SYNTHESES AND STUDIES OF CARBONYLCHROMIUM COMPLEXES OF SOME METAL CHELATES

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A Thesis

by

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Submitted in partial fulfillment of the requirement
for the degree of Doctor of Philisophy

February 1974

Memorial University
of Newfoundland

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. N. J. Gogan who, through his helpful suggestions and encouragement, has guided the author to become a research scientist.

Thanks are also due to Dr. B. S. Ramaswamy for valuable discussion with him on electronic spectroscopy.

The author wishes to thank Mr. P. J. King for the graphic work, and Miss D. Janes for typing this manuscript.

Financial assistance from the National Research Council and from Memorial University of Newfoundland is gratefully acknowledged.

Lastly, the author expresses his deep sense of gratitude to his father for his encouragement and support throughout the academic career.

ABSTRACT

Complexes obtained by displacement of two and three carbonyl groups from hexacarbonylchromium by transition metal Schiff bases have been prepared and identified. Two carbonyl groups are replaced by a metal Schiff base forming a σ-bonded tetracarbonylchromium complex. Tricarbonylchromium π-complexes of metal Schiff bases are formed by displacement of three carbonyl groups from hexacarbonylchromium. The stereochemistry about the acceptor metal in the tetracarbonylchromium complex approximates to C_{2v} symmetry; under these conditions, four i.r. active carbonyl bands are expected and observed. Considering the local symmetry of the carbonyl groups, the tricarbonylchromium complexes belong to the C_{3v} point group, and so display two i.r. active carbonyl bands.

Carbonyl stretching vibrations are used to see if electronic effects are transmitted from the central metal to the tricarbonylchromium moiety. The i.r. data for the CO stretching region indicate a very small shift ($\sim$ 10 cm^{-1} higher in d^{10} than d^4 systems) of ν_{CO} using different transition metals at the centre. The observed trend of CO frequency is opposite to that expected in $M(R\text{-}N\text{-}sal)_n\,Cr(CO)_3$ (n = 2 or 3) complexes (M, the central metal = Cr(II), Co(III), Co(II), Ni(II), Cu(II) and Zn(II) and R = CH_3, C_6H_5 and $-CH_2-$). This reverse increase of order of CO stretching frequencies from that expected suggests that electron density of the ligand is decreasing as the number of d electrons increases in the central transition metals. This can be explained if π-bonding between M(II) and $(R\text{-}N\text{-}sal)_2$ is considered negligible compared to σ-bonding.

β, the ratio of B in complex/B of free ion determined for a few complexes with the help of electronic spectra, was high (0.75-0.85). The

high values of β suggest that the bonding is mostly ionic and a very small amount of covalency exists between the central metal and the ligand.

These complexes are fairly stable toward oxidation by air and, in some cases, are even stable in solution for more than a day.

The overall spectroscopic study (i.r., U.V./visible and near i.r.) of tricarbonylchromium complexes of metal Schiff bases provides the following information:

1. The addition of a $Cr(CO)_3$ group to a metal Schiff base has no significant effect on stereochemistry of metal Schiff bases.
2. The electronic distribution of the ligand (Schiff base) does not change very much by varying the central metal.
3. There is very little covalent bonding between the central metal and the ligand (Schiff base).

The reaction between metal phthalocyanine (metal = Cr(II), Cu(II) and Zn(II)) and hexacarbonylchromium yielded tricarbonylchromium complexes, but the purification of the complexes was not achieved.

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DISCUSSION, cont'd

LIST OF ABBREVIATIONS

$(CH_3\text{-N-sal})_2M(II)$ = Bis(N-methylsalicylaldiminato)M(II)
$(C_6H_5\text{-N-sal})_2M(II)$ = Bis(N-phenylsalicylaldiminato)M(II)
(Salen)M(II) = N,N-ethylenebis(salicylideneiminato)M(II)
M = 1st series transition metals
O_h = Octahedral
Ppt = Precipitate
P.spirit = Petroleum spirit
Py = Pyridine
Pc = Phthalocyanine
TPP = Tetraphenylporphin
T_d = Tetrahedral
C.F.S.E. = Crystal field stabilization energy
Metal Schiff base = Metal complex of Schiff base

I.

INTRODUCTION

A large number of complexes containing two different transition metals has been prepared in the past. In general in these complexes the two metals are bonded to each other through metal-metal bonds or through simple bridges. Very few complexes containing two different transition metals connected to each other through conjugated ligands have been prepared. A metal-metal interaction through the ligand can be studied by preparing and studying such complexes. In the present study complexes of this last category (tricarbonylchromium complexes of metal Schiff bases) have been prepared and studied. The developments in the field of tricarbonylchromium complexes of arenes and polynuclear aromatics are outlined. The metal Schiff bases used are also reviewed briefly.

The number of known arene tricarbonylchromium complexes has increased significantly in the past few years. It was not too long ago when Fischer and Öfele (1) first obtained tricarbonyl benzenechromium (Fig. 1) in

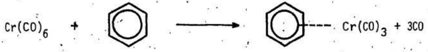


Fig. 1

27% yield by reacting hexacarbonylchromium with dibenzenechromium in benzene in a sealed system at 220^{o}C. Nicholls and Whiting (2) and Fischer and his coworkers (3) discovered a simpler and more general method for preparing compounds of this type which involves heating hexacarbonylchromium under reflux in excess aromatic compound in an inert solvent. Natta and his coworkers (4) also described the direct preparation of several of these compounds using a pressurised system and high temperature (200-235°C). The work of Fischer shows that equilibria are involved in these reactions. An excess of carbon monoxide converts the dibenzenechromium complex into the hexacarbonylchromium and therefore it is advantageous in principle and in practice to employ an open system, the free escape of carbon monoxide then driving the reaction to completion.

Recently Rausch and his coworkers (5) obtained tricarbonyl benzenechromium in 90-95% yield from the reaction of hexacarbonylchromium, benzene and 2-picoline at reflux temperatures. They presume that the reaction proceeds via a dative complex such as (2-picoline) pentacarbonylchromium, which is subsequently converted to the more thermodynamically stable product (Fig. 2).

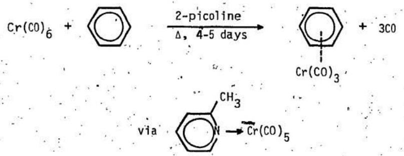


Fig. 2

Zeiss listed a number of arene and substituted arene tricarbonylchromium complexes in his 1960 review (6). A large amount of work on arene exchange reactions of (arene $Cr(CO)_3$) complexes was discussed in 1966 (7) and in the same year a general review by Dobson et al. (8) was also published.

Naphthalene, the simplest condensed six-membered ring compound reacts with hexacarbonylchromium to give the complex (9) as shown below (Fig. 3). Fischer (10) examined the tendency of condensed aromatic systems to form arene carbonyl derivatives and prepared the following complexes (Fig. 4). He suggested that the least substituted, most benzenoid ring forms the tricarbonylchromium complex. Nuclear magnetic resonance spectra were used to identify the products. Rausch et al. (11) have developed a convenient new synthesis of the reagent triamminetricarbonylchromium and shown it to be a valuable compound for the synthesis of a wide variety of arene tricarbonylchromium complexes.

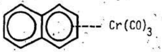


Fig. 3

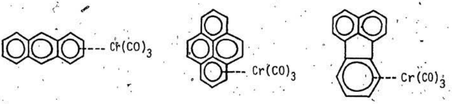


Fig. 4

$$Cr(CO)_6 + KOH \xrightarrow[\text{pressure vessel}]{\text{95\%EtOH, 100C}^\circ\text{, 6hours}} K_2[(CO)_3Cr(OH)_3Cr(CO)_3H] \text{ red orange}$$

$$\downarrow +NH_4OH$$

$$(NH_3)_3Cr(CO)_3 + H_2O + KOH$$

Yellow crystals m.p. 80-90°C(dec)

For example, the reaction between triamminetricarbonylchromium and biphenylene in refluxing dioxane produces biphenylene tricarbonylchromium and biphenylene hexacarbonyldichromium (Fig. 5).

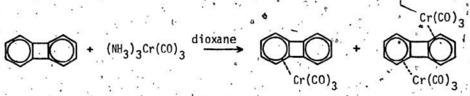


Fig. 5

Similar reactions between triamminetricarbonylchromium and various arenes have produced a variety of organometallic complexes such as: (Fig. 6),

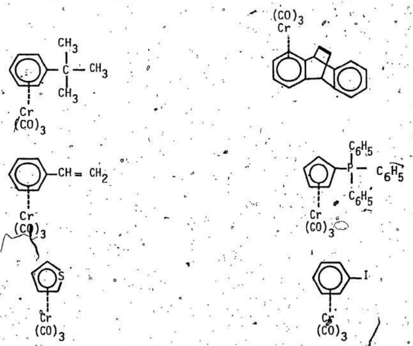


Fig. 6

Iodobenzene tricarbonylchromium reacts with magnesium in tetrahydrofuran to form a Grignard reagent, and a solution of this with trimethylchlorosilane gives trimethylsilylbenzene tricarbonylchromium.

Fischer and Öfele (12) reported that pyrolysis of N-methylpyridinium iodopentacarbonylchromate [0] gave π-C-methylpyridine tricarbonylchromium (Fig. 7A). However, on the basis of n.m.r. evidence the same authors (13) have reformulated the product as (1-methyl-1,2-dihydropyridine)tricarbonylchromium (Fig. 7B).

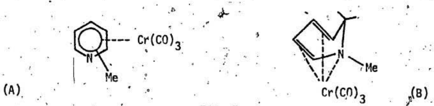


Fig. 7

Mixed iron-chromium complexes were first synthesised in 1961 (14) by the reaction of diphenylbutadiene tricarbonylchromium with Fe(CO)$_5$ or Fe$_3$(CO)$_{12}$ to give (Ph$_2$C$_4$H$_4$Cr(CO)$_3$Fe(CO)$_3$) (Fig. 8). Many other iron-

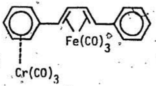


Fig. 8

chromium complexes were formed from phenylsubstituted ferrocene derivatives and Cr(CO)$_6$, e.g. Fig. 9 (15). Recently quite a number of mixed carbonyl

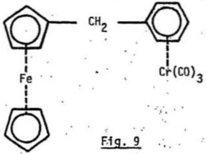


Fig. 9

complexes have been prepared by refluxing $Mn_2(CO)_{10}$ and $Cr(CO)_6$ with 2-phenylpyrrole (16), 2-benzylpyrrole (17), and $C_6H_5COC_5H_4Mn(CO)_3$ (18) in an inert solvent (Fig. 10). Rausch and coworkers (5) have reported a new route for synthesizing organochromium complexes which would be impossible to obtain by the direct complexation method (Fig. 11). The ^1H n.m.r. studies of $(C_6H_6M(CO)_3)$ complexes by various workers between 1964 and 1969 have shown that the most obvious characteristic is the upfield shift of the ring proton resonance upon complexation. A recent paper (19) has correlated these shifts with three effects, namely, withdrawal of π-electron density from the ring, the magnetic anisotropy of the $-Cr(CO)_3$

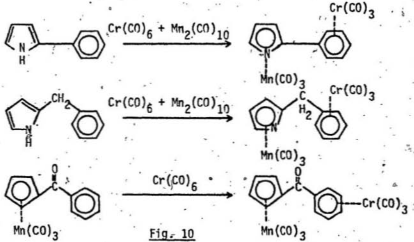


Fig. 10

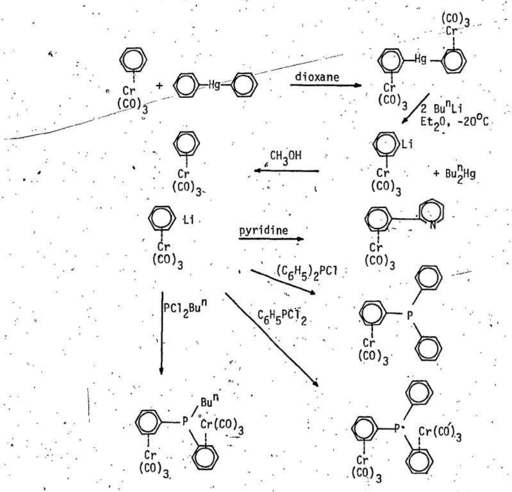
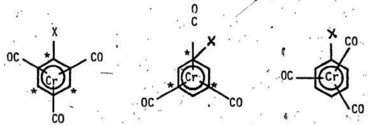


Fig. 11

moiety, and the quenching of the ring current. The decrease of coupling constant between ring protons on complex formation was also discussed in terms of reduced π-electron density on the complexed arene ring.

Extensive infra-red studies have been done by various workers (7,20,21). I.R. studies on the variation of ν_{CO} with substituents on the arene ring show that electronic effects are transmitted from the ring to the carbonyls. This is reflected in a reduction of the CO bond order (and hence stretching frequency) as more π-electron density is transmitted to the carbonyl group. The work of Brown and Hughes (22) on the effects of solvents on ν_{CO} shifts indicates that π-bonding between the metal and carbonyl groups increases in the sequence Cr < Mo < W.

A substantial number of crystal structures (23,24,25) on mono-substituted benzene tricarbonylchromium have established that the eclipsed orientation of the $-Cr(CO)_3$ group, with respect to the arene ring, exists in the solid state. This orientation is controlled by electron repulsion or withdrawal by the substituent, such that when the substituent X is a +M group, conformer (B) is more stable. When X is a -M group, conformer (A) is stabilised and for more bulky substituents the staggered orientation (C) is favoured in order to minimise steric effects (Fig. 12).



(A) (B) (C)

Fig. 12

Emanuel and Randall (19) have suggested that in the eclipsed conformers the effect of the magnetic anisotropy of the $-Cr(CO)_3$ group will produce different chemical shifts at the starred and unstarred ring protons. Thus if either conformer is preferred in solution, there will be a differential shift of the two sets of ring protons. On consideration of their n.m.r. data, they concluded that (B) is the preferred conformer for $(CH_3C_6H_5Cr(CO)_3)$. Similar observations by Price and Sorenson (26) are explained by partial three-point bonding of the -$Cr(CO)_3$ moiety to the arene ring. However, the X-ray structure of $C_6H_6Cr(CO)_3$ (27) shows no evidence for bond alternation in the same ring. Therefore, the interpretation of Emanuel and Randall (19) that preferred conformers are retained in solution and that the n.m.r. variations are due to differential magnetic anisotropy effects present in the conformers seems very reasonable. It is also very probable that the differences in isomer distribution in electrophilic reactions of free and complexed arenes are due to the electronic and steric effects.

The author has prepared and studied (28,29,30) the electronic effects of tricarbonylchromium complexes of α,β,γ,δ-tetraphenylporphine and its Cr(II), Mn(III), Ni(II), Cu(II), and Zn(II) chelates (Fig. 13). The

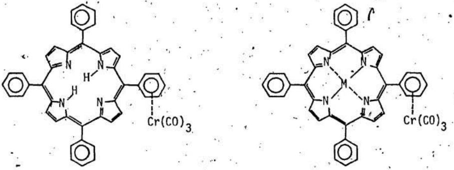


Fig. 13

complexes were prepared by refluxing hexacarbonylchromium with metalloporphines in di-n-butyl ether under nitrogen. In the case of zinc, two complexes were obtained, one with only one -$Cr(CO)_3$ group and the other with two -$Cr(CO)_3$ groups attached. The structures were established with the help of n.m.r.

The electronic effects were studied with i.r. spectroscopy. The frequencies of the carbonyl stretching vibrations are sensitive to changes of electron distribution in the benzene ring. If benzene is part of a conjugated ligand, any changes in the electron distribution of the ligand by varying the central metal will be reflected by changes in the position of carbonyl stretching vibrations (Table I). The i.r. spectra of these complexes show similarity in the positions of the carbonyl stretching vibrations. These occur at the same frequency within experimental error, except for the free base complex, $TPPCr(CO)_3$, which shows a significant difference in this respect. The higher frequencies (1930, 1990 cm^{-1}) observed for this complex mean that there is less π-electron density in the antibonding orbitals of the carbonyl groups than in the metal complexes.

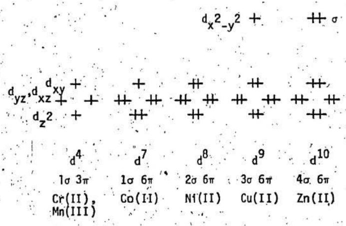
TABLE I

The i.r., CO stretching region for $M\text{-}TPPCr(CO)_3$, cm^{-1} ($CHCl_3$)

M = Cr(II)	Mn(III)Cl	Co(II)	Ni(II)	Zn(II)	H_2
1970	1972	1972	1973	1972	1990
1900	1904	1904	1903	1902	1930

A qualitative molecular orbital diagram (Fig. 14) for the higher bonding orbitals of the metalloporphine system shows the variation in the number of σ- and π-electrons. Any σ- or π-effect or both, transmitted from the central metal to the carbonyl groups, should be observable in a

Fig. 14



variation in the frequency of the carbonyl stretching vibrations. However, no variation was observed. If there was significant interaction between the π-system of the porphine ring and the phenyl ring, one would expect an appreciable effect on the tricarbonylchromium group. On the other hand, if the systems could interact only through the σ-framework the effect would be very small as the σ-orbitals are localised between pairs of atoms. This interpretation is consistent with the x-ray work of Fleischer et al. (31) who showed that the phenyl rings in ZnTPP were perpendicular to the plane of the porphine system. This configuration would not allow any π-interaction between the porphine and the phenyl ring. From this work it was suggested that the mutual configuration of the porphine and the phenyl system are perpendicular to one another in solution as well as in the solid state.

In the present work the tricarbonylchromium π-complexes of phthalocyanines and metal phthalocyanines were prepared. The phthalocyanines were chosen because the benzene ring is fused into the basic frame and there is a strong possibility of a conjugated π-system. Upon complexation significant changes in CO stretching vibrations were expected by varying the central metal. The reaction between the metal phthalocyanines and hexacarbonylchromium in di-n-butyl ether produced tricarbonylchromium complexes. Unfortunately, purification of these complexes was difficult. The details are given in the last chapter of this thesis.

Finally, metal Schiff bases were chosen as ligands. These metal Schiff bases are familiar for their diversity in stereochemistry and, at the same time, the ligand (Schiff base) when coordinated to a metal is known to have a conjugated system. The author has prepared and purified the tricarbonylchromium π-complexes of Cr(II), Co(II), Co(III), Ni(II), Cu(II) and Zn(II) metal Schiff bases and their study will reveal the following:

1. The changes in stereochemistry caused by the addition of a tricarbonylchromium group.
2. The changes in electron distribution in the ligand produced by changing the central metal.
3. The extent of covalent bonding between the central metal and the ligand.

II.

Metal complexes of Schiff bases

Metal complexes of Schiff bases are among the oldest known complexes. Ettling (32) in 1840 isolated bis (salicylaldiminato) copper (II) from the reaction of copper (II) acetate, salicylaldehyde and aqueous ammonia as dark-green crystals (Fig. 15).

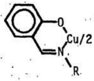


Fig. 15

In 1869, Schiff (33) prepared the corresponding R = phenyl and aryl derivatives and showed 1:2 metal:ligand stoichiometry. The complexes with R = methyl and benzyl were prepared by Delepine in 1899, who also (34) demonstrated 1:2 stoichiometry. No work was done after 1899, until 1931-1942, when Pfeiffer and his coworkers (35,36,37) isolated a variety of complexes from Schiff bases of salicylaldehyde and its substitution products, o-aminobenzaldehyde and pyrrole-2-aldehyde (Fig. 16). Dubsky and Sokol (38) in 1931 isolated N-N-ethylenebis (salicylidineaminato) copper (II) and nickel (II) and formulated the structure as shown in Fig. 17. The emphasis

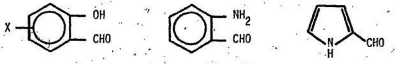


Fig. 16

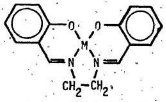


Fig. 17

was placed on the synthesis of complexes and recognition of their structure by measurement of dipole and magnetic moments and optical resolution experiments before 1950.

The physicochemical investigations during the past 15 years of these complexes have made it easy to understand their electronic and stereochemical properties. These compounds have been widely studied because simple synthetic procedures make it possible to synthesize them by varying the ligand (Schiff base) with the same metal. The variation of ligand changes the electronic and stereochemical properties of compounds. Thus it is ~~possible~~ to study the effects of these changes in a series of compounds.

The effect of medium on stereochemistry is important; therefore a non-coordinating solvent was chosen by previous workers. In this non-coordinating medium the stereochemistry presumably remains the same during the investigation. The best media in which to study the structures are weakly interacting solvents where medium effects can be ignored. The two most significant stereochemical patterns studied were (39):

1. "Variation in stereochemistry as a function of metal ion in a series of complexes with a constant ligand structure. From this point of view, much work has not been done because the chemistry of four coordinate complexes of metals ions lighter than Co(II) is poorly and unsystematically developed at the present time."

2. "Variation in stereochemistry as a function of ligand structure in a series of complexes with the same metal ion" (Fig. 18). A large number of compounds can be easily prepared by varying the nitrogen substituent R. Different electronic and steric effects are observed by changing the R group. The ring substituent X may also be varied but these changes have secondary effects on the stereochemistry as compared to alteration of R.

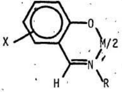


Fig. 18

The complexes of tetradentate Schiff bases are, in general, planar or nearly planar due to the steric constraints of the ligand system and therefore these complexes are less attractive than neutral bis-chelate species for the purpose of investigating the stereochemical patterns.

Basic structural features of bis-chelate complexes

The possible structures of monomeric bis-chelate complexes are planar and tetrahedral. The cis and trans geometrical isomers (Fig. 19)

Fig. 19

are possible for planar stereochemistry. In the tetrahedral case it has been proposed (40) that the configurations of right- and left-handed helicity along the twofold rotation axis be designated Δ and Λ, respectively (Fig. 20). The notation is analogous to that employed with trigonal

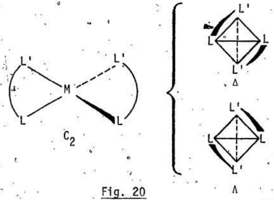


Fig. 20

complexes and describes the absolute stereochemistry without reference to any known structure. The structural parameters required to define complete geometry of the coordination sphere are shown in Fig. 21. Both the ϕ and θ, the dihedral angle between the planes MLL, are found to be $< 90^{\circ}$, if the structure of the coordination sphere contains a twofold rotation axis. In either the planar or tetrahedral case the specification of all the distances and angle parameters is unnecessary because $a = c$, $b = d$, $\alpha = \alpha'$, $\beta = \beta'$.

From the available X-ray results, several structural features of general importance are derived in the crystalline state (40). The planar complexes possessing or closely approaching the maximum possible coplanarity of metal ion and ligand atoms are not common compared to those which exhibit the so-called "stepped structures". The stepped structures are those in which ligands are individually planar or nearly so, but are not

Planar tetrahedral

dihedral (fold) angle φ planar, tetrahedral

dihedral angle θ between ML_2 planes, tetrahedral

Fig. 21

coplanar. The structure is illustrated in Fig. 22, where S is the

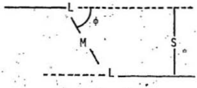


Fig. 22

perpendicular separation of chelate ring mean plane. In some cases the step is very slight, as with bis (salicylaldiminato) Cu(II), while the isomorphous nickel analog has a step S = .29 Å. The corresponding N-phenyl Cu(II) has a much larger step with S = .89 Å and φ = 18.° The interactions producing the stepped structures are not clear and may arise from specific intermolecular interactions; although this is definitely not a necessary condition, Van der Waal's forces or a combination of both may be acting.

At present we can say there are two general types of structures, tetrahedral and stepped, in these metal Schiff base chelates.

The usual type of spectral and magnetic measurements which are employed to assess the stereochemistry of metal complexes in the solution and solid phase are incapable of distinguishing between complexes that are planar and those that possess the stepped configuration. The term planar implies exact or essential planarity of the ML_4 coordination sphere only. Likewise, the description of tetrahedral is meant to imply a sufficiently large dihedral angle such that the ground state spin multiplicity of the coordination metal ion is consistent with a simple ligand field theory for effective tetrahedral symmetry.

Planar and tetrahedral distinctions are generally quite clear when the two forms have different multiplicities, as in the case for the verified stereoisomers of bis-chelate cobalt (II) and nickel (II) complexes. Intermediate structures are frequently designated as pseudotetrahedral in order to convey the lack of close approach to the limiting ($\Theta = 90^0$) tetrahedral configuration.

The two stereochemical patterns specified before (page 14) are summarized in Table II for the more important type of first transition series complexes by Holm et al. (40). Horizontal and vertical rows comprise patterns 1 and 2 (page 14) for each type of complex. The information given refers to the established or most likely stereochemistry in non-coordinating solvents near room temperature. Structures of the crystalline complexes are in most cases the same as those indicated in solution.

TABLE II (40)

Stereochemical patterns of bis-chelate metal (II) complexes of the first transition series

Complexes		Studies in $CHCl_3$ solution						
		M						
		Cr(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
$M(R\text{-}sal)_2$	R=Me	—	(T^f)	—	T	P^k	P	T^f
	Et	—	—	—	T	P^k	pT, P	T
	n-Pr	—	—	—	T	P^k	P	T
	i-Pr	—	—	—	T	$T \rightleftharpoons P$	pT	T
	n-Bu	—	—	—	T	P^k	P	T
	t-Bu	—	—	—	T	T	pT	T
	Ph	—	—	(T)	T	P^k	P	T

P^k = Mixture of planar monomer and paramagnetic associated species in solution

T^f = Monomer in solution and dimeric in solid state

T = Tetrahedral

P = Planar

pT = Pseudotetrahedral.

Structural information for Cr(II), Fe(II), Co(II), Ni(II) and Cu(II) is based upon various combinations of magnetic, spectral and dipole moment data, and complete X-ray studies, isomorphic relationship and, where available, comparisons of certain of these data in solution and solid phases. Established structures of Zn(II) complexes follow from X-ray and dipole moment results.

$Co(II)\ (CH_3\text{-}N\text{-}sal)_2$

The complex $Co(II)\ (CH_3\text{-}N\text{-}sal)_2$ exists in the form of triclinic emerald green crystals. The magnetic moment of Co(II) is 4.62 B.M. at room temperature. The magnetic susceptibility follows the Curie-Weiss law with a value of $\theta = < 5^0$. This complex represents the first example of penta-coordinate high spin cobalt (II) complex, whose structure has been established by X-ray analysis (41). Cryoscopic measurement in benzene solution has shown it to be monomeric (42). On the basis of a simple model three spin allowed crystal field bands are expected (in solution) in tetrahedral cobalt (II) (43):

$$ {}^4T_2 \xleftarrow[\nu_1]{} {}^4A_2, \quad {}^4T_1(F) \xleftarrow[\nu_2]{} {}^4A_2, \quad {}^4T_1(P) \xleftarrow[\nu_3]{} {}^4A_2 \ . $$

ν_1 is generally too far in the near infra-red to be easily observed. ν_2 and ν_3 are often found to be resolved into several components. "Co(II) $(Alkyl\text{-}N\text{-}sal)_2$ complexes show two bands at 7,700 and 11,200 cm^{-1} which may be assigned as ν_2. The rapid rise in absorption obscures part of ν_3, however a well-defined shoulder at 17,000 cm^{-1} is clearly seen. The charge transfer bands at 25,000 cm^{-1}, 28,000 cm^{-1} and 34,000 cm^{-1} occur at frequencies which are nearly identical with those of $Cu(II)\ (CH_3\text{-}N\text{-}sal)_2$" (39).

The reflectance spectrum of $Co(II)\ (CH_3\text{-}N\text{-}sal)_2$ shows four bands with peaks at 5,600, 11,400, 15,000 and 19,000 cm^{-1}. It differs considerably from that of other high spin complexes of Co(II) with N-substituted salicylaldimines with tetrahedral configuration or octahedral symmetry.

The magnetic moments of tetrahedral and octahedral complexes fall in the range 4.3 - 4.5 B.M and 4.8 - 5.2 B.M, respectively.

$Zn(II)\ (CH_3\text{-}N\text{-}sal)_2$

The complex $Zn(II)\ (CH_3\text{-}N\text{-}sal)_2$ exists in a straw-coloured triclinic form. A complete three-dimensional X-ray (45) analysis has shown that this complex exists as a dimer in the solid state.

Each atom of zinc, bound to two atoms of oxygen and two atoms of nitrogen, has a coordination of five via sharing with an oxygen atom from a neighboring molecule. The ligand atoms are situated at the vertices of two trigonal bipyramids with a common edge. The zinc atoms are at the centre of bipyramids according to the following sketch (Fig. 23).

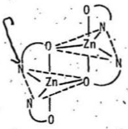


Fig. 23

$Ni(II)\ (CH_3\text{-}N\text{-}sal)_2$

Three crystalline forms of this compound are known to exist (46). The α-orthohombic and β-monoclinic forms are those usually obtained by crystallization from organic solvents. They are diamagnetic with planar configuration about nickel as shown by X-ray. The γ-form is obtained by heating diamagnetic

Ni(II) $((CH_3\text{-N-sal})_2$ to about 180°C; this high temperature form is paramagnetic with μ_{eff} = 3.4 B.M. and is a yellow-green microcrystalline powder, it is insoluble in all inert solvents and this can be attributed to its polymeric structure. The complex has been studied as the first example of a magnetically anomalous nickel (II) complex. The discovery of magnetically anomalous nickel complexes was made in the period 1947-1957. The observed magnetic moments per nickel atom of these complexes in non-coordinating solvents corresponds to a nonintegral number of unpaired electrons. These unusual magnetic moments were explained by considering an equilibrium between high spin and low spin complexes.

Further work in 1960-1962 (46) showed that magnetic moments in solution depend upon the degree of association of these complexes. In 1962-1963 (47) the magnetically anomalous behavior of nickel complexes was explained by the existence of a structural equilibrium between Planar $\rightleftharpoons$ Tetrahedral in the solution (48,49).

Cu(II) $(CH_3\text{-N-sal})_2$

The structure is trans planar and exists in three forms, α, γ orthohombic and β monoclinic form (50). The molecular packing is similar to Ni-dimethylglyoxime with inter-molecular Cu-Cu distance being 3.33 Å for the α-form.

The structure for the copper (II) n-alkyl complex is planar in the solid form, while the sec-alkyl complexes have a pseudotetrahedral coordination probably imposed by forces of a steric nature.

These two different types of structure correspond to two different reflectance spectra in the region 5,000-25,000 cm^{-1}. For example, the planar N-butyl complex (51) has a single broad band at 16,000 cm^{-1} and a shoulder at 22,000 cm^{-1}. This is analogous to the results obtained by Ferguson (52). The N-methyl complex probably also contains more than one transition under its envelope. On the other hand, the pseudotetrahedral N-isopropyl copper (II) complex, both as pure solid and in solid solution with the analogous zinc (II) compound, has bands at 8,500, 13,500 and 21,000 cm^{-1}. For a truly tetrahedral copper (II) complex, the crystal field theory predicts only one transition, $^2T_2 \rightarrow {}^2E$. Furlani and Morpurgo (53) have shown that the flattening of the tetrahedron results in the splitting of both the ground and excited levels, so that four transitions are to be expected in the crystal field spectrum for a salicylaldiminato copper (II) complex. Hence both bands at 8,500 and 13,500 cm^{-1} on the basis of their frequencies and of their relatively low intensities can be assigned to crystal field transitions of the copper (II) ions. The other two bands expected may be located below 5,000 cm^{-1}.

The salicylaldiminato complexes of copper (II), to which a pseudotetrahedral structure has been assigned on the basis of the spectral criterion have magnetic moments (1.89-1.92 B.M at room temperature) slightly but consistently higher than those of planar compounds (53) (1.83-1.86 B.M).

Co(III) $(CH_3\text{-N-sal})_3$ (39)

"The interesting feature of this complex is the possibility of geometrical isomerism. Tris-chelate complexes containing three identical unsymmetrical bidentate ligands can exist in two geometrically isomeric configurations, cis and trans (Fig. 24).

cis trans

Fig. 24

The complex has been isolated in only one form. West (54) observed that, because of steric overcrowding, molecular models of the cis isomer could not be assembled and that models of the trans form could be made but still show considerable steric strain. West tentatively suggested a trans structure for the isolated complexes. The trans stereochemistry of the tris complexes has now been definitely established by dipole moment and n.m.r. studies (55). The n.m.r. uses the argument that the trans isomer has no symmetry at all. Thus, in the trans isomer, a given substituent (R) on nitrogen can, in principle, produce a separate resonance, generating three signals in all. A single signal is predicted for the same substituent in the cis form. The spectrum of the complex $(R=CH_3)$ shows three distinct and equally intense resonances of the methyl group, clearly demonstrating the predominant trans configuration."

The electronic spectra of these complexes show only one ligand field band ($^1A_{1g} \rightarrow {}^1T_{1g}$), and from its energy it has been argued that the salicylaldiminato group lies slightly toward the strong field side of water and acetylacetone in the spectrochemical series (56). The complex is diamagnetic as is expected for spin paired Co(III) complex.

Co(III) (C_6H_5-N-sal)$_3$

This complex has been isolated only in the trans form. It is diamagnetic and shows only one broad ligand field band when the electronic spectrum is studied (54)

Co(II) (C_6H_5-N-sal)$_2$

A large number of magneto-chemical investigations have been reported for the complexes of Co(II) which are often assigned structures on this basis. For example, tetracoordinated Co(II) complexes are assigned tetrahedral structures if the values of magnetic moment are in the range 4.2-4.7 B.M, whereas the values of 2.1-2.9B.M are said to indicate square planar structures. Octahedral Co(II) complexes have μ_{eff} values of (44) 1.7-2.0 or 4.4-5.6 B.M. As far as the spectral properties are concerned, it was observed that the crystal field bands in the spectra of the tetrahedral complexes of Co(II) have molar extinction coefficients which are much larger than those found in either planar or octahedral complexes.

The magnetic susceptibility of the Co(II) (C_6H_5-N-sal)$_2$ complex, as measured (57) in the solid state over the 89-297°K range of temperature, follows strictly the Curie-Weiss law and has values of θ from -3 to 3°. These very low values of θ indicate that intermolecular interactions are very small.

The values of the magnetic moments between 4.27 and 4.48 B.M. are those predicted for a tetrahedral structure. The temperature independence of μ_{eff} is also in agreement with the ground state being an orbital singlet as expected for a tetrahedral arrangement. The magnetic moments in benzene solution are identical (4.41-4.42 B.M.) with those of the solids. Cryoscopic measurements also show that the complex is monomeric in benzene solution. This is supported by a comparison of the spectra of the complex in the solid state with that in benzene solution over the range 600-3,500 cm^{-1}. The reflectance spectrum is very similar in shape to the absorption spectrum taken in benzene solution which shows maxima at 7,700, 11,200, 25,000 and 34,100 cm^{-1} and shoulders at about 17,000 and 28,000 cm^{-1}. The bands beyond 20,000 cm^{-1} are very intense and may be attributed either to intraligand transitions or to charge transfer between the ligand and the metal. The weak bands at lower frequency may be due to crystal field transitions.

The magnetic moment of the complex in pyridine solution (4.78 B.M.) is higher than in benzene solution. This suggests that in pyridine the complex coordinates to two molecules of solvent thus being six coordinated and octahedral. This was confirmed by isolation of the solid adduct bis (C_6H_5-N-sal) Co(II).2 pyridine, with μ_{eff} of 4.81 B.M. Further evidence for the formation of this adduct is provided by the reflectance spectrum of the dipyridine derivative and that of pyridine solution of the unsolvated complex. These two are very similar. The latter shows band maxima at 10,000, 26,000, 33,100 cm^{-1} and a shoulder around 17,000 cm^{-1}. This differs from the spectrum of a benzene solution of the tetrahedral complex, the major difference being the higher extinction coefficient of the crystal field bands in the tetrahedral complex.

Cu(II) $(C_6H_5\text{-N-sal})_2$

The structure is centrosymmetric but the molecule is not completely planar (58). Only the $Cu\text{-}O_2N_2$ unit is planar, and the salicylaldimine groups are parallel but not coplanar and are separated by 0.89 Å. The phenyl groups are normal to the coordinate plane ($Cu\text{-}N_2\text{-}O_2$ plane).

The magnetic susceptibility follows the Curie-Weiss law and has a very small value of θ. This low value of θ indicates that intermolecular interactions are very small. The distinction between square planar and tetrahedral structures can be made with the help of electronic spectra and magnetic susceptibility as discussed previously.

Ni(II) $(C_6H_5\text{-N-sal})_2$

X-ray crystallography (59) shows a trans planar structure with Ni-Ni distance being 7-8 Å, isomorphous with the Cu(II) complex, but with a slightly different molecular structure.

Magnetic and spectroscopic studies (60) on a series of N-aryl Ni(II) complexes in inert solvents up to a temperature of 473^oK have shown than phenyl substituted complexes which are diamagnetic both in solid state and in solution retain the square planar structure at all temperatures. For 3 and 4-substituted phenyl complexes, the decrease in the amount of association which is observed with an increase in temperature is accompanied by the appearance of a tetrahedral species whose concentration increases with temperature. Dilution, too, causes a decrease in the amount of association and favours the formation of tetrahedral species.

The sensitivity of the magnetic and spectral properties of the phenyl complex to temperature is suggestive of an equilibrium (Tet $\rightleftharpoons$ Sq.pl.) (61) such as occurs in the N-methyl complex.

The μ_{eff} value decreases with temperature and is 3.10 B.M at 20^0. The electronic spectrum shows three bands around 16,270, 12,820 and 9,950 cm^{-1} at 25^0 in chloroform. The intensity of the bands at 16,270 and 9,950 cm^{-1} decreases as the temperature is raised.

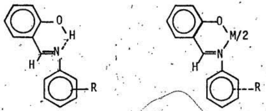
$Zn(II)\ (C_6H_5\text{-}N\text{-}sal)_2$

X-ray crystallography has shown (62) a tetrahedral structure for the complex. The complex has not been widely studied because of its d^{10} configuration.

Infra-red studies of $M(II)\ (aryl\text{-}N\text{-}sal)_2$

The limited i.r. study is due to structural diversity of the complexes, and the difficulty of applying normal coordinate methods to the assignment of bands and the complexity of the spectra resulting from the presence of phenyl vibrations, two different metal ligand bands (M-N, M-O) and extensive vibrational coupling.

The application of ^{15}N-labelling (63) has helped in interpreting i.r. spectra of metal complexes of Schiff bases. This technique yields reliable assignments and provides an estimate of the vibrational purity of the frequency. Two ^{15}N sensitive bands near 1,600 cm^{-1} occur in the spectrum of the N-aryl compound (Fig. 25A); the higher frequency band has



(A) (B)

Fig. 25

been assigned to ν C=N but the lower frequency band shows the greater ^{15}N induced shift and is therefore vibrationally purer. A shift to higher frequency was expected for uncomplexed ν C=N but a shift to lower frequency is observed indicating that both bands are extensively coupled. The assignment of both bands to ν C=N is supported by their sensitivity to metal ion complexation and to the variation of substituent R.

Two other bands in the range 1,375-1,475 cm^{-1} exhibit shifts of -7 cm^{-1} on ^{15}N labelling and their assignment to ν C-N was therefore indicated. The following shifts on ^{15}N labelling in the copper (II) (R=4CH$_3$ (Fig. 25B)) chelate were observed: 1,615 ($\Delta\nu$-3), 1,596 ($\Delta\nu$-10), 1,450 ($\Delta\nu$-3), 1,387 ($\Delta\nu$-6), 1,256 ($\Delta\nu$-6), 867 ($\Delta\nu$-6) and 829 ($\Delta\nu$-4) cm^{-1}. The bands at 1,615 cm^{-1} and 1,596 cm^{-1} were assigned to ν C=N. Two ^{15}N sensitive bands at 1,450 and 1,387 cm^{-1} are due to ν(C-N aryl) and the two bands near 850 cm^{-1} are probably C=N-C deformation frequencies.

Below 600 cm^{-1} only three bands exhibit shifts exceeding 2 cm^{-1}. That at 595 cm^{-1} is very little affected by substitution in the N-aryl ring or by replacement of Cu(II) by other metal (II) ions.

The remaining bands at 505 and 427 cm^{-1} are sensitive to both modes of substitution and therefore assigned to ν Cu-N although there is undoubtedly a significant contribution to each from coupled ν Cu-O.

Crystal field theory predicts (64) that a series of three complexes with identical ligand composition containing tetrahedral Co(II) and Zn(II) and square planar Cu(II) will have C.F.S.Es in the order Co<Cu>Zn. Accordingly, any band assignment as ν Cu-N is expected to exhibit a similar order of frequency variation on substitution of Co(II) or Zn(II) for Cu(II).

The frequencies of the bands assigned to ν Cu-N reflect (Table III) the predicted C.F.S.E. sequence for differently substituted salicylaldimine complexes.

TABLE III

	ν C=N cm^{-1}	ν M-N cm^{-1}	ν M-0 cm^{-1}
Co(II) $(C_6H_5$-N-sal$)_2$	1,607, 1,580	519, 457	494
Ni(II) $(C_6H_5$-N-sal$)_2$	1,618, 1,588	542, 466	516
Cu(II) $(C_6H_5$-N-sal$)_2$	1,611, 1,595	529, 448	495
Zn(II) $(C_6H_5$-N-sal$)_2$	1,609, 1,589	516, 454	493
C_6H_5-N-sal H	1,625, 1,576		

Percy and Thornton (65), in a further test of the assignment, included a Ni(II) complex of known structure (square planar) similar to Cu. Crystal field theory predicts the stability order Ni>Cu for the pair of complexes since the orbital of highest energy is necessarily occupied in the Cu(II) chelate but is unoccupied in the diamagnetic Ni(II) analogue. The ν C-N bands are observed to exhibit this frequency order.

The effect of varying the N-aryl substituents R is noticeable in the i.r. spectra of copper (II) complexes. The ν C-N band shifts to higher frequency with an electron withdrawing substituent R. The N π-bonding is facilitated by electron withdrawing substituents. It is unlikely that the electronic effect is transmitted via the conjugation of the chelate ring, as ν C=N and ν C-0 are insensitive to substitution in the N-aryl ring.

The assignment of ν Cu-O has not been conclusively established yet, but ν Cu-O is coupled with ν Cu-N so that ^{15}N-substitution will induce some shift in ν Cu-O. The confirmation of the Cu-O band has to come from ^{18}O labelling.

Infra-red studies of M(II) (alkyl-N-sal)$_2$ (65)

The i.r. spectra of the N-alkyl salicylaldimines have fewer bands than observed for N-aryl salicylaldimine. This feature suggests less vibrational coupling in the N-alkyl compounds. There is only one ^{15}N sensitive ν C=N band in N-alkyl base as compared to two bands in N-aryl base. The shift in ν C=N on labelling is (Δν, - 18 cm^{-1}) for the N-alkyl base while the shift in the case of N-aryl is much less (Δν, - 5 and - 8 cm^{-1}) for both bands. If there was no vibrational coupling, a shift of ~ Δν, - 40 cm^{-1} was expected in both cases.

The i.r. spectra of the Cu(II) complexes (Fig. 26B) also exhibit

(A) (B)

Fig. 26

only one substituent sensitive band in the ν C=N region and only one band in this region has been observed to shift on ^{15}N labelling of the Cu(II) complex. The ν C=N assignment is supported by the fact that increased electron delocalization accompanying metal ion complexation of the free ligand leads to the expected frequency decrease.

Compound	ν C=N cm^{-1}	ν M-N cm^{-1}	ν M-O cm^{-1}
Cu(II) $(CH_3\text{-N-sal})_2$	1,638	467, 410	587
CH_3-N-sal H	1,645		

Two bands in the far infra-red spectra of the N-alkyl Cu(II) complexes are sensitive to the substituent. An electron withdrawing group causes an increase in frequency. The bands are assigned to ν Cu-N similarly as in the case of N-aryl complex. A band in the region 550-600 cm^{-1} was observed to shift in the opposite direction to ν Cu-N and on this basis was tentatively assigned to ν Cu-O.

Percy and Thornton did not confirm the assignment of metal ligand vibrations by observing the band shifts induced by substitution of other metal (II) ions, but instead adopted an alternative approach of introducing substituents into the phenyl ring (R' and R", Fig. 27) with the assumption

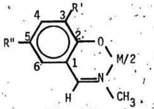


Fig. 27

that these substituents would shift the metal ligand bands, if correctly assigned. The substantial shifts in the frequencies of these bands occur in the substituent sequence: H ~ 5-Cl<3,5-di-Br<3,5-di Cl<3-OCH_3. Except for the 5-Cl substituent which yields a rather low frequency shift is also the sequence of electron releasing capacity of the substituents.

Finally, in order to determine whether the order of substituents effect is peculiar to the Cu(II) complexes, they succeeded in obtaining a series of stable tetrahedral Co(II) complexes of N-isopropylsalicylaldimine with an identical range of R' and R" substituents and found a similar order of substituent effect in their spectra.

N-N-ethylenebis- (salicylaldiminato) cobalt (II)

The compound has attracted a lot of attention because of its property to form an adduct with oxygen reversibly. It was found that different crystalline and solvated forms existed, each with differing capacity for oxygenation, including one completely inactive form. The variation in oxygenation activity in the solid state has been related to the presence of voids in the crystal lattice, of sufficient size to allow the passage of oxygen.

This suggestion is supported by structural determination of the active and inactive forms. The inactive form is dimeric $[Co(II)\ (salen)]_2$ (Fig. 28). Dimerization is accompanied by an interaction

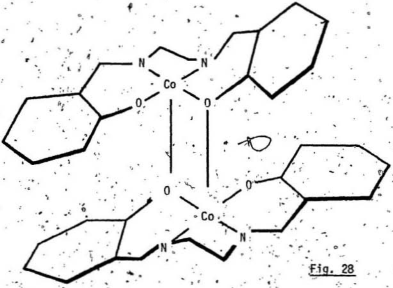


Fig. 28

between the cobalt atoms and the phenolic oxygen atoms of an adjacent pair of molecules. In this manner the cobalt becomes five coordinate in a distorted rectangular-based pyramid. The intermolecular cobalt-oxygen distance is 2.25 Å. The close stacking of the dimeric units prevents the formation of voids in the lattice and possibly explains the compound's oxygenation inactivity.

The first study (66,67) of cobalt (II) Schiff base complexes of the planar tetradentate type revealed an absorption in the near infra-red region of the spectrum characteristic of a planar configuration. Similar results were obtained in other studies (68) where solution magnetic properties were also consistent with planar stereochemistry. The diffuse reflectance spectrum (69) of Co(II) (salen) differs from the solution spectrum in that the near infra-red absorption shows a positive shift of 3,100 cm^{-1} on going from solution to the solid state.

The absorption at 15,500 cm^{-1} was assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. In those cases where the d-d bands could be clearly observed, the second band at about 17,500 cm^{-1}, was assigned to the low energy component of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. The highest energy d-d band observed (19,000 cm^{-1}) is assigned to the lower energy component of the $d_{xz} \pm d_{yz} \rightarrow d_{x^2-y^2}$ transition. The remaining bands in the visible region are either charge transfer or intraligand in origin.

Variation of the substituent R and X in low spin planar Co(II) complexes results in magnetic moment values at room temperature in the range 2.1-2.9 B.M. No high spin planar complexes are known. Co(II) (salen) as the active form possesses an effective moment reported as 2.24 B.M. at 300 K, 2.52 B.M. at 298 K and 2.72 B.M. at 297 K. The reciprocal susceptibility of Co(II) (salen) follows Curie-Weiss variation with temperature, and θ (the Weiss constant) is reported as 20^o(70) and 25^o(71). The inactive form (72) of this compound does not obey a Curie-Weiss law and has $\mu_{eff} = 1.90$ B.M. at room temperature.

N-N-ethylenebis (salicylaldiminato) nickel (II)

Ni(II) (salen) has been shown to exist as the centrosymmetric dimer in the solid state, incorporating planar Ni(II) (salen) units. This is the only example of a dimeric structure formed by direct metal-metal interactions. The nickel-nickel distance is 3.21 Å and this results in only a weak interaction. The diamagnetism of the complex is typical of planar nickel compounds. The diamagnetism of Ni(II) (salen) is also maintained in solution of coordinating and noncoordinating solvents.

The electronic spectrum of this planar nickel Schiff base complex has been widely studied (73,74). Depending on the symmetry of the complex, three or four transitions are expected within the d orbitals of the metal ion. For optically active Schiff base complexes of the tetradentate (salen) type, three circular dichroism d-d bands are observed. These correspond to a single shoulder in the absorption spectra. Bands occurring in the approximate region 17,000-22,000 cm^{-1} were assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$, $(A_1 \rightarrow B_2)$ $d_{xy} \rightarrow d_{z^2}$ $(A_1 \rightarrow B_2)$ and $d_{xy} \rightarrow d_{xz}$ $(A_1 \rightarrow A_1)$ plus $d_{xy} \rightarrow d_{yz}$ $(A_1 \rightarrow B_1)$ transitions. The latter two transitions are observed as one band since the d_{xz} and d_{yz} orbitals are not expected to differ much in energy in these compounds. For purposes of general characterisation, planar complexes of nickel can be distinguished from octahedral and tetrahedral symmetries by the lack of electronic absorption below 10,000 cm^{-1} - a consequence of large crystal field splitting. Clark and Odell (75) have reported the solution absorption spectrum of nickel(II) (salen) in coordinating solvents and found both temperature variable solid and solution magnetic properties consistent with a planar arrangement.

N-N-ethylenebis-(salicylaldiminato) copper (II)

The interest in copper Schiff base complexes has centred around their spectral, magnetic and structural properties. The structure of Cu(II) (salen) has been determined by X-ray diffraction methods (76). This reveals a dimeric situation involving intermolecular copper-oxygen bonding interactions. The resulting stereochemistry about the copper is approximately square pyramidal with an intermolecular copper-oxygen distance of 2.41 Å (2.25 Å in the inactive Cu(II) (salen) dimer) (77).

The color isomerism of copper (II) Schiff base complexes has been related to the coordination number of the metal ion. It is proposed that (78) the green-colored copper complexes possess an effective coordination exceeding four, due to either intermolecular association or adduct formation with Lewis bases, whereas brown or violet complexes contain four-coordinate copper. The green complex has low ε in the 20,000 cm^{-1} region and high ε in the 14,280 cm^{-1} region as compared to the violet or brown complexes. The rule applies in a substantial number of cases but there are a few exceptions (79).

The susceptibility of Cu(II) (salen) obeys the Curie-Weiss law. The magnetic moments determined by different workers are 1.84 B.M. (80) and 1.90 B.M. (81) with $\theta = 4^0$ and -13.5^0, respectively.

For Cu(II) ions, crystal field theory predicts that three or four transitions should occur within the 3d orbital manifold, depending upon the symmetry involved. In most cases the spectra of planar Cu(II) complexes posses only a single broad band, making assignment of individual electronic transitions difficult. Circular dichroism spectra of optically active tetradentate copper complexes have been applied to the problem of assigning transitions (82). Circular dichroism spectra indicate the presence of three transitions. These have been assigned to $d_{xy} \rightarrow d_{z^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and tentatively $d_{xy} \rightarrow d_{yz}$ in order of increasing energy and under C_2 symmetry.

N-N-ethylenebis (salicylaldiminato) zinc (II)

The solid state of Zn(II) (salen) as the monohydrate reveals almost planar ligand arrangement or square pyramidal stereochemistry about the metal. The water molecule occupies the apical position (83).

The crystal structure (84) shows that N_2O_2 unit is planar, where the zinc is 0.34 Å above the N_2O_2 plane; the distance of zinc to water is 2.13 Å.

The fully occupied d-orbital levels in the (salen) zinc (II) . H_2O result in simplified physical and chemical properties of this compound.

Metal Schiff bases as ligands

The donor bonding properties of the phenolic oxygen atoms in metal Schiff bases have been extensively studied in the past few years by Gruber, Harris and Sinn and others (138).

The metal Schiff base complex has been found to act as a neutral bidentate ligand towards metal halides and perchlorates, forming both homo- and hetero-binuclear and trinuclear adducts. These complexes are represented as Cu(II) (salen)MX (X=halide) and [Cu(II) (salen)] $M(ClO_4)_2$ (where M may be copper or another metal). Complex formation is not restricted to Cu(II) (salen). Similar compounds may be formed using nickel or vanadyl complexes, and the nature of the Schiff base ligand may also be varied (85,86).

The investigations of the Lewis base properties of transition metal Schiff base complexes have shown that M(II) (salen) complexes where the metal ion is Cu(II), Ni(II) and Co(II) react with SnX_4 (where X = Cl or Br) to form 1:1 adducts. Characterisation of the adducts using magnetic data and diffuse reflectance and infra-red spectroscopy indicates a retention of planarity about the transition metal ion and that adduct formation involves cis addition to SnX_4. In polar solvents the Co(II) (salen) SnX_4 adduct was found to undergo exchange reactions to produce Co(II) (salen) SnX_2 (87).

Reaction of $SbCl_3$, $SbBr_3$ and $SbCl_5$ with M(II) (salen) complexes, where M is Co(II), Ni(II) and Cu(II) also leads to the formation of adducts in which the planarity of the transition metal is retained (Fig. 29).

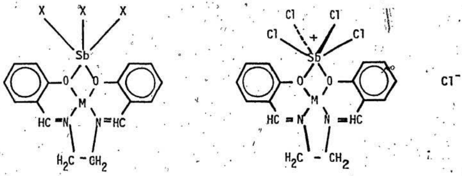


Fig. 29

To clarify the question of local symmetry about the acceptor metal, Hobday and Smith (88) isolated compounds involving metal carbonyls because the metal carbonyl i.r. absorptions are more sensitive to local symmetry than metal chlorine absorptions. They isolated the following compounds:

Ni(II) (salen) $Mn(CO)_3Cl$
Ni(II) (salen) $Mn(CO)_3Br$
Ni(II) (salen) $Mo(CO)_4$
Ni(II) (salen) $W(CO)_4$.

"Group VI transition metal carbonyls allow from one to four CO groups to be displaced by Lewis bases, stereochemical changes being reflected in the carbonyl region of the i.r. spectrum. Neutral bidentate ligands, under appropriate conditions, displace two carbonyl groups. In Ni(II) (salen) $Mn(CO)_3Br$ the stereochemistry about the acceptor metal may be either C_{2v} or C_{3v}. The former requires three i.r. active carbonyl stretching vibrations and the latter only two. Three carbonyl absorptions are found in this case indicating C_{2v} symmetry about the manganese." (88).

Ni(II) (salen) displaces two carbonyl groups from hexacarbonyl molybdenum and hexacarbonyl tungsten to form the diamagnetic compound Ni(II) (salen) $M(CO)_4$. The stereochemistry about the acceptor metal is analogous to that in the SnX_4 adduct and approximates to C_{2v} symmetry. Under these conditions, four i.r. active carbonyl bands are expected and observed, confirming the local group symmetry about the metal.

The substitution of two carbonyl groups from $Mn(CO)_5X$ by nickel Schiff base complexes produces compounds with two (Fig. 30) alternative structures. On the i.r. evidence, Hobday and Smith assigned the correct structure as (30A) with C_{2v} local symmetry about the manganese.

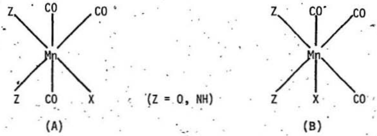


Fig. 30

Ni(II) (salen) $M(CO)_4$ shows four bands in the CO stretching region indicating the presence of C_{2v} local symmetry around M. On the basis of C_{2v} symmetry Hobday and Smith (88) assigned the following structure (Fig. 31).

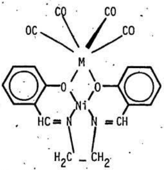


Fig. 31

The carbonyl absorptions are removed to lower frequencies than those of the parent molecules.

	i.r. ν_{CO} region cm^{-1}			
Ni(II) (salen) $Mo(CO)_4$	1910	1798	1696	1665
Ni(II) (salen) $W(CO)_4$	1899	1790	1667	1630

It was suggested (by Hobday and Smith) that Ni(II) (salen) is a strong electron donor and the bonds to the acceptor metal are strong. Their explanation for low ν_{CO} values is not satisfactory which makes their proposed structure rather doubtful.*

	i.r. ν_{CO} region cm^{-1}		
Ni(II) (salen) $Mn(CO)_3Cl$	2030	1939	1900
Ni(II) (salen) $Mn(CO)_3Br$	2029	1940	1900

Two reasons were given why, in the manganese compounds, the carbonyl frequencies are not shifted to low values. The strongly electronegative halogen could accommodate a large degree of electron density, which is solely accommodated on the carbonyl group in the molybdenum and tungsten cases or alternatively a metal-metal bond may

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*See page 184 for detailed argument.

be present in manganese compounds forming a synergic type of bonding system, reducing the electron density on the carbonyl groups. Hobday and Smith did react hexacarbonylchromium with these metal Schiff bases but apparently did not get any carbonyl complex. The work was repeated in the present study using di-n-butyl ether as a solvent and tricarbonylchromium complexes of these metal Schiff bases were obtained.

III.

EXPERIMENTAL

I.R. spectra were recorded on a Perkin Elmer 457 grating spectrophotometer using nujol mulls, solutions in chloroform and potassium bromide discs. Moisture (water vapour) and polystyrene were used for calibration.

U.V. and visible spectra were determined on a Perkin Elmer 202 or Unicam S.P. 800 D spectrophotometer in chloroform solution. The spectra were recorded using 1-cm quartz cells with the solvent in the reference beam. Holmium oxide was used for calibration.

Near infra-red spectra were taken on a Beckman DK-2A ratio recording spectrophotometer as nujol mulls (89).

Magnetic susceptibilities of solids were obtained by the Faraday method and of solution by the n.m.r. method (90).

N.M.R. spectra were recorded on a Varian A-60 or HA-100 spectrometer.

Precautions during the process of separation and purification

Most of the tricarbonylchromium complexes of metal Schiff bases are fairly stable in air and solution for some time. Therefore, the processes of separation and purification were carried out in an open atmosphere.

The Co(II) and Mn(II) complexes oxidized easily in solution. For these complexes the purification and separation were carried out in an atmosphere of nitrogen, and nitrogen was passed through dried solvents before they were used. In most of the cases thin layer chromatography was used to test the purity of the compounds.

All the compounds were recrystallised (reprecipitated) from the same solvents used for separation.

Bis (methyl-N-salicylaldiminato) zinc (II) (91)

A solution of 0.10 mole of zinc acetate was added to a solution of 0.20 mole of salicylaldehyde and 0.30 mole of methylamine in 100 ml of ethanol. The mixture was refluxed for 30 minutes. On cooling, pale yellow-colored crystals separated which were recrystallized from chloroform.

M.P. reported (260-262°C)
M.P.* found (262-264°C)

Purification of di-n-butyl ether

The peroxides were removed by shaking the ether with acidic iron (II) sulphate in a separating funnel. The ether layer was separated after washing with distilled water. The presence of peroxide was tested using acidic iron (II) sulphate and potassium thiocyanate which gives a red color if peroxide is present.

$$4\ Fe^{++} + 2\text{-}O\text{-}O^{-2} \rightarrow 4\ Fe^{+++} + 2\text{-}O^{-2} + O_2$$

$$Fe^{+++} + SCN^{-} \rightarrow [Fe\ (SCN)]^{++}\ \text{red}$$

After removing the peroxide, the ether was dried with $CaCl_2$ and then refluxed for 30 minutes with sodium and finally distilled in an atmosphere of pure nitrogen. The nitrogen used was purified by passing through Fieser's solution and drying agents to remove oxygen and moisture. Hydrogen sulphide produced by Fieser's solution was absorbed by lead acetate solution, and traces of sulphuric acid were removed by soda lime.

Reagent grade di-n-butyl ether contained xylene as an impurity which forms a π-complex with hexacarbonylchromium. Di-n-butyl ether was

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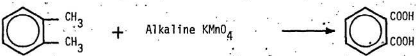
*Melting points were recorded using Thomas Hoover Capillary melting point apparatus. Melting points are uncorrected.

treated with alkaline $KMnO_4$ to oxidize xylene to phthalic acid which has a higher boiling point and could be removed by fractional distillation.



The oxidation was not complete even by repeating the process several times. Fractional distillation of di-n-butyl ether to separate xylene from it did not work as their boiling points are very close.

Di-n-butyl ether B.P = 142°C
p-xylene B.P = 144°C
o-xylene B.P = 138°C
m-xylene B.P = 139°C

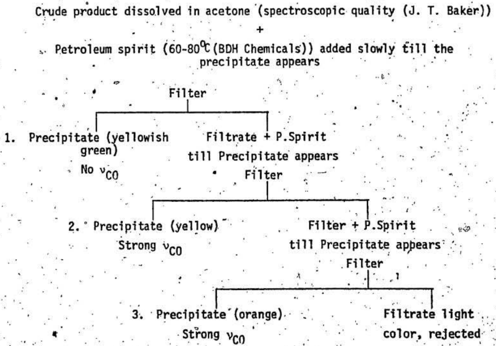
Xylene was removed successfully by refluxing di-n-butyl ether with hexacarbonylchromium under pure nitrogen. The tricarbonylchromium complex of xylene was formed. The di-n-butyl ether was separated from the complex by distillation under vacuum, the complex was left as a solid and the ether obtained was free of xylene. Spectroscopic quality di-n-butyl ether (Matheson, Coleman and Bell, U.S.A.) was used subsequently due to these difficulties involved in purification.

Hexacarbonylchromium (Pressure Chemical Co., U.S.A.) was purified by vacuum sublimation.

Tri and tetra carbonylchromium complexes of bis (methyl-N-salicylaldiminato) zinc (II)

Bis (methyl-N-salicylaldiminato) zinc (II) (0.0045 moles) was refluxed with hexacarbonylchromium (0.009 moles) in 150 ml di-n-butyl ether for six hours in an atmosphere of pure nitrogen using a Soxhlet extractor (Diagram 1). When the reaction was over, the solvent was evaporated *in vacuo*. The i.r. of the dried product showed four bands in the CO stretching region indicating that a tetracarbonyl complex was formed, as a tricarbonylchromium complex has only two bands, or the crude product was a mixture of complexes.

All the attempts to separate the complexes by chromatography using different adsorbants and eluents failed. The complexes were separated successfully by fractional precipitation.



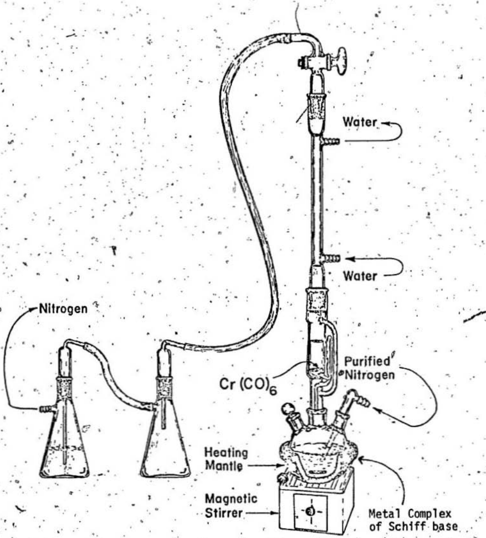

Water
Water
Nitrogen
Purified Nitrogen
Cr (CO)$_6$
Heating Mantle
Magnetic Stirrer
Metal Complex of Schiff base

Diagram I

1. The first fraction showed no CO stretching vibrations indicating absence of carbonyl complex.

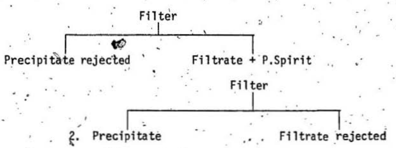
2. Tricarbonylchromium π-complex of Zn(II) $(CH_3\text{-N-sal})_2$

This fraction was further purified by repeating the process.

Precipitate (2) dissolved in acetone

\+

P.Spirit till ppt appears



Finally this fraction (2) was recrystallised yielding an amorphous yellowish-colored solid. The complex was fairly stable in air and was found to be hygroscopic. There is a marked increase in weight if left in air and the weight decreases when dried under vacuum. The i.r. of the dried complex, in the region 3200-3600 cm^{-1}, shows a broad band indicating the presence of lattice water. The elemental analysis of the dried complex agrees with the presence of three water molecules.

Zinc (II) $(CH_3\text{-N-sal})_2\ (Cr(CO)_3)_2.3H_2O$

Calculated = C 40.10, H 3.34, N 4.26, and Cr 15.7%

Found = C 39.34, H 3.53, N 4.60, and Cr 15.2%

The complex starts losing CO's when heated above 100°C and no CO's are left when the temperature reaches 185°C. (This study was followed by studying the i.r. of the solid taken out from the melting point apparatus at different temperatures. The intensity of CO's was compared with ligand bands and no CO stretchings were left when the complex was completely decomposed.) The rate of decomposition increases as the temperature is raised.

Yield, 800 mg, 27% based on $Zn(II)\ (CH_3\text{-}N\text{-}sal)_2$

3. Tetra carbonylchromium complex of $Zn(II)\ (CH_3\text{-}N\text{-}sal)_2$

The third fraction was purified by the same process used for fraction number two and finally recrystallised to give an orange-colored powder. This complex is stable in air and also hygroscopic as shown by the i.r. and drying tests. The elemental analysis of the dried complex corresponds to a formula with one water molecule:

$$Zn(II)\ (CH_3\text{-}N\text{-}sal)_2\ (Cr(CO)_4).H_2O$$

Calculated = C 46.60, H 3.49, N 5.44, and Cr 10.07%

Found = C 46.56, H 3.46, N 5.07, and Cr 10.23%

The complex started decomposing above 100°C and was completely decomposed around 180°C.

$(Zn(II)\ (CH_3\text{-}N\text{-}sal)_2\ Cr(CO)_4.H_2O)$

Yield/, 370 mg, 16% based on $Zn(II)\ (CH_3\text{-}N\text{-}sal)_2$

Bis (methyl-N-salicylaldiminato) cobalt (II) and manganese (II) (91)

The complexes of cobalt (II) and manganese (II) were prepared and collected under a nitrogen atmosphere in order to avoid oxidation by atmospheric oxygen. In the crystalline state both these complexes are fairly stable to air, while in solution they are readily oxidised.

Cobalt (II) complex

A concentrated aqueous solution of 0.02 moles of cobalt (II) acetate was added to a warm solution of 0.04 moles of salicylaldehyde and 0.06 moles of methylamine in 80 ml of ethanol. After a few minutes, deep green crystals began to separate from solution. When recrystallisation was complete, the crystals were collected on a filter, washed with petroleum ether and dried.

M.P. reported 231-234°C
M.P. found 233-235°C

Manganese (II) complex

The same procedure used for the preparation of the cobalt complex was employed. This complex is not as stable as the cobalt and decomposes in air after a few days.

M.P. reported 305-307°C
M.P. found 307°C

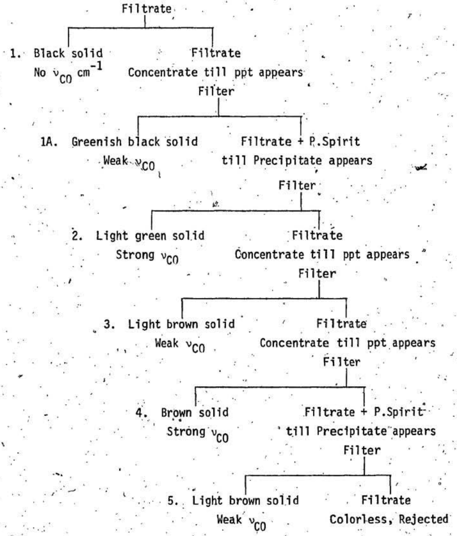
Bis (methyl-N-salicylaldiminato) iron (II) (91)

Attempts to prepare the analogous iron (II) compound led to the formation of a red crystalline product which readily decomposed in air, becoming black even when dry.

Tricarbonylchromium π-complexes of bis (CH_3-N-sal) Co(II)

The same procedure used for the preparation of the zinc complex was employed. All attempts to separate and purify the complexes by columnchromatography using different adsorbants and eluents failed. The complexes were separated successfully by fractional precipitation.

Crude product partially soluble in chloroform (spectroscopic quality (J. T. Baker)).



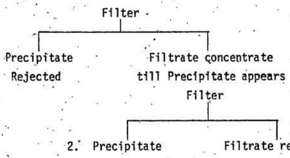
1. The first fraction showed no CO stretching vibrations indicating absence of any carbonyl complex.

Fractions 1A, 3 and 5 showed weak CO stretching vibrations indicating that these fractions were impure.

2. Tricarbonylchromium π-complex of bis (CH$_3$-N-sal) Co(II).

This fraction was further purified by repeating the process.

Light green solid dissolved in chloroform
+
P.Spirit till ppt appears



Finally the fraction 2 was recrystallised and an amorphous greenish solid obtained. The complex is fairly stable in air. The i.r. of the dried complex in the region 3200-3600 cm^{-1} shows a broad band indicating the presence of lattice water. The elemental analysis of the dried complex agrees with the presence of one water molecule.

$$\mathrm{Co(II)\ (CH_3\text{-}N\text{-}sal)_2\ Cr(CO)_3.H_2O}$$

Calculated = C 47.4, H 3.74, N 5.84, and Co 12.24%

Found = C 47.13, H 4.78, N 5.32, and Co 12.37%

The complex starts losing CO's when heated above 100°C. The rate of decomposition increases as the temperature is raised.

Yield, 27% based on Co(II) $(CH_3\text{-N-sal})_2$

4. Tricarbonylchromium π-complex of bis $(CH_3\text{-N-sal})$ Co(II)

This fraction was purified further by the same procedure as employed for fraction number 2, and a brownish solid was obtained. The details of this complex are given in Table IV.

Tricarbonylchromium π-complex of bis $(CH_3\text{-N-sal})$ Mn(II)

The same procedure used for the zinc complex was employed for this preparation. The process of separation and purification was carried out in an atmosphere of nitrogen. Nitrogen was passed through the solvents before they were used. The complex decomposed during the process of separation and purification either by chromatography or by fractional precipitation.

Bis (methyl-N-salicylaldiminato) copper (II) (92)

To 0.05 moles of salicylaldehyde dissolved in 100 ml of methyl alcohol was added 0.10 moles of primary amine (as 40% solution in water) and the mixture was allowed to stand for a few minutes at room temperature. A solution of 0.025 moles of copper acetate in 100 ml of distilled water was added. The mixture was heated nearly to boiling and stirred for 30 minutes. After heating it was allowed to stand at room temperature for two hours, and the solid chelate was filtered on a buchner funnel. The compound was recrystallised from methanol.

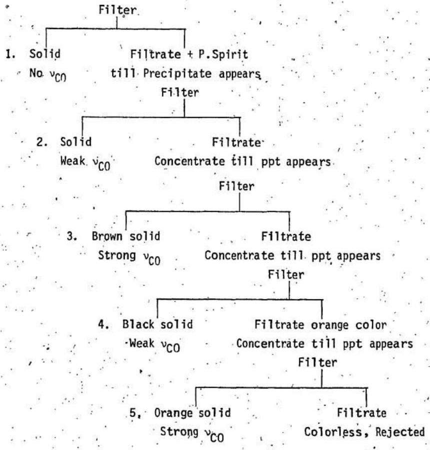
M.P reported 158.5°C

M.P found 159.5°C

Tricarbonylchromium π-complex of bis (CH_3-N-sal) Cu(II)

The same procedure used for zinc complex was employed for the preparation. The complexes were separated and purified by fractional precipitation.

Crude product partially soluble in acetone.



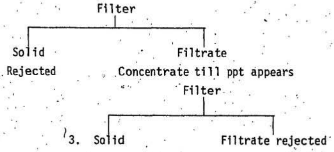
1. The first fraction showed no CO stretching vibrations indicating absence of any carbonyl complex.

Fractions 2 and 4 showed weak CO stretching vibrations indicating that these fractions were impure.

3. Tricarbonylchromium π-complex of bis (CH_3-N-sal) Cu(II)

This fraction was further purified by repeating the process.

Brown solid 3, dissolved in chloroform
+
P.Spirit till precipitate appears



Finally this fraction was recrystallised and an amorphous brown-colored solid obtained. The elemental analysis corresponds with the following formula:

$$Cu(II)\ (CH_3\text{-N-sal})_2\ Cr(CO)_3$$

Calculated = C 48.70, H 3.42, N 5.97, and Cr 11.12%

Found = C 48.46, H 4.74, N 6.10, and Cr 11.03%

The complex starts losing CO's above 100°C and no CO's are left when the temperature reaches 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 31% based on Cu(II) $(CH_3\text{-N-sal})_2$

5. Tricarbonylchromium π-complex of bis (CH_3-N-sal) Cu(II)

This fraction was purified further by the same procedure used for fraction 3 and an orange-colored solid was obtained. The details of this complex are given in Table IV.

Bis (methyl-N-salicylaldiminato) nickel (II) (92)

The same procedure used for copper (II) chelate was employed for preparation.

M.P. reported 206-207°C

M.P. found 208-210°C

Tricarbonylchromium π-complex of bis (CH_3-N-sal) Cr(II)

The same procedure used for the zinc complex was employed for the preparation. A mirror was observed on the wall of the flask and on the lower portion of the Soxhlet when the reaction was completed (Diagram 1). To the (HNO_3) solution of mirror was added 6 molar ammonium hydroxide, drop by drop, until alkaline, then a few drops of dimethylglyoxime gave the plum-red precipitate of bis (dimethylglyoxime) nickel (II), indicating the presence of nickel. A negative test of nickel was shown on the dried product, indicating the replacement of nickel by chromium which was confirmed by quantitative chromium analysis on the complex formed.

$$Ni(CH_3\text{-}N\text{-}sal)_2 + Cr(CO)_6 \longrightarrow Cr(CH_3\text{-}N\text{-}sal)_2 + Ni(CO)_4 + 2CO$$

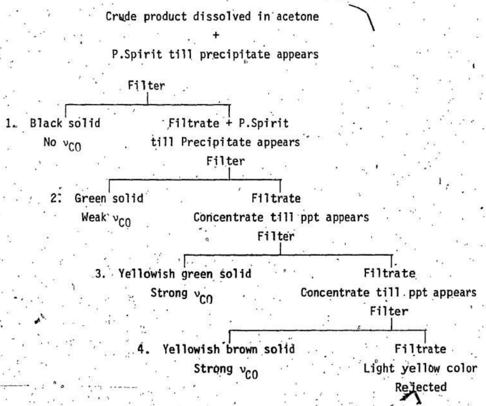
$$Ni(CO)_4 \longrightarrow Ni(0) + 4CO$$

$$Cr(CH_3\text{-}N\text{-}sal)_2 + Cr(CO)_6 \longrightarrow Cr(CH_3\text{-}N\text{-}sal)_2\ Cr(CO)_3 + 3CO$$

The formation of a nickel mirror on the lower part of the Soxhlet cannot be explained unless a very volatile compound of nickel was formed which decomposes readily at that temperature (temperature of reaction 141°C).

Tetracarbonylnickel (B.P 43°C) vaporises quickly and decomposes to the metal readily. No further study has been done to confirm the formation of $Ni(CO)_4$ as an intermediate.

The complexes were separated and purified by fractional precipitation.

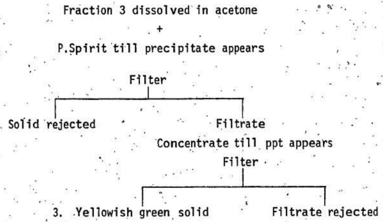


1. The first fraction showed no CO stretching vibrations indicating absence of any carbonyl complex.

2. Second fraction showed weak CO stretching vibrations indicating that this fraction was impure.

3. Tricarbonylchromium π-complex of Cr(II) $(CH_3\text{-N-sal})_2$

This fraction was further purified by repeating the process.



Finally this fraction was recrystallised, an amorphous yellowish-green solid obtained. The elemental analysis corresponds with the following formulae:

$$Cr(II)\ (CH_3\text{-N-sal})_2\ Cr(CO)_3$$

Calculated = C 50.00, H 3.51, N 6.13, and Cr 22.78%

Found = C 49.73, H 4.66, N 6.44, and Cr 2[illegible]00%

The complex starts losing CO's above 100°C and no CO's are left when the temperature reaches 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 8% based on Ni(II) $(CH_3\text{-N-sal})_2$

4. Tricarbonylchromium π-complex of Cr(II) $(CH_3\text{-N-sal})_2$

This fraction was purified further by the same procedure used for fraction 3 and a yellowish-brown solid was obtained. The details of this complex are given in Table IV.

Tris $(CH_3\text{-N-sal})$ Co(III) (93)

To 0.06 moles of salicylaldehyde in 100 ml ethanol was added 0.06 moles of methylamine and to this solution 0.02 moles of cobalt (II) acetate tetrahydrate dissolved in 50 ml of water was added. To the resulting mixture was added dropwise a slight excess of hydrogen peroxide (0.013 moles) with vigorous stirring for 30 minutes. The product obtained was filtered through a buchner funnel and recrystallised from methylene chloride and ethanol mixture as dark green crystals.

M.P reported 246-247°C

M.P found 247-249°C

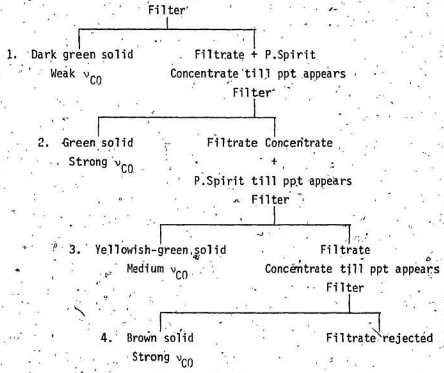
Tricarbonylchromium π-complex of tris $(CH_3\text{-N-sal})$ Co(III)

The same procedure used for the zinc complex was employed for preparation. The complexes were purified and separated by fractional precipitation.

Crude product dissolved in chloroform

\+

P.Spirit till precipitate appears



1. First fraction showed weak CO stretching vibrations indicating that it was impure.

3. Third fraction was considered impure, and was rejected.

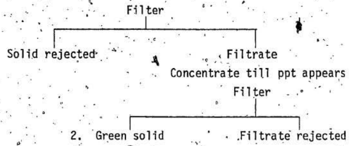
2. Tricarbonylchromium π-complex of tris (CH_3-N-sal) Co(III)

This fraction was purified by repeating the process.

Fraction 2 dissolved in chloroform

+

P.Spirit till precipitate appears



Finally the fraction 2 was recrystallised and an amorphous green solid obtained. A weight loss occurred on drying, and also the weight increases if the complex is left in air. The i.r. of the dried complex in the region 3200-3600 cm^{-1} shows a broad band indicating the presence of lattice water. The elemental analysis corresponds to the presence of two water molecules.

$$Co(III)\ (CH_3\text{-}N\text{-}sal)_3\ Cr(CO)_3.2H_2O$$

Calculated = C 51.20, H 4.42, N 6.64, and Co 9.32%

Found = C 51.87, H 4.56, N 6.83, and Co 9.93%

The complex started losing CO's above 100°C and no CO's were left when the temperature reached 180°C. The rate of decomposition increases when the temperature is raised.

Yield, 22% based on Co(III) $(CH_3\text{-}N\text{-}sal)_3$

4. Tricarbonylchromium π-complex of Co(III) $(CH_3\text{-}N\text{-}sal)_3$

This fraction was purified in the same way as fraction 2. The i.r. of the dried complex shows a broad band in the region 3200-3600 cm^{-1} indicating the presence of lattice water.

The elemental analysis corresponds to the presence of three water molecules.

$Co(III)(CH_3\text{-N-sal})_3(Cr(CO)_3)_2.3H_2O$

Calculated = C 45.75, H 3.84, N 5.34, and Co 7.50%

Found = C 46.10, H 4.46, N 5.15, and Co 8.37%

The complex starts losing CO's above 100°C and is completely decomposed around 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 13% based on $Co(III)(CH_3\text{-N-sal})_3$

Tris (phenyl-N-salicylaldiminato) cobalt (III) (94).

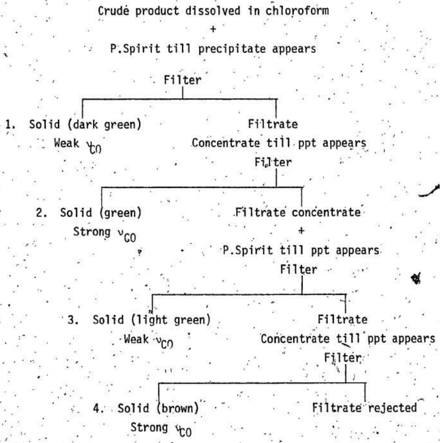
Cobalt (II) acetate tetrahydrate (5.0 g, 0.02 mole) was dissolved in water (50 ml), and the solution filtered and added to a solution of salicylideneaniline (11.0 g, 0.06 mole) in ethanol (300 ml). To the resulting dark red solution was added dropwise a slight excess of hydrogen peroxide (0.013 mole) with vigorous stirring. The dark yellow-brown solution was kept until crystallisation was complete. The product was recrystallised from alcohol and obtained as black green needles.

M.P. reported 194°C

M.P. found 195°C

Tricarbonylchromium π-complex of tris (C_6H_5-N-sal) Co(III)

The same procedure used for the zinc complex was employed for the preparation. The complexes were separated and purified by fractional precipitation.



Fractions 1 and 3 showed weak CO stretching vibrations indicating that they were impure.

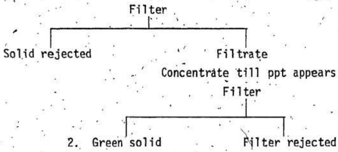
2. Tricarbonylchromium π-complex of Co(III) $(C_6H_5\text{-N-sal})_3$

This fraction was purified by repeating the process,

Fraction 2 dissolved in chloroform

+

P.Spirit till precipitate appears



Finally the fraction 2 was recrystallised and an amorphous green solid was obtained. The details of the complex are given in Table IV.

4. Tricarbonylchromium π-complex of $Co(III)\ (C_6H_5\text{-}N\text{-}sal)_3$

This fraction was purified in the same way as fraction 2. The i.r. of the dried complex shows an intense broad band in the region 3200-3600 cm^{-1} indicating the presence of lattice water. A weight loss occurred on drying, and also the weight increases if the complex is left in the air, suggesting it to be hygroscopic. The elemental analysis of the dried complex corresponds to the presence of 13 water molecules. The complex had perhaps picked up water molecules before elemental analysis.

$$Co(III)\ (C_6H_5\text{-}N\text{-}sal)_3\ (Cr(CO)_3)_2.13H_2O$$

Calculated = C 47.58, H 4.79, N 3.69, and Co 5.18%

Found = C 46.94, H 4.19, N 3.58, and Co 5.45%

The complex starts losing CO's above 100°C and is completely decomposed around 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 7.5% based on $Co(III)\ (C_6H_5\text{-}N\text{-}sal)_3$

In view of the bad C:N ratio the identity of the complex is suspect. It is very likely impure.

Bis (salicylaldehyde) cobalt (II).$2H_2O$ (95)

This complex was prepared by treating a saturated solution of cobalt (II)acetate in 50% alcohol with a stoichiometric amount of salicyldehyde. The reactants were thoroughly mixed and allowed to stand at room temperature until the reaction was complete. The precipitated product was filtered, washed successively with water, alcohol and ether and finally dried.

Bis (phenyl-N-salicylaldiminato) cobalt (II) (42)

To (0.01 mole) bis (salicylaldehyde) cobalt (II) in (50 ml) ethanol was added (0.02 mole) aniline and refluxed on a steam bath for several hours till brick-red crystals started appearing. Crystals obtained were filtered on a buchner funnel, washed with ethanol and then recrystallised from ethanol.

M.P reported 193°C

M.P found 193°C

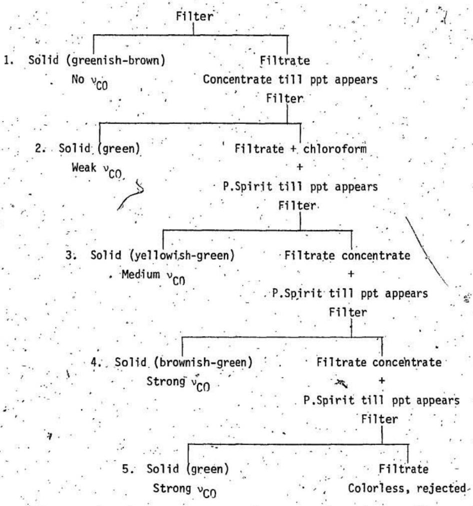
Tricarbonylchromium π-complexes of bis (C_6H_5-N-sal) Co(II)

The same procedure used for the zinc complex was employed for the preparation. The complexes were separated and purified by fractional precipitation.

Crude product dissolved in chloroform

\+

P.Spirit till precipitate appears

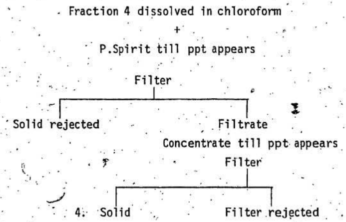


1. First fraction showed no CO stretching vibrations indicating absence of any carbonyl complex.

Fractions 2 and 3 showed weak and medium CO stretching vibrations indicating that they were impure.

4. Tricarbonylchromium π-complex of Co $(C_6H_5\text{-N-sal})_2$

This fraction 4 was purified by repeating the process.



Finally this fraction was recrystallised and an amorphous green solid was obtained. The i.r. of the dried complex shows the presence of water. The elemental analysis corresponds to the presence of three water molecules.

$$Co(II)\ (C_6H_5\text{-N-sal})_2\cdot Cr(CO)_3.3H_2O$$

Calculated = C 54.30, N 4.36, H 4.08, and Co 9.18%

Found = C 54.50, N 4.51, H 4.20, and Co 9.15%

The complex starts losing CO's above 100°C and is completely decomposed around 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 10% based on Co(II) $(C_6H_5\text{-N-sal})_2$

5. Tricarbonylchromium π-complex of Co(II) $(C_6H_5\text{-N-sal})_2$

This fraction was purified the same way as fraction 4. The i.r. of the dried complex shows the presence of water. The elemental analysis of the dried product corresponds to the presence of two water molecules.

$$Co(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3.2H_2O$$

Calculated = C 55.87, H 3.86, N 4.49, and Co 9.45%

Found = C 55.99, H 4.12, N 4.56, and Co 8.27%

The complex starts losing CO's above 100°C and no CO's are left around 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 5% based on $Co(II)(C_6H_5\text{-N-sal})_2$.

Bis (salicylaldehyde) nickel (II).$2H_2O$ (95)

The same procedure used for the cobalt complex was employed for the preparation (page 65).

Bis (phenyl-N-salicylaldiminato) nickel (II) (96)

To (0.01 mole) bis (salicylaldehyde) nickel (II) in 50 ml ethanol was added (0.02 mole) aniline and refluxed for 30 minutes, on cooling dark green crystals were filtered using a buchner funnel and then recrystallised from p-xylene.

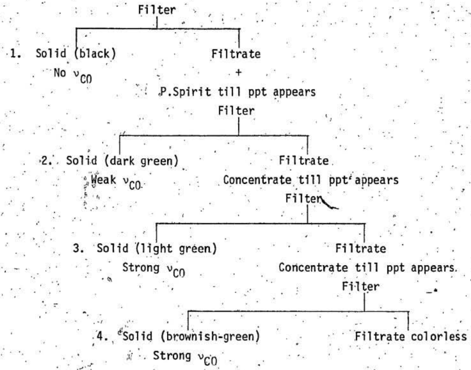
Tricarbonylchromium π-complexes of bis $(C_6H_5\text{-N-sal})$ Cr(II)

The same procedure used for the zinc complex was employed for the preparation. The nickel metal was replaced by chromium, the details of metal replacement are the same as were discussed in the case of bis-$(CH_3\text{-N-sal})$ Cr(II).

$$Ni^{++} + Cr(0) \longrightarrow Cr^{++} + Ni(0)$$

The complexes were separated and purified by fractional precipitation.

The crude product was partially soluble in chloroform.



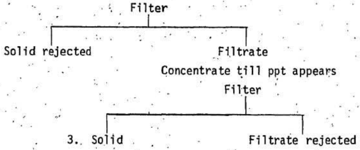
1. First fraction showed no CO stretching vibrations indicating the absence of any carbonyl complex.

2. Second fraction has weak CO stretching vibrations indicating that this fraction was impure.

3. <u>Tricarbonylchromium π-complex of bis (C_6H_5-N-sal) Cr(II)</u>

This fraction was further purified by repeating the process.

Fraction 3 dissolved in acetone
+
P.Spirit till ppt appears



Finally this fraction was recrystallised and an amorphous yellowish-green solid obtained. The i.r. of the dried complex shows the presence of water. The elemental analysis of the dried complex corresponds to the presence of three water molecules.

$$Cr(II)\ (C_6H_5\text{-N-sal})_2\ Cr(CO)_3,3H_2O$$

Calculated = C 54.89, H 4.13, N 4.41, and Cr 16.38

Found = C 54.93, H 4.35, N 4.28, and Cr 16.12%

The complex starts losing CO's above 100°C and no CO's are left when the temperature reaches 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 35% based on Ni(II) $(C_6H_5\text{-N-sal})_2$

4. Tricarbonylchromium π-complex of bis $(C_6H_5\text{-N-sal})_2$ Cr(II)

This fraction was purified as fraction 3. The i.r. of the dried complex shows the presence of water. The elemental analysis of the dried complex corresponds to the presence of four water molecules.

$$Cr(II)\ (C_6H_5\text{-N-sal})_2\ (Cr(CO)_3)_2.4H_2O$$

Calculated = C 48.73, H 3.57, N 3.55, and Cr 19.85%

Found = C 49.93, H 3.98, N 3.88, and Cr 19.63%

The complex starts losing CO's above 100°C and is completely decomposed around 180°C. The rate of decomposition increases as the temperature is raised.

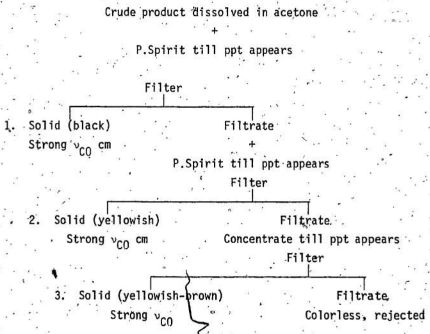
Yield, 5% based on Ni(II) $(C_6H_5\text{-N-sal})_2$

Bis (phenyl-N-salicylaldiminato) zinc (II) (97).

To (0.01 mole) bis (salicylaldehyde) zinc (II) in (50 ml) ethanol was added (0.02 mole) aniline and stirred for 3 hours at 25°C. The yellow crystals formed were filtered, washed with a slight amount of ethanol and then recrystallised from ethanol.

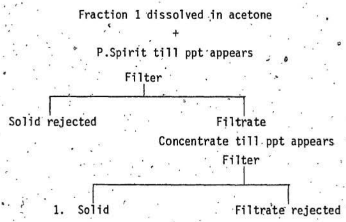
Tricarbonylchromium π-complexes of bis $(C_6H_5\text{-N-sal})$ Zn(II)

The same procedure used for the zinc complex was employed for the preparation. The complexes were separated and purified by fractional precipitation.



1. Tricarbonylchromium π-complex of bis $(C_6H_5\text{-N-sal})$ Zn(II)

This fraction was further purified by repeating the process.



Fraction 1 dissolved in acetone
+
P.Spirit till ppt appears
Filter
Solid rejected
Filtrate
Concentrate till ppt appears
Filter
1. Solid
Filtrate rejected

Finally the fraction 1 was recrystallised and an amorphous light brown solid obtained. The i.r. of the dried complex shows the presence of water. The details of this complex are given in Table IV.

2. This fraction was considered a mixture of 1 and 3 and was rejected.

3. Tricarbonylchromium π-complex of Zn(II) $(C_6H_5\text{-N-sal})_2$

This fraction was purified as fraction 1. The i.r. of the dried complex shows the presence of water. The elemental analysis of the dried complex corresponds to the presence of four water molecules.

$$\mathrm{Zn(II)}\ (C_6H_5\text{-N-sal})_2\ (Cr(CO)_3)_3 \cdot 4H_2O$$

Calculated = C 44.81, H 3.00, N 2.99, and Cr 16.62%
Found = C 45.37, H 3.79, N 2.70, and Cr 16.50%

The complex starts losing CO's above 100°C and no CO's are left above 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 14% based on Zn(II) $(C_6H_5\text{-N-sal})_2$

Bis (phenyl-N-salicylaldiminato) copper (II)

The same procedure used for nickel (II) complex was employed for the preparation.

Tricarbonylchromium π-complex of Cu(II) $(C_6H_5\text{-N-sal})_2$

The same procedure used for the zinc complex was employed for the preparation. The complexes were separated and purified by fractional precipitation.

Crude product partially soluble in acetone.

Filter

1. Solid (dark green) — No ν_{CO}

Filtrate + P.Spirit till ppt appears

Filter

2. Solid (green) — Weak ν_{CO}

Filtrate — Concentrate till ppt appears

Filter

3. Solid (light green) — Strong ν_{CO}

Filtrate — Concentrate till ppt appears

Filter

4. Solid (brown) — Strong ν_{CO}

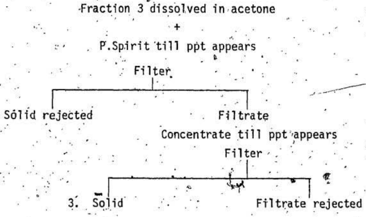
Filtrate — Light color, rejected

1. First fraction showed no CO stretching vibrations indicating absence of any carbonyl complex.

2. Second fraction showed weak CO stretching vibrations indicating that this fraction was impure.

3. Tricarbonylchromium π-complex of Cu(II) $(C_6H_5\text{-N-sal})_2$

This fraction was purified by repeating the process.



Finally this fraction was recrystallised and an amorphous green solid obtained.

The i.r. of the dried complex shows the presence of water. The elemental analysis of the dried complex corresponds to the presence of five water molecules.

$$Cu(II)\ (C_6H_5\text{-N-sal})_2\ Cr(CO)_3\ 5H_2O$$

Calculated = C 51.08, H 4.41, N 4.11, and Cr 7.63%

Found = C 51.07, H 4.22, N 3.91, and Cr 7.93%

The complex starts losing CO's above 100°C and no CO's are left around 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 22% based on Cu(II) $(C_6H_5\text{-N-sal})_2$

4. Tricarbonylchromium π-complex of Cu(II) $(C_6H_5\text{-N-sal})_2$

This fraction was purified in the same way as fraction 3. The details of this complex are given in Table IV.

N-N-ethylenebis (salicylideneiminato) cobalt (II) (98,99,100)

Cobalt acetate tetrahydrate (0.02 mole) was dissolved in a mixture of solvents (EtOH 100 ml + H_2O 20 ml) by heating under nitrogen. This solution was added to the Schiff base (0.02 moles in 50 ml EtOH) already heated (below the boiling point of EtOH) in a nitrogen atmosphere and stirred at that temperature for 15 minutes. On cooling, small violet-brown crystals were obtained. The crystals obtained were washed with distilled water, alcohol and petroleum ether in an atmosphere of nitrogen. The crystals were dried under vacuum.

Tricarbonylchromium π-complex of Co(II) (salen)

The same procedure used for the zinc complex was employed for the preparation. The complex was separated from the reaction product by fractional precipitation. The whole process of separation and purification was carried out under nitrogen and nitrogen was passed through solvents (chloroform and P.Spirit) before they were used. Three fractions were obtained: 1. First and third fractions showed weak CO stretching vibrations indicating that these fractions were impure. 2. Second fraction showed strong CO stretching vibrations and was purified by repeating the precipitation process. Finally, fraction 2 was recrystallised and an amorphous brown solid was obtained.

The i.r. of the dried complex shows the presence of water. The elemental analysis of the dried complex corresponds to the presence of two water molecules.

$$\mathrm{Co(II)\ (salen)\ Cr(CO)_3.2H_2O}$$

Calculated = C 46.00, H 3.63, N 5.67, and Cr 10.46%

Found = C 46.75, H 3.89, N 5.65, and Cr 10.63%

The complex starts losing CO's above 100^{o}C and was completely decomposed around 185^{o}C. The rate of decomposition increases as the temperature is raised.

Yield, 53% based on Co(II) (salen)

N-N-ethylenebis (salicylideneiminato) zinc (II) (101)

To (0.04 mole) salicylaldehyde in 100 ml ethanol was added (0.02 mole) zinc acetate and kept warm while stirring for 20 minutes. To this warm solution was added (0.02 mole) ethylenediamine and stirred for another 30 minutes. The Zn(II) (salen) formed was filtered, washed with distilled water and then recrystallised from ethanol.

Tricarbonylchromium π-complex of Zn(II) (salen)

The same procedure used for the zinc complex was employed for the preparation. The separation of the complex from the reaction product was achieved by extracting the complex with chloroform using a Soxhlet in a nitrogen atmosphere. The extracted complex was recrystallised from chloroform and petroleum spirit and an amorphous yellowish solid was obtained. The i.r.

of the dried complex shows the presence of water. The elemental analysis of the dried complex corresponds to the presence of two water molecules.

$$Zn(II)\ (salen)\ Cr(CO)_3.2H_2O$$

Calculated = C 45.40, H 3.58, N 5.57, and Cr 10.32%

Found = C 45.51, H 3.67, N 5.53, and Cr 10.71%

The complex starts decomposing above 100°C and was completely decomposed around 185°C. The rate of decomposition increases as the temperature is raised.

Yield, 7% based on Zn(II) (salen)

N-N'-ethylenebis (salicylideneiminato) copper (II) (102)

The same procedure used for Zn(II) (salen) was employed for the preparation.

M.P reported 322°C

M.P found 324°C

Tricarbonylchromium π-complex of Cu(II) (salen)

The same method used for the zinc complex was employed for this preparation. The separation and purification was achieved by fractional precipitation using chloroform and petroleum spirit. There were four fractions: the fractions 1, 2 and 3 showed weak CO stretching vibrations and were considered impure. The fourth fraction had strong CO stretching vibrations and was further purified by repeating the precipitation process. Finally on recrystallisation an amorphous brownish-green solid was obtained. The i.r. of the dried complex shows the presence of water. The elemental analysis of the dried complex corresponds to the presence of two water molecules.

Cu(II) (salen) $Cr(CO)_3 \cdot 2H_2O$

Calculated = C 45.46, H 3.99, N 5.58, and Cr 10.36%

Found = C 45.38, H 4.92, N 5.77, and Cr 10.52%

The complex starts losing CO's above 100°C and was completely decomposed around 180°C. The rate of decomposition increases as the temperature is raised.

Yield, 11% based on Cu(II) (salen)

<u>N-N-ethylenebis (salicylideneiminato) nickel (II) (102)</u>

The same procedure used for Cu(II) (salen) was employed for the preparation.

M.P. reported 330°C

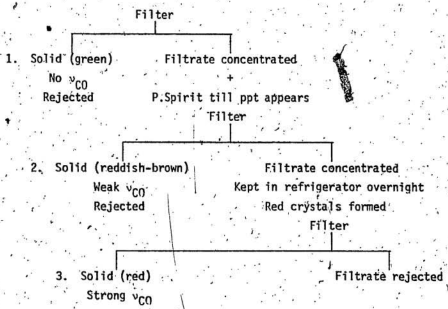
M.P. found 332°C

<u>Tricarbonylchromium π-complex of Ni(II) (salen)</u>

The same procedure used for the zinc complex was employed for the preparation. In this reaction nickel metal was not replaced by chromium as compared to CH_3 and C_6H_5 Schiff base nickel chelates (where it was replaced by chromium).

The separation and purification was achieved by fractional precipitation.

Reaction product was partially soluble in chloroform.



Fraction 3 was recrystallised and red crystals were obtained. The i.r. of the dried complex showed the presence of water. The elemental analysis of the dried complex corresponds to the presence of one water molecule.

$$\mathrm{Ni(II)\,(salen)\,Cr(CO)_3 \cdot H_2O}$$

Calculated = C 47.63, H 3.76, N 5.84, and Cr 10.86%

Found = C 47.93, H 3.56, N 5.86, and Cr 10.71%

This complex is not as stable as other complexes; if stored for some time it decomposes.

Yield, 9% based on Ni(II) (salen)

<u>Some Unidentified Complexes</u>

The details of these complexes are given in Table IV. The i.r. of the dried complexes (where molecular formula includes xH_2O) show a broad band in the region 3,200-3,600 cm^{-1} indicating the presence of lattice water. The weight measurements before and after drying show the loss of weight, and also the weight increases if the complexes are left in the air. The molecular weight could not be determined because of lack of sufficient solubility and mass spectra could not be recorded because of decomposition and non-volatility of all these complexes.

The purity of these complexes was checked by thin layer chromatography.* The elemental analysis does not agree with the expected molecular formula and various other possibilities.

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*In most of the cases the TLC method was not effective because the spot did not move at all, but in some cases the spot did move with a tail and in others without a tail. The places where only one spot was seen were considered to be pure. The adsorbed compound could not be eluted.

TABLE IV

Some unidentified complexes

Complex	Elemental Analysis	Yield	Decomposition Temperature
$[Co(II)\ (CH_3\text{-N-sal})_2]_x[Cr(CO)_3]_x \times H_2O$	Found = C 52.26, H 5.08, N 5.97, and Cr 14.20%	23% based on $Co(II)\ (CH_3\text{-N-sal})_2$	180°C
$[Cu(II)\ (CH_3\text{-N-sal})_2]_x[Cr(CO)_3]_x$	Found = C 58.80, H 5.33, N 7.17, and Cr 13.9%	5% based on $Cu(II)\ (CH_3\text{-N-sal})_2$	160°C
$[Cr(II)\ (CH_3\text{-N-sal})_2]_x[Cr(CO)_3]_x$	Found = C 56.42, H 5.43, N 6.90, and Cr 20.12%	30% based on $Ni(II)\ (CH_3\text{-N-sal})_2$	180°C
$[Co(III)\ (C_6H_5\text{-N-sal})_3]_x[Cr(CO)_3]_x \times H_2O$	Found = C 59,66, H 4.49, and N 46.30	35% based on $Co(III)\ (C_6H_5\text{-N-sal})_3$	180°C
$[Zn(II)\ (C_6H_5\text{-N-sal})_2]_x[Cr(CO)_3]_x \times H_2O$	Found = C 33.28, H 3.34, N 1.65, and Cr 17.25%	19% based on $Zn(II)\ (C_6H_5\text{-N-sal})_2$	180°C
	Identified Complex		
$Cu\ (C_6H_5\text{-N-sal})_2\ Cr(CO)_3\ 3H_2O$	Found = C 5528, H 417, and N 4.47 Cal = C 55.47, H 3.85, and N 4.46	13% based on $Cu(II)\ (C_6H_5\text{-N-sal})_2$	180°C

IV.

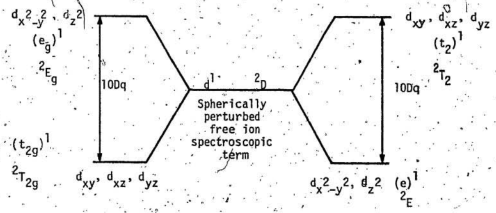
INTRODUCTION TO DISCUSSION

Electronic spectra of transition metal complexes

The energy required for the promotion of an electron from one orbital to another or more precisely the excitation of a molecule from its electronic ground state to an electronic excited state corresponds to absorption of light in the near infra-red, visible or ultraviolet region of the spectrum. For first row transition metal complexes the absorption bands in the first two of these regions are relatively weak and are associated with transitions largely localized on the metal atom. The ultraviolet bands are usually intense. They are associated with the transfer of an electron from one atom to another and so are called charge transfer bands.

The weak bands in the near infra-red and visible region are explained by crystal field theory and the predictions of the spectra can be made on the basis of crystal field theory and the electronic configuration of the transition metal. The crystal field spectrum of a d^1 system is considered first. The free ion state for d^1 is ^2D. The D state is split into T_{2g} and E_g levels by the octahedral ligand field. In the case of a strong crystal field the single electron may either occupy the t_{2g} level or the e_g level. Hence there are two possible configurations, $t_{2g}{}^1$ and $e_g{}^1$. The crystal field splitting of a d^1 system in an octahedral and tetrahedral environment is shown in Fig. 32.

One band is predicted corresponding to the electronic transition in the d^1 system ($T_{2g} \longrightarrow E_g$ or $E \longrightarrow T_2$). The d^9 ion (one hole in the d shell) behaves in an electrostatic field just like the d^1 ion, except for a reversal in the sign of the energy of interaction. The situation is a bit complicated



Octahedral Field   Tetrahedral Field

Fig. 32

in the d^9 case because of Jahn-Teller distortion. The splitting of the electronic energy levels of a d^9 ion in crystal fields of octahedral, tetrahedral and lower symmetries are shown below (Fig. 33). The number

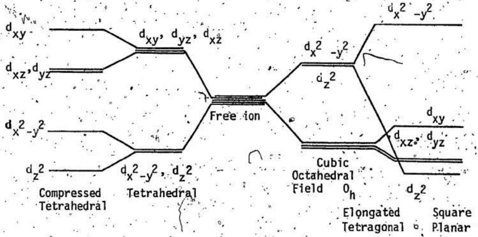


Fig. 33

of bands in the d^9 case will depend upon the distortion from octahedral or tetrahedral environment. If there is no distortion only one band is predicted. The spectrum of the d^2 system is not as simple as a one electron system. The electrons can be placed in several different ways in the e_g and t_{2g} levels in an octahedral field (Fig. 34).

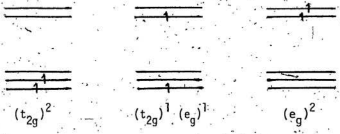


Fig. 34

The free ion d^2 terms would split in a weak octahedral field as follows:

$^3F \longrightarrow {}^3A_{2g};\ {}^3T_{2g};\ {}^3T_{1g}$

$^3P \longrightarrow {}^3T_{1g}$

$^1D \longrightarrow {}^1T_{2g};\ {}^1E_g$

$^1G \longrightarrow {}^1A_{1g};\ {}^1T_{2g};\ {}^1T_{1g};\ {}^1E_g$

$^1S \longrightarrow {}^1A_{1g}$

However, if we use a strong field approach, the ground state configuration would be $(t_{2g})^2$. From Fig. 34 the first and second excited states would then be $(t_{2g})^1\,(e_g)^1$ and $(e_g)^2$. The energy separation between $(t_{2g})^2$ and $(t_{2g})^1\,(e_g)^1$ would then be 10 Dq. In the absence of interelectronic interaction the energy difference between the $(t_{2g})^1 (e_g)^1$ and $(e_g)^2$ would also be 10 Dq. However, in the presence of interelectronic repulsion, the different electronic configurations give rise to a number of terms. The direct products can be obtained from group theory (103). The direct products would then be:

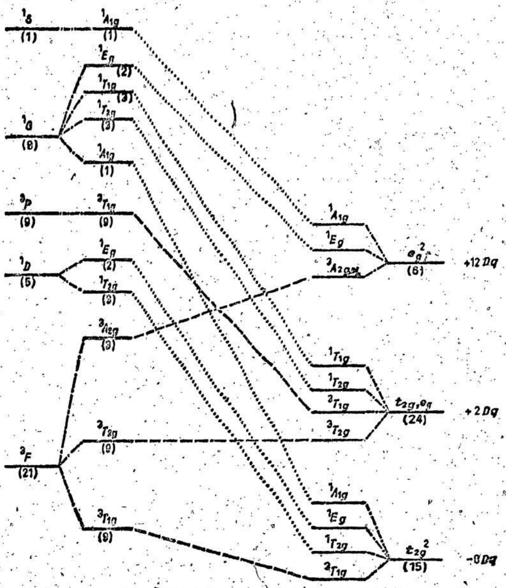
$$t_{2g} \times t_{2g} = {}^1A_{1g} + {}^1E_g + {}^3T_{1g} + {}^1T_{2g}$$
$$t_{2g} \times e_g = {}^1T_{1g} + {}^1T_{2g} + {}^3T_{1g} + {}^3T_{2g}$$
$$e_g \times e_g = {}^1A_{1g} + {}^3A_{2g} + {}^1E_g$$

A complete correlation diagram for the d^2 case in a strong and weak field environment is given in Fig. 35 (104). The method of constructing such diagrams may be found in standard textbooks (104-106). The strong field terms are listed to the right and the weak field terms to the left in the diagram. The spectroscopic terms can be obtained from atomic spectroscopy (104).

The spin selection rule allows transitions only within the same spin multiplicity. Three allowed transitions are predicted in a d^2 octahedral spectrum.

$${}^3T_{1g}(F) \longrightarrow {}^3T_{2g} \ (\nu_1)$$
$${}^3T_{1g}(F) \longrightarrow {}^3A_{2g} \ (\nu_2)$$
$${}^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P) \ (\nu_3)$$

The ${}^3T_{1g}(F) \longrightarrow {}^3A_{2g}$ is a two-electron transition in a d^2 system and is forbidden by the spin selection rule. This band is at times observed as a



^1S (1)
^1G (9)
^3P (9)
^1D (5)
^3F (21)
$^1A_{1g}$ (1)
^1E_g (2)
$^1T_{1g}$ (3)
$^1T_{2g}$ (3)
$^1A_{1g}$ (1)
$^3T_{1g}$ (9)
^1E_g (2)
$^1T_{2g}$ (3)
$^3A_{2g}$ (3)
$^3T_{2g}$ (9)
$^3T_{1g}$ (9)
$^1A_{1g}$
^1E_g
$^3A_{2g}$
e_g^2 (6)
+12 Dq
$^1T_{1g}$
$^1T_{2g}$
$^3T_{1g}$
$^3T_{2g}$
t_{2g}, e_g (24)
+2 Dq
$^1A_{1g}$
^1E_g
$^1T_{2g}$
$^3T_{1g}$
t_{2g}^2 (15)
-8 Dq

Fig. 35 (104)

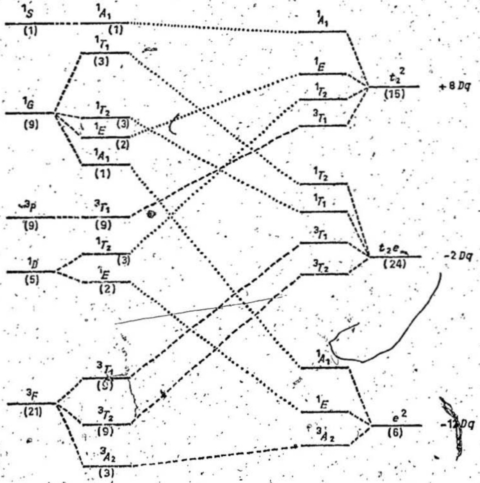

^1S
(1)
$^1A_1$
(1)
$^1T_1$
(3)
^1G
(9)
$^1T_2$
(3)
^1E
(2)
$^1A_1$
(1)
^3P
(9)
$^3T_1$
(9)
^1D
(5)
$^1T_2$
(3)
^1E
(2)
^3F
(21)
$^3T_1$
(9)
$^3T_2$
(9)
$^3A_2$
(3)
$^1A_1$
^1E
$^1T_2$
$^3T_1$
t_2^2
(15)
+8 Dq
$^1T_2$
$^1T_1$
$^3T_1$
$^3T_2$
t_2e
(24)
-2 Dq
$^1A_1$
^1E
$^3A_2$
e^2
(6)
-12 Dq

Fig. 36 (104)

weak band. The energy of transition ν_2 may occur at a higher or lower energy than ν_3 according to the strength of the crystal field.

The tetrahedral d^2 system has a correlation diagram which is the inverse of the octahedral d^2 case (Fig. 36). The d^8 ion can be considered a two-hole system and will be the reverse of a d^2 case. Three transitions are also predicted for a d^8 system.

In a d^3 ion the spin quartet states are ^4F and ^4P. The ^4F term will give rise to a $^4A_{2g}$ ground term and $^4T_{1g}$ and $^4T_{2g}$ terms at higher energies. The ^4P will give rise to the $^4T_{1g}(P)$ term. The energy level splitting diagram for d^3 ion is given in Fig. 37.

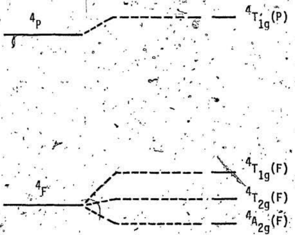


Fig. 37

One would also expect in principle three bands from the orbital singlet ground state $^4A_{2g}$. The $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ is a two-electron transition but becomes allowed because of the mixing of the $^4T_{1g}(F)$ and $^4T_{1g}(P)$ terms. The detailed energy correlation diagrams for d^3, d^4, d^6, and d^7 can be found in standard textbooks. The Orgel diagram can be consulted (Fig. 38) only for spin allowed transitions in purely octahedral

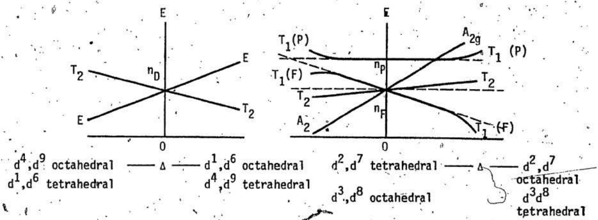


Fig. 38

and tetrahedral cases. According to the Orgel (107) diagram one spin allowed absorption is expected for d^1, d^9, d^6, d^4 systems and three spin allowed absorptions for d^2, d^3, d^7, and d^8 systems. In practice, all observed bands cannot b explained by Orgel diagrams. A complete correlation diagram or Tanabe and Sugano graphs are needed to explain all the bands.

Tanabe and Sugano (108) calculated the energies of the various terms as a function of the octahedral field splitting parameter 10 Dq and interelectronic parameter B. (The same diagram can be used to interpret tetrahedral complexes by reversing the sign and dropping the g suffix.) Tanabe and Sugano diagrams (Figs. 39, 40) have two special features Firstly, they are plots of 10 Dq/B versus E/B so that B is a function of ligand and of the metal. (The diagrams can be used for any ligand assuming spin orbit coupling phenomena to be negligible.) Secondly, the ground term is made the horizontal base line so that absorption transition energies may be estimated simply by vertical measurements from the base line. In this way experimental results may be compared with theory by fitting the observed bands to the Tanabe and Sugano diagrams with an appropriate value of 10 Dq/B.

Accurate values of Dq and B can be obtained by solving the simultaneous equations (109).

Octahedral d^3 and d^8, and tetrahedral d^2 and d^7 species

$$T_{2g} \longleftarrow A_{2g}\ (\nu_1)\ 10\ Dq$$

$$T_{1g}(F) \longleftarrow A_{2g}\ (\nu_2)\ 7.5\ B + 15\ Dq - \tfrac{1}{2}(225\ B^2 + 100\ Dq^2 - 180\ DqB)^{\frac{1}{2}}$$

$$T_{1g}(P) \longleftarrow A_{2g}\ (\nu_3)\ 7.5\ B + 15\ Dq + \tfrac{1}{2}(225\ B^2 + 100\ Dq^2 - 180\ DqB)^{\frac{1}{2}}$$

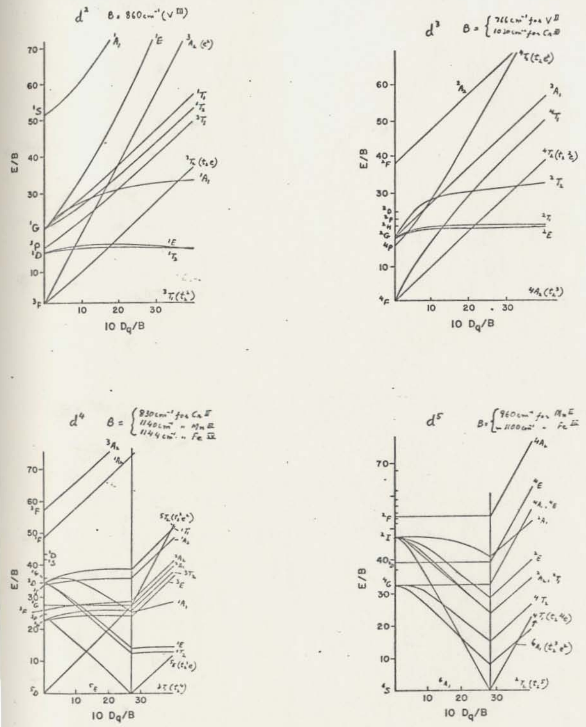

d²
B = 860 cm⁻¹ (V III)
d³
B = { 766 cm⁻¹ for V II / 1030 cm⁻¹ for Cr III
d⁴
B = { 830 cm⁻¹ for Cr II / 1140 cm⁻¹ " Mn III / 1144 cm⁻¹ " Fe IV
d⁵
B = { 960 cm⁻¹ for Mn II / ~1100 cm⁻¹ " Fe III
E/B
10 Dq/B
10
20
30
40
50
60
70
¹S
¹G
³P
¹D
³F
¹A₁
¹E
³A₂ (e²)
¹T₁
¹T₂
³T₁
³T₂ (t₂e)
¹A₁
¹E
¹T₂
³T₁ (t₂²)
²A₂
⁴T₁ (t₂e²)
²A₁
⁴T₁
⁴T₂ (t₂²e)
²T₂
²T₁
²E
²F
²D
²P
²H
²G
⁴P
⁴F
⁴A₂ (t₂³)
³A₂
¹A₂
³F
¹F
¹D
¹S
³G
³D
¹G
³H
³P
⁵D
⁵E
⁵T₂ (t₂³e²)
¹T₁
¹A₂
³A₂
³T₂
³E
¹A₁
¹E
¹T₂
⁵E (t₂³e)
³T₁ (t₂⁴)
⁴A₂
⁴E
⁴A₁, ⁴E
²A₁
²E
²A₂, ²T₁
⁴T₂
⁴T₁ (t₂⁴e)
⁶A₁ (t₂³e²)
⁶A₁
²T₂ (t₂⁵)
²F
²I
⁴D
⁴G
⁶S

Fig. 39 (108)

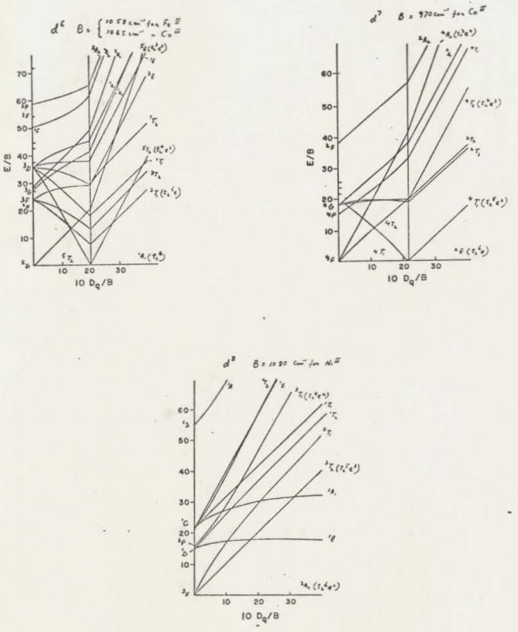

d6 B = { 1058 cm-1 for Fe II
1065 cm-1 - Co III
E/B
10 Dq/B
5D
3H
3F
3G
3D
1F
3P
5T2
5E(t2^3e^2)
1E
3E
1T2
5T2(t2^4e^2)
1T1
3T2
3T1(t2^5e)
1A1(t2^6)
d7 B = 970 cm-1 for Co II
E/B
10 Dq/B
4F
4P
2G
2F
4T1
4T2
2A2
4A2(t2^3e^4)
4T1
4T2(t2^4e^3)
2T2
2T1
4T1(t2^5e^2)
2E(t2^6e)
d8 B = 1080 cm-1 for Ni II
E/B
10 Dq/B
3F
1D
3P
1G
1S
1A1
1T2
1E
3T1(t2^4e^4)
1T1
1T2
3T1
3T2(t2^5e^3)
1A1
1E
3A2(t2^6e^2)

Fig. 40 (108)

Octahedral d^2 and d^7, tetrahedral d^3 and d^8 species

$$T_{2g} \longleftarrow T_{1g}(\nu_1)\ 5\ Dq - 7.5\ B + \tfrac{1}{2}(225\ B^2 + 100\ Dq^2 + 180\ DqB)^{\frac{1}{2}}$$

$$A_{2g} \longleftarrow T_{1g}(\nu_2)\ 15\ Dq - 7.5\ B + \tfrac{1}{2}(225\ B^2 + 100\ Dq^2 + 180\ DqB)^{\frac{1}{2}}$$

$$T_{1g}(P) \longleftarrow T_{1g}(\nu_3)\ (225\ B^2 + 100\ Dq^2 + 180\ DqB)^{\frac{1}{2}}$$

(The g suffix should be dropped for tetrahedral species.)

$$\nu_2 + \nu_3 - 3\nu_1 = 15\ B$$

Overall, if we consult the Tanabe and Sugano diagrams, the equations (above) and transition energy ratios (Table V) (109), the valuable quantities like 10 Dq, B, C, and the position of an unknown band (ν_1, ν_2 or ν_3) can be calculated from the observed spectrum.

The parameter B can throw light on the nature of bonding between metal and ligand. The value of B increases with increasing oxidation state and with the number of electrons in the d shell. The primary factor is the size of the ion. Since the size of the ion is related to the effective nuclear charge experienced by the d electrons, it follows that B is not only a measure of size, but also of effective nuclear charge.

If the bonding between metal and ligand becomes partially covalent a decrease in B is expected. The e_g electrons will become σ antibonding and will therefore spend some of their time on the ligand (O_h complex). The t_{2g} electrons may become π-bonding or antibonding, depending upon the ligand, and will also spend some time on the ligand. A small amount of σ and π-electron density on the metal may be transferred onto the ligand. Such a delocalization will increase the mean distance between the d

TABLE V (109)

Transition Energy Ratios

Dq/B	A_2 Ground State				T_1 Ground State			
	ν_1/B	ν_2/ν_1	ν_3/ν_1	ν_3/ν_2	ν_1/B	ν_2/ν_1	ν_3/ν_1	ν_3/ν_2
0.05	15.60	1.794	31.21	17.39	15.31	2.242	38.02	16.96
0.1	16.21	1.789	16.21	9.062	15.62	2.234	19.28	8.629
0.15	16.83	1.783	11.22	6.291	15.95	2.227	13.04	5.857
0.2	17.45	1.777	8.723	4.909	16.28	2.220	9.930	4.473
0.25	18.07	1.771	7.230	4.083	16.62	2.213	8.067	3.645
0.3	18.71	1.764	6.236	3.535	16.97	2.207	6.828	3.094
0.35	19.35	1.757	5.529	3.147	17.33	2.201	5.947	2.702
0.4	20.00	1.750	5.000	2.857	17.69	2.196	5.288	2.408
0.45	20.66	1.743	4.591	2.634	18.06	2.190	4.777	2.181
0.5	21.32	1.735	4.265	2.458	18.44	2.185	4.370	2.000
0.55	22.00	1.727	4.000	2.316	18.82	2.180	4.038	1.852
0.6	22.69	1.719	3.781	2.199	19.21	2.175	3.763	1.730
0.65	23.38	1.711	3.597	2.102	19.60	2.171	3.531	1.627
0.7	24.08	1.703	3.440	2.021	20.00	2.167	3.333	1.539
0.75	24.80	1.694	3.306	1.952	20.40	2.163	3.163	1.462
0.8	25.52	1.685	3.190	1.893	20.81	2.159	3.014	1.396
0.85	26.26	1.676	3.089	1.843	21.22	2.155	2.883	1.338
0.9	27.0	1.667	3.000	1.800	21.63	2.151	2.768	1.286
0.95	27.76	1.657	2.922	1.763	22.05	2.148	2.665	1.241
1.0	28.52	1.648	2.852	1.731	22.47	2.145	2.572	1.199
1.1	30.08	1.629	2.735	1.679	23.32	2.139	2.414	1.129
1.2	31.69	1.610	2.640	1.640	24.19	2.133	2.283	1.071
1.3	33.33	1.590	2.563	1.612	25.06	2.128	2.174	1.022
1.4	35.00	1.571	2.500	1.591	25.94	2.123	2.080	0.980
1.5	36.70	1.553	2.447	1.576	26.83	2.118	2.000	0.944
1.6	38.45	1.535	2.403	1.566	27.73	2.114	1.930	0.913
1.7	40.21	1.517	2.365	1.559	28.64	2.110	1.869	0.886
1.8	42.00	1.500	2.333	1.556	29.55	2.106	1.816	0.862
1.9	43.81	1.484	2.306	1.554	30.46	2.103	1.768	0.841
2.0	45.64	1.468	2.282	1.554	31.39	2.099	1.725	0.822
2.1	47.49	1.453	2.261	1.556	32.31	2.096	1.687	0.805
2.2	49.35	1.439	2.243	1.559	33.24	2.093	1.652	0.789
2.3	51.22	1.425	2.227	1.563	34.18	2.091	1.621	0.775
2.4	53.11	1.412	2.213	1.567	35.11	2.088	1.592	0.762
2.5	55.00	1.400	2.200	1.571	36.06	2.086	1.566	0.751
2.6	56.90	1.388	2.189	1.577	37.00	2.083	1.542	0.740
2.7	58.82	1.377	2.178	1.582	37.95	2.081	1.520	0.730
2.8	60.74	1.367	2.169	1.587	38.90	2.079	1.499	0.721
2.9	62.66	1.357	2.161	1.593	39.85	2.077	1.480	0.713
3.0	64.59	1.347	2.153	1.599	40.80	2.075	1.462	0.705
3.1	66.53	1.338	2.146	1.604	41.76	2.073	1.446	0.697
3.2	68.47	1.329	2.140	1.610	42.72	2.072	1.431	0.691
3.3	70.42	1.321	2.134	1.616	43.68	2.070	1.416	0.684
3.4	72.37	1.313	2.128	1.621	44.64	2.069	1.403	0.678
3.5	74.32	1.305	2.123	1.627	45.61	2.067	1.390	0.673
3.6	76.27	1.298	2.119	1.632	46.57	2.066	1.378	0.667
3.7	78.23	1.291	2.114	1.638	47.54	2.064	1.367	0.662
3.8	80.19	1.284	2.110	1.643	48.51	2.063	1.357	0.658
3.9	82.16	1.278	2.107	1.648	49.48	2.062	1.347	0.653
4.0	84.12	1.272	2.103	1.653	50.45	2.060	1.337	0.649
4.1	86.09	1.266	2.100	1.658	51.42	2.059	1.328	0.645
4.2	88.06	1.261	2.097	1.663	52.39	2.058	1.320	0.641
4.3	90.03	1.256	2.094	1.668	53.37	2.057	1.312	0.638
4.4	92.00	1.250	2.091	1.673	54.34	2.056	1.304	0.634
4.5	93.97	1.245	2.088	1.677	55.32	2.055	1.297	0.631
4.6	95.95	1.240	2.086	1.682	56.29	2.054	1.290	0.628
4.7	97.93	1.235	2.084	1.686	57.27	2.053	1.283	0.625
4.8	99.90	1.231	2.081	1.691	58.25	2.052	1.277	0.622
4.9	101.9	1.227	2.079	1.695	59.22	2.051	1.271	0.619
5.0	103.9	1.223	2.077	1.699	60.21	2.050	1.265	0.617

electrons and thereby reduce B. Central field covalency probably plays the major part in the reduction of B in transition metal complexes.

It can be reasonably argued that the greated the reduction in β as represented by the ratio

$$\frac{\text{B in complex}}{\text{B in free ion}} = \frac{B}{B_0} = \beta$$

the greated the covalency in the metal ligand bond and the smaller the effective charge experienced by the d electrons.

V.

Magnetic properties of inorganic compounds (110-113)

Magnetic moments of transition metal ions in units of Bohr magnetons are very useful in determining the stereochemistry and bonding of complexes. The main contribution to bulk magnetic properties of substances arises from magnetic moments resulting from motion of charged electrons. Effects from nucleons are minor and can be ignored.

Substances which contain one or more unpaired electrons have a permanent magnetic moment which exists in the absence of the magnetic field and arises from the net spin and orbital angular momentum of the unpaired electrons. Such a substance is attracted into a magnetic field with a force proportional to the field strength times the field gradient and is called paramagnetic.

Magnetic moments cannot be measured directly. Instead, one measures the susceptibility of a material from which it is possible to calculate magnetic moments. When a substance is placed in a magnetic field H, the magnetic induction B is given by

$$B = H + 4\pi I/H$$

$$I/H = k$$

$$B/H = I + 4\pi k$$

The ratio B/H is called the magnetic permeability of the material, I the intensity of magnetization and k the magnetic susceptibility per unit volume.

It is convenient to measure the gram susceptibility, and the following relationship exists:

$$\chi_g = \frac{k}{\text{density}}$$

The molar susceptibility is given by

$$\chi_M = \chi_g \times \text{mol wt} \quad .$$

The molar susceptibility is corrected for diamagnetic contribution and TIP (temperature independent paramagnetism).

The corrected molar susceptibility χ_M^{corr} in a noninteracting magnetic dipole has the following relationship with the temperature:

$$\chi_M^{corr} = \frac{C}{T} \quad .$$

where C is the Curie constant which is

$$C = N \mu^2/3k \quad .$$

N is Avogadro's number, k is the Boltzmann constant and μ is the magnetic moment in B.M. (Bohr magnetons). Applying the statistical treatment, the molar susceptibility of a substance containing independent atoms, molecules or ions of magnetic moment, μ will vary with temperature

$$\chi_M^{corr} = \frac{N \mu^2/3k}{T}$$

and at a fixed temperature

$$\mu = \sqrt{3k/N} \sqrt{\chi_M^{corr} T} \quad .$$

The effective magnetic moment is given by

$$\mu_{eff} = 2.84 \sqrt{\chi_M^{corr} T} \quad .$$

Some compounds follow the Curie-Weiss law

$$\chi_M^{corr} = \frac{C}{T-\theta} \quad .$$

Here, θ is known as Weiss constant; in this case, the correction should be made while calculating the magnetic moment.

$$\mu = 2.84 \sqrt{\chi_M^{corr} (T-\theta)} .$$

For compounds which do not follow the Curie-Weiss law this equation should not be used. For practical purposes μ_{eff} is generally used at a given temperature. The Bohr magneton is a fundamental quantity in the quantum theory of magnetism and is defined as

$$1 \text{ B.M.} = \frac{eh}{4\pi mc}$$

where e is the electronic charge, h is Planck's constant, m is electron mass and c the speed of light. This is not the moment of one electron.

The spin only value, i.e., the contribution to the moment from only the electron spin effect, is given by the equation:

$$\mu_S = g \sqrt{s(s+1)} \text{ B.M.}$$

where s is the absolute value of the spin quantum number and g is the gyromagnetic ratio; for a free electron g has the value 2.00023 which may be taken as 2 for most purposes, the spin only value is also given by the formula

$$\mu_S = \sqrt{n(n+2)} \text{ B.M.}$$

where n is the number of unpaired electrons. If the orbital motion makes its full contribution, then the value is calculated by

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} .$$

L = orbital angular momentum quantum number. When there is appreciable spin orbit coupling in a molecule or ion which gives splitting of the ground state, there will be an appreciable contribution to the moment from this coupling. The value is then given by the equation

$$\mu = g\sqrt{J(J+1)} \ .$$

This situation prevails for atoms in the gas phase and for most rare earth ions. J is the total angular momentum of the ground state given, according to LS coupling. The calculated values are given in Table VI (110).

TABLE VI

No. of unpaired d electrons	Ions	Ground term	μ_{eff}(B.M)			
			$[L(L+1) + 4S(S+1)]^{\frac{1}{2}}$	$g[J(J+1)]^{\frac{1}{2}}$	$[4S(S+1)]$	Expt
1	Ti^{3+}	$^2D_{3/2}$	3.00	1.55	1.73	1.7-1.8
2	Ti^{2+}, V^{3+}	$^3F_2$	4.47	1.63	2.83	2.7-2.9
3	V^{2+}, Cr^{3+}	$^4F_{3/2}$	5.20	0.70	3.87	3.7-3.9
4	Cr^{2+}, Mn^{3+}	$^5D_0$	5.48	0	4.90	4.8-4.9
5	Mn^{2+}, Fe^{3+}	$^6S_{5/2}$	5.92	5.92	5.92	5.7-6.0
4	Fe^{2+}, Co^{3+}	$^5D_4$	5.48	6.71	4.90	5.0-5.6
3	Co^{2+}	$^4F_{9/2}$	5.20	6.63	3.87	4.3-5.2
2	Ni^{2+}	$^3F_4$	4.47	5.59	2.83	2.9-3.5
1	Cu^{2+}	$^2D_{5/2}$	3.00	3.55	1.73	1.8-2.1

The experimental magnetic moments for first row transition metal ions are often found to be close to those calculated for the spin only values.

The discrepancy between the measured values and those calculated from equations including orbital contribution arises because ligands remove the degeneracy of the d orbitals. The orbital angular moment could arise from rotation of the electron about the nucleus. This simple picture is complicated in the wave mechanical model of the atom where the orbital angular momentum may be pictorially associated with the interchange or transformation of one orbital with another by rotation about an appropriate axis. For this to be possible the orbitals must be degenerate and of the same shape and should not contain electrons of the same spin. The d_{xy}, d_{yz} and d_{xz} orbitals can transform into each other by 90^0 rotation about the relevant axes, while 45^0 rotation of the d_{xy} orbital about the z axis transforms it into $d_{x^2-y^2}$ orbital.

A ligand field lifts the degeneracy of the $d_{x^2-y^2}$ and d_{xy} orbitals and spin orbit coupling cannot occur via this model for this set of orbitals. In O_h or T_d complex ions, the e_g set of orbitals ($d_{x^2-y^2}$, d_{z^2}) cannot be used by electrons to rotate about an axis, therefore e_g orbitals do not contribute to orbital angular momentum. If the t_{2g} set of orbitals in a complex is half filled, rotation involving d_{xy}, d_{yz} and d_{xz} orbitals is not possible and orbital contribution from this set is quenched.

The orbital contribution in octahedral and tetrahedral complexes for different electronic configurations of d orbitals is given in Table VII. In complexes of lower symmetry, the more the d orbitals lose their degeneracy, the greater the likelihood of the orbital contribution being quenched. The presence or absence of orbital contribution may be taken to distinguish octahedral and tetrahedral shapes, since in no case does it

TABLE VII (110)

	Spin-paired oct.		Spin-free oct.		Spin-free tet.	
No. of d electrons	Orb. cont.	No orb. cont.	Orb. cont.	No orb. cont.	Orb. cont.	No orb. cont.
1			d_ε^1			d_γ^1
2			d_ε^2			d_γ^2
3				d_ε^3	$d_\gamma^2 d_\varepsilon^1$	
4	d_ε^4			$d_\varepsilon^3 d_\gamma^1$	$d_\gamma^2 d_\varepsilon^2$	
5	d_ε^5			$d_\varepsilon^3 d_\gamma^2$		$d_\gamma^2 d_\varepsilon^3$
6		d_ε^6	$d_\varepsilon^4 d_\gamma^2$			$d_\gamma^3 d_\varepsilon^3$
7		$d_\varepsilon^6 d_\gamma^1$	$d_\varepsilon^5 d_\gamma^2$			$d_\gamma^4 d_\varepsilon^3$
8				$d_\varepsilon^6 d_\gamma^2$	$d_\gamma^4 d_\varepsilon^4$	
9				$d_\varepsilon^6 d_\gamma^3$	$d_\gamma^4 d_\varepsilon^5$	

appear that it should occur in both. Tetrahedral Co(II) seems to be an exception which does not fit in the scheme above.

In general, orbital contributions are expected in these complexes in which the ground state is triply degenerate (e.g. t_{2g}) and values approximating the spin only values are obtained for non-degenerate and doubly degenerate ground states (e.g. A_{2g}, E_g). Information regarding the ground state can be obtained from the Tanabe and Sugano diagrams for octahedral and tetrahedral complexes.

The terms A and E give no orbital contribution. However, if there is a T term of the same multiplicity at a higher energy, it is possible for spin orbit coupling to mix some of this into the ground term, so introducing a certain amount of orbital angular momentum into the latter.

There are two cases in which the ground term is A. These are weak field octahedral d^5 and strong field octahedral d^6. In the d^5 case there is no higher T term of the same multiplicity and it therefore is expected to give a spin only moment of 5.92 B.M. independent of temperature. The strong field d^6 is diamagnetic. A_2 and E terms arising from F and D terms must be accompanied by a higher T term of the same multiplicity; for these the mixing is expressed by the following formula:

$$\mu_{eff} = \mu_{s.o}\left(1-\alpha\,\frac{\lambda}{10\,Dq}\right)$$

where α is 2 for an E and 4 for an A term, 10Dq is the energy separating the interacting terms and λ is the spin orbit coupling constant for the terms involved. It refers to the particular term and is related to the spin orbit coupling constant ζ, of an individual electron.

$$\lambda = \pm\,\frac{\zeta}{2s}$$

This is important in dealing with the strong field case. The free ion values of spin orbit coupling constants for first row transition metal ions are given in Table VIII. An example will illustrate the calculation of μ_{eff} or λ if μ_{eff} is known experimentally (110).

$d^8\,O_h = Ni(H_2O)_6^{+2}$ 10 Dq = 8,900 cm^{-1} (spectroscopically)

$\lambda = -\,315\ cm^{-1}$ (free ion value) Ground term is A_2 therefore $\alpha = 4$.

$$\mu_{eff} = 2.83\left(1 + \frac{1260}{8900}\right) = 3.23\ \text{B.M.}$$

TABLE VIII (110)

Free ion values (cm^{-1}) of spin-orbit coupling constants for first row transition metal ions

Ligand field:			Weak oct.		Strong oct.		Weak tet.	
Ion	ζ	No. of d electrons	Ground term	λ	Ground term	λ	Ground term	λ
Ti^{3+}	155	1	$^2T_{2g}$	+155	$^2T_{2g}$	+155	^2E	+155
V^{3+}	210	2	$^3T_{1g}$	+105	$^3T_{1g}$	+105	$^3A_2$	+105
V^{2+}	170	3	$^4A_{2g}$	+57	$^4A_{2g}$	+57	$^4T_1$	+57
Cr^{3+}	275	3	$^4A_{2g}$	+92	$^4A_{2g}$	+92	$^4T_1$	+92
Cr^{2+}	230	4	^5E_g	+58	$^3T_{1g}$	-115	$^5T_2$	+58
Mn^{3+}	355	4	^5E_g	+89	$^3T_{1g}$	-178	$^5T_2$	±89
Mn^{2+}	300	5	$^6A_{1g}$	—	$^2T_{2g}$	-300	$^6A_1$	—
Fe^{3+}	460	5	$^6A_{1g}$	—	$^2T_{2g}$	-460	$^6A_1$	—
Fe^{2+}	400	6	$^5T_{2g}$	-100	$^1A_{1g}$	—	^5E	-100
Co^{3+}	580	6	$^5T_{2g}$	-145	$^1A_{1g}$	—	^5E	-145
Co^{2+}	515	7	$^4T_{1g}$	-172	^2E_g	-515	$^4A_2$	-172
Ni^{3+}	715	7	$^4T_{1g}$	-238	^2E_g	-715	$^4A_2$	-238
Ni^{2+}	630	8	$^3A_{2g}$	-315	$^3A_{2g}$	-315	$^3T_1$	-315
Cu^{2+}	830	9	^2E_g	-830	^2E_g	-830	$^2T_2$	-830

For A and E terms of weak field d^1 to d^4 configurations, λ is positive and should lead to a reduction in the moment below the spin only values, for A and E terms of weak field d^6 to d^9 configurations, λ is negative and should lead to an increase in the moment above the spin only values. The only relevant strong field case is d^7, for which $2S = 1$, therefore $\lambda = -\zeta$ leading to the moment above 1.73 B.M." (110)

VI.

DISCUSSION

NEAR INFRA-RED SPECTRA AND MAGNETIC SUSCEPTIBILITY

Tricarbonylchromium complexes of cobalt (II) Schiff bases (O_h)

Electronic spectra and magnetic susceptibility data are widely used for determining the stereochemistry of complexes.

The distinction between octahedral and tetrahedral cobalt (II) complexes can be made by values of magnetic moments. Higher moments (4.8-5.2 B.M.) were predicted and observed for octahedral and lower moments (4.2-4.6 B.M.) for tetrahedral complexes. The parent compound Co(II) $(C_6H_5\text{-N-sal})_2$ has a higher magnetic moment in pyridine solution (4.78 B.M.) as compared to benzene solution (4.41 B.M.). The higher value was explained by adduct formation of Co(II) $(C_6H_5\text{-N-sal})_2$ with pyridine. The adduct has an octahedral stereochemistry and in this stereochemistry orbital contribution is possible and this effect increases the magnetic moments higher than the spin only values. The formation of adduct was confirmed by isolation of a solid pyridine adduct, and its magnetic moment was 4.81 B.M. (57).

The magnetic moments of tricarbonylchromium complexes of Co(II)-$(C_6H_5\text{-N-sal})_2$ both in solid and solution are in the octahedral range (Table IX), indicating the presence of octahedral stereochemistry in these complexes.

The electronic spectra of cobalt (II) six-coordinate complexes in general give rise to two transitions.

${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}$ (ν_1) and ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ (ν_3). The transition ${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ (ν_2) is a two-electron transition and is not always observed. The electronic spectra of these complexes are interpreted

TABLE IX

Electronic spectra and magnetic susceptibility data

Complex	Structure	Colour	Electronic spectra	Magnetic susceptibility μ_{eff} (B.M)	
				Solid	Solution
$Co(II)(C_6H_5\text{-}N\text{-}sal)_2$	T_d	Red	7,700, 11,200, 25,000, and 34,000 cm^{-1}		4.41 (Benzene)
$Co(II)(C_6H_5\text{-}N\text{-}sal)_2\ 2Py$	O_h		10,000, 17,000 (Sh), 26,000, and 33,100 cm^{-1}	4.81	4.87 (Pyridine)
$Co(II)(C_6H_5\text{-}N\text{-}sal)_2Cr(CO)_3 3H_2O$	O_h	Green	8,350, 17,840, 20,130, 23,000, 25,350, 30,500, and 33,100 cm^{-1}	4.84	4.93 (Chloroform)
$Co(II)(C_6H_5\text{-}N\text{-}sal)_2\ Cr(CO)_3 2H_2O$	O_h	Greenish-brown	7,871, 16,750, 18,000, 23,000, 24,500, 30,500, and 33,400 cm^{-1}	4.83	4.95 (Chloroform)

considering these complexes of octahedral stereochemistry as indicated by magnetic moments.

The bands at 8,300 and 20,130 cm^{-1} are considered to be ν_1 and ν_3 for Co(II) $(C_6H_5\text{-N-sal})_2$ $Cr(CO)_3$. The position of ν_2 (17,840 cm^{-1}) is calculated from ν_1 and ν_3.

From ν_1, ν_2 and ν_3 the Racah parameter B, the crystal field parameter Dq and β, the ratio of B in complex/B in free ion are calculated.

$B = 864\ cm^{-1}$

$Dq = 950\ cm^{-1}$

$\beta = 0.89$

The band assignment ν_1, ν_2 and ν_3 is checked from Tanabe and Sugano plots. This is done by making the ground term the horizontal line so that the transition energy may be estimated by vertical measurement from the base line. The value of 10 Dq/B is obtained from the above calculated values. The value of ν_1, ν_2 and ν_3 obtained from Tanabe and Sugano plots are 8,850, 18,300 and 21,000 cm^{-1}, respectively.

From the agreement between observed positions of ν_1, ν_2 and ν_3 and those calculated from Tanabe and Sugano plots, it can be inferred that the complex is d^7 six-coordinate. The chances of getting similar values from Tanabe and Sugano plots are extremely low if the complex is not octahedral.

The bands at 7,781 and 18,000 cm^{-1} are considered to be ν_1 and ν_3 for Co(II) $(C_6H_5\text{-N-sal})$ $(Cr(CO)_3)_2$. The position of ν_2 (16,750 cm^{-1}) is calculated from ν_1 and ν_3. From ν_1, ν_2 and ν_3 the B, 10 Dq and β are calculated.

$B = 745\ cm^{-1}$

$Dq = 895\ cm^{-1}$

$\beta = 0.766$

The value of β throws some light on the nature of bonding between central metal and ligand. The value of β in complexes of sulphur ligands (e.g. diethylthiophosphate) is nearly 0.30, and this is attributed to the strong covalency between central metal and ligand. Ions, like fluoride, give values of β close to one; the fluoride complexes are known to be ionic. In $Co(II)\ (C_6H_5\text{-}N\text{-}sal)_2\ Cr(CO)_3\ 3H_2O$ and $Co(II)\ (C_6H_5\text{-}N\text{-}sal)_2\ Cr(CO)_3 2H_2O$ complexes, the values of β are 0.89 and 0.766, respectively. The higher values in these complexes indicate poor covalent bonding. The comparison of tricarbonylchromium complexes with the parent compound $Co(II)\ (C_6H_5\text{-}N\text{-}sal)_2$-2Py is not made because there is no pyridine in these tricarbonylchromium complexes of $Co(II)\ (C_6H_5\text{-}N\text{-}sal)_2$. The position of pyridine is taken by water molecules.

Tricarbonylchromium complex of cobalt (II) Schiff bases (T_d)

The electronic spectra and magnetic susceptibility of the parent compound $Co(II)\ (CH_3\text{-}N\text{-}sal)_2$ are compared with those of tricarbonylchromium complexes in Table X. In general, cobalt (II) tetrahedral complexes have μ_{eff} values in the range 4.3-4.56 B.M. The magnetic susceptibility of these tricarbonylchromium complexes falls in the range of tetrahedral values and therefore a tetrahedral stereochemistry is suggested for these complexes. The reason for studying the magnetic susceptibility in solution was to check the possibility of having different stereochemistries in solution and solid. The cobalt (II) square planar complexes are expected to give lower moments

TABLE X

Electronic spectra and magnetic susceptibility data

Complex	Structure	Colour	Electronic spectra	Magnetic susceptibility μ_{eff} (B.M) Solid	Solution
$Co(II)(CH_3\text{-}N\text{-}sal)_2$	T_d	Green	7,700, 11,200, 17,000, 25,000, 34,000, and 34,000 cm^{-1}	4.62	
$Co(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3 2H_2O$	T_d	Light green	6,650, 16,700, 24,000, 26,000, 30,000, and 33,500 cm^{-1}	4.43	4.51 (Chloroform)
$Co(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_x$		Brown	6,670, 16,500, 23,500, 25,900, 30,500, and 33,500 cm^{-1}	4.40	4.49* (Chloroform)

*The magnetic susceptibility values quoted for this complex are based on assumed molecular weight (600).

(1.73 B.M.) while higher values are expected for tetrahedral. The higher values found are more or less the same in solid and solution suggesting that tetrahedral stereochemistry exists in the two phases.

Moments much higher than the spin only (3.87 B.M.) found in these complexes can be explained by mixing of the A_2 ground state with the T state by spin orbit coupling; this spin orbit coupling allows some orbital contribution and this contribution raises the magnetic moments. The spin orbit coupling constant λ is calculated from μ_{eff} values. The Dq is known from the electronic spectrum.

$$\mu_{eff} = \text{s.o}\left(1 - \frac{\alpha \cdot \lambda}{10\ Dq}\right)$$

$$\lambda = -109\ cm^{-1}\quad [Co(II)(CH_3\text{-}N\text{-}sal)_2\ Cr(CO)_3\ 3H_2O]$$

The free ion value for λ in the case of cobalt (II) is 172 cm^{-1}. The lower value of λ is because the ligand electrons quench the spin orbit coupling and therefore the value of λ is always lower than free ion value.

Tetrahedral cobalt (II) complexes are expected to give three bands by considering crystal field theory. One band $[A_2 \longrightarrow T_2\ (\nu_1)]$ is not observed because it is of very low energy and is obscured by ligand absorptions in the infra-red region. The bands around 7,000 and 17,000 cm^{-1} in these tricarbonylchromium complexes and the parent compound are considered to be $\nu_2\ [A_2 \longrightarrow T_1(F)]$ and $\nu_3\ [A_2 \longrightarrow T_1\ (P)]$. The value of ν_1 is calculated from ν_2 and ν_3 in all the complexes. From these ν_1, ν_2 and ν_3 bands the Racah parameter B and β the ratio of B in complex/B in free ion are calculated.

$Co(II)(CH_3\text{-N-sal})_2$ $B = 751\ cm^{-1}$, $\beta = 0.774$

$Co(II)(CH_3\text{-N-sal})_2Cr(CO)_32H_2O$ $B = 791\ cm^{-1}$, $\beta = 0.815$

$Co(II)(CH_3\text{-N-sal})_2(Cr(CO)_3)_xxH_2O$ $B = 776\ cm^{-1}$, $\beta = 0.800$

The calculated values shown above, are not reliable as ν_3 is seen as a shoulder and its exact position cannot be determined accurately. The values of B and β are high as compared to other cobalt (II) tetrahedral complexes which makes these figures even more doubtful. However, the similarity of the spectrum of both the tricarbonylchromium complexes with the parent compound whose tetrahedral stereochemistry is already established by Sacconi (42) does support a tetrahedral stereochemistry. The values of β may not be reliable but the values are close enough in all the three compounds to indicate that the bonding between central metal and ligand is not changed by the addition of $Cr(CO)_3$ group.

Tricarbonylchromium complexes of copper (II) Schiff bases

The crystal field theory predicts a single transition ($^2T_2 \longrightarrow {}^2E$) for copper (II) complexes in a regular tetrahedral field. If the tetrahedron is distorted, the ground or excited state may split, giving rise to more than one band.

The electronic spectra of copper (II) $(R\text{-N-sal})_2$ compounds are shown in Table XI, where a clear distinction is made between square planar and tetrahedral (pseudotetrahedral) complexes by Sacconi (51) on the basis of differences in the electronic spectrum.

The parent compounds Cu(II) $(CH_3\text{-N-sal})_2$ and Cu(II) $(C_6H_5\text{-N-sal})_2$ are shown to be square planar by electronic spectra. The square planar

TABLE XI

The structure of some copper (II) $(R\text{-}N\text{-}sal)_2$ complexes substituted in the benzene ring as indicated by their electronic spectra (51)

R	H	$3\text{-}CH_3$	$5\text{-}CH_3$	3-Cl	5-Cl	3-Br	$5\text{-}NO_2$
Pr^n.	P	P	P	P	P		P
Pr^i.	T_d	T_d	T_d	P	P	P	P
Bu^t.	T_d	T_d	T_d	T_d	T_d		T_d

P = Planar

T_d = Tetrahedral

ν_{max} (planar form) 14,000-16,000 cm^{-1}

ν_{max} (tetrahedral form) 8,700-10,000, 12,800-14,000, 19,200-20,800 cm^{-1}

structure in both parent compounds has been confirmed by X-ray crystallography (50,58). The complexes Cu(II) $(CH_3\text{-N-sal})_2$ $Cr(CO)_3$ and Cu(II) $(CH_3\text{-N-sal})_2$ $(Cr(CO)_3)_x$ have similar spectra in the near infra-red region to those of square planar copper (II) complexes (Table XII). Therefore, a square planar stereochemistry is suggested for these two complexes.

The spectra of Cu(II) $(C_6H_5\text{-N-sal})_2$ $Cr(CO)_3 5H_2O$ and Cu(II) $(C_6H_5\text{-N-sal})_2$ $(Cr(CO)_3)_2 4H_2O$ complexes have extra bands in the near infra-red region which are similar to other tetrahedral (pseudotetrahedral) copper (II) complexes. There is also the possibility of octahedral structure because of the presence of water molecules in these complexes. Generally, octahedral copper (II) complexes do not have any absorption in the region 5,000-15,000 cm^{-1}. The similarity of spectra of these two tricarbonylchromium complexes to other copper (II) tetrahedral complexes suggests a tetrahedral (pseudotetrahedral) structure.

The tetrahedral (pseudotetrahedral) structure is favoured from the steric point of view in these tricarbonylchromium complexes of Cu(II) $(C_6H_5\text{-N-sal})_2$ as compared to Cu(II) $(CH_3\text{-N-sal})_2$.

TABLE XII

Electronic spectra and magnetic susceptibility data

Complex	Structure	Colour	Electronic spectra	Magnetic susceptibility μ_{eff} (B.M)
$Cu(II)(CH_3\text{-N-sal})_2Cr(CO)_3$	P	Brown	14,300-18,200 (sh), 22,800, 25,670, 30,000, and 33,200 cm^{-1}	1.82
$Cu(II)(CH_3\text{-N-sal})_2(Cr(CO)_3)_xH_2O$	P	Orange-brown	14,000-18,200 (sh), 23,000, 25,800, 30,500, and 33,400 cm^{-1}	1.81*
$Cu(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3 5H_2O$	T_d	Green	6,670, 8,350, 11,780-16,700 (sh), 22,800, 25,180, 29,500, and 33,300 cm^{-1}	1.89
$Cu(II)(C_6H_5\text{-N-sal})_2(Cr(CO)_3)_2 4H_2O$	T_d	Brownish-green	6,660, 8,700, 12,500-16,650 (sh), 22,900, 25,110, 30,000, and 33,500 cm^{-1}	1.93

*The magnetic susceptibility value quoted for this complex is based on assumed molecular weight (600).

Sacconi has reported that a higher magnetic moment is expected for tetrahedral complexes over square planar because of higher orbital contribution (51).

Magnetic data for X-substituted
$Cu(II)\ (R\text{-}N\text{-}sal)_2$ complexes

X	R	Temp.	μ_{eff} (B.M)	Stereochemistry
H	Pr^n	23	1.86	Planar
	Pr^i	28	1.90	Pseudotetrahedral
	Bu^n	23	1.85	Planar
	Bu^s	21	1.91	Pseudotetrahedral
	Bu^t	21	1.91	Pseudotetrahedral
3-Cl	Bu^t	22	1.92	Pseudotetrahedral
5-Cl	Pr^i	21	1.84	Planar
5-Cl	Bu^t	22	1.91	Pseudotetrahedral
3,4 Benzo	Bu^t	24	1.89	Pseudotetrahedral

The magnetic moments obtained for tricarbonylchromium complexes of $Cu(II)\ (CH_3\text{-}N\text{-}sal)_2$ fall in the square planar range (1.83-1.86 B.M). This supports the square planar stereochemistry suggested with the help of electronic spectra. The pseudotetrahedral structure of $Cu(II)\ (C_6H_5\text{-}N\text{-}sal)_2$

$Cr(CO)_3$ and Cu(II) $(C_6\text{-N-sal})_2$ $(Cr(CO)_3)_2$ complexes is also supported by magnetic moments (1.89 and 1.93 B.M., respectively) (Table XII).

Tricarbonylchromium complexes of chromium (II) Schiff bases.

All the four-coordinate chromium (II) complexes are known to have tetrahedral stereochemistry with the exception of chromium (II) phthalocyanine, which is square planar.

The magnetic moments show that all these carbonyl complexes have high spin. The electronic spectra of tricarbonylchromium complexes of chromium (II) Schiff bases exhibit a broad band (14,000-20,000 cm^{-1}). Chromium (II) $(C_6H_5$ or $CH_3\text{-N-sal})_2$ compounds are not known to exist. Tricarbonylchromium complexes of Cr(II) Schiff bases were obtained by replacement of Ni(II) by chromium from Ni(II) $(C_6H_5$ or $CH_3\text{-N-sal})_2$ and, at the same time, forming the tricarbonylchromium complex. The nonavailability of electronic spectra of parent compounds makes it difficult to interpret a broad band observed in the near infra-red region of these complexes. A broad band in the range 14,000-20,000 cm^{-1} is generally typical of octahedral Cr(II). Therefore an octahedral stereochemistry is suggested for Cr(II) $(C_6H_5\text{-N-sal})_2 \cdot (Cr(CO)_3)_n$ complexes.

Tricarbonylchromium complexes of cobalt (III) Schiff bases

All the four tricarbonylchromium complexes are diamagnetic. Their electronic spectra show a broad band in the 13,000-19,000 cm^{-1} region. Crystal field theory predicts two spin allowed and two spin forbidden bands. In practice the two spin allowed bands are seen as one band, and two spin allowed bands are not seen (56). In these Co(III) $(C_6H_5$ or CH_3-N-sal$)_3$ $Cr(CO)_3$ complexes the two spin allowed bands are probably hidden in the broad band, and no spin forbidden bands are observed.

The parent Co(II) $(C_6H_5$ or CH_3-N-sal$)_3$ compounds were shown to have a trans structure because of steric reasons. The trans structure was confirmed by n.m.r. studies (55). In these Co(III) $(C_6H_5$ or CH_3-N-sal$)_3$-$Cr(CO)_3$ complexes the crowding is even greater than the parent compound because of additional $Cr(CO)_3$ groups, therefore the possibility of trans structure is very high.

Tricarbonylchromium complexes of zinc (II) Schiff bases

All the four tricarbonylchromium complexes are diamagnetic. The parent Zn(II) $(C_6H_5$-N-sal$)_2$ compound was shown to be tetrahedral by X-ray crystallography (62). In the absence of X-ray crystallographic studies for these tricarbonylchromium complexes the stereochemistry cannot be proposed with certainty, although most zinc (II) complexes are known to have tetrahedral stereochemistry. N.M.R. could not be obtained because of lack of sufficient solubility.

Tricarbonylchromium complexes of cobalt (II) (salen)

The magnetic susceptibility of the complex corresponds to one electron, which is only possible if the structure is square planar. All the tetrahedral cobalt (II) complexes have three unpaired electrons.

The electronic spectra exhibit bands at 6,540, 8,350, 17,300, and 21,780 cm^{-1}. The band around 8,500 cm^{-1} is considered to be a characteristic of Co(II) square planar complexes (114).

Tricarbonylchromium complex of nickel (II) (salen)

The complex is diamagnetic and the electronic spectrum shows a broad band (12,000-16,400 cm^{-1}). Planar complexes can be distinguished from octahedral and tetrahedral symmetries by the lack of electronic absorption below 10,000 cm^{-1} (74). The Ni(II) (salen) $Cr(CO)_3$ exhibits no absorption below 10,000 cm^{-1}, therefore this complex is considered square planar. The tetrahedral complexes are paramagnetic and this complex is diamagnetic, which further supports square planar stereochemistry.

Tricarbonylchromium complex of copper (II) (salen)

The electronic spectrum shows bands at 16,000 cm^{-1} and 22,000 cm^{-1} which are similar to the parent compound. The parent compound Cu(II) (salen) is shown to have a square planar structure by X-ray crystallography (76). A square planar stereochemistry is therefore suggested for this complex.

Tricarbonylchromium complex of Zinc (II) (salen)

The complex is diamagnetic. N.M.R. could not be studied because of lack of sufficient solubility. In the absence of X-ray crystallographic studies, the stereochemistry cannot be proposed with certainty, although the parent compound is planar (84).

U.V. and visible spectra of tricarbonylchromium complexes of metal Schiff bases

The U.V. and visible spectra of these complexes are complicated because of the large number of absorptions in this region. The U.V. and visible spectra of various arene tricarbonylchromium complexes have already been studied by Ercoli and Mangani (115). Their spectra resemble the spectra obtained by Yamada (116). Generally there are three bands observed for arene and substituted arene tricarbonylchromium complexes in the region given below.

30,800-32,000 cm^{-1} (log ε, 4-4.3)
36,000-40,000 cm^{-1} (log ε, 3.7-4.0)
43,500-47,000 cm^{-1} (log ε, 4.3-4.8)

The U.V. and visible spectra of metal Schiff bases used fall in the following general range:

24,000-28,000 cm^{-1} (log $\varepsilon \sim 4.0$)
33,000-34,000 cm^{-1} (log $\varepsilon \sim 4.0$)

In some cases bands with their maxima in the near i.r. extend up to 21,000 cm^{-1}. If the U.V. and visible spectra of metal Schiff bases are combined with arene tricarbonylchromium complexes, a rather complicated result will arise. However, the observed spectral bands for the tricarbonylchromium complexes of metal Schiff bases fall in the following general range:

24,000-26,000 cm^{-1} (log ε, 3.36-3.88)
29,500-32,000 cm^{-1} broad shoulder
33,000-34,000 cm^{-1} (log ε, 3.96-4.30)
34,000-37,000 cm^{-1} shoulder

The detailed spectrum of each complex is tabulated in Table XIV.

One of the previous workers (117) has studied the U.V. and visible spectra of $Cr(CO)_6$, $[Mn(CO)_5]_2$, and $Fe(CO)_5$ and their derivatives. They (117) assigned the absorption to electron transition involving the metal carbon bond and this could be considered a characteristic feature of all compounds containing such bonds. These bands were referred to by them as M-C (metal carbon bands). Their study, in general, reveals three features:

1. Replacement of electron releasing group by strongly electron withdrawing groups causes a hypsochromic shift; for example, in methyl pentacarbonyl manganese the replacement of the methyl group by a trifluromethyl group causes a shift of M-C band from 36,000 cm^{-1} to 37,000 cm^{-1}.

2. The number of carbonyl groups attached to the metal atom has a direct influence on the intensity of absorption of the M-C bands, the higher the number of carbonyl groups the greater the intensity of the bands.

3. A bathochromic shift is expected if the conjugation increases in the ligand part other than carbonyl.

In molecular orbital terms the M-X bands are referred to as charge transfer bands. The charge transfer bands arise by transfer of an electron from one of the orbitals of the metal to a ligand orbital or from ligand to metal.

The effect of solvent was studied for tricarbonylchromium complexes of metal Schiff bases using polar and nonpolar solvents to assign the bands wherever possible. The band positions due to carbonyl groups are sensitive to the polarity of the solvents. Polar solvents generally shift the $n \longrightarrow \pi^*$ and $n \longrightarrow \sigma^*$ bands to shorter wavelengths and $\pi \longrightarrow \pi^*$ bands to longer wavelengths. No significant changes were noticed in band positions using polar and nonpolar solvents. It was difficult to assign the exact position of bands because they were very broad. The band assignment is very difficult, it is hard even to say whether certain transitions are due to the tricarbonylchromium part of the complex or the metal Schiff base part.

The spectra of all the tricarbonylchromium complexes of metal Schiff bases (excluding zinc and nickel) are very similar except for their positions and intensities. The spectra of zinc and nickel complexes have an extra band around 30,000 cm^{-1}. It is very hard to draw any conclusions from the U.V and visible spectra of these complexes. However, there is a noticeable change in intensity of certain bands by varying the number of carbonyl groups (Table XIII). The extinction coefficient increases as the

TABLE XIII

Complex	$X = Cr(CO)_3$	$X = (Cr(CO)_3)_2$
$Cr(II)(C_6H_5\text{-N-sal})_2\ X$	25,500 cm^{-1} (ε 5,330)	25,000 cm^{-1} (ε 7,860)
	33,500 cm^{-1} (ε 13,090)	33,000 cm^{-1} (ε 16,600)
$Cr(II)(CH_3\text{-N-sal})_2\ X$	25,600 cm^{-1} (ε 6,640)	25,700 cm^{-1} (ε 1,000)
	33,800 cm^{-1} (ε 11,570)	33,500 cm^{-1} (ε 18,450)
$Cu(II)(C_6H_5\text{-N-sal})_2\ X$	25,180 cm^{-1} (ε 6,710)	25,110 cm^{-1} (ε 6,730)*
	33,300 cm^{-1} (ε 14,410)	33,300 cm^{-1} (ε 17,100)
$Co(II)(C_6H_5\text{-N-sal})_2\ X$	25,350 cm^{-1} (ε 5,690)	24,500 cm^{-1} (ε 7,094)*
	33,100 cm^{-1} (ε 16,810)	33,400 cm^{-1} (ε 18,984)
$Co(III)(CH_3\text{-N-sal})_3\ X$	25,500 cm^{-1} (ε 8,820)	26,000 cm^{-1} (ε 7,890)
	33,800 cm^{-1} (ε 15,490)	33,600 cm^{-1} (ε 15,420)

*These complexes have one $Cr(CO)_3$ group.

number of $Cr(CO)_3$ groups is increased from one to two in these complexes. The extinction coefficient does not increase in the case of Co(III)-$(CH_3$-N-sal$)_3$ with two $Cr(CO)_3$ groups for some unknown reason. The dependence of intensity on the number of $Cr(CO)_3$ groups suggests that these bands are associated with the $Cr(CO)_3$ or $Cr(CO)_3$ groups have some effect on these bands. A similar effect was noticed by Lundquist and Cais (117) with other metal carbonyl complexes.

TABLE XIV

Electronic Spectra (cm^{-1})

Compound	Nujol Mull			$CHCl_3$
	ν_1 ($^4T_{2g} \leftarrow {}^4T_{1g}$)	ν_2 ($^4A_{2g} \leftarrow {}^4T_{1g}$) Calculated	ν_3 ($^4T_{1g}(P) \leftarrow {}^4T_{1g}$)	
$Co(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3 3H_2O$	8,350	17,840	20,130	25,350 (ε5,690), 33,100 (ε16,810) Broad shoulders 23,000 and 30,000
$Co(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3 2H_2O$	7,871	16,750	18,000	24,500 (ε7,094), 33,400 (ε18,980) Broad shoulders 23,000 and 30,500
	ν_2 $^4T_1(F) \leftarrow {}^4A_2$	ν_3 ($^4T_1(P) \leftarrow {}^4A_2$)		
$Co(II)(CH_3\text{-N-sal})_2Cr(CO)_3H_2O$	6,650	16,700		26,000 (ε3,863), 33,500 (ε9,200) Broad shoulders 24,000 and 30,000
$Co(II)(CH_3\text{-N-sal})_2(Cr(CO)_3)_x xH_2O$	6,670	16,500		25,900, 33,500 Shoulders 23,500 and 30,500

TABLE XIV, continued

Electronic Spectra (cm^{-1})

Compound	Nujol Mull	$CHCl_3$
$Co(III)(CH_3\text{-}N\text{-}sal)_3Cr(CO)_3 2H_2O$	Broad band extends from 13,000 to 19,000 cm^{-1}	25,500 (ε8,820), 33,800 (ε15,490) Broad shoulders 23,500 and 30,500
$Co(III)(CH_3\text{-}N\text{-}sal)_3(Cr(CO)_3)_2 3H_2O$	Broad band extends from 13,000 to 19,000 cm^{-1}	26,000 (ε7,890), 33,600 (ε15,420) Broad shoulders 24,000 and 31,000
$Co(III)(C_6H_5\text{-}N\text{-}sal)_3Cr(CO)_3$	Broad band extends from 13,000 to 19,000 cm^{-1}	25,400, 33,700 Broad shoulders 23,500 and 31,000
$Co(III)(C_6H_5\text{-}N\text{-}sal)_3(Cr(CO)_3)_2 7H_2O$	Broad band extends from 13,000 to 19,000 cm^{-1}	25,000, 33,600 Broad shoulders 23,000 and 30,500
$Cr(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3$	Band extends from 14,000 to 20,000 cm^{-1}	25,700 (ε6,640), 33,800 (ε11,570) Broad shoulders 24,000 and 31,500
$[Cr(II)(CH_3\text{-}N\text{-}sal)_2]_2Cr(CO)_3$	Band extends from 14,000 to 20,000 cm^{-1}	25,700 (ε10,000), 33,500 (ε18,450) Broad shoulders 23,500 and 30,500

TABLE XIV, continued

Electronic Spectra (cm^{-1})

Compound	Nujol Mull	$CHCl_3$
$Cr(II)(C_6H_5\text{-}N\text{-}sal)_2Cr(CO)_3 5H_2O$	Band extends from 14,000 to 20,000 cm^{-1}	25,500 (ε5,330), 33,500 (ε13,090) Broad shoulders 23,000 and 30,500
$Cr(II)(C_6H_5\text{-}N\text{-}sal)_2(Cr(CO)_3)_2 4H_2O$	Band extends from 14,000 to 20,000 cm^{-1}	25,000 (ε7,860), 33,000 (ε16,600 Broad shoulders 23,000 and 30,000
$Zn(II)(C_6H_5\text{-}N\text{-}sal)_2(Cr(CO)_3)_3 5H_2O$		22,300 (ε2,580), 31,600 (ε10,750), 33,700 (ε10,970) Broad shoulders 28,500
$[Zn(II)(C_6H_5\text{-}N\text{-}sal)_2]_x(Cr(CO)_3)_x xH_2O$		
$Zn(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_2 3H_2O$		
$Zn(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_4H_2O$		23,300 (ε5,560), 31,300 (ε13,450), 33,500 (ε13,620) Broad shoulders 29,000

TABLE XIV, continued

Electronic Spectra (cm^{-1})

Compound	Nujol Mull	$CHCl_3$
$Cu(II)(CH_3\text{-N-sal})_2Cr(CO)_3$	Band extends from 14,300 to 18,200 cm^{-1}	25,670 (ε1,622), 33,200 (ε4,560)
$[Cu(II)(CH_3\text{-N-sal})_2]_x(Cr(CO)_3)_x$	Band extends from 14,300 to 18,200 cm^{-1}	25,800, 33,400 Broad shoulders 23,500 and 30,500
$Cu(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3 5H_2O$	6,670, 8,350 cm^{-1} (Shoulder 11,780 to 16,700 cm^{-1}	25,180 (ε5,710), 33,300 (ε14,410 Broad shoulders 22,800 and 29,500
$Cu(II)(C_6H_5\text{-N-sal})_2\ Cr(CO)_3 3H_2O$	6,660, 8,760 cm^{-1} (Shoulder 12,520 to 16,650 cm^{-1})	25,110 (ε6,730), 33,300 (ε17,100) Broad shoulders 22,900 and 3,000
$Co(II)(salen)Cr(CO)_3 2H_2O$	17,300, 21,780 Weak bands 6,540, 8,350	25,600, 34,000 Broad shoulders 31,800 and 23,200
$Ni(II)(salen)Cr(CO)_3 2H_2O$	Band (12,500-16,400)	23,000, 29,300 and 33,700 Shoulders 22,000 and 25,900

TABLE XIV, continued

Electronic Spectra (cm^{-1})

Compound	Nujol Mull	$CHCl_3$
Cu(II)(salen)$Cr(CO)_3 2H_2O$	16,400, 22,400	26,000 (ε7,100), 33,700 (ε8,225) Broad shoulders 23,500 and 31,500
Zn(II)(salen)$Cr(CO)_3 2H_2O$		22,800 (ε2,050), 33, 800 (ε5,160), 31,300 (ε5,020) Broad shoulder at 26,500

TABLE XV

Magnetic Susceptibility

					μ_{eff} (B.M.)	
					Experimental (B.M.)	
Configuration	Compound	Stereochemistry	n	Spin only (B.M)	Solid	Solution ($CHCl_3$)
d^4	$Cr(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3$	Tetrahedral	4	4.90	4.91	
	$Cr(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_x$	Tetrahedral	4	4.90	5.01	
	$Cr(II)(C_6H_5\text{-}N\text{-}sal)_2Cr(CO)_3 5H_2O$	Tetrahedral	4	4.90	4.90	
	$Cr(II)(C_6H_5\text{-}N\text{-}sal)_2(Cr(CO)_3)_2 4H_2O$	Tetrahedral	4	4.90	4.88	
d^7	$Co(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3H_2O$	Tetrahedral	3	3.88	4.43	4.51
	$Co(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_x xH_2O$	Tetrahedral	3	3.88	4.46	4.49
	$Co(II)(C_6H_5\text{-}N\text{-}sal)_2(Cr(CO)_3 3H_2O$	Octahedral	3	3.88	4.84	4.93
	$Co(II)(C_6H_5\text{-}N\text{-}sal)_2\ Cr(CO)_3 2H_2O$	Octahedral	3	3.88	4.83	4.95
	$Co(II)(salen)Cr(CO)_3 2H_2O$	Planar	1	1.73	2.43	
d^9	$Cu(II)(CH_3\text{-}N\text{-}sal)Cr(CO)_3$	Planar	1	1.73	1.82	
	$Cu(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3)_x$	Planar	1	1.73	1.81	

n = number of unpaired electrons

TABLE XV, continued

Magnetic Susceptibility

Configuration	Compound	Stereochemistry	n	Spin only (B.M)	μ_{eff} (B.M.) Experimental (B.M.) Solid	μ_{eff} (B.M.) Experimental (B.M.) Solution ($CHCl_3$)
d^9	$Cu(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3 5H_2O$	Tetrahedral	1	1.73	1.89	
	$Cu(II)(C_6H_5\text{-N-sal})_2\ Cr(CO)_3 3H_2O$	Tetrahedral	1	1.73	1.93	
	$Cu(II)(salen)Cr(CO)_3 2H_2O$	Planar	1	1.73	1.91	

n = number of unpaired electrons

VIII.

INFRA-RED

INTRODUCTION

Infra-red spectroscopy has played a very important role in determining the molecular structures of metal carbonyls and their derivatives. The number of infra-red and Raman active CO stretching fundamentals and symmetries for the different geometrical isomers of the octahedral derivatives $M(CO)_{6-x}L_x$ can be derived on the basis of local symmetry of the carbonyl groups left in the original octahedral environment by substituent groups (118).

Complex	Point group	Number of i.r. and Raman CO stretching modes	
$M(CO)L_5$	C_{4v}	1, i.r. (A_1)	1, Raman (A_1)
trans-$M(CO)_2L_4$	D_{4h}	1, i.r. (A_{2u})	1, Raman (A_{1g})
cis-$M(CO)_2L_4$	C_{2v}	2, i.r. (A_1, B_1)	2, Raman (A_1, B_1)
asymm-$M(CO)_3L_3$	C_{2v}	3, i.r. (A_1, B_1, A_1)	3, Raman (A_1, B_1, A_1)
symm-$M(CO)_3L_3$	C_{3v}	2, i.r. (A_1, E)	2, Raman (A_1,E)
trans-$M(CO)_4L_2$	D_{4h}	1, i.r. (E_u)	2, Raman (A_{1g}, B_{1g})
cis-$M(CO)_4L_2$	C_{2v}	4, i.r. (A_1, B_1, B_2, A_1)	4, Raman (A_1, B_1, B_2, A_1)
$M(CO)_5L$	C_{4v}	3, i.r. (A_1, E, A_1)	4, Raman (A_1, B_1, E, A_1)
$M(CO)_6$	O_h	1, i.r. (T_{1u})	2, Raman (E_g, A_{1g})

Band assignments can be made on the basis of relative band positions and intensities (119,120) and through application of the "non-rigorous" secular equations of Cotton and Kraihanzel (121). Extreme caution should be taken in assigning the bands. The spectra in both solid and solution should be taken. The band assignments from the solid-state data only may not be very reliable, as small intensity bands may be hidden in broad bands. The spectra in solution are generally reliable, provided there is no reaction with the solvent (adduct formation, dissociation and change of stereochemistry in solution).

Correct band assignments are not only important in determining the point group symmetry of the molecule but also in determining the CO stretching force constants. The assumptions as to the nature of bonding in metal carbonyls in an attempt to demonstrate the internal consistency of the force constant to bond order relationship are open to question, and the reliability of such calculations has not been satisfactorily demonstrated (122).

The deviation from local symmetry causes broadening of bands and, in some cases, the band may split; for example, the E mode in symm-M(CO)$_3$L$_3$ splits into two bands if the molecule deviates from C_{3v} symmetry (123).

The structures assigned to the carbonyl complexes on the basis of point group symmetry derived from i.r. studies are generally found to be correct by X-ray crystal structure determinations. If the same symmetry exists in other carbonyl complexes a similar structure can be proposed (124).

The i.r. studies of tricarbonylchromium complexes have been done by various workers (121,124-128). The work by Brown and Hughes (126) on the trend of carbonyl stretching frequencies in metal tricarbonyl complexes shows that

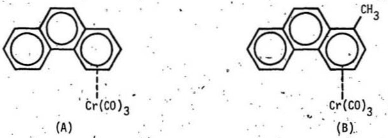
1. Carbonyl frequencies in arene metal tricarbonyls decrease in the order benzene, toluene, xylene, mesitylene and N-N dimethyl-p-toluidine in all Cr, Mo and W arene tricarbonyls studied.

2. Carbonyl frequencies in arene metal tricarbonyls increase in the order Cr, Mo and W.

3. Carbonyl frequencies in arene metal tricarbonyls are dependent upon solvent.

Earlier work of Brown and Raju (129) has shown from i.r studies on substituted condensed hydrocarbons that the $Cr(CO)_3$ group goes preferentially to the ring which has higher π-electron density. The i.r in the CO stretching region shows three bands:

Tricarbonylchromium complex of	ν_{CO} cm^{-1} (cyclohexane)
Phenanthrene (Fig. 41A)	1977, 1917, 1906
1-methyl phenanthrene (Fig. 41B)	1973, 1913, 1903



(A) (B)

Fig. 41

The methyl group is an electron donor and increases the electron density of the ring. This increase is shown by a small decrease in CO frequencies in the case of 1-methyl phenanthrene tricarbonylchromium, as compared to the phenanthrene complex.

The spectra of tricarbonylchromium complexes of substituted arenes provide clear evidence for the transmission of electronic effects of a substituent of an arene ring to the attached metal carbonyl group. However the question arises as to whether the metal atom interacts with only the π-electron system of the ring to which it is attached or whether it reacts with the π-orbitals of the complete ring system. The application of the effective atomic number rule (E.A.N.) and simple theory will support the latter, but according to Brown (130) the interaction of all orbitals should be taken into account for discussion of bonding of organometallic systems, because the E.A.N. rule has no real significance in molecular orbital theory. His (130) spectral results for the substituted biphenyl complexes suggest that there is a transmission of an electronic effect from a substituent on an adjoining ring (at least for a methyl group) (Fig. 42).

Tricarbonylchromium complex	ν_{CO} (cyclohexane)
Biphenyl	1982, 1917
4-methyl biphenyl	1978, 1913
4, 4' dimethyl biphenyl	1976, 1908

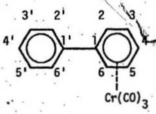


Fig. 42

The decrease in frequency is indicative of an increase in π-electron density of the ring to which the tricarbonylchromium group is attached.

Recently, Adams and Squires (127) and Kettle and coworkers (131) have studied the vibrational spectra of benzene tricarbonylchromium and related compounds in the solid state.

ν_{CO} (cm^{-1}) of $C_6H_5Cr(CO)_3$

Solution (CCl_4) i.r.	1978, 1909
Solid (KBr) i.r.	1966, 1879, 1858
Solid (powder) Raman	1945, 1887, 1865

Their studies show that there was no coincidence between the Raman and i.r. spectra in solution and solid. There are more bands in solid state than predicted by the C_{3v} point symmetry of the isolated molecules. They found that the data were best explained by use of factor group analysis of the spectra and suggested that spectra in the solid phase must be discussed on the basis of the factor group, although in some cases the molecular point group symmetry is a good approximation. The abundance of bands in the 300-700 cm^{-1} region as compared to the few bands predicted for C_{3v} local symmetry for solids also suggests the use of factor group analysis is more useful.

In the past few years the use of i.r. spectroscopy of metal carbonyl compounds has changed in emphasis from the determination of molecular symmetry to discussion of bonding and electron distribution in terms of observed frequencies in the CO stretching region. All attempts to relate stretching frequencies to bond order have been based on the assumption that in a series of compounds the observed variation can be related primarily to a change in bond character of the metal carbonyl system.

Kettle (132) has shown that for the variation of the C-O bond distance normally observed in metal carbonyl compounds the π-overlap integral 2pπ-2pπ (C-O) changes far more than the corresponding σ-overlap integral.

In the present work the changes in CO frequencies in tricarbonylchromium complexes of metal Schiff bases will be discussed in terms of changes in electron distribution on the ligand (metal Schiff base).

IX.

DISCUSSION

Band assignment

The band assignment in the CO stretching region of tricarbonylchromium complexes of metal Schiff bases is simple, as there are no other absorptions in this region. The high energy band is assigned as A_1 and low energy band as E_2.

The far infra-red for simple arene tricarbonylchromiums and some of its derivatives have been studied by some workers, and they have assigned M-C-O angle deformations, M-CO stretching vibrations and metal ring vibrations. Some of the values obtained by Brown and Carrol (133) for monosubstituted benzene tricarbonylchromium are given below.

Substituent	Cr-C-O	Cr-C-O	Cr-CO	Cr-ring
Cl	638	546	483	300
H	646	540	487	296
CH_3	645	548	485	298
NH_3	645	538	491	295
p-Tolyl	646	536	489	301

(Measured in KBr) unit, cm^{-1}

Recently, Adams and Squire (127) have reported the i.r. and far infra-red of benzene tricarbonylchromium in the solid state. They found many extra bands in the far infra-red region and an extra band in the CO stretching region. Their results and band assignment are given below.

ν_{CO} = 1966, 1899, 1858

δ (M-C-O) = 667

δ (M-C-O) = 654

δ (M-C-O) = 635

δ (M-C-O) = 612

δ (M-C-O) = 533

ν (M-CO) = 488

ν (M-CO) = 483

ν (M-ring) sym = 298

ν (M-ring) asym = 328

Adams and Squire discussed these results using the full factor group rather than point group symmetry to explain the existence of these extra bands. The complex in the solid state in a unit cell has C_{2h} symmetry; two molecules of the complex are found in the unit cell and their combined symmetry is not C_{3v}. Under C_{2h} symmetry more bands are expected. Percy and Thornton (63,65) have studied the infra-red of M(II) $(C_6H_5\text{-N-sal})_2$ and M(II) $(CH_3\text{-N-sal})_2$ compounds by ^{15}N isotope labelling. They have assigned ν C=N, M-N and M-O vibrations.

Compound	ν C=N (cm^{-1})	ν M-O (cm^{-1})	ν M-N (cm^{-1})
Cu(II)$(C_6H_5\text{-N-sal})_2$	1611, 1594	495	529, 448
Ni(II)$(C_6H_5\text{-N-sal})_2$	1618, 1588	516	542, 466
Zn(II)$(C_6H_5\text{-N-sal})_2$	1609, 1589	493	516, 454
Co(II)$(C_6H_5\text{-N-sal})_2$	1607, 1580	494	519, 457
Co(II)$(CH_3\text{-N-sal})_2$	1683	487	467, 410

The band assignment of tricarbonylchromium complexes of metal Schiff bases in the far infra-red region is rather complicated because of the Cr-C-O, Cr-CO, Cr-ring, M-O and M-N vibrations in the same region. The only way to assign the bands with some certainty is by isotope labelling. The isotopes ^{15}N, ^{18}O and ^{53}Cr are needed separately for each compound to assign vibrations mentioned above.

In the absence ~~of such~~ isotope labelling studies for these tricarbonylchromium complexes of metal Schiff bases, the bands cannot be assigned with certainty, but the bands can be assigned tentatively on the basis of analogy with the parent compounds.

The bands in the far infra-red region above 600 cm^{-1} have been assigned to Cr-C-O angle deformations as M-N, M-O, Cr-CO and Cr-ring vibrations fall below this region. The band in the region of 480 cm^{-1} is present in all other arene tricarbonylchromium complexes and has been assigned as a Cr-CO vibration (133). The presence of such a band in the above mentioned region in all tricarbonylchromium complexes of metal Schiff bases suggests that this band could be due to Cr-CO vibrations. All the other bands have been assigned tentatively on the basis of analogy with parent compounds (Table XVII).

Discussion

The bands assigned as Cr-CO stretching vibrations are listed below.

	ν Cr-CO (cm^{-1})
$M(II)(CH_3\text{-N-sal})_2Cr(CO)_3$	487, 475, 473, 472, 473, 473, 473, 477, 470, and 478 cm^{-1}
$M(II)(C_6H_5\text{-N-sal})_2\ Cr(CO)_3$	476, 473, 472, 475, 472, 473, 475, and 472 cm^{-1}
$M(II)(\text{salen})Cr(CO)_3$	483, 490, 488, and 483 cm^{-1}

Each band corresponds to one complex. The bands are grouped together for the complexes of three different series of ligands. These figures are also reported in Table XVII, where a specific assignment is given for each complex.

The band positions of Cr-CO vibrations are dependent upon the extent of bonding between chromium and carbon. The bonding between chromium and carbon depends upon the nature of X. ($X\text{-}Cr(CO)_3$ where X = $M(II)\text{-}(CH_3\text{-N-sal})_2$, $M(II)(C_6H_5\text{-N-sal})_2$ and M(II)(salen) and M = 1st series transition metals).

$$\ddot{X}\text{-}M\text{-}C \equiv O \rightleftharpoons \overset{+}{X} = M = C = \overline{O}$$

The greater the electron donation from X the higher the value of the Cr-CO stretching vibrations. The ν Cr-CO are expected to vary if there are changes in electron donation capacity of X, in all the three series with different transition metals. The ν Cr-CO values are very close in each series and are indicative of nearly the same Cr-C bond order. This is only possible if the π-interaction of X and Cr is more or less the same in each series; this result suggests that the π-electron density of the ligand X in each series does not vary very much within the first series transition metals.

The Cr-CO stretching vibrations are not as sensitive as ν_{CO} when the π-electron density on X is changed.

The other vibrations such as Cr-C-O deformations and Cr-ring vibrations have no obvious correlation with the varying nature of X, although Cr-ring vibrations involve a simple metal ring stretch and should be a measure of the metal ring bond strength.

The central metal-oxygen and metal-nitrogen band assignments are very uncertain, therefore they will not be discussed further.

<u>The ν C=N band</u>

CH_3-N-sal = 1645 cm^{-1}

$(CH_3$-N-sal$)_2$Cu(II) = 1638 cm^{-1}

Cu(II)$(CH_3$-N-sal$)_2$Cr$(CO)_3$ = 1630 cm^{-1}

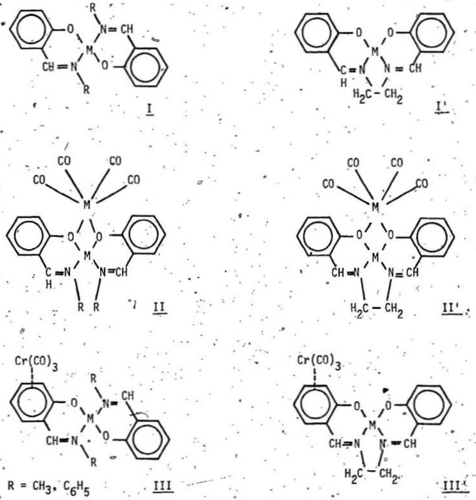
The reported values of ν C=N for Schiff base and M(II)$(CH_3$-N-sal$)_2$ are compared with tricarbonylchromium complexes of M(II)$(CH_3$-N-sal$)_2$ (e.g. above). There is a decrease of ν C=N in the tricarbonylchromium complex as compared to the parent compound which indicates a decrease of C-N bond order. This can be explained by arguing that the conjugated ligand has lost some of the π-electron density in bonding with the Cr$(CO)_3$ group. There is no significant change in ν C=N in M(II)$(C_6H_5$-N-sal$)_2$ and its tricarbonylchromium complexes. The ν C=N band in M(II)(salen) Cr$(CO)_3$ are not assigned because this band has not been assigned in M(II)(salen) by ^{15}N isotope labelling.

The ν C=0 bands

These are the most important bands in discussing the structure of the complexes and electron density distribution on the ligand. In all these complexes, two CO stretching vibrations are observed in solid state and in solution (Table XVI).

The E band is generally seen as a broad band. Perhaps the E band is split into two bands (A+B) which are not resolved in the spectrum. The broadening of the E mode may be due to deviation from the C_{3v} symmetry in these complexes.

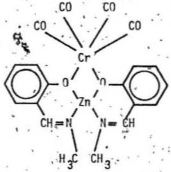
The point group symmetry predicts two i.r. active bands for C_{3v} symmetry. The presence of two CO bands in solid and solution in tricarbonylchromium complexes of metal Schiff bases indicates the presence of C_{3v} symmetry around the chromium atom. Therefore, the conclusion is drawn that a $Cr(CO)_3$ group is present in these complexes. The only reasonable place where a $Cr(CO)_3$ group can be attached is the benzene ring of the metal Schiff base. The structure of metal Schiff bases has already been established by other workers as shown in Fig. 43 (I, I'). In the case of both ligands (Fig. 43, I, I') there are two possibilities. The ligand may react with $Cr(CO)_6$ to form either a tricarbonylchromium complex (Fig. 43, III , III') or a tetracarbonylchromium complex (Fig. 43, II, II'). These two (Fig. 43, II and III) complexes can be easily differentiated from each other by the number of bands observed in the CO stretching reion. In the case of a tricarbonylchromium complex with C_{3v} symmetry only two bands are expected and in a tetracarbonylchromium complex with C_{2v} symmetry four bands are expected. There are four i.r. active bands observed in the case of



R = CH_3, C_6H_5

Fig. 43

Zn(II) (CH_3-N-sal)$_2$ $Cr(CO)_4$. Therefore, the following structure is proposed (Fig. 44).



IV

Fig. 44

The elemental analysis agrees with the above structure.

In the case (I of Fig. 43) where R is CH_3, these complexes show two i.r active bands and the following structure is suggested for M(II) $(CH_3$-N-sal$)_2$ $Cr(CO)_3$ complexes where M = Cr(II), Co(II) and Cu(II) (Fig. 45).

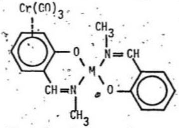


Fig. 45

The number of $Cr(CO)_3$ groups attached is determined by elemental analysis (C, H, N, and Cr). Only one group was shown to be present in these complexes.

In the zinc complex ($R = CH_3$) two $Cr(CO)_3$ groups have been shown to be present by the elemental analysis. In this case various isomers are possible (Fig. 46). It is hard to suggest which isomer exist. The n.m.r. could not be studied because of lack of sufficient solubility.

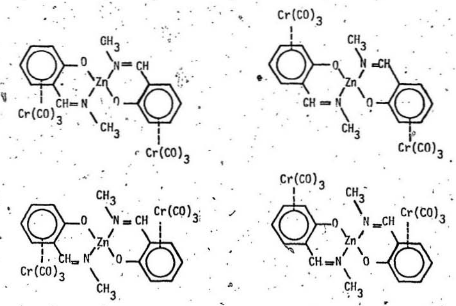


Fig. 46

Some unidentified complexes

All these complexes (Table IV) have two i.r. bands in the CO stretching region. This indicates that a Cr(CO)$_3$ group is present in these complexes. The elemental analysis suggests that, on the average, more than one and less than two Cr(CO)$_3$ groups are present per molecule of ligand in some of these complexes. The n.m.r of these complexes was not recorded because of lack of sufficient solubility. The thin layer chromatography showed only one spot with a tail in all the cases. Further attempts at purification by fractional precipitation gave the same result (a single spot with a tail on thin layer). There is a possibility that these complexes are either impure or dimeric with two and one Cr(CO)$_3$ groups per dimer of ligand (metal Schiff base). The overall mixture will have between one to two Cr(CO)$_3$ groups.

The following structures are proposed for Co(III) $(CH_3\text{-N-sal})_3$ $Cr(CO)_3$ (Fig. 47A) and Co(III) $(CH_3\text{-N-sal})_3(Cr(CO)_3)_2$ (Fig. 47B) complexes.

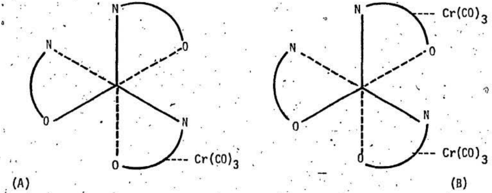


Fig. 47

N.M.R. study has already shown that these complexes have a trans stereochemistry (55). Various isomers are possible for Co(III) $(CH_3\text{-N-sal})_3$ $(Cr(CO)_3)_2$ Fig. 47B). The possible structures of M(II) $(C_6H_5\text{-N-sal})_2$ $Cr(CO)_3$ (M = Co(II), Cr(II) and Cu(II)) complexes are given below (Fig. 48A,B).

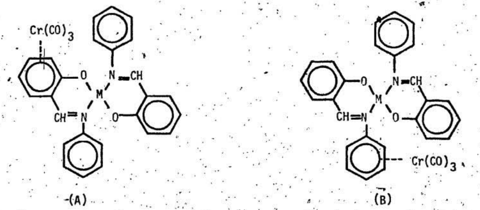


Fig. 48

The distinction between A and B would have been very simple if n.m.r. was available. (These complexes are paramagnetic and not very soluble.) From the infra-red arguments it was shown by Brown (129) that the $Cr(CO)_3$ group attaches preferentially to the ring which has higher electron density. In the parent compound, due to the following resonating structures (Fig. 49), the ring with four protons is conjugated. This conjugation increases the electron density of the ring with four protons.* The $Cr(CO)_3$ group will therefore attach itself preferentially to the ring with four protons. Therefore structure A (Fig. 48) is suggested for these complexes.

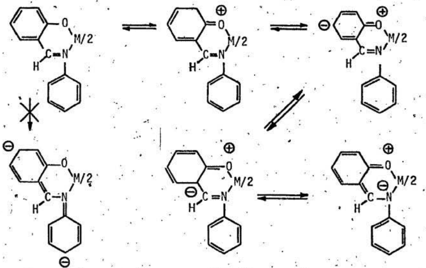


Fig. 49

Two $Cr(CO)_3$ groups are shown to be present in the following complex (Fig. 50), $Cr(C_6H_5\text{-}N\text{-}sal)_2 2Cr(CO)_3 4H_2O$. Various isomers are possible similar to zinc complex (Fig. 46).

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*See page 185 for further discussion.

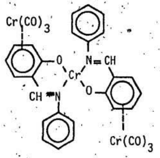


Fig. 50

The zinc complex has three $Cr(CO)_3$ groups, therefore one of the $Cr(CO)_3$ group has to be attached to a monosubstituted benzene ring (Fig. 51).

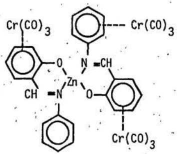


Fig. 51

The number of possible isomers is much greater for this complex. This complex is diamagnetic but is not soluble enough to study the n.m.r. The complex decomposed in deuterated dimethylsulphoxide while trying to get the n.m.r. spectrum.

<u>Tricarbonylchromium complexes of M(II) (salen)</u>

There was a strong possibility of forming a tetracarbonylchromium complex (Fig. 43 II') in the case of M(II) (salen) but the i.r. shows only two bands, suggesting a C_{3v} symmetry around the chromium metal. In this series of complexes only one $Cr(CO)_3$ group was found to be attached. This was shown by elemental analysis. The following structure is proposed for these complexes (Fig. 52), where M = Co(II), Ni(II), Cu(II) and Zn(II). The n.m.r. was not studied because of lack of solubility for Zn(II) and Ni(II) complexes.

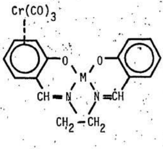


Fig. 52

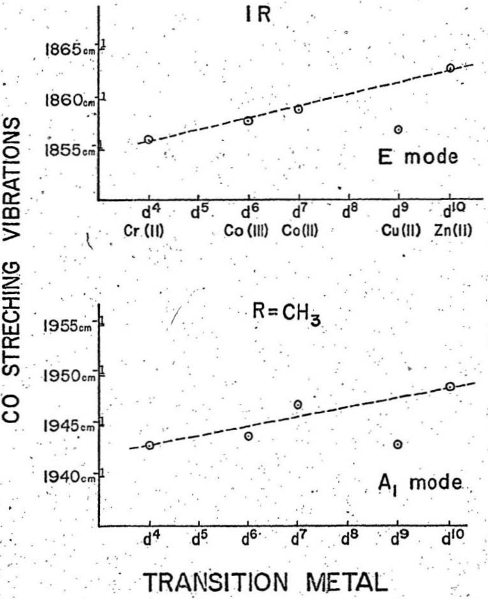
Electron distribution

The changes in CO stretching vibrations are discussed here in terms of changes in electron distribution of the ligands.

The CO stretching vibrations of tricarbonylchromium complexes of M(II) $(CH_3\text{-N-sal})_2$ are plotted against the electronic configuration of metals. The complexes containing one $Cr(CO)_3$ group are considered separately from complexes containing two $Cr(CO)_3$ groups. This way, changes of CO stretching vibrations are only dependent on the central metal.

The CO frequency increases as the number of the d electrons increases in M(II) $(CH_3\text{-N-sal})_2$ $Cr(CO)_3$ complexes (Graph I). The CO frequencies are known to be sensitive to the electron donating capacity of X(X = arenes) in arene tricarbonylchromium complexes. (Here X = M(II)-$(CH_3\text{-N-sal})_2$ where M = Cr(II), Co(II), Ni(II), Cu(II) and Zn(II).) The π-electron back donation from M(II) to $(CH_3\text{-N-sal})_2$ should increase with the increase of the number of d electrons and, as a result, the electron density of the $(CH_3\text{-N-sal})_2$ part should increase in the following order: Cr(II) < Co(III) < Co(II) < Cu(II) < Zn(II). Therefore, the CO stretching frequency should be in the reverse order, Cr(II) > Co(III) > Co(II) > Zn(II).

The observed trend of CO frequencies is opposite to that expected in M(II) $(CH_3\text{-N-sal})_2$ $Cr(CO)_3$ complexes. The increase of CO frequency from Cr to Zn is very small (7 cm^{-1}). This reversal in the order of CO stretching frequencies suggests that the electron density of the ligand is decreasing as the number of d electrons increases. This can be explained if the π-bonding between M(II) and $(CH_3\text{-N-sal})_2$ is considered negligible as compared to σ-bonding. Moving across from Cr to Zn the size of the metal ion decreases. The smaller ion with the same


IR
1865cm⁻¹
1860cm⁻¹
1855cm⁻¹
E mode
d4 d5 d6 d7 d8 d9 d10
Cr(II) Co(III) Co(II) Cu(II) Zn(II)
CO STRECHING VIBRATIONS
R=CH3
1955cm⁻¹
1950cm⁻¹
1945cm⁻¹
1940cm⁻¹
A1 mode
d4 d5 d6 d7 d8 d9 d10
TRANSITION METAL

Graph I

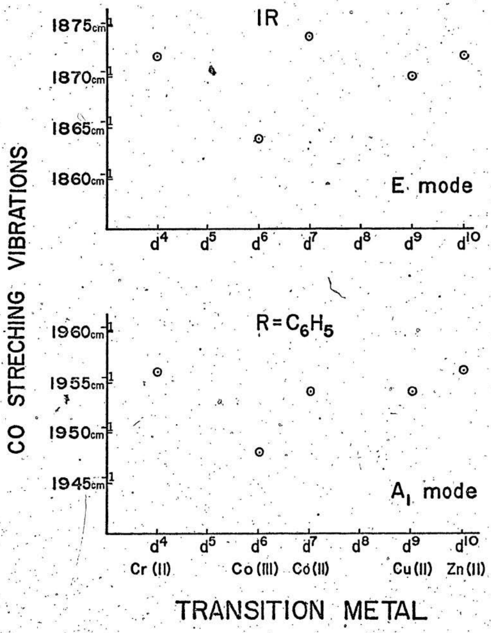
charge will withdraw more electron density from the ligand and will cause a decrease of electron density on the ligand. This effect will be observed as an increase in the CO stretching frequencies in the following order: Cr(II) < Co(III) < Co(II) < Cu(II) < Zn(II).

These results suggest that the bonding between the central metal and the ligand is mostly σ and perhaps a negligible amount of π-back bonding from the central metal to ligand exists. The oxygen atoms of the ligand do not have any suitable empty orbitals to accept π-back bonding.

β, the ratio of B in complex/B of free ion of these complexes was high (0.65-0.95) for the complexes where this parameter could be measured. The high value of β suggests that the bonding is mostly ionic and a very small amount of covalency exists between the central metal and the ligand. These results, along with i.r. observations in the CO stretching region, indicate that there is very poor covalent bonding between the central metal and the ligand.

The graph (Graph II) of CO frequencies vs. electronic configuration of metal for M(II) $(C_6H_5\text{-N-sal})_2\ Cr(CO)_3$ complexes (M = Cr(II), Co(III), Co(II), Cu(II) and Zn(II) seems to have no trend. The ν_{CO} values are more or less the same, indicating that the electron density of the Schiff base does not change much with different transition metal at its centre.

The Co(II) complex is octahedral and the stereochemistry of Cr(II) complex is not definitely known. Other complexes in the series are tetrahedral. The change of stereochemistry may be the reason for a slightly different interaction between the central metal and the ligand. This difference of stereochemistry changes the electron density on the ligand which changes the position of ν_{CO}.


IR
1875cm⁻¹
1870cm⁻¹
1865cm⁻¹
1860cm⁻¹
E mode
d4 d5 d6 d7 d8 d9 d10
R = C6H5
1960cm⁻¹
1955cm⁻¹
1950cm⁻¹
1945cm⁻¹
A1 mode
d4 d5 d6 d7 d8 d9 d10
Cr (II) Co (III) Co (II) Cu (II) Zn (II)
CO STRECHING VIBRATIONS
TRANSITION METAL

Graph II

The third series (M(II) (salen) $Cr(CO)_3$ complexes (M = Co(II), Ni(II), Cu(II) and Zn(II)) show a similar variation of CO frequencies with electronic configuration. The Cu(II) complex in this series does not follow the trend and has a higher ν_{CO} than the zinc complex. It is hard to explain this difference.

All the three series of complexes show a similar trend of increase of CO frequency with increasing electronic configuration of metals. The increase of ν_{CO} is less than 10 cm^{-1} going from d^1 to d^{10} in each series.

The overall study of tricarbonylchromium complexes of metal Schiff bases provides the following information:

1. The addition of a $Cr(CO)_3$ group to the metal Schiff bases has no significant effect on the stereochemistry of the metal Schiff bases.

2. The electronic distribution of the ligand (Schiff base) does not change very much by varying the central metal.

3. There is very little covalent bonding between the central metal and the ligand (Schiff base).

TABLE XVI

Infra-red (cm^{-1})

Compound	ν C=N Solid KBr	ν_{CO} Solid KBr	ν_{CO} Solution $CHCl_3$
$Cr(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3$	1,630 s	1,943, 1,856	L.S
$Cr(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_x$	1,628 s	1,947, 1,860	1,954, 1,869
$Co(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3H_2O$	1,630 s	1,947, 1,859	1,950, 1,864
$Co(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_x xH_2O$	1,628 s	1,950, 1,864	1,952, 1,868
$Cu(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3$	1,630 s	1,943, 1,857	1,950, 1,964
	1,618 sh		
$Cu(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_x$	1,628 s	1,942, 1,854	1,953, 1,865
$Zn(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_2 3H_2O$	1,632 s	1,949, 1,863	L.S
	1,627 sh		
	1,637 sh		
$Zn(CH_3\text{-}N\text{-}sal)_2Cr(CO)_4H_2O$	1,632 s	1,954, 1,880, 1,866, 1,826	1,948, 1,876, 1,860, 1,824

TABLE XVI, continued

Infra-red (cm^{-1})

Compound	ν C=N Solid KBr	ν_{CO} Solid KBr	ν_{CO} Solution $CHCl_3$
$Co(III)(CH_3-N-sal)_3Cr(CO)_32H_2O$	1,626 s	1,944, 1,858	1,954, 1,870
	1,616 sh		
	1,636 sh		
$Co(III)(CH_3-N-sal)_2(Cr(CO)_3)_23H_2O$	1,629 s	1,948, 1,862	1,950, 1,866
	1,637 sh		
	1,618 sh		
$Cr(II)(C_6H_5-N-sal)_2Cr(CO)_35H_2O$	1,614 s	1,956, 1,871	1,960, 1,880
	1,591 w		
$Cr(II)(C_6H_5-N-sal)_2(Cr(CO)_3)_24H_2O$	1,613 s 1,590 m	1,958, 1,873	1,960, 1,876
$Co(II)(C_6H_5-N-sal)_2Cr(CO)_33H_2O$	1,610 s	1,954, 1,874	1,956, 1,876
	1,590 w		

TABLE XVI, continued

Infra-red (cm^{-1})

Compound	ν C=N Solid KBr	ν_{CO} Solid KBr	ν_{CO} Solution $CHCl_3$
$Co(III)(C_6H_5\text{-N-sal})_2\,Cr(CO)_3 2H_2O$	1,608 s	1,954, 1,875	1,955, 1,877
	1,590 m		
$Cu(II)(C_6H_5\text{-N-sal})_2 Cr(CO)_3 5H_2O$	1,613 s	1,954, 1,872	1,956, 1,876
	1,593 m		
$Cu(II)(C_6H_5\text{-N-sal})_2\ Cr(CO)_3 3H_2O$	1,612 s	1,954, 1,875	1,955, 1,878
	1,590 m		
$Zn(II)(C_6H_5\text{-N-sal})_2(Cr(CO)_3)_x xH_2O$	1,612 s	1,956, 1,872	L.S
	1,583 m		
$Zn(II)(C_6H_5\text{-N-sal})_2(Cr(CO)_3)_3 5H_2O$	1,615 s	1,958, 1,876	1,962, 1,882
	1,593 m		
$Co(III)(C_6H_5\text{-N-sal})_3(Cr(CO)_3)_x xH_2O$	1,612 s	1,948, 1,850	1,950, 1,858
	1,593 m		

TABLE XVI, continued

Infra-red (cm^{-1})

Compound	ν C=N Solid KBr	ν_{CO} Solid KBr	ν_{CO} Solution $CHCl_3$
$Co(III)(C_6H_5-N-sal)_3(Cr(CO)_3)_2 7H_2O$	1,608 s 1,589 m	1,946, 1,864	1,948, 1,874
$Co(II)(salen)Cr(CO)_3 2H_2O$		1,938, 1,849	1,942, 1,854
$Ni(II)(salen)Cr(CO)_3 2H_2O$		1,939, 1,852	L.S
$Cu(II)(salen)Cr(CO)_3 2H_2O$		1,948, 1,866	1,956, 1,872. 1,892
$Zn(II)(salen)Cr(CO)_3 2H_2O$		1,943, 1,858	

L.S = Low Solubility

TABLE XVII

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Cr(II)(CH_3\text{-N-sal})_2Cr(CO)_3$	681 w 662 sh 632 m 613 sh	487 s	296 w	590 w	464 w
	Others 522 w, 502 sh, 401 v.w, 392 w, 368 w, 350 w, 342 w, 330 v.w, 319 m, 304 w, 280 w, 268 v.w, 260 v.w				
$Cr(II)(CH_3\text{-N-sal})_2(Cr(CO)_3)_x$	681 w 665 sh 638 m 631 m 615 sh	475 w	291 w	590 w	497 sh 416 m
	Others 549 v.w, 521 sh, 400 v.w, 391 v.w, 366 v.w, 359 v.w, 341 v.w, 299 v.w, 317 v.w, 303 v.w, 280, 267, 259				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Co(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3H_2O$	679 w 658 sh 629 s 608 s	473 m	290 w	593 w	473 m 420 m
	Others 550 sh, 500 sh, 450 sh, 390 sh, 367 w, 356 sh, 340 v.w, 329 v.w, 316 v.w, 302 v.w, 280 sh, 265 sh, 256 w				
$Co(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_x$	680 w 655 sh 628 s 612 m	472 m	295 m	590 w	472 m 420 m
	Others 555 sh, 524 v.w, 490 sh, 401 v.w, 392 w, 38 sh, 370 w, 374 w, 350 w, 344 w, 330 v.w, 318 w, 305 w, 281 w, 26 v.w				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Cu(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3$	681 sh	473 w	296 w	588 w	473 w
	663 sh				415 w
	641 m				
	610 sh				
	Others 549 w, 522 w, 422 sh, 401 v.w, 391 v.w, 370 v.w, 357 v.w, 342 w, 330 v.w, 318 w, 303 w, 280 w, 268 w, 260 w				
$Cu(II)(CH_3\text{-}N\text{-}sal)_2(Cr(CO)_3)_x$	679 w	473 m	292 v.w	590 w	473 m
	659 sh				422 m
	630 s				
	616 sh				
	Others 561 w, 521 w, 500 sh, 406 sh, 492 sh, 372 v.w, 367 v.w, 337 v.w, 328 v.w, 317 v.w, 303 v.w, 259 v.w				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Zn(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3 3H_2O$	682 w	473 v.w	293 v.w	549	488 v.w
	660 sh				420 w
	642 m				
	606 w				
	Others 521 sh, 503 sh, 449 v.w, 391 v.w, 372 w, 358 sh, 350 sh, 341 w, 321 v.w, 304 v.w				
$Zn(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_4H_2O$	681 m	477 w	297 w	576 w	489 sh
	675 sh				438 m
	630 m				
	613 w				
	Others 548 sh, 519 sh, 391, 370 m, 358 sh, 351 w, 343 w, 319 m, 305 w, 294 w, 281 w, 268 w, 260 w				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Co(II)(CH_3\text{-}N\text{-}sal)_3(Cr(CO)_3)_2 3H_2O$	675 sh	470 w	292 w	592 v.w	500 v.w
	659 v.w				417 m
	628 m				
	610 m				
	Others 562 sh, 546 sh, 525 v.w, 395 sh, 366 v.w, 352 v.w, 316 v.w, 302 v.w, 286 sh, 257 v.w				
$Co(III)(CH_3\text{-}N\text{-}sal)_3Cr(CO)_3 2H_2O$	672 sh	478 w	290 w	590 w	500 v.w
	654 w				420 m
	625 m				
	611 w				
	Others 520 v.w, 456 sh, 392 sh, 366 v.w, 354 v.w, 342 v.w, 314 v.w, 300 v.w, 280 sh, 257 v.w				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Cr(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3 5H_2O$	675 v.w	476 w	290 w	501 v.w	558 w
	670 v.w				438 m
	630 w				
	608 w				
	Others 590 v.w, 440 sh, 365 w, 356 sh, 340 w, 318 w, 302 v.w, 278 sh				
$Cr(II)(C_6H_5\text{-N-sal})_2(Cr(C\overline{O)_3)_2 4H}_2)$	672 w	470 w	290 w	497 w	556 m
	640 w				437 w
	607 m				
	Others 592 w, 535 w, 470 w, 417 w, 400 sh, 362 w, 350 sh, 340 w, 317 w, 280 w, 256				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Co(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3 2H_2O$	681 v.w	473 v.w	290 w	489 v.w	532 sh
	677 w				460 w
	622 w				
	609 s				
	Others 591 v.w, 582 v.w, 557 m, 544 sh, 532 sh, 473 v.w, 410 sh, 384 v.w, 365 m, 356 sh, 339 v.w, 328 v.w, 301 v.w, 278, 259 v.w				
$Co(II)(C_6H_5\text{-N-sal})_2(Cr(CO)_3)_2 3H_2O)$	670 w	472 v.w	290 w	488 v.w	528 v.w
	630 w				
	606 w				
	Others 590 sh, 556 m, 536 sh, 528 sh, 500 v.w, 390 sh, 365 m, 354 v.w, 338 w, 327 v.w, 313 w, 300 v.w, 276 v.w, 263 sh, 258 v.w				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Cu(II)(C_6H_5\text{-}N\text{-}sal)_2(Cr(CO)_3 5H_2O$	681 w	475 v.w	292 w	508 sh	527 sh
	635 sh				
	628 w				
	611 m				
	Others 593 w, 558 m, 412 sh, 396 v.w, 367 m, 354 sh, 340 v.w, 326 v.w, 315 w, 302 v.w, 280 sh, 258 v.w				
$Cu(II)(C_6H_5\text{-}N\text{-}sal)_2(Cr(CO)_3)_2 4H_2O$	680 w	472 v.w	290 w	481 v.w	533 sh
	643 sh				428 v.w
	628 w				
	604 s				
	Others 590 w, 558 m, 420 v.w, 408 v.w, 390 v.w, 364 w, 328 v.w, 315 v.w, 301 v.w, 276 sh, 258 v.w				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Zn(II)(C_6H_5\text{-N-sal})_2(Cr(CO)_3)_x xH_2O$	680 m 632 m		295 w		560 w 435 m
	Others 594 sh, 342 w, 317 w, 304 w, 280 w, 268 w, 260 w				
$Zn(II)(C_6H_5\text{-N-sal})_2(Cr(CO)_3)_3 5H_2O$	681 w 676 sh 640 m	473 sh	295 w		556 w 437 m
	Others 596 sh, 440 sh, 413 w, 391 w, 367 w, 358 sh, 350 w, 342 w, 338 w, 330 w, 318 m, 303 m, 193 m, 270 w, 268 w				
$Co(III)(C_6H_5\text{-N-sal})_3 Cr(CO)_3)_x$	675 v.w 640 w 608 m	475 v.w	295 w	486 v.w	558 m
	Others 590 v.w, 580 v.w, 546 sh, 511 sh, 501 sh, 416 v.w, 393 sh, 372 sh, 369 w, 356 v.w, 352 v.w, 330 v.w, 321 v.w, 254 v.w				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
$Co(III)(C_6H_5\text{-N-sal})_3(Cr(CO)_3)_2 7H_2O$	672 v.w 640 w 611 w	472 v.w	292 w	496 v.w	556 m
	Others 594 v.w, 530 v.w, 522 v.w, 408, 417 sh, 397 sh, 365 w, 356 v.w, 338 v.w, 315, 300 v.w				
$Co(II)(salen)Cr(CO)_3 2H_2O$	675 v.w 630 m	483 w	292 w		
	Others 593 sh, 582 sh, 560 sh, 546 w, 472 w, 438 w, 410 sh, 348 sh, 333 sh, 317 sh				
$Ni(II)(salen)Cr(CO)_3 2H_2O$	671 sh 656 sh 632 m 615 sh	490 w	288 w		
	Others 588 w, 545 w, 471 w, 416 sh, 363 w, 353 sh, 336 sh, 312 sh				

TABLE XVII, continued

Far infra-red (cm^{-1}) KBr

Compound	δ Cr-C-O	ν Cr-CO	ν Cr-ring	ν M-O	ν M-N
Cu(II)(salen)Cr(CO)$_3$2H$_2$O	676 w 642 m 612 sh	483 m	290 v.w		
	Others 588 w, 535 w, 464 m, 438 w, 421 m, 380 w, 366 w, 330 w				
Zn(II)(salen)Cr(CO)$_3$2H$_2$O	675 m 640 s	488 w	290 w		
	Others 580 w, 540 m, 438 w, 354 m, 348 w, 335, 325, 312, 300 w				

s = strong, m = medium, w = weak, v.w = very weak and sh = shoulder

X.

TRICARBONYLCHROMIUM COMPLEXES OF METAL PHTHALOCYANINES

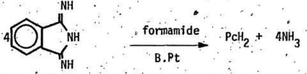
Phthalocyanines are a very widely studied group of compounds because of their peculiar structure and high thermal and chemical stability. Most of the metal phthalocyanines can be sublimed unchanged at 400°C/10^{-6} mm. Hg. Copper phthalocyanine is stable at 900°C in vacuo. These compounds are usually insoluble in common solvents but are slightly soluble in higher boiling aromatic solvents such as quinoline, chlorobenzene and chloronapthalene.

The conjugated system of metal phthalocyanine makes it a very suitable ligand to study the metal-metal interaction occurring through the ligand, (tricarbonylchromium complex of metal phthalocyanine) and changes of electron distribution by varying the central metal. The electron density of the highly conjugated metal phthalocyanine is expected to change by varying the central metal if there is significant π-back bonding from the central metal to phthalocyanine. The changes of electron density can be studied by making tricarbonylchromium complexes and studying the i.r. in the CO stretching region. The tricarbonylchromium complexes of phthalocyanine and a few metal phthalocyanines have been prepared by the reaction of hexacarbonylchromium with metal phthalocyanines. Purification of these complexes was not achieved.

General methods of preparation of phthalocyanine and metal phthalocyanines

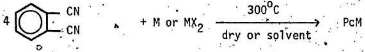
There are many methods of preparing these compounds. Some of the laboratory methods are given below (134).

1.

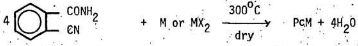


2. $PcH_2 + MX_2 \xrightarrow[\text{B.Pt}]{\text{solvent (e.g. quinoline)}} PcM + 2HX$

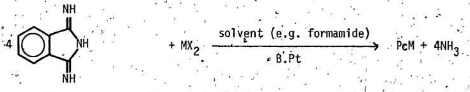
3.



4.



5.



6. $PcLi_2 + MX_2 \xrightarrow{\text{solvent}} PcM + 2LiX$

Experimental

Phthalocyanine

Phthalocyanine was bought commercially from J. T. Baker Chemical Co.

Tricarbonylchromium complex of phthalocyanine

The same method used for the preparation of Zn(II) $(CH_3\text{-N-sal})_2 Cr(CO)_3$ complex was used. Dioxane was tried first as a solvent for this reaction because of the greater solubility of Pc in it, but no carbonyl complex was formed. Finally, di-n-butyl ether was used as a solvent and a tricarbonylchromium complex was formed. The i.r. of the dried product showed weak CO stretching vibrations as compared to other bands, indicating that the greater portion of the product was starting material (phthalocyanine). The reaction was repeated three times, prolonging the duration of reaction each time (6h, 12h and 48h) in an attempt to increase the yield, but there was no significant increase.

The reaction product was sublimed in vacuo. The complex decomposed at 200°C. No sublimation occurred. The other techniques of purification such as chromatography and crystallization did not give satisfactory results.

PcZn(II)

The third method outlined above was used to prepare this compound. The purity of the compound was checked by comparing the U.V/visible spectra of the prepared compound with the literature (135).

Spectrum recorded (pyridine) = 673 nm ($\log \varepsilon = 5.44$), 647 nm
($\log \varepsilon = 4.55$), 608 nm ($\log \varepsilon = 4.58$), 347 nm ($\log \varepsilon = 481$)
Literature value = 672 nm ($\log \varepsilon = 5.45$), 646 nm ($\log \varepsilon = 4.56$)
607 nm ($\log \varepsilon = 4.59$), 347 nm ($\log \varepsilon = 4.81$).

Tricarbonylchromium complex of PcZn(II)

The same method used for the PcCr(CO)$_3$ complex was used for the preparation. The i.r. of the dried product showed two CO stretching vibrations, indicating the formation of tricarbonylchromium complex.

All attempts to purify this complex using sublimation, crystallisation and chromatographic techniques were unsuccessful.

PcCu(II)

A similar method used for PcZn(II) was used for the preparation. The purity of the compound was checked by comparing the U.V/visible spectra of the prepared compound with that of the literature (136).

Spectrum recorded = 793 nm (log ε = 5.395), 701 nm (log ε = 4.49), 441 nm (log ε = 4.28), 305 nm (log ε = 4.73), 292 nm (log ε = 4.59) and 225 nm (log ε = 4.84)

Literature value=792 nm (log ε = 5.39), 700 nm (log ε = 4.49), 440 nm (log ε = 4.28), 305 nm (log ε = 4.72), 291 nm (log ε = 4.58) and 224 nm (log ε = 4.83)

Solvent, sulphuric acid (13.8 M)

Tricarbonylchromium complex of PcCu(II)

The same method used for the PcCr(CO)$_3$ complex was used for the preparation. The i.r. of the dried product showed two weak CO stretching vibrations, indicating the formation of tricarbonylchromium complex. The purification of this compound was not achieved.

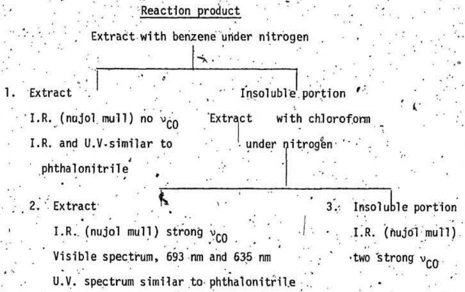
Phthalonitrile

Phthalonitrile was obtained commercially from J. T. Baker Chemical Co.

Tricarbonylchromium complex of PcCr(II)

Phthalonitrile was reacted directly with hexacarbonylchromium in refluxing di-n-butyl ether in an atmosphere of nitrogen for six hours in order to obtain PcCr(II) and its tricarbonylchromium derivative. The i.r. of the dried product showed strong CO stretching vibrations.

The reaction product was separated into the following fractions using different solvents in a Soxhlet extractor.



Reaction product

Extract with benzene under nitrogen

1. Extract
I.R. (nujol mull) no ν_{CO}
I.R. and U.V. similar to
phthalonitrile

Insoluble portion
Extract with chloroform
under nitrogen

2. Extract
I.R. (nujol mull) strong ν_{CO}
Visible spectrum, 693 nm and 635 nm
U.V. spectrum similar to phthalonitrile

3. Insoluble portion
I.R. (nujol mull)
two strong ν_{CO}

The presence of bands in the visible region of fraction 2 indicates the formation of phthalocyanine (phthalonitrile has no absorption in the visible region). The different visible spectrum of fraction 2 than phthalocyanine (702 nm and 662 nm) suggests the formation of PcCr(II). Fractions 2 and 3 could be a mixture of PcCr(II) and PcCr(II) $Cr(CO)_3$ complexes. A yellow compound was obtained by sublimation of fraction 2 (the unsublimed compound showed CO stretching vibrations). This yellow compound had two very strong CO stretching vibrations, and its U.V. spectrum was similar to phthalonitrile. This yellow compound was ignored because the author was only interested in isolating the tricarbonylchromium complexes of Pc M(II). Further purification of fractions 2 and 3 was unsuccessful.

Discussion

Due to difficulties involved in purifying these complexes no further attempt was made to make more complexes. The complexes prepared were not isolated in pure form, therefore their i.r and U.V/visible spectra may not be reliable and therefore will not be discussed.

XI.

Further scope of work

The preparation and study of tricarbonylchromium complexes of bis (thiosalicylaldiminato)M(II) (137) (Fig. 53) will be an interesting extension of this work.

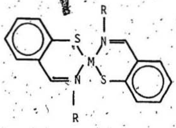


Fig. 53

Sulfur is known to form strong covalent bonds and this should bring significant changes of electron density on the ligand with different transition metals at the centre (M). Such changes will be reflected by changes in ν_{CO}. A disadvantage in pursuing this problem could be the predicted low solubility of these complexes. Lack of solubility prevents n.m.r. and molecular weight determinations and purifications also become difficult.

XII

REFERENCES

1. E. O. Fischer and K. Öfele, Angew. Chem., 69 (1957) 715; Chem. Ber., 90 (1957) 2532.
2. A. Nicholls and M. J. Whiting, J. Chem. Soc. (1959) 551.
3. E. O. Fischer, K. Öfele, H. Essler, W. Frohlich, J. P. Mortenson, and W. Semmlinger, Chem. Ber., 91 (1958) 2763.
4. G. Natta, R. Ercoli, and F. Calderazzo, Chem. e Ind., 40 (1958) 287.
5. M. D. Rausch, Pure App. Chem., 30 (1972), 523.
6. H. Zeiss, "Organometallic Chemistry" Reinhold Publishing Corp., New York, 1960, p. 399.
7. H. Zeiss, P. J. Wheatly, and H. J. S. Winkler, "Benzenoid Metal Complexes", Ronald Press Co., New York, 1966, p. 51.
8. G. R. Dobson, W. Stolz, and R. K. Sheline, Adv. Inorg. Radiochem., 8 (1966) 1.
9. E. O. Fischer and H. P. Fritz, Adv. Inorg. Radiochem., 1 (1959) 102.
10. E. O. Fischer and A. Maasbol, Angew. Chem., 76 (1964) 645.
11. M. D. Rausch, G. A. Moser, E. T. Zaiko, and A. L. Lipman, Jr., J. Organometal. Chem., 23 (1970) 185.
12. E. O. Fischer and K. Öfele, Chem. Ber., 93 (1960) 1156.
13. E. O. Fischer and K. Öfele, J. Organometal. Chem., 8 (1967) 5.
14. T. A. Emmanuel, S. L. Stafford, and F. G. A. Stone, J. Am. Chem. Soc. 83 (1961) 3597.
15. S. P. Gubin and V. S. Khandkorova, J. Organometal. Chem., 22 (1970) 449.

16. N. J. Gogan and C. S. Davies, J. Organometal. Chem., 39 (1972) 129.

17. K. J. Coleman, C. S. Davies, and N. J. Gogan, Chem. Commun. (1970) 1414.

18. N. J. Gogan and K. C. Chu, 56th C.I.C. Conference, Montreal, Canada, June 1973.

19. R. V. Emanuel and E. W. Randall, J. Chem. Soc. A (1969) 3002.

20. M. L. H. Green, "Organometallic Compounds", Methuen & Co., Ltd., London, 1968, p. 181.

21. G. Klopman and K. Noack, Inorg. Chem., 7 (1968) 579.

22. D. A. Brown and F. J. Hughes, J. Chem. Soc. A (1968) 1519.

23. O. L. Carter, A. J. McPhail, and A. T. Sinn, J. Chem. Soc. A (1966) 822.

24. O. L. Carter, A. J. McPhail, and A. T. Sinn, J. Chem. Soc. A (1967) 228.

25. O. L. Carter, A. J. McPhail, and A. T. Sinn, J. Chem. Soc. A (1967) 1619.

26. J. T. Price and T. S. Sorenson, Can. J. Chem., 46 (1968) 515.

27. M. F. Bailey and L. F. Dahl, Inorg. Chem., 4 (1965) 1314.

28. N. J. Gogan and Z. U. Siddiqui, Chem. Commun. (1970) 284.

29. N. J. Gogan and Z. U. Siddiqui, Can. J. Chem., 50 (1972) 720.

30. Z. U. Siddiqui, M.Sc. Thesis, Memorial University of Newfoundland, 1970.

31. E. B. Fleischer, C. K. Milbrand, and L. E. Webb, J. Am. Chem. Soc., 86 (1964) 2342.

32. C. Ettling, Ann., 35 (1840) 241.

33. H. Schiff, Ann., 150 (1869) 193.

34. M. Delepine, Bull. Soc. Chim. France, 21 (1899) 943.

35. P. Pfeiffer, E. Buchholz, and O. Bauer, J. Prakt. Chem., 129 (1931) 163.

36. P. Pfeiffer, E. Brith, E. Lubbe, and T. Tsumaki, Ann., 84 (1933) 503.

37. P. Pfeiffer, W. Offerman, and W. Werner, J. Prakt. Chem., 159 (1942) 313.

38. J. V. Dubsky and A. Sokol, Collection Czech. Chem. Commun., 3 (1931) 548.

39. R. H. Holm, G. W. Everett, and A. Chakravorty, Prog. Inorg. Chem., 7 (1966) 83.

40. R. H. Holm and M. G. O'Connor, Prog. Inorg. Chem., 14 (1971) 241.

41. P. L. Orioli, M. DiVaira, and L. Sacconi, Chem. Commun. (1965) 103.

42. L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, J. Am. Chem. Soc., 84 (1962) 3246.

43. F. A. Cotton, P. M. L. Goodgame, and M. Goodgame, J. Am. Chem. Soc., 83 (1961) 4690.

44. B. O. West, J. Chem. Soc. (1962) 1374.

45. P. L. Orioli, L. Sacconi, and M. DiVaira, Chem. Commun. (1965) 1.

46. E. Frasson, C. Tamattoni, and L. Sacconi, J. Phys. Chem., 63 (1959) 1908.

47. L. Sacconi, P. Paoletti, and G. Delre, J. Am. Chem. Soc., 85 (1963) 411.

48. L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, Proc. Chem. Soc. (1962) 255.

49. R. H. Holm and K. Swaminathan, Inorg. Chem., 2 (1963) 181.

50. E. C. Lingafelter, G. L. Simmons, B. Morisin, C. Sheringer, and C. Freiburger, Acta. Cryst., 14 (1961) 1222.

51. L. Sacconi and M. Ciampolini, J. Chem. Soc. (1964) 276.

52. J. Ferguson, J. Chem. Phys., 34 (1961) 611.

53. F. Furlani and G. Morpurgo, Theor. Chim. Acta., 1 (1963) 102.

54. B. O. West, J. Chem. Soc. (1960) 4944.

55. A. Chakravorty and R. H. Holm. Inorg. Chem., 3 (1964) 1521.

56. H. Nishikawa and S. Yamada, Bull. Chem. Soc. Japan., 37 (1964) 1154.

57. L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, J. Am. Chem. Soc., 84 (1962) 3246.

58. L. Wei, R. M. Stogsdill, and E. C. Lingafelter, Acta. Cryst., 17 (1964) 1058.

59. M. Dobler, Helv. Chim. Acta., 45 (1962) 1628.

60. L. Sacconi and M. Ciampolini, J. Am. Chem. Soc., 85 (1963) 1750.

61. R. H. Holm and K. Swaminathan, Inorg. Chem., 1 (1962) 599.

62. E. Frasson and C. Panattoni, Z. Kristallog., 116 (1961) 154.

63. C. E. Percy and D. A. Thornton, J. Inorg. Nucl. Chem., 34 (1972) 3357.

64. R. D. Hancock and D. A. Thornton, J. S. Af. Chem. Inst., 23 (1970) 71.

65. C. E. Percy and D. A. Thornton, J. Inorg. Nucl. Chem., 34 (1972) 3369.

66. H. Nishikawa and S. Yamada, Bull. Chem. Soc. Japan, 37 (1964) 8.

67. S. Yamada, Coord. Chem. Rev., 1 (1966) 415.

68. J. Manassen, Inorg. Chem., 9 (1970) 966.

69. H. Weigold and B. O. West, J. Chem. Soc. A (1967) 1310.

70. B. N. Figgis and R. S. Nyholm, J. Chem. Soc. (1959) 338.

71. A. Earnshaw, P. C. Howlett, E. A. King, and L. F. Larkworthy, J. Chem. Soc. A (1968) 241.

72. M. Calvin and C.H. Barkelaw, J. Am. Chem. Soc., 68 (1946) 2267.

73. B. Bosnich, J. Am. Chem. Soc., 90 (1968) 627.

74. R.S. Downing and F.L. Urbach, J. Am. Chem. Soc., 92 (1970) 5861.

75. H.C. Clark and A.L. Odell, J. Chem. Soc. (1956) 520.

76. D. Hall and T.N. Waters, J. Chem. Soc. (1960) 2644 and 2639.

77. R. De Isasi, S.L. Holt, and B. Post, Inorg. Chem., 10 (1971) 1498.

78. E.N. Baker, D. Hall, and T.N. Waters, J. Chem. Soc. A (1970) 406.

79. D. Hall, A.D. Rae and T.N. Waters, J. Chem. Soc. (1963) 5897.

80. J. Lewis and R.A. Walton, J. Chem. Soc. A, (1966) 1559.

81. J.M. Stewart and E.C. Lingafelter, Acta. Crystallogr., 12 (1959) 842.

82. R.S. Downing and F.L. Urbach, J. Am. Chem. Soc., 19 (1969) 5977.

83. D. Hall and F.H. Moore, J. Chem. Soc. A, (1966) 1822.

84. D. Hall and F.H. Moore, Proc. Chem. Soc. (1960) 256.

85. D. Smith and C.M. Harris, Coord. Chem. Rev., 4 (1969) 391.

86. R.B. Coles, C.M. Harris, and E. Sinn, Aust. J. Chem., 33 (1970) 243.

87. M.D. Hobday and T.D. Smith, J. Chem. Soc. A, (1971) 1453.

88. M.D. Hobday and T.D. Smith, J. Chem. Soc. A, (1971) 3424.

89. R.H. Lee, E. Griswold, and T. Kleinberg, Inorg. Chem., 3 (1964) 1278.

90. J. Loliger and R. Schefford, J. Chem. Ed., 49 (1972) 646.

91. L. Sacconi, M. Ciampolini, and T. Speroni, J. Am. Chem. Soc., 67 (1965) 3103.

92. R.G. Charles, J. Org. Chem., 22 (1957) 677.

93. A. Chakravorty and R.H. Holm, Inorg. Chem., 3 (1964) 1521.

94. B.O. West, J. Chem. Soc. (1960) 4944.

95. G.N. Tyson and S.C. Adams, J. Am. Chem. Soc., 62 (1940) 1228.

96. R.H. Holm and K. Swaminathan, Inorg. Chem., 1 (1962) 599.

97. C. E. Percy and D. A. Thornton, J. Inorg. Nucl. Chem., 34 (1972) 3357.

98. R. H. Bailes and M. Calvin, J. Am. Chem. Soc., 69 (1947) 1886.

99. B. O. West, J. Chem. Soc. (1954) 395.

100. T. Tsumaki, Bull. Chem. Soc. Japan., 13 (1938) 252.

101. D. Hall and F. H. Moore, J. Chem. Soc. A (1966) 1822.

102. J. V. Dubsky and A. Sokol, Collec. Czec. Chem. Comm. 3 (1931) 548-9; Chem. Abst. 26 (1932) 1538.

103. F. A. Cotton, "Chemical Applications of Group Theory", Interscience, New York, 1966.

104. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier Publishing Company, London-New York, 1968.

105. T. M. Dunn, D. S. McClure, and R. G. Pearson, "Some Aspects of Crystal Field Theory", Harper and Row Publishers, New York, 1965.

106. J. P. Fackler, Jr., "Symmetry in Coordination Chemistry", Academic Press, New York-London, 1971.

107. L. E. Orgel, J. Chem. Soc. (1952) 4756.

108. Y. Tanabe and S. Sugano, J. Phys. Soc. Japan, 9 (1954) 766.

109. A. B. P. Lever, J. Chem. Ed., 45 (1968) 711.

110. A. Earnshaw, "Introduction to Magnetochemistry", Academic Press, London-New York, 1968.

111. J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry", Interscience Publishers, New York, 1964.

112. S. F. A. Kettle, "Coordination Compounds", Appleton Century Crofts, New York, 1969.

113. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, New York-London-Sydney, 3rd ed., 1972.

114. G. W. Everett, Jr., and R. H. Holm, J. Am. Chem. Soc., 87 (1965) 5266.

115. Ercoli and A. Mangani, Ric. Sci., 28 (1958) 2135; Chem. Abs., 5323 (1959) 10947g.

116. H. Yamada, T. Nakamura, and R. Tsuchida, Bull., Chem. Soc. Japan 30 (1960) 481,

117. R. T. Lundquist and M. Cais, J. Org. Chem., 27 (1962) 1167.

118. G. R. Dobson, I. W. Stolz and R. K. Sheline, Advances in Inorganic Chemistry and Radiochemistry, 8 (1966) 1.

119. D. Steele, Quart. Rev., 18 (1964) 21.

120. W. Beck, A. Melnikoff, and R. Stahl, Chem. Ber., 99 (1966) 3721.

121. F. A. Cotton and C. S. Kraihanzel, J. Am. Chem. Soc. 84 (1962) 4432.

122. F. A. Cotton, Inorg. Chem., 3 (1964) 702.

123. L. H. Jones, J. Chem. Phys., 36 (1962) 2375.

124. G. Klopman and K. Noack, Inorg. Chem., 7 (1968) 579.

125. H. Hass and R. K. Sheline, J. Chem. Phys. (1967) 2996.

126. D. A. Brown and F. J. Hughes, J. Chem. Soc. (1968) 1519.

127. D. M. Adams and A. Squire, J. Chem. Soc. A, (1970) 814.

128. H. P. Fritz and J. Manchot, Spectrochim. Acta., 18 (1962) 171.

129. D. A. Brown and J. R. Raju, J. Chem. Soc. A, (1966) 1617.

130. D. A. Brown, J. Inorg. Nucl. Chem., 13 (1960) 212.

131. H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, J. Chem. Soc. A, (1969) 2077.

132. S. F. A. Kettle, Spectrochim. Acta., 22 (1966) 1389.

133. D. A. Brown and L. Carrol, J. Chem. Soc. (1965) 2822.

134. A. B. P. Lever, Adv. Inorg. Radiochem., 7 (1965) 28.

135. M. J. Whalley, J. Chem. Soc. (1961) 866.
Izv. Vysshikh Uchebn. Zaredenii Khim. i Khim. Tekhnol., 4 (1961) 45.
136. B. D. Berezin, Chem. Abst. 55 (1961) 17205b.

137. E. Hoyer and B. Lorenz, Z. Chem., 8 (1968) 28.

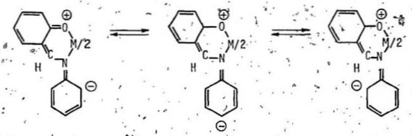
138. S. J. Gruber, C. M. Harris and E. Sinn, Inorg. Chem., 7 (1968) 268.

*See page 41.

The structure proposed by Hobday and Smith is doubtful, in view of the ν_{CO} values obtained for diglyme $Mo(CO)_3$ (lowest ν_{CO} 1823 cm^{-1}) where there are three oxygen atoms donating to the Mo and there is no back bonding from Mo to oxygen. As a result of the π-back donation from Mo to 3 CO's increases and the CO bond order is reduced and the ν_{CO} frequency is decreased.

In the case of Ni(II) (salen) $Cr(CO)_4$ there are only two oxygen atoms involved. As a result the π-back donation from Mo to CO's is distributed to 4 CO's, as compared to 3 CO's in the case of diglyme $Mo(CO)_3$, therefore the lowest ν_{CO} value should be above 1,823 cm^{-1} in the former complex. In fact, the lowest ν_{CO} value obtained by Hobday and Smith is 1,665 cm^{-1} which does not seem reasonable. The alternative possible structure could be Ni(II) (salen) $Cr(CO)_3$ H_2O where two i.r. bands are expected and the bands around 1,665 and 1,695 cm^{-1} could be due to impurity or the band at 1,665 cm^{-1} could easily be due to ν C=N. The elemental analysis for the new formula Ni(II) (salen) $Cr(CO)_3H_2O$ also agrees with the values found by Hobday and Smith.

In view of the fact that there are 3 more possible canonical forms in addition to those shown in Fig. 49 (page 147) the argument is revised. The 3 more canonical forms are shown below.



The negative charge is less likely to spend time on the ring with 5 protons than on the ring with 4 protons due to electronegativity reasons; as a result the electron density will be slightly higher at the ring with 4 protons. Therefore, it is likely that the $Cr(CO)_3$ group will prefer the ring with 4 protons.

There are two complexes obtained with one $Cr(CO)_3$ group in the case of Co(II) and Cu(II) $(C_6H_5\text{-N-sal})_2$ with the different number of water molecules. There are two possibilities. (1) Either both the complexes have the same structure ($Cr(CO)_3$ group attached to the ring with 4 protons), or (2) the complexes have different structures; one where the $Cr(CO)_3$ group is attached to the ring with 4 protons and the other where the $Cr(CO)_3$ group is attached to the ring with 5 protons.

There is a possibility of the latter case because of slightly different band positions in the near infrared and U.V./visible region and different ϵ values for these complexes. The ν_{CO} values are similar for both complexes. It is hard to suggest definitely any structure in the absence of any concrete proof for this group of complexes.