

**SYNTHESIS AND STUDY OF TRICARBONYLCHROMIUM
COMPLEXES OF SOME METALLOPORPHINES**

CENTRE FOR NEWFOUNDLAND STUDIES

**TOTAL OF 10 PAGES ONLY
MAY BE XEROXED**

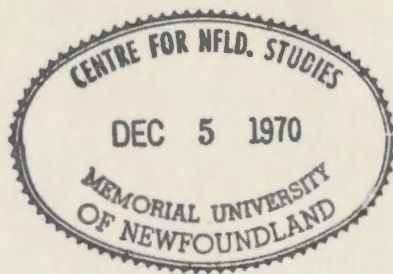
(Without Author's Permission)

ZAHIR UDDIN SIDDIQUI

16672

c1

223860



SYNTHESIS AND STUDY OF TRICARBONYLCHROMIUM
COMPLEXES OF SOME METALLOPORPHINES
A Thesis

by



Zahir Uddin Ziddiqui

Thesis submitted to the Memorial University
of Newfoundland for the partial fulfillment of
the degree of Master of Science.

DATE: August 7, 1970

Memorial University of
Newfoundland

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. N.J. Gogan for his encouragement and supervision throughout the course of this work.

Thanks are also due to Dr. D. Field for helpful advice and Mrs. C. Murphy who typed the manuscript.

The author wishes to thank Dr. E.K. Ralph, Mr. Tom Buckley and Dr. C. Loader for operation of the n.m.r. instrument and also Dr. B. Gregory for running mass spectra.

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

ABSTRACT

The tricarbonylchromium complexes of some metallocorphins have been synthesized and studied. The tricarbonylchromium complexes of 1st transition series metal porphines were prepared by refluxing hexacarbonylchromium and metal porphine in an atmosphere of pure nitrogen for 6 hours. After the preliminary studies by thin-layer chromatography on dried products the purification was done on a florisil column under nitrogen using different eluents for different compounds; in most of the cases the chromatographic technique for purification was successful. The purity of the purified products was tested by ultra violet/visible and infra red spectroscopy. The visible region spectrum of the complex had a blue or red shift in the bands as compared to starting material (metal porphine): in most cases, if the product was impure bands were mixed and broad. The infra red of pure product always had very distinct carbonyl peaks: if the compound was decomposed no CO stretching vibrations were observed.

The structures of the complexes were established with the help of infra red, ultra violet and n.m.r.. The elemental analysis confirmed the structure although the elemental analyses were not correct in some compounds due to their unstability.

Tetraphenylporphine, p-substituted porphine and metallocorphins have been studied spectroscopically (UV/visible IR) and theoretically. Zerner and Gouterman have done extended Hückel calculations on porphine systems with the metals Mn, Fe, Co, Ni, Cu and Zn. These calculations help in understanding the electronic structure of metallocorphine.



The studies on the trend of carbonyl frequencies of arene metal tricarbonyl have been done by Brown and Hughes using different arenes and different transition metals.

The preparation of tricarbonylchromium complexes of $\alpha, \beta, \gamma, \delta$ tetraphenylporphine metals and their infra red, ultra violet/visible spectra gives a better understanding of electronic distribution and bonding in metalloporphines.

The experimental results of CO stretching vibrations trend in the complexes was found in the following decreasing order: $\text{Cr}^{+2} > \text{Mn}^{+2} > \text{Co}^{+2} > \text{Zn}^{+2} > \text{Cu}^{+2} > \text{Ni}^{+2} > \text{Mn}^{+3}$.

The expected trend of CO stretching vibrations in complexes was in the following decreasing order. $\text{Cr}^{+2} > \text{Mn}^{+2} > \text{Co}^{+2} > \text{Zn}^{+2} > \text{Cu}^{+2} > \text{Ni}^{+2} > \text{Mn}^{+3}$.

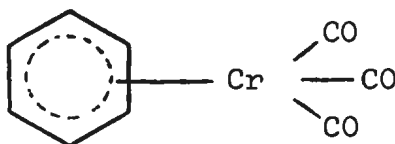
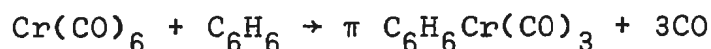
The CO stretching vibrations in all the complexes depend upon the π electron distribution in the metal porphines. A decrease of π electron distribution will increase the CO stretching vibration values and an increase of π electron distribution will decrease the CO stretching vibration values. As a result the trend in CO stretching vibration gives the qualitative values for π electron distribution in the metal porphine system and also throws light on bonding between central metal and porphine.

INDEX

	<u>Page No.</u>
INTRODUCTION	1
EXPERIMENTAL	15
DISCUSSION	31
APPENDIX	47
REFERENCES	58

INTRODUCTION

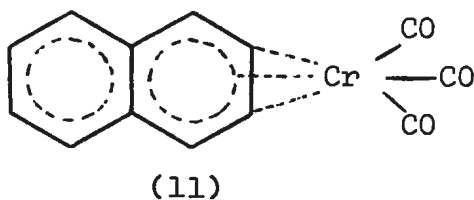
Tricarbonylbenzenechromium (Fig.I) was first obtained by Fischer and Öfele(1) in 27% yield from hexacarbonylchromium and dibenzenechromium in benzene in a sealed system at 220°. Nicholls and Whiting (2), Fischer and his coworkers(2a), discovered a simpler and more general method for preparing compounds of this type which involves heating hexacarbonylchromium under reflux in an excess of aromatic compound with a molar quantity in an inert solvent



(1)

Natta and his coworkers(3) also described the direct preparation of several of these compounds but used a pressurised system and high temperatures (200-235°). The work of Fischer shows that equilibria are involved in these reactions. An excess of carbon monoxide converts the dibenzenechromium complex into the hexacarbonyl and therefore it is advantageous in principle as well as much easier in practice to employ an open system, the free escape of carbon monoxide then driving the reaction to completion.

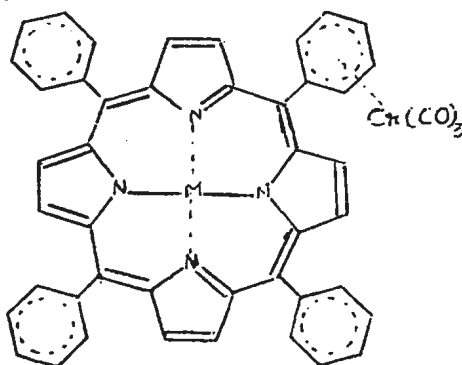
Naphthalene, the simplest condensed six membered ring compound, reacts with hexacarbonylchromium to give the complex shown in Fig.II (4).



The studies on carbonyl frequencies of arene metal tricarbonyls have been done using different arenes and different transition metals (5,6,7). I will refer briefly on recent work done by Brown and Hughes(8) on the trend of carbonyl stretching frequencies in metal tricarbonyl complexes.

- (a) Carbonyl frequencies in π -arene metal tricarbonyls decrease in the order benzene, toluene, xylene, mesitylene and N-N dimethyl-p-toluidine in all the Cr, Mo and W arene tricarbonyls.
- (b) Carbonyl frequencies in arene metal tricarbonyls increase in the order Cr, Mo and W.
- (c) Carbonyl frequencies in arene metal tricarbonyls are dependent upon solvent.

In the present study, the preparation of complexes of $\alpha,\beta,\gamma,\delta$ tetraphenylporphyrin metals with one or two tricarbonyl-chromium groups attached to a phenyl ring was done by reacting hexacarbonylchromium with metalloporphine in refluxing di-n-butyl-ether in an atmosphere of pure nitrogen.



The preparation of tricarbonylchromium complexes of $\alpha, \beta, \gamma, \delta$ tetraphenylporphine metals, and studies of their infra red, ultra violet and visible spectra should give a better understanding of electronic distribution and bonding in metalloporphines.

Tetraphenylporphine, p-substituted porphines and metalloporphines have been studied spectroscopically (u.v./visible and I.R.) and theoretically. Zerner and Gouterman(9) have done extended Hückel calculations on porphin systems with the metals Mn, Fe, Co, Ni, Cu, Zn and on the diprotic acid. These calculations move one step forward in understanding the electronic structure of porphyrins.

The extended Hückel calculations include all the valence orbitals of the metal. They accomplished the following objectives.

(a) Ordering of the d energy levels: magnetic state.

Fig.4 shows the orbital energy diagram

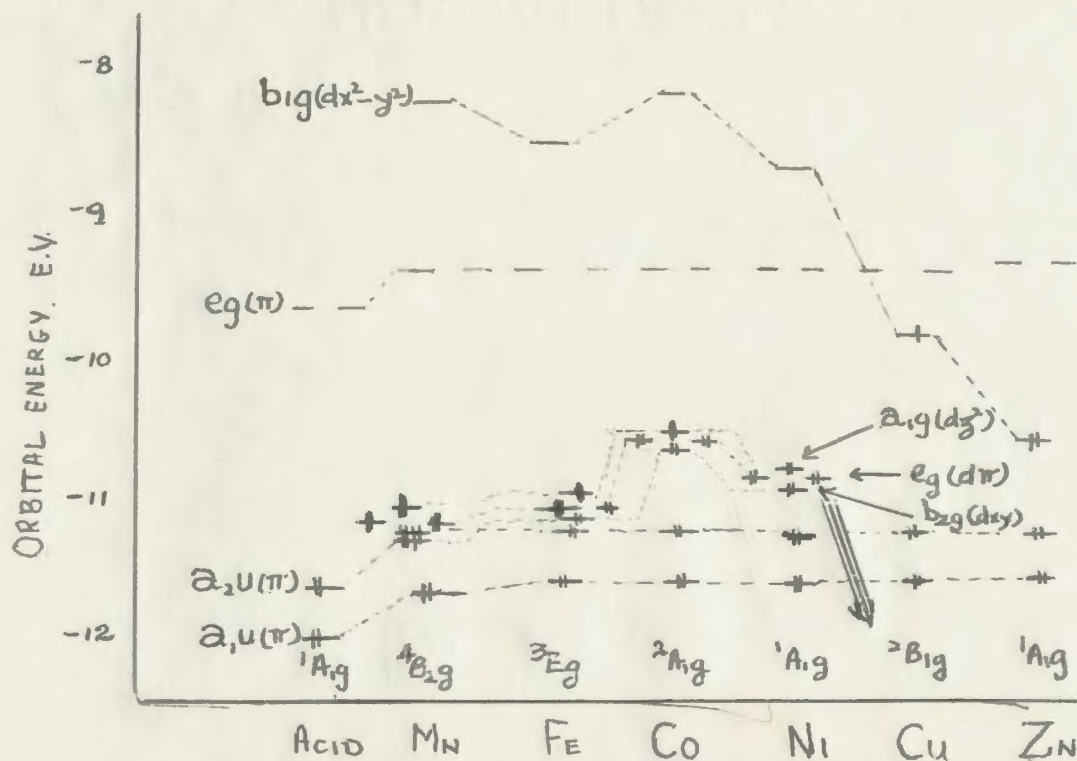


Fig. 4

obtained for the transition metal porphines. Electrons are assigned to d levels by a comparison of the d-d electronic energy gaps and the electronic repulsion estimated from atomic spectra. The Zn and Ni compounds are predicted to be diamagnetic. The calculations make Ni compound paramagnetic upon the addition of one pyridine above the metal. Cu and Co are paramagnetic. Fe (II) is predicted to exist as a triplet state. Mn (II) porphyrin exists as a quartet in the free compound. The order of the metal d-orbitals and the electronic assignments calculated from this model are in good agreement with those calculated by Lever(10) from a study of EPR and magnetic susceptibility measurements on phthalocyanines (preliminary calculations on phthalocyanines seem to indicate that the order and ligand field splitting of the metal d orbitals is almost identical to that of porphyrin). The complex experimental behavior of Mn (II) and Fe (II) porphyrins is attributed to the intermingling of the metal d orbitals with the porphyrin $a_2u(\pi)MO$.

(b) Coupling of metal and porphyrin

The original spectroscopic studies (10a) showed that except for small shifts in energy and intensity, the spectra of the various metal porphyrins are much the same. Thus the various metal orbitals must be weakly interacting with the porphyrin π system. The calculations give a picture of how this works as shown by Fig.4 and Tables 1, 2, 3, 4 and 5 as compared to spectroscopic studies.

TABLE I.

Top Filled Orbitals

A. Ligand Field Orbitals

	$3d_{x^2-y^2}$	b_{1g} N (2s)	N (2p σ)	All Others
Mn	-0.8279, 0.5455	-0.1242, 0.0264	0.3654, 0.3788	-, 0.0493
Fe	-0.8236, 0.5531	-0.1237, 0.0268	0.3568, 0.3700	-, 0.0501
Co	-0.8577, 0.6051	-0.1322, 0.0296	0.3401, 0.3284	-, 0.0369
Ni	-0.8373, 0.5882	-0.1306, 0.0300	0.3383, 0.3392	-, 0.0426
Cu	-0.6158, 0.2962	-0.1434, 0.0408	0.4076, 0.5584	-, 0.1046
Zn	-0.2346, 0.0283	-0.1349, 0.0392	0.4456, 0.7176	-, 0.2149

	$3d_{z^2}$	4s	a_{1g} N (2s)	N (2p σ)	All Others
Mn	-0.9524, 0.8908	-0.2417, 0.0620	-0.0049, 0.0000	0.0926, 0.0308	-, 0.0164
Fe	-0.9569, 0.8991	-0.2174, 0.0529	-0.0096, 0.0004	0.0945, 0.0328	-, 0.0148
Co	-0.9757, 0.9420	-0.1959, 0.0401	-0.0030, 0.0000	0.0578, 0.0112	-, 0.0067
Ni	-0.9787, 0.9491	-0.1781, 0.0341	-0.0037, 0.0000	0.0543, 0.0104	-, 0.0064

TABLE I (continued)

A. Ligand Field Orbitals				
	$3d_{xz}$	$eg(d\pi)$ N ($2p\pi$)	All Others	
Mn	0.9247, 0.8224	-0.1370, 0.0340	-, 0.1236	
Fe	0.9376, 0.8692	-0.1222, 0.0270	-, 0.1038	
Co	0.9450, 0.8862	-0.0767, 0.0100	-, 0.1038	
Ni	0.9514, 0.8981	-0.0927, 0.0152	-, 0.0867	
	$3d_{xy}$	b_{2g} N ($2p_x$)	All Others	
Mn	0.9838, 0.9592	-0.0478, 0.0072	-, 0.0336	
Fe	0.9866, 0.9663	-0.0432, 0.0056	-, 0.0281	
Co	0.9879, 0.9692	-0.0395, 0.0044	-, 0.0264	
Ni	0.9886, 0.9716	-0.0391, 0.0044	-, 0.0240	
B. Porphyrin Orbitals				
	$a_{2u}(\Pi)$		$eg(\Pi)$	
	$4p_z$	All Others	$3d\pi$	All Others
Mn	-0.1161, 0.0262	-, 0.9738	-0.1558, 0.0204	-, 0.9796
Fe	-0.1382, 0.0344	-, 0.9656	-0.1488, 0.0187	-, 0.9813
Co	-0.1654, 0.0475	-, 0.9525	-0.2066, 0.0374	-, 0.9626
Ni	-0.1520, 0.0434	-, 0.9566	-0.1647, 0.0235	-, 0.9765
Cu	-0.1555, 0.0450	-, 0.9550	-0.0659, 0.0031	-, 0.9969
Zn	-0.2177, 0.0697	-, 0.9303	-0.0242, 0.0003	-, 0.0007

(c) Electron transitions

Table (II) shows the π electron energy differences and compares them with the calculated SCMO-PPP π (Self Consistent Molecular Orbital Pariser-Parr-Pople) electron transitions.

Table II Electronic Energy Gaps

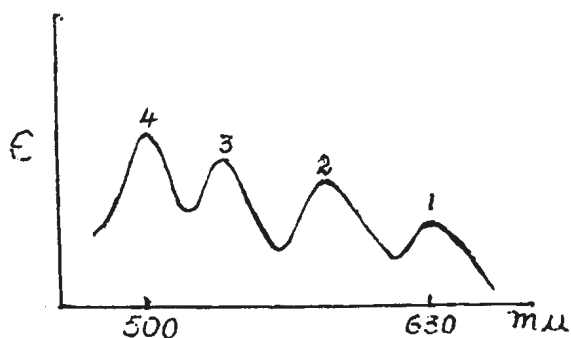
	Gouterman's work	SCMO-PPP	Experimental
$\Delta E(a_{2u} \rightarrow eg)$	2.01 eV	2.15 eV	
$\Delta E(a_{1u} \rightarrow eg)$	2.35 eV	2.23 eV	
ΔE	2.18 eV	2.19 eV	2.19 eV
$q^2(a_{2u} \rightarrow eg)$	9.61 $\text{\AA}^2$	11.06 $\text{\AA}^2$	
$q^2(a_{1u} \rightarrow eg)$	10.10 $\text{\AA}^2$	11.23 $\text{\AA}^2$	
Total q^2	19.81 $\text{\AA}^2$	22.29 $\text{\AA}^2$	5.16 $\text{\AA}^2$

q^2 = dipole strength

, Both calculated numbers are 3-4 times too large. This is a common ailment of MO theory, and has been shown to be greatly ameliorated by the inclusion of doubly excited configurations in a configuration interaction refinement. Gouterman says these calculations provide a clear insight into the relation of the metal orbitals to those of the ring and this will be subject to verification through E.P.R. and spectroscopic studies. The calculated ionic properties of the metal and ring correlate successfully to chemical stabilities and to reduction potentials(9).

The studies by Thomas and Martel(11,12) on tetraphenylporphin and other para (methoxy, methyl, chloro, nitro)

$\alpha, \beta, \gamma, \delta$ tetrasubstituted porphines have provided information and understanding of the structure and bonding in compounds derived from porphin. They described the ultra violet/visible and infra red spectra of these compounds with a view to determining the influence, if any, of the p-phenyl substituents on the porphine system and on the electron donor properties of the central nitrogen atom. Many of the absorption bands (visible region) of the parasubstituted derivatives exhibit small shifts to longer wave lengths as compared to aetio type spectrum of tetraphenylporphine, while other bands showed

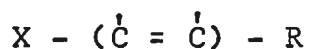


AETIO TYPE SPECTRUM

no change in position. In no case, however, was the maximum of an absorption band displaced to lower wave length than that found in the parent compound. The most pronounced bathochromic shift (a shift toward longer wave length) occurs in the methoxy derivative. In this case the main absorption peak in the visible region occurs at 519 mμ and its intensity is decreased somewhat while the intensities of most of the weaker bands in this group are considerably increased and are shifted to a greater extent than the main band. Tetra(p-chlorophenyl)-porphine, on the other hand, shows only minor shifts, but the intensities

of all the peaks are higher than those of the parent tetraphenylporphine-like the methoxy derivatives in benzene.

In general it may be concluded that the extent of the influence of substituent groups on the absorption bands of tetraphenylporphine (TPP) decrease in the order $-\text{OCH}_3$, $-\text{NO}_2 \gg -\text{Cl} > -\text{CH}_3$ if one neglects the direction of the effects of these groups that is also the relative order of interactions of these groups with aromatic systems.



The introduction of a resonating group X at one end of a general system of this type usually produces a bathochromic shift of the electronic transitions, with a corresponding intensification of the absorption bands. The bathochromic shifts and spectral intensifications observed are considerably less than what would be expected in simpler aromatic systems.

The nitrogen-hydrogen stretching frequency which occurs at 3500 cm^{-1} in pyrrole, occurs at 3350 cm^{-1} in TPP and is an indication of stronger hydrogen bonding in the condensed ring systems of the porphines. The replacement of p-hydrogen by an element more electronegative than carbon (ie. by substitution of methoxy, chloro and nitro groups) gives a slight increase in the N-H stretching frequency. Thus it appears that hydrogen bonding is somewhat decreased by substitution of these electronegative elements. The decrease in hydrogen bond strength indicates that the influence of the substituents is to decrease the electron density about the central nitrogen atom. Hence the influence of the para group is due to their inductive effects

rather than their resonance interactions. This conclusion is reasonable in view of the non-coplanarity of the porphine.

The characteristic skeletal -C=C- in plane vibrations which usually occur near 1600 cm^{-1} are frequently shifted to slightly higher frequency by para-substitution. The most pronounced shift of this type may be found in the p-methoxy band which is found at 1600 cm^{-1} compared to 1597 in tetraphenylporphine, the intensities of these bands in the p-nitro, methyl and methoxy compounds are considerably enhanced over those of tetraphenylporphine.

This work was extended (by Thomas and Martel (13,14)) on metal chelates of $\alpha,\beta,\gamma,\delta$ tetra(p-substituted phenyl)porphine.
Fig.No.5

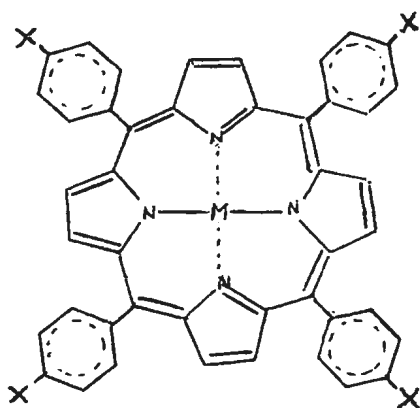
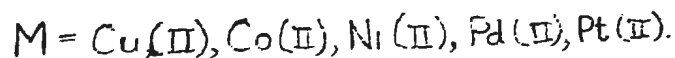
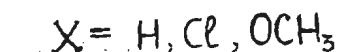


Fig. No.5



A series of metals was chosen on the basis of their tendencies to form square planer complexes with three of these ligands, tetraphenylporphine and its p-methoxy and p-chloro derivatives. A study of the infra red, ultra violet and visible spectra of each chelate was made to understand the electronic distribution, bonding, and the influence of p-phenyl substituents on the electron donor properties of the central nitrogen atoms and on the stabilities of the metal nitrogen bond.

The frequencies for all the tetraphenyl porphines increase in the order Cu(II), Co(II), Ni(II) < Pd(II) < Pt(II). In view of the nature of the metal ions involved, it is probable that the bond strength increase in the order Cu(II), Co(II), Ni(II) < Pd(II) < Pt(II).

For any one metal of the above series with the exception of the Palladium(II) and and platinum(II) chelates of the methoxy ligands, the frequencies near 1000 cm^{-1} decrease in the order TPP > p-Cl TPP > p-OCH₃ TPP.

Variation of I.R. Frequencies with Metal Ion

Metal	T.PP	p-OCH ₃ T.PP	p-ClTPP
Cu(II)	1004 cm^{-1}	998 cm^{-1}	1000 cm^{-1}
Co(II)	1005 cm^{-1}	1001 cm^{-1}	1002 cm^{-1}
Ni(II)	1007 cm^{-1}	1002 cm^{-1}	1004 cm^{-1}
Pd(II)	1014 cm^{-1}	1016 cm^{-1}	1013 cm^{-1}
Pt(II)	1019 cm^{-1}	1020 cm^{-1}	1014 cm^{-1}

If the absorption band at 1009 cm^{-1} of the palladium chelate and the less intense band at 1010 cm^{-1} for the platinum compound are tabulated for the p-methoxy derivatives, this same frequency order $\text{TPP} > \text{p-Cl TPP} > \text{p-OCH}_3\text{ TPP}$ would also be indicated for these metal chelates. The decreased frequencies for the p-substituted chelates may be due in part to the mass effect but it appears that another effect is also in operation since it is seen that these frequencies follow the electron properties of the p-substituted groups.

The visible spectra of Cu(II), Ni(II), Pd(II), Pt(II), Co(II) chelates consist of a single absorption band (K-band) which is accompanied in many cases by much weaker vibrational bands (R-band). In both ligands and chelates, however, the strong Soret peak is present above $400\text{ m}\mu$ and is relatively stable in position. The behaviour on chelation is considered to be indicative of the fact that each set of absorption bands in each of these regions correspond to separate electronic transitions with the weaker bands corresponding to vibrations. The replacement of the two imino hydrogens of the tetraphenylporphine ligands with the above cations results in a displacement of the K-absorption band maximum and its position depends upon the nature of the metal ion. The wavelength maxima for tetraphenylporphine and its p-methoxy and p-chloro derivatives follow the order $\text{Cu(II)} > \text{Co(II)} > \text{Ni(II)} > \text{Pd(II)} > \text{Pt(II)}$.

The displacement of a K-band from its position in a ligand has been correlated in certain instances with the presence or absence of conjugation between the metal ion and the ligand, with the effective electron affinity of the cation and also

with the stability of the complex.

The general order of stabilities of transition metal chelate compounds formed with a given ligand is $\text{Pd(II)} > \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$. Platinum(II) is known to form the strongest covalent bonds of this group so that the stability series would be: $\text{Pt(II)} > \text{Pd(II)} > \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$. The order of absorption maxima observed for all the tetraphenylporphine chelates is $\text{Cu} > \text{Co} > \text{Ni}$. Consequently, the absorption maxima of the K-band does appear to follow the strength of the metal-nitrogen bonds and the stability of the chelates. The observed order of the absorption maxima indicates that the bonding in the platinum(II) chelates (510-513 m μ) is the strongest and the bonding in the copper(II) compound (540-542 m μ) is the weakest in the series. In these and related porphyrin systems, a bathochromic shift is an indication of a weaker bonding in the chelates, where as a shift to lower wavelengths reflects an increase in bond strength.

The main effect of the p-methoxy and p-chloro substituents on the spectra of each of the metals studied is to shift the ligand and other weaker absorption bands to longer wavelengths in the order $\text{p-OCH}_3 > \text{p-Cl}$. The bathochromic shift of the K-bands which results from substitution of the p-methoxy and p-chloro groups suggests that for each metal chelate these functional groups weaken the metal-nitrogen bonds of the porphine system in the order $-\text{OCH}_3 > -\text{Cl}$. This behaviour indicates an electron withdrawal effect upon the porphine nitrogen atoms as a result of inductive effects of the methoxy

and chloro groups.

Thomas and Martell have studied the infra red, visible and ultra violet spectra of the Cu(II) Co(II), Ni(II), Pd(II) and Pt(II) chelates of tetraphenylporphine, tetra(p-methoxyphenyl)porphine, and of tetra(p-chlorophenyl)porphine, and attributed the variations on the basis of ligand structure and nature of the central metal ion on chemical binding. The co-ordinate bond strength seems to change in the order Cu(II) < Co(II) Ni(II) < Pt(II), and phenyl > p-chlorophenyl > p-methoxyphenyl.

In the present study it is intended to see the variations in carbonyl stretching in the infra red, ultra violet and visible spectra of the complexes, and correlate them with different transition metals at the center of the porphyrin system.

EXPERIMENTAL

Infra red spectra were recorded on a Perkin Elmer 273B and 457 grating spectrophotometer as nujol mulls or solution in carbon tetrachloride or chloroform. Ultra violet spectra were determined on a Perkin Elmer 202 and Unicam SP 800D spectrophotometer in chloroform or benzene as solvents.

Nuclear magnetic resonance spectra were recorded on a Varian HA-100 spectrometer and all resonance positions are reported on the τ scale.

Synthesis of $\alpha,\beta,\gamma,\delta$ Tetraphenylporphine (TPP) (15)

Freshly distilled pyrrole (56 ml) and 80 ml of reagent grade benzaldehyde were added to 3 l. of refluxing reagent grade propionic acid. After refluxing for 30 minutes the solution was cooled to room temperature, filtered, and the filter cake was washed thoroughly with methanol. After a hot water wash the resulting purple crystals were air dried.

The product was purified by chromatographing through a column of neutral alumina using benzene 20% and chloroform 80% as eluent and finally crystallized from benzene.

The visible spectrum of a solution of this product in (Fig.6) benzene is in agreement with that reported by other workers (16).

Preparation of $\alpha,\beta,\gamma,\delta$ Tetraphenylporphinezinc (TPP-Zn) (17)

One gram of TPP, 100 ml of chloroform, 500 mg of zinc acetate hydrate and 500 ml of glacial acetic acid were refluxed

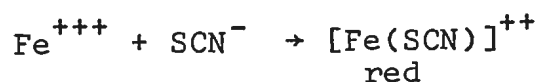
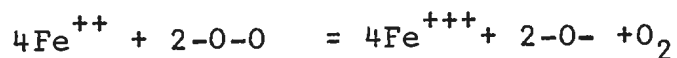
for one hour on a steam bath, the solvent was removed by vacuum distillation. A quantitative yield was obtained. The substance was extracted from a soxhlet thimble with a mixture of 100 ml of ether and 50 ml of methanol and finally crystallized from the same mixture of solvents. The ultra violet (Fig.7) spectrum of the product agreed with the literature (16).

Preparation of Tricarbonylchromium Complexes of $\alpha,\beta,\gamma,\delta$ Tetraphenylporphine zinc.

The reaction between TPP-Zn and hexacarbonylchromium was done in several solvents, under nitrogen but butyl ether was found to be the most suitable solvent.

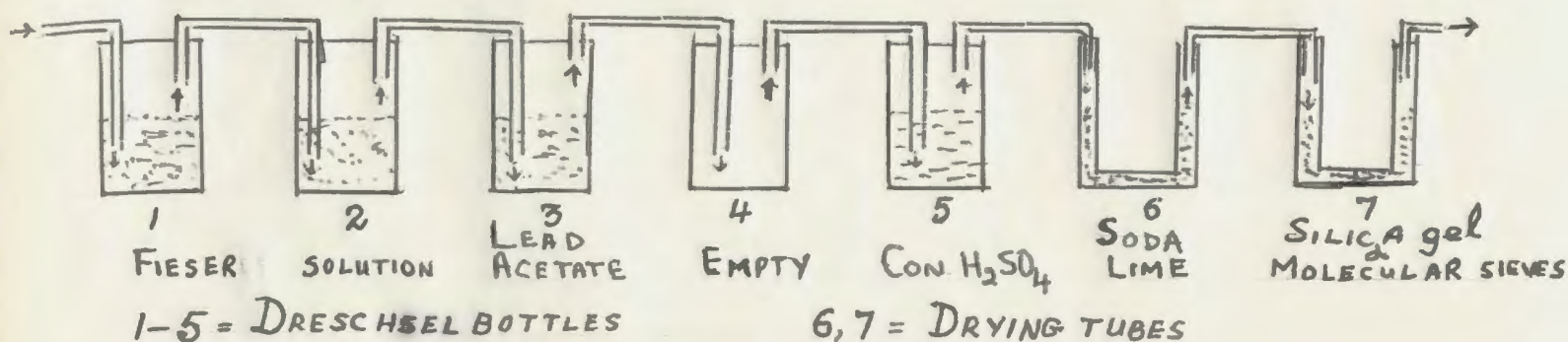
Bis-2-Methoxy Ethyl Ether as a solvent for reaction.

Ethers form peroxides which were removed. In order to remove peroxide, the ether was shaken with acidic ferrous sulphate in a separating funnel. The ether layer was separated after washing with distilled water. The presence of peroxide was tested using acidic ferrous sulphate and potassium thiocyanate which gives a red color if peroxide is present



After removing the peroxide, the ether was dried with CaCl_2 and then refluxed with sodium for 30 minutes and finally distilled under pure nitrogen. The nitrogen used was purified by passing through a series of solutions and drying agents

to remove oxygen, hydrogen sulphide and moisture:-



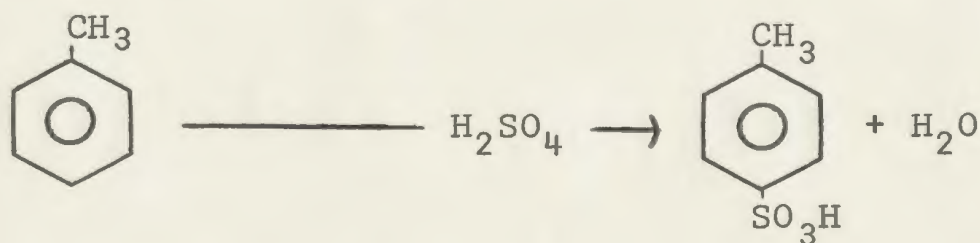
Hexacarbonylchromium was purified by sublimation.

REACTION: 500 mg of tetraphenylporphinezinc and 500 mg of hexacarbonylchromium were refluxed in 150 ml of bis-2 methoxy ethyl ether under pure nitrogen and $140^\circ C$. The infra red spectrum of the dried product showed no band in the carbonyl stretching region indicating that no tricarbonylchromium complex was formed.

Petroleum Spirit (P. Spirit) b.p. $113-119^\circ$

Since the petroleum spirit had an impurity of toluene which would react with hexacarbonylchromium to form a π -complex, it was necessary to remove it.

500 ml petroleum spirit was refluxed with 50 ml conc. sulphuric acid to form toluene sulfonic acid



The acid formed was neutralized with sodium carbonate, the p-spirit layer was decanted and washed with water. The

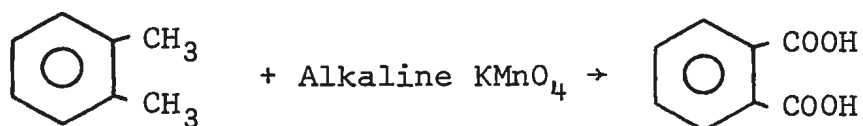
ultra violet spectrum was taken which indicated the presence of toluene, the process was repeated 6 times to get toluene-free p. spirit, which was distilled and collected the fraction between 113°C - 119°C .

REACTION: 500 mg of TPP Zn, 500 mg of hexacarbonylchromium and 120 ml of p. spirit refluxed under nitrogen for 6 hours. The product was evaporated to dryness, but its infra red spectrum showed no carbonyl peaks - indicating that no reaction had occurred.

Butyl Ether as Solvent

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

Butyl ether was 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 butyl ether to separate xylene from it did not work as their boiling points are very close.

Butyl ether	B.P. =	142°C
p-xylene	B.P. =	144°C
O-xylene	B.P. =	138°C
m-xylene	B.P. =	139°C

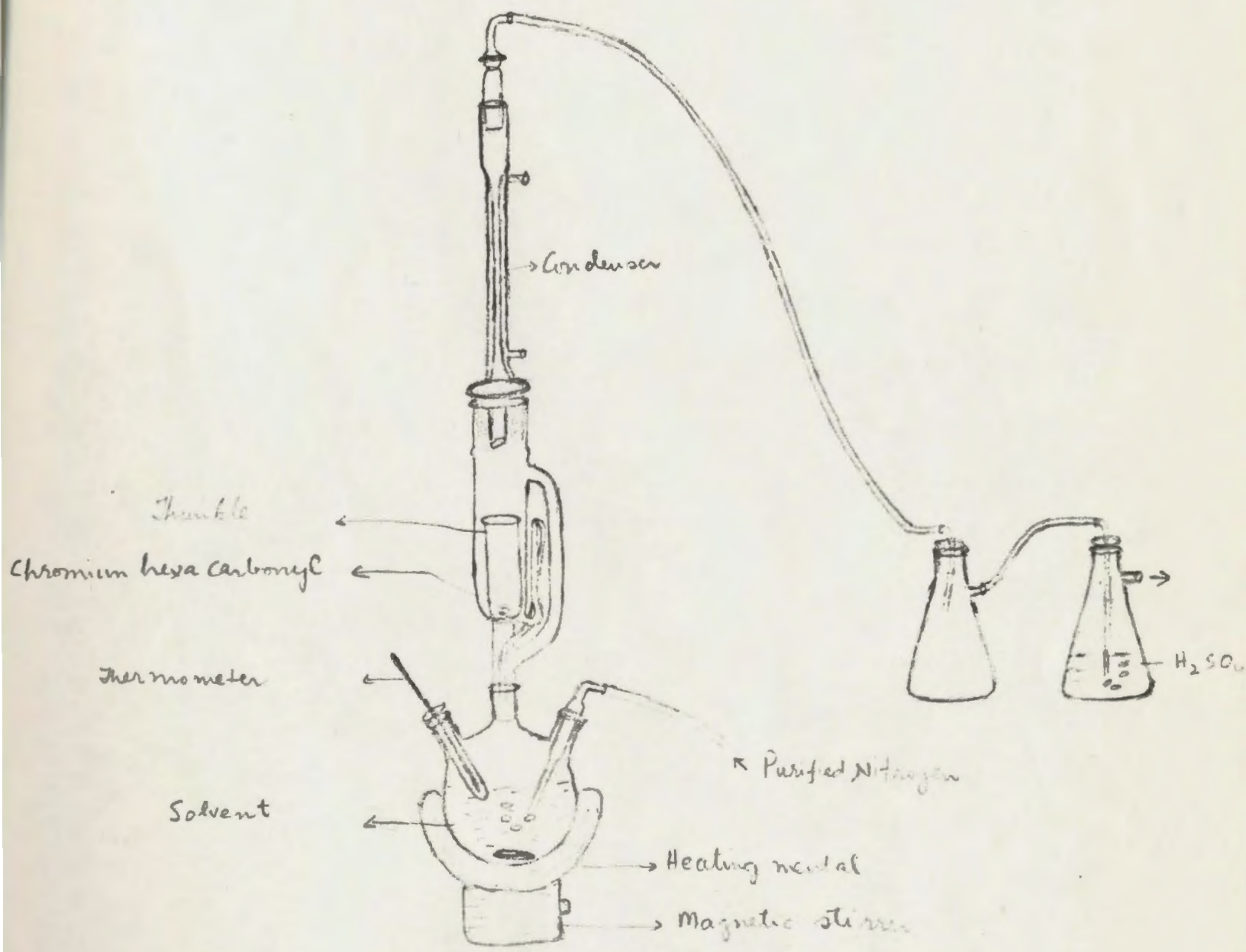


DIAGRAM NO 8

Xylene was removed successfully by refluxing butyl ether with hexacarbonylchromium under pure nitrogen, the tricarbonyl chromium complex of xylene was formed which was evaporated to dryness and the solvent obtained was free of xylene.

Removal of peroxide and drying was done in the same way as for bis-2-methoxy ethyl ether. Spectroscopic quality butyl ether was used subsequently due to these difficulties involved in its purification.

REACTION: 500 mg tetraphenylporphinezinc, 500 mg hexacarbonylchromium, and 200 ml of butyl ether (spectroscopic quality) were refluxed pure nitrogen for nine hours (Diagram No.8). The IR of the dried product showed distinct carbonyl peaks indicating that reaction had occurred. Thin layer chromatography of the product on silica gel plates gave three spots: green, which was completely adsorbed; brown, which moved slowly and red, which moved fast. The green spot was decomposed product, the brown was the new complex; the red was TPP-Zn.

The solubility of the product was checked in various organic solvents, and it was found to be partially soluble in benzene. The more soluble portion was brownish green and the less soluble was just green; the brownish green and green portions were separated by ordinary filtration. The u.v. and visible spectra of the green portion showed it to be similar to TPP-Cr. The brownish green portion showed shifted visible bands from TPP-Zn and bands in the carbonyl stretching

region indicated it to be the tricarbonylchromium complex.

Chromatography of the more soluble portion on Florisil gave a better result than silica gel using chloroform as eluent and three distinct bands were observed. (1) A red band which was TPP-Zn. (2) A brownish green band and (3) a greenish brown band. Bands 2 and 3 after analysis by n.m.r., U.V., and IR spectroscopy were found to be the following compounds -
(2) Zn TPP Cr(CO)_3 , (3) $\text{Zn TPP (Cr(CO)}_3)_2$.

Heating the products up to 300° gave no visible change. However, the visible spectrum in chloroform of the material that had been heated above 110° was that of TPP-Zn indicating that decomposition had occurred. Solution left for a few days was found to be decomposed.

UV/visible (CHCl_3) nm ($10^3\epsilon$) (Fig.9,10)

(2) 422 (230, 562 (13), 612 (6.3)

(3) 424 (200), 570 (12), 621 (6.9)

IR cm^{-1} (CCl_4) CO stretching region (Fig.11,12)

(2) 1978, 1910

(3) 1978, 1910

n.m.r. (τ) CDCl_3 (Fig.13,14)

(2) β pyrrole 1.11 Phenyl 1.81, 2.25, 3.33, 4.21

(3) β pyrrole 1.09 Phenyl 1.83, 2.26, 3.44, 4.20

Elemental Analysis

(2) Experimental C, 66.11%, H 4.06%, N 5.56%

Theoretical C, 66.3%, H 3.77%, N 6.50%

TPP-Zn $2\text{H}_2\text{O Cr(CO)}_3$

(3) Experimental C, 60.14%, H 4.23%, N 5.29%

Theoretical C, 60.08%, H 3.25%, N 5.67%

TPP-Zn $2\text{H}_2\text{O (Cr(CO)}_3)_2$

Preparation of α β γ δ tetraphenylporphine nickel (TPP-Ni)

One gram of TPP, 100 ml of chloroform, 500 mg of nickel acetate hydrate, and 500 ml of glacial acetic acid were refluxed for one hour on a steam bath. The solvent was removed by vacuum distillation. The U.V. of the dried product showed some unreacted TPP. The experiment was repeated using the same reactants with a slight excess of nickel acetate hydrate for one hour on a steam bath. A quantitative yield was obtained. Excess of Ni-acetate hydrate was removed with hot water. Impurities were extracted from a soxhlet thimble with a mixture of 100 ml of ether and 50 ml of methanol. Ni-acetate was slightly soluble in methyl alcohol and TPP slightly soluble in ether, so both impurities were removed and pure crystals of NiTPP were left in the thimble. The ultra violet spectrum agrees with the literature (12).

Preparation of Tricarbonyl Chromium Complex of $\alpha,\beta,\gamma,\delta$ Tetraphenylporphinenickel

500 mg of tetraphenylporphinenickel, 500 mg of hexacarbonylchromium, 200 ml of butyl ether (spectroscopic quality) were refluxed under pure nitrogen for six hours. The IR of the dried product showed distinct carbonyl peaks indicating a reaction between TPP-Ni and $\text{Cr}(\text{CO})_6$.

Complex Ni-TPP $\text{Cr}(\text{CO})_3$ was extracted from a soxhlet thimble with petroleum ether (bp 50°) under nitrogen, Ni-TPP was left in the thimble. Chromatography of the petroleum ether extract on Florisil using benzene 20% and chloroform 80%

as eluent under nitrogen gave two bands (1) a brown band which moved fast and showed prominent carbonyl peaks. The U.V. band was indicating that the brown band was the complex NiTPP Cr(CO)_3 . (2) A green band which was adsorbed strongly on the column and was found to be NiTPP by studying its IR and U.V.

Heating the product to 300° gave no visible change. However the visible spectrum in CHCl_3 of the material that had been heated above 110° was that of Ni-TPP indicating that decomposition had occurred.

UV/visible (CHCl_3) nm ($10^3 \epsilon$)

Ni-TPP, 417 (240), 528 (17)

Ni-TPP(Cr(CO)_3)₂ 417 (200), 534 (9.8)

IR cm^{-1} CO stretching region (CHCl_3) 1901, 1971.5

Elemental Analysis

Experimental C, 61.17%, H 7.24%, N 3.96%

Theoretical C, 60.2%, H 3.27%, N 5.7%

Preparation of $\alpha, \beta, \gamma, \delta$ Tetraphenylporphinecobalt(II)

One gram of TPP, 100 ml chloroform, 500 mg of cobalt acetate hydrate, and 500 ml of glacial acetic acid were refluxed for one hour on a steam bath, the solvent was removed by vacuum distillation. The U.V. of the dried product showed complete conversion of TPP to TPP-Co(II).

The product was washed with cold deionized water on a Büchner funnel, which removed unreacted cobalt acetate, and finally washed with acetone to remove unreacted free base.

The ultra violet spectrum of the product agrees with other workers (12).

Preparation of Tricarbonyl Chromium Complex of $\alpha,\beta,\gamma,\delta$,
Tetraphenylporphine Cobalt(II)

500 mg of tetraphenylporphinecobalt(II), 500 mg of hexacarbonylchromium and 200 ml of butyl ether (spectroscopic quality) were refluxed under nitrogen for 6 hours. The IR of the dried product showed distinct carbonyl peaks indicating a reaction between TPP-Co(II) and $\text{Cr}(\text{CO})_6$.

Complex Ni-TPP($\text{Cr}(\text{CO})_3$) was extracted from a soxhlet thimble with methyl alcohol under nitrogen; Co-TPP was left in the thimble. Chromatography of the methyl alcohol extract on florisil using benzene 20% and chloroform 80% as eluent under nitrogen gave three bands (1) a green band which was adsorbed strongly on the column (2) a light yellow band which showed bands in the carbonyl region and U.V. different from the CoTPP (other studies have to be done on this fraction), (3) an orange colored band which showed very strong carbonyl peaks and U.V. bands quite shifted from the parent compound (CoTPP) indicating that the brown band was the complex $\text{Co(II)TPPCr}(\text{CO})_3$. Heating the product up to 300°C gave no visible change, however the visible spectrum in CHCl_3 of the material that had been heated above 110°C was that of CoTPP indicating decomposition.

UV/visible (CHCl_3) nm ($10^3\epsilon$)

Co-TPP 411 (245), 530 (15)

Co-TPP $\text{Cr}(\text{CO})_3$ 410(293), 531(17.1)

IR cm^{-1} (CHCl_3) Co stretching region 1970, 1901

Experimental C, 73.0%, H 6.14%, N 6.62%

C 66.4%, H 3.78%, N 6.58%

Preparation of $\alpha,\beta,\gamma,\delta$ Tetraphenylporphinecobalt(III) Chloride(18,19)

To a solution of TPP free base (one gram) in benzene (300 ml) was added 2 ~ 3 moles of a cobaltous salt (chloride or acetate) and 2 ~ 3 moles of pyridine in ethanol (300 ml). The mixture was adjusted to pH 3 ~ 4 with hydrochloric acid or acetic acid. This solution was refluxed on a water bath until its color changed from purple to purplish-red (in about 8 hours) and then evaporated to dryness under reduced pressure. The residue was washed with benzene and ether to remove unchanged free base and by-product (Co(II)TPP). Next it was washed with dilute hydrochloric acid for removing excess of additional base and washed thoroughly with water. It was dissolved in ethanol, weakly acidified with dilute hydrochloric acid, and ether and petroleum ether were added. The cobaltic complex coordinated with TPP and additional base was crystallized from the above solution as violet palates. Recrystallization was carried out from acidic ethanol-ether.

Preparation of Tricarbonylchromium Complex of $\alpha,\beta,\gamma,\delta$ tetraphenylporphinecobalt(III)

1. 500 mg of tetraphenylporphinecobalt(III) Chloride, 500 mg of hexacarbonylchromium and 200 ml of butyl ether (spectroscopic quality) were refluxed under pure nitrogen for six hours. The IR of the dried product showed no bands in the carbonyl

region and U.V. bands were changed from Co(III)TPPPy-Cl to Co(II)TPP indicating that the Cr was oxidized and Co(III) was reduced. The reaction was repeated but the same result was obtained.

2. 5 ml of pyridine was added in the above reaction to stabilize the Co(III)TPPPy-Cl so that a reaction could take place without reduction of the Co(III)TPPPy-Cl. The reaction was not successful. The IR spectrum had no bands in carbonyl stretching region and U.V. was changed to Co(II)TPP.

3. Cyclohexene (10 ml) (cyclohexene induces oxidation of Co(II) to Co(III)mesoporphyrin IX dimethylester(20)), 235 mg of tetraphenylporphinecobalt(III), 230 mg of hexacarbonyl-chromium and 80 ml of butylether (spectroscopic quality) were refluxed under pure nitrogen for 6 hours. The IR of the dried product showed no bands in the carbonyl stretching region and the U.V. bands were shifted from Co(III)TPPPy-Cl to Co(II)TPP indicating the reduction of Co(III)TPPPy-Cl.

Preparation of $\alpha,\beta,\gamma,\delta$ Tetraphenylporphine Mn(II)

Two grams of TPP, 200 ml chloroform, one gram of manganese acetate hydrate and 100 ml of glacial acetic acid were refluxed for four hours on a steam bath under nitrogen.

The U.V. of the dried product showed complete conversion to TPPMn(II).

The product was washed with deionized water several times on a Büchner funnel, which removed unreacted manganese acetate hydrate.

Mn(II)TPP was extracted from a soxhlet thimble with methyl-alcohol under nitrogen; TPP was left in the thimble being insoluble. Mn(II)TPP was crystallized from benzene.

Preparation of Tricarbonylchromium Complex of $\alpha, \beta, \gamma, \delta$ Tetraphenylporphinemanganese(II).

500 mg of tetraphenylporphinemanganese(II), 500 mg of hexacarbonylchromium, 200 ml of butylether (spectroscopic quality) were refluxed under nitrogen for 6 hours. The IR of the dried product showed distinct carbonyl peaks indicating a reaction between TPP-Mn(II) and Cr(CO)_6 .

The product was purified by chromatography. A florisil column was made by using a slurry of florisil in chloroform; the product was dissolved in CHCl_3 and run through the column. Methyl alcohol was used as eluent which separated the product in two bands; (1) a green band which was completely adsorbed and had no bands in carbonyl region and its UV was similar to Mn(II)Tpp; (2) a brownish green band which showed distinct carbonyl bands and a shifted U.V., a gum was obtained on drying but by slowly adding petroleum ether the fraction was crystallized. The crystals when studied by IR showed no bands in carbonyl region indicating decomposition. No further studies were done as the compound had decomposed.

Preparation of $\alpha \beta \gamma \delta$ Tetraphenylporphine Mn(III)(21)

500 mg of TPP Mn(II), 50 ml chloroform, 250 ml glacial acetic acid and 2.5 ml conc. HCl were refluxed for 3 hours, air was passed at the same time for oxidation; solvents

were removed by vacuum distillation. The product was washed with deionized water several times to remove acids. (Mn(III)TPPCl) was extracted from a soxhlet thimble with methyl alcohol. The U.V. of the dried product indicated complete conversion of Mn(II)TPP to Mn(III)TPPCl . The product was crystallized from benzene.

Preparation of Tricarbonylchromium Complex of Mn(III)TPPCl

500 mg of tetraphenylporphinemanganese(III)chloride, 500 mg of hexacarbonylchromium, and 200 ml of butyl ether (spectroscopic quality) were refluxed under nitrogen for 6 hours. The IR of the dried product showed bands in the carbonyl stretching region indicating a reaction between Mn(III)TPPCl and Cr(CO)_6 .

The product was purified by chromatography. A florisil column was made in chloroform. The product was dissolved in CHCl_3 and run through the column. Methyl alcohol was used as eluent which separated the product into 2 bands; (1) a green band which was completely adsorbed and had no bands in carbonyl region and there was no change in U.V.; (2) a brownish green band which showed distinct carbonyl bands and a shifted U.V. The product on drying was decomposed as dried product showed no bands in the carbonyl region. No further studies were done as the complex had decomposed.

Preparation of $\alpha, \beta, \gamma, \delta$ Tetraphenylporphinechromium(II)

500 mg of tetraphenylporphine, 500 mg of hexacarbonylchromium and 150 ml of butyl ether (spectroscopic quality) were refluxed under nitrogen for 6 hours. The IR of the dried

product showed no bands in the carbonyl region indicating that no tricarbonyl complex of TPP was formed. The U.V. of the product was shifted and some of the TPP bands disappeared. Chromium was detected qualitatively in the product. The product TPPCr(II) was extracted from a soxhlet thimble with methyl alcohol leaving unreacted TPP in thimble.

The extracted material showed no free base band in the U.V. indicating no free base in purity in the product. Thin-layer chromatography also showed it to be free from TPP.

Preparation of Tricarbonylchromium Complex of Cr(II)TPP

500 mg of tetraphenylporphinechromium, 500 mg of hexacarbonylchromium and 200 ml of butyl ether (spectroscopic quality) were refluxed under nitrogen for 6 hours. The IR of the dried product showed bands in the carbonyl region indicating a reaction between CrTPP and Cr(CO)_6 . The product was purified by chromatography. A florisil column was made in chloroform. The product was dissolved in minimum amount of chloroform and run through the column, same solvent used as eluent which separated the product in two bands; (1) a green band completely adsorbed showed no bands in the carbonyl region and there was no change in U.V. of CrTPP ; (2) a brownish green band which showed distinct carbonyl bands and a shifted U.V. The product when dried was a gel and could not be crystallized. No further studies were done except a detailed IR in solution was taken:-

IR $\text{cm}^{-1}(\text{CHCl}_3)$ CO stretching region

Cr-TPPCr(CO)_3 1930, 1990

Preparation of α β γ δ Tetraphenylporphinecopper(II) (17)

650 mg of tetraphenylporphine, 650 mg of copper acetate hydrate, 80 ml of chloroform, and 80 ml glacial acetic acid were refluxed for two hours on a steam bath; the solvent was removed by vacuum distillation. The product was washed with deionized water several times to remove unreacted copper acetate hydrate and acid.

The product was extracted from a soxhlet thimble with benzene and was finally crystallized from benzene. The ultra violet spectrum of the product agrees with the other workers(12).

Preparation of Tricarbonyl Complex of $\alpha,\beta,\gamma,\delta$ Tetraphenylporphinecopper(II)

500 mg of Cu(II)TPP, 500 mg of hexacarbonylchromium, 200 ml of butyl ether (spectroscopic quality) were refluxed under pure nitrogen for 6 hours. The IR of the dried products showed distinct bands in carbonyl region indicating a reaction between CuTPP and $\text{Cr}(\text{CO})_6$.

The product was extracted from a soxhlet thimble with methyl alcohol under nitrogen; Cu(II)TPP was left in the thimble being insoluble. Further purification was done by chromatography. The methanol extract was run through the florisil column using chloroform as eluent which was separated into two bands; (1) a green band which was completely adsorbed; (2) an orange band which showed bands in carbonyl region and a shifted U.V. The green band was eluted with methanol after the orange band was eluted. The green band (1) also showed distinct bands in the carbonyl region and shifted U.V.

U.V./visible (CHCl_3) nm ($10^3 \epsilon$)

Cu-TPP 416(475), 542(21)

Cu-TPP $\text{Cr}(\text{CO})_3$ (Green) 439(130), 568(7.5), 606(6.3)

Cu-TPP $\text{Cr}(\text{CO})_3$ (Orange) 440, 568, 606

1R cm^{-1} (CHCl_3) CO stretching region

Cu-TPP $\text{Cr}(\text{CO})_3$ (Orange) 1902, 1969

Cu-TPP $\text{Cr}(\text{CO})_3$ (Green) 1901, 1968

Elemental Analysis

Cu-TPP $\text{Cr}(\text{CO})_3$ (Green) Experimental %, C65.5, H4.8, N6.74

Theoretical %, C66.5, H3.79, N6.6

Cu-TPP $\text{Cr}(\text{CO})_3$ (Orange) Experimental %, C74.74, H6.13, N6.28

(one $\text{Cr}(\text{CO})_3$ group attached) Theoretical %, C66.5, H3.79, N6.6

(two $\text{Cr}(\text{CO})_3$ groups attached) Theoretical %, C60.3, H3.28, N5.72.

Discussion

Many tricarbonylchromium complexes of aromatic derivatives have been prepared. Most of them have been made by refluxing the hexacarbonylchromium and the aromatic derivative in butyl ether or decane as solvent under nitrogen for 6 hours.

In the present study the tricarbonylchromium complex of $\alpha,\beta,\gamma,\delta$ TPP-Zn has been prepared in the same way, but the yield of the complex was low after 6 hours reaction. The reaction time was extended to 9 hours to increase the yield.

Thin layer chromatography of the product on silica gel plates showed three spots indicating the presence of 3 compounds, one spot was identified as Zn-TPP by running a blank of Zn-TPP on a separate silica gel plate and comparing the r_f (rate of flow) value on reference and sample plate. The other two spots had slightly lower r_f values.

The three compounds were separated from each other on a florisil column. Purification was done by rerunning the fractions on the column.

Each purified fraction was studied in detail spectroscopically (U.V./visible, IR, nmr) and analytically.

The red band was identified as Zn-TPP, the nmr spectra of the greenish brown (Zn-TPPCr(CO)_3) and brownish green ($\text{Zn-TPP(Cr(CO)}_3)_2$) fractions were taken using a Varian HA100 instrument in CDCl_3 . The spectra taken on the A-60 Varian instrument were too weak to be useful.

<u>n.m.r. τ (CDCl₃)</u>		
	β -Pyrrole	Phenyls
Zn-TPP	1.17	1.80, 2.23
(1) Brownish green fraction	1.11	1.81, 2.25 3.33, 4.21
(2) Greenish brown fraction	1.09	1.83, 2.26 3.44, 4.20

The n.m.r. assignments follow those of Webb and Fleisher(22) for $\alpha,\beta,\gamma,\delta$ tetraphenylporphine. In tricarbonylbenzenechromium the phenyl proton resonances are shifted 1.67 p.p.m upfield from benzene (23). Very similar shifts are observed in the tricarbonyl complexes of $\alpha,\beta,\gamma,\delta$ TPP-Zn.

The n.m.r. spectra of these compounds consist of three main areas; a single band at about τ 1.1 assigned to the β -pyrrole proton resonances, two bands at about 1.8 and 2.2 assigned to proton resonances of phenyl rings without $\text{Cr}(\text{CO})_3$ groups attached, and two bands at about 3.3 and 4.2 assigned to proton resonances of phenyl rings with $\text{Cr}(\text{CO})_3$ groups attached. For compound(1) the ratio of intensities of the proton resonances due to uncomplexed phenyls to that of complexed phenyl is 3:1, clearly indicating that only one $\text{Cr}(\text{CO})_3$ is attached to compound (1). For compound(2) this ratio is 1:1. In both compounds the ratio of intensities of the β -pyrrole resonances to the total phenyl resonances is approximately 8:20. This leads to suggest a structure for (1) in which a $\text{Cr}(\text{CO})_3$ group is π -bonded to one phenyl ring and for (11) in which $\text{Cr}(\text{CO})_3$ groups are π -bonded

to two of the phenyl rings. The structure for (1) is shown below:

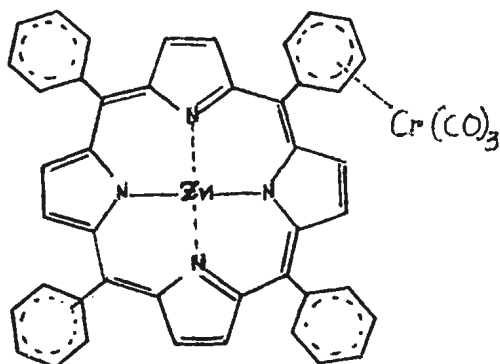


Fig.No.15

Several isomers are possible for compound (2) as there are 2 $\text{Cr}(\text{CO})_3$ attached. (Fig. below shows the isomers)

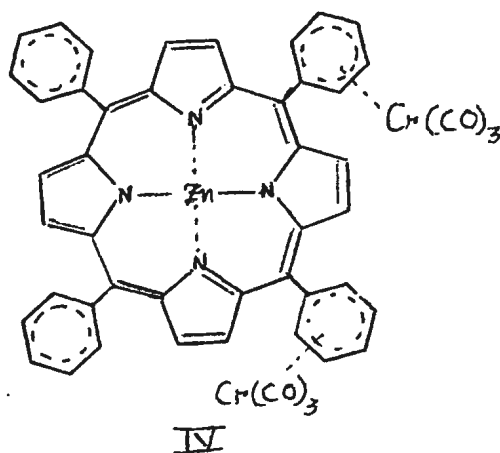
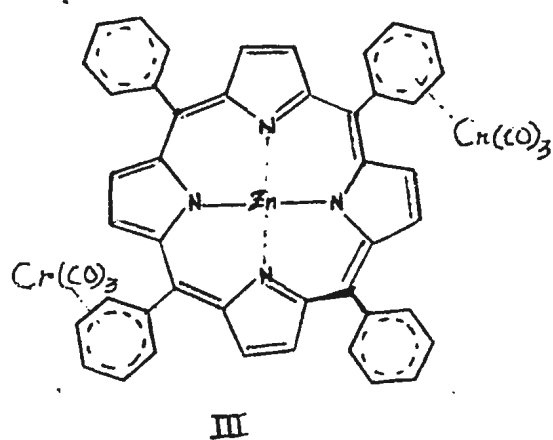
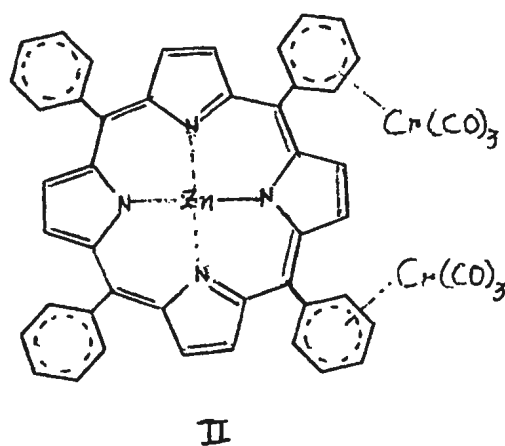
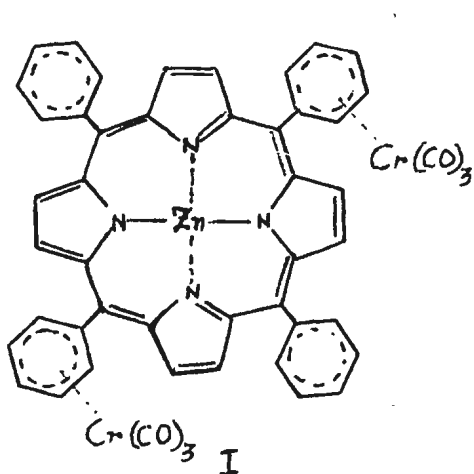


Fig.No.16

Ultra Violet

Compound	U.V./visible (CHCl_3) nm ($10^3 \epsilon$)
Zn-TPP	420 (600), 550 (22), 595 (6.0)
1. Brownish green compound	422 (230), 562 (13), 612 (6.3)
2. Greenish brown compound	424 (200, 570(12), 621(6.9)

There is no additional appearance or disappearance of bands compared with Zn-TPP, although there is a shift of bands toward longer wavelength (bathochromic effect). This indicates no basic change in porphine structure. A weakening of the central metal to porphyrin bond is indicated and could be due to a decrease in electron density at nitrogen which is only possible if there is a general decrease of electron density in the whole porphyrin system through phenyl to $\text{Cr}(\text{CO})_3$ group. The overall effect makes the nitrogen less basic and weakens the bonding. When in metalloporphyrins the bond between metal and porphyrin is weakened, there is a red shift(13). Thus ultra violet studies support the structures deduced by n.m.r.

The bathochromic effect is greater in compound(11) which supports the above explanation as there will be more loss of electron density compared with compound(1) because of the 2 $\text{Cr}(\text{CO})_3$ groups attached to the metalloporphine.

IR.

The CO stretching vibrations are typical of $\text{Cr}(\text{CO})_3$ groups π -bonded to phenyl rings. For example, in tricarbonylbenzene-chromium the bands at 1977 and 1910 cm^{-1} are assigned to CO stretching vibrations.

1R cm^{-1} (CHCl_3) CO stretching region

Zn-TPP	none
compound(1)	1902, 1969
compound(11)	1902, 1969

The 1R also support the structures as $\text{Cr}(\text{CO})_3$ groups could only be attached to the phenyl rings. (If the $\text{Cr}(\text{CO})_3$ group was attached to pyrrole the CO stretching vibrations would be different).

Mass Spectra

The mass spectra of the complexes were obtained but were of little significance as the parent peaks could not be seen.

Elemental Analysis: Finally the structures drawn above are supported by elemental analysis, as experimental and theoretical figures are very close.

Compound(1) Experimental: C66.11%, H4.06%, N6.5%

Theoretical: C66.3%, H3.77%, N6.5%

Zn-TPP $\text{Cr}(\text{CO})_3 \cdot 2\text{H}_2\text{O}$

Compound(11) Experimental: C60.1%, H4.23%, N5.29%

Theoretical: C60.00, H3.25%, N5.67%

Zn-TPP $(\text{Cr}(\text{CO})_3)_2 \cdot 2\text{H}_2\text{O}$

Ni-TPP $(\text{Cr}(\text{CO})_3)_2 \cdot 2\text{H}_2\text{O}$

This complex was prepared in the same way as Zn-TPP $(\text{Cr}(\text{CO})_3)_2 \cdot 2\text{H}_2\text{O}$. Thin-layer chromatography of the product on silica gel plate showed 2 spots indicating the presence of 2 compounds; one spot was identified as Ni-TPP by running a blank of Ni-TPP on the same silica gel plate and comparing the r_f value on

reference and sample plates. The other spot had a different R_f value. Separation and purification of the complex was done on a florisil column. Thin-layer chromatography of the complex showed it to be pure. A spectroscopic study was done on the complex.

n.m.r.

The n.m.r. of the complex was studied on a Varian HA100 in deuteroform, but the spectrum could not be recorded because complex may be paramagnetic or low solubility of it.

Ultra Violet

	U.V./visible (CHCl_3) nm ($10^3 \epsilon$)
Ni-TPP	417(240), 528(17)
Ni-TPP($\text{Cr}(\text{CO})_3$) ₂	417(200), 534(9.8)

There is no change in the spectrum of the complex except a bathochromic shift of one band, indicating no change in basic metalloporphine system and some weakening of central metal to porphyrin bonding due to electron withdrawal.

IR

The CO stretching vibrations are typical of $-\text{Cr}(\text{CO})_3$ groups π -bonded to phenyl rings and are very similar to $\alpha, \beta, \gamma, \delta$ tetraphenylporphine zinc complexes.

	IR cm^{-1} (CHCl_3) CO stretching region
Ni-TPP ($\text{Cr}(\text{CO})_3$) ₂	1901, 1971.5

The structure of the complex can be deduced as we know that there is no basic change in metalloporphine system as shown by U.V., and $\text{Cr}(\text{CO})_3$ group or groups are attached to phenyl rings as

shown by IR.

The elemental analysis is not in complete agreement with, but close to, the theoretical figures for 2 $\text{Cr}(\text{CO})_3$ groups attached to Ni-TPP.

Experimental	C61.17%, H7.24%, N3.9%
--------------	------------------------

Theoretical	C60.27%, H3.27%, N5.7%
-------------	------------------------

The analysis results for some of the tricarbonylchromium complexes of arenes are not very accurate due to the instability of the complexes. King(24) in his book states that in stable and readily purified solid organometallic transition metal compounds, the degree of accuracy is often readily obtainable. However, with unstable compounds purified with more difficulty and containing a greater variety of complicating elements, the degree of accuracy often cannot be obtained and experimental values deviate as much as 1% (or even 2% in some cases) from theoretical values for one or more elements in samples indicated to be pure by physical techniques.

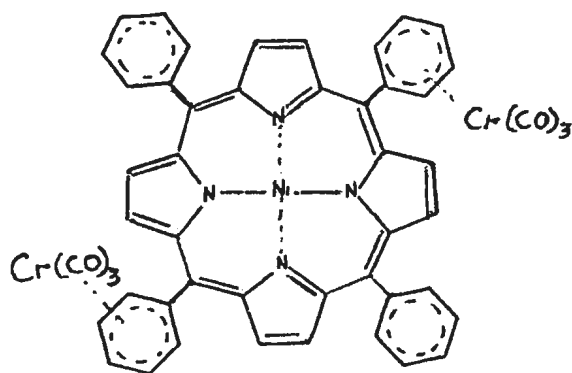


Fig.No.17

The four possible isomers of the above complex are similar to Zn-TPP $(\text{Cr}(\text{CO})_3)_2 \cdot 2\text{H}_2\text{O}$ complex as shown on page 33.

Co-TPP Cr(CO)₃

Thin-layer chromatography of the product on a silica gel plate showed three spots. One spot was identified as Co-TPP and the other two spots as complexes. Separation and purification was done on a florisil column. Thin-layer chromatography of the fractions showed that they were pure. The detailed spectroscopic studies were done on one complex (on the others, the studies could not be done due to the very small amount of complex obtained after purification).

n.m.r.

The n.m.r. of the complex could not be studied as the complex was paramagnetic.

Ultra Violet

Co-TPP	411(245), 530(15)
Co-TPP Cr(CO) ₃	410(293), 531(17.1)

There is no change in the spectrum except for the extinction coefficients of the bands indicating that there is no change in basic structure of the metalloporphyrine.

IR

The CO stretching vibrations are typical of Cr(CO)₃ groups π -bonded to phenyl rings, and are very similar to other tricarbonylchromium complexes of metalloporphines.

1R cm^{-1} (CHCl_3) CO stretching region
Co-TPP $\text{Cr}(\text{CO})_3$

The structure of the complex can be drawn as we know that there is no basic change in metalloporphine system as shown by U.V. and $\text{Cr}(\text{CO})_3$ group or groups are attached to phenyl rings which is shown by 1R.

The elemental analysis is not in complete agreement with the theoretical figures for one $\text{Cr}(\text{CO})_3$ group attached to Co-TPP. This indicates that the product could be impure.

Experimental C73.0%, H6.14%, N6.62%

Theoretical C66.4%, H3.78%, N6.58%

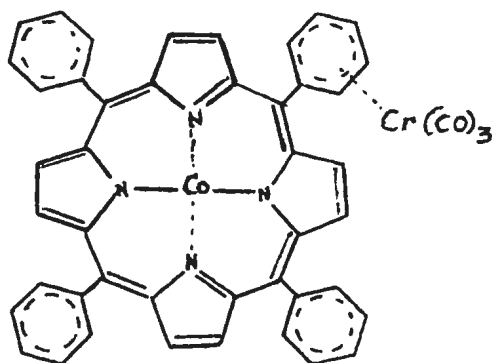


Fig.No.18

Cu-TPP $\text{Cr}(\text{CO})_3$

Thin-layer chromatography of the methanol extract of the product from soxhlet thimble on silica gel plate showed 2 spots (Cu-TPP was left in the thimble being insoluble in methanol) indicating the presence of two compounds. The two compounds were separated and purified on a florisil column.

Thin-layer chromatography of the two compounds showed them to be free from Cu-TPP. Detailed studies were done on both compounds.

n.m.r.

The n.m.r. of the complex could not be studied as the complex was paramagnetic.

Ultra Violet

U.V./visible (CHCl_3) nm ($10^3 \epsilon$)

Cu-TPP	416(475), 542(12)
Cu-TPP $\text{Cr}(\text{CO})_3$ green	439(130), 568(7.5), 606(6.3)
Cu-TPP $\text{Cr}(\text{CO})_3$ orange	440, 568, 606

There is quite a shift of bands toward longer wavelengths in both green and orange compounds and there is also an additional band around 606 nm.

The bathochromic shift is attributed to the weakening of the bond between central metal and porphyrine.

The spectra of the green and the orange complex are very similar indicating that there is no apparent difference in structure.

IR

The CO stretching vibrations are typical of $\text{Cr}(\text{CO})_3$ groups π -bonded to phenyl rings, and are very similar to other tricarbonylchromium complexes of metalloporphines.

IR cm^{-1} (CHCl_3) CO stretching region

Cu-TPP $\text{Cr}(\text{CO})_3$ green	1901, 1968
Cu-TPP $\text{Cr}(\text{CO})_3$ orange	1902, 1969

Elemental analysis results indicate that the compound could be impure, but still the figures are near to theoretical figures for one $\text{Cr}(\text{CO})_3$ group attached so the structure will be the same as for green compound. The difference between the two is not known; the U.V./visible for two complexes should be different because of their different colors, but it is very similar. The difference of color between the two compounds may be due to fluorescence.

Cr-TPP $\text{Cr}(\text{CO})_3$

The product was studied on silica gel plates and adsorption chromatography on a florisil column separated the complex from Cr-TPP. Purification was done by running the complex on the same fresh column. The complex obtained was a gum and could not be crystallized. The ultra violet and infra red of the complex were studied in solution.

Ultra Violet

	U.V./visible (CHCl_3) nm ($10^3 \epsilon$)
Cr-TPP	400(shoulder) 450(soret band) 525, 556, 606
Cr-TPP $\text{Cr}(\text{CO})_3$	421(soret band) 549, 607

The band around 525 disappeared in the complex and there is a hypsochromic effect (a shift toward shorter wave length) in the soret band. This effect is different from other tri-carbonylchromium complexes of metalloporphines which have a red shift in their ultra violet bands. The blue shift indicates that the bond between the central metal and porphine is stronger in the complex than in the Cr-TPP.

IR

The CO stretching vibrations are typical of $\text{Cr}(\text{CO})_3$ groups π -bonded to phenyl rings and are very similar to other tricarbonylchromium complexes of other metallocporphines.

IR cm^{-1} (CHCl_3) CO stretching region

Cr-TPP $\text{Cr}(\text{CO})_3$ 1930, 1990

The structure of the complex cannot be drawn as we do not know how many $\text{Cr}(\text{CO})_3$ groups are attached. The n.m.r. of the complex could not be studied as the complex was paramagnetic. Elemental analysis was not done as pure crystals were not obtained (a gel was obtained).

 Mn^{+2} TPP $\text{Cr}(\text{CO})_3$

Thin-layer chromatography of the product on silica gel plate using different eluents gave only one completely adsorbed spot. Adsorption chromatography on a florisil column using chloroform as eluent gave no band separation, but when methyl alcohol was followed by chloroform on the same column two bands were observed, one completely adsorbed green band and the other brownish green, which was eluted. The green band was identified as Mn^{+2} -TPP. The eluted fraction on drying decomposed as there were no CO stretching vibrations observed in the IR. However, the infra red of the crude product was studied.

IR

The CO stretching vibrations are typical of $\text{Cr}(\text{CO})_3$ groups π -bonded to phenyl rings and are very similar to

other tricarbonylchromium complexes of other metalloporphines.

The CO band positions may not be accurate as they are not of the purified complex; instead they are of crude product. IR cm^{-1} (CCl_4) CO stretching region, 1910, 1978.

No other studies were done as the complex decomposed on drying after eluting through the column.

$\text{Mn}^{+3}\text{TPP Cl Cr}(\text{CO})_3$

Thin-layer chromatography of the product on silica gel plate using different eluents gave only one completely adsorbed spot. Adsorption chromatography on a florisil column using chloroform as eluent gave no band separation, but when methyl alcohol was followed by chloroform on the same column two bands were observed, one completely adsorbed green band and the other brownish green, which was eluted. The green band was identified as $\text{Mn}^{+3}\text{TPPCl}$. The eluted fraction on drying decomposed as there were no CO stretching vibrations observed in the IR. However the infra red of the crude product was studied.

IR

The CO stretching vibrations are typical of $\text{Cr}(\text{CO})_3$ groups π -bonded to phenyl rings and are very similar to other tricarbonyl chromium complexes of other metalloporphines.

The CO band positions may not be accurate as they are not of the purified complex, instead they are of crude product. IR cm^{-1} (CCl_4) CO stretching region, 1906, 1978.

No other studies were done as the complex decomposed on drying after eluting through the column.

General trends in CO stretching region

The positions of the CO stretching vibrations for Cr-TPP-Cr(CO)₃ were the highest (1930, 1990 cm⁻¹) of the group as was expected. The size of the central ion Cr⁺² (0.89 Å) is slightly greater than the others (Mn⁺², Co⁺², Ni⁺², Cu⁺² and Zn⁺²) which will result in weaker bonding of Cr to TPP. The weaker bonding will decrease the extent of π orbital overlap between central metal (d_{xy}, d_{xz}, d_{yz}) orbitals and π anti-bonding orbitals of ligand (porphine). The less number of electrons in 3d orbitals of Cr will also decrease the π electron density in porphine system. The π back bonding from the phenyl rings of the porphine system to the Cr(CO)₃ group will be less as the charge density is less due to less π back bonding from the central metal. The decreased π back bonding to Cr(CO)₃ group will increase the CO stretching vibration value.

The size of the ion of Mn⁺² (0.8 Å) is slightly less than Cr⁺² which will result in increased stability of Mn-TPP and the π back bonding from the central metal will ultimately increase the π back bonding from the phenyl of the porphine system to the Cr(CO)₃ group and the CO stretching frequencies will be decreased. Experimentally the value is decreased.

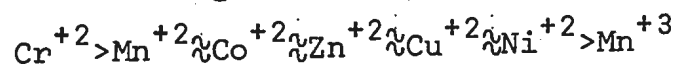
The value of the CO stretching vibrations for the Mn⁺³ complex is less than the Mn⁺² complex. The charge on the central metal is increased and its ion size decreased which results in an increased binding between Mn⁺³ and TPPCl. The greater π back bonding from the central metal will ultimately increase the π back bonding from the phenyl of the porphine system to the Cr(CO)₃ group and the CO stretching vibrations

will be decreased. Considering the size of the ions $\text{Co}=0.72\text{\AA}$, $\text{Ni}=0.69\text{\AA}$, $\text{Cu}=0.7\text{\AA}$, and $\text{Zn}=0.74\text{\AA}$) and π back bonding, the Co^{+2} complex should have a lower value for the CO stretching vibrations than the Mn^{+2} and greater than the Ni, Cu, Zn complex but the value for CO stretching vibrations are very close for Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} complexes. The theoretical calculation, by Gouterman (page 3), on the top filled and lowest empty orbitals on Mn, Fe, Co, Ni, Cu, Zn shows that comparatively Mn^{+2} π orbitals are of slightly low energy while the energy for Co, Ni, Cu and Zn π orbitals are very close which can explain the close CO positions for these metal complexes as the π charge density is close in all of these metalloporphines. The calculated energies for σ orbitals for these metals are different which is indicating that σ bonding is not effecting the π back bonding from the phenyls of the porphine system to the $\text{Cr}(\text{CO})_3$ group.

The theoretical calculations have not been done on Cr-TPP.

The expected trend of CO stretching vibrations in the 1st transition series metal porphine π complexes, based on the size of the central metal, π back bonding from central metal to porphine system, and π back bonding from the phenyl ring to chromium tricarbonyl group should be in the following decreasing order: $\text{Cr}^{+2} > \text{Mn}^{+2} > \text{Co}^{+2} > \text{Zn}^{+2} > \text{Cu}^{+2} > \text{Ni}^{+2} > \text{Mn}^{+3}$.

The experimental results of CO stretching vibrations for the 1st series of transition metal π complexes were found to be in the following decreasing order:



APPENDIX

Spectra and spectroscopic data

Elemental Analysis Results

		C	H	N
Zn-TPP $\text{Cr}(\text{CO})_3 \cdot 2\text{H}_2\text{O}$	Experimental	66.11	4.06	6.56
	Theoretical	66.3	3.77	6.50
Zn-TPP $(\text{Cr}(\text{CO})_3)_2 \cdot 2\text{H}_2\text{O}$	Experimental	60.14	4.23	5.29
	Theoretical	60.08	3.25	5.67
Ni-TPP $(\text{Cr}(\text{CO})_3)_2 \cdot 2\text{H}_2\text{O}$	Experimental	61.17	7.24	3.96
	Theoretical	60.27	3.27	5.7
Co-TPP $\text{Cr}(\text{CO})_3 \cdot 2\text{H}_2\text{O}$	Experimental	73.0	6.14	6.62
	Theoretical	66.4	3.78	6.58
Cu-TPP $\text{Cr}(\text{CO})_3 \cdot \text{H}_2\text{O}(\text{green})$	Experimental	65.5	4.8	6.74
	Theoretical	66.5	3.79	6.6
Cu-TPP $\text{Cr}(\text{CO})_3 \cdot 2\text{H}_2\text{O}$ (orange)	Experimental	74.74	6.13	6.28
	Theoretical			
	one $\text{Cr}(\text{CO})_3$ group attached	66.5	3.79	6.6
	two $\text{Cr}(\text{CO})_3$ group attached	60.3	3.28	5.72

Compound	U.V./visible (CHCl) nm($10^3 \epsilon$)
Zn-TPP	420(600), 550(22), 595(6.0)
Zn-TPP Cr(CO) ₃	422(230), 562(13), 612(6.3)
Zn-TPP (Cr(CO) ₃) ₃	424(200, 570(12), 621(6.9)
Ni-TPP	417(240), 528(17)
Ni-TPP (Cr(CO) ₃) ₂	417(200), 534(9.8)
Co-TPP	411(245), 530(15)
Co-TPP Cr(CO) ₃	410(293), 531(17.1)
Cu-TPP	416(475), 542(21)
Cu-TPP Cr(CO) ₃ (green)	395(shoulder), 439(130), 568(7.5), 606(6.3)
Cu-TPP Cr(CO) ₃ (orange)	440, 565, 606
Cr-TPP Cr(CO) ₃	421 (soret band) 549, 607
Cr-TPP	400(shoulder) 450(soret band) 525, 556, 606

Compound	$\text{CHCl}_3(\text{cm}^{-1})$ Calibration		$\text{CCl}_4(\text{cm}^{-1})$ Calibration	
Cr-TPPCr(CO) ₃	1930, 1990	(moisture)		
MnTPP Cr(CO) ₃	-	-	1910, 1978	(polystyrene)
CoTPP Cr(CO) ₃	1901, 1970	(moisture)	1912, 1974	(moisture)
ZnTPP Cr(CO) ₃	1902, 1969	(moisture)	1910, 1978	(polystyrene)
			1911, 1974	(moisture)
ZnTPP(Cr(CO) ₃) ₂	-	-	1910, 1978	(polystyrene)
CuTPP Cr(CO) ₃ (orange)	1901, 1968	(moisture)	-	-
			-	-
CuTPP Cr(CO) ₃ (green)	1901, 1968	(moisture)	-	-
			-	-
NiTPP Cr(CO) ₃	1901, 1971.5	(moisture)	1912, 1976	(polystyrene)
M _n ⁺³ TPPCl(Cr(CO) ₃)	-	-	1906, 1978	(polystyrene)

The CO stretching vibrations were measured using an expanded scale and measuring the centre of the minima of the band.

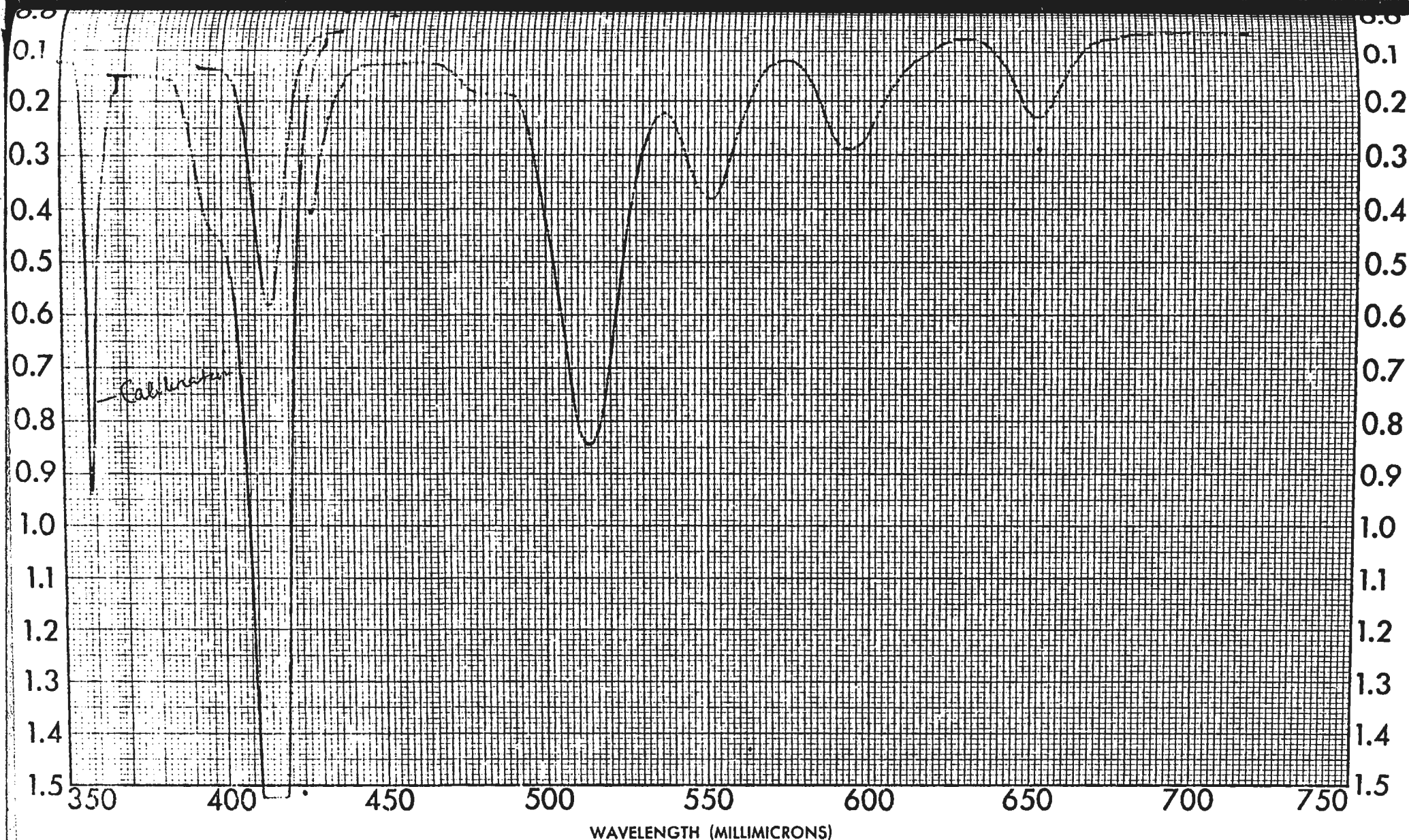


Fig no 6

SAMPLE <u>T.P.P</u>	CURVE NO. _____	SCAN SPEED <u>Slow</u>	OPERATOR <u>Z.U.S</u>
ORIGIN _____	CONC. _____	SLIT <u>N</u>	DATE <u>11-4-70</u>
SOLVENT <u>CHCl₃</u>	CELL PATH <u>1cm</u>	REMARKS _____	
	REFERENCE <u>CHCl₃</u>		

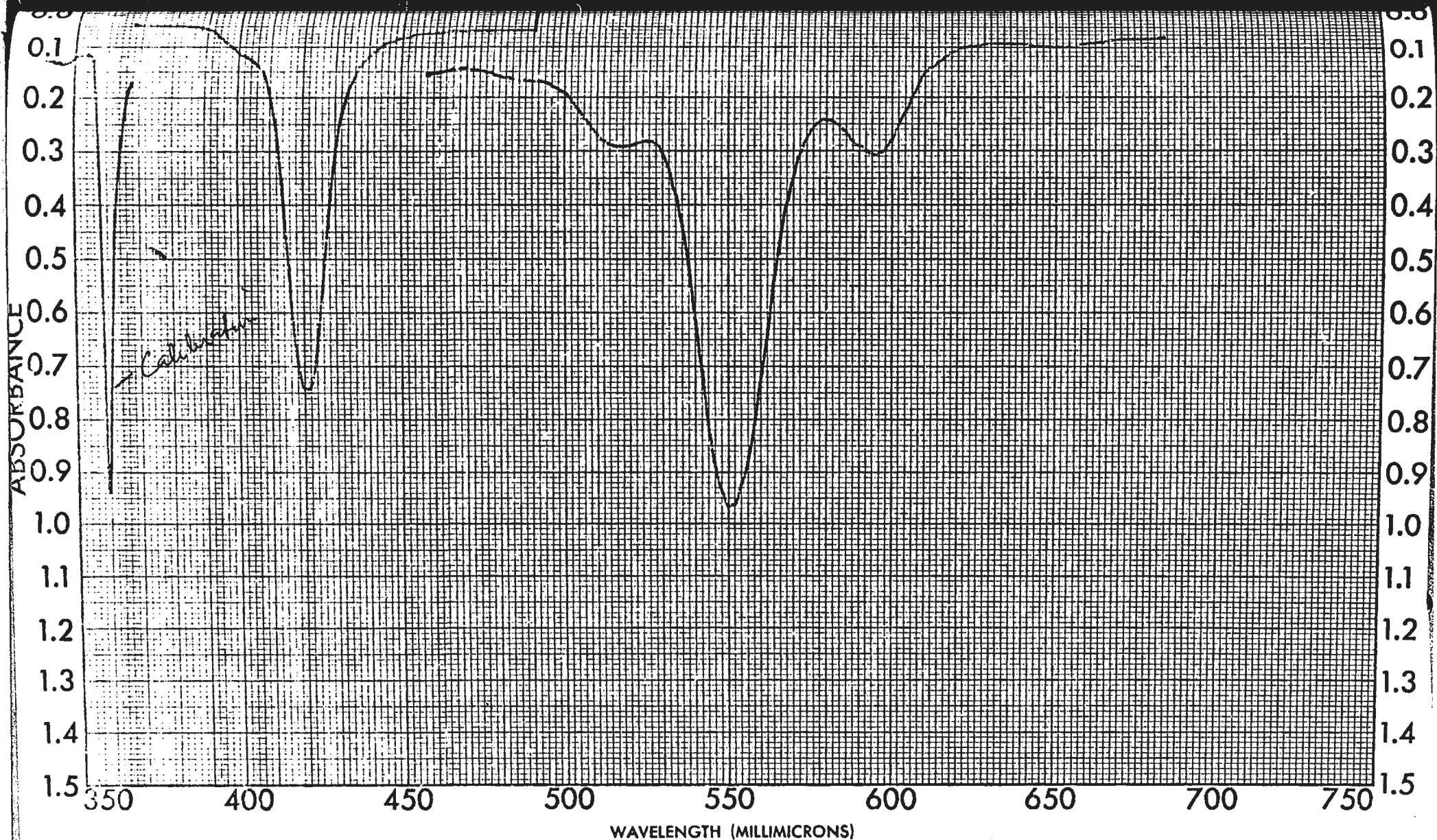


Fig no 7

SAMPLE <u>Zn (T.P.P)</u>	CURVE NO. _____	SCAN SPEED <u>Slow</u>	OPERATOR <u>Z.U.S</u>
<u>Sample 27.6.68</u>	CONC. _____	SLIT <u>N</u>	DATE <u>13-11-69</u>
ORIGIN _____	CELL PATH <u>1cm</u>	REMARKS _____	
SOLVENT <u>CHCl₃</u>	REFERENCE <u>CHCl₃</u>		

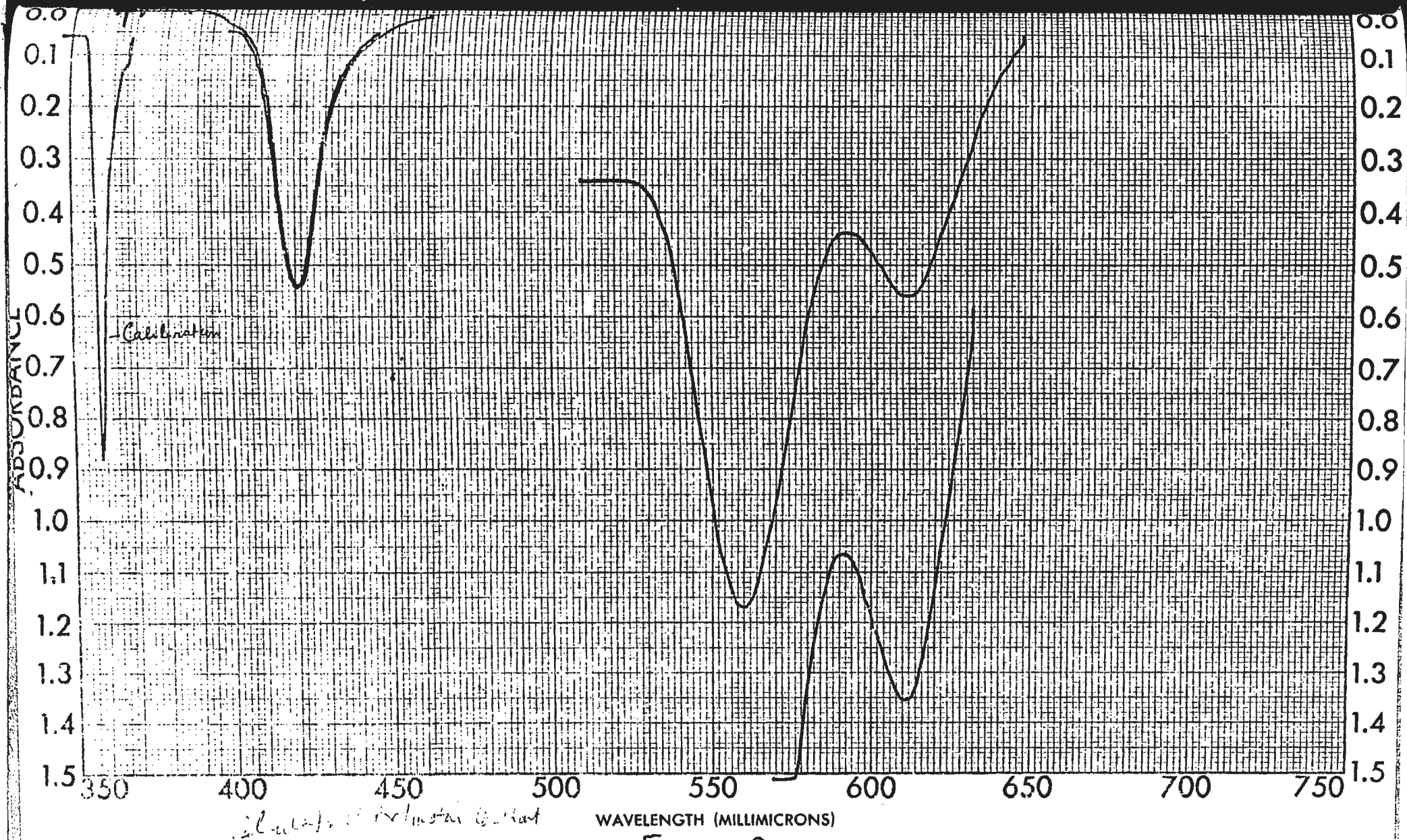
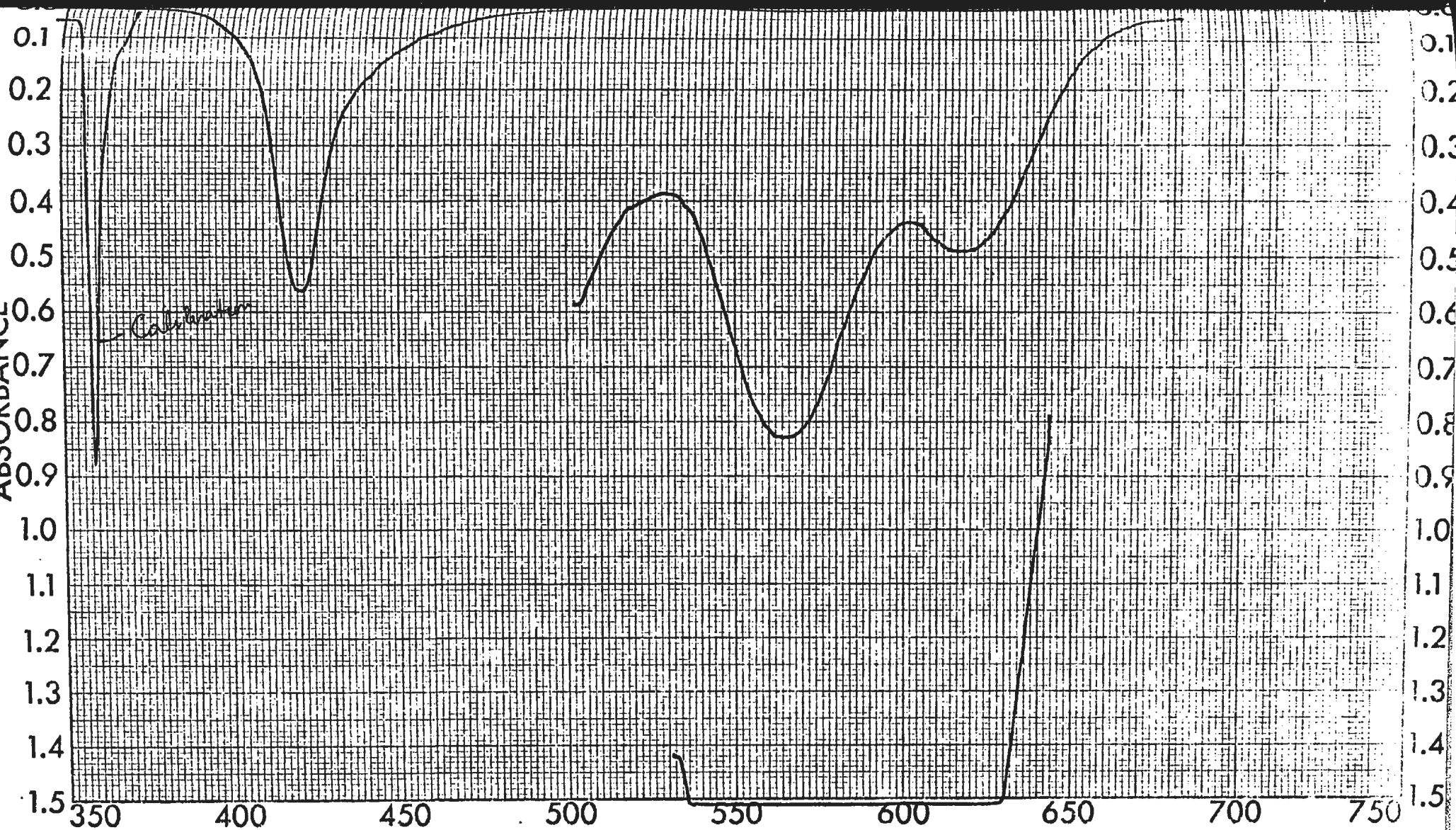


Fig no 9

SAMPLE <u>Zn T. Pt (15 (10))</u>	CURVE NO. _____	SCAN SPEED <u>Slow</u>	OPERATOR <u>Z.U.S</u>
ORIGIN _____	CONC. _____	SLIT _____	DATE <u>15-12-82</u>
SOLVENT <u>(4 Cl₂)</u>	CELL PATH <u>1cm</u>	REMARKS _____	
REFERENCE <u>Cl₂</u>			

ABSORBANCE



Calculation of Extinction Coefficient

Fig no 10

SAMPLE <u>$Zn \cdot 1.8 \cdot 9(CrO_4)_2$</u>	CURVE NO. _____	SCAN SPEED <u>slow</u>	OPERATOR <u>Z. U. S.</u>
ORIGIN _____	CONC. _____	SLIT _____	DATE <u>15-11-65</u>
SOLVENT <u>CH₂Cl₂</u>	CELL PATH <u>1 cm</u>	REMARKS _____	
PART NO. 202-1512	REFERENCE <u>CH₂Cl₂</u>		

PERKIN-ELMER®

53

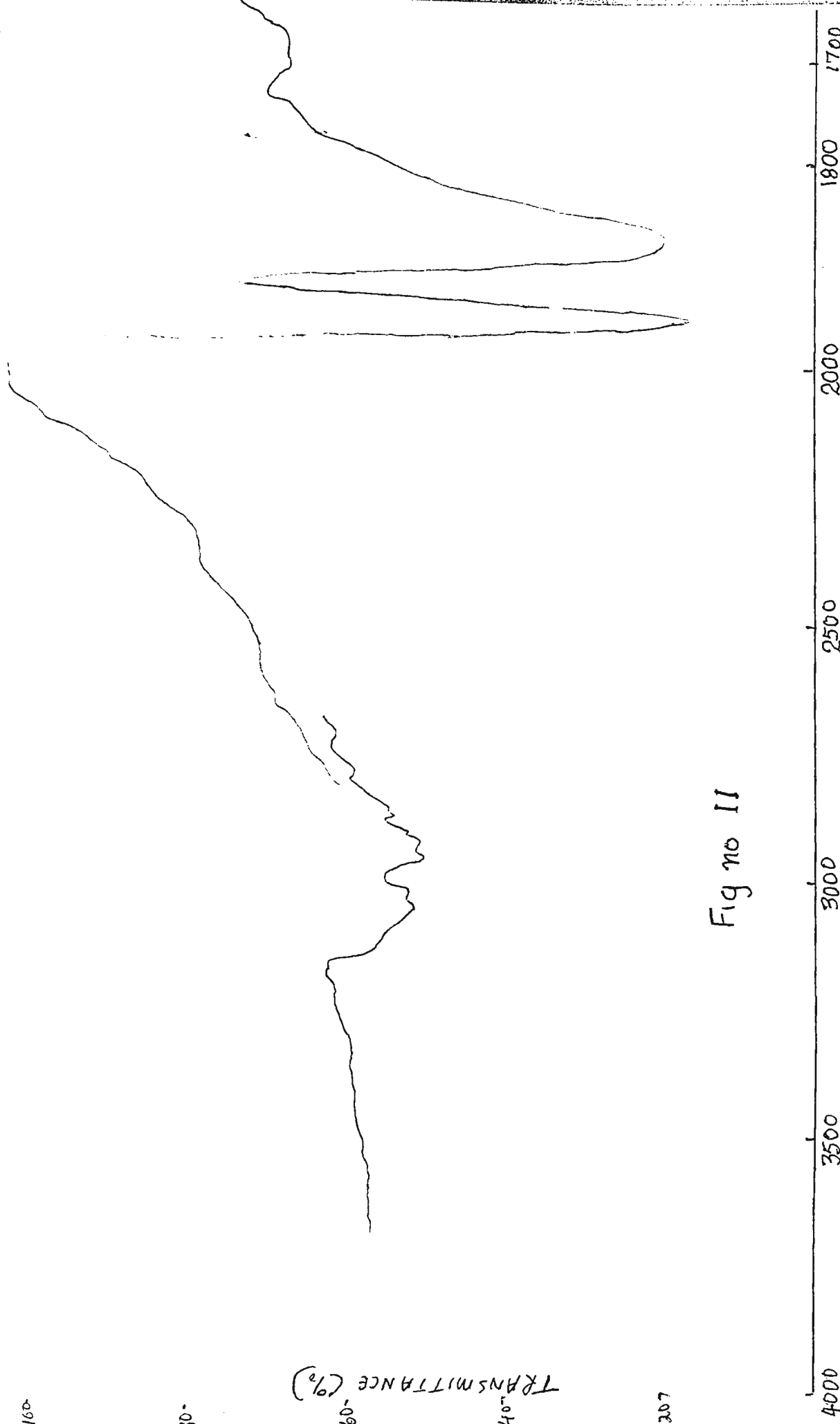


Fig no 11

SAMPLE	$Zn\ TPP\ Cr(CO)_3$	SCAN SPEED	5000	DATE	25.4.20
		SPLIT	N		
SOLVENT.	KBr disk.	REFERENCE	KBr disk.		

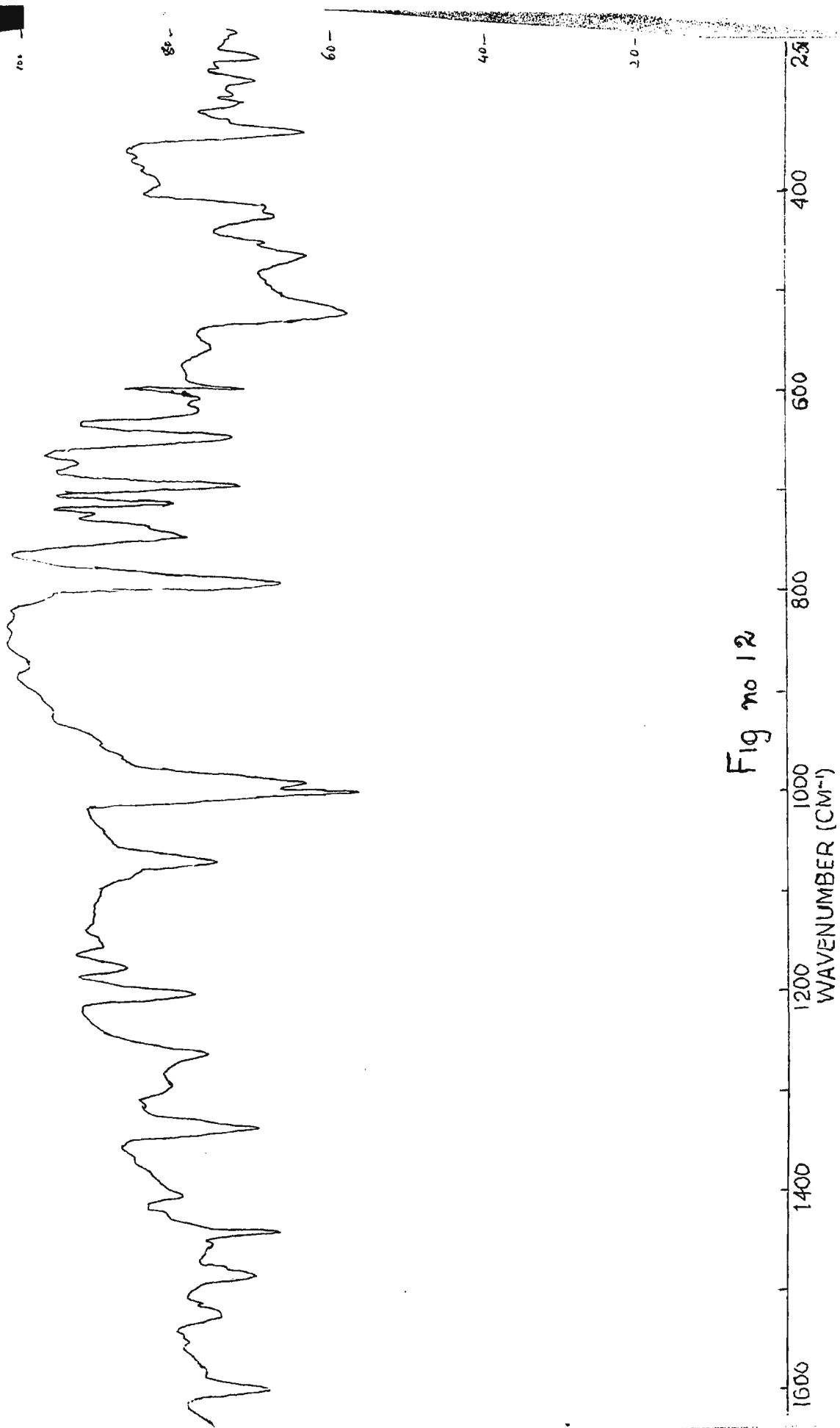


Fig no 12

Zn TPP Cr(CO)₃
KBr disk

SCAN SPEED Slow
SLIT N

DATE 25- 4- 70

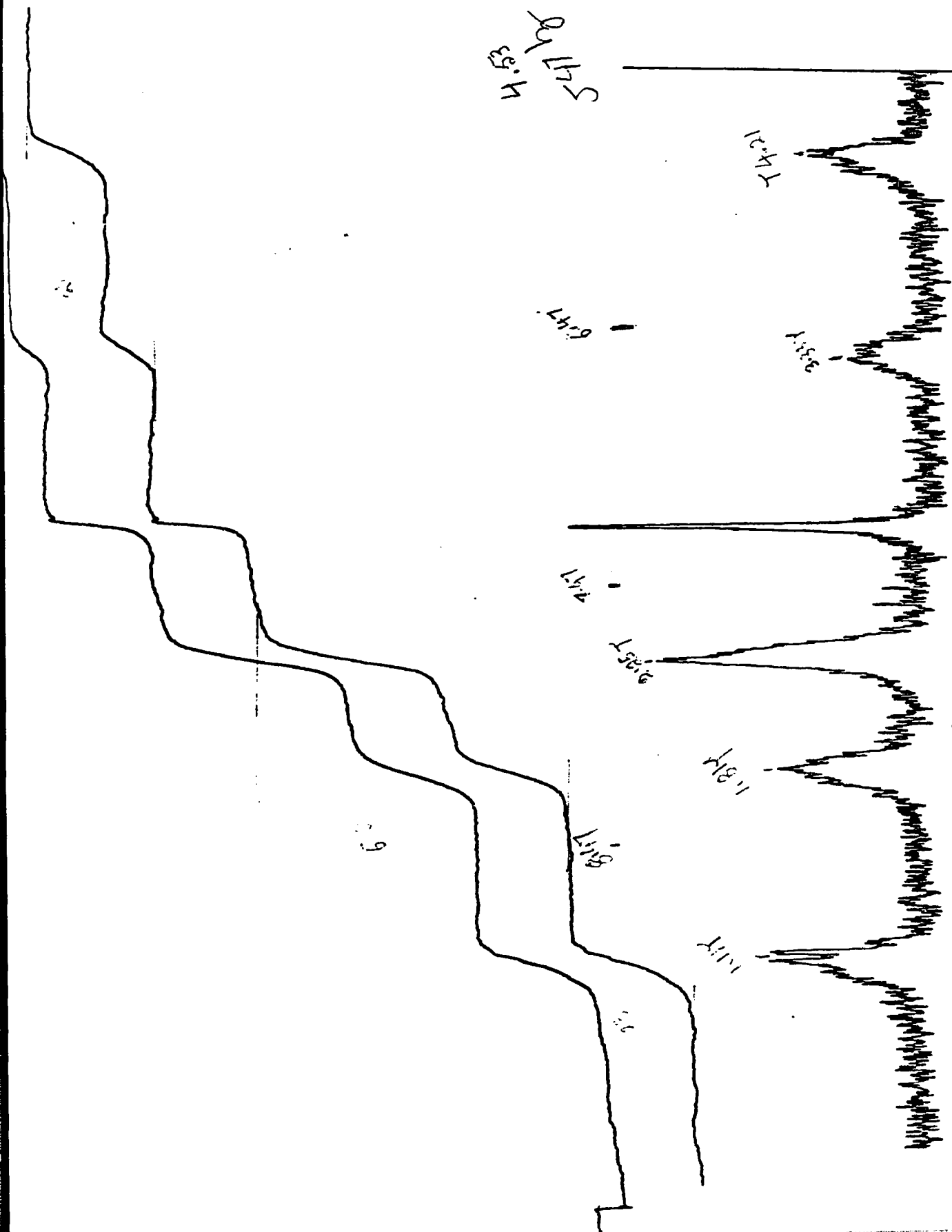


Fig no 13

Zn-TPPCr(CO)₃

SAMPLE

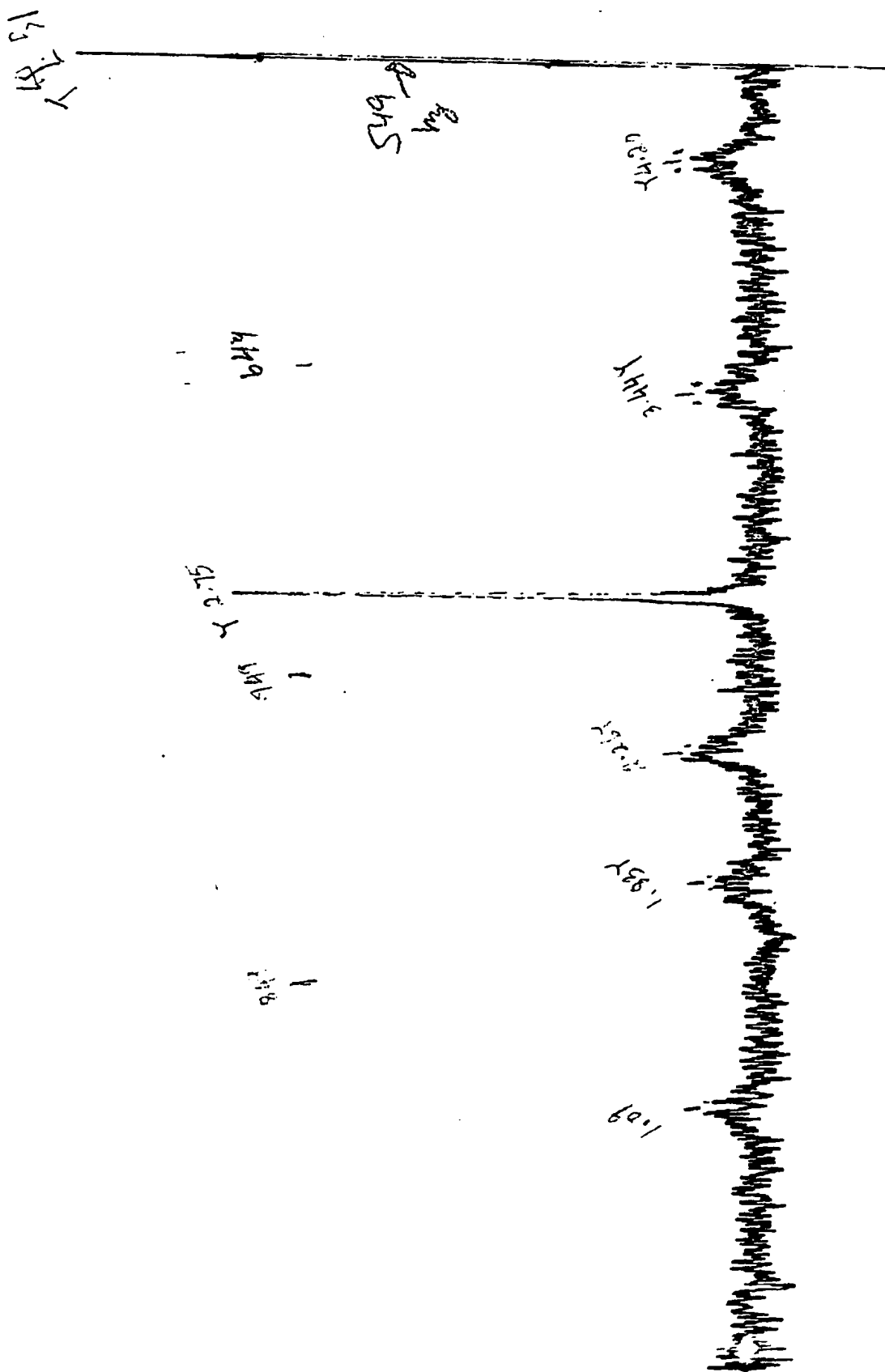


Fig no 14

SAMPLE $ZnTPP(C_2(CO)_3)_2$ $ZnTPP(C_2(CO)_3)_2$

Reference:

1. E.O. Fischer and K. Ofele, Angew. Chem., 69, 715, (1957)
Chem. Ber. 90, 2532, (1957).
2. A. Nicholls and Whiting. J. Chem. Soc. 551, (1959).
- 2A. E.O. Fischer, K. Ofele, H. Essler, W. Frohlich, J.P.
Mortenson and W. Semmlinger, Chem. Ber. 91, 2763 (1958).
3. Natta Ercoli and Calderazzo, Chem. e Ind., 40, 287 (1958).
4. Advances in Inorganic Chemistry and Radiochemistry,
Vol.I., 102(1959).
5. D.A. Brown and H. Sloan, J. Chem. Soc., 3849 (1962).
6. D.A. Brown, Transition Metal Chemistry, Vol.3.
M. Dekker, New York (1966).
7. T.L. Brown and D.J. Darensbourg, Inorg. Chem.,
6, 971 (1967).
8. D.A. Brown and F.J. Hughes, J. Chem. Soc., 1519(1968).
9. Zerner and Gouterman, Theoretica Chemica Acta 4,
(44-63)(1966).
10. Lever, A.B.P. J. Chem. Soc.(London) 1821(1965).
- 10A. Gouterman,M., J. Chem. Physics, 30, 1139(1959).
11. Thomas, D. Ward, Martell, A.E., J. Am. Chem. Soc. 78,
1335(1956).
12. Thomas, D.W. and Martell, A.E., J. Am. Chem. Soc. 78,
1338(1956).
13. Thomas, D.W., and Martell, A.E., Archiv, Biochem and
Bio Phys. 76, 286(1958).
14. Thomas, D.W., and Martell, A.E., J. Am. Chem. Soc.,
80, 5111(1959).

15. Alan D. Adler, Frederick R. Longo, John D. Finarelli, Joel Goldmacher, Jacquel Assour, and Leonard Korsakoff, J. Org. Chem. 32, 476 (1967).
16. G.D. Dorough, J.R. Miller and Frank M. Hunnekene, J. Am. Chem. Soc., 73, 4315(1951).
17. Paul Rothmund and Amer. R. Menotti, J. Am. Chem. Soc. 70, 1808 (1948).
18. Kiyoko Yamamoto and Shizu Tonomura, Sci. Papers I.P.C.R., Vol.58, No.3 (1964).
19. A.W. Johnson and I.T. Kay., J. Chem. Soc. 2970 (1960).
20. M. Tsutsui, R. Velapoldi, K. Susuki, A. Ferrari, J. Am. Chem. Soc. |90:10| May 8 (1968).
21. L.J. Boucher, J. Am. Chem. Soc. |90:24| November 20 (1968).
22. L.E. Webb and E.B. Fleischer. J. Chem. Phys. 43, 3100 (1965).
23. E.O. Fischer and H.P. Fritz. Angew. Chem. 73, 353 (1961).
24. Organometallic Synthesis, Volume I by R. Bruce King, (Pages 50-51).

Addenda

Page 11. The band around 1000 cm^{-1} is assigned to the C-H rocking vibrations. The author did not state why it was chosen for the comparative study, however it is a relatively intense band and this may have been the reason.

Page 32. The n.m.r. spectra with integration were recorded three times and the mean value for the ratio of substituted phenyl protons to phenyl protons was found to be 1:2.6. As expressed in phenyl groups this is close to a 1:3 ratio.

Errata

The words infra red, ultra violet and wave length should read as single words infrared, ultraviolet and wavelength.

The extinction coefficient values for visible bands will be the values multiplied by 10^{-3} instead 10^3 throughout.

The words Florisil, Nujol and Molecular Sieve are trade mark names for activated magnesium silicate, paraffin oil and aluminum sodium silicate.

