PHENYLSULFOXYACETIC ACID, A POTENTIAL AMBIDENT LIGAND

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A Thesis

by

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ABSTRACT

Phenylsulfoxyacetic acid has been investigated as a potential ambident ligand. The following inorganic derivatives have been synthesized: bidentate chelated platinum(II) complexes of the type $M\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ where $M = H^+, K^+, Cs^+$; bidentate chelated cadmium(II) complex $(C_6H_5SOCH_2CO_2)_2Cd \cdot 2H_2O$; chlorine-bridged platinum(II) complex $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ and a series of phenylsulfoxyacetates of general formula $(C_6H_5SOCH_2CO_2)_nM \cdot xH_2O$ where M = Mg(II), Ca(II), Ba(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Hg(I), n = 1 or 2 and x = 0, 1, 2, or 3/2.

Analytical data and several spectroscopic techniques have been used to help understand the chemistry of these compounds and to confirm proposed structures. In all of the platinum(II) complexes, the sulfoxy group utilizes sulfur in bonding, while the cadmium(II) complex is O-bonded. In the series of phenylsulfoxyacetates studied here, the sulfoxy group remains uncoordinated.

ACKNOWLEDGEMENTS

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(I) INTRODUCTION

Recent researches on coordination chemistry have revealed the wide occurrence and good coordinating property of sulfur-containing ligands. Among the complexes of sulfur derivatives, the following types of complexes have been reported: (i) complexes of sulfide ion; (ii) complexes of negatively charged unidentate ligands such as thiols, sulfite ion, thiosulfate ion, and thiocyanate ion; and (iii) complexes of neutral unidentate ligands of thioethers, thiourea and its derivatives, thioacetamide, and dialkyl or diaryl sulfoxides. Some complexes of sulfur chelate ligands with two sulfur atoms as donors, sulfur and oxygen atoms as donors, and sulfur and nitrogen atoms as donors have also been reported.[1]

A survey of the relative affinities of ligand atoms for metal ions was made by Ahrland, Chatt, and Davies[2] who divided metals into two classes: (a) those which form the most stable complexes with the first ligand atom of each group; (b) those which form the most stable complexes with the second or subsequent ligand atom. For class (a) metals O>>S and for class (b) metals S>>O. The oxidation state of the metal affects the degree of 'b' character, which is stronger for transition metals in low oxidation states, i.e., metals having non-bonding d electrons and thus capable of forming $d\pi$-$p\pi$ and $d\pi$-$d\pi$ bonds by donating a pair of electrons to the ligand.

Pearson[3] has classified metal ions and ligands into "hard" and "soft" Lewis acids and bases, and he has suggested a general rule that "hard acids" bind strongly to "hard bases" and "soft acids" to "soft bases". "Hard acids" are those that bind to bases which bind strongly to the proton, i.e., basic in the usual sense, while "soft acids" bind strongly to highly polarisable or unsaturated bases which often have negligible proton basicity, e.g. R_2S. Yet it is possible for a base to be "soft" and strongly binding to the proton; such a case is the highly polarisable sulfide ion. Pearson's "hard" and "soft" acids correspond roughly to 'a' and 'b' metals respectively.

Thiocyanate ion is an ambident ligand, which coordinates in general to 'a' class metals through nitrogen and to 'b' class metals through sulfur. However, the oxidation state of the metal, the nature of the other ligands in the complex, and steric factors may determine the way in which the thiocyanate group is bound.

Phenylsulfoxyacetic acid is used as a ligand in the present investigation, therefore it is necessary to introduce the parent acid and some of its known related complexes. A brief review of phenylsulfoxyacetic acid, sulfur-oxygen linkage in sulfoxide, sulfoxide complexes and phenyl or alkylthioacetic acid complexes is given below.

A. Phenylsulfoxyacetic Acid

Phenylsulfoxyacetic acid was first prepared by R. Pummerer[4] in 1909 from water and phenylthioglycollic acid dibromide.

$$C_6H_5SBr_2CH_2CO_2H + H_2O \longrightarrow C_6H_5SOCH_2CO_2H + 2HBr$$

There are several methods to prepare phenylsulfoxyacetic acid. Although higher yield may be obtained by oxidation with hydrogen peroxide (30%) in glacial acetic acid or by sodium metaperiodate in aqueous methanol[5], the most convenient preparation of phenylsulfoxyacetic acid is by oxidation of phenylthioglycollic acid with hydrogen peroxide (30%) in absolute ethanol, which involves a one step isolation of phenylsulfoxyacetic acid.

$$C_6H_5SCH_2CO_2H + H_2O_2 \xrightarrow[\text{cold}]{C_2H_5OH} C_6H_5SOCH_2CO_2H + H_2O$$

Unlike phenylthioglycollic acid, phenylsulfoxyacetic acid contains an asymmetric centre at the sulfur atom and forms a racemic mixture of two enantiomers which has been resolved through the cinconidine salts.[6]

Phenylsulfoxyacetic acid with pKa 2.66 in aqueous solution[7] is a fairly strong organic acid, and is stronger than monochloroacetic acid as is seen in Table 1 below:

Table 1[8]

Ionization Constants of Acids in Water at 25°C

Acid	pKa
$C_6H_5SOCH_2COOH$	2.66
CH_3COOH	4.76
$C_6H_5CH_2COOH$	4.31
$ClCH_2COOH$	2.86
$CNCH_2COOH$	2.43
C_6H_5COOH	4.17

The acidity of phenylsulfoxyacetic acid is solvent dependent, and decreases on passing to non-aqueous* solvent systems. That the polar sulfur-oxygen linkage increases the acidity of the acid is obvious by comparing the ionization constants of some related acids[8] as is seen in Table 2 below:

Table 2[8]

Ionization Constants of Acids in Water at 25°C

Acid	pKa
$C_6H_5OCH_2COOH$	3.12
$C_6H_5SCH_2COOH$	3.52
$C_6H_5SOCH_2COOH$	2.66
$C_6H_5SO_2CH_2COOH$	2.44

The highly polar sulfur-oxygen bond has a strong electron withdrawing inductive effect which is also indicated by the reduced ability of the sulfoxy group to transmit

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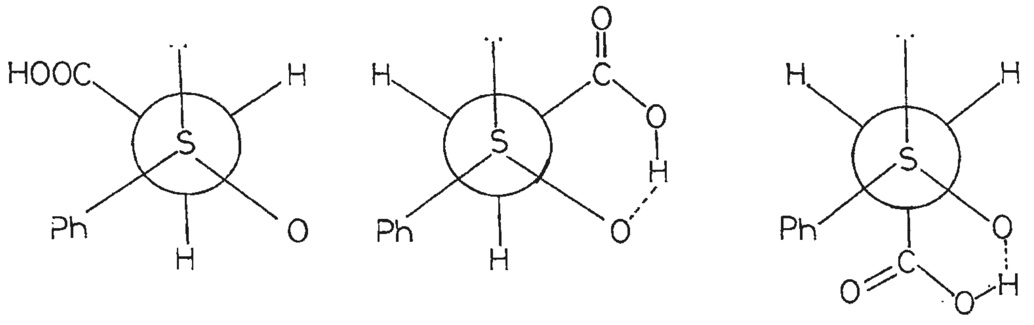
*organic

substituent inductive effects. D. J. Pasto and others have suggested that transmission of the inductive effects by the sulfoxy group may be partially shunted into the highly polar sulfur-oxygen bond instead of being directed through the methylene group to the carboxyl group, thus reducing the overall ability of the sulfoxy group to transmit substituent effects.[5b]

The major conformations of phenylsulfoxyacetic acid may be represented as a, b, and c (Figure 1). D. J. Pasto and R. Kent[7] have proposed that phenylsulfoxyacetic acid exists predominantly in the conformation a in which no intramolecular hydrogen-bonding is possible.



a b c

Figure 1

Intramolecular hydrogen-bonding may exist in conformers b and c, but not in conformer a. Conformer b would be preferred over c on the basis of steric consideration. Conformer a, however, would be expected to be more favourable because of the separation and opposition of the dipoles in the carboxyl and sulfoxy groups, particularly in the anion.

Phenylsulfoxyacetic acid undergoes a facile cleavage to benzenethiol and glyoxylic acid in the presence of mineral acids,

$$C_6H_5SOCH_2COOH \xrightarrow{H^+} C_6H_5SH + OHCCOOH$$

and auto-catalyzed cleavage in aqueous supersaturated solution, in methyl ethyl ketone, and in benzene.[9]

B. Sulfur-Oxygen Linkage

There has been a controversy[10] regarding the nature of the sulfur-oxygen bond in sulfoxides.

On the basis of observations such as the rather small bond moment of the sulfur-oxygen linkage (2.16-2.6 D*), the shorter bond length (1.45Å), and the greater bond strength, Phillips, Hunter, and Sutton[11] suggested double bond character for the sulfur-oxygen linkage in both sulfones and sulfoxides. Cumper and Walker[12] recalculated the bond moment (average value of $\ddot{\mu}_{SO}$ = 3.0 D) and favoured the double-bonded structure for the sulfur-oxygen linkage in sulfoxides.

However, rather small bond force constants[13] calculated from the frequencies of infrared absorption spectra, the strong hydrogen bonding property of sulfoxides,[13a,14]

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* Dipole moments are usually expressed in Debye units, equivalent to 10^{-18} e.s.u.

and the smaller value of the calculated bond order[15] led many workers to believe that the sulfur-oxygen linkage in sulfoxide is best described as a semipolar single bond, even though that in sulfones was still suggested to be essentially a covalent double bond. Other parameters such as bond refraction[16] and parachor[17] also lead to the conclusion of semipolar character for the sulfur-oxygen linkage of sulfoxides.

The crystal structures of dimethyl sulfoxide[18] and diphenyl sulfoxide[19] have been determined by x-ray diffraction. The molecular structure of a sulfoxide is essentially pyramidal with the sulfur atom at the apex of the pyramid. Hence a sulfoxide is very different from the corresponding planar ketone. Diagrams of the structure of dimethyl sulfoxide and diphenyl sulfoxide with important bond lengths and angles are given below: (Figure 2)

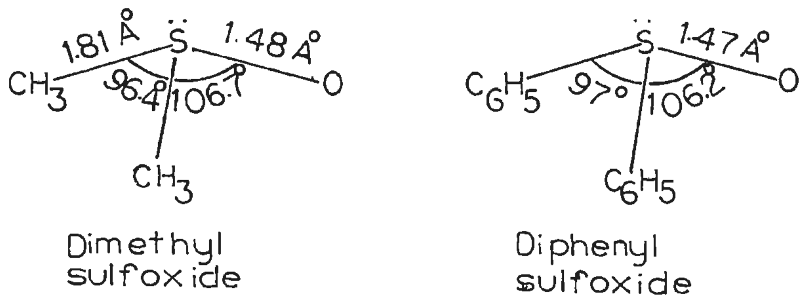
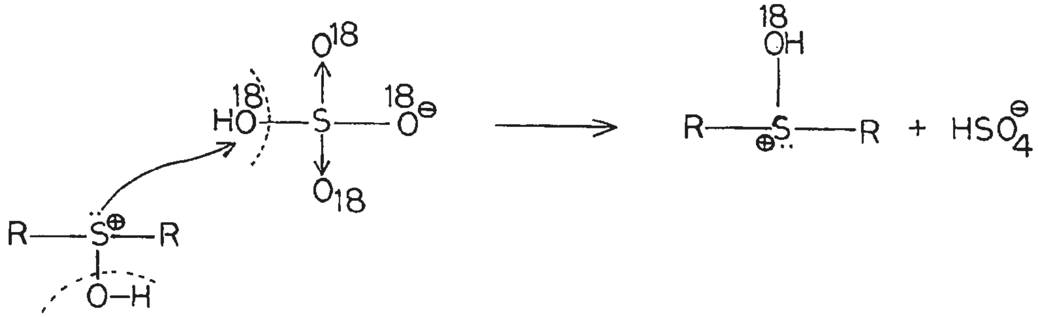


Figure 2

The S-O bond length in sulfoxides (1.47-1.48Å) is shorter than the S-O single bond (1.69Å)*, showing the partial double bond character of the former.

The sulfoxide group still retains a lone pair of electrons on the sulfur atom and is therefore, still nucleophilic in nature in spite of its partial positive charge. Thus, the sulfoxide group readily exchanges oxygen in concentrated sulfuric acid. This is in distinction from the sulfone, N-oxide, and phosphine oxide groups, which have no lone pair of electrons on the respective sulfur, nitrogen, and phosphorus atoms respectively.[20]



D. G. Cram has suggested that the sulfoxide bond, like the amine oxide bond, is semipolar because the polar oxygen of the sulfoxide is able to abstract an adjacent hydrogen as an amine oxide does. The erythro and threo configurations of sulfoxide give the <u>trans</u> and <u>cis</u> olefins respectively.[21]

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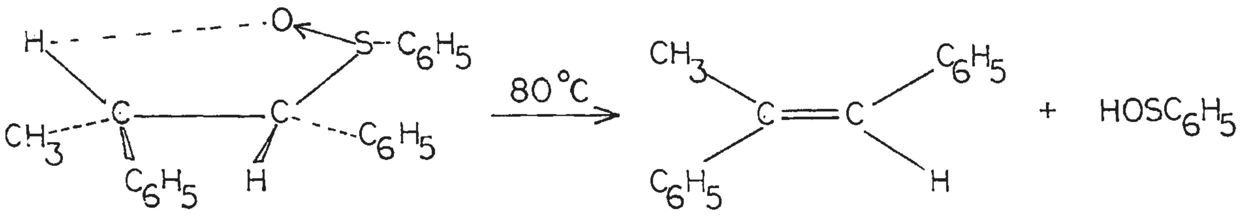
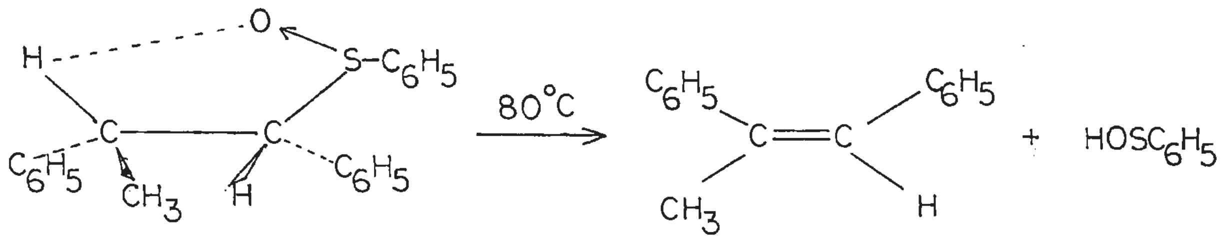
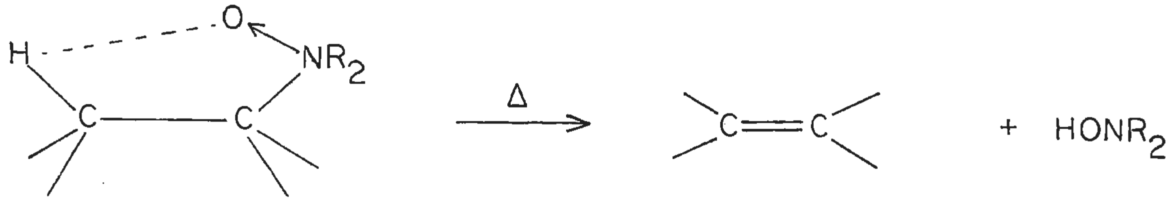
*calculated value, see ref. 10a p. 63.







The lone pair of electrons on the sulfur atom is stereochemically active which permits resolution of sulfoxides of the general type R_1R_2SO.[22] This has been considered as proof for the semipolar character of the sulfur-oxygen bond. This is not necessarily so, because one can have *sp*^{3} hybridization for the sigma bonds and the possibility of formation of π orbitals.[10b]

The bonding in sulfoxides may be assumed to involve a coordinate S→O bond, in addition to which there will be some degree of backbonding by S←O overlap of filled pπ-orbitals of oxygen with the appropriate empty dπ-orbitals of sulfur.

C. Sulfoxide Complexes

Although some diphenyl sulfoxide complexes were prepared in 1907,[23] systematic studies of sulfoxides as ligands are very recent. Dimethyl sulfoxide (DMSO) complexes have been the most widely studied. Derivatives of non-transition elements, transition elements, lanthanides and actinides have all been reported.[24]

Some complexes of diphenyl sulfoxide (DPSO) of divalent metal perchlorates and halides were prepared and investigated by Gopalakrishnan and Patel.[25] Von Leeuwen and Groenveld reported the preparation and infrared spectral data of a series of diphenyl sulfoxide complexes as well as those of pentamethylene sulfoxide and tetramethylene sulfoxide.[26] W. F. Currier and others have investigated the transition metal complexes of diphenyl sulfoxide, methyl phenyl sulfoxide (MPSO), di-n-propyl sulfoxide, and di-n-butyl sulfoxide.[27] Diphenyl sulfoxide complexes of lanthanide perchlorates of general formula $\{Ln(DPSO)_6\}(ClO_4)_3$ have also been synthesized and characterized.[28]

The number of ligands contained in a sulfoxide complex of 3d transition metals depends on the coordination nature of the anions present. When the anions are perchlorate or tetrafluoroborate, the complex contains a maximum number of sulfoxide ligands; but it takes relatively smaller number of donor molecules with halides and nitrates as anions, since the latter are better coordinating agents than perchlorate and tetrafluoroborate.

The 3d transition metal perchlorate complexes of dimethyl sulfoxide (DMSO) investigated are octahedral with general formula $\{M(DMSO)_6\}(ClO_4)_n$ (where M = Cr(III), Fe(III), Co(II), Ni(II), Zn(II), or Mn(III), and n = 2 or 3).[29] Diphenyl sulfoxide complexes of similar general formula $(M(DPSO)_6)(Anion)_n$ (where anion = tetrafluoroborate, tetraphenylborate, and hexachloroantimonate, and M = Mg(II), Mn(II), Fe(II), Ni(II), Co(II), Zn(II), Al(III), and Fe(III)) and diphenyl sulfoxide complexes of lanthanide $(Ln(DPSO)_6\}(ClO_4)_3$ (where Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, Yb and Y) are also octahedral.[24] Infrared studies of these complexes indicate that coordination is through the oxygen atom as the S-O absorption band has shifted to lower frequencies ($\Delta\nu = +61\ cm^{-1}$).[28]

It has been stated[29a, 30, 31] that it is possible to determine from infrared spectra whether coordination in sulfoxide complexes occurs via the oxygen or the sulfur atom. The shift of S-O band to higher frequencies indicates that the complex is S-bonded, while to lower frequencies indicates O-bonded. The x-ray[32] results for an iron(III) and a palladium(II) complex of dimethyl sulfoxide definitely confirm that the iron(III) complex is O-bonded and the palladium(II) complex S-bonded as predicted from infrared spectra.

Six-coordinate Hg(II) complexes of sulfoxide with general formula $(HgL_6)(ClO_4)_2$ (where L = dimethyl sulfoxide, tetramethylene sulfoxide, and thioxane oxide) have been prepared. Since the preparation of the corresponding diphenyl sulfoxide complex was not successful, it has been suggested that steric factors are important in forming these complexes.[33]

In $CdCl_2 \cdot DPSO$ and $HgCl_2 \cdot DPSO$ complexes,[25] coordination through sulfur atom has been suggested from the infrared spectra. The compounds are believed to have a halogen-bridged dimeric structure as follows (Figure 3):

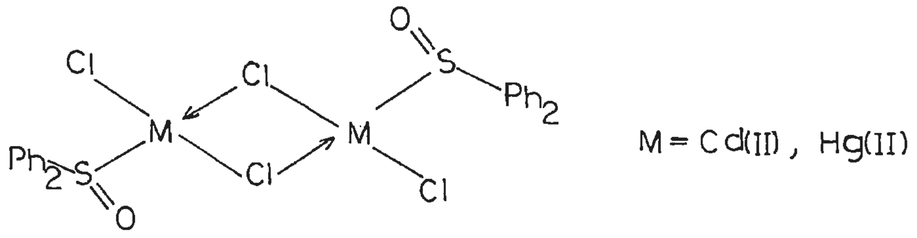


Figure 3

Very recently, W. Kitching and his collaborators[34] have synthesized a number of sulfoxide complexes of platinum(II) and palladium(II). The infrared and proton magnetic resonance spectra of these compounds indicate that sulfur is the donor atom. Three groups of complexes have been prepared:

$PtCl_2L_2$ L = $(C_2H_5)_2SO$, $CH_3SOCH_2C_6H_5$, $(C_6H_5CH_2)_2SO$, $CH_3SOCH(CH_3)_2$.

$PdCl_2L_2$ L = $(C_2H_5)_2SO$, $CH_3SOCH_2C_6H_5$, $CH_3SOCH(CH_3)_2$.

$[PdCl_2L]_2$ L = $CH_3SOCH_2C_6H_5$, $(C_6H_5CH_2)_2SO$, $(C_6H_5)_2SO$, $\{(CH_3)_2CH\}_2SO$, $(CH_3CH_2)_2SO$.

Far infrared and proton magnetic resonance data indicate a cis configuration for $PtCl_2L_2$ except for the complex with L = $\{(CH_3)_2CH\}_2SO$. The palladium(II) complexes, $PdCl_2L_2$, are trans in the solid state, but in solution most appear to revert to the halogen-bridged binuclear structures $(PdCl_2L)_2$.

D. Inorganic Derivatives of $RSCH_2COOH$

Although inorganic derivatives of simple carboxylic acids and amino acids have been studied, there appear to be no reports of ligands containing both carboxylic and sulfoxy groups.

In the study of formation constants and relative stability of the complexes of phenoxyacetic acid, phenylthioacetic acid with divalent metal ions, Suzuki and Yamasaki[35] found that the stability of the metal complexes formed decreases in the order

$$Pb > Cu > Cd > Zn > Ni$$

Since this order is the same as shown by the carboxylic acids which form seven membered or larger chelate rings,[36] it was suggested that sulfur and oxygen of these two ligands are perhaps not involved in coordination.

L. D. Pettit and his collaborators, in the study of the stabilities of a series of silver complexes of substituted phenylthioacetic acids, and phenylselenoacetic acids, proposed that for phenylthioacetic acids (HL) of general formula $RC_6H_4SCH_2COOH$ (where R = H, o, m, p-CH_3; o, m, p, -OCH_3; o, m, p, -Cl; o, m, p, -COOH; o, p, -NO_2; m-CF_3; p-CN; p-Br; p-NH_2; o, p, -SCH_3), the stability of the species AgL, $AgHL^+$ and AgL_2^- tends to increase as the electron releasing nature of the phenyl substituent of the ligand increases, and to decrease as the substituent becomes more electron-attracting (with the exception of the substituents o-SCH_3 and p-SCH_3).[37]

Silver complexes of ligands containing sulfur or selenium as donor atoms are always more stable than the analogous oxygen complexes. This large increase in stability has been attributed to the back donation from filled metal ion d-orbitals to empty ligand d-orbitals.

The formation constants of the silver complexes, AgL, of $RC_6H_4SCH_2COOH$ and p-RSC_6H_4COOH(HL) and of the protonated silver complexes AgHL of $RC_6H_4SCH_2COOH$ have been measured. The stabilities of the complexes are found to vary with the inductive effects of the substituents. From the above, L. D. Pettit and his co-worker suggested that changes in sigma bonding between sulfur and silver atoms are the major contributing factors to the free energy changes observed. Hence, they predicted that the bonding of the phenyl group to the sulfur atom would markedly reduce the stabilities of the complexes.[38]

Since removal of negative charge from the sulfur atom would encourage dissociation of the carboxyl proton, the increase in acidity by 0.76 pK unit on coordination of silver to the sulfur atom is to be expected if the silver-sulfur bond is largely sigma in character. The substitution of phenyl group on the sulfur atom reduces the stability of the complex considerably and this shows that a reduction in donor capacity of the sulfur atom is not matched by any increase in its π-acceptor capacity.[39]

Thermodynamic studies of the silver complexes of substituted phenoxyacetic acids, phenylthioacetic acids and phenylselenoacetic acids shows that the stability of the complexes decreases in the order of Se>S>>O. It was thus concluded that for the substituted phenylthioacetic acids and phenylselenoacetic acids, the Ag-L bond is enthalpy-stabilized and the increased stability of the selenium complexes is due entirely to an enthalpy effect.[40]

L. Ramberg and A. Tieberg[41] studied some reactions of platinum(II) with ethylthioacetic acid and ethylenethioglycollic acid at the beginning of the present century, but no spectrochemical data were provided in their works.

Other sulfur-containing carboxylic acid such as thioglycollic and β-mercaptopropionic acid have also been studied as ligands. Since these ligands involve charged sulfur in the reaction, they will not be treated here.

From the whole discussion above it is clear that only simple sulfoxide as ligand has been investigated. It seems that no research has been done on how the presence of other competing donor groups in the same ligand will affect the donor power of sulfoxide. It would be interesting to see how the sulfoxide behaves in reactions in the presence of other donor groups in the same ligand.

(II) EXPERIMENTAL

Analyses

Microanalyses of carbon, hydrogen, sulfur and chlorine were carried out by Alfred Bernhardt, West Germany. Calcium, manganese, cobalt, and copper were determined by the method of atomic absorption. Magnesium, nickel, zinc and cadmium were determined by EDTA titrations, while silver was precipitated as silver chloride and barium as barium chromate and determined gravimetrically.

Infrared Spectra (i.r.)

The solid state infrared spectra were obtained in KBr discs in the range (4000–250 cm^{-1}) with a Perkin-Elmer 457 grating spectrometer.

Ultraviolet and Visible Spectra (u.v. and visible)

The ultraviolet and visible spectra were recorded in aqueous or alcohol solution with a Unicam SP 800 spectrometer.

Electron Spin Resonance Spectra (e.s.r.)

A JES-ME-3X spectrometer, operating at x-band frequency, was used to record the electron spin resonance spectra at various temperatures.

Nuclear Magnetic Resonance Spectra (n.m.r.)

Nuclear magnetic resonance spectra were recorded in d_6-dimethyl sulfoxide solvent, with a Varian A-60 instrument at 60 Mhz.

Melting points (uncorrected) were determined on a Fisher-John's melting point apparatus.

Reagents

Commercial phenylthioacetic acid, which was purchased from Aldrich Chemical Co., was employed directly for the preparation of phenylsulfoxyacetic acid.

Preparation of phenylsulfoxyacetic acid

To the solution of $C_6H_5SCH_2CO_2H$ (16.8210 g., 0.100 mole) in absolute ethanol at 0-5°C, 30% H_2O_2 (12.2100 g., 0.110 mole) was added dropwise. The solution was stirred for six hours at 0°C. The excess hydrogen peroxide and solvent were removed by distillation under reduced pressure. The oily residue was dissolved in hot benzene-ethyl acetate (3:1 by volume) and, on cooling, yielded white prisms of phenylsulfoxyacetic acid (ca 80% yield). Phenylsulfoxyacetic acid was recrystallized three times from benzene-ethyl acetate (3:1 by volume) to yield crystals of m.p. 117-118.5°C. It is a racemic mixture and therefore the melting point varies with the proportion of the conformers present as seen by comparing the literature values below: (lit.m.p. 112.5-113.0°C),[42] (lit.m.p. 116.0-117.6°C),[5b] and (lit.m.p. 118.0-119.5°C).[43]

Preparation of coordination complexes of phenylsulfoxyacetic acid

(a) Hydrogen dichloro-monophenylsulfoxyacetato-platinate(II)

A solution of K_2PtCl_4 (0.4152 g, 1.0 mmole) in 3 ml water was added to a solution of $C_6H_5SOCH_2CO_2H$ (0.1840 g, 1.0 mmole) in 5 ml water. A pale yellow product began to precipitate after the reaction mixture had been stirred at 45°C for five hours. The precipitate was filtered, washed with cold water, and then dried in vacuum. The complex $H\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ was recovered in a yield of 0.3378 g (75.0%).

(b) Potassium dichloro-monophenylsulfoxyacetato-platinate(II)

A solution of K_2PtCl_4 (0.8304 g, 2.0 mmole) in 3 ml water was added to a solution of $C_6H_5SOCH_2CO_2K$, which was prepared by neutralizing $C_6H_5SOCH_2CO_2H$ (0.3680 g, 2.0 mmole) in 10 ml water with stoichiometric amount of K_2CO_3. The reaction mixture was stirred at room temperature until the reddish colour turned yellow. On cooling, a yellow compound crystallized out. This was filtered, washed with cold water, then with cold 95% ethanol, and dried in vacuum. $K\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ was recovered in a yield of 0.2363 g (24.2%).

(c) Cesium dichloro-monophenylsulfoxyacetato-platinate(II) and Di-μ-chloro-dichloro-bisphenylsulfoxyacetic acid-diplatinum(II)

A mixture of K_2PtCl_4 (0.4152 g, 1.0 mmole), $C_6H_5SOCH_2CO_2H$ (0.1840 g, 1.0 mmole) and CsCl (0.1684 g, 1.0 mmole) was dissolved in 10 ml water. A yellow precipitate was formed after the reaction solution had been stirred for fourteen hours at room temperature. It was filtered, washed with cold water and dried in vacuum. $Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ was obtained in a yield of 0.2268 g (39.1%).

Binuclear chlorine-bridged $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ was isolated as needle-shaped yellow crystals from the filtrate above, after it had been stored at 0°C for three days. The yield was 0.1520 g (33.8%).

(d) Bisphenylsulfoxyacetato-cadmium(II) dihydrate

A solution of $C_6H_5SOCH_2CO_2H$ (3.6800g, 0.020 mole) in 100 ml water was added to freshly prepared $CdCO_3$.[44] The reaction mixture was stirred at about 50°C until it was neutral. After the unreacted $CdCO_3$ had been filtered off, the solvent was removed by evaporating under reduced pressure. Ethyl ether was then added to solidify the compound. Recrystallization of the compound from water yielded 4.2301 g (88.5%) of the complex $(C_6H_5SOCH_2CO_2)_2Cd\cdot 2H_2O$, while recrystallization from 95% ethanol yielded the simple salt $(C_6H_5SOCH_2CO_2)_2Cd\cdot 2H_2O$.

Preparation of phenylsulfoxyacetates

(a) Magnesium(II) phenylsulfoxyacetate dihydrate

A solution of $C_6H_5SOCH_2CO_2H$ (3.6800g, 0.020 mole) in 100 ml water was added to heavy basic magnesium carbonate $3MgCO_3Mg(OH)_2 \cdot 3H_2O$ (0.9134 g, 2.5 mmole). The reaction mixture was stirred at about 35°C until the solution was not acidic. The unreacted magnesium carbonate was filtered off and the solvent was removed under reduced pressure. The product was recrystallized from water-acetone mixed solvent and then filtered and dried under vacuum. $(C_6H_5SOCH_2CO_2)_2Mg \cdot 2H_2O$ was obtained in a yield of 4.1602g (97.5%).

(b) Calcium(II) phenylsulfoxyacetate

Calcium(II) phenylsulfoxyacetate was prepared by the same procedure described for the corresponding magnesium(II) compound by neutralizing phenylsulfoxyacetic acid with a stoichiometric quantity of calcium carbonate in aqueous solution. The yield was 87.1%.

(c) Barium(II) phenylsulfoxyacetate

A similar procedure as described for the corresponding magnesium(II) derivative was employed here. Barium(II) phenylsulfoxyacetate was recovered in a yield of 83.2%.

(d) Manganese(II) phenylsulfoxyacetate

Phenylsulfoxyacetic acid was neutralized by freshly prepared manganese carbonate[45a] by using the procedure described for the corresponding magnesium(II) derivative.

Manganese(II) phenylsulfoxyacetate was recrystallized from water. The yield was 65.2%.

(e) Cobalt(II) phenylsulfoxyacetate

The procedure similar to that described for the corresponding magnesium(II) derivative was employed here. Cobalt(II) phenylsulfoxyacetate was recrystallized from water and it was recovered in a yield of 89.2%.

(f) Nickel(II) phenylsulfoxyacetate

A solution of $C_6H_5SOCH_2CO_2H$ (1.8400g, 0.010 mole) in 50 ml water was added to freshly prepared $Ni(OH)_2$.[45b] The reaction mixture was stirred at 60-70°C for two hours, until the solution was neutral. The unreacted nickel hydroxide was filtered off and the solvent removed. Nickel(II) phenylsulfoxyacetate was recrystallized from water-acetone mixed solvent and a yield of 1.9201 g (90.0%) was obtained.

(g) Copper(II) phenylsulfoxyacetate monohydrate and Copper(II) phenylsulfoxyacetate 3/2 hydrate

Phenylsulfoxyacetic acid was reacted with basic copper(II) carbonate $CuCO_3 \cdot Cu(OH)_2$ by following the procedure of the corresponding magnesium(II) derivative. The blue precipitate could be recrystallized from water. A green powder $(C_6H_5SOCH_2CO_2)_2Cu \cdot H_2O$ was obtained when the sample was dried overnight in vacuum at 110°C while that which was dried at about 70°C in vacuum produced $(C_6H_5SOCH_2CO_2)_2Cu \cdot 3/2H_2O$ which remained blue in colour.

(h) Zinc(II) phenylsulfoxyacetate dihydrate

Phenylsulfoxyacetic acid was neutralized by zinc carbonate by following the procedure described for the corresponding magnesium(II) compound. $(C_6H_5SOCH_2CO_2)_2Zn\cdot 2H_2O$ was recovered in 94.0% yield.

(i) Silver(I) phenylsulfoxyacetate

The reaction was carried out in the dark. A solution of phenylsulfoxyacetic acid (1.8400 g, 0.010 mole) dissolved in 50 ml of water was added to Ag_2CO_3 (1.3787 g, 5.0 mmole). The reaction mixture was stirred at 66°C for one hour. A pale brown precipitate which formed was filtered off. A white precipitate crystallized out from the solution after one day and it was filtered and dried in vacuum. $C_6H_5SOCH_2CO_2Ag$ was recovered in a yield of 2.4230g (83.5%).

(j) Mercury(I) phenylsulfoxyacetate

The reaction was performed in the dark. To a solution of $Hg_2(NO_3)_2$ (2.8060g, 0.010 mole) in 15 ml water, 1-2 ml of 25% nitric acid was added slowly until all the mercurous nitrate was dissolved. To this solution, a solution of $C_6H_5SOCH_2CO_2Na$ (2.0600g, 0.010 mole) in 5 ml water was added. White precipitate began to form in the process of mixing the solutions. The mixture was stood at room temperature for two hours. $(C_6H_5SOCH_2CO_2)_2Hg_2$ was filtered, washed with cold water and dried in vacuum at about 70°C and a yield of 3.1520g (82.0%) was produced.

Unsuccessful attempts

(a) The reaction of $C_6H_5SOCH_2CO_2H$, $CrCl_3 \cdot 6H_2O$ and NaOH (in the mole ratio 3:1:3) was carried out in both water and ethanol solvents. A green product which is very soluble in alcohol but insoluble in water was obtained. Unfortunately, no analytically pure compound was successfully isolated.

(b) The reaction of $C_6H_5SOCH_2CO_2Ag$ and $FeCl_3$ (in a mole ratio 3:1) was carried out in both water and 95% ethanol. A brownish red precipitate was formed but no analytically pure compound was isolated.

(c) Attempts to prepare molybdenum(II) phenylsulfoxyacetate were not successful. The method described[46] for the syntheses of molybdenum(II) carboxylates was followed but the reaction conditions were varied. All the reactions were carried out under nitrogen:

(i) $Mo(CO)_6$ and $C_6H_5SOCH_2CO_2H$ (in a 1:2.2 mole ratio) were dissolved in the minimum amount of dry diglyme and heated to ca 150°C until gas evolution ceased. A black decomposition product was obtained.

(ii) $Mo(CO)_6$ and $C_6H_5SOCH_2CO_2H$ (in a 1:2.2 mole ratio) were allowed to react in sodium dried tetrahydrofuran (THF) at ca 50°C. A grey decomposition product was recovered.

(iii) $Mo(CO)_6$ and $C_6H_5SOCH_2CO_2H$ was refluxed at ca 110°C in dry diglyme. The reaction solution turned yellow, but the yellow colour vanished quickly and changed to green and finally to grey. Again, only the decomposition product was obtained.

(d) The reaction of $C_6H_5SOCH_2COOH$ and $Na_3Co(CO_3)_3 \cdot 3H_2O$ (in a 3:1 mole ratio) was carried out at 60°C in absolute ethanol. One-fifth by volume of water at the same temperature was added to the reaction mixture. After the gas evolution had ceased a green solution was formed. No analytically pure compound was isolated.

(III) RESULTS AND DISCUSSION

Although sulfoxide and carboxylate complexes are well known, no ligands in which both sulfoxide and carboxylate group occur have been studied. Phenylsulfoxyacetic acid, one of the simplest compounds which contains both groups, is the object of the present work.

The acid and its relatives are potentially very interesting. Since the molecule contains two different donor groups, it is potentially ambident when acting as a monodentate ligand. In addition, it could act as a chelating bidentate ligand. Finally, it is known that the hydrogens of the methylene group of the parent acid are non-equivalent from nuclear magnetic resonance studies.

In the present study, phenylsulfoxyacetic acid reacted with various metal ions to give products which may be divided into two classes: (A) coordination complexes of phenylsulfoxyacetic acid, and (B) phenylsulfoxyacetates, in which the sulfoxy group does not participate in the reaction and the compounds contain essentially ionic metal-carboxylate bonds.

(A) Coordination Complexes

Three types of coordination complexes of phenylsulfoxyacetic acid have been isolated. These include (a) chelated complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+, K^+, Cs^+$, in which the phenylsulfoxyacetic acid acts as a chelating bidentate ligand, bonded through sulfur of the sulfoxy group as well as the carboxylate group; (b) chlorine-bridged complex $\{Pt(C_6H_5SOCH_2COOH)Cl_2\}_2$, in which phenylsulfoxyacetic acid is monodentate, bonded only through sulfur of the sulfoxy group; and (c) chelated complex $(C_6H_5SOCH_2COO)_2Cd\cdot 2H_2O$, in which chelation occurs through oxygen of the sulfoxy group and the carboxylate ion.

According to S. Ahrland et al.[2], platinum(II) belongs to 'a'-class acceptor (i.e. soft acid) while cadmium(II) is in the border line of 'a' and 'b'-class. R. G. Pearson[3] classifies carboxylate ion as an 'a'-class donor (i.e. hard base). In sulfoxide complexes, sulfur usually coordinates with 'b'-class acceptors while oxygen with 'a'-class acceptor.[24] Thus in the complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+$, K^+, Cs^+, a mixed complex of 'a' and 'b' class donors occurs in the complex anion $\{Pt(C_6H_5SOCH_2COO)Cl_2\}^-$. In the chelated complex $(C_6H_5SOCH_2COO)_2Cd\cdot 2H_2O$ cadmium(II) acts as a "hard acid", forming a complex with "hard bases".

The formation of mixed complexes of 'a' and 'b' class donors in the complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+$, K^+, Cs^+, is partly attributed to the gain of stabilization energy through chelation. This phenomenon of mixed complex of 'a' and 'b' class donor in one complex may also be explained by the view of S. Ahrland[47] that "The coordination of very soft ligands to a 'b'-acceptor will decrease its 'b' character, or even turn it into an 'a'-acceptor".

A similar phenomenon has been observed by Burmeister and Basolo,[48] who found that the very soft ligand triphenylphosphine causes platinum(II) and palladium(II) to coordinate the "hard" nitrogen end of the thiocyanate ion, forming an isothiocyanate complex, while the less soft triphenylstibine causes these acceptors to attach the thiocyanate ion by its soft sulfur end, in accordance with the more general rule that soft ligands flock together.

The three types of phenylsulfoxyacetic acid complexes are discussed separately in the following sections. The structural elucidation is based mainly on the elemental analyses, the infrared spectral data together with other spectroscopic data which are available. The analytical data of these complexes are located in Table 3a.

(a) Complexes of hydrogen, potassium, and cesium (dichloro-monophenylsulfoxyacetato-platinate(II)

Elemental analyses (Table3a) of the three new complexes are consistent with the empirical formula $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+, K^+, Cs^+$, for the solid yellow compounds.

Although no well-defined nuclear magnetic resonance spectra of complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+, K^+, Cs^+$, are available owing to their low solubility in suitable n.m.r. solvent, the presence of weak n.m.r. signals for these complexes are consistent with their diamagnetism.

TABLE 3a

Analytical data for platinum(II) and cadmium(II) complexes of phenylsulfoxyacetic acid.

		Analysis (%)									
	Melting point	C		H		S		Cl		Metal	
Compound	(°C)	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$H(Pt(C_6H_5SOCH_2CO_2)Cl_2)$	230° (dec)	21.26 21.08	21.34	1.69 1.62	1.79	6.91 7.04	7.12	15.30 15.45	15.75		
$K(Pt(C_6H_5SOCH_2CO_2)Cl_2)$	260° (dec)	19.89	19.68	1.56	1.65	6.82	6.56	14.17	14.52		
$Cs(Pt(C_6H_5SOCH_2CO_2)Cl_2)$	230° (dec)	16.34	16.51	1.37	1.21	5.34	5.51	12.06	12.18		
$(Pt(C_6H_5SOCH_2CO_2H)Cl_2)_2$	125°	21.19	21.34	1.81	1.79	7.39	7.12	15.80	15.75		
†$(C_6H_5SOCH_2CO_2)_2Cd\cdot 2H_2O$	124-25°	37.37	37.33	3.61	3.52	12.26	12.46			21.91[b]	21.42
*$(C_6H_5SOCH_2CO_2)_2Cd\cdot 2H_2O$	131-32°	37.62	37.33	3.37	3.52	12.29	12.46				

† Chelated compound recrystallized from water;

* Simple salt recrystallized from 95% ethanol.

b) by EDTA titration.

Magnetic susceptibility measurements[49] indicate essential diamagnetism in the case of $PdCl_2(DMSO)_2$ in the solid which is square planar.[50] Diamagnetism of a d^8 ion is definite evidence for square planar. Hence the diamagnetism of the new platinum(II) complexes indicates little departure from square structures, so that square planar geometry seems appropriate.

Questions remaining relate to the identity of the donor atom (S or O) of the sulfoxy group and the determination of the type of platinum(II)-carboxylate bond which formed. Infrared spectra allow firm conclusions on both questions as well as the configuration (cis or trans) in the square planar structure.

Infrared spectra

Investigation of a wide variety of sulfoxide complexes suggests strongly that the direction of change in energy of the S-O stretching frequency band on coordination reflects the donor atom (S or O).[24] This has been confirmed directly by a number of x-ray determinations[50,51] and there is no exception to the generalization that an increase in ν(S-O) indicates S-coordination, and a decrease, O-coordination. Thus $\Delta\nu(S\text{-}O) = (\nu(S\text{-}O)_{ligand} - \nu(S\text{-}O)_{complex})$ if negative indicates S-coordination, while if positive indicates O-coordination.

The electronic structure of sulfoxides may be represented by a resonance hybrid of the structures (I-III)[52] (Figure 4).

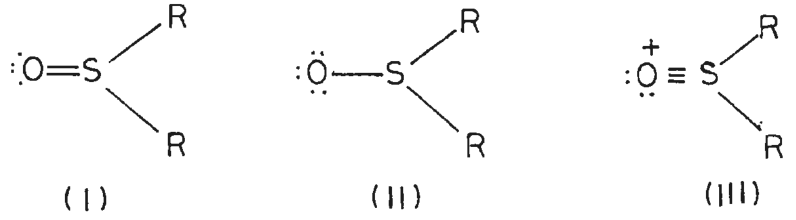


Figure 4

If coordination occurs through oxygen, the contributions of structures (I) and (III) will decrease and the result will be a decrease of the S-O stretching frequency. If coordination occurs through sulfur, the contribution of structure (II) will decrease and the result may be an increase in ν(S-O).[52]

The infrared spectra of the complexes $M[Pt(C_6H_5SOCH_2COO)Cl_2]$ where M = H^+, K^+, Cs^+, show very similar absorption peaks, which arise from the same complex anion $[Pt(C_6H_5SOCH_2COO)Cl_2]^-$. The important and characteristic infrared spectral data and assignments are collected in Table 4. The infrared spectra of $K[Pt(C_6H_5SOCH_2COO)Cl_2]$ and phenylsulfoxyacetic acid in KBr discs in the region (1800-600 cm^{-1}) are shown in Figures I_a and I_b respectively.

It is quite clear, as seen in Table 4, that the shift of the S-O stretching frequency in the three new

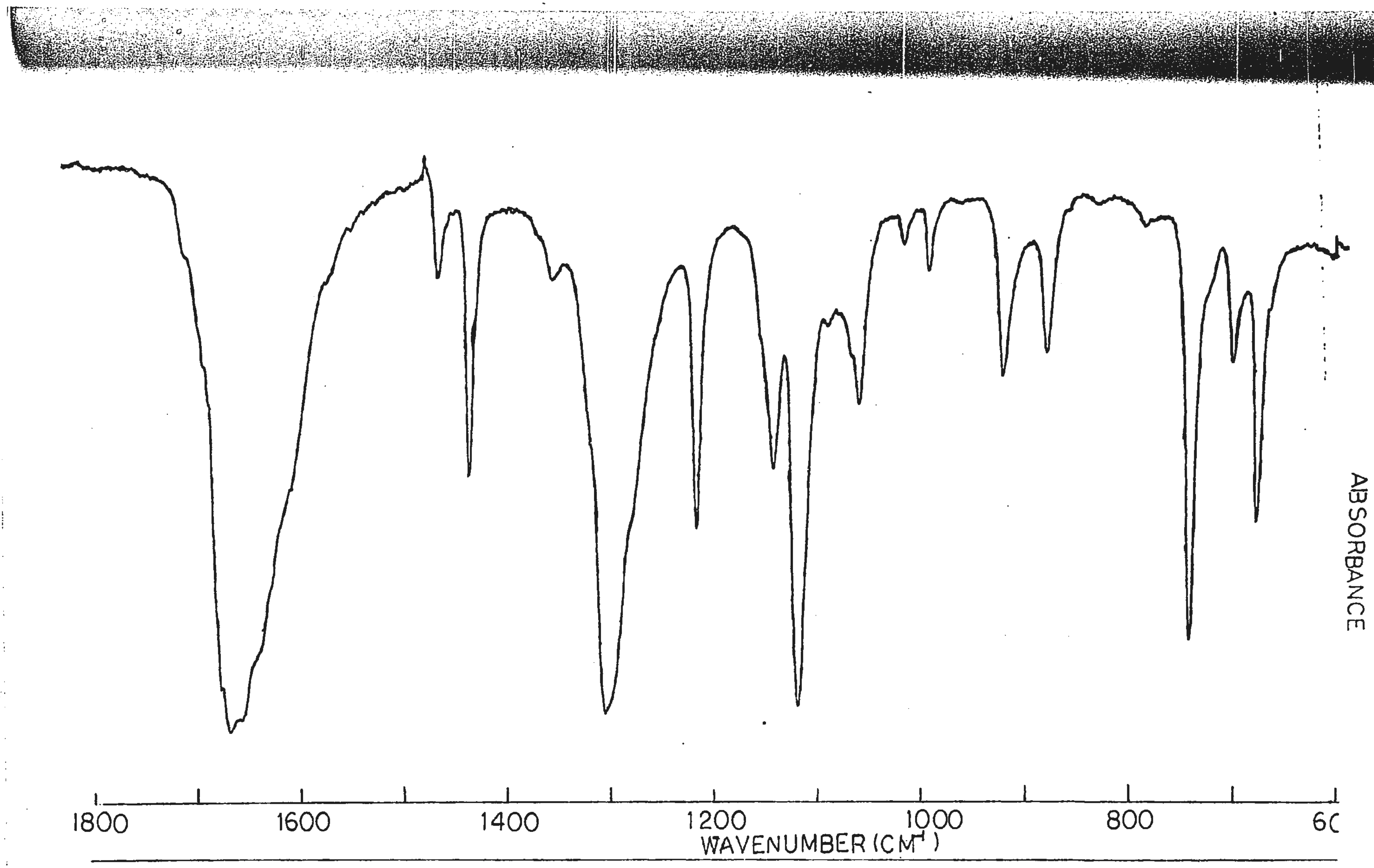


Figure Ia. I.r. spectrum (1800-600 cm^{-1}) of chelated K$\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ in KBr disc.

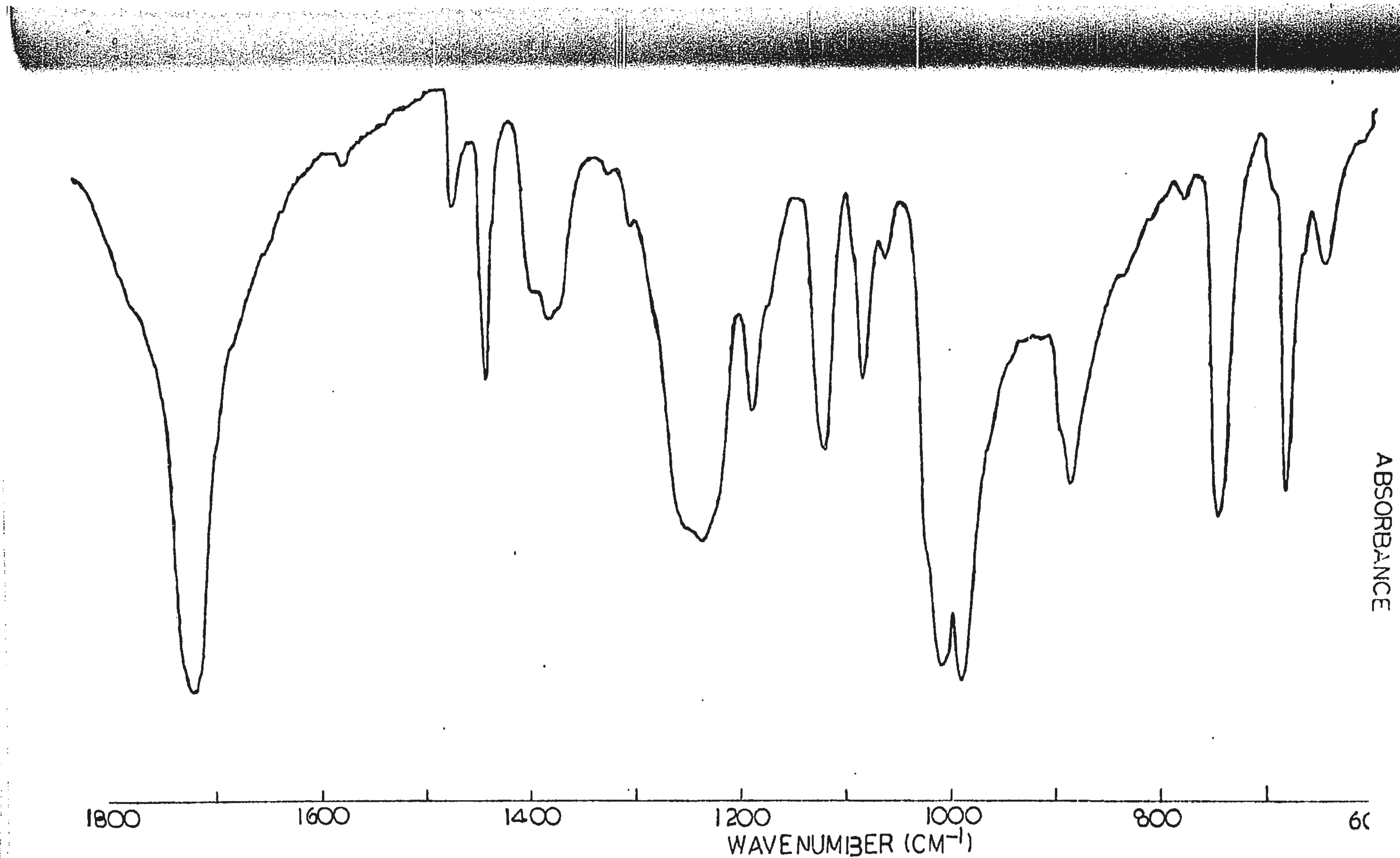


Figure Ib. I.r. spectrum (1800-600 cm^{-1}) of phenylsulfoxyacetic acid. in KBr disc.

$M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ complexes where $M = H^+, K^+, Cs^+$, is negative, thus suggesting S-coordination for these complexes. The band at 1120 cm^{-1} which has very strong intensity is assigned to ν(S-O). The moderate intensity band at 1145 cm^{-1} may also presumably be assigned to ν(S-O). The feature that in the infrared spectra of some platinum(II) sulfoxide complexes the S-O band is "split", is also observed in the complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+, K^+, Cs^+$. The duality in the S-O stretching region of $Pt(DMSO)_2Cl_2$ has been taken to indicate a cis configuration,[51a] but assignments of cis configuration on the basis of splitting of bands due to coordinated groups such as -C≡N, S=O etc. must be uncertain, particularly when measurements have been made on solid samples.

The C-S stretching vibration in sulfoxides, as reported by Bellamy[53] is a weak absorption occuring in the region 700-600 cm^{-1}. The bands at 736 and 689 cm^{-1} have been assigned to C-S stretching frequencies in the complex $Pt(DMSO)_2Cl_2$.[31] Since the monosubstituted benzene has strong absorptions in these regions (697±1 cm^{-1} for out of plane ring bending and 751±15 cm^{-1} for five adjacent H wagging),[54] it is difficult to assign the weak C-S band in the complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+, K^+, Cs^+$.

The coordination of a carboxylate ion to a metal may be either with a symmetrically bridged structure or as a unidentate ligand and this may be differentiated by using infrared spectroscopy.[55] For the carboxylate as a unidentate ligand (I), a divergence of ν_{asym}(COO) and ν_{sym}(COO), compared with the free ion is expected due to a decrease in the equivalence of the C-O bonds. For the symmetrically bridged structure (II), (Figure 5), both the ν_{asym}(COO) and ν_{sym}(COO) frequencies are shifted in the same direction upon changing the metal. Furthermore, for structure (II), the separation values $\Delta\nu$(COO) are comparable to those of the free ion, e.g. sodium salt of the acid, while the separation $\Delta\nu$(COO) for unidentate carboxylate complex (I) is usually much larger.

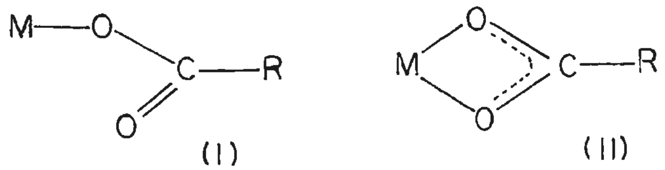


Figure 5

As seen in Table 4, the shift of carbonyl stretching frequencies of the new platinum(II) complexes from that of the free parent acid suggests the participation of the carboxylate group in the reaction. The wide separation of the carbonyl stretching frequencies $\Delta\nu$(COO) (ca 360 cm^{-1}) compared with that of free ions (220 cm^{-1}), reveals that the carboxylate group functions as a unidentate covalent ligand in the complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where M = H^+, K^+, Cs^+.

TABLE 4

Infrared absorptions of sulfoxy and carbonyl stretching frequencies in KBr discs[a]

Compound	Frequency (cm^{-1})				
	ν_{S-O}	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\Delta\nu_{CO_2}$ (average)	$\Delta\nu_{S-O}$
$H(Pt(C_6H_5SOCH_2CO_2)Cl_2)$	1145(m) 1120(s)	1665(s)	1305(s)	+360	-112
$K(Pt(C_6H_5SOCH_2CO_2)Cl_2)$	1145(m) 1120(s)	1668(s)	1305(s)	+363	-112
$Cs(Pt(C_6H_5SOCH_2CO_2)Cl_2)$	1143(m) 1120(s)	1660(s)	1305(s)	+355	-112
$((C_6H_5SOCH_2CO_2H)PtCl_2)_2$	1135(s)	1718(s)	1300(m, br)	+418	-127
† $(C_6H_5SOCH_2CO_2)_2Cd\cdot 2H_2O$	960(s)	1590(s)	1380(s)	+210	+48
* $(C_6H_5SOCH_2CO_2)_2Cd\cdot 2H_2O$	1020(s)	1565(s)	1398(s)	+167	-12
$C_6H_5SOCH_2CO_2H$	1008(s)	1720(s)	1240(s)		0
$(C_6H_5SOCH_2CO_2)Na$	1010(s)	1605(s)	1385	+220	-2

[a] abbreviations s = strong, m = medium, w = weak, v = very, br = broad

† chelated complex * simple salt

The far-infrared spectral data (600-250 cm^{-1}) are located in Table 5. The peak with moderate intensity at 405-407 cm^{-1}, which is underlined in Table 5, may be assigned to Pt-O stretching frequency. This peak is absent in the spectrum of chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2COOH)Cl_2\}_2$ in which no Pt-O bond has formed. This assignment of Pt-O stretching frequency may be compared with that reported by Kieft and Nakamoto[56] who have assigned the peak at 388 cm^{-1} in the compound $K\{Pt(Gl)Cl_2\}$ and the peak at 407 cm^{-1} in the compound Pt(GlH)Cl(Gl), where Gl = $NH_2CH_2COO^-$ and GlH = NH_2CH_2COOH = glycine, to the Pt-O stretching frequency.

The chief complication in identifying the ν(Pt-Cl) in the far-infrared region is the identification of ν(Pt-S) which arises in the same region as ν(Pt-Cl). There are also complications of various ligand skeletal bending and deformation modes. Fortunately, the Pt-Cl stretching motions are very strong absorbers, their intensity alone generally makes them readily distinguishable. Appreciable coupling of ν(Pt-Cl) and ν(Pt-S) may also occur and could be particularly serious in the cis complexes. It has been found that ν(Pt-X) of complexes cis PtX_2L_2 where X = Cl, L = neutral ligand, is sensitive to the nature of the ligand and covers a wide range of values (340-269 cm^{-1}) while the ν(Pt-X) of trans PtX_2L_2 falls in the range 339.5±3.1 cm^{-1}, and is almost insensitive to the nature of the ligand.[57]

TABLE 5

Far-i.r. absorptions(600-250 cm^{-1}) for some platinum(II) complexes. Metal-halogen and metal-oxygen stretching frequencies are tentatively assigned.[a]

Complex	Frequencies of other bands (cm^{-1})			ν(M-X) cm^{-1}
$H\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$	550(m)	528(s)	515(s)	338(m)
	444(w)	405(m)	375(w)	318(s)
$K\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$	552(w)	530(m)	518(s)	340(m)
	445(w)	407(m)		318(s)
$Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$	550(m)	530(s)	515(s)	340(m)
	442(w)	405(m)	268(w)	318(s)
$\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$	580(m)	528(s)	502(s)	338(s)
	448(w)	315(w)	305(w)	315(m, sh)
				280(w)
$\{Pt\{P(OEt)_3\}Cl_2\}_2^b$				361(vs)
				354(sh)
				325(m)
$\{Pt(PEt_3)Cl_2\}_2^b$				353(vs)
				345(sh)
				325(m)
				266(s)

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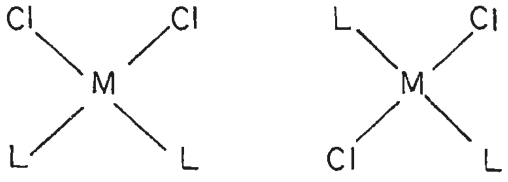
[a] abbreviation: s = strong; m = medium; w = weak; sh = shoulder.

[b] known compounds, see reference 58a.

As required by symmetry (Figure 6) the cis configuration (I) of the square planar structure should yield two ν(Pt-X) in the infrared region, while the trans configuration (II) should possess one in the infrared region.



(I) (II)

Figure 6

In the complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+, K^+, Cs^+$, two bands at ca 338 cm^{-1} are assigned to ν(Pt-Cl) and confidence in these can be derived from the observation first, that these bands have a high intensity, and second, that the frequencies fall nicely into the range (340-269 cm^{-1}) which is generally agreed upon for ν(Pt-Cl).[58] That there are two ν(Pt-Cl) bands observed for the complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ suggests a cis configuration for these complexes.

The complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+, K^+, Cs^+$, are insoluble in non-polar organic solvents and their solubility in water increases as the cations $H^+ < K^+ < Cs^+$ increase in size. This suggests that the complexes are in the ionic form, in which the very small cation as proton generally reduces the solubility in water.

From the above discussion, the structure of the complexes $M\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ where $M = H^+, K^+, Cs^+$, may be predicted as in Figure 7 below:

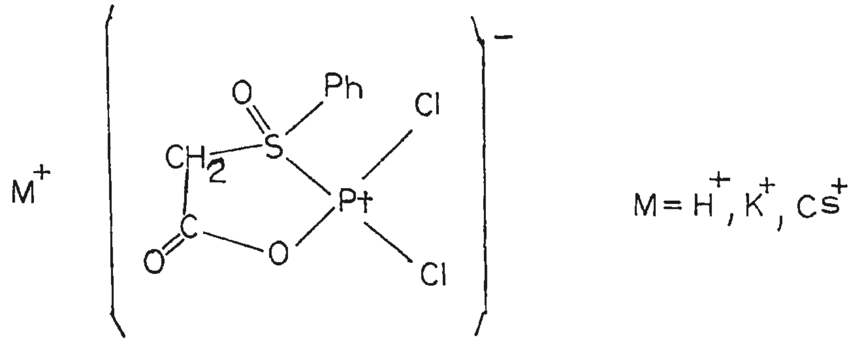


Figure 7

(b) Di-μ-chloro-dichloro-bis(phenylsulfoxyacetic acid)-diplatinum(II)

As described in the experimental section, the reaction of potassium tetrachloroplatinate(II), phenylsulfoxyacetic acid and cesium chloride (in a mole ratio 1:1:1) in aqueous solution produced two products. One of these has been characterized in the previous section to be the complex $Cs\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ and the other is discussed below.

Element analyses of chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2COOH)Cl_2\}_2$ correspond to the same empirical formula $Pt(C_6H_5SOCH_2COOH)Cl_2$ as that of the hydrogen dichloromonophenylsulfoxyacetato-platinate(II). Yet the two compounds are readily distinguished from each other through infrared spectroscopy. The infrared spectra of the chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2COOH)Cl_2\}_2$ and the chelated complex $H\{Pt(C_6H_5SOCH_2COO)Cl_2\}$ in KBr discs in the region (1800-600 cm^{-1}) are shown in Figures IIa and IIb. Comparison of the infrared spectra shows that the two compounds have quite different absorptions.

The structural elucidation of chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2COOH)Cl_2\}_2$ based on the infrared spectral data is discussed below. For chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$, the band at 1718 cm^{-1} (see Table 4) is assigned to $\nu_{asym}(COO)$. This absorption corresponds to a very small shift (+2 cm^{-1}) of $\nu_{asym}(COO)$ from the $\nu_{asym}(COO)$ of the parent acid which indicates that the carboxylic acid group in this chlorine-bridged binuclear complex has not participated in the complex formation reaction. The chelated complex $H\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$, in which the carboxylate group participates in the reaction, has the $\nu_{asym}(COO)$ shifted (+55 cm^{-1}) from the parent acid. A strong band at 1135 cm^{-1} is assigned to the S-O stretching frequency and thus the complex is S-Bonded. The 'split' of the S-O band in the spectrum of the chelated complex $H\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ is not observed in the spectrum of the chlorine-bridged complex $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$. This suggests that the structure of $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ is not a <u>cis</u> configuration.

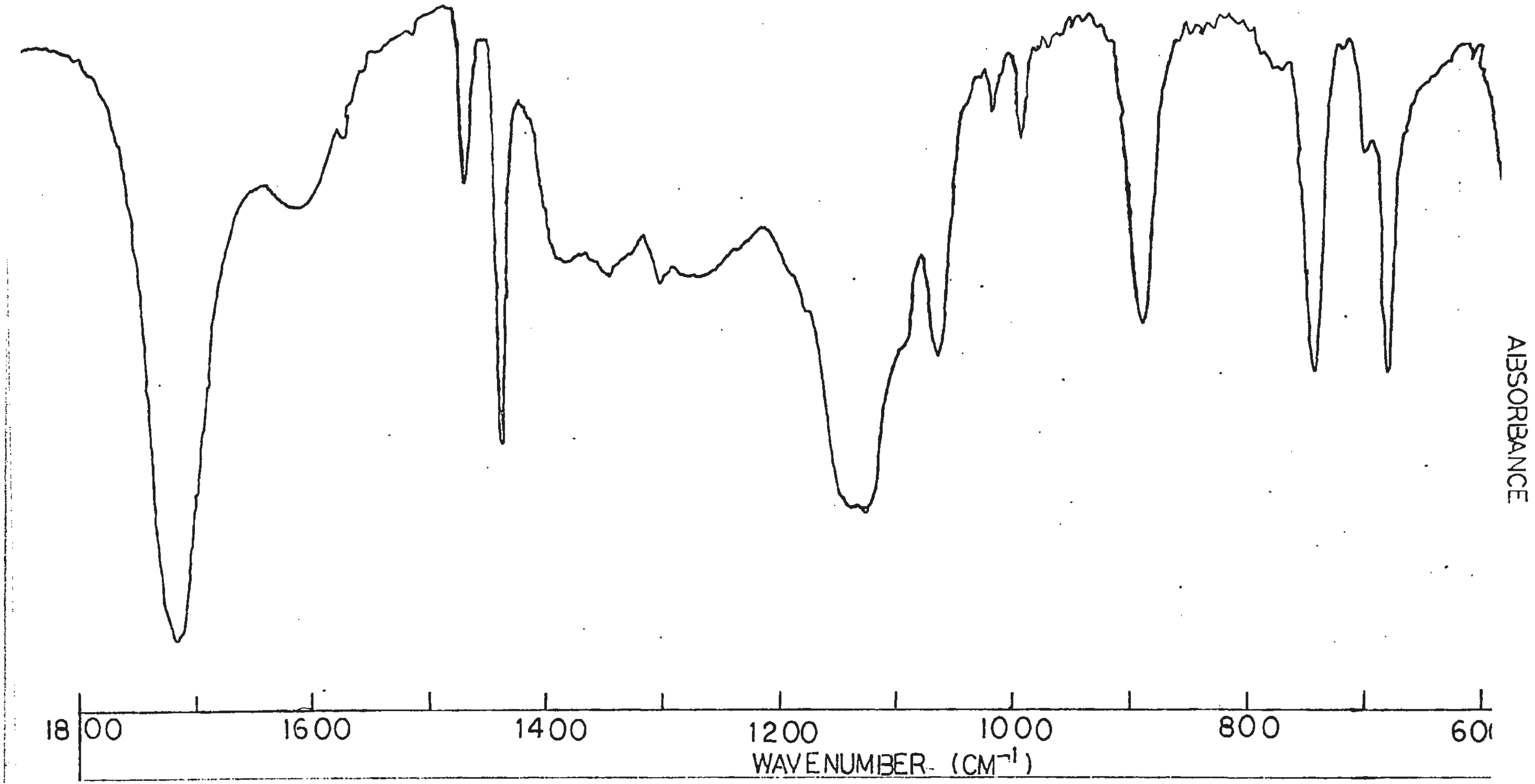


Figure IIa. I.r. spectrum (1800-600 cm^{-1}) of chlorine-bridged binuclear $(Pt(C_6H_5SOCH_2CO_2)Cl_2)_2$ in KBr disc.

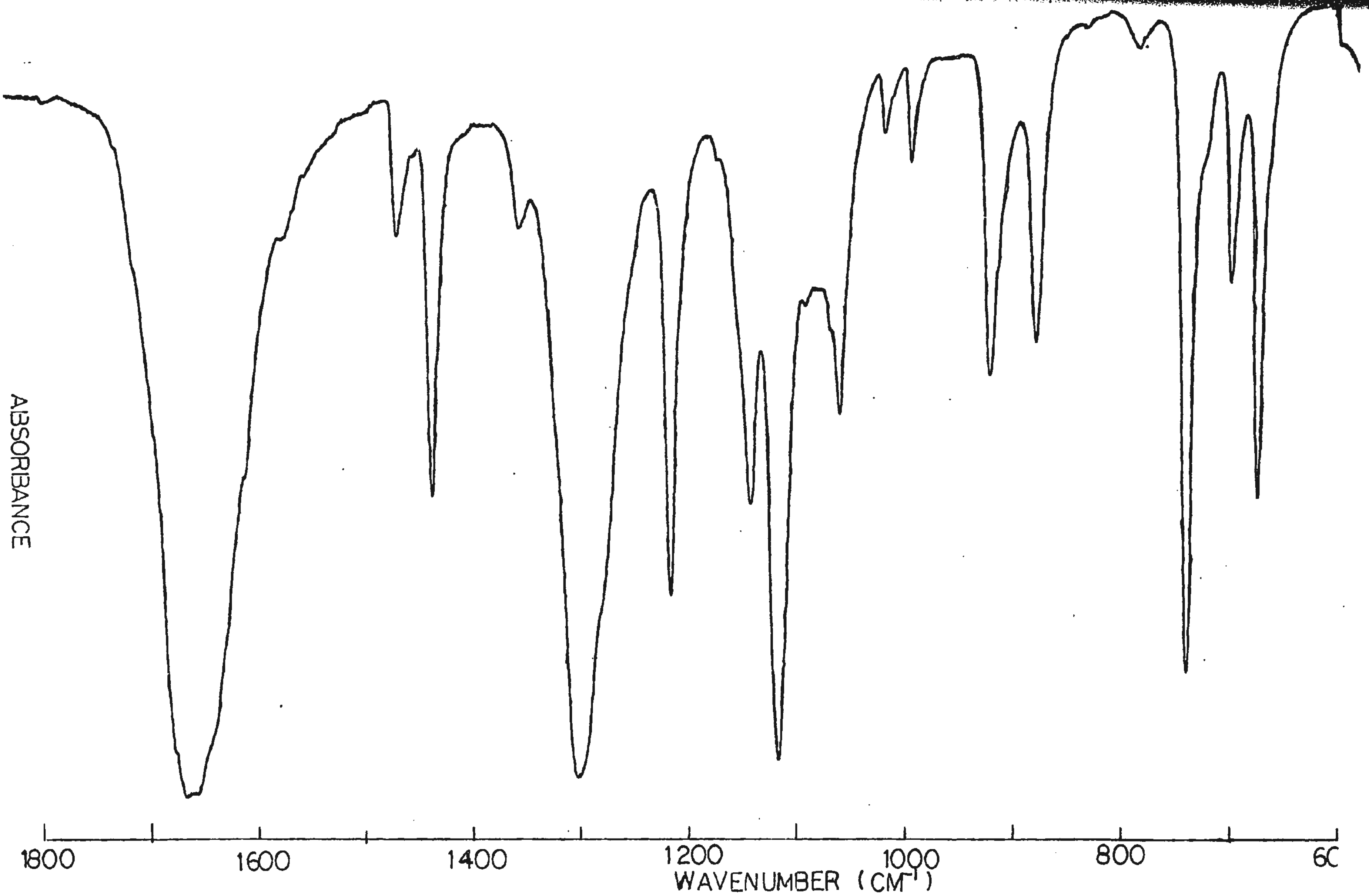


Figure IIb. I.r. spectrum (1800-600 cm^{-1}) of chelated H(Pt($C_6H_5SOCH_2CO_2$)Cl_2) in KBr disc

For the chlorine-bridged complex $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$, the absence of the band in the far-infrared region at ca 405 cm^{-1}, which has been assigned to Pt-O stretching frequency in chelated complex $H\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$, reveals that no Pt-O bond is formed in this compound. Since this is consistent with the small ν_{asym}(COO) shift from the parent acid, we can conclude that the carboxylic acid group remains unreacted.

It is known that for chlorine-bridged compound of the type $M_2X_4L_2$ (M = Pt, Pd; X = Cl, Br, I; L = neutral donor ligand), one terminal ν(Pt-X) and two bridging ν(Pt-X) stretching frequencies are expected for each of the compounds. R. J. Goodfellow et al.,[58c] and D. M. Adams[58a] have found the ranges of Pt-Cl stretching frequencies for compounds of the type $Pt_2Cl_4L_2$ as terminal $\nu(Pt\text{-}Cl)_t$ in the range 368-347(330) cm^{-1} and the two bridging $\nu(Pt\text{-}Cl)_b$ in the ranges 331-316 cm^{-1} and 301-257 cm^{-1}. Of the two bridging $\nu(Pt\text{-}Cl)_b$ frequencies, the lower one is markedly sensitive to the change of ligand (L).

Figure III shows the far-infrared spectrum of chlorine-bridged $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ and chelated $H\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$. The band at 338 cm^{-1} may be assigned to terminal ν(Pt-Cl) stretching, while the shoulder at 315 cm^{-1} is assigned to a bridge $\nu(Pt\text{-}Cl)_b$ frequency. The band at 280 cm^{-1} may or may not be assigned to the other bridged ν(Pt-Cl) frequency. Although the band at 280 cm^{-1}

falls in the region mentioned in the literature,[58a] its weak intensity seems ambiguous. As seen in Table 5 and Figure III for the cis configuration, the ν(Pt-Cl) band at 318 cm^{-1} is the strongest peak, while for the bridge ν(Pt-Cl) frequency, it is only a shoulder. The appearance of the ν(Pt-Cl) bands in chlorine-bridged $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ is very similar to that of the known chlorine bridged $Pt_2(PEt_3)_2Cl_4$.[58a] It is thus clear that the compound is a chlorine-bridged binuclear complex and the structure proposed is as in Figure 8 below:

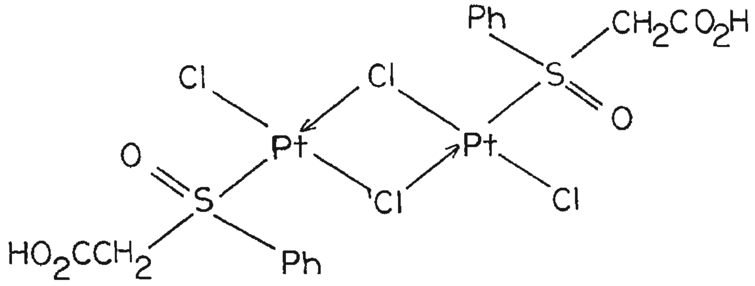
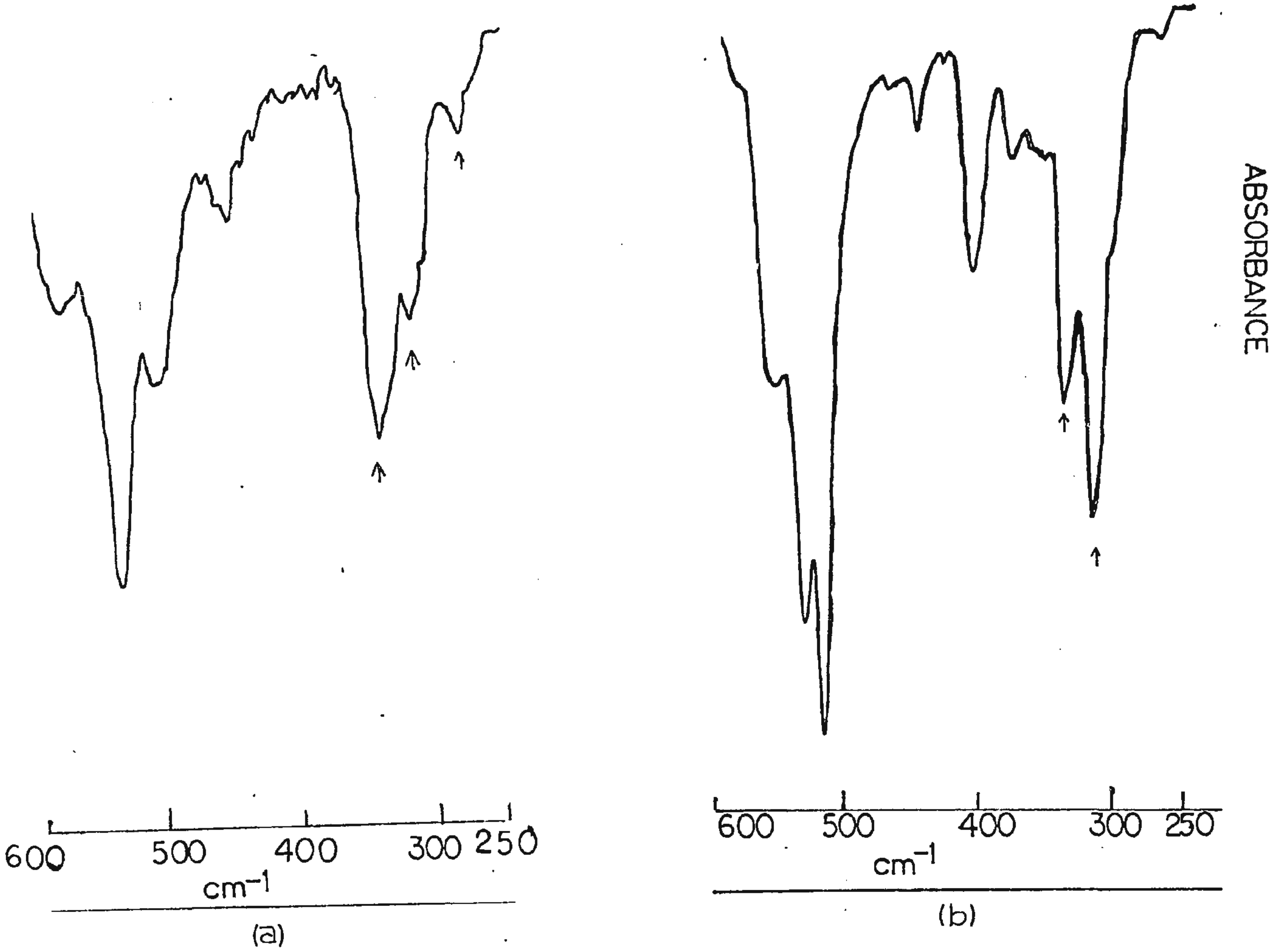


Figure 8

There are two possible ways to form the two products, chelated $Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ and chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$, from the reaction of potassium tetrachloro-platinate(II), phenylsulfoxyacetic acid and cesium chloride.(1) The two products are formed



(a)

(b)

Figure III. Comparison of far i.r. (600-250 cm^{-1}) of (a) chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ and (b) chelated $H\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$. ν(Pt-Cl) are indicated by the arrows.

simultaneously during the reaction. (2) The chelate $Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ is formed first in the reaction, then the chelate anion $\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}^-$ converts slowly in an acidic solution into the chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$. The reaction equations may be represented as shown on page 49.

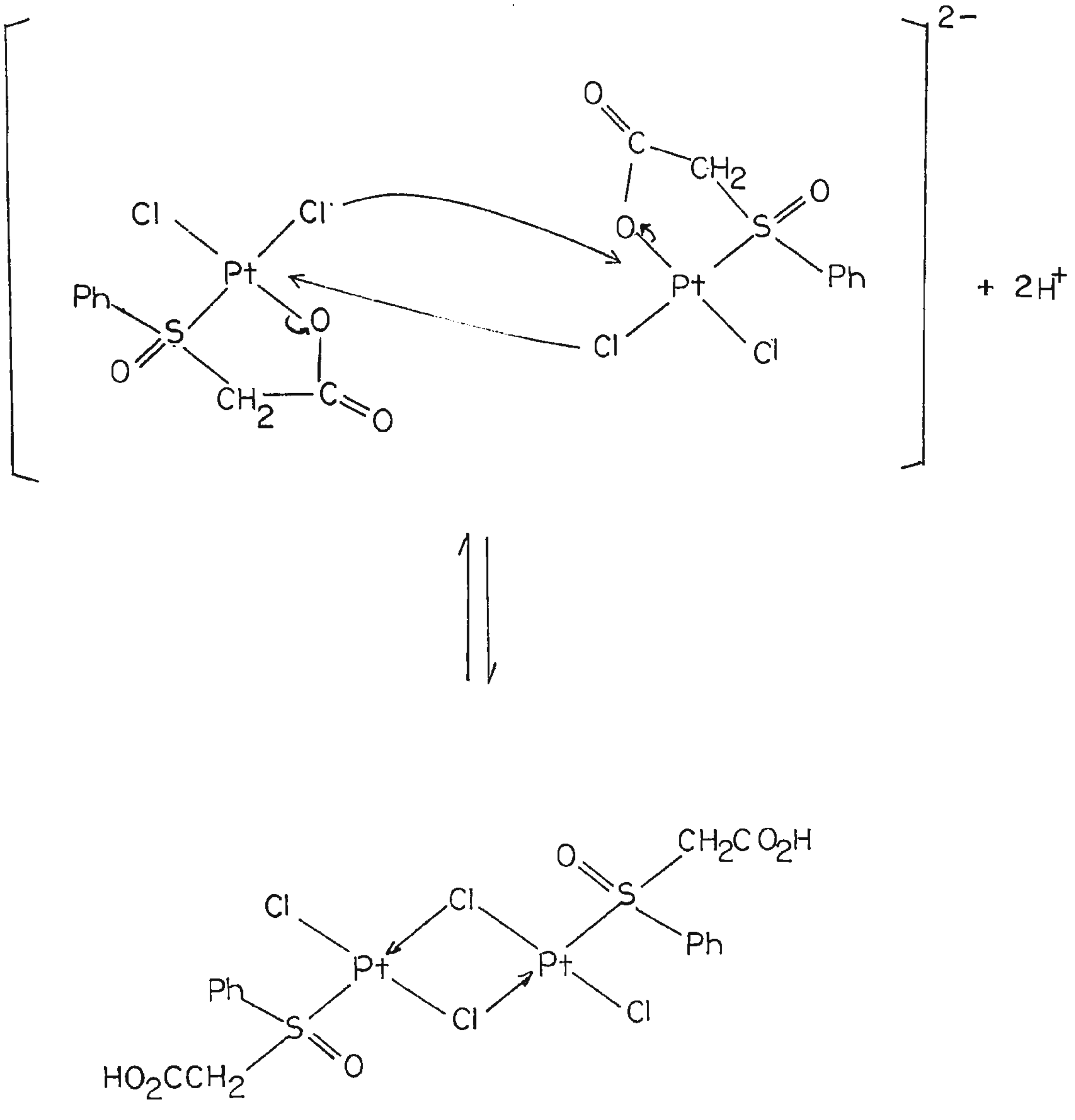
The experimental observation that the isolation of the compounds $Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ and $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ from the mother liquor yielded analytically pure compounds, but either one of them, when recrystallized from aqueous solution yielded a mixture containing the binuclear species and the chelate anion (i.r. data) may favour the reaction route via equation (2). The chelated complex $Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ is formed first in the reaction. In an acidic solution, the Pt-O bond in the complex anion $\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}^-$ is broken slowly and replaced by the formation of a new chlorine-bridged bond, and the carboxylate ion combines with an acidic proton. Thus two molecules of the complex anion $\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}^-$ would combine to form a molecule of chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ as illustrated by the equation (3) as shown on page 50.

When the chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ was dissolved in water, the first recrystallization product which formed contained chelate anion $\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}^-$ (i.r. data) while after the solution had been kept for a longer time (3-4 days), the

$$3K_2PtCl_4 + 3C_6H_5SOCH_2CO_2H \xrightarrow[H_2O]{CsCl} Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\} + \{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2 + 6KCl + HCl \qquad (1)$$

$$K_2PtCl_4 + C_6H_5SOCH_2CO_2H + CsCl \longrightarrow Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\} + 2KCl + HCl$$

$$2\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}^- + 2H^+ \xrightarrow[H_2O]{} \{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2 \qquad (2)$$



(3)

first formed $\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}^-$ anion converted into the chlorine-bridged binuclear $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ again (vide infrared). Thus, the product $Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ may be considered to be kinetically favoured while the chlorine-bridged binuclear complex $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ is the more thermodynamically stable.

(c) Bisphenylsulfoxyacetato-cadmium(II) dihydrate

As described in the experimental section the reaction product of phenylsulfoxyacetic acid and cadmium carbonate was a chelated compound(I) when recrystallized from water, while recrystallization from 95% ethanol yielded a simple salt(II). Elemental analyses (Table 3) of compound(I) and compound(II) both correspond to the formula $(C_6H_5SOCH_2CO_2)_2Cd \cdot 2H_2O$, but the infrared spectral data show that compound(I) and compound(II) are not identical (see Figures IVa and IVb).

As seen in Table 4, phenylsulfoxyacetic acid functions as a chelating bidentate ligand in compound(I). The S-O stretching frequency has shifted to a lower frequency. This indicates that compound(I) is bonded through oxygen of the sulfoxy group. The shift of the carbonyl stretching frequencies from the parent acid reveals the formation of a cadmium-carboxylate bond. Since the carbonyl stretching frequencies and the separation of ν(COO) of compound(I) is very close to that of free ion, i.e. $C_6H_5SOCH_2CO_2Na$, it is

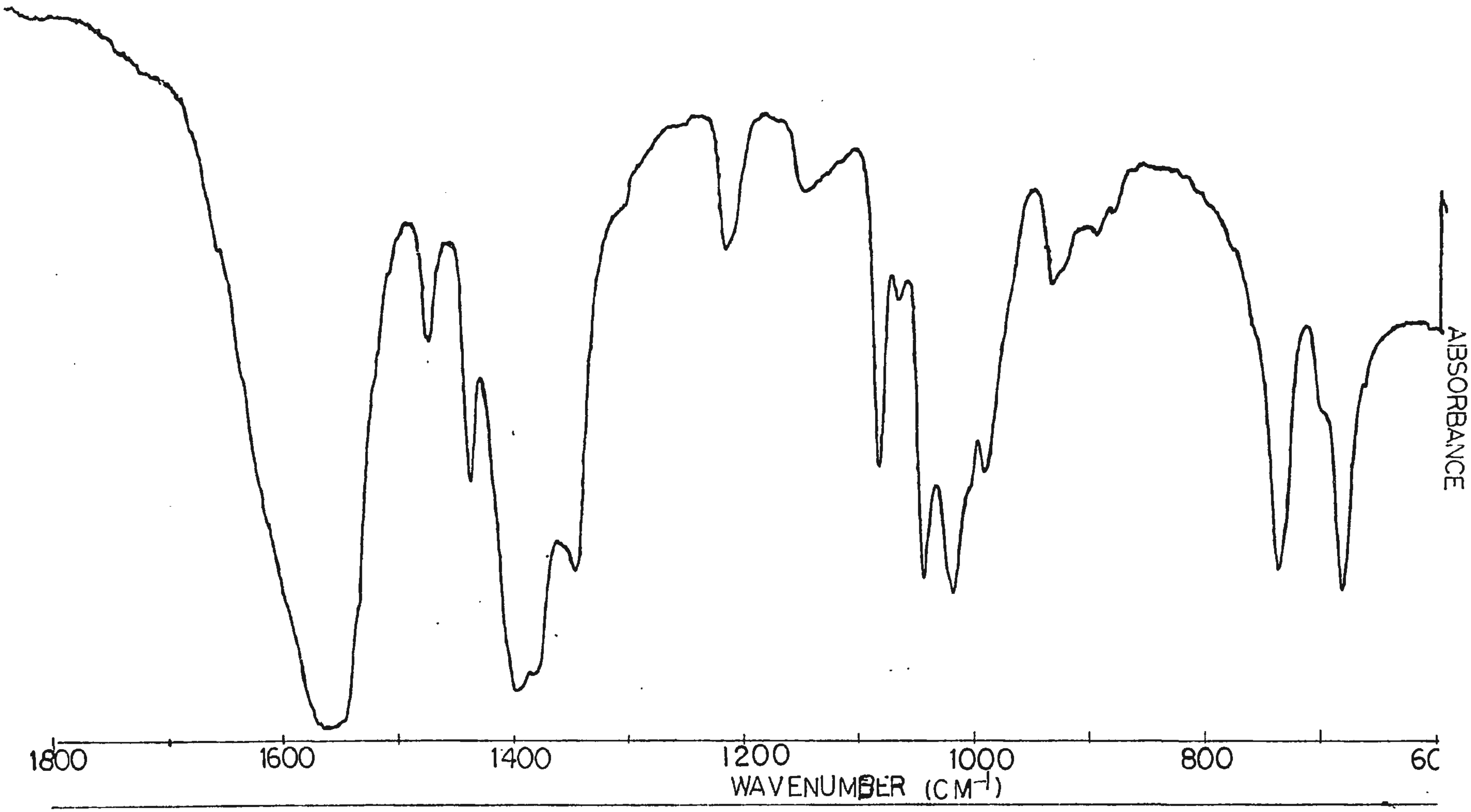


Figure IVa. I.r. spectrum (1800-600 cm^{-1}) of simple salt $(C_6H_5SOCH_2CO_2)Cd \cdot 2H_2O$.

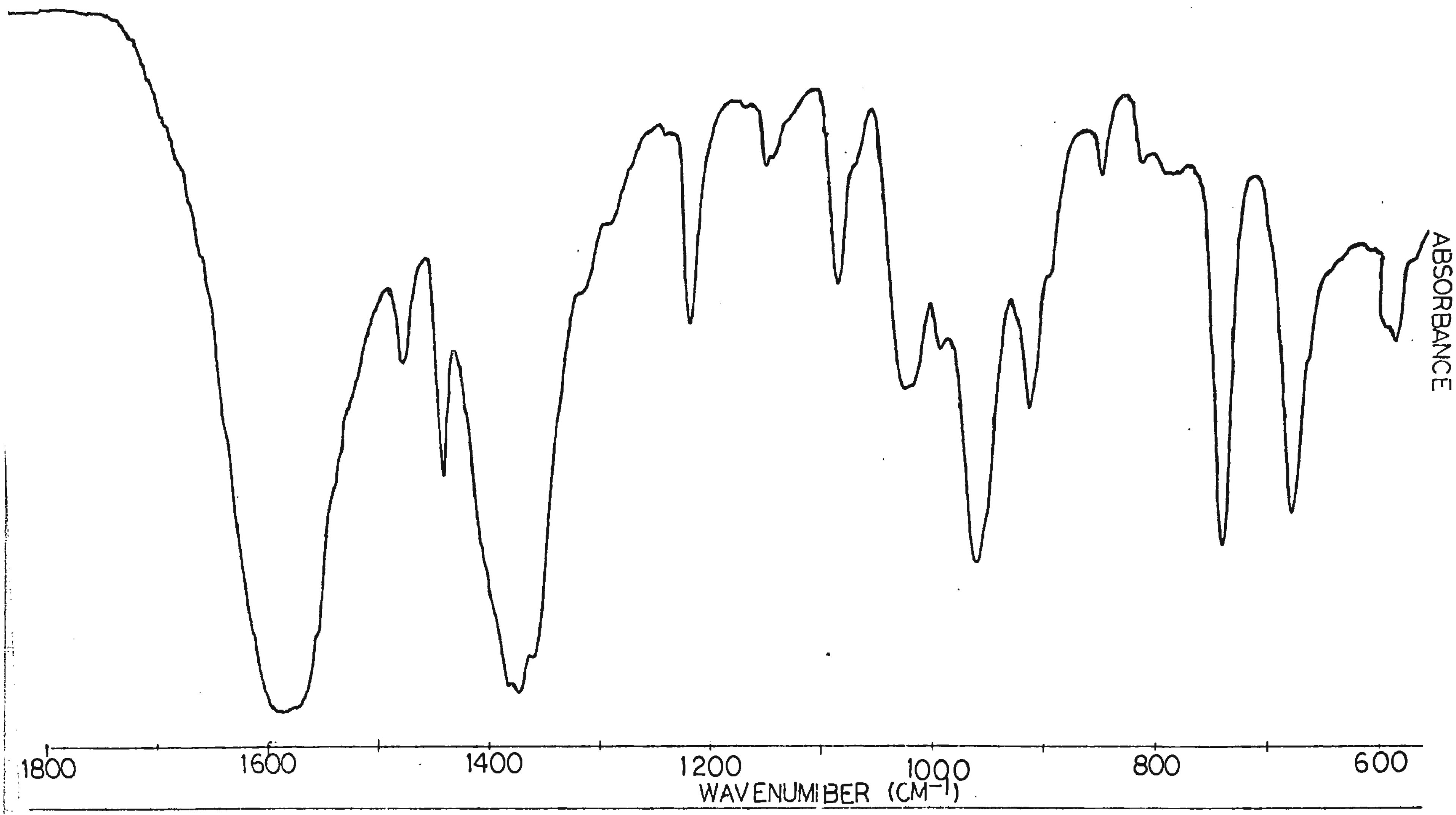


Figure IVb. I.r. spectrum (1800-600 cm^{-1}) of chelated ($C_6H_5SOCH_2CO_2$)Cd·$2H_2O$.

concluded that the cadmium-carboxylate bond has a high degree of ionic character.

Without x-ray analytical data, prediction of crystal structure seems inappropriate. In the chelated complex $(C_6H_5SOCH_2CO_2)_2Cd \cdot 2H_2O$, cadmium(II) forms four bonds with two phenylsulfoxyacetate ligands. If the two molecules of water of crystallization present are coordinated to the metal, then the six-coordinated cadmium(II) is probably octahedral. If the two water molecules are present as lattice water, then the four-coordinated cadmium(II) may involve a tetrahedral or a square planar structure. The zinc and cadmium complexes with coordination numbers four, usually have tetrahedral structures, e.g. $[Zn(CN)_4]^{2-}$, $[CdBr_4]^{2-}$, $[Cd(NH_3)_4]^{2+}$, $Zn(NH_3)Cl_2$.[59] Thus, the chelated complex $(C_6H_5SOCH_2CO_2)Cd \cdot 2H_2O$ is probably tetrahedral if it is four-coordinated.

For the simple salt $(C_6H_5SOCH_2CO_2)_2Cd \cdot 2H_2O$, the small shift of S-O stretching frequency suggests that the sulfoxy group in the ligand remains uncoordinated. The shift of carbonyl antisymmetric stretching frequency $\nu_{asym}(COO)$ to 1565 cm^{-1} indicates that the cadmium-carboxylate bond is essentially ionic. It is a simple salt which is formed by replacing the carboxylic acid protons with cadmium(II) ion.

Electronic spectra of platinum(II) complexes

The electronic spectral absorption bands of a transition metal complex may arise from the so-called "d-d" transition of the metal ion, and the charge transfer which is associated with a ligand to metal or a metal to ligand charge transfer process, or an intra ligand transition.

For d^8 diamagnetic complexes, there should be three spin-allowed d-d transitions, $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xy}d_{yz} \rightarrow d_{x^2-y^2}$. The aqueous solution d-d spectrum of $(PtCl_4)^{2-}$ shows three bands at 21.0 kK(ε = 15), 25.5 kK(ε = 59), 30.2 kK(ε = 64).[60]

The electronic spectral data of the platinum(II) complexes of $M\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ where M = H^+, K^+ and Cs^+ and the chlorine-bridged binuclear complex $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ in aqueous solution are collected in Table 6. The intense bands between 36.4-52.1 kK are assigned to charge transfer bands which are associated with either ligand to ligand electronic transition or a metal-ligand charge transfer. The two bands at 28.5±0.5 kK and 33.0 kK may be assigned to d-d transitions. Chatt et al.[61] relate the bands in the spectrum of $\{PtCl_4\}^{2-}$ to those in $\{PtCl_2(amine)_2\}$ by considering the gradual shift of bands to higher frequencies in the complexes $\{PtCl_{4-n}(amine)_n\}^{(n-2)+}$ as n is increased from 0 to 4. A. Pidcock et al.[62] extended the work to other ligand systems

TABLE 6

Electronic spectral data of platinum(II) complexes in aqueous solution

Complex	ν(kK)	logε	Transition
$H\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$	52.1	4.2810	charge
	51.4	4.2967	"
	50.8	4.3160	"
	45.0	3.9590	"
	37.5	3.3404	"
	36.5	3.2504	"
	33.0	2.7619	d-d
	28.0	2.2355	d-d
$K\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$	52.1	4.3579	charge
	51.4	4.3997	"
	50.7	4.4200	"
	50.2	4.4314	"
	45.0	4.1761	"
	37.2	3.4983	"
	36.3	3.3324	"
	33.0	2.6532	d-d
	28.0	2.1818	d-d
$Cs\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$	52.1	4.3304	charge
	51.5	4.3692	"
	51.0	4.3345	"
	45.0	3.9717	"
	37.5	3.0755	"
	36.5	2.9877	"
	33.0	2.5105	d-d
	29.0	2.0453	d-d
$\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$	52.1	4.3038	charge
	51.5	4.3345	"
	50.1	4.3345	"
	44.5	3.8756	"
	37.5	3.1553	"
	36.4	3.0607	"
	33.0	2.6444	d-d
	28.0	2.0531	d-d
trans-$\{Pt(Ph_2S)Cl_2\}$[a]	28.2	2.7782	d-d
	24.7	2.3010	d-d

[a] A known compound in chloroform solution, see reference 61b.

and found that the frequency of d-d transition bands changes considerably on replacing the chloride by other ligands.

By comparing the electronic spectral data (Table 6) of the four new platinum(II) complexes studied here with that of the known square planar complex trans-$\{Pt(Ph_2S)_2Cl_2\}$, it is seen that all these platinum(II) complexes have two d-d transition bands with comparable extinction coefficients. It is apparent that the new complexes are also square planar, involving d^8 diamagnetic species. The shift of the d-d bands of complexes $M\{Pt(C_6H_5SOCH_2CO_2)Cl_2\}$ where $M = H^+, K^+, Cs^+$ and chlorine-bridged $\{Pt(C_6H_5SOCH_2CO_2H)Cl_2\}_2$ to higher frequencies may be due to the change of ligands.

(B) Phenylsulfoxyacetates

Besides the coordination complexes of phenylsulfoxyacetic acid discussed previously, a series of phenylsulfoxyacetates of general formula $(C_6H_5SOCH_2CO_2)_nM\cdot xH_2O$ where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Mg(II), Ca(II), Ba(II), Hg(I) and Ag(I); n = 1 or 2, x = 0, 1, 2, or 3/2 were also isolated. It is known from infrared spectra that the sulfoxy groups in these derivatives remain uncoordinated. The metal-carboxylate bonds and structures of these compounds are discussed on the basis of their spectroscopic data. Elemental analyses data are located in Table 3b.

TABLE 3b

Analytical data for phenylsulfoxyacetates.

Compound	Melting point (°C)	Analysis (%)							
		C		H		S		Metal	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$(C_6H_5SOCH_2CO_2)_2Mg\cdot 2H_2O$	180-81	44.09	45.03	4.02	3.78	14.90	15.03	5.68	5.79[b]
$(C_6H_5SOCH_2CO_2)_2Ca$	140 (dec)	47.13	47.29	3.65	3.47	15.67	15.78	9.70	9.86[a]
$(C_6H_5SOCH_2CO_2)_2Ba$	154	38.30	38.15	2.98	2.80	12.57	12.73	27.51	27.26[c]
$(C_6H_5SOCH_2CO_2)_2Mn$	148.5 (dec)	45.49	45.60	3.74	3.35	15.10	15.22	13.00	13.05[a]
$(C_6H_5SOCH_2CO_2)_2Co$	167 (dec)	45.10	45.20	3.53	3.32	15.26	15.08	13.20	13.86[a]
$(C_6H_5SOCH_2CO_2)_2Ni$	170	45.06	45.21	3.51	3.32	15.02	15.09	13.28	13.81[b]
$(C_6H_5SOCH_2CO_2)_2Cu\cdot H_2O$	142 (dec)	42.84	42.89	3.80	3.59	14.21	14.32	14.00	14.21[a]
$(C_6H_5SOCH_2CO_2)_2Cu\cdot 3/2H_2O$	130 (dehydration) 150 melt	42.74	42.06	3.78	3.75	14.12	14.04	13.11	13.91[b]
$(C_6H_5SOCH_2CO_2)_2Zn\cdot 2H_2O$	140 (dec)	41.17	41.09	3.81	3.88	13.72	13.71	13.27	13.96[b]
$(C_6H_5SOCH_2CO_2)Ag$	167	33.26	33.01	2.62	2.42	10.85	11.01	37.01	37.08[d]
$(C_6H_5SOCH_2CO_2)Hg$	184	26.14	25.01	1.98	1.84	8.52	8.35		

Metal analysis method: a = atomic absorption; b = EDTA titration;
c = precipitated as $BaCrO_4$;
d = precipitated as AgCl.

Infrared spectra

The infrared spectra of complexes of carboxylic acids have been studied extensively. It is suggested that the carbonyl antisymmetric stretching frequency is most sensitive to a change in the metal, and the relationship between this frequency and some physical properties of the metal has been discussed by several investigators.[55] The carboxylate anion may coordinate with a metal in one of the four ways (Figures 9 and 5).

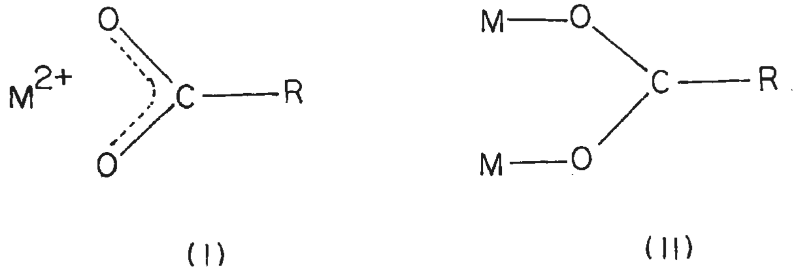


Figure 9

Since the symmetry of the free ion is low no great differences in the infrared spectra would be expected for each type. The use of the infrared ($\nu_{asym}(COO) - \nu_{sym}(COO)$) separation as a means of assessing the mode of coordination of carboxylate group to metals should be carried out with caution, because the carbonyl stretching frequencies are affected by coordination as well as inter-molecular interaction or hydrogen bonding.

The carbonyl stretching frequencies and sulfoxy stretching frequencies of the phenylsulfoxyacetates are located in Table 7. The sulfoxy frequencies of these compounds remain nearly constant and it is thus concluded that this group does not participate in the coordination.

For the purpose of comparison, the phenylsulfoxyacetates studied here are divided into three groups: (a) divalent group IIa and IIb carboxylates, (b) divalent transition metal carboxylates and (c) univalent metal carboxylates.

(a) Divalent groups IIa and IIb phenylsulfoxyacetates

The ν_{asym}(COO) of magnesium(II), calcium(II) and barium(II) are in the region 1610-1580 cm^{-1}, and the ν_{sym}(COO) in the region 1395-1378 cm^{-1} (see Table 7), which is close to the value of carbonyl stretching frequencies of free ion. The region 1610-1580 cm^{-1} of ν_{asym}(COO) of divalent alkaline earth phenylsulfoxyacetates is comparable to the region (1610-1590 cm^{-1}) observed and assigned to the ionic (COO^-) stretching frequencies of the corresponding EDTA chelates of the alkaline earths.[63] Thus, it is concluded that the metal-carboxylate bonding in the divalent alkaline earth carboxylates is primarily ionic.

The ν_{asym}(COO) frequencies decrease in the order Mg > Ca > Ba. This corresponds to a decrease in frequency with increasing ionic radius of the metal and suggests that

TABLE 7

Infrared absorptions of sulfoxy and carbonyl stretching frequencies of phenylsulfoxyacetates in KBr discs[a]

Compound	Frequency (cm^{-1})				
	ν_{S-O}	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\Delta\nu_{CO_2}$ (average)	$\Delta\nu_{S-O}$
$C_6H_5SOCH_2CO_2Na$	1010(s)	1605(s)	1385(s)	+220	-2
$(C_6H_5SOCH_2CO_2)_2Mg\cdot 2H_2O$	1018(s)	1610 1585 (s)	1378(s)	+232	-10
$(C_6H_5SOCH_2CO_2)_2Ca$	1012(s)	1595(s)	1395(s)	+200	-4
$(C_6H_5SOCH_2CO_2)_2Ba$	1018(s)	1580(s)	1395(s)	+185	-10
$(C_6H_5SOCH_2CO_2)_2Mn$	1008(s)	1588(s)	1398(s)	+190	0
$(C_6H_5SOCH_2CO_2)_2Co$	1018(s)	1590(s)	1395(s)	+195	-10
$(C_6H_5SOCH_2CO_2)_2Ni$	1012(s)	1580(s)	1395(s)	+205	-4
$(C_6H_5SOCH_2CO_2)_2Cu\cdot H_2O$	1030(s)	1600(s)	1400(s)	+190	-22
$(C_6H_5SOCH_2CO_2)_2Cu\cdot 3/2H_2O$	1008(s)	1595	1402(s) 1380(s)	+193 +215	0
$(C_6H_5SOCH_2CO_2)_2Zn\cdot 2H_2O$	1015(s)	1600(s)	1372(s)	+228	-7
$C_6H_5SOCH_2CO_2Hg$	1015(s)	1580(s)	1305(s)	+275	-7
$C_6H_5SOCH_2CO_2Ag$	1012(s)	1598 1552 (s)	1378 1360 (S)	+180	-4

[a] abbreviation s = strong.

magnesium has the most covalent character of the series and barium the least. This is in agreement with the general rules favouring covalent bonds, and indicates the order of increasing stability for these compounds should be Ba < Ca < Mg.

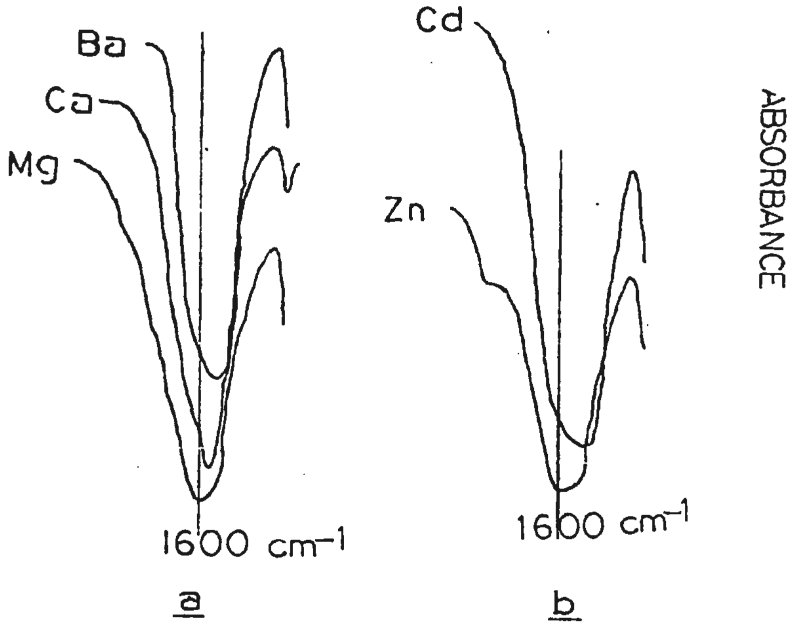
A linear relationship of the ν_{asym}(COO) versus ionic radii of the metals is shown in Figure Vc. Stretching frequencies decrease in the order of Mg > Ca > Ba as shown in Figure Va.

For the zinc(II) and cadmium(II) derivatives of formula $(C_6H_5SOCH_2CO_2)_2M\cdot 2H_2O$ where M = Zn(II), Cd(II), the metal-carboxylate bonds are believed to be essentially ionic since the ν_{asym}(COO) at 1600 cm^{-1} and 1570 cm^{-1} and the ν_{sym}(COO) at 1372 cm^{-1} and 1395 cm^{-1} respectively for zinc(II) and cadmium(II) derivatives fall in the region normally assigned to ionic carboxylate.[64]

As in the derivatives of the alkaline earth group, a similar general trend that ν_{asym}(COO) shifts to lower frequencies as the ionic radius of the metal increases also exists in the zinc(II) and cadmium(II) compounds. The peaks which correspond to ν_{asym}(COO) of zinc(II) and cadmium(II) phenylsulfoxyacetates are shown in Figure Vb.

(b) Divalent transition metal phenylsulfoxyacetates

The phenylsulfoxyacetates of manganese(II), cobalt(II), nickel(II), and copper(II), which have the ν_{asym}(COO) at 1600-1580 cm^{-1} and the ν_{sym}(COO) at 1402-1395 cm^{-1},



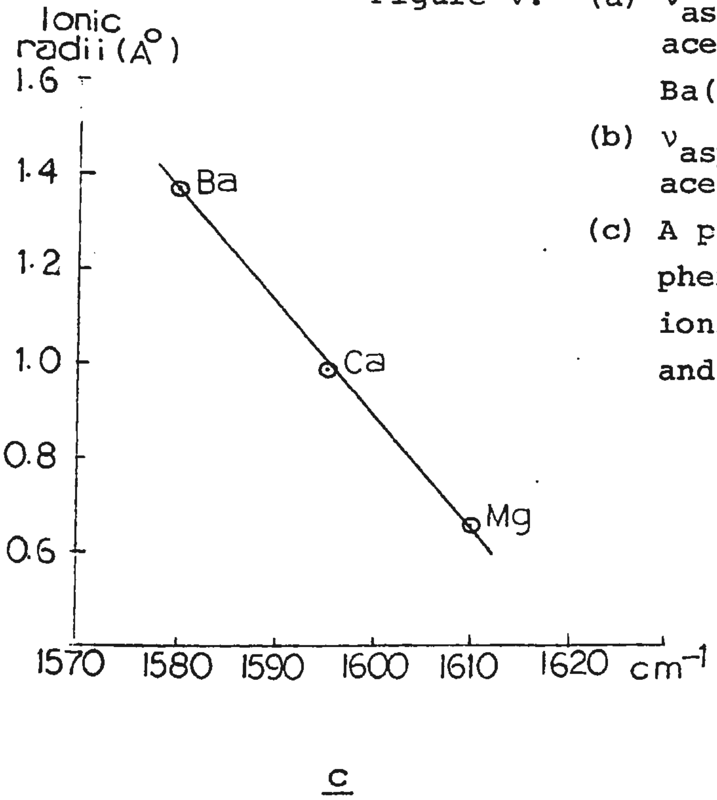


Figure V. (a) ν_{asym}(COO) of phenylsulfoxyacetates of Mg(II), Ca(II) and Ba(II).

(b) ν_{asym}(COO) of phenylsulfoxyacetates of Zn(II) and Cd(II).

(c) A plot of ν_{asym}(COO) of phenylsulfoxyacetates versus ionic radii of Mg(II), Ca(II) and Ba(II).

are predicted to be simple salts. As seen in Table 7, the ν_{asym}(COO) and ν_{sym}(COO) of these compounds are essentially the same as those of the corresponding sodium phenylsulfoxyacetate, which is ionic. It is thus concluded that the metal-carboxylate bonds of these divalent transition metal phenylsulfoxyacetates are ionic in character.

Two copper(II) phenylsulfoxyacetates with different hydration were isolated. The green powder $(C_6H_5SOCH_2CO_2)Cu \cdot H_2O$ was produced after the hydrated blue copper(II) phenylsulfoxyacetate had been dried overnight at 110°C under vacuum, while $(C_6H_5SOCH_2CO_2)_2Cu \cdot 3/2H_2O$ was obtained after the hydrated derivative was dried overnight at 70°C under vacuum.

It has been suggested that in the copper(II) alkanoates where there is a dimeric (or polymeric) structure involving a bridging of two copper atoms by four carboxylate groups, the ν_{asym}(COO) mode occurs as a sharp band at 1600 cm^{-1}, while in the monomeric copper(II) alkanoates, only a broad band in the region 1560-1600 cm^{-1} is observed.[65]

According to this explanation, the presence of a broad band of ν_{asym}(COO) at 1590 cm^{-1} for the blue $(C_6H_5SOCH_2CO_2)_2Cu \cdot 3/2H_2O$ suggests a monomeric structure, while the band of ν_{asym}(COO) at 1600 cm^{-1} for green $(C_6H_5SOCH_2CO_2)_2Cu \cdot H_2O$ indicates the formation of a dimeric (or polymeric) structure. But the band at 1600 cm^{-1} for the green $(C_6H_5SOCH_2CO_2)_2Cu \cdot H_2O$ is not sharp, therefore the prediction of a dimeric structure from the infrared spectral data of ν_{asym}(COO) for the compound seems ambiguous. The dimeric structure of $(C_6H_5SOCH_2CO_2)_2Cu \cdot H_2O$ could be ascertained from the information of electron spin resonance spectra, which will be discussed later in this thesis.

(c) <u>Univalent phenylsulfoxyacetates</u>

Among the phenylsulfoxyacetates studied here, silver(I) derivative is the only case in which the ν_{asym}(COO) is "split". Both the strong bands at 1598 cm^{-1} and 1552 cm^{-1} are assigned to ν_{asym}(COO). The band at 1378 cm^{-1} with a shoulder at 1360 cm^{-1} is assigned to ν_{sym}(COO).

The splitting of ν_{asym}(COO) leads to the proposal that silver(I) phenylsulfoxyacetate possesses a dimeric structure in which the carboxylate groups bridge two Ag atoms. The structure proposed is shown in Figure 10. An eight-membered ring is formed and the bridging carboxylate group contains two non-equivalent carbon-oxygen bonds.

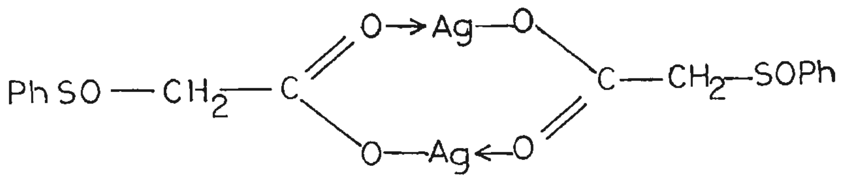


Figure 10

The proposed dimeric structure of silver(I) phenylsulfoxyacetate may be compared with the structures of silver(I) perfluorobutyrate[66] and silver(I)oxalate[67], which have been shown by x-ray analyses to possess dimeric structures. The Ag...Ag distance (2.90 Å) of silver perfluorobutyrate is nearly identical with the interatomic distance in metallic silver.

Since x-ray analysis for silver(I) phenylsulfoxyacetate has not been carried out, the proposal of dimeric structure is only tentative.

The infrared spectrum of mercury(I) phenylsulfoxyacetate shows a strong band at 1580 cm^{-1} which is assigned to $\nu_{asym}(COO)$. The band at 1305 cm^{-1} is assigned to the $\nu_{sym}(COO)$. The mercury(I)-carboxylate bond is predicted to be ionic since the $\nu_{asym}(COO)$ falls in the region of ionic carboxylate, yet the wide separation of $(\nu_{asym}(COO) - \nu_{sym}(COO))$ (275 cm^{-1}) is unusual for an ionic compound.

It is well known[68a] that mercury(I) ion which possesses the binuclear nature of Hg_2^{2+} forms few complexes. This has been attributed to a low tendency for mercury(I) ion to form coordinate bonds while mercury(II) ion forms more stable complexes with most ligands, so that the Hg_2^{2+}, disproportionates.[68a] However, complexes of mercury(I) have been obtained in solution with ligands which form essentially ionic metal-carboxylate bonds. Such ligands are oxalate, succinate, pyrophosphate and tripolyphosphate.[69] Thus, the formation of ionic mercury(I)-carboxylate in mercury(I) phenylsulfoxyacetate seems reasonable.

Electronic spectra

The u.v. spectra of aqueous and methanolic solutions of phenylsulfoxyacetates studied here show absorption peaks arising from the ligand phenylsulfoxyacetate, which has no apparent difference from its sodium salt. Hence, it may be assumed that the phenylsulfoxyacetates of the compounds studied retain their ionic structures as in the corresponding sodium phenylsulfoxyacetate.

The visible spectra of cobalt(II) and nickel(II) phenylsulfoxyacetates in aqueous solution are compared with the corresponding aqueous solution of cobalt(II) and nickel(II) nitrates while copper(II) phenylsulfoxyacetate, due to its low solubility in water, was compared with its inorganic salt in 95% ethanol. The absorption bands with the extinction coefficients of these compounds are located in Table 8.

As can be seen in Table 8, aqueous cobalt(II) and nickel(II) exhibit absorptions similar to the corresponding inorganic salts.

The aqueous solution spectra of cobalt(II) and nickel(II) inorganic salt show the absorption bands characteristic of $M(H_2O)_6^{2+}$ ion, where M = Co(II) and Ni(II).[68b] The resemblance of absorption spectra of aqueous solutions

TABLE 8

Visible spectral data

Compound	ν (kK)	ε_{max}	Assignment	solvent
$(C_6H_5SOCH_2CO_2)_2Co$	19.5	2.98	d-d	H_2O
	21.5 (sh)	1.98	d-d	
	34.7	22.54	charge	
$(C_6H_5SOCH_2CO_2)_2Ni$	13.5	3.42	d-d	H_2O
	14.8	3.59	d-d	
	25.2	10.25	d-d	
	34.0	17.98	charge	
$(C_6H_5SOCH_2CO_2)_2Cu\cdot 3/2H_2O$	13.0	48.47	d-d	95% EtOH
	34.0	637.05	charge	
$Co(NO_3)_2\cdot 6H_2O$	19.5	4.63	d-d	H_2O
	21.5	3.04	d-d	
	32.8	12.41	charge	
$Ni(NO_3)_2\cdot 6H_2O$	13.5	2.97	d-d	H_2O
	15.1	2.14	d-d	
	25.0	7.14	d-d	
	32.8	11.06	charge	
$Cu(NO_3)_2\cdot 3H_2O$	12.5	27.31	d-d	95% EtOH
	34.0	332.19	charge	

of cobalt(II) and nickel(II) phenylsulfoxyacetates to the octahedral $M(H_2O)_6^{2+}$ where M = Co(II), and Ni(II), leads to the conclusion that these two compounds dissociate in aqueous solution giving octahedrally solvated metal ions.

The spectrum of copper(II) phenylsulfoxyacetate in 95% ethanol or methanol shows essentially the solvated copper(II) ion. Copper(II) ion with d^9 configuration is a one positron case. In both copper(II) phenylsulfoxyacetate and copper(II) nitrate, only one d-d band at 13.5 kK and 12.5 kK respectively has been observed. This may lead to the conclusion that copper(II) ions in both cases have a similar environment and the one band observed may result from a d-d transition in a distorted octahedral environment of solvated copper(II) ion.

Nuclear magnetic resonance spectra

The nuclear magnetic resonance spectra of phenylsulfoxyacetic acid and its sodium(I), calcium(II), magnesium(II), barium(II), zinc(II), cadmium(II) and silver(I) derivatives in d_6-DMSO are located in Table 9. The non-equivalent methylene protons of the parent acid are removed in these derivatives. By comparing the chemical shift of the methylene protons of the phenylsulfoxyacetates studied here with that of the corresponding sodium phenylsulfoxyacetate, it can be seen that there is no appreciable

TABLE 9

Proton magnetic resonance spectra of phenylsulfoxyacetate
in d_6 dimethyl sulfoxide.

Compound	Chemical shift (τ)		
	C_6H_5	CH_2	J_{CH_2}
$C_6H_5SOCH_2CO_2H$	2.35 (multiplet)	5.8-6.35 (quartet)	14.5 c.p.s.
$(C_6H_5SOCH_2CO_2)_2Ca$	2.40 (")	6.38 (singlet)	
$(C_6H_5SOCH_2CO_2)_2Mg$	2.24 (")	6.30 (")	
$(C_6H_5SOCH_2CO_2)_2Ba$	2.32 (")	6.22 (")	
$(C_6H_5SOCH_2CO_2)_2Zn\cdot 2H_2O$	2.20 (")	6.18 (")	
$(C_6H_5SOCH_2CO_2)_2Cd\cdot 2H_2O$	2.20 (")	6.21 (")	
$C_6H_5SOCH_2CO_2Ag$	2.24 (")	6.21 (")	
$C_6H_5SOCH_2CO_2Na$	2.39 (")	6.50 (")	

change. Thus, the chemical environments of these phenylsulfoxyacetates may be assumed to be essentially the same as that of the sodium derivative.

Electron spin resonance spectra of manganese(II) and copper(II)

It has been suggested that the bonding of paramagnetic ions in unknown surroundings can be studied on the basis of their electron spin resonance spectra (e.s.r.). Abragam and Pryce[70] have accounted for the g-factors and hyperfine splitting when essentially ionic bonding occurs between the paramagnetic ion and its neighbours. Stevens and Owen[71] have proposed a theory for the case of covalent bonding. By extending the theory of Abragam and Pryce, van Wieringen[72] finds a direct relationship between the magnitude of the hyperfine structure interval in manganese(II) and the percentage ionic character in the bonds between this ion and its neighbours. The e.s.r. spectra of manganese(II) phenylsulfoxyacetate and manganese(II) chloride were measured in methanol solution at x-band frequency at various temperatures. Figure VI shows the spectra of a 0.025M methanol solution of manganese(II) phenylsulfoxyacetate at 21°C, -82°C and in the frozen state. Figure VII shows the spectra of 0.1M methanol solution of manganese(II) chloride tetrahydrate at 21°C and -82°C. In an electrostic field of cubic symmetry, the manganese(II) spectrum shows a nuclear hyperfine structure of six lines. All these spectra have their centres at

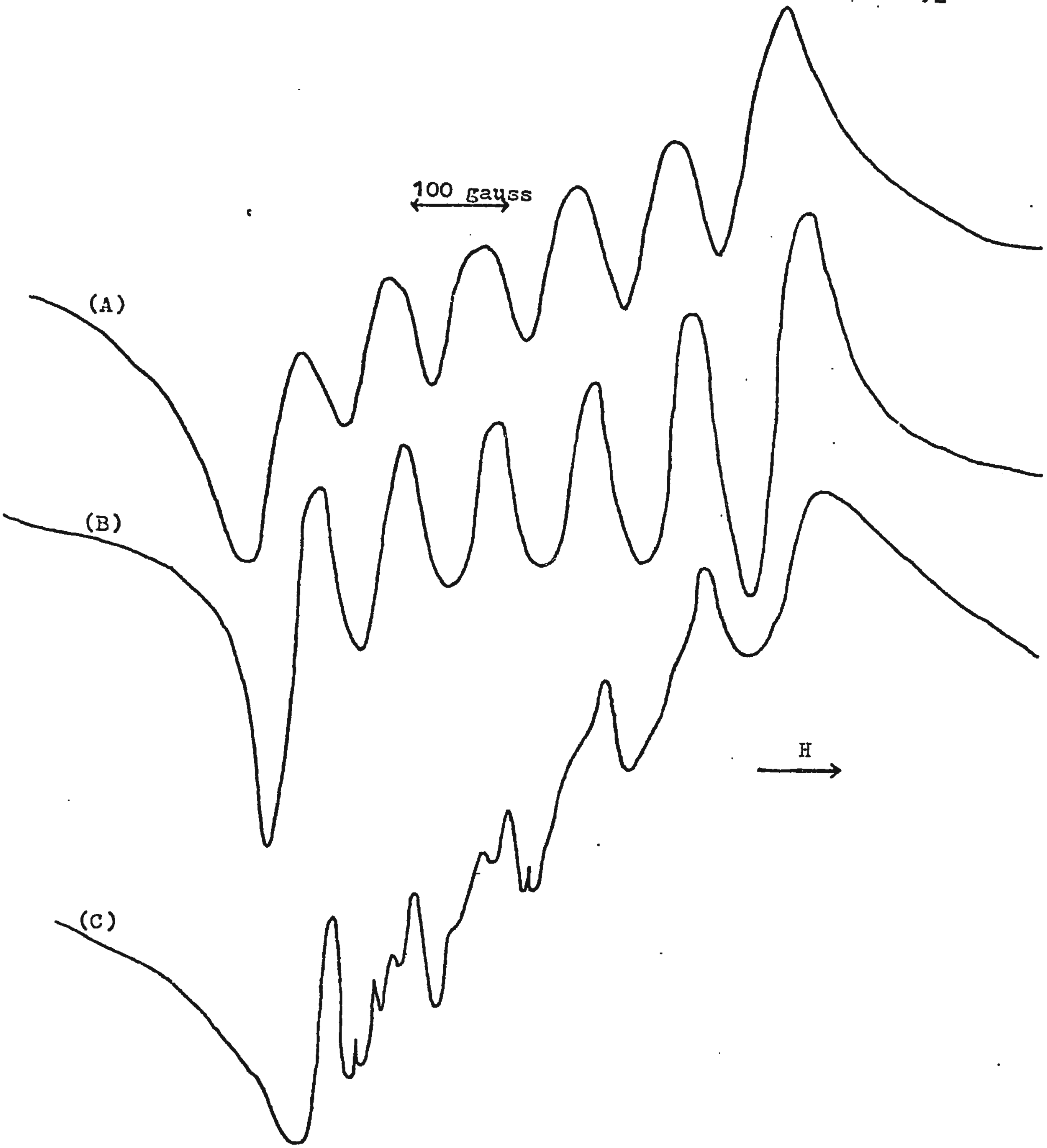


Figure VI. E.s.r. spectra of manganese(II) phenylsulfoxyacetate (0.025M) at x-band frequency in methanol (A) at room temperature, (B) at -82°C, and (C) in frozen state.

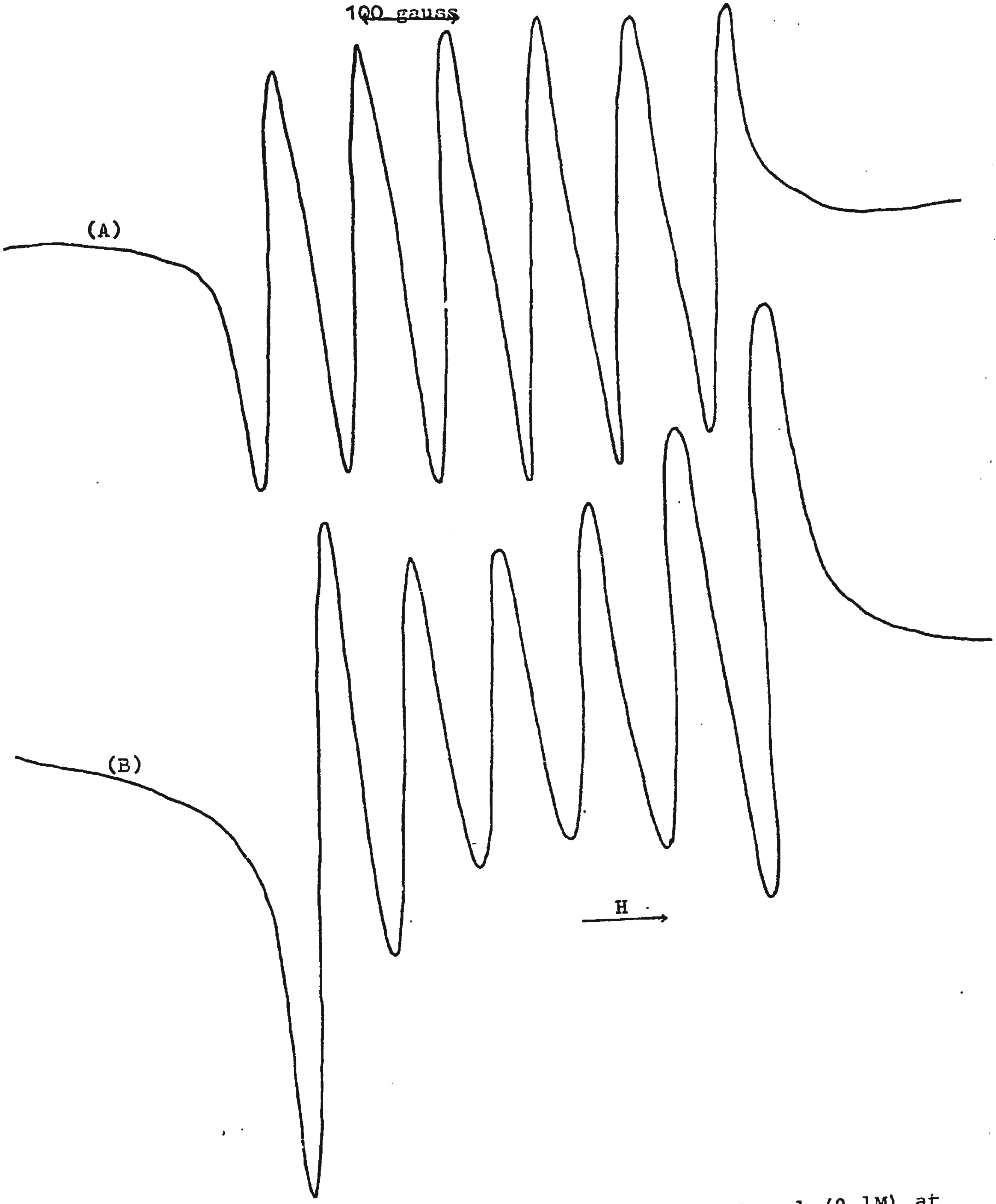


Figure VII. E.s.r. spectra of $MnCl_2 \cdot 4H_2O$ in methanol (0.1M) at x-band frequency (A) at room temperature and (B) at -82°C.

g = 2.00 ± 0.02 and a hyperfine splitting constant of 87 ± 3 gauss. For the spectrum of frozen manganese(II) phenylsulfoxyacetate, the six hyperfine structural lines are inhomogeneously broadened. This may be due to the anisotropies (directional dependences) in the dipolar interactions. In the frozen state, a solvent's viscosity may also result in line broadening.

Since the g value and the hyperfine splitting constant of manganese(II) phenylsulfoxyacetate are essentially the same as those of manganese(II) chloride, it is thus concluded that manganese(II) phenylsulfoxyacetate has an ionic character comparable to that of manganese(II) chloride. The observed g value and hyperfine splitting constants of the spectra studied here are also close to the literature value for manganese(II) in ionic crystals and in aqueous solutions.[73]

The presence of monomeric or dimeric species in copper(II) compound can be distinguished from the appearance of the line-shapes of the e.s.r. spectra. It has been found that dipolar coupling between pairs of copper(II) ions results in considerable broadening of the lines. This effect has been observed for mercaptosuccinate complexes[74] and copper(II) chelates of cyclopentanetetracarboxylic acid in non-aqueous solvents.[75]

E.s.r. measurements (x-band) of a powdered sample of the green compound $(C_6H_5SOCH_2CO_2)_2Cu \cdot H_2O$ gave a signal as shown in Figure VIII(C), which consists of two bands with $g_{\parallel} = 2.38$ and $g_m = 2.13$. In contrast to $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}H_2O$, x-band measurements made on a powdered sample of the blue compound $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}3/2H_2O$ gave a signal with $g_m = 2.17$ as shown in Figure VIII(B). This latter signal is believed to arise from monomeric species by analogy to the signal of copper(II) citrate (Figure VIIIA).[76] The signals of Figures VIIIA and VIIIB are in the reverse position. This is because the spectra were recorded in a different crystal phase.

As seen in Figure VIII, the line shape of a powdered sample of the green compound $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}H_2O$ is different from that of the blue compound $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}3/2H_2O$. If the prediction of a monomeric structure for $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}3/2H_2O$ is correct, then the green compound $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}H_2O$ may involve a dimeric or polymeric structure.

The e.s.r. spectrum of a powdered sample of the green $(C_6H_5SOCH_2CO_2)Cu{\cdot}H_2O$ is entirely different from that of copper acetate monohydrate,[77] which has been shown by x-ray analysis[78] to involve a dimeric structure in which the copper ions are held together by bridging carboxylate groups in a syn-syn arrangement (Figure 11a).

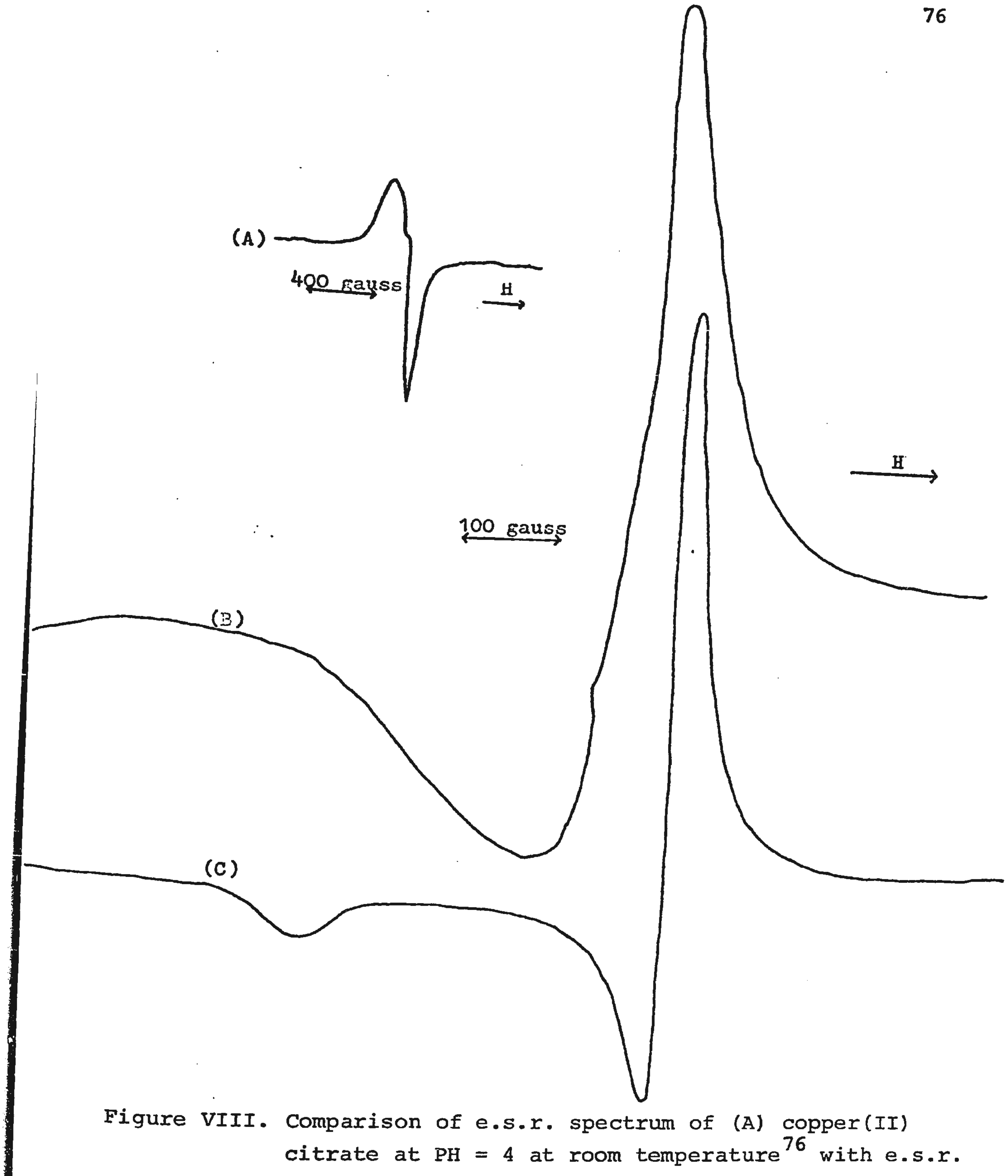


Figure VIII. Comparison of e.s.r. spectrum of (A) copper(II) citrate at PH = 4 at room temperature[76] with e.s.r. spectra of powdered samples of (B) copper(II) phenylsulfoxyacetate 3/2 hydrate and (C) copper(II) phenylsulfoxyacetate monohydrate at x-band frequency at room temperature.

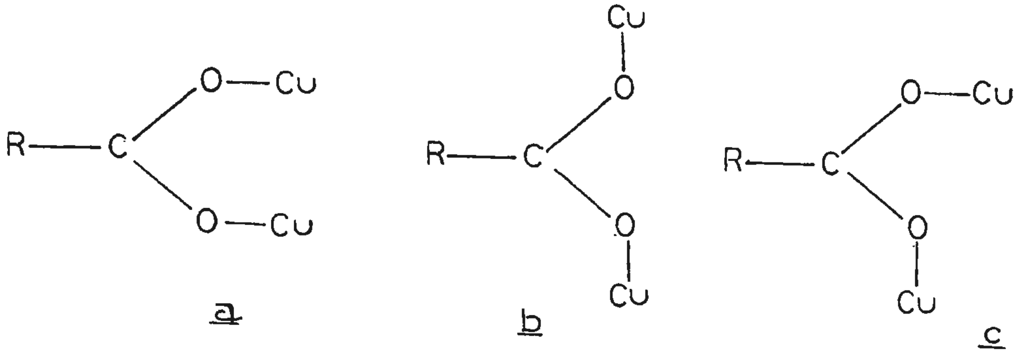


Figure 11 Carboxylate bonding configurations: a syn-syn b anti-anti c anti-syn.

Thus, it is clear that the structure of the green compound $(C_6H_5SOCH_2CO_2)_2Cu\cdot H_2O$ is most likely different from that of the copper acetate monohydrate. The green compound may probably involve a polymeric structure in which layers of copper ions are held together by bridging carboxylate groups in an anti-anti (Figure 11b) or anti-syn arrangement (Figure 11c). In the case of copper(II) acetate, the syn-syn arrangement of carboxylate groups hold the copper ions close enough together to allow the possibility of direct copper-copper interaction. The copper ions in the phenylsulfoxyacetate are probably much further apart and any spin-spin interaction between them must occur in this instance via the bridging carboxylate groups. This interaction seems to be much weaker than the direct copper-copper interaction which occurs in the "acetates".

In summing up the evidence from the various copper(II) n-alkanoates and some of their adducts, Martin and Waterman[79] conclude that because of the proximity of copper ions in the binuclear structure, this structure will be unstable and the anti-anti or anti-syn configuration favoured if a large residual charge remains on the copper ions after bonding with the carboxylate groups. The acid dissociation constants of the parent organic acids are taken as an indication of the available σ-electron density on the carboxylate oxygen atoms. Stronger acids than acetic give carboxylate ligands which are less polarisable than the acetate group and thus have less available σ-electron density on the carboxylate oxygens. This leaves greater residual charge on the copper ions and favours the anti-anti or anti-syn arrangements. Thus, the prediction of anti-anti or anti-syn configuration of $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}H_2O$ seems reasonable.

Methanol solutions of the green compound $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}H_2O$ (0.2 M) and the blue compound $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}3/2H_2O$ (0.1 M) were measured at x-band at various temperatures. At room temperature, $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}3/2H_2O$ in methanol still retains its monomeric structure. As the temperature is decreased to -30°C, $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}3/2H_2O$ shows essentially the same signal as that of $(C_6H_5SOCH_2CO_2)_2Cu{\cdot}H_2O$. These signals have an appearance similar to that of a dimer signal of copper(II) malate[80] as shown in Figure IX. The appearance of the broad line at g ≃ 2 is attributed to dipole-dipole interaction between copper(II) ions. Thus, it is concluded that both the green compound $(C_6H_5SOCH_2CO_2)_2Cu \cdot H_2O$ and the blue compound $(C_6H_5SOCH_2CO_2)_2Cu \cdot 3/2H_2O$ exist as dimers in methanol at -30°C. As the temperature is further decreased to -82°C, hyperfine splittings are observed in the e.s.r. spectra of methanol solutions of both $(C_6H_5SOCH_2CO_2)_2Cu \cdot H_2O$ and $(C_6H_5SOCH_2CO_2)_2Cu \cdot 3/2H_2O$. The four hyperfine splitting lines result from the interaction of the unpaired electron with the copper(II) nuclei which have nuclear spins of $I = 3/2$. The hyperfine lines are centred at $g = 2.27 \pm 0.06$ with a hyperfine splitting constant of 100 ± 1 gauss. Besides the hyperfine splitting lines, a dipole-dipole interaction band at $g_m = 2.085 \pm 0.005$ is also observed. The dimer formation of $(C_6H_5SOCH_2CO_2)_2Cu \cdot H_2O$ and $(C_6H_5SOCH_2CO_2)_2Cu \cdot 3/2H_2O$ in methanol solution at -82°C is obvious from comparison with the e.s.r. spectrum of copper(II) chloride at the same temperature as shown in Figure X. The signal of copper(II) chloride indicates that the monomeric species is predominant.

Molybdenum(II) phenylsulfoxyacetate (unsuccessful)

When the reaction of hexacarbonyl molybdenum and phenylsulfoxyacetic acid was carried out at about 110°C in dry diglyme, the change of appearance of reaction solution into yellow

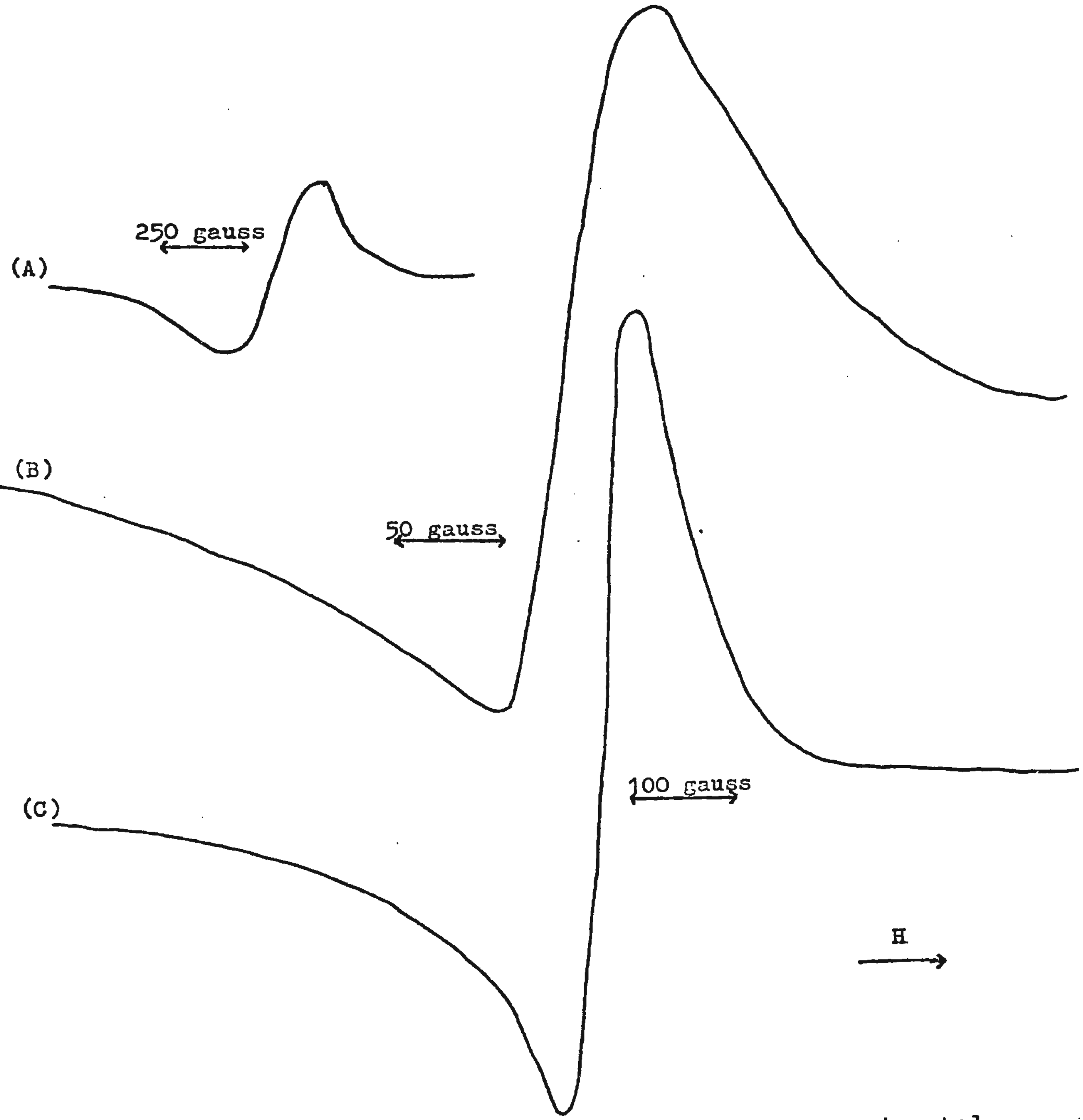


Figure IX. Comparison of (A) e.s.r. spectrum of experimental dimer signal due to copper(II) malate at 77°K[80] with the e.s.r. spectra of (B) copper(II) phenylsulfoxyacetate 3/2 hydrate and (C) copper(II) phenylsulfoxyacetate monohydrate at x-band frequency in methanol at -30°C.

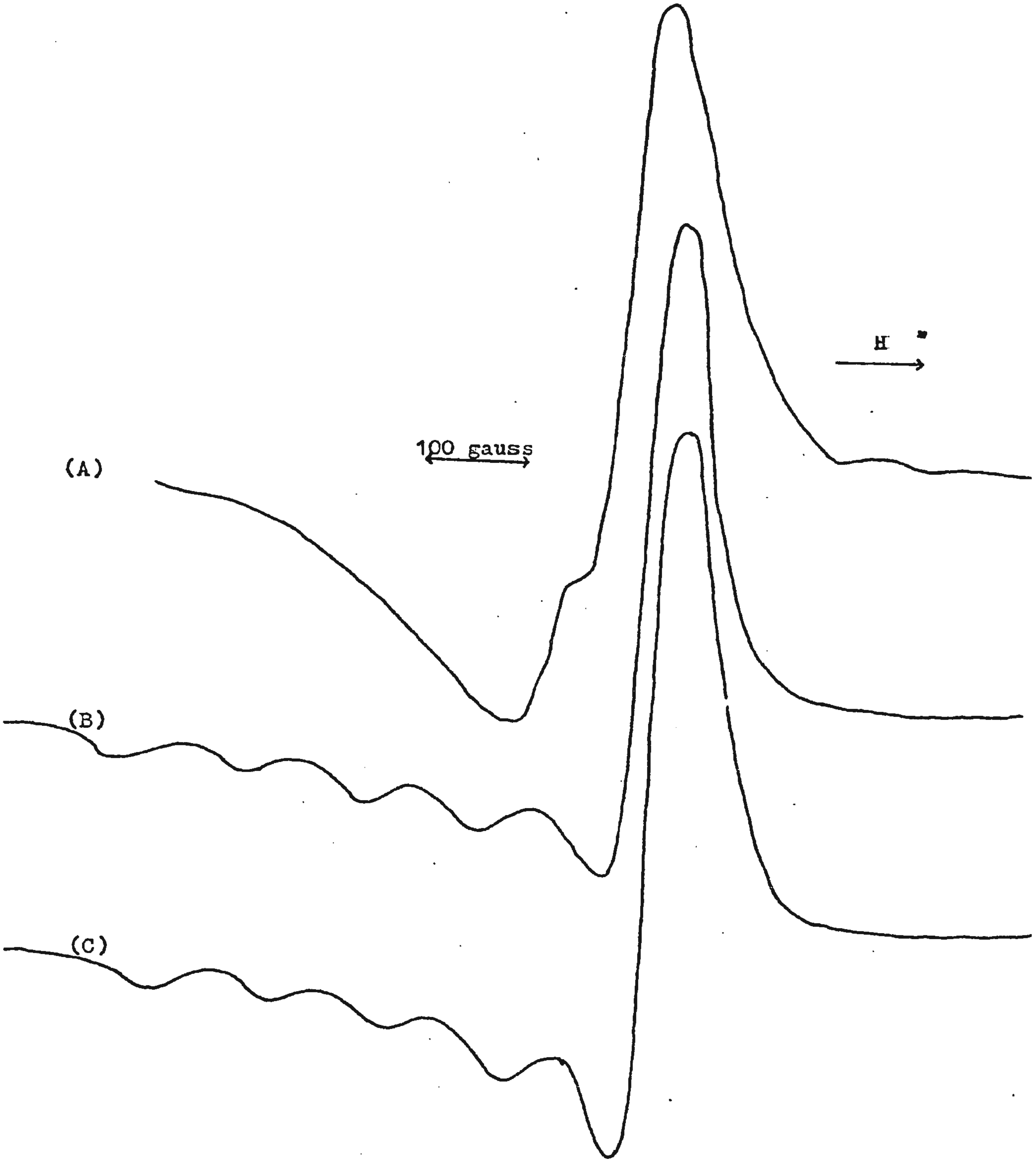


Figure X. Comparison of e.s.r. spectra of (A) copper(II) chloride (B) copper(II) phenylsulfoxyacetate monohydrate and (C) copper(II) phenylsulfoxyacetate 3/2 hydrate at x-band frequency in methanol at -82°C.

colour indicates the formation of molybdenum(II) carboxylate by analogy with yellow molybdenum(II) carboxylates reported by T. A. Stephenson et al..[46] The known reaction of preparation of molybdenum(II) acetate[46] has been carried out to compare the corresponding reaction of phenylsulfoxyacetate. The yellow solid molybdenum(II) acetate when exposed to air decomposed and turned green. Thus in the reaction of hexacarbonyl molybdenum and phenylsulfoxyacetic acid, the change of solution colour from yellow to green may involve a decomposition process. The molybdenum(II) phenylsulfoxyacetate is far less stable to the air than the corresponding molybdenum(II) acetate as the latter could be isolated readily while the former decomposed quickly during the reaction. The decomposition may probably be caused by a trace of air in the nitrogen gas or in the solvent.

(C) Conclusion

In all the "hard acids" investigated here, the sulfoxy group has not participated in the complex formation. In the cadmium(II) complex, the sulfoxy group utilizes oxygen in bonding, while the platinum(II) complexes are bonded through sulfur in all cases.

The S and O of phenylthioacetic acid and phenoxyacetic acid respectively were found to have no reaction with divalent ions of lead, copper, cadmium, zinc and nickel[35] while chelate formation through sulfur and oxygen was found for all the five divalent ions in the ethylthioacetate system.[81] Furthermore, the sulfur atom of ethylthioacetic acid is strongly bound to the central atom in the chelated copper(II) complex.[82]

The unreactive property of sulfoxy group of phenylsulfoxyacetic acid towards "hard acid" may be due to unfavourable reaction conditions, or the presence of phenyl group may probably have affected its reactivity. It seems that the X groups of the compounds of formula C_6H_5-X-CH_2CO_2H where X = S, O, SO, are not reactive towards the "hard acids".

The chlorine derivatives of platinum(II) complexes of phenylsulfoxyacetic acid have been investigated. For further investigation, it may be interesting to study other analogous derivatives which contain bromine, iodine, cyanide or isocyanate groups, and the complexes of the type $M(Pt(C_6H_5SOCH_2CO_2)X_2)_n$ where M = higher valency cations and X = univalent anionic groups.

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