November, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 3621—3624 (1982) 3621

Some Observations on the Structural Aspects of *o*-Hydroxythiobenzamide and Its Complexes with Pt(II), Pt(IV), and Au(III)

Karunamay Banerjee* and Shyamal Raychaudhury
Department of Pure Chemistry, University College of Science and Technology, Calcutta 700009, India

(Received September 22, 1981)

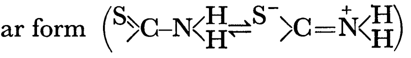
^{1}H NMR, electronic spectra, electrical conductivity studies in solution and IR study in solid phase have been done on *o*-hydroxythiobenzamide and its complexes with Pt(II), Pt(IV), and Au(III). The results indicate presence of the thioamide-thioimidic acid equilibrium in *o*-hydroxythiobenzamide, the thioamide form in the Pt(II) and Pt(IV) complexes, the thioimidate form in the Au(III) complex and free phenolic OH group in the Pt(IV) and Au(III) complexes.

o-Hydroxythiobenzamide received attention as a complexing agent for quantitative estimation of Pt(IV)[1)] and Au(III)[2)] ions. The previous workers[1,2)] predicted the possible formulas of the complexes as $[Pt^{IV}L_2L'_2]Cl_2$, $[Pt^{II}L'_2]$, and $H[Au^{III}L'_3Cl]$ (where L=*o*-hydroxythiobenzamide and L′=*o*-hydroxythiobenzamide anion), but the structural form of L′ and structure of the complexes have not been clearly revealed. The object of the present investigation is to elucidate the ionic forms of the ligand, and nature of bonding present in the above complexes on the basis of ^{1}H NMR, electronic spectra, electrical conductivity studies in solution and IR study in solid phase. In the course of our investigation it has been observed that *o*-hydroxythiobenzamide remains in thioamide-thioimidic acid ($o\text{-}HOC_6H_4CSNH_2 \rightleftharpoons o\text{-}HOC_6H_4C(SH){:}NH$) equilibrium in solution and may lose phenolic OH and/or thiomidic acid proton to satisfy primary valency of the metal ions in complex formation. The probable structures of the metal complexes have been suggested on the basis of the present study as $[Pt^{II}(o\text{-}OC_6H_4CSNH_2)_2]$, $[Pt^{IV}(o\text{-}OC_6H_4CSNH_2)_2(o\text{-}HOC_6H_4CSNH_2)_2]Cl_2$, and $H[Au^{III}(o\text{-}HOC_6H_4CS{:}NH)_3Cl]$.

Experimental

The complexes were prepared by the methods given in literature.[1,2)] The electrical conductivity data of the compounds at 25 °C in methanol were obtained by using Phillips PR 9500 conductivity bridge. The UV and visible absorption spectra of the compounds in solution were recorded at room temperature on Varian Techtron 634 spectrometer. IR shectra were obtained in KBr pellets on Beckmann IR 20 spectrometer. ^{1}H NMR spectra of the compounds in deuterated solvents were obtained on Varian NMR spectrometer EM-390; 90 MHz at 20 °C using tetramethylsilane as the internal reference.

Results and Discussion

NMR, IR, and Electrical Conductivity Studies. *o-Hydroxythiobenzamide*: ^{1}H NMR spectra in Fig. 1 indicate that *o*-hydroxythiobenzamide exists in thioamide form in $CDCl_3$ solution, and thioimidate form in DMSO-d_6 solution. $CDCl_3$ solution of *o*-hydroxythiobenzamide exhibits peaks due to the H-bonded phenolic OH at 11.9 δ, NH_2 and ring protons at 6.9—7.7 δ. ^{1}H NMR spectra of the *o*-hydroxythiobenzamide solution in DMSO-d_6 reveal a broad doublet at (9.6 δ, 9.8 δ). This doublet indicates the magnetic non-equivalence of NH_2 protons due to the restricted rotation about C–N bond in the polar form  $\left({}^{S}{>}C\text{–}N{<}^{H}_{H} \rightleftharpoons {}^{S^-}{>}C{=}\overset{+}{N}{<}^{H}_{H}\right)$ of *o*-hydroxythiobenzamide. The appearence of this doublet in the downfield region can be accounted for by the greater deshielding of protons attached with positive nitrogen in the polar form. A coalesced signal of two protons appears at 13.1 δ due to resonances of thioimidic SH and =NH groups. Analogous observation was reported in the molecular complex of dimethylamine and acetylacetone.[3)] The ^{1}H NMR signal of H-bonded phenolic OH is seen at 11.75 δ in DMSO-d_6 solution of *o*-hydroxythiobenzamide. Except the ring protons, all other signals of *o*-hydroxythiobenzamide in DMSO-d_6 disappear on deuteration.

The IR spectral data of *o*-hydroxythiobenzamide in

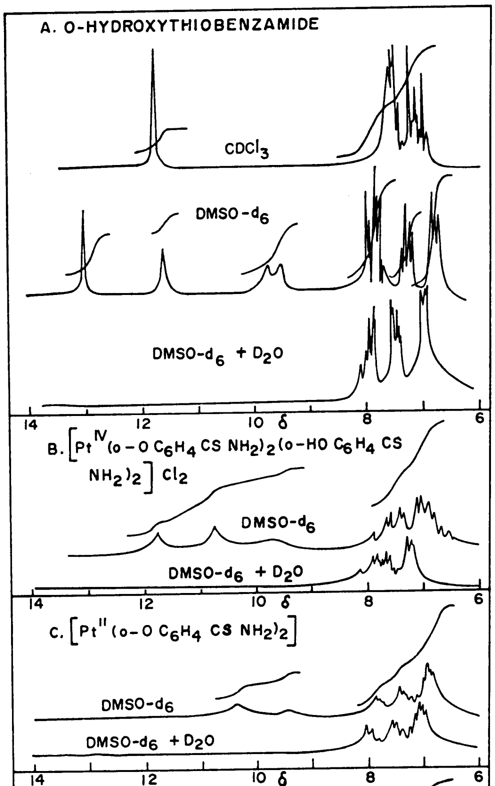


Fig. 1. ^{1}H NMR spectra.

Table 1. IR spectral bands ($\tilde{\nu}$/cm^{-1}) in KBr pellets

A	B	C	D	Probable assignments
3395 s	3400 br	3380 br	3320 m	$\nu_{OH}+\nu_{NH}$
3290 s	—	3245 br	3270 br	
3190 w	3050 br	3080 br	3100 w	
2750 w	2900 w	—	2900 w	ν_{OH}(H-Bonded)
1638 s	1600 s	1595 s	1600 s	$\delta_{NH_2}+\nu_{C-N}$
1610 w	—	1580 w	1585 w	
1473 s	1530 m	1490 w	1490 w	ν_{asym} of N–C=S
1385 s	1385 s	—	1385 w	δ_{OH}
1320 s	1315 s	1320 s	1315 s	ρ_r $NH_2+\nu_{C-S}$
1228 w	1235 w	1232 w	1235 w	ν_{sym} of N–C–S
895 m	900 w	880 s	885 s	NH_2 bending$+\nu_{C=N}+\nu_{C=S}$
757 m	750 m	750 m	748 m	$\nu_{C-N}+\nu_{C=S}$
742 s	698 s	690 w	690 br	$\nu_{C=S}$
660 s	660 s	659 s	660 s	δ_{ligand}
645 m	644 m	642 m	644 m	
595 s	598 s	595 s	595 s	
580 m	582 m	579 w	580 w	
560 w	558 w	560 w	560 w	
520 w	550 w	550 w	550 w	
470 s	490 s	480 s	480 s	ν_{M-S}
410 w	410 w	411 w	410 w	ligand vibration
—	—	381 s	380 s	ν_{M-O}
350 m	350 m	354 m	350 m	ligand vibration
—	310 m	—	—	ν_{Au-Cl}
285 w	282 w	283 w	282 w	ligand vibration

A = o-$HOC_6H_4CSNH_2$; B = $H[Au^{III}(o\text{-}HOC_6H_4CS{:}NH)_3Cl]$; C = $[Pt^{II}(o\text{-}OC_6H_4CSNH_2)_2]$; D = $[Pt^{IV}(o\text{-}OC_6H_4CSNH_2)_2(o\text{-}HOC_6H_4CSNH_2)_2]Cl_2$; s = strong; w = weak; br = broad; m = medium; M = Pt or Au.

KBr pellets are shown in Table 1. The stretching vibrations of OH and NH_2 appear in the 2750—3400 cm^{-1} region. The absence of SH band around 2550 cm^{-1} in the free ligand excludes the possible existence of thioimidic acid form in the solid state. All other band assignments according to Jensen *et al.*[4] are shown in Table 1.

Previous works[5] on the electrical conductivity in methanol indicate that molar conductance values in the 80—115 Ω^{-1} cm^2 mol^{-1} range are due to formation of the 1:1 electrolyte. The conductivity data in Table 2 indicate nonelectrolyte nature of *o*-hydroxythiobenzamide in methanol. Therefore low-field ^{1}H-NMR signal for phenolic OH, lower frequency IR band for ν_{OH} and nonelectrolyte behaviour of *o*-hydroxythiobenzamide suggest that its OH group is H-bonded in solution as well as in solid state.

[Pt^{II}(o-OC$_6$H$_4$CSNH$_2$)$_2$]. ^{1}H NMR spectra of the Pt(II) complex solution in DMSO-d_6 (Fig. 1) indicate the presence of broad doublet due to NH_2 protons at (9.5 δ, 10.4 δ) and the absence of phenolic OH proton signal. The IR data of Pt(II) complex in KBr pellets (Table 1) show slight lowering of ν_{NH_2} and absence of ν_{OH} at 2750 cm^{-1} in comparison to free ligand. It is known[4] that OH deformation band at 1385 cm^{-1} disappears on deuteration for the free ligand and also for the Ni(II) complex. We have also observed that the 1385 cm^{-1} band is absent in the Pt(II) complex. Therefore absence of phenolic OH signal in ^{1}H NMR spectra and absence of δ_{OH} band at 1385 cm^{-1} in IR spectra indicate Pt–O bonding in the Pt(II) complex. The antisymmetric vibration of the N–C=S group in *o*-hydroxythiobenzamide occuring at 1473 cm^{-1} and its subsequent shifting to higher frequency due to increased double bond character of N–C in N–C=S grouping in case of its Ni(II) complex[4] is at par with our observation in the Pt(II) complex. In the case of *o*-hydroxythiobenzamide the stretching vibration due to C=S appears at 742 cm^{-1}, but this band is shifted to 690 cm^{-1} in the Pt(II) complex due to metal-sulfur bonding. In the far IR region the bands at 480 cm^{-1} and 381 cm^{-1} are probably due to Pt–S and Pt–O bonding.

The electrical conductivity data in Table 2 indicate the nonelectrolyte behaviour of the Pt(II) complex in methanol.

Therefore in the square planar arrangement two *o*-hydroxythiobenzamide molecules are bonded through S and O with Pt^{2+} ion in Pt(II) complex.

[Pt^{IV}(o-OC$_6$H$_4$CSNH$_2$)$_2$(o-HOC$_6$H$_4$CSNH$_2$)$_2$]Cl$_2$. The ^{1}H NMR spectra of the Pt(IV) complex solution in DMSO-d_6 (Fig. 1) exhibit a broad band at (9.7 δ, 10.8 δ) for the NH_2 protons and a single proton peak at 11.8 δ for the H-bonded phenolic OH. IR spectral bands of the Pt(IV) and Pt(II) complexes in KBr pellets are alike except the case where the band due to H-bonded OH stretching of the free ligand at 2750 cm^{-1} is shifted to 2900 cm^{-1}, and OH deformation band at 1385 cm^{-1} does not disappear for the Pt(IV) complex. Therefore ^{1}H NMR signal at 11.8 δ and IR band at 1385 cm^{-1} indicate the existence of free phenolic OH in the Pt(IV) complex. The $\nu_{C=S}$ band of the free ligand appearing at 742 cm^{-1} and its subsequent shifting to 690 cm^{-1} in the Pt(IV) complex

Table 2. Electrical conductivity in methanol at 25 °C

Compound	Concentration mol dm^{-3}	Molar conductance Ω^{-1} cm^2
o-$HOC_6H_4CSNH_2$	2.2×10^{-3}	3.77
$[Pt^{II}(o\text{-}OC_6H_4CSNH_2)_2]$	1.2×10^{-3}	8.24
$[Pt^{IV}(o\text{-}OC_6H_4CSNH_2)_2(o\text{-}HOC_6H_4CSNH_2)_2]Cl_2$	1.2×10^{-3}	99.63
$H[Au^{III}(o\text{-}HOC_6H_4CS{:}NH)_3Cl]$	0.6×10^{-3}	91.02
$H[Au^{III}(o\text{-}HOC_6H_4CS{:}NH)_3Cl]$+Excess o-$HOC_6H_4CSNH_2$	0.6×10^{-3}	114.00

suggests Pt–S bonding. In far IR region, like the Pt(II) complex the appearance of two bands at 380 cm^{-1} and 480 cm^{-1} indicate Pt–O and Pt–S bonding in the Pt(IV) complex. The electrical conductivity data in Table 2 show that the Pt(IV) complex behaves as 1:1 electrolyte in methanol. The lower conductivity of the Pt(IV) complex may be due to ionic association in low dielectric medium where one of the axially S bonded o-hydroxythiobenzamide molecule is replaced by chloride ion to form $[Pt^{IV}(o\text{-}OC_6H_4CSNH_2)_2(o\text{-}HOC_6H_4CSNH_2)Cl]Cl$ and free o-$HOC_6H_4CSNH_2$.

Therefore, IR, ^{1}H NMR, and electrical conductivity studies indicate that Pt^{4+} ion is in octahedral environment where two o-hydroxythiobenzamide molecules are bonded through S and O, and the rest two are coordinated axially only through S leaving free OH.

$H[Au^{III}(o\text{-}HOC_6H_4CS{:}NH)_3Cl]$. The ^{1}H NMR spectra of the Au(III) complex solution in DMSO-d_6 (Fig. 1) exhibit a broad peak of single proton at 10 δ due to deprotonated thioamide group. Like the Pt(IV) complex a single proton signal due to H-bonded phenolic OH at 11.9 δ is also found in the Au(III) complex. The IR spectral data of the gold complex in KBr pellets (Table 1) show fewer number of bands for NH_2 stretching vibrations. The stretching vibration due to H-bonded OH of the free ligand at 2750 cm^{-1} is displaced to 2900 cm^{-1}. It is also seen that one of the split band of o-hydroxythiobenzamide at 1600 cm^{-1} is absent in the Au(III) complex. The OH deformation band at 1385 cm^{-1} does not disappear and a band due to C=S stretching appears at lower frequency (698 cm^{-1}) due to gold-sulfur bonding. In the far IR region the gold complex exhibits bands at 490 cm^{-1} and 310 cm^{-1} probably due to ν_{Au-S} and ν_{Au-Cl}; other features of IR spectral bands of the gold complex are similar to the platinum complexes. Therefore, the ^{1}H NMR and IR studies of the gold complex indicate its complexation through thioimidate anion leaving phenolic OH groups free.

The electrical conductivity data in Table 2 indicate that the gold complex behaves as 1:1 electrolyte in methanol. The amperometric study of the gold complex[6] and elemental analysis[2] indicate that the metal-ligand ratio is 1:3. Our chemical tests show that in the gold complex Cl is in the inner sphere which also includes bonded imidate anion and free OH groups. These facts suggest that the square planar arrangement exists in the gold complex. Lower pH of methanolic solution of the gold complex as compared to methanol indicates the presence of H$^+$ in the outer sphere of the complex. Tarantelli *et al.*[7] have shown that electrical conductivity of $[Pd^{II}L_4]^{2+}$ (where L= $(C_6H_5NH)_2CS$) in methanol or acetone increases on adding excess ligand. Similar increase in conductivity is observed on adding excess o-hydroxythiobenzamide to the methanolic solution of the gold complex. This behaviour may be due to displacement of Cl from the inner sphere of the gold complex by a neutral ligand molecule to form neutral species $[Au^{III}(o\text{-}HOC_6H_4CS{:}NH)_3(o\text{-}HOC_6H_4CSNH_2)]$ and free HCl. By the mole ratio method the earlier workers[2] have shown that the metal-ligand ratio is 1:4 in the gold complex and at first sight it is apparently misleading as it does not fit their elemental analysis data of 1:3. In the presence of excess reagent a reaction like $[ML_3Cl]^-H^+\xrightarrow{L}ML_4+HCl$ may have occured in the solution during the mole-ratio method of studying metal-ligand ratio.

Electronic Spectra. o-*Hydroxythiobenzamide*: Electronic spectra of thiocarbonyl derivatives[8–10] show a low intensity and long wavelength band due to the $n\rightarrow\pi^*$ transition. In the case of o-hydroxythiobenzamide interaction of nitrogen lone pair electrons with the C=S unit makes the $n\rightarrow\pi^*$ transition easy. Therefore the low intensity ($\varepsilon<100$) band at 20400 cm^{-1} of o-hydroxythiobenzamide in different solvent media is the $n\rightarrow\pi^*$ transition. Figure 2 shows that this 20400 cm^{-1} band is quenched in neutral and acidic aqueous media, whereas the band is pronounced in DMSO and alkaline aqueous media. Methanolic solution of o-hydroxythiobenzamide also exhibits a very weak intensity $n\rightarrow\pi^*$ transition at ≈20000 cm^{-1}.

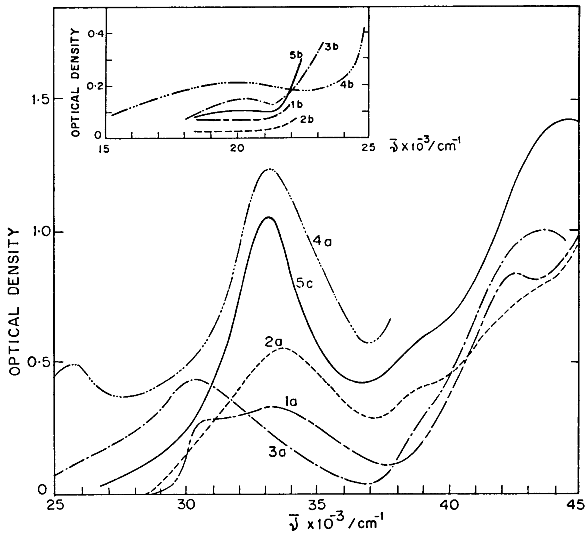
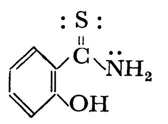
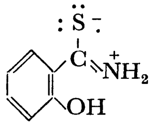


Fig. 2. Absorption spectra of o-hydroxythiobenzamide in 1(a,b) water; 2(a,b) 0.1 M HCl; 3(a,b) 0.1 M NaOH; 4(a,b) DMSO; 5(c,b) Methanol. a=10^{-4}, b=10^{-3}, c=2.2×10^{-4} mol dm^{-3}.

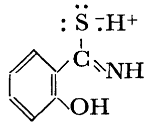
In case of thiocarbonyl compounds it has been reported[8–10] that the intense bands immediately preceding n→π* are due to the π→π* rather than the n→σ* transition. Again two different π→π* transitions should also be expected due to conjugation of C=S and C=N groups with the aromatic ring in *o*-hydroxythiobenzamide as found in methyl *N,N*-dimethyldithiocarbamate[11] and 5-amino-2-mercaptothiazoles.[12] Therefore two bands at ≈33000 cm^{-1} and 30500 cm^{-1} in aqueous solution of *o*-hydroxythiobenzamide (Fig. 2, 1a) indicate π→π* transitions. Therefore in neutral aqueous medium the existence of both i and ii or iii forms are expected. DMSO solution of *o*-hydroxythiobenzamide also exhibits two π→π* transitions (Fig. 2, 4a) of which the lower frequency one is red-shifted to 26000 cm^{-1} due to high proton binding capacity of DMSO favouring the existence of structure iii. In alkaline medium (Fig. 2, 3a) red shifting of the two (apparently nonresolvable) π→π* bands may be due to deprotonation of SH and OH groups in structure iii. In acidic aqueous medium (Fig. 2, 2a) only 33000 cm^{-1} band is present probably due to protonation of NH$_2$ group in structure i.



i



ii



iii

Very intense bands at ≈44000—44500 cm^{-1} is found in methanolic and aqueous alkaline solutions of *o*-hydroxythiobenzamide, and intensity of this band is decreased in acidic medium. Therefore the ≈44500 cm^{-1} band may be due to the n→σ* transition in the ligand molecule. The shoulders at 39000 cm^{-1} may be due to phenolic chromophore as its intensity is decreased in alkaline medium.

Pt(II), Pt(IV), and Au(III) Complexes. The phenolic chromophore band at 39000 cm^{-1} of *o*-hydroxythiobenzamide is red-shifted in the Pt complexes indicating Pt–O bonding, whereas the gold complex does not show such shift. The intensity of the n→π* band (20000 cm^{-1}) of *o*-hydroxythiobenzamide increases significantly on complexation (Fig. 3) and this band shifts to higher frequency in the sequence Au(III)<Pt(IV)<Pt(II) complexes indicating L→M charge transfer.[13,14] The d-d transitions are obscured by the intense charge transfer band. Electronic spectra of the complexes show that the positions of the bands appearing above 20000 cm^{-1} agree more or less with those of the free ligand with enhanced intensities. Hence these bands may be regarded as intraligand transitions with intensities modified on complexation.

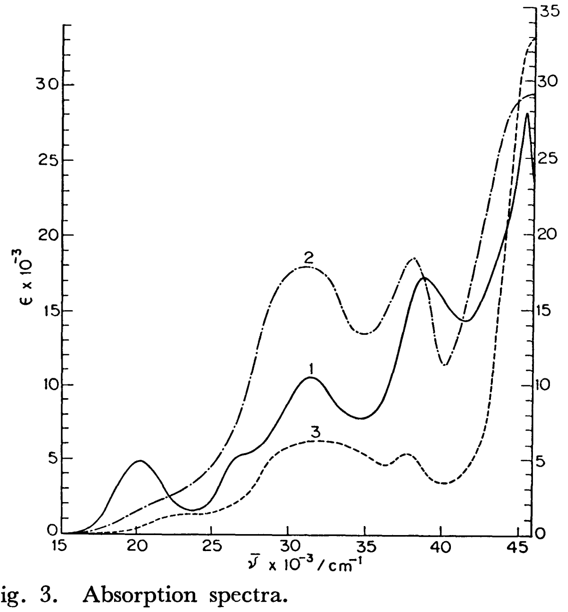


Fig. 3. Absorption spectra.
1: H[Au^{III}(*o*-HOC$_6$H$_4$CS:NH)$_3$Cl], 2: [Pt^{IV}(*o*-OC$_6$H$_4$CSNH$_2$)$_2$(*o*-HOC$_6$H$_4$CSNH$_2$)$_2$]Cl$_2$, 3: [Pt^{II}(*o*-OC$_6$H$_4$CSNH$_2$)$_2$] in methanol.

Conclusion

From the above studies it is clear that *o*-hydroxythiobenzamide exists in the thioamide-thioimidic acid equilibrium in solution. Metal-sulfur and metal-oxygen bondings are observed in the platinum complexes, whereas the gold complex shows only metal-sulfur bonding. Amide C=S coordinates with Pt(II) and Pt(IV) and the thioimidate anion is bonded with Au(III). The existence of free phenolic OH in the Pt(IV) and Au(III) complexes has been established decidedly by ^{1}H NMR, IR, and electronic spectral studies. Recent studies also indicate the presence of free phenolic OH group in the Pd(II) complex of salicylaldehyde 2-picoloylhydrazone[15] and rare earth complexes of *o*-hydroxybenzhydroxamic acid.[16]

Thanks are due to Dr. S. K. Bose, Dr. S. N. Bhattacharyya and Dr. M. P. Roy for their encouragement throughout the work and also to UGC, India for financial assistance to one of the authors (K. B.).

References

1) K. Sur and S. C. Shome, *Anal. Chim. Acta*, **57**, 20 (1971).
2) K. Sur and M. Mazumdar, *Anal. Chim. Acta*, **59**, 306 (1972).
3) L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **36**, 793 (1958).
4) Kai Arne Jensen and Per Halfden Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966).
5) W. J. Geary, *Coord. Chem. Rev.*, **7**, 112 (1971).
6) A. Basu, M. Mazumdar, and S. C. Shome, *J. Indian Chem. Soc.*, **57**, 1156 (1980).
7) T. Tarantelli and C. Furlani, *J. Chem. Soc., A*, **1968**, 1717.
8) K. S. Suresh, J. Ramachandran, and C. N. R. Rao, *J. Sci. Indust. Res. (India)*, **20B**, 206 (1961).
9) C. N. R. Rao, A. Balasubramaniam, and J. Ramachandran, *J. Sci. Indust. Res. (India)*, **20B**, 382 (1961).
10) J. Fabian and R. Mayer, *Spectrochim. Acta*, **20**, 299 (1964).
11) H. P. Koch, *J. Chem. Soc.*, **1949**, 401.
12) E. S. Stern, *J. Chem. Soc.*, **1949**, 1664.
13) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier Publishing Company, Amsterdam (1968), p. 354.
14) Donald L. Swihart and W. Roy Mason, *Inorg. Chem.*, **9**, 1749 (1970).
15) R. L. Dutta and A. K. Sarkar, *J. Inorg. Nucl. Chem.*, **43**, 57 (1981).
16) S. K. Brahma and A. K. Chakraburtty, *J. Indian Chem. Soc.*, **58**, 615 (1981).