

## Complexing Behaviour of Ethyl N-Phenyldithiocarbamate: Structural Studies of Complexes of Fe(II), Ru(II), Co(II), Rh(III), Rh(I), Ni(II), Pd(0), Pt(0), Pt(II), Ag(I), Zn(II), Cd(II) & Hg(II)

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Complexes of Fe(II), Ru(II), Co(II), Rh(III), Rh(I), Ni(II) and Pd(0), Pt(0), Pt(II), Ag(I), Zn(II), Cd(II) and Hg(II) with ethyl N-phenyldithiocarbamate have been synthesised. The complexes are characterised by elemental analyses, magnetic moment, conductivity and spectral (IR, UV-visible) data. It is proposed that bonding of metal ions with the ligand takes place through thiocarbonyl sulphur and the ligand acts as monodentate.

The current interest in the metal complexes of dithiocarbamates is mainly due to their novel structural<sup>1</sup>, electrochemical properties<sup>2,3</sup> and interesting photoredox chemistry<sup>4,5</sup>. Metal dithiocarbamate complexes have also shown promise as accelerators in the vulcanization of rubber<sup>6</sup>. However, investigations on complexes of dithiocarbamate esters are few<sup>7,8</sup> and the complexing behaviour of ethyl N-phenyldithiocarbamate is hitherto not reported. The present paper describes the synthetic and the structural aspects of the complexes of ethyl N-phenyldithiocarbamate with Fe(II), Ru(II), Co(II), Rh(III), Rh(I), Ni(II), Pd(0), Pt(0), Pt(II), Ag(I), Zn(II), Cd(II) and Hg(II).

### Materials and Methods

All the chemicals used were either chemically pure or of AR quality. The solvents were dried and freshly distilled before use. All operations were carried out under pure and dry nitrogen atmosphere.

Ethyl N-phenyldithiocarbamate (hereafter referred to as EPD) was prepared by the known method<sup>9</sup> and used after recrystallisation from ethyl alcohol. Chlorotris(triphenylphosphine)rhodium(I), tetrakis(triphenylphosphine)palladium(0) and tetrakis(triphenylphosphine)platinum(0) were prepared by reported methods<sup>10-12</sup>.

### Preparation of metal complexes:

#### *Dichlorobis(EPD)iron(II)*

A benzene solution (15 ml) of anhydrous FeCl<sub>3</sub> (0.32 g, 2 mmol) was added with stirring to a chloroform solution (15 ml) of EPD (1.6 g, 8 mmol) and the stirring continued for 1 hr. The resulting dark brown solution was concentrated to about 15 ml under reduced pressure and pet. ether (40-60°) added to it when a reddish brown precipitate of the complex was obtained. It was centrifuged, washed with ether and

recrystallised twice from chloroform-pet. ether, followed by drying *in vacuo*, m.p. 125-27°; yield 50%.

#### *Dichlorotris(EPD)ruthenium(II)*

An ethanolic solution (8 ml) of RuCl<sub>3</sub> · 3H<sub>2</sub>O (0.3 g, 1 mmol) was slowly added to chloroform solution (10 ml) of EPD (0.8 g, 4 mmol) with constant stirring. After 1 hr, the red-brown solution was concentrated to about 10 ml and ether (10 ml) added to it when a dark red complex precipitated out. It was centrifuged, washed with ether and dried in a vacuum desiccator, m.p. 137-38°; yield 58%.

#### *Dichlorobis(EPD)cobalt(II) ethanol*

A solution of CoCl<sub>2</sub> · 6H<sub>2</sub>O (0.5 g, 2 mmol) in ethanol (12 ml) was slowly added with stirring to a chloroform solution (15 ml) of EPD (1.6 g, 8 mmol). The colour of the solution changed to dark green. Stirring was continued for 1 hr more and the resulting solution concentrated to 10 ml and pet. ether (40-60°) added to it when a green oily product separated out. The oily layer was dissolved in chloroform and reprecipitated by adding ether. This process was repeated several times, till a green complex was obtained, which was centrifuged, washed with pet. ether and dried in air, m.p. 149-51°; yield 45%.

#### *Trichlorotris(EPD)rhodium(III)*

A solution of RhCl<sub>3</sub> · 3H<sub>2</sub>O (0.26 g, 1 mmol) in ethyl alcohol (10 ml) was slowly added with stirring to a benzene solution (10 ml) of EPD (0.8 g, 4 mmol). The solution was stirred at 10° for 1 hr, whereupon the colour of the light brown solution changed to dark brown. To this solution was added pet. ether (10 ml, 40-60) when a red-orange complex precipitated out. It was centrifuged, washed with *n*-pentane, dried *in vacuo* and recrystallised twice from chloroform-pet. ether

followed by washing a few times with *n*-pentane; m.p. 187-88°; yield 65%.

*Monochlorobis(EPD)triphenylphosphine-rhodium(I)*

To a chloroform solution (10 ml) of chlorotris(triphenylphosphine)rhodium(I) (0.31 g, 0.33 mmol) was slowly added with stirring the chloroform solution (10 ml) of EPD (0.3 g, 1.5 mmol). Addition of pet. ether (40-60°) to the resulting red-brown solution afforded a yellowish brown solid, which was centrifuged, washed with ethanol, ether and dried *in vacuo*. It was repeatedly recrystallised from chloroform-pet. ether, to a constant melting point; m.p. 181-83°; yield, 50%.

*Dichlorobis(EPD)nickel(II)*

A solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.48 g, 0.2 mmol) in ethanol (15 ml) was slowly added with stirring to a solution of EPD (1.6 g, 8 mmol) in dichloromethane (10 ml) and stirring continued for 1 hr. The solution was slowly evaporated to half of its original volume and addition of ether to this afforded a green oil, which was separated, dissolved in dichloromethane and precipitated by adding pet. ether. This process was repeated three to four times until a constant melting pale green complex was obtained. It was centrifuged, washed with pet. ether and dried in air; m.p. 265-70° (d); yield 40%.

*Bis(EPD)bis(triphenylphosphine)palladium(0)*

To a stirred solution of tetrakis(triphenylphosphine)palladium(0) (0.6 g, 0.5 mmol) in benzene (12 ml) was slowly added a chloroform solution (10 ml) of EPD (0.5 g, ~2.5 mmol). Stirring was continued for 3 hr more when the yellow solution slowly changed to red. Upon concentration to half of the original volume and addition of pet. ether (15 ml, 40-60°) a red oil separated out, which was redissolved in chloroform and precipitated by adding ether (40-60°). This process was repeated a few times until a yellow complex having constant melting point was obtained. It was centrifuged, washed with ethanol and ether, dried and kept in a vacuum desiccator; m.p. 124-26°; yield 45%.

*Bis(EPD)bis(triphenylphosphine)platinum(0)*

The above procedure was adopted to prepare this Pt(0) complex, using tetrakis(triphenylphosphine)platinum(0) in place of tetrakis(triphenylphosphine)palladium(0). A pale yellow complex was obtained, m.p. 164-65°; yield 50%.

*Dichlorobis(EPD)platinum(II)*

A solution of platinum chloride (0.3 g, 1 mmol) in ethanol (8 ml) was added with stirring to a chloroform

solution (10 ml) of EPD (0.8 g, 4 mmol). Stirring was continued at room temperature for 2 hr, whereby a yellow complex was slowly formed. It was centrifuged, washed with pet. ether and dried *in vacuo*; m.p. 140-42°; yield 55%.

*Bis(EPD)silver(I) nitrate*

AgNO<sub>3</sub> (0.34 g, 2 mmol) dissolved in hot aq. ethanol (20 ml) was kept stirred and to this was added slowly a chloroform solution (12 ml) of EPD (1.6 g, 8 mmol), and stirring for additional 3.5 hr after the addition of EPD was over. A dark red complex was slowly formed. It was centrifuged, washed with ethanol, benzene and pet. ether followed by drying *in vacuo*; m.p. 180-82°; yield 53%.

*Dichlorobis(EPD)zinc(II)*

An alcoholic solution (10 ml) of ZnCl<sub>2</sub>·2H<sub>2</sub>O (0.34 g, 2 mmol) was added with stirring to a solution of EPD (1.6 g, 8 mmol) in chloroform (10 ml), and stirring continued for 1 hr more followed by refluxing for 30 min. The light brown solution was cooled and treated with ether (15 ml) whereby a yellow oil was obtained. It was separated, dissolved in chloroform and precipitated by adding pet. ether (40-60°). This process was repeated several times, until a constant melting yellow solid was obtained which was dried *in vacuo*, m.p. 96-98°; yield 60%.

*Diiodobis(EPD)cadmium(II)diethanol*

A solution of CdI<sub>2</sub> (0.4 g; 1 mmol) in ethanol (8 ml) was added with stirring to a benzene solution (10 ml) of EPD (1 g, 5 mmol). The resulting solution was refluxed for 30 min, cooled and pet. ether added. The yellow oil appeared was separated, dissolved in chloroform and precipitated by the addition of pet. ether. This process of precipitation was repeated a few times until a pale yellow solid was obtained. It was dried *in vacuo*; m.p. 168-70°; yield 65%.

*Dichlorobis(EPD)mercury(II)*

Upon adding an alcoholic solution (8 ml) of HgCl<sub>2</sub> (0.27 g, 1 mmol) to a solution of EPD (1 g, 5 mmol) in ethanol (10 ml), a white precipitate was immediately formed. Stirring was continued 1 hr more, the precipitate centrifuged, washed with ethanol, ether, recrystallised from chloroform-pet. ether and dried *in vacuo*; m.p. 220°; yield 65%.

*Physical measurements*

Infrared spectra of the ligand and the metal complexes were recorded in KBr on a Perkin-Elmer model 580 spectrophotometer. Magnetic susceptibilities of the complexes were determined with the help of a Gouy balance at room temperature (25 ± 3°C) using

mercury tetrathiocyanatocobalt(II) as the calibrant. The diamagnetic corrections were made as outlined by Figgis and Lewis<sup>14</sup>.

The electronic absorption spectra of the ligand and complexes in chloroform were recorded on a Cary model 17-D spectrophotometer in the region 300-950 nm.

Melting points of the complexes are uncorrected and were observed on a Fisher-Johns melting point apparatus.

Conductance of millimolar solutions of the complexes in nitrobenzene were measured on an Elico conductivity meter type CM-80.

## Results and Discussion

The analytical data of the complexes are presented in Table I.

The IR spectrum of EPD exhibited characteristic bands due to phenyl and ethyl groups (3130, 2980, 2920, 2880, 1590, 1500, 1490, 1440, 1065, 1008, 750, 690  $\text{cm}^{-1}$ )<sup>15a</sup>. The position of these bands remained practically unchanged ( $\pm 5 \text{ cm}^{-1}$ ) in the spectra of all the complexes. This suggests that the phenyl and ethyl groups are virtually unaffected by the complex formation. It is, therefore, assumed that the metal ions in the complexes are bonded to  $-\text{N}(\text{H})\text{C}(\text{S})\text{S}-$  moiety of EPD. Further, the possibility of the ligand being in the thiol form is ruled out because of the absence of any band in the 2500  $\text{cm}^{-1}$  region due to  $\nu(\text{S}-\text{H})$ <sup>15b</sup>. The major shifts in the IR band positions are, therefore, expected to be in those which have contributions of the vibrational modes of  $(-\text{NH})$ ,  $(\text{C}=\text{S})$  and  $(\text{C}-\text{S})$  bonds. Subsequent discussion of IR data of the complexes are confined to these modes.

The free ligand exhibited a broad band at 3130  $\text{cm}^{-1}$  along with a shoulder at 3200  $\text{cm}^{-1}$  assignable to  $\nu(\text{CH})$  of the phenyl group and  $\nu(\text{NH})$  respectively. These free ligand modes appeared as two separate bands around 3030(w) and 3200  $\text{cm}^{-1}$  in the spectra of the complexes. The broadness of the free ligand band at 3130  $\text{cm}^{-1}$  may be due to hydrogen bonding, which got considerably reduced in the complexes. This resulted in the separation of the band into two bands around 3030 ( $\nu\text{C}-\text{H}$ ) and 3200 ( $\nu\text{N}-\text{H}$ )  $\text{cm}^{-1}$ . The appearance of  $\nu(\text{NH})$  at approximately the same position in the spectra of the ligand and the complexes suggests that (i) the NH group is not deprotonated and (ii) the nitrogen atom possibly is not linked to the metal ions in complexes.

Since the moiety,  $-\text{N}(\text{H})\text{C}(=\text{S})\text{S}-$  contains a thioamide group  $[\text{N}(\text{H})\text{CS}]$ , it should exhibit four characteristic thioamide bands<sup>15c</sup>. The free ligand band at 1540  $\text{cm}^{-1}$  has been assigned to the thioamide-I band having major contributions from  $\nu\text{C}=\text{N}$  and  $\delta\text{NH}$ . This band shifted towards higher wavenumbers

(1550  $\text{cm}^{-1}$ ) in the spectra of the complexes, suggesting bonding through thiocarbonyl sulphur atom.

A slightly broad band at 1330  $\text{cm}^{-1}$  in the spectrum of the ligand assignable to thioamide-II band having major contributions from  $\nu\text{C}=\text{N}$  and  $\delta\text{NH}$  was shifted towards higher wavenumbers ( $\sim 30 \text{ cm}^{-1}$ ) in the spectra of the complexes further supporting the bonding of the metal ions through thiocarbonyl sulphur.

The thioamide-III band of the free ligand at 1050  $\text{cm}^{-1}$  was shifted to lower wavenumbers ( $\sim 15 \text{ cm}^{-1}$ ) in the complexes. This is as per expectation and suggests bonding of the metal ions to carbonyl sulphur.

The thioamide-IV band of the free ligand at 970  $\text{cm}^{-1}$ , having a major contribution from  $\nu\text{C}=\text{S}$  was shifted towards lower wavenumbers ( $\sim 50 \text{ cm}^{-1}$ ) in the spectra of the complexes<sup>16</sup>. This observation again suggests metal-sulphur bonding in the complexes.

The free ligand band at 730  $\text{cm}^{-1}$  assigned to  $(\text{C}-\text{SEt})$  slightly shifted to higher wavenumbers ( $\sim 5 \text{ cm}^{-1}$ ), indicating a bonding pattern of the type  $\text{M}-\text{S}-\text{C}$ .

All the characteristic bands due to  $\text{PPh}_3$  or  $\text{AsPh}_3$  were present in the spectra of the complexes having  $\text{PPh}_3$  or  $\text{AsPh}_3$  as coligands<sup>17</sup>.

The new bands around 300  $\text{cm}^{-1}$  (one broad or two relatively less broad) in the spectra of the complexes have been assigned to the coupled vibrations of  $\nu(\text{M}-\text{S})$  with other bonding modes of the ligand molecule<sup>18</sup>. Another new band in the complex of Ru(II) at 280  $\text{cm}^{-1}$  has been assigned to  $\text{Ru}-\text{Cl}-\text{Ru}$  bridge<sup>19</sup>.

The characteristic bands of  $\text{NO}_3^-$  in the spectrum of the silver complex were present, suggesting the presence of  $\text{NO}_3^-$  group<sup>20</sup>.

Thus, the above discussion of the IR data clearly reveal that the metal ions in the complexes are linked to thiocarbonyl sulphur atom of the ligand, which is acting as monodentate towards the metal ions.

All the complexes, except those of iron(II) and cobalt(II) exhibited diamagnetic behaviour.  $\text{CoCl}_2(\text{EPD})_2$ . EtOH was paramagnetic with an observed moment of 2.05 B.M. on the basis of magnetic moment alone, it is difficult to distinguish between spin-paired octahedral and square planar complexes of cobalt(II), as in principle, for both the cases the moment should be close to spin only value corresponding to one unpaired electron. In practice, very few low-spin octahedral complexes of Co(II) are known, and in such complexes especially with sulphur ligands of low crystal field strength, the magnetic moments lying in the range 1.8-2.0 B.M. are rather unknown<sup>18</sup>. However, the magnetic moments of several Co(II) complexes having definite square

planar configuration fall in the range of 2.1-2.8 B.M. (ref. 18, 21). On the basis of the above argument, it is suggested that the complex,  $[\text{CoCl}_2(\text{EPD})_2] \cdot \text{EtOH}$  has the square planar geometry ( $d^7$  system) and cobalt exists in +2 oxidation state in the complex.

The magnetic moment of 5.2 B.M. of the iron(II) complex corresponds to four unpaired electrons. The ground state of Fe(II) in high spin  $O_h$  symmetry<sup>22</sup> is  ${}^5T_{2g}$ , whereas in  $T_d$  symmetry, it is  ${}^5E$ . Irrespective of the  $O_h$  or  $T_d$  geometry of the Fe(II) complex, the number of unpaired electrons on the iron will be four and in both the cases there will be a certain amount of orbital contribution to the spin only value of the magnetic moment. In practice, the value of the magnetic moment of tetrahedral and octahedral complexes of Fe(II) have magnetic moment of 5.2 or 5.4 B.M. respectively<sup>23c</sup>. The observed value of 5.2 B.M. for the complex under discussion suggested the tetrahedral geometry for the Fe(II) complex. This geometry is also consistent with the composition of the complex,  $[\text{FeCl}_2(\text{EPD})_2]$  in which every ligand is acting as monodentate. Although four-coordinated complex can have only two possible geometries (tetrahedral or square planar), square planar geometry is, however, ruled out on the basis that the value of the magnetic moment for such complexes should correspond to two unpaired electrons (>2.8 B.M.). Tetrahedral geometry is, therefore, assigned to the iron complex. Since all the known octahedral complexes of ruthenium(II) have been found to be diamagnetic<sup>24</sup>, it is assumed that the ruthenium complex possesses the octahedral geometry around the metal ion.

There is hardly any paramagnetic complex of Rh(I) and Rh(III) having geometries other than square planar and octahedral respectively<sup>24b</sup> is known. Therefore, the diamagnetic complexes,  $[\text{RhCl}(\text{EPD})_2(\text{PPh}_3)]$  and  $[\text{RhCl}_3(\text{EPD})_3]$  have been assigned square planar and octahedral geometries, respectively, as these are the preferred ones for Rh(I) and Rh(III) ions in their complexes.

The diamagnetic behaviour of  $[\text{NiCl}_2(\text{EPD})_2]$  and  $[\text{PtCl}_2(\text{EPD})_2]$ , reveals the square planar geometry around Ni(II) and Pt(II) complexes<sup>23b</sup>.

The diamagnetic behaviour of the four-coordinated Pd(0), Pt(0), Zn(II), Cd(II) and Hg(II) complexes ( $d^{10}$  system) suggests tetrahedral geometry of the complexes<sup>24c</sup>.

Silver complex is diamagnetic and has a coordination number two, the nitrate ion being assumed to be ionically bound. It has been assumed that the silver complex has the linear geometry<sup>24d</sup>.

The electronic spectrum of EPD exhibits three relatively weak bands at 300, 285 and 235 nm. The bands at 300 and 285 nm are shifted towards lower wavelength region in the spectra of the complexes. This

shift is due to the fact that M-S bond formation lowers the energy of the non-bonding orbitals of the thiocarbonyl sulphur atom<sup>25a</sup>. Now in the  $n \rightarrow \pi^*$  transition which is responsible for the appearance of the bands at 300 and 285 nm, one of the electrons is removed from the non-bonding orbital and promoted to  $\pi^*$ -orbital whose energy ( $\pi^*$ -orbital) remains unaffected. Therefore, the hypsochromic shifts of these bands on complexation indicate that these bands are due to  $n \rightarrow \pi^*$  transition. The position of 235 nm band remains unaffected on complexation, suggesting it to be arising due to  $\pi \rightarrow \pi^*$  transition of the phenyl ring<sup>25b</sup>.

The electronic spectrum of the cobalt complex,  $\text{CoCl}_2(\text{EPD})_2 \cdot \text{C}_2\text{H}_5\text{OH}$  exhibits very weak band in the near infrared region at 1800 nm, which is characteristic of a square planar Co(II) species<sup>26-29</sup>. This result is corroborated by its magnetic data (2.02 B.M.). The intense bands at 730, 650 and 620 nm may be assigned to charge transfer bands.

The spectrum of nickel complex displays a relatively weak band at 560 nm with a shoulder at 500 nm. This low intensity band is ascribed to  $d-d$  transition in square planar complexes and assigned to  ${}^1A_{1g} \rightarrow {}^1B_{1g}$ , based on  $D_{2h}$  micro-symmetry<sup>30</sup>. The absence of bands around 2000, 1000 and 400 nm rules out the tetrahedral or octahedral geometry of the complex. This is consistent with the diamagnetic behaviour of the complex.

One should expect four bands due to transitions from  ${}^1A_{1g}$  to  ${}^3T_{1g}$ ,  ${}^3T_{2g}$  and  ${}^1T_{2g}$  in the spectra of octahedral complexes of Ru(II) and Rh(III) ions<sup>31</sup>. In general, singlet-triplet transitions are very weak and are not usually observed. Further, the spectrum of the Ru(II) complexes displays charge transfer bands upto 550 nm and most of the weak  $d-d$  bands are, therefore, masked by these CT bands. However, one weak and broad band at 620 nm which appears in the spectrum of the Ru(II) complex can possibly be assigned to either  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  or  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition, analogous to other Ru(II) complexes<sup>32-34</sup>.

In the spectrum of Rh(III), a weak band at 470 nm is assigned to either  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  or  ${}^1T_{2g}$  transition. The shift in the position of band in Rh(III) complex towards higher energy region compared to that in Ru(II) complex may be due to the increased charge on rhodium (+3 versus +2) because of which the crystal field strength ( $10 Dq$ ) will be increased<sup>24a</sup>.

In the spectra of Rh(I), Pd(0), Pt(0), Ag(I), Zn(II), Cd(II) and Hg(II), no bands appear in the visible region. In the case of Rh(I), the intense charge transfer band in the visible region obscures all the weak  $d-d$  transition bands. In the rest of the complexes, the electronic configuration of the metal ions is  $d^{10}$  and

Table I—Analytical Data and Geometries of the Various Complexes

Complexes	Found (Calc)(%)					Geometry	
	C	H	N	S <sup>a</sup>	X		M <sup>b</sup>
[FeCl <sub>2</sub> (EPD) <sub>2</sub> ]	41.2 (41.5)	4.0 (4.2)	5.2 (5.4)	24.3 (24.6)	13.8 (13.6)	10.4 (10.8)	Tetrahedral
[RuCl <sub>2</sub> (EPD) <sub>3</sub> ]	41.8 (42.5)	4.1 (4.3)	5.6 (5.5)	24.8 (25.2)	9.7 (9.3)		Octahedral with possible Ru—Cl—Ru bridge
[CoCl <sub>2</sub> (EPD) <sub>2</sub> ].C <sub>2</sub> H <sub>5</sub> OH	41.8 (42.1)	4.7 (4.9)	5.1 (4.9)	22.8 (22.5)	13.1 (12.5)	9.9 (10.4)	Square planar
[RhCl <sub>3</sub> (EPD) <sub>3</sub> ]	40.1 (40.5)	3.9 (4.1)	5.0 (5.2)	23.6 (23.9)	13.6 (13.4)	12.3 (12.9)	Octahedral
[RhCl(EPD) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	53.9 (54.3)	4.4 (4.6)	3.2 (3.5)	16.2 (16.1)	4.6 (4.5)	12.5 (12.9)	Square planar
[NiCl <sub>2</sub> (EPD) <sub>2</sub> ]	41.1 (41.4)	4.1 (4.2)	5.4 (5.0)	24.5 (24.8)	13.8 (13.5)	11.1 (11.2)	-do-
[Pd(EPD) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	62.8 (63.3)	4.9 (5.1)	2.6 (2.7)	12.3 (12.5)	—	10.2 (10.3)	Tetrahedral
[Pt(EPD) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	58.1 (58.4)	4.6 (4.7)	2.6 (2.2)	11.3 (11.6)	—	—	-do-
[PtCl <sub>2</sub> (EPD) <sub>2</sub> ]	32.4 (32.7)	3.1 (3.3)	4.3 (4.0)	19.3 (19.4)	10.8 (10.4)	—	Tetrahedral
[Ag(EPD) <sub>2</sub> ](NO <sub>3</sub> )	37.9 (38.3)	3.5 (3.0)	7.3 (7.5)	22.5 (22.9)	—	19.0 (19.2)	Linear
[ZnCl <sub>2</sub> (EPD) <sub>2</sub> ]	40.4 (40.8)	3.9 (4.2)	5.4 (5.0)	24.1 (24.4)	13.8 (13.4)	11.9 (12.3)	Tetrahedral
[CdI <sub>2</sub> (EPD) <sub>2</sub> ].2C <sub>2</sub> H <sub>5</sub> OH	30.4 (31.0)	3.8 (4.0)	3.6 (3.3)	14.9 (15.2)	29.7 (29.8)	12.8 (13.2)	-do-
[HgCl <sub>2</sub> (EPD) <sub>2</sub> ]	31.9 (32.5)	3.0 (3.3)	4.4 (4.2)	19.4 (19.3)	11.0 (10.7)	30.3 (30.1)	-do-

<sup>(a)</sup>Sulphur was estimated as BaSO<sub>4</sub> after oxidising the complex with a mixture of Na<sub>2</sub>O<sub>2</sub> and KNO<sub>3</sub>.

<sup>(b)</sup>Metal ions were estimated by standard methods (see ref. 13).

one should, therefore, not expect any band in the visible or in the near IR region.

Iron(II) and platinum(II) complexes do not show any band in the visible region because of the presence of intense charge transfer bands. In consonance with the fact that all the known complexes of Pt(II) are found to be square planar, the present Pt(II) complex has been assigned the same geometry which is further supported by its diamagnetic behaviour.

On the basis of the analytical, spectral (IR, UV-visible) and magnetic moment data, it is inferred that the bonding of metal ion takes place through thiocarbonyl sulphur and the ligand acts as monodentate. The geometries assigned to various complexes are given in Table I.

## References

- Pignolet L H & Wheeler S H, *Inorg Chem*, **19** (1980) 935.
- Hendrickson J R, Hope J M & Martin R L, *J chem Soc Dalton Trans*, (1976) 2032.
- Wheeler S H, Mattson B M, Miersler G L & Pignolet L H, (unpublished work).
- Given K W, Mattson B M, McGuiggan M F, Miessler G L & Pignolet L H, *J Am chem Soc*, **99** (1977) 4855.
- Miessler G L & Pignolet L H, *Inorg Chem*, **18** (1979) 210.
- Coleman N M, Shelton J R & Koering J L, *Ind Engng Chem Prod Res Develop.* **13** (1974) 154.
- Brinkoff H C & Dauzenberg J M A, *Recl Trav Chim*, **91** (1972) 117.
- Gayathri Devi K R & Sathyanarayana D N, *Indian J Chem*, **20A** (1981) 980.
- Garin J, Martinez V, Mayoral J, Melendez E & Merchan F, *Synthesis*, **12** (1981) 961.
- Osborn J A, Jardine F H, Young F H & Wilkinson G, *J chem Soc(A)*, (1966) 1711.
- Malatesta L & Angoletta M, *J chem Soc (A)*, (1957) 1188.
- Ugo R, Carioti F & LaMonica G, *Inorg Syn*, **11** (1966) 105.
- Basett J, Denney R C, Jeffery G H & Mendhan J, *Vogel's textbook of quantitative inorganic analysis*, 1978, 447 and 474; (a) 461; (b) 462; (c) 466.
- Figgis B N & Lewis J, *Modern coordination chemistry*, edited by J Lewis & R G Wilkins (Interscience, New York) 1960, 403.
- (a) Cotton F A & Wilkinson G, *Advanced inorganic chemistry*, (John-Wiley, New York), 1980, (a) 61; (b) 99.  
(b) Rao C N R, *Chemical applications of infrared spectroscopy* (Academic Press, New York) 1963 (a) 125; (b) 297; (c) 300.
- Agarwala U, Lakshmi & Bhaskara Rao P, *Inorg chem Acta*, **2** (1968) 337.
- Shobatake K, Postmus C, Ferraro J R & Nakamoto K, *Appl Spectrosc*, **23** (1969) 12.
- Carlin R L, *Transition Met Chem*, **1** (1965) 28.

- 19 Adams D M, *Laboratory methods in infrared spectroscopy*, edited by R G J Miller & B C Stace (Academic Press, London) 1972.
- 20 Nakamoto K, *Infrared and Raman spectra of inorganic and Raman spectra of inorganic and coordination compounds*, (John Wiley, New York) 1978, 246.
- 21 Figgis B N & Lewis J, *Progr Chem*, **6** (1964) 192.
- 22 Ballhausen C J & Gray H B, *Molecular orbital theory* (W A Benjamin, New York) 1965.
- 23 Figgis B N, *Introduction to ligand fields* (Wiley Eastern, New Delhi) 1966, (a) pp 278, (b) pp 312.
- 24 Cotton F A & Wilkinson G, *Advanced inorganic chemistry*, (John-Wiley, New York), 1980 (a) 912; (b) 934; (c) 591; (d) 969.
- 25 Jaffe' H H & Orchin M, *Theory and applications of UV spectroscopy* (John Wiley, New York) 1962, (a) 182; (b) 98.
- 26 Yamada S, *Coord Chem Rev*, **1** (1966) 415.
- 27 Nishikawa N & Yamaja S, *Bull chem Soc Japan*, **92** (1970) 795.
- 28 Hipp C J & Baker (Jr) W A, *J Am chem Soc*, **88** (1966) 2442.
- 29 Enerett (Jr) G W & Holm R H, *J Am chem Soc*, **88** (1966) 2442.
- 30 Yamada S, Nishikawa H & Yoshida E, *Bull Chem Soc Japan*, **39** (1966) 994.
- 31 Thorn G D & Ludwig R A, *The dithiocarbamates and related compounds* (Elsevier, New York) 1962.
- 32 Jørgensen C K, *Acta Chem Scand*, **10** (1956) 500.
- 33 Jørgensen C K, *Advan Chem Phys*, **5** (1963) 33.
- 34 Jørgensen C K, *Molec Phys*, **5** (1962) 485.