

## Diethylenetriamine *bis*(dithiocarbamate) derivatives of some first row transition metals

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**Abstract.** Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) complexes of diethylenetriamine *bis*(dithiocarbamate), L, have been synthesized and characterized by elemental analysis, magnetic measurements, electronic, esr and infrared spectral studies. The Cr(III) and Fe(III) complexes are octahedral with composition  $[M(L)(H_2O)Cl]$ , whereas Co(II), Ni(II) and Cu(II) derivatives,  $[CoL] \cdot 2H_2O$ ,  $[NiL]$  and  $[CuL]$ , are square-planar. The esr spectral features indicate significant distortion from ideal symmetry.

**Keywords.** Diethylenetriamine*bis*(dithiocarbamate); magnetic moment; reflectance spectra; ESR spectra; infrared spectra.

### 1. Introduction

Synthesis and characterization of metal dithiocarbamates have been a subject of extensive studies (Marcotrigiano *et al* 1974; Fabretti *et al* 1985; Polzonetti *et al* 1986; Pandeya *et al* 1987) due to their wide applications, biocidal activities (Thorn and Ludwig 1962; Siddiqi *et al* 1987) and interesting structure–property relationship (Eley *et al* 1972; Hall and Hendrickson 1976). The sodium salt of ethylene*bis*dithiocarbamate was introduced in the early 1940s as an important fungicide. The Fe(III) dithiocarbamates were the earliest examples exhibiting the influence of N-substituents on low spin  $\rightleftharpoons$  high spin cross-over phenomena (Ewald *et al* 1964). Compared to alkyl- and aryl-substituted dithiocarbamates, those with heterocyclic and long chain N-substitution are very few. In this communication we report the synthesis and characterization of some first row transition metal complexes with diethylenetriamine*bis*(dithiocarbamate).

### 2. Experimental

Hydrated  $CrCl_3$ ,  $FeCl_3$ ,  $CoCl_2$ ,  $NiCl_2$  and  $CuCl_2$  were of BDH grade.

#### 2.1 Preparation of the disodium salt of the ligand, $C_6H_{11}N_3S_4Na_2 \cdot 6H_2O$

The disodium salt of diethylenetriamine*bis*(dithiocarbamate) was prepared as reported earlier (Gogoi and Phukan 1989).

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2.2a  $[Cr(L)(H_2O)Cl]$ : The compound was prepared by refluxing the ethanolic solutions of the ligand (0.002 mol in 40 ml) and chromium (III) chloride hexahydrate (0.002 mol in 30 ml) for about an hour. The compound formed was filtered, washed several times with ethanol and dried under vacuum.

2.2b  $[Fe(L)(H_2O)Cl]$ ,  $[CoL] \cdot 2H_2O$ ,  $[NiL]$  and  $[CuL]$ : These were prepared by mixing the ethanolic solutions of the ligand (0.002 mol in 40 ml) and the corresponding metal halides (0.002 mol in 40 ml). The resulting reaction mixtures were stirred for about half an hour. The products formed were filtered, washed several times with ethanol and dried under vacuum.

### 2.3 Physical measurements

The IR spectra ( $4000-200\text{ cm}^{-1}$ ) of the complexes as KBr pellets were recorded using a Perkin-Elmer 297 spectrophotometer. Electronic spectra of solid compounds were recorded on a Shimadzu UV-240 spectrophotometer, using  $BaSO_4$  as reference material. ESR spectra of the powdered samples at liquid nitrogen temperature were recorded on a Varian E-112 ESR spectrometer (X-band) using Coppinger's radical ( $g = 2.00399$ ) as  $g$  marker. The room temperature magnetic moments were measured on a Gouy balance using  $Hg[Co(SCN)_4]$  as calibrant. Elemental analyses for C, H and N were carried out. Metal, sulphur and chlorine contents were determined by reported standard methods (Vogel 1975).

## 3. Results and discussion

All the complexes were insoluble in common organic solvents but sparingly soluble in some strongly coordinating solvents like DMSO and DMF. In view of the poor solubility of the complexes and of the reported dimeric nature of some metal dithiocarbamates (Bonamico *et al* 1965), particularly in the case of Cu(II) and Co(II) derivatives, the possibility of the complexes being dimeric in nature cannot be excluded. The analytical data are presented in table 1.

### 3.1 Magnetic measurements

The room temperature magnetic moments of 4.04 and 5.78 BM for Cr(III) and Fe(III) derivatives, respectively, were in good agreement with high-spin octahedral complexes. For the Co(II) complex the magnetic moment of 2.08 BM was indicative of a low-spin species while the value of 1.8 BM for the Cu(II) derivative was in accordance with one unpaired electron.

### 3.2 Reflectance spectra

In the reflectance spectra of Cr(III) derivatives the bands observed around 16 650 and 23 100  $\text{cm}^{-1}$  were assigned to  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  and  ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$  transitions. The  $10Dq$ ,  $B$  and  $\beta$  were calculated to be 16 650  $\text{cm}^{-1}$ , 638  $\text{cm}^{-1}$  and 0.61 respectively. Fe(III) derivatives showed bands around 8700, 15 800, 19 700, 30 100 and 37 500  $\text{cm}^{-1}$ . The bands around 30 100 and 37 300  $\text{cm}^{-1}$  were assigned to charge transfer bands while

Table 1. Analytical data of the compounds.

Compound	Colour	Yield (%)	D* (°C)	Experimental (calculated) (%)						
				M	S	C	N	H	Cl	
[Cr(C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> S <sub>4</sub> )(H <sub>2</sub> O)Cl]	Light grey	68	187	14.10 (14.49)	35.48 (35.75)	19.78 (20.07)	11.38 (11.70)	3.48 (3.62)	9.62 (9.88)	
[Fe(C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> S <sub>4</sub> )(H <sub>2</sub> O)Cl]	Dark brown	72	182	15.21 (15.42)	34.67 (35.37)	19.48 (19.85)	11.32 (11.58)	3.66 (3.58)	9.55 (9.78)	
[Co(C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> S <sub>4</sub> )·2H <sub>2</sub> O]	Bluish green	62	235	17.23 (16.92)	36.33 (36.85)	20.82 (20.67)	11.82 (12.06)	4.12 (4.30)		
[Ni(C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> S <sub>4</sub> )]	Green	80	165	18.96 (18.81)	40.65 (41.11)	22.88 (23.08)	13.14 (13.46)	3.36 (3.52)		
[Cu(C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> S <sub>4</sub> )]	Brownish yellow	76	155	19.82 (20.05)	40.06 (40.48)	22.12 (22.72)	12.95 (13.25)	3.24 (3.47)		

\*D - decomposition temperature

the lowest energy transition at  $8700\text{ cm}^{-1}$  could be due to superimposition of  ${}^6A_1 \rightarrow {}^4T_1$  and  ${}^4T_2 \rightarrow {}^4T_1$  transitions (Martin and White 1968).

For Co(II) derivatives the bands observed at  $15\,500$ ,  $20\,600$ ,  $25\,100$  and  $28\,000\text{ cm}^{-1}$  were assigned to  ${}^2A_{1g} \rightarrow {}^2B_{2g}$ ,  ${}^2A_{1g} \rightarrow {}^2E_g$ ,  ${}^2A_{1g} \rightarrow {}^2B_{1g}$  and metal-ligand charge transfer transitions, respectively, in accordance with a square planar  $\text{CoS}_4$  moiety. The diamagnetic Ni(II) derivative showed three bands around  $15\,650$ ,  $20\,350$  and  $24\,100\text{ cm}^{-1}$  which were assigned to the transitions  ${}^1A_{1g} \rightarrow {}^1B_{1g}$ ,  ${}^1A_{1g} \rightarrow {}^1B_{2g}$  and  ${}^1A_{1g} \rightarrow {}^1B_{3g}$  respectively. The orbital parameter,  $10Dq$  calculated to be  $18\,450\text{ cm}^{-1}$  from the in-plane  $d_{x^2-y^2} \rightarrow d_{xy}$  ( ${}^1A_{1g} \rightarrow {}^1B_{1g}$ ) transition (Gray and Ballhausen 1963) was in good agreement with the square planar geometry for  $\text{NiS}_4$  chromophores. The bands observed for the Cu(II) complex around  $15\,300$ ,  $21\,500$  and  $29\,700\text{ cm}^{-1}$ , were assigned to the  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ,  ${}^2B_{1g} \rightarrow {}^2E_g$  and charge transfer transitions respectively and were suggestive of a square planar coordination.

### 3.3 ESR spectra

The ESR spectrum of the Cr(III) derivative (figure 1) showed a broad single line (peak to peak difference =  $500\text{ G}$ ) with  $g_{av}$  value of  $1.988 \pm 0.01$ . The spin-orbit coupling constant,  $\lambda$  was calculated to be  $30\text{ cm}^{-1}$  and the large reduction from free ion value ( $92\text{ cm}^{-1}$ ) was indicative of significant metal-ligand covalency. The Fe(III) derivative showed three  $g$  values ( $g_1 = 2.45$ ,  $g_2 = 2.06$  and  $g_3 = 2.01$ ) indicating the trigonally distorted octahedral geometry. Three  $g$  values ( $g_1 = 2.12$ ,  $g_2 = 2.06$  and  $g_3 = 2.02$ ) observed for Co(II) derivatives were in agreement with those of other  $\text{CoS}_4$  systems (Gregson *et al* 1970; Fabretti *et al* 1985) suggesting a tetragonally distorted square

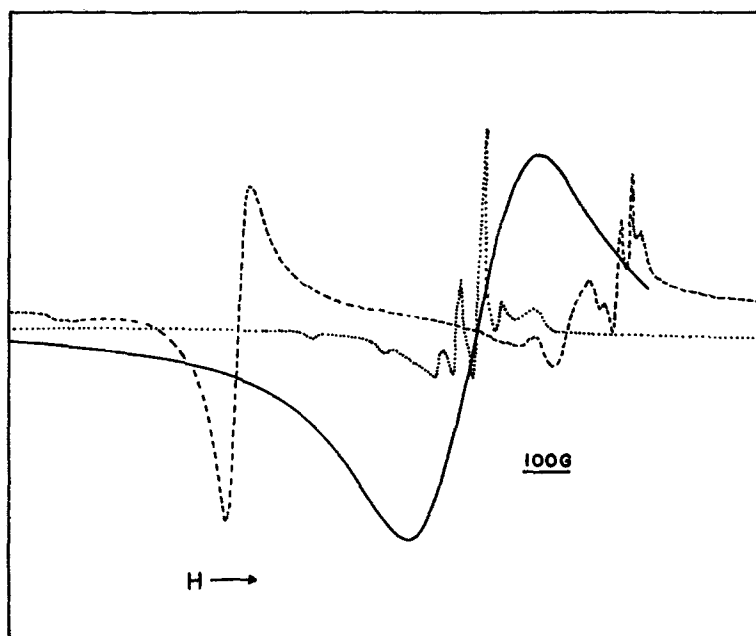


Figure 1. Solid state ESR spectrum of Cr(III) (—), Fe(III) (-----) and Cu(II) (.....) complexes at liquid nitrogen temperature.

planar geometry for the complex. The ESR spectra of Cu(II) derivatives were axial in nature with  $g_{\parallel} = 2.01$  and  $g_{\perp} = 2.067$ . The nature of the ESR spectra of the complexes were indicative of high distortion from ideal site symmetry of the complexes. This could be due to both electronic and geometric factors such as the already stated possibility of the dimeric nature of the complexes.

### 3.4 Infrared spectra

In the IR spectra of Cu(II) and Ni(II) complexes the bands at  $3200\text{--}3000$  and  $1600\text{--}1620\text{ cm}^{-1}$  were due to  $\nu\text{N-H}$  and  $\delta\text{N-H}$  respectively. The broadness of these bands in Co(II), Fe(III) and Cr(III) derivatives indicated the presence of water molecules in the complexes. The appearance of OH rocking and wagging bands around  $900 \pm 10$  and  $700 \pm 10\text{ cm}^{-1}$  for Cr(III) and Fe(III) complexes were suggestive of the presence of coordinated water (Sartori *et al* 1968). On the other hand, the presence of water molecules as lattice water in Co(II) complexes was supported by the significant weight loss corresponding to two moles of water in DTG analysis. The bands observed in the region  $1490\text{--}1520\text{ cm}^{-1}$  were characteristic thiouride bands and were assigned

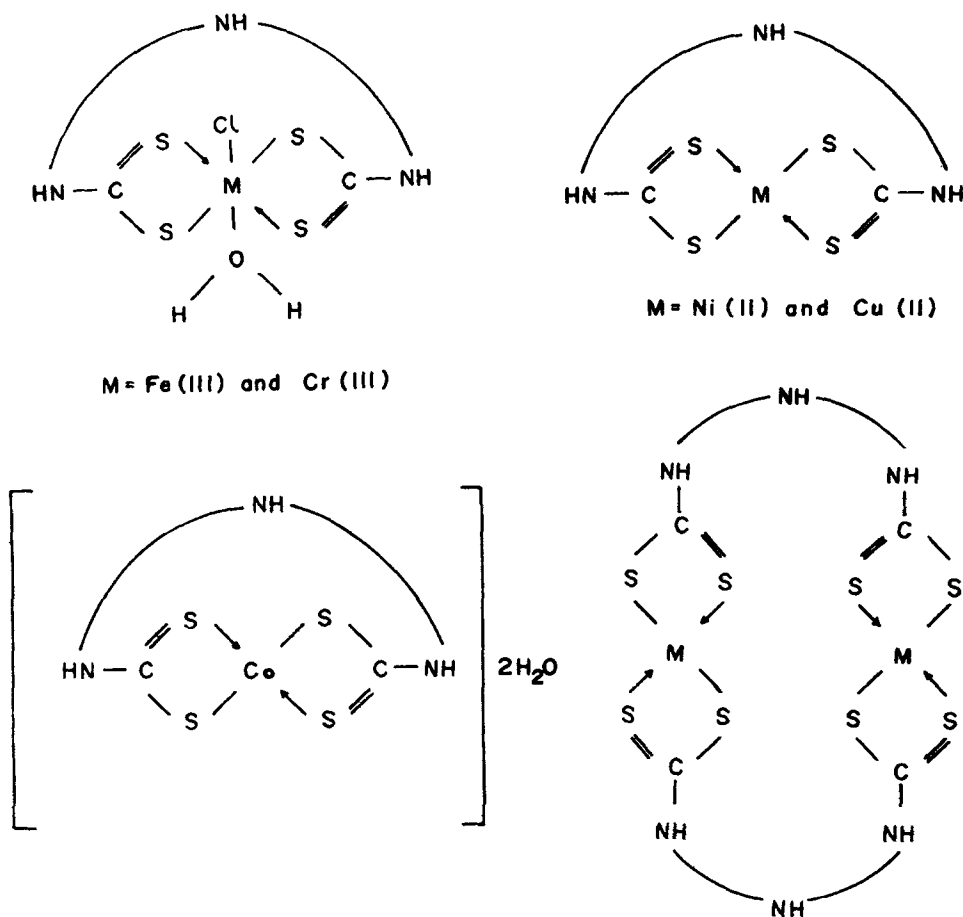


Figure 2. Proposed dimeric structures.

to  $\nu\text{C} \cdots \text{N}$ . A strong single absorption in  $995\text{--}1020\text{ cm}^{-1}$  region assigned to  $\nu\text{C} \cdots \text{S}$  was suggestive of chelating behaviour of the dithiocarbamate group (Bonati and Ugo 1967) and the quadridentate nature of the ligand. The  $\nu\text{M}\text{--S}$  vibrations were appeared in  $330\text{--}365\text{ cm}^{-1}$  region while the bands observed around the  $280\text{--}290\text{ cm}^{-1}$  region were assigned to  $\nu\text{M}\text{--Cl}$ . The structures in figure 2 may be proposed tentatively for the complexes from the above findings.

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