

**NOTE****Investigation on Transition Metal Complexes with Sulphur and Nitrogen Containing Ligand Derived from Diethylamine**

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A new series of diethylaminedithiocarbamates of transition metals has been prepared. These metal-complexes were characterized through analytical data, molar conductance and FT-IR spectral data. The most of metal-complexes were coloured. The analytical data proved the compositions  $ML_2$  for dithiocarbamates of  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $ML_3$  for those of  $Cr^{3+}$  and  $Fe^{3+}$ . All the metal-complexes were found to be non-ionic in nature. The FT-IR spectral data revealed the symmetrical coordination by the ligand in all the complexes.

**Key Words:** Transition metal complexes, Dithiocarbamates.

During past, great interest has been invoked in the study of dithiocarbamate complexes of transition metals due to their applications<sup>1-5</sup> as fungicides, pesticides, vulcanization accelerators, motor fuels, floatation agents, high pressure lubricants as well as their dual nature of coordination behaviour<sup>6</sup> to form symmetrical or asymmetrical compounds. The dialkyldithiocarbamates form complexes with a variety of transition metal which offers the scope for introducing different metals into supramolecular array. The optical and electrochemical properties of dithiocarbamate complexes can be used to construct sensors for guest molecules<sup>7,8</sup>.

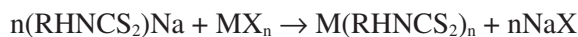
In extension of our work<sup>9-12</sup> on dithiocarbamates of transition metal ions, this communication presents the preparation and characterization of 3d transition metal dithiocarbamates derived from diethylamine. One of the most remarkable observations of this investigation was that this ligand formed four membered chelate rings during complexation with metal in all these dithiocarbamates.

Diethylamine, carbon disulphide, sodium hydroxide and salts of 3d transition metals (all E. Merck) were used as received. Solvents (all BDH) were purified by standard methods<sup>13</sup> before use.

Elemental analyses of the complexes for carbon, hydrogen and nitrogen were performed at semimicro scale by the Regional Sophisticated Instrumentation Centre (RSIC), Central Drug Research Institute (CDRI), Lucknow, India. Sulphur was estimated gravimetrically by known procedure<sup>14</sup>.

Infrared spectra in the region 4000-200  $cm^{-1}$  were recorded in Nujol mull on Perkin-Elmer Model 1620 FT-IR spectrophotometer by Jamia Millia Islamia, New Delhi, India. Conductometric measurements were done on Systronics 321 conductivity bridge.

In this work, since the sodium salts of dithiocarbamates were readily synthesized, the replacement reaction method was adopted for the synthesis. This method involves the replacement reaction of sodium salt of dithiocarbamate with the metal salt.



The sodium salts of dithiocarbamates were prepared by taking diethylamine, sodium hydroxide and carbon disulphide in 1:1:1 molar ratios, respectively. Sodium hydroxide (0.1 mol) was dissolved in 50 mL distilled water and into it 0.1 mol of diethylamine was added carefully with constant stirring. Then at 12-16 °C, 0.1 mol of carbon disulphide was added drop by drop. The stirring was continued at room temperature for about 45 min. On completion of the reaction, solid sodium diethylaminedithiocarbamate was obtained. The separated solid salt was filtered off and washed with toluene and dried at 80 °C. These salts were soluble in water. In appropriate molar ratio (1:2), the 0.01 M solutions of metal salts of the type  $\text{MCl}_2$  were added to 0.02 M aqueous solution of sodium diethylaminedithiocarbamate in distilled water at a temperature of 15-20 °C. In 1:3 molar ratio 0.01 M solutions of the metal salts of the type  $\text{MCl}_3$  were added to 0.03 M aqueous solution of sodium diethylaminedithiocarbamate. The stirring was continued for 3 h at 20 °C and then the reaction mixture was cooled to 0 °C. The precipitated solid substance was filtered, washed with ice water and dried in the air.

Dithiocarbamates derived from diethylamine and their complexes with bi- and trivalent transition metals of first series have been prepared. This method yielded compounds of high purity, which was supported by their elemental analysis. The colourless to colourful compounds were air and moisture stable at room temperature. All the metal-complexes are soluble in water, ethanol, benzene and DMF. Important

TABLE-1  
ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF  
DIETHYLAMINEDITHIOCARBAMATE COMPLEXES

Compounds (m.w.)	Yield (%)	m.p. (°C)	Colour	$\Lambda_m$ S cm <sup>2</sup> mol <sup>-1</sup>	Found (calculated) %				
					C	H	N	S	M
Na(Et <sub>2</sub> dtc) (171)	68	185	Light orange	–	35.20 (35.09)	5.90 (5.85)	8.24 (8.18)	37.34 (37.43)	–
Cr(Et <sub>2</sub> dtc) <sub>3</sub> (495.99)	69	166	Blue- green	10.2	36.53 (36.29)	6.09 (6.05)	8.35 (8.47)	38.64 (38.71)	10.39 (10.48)
Mn(Et <sub>2</sub> dtc) <sub>2</sub> (350.94)	70	170	Yellow	7.0	34.11 (34.19)	5.65 (5.70)	7.93 (7.98)	36.41 (36.47)	15.90 (15.66)
Fe(Et <sub>2</sub> dtc) <sub>3</sub> (499.85)	75	165	Dark yellow	2.1	36.17 (36.01)	5.95 (6.00)	8.43 (8.40)	38.33 (38.41)	11.12 (11.18)
Co(Et <sub>2</sub> dtc) <sub>2</sub> (354.93)	74	156	Brown	6.9	33.70 (33.81)	5.65 (5.63)	7.85 (7.89)	36.25 (36.09)	16.55 (16.58)
Ni(Et <sub>2</sub> dtc) <sub>2</sub> (354.71)	73	150	Dark green	2.4	33.69 (33.83)	5.66 (5.63)	7.92 (7.89)	36.24 (36.09)	16.49 (16.56)
Cu(Et <sub>2</sub> dtc) <sub>2</sub> (359.55)	75	159	Light brown	3.7	33.45 (33.38)	5.60 (5.56)	7.82 (7.79)	35.56 (35.60)	17.57 (17.67)
Zn(Et <sub>2</sub> dtc) <sub>2</sub> (361.37)	74	160	Colour -less	2.5	33.12 (33.21)	5.48 (5.53)	7.78 (7.75)	35.35 (35.42)	18.27 (18.09)

analytical results of the prepared complexes along with their other properties are given in the Table-1. The low molar conductance values of  $10^{-3}$  M solutions of these complexes in DMF at room temperature lying in the range 2.1 to  $10.2 \text{ S cm}^2 \text{ mol}^{-1}$  confirmed the non-ionic behaviour of all the complexes<sup>15</sup>. The monodentate or bidentate nature of dithiocarbamate group in the ligand is reflected<sup>16</sup> in the  $\nu(\text{C-S})$  stretching frequency. In the case of bidentate behaviour, a single strong band appears in the region  $1050\text{-}950 \text{ cm}^{-1}$ , while a doublet is expected in the region around  $1000 \text{ cm}^{-1}$  for the monodentate one (Table-2).

TABLE-2  
IR SPECTRAL BAND ( $\text{cm}^{-1}$ ) OF DIETHYLAMINE  
DITHIOCARBAMATE METAL COMPLEXES

Complexes	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{M-S})$
Na(Et <sub>2</sub> dtc)	1480	990	–
Cr(Et <sub>2</sub> dtc) <sub>3</sub>	1507	990	361
Mn(Et <sub>2</sub> dtc) <sub>2</sub>	1509	991	375
Fe(Et <sub>2</sub> dtc) <sub>3</sub>	1505	991	379
Co(Et <sub>2</sub> dtc) <sub>2</sub>	1520	992	365
Ni(Et <sub>2</sub> dtc) <sub>2</sub>	1522	993	387
Cu(Et <sub>2</sub> dtc) <sub>2</sub>	1508	995	356
Zn(Et <sub>2</sub> dtc) <sub>2</sub>	1505	995	380, 400

Thus the infrared spectral results of all these complexes provided the direct information about the presence of dithiocarbamate ligand and its symmetrical chelation to the metal ions through both the sulphur atoms *i.e.*, the bidentate behaviour. It is concluded that in  $\text{ML}_2$  types of complexes, the metal (M) was tetracoordinated while in  $\text{ML}_3$ , it was hexacoordinated by ligands (L) in symmetrical fashion.

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