

Research Paper :

Cr (III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II) and Zn (II) chelates with S and N containing ligand diisopropyldithiocarbamate

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ABSTRACT

The synthesis of sulphur and nitrogen containing dithiocarbamate ligand derived from diisopropylamine as well as its coordination compounds with first series transition metals has been described. These synthesized compounds were characterized through elemental analysis, conductometric measurements and IR spectral studies. The analytical data showed the stoichiometry 1:2 and 1:3 for the compounds of the types ML_2 {M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)} and $M'L_3$ {M'=Cr(III) and Fe(III)}, respectively. The conductometric measurements indicated the compounds to be non-ionic in nature. The bidentate nature of dithiocarbamate moiety was confirmed on the basis of IR spectral data.

Key words : Transition metal chelates, Dithiocarbamates, Metal complex

Dithiocarbamates the half amides of dithiocarbonic acids were discovered as a class of chemical compounds in the history of organo sulphur chemistry.^{1,2} The structures of the metal dithiocarbamate are being investigated because of (a) the fact that most of their detailed structures are unknown, (b) the theoretical interests arising from the sulphur containing four membered rings present in these compounds, (c) their biological fungitoxic activity and (d) the lack correlation between structural properties of these compounds.¹ The utilities of dithiocarbamates are several from insecticides, fungicides to therapeutic agents for alcoholism and metal intoxication.¹ They have also been reported to treat acquired immune depressive syndrome and cancer.³⁻⁵ Recently, new method for the determination of dithiocarbamate fungicidal activity has been described.⁶

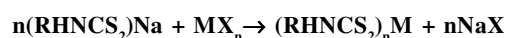
Several reports on metal complexes containing dithiocarbamates are available yet the studies on first series transition metal complexes with diisopropyldithiocarbamate are scarce. In the framework of systematic study of various dithiocarbamates,⁷⁻¹¹ we chose diisopropyldithiocarbamate complexes with main aim to explore the coordination aspects of the ligand.

MATERIALS AND METHODS

Diisopropylamine, carbon disulphide, sodium hydroxide, salts of chromium, manganese, iron, cobalt, nickel, copper and zinc (all E. Merck) were used as received. Solvents (all BDH) were purified by standard methods¹² before use. Elemental analyses of the

complexes for carbon, hydrogen and nitrogen were performed by the Regional Sophisticated Instrumentation Centre (R.S.I.C.), Central Drug Research Institute (C.D.R.I.), Lucknow (U.P.), India. Sulphur was estimated gravimetrically by known procedure.¹³ Infrared spectra in the region 4000-200 cm^{-1} were recorded in Nujol mull on Perkin Elmer Model 1620 Fourier-Transform Infrared (FT-IR) spectrophotometer by Jamia Millia Islamia University, Delhi, India. Conductometric measurements were done on Systronics 321 Conductivity Bridge.

In our work replacement reaction method was adopted for the synthesis. This method involves replacement reaction using the sodium salt of the dithiocarbamate with metal salt:



Preparation of sodium salts of dithiocarbamate:

Diisopropylamine, sodium hydroxide and carbon disulphide were taken 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 diisopropylamine was added carefully with constant stirring by means of a magnetic stirrer. 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 minutes. On completion of the reaction solid sodium diisopropyldithiocarbamate was obtained. The separated solid salts were filtered off and washed with toluene. These were dried at 80°C. These salts were soluble in water.

Preparation of complexes with transition metals:

The sodium diisopropyldithiocarbamate was used in distilled water. In appropriate molar ratio (1:2) the 0.01 M solutions of metal salts of the type MCl_2 , where $M=Mn, Co, Ni, Cu$ and Zn (1.2594 g, 1.2994 g, 1.2972 g, 1.3466 g and 1.3636 g, respectively) were added to 0.02 M aqueous solution containing 3.98 g sodium diisopropyldithiocarbamate at a temperature of 15–20°C. In 1:3 molar ratio 0.01 M solutions of the metal salts of the type M^+Cl_3 where $M^+=Cr$ and Fe (1.5850g and 1.6236 g, respectively) were added to the 0.03 M aqueous solution containing 5.97 g sodium diisopropyldithiocarbamate. The stirring was continued for 3 hours 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.

RESULTS AND DISCUSSION

There are two standard methods *viz.*, the insertion reaction method and the replacement reaction method for preparation of dithiocarbamate compounds. The second one *i.e.* the replacement reaction method throughout in the synthesis of all the compounds. This method was prepared yielded coordination compounds of high purity, which was supported by their elemental analysis (Table 1). The colourless to colourful compounds were found to be air and moisture stable at room temperature. These complexes were soluble in water, ethanol, benzene and DMF. The metal to ligand ratio for manganese, cobalt, nickel, copper and zinc was 1:2 and that for chromium and iron was 1:3. These results of elemental analysis are quite in agreement with the

proposed composition for all the complexes. The low molar conductance values of $10^{-3}M$ solutions of these complexes in DMF at room temperature lying in the range 1.9–8.2 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ confirmed the non-ionic behaviour¹⁴ of all the complexes.

The dithiocarbamate group being flexidentate ligand, can coordinate symmetrically involving both the sulphur atoms as well as unsymmetrically involving only one sulphur atom in complexation. The frequency modes $\nu(C-N)$ and $\nu(C-S)$ are diagnostic factors^{15, 16} for the nature of dithiocarbamate moiety whether it is acting as monodentate or bidentate. The IR spectra of solid complexes showed well-resolved and sharp bands (Table 2). The $\nu(C-N)$ stretching frequency appeared in the wave number range 1440–1503 cm^{-1} . Then (C-S) frequency was observed in the region 943–956 cm^{-1} .

In all the complexes studied, only one sharp and unsplit band occurred in the region 943–956 cm^{-1} . Therefore, the symmetrical coordination through both the sulphur atoms *i.e.* bidentate nature of dithiocarbamate moiety has been concluded. The $\nu(M-S)$ stretching frequency was observed in the range 376–410 cm^{-1} .

Conclusion:

The infrared spectral results of all these complexes showed the presence of bidentate dithiocarbamate ligand and its symmetrical chelation to the metal ions through both the sulphur atoms forming four membered chelate rings. Furthermore in ML_2 types of complexes, the metal (M) was tetracoordinated while in M^+L_3 , it was hexacoordinated by bidentate ligand (L) in symmetrical fashion.

Table 1 : Analytical data and other physical properties of diisopropyldithiocarbamate complexes

Compounds (Formula Wt.)	Yield (%)	M.P. (°C)	Colour	Λ_m $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	Found (calculated)%				
					C	H	N	S	M
1. Na(iPr ₂ dtc) (199)	65	170	Light yellow	----	42.35 (42.21)	7.09 (7.04)	7.09 (7.04)	32.08 (32.16)	-----
2. Cr(iPr ₂ dtc) ₃ (579.99)	69	156	Green	2.41	43.34 (43.46)	7.20 (7.24)	7.19 (7.24)	33.37 (33.10)	8.90 (8.96)
3. Mn(iPr ₂ dtc) ₂ (406.94)	68	165	Light orange	1.90	41.20 (41.29)	6.92 (6.88)	6.93 (6.88)	31.36 (31.45)	13.59 (13.50)
4. Fe(iPr ₂ dtc) ₃ (583.85)	66	163	Brown	2.67	43.10 (43.20)	7.15 (7.18)	7.14 (7.18)	33.02 (32.88)	9.59 (9.56)
5. Co(iPr ₂ dtc) ₂ (410.93)	65	175	Black	5.19	40.75 (40.89)	6.76 (6.81)	6.78 (6.81)	31.20 (31.15)	14.51 (14.34)
6. Ni(iPr ₂ dtc) ₂ (410.71)	64	173	Green	8.20	40.85 (40.91)	6.85 (6.81)	6.84 (6.81)	31.11 (31.18)	14.35 (14.29)
7. Cu(iPr ₂ dtc) ₂ (413.55)	65	170	Black	4.89	40.83 (40.63)	6.71 (6.77)	6.70 (6.77)	30.81 (30.95)	14.95 (14.88)
8. Zn(iPr ₂ dtc) ₂ (415.37)	69	163	Colourless	2.89	40.65 (40.44)	6.70 (6.74)	6.71 (6.74)	30.74 (30.82)	15.20 (15.26)

Table 2 : IR spectral data of diisopropyldithiocarbamate complexes

Complexes	$\nu(\text{C-N}) \text{ cm}^{-1}$	$\nu(\text{C-S}) \text{ cm}^{-1}$	$\nu(\text{M-S}) \text{ cm}^{-1}$
1. Na(iPr ₂ dtc)	1440	945	---
2. Cr(iPr ₂ dtc) ₃	1483	952	381
3. Mn(iPr ₂ dtc) ₂	1480	953	385
4. Fe(iPr ₂ dtc) ₃	1485	956	392
5. Co(iPr ₂ dtc) ₂	1480	947	397
6. Ni(iPr ₂ dtc) ₂	1503	945	402
7. Cu(iPr ₂ dtc) ₂	1495	943	376
8. Zn(iPr ₂ dtc) ₂	1485	945	395,410

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REFERENCES

1. **Thorn, G.D.** and Ludwig, R.A. (1962). *The dithiocarbamates and Related compounds*, New York.
2. **Schweitzer, P.A.**, Leslie, P.E. and Rudnick, R. (2003). *Lubricant additive chemistry and applications*, pp. 241.
3. **Reisinger, E.C.**, Kern, P., Ernst, M., Bock, P., Flad, H.D. and Dietrich, M. (1990). Inhibition of HIV Progression by Dithiocarb. German DTC Study Group, Lancet, 335, 679.
4. **Gandara, D.R.**, Perez, E.A., Weibe, V. and Gregorio, M.W. De (1991). *Semin. Oncol.*, **18**: 49.
5. **Kim, C.H.**, Kim, J.H., Xu, J., Hsu, C.Y. and Ahn, Y.S. (1999). Blackwell synergy. *J. Neurochem*, **72**: 1586.
6. **Singh, B.K.**, Kumar, V., Upadhyay, R. and Shukla, I.C. (2009). *Orient J. Chem.*, **25**(1): 169.
7. **Tarique, M.** and Aslam, M. (2008). *Orient. J. Chem.*, **24**(1): 267.
8. **Tarique, M.** and Aslam, M. (200). *Biosci. Biotec. Res. Asia*, **5**(1): 355.
9. **Tarique, M.** and Aslam, M. (2008). *Biosci. Biotec. Res. Asia*, **5**(2): 833.
10. **Tarique, M.** and Aslam, M. (2008). *Acta Ciencia Indica*, **34** (4): 635.
11. **Tarique, M.** and Aslam, M. (2009). *Orient. J. Chem.*, **25**(1): 207.
12. **Vogel, A.I.** (1968). *A Text Book of Practical Organic Chemistry*, (ELBS and Longmans, London).
13. **Vogel, A. I.** (1960). *A Text Book of Quantitative Inorganic Analysis*, Ed III (ELBS and Longmans, London).
14. **Geary, W. J.** (1971). *Coord. Chem. Rev.*, **7**: 81.
15. **Hulanicki, A.** (1967). *Talanta*, **14**: 1371.
16. **O'Connor, C.**, Gilbert, J. D. and Wilkinson, G. (1969). *J. Chem. Soc.*, **A**, 1398.

