



Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Diisobutyldithiocarbamate Ligand

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Abstract: The synthesis of sulphur and nitrogen containing dithiocarbamate ligand derived from diisobutylamine as well as its coordination compounds with 3d series transition metals is presented. These synthesized compounds were characterized on the basis of 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 proved the non-electrolytic behaviour of all the compounds. The bidentate nature of dithiocarbamate moiety was confirmed on the basis of IR spectral data.

Keywords: Coordination complexes, Dithiocarbamates, Transition metals

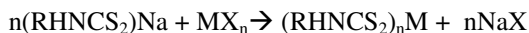
Introduction

Study of metal complexes has been of great importance. Versatile coordination behaviour of biologically active dithiocarbamate ligand has been interesting aspect in the development of coordination chemistry¹⁻³. The chemistry of transition metal-sulphur compounds has attracted much interest for their importance in the field of metalloenzymes, material precursors and catalysts. *N,N*-disubstituted dithiocarbamates are among the more frequently considered sulphur containing ligands that have been studied for the past several years^{4,6}. Recently 1:1 adducts of bis(*N,N*-diethyldithio-carbamato)oxovanadium(IV) with substituted pyridine have been studied⁷.

Although the reports on metal complexes containing dithiocarbamates are extensive, the studies on 3d series transition metal complexes with diisobutyldithiocarbamate are scarce. In the framework of systematic study of various dithiocarbamates⁸⁻¹⁷, it was decided to study the diisobutyldithiocarbamate complexes with special reference to the coordination behaviour of the ligand.

Experimental

Diisobutylamine, 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 methods¹⁸ 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 procedure¹⁹. Infrared spectra in the region 4000-200 cm⁻¹ were recorded in KBr 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 the present 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

Diisobutylamine, 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 diisobutylamine 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 dithiocarbamate 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 dithiocarbamate was used in distilled water. In appropriate molar ratio (1:2) the 0.01 M solutions of metal salts of the type MCl₂, 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 4.54 g sodium diisobutyldithiocarbamate at a temperature of 15-20 °C. In 1:3 molar ratio 0.01 M solutions of the metal salts of the type M'Cl₃ where M'=Cr and Fe (1.5850 g and 1.6236 g respectively) were added to the 0.03 M aqueous solution containing 6.81 g sodium diisobutyldithiocarbamate. 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.

Results and Discussion

Out of the two standard methods *viz.* the insertion reaction method and the replacement reaction method, the second one *i.e.* the replacement reaction method was used throughout in the synthesis of all the compounds. This method yielded coordination compounds of high purity, which was supported by their elemental analysis (Table 1). The colourless to colourful compounds were 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 1.78-4.88 ohm⁻¹cm²mol⁻¹ confirmed the non-ionic behaviour²⁰ of all the complexes.

Table 1. Analytical data and other physical properties of diisobutyldithiocarbamate complexes

Compounds (Formula wt.)	Yield, %	M.P., °C	Colour	Λ_m ohm ⁻¹ cm ² mol ⁻¹	Found (calculated)%				
					C	H	N	S	M
Na(iBu ₂ dtc) (227)	56	158	Cream	----	47.47 (47.58)	7.96 (7.93)	6.15 (6.17)	28.26 (28.19)	-----
Cr(iBu ₂ dtc) ₃ (663.99)	57	160	Blue	1.78	48.87 (48.79)	8.18 (8.13)	6.36 (6.33)	28.79 (28.92)	7.80 (7.83)
Mn(iBu ₂ dtc) ₂ (462.94)	54	159	Grey	2.67	46.88 (46.65)	7.74 (7.78)	6.01 (6.05)	27.55 (27.65)	11.82 (11.87)
Fe(iBu ₂ dtc) ₃ (667.85)	58	165	Light brown	3.22	48.40 (48.51)	8.13 (8.08)	6.24 (6.29)	28.93 (28.76)	8.30 (8.36)
Co(iBu ₂ dtc) ₂ (466.93)	60	180	Blue green	4.88	46.10 (46.26)	7.75 (7.71)	6.05 (6.00)	27.54 (27.41)	12.56 (12.62)
Ni(iBu ₂ dtc) ₂ (466.71)	65	155	Light green	1.90	46.16 (46.28)	7.76 (7.71)	6.06 (6.00)	27.50 (27.43)	12.52 (12.58)
Cu(iBu ₂ dtc) ₂ (471.55)	64	170	Blue- green	2.67	45.95 (45.80)	7.66 (7.63)	5.90 (5.94)	27.09 (27.15)	13.40 (13.48)
Zn(iBu ₂ dtc) ₂ (473.37)	63	166	Colour- less	1.78	45.52 (45.63)	7.63 (7.61)	5.95 (5.92)	27.15 (27.04)	13.75 (13.80)

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 $\nu(\text{C-N})$ and $\nu(\text{C-S})$ are diagnostic factors^{21,22} 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 (Tables 2). The $\nu(\text{C-N})$ stretching frequency appeared in the wave number range 1470-1520 cm⁻¹. The $\nu(\text{C-S})$ stretching frequency was observed in the region 980-987 cm⁻¹.

Table 2. IR spectral data of diisobutyldithiocarbamate complexes

Complexes	$\nu(\text{C-N})$ cm ⁻¹	$\nu(\text{C-S})$ cm ⁻¹	$\nu(\text{M-S})$ cm ⁻¹
Na(iBu ₂ dtc)	1470	980	----
Cr(iBu ₂ dtc) ₃	1520	981	391
Mn(iBu ₂ dtc) ₂	1520	982	395
Fe(iBu ₂ dtc) ₃	1515	982	389
Co(iBu ₂ dtc) ₂	1510	983	396
Ni(iBu ₂ dtc) ₂	1508	985	391
Cu(iBu ₂ dtc) ₂	1505	985	386
Zn(iBu ₂ dtc) ₂	1485	987	390

In all the complexes studied only one sharp and unsplit band occurred in the region 980-987 cm⁻¹, therefore the symmetrical coordination through both the sulphur atoms *i.e.* bidentate nature of dithiocarbamate moiety has been concluded. The $\nu(\text{M-S})$ stretching frequency was observed in the range 386-396 cm⁻¹.

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 forming four membered chelate rings. With respect to all experimental

facts it was concluded that 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.

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