

Studies on coordination compounds of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with butyldithiocarbamate ligand

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ABSTRACT

Some new coordination compounds of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with butyldithiocarbamate ligand have been synthesised satisfactorily by substitution reaction method in good yield. The characterization of newly synthesized compounds has been performed on the basis of elemental analyses, molar conductance and FT-IR spectroscopy. All the colourless to colourful complexes were inert to atmospheric oxygen and moisture at room temperature. The analytical data indicated the composition ML_2 for the chelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and $M'L_3$ for those of Cr(III) and Fe(III). These complexes were observed to be non-ionic in nature. These observations revealed the symmetrical coordination by the bidentate ligand forming four membered ring.

Key words : Dithiocarbamates, Transition metals, Coordination compounds

The dithiocarbamate core, $M-S_2CNR_2$, could prove to be of great synthetic utility in radio pharmacology as a wide variety of organic substituents can be incorporated in the stable bidentate ligand.¹ In some cases the bidentate anion also acts as a bridge between two transition metal centres.² In recent years, the study of transition metal complexes of substituted dithiocarbamates has been a subject of considerable interest because of their structural, magnetic, electrochemical and thermal properties. Some noble work has also been done on the formation of mixed ligand dithiocarbamates of metals and mixed heterocyclic ligand dithiocarbamates.^{3,4} The coordination chemistry of transition metal ions and Group (IV) metals with several new dithiocarbamate ligands derived from heterocyclic bases has also been explored by many chemists.⁵⁻⁷ The synthesis of acyclic and macrocyclic transition metal dithiocarbamate complexes containing positively charged imidazolium moieties has been reported.⁸

Due to the interest in the study of sulphur and nitrogen containing ligands⁹⁻¹³ this communication describes the preparation and characterization of complexes of first row transition metals with butyldithiocarbamate with the goal to observe the coordination behaviour of the dithiocarbamate moiety and some other physico-chemical characteristics of these complexes.

MATERIALS AND METHODS

Butylamine, carbon disulphide, sodium hydroxide, salts of first row transition metals (all E. Merck) were used as received. Solvents (all BDH) were purified by

standard methods¹⁴ before use. Elemental analyses of the complexes for carbon, hydrogen and nitrogen were done 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.¹⁵ Infrared spectra in the region $4000-200\text{ cm}^{-1}$ were recorded in Nujol mull on Perkin Elmer Model 1620 FT-IR spectrophotometer by Jamia Millia Islamia University, New Delhi, India. Conductometric measurements were done on Systronics 321 Conductivity Bridge.

The metal dithiocarbamate complexes may be synthesized either by insertion reaction method or by substitution reaction method. In the present work the second method was adopted for the synthesis.

Butylamine, 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 of Butylamine, was added carefully with constant stirring by means of a magnetic stirrer. 0.1 mol of carbon disulphide was then added drop by drop keeping the temperature, $12-16^\circ\text{C}$. The stirring was continued at room temperature for about 45 minutes. On completion of the reaction solid sodium butyldithiocarbamate was obtained. The separated solid salt was filtered off and washed with toluene. It was dried at 80°C . This salt was soluble in water.

In appropriate molar ratio (1:2), the 0.01 M solutions of metal salts of the type MCl_2 were added to 0.02 M aqueous solution of sodium butyldithiocarbamate dissolved in distilled water at 20°C . In 1:3 molar ratio, 0.01 M

solutions of the metal salts of the type $M'Cl_3$ were added to the 0.03 M solutions of sodium butyldithiocarbamate. 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

Dithiocarbamates derived from butylamine and its complexes with bi and trivalent transition metals of first row were prepared. The substitution reaction method yielded compounds of high purity, which was supported by analytical data (Table 1). The colourless to colourful compounds were air and moisture stable at room

cm^2mol^{-1} confirmed the non-electrolytic behaviour¹⁶ of all the complexes.

The monodentate or bidentate nature of dithiocarbamate group in the ligand is reflected¹⁷ in the $\nu(C-S)$ stretching frequency. In the case of bidentate behaviour, a single strong band appears in the region 950-1050 cm^{-1} , while a doublet is expected in the region around 1000 cm^{-1} for the monodentate one.

According to Chatt *et al.*¹⁸ the infrared spectra of alkyl dithiocarbamates should exhibit a strong band between (1480-1550 cm^{-1}) assigned to polar S_2C-N stretching frequency. This frequency lies intermediate to those associated with the C-N single bond (1250-1350 cm^{-1}) and C=N double bond (1640-1690 cm^{-1}) indicating

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

Compounds (Formula Wt.)	Yield (%)	M.P. (°C)	Colour	Λ_m $ohm^{-1}cm^2mol^{-1}$	Found (calculated)%				
					C	H	N	S	M
1. Na(Bu dtc) (171)	76	156	Colourless	----	35.16 (35.09)	5.89 (5.85)	8.10 (8.19)	37.35 (37.42)	----
2. Cr(Bu dtc) ₃ (495.99)	66	176	Blue	2.86	36.19 (36.29)	6.07 (6.05)	8.51 (8.47)	38.60 (38.71)	10.63 (10.48)
3. Mn(Bu dtc) ₂ (350.94)	68	158	Cream	3.44	34.31 (34.19)	5.75 (5.70)	7.92 (7.98)	36.33 (36.47)	15.69 (15.66)
4. Fe(Bu dtc) ₃ (499.85)	58	165	Light brown	1.29	36.19 (36.01)	5.95 (6.00)	8.35 (8.40)	38.28 (38.42)	11.23 (11.17)
5. Co(Bu dtc) ₂ (354.93)	75	163	Black	0.02	33.73 (33.81)	5.66 (5.63)	7.94 (7.89)	35.97 (36.07)	16.70 (16.60)
6. Ni(Bu dtc) ₂ (354.71)	68	172	Dark green	9.07	33.95 (33.83)	5.62 (5.64)	7.86 (7.89)	35.96 (36.09)	16.61 (16.55)
7. Cu(Bu dtc) ₂ (359.55)	67	170	Green- blue	8.90	33.25 (33.38)	5.52 (5.56)	7.75 (7.79)	35.76 (35.60)	17.72 (17.67)
8. Zn(Bu dtc) ₂ (361.37)	76	169	Colourless	7.49	33.09 (33.21)	5.58 (5.53)	7.80 (7.75)	35.30 (35.42)	18.23 (18.09)

temperature. These complexes were soluble in water, ethanol, benzene and DMF. The low molar conductance values of $10^{-3}M$ solutions of these complexes in DMF at room temperature lying in the range 0.02 to 9.07 $ohm^{-1}cm^2mol^{-1}$

partial double bond character of the thioureide bond.

The IR spectra of solid complexes showed well-resolved and sharp bands (Table 2). In present study, the bands observed in the wave number range 1490-1515 cm^{-1} , 1000-1010 cm^{-1} and 450-465 cm^{-1} were clearly attributable to $\nu(C-N)$, $\nu(C-S)$ and $\nu(M-S)$, respectively.

Table 2 : IR spectral data of butyldithiocarbamate complexes

Complexes	$\nu(C-N) cm^{-1}$	$\nu(C-S) cm^{-1}$	$\nu(M-S) cm^{-1}$
1. Na(Bu dtc)	1490	1000	---
2. Cr(Bu dtc) ₃	1495	1003	456
3. Mn(Bu dtc) ₂	1500	1005	450
4. Fe(Bu dtc) ₃	1510	1001	453
5. Co(Bu dtc) ₂	1512	1010	465
6. Ni(Bu dtc) ₂	1505	1007	460
7. Cu(Bu dtc) ₂	1515	1008	460
8. Zn(Bu dtc) ₂	1503	1009	462

Conclusion:

In view of all these experimental facts, we could conclude that this dithiocarbamate ligand showing bidentate nature, formed four membered chelate rings in complexation with metals. The metal(M) was tetraordinated in ML_2 type chelates and in $M'L_3$ type, it was hexacoordinated.

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