

Coordination Aspects of Dimethyldithiocarbamate Ligand towards the First Series Transition Metal Ions

MOHAMMAD TARIQUE

Department of Chemistry, B.I.T.S. Masuri, Ghaziabad (U.P.)-201302, India
mohammadtarique0@gmail.com

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Abstract: A series of chelates of first series transition metals with dimethyldithiocarbamate has been prepared. Physicochemical characterization of these chelates was done with the help of analytical data, 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. The FT-IR spectral data revealed the symmetrical coordination by the ligand.

Keywords: Dithiocarbamates, Transition metal chelates, Coordination aspects, Metal ions

Introduction

Carbon disulphide, proved to be a versatile ligand¹ greater tendency to react with various amines resulting the formation of an important class of compounds known as dithiocarbamates. Apart from their application in industry and agriculture, dithiocarbamates have achieved much more academic interest owing to their synthetic flexibility and dual nature of acting as monodentate as well as chelating ligand. The literature shows that the alkyl, haloalkyl, cycloalkyl, phenyl, benzyl, pyridyl, aniline, pyrrolidine, indole, indoline and carbazole dithiocarbamates together with their derivatives have been synthesized and studied in detail²⁻⁸.

Due to the interest in the study of sulphur and nitrogen containing ligands⁹⁻¹⁹, this communication describes the preparation and characterization of complexes of first row transition metals with dimethyldithiocarbamate with the aim to observe the coordination behaviour of the dithiocarbamate moiety and some other physicochemical characteristics of these complexes.

Experimental

Dimethylamine, carbon disulphide, sodium hydroxide, salts of first row transition metals (all E. Merck) were used as received. Solvents (all BDH) were purified by standard methods²⁰ 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 procedure²¹.

Infrared spectra in the region 4000-200 cm^{-1} were recorded in KBr 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 replacement reaction method. In the present work the second was adopted for the synthesis.

Dimethylamine, 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 dimethylamine 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 °C. The stirring was continued at room temperature for about 45 minutes. On completion of the reaction solid sodium dimethyldithiocarbamate 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 dimethyldithiocarbamate 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 dimethyldithiocarbamate. 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

The replacement 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 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 6.03 to 10.87 $\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$ confirmed the non-electrolytic behaviour²² of all the complexes.

Table 1. Analytical data and other physical properties of dimethyldithiocarbamate

Compounds (Formula Wt.)	Yield, %	M.P. °C	Colour	Λ_m $\text{ohm}^{-1}\text{cm}^2\text{mol}$	Found (calculated)%				
					C	H	N	S	M
1. Na(Me ₂ dtc) (143)	68	165	Orange	----	25.11 (25.17)	4.17 (4.20)	9.83 (9.79)	44.85 (44.76)	-----
2. Cr(Me ₂ dtc) ₃ (411.99)	70	156	Green	8.75	26.42 (26.26)	4.33 (4.36)	10.15 (10.19)	46.45 (46.58)	12.65 (12.61)
3. Mn(Me ₂ dtc) ₂ (294.94)	71	173	Light yellow	10.87	24.32 (24.41)	4.08 (4.06)	9.55 (9.49)	43.29 (43.41)	18.76 (18.63)
4. Fe(Me ₂ dtc) ₃ (415.85)	69	180	Dark brown	9.87	25.88 (25.97)	4.37 (4.33)	10.17 (10.10)	46.08 (46.17)	13.50 (13.43)
5. Co(Me ₂ dtc) ₂ (298.93)	73	181	Light green	7.30	24.28 (24.09)	4.03 (4.01)	9.33 (9.37)	42.71 (42.82)	19.65 (19.71)
6. Ni(Me ₂ dtc) ₂ (298.71)	67	342	Green	7.83	24.01 (24.11)	3.99 (4.01)	9.40 (9.37)	42.78 (42.86)	19.82 (19.65)
7. Cu(Me ₂ dtc) ₂ (303.55)	65	169	Brown	10.23	23.61 (23.72)	3.97 (3.95)	9.18 (9.22)	42.39 (42.17)	20.85 (20.94)
8. Zn(Me ₂ dtc) ₂ (305.37)	72	160	Colourless	6.03	23.49 (23.58)	3.91 (3.93)	9.21 (9.17)	42.04 (41.91)	21.35 (21.41)

The monodentate or bidentate nature of dithiocarbamate group in the ligand is reflected²³ in the $\nu(\text{C-S})$ stretching frequency. In the case of bidentate behaviour, a single strong band appears in the region $950\text{-}1050\text{ cm}^{-1}$, while a doublet is expected in the region around 1000 cm^{-1} for the monodentate one.

The IR spectra of solid complexes showed well-resolved and sharp bands (Table 2). The bands observed in the wave number range $1485\text{-}1496\text{ cm}^{-1}$, $1002\text{-}1010\text{ cm}^{-1}$ and $473\text{-}480\text{ cm}^{-1}$ were clearly attributable to $\nu(\text{C-N})$, $\nu(\text{C-S})$ and $\nu(\text{M-S})$ respectively.

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 observed to be tetracoordinated in ML_2 type chelates and in $\text{M}'\text{L}_3$ type, it was hexacoordinated.

Table 2. IR spectral data of dimethyldithiocarbamate complexes

Complexes	$\nu(\text{C-N})\text{ cm}^{-1}$	$\nu(\text{C-S})\text{ cm}^{-1}$	$\nu(\text{M-S})\text{ cm}^{-1}$
1. $\text{Na}(\text{Me}_2\text{ dtc})$	1490	989	---
2. $\text{Cr}(\text{Me}_2\text{ dtc})_3$	1495	970	380
3. $\text{Mn}(\text{Me}_2\text{ dtc})_2$	1494	972	350
4. $\text{Fe}(\text{Me}_2\text{ dtc})_3$	1502	970	366
5. $\text{Co}(\text{Me}_2\text{ dtc})_2$	1510	975	371
6. $\text{Ni}(\text{Me}_2\text{ dtc})_2$	1532	974	384
7. $\text{Cu}(\text{Me}_2\text{ dtc})_2$	1528	976	352
8. $\text{Zn}(\text{Me}_2\text{ dtc})_2$	1525	975	379

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