



Advances in the coordination chemistry of transition metal compounds applying nitrogen and sulphur containing ligand : Synthesis, Structural and properties consideration.

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Abstract: This paper deals with the synthesis of sulphur and nitrogen containing dithiocarbamate ligand derived from 2-naphthylamine as well as its coordination compounds with d-block metals of first series. Characterization of these compounds was made 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 FT-IR spectral data.

Keywords: Transition metal chelates, Dithiocarbamates, IR and conductance.

1. Introduction

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, biological and thermal properties. Some noble work has also been done on the formation of mixed ligand dithiocarbamates of metals and mixed heterocyclic ligand dithiocarbamates.^{1,2} The coordination chemistry of transition metal ions and Group (IV) metals with several new dithiocarbamate ligands derived from heterocyclic bases has also been explored³⁻⁵ by many chemists. The synthesis of acyclic and macrocyclic transition metal dithiocarbamate complexes containing positively charged imidazolium moieties has been reported.⁶ In extension of the previous study⁷⁻¹⁸ of sulphur and nitrogen containing ligands, this communication deals with the synthesis and characterization of coordination compounds of d-block metals of first series with dithiocarbamate ligand derived from 2-naphthylamine for observing the coordination behaviour of the dithiocarbamate moiety as well as some other physicochemical properties of these compounds.

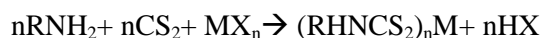
2. Experimental Details

2-naphthylamine, carbon disulphide, sodium hydroxide, salts of chromium, manganese, iron, cobalt, nickel, copper and zinc (all E. Merck) were used as received. Solvents (DMF and nitrobenzene) (all BDH) were purified by standard methods¹⁹ before use. Elemental analyses of the complexes for carbon, hydrogen and nitrogen were performed at semimicro scale 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.²⁰

Infrared spectra in the region $4000-200\text{ cm}^{-1}$ were recorded in Nujol mull on Perkin Elmer Model 1620 Fourier-Transform Infrared (FT-IR) spectrophotometer. Conductometric measurements were done on Systronics 321 Conductivity Bridge.

The metal dithiocarbamate complexes may be synthesized by one of the following standard and reliable methods:²¹

(a) Insertion Reaction Method: This method involves direct insertion of a $-CS_2$ group in the presence of an amine and the metal salt (MX_n where $n=2$ or 3).



(b) Replacement Reaction Method: This method involves replacement reaction using the sodium salt of the dithiocarbamate with metal salt.



In this research work, since the sodium salts of dithiocarbamate of 2-naphthylamine were readily synthesized, the second method viz. replacement reaction method was adopted for the synthesis. Amine, carbon disulphide and sodium hydroxide were taken in 1:1:1 molar ratios respectively. To an ethanolic 0.1 M solutions of amine (14.3 gm 2-naphthylamine), carbon disulphide (0.1 mol, 6.03 ml) and aqueous solution of sodium hydroxide (0.1 mol, 4.0 gm) were added drop-wise with continuous stirring. The reaction mixture was stirred for about an hour. On completion of the reaction, sodium dithiocarbamate of 2-naphthylamine was obtained. This was soluble in DMF.

The metal dithiocarbamate was synthesized as follows: In a molar ratio 1:2, the 0.01 M solutions of metal salts (1.2594 gm $MnCl_2$, 1.2994 gm $CoCl_2$, 1.2972 gm $NiCl_2$, 1.3466 gm $CuCl_2$ and 1.3636 gm $ZnCl_2$) were added to sodium dithiocarbamate dissolved in DMF (4.82 gm sodium 2-naphthylamine dithiocarbamate) at room temperature. In a molar ratio 1:3, 0.01 M solutions of metal salts (1.5850 gm $CrCl_3$ and 1.6234 gm $FeCl_3$) were added to 0.03 M solutions of sodium dithiocarbamates of corresponding amines (7.23 gm sodium 2-naphthylamine dithiocarbamate). The reaction mixture was stirred for one hour. The crystalline solid thus formed was washed with diethyl ether and dried in air.

3. Results and Discussion

The replacement reaction method was used throughout in the synthesis of all the compounds. This method yielded compounds of high purity, which was supported by their elemental analysis (Tables:1). The colourful compounds were air and moisture stable at room temperature. These complexes were found to have melting points ranging from 202 to 290°C. The metal to ligand ratio for manganese, cobalt, nickel, copper and zinc was 1:2 and that for chromium and iron was 1:3. The molar conductivity value should be 65-90 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ for 1:1 electrolytes.²² The low molar conductance values of 10^{-3}M solutions of these complexes in DMF at room temperature lying in the range 0.0178 to 0.0897 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ confirmed the non-electrolytic behaviour of all the complexes. The conductances of Cu(II) complexes of 2-naphthylamine could not be measured due to their very low solubility in nitrobenzene.

The evidence regarding bonding and structures of these complexes has been deduced after thoroughly examining the observed frequencies characteristic of dithiocarbamate group in their infrared spectra. The IR spectra of solid complexes (Table2) showed well-resolved and sharp bands. The characteristic frequencies arising from dithiocarbamates can be examined by comparing the observed spectra reported for the free dithiocarbamate ion (dithiocarbamic acid) and those of complexes. The free dithiocarbamate ion, as it exists in ionic compound, is expected to show IR active fundamental bands. It is expected that if there exists an increased cation-anion interaction in these dithiocarbamates, as has been observed in covalent compounds, the vibrational frequencies are very much affected and undergo a positive shift.

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 for the nature of dithiocarbamate moiety whether it is acting as monodentate or bidentate.

The monodentate or bidentate nature of dithiocarbamate group in the ligand is reflected^{23,24} in the $\nu(\text{C-S})$ 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.

It is further reflected¹ that the strong band appearing near 1500 cm^{-1} in the infrared spectra of the ligand can be assigned to the thioureide group, $\text{S}=\text{C}-\text{N}$. The energy of this band lies intermediate to the stretching frequency associated with C-N bond (1250-1350 cm^{-1}) and C=N bond (1640-1690 cm^{-1}) and can best be explained²⁵ as a vibration of a polar $\text{C}=\text{N}^+$ bond. Thus the thioureide band near 1500 cm^{-1} implies a considerable double bond character in the $\text{SC-NRR}'$ bond. In general, $\nu(\text{C-N})$ frequency shows a blue shift in the complexes as compared to the respective dithiocarbamate ligand as compared to the respective dithiocarbamate ligands, if the dithiocarbamate group behaves as a bidentate ligand. For a monodentate dithiocarbamate moiety, this frequency should exhibit either no change in position or undergo a red shift with respect to the corresponding free ligand frequency.

The $\nu(\text{C-N})$ frequency in these complexes occurred in the region 1440-1475 cm^{-1} .

Since these frequency modes lie in between those associated with single C-N and double C=N bonds hence the partial double bond character of thioureide bond was confirmed²⁶ for all the complexes studied.

The $\nu(\text{C-S})$ mode for these complexes was observed in the region 950-1020 cm^{-1} .

The absorption bands occurring in the wave number range 420-480 cm^{-1} for these complexes were attributed to $\nu(\text{M-S})$ stretching frequency.

In the light of all these experimental data as well as theoretical facts it could be concluded that this dithiocarbamate ligand showing bidentate nature, formed four membered chelate rings in complexation with metals. The metal(M) was observed to be tetraordinated in ML_2 type chelates and in $\text{M}'\text{L}_3$ type, it was hexacoordinated.

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Table-1: Analytical data and other physical properties of 2-naphthylamine dithiocarbamate compounds

Compounds (Formula Wt.)	Yield (%)	M.P. ($^{\circ}\text{C}$)	Colour	Δ_m $\frac{\text{ohm}^{-1}}{\text{cm}^2\text{mol}^{-1}}$	Found (calculated)%				
					C	H	N	S	M
1. Na(2-NA dtc) (241)	62	290	Light violet	----	54.62 (54.77)	3.33 (3.31)	5.85 (5.80)	26.48 (26.55)	-----
2. Cr(2-NA dtc) ₃ (705.99)	59	210	Green	0.0267	56.27 (56.09)	3.37 (3.40)	5.90 (5.95)	27.18 (27.20)	7.28 (7.36)
3. Mn(2-NA dtc) ₂ (490.94)	69	204	Grey	0.0897	53.65 (53.78)	3.22 (3.26)	5.65 (5.70)	26.25 (26.07)	11.23 (11.19)
4. Fe(2-NA dtc) ₃ (709.85)	65	230	Brown	0.0347	55.97 (55.79)	3.35 (3.38)	5.87 (5.92)	26.99 (27.05)	7.82 (7.86)
5. Co(2-NA dtc) ₂ (494.93)	62	202	Black	0.0178	53.41 (53.35)	3.27 (3.23)	5.69 (5.66)	25.78 (25.86)	11.85 (11.90)
6. Ni(2-NA dtc) ₂ (494.71)	66	220	Dark	0.0324	53.27 (53.38)	3.26 (3.23)	5.67 (5.65)	25.99 (25.88)	11.81 (11.86)
7. Cu(2-NA dtc) ₂ (499.55)	72	270	green Reddish-	----	53.06 (52.85)	3.17 (3.20)	5.55 (5.61)	25.57 (25.62)	12.65 (12.72)
8. Zn(2-NA dtc) ₂ (501.37)	70	210	brown Grey	0.0457	52.50 (52.66)	3.22 (3.19)	5.54 (5.58)	25.65 (25.53)	13.09 (13.04)

Table-2: IR spectral data of 2-naphthylamine dithiocarbamate compounds

Complexes	$\nu(\text{C-N}) \text{ cm}^{-1}$	$\nu(\text{C-S}) \text{ cm}^{-1}$	$\nu(\text{M-S}) \text{ cm}^{-1}$
1. Na(2-NA dtc)	1460 (s)	1005 (s)	-----
2. Cr(2-NA dtc) ₃	1440 (s)	1010 (s)	465(s)
3. Mn(2-NA dtc) ₂	1450 (s)	1020 (s)	470(s)
4. Fe(2-NA dtc) ₃	1465 (s)	1010(m)	455(s)
5. Co(2-NA dtc) ₂	1460 (s)	1005 (s)	470(s)
6. Ni(2-NA dtc) ₂	1475 (s)	980 (s)	480(s), 420(m)
7. Cu(2-NA dtc) ₂	1465 (s)	1010(m)	465(s), 420(m)
8. Zn(2-NA dtc) ₂	1470 (s)	950 (s)	440 (s)

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