

Physico-chemical study of complexes of some 3d-series transition metals with piperazine 1,4-dicarbodithioate

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ABSTRACT

Complexes of some 3d-series transition metals with Piperazine 1,4-dicarbodithioate [piperazine bis(dithiocarbamate), Pz bis dtc] of the types $M(\text{Pz bis dtc})$ and $M'_2(\text{Pz bis dtc})_3$ have been prepared satisfactorily by using the substitution reaction method. These complexes have been characterized through elemental analyses, molar conductance and infrared spectroscopy. The air and moisture stable complexes showed non-ionic nature. The metal was found to be tetra-coordinated in the $M(\text{Pz bis dtc})$ type complexes and hexa-coordinated in the type $M'_2(\text{Pz bis dtc})_3$ by bidentate ligand.

Key words: Complexes, 3d-series, transition metals.

INTRODUCTION

Various bis(dithiocarbamate) complexes have been studied thoroughly and particularly bis(dithiocarbamate)nickel(II) complexes were found¹ to be square planar and diamagnetic. It is also known²⁻⁵ that the reactions of bis(dithiocarbamate)nickel(II) complexes with triphenyl phosphine (PPh_3) or 1,2-bis(diphenylphosphino)ethane (dppe) ligands in the presence of $\text{NiX}_2 \cdot n\text{H}_2\text{O}$ (Cl, Br, I) lead to the formation square planar and diamagnetic complexes with the NiS_2XP or NiS_2P_2 chromophores. However bis(5-aminoindazolidithiocarbamate) nickel(II) complex was reported⁶ to have magnetic effective moment equal to 2.90. Similarly bis(thiazolidinedithiocarbamate) nickel(II) complex was also found⁷ to be paramagnetic ($\mu_{\text{eff}}/\mu_B = 1.84$). Methods of creating extended multi-metallic arrays through bridging bis(dithiocarbamate) ligands have also been developed⁸.

In the framework of our systematic study of complexes of Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} metal ions with few sulphur and nitrogen containing ligands we focused our attention to

piperazine bis(dithiocarbamate) complexes which have not yet been discussed in literature. The goal of the present work was to synthesize these complexes by substitution reaction method and then to investigate the coordination behaviour of piperazine bis(dithiocarbamate) moiety in these complexes and the various other properties of these complexes using current physico-chemical methods.

EXPERIMENTAL

Piperazine hexahydrate, 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 methods⁹ before use.

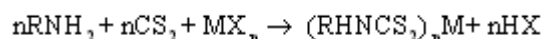
Elemental analyses of the complexes for carbon, hydrogen and nitrogen were performed at semimicro scale by the Regional Sophisticated Instrumentation Centre (R.S.I.C.), Central Drug Research Institute (C.D.R.I.), Lucknow (U.P.), India. Sulphur was estimated gravimetrically by known procedure¹⁰. Infrared 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.

The metal dithiocarbamates may be synthesized by one of the following methods:¹¹

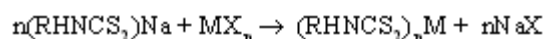
Insertion reaction method

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).



Substitution reaction method

This method involves substitution reaction using the sodium salt of the dithiocarbamate with metal salt.



In the present work the substitution reaction method was preferred for the synthesis of the complexes.

The disodium piperazine 1,4-dicarbodithioate was prepared by taking piperazine hexahydrate, carbon disulphide and sodium hydroxide in 1:2:2 molar ratios respectively. Piperazine hexahydrate (0.05 mol, 9.71 gm) dissolved in 200 ml isopropyl alcohol was kept in an ice bath at 5°C. Carbon disulphide (0.1 mol, 6.03 ml) was slowly added to this solution. Now 0.1 mol (4.0 gm) of sodium hydroxide dissolved in the minimum amount of water was added drop-wise to the above mixture with constant stirring for about 4 hours. Subsequently it was filtered and the filtrate kept overnight when needle shaped crystals of disodium piperazine 1,4-dicarbodithioate were obtained. It was soluble in ethyl alcohol.

The metal complexes of piperazine 1,4-dicarbodithioate were prepared by mixing ligand to metal salt in 1:1 molar ratio. The 0.01 M solution of disodium piperazine 1,4-dicarbodithioate (2.82 gm) in ethyl alcohol was mixed to a 0.01 M solution 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 $ZnCl_2$). In molar ratio 3:2, the 0.015 M solution (4.23 gm) of disodium piperazine 1,4-dicarbodithioate in ethyl alcohol was mixed to a 0.01 M solution of metal salts (1.5850 gm $CrCl_3$ and 1.6234 gm $FeCl_3$). It yielded precipitate immediately. The precipitate was filtered, washed with alcohol and dried in air.

RESULTS AND DISCUSSION

Complexes of piperazine 1,4-dicarbodithioate with bi and trivalent transition metals of 3d-series have been prepared by the substitution reaction method. This method yielded compounds with high purity, which was supported by their elemental analysis. The colourless to colourful compounds were air and moisture stable at room temperature. The complexes were soluble in ethanol, benzene and DMF. These complexes were found to have melting points ranging from 225 to 268°C. The metal to ligand ratio for manganese, cobalt, nickel, copper and zinc was 1:1 and that for chromium and iron was 2:3.

Important analytical results of the prepared complexes are summarized in Table 1. 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 1.0-2.60 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ confirmed the non-ionic nature¹² of all these complexes studied.

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 showed well-resolved and sharp bands (Table 2). 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. 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^{13,14}.

The thioureide band near 1500 cm^{-1} implies a considerable double bond character in the SC-NRR' bond^{15,16}. Furthermore in general, $\nu(\text{C-N})$ frequency shows a blue shift in the complexes 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, for piperazine bis(dithiocarbamate) complexes was noted around 1455 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 confirmed^{17,18} for all the complexes studied.

Table 1: Analytical data and other physical properties of piperazine 1,4-dicarbodithioate complexes

Compounds (Formula Wt.)	Yield	m.p. (°C)	Colour	Λ_m Ohm ⁻¹ cm ² mol ⁻¹	Found (calculated)%				
					C	H	N	S	M
1. Na ₂ (Pz bis dtc) (282)	68	235	Colourless	-	25.61 (25.53)	2.81 (2.83)	9.89 (9.93)	45.28 (45.39)	-
2. Cr ₂ (Pz bis dtc) ₃ (811.98)	56	256	Light green	2.0192	26.75 (26.60)	2.94 (2.96)	10.29 (10.35)	47.16 (47.29)	12.86 (12.80)
3. Mn(Pz bis dtc) (290.94)	67	268	Light yellow	1.0987	24.65 (24.74)	2.73 (2.75)	9.65 (9.62)	44.18 (44.01)	18.79 (18.88)
4. Fe ₂ (Pz bis dtc) ₃ (819.70)	58	225	Grey	2.0786	26.47 (26.35)	2.91 (2.93)	10.28 (10.25)	46.78 (46.84)	13.56 (13.63)
5. Co(Pz bis dtc) (294.93)	64	246	Blue-green	2.4567	24.29 (24.41)	2.69 (2.71)	9.45 (9.49)	43.65 (43.41)	19.92 (19.98)
6. Ni(Pz bis dtc) (294.71)	69	265	Green	1.2782	24.35 (24.43)	2.74 (2.72)	9.55 (9.50)	43.33 (43.43)	20.03 (19.92)
7. Cu(Pz bis dtc) (499.55)	68	216	Light brown	2.6789	24.19 (24.04)	2.65 (2.67)	9.30 (9.35)	42.60 (42.74)	21.26 (21.20)
8. Zn(Pz bis dtc) (301.37)	70	254	Colourless	2.1896	23.78 (23.89)	2.63 (2.65)	9.35 (9.29)	42.64 (42.48)	21.60 (21.69)

Table 2: IR spectral data of piperazine 1,4-dicarbodithioate 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 ₂ (Pz bis dtc)	1450	1000	-
2. Cr ₂ (Pz bis dtc) ₃	1465	1000	370
3. Mn(Pz bis dtc)	1455	1000	375
4. Fe ₂ (Pz bis dtc) ₃	1456	1000	379
5. Co(Pz bis dtc)	1453	1000	385
6. Ni(Pz bis dtc)	1460	1000	390
7. Cu(Pz bis dtc)	1452	1000	380
8. Zn(Pz bis dtc)	1463	1000	385

The $\nu(\text{C-S})$ stretching frequency for these complexes did not show any shift from its position at 1000 cm^{-1} . In all these complexes only one sharp and unsplit band occurred at 1000 cm^{-1} , therefore the symmetrical coordination through both the sulphur atoms i.e. bidentate nature of dithiocarbamate moiety has been concluded.^{18,19}

In addition, new bands occurring in the wave number range $370\text{-}390\text{ cm}^{-1}$ which were not observed in the case of free ligands, were reasonably attributed to the $\nu(\text{M-S})$ stretching frequency²⁰.

Thus 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 its both the sulphur atoms i.e. the bidentate behaviour. With respect to all these experimental facts it was concluded that in $\text{M}(\text{Pz bis dtc})$ type of complexes, the metal(M) was tetra-coordinated while in the type $\text{M}'_2(\text{Pz bis dtc})_3$, it was hexa-coordinated by ligands(L) in symmetrical fashion.

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