

SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES WITH SULPHUR CONTAINING LIGAND

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ABSTRACT

The ligand was prepared by reacting piperdine with carbon disulphide and sodium hydroxide. Its transition metal complexes were synthesized by substitution reaction by reacting sodium salt of piperdine dithiocarbamate with salt solutions. These complexes were characterized by elemental analysis and spectral studies. Based upon these analyses, it was confirmed that In all these complexes dithiocarbamate group is coordinated symmetrically as bidentate ligand. In all these complexes the metal is either tetra or hexa-coordinated giving square planer or octahedral geometry.

KEYWORDS : Dithiocarbamate, metal complexes, symmetrical coordination, square planer and octahedral geometry.

INTRODUCTION

Extensive work has been done in the field of coordination chemistry due to its application in industry, agriculture and medicine as well as a subject of interest of different modes of coordination to synthesize interesting compounds. The transition metal compounds with various biologically significant ligand bearing nitrogen or /and sulphur are known to possess fungitoxic properties. The carbon disulphide has been proved to be a versatile ligand and has been utilized for the synthesis of a large number of important compounds. This ligand has great tendency of reacting with aliphatic and aromatic amines forming dithiocarbamates, which is capable of coordinating to transition metals through one or both the sulphur atoms.¹⁻⁷ In view of the versatility of this ligand it was worth interesting to synthesize, its dithiocarbamates with piperdine and its complexation with some transition metal element with the hope than these complexes will exhibit great activity.

EXPERIMENTAL

Piperdine, carbon disulphide, sodium hydroxide and transition metal salts(All E. Merck) were used as received. The solvents (All BDH) were used after purification by standard methods⁸. The Elemental analysis of all the ligand and complexes for C,H and N were carried out at R.S.I.C, C.D.R.I., Lucknow (U.P).Sulphur was estimated gravimetrically by known procedure⁹.The I.R. spectra in the region 4000-200cm⁻¹were recorded in Nujol mull on a Perkin Elmer Model 1620 FTIR spectrophotometer.

Preparation of dithiocarbamates

The metal dithiocarbamates can be prepared by either of the two methods,by insertion method or by replacement or substitution method. In the present study we synthesized these by substitution method which involves the substitution reaction using sodium salt of dithiocarbamates with metal salt. The sodium salt of piperdine dithiocarbamates was prepared by talking piperdine, carbon disulphide and sodium hydroxide in equimoler ratio. To an ethanolic solution of piperdine (0.1M., 9.9ml), carbondisulphide (0.1M, 6.02ml) and aqueous solution of sodium hydroxide (0.1M, 4.0gm) was added slowly drop-wise with constant stirring. The stirring was continued for one hour, when the sodium salt of piperdine dithiocarbamate was separated out. This was filtered,washed and dried in vacuum.

Preparation of Metal Complexes

The complexes of metal salt with piperdine dithiocarbamate were prepared by the combination of metal salt to ligand in 1:2{(for Mn(II),Ni(II)Cu(II)} and 1:3 for Fe(III). In the preparation of complexes 0.01M solution of metal salt (1.26gm MnCl₂, 1.30gm NiCl₂, and 1.35gm CuCl₂) was added to 0.02M solution of sodium salt of piperdine dithiocarbamate (3.66gm) dissolved in DMF. For preparation of Fe(III) complexes feCl₃ (0.01M, 1.62gm) dissolved in water was added to a 0.03M solution of piperdine dithiocarbamate (5.50gm) in DMF. These solutions were refluxed for one to two hours until a solid was separated. These complexes were filtered, washed with ether and dried in vacuum.

RESULT AND DISCUSSION

The newly synthesized compounds so formed by substitution process were found in good yield. The elemental analyses data, melting point and colors are summarized in table-1. These date are quite in agreement with the proposed stoichiometry of the compounds. The evidence regarding the bonding and structure of these complexes has been deduced after thoroughly

examining the observed frequencies characterized of free dithiocarbamate group in its infrared spectrum and comparing with those of complexes. The I.R. spectral vibrational frequencies of ligand and those of complexes are summarized in table-2. The free dithiocarbamate ion, as it exists in ionic compounds, is expected to show I.R. active fundamental modes. It is expected that if it reexists an increased cation-anion interaction, as has been observed in covalent compounds, these vibrational frequencies are very much affected and undergo positive shift. Furthermore, the dithiocarbamate group can coordinate symmetrically involving both the sulphur atoms as well as asymmetrically involving only one sulphur atom in coordination. These frequency modes are diagnostic factors for determining the nature of dithiocarbamate moiety whether it is acting as monodentate or bidentate. The appearance of a single absorption band in the region 1000cm^{-1} or splitting of this band within the same region is a diagnostic factor for symmetric and asymmetric coordination of dithiocarbamate group¹⁰⁻¹³.

In the I.R. spectra of the complexes (Table-2) the band appearing in the region 1500cm^{-1} were clearly assigned to C-N str. vibration of thioureide group of the ligand. This frequency mode is intermediate to C-N and C=N bond giving evidence of partial double bond character of thioureide bond. A sharp unsplit band appeared in the I.R. spectra of the complexes at 1000cm^{-1} was reasonably due to C-S str. vibration. This implies a symmetrical coordination of the ligand through both the sulphur atoms giving bidentate nature of dithiocarbamate moiety. A new band, which was not observed in free dithiocarbamate, was observed at 300cm^{-1} due to M-S str. vibration confirming the metal ligand coordination¹⁴.

On the basis of above observation it was concluded that in all these complexes dithiocarbamate group is coordinated symmetrically as bidentate ligand. In these complexes metal (Mn, Ni, Cu) are tetra coordinated giving square planar geometry and Fe is hexacoordinated forming an octahedral molecule.

Table-1

S.No.	Compound	Yield	mp	Color	Analytical Data % found/(Calculated)				
					C	H	N	S	M
1	C ₆ H ₁₀ NS ₂ Na	80	210	Cream	39.34 (39.09)	5.46 (5.92)	7.65 (7.01)	34.97 (34.16)	- -
2	C ₁₂ H ₂₀ N ₂ S ₄ Mn	70	200	Grayish	38.40 (38.95)	5.33 (5.01)	7.46 (7.66)	34.13 (34.96)	14.66 (14.78)
3	C ₁₂ H ₂₀ N ₂ S ₄ Ni	76	175	Light green	37.99 (37.15)	5.27 (5.64)	7.38 (7.02)	33.77 (33.86)	15.56 (15.16)
4	C ₁₂ H ₂₀ N ₂ S ₄ C ₄	58	205	Brownish	37.50 (37.85)	5.21 (5.88)	7.29 (7.65)	33.33 (33.67)	16.66 (16.51)
5	C ₁₈ H ₃₀ N ₃ S ₆ Fe	60	200	Dark brown	40.30 (40.03)	5.60 (5.25)	7.84 (7.12)	35.82 (35.95)	10.45 (10.04)

Table-2

S.No.	Compound	$\gamma(\text{C-N}) \text{ cm}^{-1}$	$\gamma(\text{C-S}) \text{ cm}^{-1}$	$\gamma(\text{M-S}) \text{ cm}^{-1}$
1	C ₆ H ₁₀ NS ₂ Na	1500	1005	-
2	C ₁₂ H ₂₀ N ₂ S ₄ Mn	1510	1000	388
3	C ₁₂ H ₂₀ N ₂ S ₄ Ni	1515	998	390
4	C ₁₂ H ₂₀ N ₂ S ₄ C ₄	1505	996	380
5	C ₁₈ H ₃₀ N ₃ S ₆ Fe	1510	1000	392

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