

# Coordinating behaviour of dithiocarbamate group. Synthesis and characterization of new dithiocarbamates derived from 4-amino-3,5-bis(pyridine-2-yl)-1,2, 4-triazole and its complexes with transition metals

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## ABSTRACT

Some new first row transition metal complexes of types  $ML_2$  { $M=Mn(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$  and  $Zn(II)$ } and  $M'L_3$  { $M'=Cr(III)$  and  $Fe(III)$ } with dithiocarbamate ligand derived from 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole have been prepared by the replacement reaction. These complexes have been characterized by elemental analysis, conductivity measurements and infrared spectral studies. All the complexes were non-electrolyte in nature. Infrared spectral data of these complexes showed the bidentate behaviour of ligand and metals were found to be tetra and hexa-coordinated in  $ML_2$  and  $M'L_3$  type of complexes respectively.

**Key words:** Transition metal complexes, ligands and IR studies.

## INTRODUCTION

The chemistry of coordination compounds has been an interesting subject for last few decades owing to its application in industry, agriculture and medicine. Apart from their application in various fields, these compounds have also been a subject of interest due to their different modes of coordination. Extensive work has been done in this field and a large number of coordination compounds of transition metals with organic bases having potential biological activities have been reported. The coordination compounds of transition metals specially copper, zinc, cadmium and mercury which are known to possess fungitoxic properties with various biologically significant ligands viz. indazole, pyrazole and imidazole have been found to be of much interest. Due to the biological activeness of various sulphur and nitrogen containing ligands viz. acridine, piperazine, pyrrolidine, 1,10-phenanthroline, bipyridine, pyrazoles, imidazoles, triazoles, dithiazoles and their complexes with various transition metals have been prepared and studied in detail<sup>1-16</sup>.

The coordination chemistry of carbon disulphide, proved to be a versatile ligands, has also been extensively studied<sup>17</sup>. It forms complexes with almost every transition metal, capable of coordinating to one or more metal(s) and shows a variety of insertion and disproportionation reactions<sup>18-20</sup>. In addition to react with various metals, carbon disulphide has greater tendency of reacting with different amines resulting the formation of important class of compounds known as dithiocarbamates.

A literature survey reveals that no work has been done on complexes of dithiocarbamate ligand derived from 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole with first row transition metal ions. We report here, a study of the complexes of  $Cr(III)$ ,  $Mn(II)$ ,  $Fe(III)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$  and  $Zn(II)$  with dithiocarbamate ligand derived from 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole.

## EXPERIMENTAL

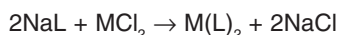
4-amino-3,5-bis(pyridine-2-yl)-1,2,4-

triazole (Fluka), salts of 3d series transition metal, carbon disulphide and sodium hydroxide (all E. Merck) were used as received. Solvents (all BDH) were used after purification by reported method<sup>21</sup>.

Elemental analyses for carbon, hydrogen and nitrogen were carried out at semi micro scale by R.S.I.C., C.D.R.I., Lucknow (U.P.). Sulphur was estimated by a known procedure<sup>22</sup>.

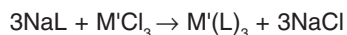
The IR spectra were recorded in KBr on Perkin Elmer model 1620 (Fourier Transform Infrared) spectrophotometer from the Jamia Millia Islamia University, Delhi, India. The molar conductivity of complexes was measured by means of Systronics 321 Conductivity Bridge.

The metal dithiocarbamates can be synthesized either by the insertion method or by substitution reaction method. In the present study we synthesized these dithiocarbamates by substitution reaction method. In the present study we synthesized these dithiocarbamates by substitution reaction method.



where

$\text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+} \text{ and } \text{Zn}^{2+}$ ;  $\text{L} = \text{C}_{13}\text{H}_9\text{N}_6\text{S}_2$



where

$\text{M}' = \text{Cr}^{3+} \text{ and } \text{Fe}^{3+}$ ;  $\text{L} = \text{C}_{13}\text{H}_9\text{N}_6\text{S}_2$

The ligand dithiocarbamate was synthesized by the interaction of 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole, carbon disulphide and sodium hydroxide in equimolar ratio (1:1:1). To a 0.05 M solution of 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole (11.9 gm) in isopropyl alcohol, carbon disulphide (0.05 mol, 3.015 ml) and aqueous solution of sodium hydroxide (0.05 mol, 2.0gm) were added drop wise with continuous stirring with the use of a magnetic stirrer. The reaction mixture was stirred for about half an hour. Thus sodium salt of 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole was obtained on completion of reaction. This ligand was found to be soluble in dimethylformamide.

Complexes with transition metals 3d-series were prepared in 1:2 metal-ligand ratio except Cr and Fe where the ratio was 1:3.

To a 0.01 M solution (3.36gm) of sodium salt of dithiocarbamate in DMF, the 0.005M solutions of metal salts (0.6298 gm  $\text{MnCl}_2$ , 0.6496 gm  $\text{CoCl}_2$ , 0.6486gm,  $\text{NiCl}_2$ , 0.6732 gm  $\text{CuCl}_2$  and 0.6818 gm  $\text{ZnCl}_2$ ) were added gradually at room temperature. In 3:1 molar ratios to a 0.01M solution of ligand dithiocarbamate, 0.0033 M solution of  $\text{CrCl}_3$  (0.5230 gm) and  $\text{FeCl}_3$  (0.5358 gm) were added gradually at room temperature. The reaction mixture was then stirred for 45 minutes. The solid thus obtained was washed with diethyl ether and dried in air.

## RESULTS AND DISCUSSION

The substitution reaction method gave the product of good purity and in good yield ranging in 67-75%.

Composition of the complexes synthesized has been established from their elemental analyses. Analytical results of the prepared complexes, their proposed formulae, formula weights, yields, melting points, colours, molar conductances and compositions are mentioned in Table 1.

These complexes were colourless to brown, inert to atmospheric oxygen and moisture. These are insoluble in water and common organic solvents but soluble in DMF and DMSO.

The low molar conductances of  $10^{-3}$  M solutions of complexes in DMSO ranging 2-13  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  showed these complexes to be non-ionic in nature. The elemental analyses indicated 1:3 (metal:dithiocarbamate) stoichiometry for Cr and Fe complexes and 1:2 stoichiometry for all other complexes.

The complexes were characterized by thoroughly examining the infrared spectra of free ligand and comparing with those of complexes (Table 2). The IR spectra of all the complexes demonstrated well-resolved absorption bands to pyridine, triazole and dithiocarbamate group.

In the IR spectra, the appearance of a single absorption band in the region  $1000\text{cm}^{-1}$  or splitting of this band within the same region is diagnostic factor of dithiocarbamate whether it is acting as bidentate or monodentate. Similarly the existence of thioureide band also an important role in deciding the symmetrical or unsymmetrical coordination of dithiocarbamate group.

The IR spectra of all compounds showed absorption bands in the region  $3200\text{-}3300\text{cm}^{-1}$ ,

which are identical to those observed in free dithiocarbamate ligand confirming the non-involvement of amine in coordination. The bands observed in the region  $1430\text{-}1600\text{cm}^{-1}$  in free dithiocarbamate were due to C-C and C-N stretching vibration of pyridine ring. These frequencies remained unaffected in complexes suggesting non-involvement of pyridine ring nitrogen in coordination. A doublet observed in the region  $980\text{-}1010\text{cm}^{-1}$  in free ligand was assigned to  $\nu(\text{C-S})$  stretching vibration. In complexes,

**Table 1: Analytical data and other physical properties of complexes derived from 4-amino-3,5-bis(pyridine-2-yl)1,2,4-triazole**

Compounds (Formula Wt.)	Yield (%)	m.p. (°C)	Colour	$\Lambda_m$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	C	Found (Calculated) %			
						H	N	S	M
1. Na(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> ) (336)	67	240	Yellowish	3.4972	46.31 (46.23)	2.69 (2.67)	25.09 (25.01)	18.96 (19.04)	-
2. Cr(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> ) <sub>3</sub> (990.99)	73	205	Greenish brown	9.7896	47.19 (47.23)	2.70 (2.72)	25.50 (25.44)	19.43 (19.37)	5.18 (5.24)
3. Mn(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> ) <sub>2</sub> (680.94)	72	218	Black	12.2233	45.86 (45.83)	2.62 (2.64)	24.52 (24.67)	18.85 (18.79)	8.15 (8.06)
4. Fe(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> ) <sub>3</sub> (994.85)	75	300	Brown	13.1325	46.96 (47.05)	2.72 (2.71)	25.41 (25.33)	19.24 (19.30)	5.67 (5.61)
5. Co(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> ) <sub>2</sub> (684.93)	75	250	Pink	10.1124	45.46 (45.54)	2.65 (2.63)	24.45 (24.53)	18.75 (18.69)	8.69 (8.60)
6. Ni(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> ) <sub>2</sub> (684.71)	71	241	Light green	2.0306	45.69 (45.57)	2.62 (2.63)	24.60 (24.53)	18.57 (18.69)	8.52 (8.57)
7. Cu(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> ) <sub>2</sub> (689.55)	70	255	Light Blue	12.1904	45.29 (45.38)	2.60 (2.62)	24.52 (24.43)	18.67 (18.61)	8.92 (8.95)
8. Zn(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> ) <sub>2</sub> (691.37)	68	290	Colour- less	8.2827	45.16 (45.25)	2.63 (2.61)	24.46 (24.37)	18.50 (18.57)	9.25 (9.19)

**Table 2: IR spectra of complexes derived from 4-amino-3,5-bis(pyridine-2-yl) 1,2,4-triazole and their assignments**

Complexes	$\nu(\text{C-N})\text{cm}^{-1}$	$\nu(\text{C-S})\text{cm}^{-1}$	$\nu(\text{M-S})\text{cm}^{-1}$
1. Na(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> )	1440	999	-
2. Cr(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> )	1456	1000	385
3. Mn(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> )	1450	1000	395
4. Fe(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> )	1466	1000	372
5. Co(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> )	1470	1000	384
6. Ni(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> )	1455	990	365
7. Cu(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> )	1457	995	380
8. Zn(C <sub>13</sub> H <sub>9</sub> N <sub>6</sub> S <sub>2</sub> )	1460	1000	379

however, this was disappeared and instead a single sharp band was observed at  $990\text{-}1000\text{cm}^{-1}$  suggesting a symmetrical coordination of a dithiocarbamate group. In the spectrum of complexes the peaks due to thiouride band ( $\text{S}_2\text{C-NR}_2$ ) have been observed in the region ( $1440\text{-}1470\text{cm}^{-1}$ ). This range is intermediate to C-N ( $1350\text{-}1250\text{cm}^{-1}$ ) and C=N ( $1690\text{-}1610\text{cm}^{-1}$ ) and considered to be due to delocalization of electrons leading to increase in  $\pi$ -bond character. The narrow range of C-N stretching frequency in these complexes indicated that the bond was insensitive to the nature of metal ion. For a symmetrically bonded dithiocarbamate, this band normally appears at higher wavelength than asymmetrically bonded dithiocarbamate. In addition

of this, a new band, which was not observed in free dithiocarbamate, was also observed at  $370\text{-}395\text{cm}^{-1}$  due to M-S stretching vibration.

In view of above findings, it is evident that the dithiocarbamate group in all these compounds is symmetrically bonded behaving as bidentate and metal is either tetra or hexa-coordinated towards the ligand.

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