

Bi and Trivalent transition metal complexes of dithiocarbamates derived from 2,6- diacetyl pyridine

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(Received: January 25, 2008; Accepted: March 17, 2008)

ABSTRACT

Some new 3d-series transition metal complexes of types $ML\{M=Mn(II), Co(II), Ni(II), Cu(II) \text{ and } Zn(II)\}$ and $M'_2L_3\{M'=Cr(III) \text{ and } Fe(III)\}$ with dithiocarbamate ligand derived from 2,6-diacetyl pyridine have been prepared by the replacement reaction method. 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 the metals were found to be tetra and hexa-coordinated in ML and M'_2L_3 type of complexes respectively.

Key words: Bi and Trivalent transition metal complexes, dithiocarbamates.

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, pyrolidine, 1,10-phenanthroline, bipyridine, pyrazoles, imidazoles, triazoles, dithiazoles and their complexes with various transition metals have been prepared and studied in detail¹⁻¹⁶.

The coordination chemistry of carbon disulphide, proved to be a versatile ligand, has also been extensively studied.¹⁷ 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.¹⁸⁻²⁰ 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.

Here we are reporting the synthesis of new dithiocarbamates derived from 2,6-diacetyl pyridine and its complexes with some bi and tri-valent transition metal salts.

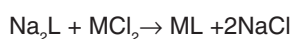
EXPERIMENTAL

2,6-diacetyl pyridine, hydrazine hydrate (both BDH), salts of 3d series transition metals, carbon disulphide, sodium hydroxide (all E. Merck) were used as such. Solvents (all BDH) were purified before use by reported methods²¹.

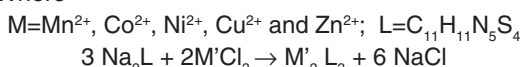
Elemental analyses for carbon, hydrogen and nitrogen were carried out at semi micro scale by R.S.I.C., C.D.R.I., Lucknow. (U.P.). Sulphur was estimated by a known procedure²².

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 was measured on a Systronics 321 conductivity bridge.

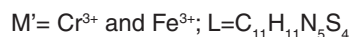
The sodium salt of dithiocarbamate was synthesized by replacement reaction method:



Where



Where



Firstly 0.05 moles (8.15 gm) of 2,6-diacetyl pyridine in isopropyl alcohol (50ml.) treated with 0.1 mole (2.9 ml) of hydrazine to obtain intermediate

hydrazide. The ligand dithiocarbamate was prepared by reacting 0.05 mole (9.35 gm) solution of this intermediate hydrazide in DMF with 0.1 mole (6.03ml) carbon disulphide and 0.1 mole (4.0 gm) of sodium hydroxide dissolved in small amount of water with constant stirring for one hour. After completion of this reaction sodium salt of dithiocarbamate was obtained which was washed, filtered and dried in vacuum.

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

To a 0.025 M solution (9.6750 gm) of sodium salt of dithiocarbamate in isopropyl alcohol, 0.025 M solutions of salts (3.1486 gm MnCl_2 , 3.2428 gm CoCl_2 , 3.2428 gm NiCl_2 , 3.3662 gm CuCl_2 , 3.4092 gm ZnCl_2) were added dropwise at room temperature. The complexes of Cr and Fe were also prepared in the similar fashion by mixing 0.03 M solution of sodium salt of dithiocarbamate (11.61 gm) in 50 ml isopropyl alcohol to 0.02 M solutions of metal chlorides (3.1698 gm CrCl_3 and 3.2470 gm FeCl_3) dropwise at room temperature. The

Table 1: Analytical data and other physical properties of complexes derived from 2,6-diacetyl pyridine

Compounds (Formula Wt.)	Yield (%)	m.p. (°C)	Colour	Λ_m Ohm ⁻¹ cm ² mol ⁻¹	C	Found (calculated)%			
						H	N	S	M
1. $\text{Na}_2(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$ (387.00)	61	240	Light yellow	12.0461	36.18 (36.26)	3.04 (3.02)	19.28 (19.23)	35.11 (35.16)	-
2. $\text{Cr}_2(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)_3$ (1126.99)	65	205	Blue	11.2503	35.31 (35.13)	2.90 (2.93)	18.58 (18.63)	33.96 (34.08)	9.25 (9.23)
3. $\text{Mn}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$ (395.94)	67	218	Brown	13.7284	33.48 (33.34)	2.79 (2.77)	17.75 (17.68)	32.41 (32.33)	13.57 (13.88)
4. $\text{Fe}_2(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)_3$ (1134.68)	63	300	Blackish brown	10.0925	34.82 (34.90)	2.93 (2.91)	18.41 (18.50)	33.93 (33.85)	9.94 (9.84)
5. $\text{Co}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$ (399.93)	68	250	Blackish green	11.3321	32.80 (33.01)	2.73 (2.75)	17.48 (17.50)	32.21 (32.01)	14.78 (14.73)
6. $\text{Ni}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$ (399.71)	70	241	Green	17.2347	32.89 (33.03)	2.77 (2.75)	17.59 (17.51)	32.13 (32.03)	14.62 (14.68)
7. $\text{Cu}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$ (404.55)	69	255	Blue	18.0028	32.72 (32.64)	2.72 (2.71)	17.35 (17.30)	31.56 (31.65)	15.65 (15.70)
8. $\text{Zn}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$ (406.37)	64	290	Colour less	15.7609	32.27 (32.49)	2.71 (2.70)	17.26 (17.22)	31.58 (31.51)	16.18 (16.08)

reaction mixture was then continuously stirred for 1 hour. The solid thus obtained was washed with diethyl ether and dried in air.

RESULTS AND DISCUSSION

These complexes, prepared by replacement reaction method were obtained in good yield ranging 60%-70%. All the complexes were of good purity as supported by their elemental analysis.

The elemental analyses of these complexes established their composition. Important analytical data along with their proposed formulae, yields, melting points, colours, molar conductances and compositions are summarized in Table 1.

The low molar conductances of 10^{-3} M solutions of complexes in DMSO ranging 10-18 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ show the non-ionic behaviour of these complexes. Most of these complexes were coloured and were quite stable in atmospheric and moisture. These were soluble in THF, DMF, DMSO and nitrobenzene but insoluble in water and common organic solvents.

The evidence regarding the bonding and structure of these complexes has been deduced after thoroughly examining the observed frequencies characteristic of free dithiocarbamate group in its infrared spectrum and comparing with those of complexes. (Table 2)

Table 2: IR spectra of complexes derived from 2,6-diacetylpyridine and their assignments

Complexes	ν (C-N) cm^{-1}	ν (C-S) cm^{-1}	ν (M-S) cm^{-1}
1. $\text{Na}_2(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$	1501	990	-
2. $\text{Cr}_2(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)_3$	1505	992	392
3. $\text{Mn}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$	1516	991	390
4. $\text{Fe}_2(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)_3$	1504	996	395
5. $\text{Co}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$	1511	995	396
6. $\text{Ni}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$	1510	999	393
7. $\text{Cu}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$	1502	1005	390
8. $\text{Zn}(\text{C}_{11}\text{H}_{11}\text{N}_5\text{S}_4)$	1503	1004	400

The free dithiocarbamate ion, as it exists in ionic compounds, is expected to show IR active fundamental modes. It is expected that if there exists an increased cation-anion interaction, as has been observed in covalent compound, these vibrational frequencies are very much affected and undergo positive shift.

The dithiocarbamate group can coordinate symmetrically involving both the sulphur atoms as well as unsymmetrically involving only one sulphur atom in coordination. These frequency modes are diagnostic factor for the nature of dithiocarbamate moiety whether it is acting as monodentate or bidentate.

The preliminary information regarding the ligand dithiocarbamate (L) has been inferred from

the bands observed in its IR spectrum which clearly exhibited characteristic absorption bands due to pyridine ring as well as dithiocarbamate moiety. The non-existence of any band corresponding to $\nu(\text{C}=\text{O})$ and instead appearance of a band at $\sim 1625 \text{ cm}^{-1}$ assignable to $\nu(\text{C}=\text{N})$ of imine group suggest the formation of hydrazide. A strong intensity band appeared in the region $3210\text{-}3260 \text{ cm}^{-1}$ was attributed to $\nu(\text{N-H})$ stretching mode of secondary amine. A strong intensity doublet observed in the region $980\text{-}1020 \text{ cm}^{-1}$ was clearly assignable to $\nu(\text{C-S})$ stretching mode. The appearance of bands in the region $2870\text{-}2970 \text{ cm}^{-1}$, $940\text{-}975 \text{ cm}^{-1}$ and $1140\text{-}1220 \text{ cm}^{-1}$ may reasonably be ascribed to $\nu(\text{C-H})$, $\nu(\text{N-N})$ $\nu(\text{C-N})$ stretching modes respectively. In addition the infrared spectrum of the ligand also exhibited the band around 403, 601 and 1570 cm^{-1} consistent with the pyridine ring

vibration assignable out of plane and in plane ring deformation. These vibrations do not suffer any significant shift toward high frequency suggesting non-involvement of pyridine nitrogen in coordination.

The infrared spectrum of all the complexes were found to be very similar to the free ligand except the appearance of a new strong intensity absorption band around 1000 cm^{-1} clearly assignable to $\nu(\text{C-S})$ stretching mode, characteristic of a symmetrical coordination of dithiocarbamate moiety. A strong intensity band around 1500 cm^{-1} was reasonably due to thioureide $\text{S}_2\text{C-N}$ stretching mode. This frequency mode lies in between C-N and C=N bond giving a partial double bond character of thioureide bond. Since no change have been observed in the absorption bands related to pyridine ring vibration, therefore the involvement of pyridine ring nitrogen in coordination was ruled out. In

addition a new absorption band was observed around 400 cm^{-1} region, which was not found in free ligand has been reasonably assigned to M-S stretching mode.

From the above observations it is evident that the dithiocarbamate group was coordinated to metal in bidentate manner involving both the sulphur atoms. In ML_2 type of complexes the metal was tetra-coordinated while in hexa-coordinated nature was exhibited by the metals in $\text{M}'_2\text{L}_3$ type complexes.

ACKNOWLEDGEMENTS

The authors are highly thankful to the Principal and the Chairman, Department of Chemistry, Gandhi Faiz-e-Aam (P.G.) College, Shahjahanpur (U.P.) India, for providing necessary laboratory facilities.

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