

## Synthesis of bivalent Co, Ni and Cu complexes with 1-methyl,5-substituted -2,4- dithiobiurets

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### ABSTRACT

The complexes of divalent cobalt, nickel and copper with 1-methyl-5 (phenyl/tolyl/phenetyl)-2,4-dithiobiurets were prepared and characterized by elemental analysis, melting point, magnetic moment, molar conductance, potentiometric, IR and <sup>1</sup>H NMR studies. It was observed that in all these complexes the metal-ligand coordinate in 1:2 ratio. A tetrahedral geometry has been proposed for all these complexes.

**Key words:** Synthesis, metal, complexes.

### INTRODUCTION

In recent years the chemistry of coordination compounds bearing hetero-atom particularly Nitrogen and Sulphur has been of much interest due to their dual behavior in coordination as well as a vulnerable source as fungicide in the field of agriculture. Dithiobiurets are one of the interesting ligands used in agriculture field. This ligand is also important due to the presence of delocalized electron pairs which make it possible to chelate through sulphur or nitrogen or both the donor atoms forming six membered rings. Therefore, this ligand can act as neutral, uninegative as well as binegative ligand. There are certain reports in literature that the transition metal complexes of this ligands are planer, coordinating two molecules of ligand through thiocarbonyl sulphur. The Cu (II) complex of the ligand was reported to be fungitoxic.<sup>1-5</sup>

### EXPERIMENTAL

All the chemicals used were of analytical grade either BDH or E. Merck and were used as received. The solvents were double distilled before use. The elemental analyses of the complexes were carried out at SAIF, CDRI, Lucknow, magnetic susceptibility was measured by Gouy method, molar

conductance was measured by conductivity bridge LBR of Wissenchaffich Tech. Germany at 10<sup>-3</sup>M in DMF and potentiometric studies were carried out with Iodine solution in THF using clonel and Pt electrodes. The I.R. spectra were recorded as KBr disc with range 4000-200 cm<sup>-1</sup> and <sup>1</sup>H NMR in DMSO using TMS as internal reference at AMU, Aligarh.

The ligands were prepared by refluxing the respective constituents in equimolar ratio for about two hours in ethanol<sup>5</sup>. After the completion of reaction, the mixture was evaporated and from the concentrates the compounds were extracted and crystallized with suitable solvents.

The complexes were prepared by reacting metal salt and ligands in 1:2 molar ratios. To a 0.1M metal chloride solution in ethanol (50ml) taken in three necked round bottomed flask fitted with mechanical stirrer, kept in ice bath maintaining the temperature of 10<sup>0</sup>c, was added (0.2 M) solution of ligand in ethanol drop by drop with constant stirring. After the completion of reaction, the mixture was allowed to stand at room temperature for an hour. The compound separated was then filtered, washed with ethanol and finally with ether and dried in vacuum.

The compounds so obtained were characterized by melting point, elemental analysis, conductivity and potentiometric study, magnetic susceptibility measurements and spectral analyses like I.R. and  $^1\text{H}$  NMR studies to ensure the formation of desired product and establishment of structure of synthesized compounds.

## RESULTS AND DISCUSSION

The analytical data (Tables I & II) are well in agreement with a 1:2 metal to ligand stoichiometry of all the complexes. The molar conductance values also suggested 1:2 electrolytic nature of these compounds.

The spin only values of magnetic moment for all cobalt complexes were observed in the range of 4.50 BM suggesting the presence of three unpaired electrons in high energy  $t_{2g}$  state arising from the tetrahedral ligand field. In case of nickel complexes the spin only values of magnetic moment were found to be in the range of 3.75 BM corresponding to the two unpaired electrons in the high field  $t_{2g}$  state arising from the tetrahedral ligand field. The spin only value of magnetic moment for copper complexes were observed in the range of 1.30 BM suggestive of only one unpaired electron<sup>5,6</sup>.

The I.R. spectra of the ligand 1-methyl-5-p-phenetyl, 1-methyl 5-O- tolyl, 1-methyl-5-phenyl 1,4-dithioburets and their Co(II), Ni (II) and Cu(II) complexes showed well resolved signals characteristic of C-C, C-H, N-H, C-S and M-S frequencies. It is well known fact that these frequencies get affected on coordination. It was found that in complexes only the C-S frequency get lowered when compared with the I.R spectra of pure ligands, suggesting the coordination through thionyl sulphur only where as the azomethyl nitrogen remain unaffected. In addition, the I.R-spectra of all the complexes observed a new absorption signal corresponding to M-S frequency. This was further supported by  $^1\text{H}$  NMR spectra of the ligand as well as complexes which exhibited proton signals for methyl, methylene, aromatic ring proton and NH protons. These signals remained unaffected in complexes suggesting non-involvement of NH group in coordination. The fact was also ensured by potentiometric studies of the complexes.

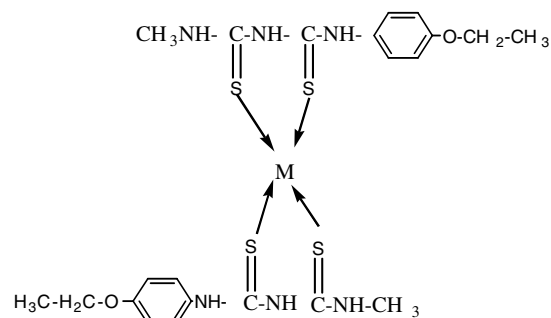
Table 1: Analytical Data

S. No.	Compound	Molecular Formula	For. Wt.	Carbon		Hydrogen		Nitrogen		Sulphur	
				Found	Cald.	Found	Cald.	Found	Cald.	Found	Cald.
1	MPhDTB	$\text{C}_{11}\text{N}_3\text{S}_2\text{OH}_{15}$	269.38	48.96	49.01	5.01	5.55	15.23	15.41	23.68	23.79
2	Co(MPhDTB) $_2\text{Cl}_2$	$\text{CoC}_{22}\text{N}_6\text{S}_4\text{O}_2\text{H}_{30}\text{Cl}_2$	668.39	38.98	39.51	4.56	4.49	12.41	12.55	20.91	21.03
3	Ni(MPhDTB) $_2\text{Cl}_2$	$\text{NiC}_{22}\text{N}_6\text{S}_4\text{O}_2\text{H}_{30}\text{Cl}_2$	668.09	39.06	39.50	4.22	4.48	12.33	12.56	20.88	21.04
4	Cu(MPhDTB) $_2\text{Cl}_2$	$\text{CuC}_{22}\text{N}_6\text{S}_4\text{O}_2\text{H}_{30}\text{Cl}_2$	672.94	39.10	39.22	4.19	4.46	12.56	12.46	19.23	19.02
5	MOTDTB	$\text{C}_{10}\text{N}_3\text{S}_2\text{H}_{13}$	239.36	49.98	50.13	5.31	5.43	17.44	17.57	26.50	26.77
6	Co(MOTDTB) $_2\text{Cl}_2$	$\text{CoC}_{20}\text{N}_6\text{S}_4\text{H}_{26}\text{Cl}_2$	608.28	39.11	39.43	4.29	4.27	13.60	13.80	21.10	21.03
7	Ni(MOTDTB) $_2\text{Cl}_2$	$\text{NiC}_{20}\text{N}_6\text{S}_4\text{H}_{26}\text{Cl}_2$	608.21	39.02	39.44	4.33	4.27	13.57	13.81	20.98	21.04
8	Cu(MOTDTB) $_2\text{Cl}_2$	$\text{CuC}_{20}\text{N}_6\text{S}_4\text{H}_{26}\text{Cl}_2$	613.06	38.88	39.14	4.19	4.24	13.78	13.70	21.03	20.88
9	MPDTB	$\text{C}_9\text{N}_3\text{S}_2\text{H}_{11}$	255.33	47.50	47.93	4.78	4.88	18.60	18.66	28.22	28.44
10	Co(MPDTB) $_2\text{Cl}_2$	$\text{CoC}_{18}\text{N}_6\text{S}_4\text{H}_{22}\text{Cl}_2$	580.39	37.01	37.21	3.81	3.79	14.41	14.47	22.11	22.04
11	Ni(MPDTB) $_2\text{Cl}_2$	$\text{NiC}_{18}\text{N}_6\text{S}_4\text{H}_{22}\text{Cl}_2$	580.15	37.44	37.22	3.80	3.79	14.43	14.48	21.96	22.06
12	Cu(MPDTB) $_2\text{Cl}_2$	$\text{CuC}_{18}\text{N}_6\text{S}_4\text{H}_{22}\text{Cl}_2$	585.11	36.42	36.92	3.68	3.77	14.21	14.35	21.88	21.86

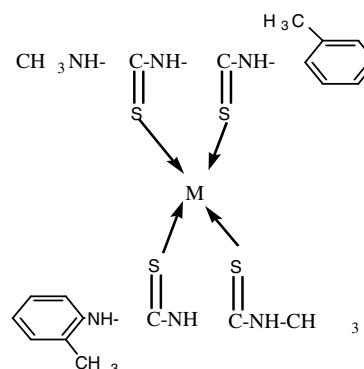
Table 2: Analytical Data

S. No.	Compound	Melting Point	Colour	Meg.Moment (B.M.)	Molar Cond. (mohs.)	N-H frequencies	C=S frequencies
1	MPhDTB	130				3220s, 1620sh	1460m, 1415s, 1260s, 760s
2	Co(MPhDTB) <sub>2</sub> Cl <sub>2</sub>	143	Brown	4.37	139	3220w, 1615sh	1420s, 1225w, 735m
3	Ni(MPhDTB) <sub>2</sub> Cl <sub>2</sub>	138	Dark Brown	3.68	160	3230s, 1615w	1420s, 1220m, 735m
4	Cu(MPhDTB) <sub>2</sub> Cl <sub>2</sub>	148	Golden Yellow	1.13	158	3220m, 1610sh	1420s, 1230w, br, 725m
5	MOTDTB	136				3220s, 1625sh	1440s, 1260s, 750s
6	Co(MOTDTB) <sub>2</sub> Cl <sub>2</sub>	156	Brownish Green	4.38	150	3220m, 1620s	1435sh, 1220m, 740w
7	Ni(MOTDTB) <sub>2</sub> Cl <sub>2</sub>	152	Brown	3.79	154	3220s, 1615w	1430s, 1215m, 730m
8	Cu(MOTDTB) <sub>2</sub> Cl <sub>2</sub>	150	Yellow	1.16	156	3210m, 1610s	1425sh, 1220m, 730w
9	MPDTB	135				3250vs, 1600s	1460br, 1260s, 750s
10	Co(MPDTB) <sub>2</sub> Cl <sub>2</sub>	152	Brown	4.20	138	3230m, 1605s	1420s, 1220m, 730m, br
11	Ni(MPDTB) <sub>2</sub> Cl <sub>2</sub>	146	Brown	3.80	158	3250m, 1595m	1425s, 1210m, 735m
12	Cu(MPDTB) <sub>2</sub> Cl <sub>2</sub>	150	Golden Yellow	1.16	156	3250m, 1610m	1420s, 1230m, 725m, br

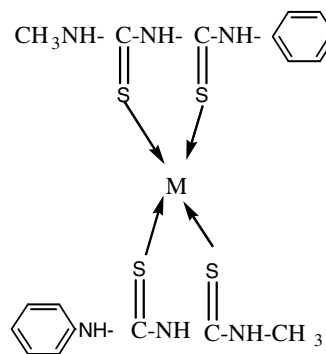
On the basis of above discussion the structures of the compounds were established as:



1-methyl-5-p-phenetyl-2,4-dithiobiuret (MPHDTB)



1-methyl-5-o-tolyl-2,4-dithiobiuret (MOTDTB)



1-methyl-5-phenyl-2,4-dithiobiuret (MPDTB)

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