

## Synthesis of 1,5-disubstituted 2,4 dithiobiurets and studies on their complexation behaviour

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### ABSTRACT

1,5-Disubstituted 2,4-dithiobiuret selected for the present studies were, 1,5 di-o-tolyl 2,4-dithiobiuret (DOTDTB), 1,5-di-p-phenetyl 2,4-dithiobiuret(DPhDTB), 1,5-dimethyl 2,4 dithiobiuret(DMDTB). The ligands were synthesized by the standard method and characterized by TLC, elemental analyses I.R. spectra and melting-points. The complexes of these ligands with the metals Co, Ni & Cu were prepared and characterized by elemental analyses, melting-points, magnetic moments, molar conductance I.R. spectra & Potentiometric studies. Tetrahedral structure have been proposed for these complexes.

**Key words:** Tetrahedral 2,4 dithiobiurets.

### INTRODUCTION

Dithiobiurets are interesting ligands for formation of Complexes with metal ions. It has an abundance of delocalized lone pair of electrons, that make it suitable for the stabilization of unusual oxidation states. Moreover, it could possibly chelate through the two sulphur atoms or through two nitrogen atoms or through a sulphur atom and a nitrogen atom, in each case it forms a six membered ring. This ligand can chelate either as a neutral donor or an uninegative or as dinegative ion, depending upon conditions.

G.A.Melson<sup>1</sup> prepared complexes of dithiobiuret with Cu(II) and Ni(II) and studies their properties using visible, reflectance and I.R. spectra and magnetic measurements. Cuprous complex of dithiobiuret has been proposed as fungicide<sup>2</sup>. Silver dithiobiuret complex was isolated and characterized by Stephen and Townshend<sup>3</sup> on the basis of I.R.

studies and suggested that dithiobiuret coordinate through thiocarbonyl sulphur atoms, Peyronel and Pignadoli<sup>4</sup>, prepared red coloured complexes of dithiobiuret with general formula  $[\text{Ni}(\text{DBT})_2]\text{X}_2$  (where  $\text{X} = \text{CH}_3\text{COO}, \text{Cl}, \text{ClO}_4$  OR DMF), and characterized on the basis of magnetic moment and I.R. studies. Girling<sup>5</sup> and Luth<sup>6</sup> isolated bis-chelate complexes of dithiobiuret with Co(II), Ni(II)Cu(II), Pd(II), and Zn(II), complete X-ray structural. Determination show that Ni(II) and Pd(II) complexes are planar.

### EXPERIMENTAL

The ligands were prepared by refluxing the respective constituents in equimolar mixture for about two hours in ethanol. After the completion of the reaction, mixture was evaporated and the concentrate was extracted with a suitable solvent and crystallized.

Table 1:



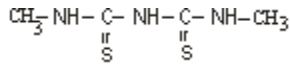
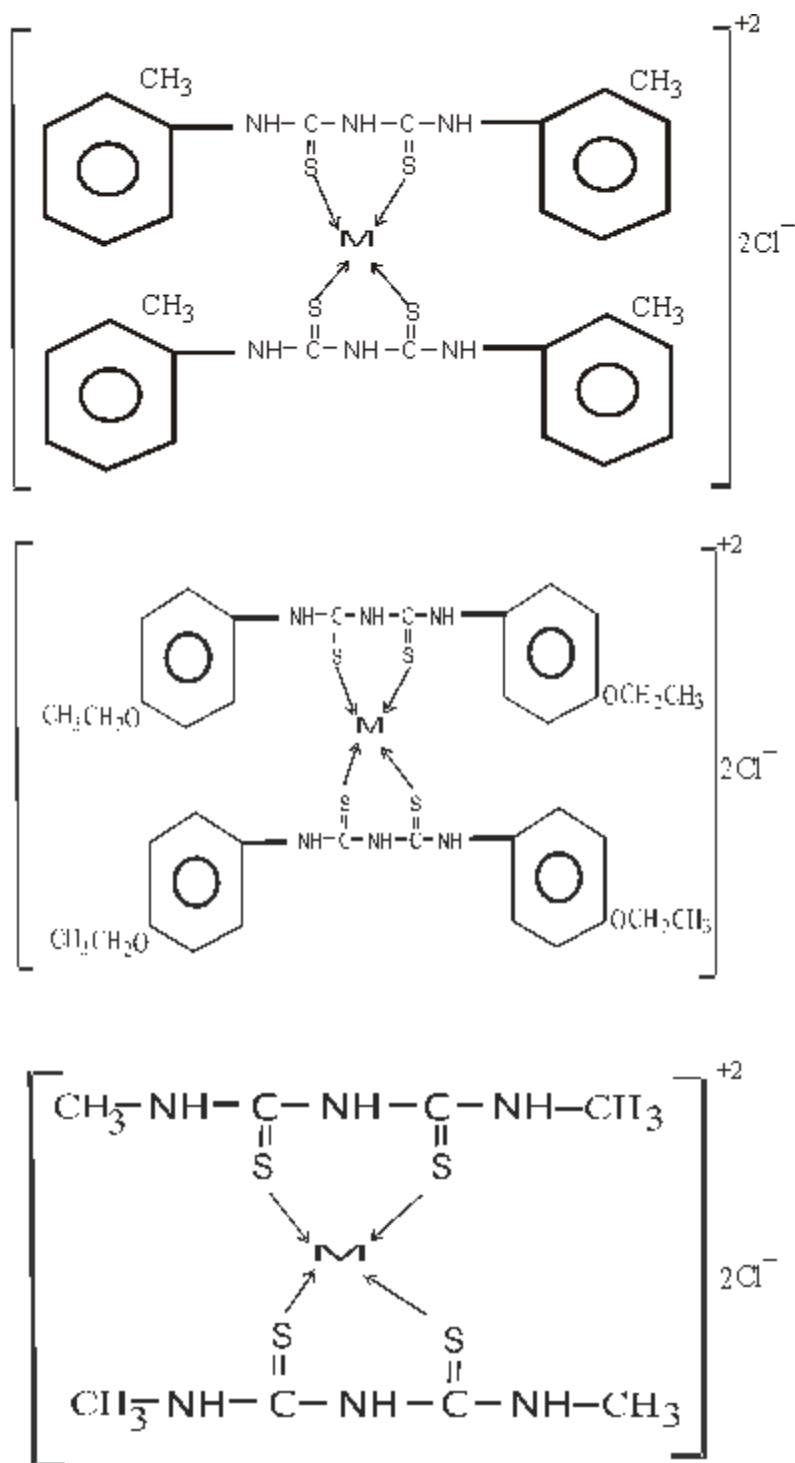
S. No	Compound abbreviation	Structure	M.pt	Mol. wt	Analysis	
					Calculated %	observed%
1.	1,5-Di-o-tolyl		115	315.46	N=13.33	13.10
	2,4-dithiobiuret (DOTDTB)	S=20.31			20.35	
2.	1,5-Di-p-phenetyl		134	375.55	N=11.25	11.20
	2,4-dithiobiuret (DPhDTB)	S=17.06			17.15	
3.	1,5-Di-methyl		148	163.26	N = 25.76	26.01
	2,4-dithiobiuret (DMDTB)	S=39.26			39.32	

Table 2: Potentiometric titration of 1,5-disubstituted 2,4-dithiobiuret with iodine in THF

Volume of iodine (in ml)	EMF OF (DOTDTB) (in ml)	EMF OF (DPhDTB) (in ml)	EMF OF (DMDTB) (in ml)
0.50	245	230	210
1.00	255	238	215
0.50	257	245	218
1.20	262	247	222
1.40	263	250	225
1.60	270	260	232
1.80	305	275	245
1.90	325	293	270
2.00	370	315	295
2.10	395	345	335
2.20	405	370	350
2.30	419	380	308
2.40	414	388	365
2.60	418	392	368
2.80	420	396	370
3.00	424	400	373
3.40	426	405	375
3.60	430	409	376
3.80	435	410	377
4.00	436	411	377

Table 3: The analytical data

S. No.	Mol. formula of the complex	Colour	M.P. °C	Elemental Analyses			Magnetic Moment in B.M.	Molar conductance Ohm <sup>-1</sup> Cm <sup>-2</sup> Mole <sup>-1</sup>
				C%	H%	N%		
1	1,5-Di-o-tolyl 2,4-dithiobiuret Cobalt(II) Chloride Complex [Co(DOTDTB) <sub>2</sub> ]Cl <sub>2</sub>	Brownish Green	128	50.51 (50.10)*	4.46 (4.38)	11.04 (10.92)	4.41	142
2	1,5-Di-p-phenetyl 2,4-dithiobiuret Cobalt(II) Chloride Complex [Co(DPhDTB) <sub>2</sub> ]Cl <sub>2</sub>	Greenish Brown	132	49.07 (49.00)	4.76 (4.70)	9.54 (8.72)	4.45	145
3	1,5-Di-methyl 2,4-dithiobiuret Cobalt (II) Chloride Complex [Co(DMDTB) <sub>2</sub> ]Cl <sub>2</sub>	Brownish Green	152	21.05 (20.50)	3.94 (3.82)	18.42 (17.89)	4.48	140
4	1,5-Di-o-tolyl 2,4-dithiobiuret Nickel (II) Chloride Complex [Ni(DOTDTB) <sub>2</sub> ]Cl <sub>2</sub>	Brown	134	50.53 (50.20)	4.47 (4.42)	11.05 (10.60)	3.72	140
5	1,5-Di-p-phenetyl 2,4-dithiobiuret Cobalt(II) Chloride Complex [Ni(DPhDTB) <sub>2</sub> ]Cl <sub>2</sub>	Dark brown	154	49.09 (49.00)	4.76 (4.71)	9.5 (8.67)	3.74	144
6	1,5-Di-methyl 2,4-dithiobiuret Cobalt (II) Chloride Complex [Ni(DMDTB) <sub>2</sub> ]Cl <sub>2</sub>	Blackish Brown	140	21.06 (21.00)	3.94 (3.89)	18.42 (17.89)	3.77	151
7	1,5-Di-o-tolyl 2,4-dithiobiuret Copper (II) Chloride Complex [Cu(DOTDTB) <sub>2</sub> ]Cl <sub>2</sub>	Golden Yellow	151	50.21 (50.00)	4.44 (4.01)	10.98 (9.34)	1.35	150
8	1,5-Di-p-phenetyl 2,4-dithiobiuret Cobalt(II) Chloride Complex [Cu(DPhDTB) <sub>2</sub> ]Cl <sub>2</sub>	Golden yellow	140	48.82 (48.40)	4.74 (4.69)	9.49 (8.88)	1.32	154
9	1,5-Di-methyl 2,4-dithiobiuret Cobalt (II) Chloride Complex [Cu(DMDTB) <sub>2</sub> ]Cl <sub>2</sub>	Yellow	144	20.84 (20.70)	3.90 (3.86)	18.23 (17.79)	1.21	152



where Metal M=Co,Ni,Cu

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The Purity of these ligands was checked by TLC & melting points, characterized by elemental analyses and I.R. spectra. The analytical data is given in data(I).

### Synthesis of complexes

A Known amount of etheral or ethanolic solution (0.01M) of anhydrous metal chloride was taken in a three necked round bottom flask fitted with a mechanical stirrer, a separating funnel and a calcium chloride tube. Flask containing metal chloride solution was cooled in ice bath at 10°C and then etheral solution (0.02M) of the ligand was added drop by drop to the metal chloride solution with constant string. After the addition was completed, the mixture was allowed to stand for an hour and then filtered, washed free of ligand first with ethanol and finally with ether. Complex compound was dried in vacuum.

The melting points of the complexes were determined in order to establish the formation of the adducts. These were subjected to elemental analyses at C.D.R.I. Lucknow, the magnetic susceptibility was measured by Gouy method at Bareilly College Bareilly. I.R. spectra were recorded in the range of 4000-200-cm<sup>-1</sup> the molar conductance was measured by conductivity meter type LBR of Wissenschaftlich Technische, Werkstätten, Germany, at 10<sup>-3</sup>M in DMF. Potentiometric studies were Carried out with iodine solution in THF using calomal and platinumium electrode. The data is given in table2.

### RESULTS AND DISCUSSION

The analytical data suggested 1:2 M:L stitiometry for all the complexes reported herein. The measurement of molar conductance at room temperture and 10<sup>-3</sup> M dilution suggested 1:2

electrolytic nature for all the complexes.

The spin only value of magnetic moment for cobalt complexes was observed in the range of 3.8-4.48 B.M. which is in the range reported for tetrahedral complexes<sup>7</sup>. These values of magnetic moments suggested the presence of three unpaired electron in the high energy t<sub>2g</sub> state arising from the tetrahedral ligand field. In case of Ni(II) complexes the spin only value of magnetic moment was found in the range of 3.72-3.77 B.M. which is suggestive of two unpaired electron in the High energy t<sub>2g</sub> state arising from tetrahedral ligand field. In case of Cu(II) complexes the value ranges from 1.7-2 B.M. The values suggested the presence of one unpaired electron and square planner gemoetry for the complex<sup>10</sup>.

The I.R spectra of the ligands 1,5 di-o-tolyl, 2,4 dithiobiuret (DOTDTB), 1,5-di-p-phenetyl 2,4-dithiobiuret(DPhDTB), 1,5-dimethyl 2,4-dithiobiuret(DOTDTB), 1,5-di-p-phenetyl 2,4-dithiobiuret(DPhDTB), 1,5-dimethyl 2,4 dithiobiuret (DMDTB) and their corresponding cobalt, Nickel and Copper Complexes were recorded in KBr phase & compared. The comparision revealed the coordination sites. The decrease in density and lowering in  $\nu_{C=S}$  frequency and lowering of  $\nu_{C=N}$  frequecey in case of all the complexes suggested the coordination through thionyl sulphur<sup>8</sup> atom and Nitrogen atom of azomethyne group(9). Coordination through thionyl group is also supported by potentiometric studies of the complexes. All other frequencies appeared unchanged in the I.R. spectra of the complexes.

On the basis of above mentioned facts tetrahedral structure has been proposed for all the complexes.

### REFERENCES

1. G.A Melson, Proceedings of IXth International Conference on Co-ordination Chemistry 243 (1966).
2. M.M.Baldwin, U.S.Patent, 2: 959,515 (1960).
3. W.I.stephen and A Townshend, *J. Chem. Soc. A*: 166 (1966).
4. G.Peyronel and A.Pignadoli, Proceeding of Xth International conference on co-ordination chemistry 290 (1967).
5. R.L.Giriling and E.L.AMMA, *Chem. Commun*, 1487(1968).
6. H.Luth, E.A. Hall., W.A. Spofford. and

- E.L.Amma, *Chem. Commun*, 520 (1969).
7. D.P Graddon An Introduction to Co-ordination Chemistry "Pergaman Press, Second edition P.32.
8. G.Peyronel and A.Pignedoli, Proceeding of Xth International conference on co-ordination chemistry, 290 (1967).
9. W.I.stephen and A.Townshend, *J.Chem.Soc A*: 166 1966).
10. R.D.Wilet, *J. Chem. Phys.* **41**: 2243 (1964).