

## Binuclear Ni(II), Co(II), VO(II) and Pt(II) Chelates of Bidentates Possessing N-N-S Moieties

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Metal-chelates of Co(II), Ni(II), Cu(II), VO(II) and Pt(II) with N-(3)-pyridine carboxaldehyde benzene thiol (HPCBT) and N-(3)-pyridine carboxaldehyde ethane thiol (HPCET) were synthesized and characterized by elemental analysis, molar conductance, magnetic moment IR and thermogravimetric analysis. These chelates exhibited sub-normal magnetic moments at room temperature indicating magnetic interaction between the metal(II) centres *via* bridging thiolic sulphur.

**Key Words:** Binuclear, Chelates, Bidentates, N-N-S Moieties.

### INTRODUCTION

Because of the possibility of interaction between the two metal centres, there is a demanding interest in the synthesis of dimeric chelates of Schiff's bases. One of the distinguishing features of such dimeric chelates is their subnormal magnetic moments<sup>1, 2</sup> which arise due to either direct metal-metal interaction or interaction through bridging ligand moieties.

### EXPERIMENTAL

Ligands N-(3 -pyridine carboxaldehyde)benzene thiol (HPCBT) and N-(3-pyridine carboxaldehyde) ethane thiol (HPCET) were synthesized by the condensation of 3-pyridine carboxaldehyde with 2-amino benzene thiol or 2-amino ethane thiol in the presence of piperidine. After refluxing equimolar DMF-ethanolic solution of these compounds for 4–5 h, concentrated and cooled to give coloured crystals, which were recrystallized from DMF. HPCBT 125° HPCET 142°C.

The metal-chelates were synthesized by refluxing for 5–6 h, the ligand (0.1 M) and the metal acetate or chloride (0.1 M) dissolved in minimum quantities of DMF-ethanol (4 : 1) mixture. Chelates so formed were filtered, washed with ethanol and recrystallized.

### RESULTS AND DISCUSSION

The solid metal-chelates synthesized were subjected to elemental analysis<sup>3</sup>, molar conductance values<sup>4</sup>, molecular mass<sup>4</sup> and magnetic susceptibility determination<sup>5-7</sup>. All were found to be coloured, stable towards air and moisture, decomposed at high temperature (> 380°C), soluble in DMF, DMSO and dioxane. Low molar conductance values reveal their non-electrolytic nature and the

analytical data suggest 1 : 1 metal-ligand stoichiometry. The molecular mass data indicate the dimeric nature of the complexes as shown in Table-3.

### Magnetic Measurements

The magnetic moments are quite interesting and are much lower than those of the usual mononuclear chelates at 308 K. This behaviour of showing sub-normal magnetic moments at room temperature is due to the phenomenon of anti-ferromagnetic interaction between the two metal(II) centres *via* the intermediate two bridging sulphur atoms and can be attributed to the dimeric nature of these chelates. In such chelates the M-M distance is too long to allow direct interaction between the two metal atoms.

The magnetic moments of Cu(II)-chelates were found to be 0.68 and 0.63 BM and those of VO(II) were 1.55 and 1.59 BM. In Co(II)-chelates the lowering in magnetic moments to 4.12 and 4.09 BM is attributed to anti-ferromagnetism *via* a super exchange mechanism.

The Pt(II) and Ni(II)-chelates were found diamagnetic as expected.

The relative decrease in magnetic moments is in the order Cu(II) > VO(II) > Co(II). All the chelates have similar structures but different magnetic behaviour. However, the electronic symmetry is supposed to play an important role in order to explain the strength of interactions in binuclear chelates.

### IR Spectra

Spectra of HPCBT and HPCET show a medium strong band at  $2660\text{ cm}^{-1}$  due to SH group,  $1645\text{ cm}^{-1}$  for  $\nu(\text{C}=\text{N})$  of the azo-methine and  $1585$  for  $\nu(\text{C}=\text{N})$  of the pyridine ring. A shift is observed towards lower region for the  $\nu(\text{C}=\text{N})$  of azomethine in complexes showing the involvement in coordination  $\nu(\text{C}=\text{N})$  for pyridine band shifts to higher value by  $45\text{--}35\text{ cm}^{-1}$  indicating coordination<sup>8</sup>.

The disappearance of the band ( $2660\text{ cm}^{-1}$ ) assigned to S—H group indicates that the chelation has taken place through the sulphur of the thiol group<sup>9</sup>.

The presence of coordinated water in all the complexes is indicated by a sharp band around  $3460\text{ cm}^{-1}$ . Medium intense broad band around  $450\text{ cm}^{-1}$  for  $\nu(\text{M}—\text{O})$  and  $295\text{ cm}^{-1}$  for  $\nu(\text{M}—\text{S})$ <sup>10, 11</sup> are assigned in complexes. A band of  $640\text{ cm}^{-1}$  is said to be for  $\nu(\text{C}—\text{S})$  mode.

### Thermogravimetric analyses

A perusal of Table-1 clearly indicates that all the complexes show loss in weight in the temperature range of  $150\text{--}180^\circ\text{C}$  corresponding to the coordinated water molecules. And in the second stage on heating above  $180^\circ\text{C}$  the compound loses mass of organic part up to  $310^\circ\text{C}$  and on further heating complete decomposition takes place resulting in the formation of oxides.

### Antimicrobial Activity

Examination of the ligands HPCBT and HPCET against bacteria, *viz.*, *B. pumilis*, *B. subtilis* and *S. aureus* was done. A perusal of Table-1 reveals that the diameter of zone of inhibition for the bacteria is in the order *B. subtilis* > *S. aureus* > *B. pumilis*.

TABLE-1  
THERMOGRAVIMETRIC ANALYSIS

Compound	Loss in weight (%)		Yield (%)		Temperature (°C)
	HPCBT	HPCET	HPCBT	HPCET	
Co(II)	3.82	3.62	96.32	94.10	150–180°
	69.02	69.92	31.21	34.27	310–450°
Ni(II)	3.89	3.52	96.82	96.80	150–180°
	87.68	89.32	13.21	13.94	310–450°
Cu(II)	3.12	3.19	96.35	92.14	150–180°
	82.73	89.11	16.15	15.32	310–450°
VO(II)	2.90	1.92	97.10	96.80	150–180°
	79.26	82.12	28.10	20.74	310–450°

Spore producing tendency of *B. subtilis* and *B. pumilis* provided them more resistivity towards toxic chemicals whereas *S. aureus* has a tendency to produce antichemicals like hydrolytic enzymes, e.g., penicillinase.

Metal-chelates show higher activity than the ligand itself as shown in Table-2. The antibacterial efficacy of these complexes was found in the order Co(II) > Cu(II) > Ni(II)<sup>13, 14</sup>. The increased activity after metallation is due to an increase in lipophilicity of the ligand which facilitates its binding to the bacterial cell followed by the removal of autolytic enzymes. Finally the result is the lysis of bacterial cells. It is worth mentioning that in the case of free ligands the co-ordinating sites were free for chelation; therefore they showed enhanced toxicity. But after complexation, the coordinating sites were satisfied with the metal ions; so their toxicity decreased appreciably.

TABLE-2  
ANTIMICROBIAL ACTIVITY

Compound	Diameters of zone of inhibition in mm		
	<i>B. subtilis</i>	<i>S. aureus</i>	<i>B. pumilis</i>
HPCBT	9.6	7.8	6.7
HPCET	8.2	6.3	5.2
Co(II)HPCBT	10.3	12.7	8.9
Ni(II)HPCBT	6.7	8.4	4.9
Cu(II)HPCBT	8.5	10.9	6.2
Co(II)HPCET	12.6	9.7	6.1
Ni(II)HPCET	8.4	6.3	3.4
Cu(II)HPCET	10.7	8.2	–

TABLE-3  
COLOURS, MOLECULAR MASSES AND ELEMENTAL ANALYSES OF LIGANDS AND THEIR METAL-CHELATES

Composition of ligands and their chelates	Colour	Molecular mass		% Analysis									
				C		H		N		S		Metal	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
HPCBT-C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> S	Dirty yellow	210	212	66.12	67.92	3.01	3.77	12.70	13.20	14.12	15.09	-	-
HPCET-C <sub>8</sub> H <sub>9</sub> N <sub>2</sub> S	Off yellow	162	164	57.12	58.53	3.91	4.87	16.10	17.07	18.23	19.51	-	-
Ni-HPCBT	Light green	532	536	51.90	53.73	2.02	2.98	9.41	10.44	10.11	11.94	9.01	10.82
Ni-HPCET	Greenish yellow	436	440	42.30	43.63	2.91	3.63	13.72	12.72	13.11	14.54	12.11	13.18
Co-HPCBT	Dark green	533	537	51.63	53.63	1.82	2.97	9.42	10.42	10.13	11.91	9.71	10.98
Co-HPCET	Olive green	537	441	41.53	43.53	2.91	3.62	13.10	12.69	13.41	14.51	12.51	13.37
Cu-HPCBT	Pale blue	483	487	57.13	59.13	2.85	3.28	10.17	11.49	12.51	13.14	11.31	12.93
Cu-HPCET	Blue	387	391	48.21	49.10	3.75	4.09	13.62	14.32	14.42	15.42	15.11	16.11
Vo-HPCBT	Grey	507	511	55.31	56.36	2.10	3.13	9.75	10.95	11.01	12.52	8.87	9.98
Vo-HPCET	Pale grey	411	415	45.12	46.26	2.17	3.85	12.30	13.49	13.10	15.42	11.82	12.28
Pt-HPCBT	Off white	615	619	45.15	46.52	1.05	2.58	10.01	9.04	9.10	10/33	29.11	31.50
Pt-HPCET	Light yellow	519	523	35.91	36.71	2.15	3.05	9.12	10.70	11.11	12.23	36.01	37.21

## REFERENCES

1. R.K. Mehta, V.C. Singhvi, R.K. Gupta and S.L. Pania, *J. Indian Chem. Soc.*, **6**, 721 (1973).
2. R.P. Mathur, P. Mathur and R.K. Mehta, *Curr. Sci. (India)*, **52**, 481 (1983).
3. A.I. Vogel, *A Text Book of Practical Organic Chemistry Including Quantitative Organic Analysis*, Longmans, London (1956).
4. I.M. Kolthoff, Phillip, J. Elving and E.B. Sandell, *Treatise of Analytical Chemistry, Part I: Theory and Practice*, Vol. 4, Interscience, New York, pp. 1785, 1827, 1828 (1963).
5. L.G. Gouy, *Compt. Rend.*, **109**, 935 (1889).
6. L.F. Bates, *Modern Magnetism*, Cambridge University Press, London (1961).
7. E.P. Stoner, *Magnetism and Atomic Structure*, Methuen, London (1926).
8. M.K. Patel, N.H. Patel, K.N. Patel and M.N. Patel, *J. Indian Council Chemists*, **17**, 19 (2000).
9. C. Natarajan, C.D. Sheela and P.R. Athappan, *Indian J. Chem.*, **30A**, 357 (1991).
10. M.K. Rastogi, R.C. Sharma and A.C. Gupta, *Indian J. Chem.*, **21A**, 190 (1982).
11. S.V. Singh, S. Gupta, A.C. Ojha and M.K. Rastogi, *Indian J. Chem.*, **30A**, 545 (1991).
12. M.A. Nakolaev, V.A. Longvinenko and L.T. Mychino, *Thermal Analysis*, Vol. 2, Academic Press, New York, p. 779 (1963).
13. F. Cavanage, *Analytical Microbiology*, Academic Press, New York p. 126 (1963).
14. V.S. Srivastava, C.P. Bhasin and G.C. Saxena, *J. Indian Chem. Soc.*, **63**, 865 (1986).

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