

Magneto, Spectral and Thermal Studies on Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , UO_2^{2+} and VO^{2+} chelates of *o*-(*N*- α -pyridimino) phenol and *o*-(*N*- α -pyrrolidimino) phenol

ANJU SHARMA, VIMLA CHOUDHARY and SHOBHA SHARMA*

Department of Chemistry, Faculty of Science J.N.V. University, Jodhpur-342 001, India

Solid chelates of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , UO_2^{2+} and VO^{2+} with *o*-(*N*- α -pyridimino) phenol (H_2PP) and *o*-(*N*- α -pyrrolidimino) phenol ($\text{H}_2\text{PP}'$) have been synthesised and characterised by different physico-chemical techniques. Elemental analysis, magnetic, conductance, spectroscopic (electronic, IR and ^1H MNR) and thermal studies conducted on solid chelates suggest an octahedral stereochemistry for Co^{2+} , Ni^{2+} , UO_2^{2+} and VO^{2+} chelates. Various bonding parameters were also evaluated.

Key words: Magnetic, spectral, thermal, Zn(II), Cd(II), $\text{UO}_2(\text{VI})$, VO(II), chelates.

INTRODUCTION

Transition metal complexes with azomethines have played a vital role in the development of coordination chemistry. A literature survey¹⁻³ has indicated that no work has been done on Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , UO_2^{2+} and VO^{2+} with *o*-(*N*- α -pyridimino) phenol (H_2PP) and *o*-(*N*- α -pyrrolidimino) phenol ($\text{H}_2\text{PP}'$). In continuation of our earlier work⁴⁻⁷, here we are reporting the preparation and characterization of bivalent metal chelates with H_2PP and $\text{H}_2\text{PP}'$.

EXPERIMENTAL

Synthesis of Ligand: The ligands H_2PP and $\text{H}_2\text{PP}'$ were synthesised by the condensation of 2-pyridone and 2-pyrrolidone with *o*-aminophenol respectively, in presence of piperidine as the condensing agent. On refluxing equimolar ethanolic solution of the reactants for 2-3 h, the brown and light yellow solutions obtained were filtered hot, concentrated and cooled when brown (H_2PP) and yellow ($\text{H}_2\text{PP}'$) crystals were obtained. These were recrystallised from ethanol. H_2PP and $\text{H}_2\text{PP}'$ were obtained in quantitative yields. m.p. 130°C (H_2PP) and 141°C ($\text{H}_2\text{PP}'$). [For H_2PP found: C, 70.65; H, 5.05; N, 14.74%; calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$: C, 70.97; H, 5.38; N, 15.05%; and for $\text{H}_2\text{PP}'$ found: C, 67.86; H, 6.52; N, 15.58%; calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$: C, 68.18; H, 6.82; N, 15.91%.] The purity of the ligands was checked by TLC and spectral data.

Synthesis of Metal Chelates and Their Adduct: The metal chelates were obtained as crystalline solids by refluxing ethanolic solutions of $\text{H}_2\text{PP}/\text{H}_2\text{PP}'$ (0.01

M in 20 mL 80% ethanol) and metal nitrate (0.01 M in 10 mL 80% ethanol for 2–3 h in nitrogen atmosphere. These were recrystallised from suitable solvents. Their chelates with pyridine adducts were also synthesised.

The hydrated metal-chelates were warmed in distilled pyridine on steam-bath and concentrated in a vacuum desiccator over calcium chloride, when coloured crystals of the pyridine adduct deposited. The crystals were separated, washed with a little absolute alcohol and ether, dried and preserved in a vacuum desiccator.

RESULTS AND DISCUSSION

The potentiometric studies⁸ were carried out by the Calvin-Bjerrum pH titration technique and the hydrated solid chelates H₂PP and H₂PP' with Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, UO₂²⁺ and VO²⁺ and their pyridine adducts were prepared by the method reported earlier⁹.

Micro-analysis of the metal chelates display 1 : 1 (metal : ligand) stoichiometry. Thermograms of the hydrated chelates revealed that on gradual heating from room temperature the hydrated salts were completely dehydrated and decomposed in the temperature range 190–800°C. From the mass-loss curves of the metal-chelates it is observed that no change occurs around 80–190°C indicating the absence of crystal held water in them. TGA of these chelates revealed mass-loss corresponding to three water molecules ($n = 3$) when M = Co²⁺, Ni²⁺ and Cu²⁺; two water molecules ($n = 2$) when M = VO²⁺ and one water molecule ($n = 1$) when M = Zn²⁺, Cd²⁺ and UO₂²⁺.

The molar conductance values of 10⁻³ M solutions of metal chelates in DMF lie in the range 3.0–7.2 (H₂PP) and 2.7–7.0 (H₂PP') ohm⁻¹ cm² mol⁻¹ indicating their non-electrolytic nature. All the metal chelates, except those of Zn²⁺, Cd²⁺ and UO₂²⁺ were found to be paramagnetic. The magnetic moments of the hydrated chelates of Co²⁺, Ni²⁺, Cu²⁺ and VO²⁺ with H₂PP/H₂PP' were found to be 4.68/4.90, 2.97/3.04, 1.82/1.93 and 1.74/1.71 B.M. respectively, indicating the presence of 3, 2, 1 and 1 unpaired electrons respectively in these metal ions.

The electronic spectral data of hydrated metal chelates in benzene and some spectral parameters like Racah inter-electronic repulsion parameters B and C, Condon-Slater parameters F₂ and F₄, nephelauxetic ratio β, Sinha's parameter δ%, D_q and LFSE of H₂PP and H₂PP' metal chelates so calculated have been summarised in Table-1.

Infrared Spectra: A comparison of the IR spectra of H₂PP and H₂PP' with those of their bivalent metal-chelates indicated coordination of the ligands through azomethine nitrogen, phenolic oxygen and ring nitrogen. In the spectra of H₂PP and H₂PP' three major peaks were observed in the regions 3380–3360, 1625–1615 and 3640–3620 cm⁻¹ assignable to ν(NH), ν(C=N) and ν(OH) modes respectively.

In the metal-chelates of H₂PP and H₂PP' the bands in the ranges 3380–3360 and 3640–3620 cm⁻¹ disappeared suggesting deprotonation of —NH and —OH groups and their participation in chelation. ν(C=O) shift of the phenolic group (1105 cm⁻¹) as obtained towards the higher region (*ca.* 25 cm⁻¹) suggests bonding

TABLE-1
ELECTRONIC SPECTRAL DATA AND BONDING PARAMETERS OF H₂PP AND H₂PP' HYDRATED METAL-CHELATES

Metal - chelates	Absorption bands (cm ⁻¹)	Assignments	Dq (cm ⁻¹)	B	β	δ	C	F ₄	F ₂	v ₂ /v ₁	LFSE (kJ mole ⁻¹)
Co ²⁺	8700 (8610)	⁴ T _{1g} → ⁴ T _{2g} (F)	870 (861)	940.00 (857.00)	0.9681 (0.8826)	0.0329 (0.1330)	4352.20 (3967.91)	124.35 (113.37)	1561.74 (1423.85)	1.9368 (1.9520)	62.28 (61.64)
	16850 (16820)	→ ⁴ A _{2g} (F)									
	23350 (21860)	→ ⁴ T _{1g} (F)									
	10330 (10220)	⁴ A _{1g} → ³ T _{2g} (F)	1033 (1022)	812.66 (836.00)	0.7524 (0.7740)	0.3290 (0.2919)	3827.62 (3937.56)	109.36 (112.50)	1359.46 (1398.50)	1.623 (1.6418)	147.89 (146.32)
16770 (16780)	→ ³ T _{1g} (F)										
26410 (26420)	→ ³ T _{1g} (F)										
Cu ²⁺	12450 (12350)	² E _g → ² T _{2g}	1245 (1235)	-	-	-	-	-	-	-	89.12 (88.41)
	11990 (11780)	² B _{2g} → ² E _{1g}	1190 (1178)	-	-	-	-	-	-	-	57.22 (56.21)
VO ²⁺	20260 (20090)	→ ² B _{1g}		-	-	-	-	-	-	-	-

*Values in parentheses for H₂PP' chelates.

between metal and phenolic oxygen atom. The band in the region 1625–1615 cm^{-1} was shifted to lower region 1605–1595 cm^{-1} in the chelates, indicating coordination through azomethine nitrogen. In the IR spectra of metal-chelates, new bands in the far infrared regions in the ranges 580–550 and 440–420 cm^{-1} were observed and assigned to $\nu(\text{M—N})$ and $\nu(\text{M—O})$ modes¹⁰, respectively. All the hydrated-chelates showed one band in the range 3350–3315 cm^{-1} due to $\nu(\text{OH})$ of coordinated water which was absent in their pyridine adducts. A band in the region 755–720 cm^{-1} in the IR spectra of the chelates indicated that the water molecules were coordinated and not lattice held.

¹H NMR Spectra

To substantiate further bonding in these chelates ¹H NMR spectra of H₂PP and H₂PP' and their bivalent metal-chelates were recorded in CDCl₃/TMS. The chemical shift value (δ , ppm) of the different protons are as follows.

¹H NMR spectra of H₂PP and H₂PP' signals due to —OH and >NH protons appeared at δ 8.02 and 7.40, δ 8.15 and 6.61 ppm respectively. The signals due to OH and NH protons disappeared in the spectra of the corresponding metal-chelates. Multiplets due to pyridine and pyrrole ring protons appeared at δ 7.45–7.88 and δ 6.12–6.54 ppm in H₂PP and H₂PP' were shifted towards higher field in the corresponding metal-chelates (*ca.* 0.10–0.15 ppm) indicating donation of lone pair of electrons of ring nitrogen to the central metal atom. The positions of signals due to aromatic protons at δ 6.98 and 7.10 in H₂PP and H₂PP' respectively were found unchanged in the metal-chelates.

Based on the above evidences Co²⁺, Ni²⁺, Cu²⁺ and VO²⁺ chelates and their adducts are assigned an octahedral stereochemistry; Zn²⁺ and Cd²⁺ chelates and their adducts tetrahedral configuration; and Cu²⁺ chelates and its adduct distorted octahedral geometry (due to Jahn-Teller effect)¹¹

REFERENCES

1. F.A. Cotton, *Prog. Inorg. Chem.*, **7**, 88 (1996).
2. D.J. Hodgson, *Prog. Inorg. Chem.*, **19**, 1 (1975).
3. A. Syamal, *Coord. Chem. Rev.*, **16**, 309 (1975).
4. S. Sharma, A. Jain, A. Sharma, L. Jain, V. Chowdhary and R.K. Mehta, *Nat. Acad. Sci. Letters*, **15**, 179 (1992).
5. S. Sharma and A. Sharma, *Orient. J. Chem.*, **16**, 349 (2000).
6. V. Chowdhary, M. Parihar and R.K. Mehta, *Z. Phys. Chemis. (Leipzig)*, **271**, 413 (1990).
7. M. Parihar, R. Goyal, V. Gupta, B.R. Patel and R.K. Mehta, *J. Indian Inst. Sci.*, **71**, 35 (1991).
8. A. Sharma, U. Bhardwaj, G.R. Kachhawah, S. Sharma and R.K. Mehta, *Trans. SAEST*, **26**, 246 (1991).
9. S. Sharma, S. Gaur and R.K. Mehta, *J. Indian Inst. Sci.*, **68**, 295 (1988).
10. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, p. 233 (1970).
11. H.A. Jahn, E. Teller, *Proc. R. Soc. London*, **161A**, 220 (1937).