

Synthesis and Characterization of Complexes of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , UO_2^{2+} and VO^{2+} with Biprotic Tridentate Ligand

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The stability constants of chelates of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , UO_2^{2+} and VO^{2+} with O-(N-pyrrole-2-methyl imino) propanoic acid (H_2PP) were determined potentiometrically by Calvin's extension of Bjerrum's method in 30% (v/v) water-ethanol-mixture ($\mu = 0.1, 0.05$ and 0.1 M NaClO_4) at 25, 35, 45°C respectively. The thermodynamic parameters have also been evaluated. These chelates are characterized by molecular mass measurement, elemental analyses, magnetic moment, ^1H NMR and electronic spectral data.

Key words: Co(II), Cu(II), Zn(II), Cd(II) $\text{UO}_2(\text{II})$, $\text{VO}(\text{II})$ complexes, biprotic tridentate ligand.

INTRODUCTION

Survey of literature¹⁻³ indicated that no work has been done in Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , UO_2^{2+} and VO^{2+} chelates of O-(N-Pyrrole-2 methyl/ imino) propanoic acid (H_2PP). Keeping this in view we report here the synthesis and analytical properties of these chelates.

The solid metal chelates were analysed for the element microanalytically. The experimental values were found in agreement with their theoretical values. The metal chelates display 1 : 1 (metal-ligand) stoichiometry. Pyrolysis (TGA) thermograms of the hydrated metal chelates showed mass loss at 110°C corresponding to three water molecules ($n = 3$) when $M = \text{Co}^{2+}$, Ni^{2+} or Cu^{2+} ; two water molecules ($n = 2$) when $M = \text{VO}^{2+}$ and one water molecule ($n = 1$) when $M = \text{Cd}^{2+}$, Zn^{2+} and UO_2^{2+} . Molar conductance of 10^{-3} M solution of the metal chelates in DMF lies in the range of $2.4\text{--}5.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating their non-electrolytic nature.

EXPERIMENTAL

The dissociation constants of O-(N-pyrrole-2-methylimino) propanoic acid (H_2PP) and stability constants of its chelates with Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , UO_2^{2+} and VO^{2+} have been determined by Calvin's extension of Bjerrum's method in 30% (v/v) water-alcohol mixture.

The ligand H_2PP was synthesized by the condensation of 2-acetyl pyrrole with β -alanine in presence of a drop of piperidine. On refluxing the equimolar ethanolic solution of the reactants for 2–3 h, the light yellow solutions obtained was filtered hot, concentrated and cooled when yellow crystals separated out. m.p. 104°C

Found: C, 58.57; H, 6.52; N, 15.38; requires: C, 60.00; H, 6.60; N, 15.55%. The purity of the ligands was checked by TLC and spectral data.

The following solutions (A–C) in 30% v/v (water-alcohol mixture, total volume 40 mL) were prepared and titrated potentiometrically against carbonate-free sodium hydroxide solution (0.1, 0.05, 0.01 M NaClO₄) at 25, 35 and 45°C:

- 10.0 mL of 0.01 M H₂PP + 4.0 mL of 1.0 M NaClO₄ + 26.0 mL of 30% water-alcohol mixture.
- 10.0 mL of 0.01 M H₂PP + 4.0 mL 1.0 M NaClO₄ + 10.0 mL of 0.01 M metal-ion solution + 16.0 mL of 30% water-alcohol mixture.
- 20.0 mL of 0.01 M H₂PP + 4.0 mL of 1.0 M NaClO₄ + 10.0 mL of 0.01 M metal-ion solution + 6.0 mL of 30% water-alcohol mixture.

The pH were corrected for the non-aqueous medium³.

The solid metal chelates were obtained by refluxing an ethanolic solution of H₂PP (0.02 M) with metal nitrate (0.02 M) solution in 75% ethanol. During refluxing the mixture was stirred magnetically and a few drops of ammonia (1 : 20) were added till the solid mass separated. It was filtered, washed and dried *in vacuo*. Their pyridine and picoline adducts were also synthesised by the method reported earlier.

RESULTS AND DISCUSSION

The values of pK₁ and pK₂ of H₂PP, as determined by interpolation of half n values method and algebraic method were found to be 4.73, 9.33 at 25°C; 4.48, 9.30 at 35°C, 4.24, 9.00 at 45°C respectively (at μ = 0.1 M NaClO₄), revealing biprotic nature of the ligands. By plotting \bar{n} vs. log [A⁻²], the formation curves of the metal ligand systems were obtained. The values of stability constants derived from the formation curves were refined by different computational methods⁴. The average values of stabilities follow the order:



in agreement with Irving-Williams rule⁵.

The values of overall changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were evaluated using Gibbs Helmholtz equation. The negative ΔH° values suggest exothermic nature of reaction. The positive entropy (ΔS°) term is favourable for chelation (Table-1).

On incorporating the data in Harned's equation⁶, the values of 0, pK_M^H and ΔH were found to be 514.2, 13.7, 0.56 and 708.57, -7.75 and 122.35 for H₂PP complexes of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, UO₂²⁺ and VO²⁺.

The electronic spectrum of Co²⁺ chelates in benzene exhibits three bands at 8580, 17300 and 21200 cm⁻¹ which can be assigned to the transitions ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g} → ⁴T_{1g}(P) respectively. These bands suggest an octahedral geometry around Co²⁺ in the complexes. In the case of Ni²⁺ chelate two bands are obtained at 10050 and 26400 cm⁻¹, which may be assigned to the transitions ³T_{2g} → ³T_{1g}(F) and ³A_{2g} → ³T_{1g}(P) respectively. These bands suggest an octahedral stereochemistry for Ni²⁺ complex. In Cu²⁺ chelate the band at 12750 cm⁻¹ is assigned to ³E_g → ²T_{2g} transition. VO²⁺ chelates display

two bands at 11900 and 20400 cm⁻¹ assignable to the transitions ³B₂ → ²E₁ and ²B₂ → ²B₁ respectively suggesting octahedral geometry for their chelates.

TABLE-1
THERMODYNAMIC STABILITY CONSTANTS AND RELATED PARAMETERS AT
35°C OF BIVALENT METAL CHELATES OF O-(N-PYRROLE-2-METHYL IMINO)
PROPANOIC ACID (H₂PP)

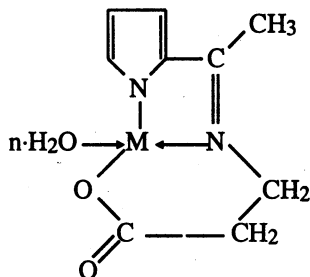
Metal ion	log β ₀ (Temp. °C)			ΔG° (kJ mol ⁻¹)	-ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹)
	25	35	45			
Co ²⁺	10.18	9.88	9.60	58.26	52.62	18.31
Ni ²⁺	10.73	10.42	10.12	61.45	55.34	19.83
Cu ²⁺	11.44	11.11	10.79	65.52	58.97	21.26
Zn ²⁺	5.69	5.52	5.37	32.55	29.03	11.42
Cd ²⁺	5.06	4.91	4.77	28.95	26.31	8.57
UO ₂ ²⁺	13.85	13.45	13.08	79.32	69.85	30.74
VO ²⁺	14.72	14.30	13.91	84.33	78.48	35.23

Infrared spectra of the ligand H₂PP in KBr/ Nujol mull reveals three bands in the range 3350–3250, 1630–1620, 1760 cm⁻¹ assignable to ν(N—H) respectively. On complexation the band at 1760 cm⁻¹ in H₂PP disappears and instead gives rise to ν_{asym}(COO⁻) and ν_{sym}(COO⁻) at 1600 and 1400 cm⁻¹ respectively. In the metal chelates under examination the band in the region 3350–3250 cm⁻¹ could not be located, suggesting the elimination due to lower wave numbers indicating participation of azomethine nitrogen in complexation. Hydrated metal chelates of this ligand display additional bands in the regions 580–500 and 410–370 cm⁻¹ assignable to ν(M—N) and ν(M—O) modes respectively. All the hydrated chelates give one band in the range 3325–3315 cm⁻¹ due to OH of the coordinated water. The pyridine and picoline adducts of these metal chelates indicated no such peaks in the range 3400–3200 cm⁻¹. This observation clearly corroborates in the hydrated chelates, the coordinated nature of the water molecules as indicated by their loss at relatively high temperature (> 180°C). Further a band in the region 755–720 cm⁻¹ in the infrared spectra of the metal chelates indicates that water molecules are coordinated and not lattice held⁷.

¹H NMR spectra of H₂PP and their metal chelates were recorded in CDCl₃ TMS. The chemical shift values (δ 5 ppm) of different protons are given below:

In the ¹H NMR spectra of the ligands the signals due to the COOH and —NH protons (in H₂PP) at δ 8.05, 7.5 ppm respectively disappeared in the spectra of the corresponding metal chelates. The positions of signals due to CH₂—CH₂ protons (in H₂PP), CH₃ positions in (H₂PP) at δ 1.86, 1.92 ppm respectively remained unchanged in the metal chelates. The signals around δ 6.12 ppm in the free ligand were due to pyrrole ring protons and later shifted to δ 6.01 in the metal chelates indicating the involvement of pyrrole ring nitrogen in coordinations.

Based on the above findings, the metal chelates may be represented by the structure (I).



where $n = 3$, $M = \text{Co}^{2+}$, Ni^{2+} and Cu^{2+} ; $n = 2$, $M = \text{VO}^{2+}$; $n = 1$, $M = \text{UO}_2^{2+}$, Zn^{2+} and Cd^{2+} .

Fig. 1. Structure of the metal chelates of H_2PP

REFERENCES

1. F.A. Cotton, *Progr. Inorg. Chem.*, **7**, 88 (1966).
2. H. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1945).
3. A. Syamal, *Coord. Chem. Rev.*, **16**, 309 (1975).
4. H.S. Harned and N.D. Embree, *J. Am. Chem.*, 5095 (1934).
5. S.P. Ranga and R.K. Mehta, *J. Indian Inst. Sci.*, **69**, 131 (1989).
6. G.M. Shashidhara and T.R. Goudar, *J. Indian Chem. Soc.*, **78**, 360 (2001).
7. R.K. Mehta and S.Z. Sharma, *Z. Phys. Chem.*, **267**, 392 (1986).

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