

THERMODYNAMIC AND PHYSICO-CHEMICAL STUDIES OF Co(II), Ni(II), Cu(II), Zn(II), Cd(II), VO²⁺ AND UO₂²⁺ IONS O-(N-PYRROLE-2-CARBOXALDIMINO) PHENOLATE SYSTEMS

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Thermodynamic and physico-chemical investigation of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), VO²⁺ and UO₂²⁺ chelates with O-(N-pyrrole-2-carboxaldimino) phenol (H₂PP) have been carried out. These chelates and their picoline adducts have also been obtained as crystalline solids and characterised by elemental analyses, molecular mass, magnetic moments, conductance and spectral techniques. Appropriate geometries have been assigned to these compounds.

Key Words : Thermodynamic and Physico-chemical Studies of Co(II), Ni(II), Cu(II), Zn(II); Cd(II), VO²⁺ and UO₂²⁺ Ions-O-(N-Pyrrole-2-Carboxaldimino) Phenolate Systems

INTRODUCTION

METAL chelates containing N-N-O, N-O-O and N-S-O moieties possess strong fungicidal and antibacterial activities. O-(N-pyrrole-2-carboxaldimino) phenol possesses N-N-O moiety.

A perusal of the literature has indicated that no work has been done so far on the chelates of O-(N-pyrrole-2-carboxaldimino) phenol (H₂PP) with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), VO²⁺ and UO₂²⁺. Hence, the same is undertaken and its findings are reported in the present paper.

EXPERIMENTAL

H₂PP has been synthesised by refluxing an equimolecular mixture of O-aminophenol and pyrrole-2-carboxaldehyde in benzene for an hour at 110 °C. Water is removed azeotropically with benzene. After distilling out the benzene a yellow crystalline solid m.p. 78° is obtained. It gave satisfactory C, H and N analysis. The metal nitrates and reagents employed are Analar pure (BDH).

Magnetic susceptibility measurements were carried out using Gouy magnetic balance in which Hg [Cu(CNS)₄] was used as the reference. The electronic spectra of the compounds were recorded on a VEB Carl Zeiss Jena VSU-2P spectrophotometer at room temperature. IR spectra were taken in Nujol mull using NaCl prism.

Potentiometric titrations have been carried out in aqueous medium according to Bjerrum's extension of Irving and Rossotti method,¹ at 25, 35 and 45 °C at $\mu = 0.01, 0.05$ and $0.1M$ $NaClO_4$. A precision pH meter type OP : 205 No. 837 (Radelkis) equipped with a glass-calomel electrode assembly is used to record the pH . The titrations are carried out in the presence and absence of metal ions against carbonate-free $0.1M$ $NaOH$ and the titrations curves have the usual shapes.

RESULTS AND DISCUSSION

The pK_1 and pK_2 of H_2PP are found 5.82 and 8.98 at 25°, 5.74 and 8.40 at 35° and 5.54 and 7.97 at 45 °C, respectively. These values suggest that H_2PP is a biprotic ligand. Further, the pK values fall with rise of temperature. The metal ligand stability constants are read from the formation curves drawn by plotting \bar{n} vs pL .

The refinement is done by various computational methods² such as correction term, convergence formula, successive approximation and interpolation at various \bar{n} values and their average values ($\log \beta_2$) alongwith their deviations from the theoretical values are summarised in Table I. The $\log \beta_2$ values of the metal chelates are in the order, $VO^{2+} > UO_2^{2+} > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II)$ which follows the Irving-Williams rule.³

The thermodynamic stability constants ($\log K^\circ$) has been obtained by extrapolation of measured formation constants to zero ionic strength on a graph plotted between \log of stability constants vs $\sqrt{\mu}$, where μ is the ionic strength (Table I).

The values of the overall changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have been evaluated using Gibbs-Helmholtz equation. ΔG° values of all the chelates are more negative at higher temperature. ΔH° values are positive in all the cases indicating endothermic nature of reactions. The positive enthalpy change can be attributed both to greater steric strain resulting from the presence of fused chelate rings in the metal chelates, and to the inherently weaker M-N bond when N is a tertiary rather than a primary nitrogen atom. Nevertheless, the greater number of chelate rings leads to greater stability, owing to an entropy effect that is only partially cancelled by the unfavourable enthalpy change. The positive values of ΔS° suggest that entropy term is favourable for chelate formation.

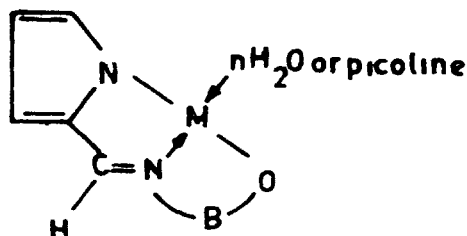
In terms of Harned equation⁴ the plots of $(pK^H - ct^2)$ vs t are found to be linear. Values of slope ($-2c\theta$) and intercept ($pK_m^H + c\theta^2$) are obtained from the plot and values of θ , pK^H and pK_m^H for H_2PP are found to be 677.9, 16.46 and -6.52 , respectively. For H_2PP , the values of ΔH obtained by Harned's equation and Gibb's-Helmholtz equation are also found in agreement.

Hydrated solid chelates of H_2PP with $Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$, $Cd(II)$, VO^{2+} and UO_2^{2+} and their picoline adducts are prepared by the methods reported earlier.⁵ The products gave satisfactory elemental analysis and display 1 : 1 metal-ligand) stoichiometry (Fig. 1). Their composition may be expressed by $(ML.nH_2O)$

TABLE I
Average stability constants and thermodynamic functions of bivalent metal chelates of *O*-(*N*-pyrrole-2-carboxaldimino) phenol (H_2P) at 25°, 35° and 45°

Metal chelates	Stability constants at $\mu = 0.1M NaClO_4$			$\log K^\circ$			$-\Delta G^\circ K cal/mole$			$\Delta H^\circ kcal/mole$ at 35°	$\Delta S^\circ deg/mole$ at 35°	
	25°	35°	45°	25°	35°	45°	25°	35°	45°	35°	at 35°	
VO ³⁺	$\log K_1$	10.46	10.69	10.92	19.97	20.64	21.10	113.95	121.73	128.48	102.52	0.73
	$\log K_2$	9.33	9.60	9.85								
	$\log \beta_2$	19.79 ± 0.07	20.29 ± 0.05	20.77 ± 0.06								
UO ₂ ²⁺	$\log K_1$	9.69	9.92	10.10	18.29	18.75	19.18	104.36	110.58	116.79	80.75	0.62
	$\log K_2$	8.47	8.69	8.88								
	$\log \beta_2$	18.16 ± 0.03	18.61 ± 0.04	18.98 ± 0.03								
Cu(II)	$\log K_1$	8.66	8.50	9.19	16.61	17.09	17.52	94.78	100.79	106.68	82.56	0.59
	$\log K_2$	7.37	7.61	8.05								
	$\log \beta_2$	16.03 ± 0.06	16.51 ± 0.07	17.24 ± 0.05								
Ni(II)	$\log K_1$	7.64	7.80	8.13	15.57	15.99	16.43	88.84	94.30	100.04	78.02	0.56
	$\log K_2$	6.47	6.75	7.05								
	$\log \beta_2$	14.11 ± 0.08	14.55 ± 0.03	15.18 ± 0.06								
Co(II)	$\log K_1$	6.75	6.96	7.21	14.56	15.02	15.49	83.08	88.38	94.32	84.38	0.56
	$\log K_2$	5.58	5.82	6.04								
	$\log \beta_2$	12.33 ± 0.04	12.78 ± 0.04	13.25 ± 0.07								
Zn(II)	$\log K_1$	6.11 ± 0.03	6.36 ± 0.07	6.57 ± 0.03	7.55	7.82	8.03	43.08	46.12	48.89	43.59	0.29
Cd(II)	$\log K_1$	5.60 ± 0.05	5.77 ± 0.06	5.99 ± 0.04	6.93	7.16	7.34	39.54	43.23	44.69	37.20	0.25

or Pic), where M = metal ion. Thermogravimetric analysis suggests a weight-loss compared to three water or picoline molecules ($n = 3$) when $M = \text{Co(II)}$ and Ni(II) , two water or picoline molecules ($n = 2$) when $M = \text{VO}^{2+}$ and one water or picoline molecule ($n = 1$) when $M = \text{Zn(II)}$, Cd(II) or UO_2^{2+} .



where, $B \equiv o\text{-C}_6\text{H}_4$
 when $n = 1$, $M(\text{II}) = \text{Zn, Cd or UO}_2$
 $n = 2$, $M(\text{II}) = \text{VO}$
 $n = 3$, $M(\text{II}) = \text{Co or Ni}$

FIG 1 Bivalent metal chelates of *o*-(*N*-pyrrole-2-carboxaldimino) phenol (H_2PP)

The magnetic moments (Table II) indicate the presence of 3, 2, 1 and 1 unpaired electron in Co(II) , Ni(II) , Cu(II) and VO^{2+} chelates, respectively. The remaining Zn(II) , Cd(II) and UO_2^{2+} -chelates are found to be diamagnetic. Excepting the Cu(II) -chelates the magnetic moments show that there is no metal-metal bonding in the chelates and hence spin exchange does not take place and they exist as monomer. However, Cu(II) chelate showed subnormal magnetic moment of 1.57 B.M. at 308 °K which indicates its dimeric nature. On the basis of evidences obtained an octahedral stereochemistry is suggested for the Ni(II) , Co(II) , UO_2^{2+} and VO^{2+} -chelates. The Cu(II) chelate may possess a dimeric bridged structure involving superexchange through bridged oxygen atom. Zn(II) and Cd(II) chelates are expected to be tetrahedral as is common with these ions. Negligibly small conductance value (Table II) of the compounds suggest them to be nonelectrolytes. Molecular masses, conductance values, magnetic moments and electronic spectra of the chelates are summarised in Table I.

Electronic Absorption Spectra

The electronic absorption spectra of the hydrated metal chelates and their picoline adducts are recorded in methanol and the results obtained are summarised in Table II. A perusal of Table II suggests an octahedral stereochemistry of the VO^{2+} , UO_2^{2+} , Co(II) and Ni(II) chelates and their adducts under study. However, the Cu(II) chelate possesses a dimeric bridged structure (Fig. 2).

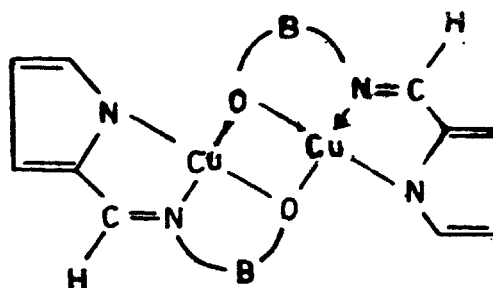
I R Spectra

The I R spectrum of H_2PP shows three bands at 3620, 3315 and 1605cm^{-1} which correspond to ν_{OH} , $\nu_{\text{N-H}}$ and $\nu_{\text{C=N}}$ respectively. In all the metal chelates

TABLE II
Molecular mass, conductance, magnetic moments and electronic spectra and possible transitions of bivalent metal chelate of O-(N-pyrrole-2-carboxaldimino) phenol (H₃PP)

Metal chelates*	Hydrated chelates				Picoline adducts				Molar extension coeff. (ε) mole ⁻¹ cm ⁻¹	Transitions (hydrated and picoline adducts)	
	Molecular mass		M u _{eff} (BM) at		Molecular mass		M u _{eff} (BM) at				
	Found	Calcd	cm ² mole ⁻¹ 308 °K	cm ² at	Found	Calcd	cm ² mole ⁻¹ 308 °K	cm ² at			
[VO(C ₁₁ H ₈ N ₂ O)X ₂]	268	269	6.8	1.67	11650	433	437	6.7	1.68	11850	$d_{xy} \rightarrow d_{xz}, d_{yz}$
[UO ₂ (C ₁₁ H ₈ N ₂ O)X]	468	472	7.0	—	20200	543	457	7.1	—	20250	$d_{xy} \rightarrow d_{x^2-y^2}$
[Cu(C ₁₁ H ₈ N ₂ O)] ₂	493	496	6.7	1.57	14150	493	496	6.8	1.57	14300	${}^3E_g \rightarrow {}^3T_{2g}$
					24500					24400	intraligand charge transfer band
[Ni(C ₁₁ H ₈ N ₂ O)X ₂]	295	297	4.3	2.96	13450	518	522	4.4	2.94	14000	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
					25900					26250	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
[Co(C ₁₁ H ₈ N ₂ O)X ₂]	294	297	4.4	4.90	8400	519	522	4.5	4.89	8550	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
					17500					17450	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
					20600					20350	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
[Zn(C ₁₁ H ₈ N ₂ O)X]	266	267	3.5	—	—	339	342	3.6	—	—	—
[Cd(C ₁₁ H ₈ N ₂ O)X]	312	314	3.3	—	—	387	389	3.5	—	—	—

X = H₂O or picoline.



where, $B = o\text{-C}_6\text{H}_4$

FIG 2 Dimeric bridged structure of copper chelate of *o*-(N-pyrrole 2-carboxaldimino) phenol (H_2PP)

the bands at 3620 and 3315cm^{-1} could not be located indicating the deprotonation of the —OH and $>\text{NH}$ groups due to chelation. $\nu_{\text{C—N}}$ was lowered to 1580cm^{-1} suggesting participation of azomethine nitrogen in complexation. The metal chelates also show two bands in the regions $560\text{--}590$ and $470\text{--}490\text{cm}^{-1}$ assignable to $\nu_{\text{M—O}}$ and $\nu_{\text{M—N}}$ respectively. Excepting the Cu(II) chelates, the remaining compounds show one band in the range $3330\text{--}3340\text{cm}^{-1}$ which may be due to ν_{OH} of water molecule present. The loss of water molecules at relatively high temperature ($>180^\circ$) and a band in the region $720\text{--}750\text{cm}^{-1}$ indicate that the H_2O molecules are coordinated and not lattice held.

Based on the above evidences structure (I) may be assigned to the metal chelates. However, the Cu(II) chelate displaying subnormal magnetic moment may be represented by the dimeric bridged structure (II).

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