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Synthesis & Characterisation of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO_2^{2+} & VO^{2+} Chelates with N-*o*-Hydroxyacetophenone-imine-*o*-aminophenol

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Potentiometric studies on Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO_2^{2+} and VO^{2+} chelates with N-*o*-hydroxyacetophenoneimine-*o*-aminophenol (H_2AP) have been carried out using Calvin's extension of Bjerrum's method in aqueous medium ($\mu = 0.1$, 0.05 and 0.01 *M* $NaClO_4$) at 25, 35 and 45°C. Related thermodynamic parameters, e.g., ΔG°, ΔH° and ΔS° have been evaluated. Magnetic, conductance and spectral data of the solid chelates have been used to characterise them.

The dissociation constants of N-*o*-hydroxyacetophenoneimine-*o*-aminophenol (H_2AP) and stability constants of its chelates with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO_2^{2+} and VO^{2+} have been determined by Calvin's extension of Bjerrum's method[1]. The results are presented in this note.

H_2AP was synthesised by the condensation of *o*-hydroxyacetophenone with *o*-aminophenol in presence of piperidine. After refluxing equimolar alcoholic solutions of these compounds for 2-3 hr, the light yellow solution obtained was filtered hot, concentrated and cooled when yellow crystals were obtained. These were purified by recrystallisation from ethanol. A quantitative yield of H_2AP was obtained, m.p. 187°C [Found: C, 73.78; H, 5.59; N, 6.03. Calc. for $C_{14}H_{13}O_2N$: C, 74.0; H, 5.73; N, 6.17%].

For potentiometric study, the following mixtures (total volume 40 ml) were prepared and titrated against 0.1 *M* NaOH solution (at 25°, 35° and 45°C) when titration curves of usual shapes were obtained. (i) 10.0 ml 0.01*M* H_2AP + 4.0 ml 1.0*M* $NaClO_4$ + 26.0 ml H_2O; (ii) 10.0 ml 0.01*M* H_2AP + 4.0 ml 1.0*M* $NaClO_4$ + 10.0 ml metal ion solution + 16.0 ml H_2O; (iii) 20.0 ml 0.01*M* H_2AP + 4.0 ml 1.0*M* $NaClO_4$ + 10.0 ml 0.01*M* metal ion solution + 6 ml H_2O.

pK_1 and pK_2 of H_2AP were found to be 5.14 and 9.23 at 25°; 4.96 and 9.00 at 35°; 4.64 and 8.70 at 45°, respectively. These values indicate the biprotic nature of the ligand. 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 methods[2]. The order of thermodynamic stabilities was found to be: $VO^{2+} > UO_2^{2+} > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II)$ which is in accordance with the Irving-Williams rule[3].

Thermodynamic parameters

The thermodynamic parameters, e.g., ΔG°, ΔH° and ΔS° have been evaluated using Gibbs-Helmholtz equation. ΔG° values of all the chelates are more negative at higher temperatures. ΔH° values are positive in all the cases indicating endothermic nature of reactions. The positive values of ΔS° for all the chelates suggest that the entropy term is favourable for their formation.

In terms of Harned equation[4], the plots of $pK^H - ct^2$ vs t were found to be linear. Values of slope ($-2c\theta$) and intercept ($pK_m^H + c\theta^2$) were obtained from the plot. Values of θ, pK^H and pK_m^H are given in Table 1.

Table 1—Thermodynamic Parameters of Bivalent Metal Chelates of N-*o*-Hydroxyacetophenoneimine-*o*-aminophenol (H_2AP)

Metal ion	log β_0			Thermodynamic parameters at 35°C		
	25°	35°	45°	$-\Delta G^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ deg^{-1} mol^{-1})
Co(II)	15.84	16.23	16.72	95.72	79.84	0.57
Ni(II)	16.52	16.99	17.44	100.20	83.47	0.60
Cu(II)	17.93	18.48	18.74	108.99	73.49	0.59
Zn(II)	7.63	7.91	8.05	46.65	38.11	0.28
Cd(II)	7.25	7.42	7.58	43.76	29.94	0.24
UO_2^{2+}	19.97	20.59	21.12	121.43	104.33	0.73
VO^{2+}	21.94	22.75	23.27	134.17	120.66	0.83

In terms of Harned's equation: pK^H at 35° is 13.94; $pK_m^H = 1.84$ and $\theta(°C) = 525.6$

Table 2—Yield, Elemental Analysis, Molecular Weight and Magnetic Moments of H_2AP and Its Bivalent Metal Chelates

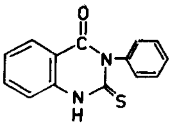
Ligand/Chelate (Yield, %)	Molec. wt	Found (Calc.), %				$\mu_{eff.}$ (B.M.) at 308°K
	Found (Calc.)	C	H	N	Metal	
H_2AP	225	72.98	5.59	6.03	—	—
(100)	(227)	(74.00)	(5.73)	(6.17)		
$[Co(C_{14}H_{11}O_2N)(H_2O)_3]$	335	49.49	4.98	4.05	16.69	4.88
(72)	(338)	(49.70)	(5.03)	(4.14)	(17.46)	
$[Ni(C_{14}H_{11}O_2N)(H_2O)_3]$	336	49.37	4.96	4.08	16.77	2.93
(66)	(338)	(49.70)	(5.03)	(4.14)	(17.46)	
$[Cu(C_{14}H_{11}O_2N)]_2$	574	57.95	3.73	4.66	21.98	1.58
(73)	(578)	(58.13)	(3.80)	(4.84)	(22.15)	
$[Zn(C_{14}H_{11}O_2N)(H_2O)]$	304	54.28	4.15	4.29	20.54	—
(64)	(308)	(54.55)	(4.22)	(4.55)	(21.10)	
$[Cd(C_{14}H_{11}O_2N)(H_2O)]$	351	47.09	3.52	3.75	30.87	—
(68)	(355)	(47.32)	(3.66)	(3.94)	(31.55)	
$[UO_2(C_{14}H_{11}O_2N)(H_2O)]$	508	32.31	2.31	2.63	52.09	—
(71)	(513)	(32.74)	(2.53)	(2.73)	(52.63)	
$[VO(C_{14}H_{11}O_2N)(H_2O)_2]$	306	53.88	4.59	4.40	20.82	1.65
(59)	(310)	(54.19)	(4.84)	(4.52)	(21.61)	

Synthesis of solid chelates

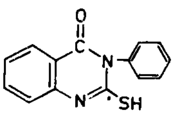
The metal chelates were obtained as crystalline solids by refluxing ethanolic solution of H_2AP (0.02*M*) with the metal nitrate (0.02*M*) solution in 70% ethanol. After reflux, the mixture was stirred magnetically and a few drops of dilute ammonia (1:20) were added gradually till the solid mass appeared. The mass was filtered under suction, washed with hot ethanol, dried and preserved. Analytical and molecular weight data of the solid metal chelates (Table 2) suggest 1:1 (metal-ligand) stoichiometry. Conductance ($\Lambda_M = 3.5-6.9$ ohm^{-1} cm^2 mol^{-1}) data suggest nonelectrolytic nature of the metal chelates. Excepting the Zn(II), Cd(II) and UO_2^{2+} chelates, which were found to be diamagnetic as usual, the rest of the complexes were found to be paramagnetic. However, Cu(II) chelate showed subnormal magnetic moment of 1.58 B.M. at 308° which indicated its dimeric nature. On this basis 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[5]. Zn(II) and Cd(II) chelates are expected to be tetrahedral as is common with these ions.

The electronic spectrum of the Co(II) chelate in benzene shows three bands at 8350, 17450 and 20500 cm^{-1} which can be assigned to the transitions ${}^4T_{1g}(F) \to {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \to {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \to {}^4T_{1g}(P)$ respectively. These bands indicate an octahedral geometry for Co(II) chelates. In the case of Ni(II) chelate, two bands are obtained at 13500 and 25800 cm^{-1} which may be assigned to the transitions ${}^3A_{2g} \to {}^3T_{1g}(F)$ and ${}^3A_{2g} \to {}^3T_{1g}(P)$, respectively. These bands suggest an octahedral stereochemistry for the Ni(II) compound. The electronic absorption spectrum of the Cu(II) chelate in benzene consists of two absorption bands at 24,600 and 14,200 cm^{-1}. The band at 24,600 cm^{-1} is stronger than the other and it may be due to intra-ligand charge-transfer. The band at 14,200 cm^{-1} may be due to the electronic transition ${}^2E_g \to {}^2T_{2g}$. In the case of VO^{2+} chelate two bands obtained at 11600 cm^{-1} and 20100 cm^{-1} may be due to the transitions $d_{xy} \to d_{xz}$, d_{yz} and $d_{xy} \to d_{x^2-y^2}$ respectively, suggesting octahedral stereochemistry for this chelate.

The IR spectrum of H_2AP shows three bands at 3640, 3450 and 1610 cm^{-1} which correspond to νO$-$H, νOH---N (hydrogen bonded $-$OH) and νC$=$N, respectively. In all the metal chelates the bands at 3640 and 3450 cm^{-1} could not be located indicating the deprotonation of both the $-$OH groups due to chelation. νC$=$N was lowered to 1590 cm^{-1} suggesting participation of azomethine nitrogen in complexation. The metal chelates also showed two bands in the regions 550-580 and 480-500 cm^{-1} assignable to νM$-$O and νM$-$N respectively. Excepting the Cu(II) complex, all the chelates showed one band in the range 3310-3320 cm^{-1} which may be due to νOH of water molecule present. The loss of water molecules at relatively high temperature (> 190°) and a band in the region 720-750 cm^{-1} indicate that the H_2O molecules are coordinated and not lattice held. Based on the above evidences structure (I) may be



(I)



(II)

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

References

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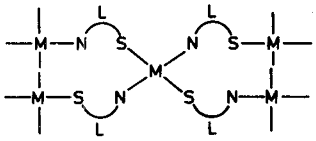

(III)

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