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II. CHEMISTRY

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THERMODYNAMIC AND PHYSICO-CHEMICAL STUDIES OF Vo^{2+}, Uo_2^{2+}, Cu(II), Ni(II), Co(II), Zn(II) AND Cd(II) IONS-3-(α-BENZOYL) METHYL-BENZYLIDENE IMINO) PROPANOATE SYSTEMS

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The dissociation constants of 3-(α-benzoyl methyl-benzylidene imino) propanoic acid (H_2BP) and overall stability constants (log β_2) of its chelates with Vo^{2+}, Uo_2^{2+}, Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) have been determined potentiometrically at 25°, 35° and 45 °C in aqueous medium (0.01M, 0.05M and 0.1M sodium perchlorate) by Bjerrum's method as modified by Irving and Rossotti. The log β_2 values have been computed by standard methods. The deviations between the theoretical and experimental values of log β_2 at 25 °C ($\mu = 0.1$M) are 17.31 ± 0.04, 16.19 ± 0.06, 15.06 ± 0.06, 14.63 ± 0.03, 14.34 ± 0.07, 7.20 ± 0.05 and 6.65 ± 0.04 for Vo^{2+}, Uo_2^{2+}, Cu(II), Ni(II), Co(II), Zn(II) and Cd(II)-chelates, respectively. The stability sequence is in agreement with the Irving-Williams rule. The thermodynamic stability constants, free energy, enthalpy and entropy changes of the metal chelates have also been evaluated. The solid chelates have also been synthesised and characterised by magnetic, conductance and spectral techniques.

Keywords : Vo^{2+}, Uo^{2+}, Cu(II), Ni(II), Co(II), Zn(II), & Cd(II) ions; 3-(α-benzoyl methyl-benzylidene imino propanoate systems

INTRODUCTION

A perusal of the literature (Cotton, 1966) has indicated that no work has been done so far on the chelates of 3-(α-benzoyl methyl-benzylidene imino) propanoic acid (H_2BP) with Vo^{2+}, Uo_2^{2+}, Cu(II), Ni(II), Co(II), Zn(II) and Cd(II), hence the same has been undertaken and reported in the present paper.

EXPERIMENTAL

H_2BP was synthesised from dibenzoyl methane and β-alanine (supplied by Fluka) by the general procedure reported (Mehta & Gupta, 1973) earlier. It gave satisfactory elemental analyses at m.p. 130 °C. The metal nitrates and reagents used were Analar pure (BDH). A precision *p*H-meter type OP : 205 No. 837 (Rade & Kis) equipped with a glass-calomel electrode assembly was used to record the *p*H.

Potentiometric titrations were carried out according to Bjerrum's extension of Irving and Rossotti method (Bjerrum, 1957), at 25°, 35° and 45 °C at $\mu = 0.01$, 0.05 and 0.1M $NaClO_4$. For this purpose the following mixtures were prepared : (1) 5.0ml 0.01M $HClO_4$ + 2.5ml 1.0M $NaClO_4$ + 17.5ml water. (2) 5.0ml 0.01M $HClO_4$ + 10.0ml 0.01M H_2BP + 2.5ml 1.0M $NaClO_4$ + 7.5ml water.

(3) 5.0ml 0.01M $HClO_4$ + 10.0ml 0.01M H_2BP + 2.0ml 0.01M metal-ion solution + 2.5ml 1.0M $NaClO_4$ + 5.5ml water. These mixtures were titrated against carbonate-free 0.1M NaOH and the titration curves were found to be of usual shapes.

Results and Discussions

The pK_1 and pK_2 of H_2BP were found 9.35 and 7.10 at 25°, 9.05 and 6.90 at 35° and 8.70 and 6.50 at 45 °C, respectively. Thus the pK values fall with rise of temperature. These values suggest that H_2BP is a biprotic ligand. The metal-ligand stability constants were read from the formation curves drawn by plotting $\bar{n}$ vs. PL.

The refinement was done by various computational methods such as correction term, convergence formula, successive approximation and interpolation at various $\bar{n}$ values and their average values (log β_2) alongwith their deviations from the theoretical values are summarised in Table I. The log β_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.

The thermodynamic stability constants (log K°) (Table I) have been obtained by extrapolation of measured formation constants to zero ionic strength. The values of overall changes in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) have been evaluated (Table I). The $\triangle G$ of the chelates have more negative values at 45 °C than at lower temperatures. $\triangle H$ is positive in all cases which suggest that there exists some steric strain around the metal-ion in the chelates due to fused rings. The entropy term $\triangle S$, seems favourable for the formation of these compounds.

Harned's gave the relation between log K^H and temperature as

$$[(PK^H - ct^2) = -2\,c\theta\,t + (PK_m^H - c\theta^2)].$$

In this case the plots of $(PK^H - ct^2)$ versus t were found linear. θ° and PK_m^H for H_2BP were found 372.8° and 2.24, respectively. $\triangle H$ values as obtained from Harned's equation are 14.13, 13.68 and 13.27 at 298°, 308° and 318 °K, respectively.

Solid Chelates

The bivalent metal chelates of H_2BP were obtained in solid state by the method reported earlier. The results of elemental analysis, molecular weight, magnetic moment, conductance and electronic absorption spectra of these chelates are given in Table II. Their non-electrolytic nature is revealed by the low molar conductance (Table II).

Based on elemental analysis and molecular weight data, the hydrated metal chelates display 1 : 1 (metal-ligand) stoichiometry and posses the composition ($ML \cdot n\,H_2O$), where M = metal ion and $LH_2 = C_{18}H_{17}NO_3$. Thermogravimetric analyses of these chelates show a weight loss compared to three water molecules

TABLE I

Average stability constants and thermodynamic functions of bivalent metal chelates of 3-(α-*benzoyl methyl-benzylidene imino*) *propanoic acid at* 25°, 35° *and* 45 °C

Metal Chelates		Stability constants at $\mu = 0.1$ M $NaClO_4$			log K°			$-\Delta G$ °K. Cal./mole			ΔH K. Cal/ mole at	ΔS Cal/ deg/mole at
		25°	35°	45°	25°	35°	45°	25°	35°	45°	35°	35°
VO^{2+}	log K_1	8.89	9.25	9.40	18.45	18.90	19.25	25.06	26.61	27.93	13.43	22.49
	log K_2	8.42	8.45	8.50								
	log β_2	17.31 ± 0.04	17.70 ± 0.05	17.90 ± 0.03								
UO_2^{2+}	log K_1	8.55	9.01	9.15	18.25	18.80	19.10	24.77	26.49	27.73	25.23	250.90
	log K_2	7.64	7.79	8.20								
	log β_2	16.19 ± 0.06	16.80 ± 0.07	17.35 ± 0.08								
Cu(II)	log K_1	7.82	8.05	8.47	17.17	17.52	18.15	23.28	24.10	26.30	21.38	68.08
	log K_2	7.23	7.50	7.58								
	log β_2	15.06 ± 0.06	15.55 ± 0.04	16.04 ± 0.05								
Ni(II)	log K_1	7.67	7.85	8.30	16.98	17.00	17.80	23.01	23.93	25.88	22.54	139.00
	log K_2	6.94	6.95	7.39								
	log β_2	14.63 ± 0.03	14.67 ± 0.04	15.67 ± 0.05								
Co(II)	log K_1	7.57	7.70	8.15	16.40	16.10	17.50	21.78	22.65	25.41	25.64	119.70
	log K_2	6.66	6.70	7.36								
	log β_2	14.34 ± 0.07	14.40 ± 0.08	15.53 ± 0.08								
Zn(II)	log K_1	7.20 ± 0 05	7.64 ± 0.06	8.07 ± 0.02	8.25	8.74	9.12	11.25	12.30	13.27	18.84	102.30
Cd(II)	log K_1	6.65 ± 0.04	7.25 ± 0.03	7.60 ± 0.05	7.90	8.30	8.70	10.76	11.69	12.66	20.51	25.29

TABLE II

Molecular weights, magnetic moment, conductance values, electronic spectral data and possible transitions of the bivalent chelates of 3-(α-*benzoyl methyl-benzylidene imino) propanoic acid*

Complex	Mol. wt. Found (calc.)	μ_{eff}(B. M.) at 308 °K	ΔM (ohm^{-1} cm^2 mole^{-1})	Absorption bands (cm^{-1})	Assignments
[Vo($C_{18}H_{15}NO_3$) (H_2O)$_2$	387 (394)	1.64	4.1	11300 19500	$dxy \rightarrow dxz, dyz$ $dxy \rightarrow dx^2 - dy^2$
[Uo_2($C_{18}H_{15}NO_3$) (H_2O)]	575 (581)	—	4.8	—	—
[Cu($C_{18}H_{15}NO_3$) (H_2O)$_2$]	401 (410)	1.93	4.2	13200	$^2Eg \rightarrow {}^2T_{2g}$
[Ni($C_{18}H_{15}NO_3$) (H_2O)$_3$]	396 (405)	2.92	3.9	13800 26100	$^3A_2g \rightarrow {}^3T_{1g}$(F) $^3A_2g \rightarrow {}^3T_{1g}$(P)
[Co($C_{18}H_{15}NO_3$) (H_2O)$_3$]	392 (405)	4.91	3.6	8800 21200	$^4T_{1g}$(F)$\rightarrow {}^4T_{2g}$(F) $^4T_{1g}$(F)$\rightarrow {}^4T_{1g}$(P)
[Zn($C_{18}H_{15}NO_3$) (H_2O)]	362 (376)	—	2.6	—	—
[Cd($C_{18}H_{15}NO_3$) (H_2O)]	410 (423)	—	3.2	—	—

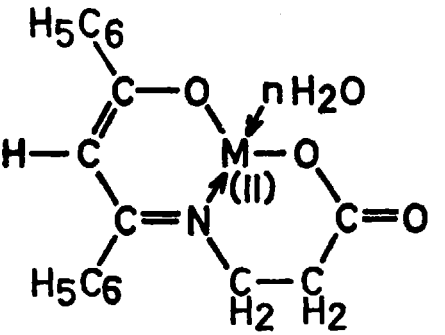
*All the chelates gave satisfactory C, H, N & metal analysis.

($n = 3$) when M = Co(II), Ni(II) or Cu(II), two water molecules ($n = 2$) when $M = Vo^{2+}$ and one water molecule ($n = 1$) when M = Zn(II), Cd(II) or Uo_2^{2+}.

The magnetic moments indicate the presence of 3, 2, 1 and 1 unpaired electrons in Co(II), Ni(II) Cu(II), and Vo^{2+} chelates and the remaining chelates were formed to be diamagnetic. From the magnetic moments (Table II) it is apparent that there is no metal-metal bonding in the chelates and hence spin exchange does not take place and they exist as monomer. Negligibly small conductance values (Table II) of the compounds suggest them to be non-electrolytes.

I. R. Spectra

In the I. R. Spectra of H_2BP five bands are observed at 3385, 2580, 1695, 1645 and 1610 cm^{-1} which correspond to $\sqrt{OH}$, $\sqrt{COOH}$, $\sqrt{C=O}$, $\sqrt{C=C}$ and $\sqrt{C=N}$, respectively. In the metal chelates, the $\sqrt{C=N}$ is lowered to 1590–1580 cm^{-1} suggesting involvement of azomethine nitrogen in chelation. Appearance of a band in the range 415–430 cm^{-1} suggest metal-nitrogen bondings in the chelates. Formation of $M - O$ bonds due to deprotonation of —COOH and enolic —OH groups is supported by the appearance of bands in the range 510–525 cm^{-1}. All the chelates gave one broad band in the region 3320–3160 cm^{-1} due to $\sqrt{OH}$ of water. The loss of water molecules at a relatively high temperature (170–285 °C) suggest that they are coordinated and not lattice held.



When n = 1, M(II) = Zn, Cd or UO_2.
n = 2, M(II) = Vo.
n = 3, M(II) = Co, Ni or Cu.

FIG. 1. Bivalent metal chelates of 3-(α-benzoyl-methyl-benzylidene imino) propanoic acid (H_2BP).

Based on the above evidences Co(II), Ni(II), Uo_2^{2+} and Vo^{2+}-chelates display an octahedral stereochemistry. Zn(II), Cd(II)-chelates posses tetrahedral configuration where as the Cu(II)-chelate displays distorted octahedral geometry in terms of Jahn-Teller effect. These structures may be represented as shown in Fig. 1.

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