©*Proc. Indian natn. Sci. Acad.*, **52**, A, No. 3, 1986, pp. 657–661
Printed in India.

COMPLEXES OF 3-(N-α-PHENYL-2-HYDROXYBENZYLIDENEIMINO) PROPANOIC ACID WITH Cu(II), Ni(II), Co(II), Zn(II), Cd(II), VO^{2+} AND UO_2^{2+}

(Ms) Preeti Mehta, Ashok Gahlot *and* R K Mehta

Department of Chemistry, University of Jodhpur, Jodhpur 342 001, India

3-(N-α-phenyl-2-hydroxybenzylideneimino) propanoic acid chelates with Cu(II), Ni(II), Co(II), Zn(II), Cd(II), VO^{2+} and UO_2^{2+}, have been investigated both in solution and solid phase by physicochemical methods. The stability of the chelates, determined by Calvin-Bjerrum *p*H-titration technique, follows Irving-Williams order. Thermal behaviour of the complexes has been investigated.

Key Words : Bivalent Chelates; Propanoate System; Physicochemical Methods; Irving-Williams Rule

Introduction

A survey of the literature[1] shows that no systematic studies have been carried out on the chelates of Cu(II), Ni(II), Co(II), Zn(II), Cd(II), VO^{2+} and UO_2^{2+} with 3-(N-α-phenyl-2-hydroxybenzylideneimino) propanoic acid (H_2PP); hence, the same is undertaken and its findings are reported in the present communication. A large number of such metal-chelates have been prepared and studied in these laboratories.[2,3]

Experimental

H_2PP is synthesized from 2-hydroxy acetophenone and 2-amino propanoic acid by the general procedure reported earlier.[3] It gives satisfactory elemental analysis. M.P. 179 °C. The metal nitrates and the reagents used are AnalaR pure (BDH).

The hydrated metal chelates have been synthesized by refluxing a mixture of the metal acetate (0.01 mole in 10–15ml 80 per cent alcohol) and H_2PP (0.01 mole in 30–50ml 80 per cent alcohol) on a steam-bath for 4 to 5hr. The solid mass separated is recrystallised from methanol.

Gallen-Kamp semi-micro ebulliometer has been used to determine the molecular weight of the solid chelates in dioxan as the solvent.

A digital *p*H-meter of the type DPH-77 (Unitec) is used and other instruments employed are the same as reported earlier.[5] Potentiometric titrations have been carried out according to Calvin-Bjerrum's method[6] at 25, 35 and 45 °C at (μ = 0.01M, 0.05M and 0.1M $NaClO_4$). The following mixtures have been prepared (total volume 40ml) for stability determinations : (1) 10.0ml of 0.01M H_2PP + 4.0ml 1.0M $NaClO_4$ + 26.0ml water (2) 10.0ml 0.01M H_2PP + 4.0ml 1.0M $NaClO_4$ + 10.0ml 0.01M metal-ion solution + 16.0ml water (3) 20.0ml

0.01M H_2PP + 4.0ml 1.0M $NaClO_4$ + 10.0ml 0.01M metal-ion solution + 6.0ml water.

These mixtures are titrated against carbonate-free 0.1M NaOH in an inert atomsphere and the titration curves possess usual shapes.

Thermal decomposition has been studied by heating the samples at the rate of 5–6° minute manually and heated upto 600 °C.

Gouy magnetic balance has been used for the susceptibility determinations.

Results and Discussion

The pK_1 and pK_2 of H_2PP are found 7.90 and 10.90 at 25°, 7.50 and 10.50 at 35° and 7.21 and 9.92 at 45 °C at μ = 0.01M; and 7.63 and 10.32 at 25°, 7.25 and 9.95 at 35° and 6.98 and 9.45 at 45° at μ = 0.05M (7.14 and 9.91 at 25°, 6.73 and 9.60 at 35° and 6.40 and 9.18 at 45 °C at μ = 0.1M respectively). Thus the pK values fall with rise of temperature and increase of ionic strength. These values suggest that H_2PP is a biprotic ligand. The metal-ligand stability constants have been read from the formation curves drawn by plotting $\bar{n}$ *vs* − log $[A^=]$. The refinement has been done by various computational methods[7] such as, correction terms, convergence formula, successive approximation and interpolation at various $\bar{n}$ values and their average values along with the deviations are summarised in Table I. The log β_0 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 agrees with the Irving-Williams rule.[7]

The $\Delta G°$ of all the chelates have more negative values at 45° that at 35° and 25 °C. It is also observed that $\Delta H°$ is positive in all the cases suggesting existance of some steric strain around the metal-ion in the fused rings. The positive values of $\Delta S°$ suggest that the entropy term is favourable for the formation of the chelates. In terms of Harned's relation the values of θ (the temperature at which pK^H is minimum) and pK_m^H (pK^H at $t° = \theta$ °C) for the ligand, are found to be 875.3 and − 17.41 at μ = 0.01M, 830 and 14.45 at μ = 0.05M and 796.6 and − 12.73 at μ = 0.1M, respectively.

Solid Chelates

The molecular formulae of the complexes may be represented as $[M(PP)\ n.x]$, where M = Bivalent-metal-ion, PP is the deprotonated form of H_2PP ($C_{11}H_{13}NO_3$) and $n.x$ is the number of H_2O molecules, as is evident from the results of micro-analysis (elemental analysis and molecular weight), magnetic moments and electronic absorption spectra of the solid chelates.

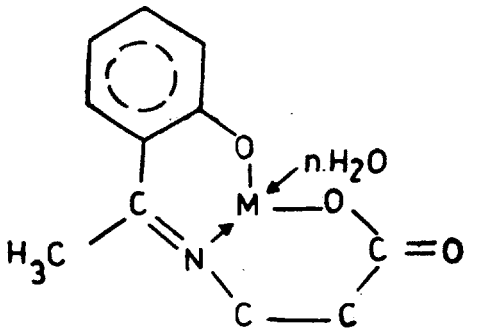
Based on micro analysis the metal-chelates display 1 : 1 (metal-ligand) stoichiometry. Pyrolysis (T.G.A.) thermogram of the hydrated chelates reveal that on gradual heating from room temperature the hydrated salts are completely dehydrated and decomposed within the temperature range 180–600°. In general, the water of hydration may be considered either as the crystal or as co-ordination water.

TABLE I

Average stability constants and thermodynamic parameters of bivalent metal chelates of 3-(N-α-phenyl-2-hydroxybenzylideneimino) propanoic acid (H_2PP) at 25, 35 and 45 °C

Metal Ion		Stability constants with deviation from theoretical values			log K°			(− ΔG°) K. Joule mole^{-1}			(ΔH°) K. Joule mole^{-1}	(ΔS°) Joule mole^{-1}
		25°	35°	45°	25°	35°	45°	25°	35°	45°	at 35 °C	at 35 °C
VO^{2+}	log K_1	8.69 (± 0.03)	9.01 (± 0.01)	9.49 (± 0.04)	19.23	19.72	20.10	109.72	116.30	122.39	70.77	147.82
	log K_2	5.35 (± 0.06)	5.95 (± 0.07)	6.54 (± 0.02)								
UO_2^{2+}	log K_1	8.21 (± 0.02)	8.63 (± 0.04)	9.05 (± 0.06)	17.66	18.06	18.40	100.77	106.51	112.04	67.14	127.82
	log K_2	5.05 (± 0.04)	5.61 (± 0.07)	5.95 (± 0.04)								
Cu(II)	log K_1	8.05 (± 0.03)	8.45 (± 0.01)	8.80 (± 0.09)	16.18	16.48	16.95	92.32	97.19	103.21	69.86	88.73
	log K_2	4.78 (± 0.01)	5.36 (± 0.03)	5.79 (± 0.08)								
Ni(II)	log K_1	7.06 (± 0.03)	8.11 (± 0.01)	8.58 (± 0.04)	14.85	15.25	15.57	84.74	89.94	94.81	63.51	85.81
	log K_2	4.51 (± 0.05)	5.17 (± 0.06)	5.56 (± 0.03)								
Co(II)	log K_1	7.51 (± 0.02)	7.98 (± 0.03)	8.35 (± 0.04)	14.69	15.10	15.55	83.82	89.05	94.68	79.84	29.90
	log K_2	4.30 (± 0.06)	5.01 (± 0.02)	5.48 (± 0.05)								
Zn(II)	log K_1	5.04 (± 0.06)	5.53 (± 0.03)	5.92 (± 0.03)	7.93	8.23	8.40	45.25	48.54	51.15	42.64	19.16
Cd(II)	log K_1	4.23 (± 0.04)	4.49 (± 0.05)	4.91 (± 0.02)	6.95	7.24	7.38	39.66	42.70	44.94	39.01	11.98

The deviations are given in parentheses.



When, n = 3, M = Co(ii), Ni (ii) & Cu(ii).

n = 2, M = VO^{2+}.

n = 1, M = UO_2^{2+}, Zn (ii) & Cd(ii).

Water expelled below 150° can be considered as the crystal water and that eliminated above 150° is the water of coordination. From the mass loss curves of the metal-chelates it is observed that no change occurs around 80–180° indicating the absence

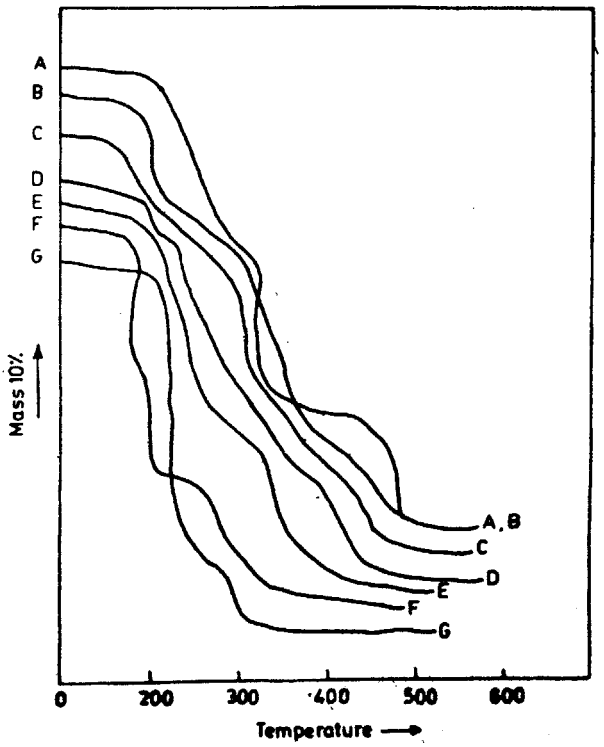


FIG 1

of crystal water in them. The weight-loss values observed in the TG-curves, amounts to the loss of three water molecules ($n = 3$) when M = Co(II), Ni(II), and 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+}. All complexes are monomeric in nature.

The magnetic moments of the hydrated Co(II), Ni(II) and Cu(II) chelates namely 3-(N-α-phenyl-2-hydroxy benzylideneimino) propionato triaquo M(II) are 5.01, 3.55 and 2.15 B.M. respectively, indicating the presence of 3, 2, and 1 unpaired electrons in them. The hydrated VO^{2+} chelate showing 1.81 B.M. as the magnetic moment possess one unpaired electron. The remaining metal chelates are found diamagnetic.

Thus based on the above data, an octahedral geometry is suggested for the Co(II), Ni(II), UO_2^{2+} and VO^{2+} chelates. Zn(II) and Cd(II) chelates possess tetrahedral stereochemistry, as is common with these ions. The Cu(II) chelate may exhibit a distorted octahedral configuration in terms of Jahn-Teller effect. These structures are represented as shown in Fig. 1.

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