Short Communication

Synthesis, characterisation and structural determination of VO^{2+}, UO_2^{2+}, Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) chelates of o-(N-2-pyrrolidimino)ethane sulphonic acid

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Abstract

The dissociation constants of o-(N-2-pyrrolidimino)ethane sulphonic acid (H_2PE), stability constant and thermodynamic parameters of its chelates with VO^{2+}, UO_2^{2+}, Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) have been determined potentiometrically in aqueous medium ($\mu = 0.01$ M, 0.05 M and 0.1 M $NaClO_4$) by Bjerrum's method at 25, 35 and 45°C. The solid complexes and their pyridine and picoline adducts have been synthesised and physicochemically studied.

Key words: o-(N-2-pyrrolidimino)ethane sulphonic acid chelates, stability constants, dissociation constants.

1. Introduction

The medicinal value of pyrrole derivatives is well known[1-2] but their complexing behaviour with metal ions has not been thoroughly studied. A survey of literature[3-4] reveals that no work has so far been reported on the bivalent metal chelates of o-(N-2-pyrrolidimino)ethane sulphonic acid (H_2PE) and hence the same has been reported in the present communication.

2. Experimental

H_2PE was synthesised by the condensation of N-2-pyrrolidone with taurine by the reported procedure[5]. It gave satisfactory elemental analysis (m.p. 182°C). The reagents used were AnalaR pure (BDH). The solid chelates, their pyridine and picoline adducts were synthesised as reported earlier[6]. The physicochemical measurements were carried out as reported earlier[7].

Potentiometric titrations of the following mixtures (total volume 40 ml) were carried out according to Calvin-Bjerrum's method[8] at 25, 35 and 45°C ($\mu = 0.01$ M, 0.05 M and 0.1 M $NaClO_4$): (i) 10 ml 0.01 M H_2PE + 4 ml 1 M $NaClO_4$ + 26 ml H_2O; (ii) 10 ml 0.01 M H_2PE + 4 ml 1 M $NaClO_4$ + 10 ml 0.01 M metal ion solution + 16 ml water; (iii) 20 ml 0.01 M H_2PE + 4 M $NaClO_4$ + 10 ml 0.01 M metal ion solution + 6 ml water.

These mixtures were titrated against carbonate-free 0.1 M NaOH in an inert atmosphere and the titration curves were found to follow standard trend.

3. Results and discussion

The pK_1 and pK_2 of H_2PE were found (4.43 and 10.18 at 25°, 4.21 and 9.82 at 35°, 3.95 and 9.27 at 45°C; $\mu = 0.1$ M $NaClO_4$) to fall with rise of temperature, suggesting that H_2PE is a biprotic ligand. Formation curves of the metal-ligand systems were obtained by plotting $\bar{n}$ v/s $-\log[A^-]$ and the values of stability constants obtained were further refined by various computational methods (interpolation at various $\bar{n}$ values, correction-term, convergence formula and successive approximation method, etc.). The stabilities of these chelates were found to follow the order $VO^{2+} > UO_2^{2+} > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II)$, in agreement with Irving-Williams rule[9].

The values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ have been evaluated using Gibbs-Helmholtz equation (Table I). The $\Delta G°$ values are more negative at higher temperatures than at 25 and 35°C while the $\Delta H°$ values are positive in all cases indicating endothermic nature of the reaction. The positive values of $\Delta S°$ for all the chelates suggests that the entropy term is favourable for their formation.

The data were also analysed in terms of Harned's relation[10], $[(pK^H - c\tau^2) = -2c\theta t + (pK_m^H - c\theta^2)]$ and the values of θ, pK^H and pK_m^H were evaluated (Table I). The $\Delta H°$ obtained by Harned's equation and Gibbs-Helmholtz equation are found in agreement with each other.

Table I
Thermodynamic parameters of bivalent metal chelates of o-(N-2-pyrrolidimino)ethane sulphonic acid (H_2PE)

Metal ion	$\log \beta°$			Thermodynamic parameters at 35°C		
	25°C	35°C	45°C	$-\Delta G°$ (KJ mol^{-1})	$\Delta H°$ (KJ mol^{-1})	$\Delta S°$ (KJ mol^{-1} deg^{-1})
CO(II)	12.17	12.42	12.94	73.25	69.86	0.465
Ni(II)	13.25	13.64	14.10	80.44	77.12	0.512
Cu(II)	14.70	15.12	15.75	89.17	87.10	0.572
Zn(II)	6.22	6.57	6.76	38.75	48.99	0.285
Cd(II)	5.85	6.13	6.32	36.15	42.64	0.256
UO_2^{2+}	16.33	16.90	17.36	99.67	93.45	0.627
VO^{2+}	17.75	18.36	18.90	108.27	104.34	0.690

In terms of Harned's equation pK^H at 35° is 14.03; $pK_m^H = -6.12$ and $\theta°C = 669.67$.

3.1. Solid chelates

The results of elemental analysis, molecular mass and magnetic moment of the hydrated solid chelates [of VO^{2+}, UO_2^{2+}, Cu(II), Ni(II), Co(II), Zn(II) and Cd(II)] alone are shown in Table II, although the adducts with pyridine and picoline were also prepared. The elemental analysis and molecular mass indicated 1 : 1 (metal-ligand) stoichiometry of the composition $[M(PE)X_n]$ where M = bivalent metal ion, $PE = C_6H_{10}N_2SO_3$ (the deprotonated form of H_2PE) and $X = H_2O$, C_5H_5N or C_6H_7N. The TCA analysis showed a weight-loss of water molecules as indicated in Table II. Negligibly small conductance values of the compounds in DMF suggested them to be non-electrolytes. 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, respectively.

The infrared spectra of H_2PE show bands at 3320, 1620 and 1160 cm^{-1} assignable to νN–H, ν>C=N and νSO$_2$OH respectively. On complexation ν>C=N of H_2PE gets shifted to lower frequency (1605–1610 cm^{-1}), indicating coordination through N of >C=N. All the complexes give one broad band in the region 3210–3230 cm^{-1} due to νOH of water molecule. The loss of water molecule at high temperature beyond 180°C and a band in the region 720–760 cm^{-1} in IR spectra suggests that these are coordinated. Besides, the appearance of two new bands in the region 420–440 cm^{-1} and 590–610 cm^{-1} suggest the formation of M–N and M–O bonds.

On the basis of the magnetic and electronic spectra measurements (Table II) an octahedral stereochemistry is suggested for Ni(II), Co(II), UO_2^{2+} and VO^{2+} chelates[11], while Cu(II) chelates appear to display tetragonally distorted octahedral configuration in terms of Jahn-Teller effect. Zn(II) and Cd(II) chelates are expected to be of tetrahedral geometry as is common with these ions[12].

Although no clear spectral evidence for the formation of >C=N–M, besides ≥C–N–M, is available, various physico-chemical measurements do point out the bonding of only one –nX moiety to the metal ion. This indirectly suggests the presence of ≥C–N–M band and hence a probable structure involving four-membered ring around the metal ion (fig. 1).

$X = H_2O$, C_5H_5N or C_6H_7N

when $n = 3$, $M = $ CO(II), Ni(II) and Cu(II)

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

$n = 1$, $M = UO_2^{2+}$, Zn(II) and Cd(II).
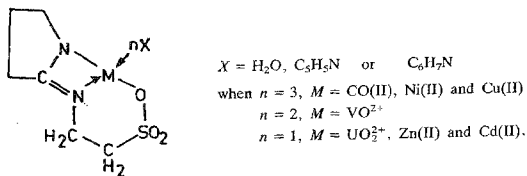
FIG. 1. Bivalent metal chelates of H_2PE.

Table II

Yield, elemental analysis, molecular mass, magnetic moments, electronic spectral data and possible transitions of H_2PE and its hydrated metal chelates

Ligand/metal chelate (Yield, %)	Molecular mass, Found (Calcd.)	Elemental analysis, Found (Calcd.)%						μ_{eff} (B.M) at 308° K	Absorption bands (cm^{-1})	Assignments
		C	H	N	S	Metal	Water			
[C₆H₁₂N₂SO₃)] (85)	183 (192)	37.29 (37.50)	6.11 (6.25)	14.14 (14.58)	16.50 (16.67)	—	—	—	—	—
[Co(C₆H₁₀N₂SO₃)(H₂O)₃] (63)	291 (303)	23.70 (23.76)	3.26 (3.30)	9.16 (9.24)	10.42 (10.56)	19.35 (19.44)	17.76 (17.82)	4.92	8,280 17,530 21,650	$^4T_{1g}(F) \to ^4T_{2g}(F)$ $^4T_{1g}(F) \to ^4A_{2g}(F)$ $^4T_{1g}(F) \to ^4T_{1g}(P)$
[Ni(C₆H₁₀N₂SO₃)(H₂O)₃] (68)	289 (303)	23.66 (23.76)	3.20 (3.30)	9.18 (9.24)	10.46 (10.56)	19.24 (19.37)	17.74 (17.82)	3.06	10,308 26,150	$^3A_{2g} \to ^3T_{2g}$ $^3A_{2g} \to ^3T_{1g}(P)$
[Cu(C₆H₁₀N₂SO₃)(H₂O)₃] (73)	296 (308)	23.31 (23.38)	3.16 (3.25)	8.99 (9.09)	10.27 (10.39)	20.55 (20.62)	17.42 (17.53)	1.89	12,268	$^2T_g \to ^2T_{g}$
[Zn(C₆H₁₀N₂SO₃)H₂O)] (70)	262 (273)	26.29 (26.37)	3.53 (3.66)	10.12 (10.26)	11.65 (11.72)	23.82 (23.96)	6.52 (6.59)	Dia.	—	—
[Cd(C₆H₁₀N₂SO₃)H₂O)] (65)	313 (320)	22.41 (22.50)	3.04 (3.13)	8.64 (8.75)	9.91 (10.00)	35.06 (35.13)	5.60 (5.63)	Dia	—	—
[UO₂(C₆H₁₀N₂SO₃)H₂O)] (76)	469 (478)	14.98 (15.06)	2.00 (2.09)	5.77 (5.86)	6.60 (6.69)	56.37 (56.49)	3.72 (3.77)	Dia.	—	—
[VO(C₆H₁₀N₂SO₃)(H₂O)₂] (69)	284 (293)	24.40 (24.57)	3.32 (3.41)	9.41 (9.56)	10.84 (10.92)	22.79 (22.85)	12.18 (12.29)	1.72	11,850 19,800	$^2B_2 \to ^2E_1$ $^2B_2 \to ^2B_1$

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