

## Short Communication

### **Tridentate schiff base complexes of some bivalent metal ions**

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#### **Abstract**

2-(N-3, 5-dichloro-*a*-pyridoneimino) ethane sulphonic acid Schiff base ( $H_2PE$ ) 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 physico-chemical methods and their stereochemistry established. The stabilities of the chelate, determined by Calvin-Bjerrum pH-titration technique, follow Irving-William's order. The pyridine and picoline adducts have also been synthesised and studied.

**Key words:** Bivalent chelates of 2-(N-3, 5-dichloro-*a*-pyridoneimino) ethane sulphonic acid,  $H_2PE$ .

#### **1. Introduction**

Pyridones have shown a strong complex forming tendency<sup>1</sup>, and it is very intense with the Schiff bases derived from pyridones. A perusal of the literature<sup>2-4</sup> reveals that much work has not been done on the chelates of  $Cu(II)$ ,  $Ni(II)$ ,  $Co(II)$ ,  $Zn(II)$ ,  $Cd(II)$ ,  $UO_2^{+2}$  and  $VO^{+2}$  with 2-(N-3, 5-dichloropyridone imino) ethane sulphonic acid ( $H_2PE$ ); hence the same was undertaken and the findings received are reported in the present communication.

#### **2. Experimental**

$H_2PE$  was synthesised from 3, 5-dichloro-*a*-pyridone and 2-amino ethane sulphonic acid by the general procedure reported earlier<sup>5</sup>. It gave satisfactory elemental analysis.

M.P. 159° C. The metal nitrates and the reagents used were AnalaR pure (BDH). The solid chelates and their pyridine and picoline adducts were synthesised as reported earlier<sup>6</sup>. A digital pH-meter of type DPH-77 (Unitec) was used and other instruments used were the same as reported earlier<sup>7</sup>. Potentiometric titrations were carried out according to Calvin-Bjerrum's method<sup>8,9</sup> at 25°, 35° and 45° C (at  $\mu = 0.01$  M, 0.05 M, and 0.1 M NaClO<sub>4</sub>). The following mixtures were prepared (total volume 40.0 ml. for stability determinations: (i) 10.0 ml. 0.01 M H<sub>2</sub>PE + 4.0 ml. 1.0 M NaClO<sub>4</sub> + 26.0 ml. water, (ii) 10.0 ml. 0.01 M H<sub>2</sub>PE + 4.0 ml. 1.0 M NaClO<sub>4</sub> + 10.0 ml. 0.01 M metal ion solution + 16.0 ml. water, (iii) 20.0 ml. 0.01 M H<sub>2</sub>PE + 4.0 ml. 1.0 M NaClO<sub>4</sub> + 10.0 ml. 0.01 M metal ion solution + 6.0 ml. water.

These mixtures were titrated against carbonate-free 0.1 M NaOH in an inert atmosphere and the titration curves had the usual shapes.

### 3. Results and discussion

The pK<sub>1</sub> and pK<sub>2</sub> values of H<sub>2</sub>PE were found (6.28 and 10.84 at 25° C, 5.52 and 10.20 at 35° C and 4.89 and 9.63 at 45° C) at  $\mu = 0.01$  M; (6.05 and 10.53 at 25° C, 5.32 and 9.92 at 35° C and 4.69 and 9.20 at 45° C) at  $\mu = 0.05$  M and (5.61 and 10.20 at 25° C, 4.96 and 9.52 at 35° C and 4.42 and 8.75 at 45° C) at  $\mu = 0.1$  M, respectively. Thus the pK values fall with the rise in temperature and increase in ionic strength. These values suggest that H<sub>2</sub>PE is a biprotic ligand. The metal-ligand stability constants were read from the formation curves drawn by plotting  $\bar{n} v/s - \log[A^-]$ . The refinement was done by various computational methods<sup>10</sup> such as, correction terms, convergence formula, successive approximation and interpolation at various  $\bar{n}$  values and their average values ( $\log \beta_2$ ) are summarised in Table I. The  $\log \beta_2$  values of the metal chelates are in the order VO<sup>2+</sup> > UO<sub>2</sub><sup>2+</sup> > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II), which agrees with the Irving-Williams rule<sup>11</sup>.

The thermodynamic stability constants ( $\log K^\circ$ ) (Table I) is obtained by extrapolation of measured formation constants to zero ionic strength. The values of overall changes in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) have been evaluated (Table I). The negative values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of the metal chelates suggest spontaneity of the chelation reaction.

In terms of Harned's relation<sup>12,13</sup> the values of  $\theta$  (the temperature at which pK<sub>2</sub> is minimum) and pK<sub>m</sub><sup>H</sup> (pK<sup>H</sup> at  $t^\circ = 0^\circ$  C) for the ligand, are found to be 1308 and -66.64 at  $\mu = 0.01$  M, 1285 and -62.96 at  $\mu = 0.05$  M and 1255 and -58.35 at  $\mu = 0.1$  M, respectively. The values of  $\Delta H$  obtained by Harned's equation and Gibbs-Helmholtz equation are also found similar.

**Table I.**  
Average stability constants and thermodynamic parameters of bivalent metal chelates of 2-(N-3,5-dichloro- $\alpha$ -pyridone imino) ethane sulphonic acid at 25°, 35° and 45° C

Metal ions		Average stability constants at $\mu = 0.1\text{M NaClO}_4$			Log $K^\circ$			$(-\Delta G^\circ)$ K. Joules mole <sup>-1</sup>			$(-\Delta H^\circ)$ K. Joules mole <sup>-1</sup>	$(-\Delta S^\circ)$ Joules mole <sup>-1</sup>
		25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C	at 35° C	at 35° C
VO <sup>+2</sup>	log $K_1$	8.62	8.02	7.29	17.01	15.98	14.08	97.06	94.24	85.73	265.83	557.11
	log $K_2$	6.73	6.06	5.27								
	log $\beta_2$	15.35	14.08	12.56								
UO <sub>2</sub> <sup>+2</sup>	log $K_1$	8.14	7.36	6.55	16.26	14.54	12.82	92.78	85.75	78.06	312.09	734.87
	log $K_2$	6.17	5.42	4.61								
	log $\beta_2$	14.31	12.78	11.16								
Cu(II)	log $K_1$	7.43	6.62	5.82	14.34	12.98	11.66	81.83	76.55	70.99	243.15	540.91
	log $K_2$	5.55	4.82	4.03								
	log $\beta_2$	12.98	11.44	9.85								
Ni(II)	log $K_1$	6.79	5.98	5.09	12.86	12.12	10.16	73.38	71.48	61.86	244.96	563.25
	log $K_2$	4.91	4.22	3.44								
	log $\beta_2$	11.70	10.20	8.53								
Co(II)	log $K_1$	6.17	5.37	4.43	12.12	11.08	8.98	69.16	65.34	54.68	284.88	712.79
	log $K_2$	4.42	3.75	2.92								
	log $\beta_2$	10.59	9.12	7.35								
Zn(II)	log $K_1$	5.45	4.71	3.91	6.96	6.14	5.24	39.71	36.21	31.91	156.05	389.09
Cd(II)	log $K_1$	4.82	4.11	3.34	6.14	5.62	4.76	35.04	33.14	28.98	125.20	298.89

### 3.1. Solid chelates

The results of microanalysis (elemental analysis and molecular weight), magnetic moment, electronic absorption spectra of the solid chelates and their pyridine and picoline adducts are given in Table II.

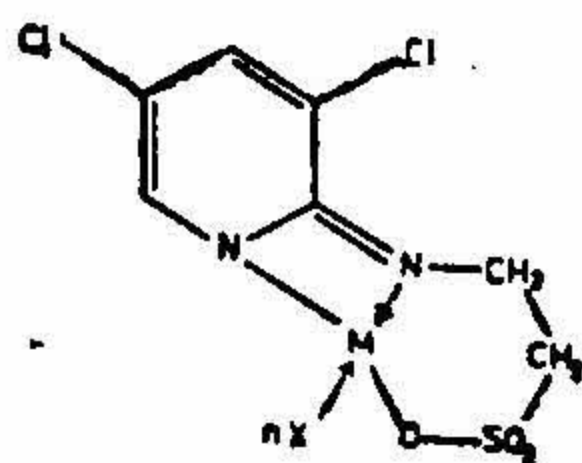
Based on microanalysis, the metal chelates and their adducts display 1:1 (metal:ligand) stoichiometry and possess the composition  $[M(PE)X_n]$  where M = bivalent metal ion, PE =  $C_7H_6Cl_2N_2SO_3$ , the deprotonated form of  $H_2PE$  ( $C_7H_8Cl_2N_2SO_3$ ) and X may be  $H_2O$ ,  $C_5H_5N$  or  $C_6H_7N$ . Pyrolysis (T.G.A.) of the hydrated chelates show a weight loss compared to three molecules ( $n = 3$ ) when M = Mn(II), Fe(II), Co(II), Ni(II) or Cu(II), two molecules of water ( $n = 2$ ) when M =  $VO^{+2}$ , and one water molecule ( $n = 1$ ) when M = Zn(II), Cd(II) or  $UO_2^{+2}$ .

The magnetic moments (Table II) indicate the presence of 5, 4, 3, 2, 1 and 1 unpaired electrons in Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and  $VO^{+2}$  chelates and their adducts respectively. The remaining chelates were found diamagnetic as expected. From the magnetic moment data it is apparent that there is no metal-metal bonding in these chelates and therefore spin-exchange does not take place and they exist as monomer.

The molar conductance values ( $3.4-6.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ) of all these chelates in dioxane and D.M.F. suggest them to be non-electrolytes.

### 3.2. Infrared spectra

The I.R. spectra of  $H_2PE$  was found to consist of three bands at 3210, 1650 and 1190  $\text{cm}^{-1}$  assignable to  $\nu_{N-H}$ ,  $\nu_{C=N}$  and  $\nu_{SO_2H}$ , respectively. In the spectra of metal chelate the bands at 3210 and 1190  $\text{cm}^{-1}$  were found absent indicating their elimination due to chelation. The metal chelates showed three bands in the ranges of 1630-1610, 500-480 and 400-370  $\text{cm}^{-1}$  attributed to the presence of  $\nu_{C=N}$ ,  $\gamma_{M-N}$  stretching and  $\nu_{M-O}$  stretching



where X may be  $H_2O$ ,  $C_5H_5N$  or  $C_6H_7N$

when  $n = 1$  M(II) Zn, Cd, or  $UO_2$

$n = 2$  M(II) VO

$n = 3$  M(II) Mn, Fe, Co, Ni, or Cu

FIG. 1. Bivalent metal chelates of 2-(N-35-dichloro- $\alpha$ -pyridoneimino) ethane sulphonic acid ( $H_2PE$ ).

**Table II**  
Molecular weight\*, magnetic moment, electronic spectral data and possible transitions of the bivalent chelates of H<sub>2</sub>PE and its pyridine and picoline adducts

Hydrated chelates			Pyridine adducts			Picoline adducts			Assignments			
Composition	Mol. wt. found (calc.)	$\mu_{eff}$ (B.M.) at 308° K	Absorption (cm <sup>-1</sup> )	Composition	Mol. wt. found (calc.)	$\mu_{eff}$ (B.M.) at 308° K	Absorption (cm <sup>-1</sup> )	Composition	Mol. wt. found (calc.)	$\mu_{eff}$ (B.M.) at 308° K	Absorption (cm <sup>-1</sup> )	Assignments
[Mn(PE)(H <sub>2</sub> O) <sub>3</sub> ]	367 (378)	5.91	23700 28800 34900	[Mn(PE)(Py) <sub>3</sub> ]	553 (561)	5.99	23000 28300 34000	[Mn(PE)(pic) <sub>3</sub> ]	594 (603)	6.10	23800 29200 35100	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> E <sub>g</sub> (G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> E <sub>g</sub> (D) <sup>6</sup> A <sub>g</sub> → <sup>4</sup> A <sub>2g</sub> (F)
[Fe(PE)(H <sub>2</sub> O) <sub>3</sub> ]	362 (379)	5.36	10900	[Fe(PE)(py) <sub>3</sub> ]	555 (562)	5.43	10250	[Fe(PE)(pic) <sub>3</sub> ]	598 (604)	5.58	11100	<sup>5</sup> T <sub>2g</sub> → <sup>5</sup> E <sub>g</sub> (D)
[Co(PE)(H <sub>2</sub> O) <sub>3</sub> ]	372 (382)	4.99	8450 17400 20800	[Co(PE)(py) <sub>3</sub> ]	551 (565)	5.12	9100 16900 20100	[Co(PE)(pic) <sub>3</sub> ]	599 (607)	5.18	8600 18100 21050	<sup>4</sup> T <sub>2g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F) <sup>4</sup> T <sub>2g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)
[Ni(PE)(H <sub>2</sub> O) <sub>3</sub> ]	371 (382)	3.28	9900 15100 26200	[Ni(PE)(py) <sub>3</sub> ]	550 (565)	3.35	9500 14410 25600	[Ni(PE)(pic) <sub>3</sub> ]	596 (607)	3.51	9950 15200 26300	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub> (F) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)
[Cu(PE)(H <sub>2</sub> O) <sub>3</sub> ]	372 (387)	2.03	12650	[Cu(PE)(py) <sub>3</sub> ]	553 (570)	2.09	12000	[Cu(PE)(pic) <sub>3</sub> ]	601 (612)	2.12	12700	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>
[Zn(PE)(H <sub>2</sub> O)]	341 (352)	dia.		[Zn(PE)(py)]	399 (413)	dia.		[Zn(PE)(pic)]	415 (427)	dia.		
[Cd(PE)(H <sub>2</sub> O)]	381 (399)	dia.		[Cd(PE)(py)]	451 (460)	dia.		[Cd(PE)(pic)]	465 (474)	dia.		
[UO <sub>2</sub> (PE)(H <sub>2</sub> O)]	550 (557)	dia.		[UO <sub>2</sub> (PE)(py)]	609 (618)	dia.		[UO <sub>2</sub> (PE)(pic)]	624 (632)	dia.		
[VO(PE)(H <sub>2</sub> O) <sub>2</sub> ]	365 (372)	1.79	11950 20500	[VO(PE)(py) <sub>2</sub> ]	483 (494)	1.90	11450 19050	[VO(PE)(pic) <sub>2</sub> ]	515 (522)	1.99	12300 20950	<sup>2</sup> B <sub>2</sub> → <sup>2</sup> E <sub>1</sub> <sup>2</sup> B <sub>2</sub> → <sup>2</sup> B <sub>1</sub>

\* All the complexes gave satisfactory C, N, S and metal analysis. py = pyridine and pic. = picoline,

frequencies, respectively. The presence of a broad band at  $3350\text{ cm}^{-1}$  due to the loss of water molecules in all the metal chelates. The loss of water molecules in the temperature range of  $180\text{--}290^\circ\text{C}$  suggest them to be present as coordinated and not lattice held.

Thus based on the above data, an octahedral geometry may be suggested for the Mn(II), Fe(II), Co(II), Ni(II),  $\text{UO}_2^{+2}$  and  $\text{VO}^{+2}$  chelates and their adducts. Zn(II) and Cd(II) chelates may possess tetrahedral stereochemistry, as expected. The Cu(II) chelates and its adducts may exhibit a distorted octahedral configuration in terms of Jahn-Teller effect<sup>14</sup>. These structures may be represented as shown in fig. 1.

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