

## Interaction of picolinic acid N-oxide and its derivatives with cobalt(II) involving some selected ligands in aqueous medium

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The formation constants of 1:1 binary chelates (ML) of Co(II) with (L) picolinic acid N-oxide (Pico) and its derivatives 4-aminopicolinic acid N-oxide (4-NH<sub>2</sub> Pico), 4-chloropicolinic acid N-oxide (4-Cl Pico) and 4-hydroxypicolinic acid N-oxide (4-OH Pico) and the corresponding 1:1:1 ternary chelates (MAL or MLA) involving (A) glycine, proline (N, O<sup>-</sup> donors); ethylenediamine, 1,10-phenanthroline (N,N donors); catechol, salicylic acid (O<sup>-</sup>, O<sup>-</sup> donors) and thioglycolic acid (S, O<sup>-</sup> donor) have been determined from pH-metric measurements at 30°C and 0.1 M (KNO<sub>3</sub>) ionic strength in aqueous medium. The stabilities of the binary chelates (ML) follow the order: 4-Cl Pico < Pico < 4-OH Pico < 4-NH<sub>2</sub> Pico, while those of ternary complexes show a quite reverse trend. The relative stabilities of the ternary complexes are quantitatively expressed in terms of the statistical parameter,  $\Delta \log K$ . The results are discussed in the light of statistical and different astatistical factors. The thermodynamic parameters determined for the binary systems are found to be favourable for chelation.

The studies on the chelating behaviour of picolinic acid and its N-oxide derivatives both in solid and solution states are of great importance in different fields of chemistry and biology<sup>1-4</sup>. In continuation of our work in this field<sup>5-7</sup>, the present note reports the pH-metric studies of the Co(II) complexes formed by (L) picolinic acid N-oxide (Pico), 4-aminopicolinic acid N-oxide (4-NH<sub>2</sub> Pico), 4-chloropicolinic acid N-oxide (4-Cl Pico) and 4-hydroxypicolinic acid N-oxide (4-OH Pico) in presence of (A) some selected N,N donors viz., ethylenediamine (en), 1,10-phenanthroline (phen); N,O<sup>-</sup> donors: glycine (gly), proline (pro); O<sup>-</sup>, O<sup>-</sup> donors: Catechol (cat), salicylic acid (sal); S,O<sup>-</sup> donor: thioglycolic acid (tga) at 30°C and 0.1 M (KNO<sub>3</sub>) ionic strength in aqueous medium. The thermodynamic quantities associated with the bi-

Table 1 – Acid dissociation constants and formation constants of secondary ligands and thermodynamic parameters of Co(II)-L- systems  
[Temp. = 30°C; I = 0.1 M (KNO<sub>3</sub>)].

Ligand	$pK_a$	$\log K_{ML}^M$	$\log K_{MA}^M$
gly	2.45	—	4.93
	9.65		
pro	10.55	—	5.35
cat	9.25	—	7.21
	10.55		
sal	2.93	—	7.95
	13.65		
en	6.94	—	6.37
	9.73		
tga	3.59	—	5.97
	10.09		
Pico	3.54	3.45	—
4-OH Pico	3.82	3.48	—
4-NH <sub>2</sub> Pico	5.20	3.57	—
4-Cl Pico	3.32	3.08	—
System	$-\Delta H$	$-\Delta G$	$\Delta S$
	(kJ mol <sup>-1</sup> )	(kJ mol <sup>-1</sup> )	(J mol <sup>-1</sup> deg <sup>-1</sup> )
Co(II)-Pico	16.42	20.01	11.85
Co(II)-NH <sub>2</sub> Pico	18.97	20.71	5.74
Co(II)-OH Pico	15.37	20.19	15.91
Co(II)-Cl Pico	14.52	17.87	11.06

nary complexes, ML are also determined by pH measurements at various temperatures.

### Experimental

The ligands Pico, 4-NH<sub>2</sub> Pico, 4-Cl Pico and 4-OH Pico were synthesised by known procedures<sup>7,8</sup> and all other ligands and chemicals used in the experiment were of AR grade. The pH-metric titrations of binary systems were carried out at 20, 30, 40 and 50°C and those of ternary systems at 30°C. In all the systems, an ionic strength of 0.1 M (KNO<sub>3</sub>) was maintained. The general experimental procedure and method of calculation of acid dissociation constants, formation constants and thermodynamic parameters were similar to those described earlier<sup>9</sup>. The accuracy of the constants reported is  $\pm 0.06$  log units.

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Table 2 – Formation constants and  $\Delta \log K$  values for Co(II) ternary complexes[Temp. = 30°C; I = 0.1 M (KNO<sub>3</sub>)]

(A)	Pico (L)			4-OH Pico (L)			4-NH <sub>2</sub> Pico (L)			4-Cl Pico (L)		
	$\log K_{MLA}^{ML}$	$\log K_{MAL}^{MA}$	$\Delta \log K$	$\log K_{MLA}^{ML}$	$\log K_{MAL}^{MA}$	$\Delta \log K$	$\log K_{MLA}^{ML}$	$\log K_{MAL}^{MA}$	$\Delta \log K$	$\log K_{MLA}^{ML}$	$\log K_{MAL}^{MA}$	$\Delta \log K$
gly	4.52	-	-0.41	4.48	-	-0.45	4.46	-	-0.47	4.56	-	-0.37
pro	4.96	-	-0.39	4.91	-	-0.44	4.86	-	-0.49	4.93	-	-0.42
cat	7.04	-	-0.17	6.82	-	-0.39	5.92	-	-1.29	7.07	-	-0.14
sal	-	-	-	5.62	-	-2.33	5.58	-	-2.37	5.64	-	-2.31
en	6.08	-	-0.29	6.04	-	-0.33	5.98	-	-0.39	6.11	-	-0.26
phen	-	-	-	-	3.44	-0.04	-	3.49	-0.08	-	3.09	-0.01
tga	-	-	-	8.02	-	+2.05	7.75	-	+1.78	8.79	-	+2.82

Constants are accurate up to  $\pm 0.06$  log units

### Results and discussion

The acid dissociation constants ( $pK_a$ ) of ligands, the formation constants and thermodynamic parameters of binary complexes, ML are presented in Table 1. The acid dissociation constants and the binary formation constants of all other (secondary) ligands, 'A' were redetermined under identical experimental conditions for better comparison with the corresponding ternary complexes (Table 1).

The stabilities of the binary complexes, ML followed the sequence: 4-Cl Pico < Pico < 4-OH Pico < 4-NH<sub>2</sub> Pico. This order of stability is in accordance with the increasing basicity ( $pK_a$ ) of these ligands. As the electron releasing nature of the substituent present on the 4th position of Pico increases, the basicity ( $\sigma$  donor ability) of the ligands (L) increases and consequently their binary stabilities. The lower stability of 4-Cl Pico can be attributed to its lower basicity due to the electron withdrawing nature of the chloro group.

The formation constants of binary complexes, ML decreases with increase in temperature indicating that the formation equilibria are exothermic in nature, which is also evidenced by their negative  $\Delta H$  (enthalpy) values. The negative values of  $\Delta G$  (free energy) indicate the spontaneity of the complexation reactions whereas the positive values of  $\Delta S$  (entropy) suggests the chelation process to be entropy favoured.

From the experimental results, the formation of all the ternary complexes (MLA or MAL) were found to occur in stepwise equilibria<sup>6,9</sup>, in which the ligands 'L' (Pico or its derivative) acted as primary ligand except those of 'Phen' systems, where 'L' behaved as a secondary ligand. The species distribution curves generated for some representa-

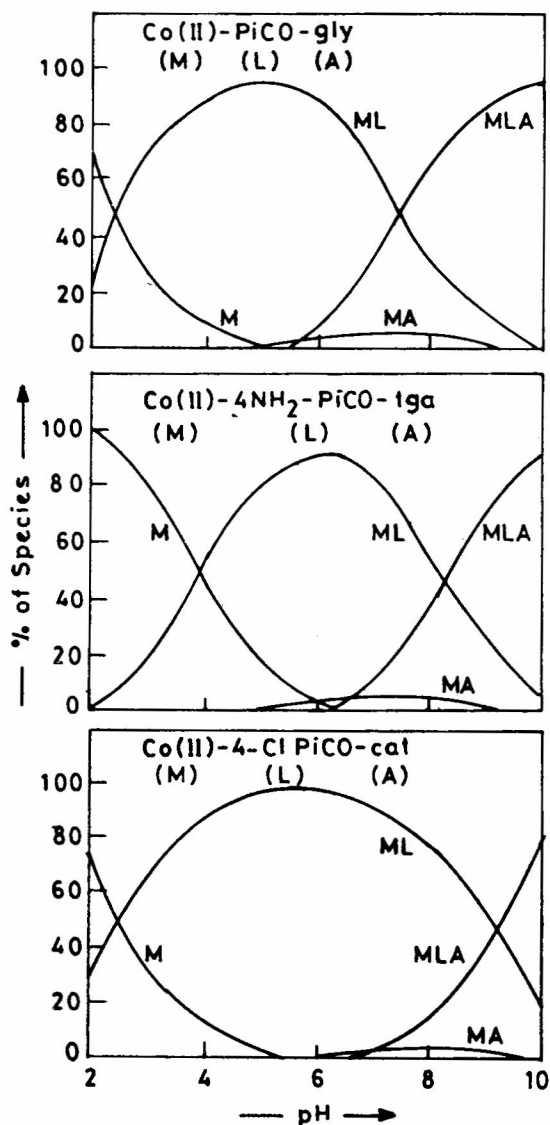


Fig. 1—Species distribution curves for Co(II)-L-A ternary systems

tive systems (Fig. 1) using the Computer Program BEST<sup>10</sup> also suggests the stepwise formation of ternary complexes in which the percentage of the ternary species increases with increase in pH, indicating the formation of stable ternary complexes at higher pH region. The relative stabilities of the ternary complexes (MAL or MLA) have been characterised in terms of the statistical<sup>11</sup> parameter,  $\Delta \log K$  (from Eq. 1) and are listed in Table 2 along with the corresponding stepwise ternary formation constants.

$$\Delta \log K = \log K_{MLA}^{ML} - \log K_{MA}^M = \log K_{MAL}^{MA} - \log K_{ML}^M \dots (1)$$

The results (Table 2) show that the  $\Delta \log K$  values for all the systems except those of 'tga' are negative as expected on statistical grounds. The observed less negative  $\Delta \log K$  values for all the systems indicates their stabilised nature due to greater contribution from different astatistical<sup>12</sup> factors, such as basicity of the ligands, nature of donor atoms, metal-ligand  $\pi$ -interactions, charge neutralisation in ternary complex, electrostatic repulsions, chelate ring size etc. The overall order of stability of ternary chelates (MAL/MLA) with respect to the ligands 'A' is: tga > phen > gly > pro > cat > sal. The higher stability (positive  $\Delta \log K$ ) of the 'tga' (S, O<sup>-</sup> donor) systems can be attributed to the strong Co(II) → tga (M-S)  $d_{\pi} - d_{\pi}$  interaction<sup>12</sup>, in addition to the M-L  $\pi$ -interactions. The higher stability (less negative  $\Delta \log K$ ) of 'Phen' systems than 'en' can be attributed to its known M → N  $d_{\pi} - p_{\pi}$  interactions<sup>11-13</sup>. The greater stability of both 'Phen' and 'en' (N,N donor) systems can be due to effective charge neutralisation and lesser electrostatic repulsions in their ternary systems. The relative stability of the 'cat' systems are much greater than 'sal'. This may be due to its greater  $\pi$ -interactions and lesser steric effects. The forma-

tion of one 5-membered and one 6-membered chelate rings in 'cat' systems than two 6-membered rings in 'sal' may also be responsible for its higher stability<sup>12</sup>.

The stabilities of the ternary complexes (MAL/MLA) with respect to the ligand 'L' follow the sequence: 4-NH<sub>2</sub> Pico < 4-OH Pico < Pico < 4-Cl Pico. A comparison of this order with that of binary complexes, ML indicates a reverse trend, which follows the  $\pi$ -acceptor ability of the ligand than ( $\sigma$  donor) basicity. The presence of more basic (electron releasing) substituent on 4th position of 'Pico' may decrease its  $\pi$ -acceptor nature and thus resonance stabilisation of the ternary metal chelates formed, as observed in the present study. Thus, the higher stability of 4-Cl Pico is due to its electron withdrawing chloro substituent. Thus in the ternary systems studied, the  $\pi$ -acceptor nature predominates over ' $\sigma$ ' donor nature (basicity) of the ligands 'L'.

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