

Enthalpy and entropy changes associated with mixed ligand chelates of Cu(II) and Ni(II) with 4-methoxy picolinic acid N-oxide and some amino acids in aqueous medium

C H SARALA DEVI and M G RAM REDDY*

Department of Chemistry, Osmania University, Hyderabad 500 007, India

MS received 26 November 1985

Abstract. The stability constants of mixed complexes of Cu(II) and Ni(II) with 4-methoxy picolinic acid N-oxide, and glycine, α -alanine, proline and hydroxy-proline have been determined at various temperatures by the potentiometric method in 0.1 M ionic strength. The formation constants of the mixed complexes have been evaluated and are in good agreement with statistically expected values. The enthalpy and entropy values have been calculated from 1:1 stability constants temperature coefficient data. From the enthalpy values of the mixed complexes it may be concluded that the bond strengths are not equal to the average of the bond strengths in MA_2 and MB_2 type parent complexes. The entropy values have been found to be favourable for ternary complex formation.

Keywords. 4-methoxy picolinic acid N-oxide; amino acids; mixed ligand complexes; formation constants; thermodynamic parameters.

1. Introduction

The study of formation of ternary complexes of picolinic acid N-oxide (PicO) and some amino acids with Cu(II) have been reported earlier (Sarala Devi and Ram Reddy 1986). In this paper we present the formation constants of Cu(II) and Ni(II) ternary complexes employing 4-methoxy PicO as primary ligand and glycine, alanine, proline and hydroxy proline as secondary ligands. Formation constants were determined by potentiometric methods and calculated with known equations (Ramamoorthy and Santappa 1971; Singh and Srivastava 1973). The proton-ligand and metal-ligand stability constants of binary systems were calculated under the present experimental conditions using the expressions given by Irving and Rossotti (1954) and are presented in table 1. The values thus obtained were found to be in agreement with literature values (Martell and Smith 1971). The enthalpy (ΔH°) and entropy (ΔS°) values associated with above ligands were calculated by known equations and are presented in table 2.

2. Experimental

All the chemicals used were of AR grade. Glycine, α -alanine, proline and hydroxy proline were used as such while 4-methoxy picolinic acid N-oxide was prepared in our laboratory (Ram Reddy *et al* 1981). All solutions were prepared in doubly distilled water. Solutions of Cu(II) and Ni(II) were estimated by titrating with the disodium salt

* To whom all correspondence should be addressed.

Table 1. Stability constants of binary and ternary complexes at 30°C and 0.1 M ionic strength.

	log K	$\Delta \log K$	log X
<i>Cu(II) complexes</i>			
4-OCH ₃ PicO	3.94		
Gly	8.27	-1.10	0.53
4-OCH ₃ PicO-Gly	7.17		
Ala	8.15	-1.26	0.12
4-OCH ₃ PicO-ala	6.89		
Pro	8.69	-0.85	0.54
4-OCH ₃ PicO-pro	7.84		
Hpro	8.50	-1.05	0.52
4-OCH ₃ PicO-hpro	7.45		
<i>Ni(II) complexes</i>			
4-OCH ₃ PicO	3.10		
Gly	5.81	-0.21	1.21
4-OCH ₃ PicO-gly	5.60		
Ala	5.35	-0.24	1.02
4-OCH ₃ PicO-ala	5.11		
Pro	6.23	-0.38	0.76
4-OCH ₃ PicO-pro	5.85		
Hpro	6.11	-0.31	1.04
4-OCH ₃ PicO-hpro	5.80		

Table 2. Thermodynamic parameters of binary and ternary complexes at 0.1 M ionic strength.

	$-\Delta H^\ddagger$ kJ mole ⁻¹	$-\Delta G^\ddagger$ (30°C) kJ mole ⁻¹	$-\Delta S^\ddagger_{111}$ (30°C) JK ⁻¹ mole ⁻¹	$-\Delta H^\ddagger_{111}$	ΔS^\ddagger_{111}
<i>Cu(II) complexes</i>					
4-OCH ₃ PicO	22.02	22.87	2.80		
Gly	25.53	47.99	94.12	42.91	51.30
4-OCH ₃ PicO-gly	29.05	41.61	41.46		
Ala	18.20	47.30	96.03	41.89	52.57
4-OCH ₃ PicO-ala	25.43	39.96	47.97		
Pro	18.41	50.43	105.67	43.45	62.08
4-OCH ₃ PicO-pro	18.74	45.43	88.31		
Hpro	35.91	49.33	46.94	47.75	39.45
4-OCH ₃ PicO-hpro	37.49	32.50	18.94		
<i>Ni(II) complexes</i>					
4-OCH ₃ PicO	29.05	17.80	-37.14		
Gly	17.15	33.68	54.51	42.41	16.06
4-OCH ₃ PicO-gly	23.43	32.50	29.93		
Ala	11.46	31.00	64.47	38.37	21.80
4-OCH ₃ PicO-ala	16.87	29.68	42.17		
Pro	12.42	35.64	62.59	38.61	34.18
4-OCH ₃ PicO-pro	18.02	33.95	52.57		
Hpro	19.56	35.43	52.37	43.51	17.97
4-OCH ₃ PicO-hpro	28.10	33.66	18.31		

of EDTA. The following solutions (total volume 50 ml) were titrated potentiometrically against standard potassium hydroxide at 30°, 40°, 50°C containing (i) acid (4×10^{-3} M); (ii) primary ligand (2×10^{-3} M); (iii) metal nitrate (2×10^{-3} M) and primary ligand; (iv) secondary ligand (2×10^{-3} M); (v) metal nitrate and secondary ligand; (vi) metal nitrate, primary ligand and secondary ligand. The ionic strength was maintained at 0.1 M by adding KNO_3 . All titrations were performed under nitrogen atmosphere. The metal:ligand:ligand ratio was maintained as 1:1:1.

3. Results and discussion

The mixed ligand titration curves of M (II)-4-methoxy PicO ($M = \text{Cu(II)}, \text{Ni(II)}$) with glycine alanine, proline and hydroxy proline at 30°C gave an inflection at $m = 4$ (m refers to moles of base added per mole of metal ion) corresponding to the formation of a ternary complex. These curves were superimposable on the previous 1:1 Cu(II)-4-methoxy PicO and 1:1 Ni(II)-4-methoxy PicO curves respectively upto $m = 3$. This was indicative of 4-methoxy PicO acting as the primary ligand. Similar titration curves were obtained at 40°C and 50°C also indicating the formation of a ternary complex from normal 1:1 M (II)-4-methoxy PicO complex in a stepwise manner. This was further confirmed by a shift of the pH of precipitation in ternary systems compared to binary systems. The data in table 1 show that the stability constants of ternary complexes are lower than those of the 1:1 binary systems of secondary ligand. This can be attributed to the lesser tendency of secondary ligand towards formation of $(MA)^+$ (A is the primary ligand) as compared to that towards formation of $M(\text{H}_2\text{O})_n^{2+}$.

There are two common ways of expressing the stability of ternary complexes: (i) the one approach is based on the disproportionation constant (X), which may be defined as:

$$\log X = 2 \log \beta_{MAB} - (\log \beta_{MA} + \log \beta_{MB})$$

The data in table 1 show that the $\log X$ values are in good agreement with statistically expected values;

(ii) the other approach compares the difference in the stability constants of binary and ternary systems:

$$\Delta \log K = \log K_{MAB}^{MA} - \log K_{MB}^M$$

The $\Delta \log K$ values are calculated and presented in table 1. The experimental values are in the range of (-1.0) to (-1.2) and (-0.22) to (-0.44) for Cu-4-methoxy PicO-AA and Ni-4-methoxy PicO-AA respectively, suggesting distorted octahedral and square planar geometries (Sigel 1975) for the same systems. However, these values are lower compared to the $\Delta \log K$ values of M -PicO-AA systems (Sarala Devi and Ram Reddy 1986). This can be attributed to electron donating groups in 4-methoxy PicO, which decreases the π -acceptor capacity of ligand.

The thermodynamic data in table 2 show that the reactions are exothermic and spontaneous in nature as evidenced by the negative values of ΔH^\ddagger and ΔG^\ddagger . The enthalpy and entropy values in ternary complexes vary from the binary complexes. The enthalpy (ΔH^\ddagger) values in M -4-methoxy PicO-AA systems are lower compared to the values in M -PicO-AA systems. This may be due to the greater electrostatic character of

M-AA bonds in M-PicO-AA resulting from the higher π -acceptor capacity of PicO as compared to 4-methoxy PicO.

The enthalpy and entropy changes of the mixed ligand complexes are calculated according to statistical considerations by the following equations (Gergely and Sovago 1973):

$$\Delta H_{111}^x = 1/2 (\Delta H_{12}^A + \Delta H_{12}^B),$$

$$\Delta S_{111}^x = 1/2 (\Delta S_{12}^A + \Delta S_{12}^B) + 4.574 \log 2,$$

and the data is listed in table 2. The enthalpy change ΔH_{111} and entropy change ΔS_{111} accompanying the mixed complex formation are smaller than the statistical values ΔH_{111}^x and ΔS_{111}^x respectively. This can be attributed to factors like the π -acceptor property of ligands, and the electrostatic character of metal ligand bonds. Hence, the strength of the metal ligand bonds in mixed complexes are not equal to the average bond strength in parent complexes.

Acknowledgements

The authors wish to thank Prof T Navneeth Rao, for his interest and CSIR, Delhi for a fellowship to CHS.

References

- Gergely A and Sovago I 1973 *J. Inorg. Nucl. Chem.* **35** 4355
Irving H M and Rossotti H S 1954 *J. Chem. Soc.* 2904
Martell A E and Smith R M 1971 *Stability constants of metal ion complexes: Special publication 25* (Oxford: Alden and Mowbray)
Ramamoorthy S and Santappa M 1971 *Indian J. Chem.* **9** 38
Sarala Devi C H and Ram Reddy M G *Indian J. Chem.* (in press)
Sigel H 1975 *Angew. Chem., Int. Ed. Engl.* **14** 394
Singh M K and Srivastava M N 1973 *J. Inorg. Nucl. Chem.* **35** 2433
Sudhaker Reddy M and Ram Reddy M G 1981 *Indian J. Chem.* **20A** 1134