Equilibrium studies on transition metal binary and ternary complexes containing N-hydroxyphthalimide and other ligands in solution

CH VENKATA RAMANA REDDY and M G RAM REDDY*

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

MS received 28 April 1994; revised 7 July 1994

Abstract. The formation constants of binary, ML , ML_2 and ternary, MAL complexes where, $M = Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$; $L = N$ -hydroxyphthalimide (2-hydroxy-1,3-*iso* indoleione) and $A =$ alanine, valine, ethylenediamine, 2,2'-bipyridyl, oxalic acid and catechol have been determined from solution equilibrium studies by pH-metric method at 30°C and 0.1 M (KNO_3) ionic strength. 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 both statistical and various astatistical factors. The stabilities of both the binary and ternary complexes were found to follow the Irving–Williams (natural) order.

Keywords. Formation constants; binary complexes; ternary complexes; stability; N-hydroxyphthalimide.

1. Introduction

The N-hydroxyphthalimide is an important chemical reagent used in the synthesis of peptides (Nefkens *et al* 1962; Zimmerman and Anderson 1967), pesticides (Harfough *et al* 1986), antibacterials (Kato *et al* 1988), antibiotics (Newall and Looker 1988) etc. Generally the physiological activity of many organic compounds undergo significant changes on complexation (Koteswara Rao and Ram Reddy 1990). Although the complex-forming ability of N-hydroxyphthalimide has been the subject matter of several investigations (Biederman and Schwarzhans 1970; Bhakshi *et al* 1989), no significant quantitative studies were made regarding the formation and stability of such complexes in solution. Accordingly, the present paper reports the pH-metric study of the binary (ML , ML_2) and ternary (MAL or MLA) complexes formed by the N-hydroxyphthalimide (NHP), L with (M) $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ in presence of other ligands 'A' containing N,N; N,O^- and O^- , O^- donor atoms viz., ethylenediamine (en), 2,2'-bipyridyl (bipy), alanine (Ala), valine (Val), catechol (cat) and oxalic acid (oxa) in 5% (v/v) ethanol–water medium at 30°C and 0.1 M (KNO_3) ionic strength.

2. Experimental

The ligand NHP was obtained from E. Merck. All other ligands, metal nitrate salts and other chemicals used in the experiment were of BDH AnalaR grade. All the solutions

*For correspondence

were prepared in doubly distilled water, except that of NHP which was prepared in 5% (v/v) ethanol–water medium. The stock solutions of metal ions were standardised volumetrically as outlined by Flashka (1964). The solution of carbonate-free potassium hydroxide was standardised by titrating with potassium hydrogen phthalate.

The experimental method consisted of pH-metric titration of ligands in absence and presence of metal ions against standard potassium hydroxide solution at 30°C and 0.1 M (KNO₃) ionic strength in 5% (v/v) ethanol–water medium under nitrogen atmosphere. The other experimental details are similar to those described earlier (Venkata Ramana Reddy *et al* 1991, 1993). The necessary pH correction for the measurements were made as reported by Van Uitert *et al* (1953). The acid dissociation constants of ligands and binary formation constants were calculated by the method of Irving and Rossotti (1953, 1954) and the ternary formation constants using known expressions (Ramamoorthy and Santappa 1970, 1971). The results obtained (with an accuracy of ± 0.05 log units) are listed in table 1.

3. Results and discussion

3.1 Acid dissociation constants and binary systems

The acid dissociation constants of all the ligands (A and L) and the formation constants of binary complexes, MA were redetermined under present experimental conditions, and are in close agreement with the reported values (Venkata Ramana Reddy *et al* 1994). The formation constants of the (1:1 and 1:2) binary complexes, ML and ML₂ of NHP (L) have been evaluated from the experimental data by analysing the titration curves in the pH range of 4.5 to 6.8 and are listed in the table 1. The ligand, NHP (structure 1) possesses three coordination sites and binds with the metal ion either through 1, 2 or 2, 3 donor sites during complexation (Venkata Ramana Reddy and Ram Reddy 1995). The stabilities of the binary complexes, ML, follow the sequence: Co(II) < Ni(II) < Cu(II) > Zn(II), which is in accordance with the Irving–Williams (1948) (natural) order.

1

3.2 Ternary systems

From the experimental data, the formation of ternary complexes (MAL or MLA) were found to occur in three different ways. In all the cases distinct inflections were found in the titration curves, indicating the nature of complexation.

(i) The complexes, MAL consisting of A = bipy/oxa were formed in stepwise equilibria, in which the 'L' (NHP) acted as secondary ligand

(ii) The complexes, MLA containing M = Co(II), Ni(II), Zn(II) and A = Ala, Val, cat

Table 1. Formation constants and $\Delta \log K$ values of transition metal complexes containing N-hydroxyphthalimide and other ligands at 30°C and $\mu = 0.1$ M (KNO_3).

System	$\log K_{\text{ML}}^{\text{M}}$	$\log K_{\text{ML}_2}^{\text{ML}}$	$\log K_{\text{MAL}}^{\text{MA}}$	$\log K_{\text{MLA}}^{\text{ML}}$	$\log \beta_{\text{MAL}}^{\text{M}}$	$\Delta \log K$
Co(II)-Ala-NHP			—	3.98	7.36	-0.55
Co(II)-Val-NHP			—	3.77	7.15	-0.57
Co(II)-en-NHP			—	—	9.21	-0.49
Co(II)-bipy-NHP			2.94	—	8.92	-0.44
Co(II)-oxa-NHP			2.72	—	7.71	-0.66
Co(II)-cat-NHP			—	6.91	10.29	-0.56
Ni(II)-Ala-NHP			—	5.07	8.50	-0.49
Ni(II)-Val-NHP			—	5.03	8.46	-0.51
Ni(II)-en-NHP			—	—	10.55	-0.44
Ni(II)-bipy-NHP			3.03	—	10.16	-0.40
Ni(II)-oxa-NHP			2.79	—	8.07	-0.64
Ni(II)-cat-NHP			—	7.15	10.58	-0.52
Cu(II)-Ala-NHP			—	—	11.47	-0.46
Cu(II)-Val-NHP			—	—	11.41	-0.48
Cu(II)-en-NHP			—	—	13.89	-0.41
Cu(II)-bipy-NHP			3.42	—	11.49	-0.36
Cu(II)-oxa-NHP			3.17	—	7.99	-0.61
Cu(II)-cat-NHP			—	—	15.61	-0.49
Zn(II)-Ala-NHP			—	4.50	8.06	-0.51
Zn(II)-Val-NHP			—	4.23	7.79	-0.53
Zn(II)-en-NHP			—	—	8.97	-0.46
Zn(II)-bipy-NHP			3.13	—	8.39	-0.43
Zn(II)-oxa-NHP			2.94	—	8.28	-0.62
Zn(II)-cat-NHP			—	7.78	11.34	-0.54
Co(II)-NHP	3.38	2.58				
Ni(II)-NHP	3.43	2.62				
Cu(II)-NHP	3.78	2.73				
Zn(II)-NHP	3.56	2.66				

 pK_a of NHP = 6.45

were also formed in stepwise equilibria, in which 'L' (NHP) behaved as a primary ligand

(iii) The ternary complexes (MAL/MLA) containing 'A' as 'en' and $\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$ and also 'A' as Ala/Val/cat and $\text{M} = \text{Cu(II)}$ were formed in simultaneous equilibria

charges omitted for clarity.

The formation of the ternary complexes in the above three equations can possibly be explained by considering the basicities (pK_a) of the ligands involved in the corresponding systems. In the systems $\text{M(II)-bipy/oxa-NHP}$ (type i), the acid dissociation constants (pK_a) of the primary ligands (A) bipy/oxa are much lower than NHP. Hence these ligands bind with the metal ion in the first step followed by NHP in the second step. Similarly in systems (type ii) the basicity (pK_a) of the NHP (L) is much

lower than (A) Ala/Val/cat and hence the NHP acts as a primary ligand while the others as secondary ones. In case of $M(II)$ -en-NHP systems (type iii), the basicities, pK_a of the NHP and pK_{1a} of en are comparable. So the formation of these complexes in simultaneous equilibria can be justified. However, the simultaneous formation of $Cu(II)$ -Ala/Val/cat-NHP systems cannot be attributed to any single factor.

In order to understand the chelating behaviour of ligands with the metal ion, the species distribution curves for major species are given as a function of pH in figure 1 for $Cu(II)$ -en-NHP and $Cu(II)$ -Ala-NHP ternary systems, obtained by using the computer program BEST (Motekaitis and Martell 1982). From the figure it can be seen that the general pH range of complexation for both the ligands A (en/Ala) and L (NHP) is same (~ 4 to 7 pH). Thus the ligands (A) en/Ala and (L) NHP can coordinate simultaneously with the metal ion, $Cu(II)$ as also observed from experimental results. The percentage of ternary species increases with increase in pH and predominates over binary species beyond pH 6.5. A similar examination of species distribution profiles for all other ternary systems also clearly revealed the mode of complexation, keeping in conformity with the experimental results.

Figure 1. Species distribution curves of $Cu(II)$ -en/Ala-NHP ternary systems.

The stepwise ($\log K_{\text{MAL}}^{\text{MA}}/\log K_{\text{MLA}}^{\text{ML}}$) and overall ($\log \beta_{\text{MAL}}^{\text{M}}$) formation constants of the ternary systems are presented in the table 1. The relative stabilities of the ternary complexes, compared to the corresponding binary systems are quantified in terms of the statistical parameter, $\Delta\log K$, using the following expressions.

$$\Delta\log K = \log K_{\text{MAL}}^{\text{MA}} - \log K_{\text{ML}}^{\text{M}} = \log K_{\text{MLA}}^{\text{ML}} - \log K_{\text{MA}}^{\text{M}}, \quad (4)$$

or

$$\Delta\log K = \log \beta_{\text{MAL}}^{\text{M}} - (\log K_{\text{MA}}^{\text{M}} + \log K_{\text{ML}}^{\text{M}}). \quad (5)$$

The results (table 1) show that the $\Delta\log K$ values for all the ternary systems are negative as expected on statistical grounds (Sigel 1975). The overall order of stabilities of the ternary complexes (MAL/MLA) with respect to the ligands 'A' is: oxa < cat < Val < Ala < en < bipy. This sequence of stability can be explained by considering a number of statistical factors (Bhattacharya 1981), such as basicity of the ligands, nature of donor atoms, charge neutralisation and electrostatic repulsions in the ternary complex, metal–ligand π -interactions, steric factors etc.

The higher stability (less negative $\Delta\log K$) of N, N donor (en/bipy) systems can be attributed to the absence of any electrostatic repulsions, between the donor atoms (N, N) of 'A' and (O, O⁻) of L in the ternary complexes (MAL/MLA). The greater stability of 'bipy' systems over 'en' is due to metal $\rightarrow$ bipy ($M - N$) $d_{\pi} - p_{\pi}$ interactions, as a result of which the effective positive charge on the metal ion increases and thus facilitates greater interaction with the O, O⁻ donor ligand, NHP, in the second step of complexation (Sigel 1975). The lower stability (more negative $\Delta\log K$) of the ternary systems containing 'A' as O⁻, O⁻ donors (oxa/cat) could be due to the formation of negatively charged complexes, which involves greater electrostatic repulsions (Bhattacharya 1981) between negatively charged oxygens of both the ligands (A and L), resulting in greater destabilization. The higher stability of 'cat' systems over 'oxa' can be attributed to its higher basicity and metal–ligand π -interactions. The stabilities of N, O⁻ donor (A) Ala/Val systems are intermediate to both N, N and O⁻, O⁻ donor systems, possibly due to the effective charge neutralisation and minimum electrostatic repulsions. The higher stability of 'Ala' systems over 'Val' can be attributed to its higher basicity and lesser steric effects.

Thus, the chelating behaviour of NHP and the stabilities of the resultant complexes were significantly influenced by a variety of factors as discussed.

References

- Bhakshi P K, Chowdhury S R, Haider S Z, Khan M S, Malik K M A and Pasha N A 1989 *J. Bangladesh Acad. Sci.* 13 225
 Bhattacharya P K 1981 *J. Sci. Ind. Res.* 40 382
 Biederman H G and Schwarzhans K E 1970 *Z. Naturforsch.* 25 889
 Flashka H A 1964 *EDTA titrations* (Oxford: Pergamon)
 Harfough A A, Idress K A and El-Kholy A 1986 *Curr. Sci.* 55 93
 Irving H M and Rossotti H S 1953 *J. Chem. Soc.* 3397
 Irving H M and Rossotti H S 1954 *J. Chem. Soc.* 2904
 Irving H and Williams R J P 1948 *Nature (London)* 162 746
 Kato K, Murakami K, Mochizuki H and Mochida E 1988 *Eur. Pat. Appl. Ep* 269087; 1988 *Chem. Abstr.* 109 p210792c
 Koteswara Rao N S R R M M and Ram Reddy M G 1990 *Biol. Met.* 3 19
 Motekaitis R J and Martell A E 1982 *Can. J. Chem.* 60 2403
 Nefkens G H L, Tesser G I and Nivard R J F 1962 *Recl. Trav. Chim.* 81 683

- Newall C E and Looker B E 1988 *Eur. Pat. Appl.* Ep 266060; 1988 *Chem. Abstr.* **110** p57409j
Ramamoorthy S and Santappa M 1970 *J. Inorg. Nucl. Chem.* **32** 1623
Ramamoorthy S and Santappa M 1971 *Indian J. Chem.* **9** 381
Sigel H 1975 *Angew. Chem. Int. Ed. Engl.* **14** 394
Van Uitert L G, Cornelius W C and Douglas B E 1953 *J. Am. Chem. Soc.* **75** 2736
Venkata Ramana Reddy Ch and Ram Reddy M G 1995 *J. Indian Chem. Soc.* (in press)
Venkata Ramana Reddy Ch, Sarala Devi Ch and Ram Reddy M G 1991 *Indian J. Chem.* **A30** 385
Venkata Ramana Reddy Ch, Shivaraj and Ram Reddy M G 1994 *J. Indian Chem. Soc.* **71** 59
Zimmerman J E and Anderson G W 1967 *J. Am. Chem. Soc.* **89** 7151