Equilibrium Studies of Some Ni(II) Ternary Complexes: A Comparative Study

SANGITA SHARMA, JABALI J. VORA and J.D. JOSHI*
Department of Chemistry, North Gujarat University, Patan-384 265, India

pH-metric method has been used to find out $\log K_{MAL}^{MA}$ at $25 \pm 0.1°C$ and at constant ionic strength, $\mu = 0.2$ M ($NaClO_4$), where A = 2,2′-bipyridyl, 2-2′-bipyridylamine, or o-phenanthroline and L = glycollic acid, lactic acid or malic acid. The coordinating tendencies of various ligands depend on the basicities of the ligand, size of the ligand and chelate ring of the ligand. It is found that along with size of secondary ligand, primary ligand size also plays a deciding role in the stability of mixed ligand complexes. Also an attempt is made to correlate the coordinating tendencies of O—O, N—O and O—S donor atoms as secondary ligands.

INTRODUCTION

Ternary complexes are well known for their pivotal role in various fields, such as biological systems[1, 2], chemotherapy[3], catalysis[4] etc. The study of formation, stabilities and reactivities of these complexes is an active field of research even today[5–7]. Super acid catalysis by metals contained in systems is essential for all organisms including mammals[8].

In the present studies mixed ligand formation constants, $\log K_{MAL}^{MA}$, where A = 2,2′-bipyridylamine or o-phenanthroline and L = glycollic acid, lactic acid or malic acid are determined by using modified form of Irving-Rossotti titration method[9]. It is also interesting to compare the effect of stuctural changes due to donor atoms on the stabilities of mixed ligand complexes of Ni(II) in aqueous media containing O—O, O—S or N—O donor atoms. For comparison, values are taken from literature. The comparison is useful for understanding the nature and coordinating behaviour of ligands.

EXPERIMENTAL

All reagents used were AR grade and solutions for the equilibrium study were prepared in the conductivity water. Acid and metal content of the solutions was determined by acid base[10] and complexometric methods[11]. Digital pH-meter Equiptronics EQ-610 with a readability of ±0.01 unit has been used for pH-measurements. The calibration was intermittently checked using standard buffer solution of potassium hydrogen phthalate (pH = 4.05) and borax

(pH = 9.18). Metal perchlorate was used to minimise the coordinating tendency of anion and ionic strength was maintained at 0.2 M using sodium perchlorate solution.

The representative potentiometric titration curves of 1 : 1 : 1 ternary complex involving Ni(II)-2,2'-bipyridyl-glycollic acid is shown in Fig. 1. From pH-metric titration data $\bar{n}H$, $\bar{n}$ and pL values were calculated and ternary formation constant values were determined by modified form of Irving-Rossotti titration technique[9].

1. ACID
2. 2,2'-BIPYRIDYLAMINE
3. GLYCOLLIC ACID
4. 1:1 MOLAR RATIO OF Ni(II)-2,2'-BIPYRIDYLAMINE
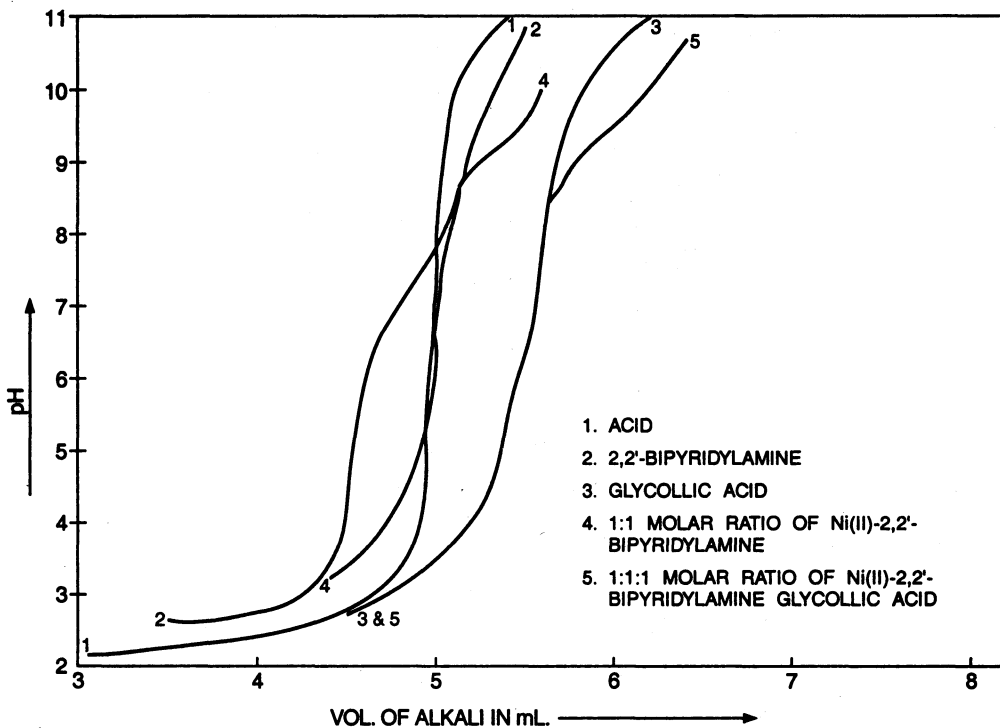5. 1:1:1 MOLAR RATIO OF Ni(II)-2,2'-BIPYRIDYLAMINE GLYCOLLIC ACID

Fig. 1.   2,2'-Bipyridylamine Glycollic Acid System at 25°C

RESULTS AND DISCUSSION

The formation of binary complex takes place due to interaction of Ni(II) ion with oxy acid anion. The average values of pK_1^H, pK_2^H and pK_3^H of acids are obtained by linear plot method[12] and these values agree with values reported in literature. The binary formation constant values of $\log K_{ML_1}^M$ and $\log K_{ML_2}^{ML}$ were obtained by least square method[13]. Precise values of $\log K_{MAL}^{MA}$ were calculated by method of averages[14] and results are presented in Table-1.

TABLE-1
COMPARISON AMONG Ni(II) TERNARY COMPLEXES

Donor atoms oxyacids	Ligand	$\log K_{NiL}^{Ni}$	$\log K_{NiL_2}^{NiL}$	$\log K_{Ni\text{-}2,2'\text{-}dipy\,L}^{Ni\text{-}2,2'\text{-}dipy}$	$\log K_{Ni\text{-}2,2'\text{-}dipy\,AL}^{Ni\text{-}2,2'\text{-}dipy\,L}$	$\log K_{Ni\text{-}O\text{-}phen\,L}^{Ni\text{-}O\text{-}phen}$
Ō—Ō	1. Glycollic acid	4.76	4.35	5.09	4.34	—
	2. Lactic acid	5.01	4.59	5.12	5.01	—
	3. Malic acid	5.50	4.89	5.22	5.06	—
Thio acids* S—Ō	1. Thioglycollic acid	6.78	6.63	6.71	6.59	—
	2. Thiolactic acid	7.31	6.97	6.87	6.78	—
	3. Malic acid	7.68	6.62	7.88	7.99	—
Amino acids* N—Ō	1. Glycine	5.90	5.05	5.50	5.48	—
	2. α-Alanine	5.55	4.53	5.14	5.28	—
	3. Aspartic acid	7.12	5.32	6.72	6.74	—

*Values are taken from literature

Mixed ligand complexes of Ni(II) with 2,2'-dipyridyl, 2,2'-dipyridylamine and o-phenanthroline as primary ligands and oxyacids, thioacids and amino acids as secondary ligands.

2,2'-dipy = 2,2'-dipyridyl; 2,2'-dipy A = 2,2'-dipyridylamine; o-phen = o-phenanthroline

The binary as well as ternary formation constant values indicate the order glycollic acid < lactic acid < malic acid. The order is explained in accordance with the basicities of the ligands. Glycollic and lactic acid both the monocarboxylic acids, the inductive effect of —CH_3 group makes lactic acid less acidic than glycollic acid. Malic acid is a tridentate ligand; the dissociation of first —COOH group brings inductive effect that reduces the dissociation of second —COOH or —OH group and makes it more ligating. From statistical consideration also the driving force for the binding of secondary ligand with $[M(A)]^{2+}$ should be less than for binding of L with $[M(aq)]^{2+}$ in binary systems. It has been observed that mixed ligand complex formation values are slightly higher than would have been expected from statistical considerations[15]. In presence of secondary ligand hydrolysis of $[MA]^{2+}$ is suppressed; therefore there is formation of mixed ligand complexes[16] at higher pH. Studies on ternary complexes have shown[17] that the presence of aromatic nitrogen donating ring becomes more selective and discriminating towards the incoming secondary ligand.

The 2,2'-bipyridylamine, 2,2'-bipyridyl and *o*-phenanthroline are neutral in behaviour and dπ–pπ interaction between metal ion and neutral molecule does not allow the concentration of charge on the metal ion to increase significantly. As a result, the electronegativity of $[M(aq)_n]^{2+}$, $[M(2,2'-bipy)]^{2+}$, $[M(2,2'-bipy\ A)]^{2+}$ and $[M(o-phenan)]^{2+}$ is almost same[18]. 1,10-Phenanthroline is bigger in size which creates steric hindrance for incoming secondary ligand. There is no separation of curves in case of *o*-phenanthroline system and so calculation of log K_{MAL}^{MA} was not possible.

It is noteworthy to compare mixed ligand formation constants of Ni(II) oxy acids (glycollic, lactic and malic acid) with thio acids (thioglycollic, thiolactic and thiomalic acid) and amino acids (glycine, α-alanine and aspartic acid) when used as secondary ligand. Structurally all ligands are alike; there is difference of only one atom among all groups of atoms, *i.e.*, O, S, N. Oxygen donor atom is common in all ligands. The order of coordinating tendencies of oxy, thio and amino acids is as follows:

$$\text{Oxyacids} \quad > \quad \text{Thio acids} \quad > \quad \text{Amino acids}$$

$$\bar{O}—\bar{O} \qquad\qquad S—\bar{O} \qquad\qquad N—\bar{O}$$
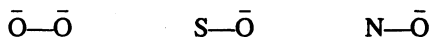
The proton ligand formation values of oxy acids are higher than amino acids and thio acids[18]. So the more electronegative oxygen atom is expected to form stable complex with metal ion. This explains that (M—O) bond is more stable than (M—N) due to presence of two negative charges in oxy acids than amino acids; a metal ion will experience more attraction with oxy acid anion as compared to amino acid anion. The charge transfer into continum orbitals of sulphur is more probable than charge transfer in the orbitals of oxygen. Sulphur has vacant d-orbitals which can be used for dπ-pπ bonding. These two factors are responsible for higher values of formation constants of thio acids[19] than amino acids.

REFERENCES

1. G.L. Eichhom, Inorganic Biochemsitry, Vol. 1 and 2, Elsevier, Amsterdam (1973)

2. H. Sigel, Metal Ions in Biological Systems, Vol 2, Marcell-Dekker, New York, p. 64 (1973).

3. S.E. Sherman and S. Lippard, *J. Chem. Rev.*, **87,** 1153 (1987).

4. E. James Huheey, Ellen A. Keiter and L.R. Keiter, Inorganic Chemistry, 4th Edn., Harper Collins College, New York, p. 708 (1993).

5. Vishnu Kolhe and K. Dwivedi, *J. Indian Chem. Soc.*, **73,** 265 (1996).

6. Suresh K. Agarwal and Manohar Lal, *Bulletin of Pure and Applied Chemistry*, **16,** 37 (1997).

7. Devdas Manwal and D. Shankaraiah, *J. Electrochem. Soc. India*, **47,** 59 (1998).

8. D. Banergea, Coordination Chemistry, Tata McGraw-Hill, New Delhi, p. 358 (1994).

9. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954); M.V. Chidambaram and P.K. Bhattacharya, *J. Inorg. Nucl. Chem.*, **32,** 3271 (1970).

10. A.I. Vogel, Text Book of Quantitative Inorganic Analysis, 4th Edn., Longman, London, p. 296 (1978).

11. H.A. Flaschka, *Mikrochim Acta*, **55,** 37 (1955).

12. F.J.C. Rossotti and H.S. Rossotti, *Acta Chem. Scand.*, **9,** 1166 (1955).

13. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 3397 (1953).

14. R.C. Mehrotra and S.N. Dubey, *J. Indian Chem. Soc.*, **43,** 881 (1970).

15. R. Griesser and H. Sigel, *Inorg. Chem.*, **9,** 1238 (1970).

16. G. Aderegg, *Helv. Chem. Acta,* **46,** 2397 (1963).

17. Condike C.F. and A.E. Martell, *J. Inorg. Nucl. Chem.* **31,** 2455 (1969); M.S. Mohan, D. Bancroft and E.H. Abott, *Inorg. Chem.*, **18,** 344 (1979); M.S. Mohan, *Indian J. Chem.*, **20A,** 252 (1981).

18. J.D. Joshi, *J. Indian Chem. Soc.*, **65,** 590 (1988).

19. G.K. Lopman, *J. Am. Chem. Soc.*, **90,** 223 (1968).