Studies on Binary and Ternary Metal Chelates II - Fe(III) and Al(III) Chelates with NTA and Coordinated amino acids

Suvendu Kumar Mazumdar[a] and Prakash Mohanty[b]

Department of Chemistry, Utkal University, Vani Vihar, BHUBANESWAR - 751 004
[b] Central Laboratory, Nalco, ANGUL

The proton ligand association constants of Trans-[Co(en)$_2$ Cl GlyH]$^{2+}$ and Trans-[Co(en)$_2$ Cl ß-AlaH]$^{2+}$ the mixed metal binuclear complexes of trivalent ions [Trans-[Co(en)$_2$ Cl Gly M]$^{4+}$ & Trans-[Co(en)$_2$ Cl ß-Ala M]$^{4+}$] and their mixed ligand complexes with NTA have been determined by pH titration method. Thermodynamic parameters of the complexation reaction are also presented.

We have reported the formation of various binuclear complexes with coordinated amino acids [1]. Recently Grace and Tregloan [2] studied the complexation reaction between $[Co(NH_3)_5OH_2]^{3+}$ and $HCrO_4^-$ spectrophotometrically. Very little attempt has yet been made to study the formation of mixed ligand complexes using NTA as primary ligand and coordinated amino acids as secondary ligand. Hence this Study.

EXPERIMENTAL

The two Co(III) complexes, [Trans-[Co(en)$_2$ Cl GlyH]$^{2+}$ and Trans-[Co(en)$_2$ Cl ß-AlaH]$^{2+}$], were prepared by the reported method [3] and characterised by elemental and spectral analysis. Stock solutions of Fe^{3+} and Al^{3+} were prepared using AR grade metal nitrate and standardised.

The following solutions were prepared and titrated pH-metrically against 0.1 M NaOH.

(i) Blank (0.004 M wrt HNO_3 and 0.1 M wrt $NaNO_3$)

(ii) Blank + 0.003 M Co(III) complex

(iii) Blank + 0.003 M Co(III) complex + 0.003 M M^{3+} (Fe^{3+} / Al^{3+})

(iv) Blank + 0.001 M NTA + 0.003 M M^{3+} (Fe^{3+} / Al^{3+})

(v) Blank + 0.003 M Co(III) complex + 0.001 M NTA + 0.003 M M^{3+} (Fe^{3+} / Al^{3+})

Titrations of solutions (i), (ii) and (iii) were used for the study of binary complex formation and titrations of (i), (ii), (iv) and (v) were considered for ternary complexation studies. Titrations were repeated at three temperatures in the range 20 - 45°C. Each titration was repeated twice to check reproducibility.

Toshniwal digital pH meter (Model CL-46) with combined electrode (Glass-Ag/AgCl) was standardised using NBS buffer and used to follow titrations. pH readings were converted to H^+ concentration. A suitable computer programme was developed to calculate the proton - ligand association constant and complex formation constant using Irving - Rossotti method [4].

© E.C.S.I. Bangalore

RESULTS

The acid dissociation equilibria of the N-protonated glycinato and alaninato complexes are given by equation 1 and 2 respectively.

$$\text{Trans-[Co(en)}_2\text{ Cl GlyH]}^{2+} \rightleftharpoons \text{Trans-[Co(en)}_2\text{ Cl Gly]}^{+} + H^{+} \quad \ldots (1)$$

$$\text{Trans-[Co(en)}_2\text{ Cl ß-AlaH]}^{2+} \rightleftharpoons \text{Trans-[Co(en)}_2\text{ Cl ß-Ala]}^{+} + H^{+} \quad \ldots (2)$$

The $\bar{n}_A$ [average number of protons bound per Co(III) complex by the amino function] were evaluated at various pH values from titration curves of solutions (i) and (ii) using the formula of Irving and Rossotti. The protonation constants were calculated and included in Table 1. The stability constants of the binuclear complexes - Trans-[Co(en)$_2$ Cl Gly M]$^{4+}$ and Trans-[Co(en)$_2$ Cl ß-Ala M]$^{4+}$ (where M = Fe^{3+} or Al^{3+}) - were calculated from titrations of solution (iii) by determining $\bar{n}$ and pL values at different pH. The stability constants of the mixed ligand complexes were calculated from titration of solution (iv) and (v) using the method of Dixit and Munshi [5].

It is worth noting that the stability of the 1:1 binuclear species of M^{3+} with Trans-[Co(en)$_2$ Cl GlyH]$^{2+}$ and Trans-[Co(en)$_2$ Cl ß-AlaH]$^{2+}$ follow the order $Fe^{3+} > Al^{3+}$. This can be explained on the basis of ionic potential (charge/radii). The same trend has been observed by Martell [6].

The proton ligand association constant (K_{11}) of the glycinato and alaninato complexes increased when temperature was increased from 20 to 45°C (Table1).

The chloro ß-alaninato complex is found to be less acidic than the chloroglycinato complex. (K_{11} of

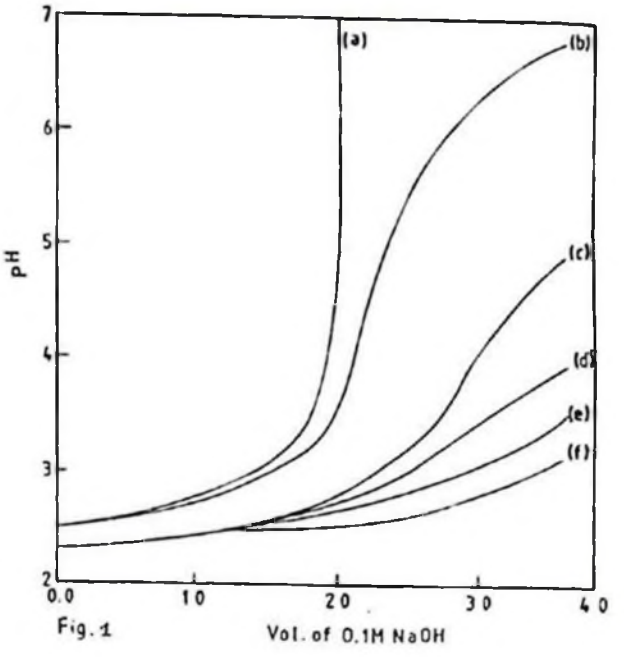


Fig. 1

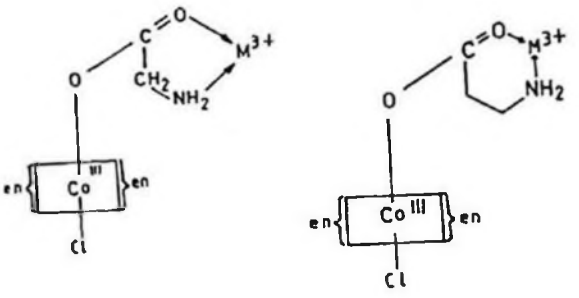
Fig 1 Titration curves of mixed ligand Complexes M^{3+}-NTA-[Co(NH$_3$)$_5$ ClglyH]$^{2+}$
I = 0.1 M ; T = 30±0.1°C
a. Blank (0.004 M wrt HNO_3 and 0.1 M wrt $NaNO_3$)
b. Blank + 0.003 M Co(III) complex
c. Blank + 0.001 M NTA + 0.003 M Al^{3+}
d. Blank + 0.001 M NTA + 0.003 M Fe^{3+}
e. Blank + 0.001 M NTA + 0.003 M Co(III) complex + 0.003 M Al^{3+}
f. Blank + 0.001 M NTA + 0.003 M Co(III) complex + 0.003 M Fe^{3+}

chloro alaninato complex > that of chloro glycinato copmlex). This is because the -NH_2 is on the ß-carbon atom in alaninato moity and gives rise to a six membered ring during chelation. In the case of glycinato group, only a five membered ring is formed. Favourable electrostatic repulsion effect of the protonated amine and cobalt(III) centre in glycinato complex also could be a cause of the higher acidity of this complex.

From the formation curve (Fig 1), it is revealed that the primary complex formation takes place at very low pH. The curves c & d (primary complex) and curves e & f (mixed ligand complex) overlap

each other at low pH values indicating that in this range (where the primary ligand combines with the metal ion) the secondary ligand does not get attached. The mixed ligand complex curves (e & f) separate from the primary complex [M(NTA)] curves (c & d) at pH 2.75 due to self dissociation of the secondary ligand [the Co (III) amino acid complex or co-ordinated amino acid]. After pH 3.0, the mixed ligand complex curve shows the indication of attachment of the secondary ligand with Fe^{3+} and Al^{3+}. Since the dissociation of $[Fe^{3+}(NTA)]$ and $[Al^{3+}(NTA)]$ does not take place in the range of dissociation of the secondary ligand, it can be considered that secondary ligand combines with $[Fe^{3+}(NTA)]$ or $[Al^{3+}(NTA)]$. The values of log K_{MAL}^{MA} and log K_{MA}^{M} are collected in the Table 1.

log K_{MAL}^{MA} and log K_{MA}^{M} where L = NTA and A = coordinated amino acid) values for the glycinato complex is found to be greater than that of the ß-alaninato complex. Such values are also explained on the basis of chelate ring formation. A six membered chelate is formed in the case of ß-alaninato complex while a five membered ring is formed in the case of glycinato complex (See the



structures).

The stability constants of the binary complexes of Fe^{3+} or Al^{3+} at any given temperature is found to be greater than that of the stability of the ternary

Table 1

log Stability Constants and Thermodynamic Parameters for Binary and Ternary Complex Formation Equilibria of Glycinato and ß-Alaninato Complex with Al^{3+} and Fe^{3+}

Species	log K±0.01 at			ΔH°, kJ.mol^{-1}	ΔS°j.K^{-1}.mol^{-1}
	20	30	45°C		
Trans[$Co(en)_2$.Cl.GlyH]$^{2+}$ (K_{II})	6.02	6.04	6.08	4.19±0.063	129.6±0.05
Trans[$Co(en)_2$.Cl.Gly Al]$^{4+}$	5.89	5.94	5.99	7.20±0.48	137.4±0.40
Trans[$Co(en)_2$.Cl.Gly Al(NTA)]	5.14	5.33	5.40	19.65±9.7	165.5±0.73
Trans[$Co(en)_2$.Cl.Gly Fe]$^{4+}$	6.26	6.30	6.34	5.72±0.80	139.4±0.05
Trans[$Co(en)_2$.Cl.Gly Fe(NTA)]	5.74	5.94	6.06	24.58±8.5	194.0±0.66
Trans[$Co(en)_2$.Cl.ß-AlaH]$^{2+}$(K_{II})	6.06	6.09	6.15	6.31±0.95	137.5±0.07
Trans[$Co(en)_2$.Cl.ß-Ala Al]$^{4+}$	5.78	5.82	5.97	12.66±4.6	153.8±0.35
Trans[$Co(en)_2$.Cl.ß-AlaAl(NTA)]	5.06	5.15	5.26	14.33±0.08	145.8±0.02
Trans[$Co(en)_2$.Cl.ß-Ala Fe]$^{4+}$	6.07	6.18	6.27	14.22±3	164.9±0.23
Trans[$Co(en)_2$.Cl.ß-Ala Fe(NTA)]	5.67	5.81	5.91	17.47±4.9	168.4±0.38

complex. This is expected in most of the cases. $\Delta\log K$ (=$\log K^{MA}_{MAL} - \log K^{M}_{ML}$) usually ranges from -0.5 to -0.8 for monodentate ligand and from -1 to -2 for bidentate ligand [7]. The values of the overall change in enthalpy (ΔH^{o}) and entropy (ΔS^{o}) for the binary and ternary complexation equilibria are also included in Table 1. These values indicate that the complexing ability of the half bonded glycine in trans-$[Co(en)_2 Cl Gly]^{+}$ is higher than that of ß-alanine in trans-$[Co(en)_2 Cl$ ß-ala$]^{+}$. Similar behaviour has been observed in the corresponding mono nuclear metal ligand chelate complex due to ring size effect.

REFERENCES

1. P.Mohanty, A.C.Dash and R.K.Nanda, *Indian J.Chem.*, **26A** (1987) 392; P.Mohanty, P.K.Panda and S.K.Mazumdar, *J.Electrochem. Soc. India*, **43** (1994) 81; P.Mohanty and S.K.Mazumdar, *J.Indian Chem. Soc.*, **72** (1995) 385; P.Mohanty and J.Dei, *J.Indian Chem. Soc.*, **73** (1996) 608

2. R.M.Grace and A.P.Tregloan, *Polyhedran*, **11** (1992) 2069

3. K.V.Nolan and A.A.Soudi, *J.Chem. Soc. Dalton Trans.*, **(1979)** 1419

4. H.Irving and H.S.Rossotti, *J.Chem. Soc.*, **(1954)** 2904

5. K.R.Dixit and K.N.Munshi, *J.Indian Chem. Soc.*, **57** (1980) 576

6. R.Delgado, Y.Sun, R.J.Motekaitis and A.E.Martel, *Inorg. Chem.*, **32** (1993) 3320

7. A.E.Martel and L.G.Sillen, (Eds.) *Stability Constants of Metal Ion Complexes* **The Chemical Society, London**, Special Publication nos 17 (1964) and 25 (1971)