

Studies on Binary and Ternary Metal Chelates. Ternary Iron(III), Aluminium(III) and Beryllium(II) Chelates with Nitrilotriacetic Acid and Coordinated Amino Acids

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Formation of various oxo- and hydroxo-bridged binuclear complexes of metal ions have been investigated¹ but measurement of formation constants of such binuclear species with two different metal ions has been rarely attempted. Cannon and Benjarvongkulchai² studied the complex formation of $[\text{Co}(\text{en})_2(\text{OH}_2)_2]^+$ with Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} and reported the formation constants of the respective hydroxo-bridge binuclear complexes. More recently Grace and Tregloan³ studied the complexation reaction between $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{3+}$ with HCrO_4^- spectrophotometrically. No 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 such a study was attempted.

Results and Discussion

Proton-ligand stability constants of secondary ligands : The values of \bar{n}_A at various pH-meter readings were calculated using equation (1) (vide Experimental) from acid and ligand titration curves for the secondary ligands (amino acidatocobalt(III) complexes). A graph is plotted between \bar{n}_A vs pH and proton-ligand stability constants were evaluated by (i) the method of interpolation at half \bar{n}_A values and (ii) by plotting $\log(\bar{n}_A/1-\bar{n}_A)$, $\log(\bar{n}_A-1/2-\bar{n}_A)$ vs pH for mono- and dibasic acids, whereby linear plots were obtained in each case intersecting the pH axis at $\text{p}K_a$ values. At $30.0 \pm 0.1^\circ$ and $I = 0.1 \text{ mol dm}^{-3}$, the mean $\log k_H^1$ (proton-ligand association constant) for coordinated glycinate, β -alaninate and histidinate were found to be 8.41 ± 0.04 , 9.28 ± 0.2 and 8.45 ± 0.05 . The mean $\log k_H^2$ for histidinato complex was found to be 6.47 ± 0.05 .

Metal-ligand stability constants : The formation constants have been obtained by plotting \bar{n} vs pL. The values of \bar{n} (the average number of ligand molecules attached per metal ion) were calculated using equation (2). pL (the free ligand exponent) has been calculated using equation (3) given by Irving and Rossotti⁴. For the determination of the stability constants of the mixed ligand complex the method of Dixit and Munsri⁵ was used. From the proton-ligand stability constant data it can be suggested that the acid strength decreases in the order (for the pentaammine com-

plexes) : glycinate > histidinato > β -alaninato. This is expected, shifting of the amino group to the β -carbon atom makes β -alaninatopentaammine complex a weaker acid than glycinate and histidinato complexes. From the titration curve (Fig. 1) it is revealed that a binuclear complex

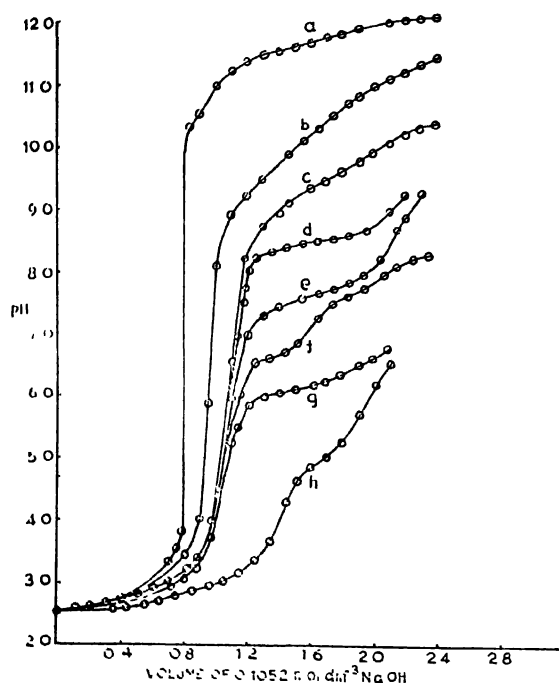


Fig 1 Titration curve for formation of binuclear complexes of $[\text{Co}(\text{NH}_3)_5 \beta\text{-alah}]^{3+}$ with different metals ions at $30 \pm 0.1^\circ$ and $I = 0.1 \text{ mol dm}^{-3}$ (a) $[\text{HClO}_4] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, (b) $[\text{HClO}_4] = 4 \times 10^{-3}$, $[\text{complex}] = 3 \times 10^{-3}$, $[\text{M}^{2+}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$, for c, d, e, f, g and h, M^{2+} is Mn, Co, Zn, Ni, Cu and Be

is formed between the Co^{III} substrate and the added metal ion. The formation of the 1 : 1 binuclear complex is supported by Job's curve. From the titration curve (Fig. 2) it is revealed that the primary complex formation (curve C) takes place at very low pH. The primary complex curve C and the mixed ligand complex curve D overlap each other at lower pH values indicating that in this range, where the

TABLE I—METAL LIGAND STABILITY CONSTANTS OF SOME DIVALENT AND TRIVALENT METAL IONS AND STABILITY OF MIXED LIGAND COMPLEXES OF Be^{II} , Al^{III} AND Fe^{III} *Temp. = $30.0 \pm 0.1^\circ$, $I = 0.1 \text{ mol dm}^{-3}$

Ligand		log K							
L ₁	L ₂	Mn ^{II}	Co ^{II}	Ni ^{II}	Cu ^{II}	Zn ^{II}	Be ^{II}	Al ^{III}	Fe ^{III}
$[\text{Co}(\text{NH}_3)_5\beta\text{-alaH}]^{3+}$		3.25	4.05	5.47	6.05	4.75	8.90	7.25	9.15
$[\text{Co}(\text{NH}_3)_5\text{HistH}_2]^{4+}$		3.21	3.90	4.50	5.70	4.01	7.60	6.94	8.75
$[\text{Co}(\text{NH}_3)_5\text{glyH}]^{3+}$		2.68	3.24	4.38	5.10	3.75	7.00	6.50	8.43
$[\text{Co}(\text{NH}_3)_5\beta\text{-alaH}]^{3+}$	NTA	—	—	—	—	—	5.55	6.75	7.63
$[\text{Co}(\text{NH}_3)_5\text{HistH}_2]^{4+}$	NTA	—	—	—	—	—	3.90	5.60	6.50
$[\text{Co}(\text{NH}_3)_5\text{glyH}]^{3+}$	NTA	—	—	—	—	—	4.21	6.05	6.90

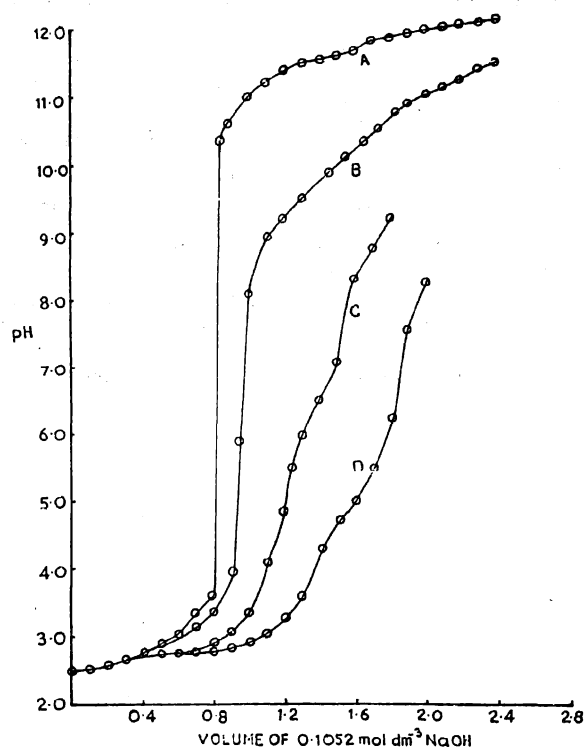
* Average deviation of log K values are ± 0.01 .

Fig. 2. Titration curve for Al^{III} -NTA- $[\text{Co}(\text{NH}_3)_5\beta\text{-alaH}]^{3+}$ mixed ligand complex at $30.0 \pm 0.1^\circ$ and $I = 0.1 \text{ mol dm}^{-3}$: (a) $[\text{HClO}_4] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, (b) $[\text{HClO}_4] = 4 \times 10^{-3}$, $[\text{complex}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$, (c) $[\text{HClO}_4] = 4 \times 10^{-3}$, $[\text{NTA}] = 1.0 \times 10^{-3}$ and $[\text{Al}^{\text{III}}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$, (d) $[\text{HClO}_4] = 4 \times 10^{-3}$, $[\text{NTA}] = 1.0 \times 10^{-3}$, $[\text{complex}] = 3 \times 10^{-3}$ and $[\text{Al}^{\text{III}}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$.

primary ligand combines with the metal ions, attachment of secondary ligand does not take place. The mixed ligand complex curve D separates from the primary complex curve C at pH 2.75 due to self-dissociation of secondary ligand. After pH 3.0, the mixed ligand complex curve shows the indication of attachment of secondary ligand with Al^{III} . Since the dissociation of $[\text{Al}(\text{NTA})]$ does not take place in the range of dissociation of the secondary ligand, it can be considered that secondary ligand combines

with $[\text{Al}^{\text{III}}(\text{NTA})]$. The values of $\log K_{\text{MAL}}^{\text{MA}}$ have been evaluated using the method of interpolation of half- \bar{n} values. The $\log K_{\text{M}}$ and $\log K_{\text{MAL}}^{\text{MA}}$ values (Table 1) show that for all the three histidinato, β -alaninato and glycina-topentaamminecobalt(III) complexes, the stability of the binuclear complexes follow the Irving-Williams order: $\text{Mn}^{\text{II}} < \text{Co}^{\text{II}} < \text{Ni}^{\text{II}} < \text{Cu}^{\text{II}} > \text{Zn}^{\text{II}}$. The stability of the binuclear complexes of tripositive Fe and Al ions are higher than that of divalent ions (except Be^{II}). This can be explained on the basis of high charge-to-radius ratio. The exceptionally high values of the stability constants of Be^{II} is also due to high charge-to-radius ratio ($6.408 \times 10^{-9} \text{ Cm}^{-1}$)⁶. For a given metal ion, the order of stability of the binuclear complex is β -alaninato $>$ histidinato $>$ glycinate. In case of β -alaninato complex, six-membered chelate ring is formed but in other cases five-membered rings are formed, and the same trend is also observed in the binuclear complexes containing M^{3+} ions. The stability constants of the mixed ligand complexes were found in the order: β -alaninato $>$ glycinate $>$ histidinato. The same explanation can also be offered for the above observation. The stability constants of glycinate and histidinato complexes are almost comparable (Table 1) as both of them form five-membered chelate rings.

Experimental

$[\text{Co}(\text{NH}_3)_5\text{glyH}](\text{ClO}_4)_3$, $[\text{Co}(\text{NH}_3)_5\beta\text{-alaH}](\text{ClO}_4)_3$ and $[\text{Co}(\text{NH}_3)_5\text{RH}_2](\text{ClO}_4)_4$ ($\text{RH}_2 = \text{histidine}$) were prepared by the reported method⁷ and characterised by spectral analysis, and cobalt⁸, carbon, hydrogen and nitrogen estimation. Solution of the metal ion perchlorates were prepared by the standard procedure. Free acid and metal ion contents were calculated by standard procedure⁹. Potentiometric measurements were made by an Elico LI 120 pH meter with glass silver-silver chloride electrode. The pH meter was standardised with NBS buffer. Electronic spectra were recorded on a JASCO 7800 spectrophotometer.

Procedure: The complexation equilibria was studied at $30.0 \pm 0.1^\circ$ with $[\text{N}_5\text{CoLH}]_1^{3+} = 3 \times 10^{-3} \text{ mol dm}^{-3}$ (where

LH = glycine or β -alanine) for histidinopentaammine complex, $[\text{complex}]_T = 2.6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ and $I = 0.1 \text{ mol dm}^{-3}$. During the experimental time, the aquation of cobalt(III)aminoacidato complexes is negligibly small. The values of \bar{n}_A were evaluated at various pH values from the titration curves for complex + HClO_4 and HClO_4 alone using equation (1),

$$\bar{n}_A = \left[Y T_L + \frac{(V' - V'')(N + E^0)}{(V^0 + V')} \right] / T_L \quad (1)$$

where, V' and V'' denote the volumes of alkali added to reach the same value of pH in the titration of acid and ligand (in case of ternary complex formation secondary ligand) respectively, Y is the number of displacable protons of the ligand, N the normality of alkali, E^0 the total initial strength of the acid and $T_L = [\text{ligand}]_T$. The value of \bar{n} was calculated by equation (2),

$$\bar{n} = \frac{(V''' - V'')(N + E^0)}{(V^0 + V') \bar{n}_A T_m} \quad (2)$$

where, $T_m = [M^{n+}]_T$. V''' and V'' are the volumes of alkali referring to the same pH for titration of M^{n+} + complex + HClO_4 and complex + HClO_4 mixture (Fig. 1). The free ligand exponent pL was calculated using equation (3) (for the non-ternary complex $(V^0 + V''')/V^0$ factor is unity),

$$pL = \log_{10} \frac{\sum_{n=0}^{n=j} \beta_n^H (1/\text{anti log } [\text{H}^+])^n}{(T_L - \bar{n} T_m)} \frac{(V^0 + V''')}{V^0} \quad (3)$$

For mixed ligand complex (Fig. 2), V''' and V'' are the difference in volume of alkali added between curve D and C, and B and A respectively, to attain the same pH. β_n^H is the overall practical proton ligand stability constant and V''' is the volume of alkali required for curve D at the same pH.

References

1. L. G. SILLEN, *Quart. Rev. Chem.*, 1959, **13**, 146; "Stability Constants of Metal Ion Complexes", Special Publication nos 17 (1964) and 19 (1971), eds A. E. MARTELL and L. G. SILLEN, Chemical Society, London.
2. R. D. CANNON and S. BENJARVONGKULCHAI, *J. Chem. Soc., Dalton Trans.*, 1981, 1924; R. D. CANNON and S. BENJARVONGKULCHAI, *J. Sci. Soc. Thailand*, 1982, **8**, 147.
3. R. M. GRACE and A. P. TREGLOAN, *Polyhedron*, 1992, **11**, 2069.
4. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
5. K. R. DIXIT and K. N. MUNSHI, *J. Indian Chem. Soc.*, 1980, **57**, 576.
6. F. A. COTTON and G. WILKINSON in "Advanced Inorganic Chemistry", 5th. ed., Wiley, New York, 1988, p. 1386
7. J. FUJITA, T. YASUI and Y. SHIMURA, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 654; C. J. HAWKINS and P. J. LAWSON, *Inorg. Chem.*, 1970, **9**, 6.
8. H. A. LAITINEN and L. M. BURDETT, *Anal. Chem.*, 1951, **23**, 1268.
9. A. C. DASH, *Inorg. Chem.*, 1983, **22**, 837.