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Equilibrium Studies on Some Heteroligand Hydroxo Complexes of Lanthanons with Iminodiacetic Acid and Citraconic or Maleic Acid

Rajiv Kumar, S. P. Tripathi, and **G. K. Chaturvedi***

Inorganic Chemical Laboratories, Agra College, Agra, India

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Mixed-ligand ternary complexes of La(III), Pr(III), Nd(III), Gd(III), and Dy(III) with iminodiacetic acid (*IMDA*) and citraconic (*CCA*) or maleic acid (*MIA*), have been studied *pH*-metrically. Their formation takes place through the stepwise addition of the secondary ligand (*IMDA*) to the initially formed 1:1, Ln(III)—*CCA*/*MIA* binary species. The resulting ternary complexes undergo hydrolysis to form their hydroxo derivatives simultaneously. The stability constants of the hydroxo species are calculated for constant temperature (27 ± 1 °C) and ionic strength ($I = 0.1\,M$ KNO_3). The relative order of stability is: La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III).

(Keywords: Hydrolysis of ternary complexes; pH-metric measurements; Stability constants of monohydroxy ternary complexes)

Gleichgewichtsuntersuchungen an einigen Heteroliganden-Hydroxo-Komplexen von Lanthanid-Ionen mit Iminodiessigsäure und Citracon- oder Maleinsäure

Es wurden ternäre Komplexe von La(III), Pr(III), Nd(III), Gd(III) und Dy(III) mit gemischten Liganden [Iminodiessigsäure (*IMDA*) und Citraconsäure (*CCA*) oder Maleinsäure (*MIA*)] mittels *pH*-metrischer Methoden untersucht. Diese Komplexe werden über die stufenweise Addition des Sekundärliganden (*IMDA*) zu den primär gebildeten 1:1 Ln(III)—*CCA*/*MIA* Spezies gebildet. Zugleich erleiden die resultierenden ternären Komplexe Hydrolyse und gehen in die entsprechenden Hydroxo-Komplexe über. Die Stabilitätskonstanten der Hydroxo-Komplexe wurden für konstante Temperatur (27 ± 1 °C) und Ionenstärke ($I = 0.1\,M$ KNO_3) berechnet. Die relative Reihung bezüglich der Stabilitäten ergab sich folgendermaßen: La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III).

Introduction

In earlier publications from this laboratory we have reported the formation of normal mixed-ligand complexes of lanthanons with multidentate chelones—*DTPA*[1], *CDTA*[2,3], *EDTA*[4], *HEDTA*[5], *NTA*[6] and some of the dicarboxylic acids—phthalic, malonic, citraconic, maleic acids, and with *IMDA*[7] and phthalic or malonic acid. In the present communication now we report the formation of 1 : 1 : 1, Ln(III)—*CCA*/*MIA*—*IMDA*-hydroxo ternary species formed by the stepwise addition of the secondary ligand *IMDA* to the initially formed 1 : 1, Ln(III)—*CCA*/*MIA* binary complex in a comparatively higher *pH*-range. The stability constants for such 1 : 1 : 1 hydroxo ternary species are given.

Experimental

All the chemicals used were of A.R., BDH/E. Merck grade. The solutions of metal nitrates were prepared and standardised as reported earlier[5]. Monopotassium iminodiacetate was prepared by dissolving the calculated amount of *IMDA* in the required volume of 0.1 *M* potassium hydroxide. Other solutions were prepared by the direct weighing method in double distilled water. The instruments used and experimental conditions were the same as reported earlier[1].

Results and Discussion

pH titration curves representing the titration of free metal ions, dicarboxylic acids (*CCA*/*MIA*), *KHIMDA* and those for 1 : 1, Ln(III)—*CCA*/*MIA* and for 1 : 1, Ln(III)—*IMDA* binary systems have already been discussed elsewhere[3, 6–8].

Curve f (Fig. 1), representing the 1 : 1 : 1, La(III)—*CCA*/*MIA*—*IMDA* system, almost overlaps the curve e (for 1 : 1, La(III)—*CCA*/*MIA*) upto $m \sim 2$ indicating the greater affinity of the dicarboxylic acids to the metal ion forming 1 : 1 binary species in the beginning. Another inflection at $m = 3$ and the lowering in *pH* between the buffer region of $m = 2$ to 3, may be attributed to the addition of the secondary ligand *IMDA* to the initially formed 1 : 1, La(III)—*CCA*/*MIA* species resulting in the formation of 1 : 1 : 1, La(III)—*CCA*/*MIA*—*IMDA* ternary complexes. The appearance of a solid phase at $m > 3$ and one more inflection at $m \sim 4.5$ may further be correlated with the disproportionation of the resulting ternary species into 1 : 2, La(III)—*IMDA*—hydroxo[7] and 1 : 3, La(III)—*CCA*/*MIA* binary complexes and the metal hydroxide.

A gradual increase in the values of stability constants for 1 : 1 : 1 ternary species indicates their hydrolysis before their complete formation, keeping the solution more acidic than it would have been in the absence of hydroxo species.

The stability constants of the ternary species formed by the stepwise addition of the ligands to the metal ion, without considering the

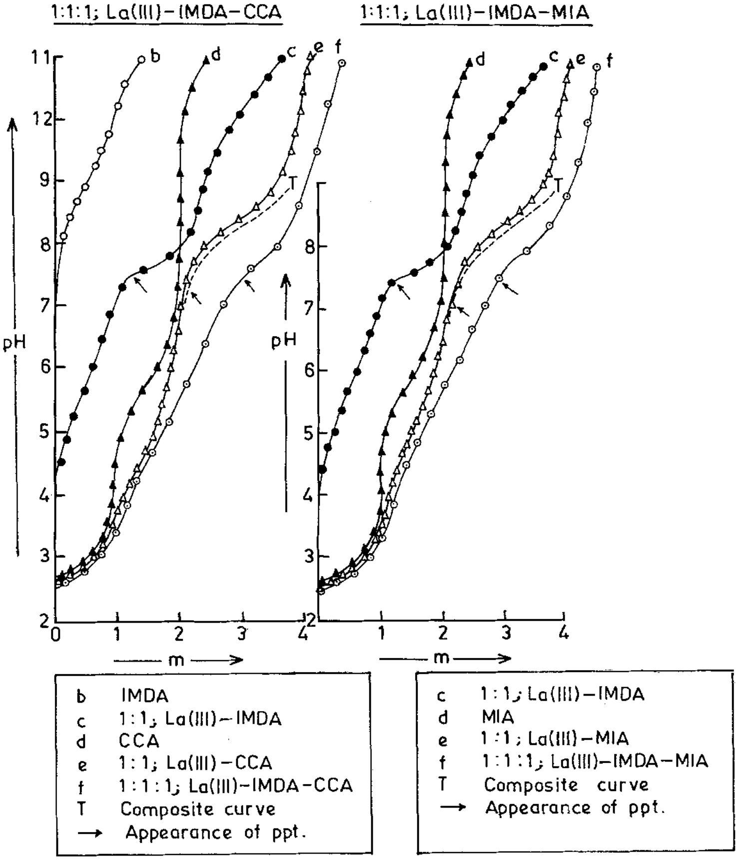

Fig. 1

formation of hydroxo species, were calculated by the method of *Thompson* and *Loraas*[9] and those for 1 : 1 : 1, Ln(III)—*CCA/MIA—IMDA*—hydroxo species by using the expressions shown below.

For the reaction equilibrium:

$$MA + B \rightleftharpoons MAB; \quad K = \frac{[MAB]}{[MA]\,[B]} \tag{1}$$

(The charges on various species are omitted here and hereafter for clarity's sake.) Using different pertinent material balance equations, K is calculated by following expressions[9]:

$$K = \frac{T_M - ([B] \cdot X)}{[B]^2 \cdot X} \tag{2}$$

where
$$[B] = \frac{T_M - aT_M - [\mathrm{H}] + [\mathrm{OH}]}{[\mathrm{H}]/K_1}$$
$$X = ([\mathrm{H}]/K_1) + 1$$

(T_M, a and K_1 are the total metal ion concentration, moles of base added per mole of monobasic ligand HB and its dissociation constant, respectively.)

The values of the stability constants of these 1 : 1 : 1 ternary species show a significant and gradual increase (simultaneous hydrolysis before their complete formation between $m = 2$ and 3).

Hence for the reaction:

$$MA + B + \mathrm{OH} \overset{2<m<3}{\rightleftharpoons} MAB(\mathrm{OH});\ K_{MAB(\mathrm{OH})} = \frac{[MAB(\mathrm{OH})]}{[MA]\,[B]\,[\mathrm{OH}]} \qquad (3)$$

Considering the existence of MA, MAB and MAB(OH) species in the equilibrium it follows:

$$T_M = [MA] + [MAB] + [MAB(\mathrm{OH})] \qquad (4)$$
$$T_B = [\mathrm{H}B] + [B] + [MAB] + [MAB(\mathrm{OH})] \qquad (5)$$

Since the calculations are done in the buffer region between $m = 2$ and 3 where the total moles of protons liberated due to the formation of both MAB and MAB(OH) species are neutralised by only one mole of alkali, as shown by the curve f (Fig. 1), it follows according to electroneutrality (mass and charge balance) principles:

$$aT_B + [\mathrm{H}] - [\mathrm{OH}] = [B] + 1/2\ \{[MAB] + 2\,[MAB(\mathrm{OH})]\} \qquad (6)$$

combining equations (4) and (5),

$$2\,T_M = [MA] + [\mathrm{H}B] + [B] + 2\,[MAB] + 2\,[MAB(\mathrm{OH})]\ (\therefore T_M = T_B)$$

or $\quad [MAB(\mathrm{OH})] = T_M - [MAB] - 1/2([MA] + [\mathrm{H}B] + [B])$.

Substituting this value of $[MAB(\mathrm{OH})]$ from above equation in eq. (6):

$$aT_B + [\mathrm{H}] - [\mathrm{OH}] = T_M + 1/2\,[B] - 1/2([MAB] + [\mathrm{H}B] + [MA])$$

or $T_M - aT_M - [\mathrm{H}] + [\mathrm{OH}] = 1/2([MAB] + [MA] + [\mathrm{H}B] - [B])$ (7)

Since $[B] = [MA]/X$ and $[MAB] = K \cdot [MA] \cdot [B]$ (from eqs. 1 and 2), putting these values of $[B]$ and $[MAB]$ in eq. (7), and introducing the ionisation constant of ligand HB, we get

$$T_M - aT_M - [\mathrm{H}] + [\mathrm{OH}] = 1/2\left\{([MA]^2 \cdot K/X) + MA\left(\frac{X}{Y} + 1\right)\right\}$$

Table 1. *Stability constants of the ternary species*

Metal ion	1 : 1 : 1, *Ln*(III)—*CCA*—*IMDA*		1 : 1 : 1, *Ln*(III)—*MIA*—*IMDA*	
	$\log K_{MAB}{}^{a}$	$\log K_{MAB(\mathrm{OH})}{}^{b}$	$\log K_{MAB}{}^{a}$	$\log K_{MAB(\mathrm{OH})}{}^{b}$
La(III)	5.25 ± 0.13	14.15 ± 0.13	5.11 ± 0.12	13.86 ± 0.11
Pr(III)	5.36 ± 0.12	14.35 ± 0.13	5.18 ± 0.14	14.06 ± 0.10
Nd(III)	5.40 ± 0.11	14.42 ± 0.14	5.24 ± 0.14	14.10 ± 0.08
Gd(III)	5.51 ± 0.12	14.65 ± 0.13	5.38 ± 0.14	14.36 ± 0.11
Dy(III)	5.61 ± 0.12	14.82 ± 0.12	5.48 ± 0.13	14.55 ± 0.13

[a, b] Average of the values calculated at $m = 2.2$ to 2.6 and 2.1 to 2.8, respectively.

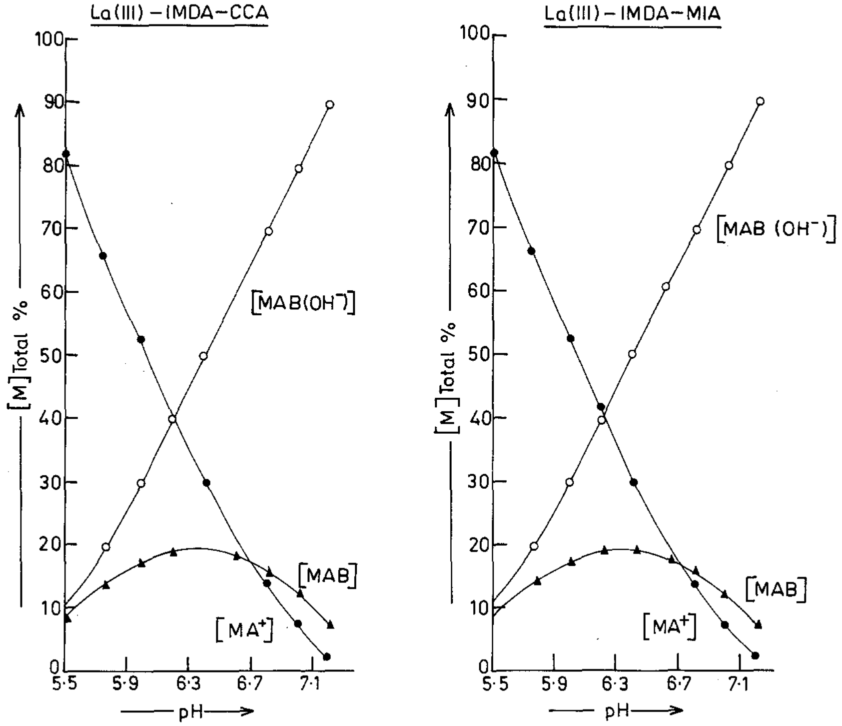

Fig. 2

or

$$[MA]^2(K/2X) + [MA]\,1/2(Y/X+1) - (T_M - aT_M - [\mathrm{H}] + [\mathrm{OH}]) = 0$$

or

$$[MA] = \frac{-b \pm \sqrt{(b)^2 + 4ac}}{2a} \tag{8}$$

where $a = K/2X$; $b = Y/X + 1$

$c = (T_M - aT_M - [\mathrm{H}] + [\mathrm{OH}])$ and $Y = ([\mathrm{H}]/K_1 - 1)$

For calculating $[MAB(\mathrm{OH})]$ from eq. (4) $[MA]$ and $[MAB]$ can be evaluated from eq. (8) and (1), respectively, and with the help of above equations $K_{MAB(\mathrm{OH})}$ can be evaluated from eq. (3).

The values of stability constants both for 1:1:1, *Ln*(III)—*CCA*/*MIA*—*IMDA* complexes and for their monohydroxo species are recorded in Table 1.

The dependence of different species MA^+, MAB and $MAB(\mathrm{OH})^-$ upon *pH* is shown in Fig. 2 where the percentage of total metal ion concentration T_M, distributed in different species, is plotted against *pH*. The analysis of these curves inferred that the concentration of hydroxo species i.e. $MAB(\mathrm{OH})^-$ predominates the equilibria and increases gradually. The short range for K_{MAB} (m = 2.2–2.6 only at 5 points out of 9) in comparison to that for $K_{MAB(\mathrm{OH})}$ (m = 2.1–2.8, at 8 points out of 9) indicates the predominating existence of $MAB(\mathrm{OH})$ in the equilibrium as is evidenced by more constant values of $K_{MAB(\mathrm{OH})}$ obtained than those of K_{MAB}.

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