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Formation of Mixed Ligand Complexes of Some Tripositive Rare Earth Ions

RASHMI VIMAL and RAM NAYAN*
Department of Chemistry
Hindu College, Moradabad-244 001, India

Quantitative complex equilibrium reactions of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} with *o*-aminophenol (HA) (and catechol (H_2B) involving the formation of binary complexes MA^{2+}, MA_2^{2+}, MA_3, MB^+, MB_2^-, MB_3^{3-} (where M = $La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}$, $Sm^{3+}$and Eu^{3+}) and the ternary complexes MAB, MA_2B^-, MB_2A^{2-} due to simultaneous coordination of A^- and B^{2-} with the metal ion, have been studied at 25°C and an ionic strength of 0.10 M KNO_3. The corresponding equilibrium constants calculated by the methods reported earlier by Nayan and Dey, have been discussed.

INTRODUCTION

In spite of the extremely rapid development of coordiantion chemistry, the equilibrium studies on nitrogen and oxygen donor molecules with the metal ions, specially the rare earths ions, involving the formation of mononuclear complex species have not reached yet maturity. In addition, these complexes have potential for further developments. Informations on the mononuclear species provide an important tool in the investigation of other complicated complex species including the mixed ligand complexes existing in solution.

Sufficient attention has not yet been paid on the formation of mixed ligand complexes of the rare earth ions. Most of the systems studied, reported in literature, involve coordination of polynucleating ligands, and the biologically important electron donor molecules with the metals in different steps[1, 2]. But, the reactions, where association of the two ligands with metal occurs in a single step, have been least studied.

Here, an attempt has been made to study the complexing properties of some rare earth ions, *e.g.*, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} using the pH-titration technique as described by Nayan and Dey[3, 4]. Simultaneous coordination of *o*-aminophenol (HA) and catechol (H_2B) with these metal ions in the formation of mixed ligand complexes containing two and three ligand molecule units, has been investigated at 25°C ($\mu = 0.10$ M KNO_3/NaCl)

EXPERIMENTAL

Standard solutions of 0.1786 N NaOH, 1.0 M KNO_3 and KCl, and 0.07856 N

HNO_3 and HCl were prepared using analytical grade reagents. Aqueous solution of Ce^{3+} ion was obtained by using its chloride salt (Johnson Matthey). La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} carbonates were precipitated from their chloride salts (Johnson Matthey). Excess of metal carbonate was treated with known amount of nitric acid and filtered. Metal content was determined in the filtrate (and Ce^{3+} ion in its solution) gravimetrically after precipitation as oxalate and subsequent ignitions to oxide. Aqueous solution of *o*-aminophenol was obtained by dissolving the ligand in one equivalent alkali which was neutralized before each titration. Solution of catechol was prepared by direct weighing and dissolving in distilled water.

The titration mixtures (ligand: 1:1, 1:2, 1:3, metal-ligand: 1:1:1, 1:1:2, 1:2:1, metal—pair of ligand mixtures) were prepared and titrated as described earlier[5] against sodium hydroxide solution (0.1786 N) using Systronic 335 pH-meter. Experiments of Ce^{3+} systems were carried out in chloride medium while those of the rest tripositive rare earths were performed in nitrate medium, keeping the ionic strength 0.1 M KNO_3/NaCl and temperature 25°C. The titration curves obtained from experimental data were analysed.

RESULTS AND DISCUSSION

Proton-ligand dissociation

Two protons are liberated in steps from the protonated amino group and the phenolic group, respectively, in *o*-aminophenol system. There is no sharp change in colour due to dissociation of protons from the ligand, However, a gradual colour change from brown to yellow and finally to yellowish green at higher pH values has been noted. The brown, yellow and the yellowish green colours may be expected due to existence of protonated, neutral and anionic ligands, respectively. The evaluated proton-ligand dissociation constants are

$$K_1^H = 10^{-4.17 \pm .05} \quad \text{and} \quad K_2^H = 10^{-10.51 \pm .01}$$

Existence of proton-ligand equilibria corresponding to dissociation of protons from the two phenolic groups of 1,2-dihydroxybenzene (catechol) is evident from the titration curve (Fig. 1). The dark reddish brown colour of neutral ligand molecule gradually turns into yellowish brown (at pH *ca.* 8.6), and subsequently the mixture appears light reddish brown beyond pH *ca.* 10.0. The proton-ligand dissociation constant for the two phenolic groups, $K_1^H = 10^{-9.38 \pm 0.5}$ and $K_2^H = 10^{-11.60 \pm 0.6}$ can be compared with those earlier reported by Martell *et al.*[6] and Singh[7].

Formation of binary complexes

The 1:1 metal-*o*-aminophenol mixtures remain turbid above pH *ca.* 6.8, 6.7, 6.6, 6.4, 6.3 and 6.2, respectively, in La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} systems. The titration curves (Fig. 1: La^{3+} system, others omitted) show weak inflections at *a* = 1.0 indicating formation of 1:1 metal-ligand species, MA^{2+}. The calculated log K_{1A} values are reported in Table-1. Formation of 1:2 metal-

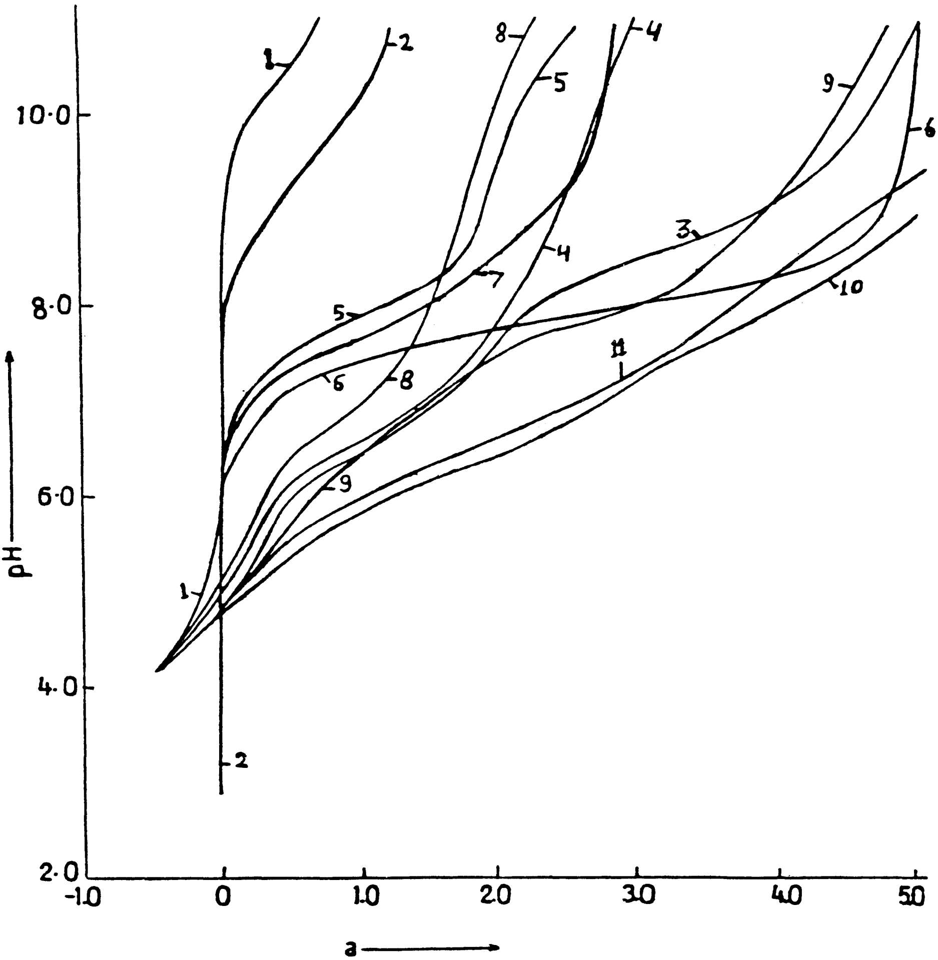

Fig. 1 pH *vs* *a* curves of La^{3+}-*o*-aminophenol (HA)-catechol (H_2B) complex systems, (1) HA, (2) H_2B, (3) La^{3+}-HA, (4) La^{3+}-2HA, (5) La^{3+}-3HA, (6) La^{3+}-H_2B, (7) La^{3+}-$2H_2B$, (8) La^{3+}-$3H_2B$ (ligand) = 5.0×10^{-4} M), (9) La^{3+}-HA-H_2B, (10) La^{3+}-2HA-H_2B, (11) La^{3+}-HA-$2H_2B$ (metal = 5.0×10^{-4} M).

ligand complexes is evident from the corresponding pH *vs* *a* curves (Fig. 1) which indicate weak inflections at $a = 1$. Equilibrium constants of complexes evaluated below pH of precipitation (pH *ca.* 6.9, 6.8, 6.6, 6.5, 6.4 and 6.2, respectively, for La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} systems) are not very close to K_{1A} values of the corresponding metal system. Also, the K_{1A} is greater than K_{2A} in each case. Like 1:1 and 1:2 metal-ligand systems, the pH *vs* *a* curves for their 1:3 ratio systems also show weak inflections. From the shape of these curves formation of MA_3 is inferred below $a = 1.0$. Equilibrium constant value is generally smaller than the corresponding K_{2A} value (Table-1). Precipitation of the reaction mixtures, like other aforesaid sytems, from pH *ca.* 6.9, 6.9, 6.7, 6.6, 6.4, 6.3, respectively, for La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} systems did not permit further analysis of the complex species existing over higher pH range.

1:1 metal-catechol mixtures of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} turn turbid at pH *ca.* 7.8, 7.6, 7.6, 7.5, 7.4, 7.3, respectively. Stability constant of the MB^+ (B^{2-} = ligand dianion) species calculated as usual are given in Table-1. 1:2 metal (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+})-ligand mixtures also turn turbid from pH *ca.* 8.3, 8.2, 8.1, 8.1, 8.0 and 7.8, respectively. K_{2B} calculated below these pH values are also very close to each other and follow almost a regular trend of increase in values with decrease of size of the metal ion. The pH *vs a* curves for 1:3 metal-ligand systems show steep inflections at $a = 2.0$ indicating the formation of MB_3^{3-} species below this *a* value without interference of the other species existing at higher *p*H range. Like other systems, the titration mixtures remain in turbid form beyond $a = 2.0$. The stability constant K_{3B} calculated below the pH of precipitation (*i.e.* below pH *ca.* 9.8, 9.7, 9.4, 9.4, 9.2 and 9.1, respectively, in La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} complex systems) are given in Table-1.

Comparing the values of equilibrium constants given in Table-1, it is concluded that oxygen donor, 1,2-dihydroxybenzene, behaves as stronger electron donor ligand than the nitrogen-oxygen mixed donor ligand, *o*-aminophenol.

Formation of mixed ligand complexes

Turbidity appears from pH *ca.* 6.5, 6.6, 6.6, 6.5, 6.5 and 6.5, respectively in 1:1:1 mixtures of metal (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+}) with *o*-aminophenol and catechol. However, a comparison of the titration curves (Ligand, 1:1, metal-ligand and the mixed ligand complex systems) indicate the formation of ternary complexes in solution below the pH of precipitation. Presence of strong and weak inflections at $a = 3.0$, in pH *vs. a* curves of all the systems also shows the formation of mixed ligand complexes. The equilibrium constants of these species are reported in Table-1. The values indicate that mixed ligand complex formation is appreciable in all the systems. For the reaction Cu(bipy) + L $\rightleftarrows$ Cu(bipy)L (where bipy = 2,2′-bipyridyl and L is the anion of salicylic acid, catechol or tiron) Martell *et at.*[8] reported higher values of the stepwise formation constants (from 0.9 to 1.5 logarithm units) than for the addition of L to the hydrated Cu^{2+} ion. Earlier findings on mixed ligand complexes of adenine, xanthine and hypoxanthine involving some tripositive rare earth ions (Y^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+})[5] and sulphosalicylic acid (ss), catechol, *o*-aminophenol, 1-amino-2-naphthol-4-sulphonic acid, 2-nitroso-1-naphthol (nn) with Th^{4+} and UO_2^{2+} (except Th^{4+}-sa-ss, Th^{4+}-ap-ca and UO_2^{2+}-sa-ss)[7] can also be compared with the results obtained by Martell *et al.* Present findings on the rare earth (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+}) complexes involving *o*-aminophenol-catechol ligand pair are mostly in agreement with those reported in previous publications.[5, 7, 8]

Formation of 1:1:2 and 1:2:1 metal-*o*-aminophenol-catechol complexes is evident from the corresponding titration curves. Analysis of the data could not be made at higher pH values (in all the systems) due to appearance of turbidity from pH *ca.* 6.2, 6.1, 6.1, 6.9, 6.1, 6.9 and 6.0, 6.1, 6.1, 6.0, 6.1, 5.9, respectively in 1:1:1 and 1:2:1 mixtures of tripositive rare earth ions (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+}) with *o*-aminophenol-catechol. The evaluated equilibrium constants for complexes existing in solution below pH of turbidity formation are given in Table-1.

TABLE-1

EQUILIBRIUM CONSTANT OF BINARY AND TERNARY COMPLEXES OF *o*-AMINOPHENOL (HA) AND CATECHOL (H_2B) (25°C, $\mu = 0.1$ M KNO_3)

Reaction	log K					
	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}
$M^{3+} + A^- \rightleftarrows MA^{2+}$	8.01 ± .14	8.17 ± .12	8.27 ± .10	8.41 ± .10	8.54 ± .12	8.64. ± .06
$MA^{2+} + A^- \rightleftarrows MA_2^+$	7.08 ± .08	7.36 ± .03	7.78 ± .07	8.07 ± .09	8.38 ± .06	8.58 ± .03
$MA_2^+ + A^- \rightleftarrows MA_3$	6.62 ± .14	7.07 ± .09	7.40 ± .21	7.66 ± .12	7.94 ± .11	8.28 ± .05
$M^{3+} + B^{2-} \rightleftarrows MB^+$	9.43 ± .30	10.02 ± .18	10.34 ± .11	10.92 ± .14	11.14 ± .02	11.52 ± .25
$MB^+ + B^{2-} \rightleftarrows MB_2^-$	7.81 ± .55	8.06 ± .08	8.42 ± .06	9.06 ± .41	10.37 ± .27	10.86 ± .08
$MB_2^- + B_2^{2-} \rightleftarrows MB_3^{3-}$	7.60 ± .05	7.66 ± .10	7.82 ± .01	7.92 ± .42	8.79 ± .23	8.99 ± .03
$M^{3+} + A^- + B^{2-} \rightleftarrows MAB$	18.95 ± .56	19.42 ± .23	20.03 ± .26	20.14 ± .25	20.28 ± .50	20.68 ± .14
$MA^{2+} + B^{2-} \rightleftarrows MAB$	10.94	11.25	11.76	11.73	11.74	12.04
$MB^+ + A^- \rightleftarrows MAB$	9.52	9.40	9.69	9.22	9.14	9.16
$M^{3+} + 2A^- + B^{2-} \rightleftarrows MA_2B^-$	26.79 ± .87	27.30 ± .76	28.62 ± .88	29.16 ± .69	28.87 ± .74	29.85 ± .47
$M^{3+} + 2B^{2-} + A^- \rightleftarrows MB_2A^{2-}$	32.78 ± .72	31.97 ± .05	33.19 ± .65	33.95 ± .94	34.05 ± .47	35.10 ± .42
$MA_2^+ + B^{2-} \rightleftarrows MA_2B^-$	11.70	11.77	12.57	12.68	11.95	12.63
$MB_2^- + A^- \rightleftarrows MB_2A^{2-}$	15.54	13.89	14.43	13.97	12.54	12.72
$MA^{2+} + 2B^- \rightleftarrows MAB_2^{2-}$	24.77	23.80	24.92	25.54	25.51	26.46
$MB^+ + 2A^- \rightleftarrows MBA_2$	17.36	17.28	18.28	18.24	17.73	18.33
$MAB + A^- \rightleftarrows MA_2B^-$	7.84	7.88	8.59	9.02	8.59	9.17
$MAB + B^{2-} \rightleftarrows MAB_2^{2-}$	13.83	12.55	13.16	13.81	13.77	14.42

The results indicate that the formation constant of mixed ligand complexes for addition of ligands A^- to MB_2^- or B^{2-} to MA_2^+ are greater than the constants for the addition of these ligands, separately, to corresponding aque-metal ion, probably due to electrostatic interaction between the ligands, as high values of equilibrium constants observed by Perrin *et al.*[9] in the reactions Ni^{2+}-(serine)$_2^+$ ethylenediamine $\rightleftarrows$ Ni^{2+}-(serine)$_2$ -ethylenediamine and Ni^{2+}-(serine)$_2$ + histamine $\rightleftarrows$ Ni^{2+}-(serine)$_2$-histamine. The values are also in agreement with those earlier reported from these laboratories[5] on mixed ligand complexes of Y^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} involving three molecules of ligand pairs, adenine-xanthine, xanthine-hypoxanthine and adenine-hypoxanthine. Similar informations have also been furnished in the interaction of A^- , nitroso R salt (nn), 5-sulpho salicylic acid (ss^{3-}), salicylic acid dianion (sa^{2-}) with ThA $(nn)^{2+}$, ThA $(sa)^+$, ThA (ss), ThB (nn^+); ThB $(ss)^-$, ThB (sa) respectively. But a reverse trend is followed on coordination of sa^{2-}, ss^{3-}, serine, histamine; ethylenediamine, ethylenediamine with ThA $(sa)^+$, ThA (ss), Ni^{2+}-(ethylenediamine)$_2$ Ni^{2+}-(histamine)$_2$, Ni^{2+}-(ethylenediamine)$_2$, Ni^{2+}-(histamine)$_2$ respectively.

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