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Complexes of Ga(III) with Thiomalic, Thiolactic, Thioglycollic, Malic Glycollic, Lactic & Aspartic Acids, & α-Alanine & Glycine

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Stepwise formation constants have been evaluated using Irving-Rossotti *p*H-titration technique of some gallium (III) complexes with thiomalic, thiolactic, thioglycollic, malic, glycollic, lactic, aspartic acids and α-alanine and glycine. The log *K* values have been computed by alternative methods. The complexes of mercapto compounds are more stable as compared to hydroxy or amino compounds. Stoichiometry of the various complexes have also been discussed.

IN continuation of our earlier work on In(III)[1] and Ga(III)[2] complexes of the title acids we report in this paper the proton ligand formation constants of thiomalic acid (TMA), thiolactic acid (TLA), thioglycollic acid (TGA), malic acid (MA), glycollic acid (GA), lactic acid (LA), aspartic acid (AA), α-alanine (AL) and glycine (GL) and the stepwise stability constants of their chelates with Ga(III) employing Irving and Rossotti[3] titration technique.

Materials and Methods

A stock solution of $Ga(NO_3)_3.8H_2O$ (Fluka) was prepared in a calculated quantity of $HClO_4$ to prevent hydrolysis. The metal content was estimated by titration with EDTA[4]. For stoichiometric experiments, freshly prepared $Ga(NO_3)_3.8H_2O$ solution was prepared without adding any acid. Extrapure ligands were used for preparing the stock solutions, viz 0·02*M* of TGA (E. Merck), TLA (Schuchardt, München), TMA (Schuchardt, München), LA, (Riedel), and GA (Riedel); 0·05*M* of MA (E. Merck); 0·015*M* of AA (BDH) and 0·025*M* AL (BDH) and GL (E. Merck) in doubly distilled water. These were standardized potentiometrically, GA and AL were standardized by adding an equal amount of solution of formaldehyde (35%) to the aqueous solution. All reagents used were 99·9% pure except TGA which was found to be only 80% pure. Suitable volume of this solution was added to maintain the desired [TGA]. Carbonate-free NaOH (AR) solution was prepared. Stock solution of $NaClO_4$ (neutral) and $HClO_4$ (AR grade) were prepared in doubly distilled water.

Expanded *p*H-meter (accuracy ±0·02 *p*H units) of (Electronics Corporation of India) with glass-calomel electrode assembly (Cambridge type GHSN 23) was used. The calomel electrode was connected externally by means of an agar-agar bridge saturated with KNO_3 to prevent the formation of chloro complexes. The *p*H-meter was calibrated with suitable buffers. Thermostat (U-10 model, Germany) was used to maintain the constant temperatures (±0·1°C accuracy). Measurements were carried out at 25°, 35°, 45° ±0·1° under nitrogen atmosphere.

Results and Discussion

Three mixtures were prepared as follows: (A) $2{\cdot}0\times10^{-2}M$ $HClO_4$, (B) $2{\cdot}0\times10^{-2}M$ $HClO_4$ $+5{\cdot}0\times10^{-3}M$ ligand and (C) $2{\cdot}0\times10^{-2}M$ $HClO^{-4}+5{\cdot}0\times10^{-3}M$ ligand $+1{\cdot}0\times10^{-3}M$ metal solution. In each case an appropriate amount of $NaClO_4$ was added to maintain $\mu = 0{\cdot}2M$ and total volume of mixtures was made 100 ml, and titrated against standard NaOH (1·004*M*). The proton ligand and metal ligand stability constants were determined from the formation curves using methods (i) Interpolation at half $\bar{n}_A(\bar{n})$ values, (ii) Interpolation at various $\bar{n}_A(\bar{n})$ values and (iii) least squares method. As all the complexes are formed in short range of *p*H, to avoid the overlap of stepwise complexes, the value by method (ii) were calculated in narrow range of $\bar{n}$ values.

Stoichiometry — For studying the stoichiometry, following four mixtures were titrated against NaOH (1·152*M*): (A) $5{\cdot}0\times10^{-3}M$ ligand; (B) $5{\cdot}0\times10^{-3}M$ ligand $+5{\cdot}0\times10^{-3}M$ metal solution, (C) $5{\cdot}0\times10^{-3}M$ ligand $+2{\cdot}5\times10^{-3}M$ metal solution and (D) $5{\cdot}0\times10^{-3}M$ ligand $+1{\cdot}66\times10^{-3}M$ metal solution.

In the case of TLA and TGA, the appearance of an inflection at $m\approx1{\cdot}0$ (m = moles of NaOH/mole ligand after the addition of 1 mole of base per mole of ligand) corresponded to the complete neutralization of single carboxyl hydrogen and the equilibrium may be represented as:

$$H_2TLA+OH^-\rightleftharpoons HTLA^-+H_2O \qquad ...(1)$$

This also indicated that second proton is not titrable under experimental conditions. Thus only two species H_2TLA and $HTLA^-$ exist in *p*H range corresponding to the value of m from 0 to 1. Addition of equimolar concentration of Ga(III) ions, greatly altered the shape of free ligand titration curve due to complex formation which was followed by hydrolysis. The large decrease in *p*H value of ligand titration and lowered buffer region between

$m = 0$ and 2 clearly showed the displacement of proton from -SH group due to complexation. When the ratio of Ga(III)-TLA (or TGA) was 1:2, an inflection at $m \approx 2$ was obtained indicating the formation of $Ga(TLA)_2^-$. The reaction equilibria may be expressed by Eq. (2)

$$Ga^{3+} + 2H_2TLA + 4OH^- \rightleftharpoons Ga(TLA)_2^- + 4H_2O \quad ...(2)$$

However, titration could not be continued because of immediate precipitation at pH ~4·5. When the ratio of Ga(III)-TLA was 1:3 the curve showed only one inflection at $m \approx 2$ indicating the formation of $Ga(TLA)_3^{3-}$. The overall reaction equilibrium may be represented by Eq. (3)

$$Ga^{3+} + 3H_2TLA + 6OH^- \rightleftharpoons Ga(TLA)_3^{3-} + 6H_2O \quad ...(3)$$

TGA-Ga(III) system also exhibited a similar behaviour and showed the formation of 1:1, 1:2 and 1:3 complexes.

In the case of TMA only one inflection was obtained, after the addition of two moles of base per mole of ligand, which corresponds to the complete neutralization of two carboxyl hydrogens in a single step. Third proton (SH) of TMA was not titrable under experimental conditions. When the ratio of Ga(III)-TMA was kept 1:1, considerable decrease in the initial pH value and a lower buffer region between $m = 0$ and 3 is observed indicating the displacement of proton due to complexation; no inflection, however was obtained before the precipitation of Ga(III) complex. In 1:2 ratio the inflection at $m \approx 3$ indicated the formation of $Ga(TMA)_2^{3-}$. The reaction equilibrium may be represented by an equation similar to Eq. (3).

The formation of only two complexes was confirmed by an inflection at $m \approx 2{\cdot}66$ when Ga(III)-TMA were taken in 1:3 ratio. In the case of MA and AA, the appearance of only one inflection after the addition of two moles of base per mole of ligand corresponded to complete neutralization of two carboxyl hydrogens. As all the three complexes are formed below pH 6·0, only lower region is considered for discussion. In the ratio 1:1 of Ga(III)-MA in lower region, the complex formation is followed by slow hydrolysis of complex. The equilibria involved are:

$$Ga^{3+} + H_3MA + 2OH^- \rightleftharpoons Ga(HMA)^+ + 2H_2O \quad ...(4)$$

$$Ga(HMA)^+ + H_2O \rightleftharpoons Ga(HMA)(OH) + H^+ \quad ...(5)$$

When the ratio of Ga(III)-MA was kept as 1:2 and 1:3 an inflection at $m = 2$ was observed, showing the formation of $Ga(HMA)^+$ and $Ga(HMA)_3^{3-}$ respectively. This showed that no proton was liberated during complexation from the -OH of MA and NH_3^+ (protonated form of $-NH_2$) of AA. In the case of LA and GA, though there was a fall in the pH value showing the displacement of proton due to complexation, no inflection was observed before the precipitation took place for all the ratios. Hence, it may be concluded that no proton was liberated during complexation from —OH of GA or LA. In all the ratios precipitation took place at pH 4·5.

Proton-ligand stability constants — The formation curves were extended from 0 to 1 for GA, LA, GL and AL whereas for AA, MA, TLA and TGA the curves were extended from 0 to 2 and in the case of TMA from 0 to 3, in the $\bar{n}_A$ scale. The values of $\log K_1^H$, $\log K_2^H$ and $\log K_3^H$ as obtained by interpolation at various $\bar{n}_A$ values have been summarized in Table 1.

Table 1 — Stepwise Proton-Ligand Stability Constants of the Ligands at Various Temperatures ($\mu = 0{\cdot}2M$)

Constant*	Values at 25°	35°	45°
	TMA		
$\log K_1^H$	10·31	10·28	9·98
$\log K_2^H$	4·51	4·44	4·44
$\log K_3^H$	2·96	2·98	3·00
	TGA		
$\log K_1^H$	10·05	9·85	9·79
$\log K_2^H$	3·45	3·46	3·47
	TLA		
$\log K_1^H$	10·38	10·29	10·24
$\log K_2^H$	3·56	3·64	3·68
	MA		
$\log K_1^H$	4·72	4·72	4·71
$\log K_2^H$	3·16	3·14	3·13
	AA		
$\log K_1^H$	3·77	3·68	3·60
$\log K_2^H$	1·90	1·88	1·86
	GA		
$\log K^H$	3·30	3·34	3·49
	LA		
$\log K^H$	3·54	3·48	3·48
	AL		
$\log K^H$	2·43	2·45	2·45
	GL		
$\log K^H$	2·37	2·40	2·43

*Uncertainty limit ± 0·05

Metal-ligand stability constants — In all the cases (except TMA) the formation curves are extended from $\bar{n} = 0$ to $\bar{n} \approx 2{\cdot}6$. Typical plots between $\bar{n}$ and pL for Ga(III)-TLA system at 25°, 35° and 45° are shown in Fig. 1. The existence of three step equilibria is thus indicated. In Fig. 1, the formation curve rises sharply and flattens at $\bar{n} = 1{\cdot}5$-$1{\cdot}8$ which then again rises in all the cases, and goes to $\bar{n} = 2{\cdot}6$ and then again it remains constant. This second sharp rise and the extension of $\bar{n}$ values beyond 2·5 is a clear indication of the formation of the

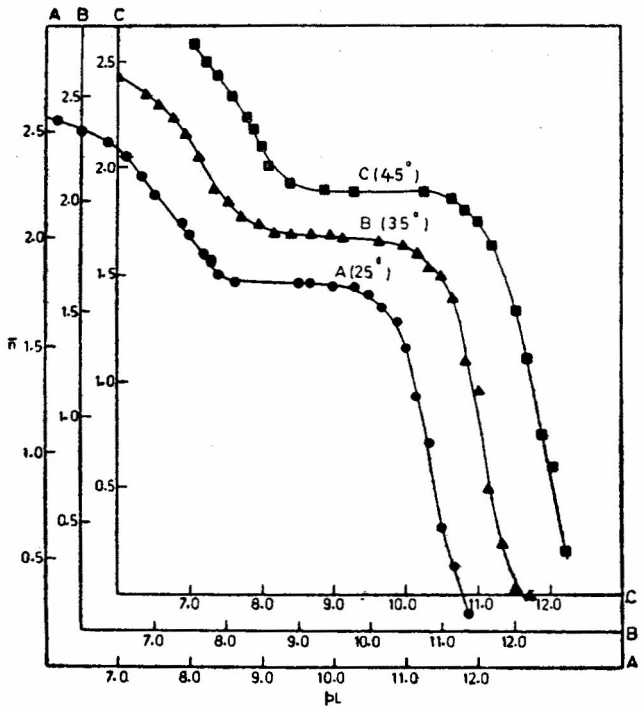

Fig. 1 — Formation curves of Ga(III)-TLA complex at $\mu = 0{\cdot}2M$

third complex which was further confirmed by stoichiometric experiment described earlier in this paper. The formation of first and second complexes in most of the cases have been found to occur in a narrow range of *p*H. The K_1 and K_2 values were also calculated by interpolation at various $\bar{n}$ values taking into account only those values where the overlapping of two complexes appeared to be negligible. In case of GA and LA, the metal curve did not become parallel with ligand curve after the formation of three complexes indicating the liberation of extra protons due to hydrolysis of metal ion. Precipitation in both the cases was observed at *p*H 4·5. Hence only portions of titrations curves in lower *p*H region were used for calculations. In the case of TMA the formation curves were extended from $\bar{n} = 0$ to 2. The existence of two step equilibria is thus indicated. In the case of AL and GL the $\bar{n}$ value rises abruptly from the very beginning and, therefore, metal-ligand stability constants could not be calculated. The values obtained by interpolation at various $\bar{n}$ values are given in Table 2.

The complexes of mercapto analogues show higher stability as compared to those of hydroxy and amino analogues. The complexes of hydroxy analogue of succinic acid are more stable than that of propionic and acetic acids. From experimental data it is clear that Ga(III)-thiomalate complexes are much more stable than malate and aspartate complexes. This can be attributed to the fact that —SH group in thiomalic acid undergoes complex formation whereas protons are not liberated from —OH of malic and —NH_2 (present in protonated form) of aspartic acid and also due to the fact that thiomalic acid acts as tridentate ligand whereas malic and aspartic acids act only as bidentate ligands. Comparison of stability constants of the thiomalate complex with those of corresponding analogues of acetic and propionic acids show large differences (approximately 2·0 log units in K_1 values). This difference is too large to be attributed solely to the inductive effect of an additional carboxylate ion in either a five or six membered bidentate. Hence it is reasonable

TABLE 2 — STEPWISE METAL-LIGAND STABILITY CONSTANTS OF Ga(III) COMPLEXES AT VARIOUS TEMPERATURES ($\mu = 0{\cdot}2M$)

Constant	Values at 25°	35°	45°
	Ga(III)-TMA		
log K_1^a	13·08	13·70	14·41
log K_2^b	7·52	8·02	8·52
log β	20·60	21·72	22·93
	Ga(III)-TGA		
log K_1^a	11·75	11·52	11·48
log K_2^b	11·08	10·86	10·74
log K_3^c	7·18	7·38	7·48
log β	30·01	29·76	29·70
	Ga(III)-TLA		
log K_1^a	11·60	11·80	12·02
log K_2^b	10·99	11·20	11·48
log K_3^c	6·47	6·95	7·25
log β	29·06	29·95	30·75
	Ga(III)-MA		
log K_1^a	5·87	5·93	6·19
log K_2^b	4·07	4·23	4·36
log K_3^c	3·04	2·96	2·96
log β	12·98	13·12	13·51
	Ga(III)-GA		
log K_1^a	3·39	3·42	3·45
log K_2^b	3·14	3·17	3·20
log K_3^c	2·67	2·85	2·98
log β	9·20	9·44	9·63
	Ga(III)-LA		
log K_1^a	3·28	3·41	3·51
log K_2^b	3·09	3·15	3·26
log K_3^c	2·92	2·94	2·97
log β	9·29	9·50	9·74
	Ga(III)-AA		
log K_1^a	3·28	3·41	3·55
log K_2^b	2·90	3·03	3·23
log K_3^c	2·84	2·98	3·03
log β	9·02	9·42	9·81

a = ±0·08, *b* = ±0·15, c = ±0·20.

to assume that thiomalic acid acts as tridentate ligand.

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