Thermochemical Studies on the Formation of Azide Complexes of Gallium(III) and Indium(III)

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The stabilities and enthalpies of the complexes formed by gallium(III) and indium(III) with azide ion have been determined in an aqueous sodium perchlorate medium of unit ionic strength at 25.0 °C. The stability constants have been determined potentiometrically and the enthalpy changes calorimetrically. In the azide system of gallium(III) only the formation of the first complex could be studied while for the indium(III) azide system studies of four successive steps are possible.

So far, thermochemical studies on the formation of the azide complexes of trivalent ions of the electron configuration d^{10} have not been attempted, except for Tl^{3+} ion, while such data are already available for the corresponding divalent ions,[1–3] *viz.* Zn^{2+}, Cd^{2+} and Hg^{2+}. In this study, among the d^{10} acceptors of group III B Ga^{3+} and In^{3+} are investigated. It is of interest to see how the thermodynamic functions change for divalent and trivalent ions of the same electron configuration.

The equilibrium and enthalpy measurements on the azide systems of gallium(III) and indium(III) show some experimental difficulties. Both acceptors hydrolyze extensively in aqueous medium. In order to suppress the hydrolysis the solutions have thus to be highly acidic.[4] The greater part of the azide will therefore be present as hydrazoic acid which very easily forms explosive corrosion products with various metallic parts of the instrument. Especially in the calorimetric studies, even minute amounts of these corrosion products may cause violent explosions.

All measurements refer to 25.0 °C and a sodium perchlorate medium of unit ionic strength.

EXPERIMENTAL

Chemicals. Gallium(III) perchlorate and indium (III) perchlorate were prepared by dissolving Ga_2O_3 (Fluka, *puriss. C*) and In_2O_3 (Fluka, *purum*) respectively, in perchloric acid (Merck, *p.a.*) and recrystallizing once from an acidic aqueous solution.
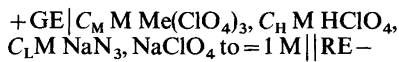
Analyses for Ga(III) and In(III) were made gravimetrically by precipitating the oxides.[5] The free acid concentrations in the stock solutions were determined potentiometrically and/or by passing aliquots through columns of Dowex-50 W cation exchange resin in the hydrogen ion form and titrating the eluate with standard sodium hydroxide solutions. Both methods gave the same results.

Sodium azide and sodium perchlorate were prepared and analyzed as described before.[6] The Ag, AgCl electrodes were prepared according to Brown.[7]
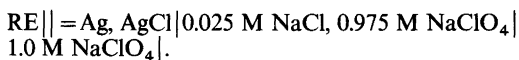
Apparatus. A Metrohm E 580 ion activity meter equipped with a Metrohm EA 109 glass electrode was used for the equilibrium measurements. The slope of the glass electrode was checked repeatedly and found to be 59.2 ± 0.2 mV. The titration calorimeter used was described previously.[8,9]

Procedure. The procedures used in the equilibrium measurements have been described before.[10,11] These measurements were arranged as titrations at constant metal ions and acid concentrations, C_M and C_H, respectively.

The emfs of the following cell were measured:

$+ GE \,|\, C_M$ M $Me(ClO_4)_3, C_H$ M $HClO_4,$
C_L M $NaN_3, NaClO_4$ to $= 1$ M $||$ RE $-$

where

RE $|| =$ Ag, AgCl $|$ 0.025 M NaCl, 0.975 M $NaClO_4|$
1.0 M $NaClO_4|$.

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Here, Me denotes gallium or indium. Each titration was repeated at least four times. Stable emfs were reached in a few minutes. The reproducibility was generally within ±0.4 mV, and even better for the indium(III) azide system.

The technique of the calorimetric studies has been described elsewhere.[10,12] The measurements were carried out as a series of titrations of a solution T into a solution S. Usually the solution S contained the metal ion and T the ligand. In order to reach higher ligand concentrations, however, some titrations were performed where the central ion was added to a ligand solution. The case of indium(III) azide system is a good example. This procedure was not possible for the gallium(III) azide system because of the extensive hydrolysis of gallium(III).

The heats of dilution were determined by similar measurements where either the ligand or the central ion solution had been exchanged for a sodium perchlorate solution of the same ionic strength.

MEASUREMENTS AND RESULTS

Gallium(III) azide. The potentiometric titrations were performed with three different values of C_M, *i.e.* 40, 60 and 80 mM. The acid concentrations, constant during the titrations, were 293, 339 and 386 mM, respectively. A free ligand ion concentration up to $\simeq 3$ mM could be reached in the measurements. Higher concentrations are not possible as most of the ligand is present as undissociated species HN_3.

In this concentration range, only the first mononuclear complex is formed and its formation constant could thus be determined. There is no indication of the formation of other azide complexes beyond the first step. However, hydrolysis of Ga(III) is observed.

In the gaphical calculation of the constant[13] the X_1 *vs.* [L] plot turns out to decrease for increasing values of [L]. From these measurements, only the first formation constant can therefore be calculated. To do this, the free ligand concentration [L] and the average ligand number $\bar{n}$ must first be calculated. Thus, it is necessary to know the ionization constant of hydrazoic acid under the same conditions. This has previously been determined[6] as $K_a = 3.61 \times 10^{-5}$ M. Hence, [L] and $\bar{n}$ can be calculated in the usual way. If only the first complex is formed then eqn. (1) can be written.

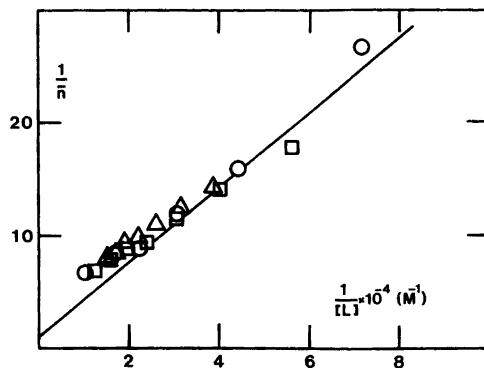$$\frac{1}{\bar{n}} = \frac{1}{\beta_1 [L]} + 1 \qquad (1)$$

Fig. 1. The determination β_1 for $Ga(Na_3)^{2+}$ [see eqn. (1)]. $\bigcirc$, $C_M = 40$ mM, $C_H = 293$ mM; $\square$, $C_M = 60$ mM, $C_H = 339$ mM; $\triangle$, $C_M = 80$ mM, $C_H = 386$ mM.

A plot of $1/\bar{n}$ *vs.* $1/[L]$ should therefore give a straight line with intercept 1 and a slope of $1/\beta_1$, Fig. 1. A value of $(3 \pm 1) \times 10^3$ M^{-1} for β_1 could thus be estimated. The errors given correspond to estimated errors from the graphical calculation.

Three different values of C_M, *i.e.* 10, 20 and 30 mM, were chosen in the calorimetric measurements. A ligand solution of $C_L = 500$ mM was added. The initial acid concentrations in the metal ion solutions were 43, 100 and 100 mM, respectively. Proton as well as gallium(III) complexes are formed in the calorimetric titrations.

Large exothermic heats are first measured during the titrations. When a certain ligand concentration is reached, however, an abrupt change to large endothermic heats is observed. A white precipitate is finally formed, probably due to hydrolytic reactions.[4] Such side reactions are so extensive that even after a few points in the titrations their influences on the measured heats can be seen. The calorimetric titrations were interrupted at these points.

From the calorimetric data, the value of ΔH_1° can be evaluated. The value of ΔH° of the HN_3 formation must then be known. In an earlier investigation[6] $\Delta H^\circ = -12.76$ kJ mol^{-1} has been found.

Using the value of β_1 found potentiometrically and the values of K ($K = 1/K_a$) and ΔH° for the formation of HN_3, a value of ΔH_1° for $Ga(N_3)^{2+}$ can be estimated by the least squares computer program "Letagrop Kalle".[14] A good fit of the calorimetric data is, however, not possible with $\beta_1 = 3 \times 10^3$ M^{-1}. On the other hand, values of β_1 varying between 10^3 and 10^5 M^{-1} do not give a

Table 1. The overall formation constants and the values of ΔG_j°, ΔH_j° and ΔS_j° for the consecutive steps of the gallium(III) and indium(III) azide systems at 25.0 °C and $I = 1$ M. The errors given correspond to confidence limits on the 99.9 % level of significance or to estimated errors.

System	j	β_j (M^{-j})	$-\Delta G_j^\circ$ (kJ mol^{-1})	$-\Delta H_j$ (kJ mol^{-1})	ΔS_j° (J mol^{-1} K^{-1})
Ga(III) $-$ N$_3^-$	1	$(3 \pm 1) \times 10^3$	20 ± 1	23 ± 6	-10 ± 20
In(III) $-$ N$_3^-$	1	$(1.54 \pm 0.05) \times 10^3$	18.2 ± 0.1	7.4 ± 0.3	36 ± 1
	2	$(4.1 \pm 0.1) \times 10^5$	13.9 ± 0.1	4.0 ± 0.8	33 ± 3
	3	$(1.8 \pm 0.1) \times 10^7$	9.4 ± 0.2	10 ± 1	-2 ± 5
	4	$(2.9 \pm 0.3) \times 10^8$	6.9 ± 0.3	9 ± 2	-6 ± 8

much better fit with the enthalpy data. Some of the results of these calculations are given below:

β_1 (M^{-1})	SIG Y(see Ref. 14)	U (Ref. 14)	$-\Delta H_1^\circ$ (kJ mol^{-1})
1×10^3	0.543	6.78	29.7 ± 4.1
3×10^3	0.454	4.84	22.9 ± 1.8
4×10^3	0.428	4.27	21.8 ± 1.4
5×10^3	0.403	3.74	21.1 ± 1.2
1×10^4	0.320	2.36	19.3 ± 0.7
1×10^5	0.329	2.49	15.7 ± 0.3

The errors given are one standard deviations. As seen, the increasing values of β_1 seem to give a somewhat better fit. However, such large values of β_1 are not computible with the potentiometric data.

Since the estimate of the potentiometric data is much more reliable this has been accepted for the value of β_1. Thus, a value of -23 ± 6 k.J. mol^{-1} can be found for ΔH_1°, Table 1.

Indium(III) azide. In the potentiometric measurements four different values of C_M have been chosen for this system. Higher ion concentrations could be used without hydrolysis occurring. For $C_M = 40$ mM, values of C_H 108 and 150 mM, for $C_M = 80$ mM 116 and 159 mM were chosen. In the other two series, the values of C_M were 120 and 160 mM, with the values of C_H 274 and 318 mM, respectively. A free ligand ion concentration of $\simeq 90$ mM could be reached. The formation function is independent of C_M and C_H, in spite of the fairly large variation of both C_M and C_H during the measure-
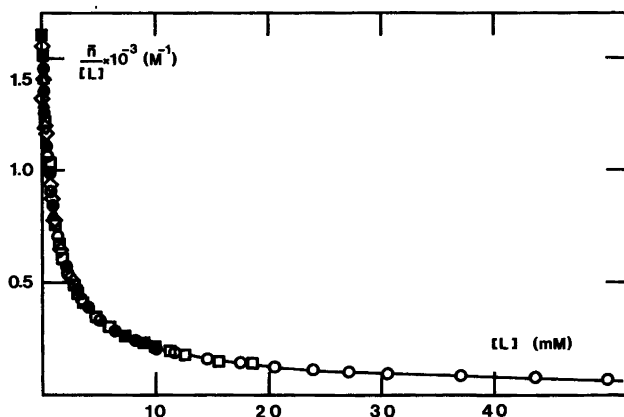

Fig. 2. $\bar{n}/[\mathrm{L}]$ as a function of $[\mathrm{L}]$ for the indium(III) azide system. Only half of the experimental points, chosen at random, have been plotted. $\bigcirc$, $C_M = 40$ mM, $C_H = 108$ mM; $\bullet$, $C_M = 40$ mM, $C_H = 150$ mM; $\square$, $C_M = 80$ mM, $C_H = 116$ mM; $\blacksquare$, $C_M = 80$ mM, $C_H = 159$ mM; $\triangle$, $C_M = 120$ mM, $C_H = 274$ mM; $\blacktriangle$, $C_M = 160$ mM, $C_H = 318$ mM.
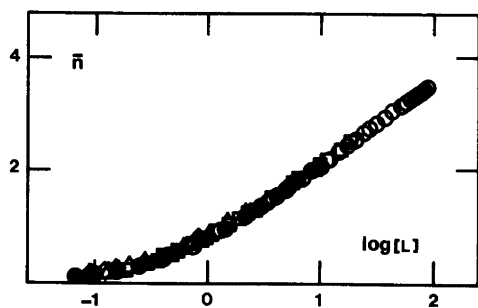
Fig. 3. The complex formation function of the indium(III) azide system. For symbols refer to Fig. 2 ([L] in mM).

ments, which proves that neither polynuclear nor acid complexes are formed, Figs. 2 and 3.

The constants have been evaluated both graphically[13] and numerically.[15] The methods gave concordant values. Four mononuclear complexes are formed in the range studied, Table 1.

In the calorimetric study, ten titration series were performed. In four of these a ligand solution, of $C_L = 500$ mM, was added to 90.0 ml of indium(III) perchlorate solutions with different values of C_M and C_H. The initial indium(III) concentrations were 10, 20 and 40 mM. For $C_M = 10$ and 20 mM a value of $C_H = 20$ mM was used while for $C_M = 40$ mM values of $C_H = 40$ and 92 mM were applied. In the other series, an indium solution, of $C_M = 100$ mM and $C_H = 100$ mM, was added to both buffered and unbuffered sodium azide solutions.

However, due to precipitation of the hydroxide an unbuffered sodium azide solution could not be used in the measurements. Free ligand ion concentrations > 100 mM were reached in the calorimetric titrations.

The enthalpy changes have been calculated by the computer program "Letagrop Kalle"[14] with the values of β_j found in the potentiometric study and the values of K and $\Delta H°$ for the formation of HN_3, determined earlier,[6] as fixed parameters.

The free energy changes $\Delta G_j°$ are calculated from the stepwise formation constants K_j and by combining these with the enthalpy changes $\Delta H_j°$ the entropy changes $\Delta S_j°$ are finally obtained. The results of this investigation are collected in Table 1.

DISCUSSION

The complex GaN_3^{2+} is slightly more stable than InN_3^{2+} though the error of β_1 (GaN_3^{2+}) is so large

that a reliable comparison is not really possible. The formation of GaN_3^{2+} is much more exothermic than that of InN_3^{2+}. The entropy change is not large as to be expected for a typically hard acceptor.[16] On the contrary, the values of $\Delta H_1°$ and $\Delta S_1°$ of the gallium(III) azide system give the impression that the interaction has indeed a soft character. Probably the nature of the ligand may play an important role in this connexion. The stability of GaN_3^{2+} is greatly determined by enthalpy change.

Much the same values of the enthalpy changes are found for the successive steps in the azide system of indium(III), except for the second step which has a slightly less exothermic value.

Probably, bonds of nearly the same character are formed. For the first and second steps almost the same values of $\Delta S°$ are obtained. The same is also valid for the third and fourth steps. In this respect, a parallelism can be seen with the corresponding azide complexes of $Cd(II)^3$. For the first and second steps, the contributions of the enthalpy and the entropy changes to the decrease of free energy are much the same, while for the last two steps the driving force is evidently the enthalpy decrease, Table 1.

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