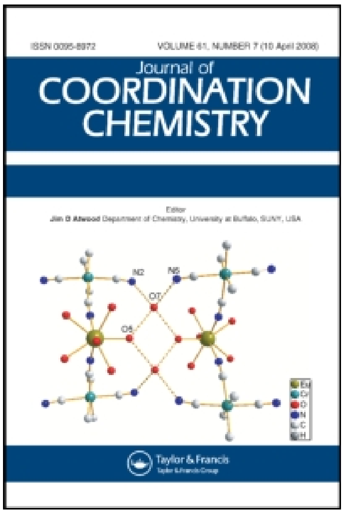

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FORMATION OF NITRITE COMPLEXES OF GALLIUM(III) AND INDIUM(III) IN AQUEOUS SOLUTION

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Stepwise complex formation between gallium(III), indium(III) and nitrite ions has been studied potentiometrically by means of a glass electrode in an aqueous sodium perchlorate medium of unit ionic strength at 25.0°C. In both systems only mononuclear complexes of moderate stability were formed over the range of concentrations used. No evidence has been found for the formation of polynuclear and/or acid complexes. Values of the overall constants for the formation of $Ga(NO_2)^{2+}$, $In(NO_2)^{2+}$, $In(NO_2)_2^+$ and $In(NO_2)_3$ are $130 \pm 40\,M^{-1}$, $390 \pm 110\,M^{-1}$, $(1.04 \pm 0.29)10^4\,M^{-2}$, and $(8 \pm 5)10^4\,M^{-3}$, respectively.

Keywords: Gallium(III), indium(III), nitrite, complexes, stability constants

INTRODUCTION

Studies of the formation of metal nitrite complexes in aqueous solution with Fe(III), Ni(II), Zn(II), Cd(II) and Hg(II)[1,2] have been extended to Ga(III) and In(III). The tervalent group IIIB acceptors have a similar outer electron shell configuration as the divalent zinc group, *viz* d^{10}, but considerably different charge/radius ratio. Thus, it would be of interest to examine the effect of this ratio on the stabilities of complexes formed with the same ligand.

In the course of systematic studies of the stepwise formation of nitrite complexes in aqueous solution, knowledge of formation constants proved useful. In nitrite complexes, metal ions display selective affinities for different donor atoms as they have a choice between N and O atoms. Therefore, *nitro* and/or *nitrito* complexes can be formed. The electronic structure of the acceptor has a dominant influence on the mode of bonding.

Among numerous techniques for the determination of formation constants, electromotive force measurements are most used. Potentiometric titrations can be applied to a central ion-ligand system if a workable electrode is available. Here, the free ligand ion concentation [L] has been determined *via* pH measurements in metal perchlorate solutions containing nitrite–nitrous acid buffers.[1,2]

EXPERIMENTAL

Chemicals

The preparation, purification and standardization of gallium(III) perchlorate, indium(III) perchlorate, sodium perchlorate and sodium nitrite was carried out as

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described previously.[1,2,3] Amounts of free perchloric acid present in stock solutions were determined potentiometrically. The Ag/AgCl electrodes were also prepared as reported elsewhere.[1,2,3]

Measurements

Measurements at $I = 1.0$ M and 25.0°C were arranged as titrations at constant metal ion and acid concentrations, C_M and C_H, respectively. Equal volumes of solutions T_1 and T_2 were added from piston burettes to V_0 cm^3 of solution S. These solutions had the composition given below.

$S: C_M$ M $Me(ClO_4)_3$, C_H M $HClO_4$, (1.0–$6C_M$) M $NaClO_4$
T_1 : 1.00 M $NaNO_2$
T_2 : $2C_M$ M $Me(ClO_4)_3$, $2C_H$ M $HClO_4$, (1.0–$12C_M$) M $NaClO_4$

By mixing the solutions practically all the free acid will be converted into HNO_2. Apart from complex formation $I = 1$ M is maintained.

The emf of the following cell was measured,

$$\ominus\,\text{Ag/AgCl}\left|\begin{array}{l}0.025\ \text{M NaCl}\\ \\ 0.975\ \text{M NaClO}_4\end{array}\right|\ 1.0\ \text{M NaClO}_4\ \left|\begin{array}{l}C_M\ \text{M Me(ClO}_4)_3\\ C_H\ \text{M HClO}_4\\ C_L\ \text{M NaNO}_2\\ \text{NaClO}_4\ \text{to}\ I = 1\text{M}\end{array}\right|\text{glass electrode}\ \oplus$$

where Me denotes Ga(III) or In(III). The solutions in the right-hand half-cell were obtained by adding increasing but equal volumes of solutions T_1 and T_2 to a known volume of solution S.

A Metrohm E 580 ion-activity meter equipped with a Metrohm EA 109 glass electrode has been used for measurements. The slope of the glass electrode has been checked repeatedly and found to be 59.2 ± 0.2 mV. A magnetic stirrer was used for mixing. Every titration was repeated at least four times and reproducible readings were obtained.

In the calculation of the constants, the acidity constant of HNO_2 under the prevailing condition is necessary. This has been determined earlier[1] and was found to be $K_a = (1.03 + 0.06) \times 10^{-3}$ M. Both graphical and numerical methods were applied. For the numerical calculations, the program UNINUX has been used.[1,2,4] In the graphical calculation, the free ligand concentration [L] and the ligand number $\bar{n}$ were obtained from (*1*) and (*2*), respectively.

$$[\text{L}] = K_a(C_H - h)/h \qquad (1)$$

$$\bar{n} = (C_L - C_H + h - [\text{L}])/C_M \qquad (2)$$

The free hydrogen ion concentration h can be measured according to equation (*3*),

$$E_H = E_H^\circ + E_j + 59.16 \log h \qquad (3)$$

where E_H° is the cell constant, and E_j the liquid junction potential. Once corresponding values of $\bar{n}$ and [L] are obtained the function (*4*)

$$X = 1 + \sum_{i=1}^{N} \beta_i [L]^i \tag{4}$$

can be evaluated from a graphical integration of $\bar{n}/[L]$ *vs* [L] plot. The overall constants are then found by plotting the functions $X_i = (X_{i-1} - \beta_{i-1})/[L]$ *vs* [L], where $1 \leqslant i \leqslant N$; $X_0 = X$; $\beta_0 = 1$.

If only the first complex is formed, as in the case of the Ga(III) – NO_2^- system, (5) is found.

$$1/\bar{n} = 1/(\beta_1[L]) + 1 \tag{5}$$

A plot of $1/\bar{n}$ *vs* 1/[L] should thus give a straight line with intercept 1 and slope $1/\beta_1$, thus permiting the evaluation of β_1.

RESULTS AND DISCUSSION

Gallium(III)-nitrite system

Titrations were performed with five different values of C_M varying from 4 to 81 mM. In order to avoid the initial hydrolysis of Ga(III), the acid concentrations were kept high. Ratios of C_H/C_M were varied between 5 and 7. A free ligand ion concentration up to $\simeq$10 mM has been reached in the measurements. Series of measurements were performed at different values of total concentrations of acid and metal, in order to ensure that complex formation is indeed independent of $[H^+]$ and C_M. It may thus be concluded not only that no acid complexes exist but also that complex formation is strictly mononuclear.

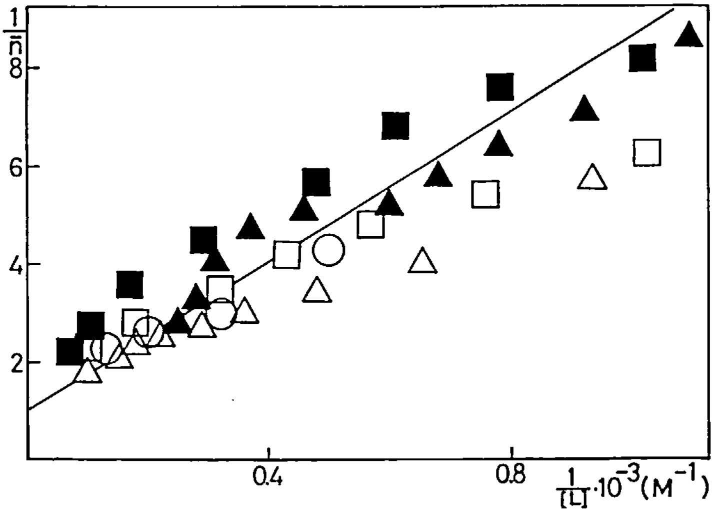

FIGURE 1 The determination of β_1 for the $GaNO_2^{2+}$ complex (see eq. (5)). (○) $C_M = 4.379$ mM, $C_H = 31.52$ mM; (□) $C_M = 8.582$ mM, $C_H = 53.25$ mM; (■) $C_M = 8.758$ mM, $C_H = 62.49$ mM; (△) $C_M = 59.03$ mM, $C_H = 344.5$ mM; (▲) $C_M = 80.76$ mM, $C_H = 376.8$ mM.

The stability of $GaNO_2^{2+}$ complex is such that this system can be characterized by a single formation constant β_1. The $1/\bar{n}$ *vs* $1/[L]$ plot is shown in Figure 1. As is seen, the experimental points do show some scatter but no systematic deviation could be observed. The uncertainties in the emf values became larger at high ligand concentrations. This is probably due to the changes in activity coefficients caused by the progressive exchange of ClO_4^- for NO_2^-. A value of $130 \pm 40\,M^{-1}$ for β_1 could be estimated. The error given corresponds to the estimated error from the graphical calculation. It must be remembered that the errors are rather large when weak complexes are determined by measurement of [L]. It seems that the first mononuclear complex formation between gallium(III) and NO_2^- is the only reaction which need be considered.

Indium(III)-nitrite system

For this system six different titration series were used. The values of C_M were varied from 3 to 21 mM, while C_H was varied from 10 to 74 mM. A free ligand ion concentration up to ≃250 mM was reached in the titrations. For the six series measured, the $\bar{n}/[L]$ *vs* [L] plot is seen to be independent of both C_M and C_H within experimental errors (Fig. 2), which proves that neither polynuclear nor acid complexes are formed.

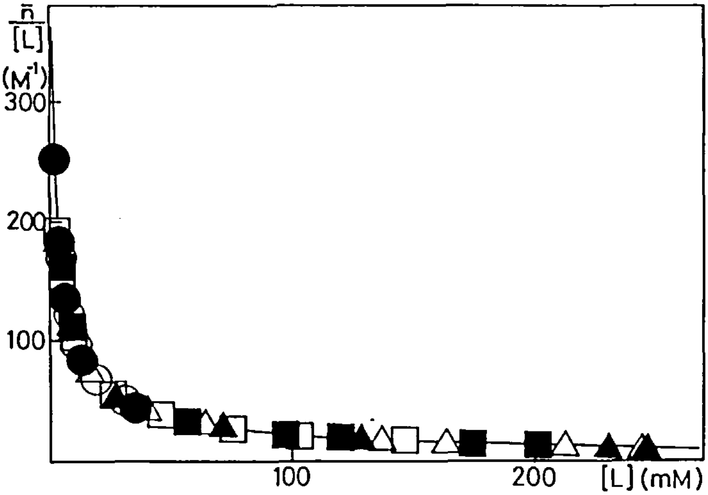

FIGURE 2 The ratio $\bar{n}/[L]$ as a function of [L] for the indium(III)-nitrite system. (○) C_M = 2.880 mM, C_H = 10.33 mM; (●) C_M = 5.600 mM, C_H = 9.374 mM; (□) C_M = 5.600 mM, C_H = 28.34 mM; (■) C_M = 8.570 mM, C_H = 27.33 mM; (△) C_M = 14.21 mM, C_H = 52.53 mM; (▲) C_M = 21.34 mm, C_H = 73.56 mM.

The formation constants have been evaluated both graphically and numerically. The methods gave concordant estimates. These calculations show the formation of three mononuclear complexes, with Table 1 giving appropriate values. If the logarithms of the first formation constants of complexes formed by divalent and tervalent acceptors of d^{10} configuration with the ligands NO_2^- and N_3^- are drawn as a function of atomic numbers, a fairly regular trend can be observed. The position of Hg^{2+} is particularly interesting due to the very soft character of the mercury(II) ion.

The high stability of mercury(II) complexes with ligands containing C, N, S, Se, and P donors is due to the formation of strong metal-ligand covalent bonds. The trends in logβ_1 for the complexes d^{10} with most of the ligands are fairly regular. It can be seen that for the azide, F^-, Cl^-, SCN^- and many other complexes of the d^{10} tervalent acceptors of group IIIB, the values of logβ_1 fall on an almost straight line.[5] This general pattern of behaviour permits an estimate of an approximate value of β_1 for any member in the group for a given complex. If therefore this trend holds for NO_2^- complexes as well, it is possible to estimate the value of β_1 for $TlNO_2^{2+}$. By interpolation, a value of log$\beta_1 \simeq 3.5$ for the complex $TlNO_2^{2+}$ was found. This value is valid at 25°C and $I = 1$ M. Both Ga^{3+} and In^{3+} are fairly hard acceptors as is obvious from the stabilities of their complexes with hard donors, while Tl^{3+} is a very soft acceptor.[5,6]

TABLE I

Overall formation constants and values of ΔG_i° for the consecutive steps of the Ga(III)- and In(III)-nitrite systems at 25.0°C and $I = 1.0$ M; errors given correspond to confidence limits at the 99.9% level of significance (in the case of In(III)) or to estimated errors.

System	i	β_i (M^{-i})	$-\Delta G_i^\circ$ (kJ mol^{-1})
Ga(III)-nitrite	1	130 ± 40	12.1 ± 0.8
In(III)-nitrite	1	390 ± 110	14.79 ± 0.70
	2	$(1.04 \pm 0.29) \times 10^4$	8.14 ± 0.99
	3	$(8 \pm 5) \times 10^4$	5.1 ± 1.7

The nitrite anion functions as an ambidentate ligand. It can bind either *via* N or O. As they are fairly hard acceptors, one might expect that Ga^{3+} and In^{3+} would prefer coordination *via* O atoms. On the other hand, the soft Tl^{3+} ion would prefer the softer N atoms.

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