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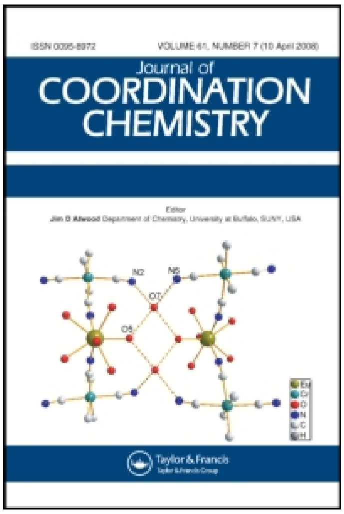

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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The Affinity of Gallium(III) and Indium(III) for Nitrogen Donor Ligands

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To cite this Article Duma, T. Walter , Marsicano, Fabrizio and Hancock, Robert D.(1991) 'The Affinity of Gallium(III) and Indium(III) for Nitrogen Donor Ligands', Journal of Coordination Chemistry, 23: 1, 221 — 232
To link to this Article: DOI: 10.1080/00958979109408253
URL: http://dx.doi.org/10.1080/00958979109408253

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J. Coord. Chem. 1991, Vol. 23, pp. 221–232
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THE AFFINITY OF GALLIUM(III) AND INDIUM(III) FOR NITROGEN DONOR LIGANDS

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(Received July 11, 1990)

Dedicated to Professor Arthur Martell on the occasion of his seventy fifth birthday.

The complexes of In(III) and Ga(III) with a variety of nitrogen donor ligands were studied in aqueous solution by glass electrode potentiometry at 25°C in 0.1 M $NaNO_3$. The ligands were 2-aminomethylpyridine (AMPY), ethylenediamine (EN), *N,N,N′,N′*-tetrakis(2-hydroxypropyl)ethylenediamine (THPED), and *N,N*-bis(2-hydroxyethyl)glycine (BICIN). A variety of mixed ligand complexes of the MLOH type were detected with many of the above ligands as L. The $\log K_1$ values obtained were with Ga(III) 8.40 (AMPY), 7.94 (THPED) 12.72 (EN), and In(III) 7.6 (AMPY), 8.20 (THPED), and 7.06 (BICIN). These formation constants are discussed in relation to previous predictions that In(III) and Ga(III) would have a substantial chemistry with nitrogen donor ligands. Of particular interest is the Ga(III) system with EN, where a very stable $Ga(EN)^{3+}$ complex is formed, but no higher complexes except for hydrolyzed species such as $Ga(EN)OH^{2+}$ and $Ga(EN)(OH)_2{}^+$.

Keywords: Gallium(III), indium(III), amines, stability constants

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INTRODUCTION

The solution chemistry of gallium(III) and indium(III) has over the last few years become of greater interest with the use[1] of these metal ions as radiopharmaceutical imaging agents in medicine. Accounts of their chemistry, as seen in reviews,[2] make no mention of solution chemistry of these ions with ligands having only saturated nitrogen donors, such as ammonia or the polyamines. Martell *et al.*[3] have reported extensive studies of the complexing of Ga(III) by a wide variety of ligands with saturated nitrogen donors, but also containing other groups such as carboxylates or phenolate. We have developed an empirical equation[4] that predicts $\log K_1$ for complexes of unidentate ligands. This equation predicts, for example, that Pb(II) should have $\log K_1$ (NH_3) of 1.6, and in previous work[5] aimed at establishing the nitrogen donor chemistry of Pb(II) this prediction was confirmed. The same equation suggests that $\log K_1$ (NH_3) for a selection of trivalent metal ions should be as follows.

	Sc^{3+}	La^{3+}	Lu^{3+}	Cr^{3+}	Co^{3+}	Al^{3+}	Ga^{3+}	In^{3+}	Fe^{3+}
$\log K_1(NH_3)$	0.7	0.2	0.7	3.4	7.3	0.8	4.1	4.0	3.8

The values of $\log K_1(NH_3)$ with Ga(III) and In(III) can be used in further equations which we have developed[6] to predict $\log K_1$ for a wide variety of polyamines such as

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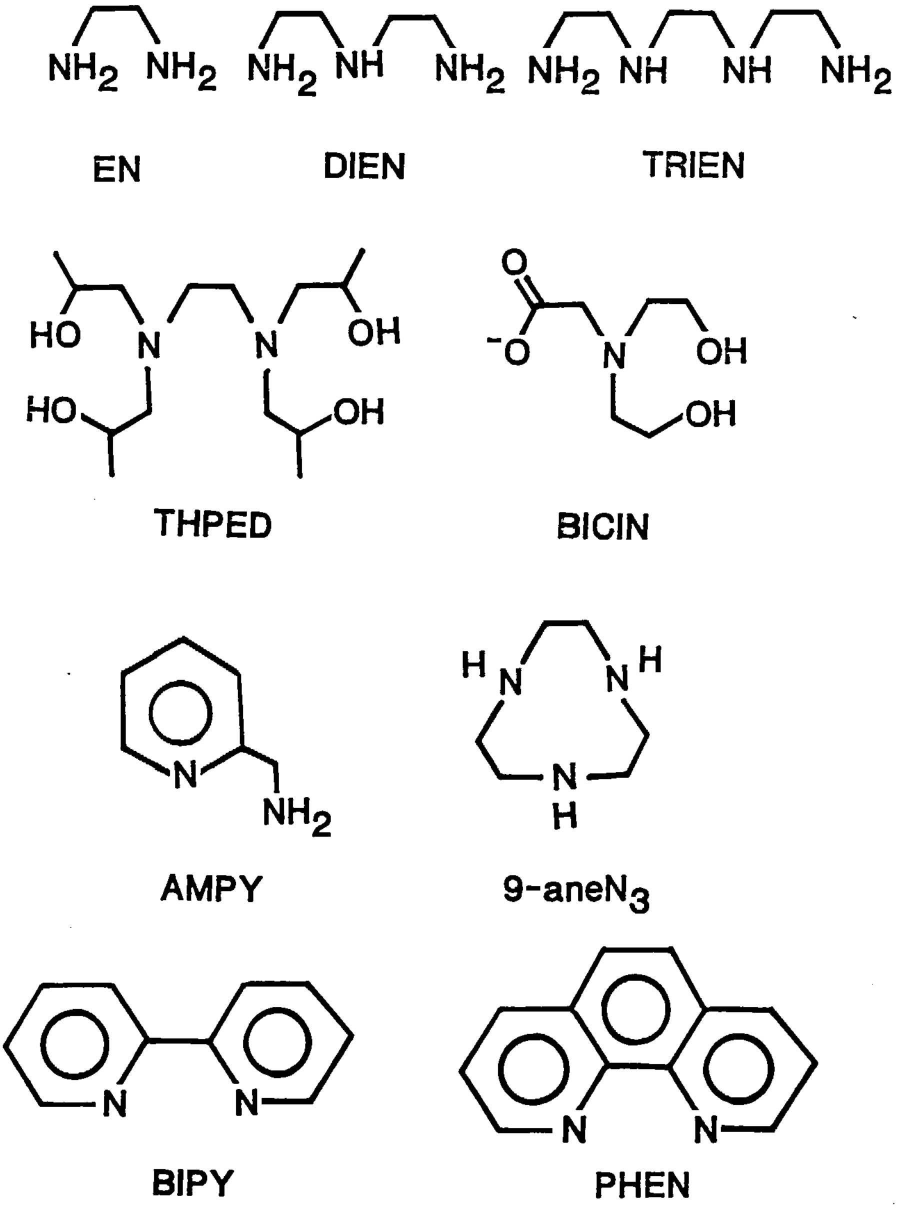


FIGURE 1 Ligands discussed in this paper.

EN, DIEN, TRIEN, and related ligands. The equations used for making such predictions are typified by equation (*1*), which is derived from the ideas of Adamson[7] on the origin of the chelate effect.

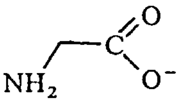
$$\log K_1(\text{polyamine}) = 1.152 \log\beta_n(NH_3) + (n - 1)\log 55.5 \qquad (1)$$

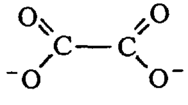
In this equation $\log K_1$(polyamine) refers to the formation constant of a polyamine such as EN, DIEN, or TRIEN having n nitrogen donors, 1.152 is an inductive effect factor which takes into account the greater basicity of alkylamines than of ammonia, and 55.5 is the molarity of pure water. It has been found[6] that where only $\log K_1(NH_3)$ is available for the metal ion, satisfactory predictions can be made using equation (*1*) assuming that $\log K_n(NH_3)$ decreases monotonically by 0.5 log units for unit increases in the value of n, so as to give $\log\beta_n(NH_3)$ values of n greater than one. If $\log K_1$ for In(III) and Ga(III) with ammonia is about four, then equation (*1*) predicts that $\log K_1$ for EN with these ions should be about 10.5. These predictions suggest that In(III) and Ga(III) might have a considerable, previously unsuspected, aqueous phase chemistry with nitrogen donor ligands. The reason why so many metal ions do not have a significant aqueous phase chemistry with ligands having only saturated nitrogen donors is often not so much because of their low affinity for nitrogen donors, but their relatively greater affinity for hydroxide ion. Thus, as an example, the Fe(III) amine complexes decompose immediately in water, as illustrated by equation (*2*).

$$Fe(NH_3)^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + NH_4^+ \qquad (2)$$

If one takes the $\log K_1$ value for $Fe(NH_3)^{3+}$ as 3.8 as shown above, and the $\log K_1$ value[8] for $Fe(OH)^{2+}$ as 11.8, combined with $pK_w = 14.0$ and pK_a for NH_4^+ as 9.2, then one calculates a reaction constant for equation (*2*) of 3.2 log units. This shows, as is observed in practice, that ferric amine complexes will be completely hydrolyzed in water. A similar analysis shows that In(III) and Ga(III) ammines will also be hydrolyzed in water. However, with their lower affinities for hydroxide [$\log K_1(OH^-) = 11.3$ for Ga(III) and 10.0 for In(III)], In(III) and Ga(III) are better candidates for having an aqueous phase chemistry with saturated nitrogen donors than is Fe(III). This is particularly true if one can bring down the pK_a values of the ligands, so helping to drive reactions such as (*1*) to the left. Hydroxyalkyl groups tend to lower the pK_a values of nitrogen donor ligands, so that we studied the coordinating properties with Ga(III) and In(III) of the ligands THPED and also BICIN (see Figure 1 for key to ligand abbreviations). Pyridyl groups have a similar effect on adjacent saturated amine groups, and so the coordination of these metal ions to AMPY was also studied.

A "rule of average environment" has been previously suggested[9] for bidentate ligands, in which the $\log K_1$ values of chelate ligands containing two different types of donor atom were found to be the average of $\log K_1$ for two bidentate ligands each containing only one of the two types of donor atom. Thus, glycine is the average of EN and oxalate, or OXINE is the average of catechol and PHEN; some $\log K_1$ values[8] illustrating the rule are shown below.





	EN	glycine	oxalate
$\log K_1$ for Cu(II):	10.50	8.57	6.23

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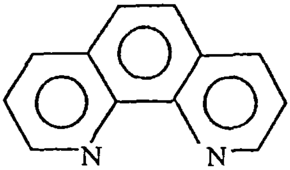
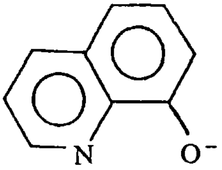
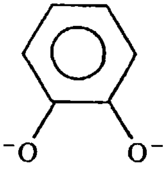
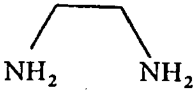
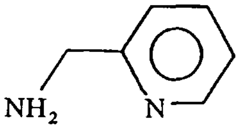

1,10-phenanthroline
(PHEN)

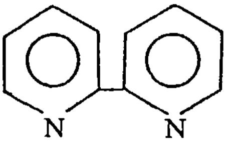

oxine


catecholate

logK$_1$ for Fe(III): 6.5 14.52 21.7


EN


AMPY


BIPY

logK$_1$ for Pb(II): 5.04 3.95 2.9

The logK$_1$ value for AMPY with Ga(III) measured in this work was 8.4. Combined with the reported[10] logK$_1$ value of 4.5 for Ga(III) with BIPY, this suggested the remarkably high logK$_1$ value for Ga(III) of $2 \times 8.4 - 4.5 = 12.3$. This is somewhat higher than predicted by equation (*1*), namely logK$_1$ for EN = 10.5. If this prediction were correct, then there seemed to be a reasonable chance that Ga(III) would form a detectable complex with ethylenediamine in solution, but not if logK$_1$ had the lower value of 10.5. The complexing of Ga(III), and also of In(III), by EN in aqueous solution was therefore studied.

In this paper is reported a study by glass electrode potentiometry of the formation of complexes of gallium(III) and indium(III) with the amine ligands THPED, EN, and AMPY, and with the amino acid BICIN. The aim of the study is to extend our knowledge of the nitrogen donor chemistry of these metal ions, and also test the predictive abilities of equations and ideas that have been proposed[4,6,9] in earlier publications.

EXPERIMENTAL

Materials

The ligand AMPY was obtained from Aldrich, THPED and BICIN from BDH, and EN from Merck. The ligands were standardized by titration with acid, a procedure which indicated that they were of at least 99% purity. Stock solutions (0.01 M) of $Ga(NO_3)_3$ and $In(NO_3)_3$ in 0.01 M HNO_3 to prevent hydrolysis were prepared from the 99.99% purity salts (Aldrich), and standardized by EDTA titration.

Potentiometry

Titrations were carried out under nitrogen in a cell thermostatted to 25°C in 0.1 M

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$NaNO_3$, using a Radiometer G202B glass electrode, and a Radiometer PHM 84 pH meter. The standard potential for the cell, E°, was obtained from calculated values of pH in a range of pH values from 2 to 12 in a standard acid/base titration. At least three titrations with variation of the metal/ligand ratio were performed for each metal ion with each ligand.

TABLE I

Protonation constants and formation constants for the ligands with gallium(III) and indium(III).[a]

Ligand[b]	Equilibrium[c]	logK	lit[d]
AMPY	$H + L \rightleftharpoons HL$	8.50 ± 0.02	8.61
	$H + L \rightleftharpoons H_2L$	2.28 ± 0.02	2.0 ± 0.1
	$Ga + L \rightleftharpoons GaL$	8.40 ± 0.06	
	$GaL + L \rightleftharpoons GaL_2$	7.58 ± 0.05	
	$GaL_2 + L \rightleftharpoons GaL_3$	4.86 ± 0.06	
	$In + L \rightleftharpoons InL$	7.6 ± 0.1	
THPED	$H + L \rightleftharpoons HL$	8.70 ± 0.03	8.75
	$HL + L \rightleftharpoons HL_2$	4.12 ± 0.01	4.24
	$Ga + L \rightleftharpoons GaL$	7.94 ± 0.03	
	$GaL + OH \rightleftharpoons GaLH_{-1}$	9.32 ± 0.08	
	$In + L \rightleftharpoons InL$	8.20 ± 0.02	
	$InL + OH \rightleftharpoons InLH_{-1}$	10.40 ± 0.01	
	$2InL + 3OH \rightleftharpoons InL_2H_{-3}$	32.24 ± 0.03	
EN	$H + L \rightleftharpoons HL$	e	9.89
	$HL + H \rightleftharpoons H_2L$	e	7.08
	$Ga + \rightleftharpoons GaL$	12.72 ± 0.05	
	$GaL + OH \rightleftharpoons GaLOH$	6.70 ± 0.09	
	$GaLOH + OH \rightleftharpoons GaLOH_2$	6.33 ± 0.09	
BICIN	$H + L \rightleftharpoons HL$	8.14 ± 0.02	8.11
	$HL + H \rightleftharpoons H_2L$	1.70 ± 0.1	(1.68)[f]
	$Ga + L + 2OH \rightleftharpoons GaLH_{-2}$	22.52 ± 0.06	
	$Ga + 2L \rightleftharpoons GaLH_2$	13.75 ± 0.09	
	$Ga + 2L + 4OH \rightleftharpoons GaL_2H_{-4}$	23.4 ± 0.01	
	$In + L \rightleftharpoons InL$	7.06 ± 0.04	
	$InL + OH \rightleftharpoons InLH_{-1}$	10.40 ± 0.05	
	$InLH_{-1} + OH \rightleftharpoons InLH_{-2}$	9.82 ± 0.05	
OH^-	$H + OH \rightleftharpoons H_2O$		13.78
	$In + OH \rightleftharpoons InOH$	10.00 ± 0.02	10.5[g]
	$3In + 4OH \rightleftharpoons In_3OH_4$	(46.0)[h]	(50.2)[i]
	$Ga + OH \rightleftharpoons GaOH$	10.63	10.8

[a] All data at 25°C in 0.1 M $NaNO_3$. [b] For key to ligand abbreviations, see Figure 1. [c] In these equilibria charges on the metal ions, ligands and complexes have been omitted for simplicity. L is the ligand indicated for the set of equilibria, Ga and In have their obvious meaning, H is the proton, and OH is the hydroxide ion. [d] Literature values at 25°C and ionic strength 0.1 except where indicated otherwise, from reference 8. [e] The literature values for the protonation constants were used for calculation of the formation constants for the metal ions. [f] At 20°C. [g] It seems unlikely that this constant should be so high, when compared with the value of $\log K_1$ at ionic strength zero of 10.0. [h] This is not fully at equilibrium, but an apparent constant obtained after equilibration for a few minutes, as discussed in the text. [i] Ionic strength zero.

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Analysis of potentiometric data

The potentiometric titrations were analyzed using the program ESTA,[11] with a large number of models considering all plausible solution species, including ML_n, ML_nH_m, ML_nOH_p, M_qL_n, and $M_qL_nOH_p$ species for a wide range of values of n, m, p and q. In a study of this nature one has to be very careful that the release of protons caused by the presence of the metal ion in the equilibrium is really due to complex formation rather than hydrolysis. To take this into account, the hydrolysis constants[8] of both Ga(III) and In(III) were included as fixed constants in calculating the formation constants. To be aware of the hydrolysis behaviour of Ga(III) and In(III), the hydrolysis of these metal ions was studied in titrations with hydroxide. A problem which became apparent here was that the rate of formation of the solution species $In_3(OH)_4{}^{5+}$ was slow, requiring several days for equilibrium to be reached. This did not make a major contribution to the species present in solution, but still could affect the outcome of the refinement. In order to complete the titrations in a reasonable time, a conditional constant for this hydroxy species was determined in titrations where equilibration times similar to those obtaining in the titrations with other ligands were employed. These hydrolysis constants, together with the other protonation and formation constants obtained in this work, are given in Table I.

In Figures 2 to 5 are shown $\bar{z}$ *versus* log[L] plots for a selection of the complexes studied, indicating both experimental points and theoretical curves calculated from the appropriate constants in Table I. The function $\bar{z}$ is[11] $\{L_T - j^{-1}(H_T - [H] - K_w[H]^{-1})\}/M_T$ where L_T is the total ligand concentration, j is $\{\beta_1{}^H[H] + 2\beta_2{}^H[H]^2 + \ldots\}/(1 + \beta_1{}^H[H] + 2\beta_2{}^H[H]^2 + \ldots)$, H_T is total proton concentration and M_T is total metal concentration. The function $-\log[A]$ in these plots refers to $A = (H_T - [H + K_w.[H]^{-1})/(\beta_1{}^H[H] + 2\beta_2{}^H[H]^2 + \ldots)$. The interpretation of the $\bar{z}$ *versus* log[A] plots is not too different from that of the more familiar $\bar{n}$ *versus* log[L] plots, except that the $\bar{z}$ plots allow[11] for theoretical curves that include species of types other than ML_n, such as ML_nOH_m, ML_nH_p or M_qL_n.

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RESULTS AND DISCUSSION

The results in Table I indicate, as we had surmised from our predictions,[4,6] that In(III) and Ga(III) have a not inconsiderable chemistry with nitrogen donor ligands. To these results must be added, of course, the formation constant studies on the BIPY and PHEN complexes of these metal ions of Kulba *et al.*[10]

Complexes with o-aminomethylpyridine

The pyridyl group has the effect of lowering the pK_a of the saturated amine donor of AMPY from the value of 10.6 found typically for saturated primary amines down to only 8.5. The pyridine nitrogen itself is of very low basicity, so that the Ga(III) complexes, in particular, are highly resistant to hydrolysis, and a *tris* complex is present in solutions of Ga(III) at higher ligand concentrations. This is seen in the $\bar{z}$ *versus* log[L] curves for Ga(III) with AMPY in Figure 2. This high resistance to hydrolysis resembles that of the BIPY and PHEN complexes, where the very low pK_a values of the pyridyl nitrogens allow the complexes to form at low pH and so avoid hydrolysis. The In(III) complex was ill defined after the addition of a single AMPY ligand, and at higher free ligand concentrations the hydroxide precipitated. The

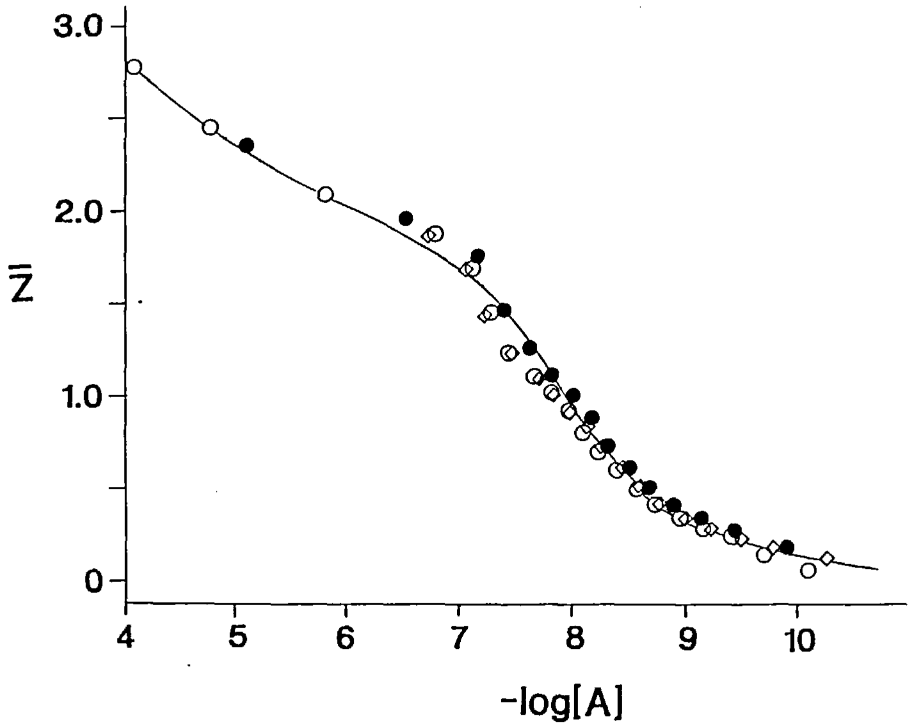

FIGURE 2 The $\bar{z}$ *versus* log[A] plot for Ga(III) with AMPY (2-aminomethylpyridine). The three separate titrations were of (—○—) 0.003333 M Ga^{3+} in 0.01667 M HNO_3, (—●—) 0.005 M Ga^{3+} in 0.025 M HNO_3, (—◇—) 0.001176 M Ga^{3+} in 0.005882 M HNO_3, all titrated with 0.01 M AMPY. Following the usual convention, the points indicate the experimental points, while the lines, solid or broken, indicate the theoretical curves calculated from the formation constants in Table I. All solutions were at 25°C and in 0.1 M $NaNO_3$ or total ionic strength 0.1 For a definition of $\bar{z}$ and A, see text and reference 11.

$\log K_1$ values of BIPY combined with those of AMPY allow us to predict formation constants for the EN complexes as follows

	BIPY observed[10]	AMPY observed this work	EN predicted A	 B
$\log K_1$[Ga(III)]	4.5	8.4	12.3	10.6
$\log K_1$[In(III)]	4.8	7.6	10.4	10.4

The predicted constants at A are obtained by the rule of average environment,[9] while those at B are predicted by equation (*1*).[6] The agreement of In(III) between the two methods of prediction is excellent. One can be reasonably sure, in the absence of any other method of obtaining this constant, that $\log K_1$ for In(III) with ammonia, derived from the EN constant by equation (*1*), and by other methods[4,6,9,12] is 4.0. As confirmed below, the EN complex also should be hydrolyzed in aqueous solution if this constant is correct.

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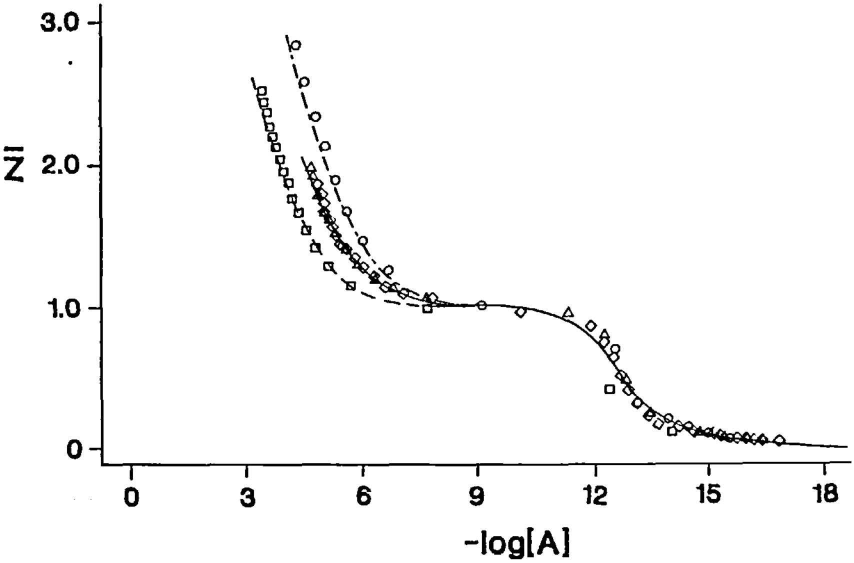

FIGURE 3 The $\bar{z}$ *versus* log[A] plot for Ga(III) with EN (ethylenediamine). See Figure 2 for a full explanation of the diagram. The separate titrations were of (·—△—·) 0.00333 M Ga^{3+} in 0.01667 M HNO_3, (—◇—) 0.004118 M Ga^{3+} in 0.02059 M HNO_3, (—○—) 0.001176 M Ga^{3+} in 0.005882 M HNO_3, all titrated with 0.01003 M EN, and (—□—) 0.005000 M Ga^{3+} in 0.0250 M HNO_3, titrated with 0.1201 M EN in 0.1 M HNO_3. All solutions were at 25°C and in 0.1 M $NaNO_3$ or total ionic strength 0.1.

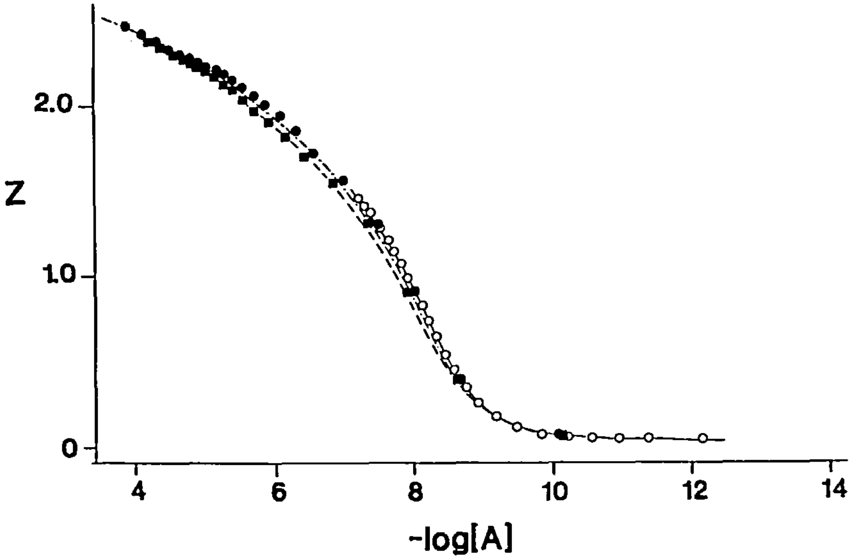

FIGURE 4 The $\bar{z}$ *versus* log[A] plot for In(III) with THPED (*N*,*N*,*N*′,*N*′-tetrakis(2-hydroxypropyl)-1,2-diaminoethane). For a full explanation of the diagram, see Figure 2. The three separate titrations were of (—○—) 0.00525 M In^{3+} in 0.00998 M HNO_3, titrated with .01213 M THPED in 0.0101 M HNO_3, and (-- ■ --) 0.00525 M In^{3+} in 0.009988 M HNO_3, (·—●—·) 0.00350 M In^{3+} in 0.006658 M HNO_3, both titrated with 0.12126 M THPED in 0.10101 M HNO_3. All solutions were at 25°C and in 0.1 M $NaNO_3$ or total ionic strength 0.1.

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Complexes with ethylenediamine

Titration of indium(III) with ethylenediamine resulted only in the precipitation of hydroxide, as we had expected. In contrast, as seen in Figure 3, where the $\bar{z}$ *versus* log[L] plot is shown for Ga(III) with EN, Ga(III) forms a very well defined mono complex with EN of unusually high stability. A total of four titrations with widely differing conditions were carried out to pin down the nature of the complexes formed, particularly at higher $\bar{z}$. The highly separated $\bar{z}$ curves at $\bar{z}$ greater than one can be accounted for by the formation of Ga(EN)OH_n species where n = 1 and 2, and the program rejected the presence of ML_2 or ML_3 species. Why no higher species such as $Ga(EN)_2$ or $Ga(EN)_3$ were observed in the titration is not clear. It is possible that the initial complex formed is tetrahedral, with higher complexes requiring octahedral coordination, an effect which produces discontinuities in $\log K_n$ sequences for other d^{10} metal ions such as Zn(II) or Cd(II) in their complexes with EN and ammonia. The similarity in magnitude for the constants for the formation of GaLOH from GaL, and $GaLOH_2$ from GaLOH, (Table I) suggests that this complex might also be tetrahedral, *i.e.* that it is $[Ga(EN)(OH)_2]^+$. The value of $\log K_1$ for EN with Ga(III) is shown in comparison with values for some other metal ions below.

	Zn(II)	Cd(II)	Ni(II)	Cu(II)	Hg(II)	Ga(III)	Co(III)	Cr(III)
$\log K_1$(EN)	5.7	5.4	7.3	10.5	14.3	12.7	(18.5)[a]	(9.1)[b]

Complexes with N,N,N',N'-tetrakis(2-hydroxypropyl)-1,2-diaminoethane (THPED)

Table I shows that well-defined complexes of THPED with In(III) and Ga(III) exist in solution. The $\bar{z}$ *versus* log[A] curve for In(III) with THPED is shown in Figure 4. It has been found[13] with small metal ions that $\log K_1$ for THPED is somewhat lower than for EN, and in keeping with the small size of Ga(III) (octahedral radius = 0.55 Å[14]) and moderately small size of In(III) (octahedral radius = 0.8 Å[14]), the observed $\log K_1$ values for these metal ions are somewhat lower than the predicted values for EN.

	Ga(III)	Cu(II)	Zn(II)	In(III)	Cd(II)	Pb(II)
Ionic radius (octahedral)/Å[14]	0.55	0.59	0.74	0.80	0.95	1.18
$\log K_1$(EN)	12.7	10.5	5.7	(10.4)	5.4	5.0
$\log K_1$(THPED)	7.9	8.2	4.8	8.2	6.5	7.6

It is noticed, as has been pointed out previously,[13] that the effect on complex stability of adding hydroxalkyl groups to a ligand such as EN to give a ligand such as THPED is strongly related to metal ion size. Larger metal ions show an increase in complex stability on addition of hydroxyalkyl groups, while smaller metal ions show a decrease.

What is interesting is the clear existence of a $M_2L_2OH_3$ complex for In(III) with THPED. A large variety of $In_qL_nOH_p$ species were tried out in the model, with q and L ranging from 1 to 4, and p ranging from 1 to 6, but that with q = n = 2, and p = 3

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[a] Estimated from $\log\beta_3$ and $\log K_3$ by assuming linear decrease in $\log K_n$ as n increases. Data from reference[8]. [b] Estimated from equation 1 and from known $\log K_3$ by comparison with other EN complexes.

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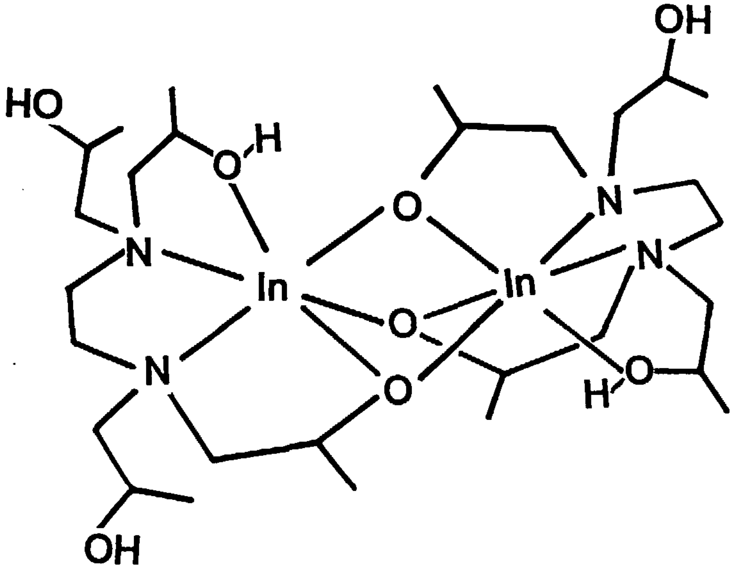
produced a dramatically better r-factor and lower standard deviation on all the constants. It should be noted that the other two constants reported for this system for the InL and InLOH species were, however, largely insensitive to the nature of the polymeric species introduced, and can be regarded with considerable confidence. Wieghardt *et al.*[15] have found crystallographically for In(III) that tetrameric complexes of the type $In_4L_4OH_6$ occur in the solid state for L = 9-aneN_3, and that dimeric $Ga_2L_2OH_3$ complexes occur in the solid state for Ga(III). It is suggested in view of the three hydroxides very specifically indicated by the program to be present that the dimer is bridged by three deprotonated alkoxide groups on the faces of the two octahedral In(III) ions, to give a complex of the type shown below.



proposed structure for In/THPED dimer

Complexes of N,N-bis(2-hydroxyethyl)glycine (BICIN)

The complexes of BICIN with In(III) and Ga(III) are dominated by the deprotonation of the complexes, and for Ga(III) no ML complex could be detected, with only $MLOH_2$ being present at the lowest pH values studied. The $\bar{z}$ *versus* log[A] curves for the In(III) complex with BICN are shown in Figure 5. It is of interest to note that the hydroxyethyl oxygen atoms deprotonate in these complexes at much the same pH as would the uncomplexed metal ions.

ML	M(BICIN)		M(THPED)		M(EN)	M	
M(III)	In	Ga	In	Ga	Ga	In	Ga
LogK for $ML + OH^- = MLOH$ or $M + OH = MOH$	10.4	> 11	10.4	9.3	6.7	9.4	10.6

In contrast, the Ga(EN)$^{3+}$ complex is much less acidic than the uncomplexed Ga^{3+} ion, supporting the idea that the protons on the BICIN and THPED complexes come from the coordinated hydroxyalkyl groups rather than coordinated water.

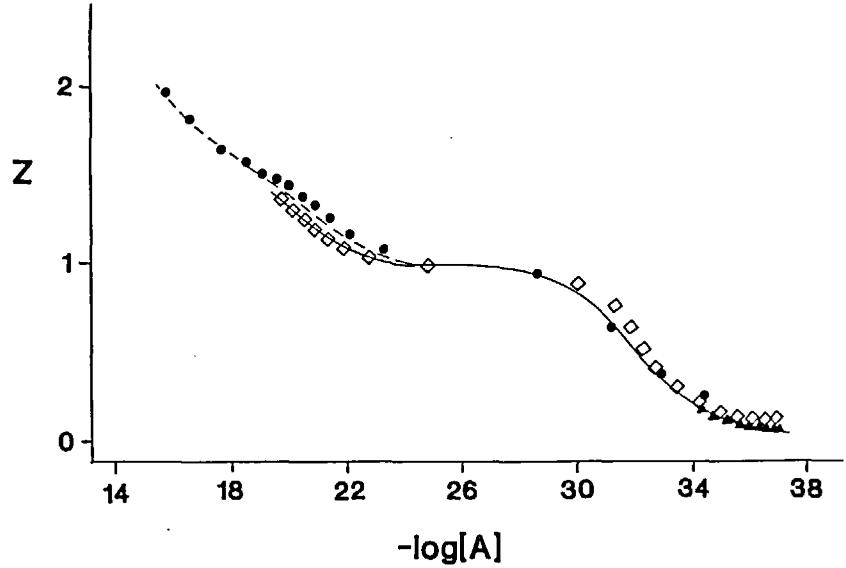


FIGURE 5 The $\bar{z}$ *versus* log[A] plot for In(III) with BICIN [*N*,*N*-bis(2-hydroxyethyl)glycine]. For a full explanation of the diagram, see Figure 2. The three separate titrations were of (—▲—) 0.00525 M In$^{3\bullet}$ in 0.03999 M HNO$_3$ and 0.01 M BICIN, (—◇—) 0.0035 M In^{3+} in 0.0466 M HNO$_3$ and 0.01333 M BICIN, and (--●--) 0.001235 M In^{3+} in 0.03764 M HNO$_3$ and 0.01176 M BICIN, all titrated with 0.02 M BICIN. All solutions were at 25°C and in 0.1 M NaNO$_3$ or total ionic strength 0.1.

This work has indicated the existence of a substantial aqueous chemistry of In(III) and Ga(III) with saturated amine ligands, and has supported the predictions of this chemistry made by a variety of approaches discussed in this paper. Particularly gratifying is the observation of a stable mono ethylenediamine complex of Ga(III) in solution in line with predictions. The only evidence of N-donor chemistry of saturated non-macrocyclic ligands for these metal ions are reports[2a,16] of the preparation in the solid state of tris(ethylenediamine) complexes of In(III). We have now isolated crystalline samples of some of the other complexes discussed here, and work is now in progress to elucidate the structures of these. The work has provided some insight into the chemistry of Ga(III) and In(III) with nitrogen donor ligands, but also raised several questions. Chief amongst these is the coordination geometry of the complexes in solution which we have discussed, particularly the complexes of ethylenediamine with Ga(III). Another interesting point raised is the nature of the deprotonated species of complexes having hydroxyalkyl groups, such as the BICIN and THPED complexes. We are currently carrying out a study of the complexing properties of Ga(III) and In(III) with macrocyclic ligands, as well as further open chain polyamine ligands, the results of which will be reported in a future paper.

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ACKNOWLEDGEMENTS

The authors thank the University of the Witwatersrand and the Foundation for Research Development for generous financial support for this work.

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