The Affinity of Indium(III) for Nitrogen-donor Ligands in Aqueous Solution. A Study of the Complexing of Indium(III) with Polyamines by Differential Pulse Voltammetry, Density Functional Theory, and Crystallography

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

The affinity of In(III) for N-donor ligands was investigated by differential pulse voltammetry, DFT calculations, and crystallography. The structure of $[In(tpen)(CH_3COO)](ClO_4)_2 \cdot 0.5\,H_2O$ (**1**) is reported (tpen = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine): Monoclinic, $P2_1/n$, a = 8.687(4), b = 7.767(8), c = 20.432(10) Å, β = 93.372(8)°, Z = 4, R = 0.0518. The In(III) center is 7-coordinate, with six In–N bonds to the tpen ligand in the range 2.306 – 2.410 Å, and a unidentate acetate group with In–O = 2.247 Å. The formation constants of In^{3+} in 0.1 M $NaNO_3$ at 25 °C are (M = In(III), L = ligand, H = proton): L = triethylenetetramine, $\log\beta(MLH_2) = 25.3 \pm 0.3$, $\log K_1 = 14.43 \pm 0.09$, and $\log\beta(ML(OH)_2) = 27.7 \pm 0.1$; tetraethylenepentamine, $\log\beta(MLH) = 20.8 \pm 0.2$, and ML ($\log\beta(ML) = 20.1 \pm 0.3$); diglycolic acid, ($\log\beta(MLH) = 8.06 \pm 0.06$), $\log K_1 = 6.02 \pm 0.06$, $\log\beta_2 = 9.40 \pm 0.08$; tpen, $\log K_1 = 17.71 \pm 0.07$; *N*,*N*′-bis(2-pyridylmethyl)ethylenediamine, $\log K_1 = 14.69 \pm 0.05$; 1,10-phenanthroline, $\log K_1 = 6.81 \pm 0.07$, $\log K_2 = 6.44 \pm 0.07$, $\log K_3 = 6.20 \pm 0.08$. Correlations are shown between the determined formation constants for the polyamines and $\log K_1(NH_3)$ values for a wide variety of metal ions. For M(II) ions, the $\log K_1(NH_3)$ values are experimental data, but for M(III) ions the data are predicted by an empirical dual-basicity equation, including $\log K_1(NH_3) = 4.0$ for In(III). DFT calculations are used to obtain ΔE for the reaction $[M(H_2O)_6]^{n+} + NH_3 \leftrightarrows [M(H_2O)_5NH_3]^{n+} + H_2O$ for M(II) through M(IV) ions in water, represented as a structureless medium with the dielectric constant of water. Correlations are found that support the predicted value of $\log K_1(NH_3)$ for In(III) of 4.0. The nature of the intercepts on such correlations are discussed.

Key words: Indium, Formation Constants, Polarography, Nitrogen Donor Ligands

Introduction

The chemistry of In(III) is of considerable interest with the use of ^{111}In and ^{113m}In in diagnostic imaging in medicine [1 – 14]. The chemistry of Ga(III) and In(III) is often viewed in terms of comparisons with Al(III), which can be somewhat misleading. All three metal ions are regarded as 'hard' in the HSAB (Hard and Soft Acids and Bases) classification of Pearson [15, 16]. However, Ga(III) and In(III) have high affinities for such soft ligands as thiols, for which Al(III) has little affinity. This can be understood in terms of the predictions [17, 18] of eq. (1), which shows that In(III) and Ga(III) are much more strongly bound by covalently binding donor atoms than is Al(III) [17 – 20]. Eq. (1) is an empirical dual-basicity equation that predicts $\log K_1$ values for metal aqua ions with unidentate ligands in aqueous solution.

$$\log K_1 = E'_a E'_b + C'_a C'_b. \quad (1)$$

In eq. (1), the E' and C' parameters refer to the ionic and covalent contributions, respectively, to ΔG of complex-formation in aqueous solution, with the subscripts indicating the acid ('a') or base ('b'). Eq. (1)

predicts that log $K_1(NH_3)$ for In(III) and Ga(III) are 4.0 and 4.1, respectively, whereas that for Al(III) is predicted to be only 0.8. The predictions of eq. (1) for Bi(III) have been extensively investigated [21 – 24], for which log $K_1(NH_3)$ = 5.1 was predicted. The reasonableness of this prediction has been confirmed [21 – 24] by studies of complexes of Bi(III) with polyamines in aqueous solution, and synthesis and structural characterization [23, 24] of complexes of Bi(III) with N-donor polyamine ligands. Further examples of Bi(III) complexes with polyamine complexes can be found in the Cambridge Structural Database [25]. The non-existence of ammonia complexes of Al(III), In(III), Ga(III), and Bi(III) in aqueous solution is due to the high acidity of the metal ions [26], which leads to hydrolysis of NH_3 complexes in aqueous solution. The hydrolysis reaction to consider is, for In(III):

$$In(NH_3)^{3+} + H_2O = In(OH)^{2+} + NH_4{}^+. \qquad (2)$$

with predicted $\log K_1(NH_3)$ [17 – 20] for In^{3+} of 4.0, pK_w = 14.0, $\log K_1(OH)^-$ for In^{3+} of 10.1 [26], and $pK_a(NH_4{}^+)$ of 9.2 [26], the value of $\log Q$ (the reaction quotient) for reaction (2) is 1.3. Thus, an NH_3 complex of In(III) will be almost completely hydrolyzed in water, particularly when the low solubility [26] of the hydroxide $In(OH)_3(s)$ is considered.

Clearly, additional approaches to confirming the predictions of eq. (1) in relation to log K_1 values for unknown NH_3 complexes would be valuable. In a recent study [27, 28], DFT (Density Functional Theory) calculations were used to calculate ΔG values for the gas-phase reaction:

$$[M(H_2O)_6]^{n+}(g) + NH_3(g) = [M(H_2O)_5NH_3]^{n+}(g) + H_2O(g). \qquad (3)$$

These gas-phase ΔG values correlated well with aqueous phase log $K_1(NH_3)$ values, both experimental where known [26], and, importantly, with values estimated [17 – 20] using eq. (1). These LFER (linear free energy relationships) support quite strongly the predicted log $K_1(NH_3)$ values of eq. (1) for M(I), M(II), M(III), and M(IV) ions. All these LFER contain large intercepts, suggesting large solvational effects not taken into account by the gas-phase calculation of ΔG for eq. (3). In this paper we report a further extension of this work for the M(III) ions of interest here by carrying out the calculations using the COSMO feature of the DMol program [29], where the aqueous phase is simulated as a structureless dielectric medium. One might expect the calculation to simulate the energetics of solvation better with the solvent included in this way.

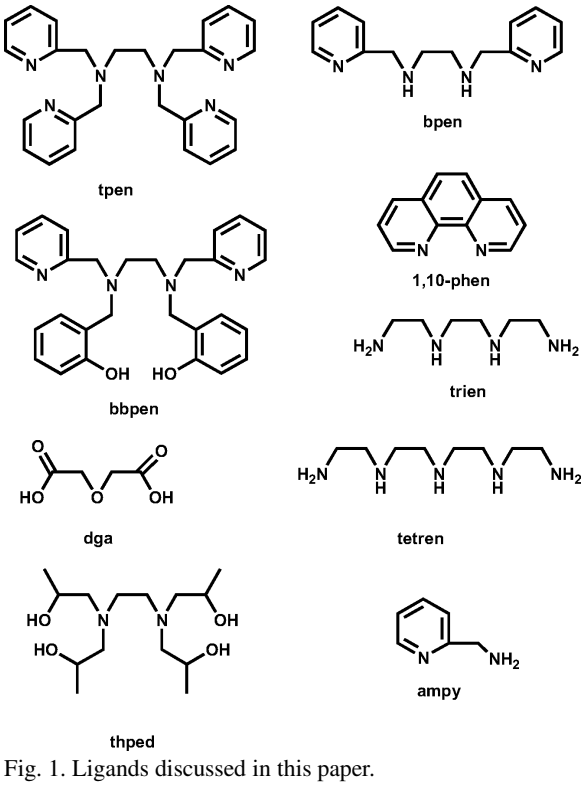


Fig. 1. Ligands discussed in this paper.

Simple NH_3 complexes of Bi(III) do not exist in appreciable quantities in aqueous solution because of hydrolysis reactions of the type in eq. (2). However, polyamine complexes can exist [21 – 24] in solution because of stabilization by the chelate [30, 31] and macrocyclic [31, 32] effects. We report here a study of complexes of In(III) with some polyamine ligands to support the estimated log $K_1(NH_3)$ value of 4.0 for In(III), and also to extend knowledge of the solution chemistry of In(III) with polyamine ligands as useful information for designing ligands for complexation of In(III) in biomedical applications [1 – 14]. This supplements a previous brief report [9] of complexation of In(III) by the diamine ligands, AmPy, and thped (Fig. 1). Studies at low total metal ion concentrations limit the precipitation of solid hydroxide, and voltammetry as a technique for measuring stability constants can easily be carried out [21 – 23] at total metal ion concentrations of 10^{-6} M. For Bi(III), complexes of dien, trien, and tetren are stable in solution at low pH

and low total Bi^{3+} concentration, but those of en are not. It was found here that only tetren and penten produced hydrolysis-resistant complexes with In(III) in solution, and log K_1 values for these complexes are reported. Pyridyl N-donor groups stabilize complexes of acidic metal ions against hydrolysis by lowering the protonation constants of the ligand, without greatly decreasing the log K_1 values, and so inhibit the type of hydrolysis in eq. (2). Accordingly, complexation of In(III) by 1,10-phen, tpen, and dpen was studied.

The number of structures of In(III) with open-chain polyamine ligands reported in the Cambridge Structural Database [25] is somewhat limited, examples being terpyridyl [33] and en [34] complexes, as well as complexes of tripodal ligands containing pyridyl groups [35], and some N-methyl substituted diamines and triamines [36]. Thus, attempts were made to grow crystals of In(III) complexes with some of the ligands in Fig. 1. Perhaps not surprisingly, at the higher In(III) concentrations needed for growing crystals, only $In(OH)_3$(s) resulted in most cases, except for the complex of the hexadentate ligand tpen, which gave the complex $[In(tpen)(CH_3CO_2)](ClO_4)_2 \cdot 0.5\ H_2O$, the structure of which is reported here.

Experimental Section

Materials

$In(NO_3)_3 \cdot 5\,H_2O$ (99.999 %), triethylenetetramine hydrate (98 %), tetraethylenepentamine pentahydrochloride (98 %), and diglycolic acid (98 %), were obtained from Aldrich, and 1,10-phenanthroline (99 %) was obtained from Acros Organics, and used as received to make stock solutions for the voltammetric titrations. Ethylenediamine (99 %), 2-picolyl chloride hydrochloride (98 %), and 2-pyridinecarboxaldehyde (99 %) were obtained from Aldrich chemicals and used in the synthesis of *N*,*N*,*N*′,*N*′-tetra(2-pyridylmethyl)ethylenediamine (tpen), and *N*,*N*′-bis(2-pyridylmethyl)ethylenediamine (bpen). Stock solutions of $In(NO_3)_3$ were standardized by usual methods.

Synthesis of tpen and bpen

Previously described methods were used for the synthesis of bpen [37] and tpen [38].

Instrumentation

Voltammetric studies were carried out with a Metrohm 663 polarograph, which was controlled by an EcoChemie PGStat 10 potentiostat and the General Purpose Electrochemical System (GPES) computer program by EcoChemie. A dropping mercury electrode was used as the working electrode in Static Mercury Drop Electrode (SMDE) mode. An Ag/AgCl electrode was used as the reference electrode, and a glassy carbon rod was used as the auxiliary electrode. The polarograph was equipped with a jacketed glass vessel to control the system to 25.0 ± 0.1 °C, and nitrogen (UHP) was bubbled through the solutions to remove O_2 and CO_2. pH was recorded with a SymPHony pH meter (VWR), and a Corning glass electrode. ^{1}H NMR experiments were performed using a Bruker 400 MHz Avance DRX spectrometer.

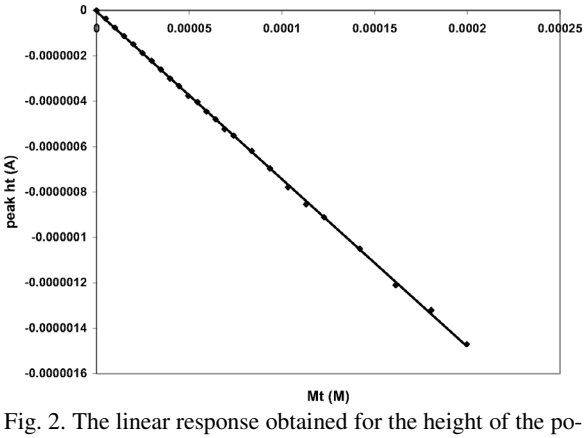


Fig. 2. The linear response obtained for the height of the polarographic peak of indium in amps *versus* the concentration of indium in solution up to 2.0×10^{-5} M in 0.010 M HNO_3/0.090 M $NaNO_3$/0.001 % gelatin.

Voltammetric titrations. The In^{3+}/trien system

Four titrations were performed for trien with $In(NO_3)_3$, giving a total of 52 titration points. These consisted of titration of 50 mL of 5.0×10^{-5} M $In(NO_3)_3$ in 0.1 M $NaNO_3$ at pH 2 in the cell, with 0.25 M trien in 0.10 M HNO_3, with additions ranging from 25 μL to 100 μL. Voltammograms were recorded giving peak positions and heights for the In^{3+} peak, as well as the pH at each point. The peak shifts and changes in peak height observed suggest three distinct species present at different pH values, an MLH_2, ML, and MLOH complex (Fig. 2).

The In(III)/diglycolic acid system

Two titrations were performed for this system, giving 57 titration points. 0.025 M diglycolic acid in a solution of 0.090 M $NaNO_3$/0.010 M HNO_3 was titrated into 50 mL of 5.0×10^{-5} M $In(NO_3)_3$ at $\mu = 0.1$. The titrations indicated three species (MLH, ML, and ML_2) in solution based on the peak heights and positions with variation of pH.

The In(III)/tetren system

Two titrations were performed for this system, giving 46 titration points. Additions ranging from 0.075 to 1.00 mL

of a 0.0050 M solution of tetren in 0.1 M $NaNO_3$ were made to a solution of 50 mL of 5.00×10^{-5} M $In(NO_3)_3$ in the cell at $\mu = 0.1$. At each addition, the pH and a voltammogram were recorded, as well as the peak position and height of the In^{3+} peak. In the second titration, additions of 2.5 mL of a 5.00×10^{-5} M $In(NO_3)_3$ and 0.2000 M tetren solution were made to 25.0 mL of a 5.00×10^{-5} M solution of $In(NO_3)_3$ solution at $\mu = 0.1$, followed by 24 additions of 0.10 M base at volumes ranging from 0.25 to 1.00 mL to adjust the pH. The titrations showed evidence of two species, an MLH and an ML complex.

The In(III)/tpen system

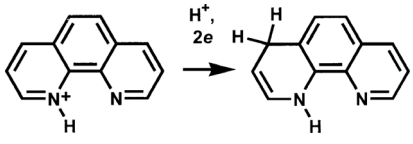
This was carried out in a similar manner to the In^{3+}/trien system. The peak shifts observed suggest that only an ML complex was present.

The In(III)/bpen solution

This was carried out in a similar manner to the In^{3+}/trien systems. The peak shifts observed suggest that only an ML complex was present.

The In(III)/1,10-phenanthroline system

Log K values for the In(III)/1,10-phen complexes were determined by titrating 25.00 mL of acidified 10^{-3} M 1,10-phen in 0.1 M $NaNO_3$ plus acidified 0.750 mL 10^{-3} M $In(NO_3)_3$ solution in 0.1 M $NaNO_3$ with 0.10 M NaOH. Voltammograms of 10^{-3} M 1,10-phen alone, and of 10^{-3} M 1,10-phen plus 3×10^{-5} M In^{3+}, are seen in Fig. 4. 1,10-Phen is polarographically active, undergoing reductions typical of, for example, quinolines [39], that resemble reduction of NAD (nicotinamide adenine dinucleotide) in biological systems:



On addition of In^{3+} to the 1,10-phen solution, a separate reduction peak due to In^{3+} occurs at around −0.53 V, typical of In^{3+}. The pH was raised progressively and voltammograms recorded for each pH obtained. The In^{3+} peak shifts to more negative potential as the pH is raised, and this shift can be analyzed as discussed below to yield values of log K_1, log K_2, and log K_3 for the In(III)/1,10-phen system. The free 1,10-phen concentration was calculated at each pH from the reported [26] pK_1 (first protonation constant) of 4.92. Since the pH in these experiments started at below 2.0, the question of the role of the second protonation constant (pK_2) of 1,10-phen, tentatively reported [26] as 1.8, became of importance

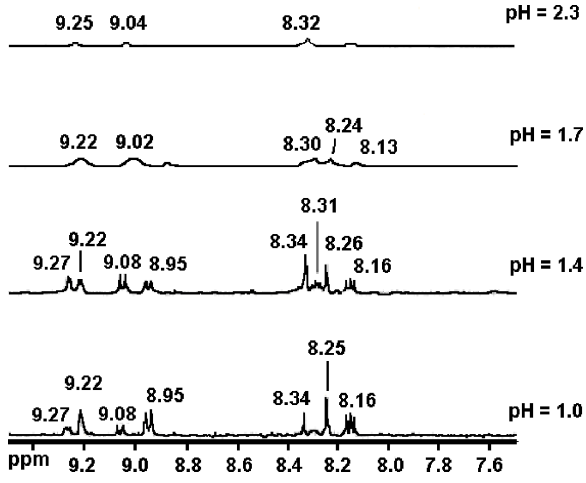


Fig. 3. A selection of ^{1}H NMR spectra of 0.001 M In(III)/1,10-phenanthroline as a function of pH. The peaks as 8.16, 8.25, 8.95, and 9.22 ppm are those of the protonated ligand LH^+, while those at 8.34, 9.06, and 9.27 ppm are those of the complex In(III)L (L = 1,10-phen).

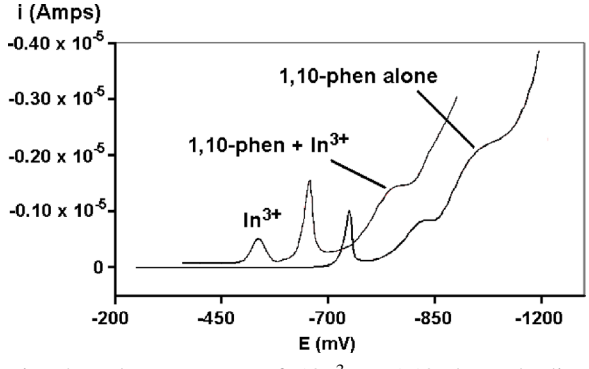


Fig. 4. Voltammograms of 10^{-3} M 1,10-phenanthroline alone, and 10^{-3} M 1,10-phen plus 3×10^{-5} M In^{3+}. Note that on coordination of In(III) to 1,10-phen the reduction potentials for 1,10-phen shift more positive.

in calculations of log K_1 for the In(III)/1,10-phen system. Such low pK values are conveniently determined by the variation of the ^{1}H NMR spectrum as a function of pH (Fig. 3).

We found no shifts in any of the peaks in the ^{1}H NMR spectrum of 1,10-phen in the pH range 1.5 to 3 that might be consistent with a pK_2 of 1.8. Small upfield shifts occurred in the pH range 0.5 – 1.5 that would be consistent with a pK_2 of less than 1.0. As confirmation of the log K_1 value determined here for In(III)/1,10-phen, the variation of the ^{1}H NMR spectrum of a 1 : 1 mixture of 1,10-phen and In^{3+} was recorded from pH 1.0 to pH 2.3. In this pH range, the peaks indicated the presence of LH^+ and InL^{3+} (L = 1,10-phen). From integration of the peaks as a function of pH, it was possible to calculate the relative concentrations of LH^+ and InL^{3+} at

each pH, and from this a value for the reaction

$$LH^+ + In^{3+} \leftrightarrows InL^{3+} + H^+ \quad (4)$$

was obtained which could be combined with the pK_1 value [26] for 1,10-phen to yield a log K_1 value for In(III)/1,10-phen in good agreement with the value obtained voltametrically.

Data treatment

In all of the titrations both the peak height and peak position changed with changing solution composition and pH. The In^{3+} aqua ion gave a single, very weak peak at about −0.470 V which increased in intensity upon addition of ligands to the solution. The program EXCEL [40] was used to determine all formation constants from the peak height, peak position, pH, and analyte concentrations. In all titrations except for the bpen titration, the initial In^{3+} peak position was used with a modified version [41] of the Lingane equation to determine E° for the metal peak.

$$\Delta E = 2.303 \times RT/nF \times \log(I_i/I) + 2.303 \times RT/nF \times \log(M_t/[M]). \quad (5)$$

Subsequent peak positions and heights upon addition of ligand were used with the determined E° and the Lingane equation to determine the free metal concentration at each point. These values were used with the metal mass balance equation to determine the concentration of each complex species in solution.

$$M_{tot} = [M] + [MLH_x] + [M(OH)_y]. \quad (6)$$

M_{tot} is the total metal ion concentration in solution, [M] is the concentration of free metal ion in solution, $[MLH_x]$ is the concentration of metal-ligand complex, with any number of protons, and $[M(OH)_y]$ is the concentration of hydrolyzed metal ion in solution. Since the pH reached values as high as 7 in some titrations, this concentration can be a significant amount since In^{3+} is easily hydrolyzed. These concentrations were determined from the pH and the equilibrium constants taken from the Critical Stability Constant Database [26]. The complex concentrations were used with the ligand mass balance equation to determine the free ligand concentration:

$$L_{tot} = [L] + [MLH_x] + [LH_z] \quad (7)$$

where L_{tot} is the total ligand concentration in solution, [L] is the concentration of free ligand in solution, and $[LH_z]$ is the concentration of protonated ligand present in solution. The peak potentials and heights were then used to determine $\bar{n}$ at each point, where $\bar{n}$ is defined as the average number of ligands bound to the metal ion in solution.

$$\bar{n} = [MLH_x]/M_{tot}. \quad (8)$$

Table 1. Table of formation constants used and determined in this paper at 25 °C and 0.1 ionic strength ($NaNO_3$). For ligand abbreviations see Fig. 1.

Equilibrium			log K	Ref.
$H^+ + OH^-$	⇆	H_2O	13.78	[26]
$In^{3+} + 2H^+ + (trien)$	⇆	$[In(trien)H_2]^{5+}$	25.3 ± 0.3	tw
$In^{3+} + trien$	⇆	$[In(trien)]^{3+}$	14.43 ± 0.09	tw
$In^{3+} + 2OH^- + (trien)$	⇆	$[In(trien)(OH)_2]^+$	27.7 ± 0.1	tw
$In^{3+} + H(tetren)^+$	⇆	$[In(tetren)H]^{4+}$	20.8 ± 0.2	tw
$In^{3+} + tetren$	⇆	$[In(tetren)]^{3+}$	20.1 ± 0.3	tw
$In^{3+} + H^+ + ODA^{2-}$	⇆	$[In(ODA)H]^{2+}$	8.06 ± 0.06	tw
$In^{3+} + ODA^{2-}$	⇆	$[In(ODA)]^+$	6.02 ± 0.06	tw
$In^{3+} + 2\ ODA^{2-}$	⇆	$[In(ODA)_2]^-$	9.40 ± 0.08	tw
$In^{3+} + tpen$	⇆	$[In(tpen)]^{3+}$	17.71 ± 0.07	tw
$In^{3+} + bpen$	⇆	$[In(bpen)]^{3+}$	14.69 ± 0.05	tw
$In^{3+} + phen$	⇆	$[In(phen)]^{3+}$	6.81 ± 0.07	tw
$[In(phen)]^{3+} + phen$	⇆	$[In(phen)_2]^{3+}$	6.44 ± 0.07	tw
$[In(phen)_2]^{3+} + phen$	⇆	$[In(phen)_3]^{3+}$	6.20 ± 0.08	tw

tw = this work.

In the bpen titration, the peak height was used as a direct indicator of extent of complex formation.

It has been found [42] that adding 0.001 % gelatin to solutions of In^{3+} gives much stronger peaks due to In^{3+}. The initial In^{3+} peak was much more intense with gelatin added, and began at −0.480 V, becoming less intense, and moving to more positive potentials upon addition of the ligand. The peak height was used to determine $\bar{n}$ from the equation

$$\bar{n} = (I \times V - I_o \times V_o)/(I_{inf} - I_o \times V_o) \quad (9)$$

where I is the peak height at each point, I_o is the initial peak height, I_{inf} is the peak height with complete complex formation, V is the volume at each point, and V_o is the initial volume. This takes into account the effect of dilution on the signal produced. I_{inf} was taken as zero for this titration, so the equation simplifies to

$$\bar{n} = (I \times V - I_o \times V_o)/(I_o \times V_o). \quad (10)$$

The value of $\bar{n}$ was used with eq. (4) above to determine the concentration of complex present in solution, which was used with eqs. (2) and (3) to determine the concentrations of free metal ion and free ligand in solution at each point. The formation constants measured in this study are shown in Table 1.

*Synthesis of [In(tpen)(CH_3COO)](ClO_4)$_2 \cdot H_2O$ (**1**)*

Crystals of the In(III) complex of tpen were synthesized by a method adapted from a synthesis of crystals of the Fe(III)/tpen complex [38]. 0.012 g of $In(NO_3)_3 \cdot 5H_2O$, 0.060 g of tpen, and 0.030 g of sodium acetate were dissolved in a minimum of absolute methanol, and after standing covered with Parafilm for a week, crystals formed in the beaker. These were collected and stored under nitrogen to prevent decomposition. Elemental analysis: calcd.

Table 2. Crystallographic data for [In(tpen)(CH_3CO_2)]-(ClO_4)$_2 \cdot 0.5\,H_2O$.

Empirical formula	$C_{28}H_{32}Cl_2InN_6O_{10.5}$
Formula weight	806.32
Temperature [K]	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	8.687(4)
b [Å]	17.767(8)
c [Å]	20.432(10)
β [deg]	93.372(8)
Volume [Å^3]	3148(3)
Z	4
μ [mm^{-1}]	0.989
Reflections collected	16229
Independent reflections	5093
Final R indices [$I \geq 2\sigma(I)$]	$R1 = 0.0518$, $wR2 = 0.1204$
R indices (all data)	$R1 = 0.0759$, $wR2 = 0.1307$

for $C_{28}H_{32}N_6O_{10.5}Cl_2In$: C 41.71, H 4.00, N 10.42; found C 41.31, H 3.90, N 10.32 %.

Crystal structure determination

A mounted crystal of **1** was placed in a cold nitrogen stream (Siemens LT-2) maintained at 110 K. A Siemens P4 four-circle diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the XSCANS software suite [43]. The structure was solved by Patterson synthesis, and refined to convergence [44]. The complex cation was disordered as two separate individuals disordered about the In(III), each with 50 % occupancy. One of the disordered individual cations is seen in Fig. 5. Details of the structure determination are given in Table 2, and bond lengths and angles of interest are given in Table 3.

CCDC 629926 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, *via* www.ccdc.cam.ac.uk/data_request/cif.

Computational method

The reaction energies (ΔE) were obtained by performing electronic structure calculations on the reactants and the products given in eq. (3). Ground state energies, E_{el}, optimized geometries and Hessians were calculated using the COSMO module of the density functional [45] software package DMol3 [29, 46, 47]. The exchange-correlation energy was approximated by the Becke-Tsuneda-Hirao gradient-corrected functional [48, 49]. Double numerical plus polarization basis sets, a 20 bohr cutoff and a fine integration grid were used in all calculations. The SCF convergence was set to 10^{-8} and convergence criteria for the gradient in geometry optimizations were set to 10^{-4} hartree per bohr. The calculations that included relativistic effects employed the all electron scalar relativity option available in DMol3 [50]. The Hessian was calculated numerically using central differencing to obtain the second derivatives. Vibration frequencies (ν_i) for each reactant and product were obtained from a normal mode analysis of the calculated Hessian matrix. For practical computational reasons, the COSMO calculations are not reported as ΔG values, but as changes in energy.

Table 3. Selected bond lengths and angles for [In(tpen)(CH_3-CO_2)](ClO_4)$_2 \cdot 0.5\,H_2O$.

In(1)–O(1)	2.247(18)	In(1)–N(4)	2.306(12)
In(1)–N(1)	2.329(12)	In(11)–N(61)	2.342(13)
In(1)–N(3)	2.356(9)	In(1)–N(2)	2.383(10)
In(1)–N(5)	2.410(11)	In(1)–N(6)	2.342(11)
O(1)–In(1)–N(4)	148.4(5)	O(1)–In(1)–N(1)	89.0(5)
N(4)–In(1)–N(1)	111.0(5)	O(1)–In(1)–N(6)	84.7(5)
N(4)–In(1)–N(6)	74.2(3)	N(1)–In(1)–N(6)	83.1(5)
O(1)–In(1)–N(3)	134.2(5)	N(4)–In(1)–N(3)	76.6(4)
N(1)–In(1)–N(3)	73.0(4)	N(6)–In(1)–N(3)	132.1(4)
O(1)–In(1)–N(2)	87.2(5)	N(4)–In(1)–N(2)	101.0(3)
N(1)–In(1)–N(2)	122.5(4)	N(6)–In(1)–N(2)	153.0(4)
N(3)–In(1)–N(2)	69.6(3)	O(1)–In(1)–N(5)	79.7(5)
N(4)–In(1)–N(5)	72.0(4)	N(1)–In(1)–N(5)	154.8(4)
N(6)–In(1)–N(5)	73.5(4)	N(3)–In(1)–N(5)	130.4(3)
N(2)–In(1)–N(5)	79.7(3)		

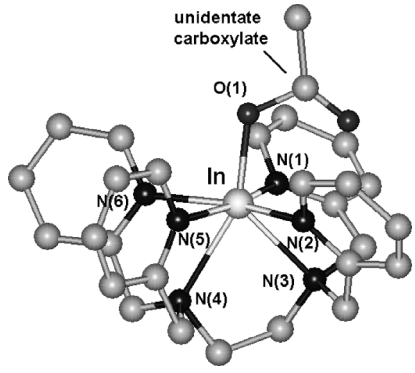


Fig. 5. Structure of the complex cation in [In(tpen)(CH_3 COO)](ClO_4)$_2 \cdot 0.5\,H_2O$, showing the numbering of the donor atoms coordinated to In(III). H-atoms omitted for clarity.

Results and Discussion

Electrochemical studies

In(III) is generally regarded as being an unfavorable metal ion for electrochemical studies [39], due to the weak signal that it gives in voltammograms. It was found, however, that upon addition of a ligand to the cell, the peak current for the metal ion peak increased considerably. This may be because the In^{3+} aqua ion has an extensive hydration sphere, which prevents it from approaching the electrode surface effectively so

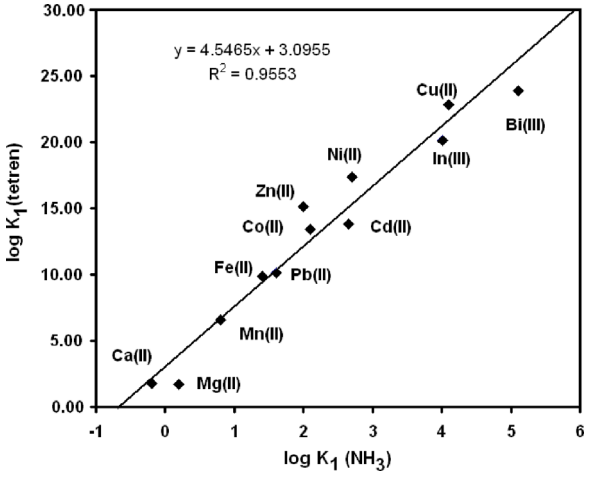


Fig. 6. Relationship between $\log K_1$ for tetren complexes (Ref. [26] and this work for In(III)) and $\log K_1(NH_3)$ for the same metal ions. The $\log K_1(NH_3)$ values are experimentally known [26], except for In(III) and Bi(III), which are predicted by eq. (1). The least squares best-fit line for the relationship is indicated, as well as the coefficient of determination (R^2) for the line.

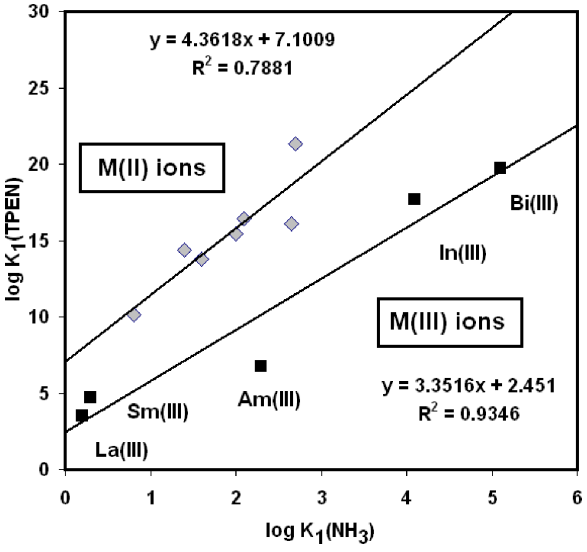


Fig. 7. Relationship between $\log K_1$ for tpen complexes (Ref. [26, 52], and [53] and this work for In(III)), and $\log K_1(NH_3)$ for the same metal ions. The $\log K_1(NH_3)$ values are experimentally known [26] for the M(II) ions, but for M(III) ions are predicted by eq. (1). The least squares best-fit lines for the relationships are indicated, as well as the correlation coefficients (R^2) for the lines.

as to be reduced. Upon coordination of a ligand, the size of the hydration sphere is decreased, allowing the metal ion to be more easily reduced. An alternative method used in a previous polarographic study [42] of indium complexes is to include 0.001 % gelatin in the electrolyte. This also gives an increased peak current, possibly because the gelatin coats the surface of the mercury drop and binds In(III), bringing it into contact with the surface of the Hg drop. The addition of In(III) to a gelatin solution was found to give a linear response for the peak current to as high as 2.0×10^{-4} M, much higher than the concentrations used in the titrations here. Upon addition of another ligand, the peak current decreases and the peak position moves more positive, preventing use of the Lingane equation. For the bpen titration, it was necessary to use gelatin, since upon addition of bpen to In^{3+} without gelatin, contrary to the previous titrations, the metal peak height decreased instead of increasing. In many of the titrations, the pH reached levels that would normally cause solubility problems for $In(OH)_3$, which has a log K_{sp} of approximately 10^{-37} [26]. However, no precipitate was observed in the titrations, possibly because there was so little free metal ion in solution that the kinetics of formation of solid hydroxides were very slow. This is supported by a previous study of crystal structures of group 13 metal ions with hexadentate ligands [10], where it was observed that the complexes of In^{3+} with bbpen were stable at both low and high pH based on ^1H NMR studies and molar conductivity of the complexes in solution.

The measured $\log K_1$ values for In(III) with the polyamines studied here support the idea [17 – 20] that In(III) has a high affinity for N-donors. In Fig. 6 is seen a correlation of $\log K_1$ for tetren complexes *versus* $\log K_1(NH_3)$ with the same metal ions. The $\log K_1$(tetren) values are all experimentally determined [26], including that reported here for In(III). It is seen that the In(III) value is consistent with the prediction [17 – 20] from eq. (1) of $\log K_1(NH_3) = 4.0$ for In(III). A similar correlation is obtained for the trien complexes, with the value of $\log K_1$(trien) = 14.43 being consistent with $\log K_1(NH_3) = 4.0$ for In(III). The $\log K$ values for In(III) with 1,10-phen, such as $\log K_1 = 6.44$, are considerably higher than a reported [51] set of $\log K$ values, such as $\log K_1 = 5.70$. The latter value was determined in 1.0 M SO_4^{2-}. $\log K_1$ for SO_4^{2-} with In(III) is 1.8 [26], so that the existence of In(III)/sulfate complexes should affect the measured value of $\log K_1$ with 1,10-phen.

In Fig. 7 is seen the correlation between $\log K_1$(tpen) and $\log K_1(NH_3)$ for both divalent and trivalent metal

ions. The $\log K_1$(tpen) values are for M(II) ions [26], for La(III), Sm(III), Am(III) [52], Bi(III) [53], and for In(III) from this work. The correlation here differs from that in Fig. 6 in that two separate relationships are obtained for M(II) and M(III) ions. This is found to be generally true. For a saturated N-donor such as tetren in Fig. 6, it appears that a single correlation between $\log K$ for the polyamine and for $\log K_1(NH_3)$ is found. However, when sp^2 hybridized N-donors from pyridyl groups are present in the ligand, the correlation is split into two based on the charge of the metal ion, as seen in Fig. 7. This is found to be generally true, as can be observed for correlations involving $\log K_1$ for ligands such as 1,10-phen or bpen studied here. It seems reasonable to assume that the lower $\log K_1$ values for M(III) as compared to M(II) ions with ligands containing pyridyl groups seen in Fig. 7 and other similar correlations, arises because the pyridyl groups are incapable of H-bonding to the solvent. H-bonding to the solvent should be more important for stabilizing complexes of M(III) ions than of M(II) ions, so that neutral pyridyl groups should have a more detrimental effect on the stability of complexes of M(III) ions than M(II) ions. Fig. 7 supports the idea [17 – 20, 52] that Am(III) is rather different from the Ln(III) (Ln = lanthanide) ions in its bonding, being more covalent ('softer'). This correlates with the predicted value [17 – 20] of $\log K_1(NH_3)$ of 2.7 for Am(III) compared to values from 0.2 to 0.7 for Ln(III) ions. It is interesting that the DFT calculations [27, 28] also predict a higher $\log K_1(NH_3)$ for Am(III) and Lr(III) than for Ln(III) ions, as discussed below.

Crystal structure of [In(tpen)(CH_3CO_2)](ClO_4)$_2$ · 0.5 H_2O

The $[In(tpen)(CH_3COO)]^{2+}$ cation is shown in Fig. 5. The fact that these crystals grew from aqueous solution supports the observation of an aqueous solution species involving In(III) and tpen by voltammetric methods. The In(III) centre is 7-coordinate in its complex with tpen, with an O-donor from an acetate anion completing the coordination sphere. The 6 N-donors of the tpen are all coordinated to the In(III) center. In–N bond lengths to saturated N-donors vary with coordination number, as shown by a search of the Cambridge Structural Database [25]. In conducting the search, structures where the In–N bonds involved N-alkyl groups such as methyl or *iso*-propyl groups were omitted, since bulky alkyl substituents that are not part of chelate rings lead to stretching of the M–L bond [54]. As seen in Table 4, the preferred coordination number for In(III) with such ligands appears to be 7, as found here for the In(III)/tpen complex. The In–N bond lengths to the saturated N-donors found here for the In(III)/tpen complex at an average length of 2.331 Å are a little shorter than the average found for other 7-coordinate complexes.

Table 4. Structures in the Cambridge Structural Database [25] of In(III) complexes with at least one chelate ring containing two neutral saturated N-donors, and no alkyl substituents that are not part of a chelate ring bonded to the N-donor. The number of structures found for each designated coordination number are indicated, as well as the average In–N bond lengths in the chelate ring for each coordination number.

Coordination number:	5	6	7	8	9
Number of structures:	1	6	17	4	0
In–N [Å]	2.27	2.31	2.39	2.42	–

DFT Calculations

In previous studies [27, 28] gas-phase energies of formation of complexes of ammonia calculated by DFT for eq. (3) correlated well with ΔG of formation of the corresponding complexes in aqueous solution calculated from the $\log K_1(NH_3)$ values [17 – 20, 26]. Separate LFERs were obtained for M(I) through M(IV) ions, and within the M(III) ions, separate LFERs appeared to be present for M(III) ions with C.N. ≥ 6. Of particular interest was that for all these LFERs, large intercepts were obtained. It was proposed that these intercepts reflected changes in solvation affecting the $\Delta G(aq)$ values, that are not modeled in eq. (3). In line with this proposal, it was found that the intercepts increased strongly with increasing charge on the metal ion, as would be expected if a greater number of H-bonding solvent molecules were displaced when a more weakly H-bonding NH_3 molecule displaced a coordinated H_2O molecule. One might assume that second sphere solvation of the $[M(H_2O)_6]^{n+}$ ion was much larger for metal ions of higher charge, and so replacement of a coordinated H_2O by a less strongly solvated NH_3 ligand would cause a greater drop in complex stability for M(IV) than for M(II) ions. In the hopes of including the effects of solvation, the energies of eq. (3) were re-calculated including the COSMO feature of DMol3, which carries out the calculations in a structureless medium of dielectric con-

M(II) ions:								
	Mg(II)	Ca(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Zn(II)	Cd(II)
ΔE	−4.280	−3.129	−7.522	−10.048	−10.334	−10.552	−11.146	−11.574
M(III) ions (C.N. = 6):								
	Al(III)	Cr(III)	Ga(III)	In(III)	Co(III)	Rh(III)	Ir(III)	Tl(III)
ΔE	−9.169	−14.532	−16.835	−17.602	−22.166	−25.050	−26.331	−23.611
M(III) ions (C.N. > 6):								
	La(III)	Y(III)	Sc(III)	Lu(III)	Lr(III)	Am(III)	Bi(III)	
ΔE	−4.346	−5.265	−6.264	−6.153	−11.347	−12.601	−15.106	
M(IV) ions:								
	Th(IV)	Zr(IV)	Hf(IV)	Pu(IV)	U(IV)	Pt(IV)		
ΔE	−6.160	−7.017	−7.606	−17.194	−17.147	−36.643		
M(I) ions[a]:								
	H(I)	Cu(I)	Ag(I)	Au(I)				
ΔE	−25.322	−11.322	−11.966	−25.613				

Table 5. DFT energies (ΔE) for reactions represented by eq. (3), calculated using the COSMO feature of DMol3 [46], which places the reactions in a structureless medium with the dielectric constant of water. Units are kcal mol^{-1}.

[a] Reaction for M(I) ions refers [27, 28] to $[M(H_2O)_2]^+ + NH_3 \leftrightarrows [M(H_2O)NH_3]^+ + H_2O$.

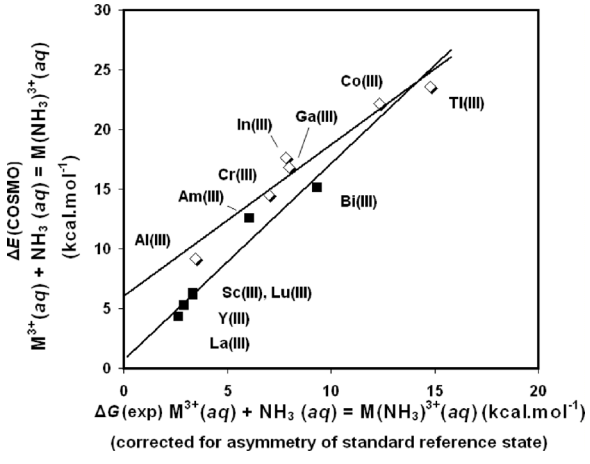


Fig. 8. Relationship between ΔE calculated by COSMO/DFT calculation, and ΔG experimental, for the formation of $M(NH_3)$ complexes of trivalent metal ions in aqueous solution. The two lines are for metal ions for which [27, 28] the aqua ions are 6-coordinate (◊), or more than 6-coordinate ■).

stant of the chosen solvent, in this case water. Using COSMO, only ΔE values can be obtained, since the required partition functions cannot be calculated. These energies are seen in Table 5. It was found that the use of COSMO ΔE values in place of the gas-phase ΔG values for eq. (3) had little influence on the occurrence of intercepts. This is seen for trivalent metal ions in Fig. 8. Again, it appears that there is a separation of M(III) ions based on whether the coordination number is greater than or equal to 6, although an argument could be made that a single LFER would be sufficient. An apparent separation by coordination number was also found [55] for the formation of hydroxo complexes from the M(III) hexa-aqua ions using DFT calculated gas-phase ΔE values. The LFERs of ΔE calculated using COSMO for all sets of metal ions, for M(I) through M(IV), differ little from those for ΔG calculated in the gas phase. This result suggests that one needs to include a set of specific water molecules in the second sphere [56], rather than use a simple structureless dielectric medium. Thus, future work will be aimed at incorporating a limited number of water molecules H-bonded to H_2O and NH_3 molecules in the inner coordination sphere of the $[M(H_2O)_6]^{n+}$ or $[M(H_2O)_5NH_3]^{n+}$ cations.

One factor not considered [27, 28] in drawing up these correlations is the asymmetry of the standard reference state [57]. By this is meant that in the normal reference state, the concentration of the solvent is expressed as unity, whereas the concentrations of all other species are expressed as molarity. In the DFT calculations of ΔG for the reaction represented by eq. (3) no solvent is included, so that this problem does not arise. One can remove the problem [57] of the standard reference state by expressing the concentrations as mole-fractions, which effectively adds the log of the molarity of the solvent, water ($\log 55.51$), to all the $\log K_1(NH_3)$ values used to calculate $\Delta G(NH_3)$. This correction reduces the size of the intercepts, but generally does not remove them. At this stage it is probably best to use correlations such as those in Fig. 8 as LFERs, which confirm or predict $\log K_1(NH_3)$ values estimated from eq. (1), much in the same way as do the LFER in Figs. 6 and 7. Future DFT calculations will be aimed at including specific H_2O molecules H-bonded in the outer-sphere of the metal aqua and ammonia complexes in order to understand the role of solvation of the complexes in complex formation.

Conclusions

1) The log *K* values determined in this work support the idea that In(III) has a high affinity for N-donor ligands, and that the difficulty of synthesizing and detecting the complexes of In(III) with polyamine ligands is due only to the high affinity of In(III) for the competing OH^- ligand. 2) The predictions of eq. (1) are validated by this research. 3) Ligands such as tpen, because of their high denticity and low protonation constants, are particularly well suited for complexing acidic metal ions such as In(III), and should form complexes of high stability with other very acidic metal ions such as Ga(III) or U(IV) that are predicted by eq. (1) to have high affinity for N-donor ligands. 4) The affinity of M(III) ions for pyridyl groups in polydentate ligands such as tpen or 1,10-phen is lower than might be anticipated from their affinity for saturated N-donors, which may be due to the inability of pyridyl groups to H-bond with the solvent. 5) DFT provides a powerful method for predicting formation constants of metal ions in aqueous solution. The relative insensitivity of the intercepts on LFERs such as in Fig. 8 to use the COSMO module of DMol3 to calculate energies of formation of ammonia complexes in a dielectric constant appropriate to water suggests that specific solvation by actual water molecules will have to be included to further advance understanding in this area.

Acknowledgements

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