The Affinity of Bismuth(III) for Nitrogen-donor Ligands

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Differential pulse polarography has been used to determine the formation constants of Bi^{3+} at ionic strength 0.5 mol dm^{-3} and 25 °C with the ligands glycine, trien (triethylenetetramine), bipy (2,2′-bipyridine), [15]aneN$_4$ (1,4,8,12-tetraazacyclopentadecane) and triethanolamine. The equilibria between Bi^{3+} and these ligands are established slowly on the polarographic time-scale, so that separate peaks occur in the differential pulse polarograms for free metal ion and complex, greatly simplifying calculation of the formation constants. Stability constant values (log K_1) for the complexes of Bi^{III} with these ligands were 10.0 (glycinate), 21.9 (trien), 4.5 (bipy) and 9.2 (triethanolamine). For the macrocycle [15]aneN$_4$, log K_1 ($M^{3+} + L \rightleftharpoons ML^{3+}$) = 23.5; for the equilibria $ML^{3+} + OH^- \rightleftharpoons ML(OH)^{2+}$ and $ML^{3+} + H^+ \rightleftharpoons M(HL)^{4+}$, values of log K were 8.5 and 3.5 respectively. These results are shown to be reasonable in terms of the formation constant log $K_1(NH_3)$ = 5.0 for Bi^{3+} predicted by a dual basicity equation developed previously.

Ligand design has become of considerable interest,[1] particularly in biomedical applications such as radiography,[2] positron emission tomography,[3] magnetic resonance imaging,[4] and cancer therapy.[5] Bismuth, as ^{212}Bi, shows promise in cancer therapy when attached *via* complexing ligands to monoclonal antibodies,[5] and bismuth(III) complexes are of interest in the treatment of gastric ulcers.[6] There is[7] very little in the way of formation constants for bismuth(III) complexes to allow for development of ligand design strategies. For example, what is the affinity of Bi^{III} for nitrogen donors and how will incorporating them into ligands affect complex stability with Bi^{III}

Attempts to understand Lewis acid–base behaviour in aqueous solution are of continuing interest.[8] Several predictions[1] suggest that the affinity of bismuth(III) for nitrogen donors is high. First, equation (1) can be used[9,10] to estimate log $K_1(NH_3)$ for Bi^{III}.

$$\log K_1 = E_A{}^{aq} \cdot E_B{}^{aq} + C_A{}^{aq} \cdot C_B{}^{aq} \qquad (1)$$

In equation (1), which is similar to the 'E and C' equation of Drago and Wayland,[11] E and C are the ionic and covalent contributions to the strength of the M–L bond, the subscript A denotes the contribution from the Lewis acid, and B denotes that from the Lewis base. The superscript 'aq' differentiates these parameters from those of Drago and Wayland, which apply to solvents and low relative permittivity rather than aqueous solution. The parameters in equation (1) are derived empirically, and, with substitution of the appropriate E and C values, equation (1) can be rearranged to give equation (2).

$$\log K_1(NH_3) = 0.881 \log K_1(OH^-) - 1.08 \log K_1(F^-) \qquad (2)$$

If log $K_1(OH^-)$ and log $K_1(F^-)$ are known for any metal ion, then log $K_1(NH_3)$ can be predicted to an accuracy for experimentally known log $K_1(NH_3)$ values of about 0.3 log units. From log K_1 = 12.9 for the OH^- complex of Bi^{III}, and log K_1 = 5.9 for the F^- complex,[7] a value of log $K_1(NH_3)$ of 5.0 is predicted.

A second approach[12] uses equations that model the chelate effect, such as in equation (3) below, that applies to n-dentate

$$\log K_1(\text{polyamine}) = 1.152 \log \beta_n(NH_3) + (n-1)\log 55.5 \qquad (3)$$

polyamines. Here the polyamine is, for example, ethylenediamine (en) (n = 2) or triethylenetetramine (trien) (n = 4), the factor of 1.152 is the inductive effect factor, and the (n − 1)-log 55.5 term is the entropy contribution[13] to the chelate effect. Equation (3) has been extended[12] to polyaminocarboxylates such as nitrolotriacetate (nta) or ethylenediaminetetraacetate (edta). Where log K_1 is known for several such polydentate ligands, then an estimate of log $K_1(NH_3)$ of *ca.* 5.0 can be obtained for Bi^{III}.

Ideas on Lewis acid-base interaction in aqueous solution, which can be traced through the Edwards equation,[14] the a and b type metal ions of Ahrland, Chatt and Davies,[15] to the hard and soft acids and bases (HSAB) of Pearson[16] may now be leading through equation (1) to a better understanding of such behaviour. We report here formation constants of complexes of Bi^{III}, determined by polarography, for its complexes with glycine, trien, 2,2′-bipyridine (bipy), 1,4,8,12-tetraazacyclopentadecane ([15]aneN$_4$) and triethanolamine, as tests of the various approaches discussed above.

Polarography has not been widely used in stability constant studies, perhaps because of greater convenience and simpler interpretation provided by glass electrode studies. However, glass electrode studies are not accurate below pH 2 because of junction potential problems, and are not useful for very acidic metal ions such as Bi^{3+}, which are extensively hydrolysed above pH 1.[7] Any ligand which will form a stable complex with Bi^{3+} must thus be able to do so below pH 1, or hydrolysis will occur instead. Polarography works well under acidic conditions, and is, moreover, convenient for the study of very acidic metal ions such as Bi^{3+}, because one can easily work with total metal ion concentrations of 10^{-6} mol dm^{-3}, which limit the precipitation of the solid hydroxide. A further convenient aspect of differential pulse polarography used here, is that,[17] where the rate of equilibration of the metal ion with the ligand is slow compared with the rate of reduction of the metal ion and its complexes at the surface of the mercury drop, separate peaks are observed for the different species, greatly facilitating the analysis of speciation.

Experimental

Materials.—The free ligands glycine, triethanolamine, bipy, and trien were obtained from BDH, [15]aneN$_4$ was obtained from Aldrich, and the ligands were used as received. Stock solutions in 0.5 mol dm^{-3} HNO_3, approximately 0.01 mol dm^{-3} in free ligand, were prepared, and used with the stock solution of

Table 1 Formation constants for bismuth(III) complexes with hydroxide and ligands studied in this paper[a]

Ligand	Equilibrium	log K	Ref.
OH^-	$H^+ + OH^- \rightleftharpoons H_2O$	13.74	7
	$Bi^{3+} + OH^- \rightleftharpoons Bi(OH)^{2+}$	12.36[b]	7
	$Bi^{3+} + 3OH^- \rightleftharpoons Bi(OH)_3$	31.9[b]	7
	$Bi^{3+} + 4OH^- \rightleftharpoons Bi(OH)_4^-$	32.8[b]	7
	$6Bi^{3+} + 12OH^- \rightleftharpoons [Bi_6(OH)_{12}]^{6+}$	164.95[b]	7
glycinate	$H^+ + L^- \rightleftharpoons HL$	9.54	7
	$HL + H^+ \rightleftharpoons H_2L^+$	2.36	7
	$Bi^{3+} + L^- \rightleftharpoons BiL^{2+}$	10.0(1)	This work
	$BiL^{2+} + OH^- \rightleftharpoons BiL(OH)^+$	9.8(1)	This work
bipy	$H^+ + L \rightleftharpoons HL^+$	4.51	7
	$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	1.5	7
	$Bi^{3+} + L \rightleftharpoons BiL^{3+}$	4.5	This work
trien	$H^+ + L \rightleftharpoons HL^+$	9.87	7
	$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	9.21	7
	$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+}$	6.87	7
	$H_3L^{3+} + H^+ \rightleftharpoons H_4L^{4+}$	3.71	7
	$Bi^{3+} + L \rightleftharpoons BiL^{3+}$	21.9(1)	This work
	$Bi^{3+} + L + H^+ \rightleftharpoons Bi(HL)^{4+}$	25.0(1)	This work
	$BiL^{3+} + OH^- \rightleftharpoons BiL(OH)^{2+}$	8.0(1)	This work
triethanolamine	$H^+ + L \rightleftharpoons HL^+$	7.90	7
	$Bi^{3+} + L \rightleftharpoons BiL^{3+}$	9.2(1)	This work
	$BiL^{3+} + OH^- \rightleftharpoons BiL(OH)^{2+}$	10.3(1)	This work
ampy	$Bi^{3+} + L \rightleftharpoons BiL^{3+}$	9.6(1)	18
thpen	$Bi^{3+} + L \rightleftharpoons BiL^{3+}$	12.0(1)	18
[15]aneN_4	$H^+ + L \rightleftharpoons HL^+$	11.1	7
	$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	10.3	7
	$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+}$	5.23	7
	$H_3L^{3+} + H^+ \rightleftharpoons H_4L^{4+}$	3.62	7
	$Bi^{3+} + L \rightleftharpoons BiL^{3+}$	23.5	This work
	$BiL^{3+} + OH^- \rightleftharpoons BiL(OH)^{2+}$	8.5	This work
	$BiL^{3+} + H^+ \rightleftharpoons Bi(HL)^{4+}$	3.5	This work

[a] At 25 °C, ionic strength 0.5 mol dm^{-3}. [b] Actually reported at ionic strength 1.0 mol dm^{-3}, but used as a reasonable approximation, since none has been reported[1] at ionic strength 0.5 mol dm^{-3} for bismuth(III) hydroxide complexes.

bismuth, which was 0.001 mol dm^{-3} $Bi(NO_3)_3$ in 0.5 mol dm^{-3} HNO_3, to make up solutions used in the polarography. The pH values of the solutions in the cell were adjusted upwards with a solution of, typically, 0.5 mol dm^{-3} NaOH to a value of *ca.* pH 2, and then 0.1 mol dm^{-3} NaOH in 0.4 mol dm^{-3} $NaNO_3$ to obtain higher pH values.

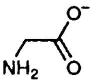
Instrumentation.—Polarograms were recorded on a Metrohm 626 POLARECORD fitted with a 626 VA stand in differential pulse mode. A multi-mode electrode (Metrohm) was employed as the working electrode, and used in the dropping mercury electrode mode with a drop time of 1 s and a pulse amplitude of 50 mV. Experiments were carried out in a three electrode system with a saturated calomel electrode and a glassy carbon electrode (both Metrohm) used as reference and auxiliary electrodes respectively. The pH of the solutions was measured to within 0.002 pH units with a PHI 72 pH-meter (Beckman). The temperature of the cell was controlled, to 25.0 ± 0.1 °C.

Polarography.—In a typical run, the cell contains Bi^{3+} (10^{-4}–10^{-6} mol dm^{-3}) with ligand added to give ligand : bismuth ratios from 1 : 1 to 1000 : 1, all in 0.5 mol dm^{-3} HNO_3. For each ligand, a minimum of three widely differing ligand : bismuth ratios were used to aid in establishing the correct species model. After recording a polarogram, the pH of the solution would be adjusted upwards in steps of about 0.1–0.2 pH units, by addition of NaOH solution from a microburette graduated to 0.01 cm^3, and a new polarogram recorded. In this way a set of polarograms of the species present in the solution as a function of pH was obtained. For each ligand with Bi^{III}, typically four different ligand : metal ratios ranging from 1000 : 1 to 1 : 1 were studied, and between 10 and 20 polarograms were obtained at a range of pH values for each different ligand : metal ratio. Polarograms of the ligand alone as a function of pH, to identify ligand peaks on the polarogram, were also run for each ligand. Equilibration of the metal–ligand solutions occurred within a few minutes, except for the macrocycle [15]aneN_4. Here solutions of metal and ligand at different ratios and pH values were prepared in stoppered flasks, and kept at 25 °C. Polarograms were recorded from time to time, and it was found that after two to three weeks the solutions had equilibrated.

Calculation of Formation Constants.—A computer program METSPEC[18] was written for the IBM PC that allowed for correction for the hydrolysis of Bi^{3+} to give species such as $Bi(OH)^{2+}$ or $[Bi_6(OH)_{12}]^{6+}$ reported[7] in solutions of Bi^{III}. The program essentially solves the appropriate mass-balance equations incorporating the estimated formation constants for the Bi^{III}–ligand complexes thought to be present in solution [equation (4)], where x is the number of metal atoms M in the

$$M_{total} = \Sigma M_x L_y H_z \qquad (4)$$

solution species, y is the number of ligands L present, and z is the number of protons H (a hydroxide is a negative proton, *i.e.* $z = -1$). For hydroxo complexes such as $Bi(OH)^{2+}$ ($x = 1$, $y = 0$, $z = -1$) the known[7] formation constants were kept fixed in solving the mass balance equation. The predicted species distribution with trial values of the unknown formation constants and the relevant solution concentrations and pH were then compared with those indicated by the polarograms, and the formation constants adjusted to give as close a fit as possible. The criterion for which species were present was then simply, as is usual in stability constant studies, which model fitted the data best. Types of model tried included species such as BiL, BiL_2, BiL(OH) and Bi(HL). Peak currents rather than integrated peak currents were used as a measure of



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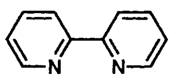

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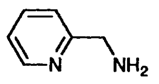

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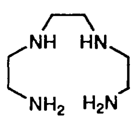

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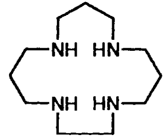
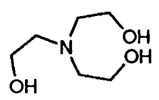


[15]aneN$_4$



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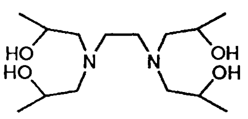
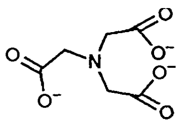
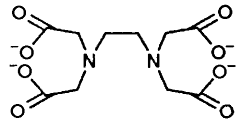


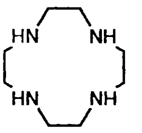
thpen



nta



edta



[12]aneN$_4$

concentration. No evidence for adsorption effects or kinetic effects was observed in the polarograms.

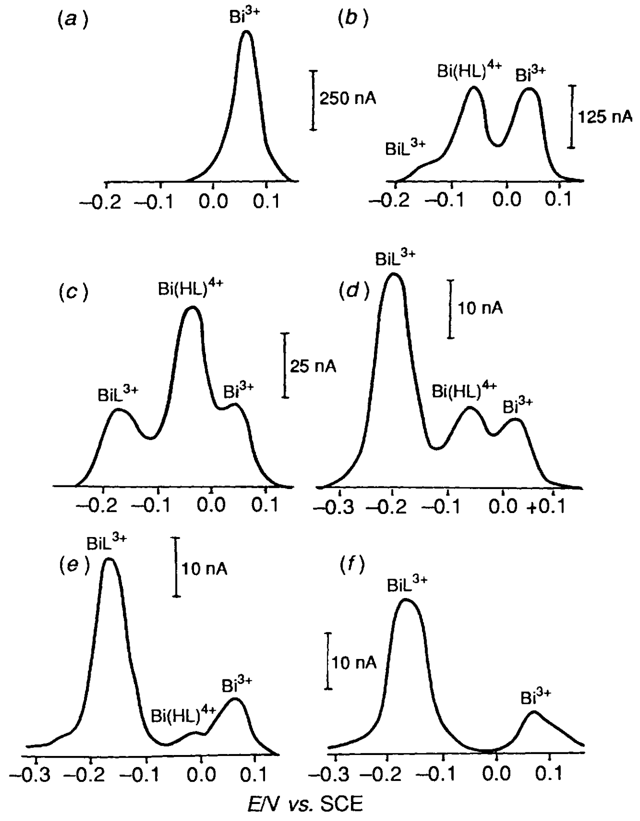


Fig. 1 Differential pulse polarograms [(*a*)–(*f*)] for the Bi^{3+}–[15]aneN$_4$ system, as a function of pH. The vertical scale indicated by a bar on each polarogram corresponds to the current shown. The peaks correspond to the solution species Bi^{3+}, $[Bi([15]aneN_4)]^{3+}$, and $[Bi(H[15]aneN_4)]^{4+}$ as indicated, although, as discussed in the text, the Bi^{3+} peak represents bismuth(III) hydroxide species as well. Thus, above pH 2, the Bi^{3+} peak refers exclusively to a mixture of bismuth hydroxy species, and above pH 4 at the BiL^{3+} peak also refers to some $BiL(OH)^{2+}$ present. The concentration of [15]aneN$_4$ in solution (*a*) is 7.315×10^{-3} mol dm^{-3}, $[Bi^{3+}] = 7.975 \times 10^{-5}$ mol dm^{-3} and $[HNO_3] = 0.5018$ mol dm^{-3}. The other polarograms (*b*)–(*f*) represent this same solution with 0.5 or 0.1 mol dm^{-3} NaOH in 0.4 mol dm^{-3} $NaNO_3$ added; pH 1.0 (*a*), 2.55 (*b*), 3.58 (*c*), 4.05 (*d*), 4.46 (*e*) and 5.18 (*f*)

Results and Discussion

In Table 1 are seen the formation constants for the Bi^{3+} complexes of glycine, triethanolamine, bipy, trien and [15]-aneN$_4$ determined here. Also included are log K_1 values for Bi^{III} with 2-aminomethylpyridine (ampy), and tetrakis(2-hydroxypropyl)ethylenediamine (thpen), which have been reported elsewhere.[18] In Fig. 1 is shown a selection of polarograms for Bi^{3+} with [15]aneN$_4$ at different pH values. The rate of equilibration of the metal ion with all the ligands to form the complex appeared to be slow relative to the rate of reduction at the mercury electrode, which leads[17] to the observation of separate peaks for each species present in solution. One must take care in analysing the results, however, as equilibria involving the proton, such as the formation of M(HL) or ML(OH) complexes from ML complexes, may be rapid, leading to a single peak representing both species. The differential pulse polarograms behave rather like spectra, and it is in principle a simple matter to calculate formation constants from them. The diffusion coefficients of the species involved at different potentials are analogous to the absorption coefficients at different energies in a UV/VIS spectrum. One should, ideally, obtain diffusion coefficients for each species in the polarogram. However, the problem of the diffusion coefficients of the complex species is removed if one uses only the metal species peak to calculate the formation constants, with the concentration of the complex species being calculated by difference. It should also be considered that the single peak assigned as 'Bi^{3+}' in Fig. 1 is a composite peak, representing a mixture of $Bi_x(OH)_y^{(3x-y)+}$ species in accord with the predictions of the program METSPEC. The overall decrease in peak height apparent in (*a*)–(*f*) in Fig. 1 is due to dilution of the solution as base was added to raise the pH. Where overlap of a small peak with a large peak was considerable, the height of the smaller peak was estimated by assuming the larger peak to be symmetrical, with the contribution of the larger peak to the observed current at the potential at which the maximum of the smaller peak occurred being subtracted.

The polarograms for the [15]aneN$_4$ complex of Bi^{III} in Fig. 1 are of interest. The first complex peak to appear has been assigned as an M(HL) species. At higher pH values, a second peak appears, which we assign as the ML peak. This assignment is based on goodness of fit. The third peak, however, persists up to pH values above 8, where METSPEC shows precipitation of $Bi(OH)_3(s)$ should occur, which does not happen, even after a few weeks. This supports the fact that the fit is better if this third peak is ascribed to both a ML and a ML(OH) species. Incorporation of the ML(OH) species in METSPEC also shows why precipitation of bismuth hydroxide does not occur at higher pH values. A single peak is observed for ML and ML(OH) because the loss of a proton from a co-ordinated water on ML to give ML(OH) is fast on the polarographic time-scale. No rupture or formation of a Bi–L bond is involved. In contrast, the equilibrium involving BiL and Bi(HL) is slow on the polarographic time-scale, since formation and rupture of a Bi–N bond must be involved on deprotonating and protonating the co-ordinated [15]aneN$_4$ ligand respectively. Further evidence for the involvement of a rapid deprotonation equilibrium here is the fact that at higher pH values the peak shifts with a slope of approximately 59 mV per decade. The above analysis of the [15]aneN$_4$ system with Bi^{III} demonstrates the power of differential pulse polarography as a tool for studying metal–ligand systems in aqueous solution.

The chemistry of bismuth has been largely neglected. In the seven volume *Comprehensive Coordination Chemistry*,[19] bismuth receives a mere fifteen pages. Recently, Rogers *et al.*[20,21] have determined crystal structures of complexes of Bi^{III} with polyethylene glycols, and structures of complexes of Bi^{3+} with

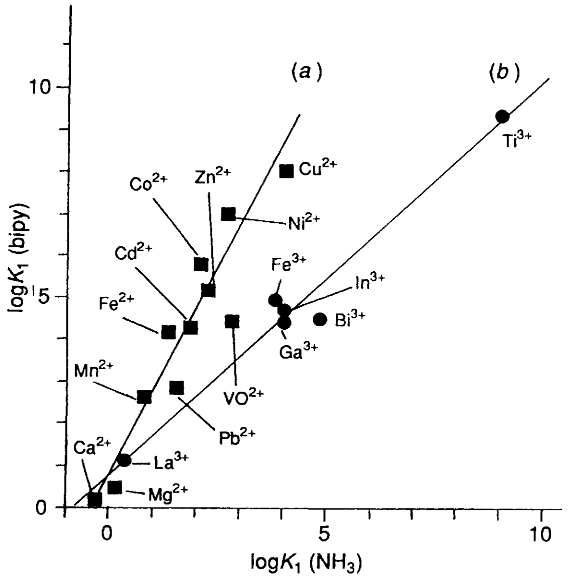


Fig. 2 The relationship between log K_1(bipy) and log K_1(NH$_3$) for divalent (■) and trivalent (●) metal ions. Data from refs. 1 and 7 and this work

crown ethers have been reported.[20,22,23] However, almost nothing is known about complexes of Bi^{3+} with nitrogen-donor ligands. We may check the predictions of the 'E and C' equation developed previously,[9,10] that logK_1 = 5.0 for Bi^{III}, against expectations from other types of correlation developed for estimating the formation constants of nitrogen-donor containing ligands.

Equation (3) works well for divalent metal ions. When only log K_1 is known for the NH$_3$ complexes of a metal ion, it becomes necessary to estimate the stepwise decrease in formation constant, λ (= log K_n − log K_{n-1}), in order to use it to predict formation constants for polyamines. For divalent metal ions it was found that a constant value of λ of 0.5 was satisfactory. If we use this combined with log K_1(NH$_3$) = 5.0, we predict log K_1 for trien with Bi^{III} to be 24.8. This is somewhat higher than our measured value of 21.9 reported here, although not in bad agreement if we consider that the value of 24.8 for the trien complex is in effect predicted from a knowledge of log K_1 for the F$^-$ and OH$^-$ complexes of Bi^{III}. It may be, and more investigation is required here to establish this point, that λ obtained from equation (3) for trivalent metal ions should be somewhat larger. A value of λ of 0.9 for Bi^{III} in equation (3) would give log K_1 = 22.0 for the trien complex of Bi^{III}. Since it appears from molecular mechanics studies[24] that the physical significance of λ in equation (3) may be the build-up of steric strain in forming the complex, it is not unreasonable that this might be more severe for trivalent than divalent metal ions. This is approximately what is found[1] for λ in versions of equation (3) that apply to aminocarboxylate ligands such as edta.

The chelate effect equation for polyaminocarboxylates predicts log K_1 = 11.3 for Bi^{III} with glycine at infinite dilution. Our measured value of 10.0 is at ionic strength 0.5 mol dm^{-3}. We may correct this to infinite dilution by application of the Davies[25] form of the extended Debye–Hückel equation, which indicates that the measured value at infinite dilution would be 10.9. This reasonable agreement with the predicted value of 11.3 is a validation of the chelate effect equation developed earlier,[12] and further supports the estimate of log K_1(NH$_3$) = 5.0 for Bi^{III}.

In Fig. 2 is seen a plot of log K_1(bipy) *versus* log K_1(NH$_3$) for a selection of metal ions. It is immediately apparent that trivalent metal ions show a lower affinity for 2,2′-bipyridine than do divalent metal ions, relative to their affinity for ammonia. The value of log K_1(bipy) of 4.5 here is seen to be reasonable in relation to results for other trivalent metal ions. It is not clear why trivalent metal ions should show this relatively lower affinity for bipy. One possibility is that the nitrogen donors of bipy, being effectively tertiary nitrogens, are incapable of hydrogen bonding to the solvent. Hydrogen bonding stabilizes[10] complexes by distributing the charge on the metal ion to the solvent, which is not possible for bipy, which has no N–H hydrogens. Possibly this effect is more important for complexes of trivalent than of divalent metal ions.

Triethanolamine shows a very high formation constant with Bi^{III}, with log K_1 = 9.2, as compared with log K_1(NH$_3$) = 5.0. Most metal ions show little change in log K_1[7] in passing from the ammonia to the triethanolamine complex. However, it has been shown[26] that for very large metal ions, addition of neutral oxygens donors, such as on N-2-hydroxyalkyl groups, to amines produces large increases in log K_1 as compared with the unsubstituted amine. Octahedral Bi^{III} has an ionic radius[27] of 1.03 Å, which makes it fairly large, so that the high formation constant of the triethanolamine complex may not be unreasonable.

The measured value of log K_1 = 23.5 for [15]aneN$_4$ with Bi^{III} can be compared with values for other metal ions, which show that in relation to log K_1 for ammonia, the Bi^{III} value is reasonable (formation constants for complexes of Zn^{II}, Ni^{II} and Cu^{II} are taken from ref. 7, the values for Bi^{III} are from this work).

Metal ion	Zn^{II}	Ni^{II}	Cu^{II}	Bi^{III}
log K_1(NH$_3$)	2.18	2.7	4.1	5.0
log K_1([15]aneN$_4$)	15.0	18.4	24.4	23.5

One might have expected from the higher value of log K_1(NH$_3$) that log K_1 for [15]aneN$_4$ with Bi^{III} might have been somewhat higher. However, extensive work has shown[28] that the complexes of larger metal ions are destabilized relative to those of smaller metal ions by the presence of six-membered chelate rings rather than five-membered chelate rings. The complex of the large Bi^{3+} ion is thus likely to be destabilized by the presence of three six-membered chelate rings. The picture for Bi^{III} with tetraaza macrocycles will become clearer as our studies of other members of the series are completed. Work in progress shows that the [12]aneN$_4$ (1,4,7,10-tetraazacyclododecane) complex of Bi^{III}, which forms only five-membered chelate rings, is of very high stability, in support of the above suggestion.

The results reported here show that Bi^{III}, as expected from the predicted[9,10,12] value of log K_1(NH$_3$) = 5.0, belongs to the group of heavy post-transition metal ions, such as Cd^{II}, Hg^{II}, Ag^{I}, Pb^{II} and, as will be discussed in a future paper, Tl^{III}, that have a good to high affinity for nitrogen-donor ligands in aqueous solution. In attempts to design ligands selective for Bi^{III}, one should thus bear in mind that Bi^{III} has, in fact, a high affinity for nitrogen-donor ligands, and that incorporation of nitrogen donors into ligands should enhance both bismuth(III) complex stability and selectivity relative to most other metal ions.

Acknowledgements

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References

1 R. D. Hancock and A. E. Martell, *Chem. Rev.*, 1989, **89**, 1875.
2 S. W. Schwarz and M. J. Welch, in *Applications of Enzyme Biotechnology*, eds. J. W. Kelly and T. O. Baldwin, Plenum, New York, 1991.
3 M. E. Phelps, J. C. Mazziota and H. R. Schelbert (Editors), *Positron Emission Tomography and Autoradiography: Principles and Applications for the Brain and Heart*, Raven Press, New York, 1986.

4 R. B. Lauffer, *Chem. Rev.*, 1987, **87**, 901.
5 R. W. Kozak, T. A. Waldmann, R. W. Atcher and O. A. Gansow, *Trends Biotechnol.*, 1985, **4**, 259.
6 G. F. Baxter, *Chem. Br.*, 1992, **28**, 445.
7 A. E. Martell and R. M. Smith, *Critical Stability Constants*, Plenum, New York, vols. 1–6, 1974, 1975, 1976, 1977, 1982, 1989.
8 W. B. Jensen, *The Lewis Acid-Base Concepts*, Wiley, New York, 1980.
9 R. D. Hancock and F. Marsicano, *Inorg. Chem.*, 1978, **17**, 560.
10 R. D. Hancock and F. Marsicano, *Inorg. Chem.*, 1980, **19**, 2709.
11 R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, 1965, **87**, 3571.
12 R. D. Hancock and F. Marsicano, *J. Chem. Soc., Dalton Trans.*, 1976, 1096.
13 A. W. Adamson, *J. Am. Chem. Soc.*, 1954, **76**, 1578.
14 J. O. Edwards, *J. Am. Chem. Soc.*, 1954, **76**, 1540.
15 S. Ahrland, J. Chatt and N. R. Davies, *Q. Rev. Chem. Soc.*, 1958, 12.
16 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.
17 J. Inczédy, *Komplex Egyensúlok Analtikai Alkalmazása*, Müsaki Könyvkiadó, Budapest, 1970.
18 R. D. Hancock and I. Cukrowski, unpublished work.
19 *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, London, 1987, vols. 1–7.
20 R. D. Rogers, A. H. Bond and S. Aguinaga, *J. Am. Chem. Soc.*, 1992, **114**, 2960.
21 R. D. Rogers, A. H. Bond, S. Aguinaga and A. Reyes, *J. Am. Chem. Soc.*, 1992, **114**, 2967.
22 N. W. Alcock, N. Ravindran and G. R. Willey, *J. Chem. Soc., Chem. Commun.*, 1989, 1063.
23 M. G. B. Drew, D. G. Nicholson, I. Sylte and A. Vasudevan, *Inorg. Chim. Acta*, 1990, **171**, 11.
24 R. D. Hancock, G. J. McDougall and F. Marsicano, *Inorg. Chem.*, 1979, **18**, 2847.
25 C. W. Davies, *J. Chem. Soc.*, 1938, 2093.
26 R. D. Hancock, in *Perspectives in Inorganic Chemistry*, eds. A. P. Williams, C. Floriani and A. E. Merbach, VCH, Weinheim, Verlag Helvetica Chimica Acta, Basel, 1992, 129.
27 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
28 R. D. Hancock, *J. Chem. Educ.*, 1992, **69**, 615.

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