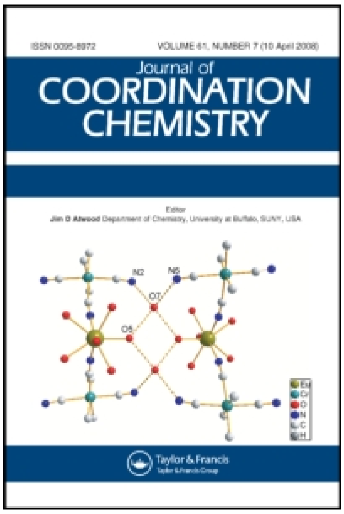

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THE AFFINITY OF LEAD(II) FOR NITROGEN-DONOR LIGANDS

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The following formation constants are reported for lead(II) with imidazole (Im) at 25°C in 0.5 M $ImHNO_3$: $\log K_1$ 1.10 ± 0.04, $\log K_2$ 0.99 ± 0.04. The pK_a of Im in 0.5 M $ImHNO_3$ at 25°C is 6.972 ± 0.003. $\log K_1$ for lead(II) with Im is fairly close to $\log K_1$ (NH_3) 1.6 for lead(II) predicted using a model of the chelate effect based on the asymmetry of the standard state. Since $\log K_1$(Im) and $\log K_1$ (NH_3) for any one metal ion are invariably close together, the agreement in $\log K_1$ for the lead(II) Im and NH_3 complexes indicates that the model can be used to estimate the formation constants of complexes that cannot exist in water because of hydrolysis.

INTRODUCTION

For the majority of metal ions, it is not possible to determine the formation constants of their complexes in water with ligands such as ammonia, because these are hydrolysed to give the metal hydroxide plus ammonium ion. In a recent paper[1] it was shown that the stabilities of such complexes could be estimated from equations which relate the formation constants of the complexes of polydentate ligands with those of their unidentate analogues. The formation constants, $\log K_1$, of the complexes of ligands such as 1,2-diaminoethane (en), 2,2′-iminobis(ethylamine) (dien), ethylenebis(2′-aminoethylamine) (trien), and 1,4,7,10,13-pentaazatridecane (tetren), are related to the ammonia formation constants with the same metal ion by[1]

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

The $(n - 1)\log 55.5$ term is the contribution from the asymmetry of the standard reference state,[2] where n is the number of donor atoms on the polydentate ligand. The factor of 1.152 takes into account the fact that the electron-donating properties of the alkyl bridges of polyamines are not present in ammonia, and is derived from $pK_a(CH_3NH_2)/pK_a(NH_3)$. The reason[1] that the formation constants of alkylamine complexes are not much higher than those of the analogous ammonia complexes is that the steric hindrance found in alkylamine complexes is not present in complexes of ammonia, or complexes of polyamines containing five-membered rings. In Figure 1, not reproduced in the original paper, $\log K_1(\text{polyamine}) - (n - 1)\log 55.5$ has been plotted against $\log \beta_n(NH_3)$ for all the metal ions for which formation constant data on such

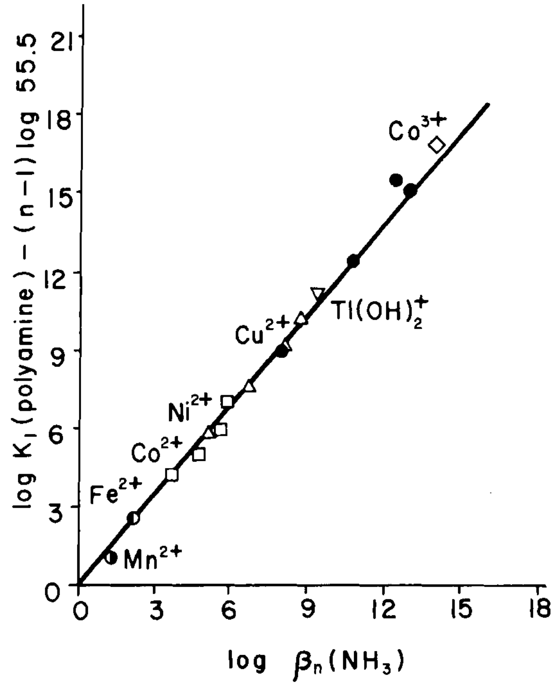

FIGURE 1 Plot of $\log K_1$ (polyamine) − $(n - 1)\log 55.5$ against $\log \beta_n(NH_3)$ for several metal ions: Mn^{II}(◑), Fe^{II} (◐), Co^{II} (□), Ni^{II} (△), Cu^{II} (●), $Tl(OH)_2^+$ (▽), Co^{III} (◇). The point at lowest stability for each metal ion is the en complex, and at successively higher stabilities are the dien, trien, and tetren complex.

complexes is available. The line drawn in has the theoretical slope of 1.152.

For a metal ion such as lead(II), although no formation constants with ammonia are reported, formation constants of the complexes with trien,[3] $\log K_1$ 10.4, and tetren,[4] $\log K_1$ 10.9, have been reported, from which $\log \beta_4(NH_3)$ 4.5 and $\log \beta_5(NH_3)$ 3.4 can be calculated for lead(II) using equation (1). If a value of λ, the logarithm of the ratio of successive formation constants, i.e. $\log K_n - \log K_{(n+1)}$, is estimated as 0.4, $\log K_1(NH_3)$ for lead(II) should be 1.6. This value is consistent with the hydrolysis of lead(II) ammonia complexes by water, since reaction (2) should proceed with a reaction constant of $\log K = 0$

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

taking $\log K_1(Pb(OH)^+) \sim 6.4$, $pK_a(H_2O)$ 14, and $pK_a(NH_4^+)$ 9.2. The $Pb(NH_3)^{2+}$ will in fact be even more decomposed than suggested by equation (2) if one considers the low solubility of lead hydroxide with $K_{so} - 16$.

Examination of the literature shows that the formation constants of imidazole (im) complexes are close to those of their ammonia analogues while, perhaps anomalously, the pK_a of imidazole at 6.9 is very much lower than the pK_a of ammonia. This renders the $Pb(im)^{2+}$ complex very much more resistant to hydrolysis, as can be seen by substituting im for ammonia in equation 2, with the reaction constant now being 2.3 log units to the left. As a check on the reliability of equation 1 for estimating the formation constants of hydrolysis-prone ammonia complexes, it was decided that a study of the lead(II) imidazole complexes would be undertaken.

EXPERIMENTAL

Materials

Extra pure lead nitrate was obtained from KANTO Chemical Co., and "guaranteed" imidazole from Merck. These were used for the preparation of the respective 0.1667 M and 0.100 M stock solutions. The imidazolinium nitrate used to adjust the ionic strength to 0.50 was prepared by adding the required quantity of nitric acid and imidazole, and then adjusting the pH according to the pK_a of imidazole.

Experimental Procedure

The system was studied potentiometrically in an Ingold titration cell thermostatted to 25°C. Nitrogen was bubbled through the solutions to exclude CO_2. Potentials were recorded on a Radiometer pHM 64 research pH meter, using an Ingold glass electrode, and a Ag/AgCl reference electrode consisting of a silver wire coated with silver chloride dipping into a reference solution that was 0.01 M NaCl + 0.49 M $NaNO_3$. A drop of $Ag(NO_3)$ solution was added to the reference electrode to ensure saturation with AgCl. The reference electrode was connected to the solution in the titration cell by way of a salt bridge containing 0.5 M $NaNO_3$.

$ImHNO_3$ was used to adjust the ionic strength to 0.5 M in order to minimise hydrolysis of the Pb^{2+}. The standard electrode potential, E°, for the cell was determined from the e.m.f. values obtained from the titration of a 0.05 M solution of HNO_3 in 0.45 M $ImHNO_3$ into 0.50 M $ImHNO_3$. Deprotonation of the ImH^+ at the start of the titration was corrected for using the HALTAFALL facility of the LETAGROP[5] suite of computer programs. The pK_a of imidazole in 0.50 M $ImHNO_3$ was determined by titrating 20 ml of 0.50 M $ImHNO_3$ with a solution containing 0.10 M Im in 0.50 M $ImHNO_3$. Additions were made from a Mettler automatic piston burette graduated to 0.01 ml. The same procedure was used for e.m.f. measurements on the Pb^{2+} – Im system, the concentration of Pb(II) in the system being ca. 3.3×10^{-2} M.

RESULTS

The pK_a of imidazole and the formation constants of the lead(II) im complexes were calculated using the program LETAGROP.[5] The values obtained are: $pK_a(im) = 6.972 \pm 0.003$ and $\log K_1 = 1.10 \pm 0.04$, $\log K_2 = 0.99 \pm 0.04$ for the lead(II) imidazole complexes. A value of $\log K_3 = -0.59$ was indicated by the program, which is probably not significant because such low concentrations of this complex were present. The standard deviations quoted above are three times the value of σ indicated by the program, which then corresponds to a 95% confidence limit.

It is difficult in glass electrode experiments to distinguish between hydroxy species and ligand species being formed, since the consequence of both reactions for the observed pH is the same. Normally, fixing the known values of the formation constants overcomes this problem. However, for lead(II), log K for the formation of the dominant hydroxy species, $PbOH^+$, is somewhat uncertain, since the values reported[6] span a range of from $\log K_1$ 6.2 to 7.2. In order to see whether the values of $\log K(\text{Im})$ determined for lead(II) were cross-correlated with $\log K_1(\text{Pb(OH)}^+)$, the $\log K(\text{Im})$ values were refined with each of a series of $\log K_1(\text{Pb(OH)}^+)$ values representative of the range. No cross-correlation was found, except that at the upper extreme of the range $\log K_1$ was affected to an extent of 5%, and $\log K_2$ to an extent of 1%, which is not considered to be significant.

DISCUSSION

A selection of $\log K_1(\text{Im})$ values for several metal ions, with $\log K_1(NH_3)$ for comparison, is seen below. It is seen that $\log K_1(\text{Im})$ for lead(II) agrees with $\log K_1$ for its ammonia complex estimated from equation 1 reasonably well in comparison with the other metal ions. Constants are from reference 6.

	Pb^{II}	Ag^{I}	Cu^{II}	Ni^{II}	Co^{II}	Zn^{II}	Mn^{II}
$\log K_1(\text{Im})$	1.1	3.2	4.3	3.1	2.5	2.6	1.7
$\log K_1(NH_3)$	1.6	3.3	4.2	2.8	2.2	2.3	0.8

The value of $\log K_1$ 1.6 for lead(II) with ammonia is estimated in several ways other than equation 1. Other equations were developed[1] which relate the stabilities of complexes of aminocarboxylate ligands (e.g. glycine (Gly), or (ethylenedinitrilo)tetraacetate (edta)) to the stabilities of the acetate (CH_3COO^-) and ammonia complexes:

$$\log K_1(\text{aminocarboxylate}) = 1.152 \log\beta_n(NH_3) + m \log K_1(CH_3COO^-) - \left(\sum_{i=1}^{m} i\right)\lambda' + (n + m - 1)\log 55.5 \qquad (3)$$

Equation 3 is appropriate to complexes of aminocarboxylate ligands with n nitrogen-donor groups, and m carboxylate groups. The principle here is the same as used in the derivation of equation 1, except that λ', which is λ appropriate to negatively charged oxygen-donor groups (phenolate or carboxylate), is an adjustable parameter. Because the large values of λ found for charged ligands are supposedly due to mutual electrostatic repulsion of the charges, which is no longer so important when the groups are held together in a single polydentate ligand, λ' is adjusted downwards in the polydentate ligand from the larger values found in the acetate complexes themselves. It is found empirically that if λ' is set equal to 0.175 $\log K_1(CH_3COO^-)$ for all metal ions, the formation constants of amino-carboxylate complexes can be predicted satisfactorily. Thus, for example, from $\log K_1(CH_3COO^-)$ 2.68 for lead(II),[7] using the estimated $\log K_1(NH_3)$ 1.6 we can estimate lead(II) formation constants with aminocarboxylate ligands as follows: $\log K_1(\text{Gly})$ 5.8 (observed[8] 5.5), $\log K_1(\text{NTA})$ 12.2 (NTA = nitrilotriacetate, observed[9] 11.8), $\log K_1(\text{EDDA})$ 12.3 (EDDA = ethylenediamine-*N*,*N*-diacetate, observed[10] 12.2), and $\log K_1(\text{edta})$ 18.0 (observed[11] 18.0).

Ligands such as bipyridyl form lead(II) complexes, so that one might expect to be able to predict $\log K_1$ for lead(II) with pyridine using an equation analogous to 1, with bipy formation constants in the place of en constants. However, the stabilities of pyridine complexes so predicted are always much higher than observed. The anomalously high stability of bipy complexes which this implies is not[12] due to electronic delocalisation over the chelate ring, since the same anomalously high stability is observed in the complexes of 2-aminomethylpyridine (amp), in which such delocalisation cannot occur. That pyridyl groups in bipy complexes are electronically equivalent to those in amp complexes is seen in that 10Dq (the orbital splitting energy) for amp complexes are intermediate[12] to those of the analogous bipy and en complexes, following the rule of average environment,[13] which would not be expected if delocalisation of the chelate ring played any part in the high 10Dq values found in bipy complexes. In spite of the inability to predict the formation constants of complexes of ligands containing the pyridyl group from rigorously derived equations such as 1, these stability constants are empirically related to those of ligands that contain the alkylamine group. In Figure 2 is shown the linear free energy relation (l.f.e.r.) between $\log K_1(NH_3)$ and $\log K_1(\text{bipy})$, and $\log K_1(\text{phen})$ (phen = 1,10-phenanthroline). It is seen that, apart from Cu(II), whose unexpectedly low stability is explicable[12] in terms of the unusually small tetragonal distortion found[14] in Cu^{II} bipy and phen complexes, a reasonably good l.f.e.r. is observed. The position of the points for $\log K_1(\text{bipy})$ and $\log K_1(\text{phen})$ for lead(II) on this l.f.e.r. suggests that the estimated $\log K_1(NH_3)$ 1.6 is a reasonable estimate.

Estimates of $\log K_1(NH_3)$ for several other metal ions were made using equation 3, which are seen below together with the $\log K_1(CH_3COO^-)$ values used (values in brackets were estimated in same way

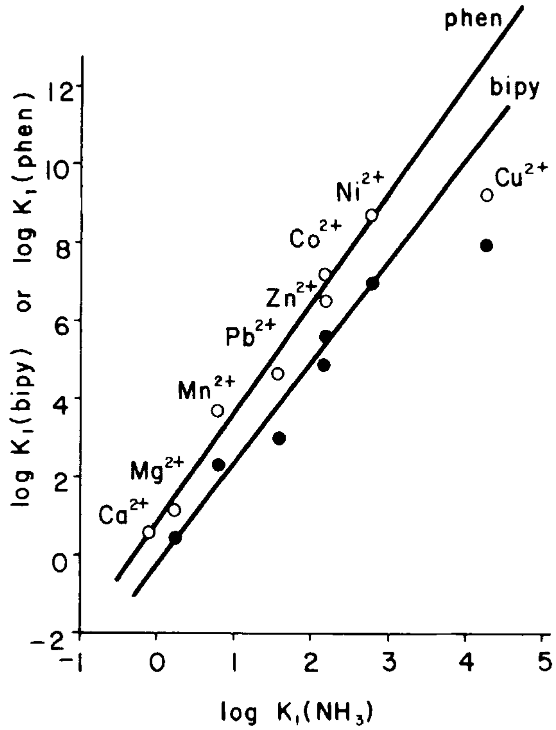

FIGURE 2 l.f.e.r. for log K_1 (NH$_3$) for several metal ions against log K_1 (bipy) (●), and log K_1 (phen) (○).

as ammonia constants). From the log $K_1(OH^-)$ values also tabulated (all from reference 6), it can be seen that imidazole complexes of all the metal ions will be hydrolysed, except for the lead(II) complex.

log K_1	Pb^{II}	Fe^{III}	Ga^{III}	UO$_2^{2+}$	La^{III}	Zr^{IV}
NH$_3$	1.6	4.3	2.9	3.1	0.7	≈4
CH$_3$COO$^-$	2.7	3.4	(3.4)	2.6	2.5	(4.6)
OH$^-$	6.4	11.8	10.4	9.3	≈8.0	≈14.0

The agreement obtained between the estimated log K_1(NH$_3$) 1.6 and log K_1(Im) 1.1 for lead(II) is sufficiently close to suggest that the estimates made for log K_1(NH$_3$) for other metal ions are, however, reliable. It is envisaged that such constants will be useful in attempts to model formation constants of unidentate ligands, such as that recently described by Yamada and Tanaka.[15] Their model is able, to a certain extent, to reproduce known formation constants, but fails in that it predicts that species such as Zr(NH$_3$)$^{4+}$ should exist, which are completely hydrolysed, as indicated both by experience and the above chelate effect model.

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