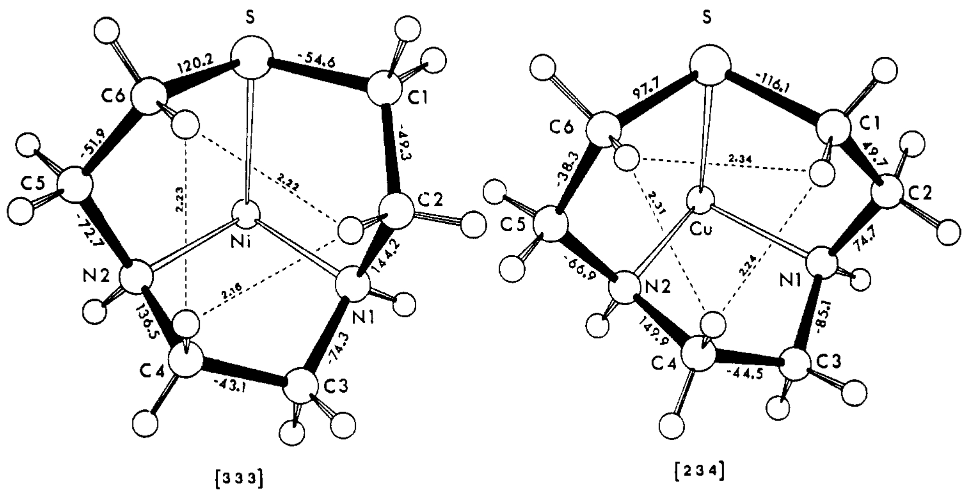

Figure 4. The two different conformations for a coordinated tridentate cyclononane ring: (a) the [333] conformation for the nickel(II) complex and (b) the [234] conformation for the copper(II) complex.

the three rings in the copper complex than in the nickel complex (Table VI).

Conformation of the 9-Membered ring. This flip of conformation of one chelate ring relative to the other two is also manifested in the conformation of the 9-membered ring, as might be expected. The macrocycle has a [234] conformation[16] in the copper complex (Figure 4), and this is the first X-ray diffraction study of a complex containing a tridentate 9-membered ring with this conformation. Previously, Dale et al.,[17] using IR techniques, proposed that the free ligand 9-ane-O_3 has this conformation. Crystal structures of $[Ni(9\text{-ane-}N_3)_2]^{2+}$ and $[Ni(9\text{-ane-}N_2S)_2]^{2+}$ and of 9-ane-S_3 as a free ligand[18] and coordinated to nickel, cobalt, and copper[13] all have a [333] conformation in the 9-membered ring.

The free ligand 9-ane-S_3 has a 3-fold axis perpendicular to the ring and as such has a conformation that most resembles the minimum energy [333] conformation calculated for cyclononane.[18] When two macrocycles are bonded to a metal ion, there is an increase in the number and/or magnitude of nonbonded interactions, either interligand or intraligand. Figure 4 shows that in the [333] conformation, there are three hydrogen atoms "above" the ligand, which are fairly close together (2.16, 2.22, and 2.23 Å), but in the [234] conformation these nonbonded interactions are reduced since these three distances are increased (2.24, 2.31, and 2.34 Å).

We propose that the larger Cu–S bond distance allows this change in conformation from [333] to [234] to take place and that this in turn reduces unfavorable nonbonded interactions and therefore the strain energy of the complex.

In Figure 4 it is also possible to see another result of this conformation change. If the hydrogens on the carbon atoms of the N–C–C–N linkage are to be staggered, then one N–Cu–S angle must be compressed and the Cu–N bond is stretched while the N–Cu–S angle in the other ring must be opened out and the bond compressed.

Electronic Spectra. The spectrum of the macrocyclic complex contains bands at higher wavenumbers (17 990 and 37 040 cm^{-1}) than the spectrum of the open-chain complex (16 260 and 30 960 cm^{-1}, respectively). The increase in ligand field strength indicated by the bands in the 17 000-cm^{-1} region of the spectrum is a phenomenon commonly observed in macrocyclic complexes. Two theories exist for cyclononane ligands: (1) trigonal distortion around the metal[5] and (2) an increase in the number of secondary nitrogens without an increase in steric hindrance.[19] In these two structures the coordination sphere around the metal is the same. The bond lengths to the donor atoms and the bond angles around the metal are similar. The average Cu–N bond lengths are 2.05 and 2.06 Å, and the average N–Cu–S bond angles are 82.0 and 81.4° for the macrocyclic and open-chain complexes, respectively. The differences are within the limits of experimental error. As mentioned earlier the Cu–S bond length is shortened by 0.05 Å in the macrocyclic complex (a similar shortening is found in the nickel complex). It seems likely that the constraints imposed by the macrocyclic ligand are responsible for the bond shortening. However, this does not seem a sufficient effect to account for a large different in 10*Dq* between the macrocyclic and open-chain complex. This is particularly so in relation to the bond angles around copper, which were very similar for the macrocyclic and open-chain complexes.

Acknowledgment. Generous financial support from the Council for Scientific and Industrial Research and the Senate Research Grant Committee of the University of the Witwatersrand is acknowledged. J. Albain is thanked for carrying out the X-ray data collection.

Registry No. 9-ane-N_2S, 88194-17-6; $[Cu(9\text{-ane-}N_2S)_2](NO_3)_2$, 96760-86-0; $[Cu(daes)_2](NO_3)_2$, 96760-88-2; *N,N'*-bis((4-methylphenyl)sulfonyl)bis(2-aminoethyl) sulfide, 85775-49-1; 1,2-bis((4-methylphenyl)sulfonyl)ethane, 22952-14-3.

Supplementary Material Available: Listings of calculated and observed structure factors, temperature factors, coordinates for hydrogen atoms, and bond lengths and angles for the two complexes (23 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
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Stability of Ammonia Complexes That Are Unstable to Hydrolysis in Water

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An interesting feature of aqueous phase coordination chemistry is that most metal ions do not form complexes with ammonia. One

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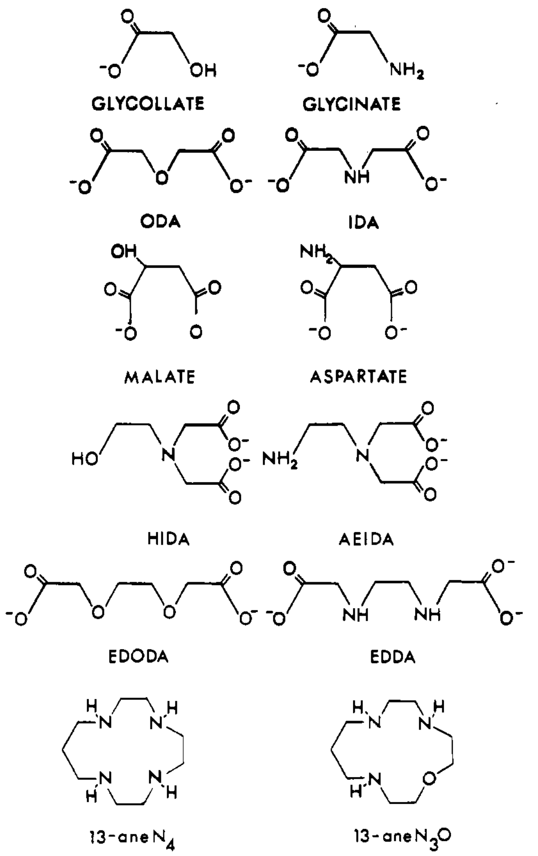

Figure 1. Ligands discussed in this paper. The ligands are pairs which differ only in that where the ligand in the left-hand column has oxygen donor, that in the right-hand column has a nitrogen donor. Abbreviations are as follows: ODA, oxydiacetate; IDA, iminodiacetate; HIDA, ((2-hydroxyethyl)imino)diacetate; AEIDA, ((2-aminoethyl)imino)diacetate; EDODA, (ethylenedioxy)diacetate; EDCA, ethylenediamine-*N*,*N'*-diacetate.

might form the impression from this that these metal ions, e.g. Fe^{3+}, In^{3+}, La^{3+}, UO_2^{2+}, and Pb^{2+}, have very little affinity for nitrogen donor ligands. On the other hand, coordination to chelating ligands appears to be enhanced by the presence of saturated nitrogen, suggesting some affinity for nitrogen as a donor. Thus, for Pb^{2+}, the formation constant $\log K_1$ is 5.47[1] for glycine, a considerable enhancement in stability over the acetate complex with $\log K_1 = 2.68$ or the hydroxyacetate with $\log K_1 = 2.61$. (All formation constants in this work are at 25 °C and infinite dilution and are taken from the critical compilation of Martell and Smith.[1])

The fact of the above enhancement prompted us[2] to attempt an estimation of $\log K_1$ values for the ammonia complexes of these metal ions. A knowledge of these values is of considerable importance in modeling Lewis acid–base behavior in aqueous solution[3,4] and in understanding the chelate[2] and macrocyclic effects.[5,6] Our original estimates of ammonia constants were based on an empirical model of the chelate effect.[2] Briefly, this model was based on Adamson's[7] ideas on the asymmetry of the standard reference state. A chelating ligand such as glycine is considered to be composed of the unidentate ligands acetate and ammonia, and its stability is related to that of its unidentate components by the expression

$$\log K_1(\text{polyamino carboxylate}) = 1.152n \log K_1(NH_3) - \left(\sum_{i=1}^{n-1} i\right)\lambda_N + m \log K_1(CH_3COO^-) - \left(\sum_{i=1}^{m} i\right)\lambda_O + (m + n - 1) \log 55.5 \quad (1)$$

Expression 1 predicts $\log K_1$ values for polyamino carboxylate ligands such as glycine, IDA, or EDTA (see Figure 1 for structures of ligands) with a fair degree of success for metal ions where $\log K_1$ values for acetate and ammonia are known. The numbers *m* an *n* are the numbers of acetate and ammonia groups on the polyamino carboxylate, e.g. for EDTA $m = 4$ and $n = 2$. The term in log 55.5 corrects for the asymmetry of the standard reference state. The terms in λ involve two constants, λ_N and λ_O, which are empirically adjusted for each metal ion to give a best fit. The physical significance of these terms is uncertain. It was originally thought that they were statistical in origin,[2] but it has since become clear that they are more related to the increase in steric strain on complex formation.[8] Thus metal ions such as Ca^{2+} or La^{3+}, which have highly ionic metal to ligand bonding, where bond deformation so as to accommodate the steric requirements of the ligand will not lead to much strain energy, have small λ values. For metal ions with much more covalent metal to ligand bonding, which is likely to be sensitive to steric deformation, such as Cu^{2+} or Co^{3+}, λ values are large.

Equation 1 can be used to estimate unknown $\log K_1(NH_3)$ values if $\log K_1(CH_3COO^-)$ and $\log K_1$ for some polyaminocarboxylate ligands, such as glycine and EDTA, are known. Thus, for Pb^{2+}, with $\log K_1(CH_3COO^-) = 2.68$, $\log K_1(NH_3)$ is estimated to be 1.6, and the λ values are $\lambda_N = 0.5$ and $\lambda_O = 0.4$. Predicted values are given first, followed by observed[1] values in parentheses, for some ligands: diethylenetriamine, 7.5 (7.5); triethylenetetramine, 9.6 (10.4); tetraethylenepentamine, 11.2 (10.9); glycine, 5.86 (5.47); NTA, 12.70 (12.66); EDTA, 19.0 (19.6); ethylenediaminemonoacetate, 8.95 (8.67); AEIDA, 12.57 (13.1).

For metal ions such as Pb^{2+} where many formation constants are available, particularly with polyamines, where no carboxylate groups are present, the estimate of $\log K_1(NH_3)$ appears to be reliable. For many others, such as La^{3+} or Sc^{3+}, there appears to be a considerable degree of cross-correlation of the adjustable parameters in eq 1, and the estimated values of $\log K_1(NH_3)$ appear to be less certain.

It was thus decided to develop another approach to the problem. Consider pairs of ligands such as IDA and ODA, or AEIDA and HIDA (Figure 1), which differ only in that the first member of the pair has a saturated amine where the second member has an alcoholic or ethereal oxygen. A complex-formation reaction in which the amine donor replaces the oxygen donor ligand resembles the complex-formation reaction where an ammonia molecule replaces the coordinated water from the metal ion.

What is important is that, if the complexes formed by the pair of ligands, e.g. IDA and ODA, are structurally similar, we might reasonably expect the increase in strain energy on complex formation to be similar in the two cases, with any one metal ion. This then circumvents the problem of estimating λ values for eq 1, and we have in fact factored out differences in strain energy. This assumption of structural similarity, and hence similarity in strain energies, is essential to the approach, seen for the IDA plus ODA pair in Figure 2.

Figure 2 is a plot of $\log K_1(\text{IDA}) - \log K_1(\text{ODA})$ vs. $\log K_1(NH_3)$ for a variety of metal ions. An excellent relationship is observed, which includes both experimental values of $\log K_1(NH_3)$ as well as estimated values. What is of interest if we examine these estimated values is that we see that many metal

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Table I. Thermodynamic Quantities Determined in This Work[a]

ligand	equilibrium	medium	log K^b	lit. values
NH_3	$Pb^{2+} + NH_3 \rightarrow PbNH_3^{2+}$	5 M NH_4NO_3	1.55 ± 0.1	
	$NH_3 + H^+ \rightarrow NH_4^+$		9.85 ± 0.01	
OH^-	$Pb^{2+} + OH^- \rightarrow Pb(OH)^+$	5 M $NaNO_3$	6.05 ± 0.05	
IDA[c]	$In^{3+} + IDA^{2-} \rightarrow In(IDA)^+$	1 M $NaClO_4$	10.2 ± 0.2	9.54[d]
	$In^{3+} + 2IDA^{2-} \rightarrow In(IDA)_2^-$		20.3 ± 0.1	18.41[d]
	$In^{3+} + 3IDA^{2-} \rightarrow In(IDA)_3^{3-}$		29.0 ± 0.2	
	$In^{3+} + H^+ + IDA \rightarrow In(IDA)H^{2+}$		12.6 ± 0.2	
	$2In^{3+} + IDA \rightarrow In_2(IDA)^{4+}$		14.0 ± 0.2	
ODA	$Hg^{2+} + ODA^{2-} \rightarrow Hg(ODA)$[e]		6.7 ± 0.15	
	$Hg^{2+} + H^+ + ODA^{2-} \rightarrow Hg(ODA)H^+$		8.50 ± 0.06	

[a] At 25.0 °C. [b] Standard deviations are those indicated by the program MINIQUAD.[10] [c] For abbreviations, see Figure 1. [d] Misumi, S.; Aihara, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2677. Medium is 0.3 M KCl. The lower values reflect the presence of chloride complexes of In^{3+}, for which no corrections were made. [e] These constants were determined for Hg^{2+} in an attempt to use a mercury electrode to monitor the competition reaction between Hg^{2+} and In^{3+} so as to determine log K values for the In^{3+}/ODA system.

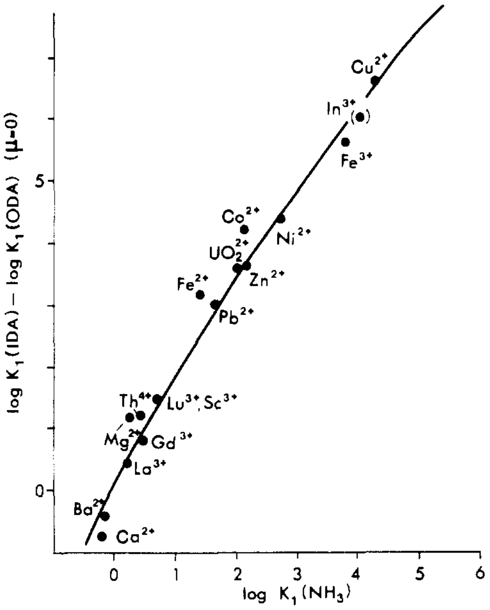

Figure 2. Relationship between log K_1(IDA) – log K_1(ODA) and log $K_1(NH_3)$ for a variety of metal ions. The log $K_1(NH_3)$ values for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, and Pb^{2+} (this work) are experimental, while all the remainder are estimates, as discussed in the text.

ions have a high affinity for ammonia, which is masked by an even higher affinity for hydroxide, so that hydrolysis in water will occur according to eq 2 or 3. As a guide, from pK_w, the ionization

$$M(NH_3)^{y+} + H_2O \rightleftharpoons M(OH)^{(y-1)+} + NH_4^+ \quad (2)$$

$$yM(NH_3)^{y+} + yH_2O \rightleftharpoons M(OH)_y(s) + yNH_4^+ + (y-1)M^{y+} \quad (3)$$

constant of water of 14, and pK_a of ammonia of 9.2, we may say from eq 2 that if log $K_1(OH^-)$ for a metal ion is larger than log $K_1(NH_3)$ by more than 14 – 9.2 = 4.8 log units, the ammine will be unstable in solution. Thus, for Cu^{2+}, Ag^+, and Ni^{2+}, log $K_1(OH^-)$ – log $K_1(NH_3)$ are respectively 2.4, –1.3, and 1.4 log units, so that hydrolysis will not readily occur. For Fe^{3+} and Pb^{2+}, with log $K_1(NH_3)$ values[2] of 3.8 and 1.6, log $K_1(OH^-)$ – log$K_1(NH_3)$ amounts to 8.0 and 4.7 log units. Thus, the equilibrium in eq 2 will lie far to the right for Fe^{3+}, in accordance with experience. A satisfying feature of the estimates made of log $K_1(NH_3)$ was that these metal ions had ammine complexes that should decompose according to eq 2, in agreement with their nonexistence. An exception to this is Pb^{2+}, a borderline case with log $K_1(OH^-)$ – log $K_1(NH_3)$ = 4.7. We should thus, in the presence of sufficient ammonium ion, be able to drive reaction 2 over to the left for Pb^{2+}, and measure log $K_1(NH_3)$. Accordingly, we report in this paper a study of the Pb^{2+}/ammonia complex in 5 M NH_4NO_3. In order to check for hydrolysis, a study of the hydroxy complexes of Pb^{2+} in 5 M $NaNO_3$ was made, for use in the data reduction in 5 M NH_4NO_3. In addition, log K_1(en) is predicted by eq 1 to be 4.93, which should make it reasonably resistant to hydrolysis, so that a study of the Pb^{2+} complex with ethylenediamine is also reported here, along with a check on the log K_1 values for Pb^{2+} with dien and trien.

We have started a program of determining log K_1 values for IDA and ODA with metal ions not shown in Figure 2, and report here a study of the complexing of In^{3+} by these ligands.

Experimental Section

Materials. Iminodiacetate was obtained from BDH. Mass spectrometry showed that, on standing, a compound of molecular mass 230 formed in solution, indicating decomposition. This problem was circumvented by preparing a fresh solution for each experiment and standardizing with acid. Oxydiacetic acid (Fluka, Puriss Grade) was purified by recrystallization from boiling water and dried at 80 °C under vacuum. $In(ClO_4)_3$ was obtained from Alfa Ventron, and the 10^{-2} M stock solution was standardized by titration with EDTA. $Pb(NO_3)_2$ was obtained from Merck ("Extra Pure"), and a stock solution was prepared, which has standardized with EDTA. NH_4NO_3 and NH_3 (25% solution, extra pure) were obtained from Merck and used to make up the solutions containing the 5 M NH_4NO_3 background electrolyte plus the titrant, which contained approximately 0.05 M NH_3 in 5 M NH_4NO_3. Ethylenediamine (Merck "Gold Label") was used for the study of the Pb^{2+} complex.

Potentiometry. The apparatus used for the glass-electrode study has been described before.[9] For the study of the Pb^{2+} system, salt bridges filled with 5 M $NaNO_3$ were used to eliminate junction potentials.

Data Reduction. The five separate titrations for Pb^{2+}/NH_3 and three titrations for In^{3+}/IDA were successfully analyzed by using the program MINIQUAD of Sabatini et al.[10] The constants thus obtained are seen in Table I. It was found that a successful analysis of the In^{3+}/ODA system was not possible, beyond an estimate that log K_1 was about 5. This was due to the fact that the complex was not effectively decomposed by acid down to a pH value of 2, where junction potentials begin to make potentiometry unreliable. In addition, several mixed ODA/hydroxy complexes appeared to be present, which hindered refinement. An attempt was made using a mercury electrode to conduct a competition experiment with the Hg^{2+} ion so as to determine log K_1(ODA) with In^{3+}. However, this was bedeviled by the formation of insoluble [Hg(ODA)] precipitates, and no useful results were obtained.

Results and Discussion

The plot of $\bar{n}$, the average number of NH_3 molecules bound per metal ion, as a function of the concentration of free NH_3, is seen for Pb^{2+} in Figure 3. The maximum value of $\bar{n}$ achieved before precipitation of lead hydroxide occurred was just short of 0.5, which gives one reasonable confidence in the value of log $K_1(NH_3)$ of 1.55 ± 0.1 determined for Pb^{2+} here. Calculations with the program MINIQUAD[10] showed that the concentration of lead hydroxide species in the titration before precipitation occurred was negligible.

The agreement between the measured value of log $K_1(NH_3)$ of 1.55 and the predicted value of 1.6 is heartening. As pointed out by a reviewer, Pb^{2+} does form complexes with NO_3^- of some

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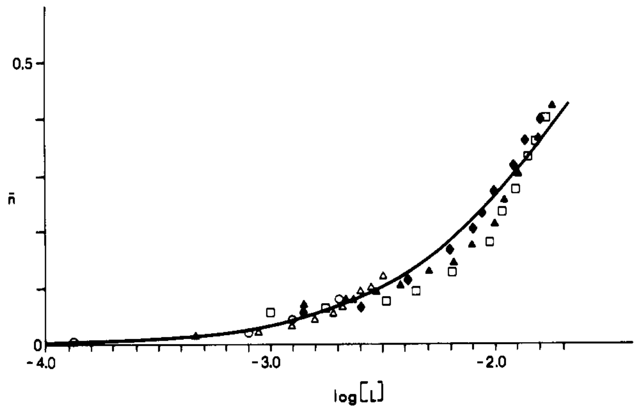

Figure 3. Plot of $\bar{n}$, the average number of ammonia molecules bound to Pb^{2+}, vs. log [L] for the Pb^{2+}/NH_3 system at 25 °C in 5 M NH_4NO_3. The scatter in the points may appear somewhat larger than usual, but it should be noted that the curve is plotted on a very large scale. The different titrations are for differing concentrations of Pb^{2+}: (▲) Pb^{2+} = 5.88×10^{-3}M; (♦) 8.82×10^{-3}M; (□) 1.33×10^{-2}M; (△) 3.21×10^{-2}M; (○) 5.47×10^{-2}M. Each titration was terminated by precipitation of lead hydroxide, which happedn earlier as the concentration of Pb^{2+} in the titration increased. The solid line drawn in is the theoretical curve calculated with log $K_1(NH_3)$ = 1.55.

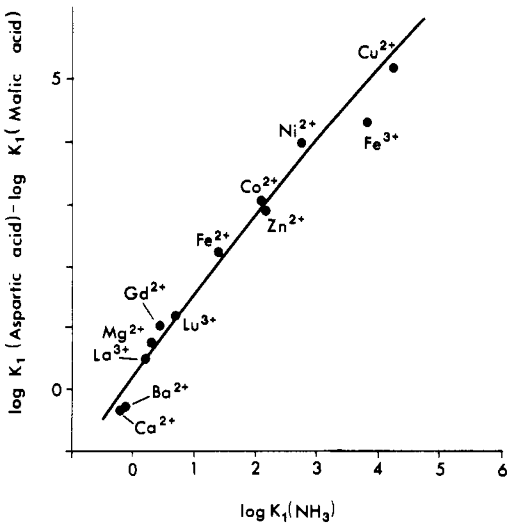

Figure 4. Relationship between log K_1(aspartate) – log K_1(malate), and log $K_1(NH_3)$ for a variety of metal ions.

Table II. Values of log K_1, Estimated and Experimental, for NH_3 Complexes of Various Metal Ions[a]

	Ba^{2+}	Ca^{2+}	Mg^{2+}	La^{3+}	Gd^{3+}	Lu^{3+}	Sc^{3+}	Y^{3+}
log K_1 (NH_3)	-0.15	-0.2[b]	0.26[b]	0.2	0.45	0.7	0.7	0.4
	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	UO_2^{2+}
log K_1 (NH_3)	0.8	1.4	2.1[b]	2.71[b]	4.27[b]	2.18[b]	1.6	2.0
	In^{3+}	Fe^{3+}	Bi^{3+}	Th^{4+}	U^{4+}	Ga^{3+}		
log K_1 (NH_3)	4.0[c]	3.8	(5.0)[d]	0.4[c]	(4.2)[d]	4.1		

[a] Estimated as described in the text from linear relations such as those seen in Figures 2–6. [b] Experimental values from ref 1. [c] Somewhat less reliable values since the ODA log K_1 values are not known with any reliability. The Th^{4+} values are from: Di Bernado, P.; Cassol, A.; Tomat, G.; Bismondo, A. "Abstracts of Papers", Vth International Symposium on Solute–Solute–Solute Interactions, Florence, Italy, 1980. [d] Values based only on eq 1 in the text, which is a less reliable method of estimation.

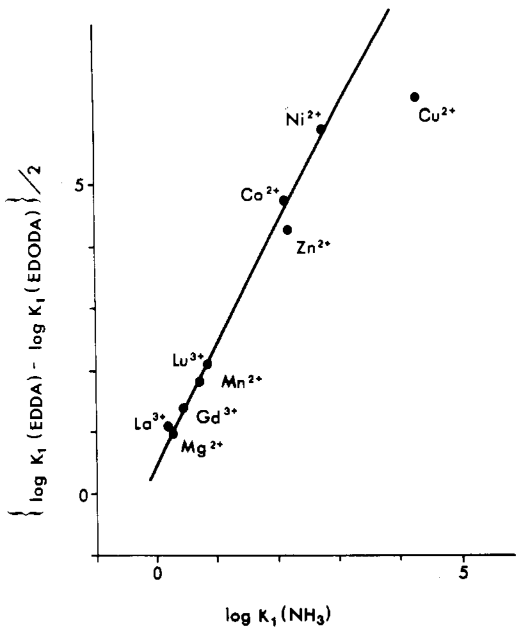

Figure 5. Relationship between log K_1(EDDA) – log K_1(EDODA) and log $K_1(NH_3)$ for a variety of metal ions. Note that the quantities on the *y* axis have been divided by 2 to make them comparable with other such plots EDDA has two nitrogen donor atoms, so that to make the slope refer to the increase per nitrogen donor, there has been a division by 2. See Figure 1 for the structure of ligands.

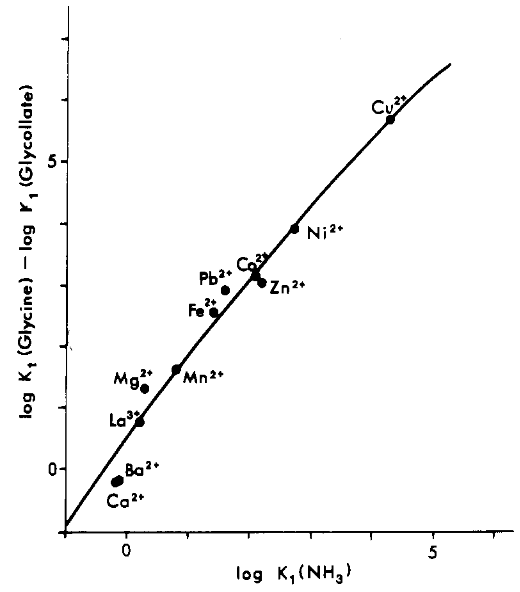

Figure 6. Relationship between log K_1(glycinate) – log K_1(glycolate) and log $K_1(NH_3)$ for a variety of metal ions. The value for log K_1(glycine) for La^{3+} is from: Hancock, R. D.; Jackson, G.; Evers, A. *J. Chem. Soc., Dalton Trans.* **1979**, 1384.

stability, so that results in 5 M NO_3^- ion should be somewhat affected by this. The level of agreement is thus possibly better than might have been anticipated, but the lowering of log $K_1(NH_3)$ that might have been produced by competition with NO_3^- for the Pb^{2+} ion is probably offset by the fact that log $K_1(NH_3)$ values increase quite strongly with increasing ionic strength. A large number of estimates of log $K_1(NH_3)$ for a variety of metal ions have been made by using the relationship in Figure 2 and Figures 4–7 for the ligand pairs indicated. These estimated values are seen in Table II. The value of log K_1(IDA) of 10.2 determined here combined with the estimated value of 5.0 for log K_1(ODA) gives the estimated log $K_1(NH_3)$ of 4.0 for In^{3+}. The changes in our values of log $K_1(NH_3)$ estimated by using Figure 2 and Figures 4–7 from those reported previously[2] using eq 1 are generally small. Thus, log $K_1(NH_3)$ for La^{3+} moves down from 0.7 to 0.2 and for Sc^{3+} from 1.4 down to 0.7, which was the largest change made. All of the values of log $K_1(NH_3)$ reported in Table II are consistent with the chemistry of the metal ions present. Thus, for metal ions such as Sc^{3+} or La^{3+} for which no ammonia complexes in aqueous solution are known, the ammonia complex is

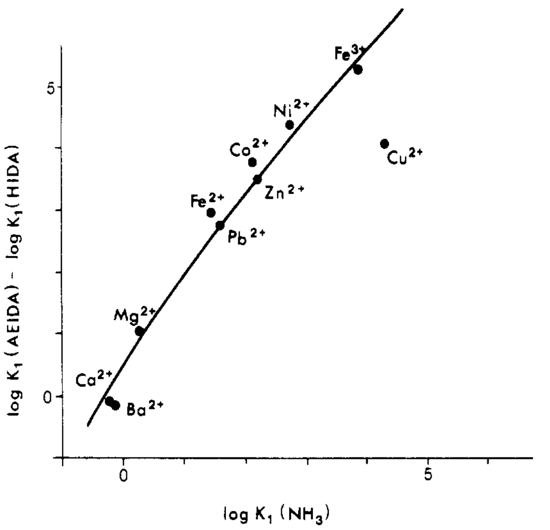

Figure 7. Relationship between log K_1(AEIDA) – log K_1(HIDA), and log $K_1(NH_3)$. The downward deviation for the point for Cu^{2+} is discussed in the text in terms of possible differing structures for the HIDA and AEIDA complexes of Cu^{2+}.

unstable according to eq 2 and 3 and the value of log $K_1(NH_3)$ estimated.

The plots in Figure 2 and Figures 4–7 are of interest in several ways. The most striking feature is that all of them have slopes well in excess of unity. This feature has a ready explanation in terms of our proposals[11,12] on the inductive effects of alkyl groups. Thus, in the gas phase,[13-16] saturated amines increase in basicity along the series NH_3 < primary < secondary < tertiary amine. This effect is masked in water for the proton because of solvation effects[12,17] and steric effects.[12] Our treatment here effectively factors out steric effects, as discussed in the introduction, and what we are left with in the slopes are the pure inductive effects. If we divide the relationships into those involving primary amines and alcohols and those involving secondary amines and ethers, we see that the slopes are in the region of 1.5 for the former and 1.9 for the latter, exactly as would be expected if secondary amines are more basic than primary amines. A second factor which emerges is that alkyl groups in the form of ethylene bridges appear to increase basicity more than do acetate groups. Thus, the slope of the EDODA/EDDA relationship in Figure 7 is 2.2, in comparison with a slope of 1.6 for ODA/IDA in Figure 2. We have studied[18] the formation constants of the ligand [13]aneN_3O, and a plot similar to those in Figure 2 and Figures 4–7 may be drawn up by using the all-nitrogen analogue [13]aneN_4. As expected from the above argument, the slope of log K_1([13]aneN_4) – log K_1([13]aneN_3O) vs. log $K_1(NH_3)$ is about 2.2, reflecting the ethylenes adjacent to the ethereal oxygen in [13]aneN_3O, which is replaced by a nitrogen to give a secondary amine in [13]aneN_4.

A further point of interest is that all the relationships in Figure 2 and Figures 4–7 have, if plotted on a single graph, a common intersection point at the Mg^{2+} ion. At stabilities lower than this, we find that for Ca^{2+}, Sr^{2+}, and Ba^{2+}, a change from oxygen donor to nitrogen donor leads to a destablization, whereas for all metal ions above this crossover point, stabilization results. Moreover, the destabilization is greater if a secondary rather than a primary nitrogen is involved. This effect relates to the different way in which metal ions respond to changing hydrogens for alkyl groups on the donor atom in the gas phase.[12] Thus, if the metal ion is extremely ionic in its metal–ligand bonding, such as Li^+, the increase in enthalpy of complex formation along a series such as XH_n, $(CH_3)XH_{n-1}$, $(CH_3)_2XH_{n-2}$,... is much greater if X is oxygen than if X is nitrogen, whereas for covalently bonded metal ions such as Ni^+ the reverse is true. Thus, the ionically bound Ca^{2+} and Ba^{2+} ions respond more strongly to the increasing basicity in passing from alcohol to ether than in passing from primary to secondary amine as donor atom. For all the metal ions above the crossover point at Mg^{2+}, the reverse is true.

Table III. Values of the Formation Constants of Pb^{2+} with Ammonia and Polyamines[a]

ligand[b]	NH_3	en	dien	trien	tetren
log $K_1(Pb^{2+})$	1.55 ± 0.1	5.04 ± 0.05[c]	7.56 ± 0.04[c]	10.35 ± 0.04[c]	
calcd	1.6[d]	4.93[e]	7.51[e]	9.59[e]	11.18[e]
lit. values		7.0[f]	8.5[f]	10.4[g]	10.9[h]

[a] At 25 °C and ionic strength 0.1. [b] Abbreviations are en = ethylenediamine, dien = diethylenetriamine, and trien = triethylenetetramine. [c] Observed values, this work, at 25 °C in 0.1 M $LHNO_3$ (en) or 0.1 M $NaNO_3$ (dien, trien). [d] Estimated from relationships such as Figure 2 and Figures 4–7, and also eq 1. [e] Estimated from eq 1 with log $K_1(NH_3)$ = 1.6 and λ_N = 0.5 for Pb^{2+}. [f] Ivanova, E. D.; Migal, P. K. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1969**, *14*, 1723. No $LiHNO_3$ was present as excess background electrolyte to prevent hydrolysis, so that the reaction being followed would have been hydrolysis of the Pb^{2+} ion. [g] Reilly, C. N.; Schmid, R. W. *J. Elisha Mitchell Sci. Soc.* **1957**, *73*, 279. [h] Jacobsen, E.; Schroder, K. *Acta Chem. Scand.* **1962**, *16*, 1393.

A final point of interest is seen in Figure 7 for the HIDA/AEIDA relationship. We see that the point for the Cu^{2+} ion is displaced downward from the relationship formed by the other metal ions. This must relate to the distorted geometry normally found around Cu^{2+} with four short in-plane bonds, and two long axial ones. HIDA and AEIDA are "tripod" ligands, which force coordination to the unfavorable axial site on the Cu^{2+}. This effect is apparently more serious for AEIDA than IDA, and in all probability the two complexes are not structurally the same. We might thus find that, for HIDA, the hydroxyethyl group occupies the unfavorable axial site, whereas in AEIDA one of the acetates would almost certainly be forced into this position. The Cd^{2+}, Hg^{2+}, and Ag^+ ions are not included in any of the relationships in Figure 2 and Figures 4–7. For the latter two ions, the favored linear coordination geometry found in the ammonia complexes is not possible in any of the polyamino carboxylate ligands used in Figure 2 and Figures 4–7. For Hg^{2+} a log $K_1(NH_3)$ value in the vicinity of 4.0 is suggested by the latter relationships in comparison with the experimentally determined value of 8.8. One must presume that the value of log $K_1(NH_3)$ of 4.0 would apply to a hypothetical ammonia complex of Hg^{2+} possessing coordination geometry similar to that in complexes of ligands such as HIDA or EDDA, possibly being octahedral. For Cd^{2+}, the relationships in Figure 2 and Figures 4–7 are consistent with log K_1 = 1.9, rather than the experimental value of 2.65. Again, this must be log $K_1(NH_3)$ appropriate to octahedral Cd^{2+}, rather than the 2.65 value appropriate to tetrahedral Cd^{2+}.

The deviations found for Cu^{2+}, Hg^{2+}, Cd^{2+}, and Ag^+, from the relationships such as that shown in Figure 2, mean that the estimated values of log $K_1(NH_3)$ in Table II should be regarded with caution unless they are established by using several ligand pairs and no deviations or differences in coordination geometry are apparent. In spite of this caveat, we believe that the estimates in Table II will prove useful in understanding solution chemistry of metal ions with nitrogen and also oxygen donor ligands.

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