Inorg. Chem. **2005**, *44*, 7175–7183

Inorganic Chemistry

Article

Density Functional Theory-Based Prediction of the Formation Constants of Complexes of Ammonia in Aqueous Solution: Indications of the Role of Relativistic Effects in the Solution Chemistry of Gold(I)

Robert D. Hancock,*,† and Libero J. Bartolotti*,‡

Department of Chemistry and Biochemistry, University of North Carolina,
Wilmington, North Carolina 28403, and Department of Chemistry, East Carolina University,
Greenville, North Carolina 27858

Received March 30, 2005

A prediction of the formation constants (log K_1) for complexes of metal ions with a single NH_3 ligand in aqueous solution, using quantum mechanical calculations, is reported. ΔG values at 298 K in the gas phase for eq 1 (ΔG(DFT)) were calculated for 34 metal ions using density functional theory (DFT), with the expectation that these would correlate with the free energy of complex formation in aqueous solution (ΔG(aq)). $[M(H_2O)_6]^{n+}(g) + NH_3(g) = [M(H_2O)_5NH_3]^{n+}(g) + H_2O(g)$ (eq 1). The ΔG(aq) values include the effects of complex changes in solvation on complex formation, which are not included in eq 1. It was anticipated that such changes in solvation would be constant or vary systematically with changes in the log K_1 value for different metal ions; therefore, simple correlations between ΔG(DFT) and ΔG(aq) were sought. The bulk of the log $K_1(NH_3)$ values used to calculate ΔG(aq) were not experimental, but estimated previously (Hancock 1978, 1980) from a variety of empirical correlations. Separate linear correlations between ΔG(DFT) and ΔG(*aq*) for metal ions of different charges (M^{2+}, M^{3+}, and M^{4+}) were found. In plots of ΔG(DFT) versus ΔG(aq), the slopes ranged from 2.201 for M^{2+} ions down to 1.076 for M^{4+} ions, with intercepts increasing from M^{2+} to M^{4+} ions. Two separate correlations occurred for the M^{3+} ions, which appeared to correspond to small metal ions with a coordination number (CN) of 6 and to large metal ions with a higher CN in the vicinity of 7–9. The good correlation coefficients (*R*) in the range of 0.97–0.99 for all these separate correlations suggest that the approach used here may be the basis for future predictions of aqueous phase chemistry that would otherwise be experimentally inaccessible. Thus, the log $K_1(NH_3)$ value for the transuranic Lr^{3+}, which has a half-life of 3.6 h in its most stable isotope, is predicted to be 1.46. These calculations should also lead to a greater insight into the factors governing complex formation in aqueous solution. All of the above DFT calculations involved corrections for scalar relativistic effects (RE). Au has been described (Koltsoyannis 1997) as a "relativistic element". The chief effect of RE for group 11 ions is to favor linear coordination geometry and greatly increase covalence in the M–L bond. The correlation for M^+ ions (H^+, Cu^+, Ag^+, Au^+) involved the preferred linear coordination of the $[M(H_2O)_2]^+$ complexes, so that the DFT calculations of ΔG for the gas-phase reaction in eq 2 were carried out for M = H^+, Cu^+, Ag^+, and Au^+. $[M(H_2O)_2]^+(g) + NH_3(g) = [M(H_2O)NH_3]^+(g) + H_2O(g)$ (eq 2). Additional DFT calculations for eq 2 were carried out omitting corrections for RE. These indicated, in the absence of RE, virtually no change in the log $K_1(NH_3)$ value for H^+, a small decrease for Cu^+, and a larger decrease for Ag^+. There would, however, be a very large decrease in the log $K_1(NH_3)$ value for Au(I) from 9.8 (RE included) to 1.6 (RE omitted). These results suggest that much of "soft" acid behavior in aqueous solution in the hard and soft acid–base classification of Pearson may be the result of RE in the elements close to Au in the periodic table.

Introduction

Formation constants (log K_1) for the complexation of metal ions by ligands in aqueous solution are vital for understanding the role of metal ions in biology[1] and the behavior of metal ions in the environment.[2] They are also an essential tool in the design of metal ion complexes for biomedical applications.[3] In many cases, the log K_1 values are unknown, and there may be insuperable experimental difficulties preventing their measurement. Empirical approaches to the prediction of the log K_1 values for complexes of metal ions

---

* To whom correspondence should be addressed. Email: hancockr@uncw.edu (R.D.H); BARTOLOTTIL@MAIL.ECU.EDU (L.J.B.).

† University of North Carolina at Wilmington.

‡ East Carolina University.

10.1021/ic050471s CCC: $30.25

have been proposed by one of the present authors,[4−9] in which papers empirical approaches by other authors are also discussed. The reliability of DFT (density functional theory) calculations for the prediction of the energies of formation of complexes between metal ions and unidentate ligands in the gas phase has advanced[10] to the point where these might be used to predict the formation constants of, for example, ammonia complexes, the subject of interest of this paper.

Log $K_1(NH_3)$ is not known experimentally for most metal ions, such as Bi^{3+}, because[4−9] the ammonia complexes are unstable to hydrolysis, as shown in eq 1

$$Bi(NH_3)^{3+} + H_2O = Bi(OH)^{2+} + NH_4^{+} \qquad (1)$$

With a predicted log $K_1(NH_3)$ for[4−9] Bi^{3+} of 5.1, pK_w = 14.0, log $K_1(OH)^-$ for Bi^{3+} = 12.4,[11] and pK_a NH_4^+ = 9.2,[11] the value of log Q (the reaction quotient) for the reaction (eq 1) is 2.5. This means that the NH_3 complex will be effectively completely hydrolyzed in water. Particularly satisfying is that all predicted[4−9] log $K_1(NH_3)$ values are consistent with the nonexistence of NH_3 complexes of particular metal ions, following reactions of the type in eq 1, where these complexes have not been observed experimentally in aqueous solution. An approach not previously reported involves the LFER (linear free-energy relationship) between log K_1(dien) (see Figure 1 for key to ligand abbreviations) and log $K_1(NH_3)$, shown in Figure 2. The log $K_1(NH_3)$ of 5.1 for Bi^{3+} allowed, for example, the prediction[7] of log K_1 for the [12]aneN$_4$ complex of Bi^{3+}, and synthesis of its complex.

Despite the success of empirical approaches to the prediction of log $K_1(NH_3)$ and the large amount of data supporting the estimated log $K_1(NH_3)$ values, it is clear that a different avenue of prediction for the unknown log $K_1(NH_3)$ values would greatly increase the confidence with which these log $K_1(NH_3)$ values can be regarded. The calculation of all the solvational changes that would occur in a complex formation equilibrium in aqueous solution would present considerable difficulties. To get around this problem, the approach adopted here is to use the simplest "cluster" that will give a reasonable model of the complex formation reaction. A cluster might be the hydrated metal ion, including the inner-sphere waters and one layer of second sphere waters. There has been some success with this approach[12] in using DFT to model water-exchange reactions on metal ions in aqueous solution. The simplest cluster that might give a satisfactory representation of a complex formation reaction where a water molecule is replaced by an ammonia would be the metal aqua ion including only the inner sphere waters coordinated directly to the metal ion.

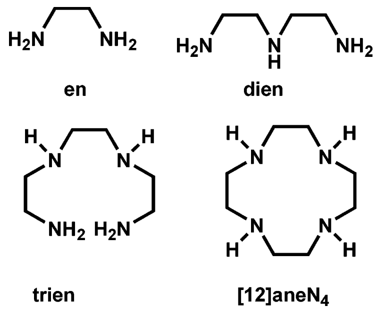


Figure 1. Ligands discussed in this paper.

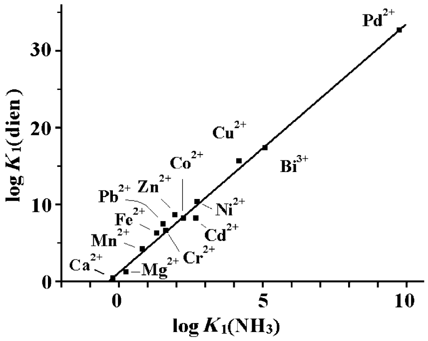


Figure 2. Linear free-energy relationship for log K_1(dien) versus log $K_1(NH_3)$ for a variety of metal ions. The important point of the diagram is the fit of the point for Bi^{3+}. No experimentally known log $K_1(NH_3)$ value is known[7] for Bi^{3+} because of its instability to hydrolysis in water (see eq 1). The value of log $K_1(NH_3)$ for Bi^{3+} of 5.1 comes from eqs 4 and 7. This value of 5.1 is consistent with dozens of correlations of the type presented in this figure. Some involve other N-donor ligands such as trien or [12]aneN$_4$ or a variety of LFER that involve ligands such as aminopolycarboxylates. Formation constant data were taken from ref 11, and the log K_1 value for Bi(III) with dien was taken from from ref 7.

The use of density functional theory (DFT) to calculate the free energies (ΔG) of reaction of metal aqua ions in the gas phase with NH_3 ligands,[13] according to eq 2, is reported here.

$$[M(H_2O)_6]^{n+}(g) + NH_3(g) = [M(H_2O)_5NH_3]^{n+}(g) + H_2O(g) \quad (2)$$

As in reported [14,15] DFT studies of the hydrolysis of trivalent metal ions, the ΔG for eq 2 is not expected to equal

---

(1) Burger, K., Ed. *Biocoordination Chemistry: Coordination Equilibria in Biologically Active Systems*; Ellis Horwood: New York, 1990. (b) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994. (c) Frausto da Silva, J. J. R.; Williams, R. J. P. *The Biological Chemistry of the Elements*; Oxford University Press: Oxford, U.K., 1991. (d) Cowan, J. A. *Inorganic Biochemistry: An Introduction*, 2nd ed.; Wiley-VCH: New York, 1997. (e) Kaim, W.; Schwederski, B. *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*; Wiley-VCH: Weinheim, Germany 1994.

(2) Steinnes, E., Salbu, B., Eds. *Trace Elements in Natural Waters*; CRC Press: Boca Raton, FL, 1995.

(3) Bianchi, A.; Calabi, L.; Corana, F.; Fontana, S.; Losi, P.; Maiocchi, A.; Paleari, L.; Valtancoli, B. *Coord. Chem. Rev.* **2000**, *204*, 309. (b) See Orvig, C.; Abrams, M. *Chem. Rev.* **1999**, *99*, 2201 and the following papers in that issue.

(4) Hancock, R. D.; Marsicano, F. *Inorg. Chem.* **1978**, *17*, 560.

(5) Hancock, R. D.; Marsicano, F. *Inorg. Chem.* **1980**, *19*, 2709.

(6) Hancock, R. D.; Marsicano, F. *J. Chem. Soc., Dalton Trans.* **1976**, 1096.

(7) Hancock, R. D.; Cukrowski, I.; Baloyi, J.; Mashishi, J. *J. Chem. Soc., Dalton Trans.* **1993**, 2895.

(8) Mulla, F.; Marsicano, F.; Nakani, B. S.; Hancock, R. D. *Inorg. Chem.* **1985**, *24*, 3076.

(9) Hancock, R. D. *Analyst* **1997**, *122*, 51R.

(10) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2001.

(11) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1974−1985; Vol. 1−6.

(12) Erras-Hanauer, H.; Clark, T.; van Eldik, R. *Coord. Chem. Rev.* **2003**, *233*, 238.

(13) The present work has been reported as a preliminary communication: Hancock, R. D.; Bartolotti, L. J. *J. Chem. Soc., Chem. Commun.* **2004**, 534.

(14) Rustad, J. R.; Dixon, D. A.; Rosso, K. M.; Felmy, A. R. *J. Amer. Chem. Soc.* **1999**, *121*, 3234. (b) Rosso, K. M.; Rustad, J. R.; Gibbs, G. V. *J. Phys. Chem.* **2002**, *106*, 8133.

numerically the ΔG for the same reaction in aqueous solution. Important solvational effects in aqueous solution are not included in eq 2. However, one could expect these effects to be constant or vary systematically along a series of metal ions with the change in ΔG, so that a simple correlation between the calculated values of ΔG for eq 2 and the ΔG values for the same reaction in aqueous solution (or, equivalently, the log K_1 value) could be anticipated.

Of particular interest is the role of relativistic effects (RE) in the stability of complexes of heavy metal ions such as Au(I), where it has been suggested[16] that the chemistry is largely dominated by RE. The energy of the 6s subshell in heavy elements such as Au and Hg is greatly decreased by RE, leading to greatly increased covalence[16] in the M−L bonds. The DFT calculations offer the possibility of repeating the calculations with and without corrections for RE, to see what role is played by RE in producing the soft behavior in the HSAB[17,18] (hard and soft acids and base) sense of a metal ion such as Au(I).

Computational Method

The reaction free energies were obtained by performing electronic structure calculations on the reactants and the products given in eq 2. Ground-state energies, E_{el}, optimized geometries, and Hessians were calculated using the density-functional[19] software package DMol3.[20−22] The exchange-correlation energy was approximated by the Becke−Tsuneda−Hirao gradient-corrected functional.[23,24] 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 the convergence criteria for the gradient in geometry optimizations was set to 10^{-4} hartree per bohr. The calculations that included relativistic effects employed the all-electron scalar-relativity option available in DMol3.[25] 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, from which translational and rotational degrees of freedom were projected.[26] The E_{el}, geometries, and ν_i allowed us to calculate the temperature-dependent partition functions needed in the statistical mechanical expression for molecular free energies.[27]

Results and Discussion

The values calculated here by DFT for the gas-phase reaction energies (ΔE) and the reaction energies corrected for zero-point energy (ΔE(zpe corr)), as well as the enthalpies (ΔH) and free energies (ΔG) for the formation of the $[M(H_2O)_5NH_3]^{n+}$ complexes from the hexa-aqua ions in the gas phase, for the divalent (M(II)), trivalent (M(III)), and tetravalent (M(IV)) metal ions, respectively, are given in Tables 1−3 . All these calculations include corrections for relativistic effects (RE). The same thermodynamic values calculated by DFT for the gas-phase formation of the

Table 1. Values of ΔE, ΔH, and ΔG at 298 K for the Reaction Involving the Replacement of an H_2O by an NH_3 on the Hexa-Aqua Ion in the Gas Phase (eq 2) for Divalent Metal Ions, Calculated in This Work from DFT as Described in the Text[a]

	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
ΔE	−11.3166	−11.5313	−11.5027	−9.8667
ΔE (zpe corr)	−10.5314	−11.3454	−12.1156	−8.4185
ΔH	−10.5811	−11.6707	−12.9672	−8.2953
ΔG	−10.4521	−11.6598	−11.1801	−8.4868

	Fe^{2+}	Mn^{2+}	Mg^{2+}	Ca^{2+}
ΔE	−9.9202	−7.7301	−4.4134	−3.3067
ΔE (zpe corr)	−8.3130	−7.0388	−3.0182	−3.4091
ΔH	−7.7433	−7.0748	−2.8964	−3.6546
ΔG	−8.7032	−6.7903	−2.9294	−3.0603

[a] Units are kcal mol^{-1}.

Table 2. Values of ΔE, ΔH, and ΔG at 298 K for the Reaction Involving the Replacement of an H_2O by an NH_3 on the Hexa-Aqua Ion in the Gas Phase (eq 2) for Trivalent Metal Ions, Calculated in This Work from DFT as Described in the Text[a]

	Al^{3+}	Ga^{3+}	In^{3+}	Tl^{3+}	Sc^{3+}
ΔE	−11.4846	−19.0752	−19.7761	−24.7599	−8.4454
ΔE (zpe corr)	−11.2675	−18.4101	−18.4211	−24.2902	−8.1174
ΔH	−10.8650	−18.3060	−18.6648	−24.2354	−7.9063
ΔG	−12.2954	−18.5942	−17.7600	−23.9010	−8.3879

	Y^{3+}	La^{3+}	Lu^{3+}	Am^{3+}	Lr^{3+}
ΔE	−7.2216	−6.4054	−8.2683	−10.8692	−9.6156
ΔE (zpe corr)	−6.8341	−6.4041	−8.1577	−10.6144	−9.1861
ΔH	−6.7032	−6.0855	−7.8655	−10.4087	−9.0655
ΔG	−7.0685	−7.3678	−8.5680	−10.7684	−9.3735

	Cr^{3+}	Co^{3+}	Rh^{3+}	Ir^{3+}	Bi^{3+}
ΔE_R	−16.2915	−24.1318	−26.9128	−27.9196	−16.6459
ΔE_R (zpe corr)	−15.5401	−23.3933	−26.3837	−27.3759	−15.7732
ΔH	−15.4805	−23.1871	−26.0940	−27.1344	−15.7407
ΔG	−15.5787	−23.5978	−27.1200	−27.7315	−15.7823

[a] Units are kcal mol^{-1}.

Table 3. Values of ΔE, ΔH, and ΔG at 298 K for the Reaction Involving the Replacement of an H_2O by an NH_3 on the Hexa-Aqua Ion in the Gas Phase (eq 2) for Tetravalent Metal Ions, Calculated in This Work from DFT as Described in the Text[a]

	Zr^{4+}	Hf^{4+}	Th^{4+}
ΔE	−12.2325	−12.8587	−10.8010
ΔE (zpe corr)	−12.4264	−13.0098	−10.5141
ΔH	−11.8615	−12.4443	−10.2586
ΔG	−13.7841	−14.4003	−11.2736

	U^{4+}	Pu^{4+}	Pt^{4+}
ΔE	−13.5693	−15.4623	−40.1293
ΔE (zpe corr)	−13.3904	−14.7290	−38.9631
ΔH	−13.0769	−14.6526	−38.8990
ΔG	−14.2004	−14.9903	−38.8236

[a] Units are kcal mol^{-1}.

---

(15) Li, J.; Fisher, C. L.; Chen, J. L.; Bashford, D.; Noodleman, L. *Inorg. Chem.* **1996**, *35*, 4649.
(16) Koltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1997**, 1.
(17) Pearson, R. G.; Mawby, R. *J. Halogen Chem.* **1967**, *3*, 55. (b) Pearson, R. G. *Coord. Chem. Rev.* **1990**, *90*, 403.
(18) Pearson, R. G. *Chemical Hardness*; Wiley-VCH: Weinheim, Germany 1997.
(19) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
(20) DMol3 is available from Accelrys, San Diego, CA.
(21) Delley, B. *Modern Density Functional Theory: A Tool for Chemistry, Vol. 2 of Theoretical and Computational Chemistry*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995.
(22) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508.
(23) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 105.
(24) Tsuneda, T.; Hirao, K. *Chem. Phys. Lett.* **1997**, *268*, 510.
(25) Delley, B. *Int. J. Quant. Chem.* **1998**, *69*, 423.
(26) Miller, W. H.; Handy, N. C.; Adams, J. E. *J. Chem. Phys.* **1980**, *72*, 99.
(27) McQuarrie, D. A. *Statistical Mechanics*; Harper & Row: New York, 1976.

Table 4. Values of ΔE, ΔH, and ΔG at 298 K for the Reaction Involving the Replacement of an H_2O by an NH_3 on the Diaqua Ion in the Gas phase (eq 9) for Univalent Metal Ions, Calculated in This Work from DFT as Described in the Text,[a] Incorporating Relativistic Effects and Excluding Relativistic Effects

	H^+	Cu^+	Ag^+	Au^+
		Relativistic		
ΔE	−26.7704	−19.8860	−16.9575	−28.1358
ΔE (zpe corr)	−24.7710	−18.8958	−16.0456	−27.0475
ΔH	−24.1129	−19.1018	−16.2239	−27.1894
ΔG	−26.0913	−18.8090	−16.1144	−27.1699
		Nonrelativistic		
ΔE	−26.7293	−18.7268	−13.5182	−13.6358
ΔE_R (zpe corr)	−24.8397	−17.8284	−12.4743	−12.5517
ΔH	−24.1016	−18.5454	−12.7693	−12.8701
ΔG	−26.5195	−16.9901	−12.2004	−12.2253

[a] Units are kcal mol^{-1}.

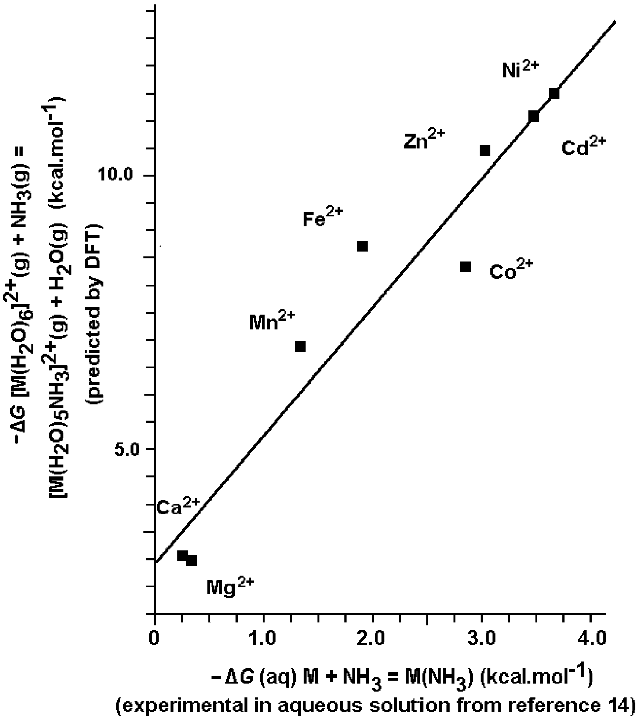


Figure 3. ΔG for the formation of the mono-NH_3 complexes of the divalent metal ions calculated by DFT in the gas phase (eq 3) and plotted against experimental[11] values in aqueous solution. The line fitted to the points is the least-squares best-fit line with $y = 2.201x + 2.951$.

$[M(H_2O)NH_3]^+$ cations from the di-aqua ions, both with and without corrections for RE, and for the univalent (M(I)) Lewis acids H^+, Cu^+, Ag^+, and Au^+ are given in Table 4.

Ammonia Complexes of Divalent Cations. In Figure 3, the relationship between the DFT-calculated ΔG for reaction 2 (ΔG(DFT)) for the M(II) ions and the experimental values[11] (ΔG(aq)) is shown. The equation for the best-fit straight line is given by eq 3, for divalents

$$\Delta G(\text{DFT}) = 2.201(\Delta G(\text{aq})) + 2.951 \tag{3}$$

The correlation coefficient (R^2) for Figure 4 is 0.976, while for Figure 4 (M(III) ions) R^2 is 0.976 and 0.989 for the two separate correlations for metal ions of coordination numbers greater than 6 and equal to 6. For Figure 5, for the M(IV) ions, R^2 is 0.952, while in Figure 6 for the univalent metal ions, it is 0.970 for the data that include RE. An R^2 value of 0.952 is reasonable in terms of the correlation sought of ΔG(DFT) with ΔG(aq), with complex solvational changes occurring in the latter case, and gives one some confidence that the relationships found in Figures 3−5 are significant. One problem with the correlation for M(II) ions in Figure 3 may be that the coordination number (C.N.) is not constant

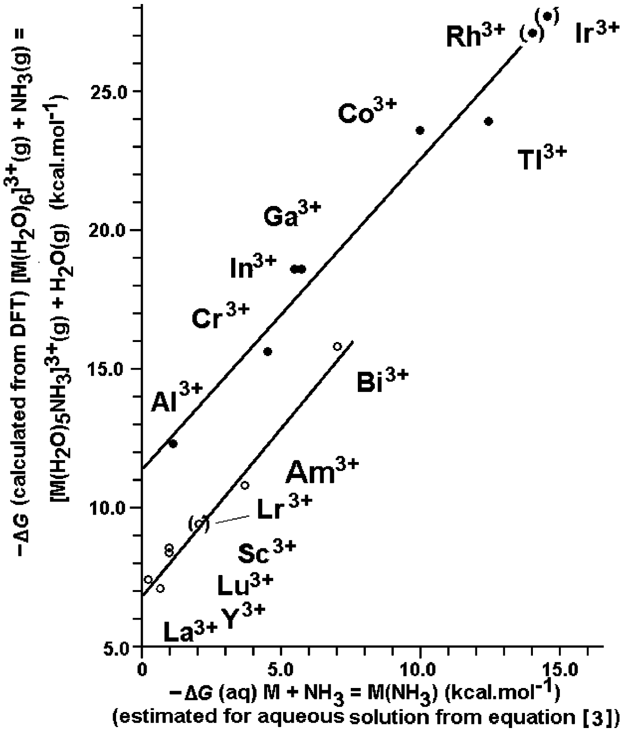


Figure 4. Relationship between the ΔG values calculated from DFT for the formation in the gas phase of the ammonia complexes of trivalent metal ions (eq 5) and the ΔG values for the formation of the monoammonia complexes (ref 35) in aqueous solution. Separate relationships are found for metal ions that form octahedral aqua ions (●) and aqua ions of higher coordination numbers (○) (see Table 5). Points in parentheses are for metal ions (Lr^{3+}, Rh^{3+}, and Ir^{3+}) where no ΔG value in aqueous solution is known, but ΔG, and hence log $K_1(NH_3)$, can be estimated from the ΔG calculated by DFT from eqs 5 and 6. This approach indicates that the log $K_1(NH_3)$ value for Lr^{3+} is 1.46, for Rh^{3+} is 10.5, and for Ir^{3+} is 10.9.

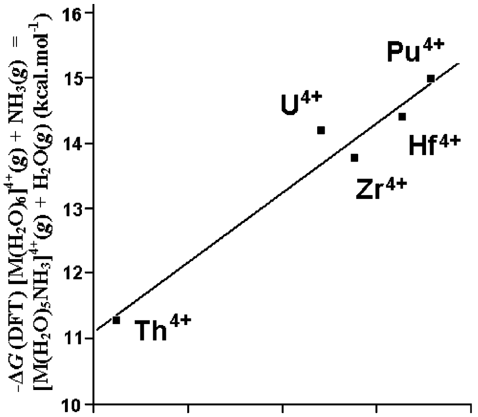


Figure 5. Relationship between the ΔG value calculated from DFT for the formation in the gas phase of the ammonia complexes of tetravalent metal ions (eq 8) and the ΔG values for the formation of the monoammonia complexes (eq 7) in aqueous solution.

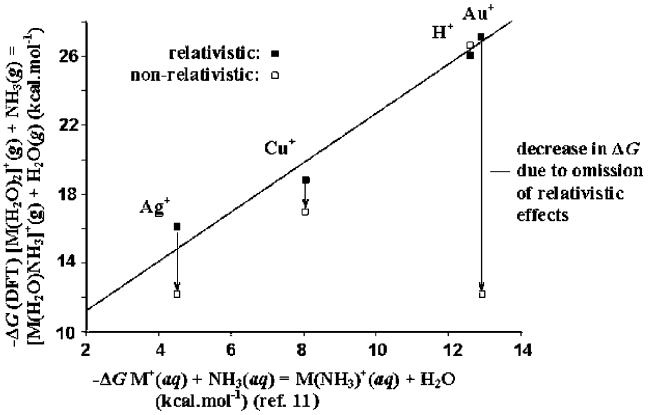


Figure 6. Relationship between the ΔG values calculated from DFT for the formation in the gas phase of the ammonia complexes of univalent metal ions (eq 9) and the ΔG values for the formation of the monoammonia complexes (ref 35) in aqueous solution. The calculation of ΔG(DFT) was carried out with (■) and without (□) corrections for relativistic effects.

Table 5. Coordination Numbers of the Aqua Ions of Trivalent Metal Ions in the Solid State Indicated in the Cambridge Structural Database (CSD) and Elsewhere in the Literature,[a] Together with Wag-Angles (θ) Calculated Here by DFT for Coordinated Waters

	Al^{3+}	Ga^{3+}	In^{3+}	Tl^{3+}	Cr^{3+}	Co^{3+}	Rh^{3+}
ionic radius[b] (Å)	0.54	0.62	0.80	0.88	0.58	0.55	0.67
C.N.	6	6	6	6	6	6	6
no. of examples in CSD	12	1	1	1[c]	6	1[d]	1[d]
wag-angle, θ (deg)	180	180	180	144.7	180	159.0	154.7

	Ir^{3+}	La^{3+}	Y^{3+}	Lu^{3+}	Sc^{3+}	Bi^{3+}
ionic radius[b] (Å)	0.68	1.16	1.02	0.98	0.87	1.03
C.N.	6[d]	9	9	8,9	6,7,9	9
no. of examples in CSD	1[d]	5	6	3,2	1,1,1	1
wag-angle, θ (deg)	141.7	180	180	180	180	180

[a] CSD is ref 29. See ref 38 for solution C.N. and ref 42 for the C.N. of Ga^{3+}, In^{3+}, and Cr^{3+} in aqueous solution, as well as ref 43 for metal hexa-aqua ions in the solid state. [b] Ref 33. Ionic radius is for C.N. = 6 for smaller metal ions and C.N. = 8 for metal ions with C.N. > 6. [c] From ref 44 and 45, but Tl(III) shows a C.N. value as high as 10 in other complexes (see ref 46). [d] Structures of alums in ref 42.

Table 6. Log $K_1(NH_3)$ Values for Metal Ions in Aqueous Solution Studied in This Paper

	Ca^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}
exptl[a]	0.1	0.24	0.90	1.53	2.33	2.10	2.73	2.62
eq 4	0.09	0.19	0.98	1.65	2.31	1.97	2.61	2.63
DFT[b] (eq 3)	0.02	−0.02	1.24	1.86	2.43	1.79	2.67	2.62

	Al^{3+}	Cr^{3+}	Ga^{3+}	In^{3+}	Co^{3+}	Rh^{3+}	Ir^{3+}	Tl^{3+}
exptl[c]		(3.4)			(7.3)			
eq 4	0.55	3.34	3.80	3.96	7.23			9.09
DFT[b] (eq 5)	0.94	2.75	4.76	4.21	8.12	10.5	10.9	8.32

	La^{3+}	Y^{3+}	Lu^{3+}	Sc^{3+}	Am^{3+}	Bi^{3+}	Lr^{3+}
eq 4	0.46	0.38	0.67	0.69	2.71	5.04	
DFT (eq 6)	0.27	0.09	0.99	0.88	2.29	5.27	1.46

	Th^{4+}	U^{4+}	Zr^{4+}	Hf^{4+}	Pu^{4+}	Pt^{4+}
eq 7	0.40	1.77	2.02	2.4	2.6	
DFT (eq 8)	0.12	2.11	1.83	2.25	2.65	~16

	H^+	Cu^+	Ag^+	Au^+
exptl	9.26	5.93	3.31	
eq 4	9.14	5.91	3.41	9.47
DFT (eq 10)	9.20	5.21	3.72	9.79

[a] Experimental values from ref 11. [b] Calculated using eqs 3, 5, 6, 8, and 10. [c] For these metal ions log $K_1(NH_3)$ is not known, but an experimental value of log $\beta_6(NH_3)$ has been reported,[11] which allows for the estimation of log $K_1(NH_3)$ by comparison with other metal ions where both log $K_1(NH_3)$ and log $\beta_6(NH_3)$ are known.

Table 7. Statistical Validation of the Least-Squares Correlations in Figures 3−6 and Eqs 3, 5, 6, 8, and 10, for the Relationship between ΔG(DFT) and ΔG(aq)

correlation	R^2	F^a	P	se(LOO)[b]
M^{2+} ions (Figure 3, eq 3)	0.952	119.8	3.449×10^{-5}	0.38
M^{3+} ions, C.N. = 6 (Figure 4, eq 5)	0.951	77.8	0.000911	1.42
M^{3+} ions, C.N. > 6 (Figure 4, eq 6)	0.978	181.5	0.000176	0.65
M^{4+} ions (Figure 5, eq 8)	0.952	59.8	0.00449	0.41
M^+ ions (Figure 6, eq 10)	0.970	64.4	0.01517	1.23

[a] For a discussion of the F test see ref 38. Note that the P parameter is calculated by the EXCEL function P = FDIST(F-value,1,ndf), where ndf = number of degrees of freedom = $N - 2$, where N is the number of data points. The smaller the P parameter, the greater is the significance of the linear correlation. [b] se(LOO) = standard error for the LOO cross validation. For a discussion of LOO cross-validation, see text and ref 39. Note that the standard errors given here are on x rather than y for the $y = mx + b$ expressions, since one is interested in knowing how accurately an unknown ΔG(aq) (x) would be predicted from the calculated ΔG(DFT) (y) values.

at 6, as implied by eq 2. This is the case for Ca^{2+}, where the preferred C.N. is[1,28,29] 7, although the point for Ca^{2+} in Figure 3 does not deviate much from the fitted line. Other possibilities are that ions such as Zn^{2+} and Co^{2+} may have considerable concentrations of tetrahedral aqua ion present in solution, which may affect the outcome. The statistical significance of the correlations in Figures 3−6 is summarized in Table 7.

The slope of the relationship in Figure 3 is quite large, 2.201, which suggests that there are large systematic changes in solvational effects as one proceeds along the series of metal ions with increasing ΔG(aq) for the formation of $[M(H_2O)_5NH_3]^{2+}$. Gas-phase basicities of the *p*-substituted pyridines obtained from the HF-type calculations were found[30] to correlate with aqueous phase basicities. In this case, a slope of 3.5 rather than unity was obtained, showing that, in solution, solvation greatly dampened the electronic effects of the substituents. The slope of 2.201, obtained in Figure 3, suggests that as the value of ΔG for the formation of the ammonia complex increases in the gas-phase, the charge on the H atoms of the inner-sphere waters decreases, altering the strength of solvation by the bulk solvent. The variation of ΔG for reaction 6 is thus dampened by solvation, much as was found[30] for the gas-phase energies of protonation of differently substituted pyridines.

Ammonia Complexes of Trivalent Metal Ions. Figure 4 shows the relationship between ΔG(DFT) and ΔG(aq) for the M(III) ions. Virtually all of the ΔG(aq) values used in Figure 4 have been estimated[4−9] from numerous correlations, such as those seen in Figure 2, as well as from a variety of

---

(28) Hancock, R. D.; Siddons, C. J.; Oscarson, K. A.; Reibenspies, J. H. *Inorg. Chim. Acta* **2004**, *357*, 723.

(29) Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom.

(30) Taagapera, M.; Henderson, W. G.; Brownlee, R. T. C.; Beauchamp, J. L.; Holtz, D.; Taft, R. W. *J. Amer. Chem. Soc.* **1972**, *94*, 1369.

equations. The one of most interest is eq 4, which is based[4,5−9] on the "E and C" equation of Drago,[31,32] but refers to aqueous solutions rather than solvents with low dielectric constants.

$$\log K_1 = E'_aE'_b + C'_aC'_b \qquad (4)$$

In eq 4, the E' and C' parameters refer to the ionic and covalent contributions, respectively, to the ΔG of complex formation in an aqueous solution, referring to the acid (a) and base (b).

The estimated ΔG(aq) values used in Figure 4 have changed little from the first estimates obtained from eq 4 some 26 years ago, but they correlate well with the ΔG(DFT) values obtained in this work. The two separate correlations drawn in Figure 4 appear to be for small metal ions with a C.N. value of 6 and ionic radii[33] of $r^+ < 0.90$ Å and for large metal ions with $r^+ > 0.90$ Å and C.N. > 6. The C.N. values for the M(III) aqua ions, shown in Figure 4 as obtained from the CSD,[29] are shown in Table 5. The split according to the C.N. in Figure 4 reflects the effects of C.N. found[14] for the predicted log $K_1(OH^-)$ values. The two best-fit linear relationships can be expressed as eq 5 and 6. For trivalents with C.N. = 6

$$\Delta G(\mathrm{DFT}) = 1.094\ (\Delta G(\mathrm{aq})) + 11.484 \qquad (5)$$

and for trivalents with C.N. > 6

$$\Delta G(\mathrm{DFT}) = 1.233(\Delta G(\mathrm{aq})) + 6.910 \qquad (6)$$

It should be noted that eq 5 and 6 differ somewhat from the corresponding equations reported initially[13] because we realized that the Tl^{3+} aqua ion is better described as having a C.N. value of 6, rather than a C.N. value of >6, as was first thought. The slopes of the relationships are much less than those for the M(II) ions in Figure 4. This is effect is still greater for the M(IV) ions, as seen in Figure 5. The relationship in eq 5 can be used to estimate log $K_1(NH_3)$ = 10.5 for Rh(III) and 10.9 for Ir(III), which is reasonable in relation to log $K_1(NH_3)$ = 7.3 for Co(III) and 9.7 for Pd(II).[11] The estimated log $K_1(NH_3)$ value for Lr(III) of 1.46 that can be made from the ΔG(DFT) value for Lr(III) in Table 3, assuming it to have C.N. > 6, is also of interest. The M(III) state of Lr is its most stable, and C. N. = 8−9 seems probable because it resembles a lanthanide(III) ion in its chemistry.[34] ^{262}Lr, the most stable isotope of Lr, has a half-life[34] of only 3.6 h, so that the study of its aqueous chemistry is difficult. It is hoped that the approaches adopted here will lead to the ability to predict the aqueous-phase chemistry of metal ions, such as those of the heavier transuranics, where experimental approaches would be very problematical.

A referee has raised the very reasonable point that the separation of metal ions according to C.N., as in Figure 4, presents some problems. For example, Sc^{3+} may be fairly described as preferring a C.N. value of 6, even though it does frequently[29] display a higher C.N. A scan[28] of the C.N. numbers of Sc^{3+} complexes in the CSD[29] reveals 4 that have a C.N. value of 9, 17 with a C.N. value of 8, 23 with a C.N. value of 7, and 78 with a C.N. value of 6. In making such a scan, the structures with coordinated-unsaturated organics with high hapticity, such as cyclopentadienyl or allyl complexes, are omitted because they skew the results in the direction of high C.N. and have no bearing on ordinary coordination compounds. A similar scan for Ga^{3+}, which in Figure 4 is designated as having a C.N. value of 6, reveals no complexes with C.N. > 6, if the high-hapticity π-complexes are omitted, but there are 312 hits for complexes with a C.N. value of 6. One might say that Ga^{3+} and the other metal ions designated as having a C.N. value of 6 have, except for Tl^{3+}, a very strong tendency to not exceed C.N. = 6, while Sc^{3+} frequently does exceed C.N. = 6. It may turn out with future work on other ligands that the separation of M^{3+} ions here by C.N. is not justified, although, as noted above, the same phenomenon[14] appeared to be present with DFT calculations on OH^- complexes. If one combines all of the points on Figure 4, as a single correlation, one obtains a still-respectable R = 0.94 from the best-fit line.

Ammonia Complexes of Tetravalent Metal Ions. Figure 5 shows a good relationship between ΔG(DFT) and ΔG(aq) for the M(IV) ions. Unlike Figures 3 and 4, the ΔG(aq) values are somewhat revised from those estimated previously.[35] Because of the high acidity[11] and slow rates of ligand exchange of the M(IV) ions, it is very difficult to determine the log K_1 values for these ions. The values of log $K_1(NH_3)$, used in Figure 5, were thus all calculated here from a rearranged version of eq 4, incorporating the E'_a and C'_a parameters for F^-, OH^-, and NH_3 because the log $K_1(OH^-)$ and log $K_1(F^-)$ values[11] of these ions appeared to be the most accurately known

$$\log K_1(\mathrm{NH_3}) = 0.881 \log K_1(\mathrm{OH^-}) - 1.08 \log K_1(\mathrm{F^-}) \qquad (7)$$

The values for log $K_1(NH_3)$ obtained from eq 7 for M(IV) ions are given in Table 6. The relationship between the ΔG(DFT) and ΔG(aq) values for the M(IV) ions is given in eq 8 (R = 0.976). For tetravalents

$$\Delta G(\mathrm{DFT}) = 1.076(\Delta G(\mathrm{aq})) + 11.095 \qquad (8)$$

The progressive decrease in slope for the correlations $M^{2+} > M^{3+} > M^{4+}$ has continued here, with a slope in eq 10 close to unity. At the same time, the intercepts in the relationships have continued to increase, $M^{2+} < M^{3+} < M^{4+}$. The variation in slopes suggests that the M(II) ions show the greatest variation in the solvational effects as ΔG(aq) varies, while the M(IV) ions show the least. Conversely, the variation in the intercepts in eq 3, 5, 6, and 8 suggests small constant changes in solvation for the M(II) ions and large constant changes in solvation for the M(IV) ions.

---

(31) Drago, R. S.; Vogel, G. C.; Needham, T. E. *J. Am. Chem. Soc.* **1971**, *93*, 6014.

(32) Drago, R. S. *Struct. Bonding* **1973**, *15*, 73.

(33) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(34) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heineman: Oxford, U.K., 1997; p 1263.

(35) Martell, A. E.; Hancock, R. D. *Metal Complexes in Aqueous Solutions*; Plenum: New York, 1996; p 48.

Table 3 contains a ΔG(DFT) value for the Pt(IV) ammonia complex, which is very large at about -40 kcal.mol^{-1}. Equation 10 suggests, from this ΔG(DFT) value, a ΔG(aq) value of 27 kcal.mol^{-1}. One notes that the M(IV) ions in Figure 4 all have[34] have a C.N. value of ~8, while Pt(IV) always has a C.N. value of 6. One would guess that a relationship for the M(IV) ions with a C.N. value of 6 would have a larger intercept by about 4 kcal mol^{-1}, as can be seen in Figure 3 for the M(III) ions. Thus, ΔG(aq) for the Pt(IV) ammonia complex would probably be reduced to $27 - 4 = 23$ kcal mol^{-1}. The latter suggests a log $K_1(NH_3)$ value at 298 K of about 17 for Pt(IV), which seems reasonable in comparison with the log $K_1(NH_3)$ values for the trivalent low-spin d^6 ions estimated here, namely, Co(III), 7.3; Rh(III), 10.5; and Ir(III), 10.9.

Ammonia Complexes of Univalent Metal Ions. The M(I) ions Cu(I), Ag(I), Au(I), and H(I) tend to favor a low C.N.[34] value of 2 in their aqua ions, with only Cu(I) commonly favoring a C.N. value of 3 or 4. A solid-state structure of the aqua ion of Ag(I) shows it to be the $[Ag(H_2O)_2]^+$ ion,[36] although it has been suggested[37] that the Ag(I) aqua ion is tetrahedral in solution. Some 40 structures of the $[H(H_2O)_2]^+$ ion reported in the CSD[29] all show a C.N. value of 2, usually with two symmetric bonds to the central proton. Where additional waters are present, as in ions such as $[H_9O_4]^+$ or $[H_{13}O_6]^+$, the structure[29] is the same as for $[H(H_2O)_2]^+$, with the additional water molecules H-bonded to the two waters already coordinated to the proton. The correlation with ΔG(aq) that was set up involved di-aqua ions $[M(H_2O)_2]^+$ in eq 9, rather than the $[M(H_2O)_6]^+$ ions.

$$[M(H_2O)_2]^+(g) + NH_3(g) = [M(H_2O)NH_3]^+(g) + H_2O(g) \tag{9}$$

The plot of ΔG(DFT) for eq 9 versus ΔG(aq) for the formation of the monoamine complexes of H(I), Cu(I), Ag(I), and Au(I) is in Figure 6. The correlation in Figure 6 gives the best-fit linear relationship below with $R = 0.984$. Figure 6 suggests that use of a C.N. value of 2 for these univalent metal ions is reasonable. For the univalents with C.N. = 2

$$\Delta G(\mathrm{DFT}) = 1.336(\Delta G\ (aq)) + 9.32 \tag{10}$$

Since these are di-aqua ions, the slope and intercept of eq 10 probably cannot be compared with those of eq 3, 5, 6, and 8, which refer to hexa-aqua ions. The log $K_1(NH_3)$ values for M(I) = Cu(I), Ag(I), and H(I) are experimental,[11] while that for Au(I) is derived from eq 4 and a best fit to the scanty log K_1 values available[11] for Au(I). The calculated value of ΔG(DFT) for Au(I) is consistent with an estimated log $K_1(NH_3)$ for Au(I) of 9.8, which seems reasonable in relation to the log $K_1(NH_3)$ values for metal ions close to Au in the periodic table, such as the log $K_1(NH_3)$ value for Hg(II) which is 8.8[11] or that for Tl(III) which is 9.1.[4,5]

Au has been described[16] as a "relativistic element", which means that its chemistry is dominated by RE. The electrons in the 1s shell of Au are traveling[16] at some 60% of the speed of light, which increases their mass by about 25%. The effect of this is a considerable decrease in the energy of the 1s shell and a contraction in the radius of all the *n*s shells in Au, including its 6s valence shell, which makes the ionic radius of Au(I) some 20% smaller than it would be otherwise. Other important effects in Au are the large spin–orbit coupling effects that split the 6p shell into two levels. This leads to the formation of sp hybrid orbitals rather than sp^3 hybrids; the sp hybridization leads to the strong tendency for linear-coordination geometry seen in Au(I) and neighbors, such as Ag(I) and Hg(II). Most importantly, the contraction of the 6s orbital leads to a tremendous increase in covalence of the M–L bond in Au and the elements adjacent to Au.

The present calculations can suggest what would happen to the aqueous phase chemistry of Au(I) in the absence of RE. Table 4 shows the calculated values of ΔG(DFT) obtained with corrections for RE omitted. As can be seen, there is only a small change in ΔG(DFT) for H(I), which is as expected. For Cu(I), ΔG(DFT) decreases by 1.8 kcal.mol^{-1}, which corresponds to a change in predicted log $K_1(NH_3)$ (assuming eq 10 still holds) from 5.2 (relativistic) to 4.2 (nonrelativistic). For Ag(I), the changes in the predicted log $K_1(NH_3)$ values are considerably larger at 3.75 (relativistic) down to 1.58 (nonrelativistic). For Au(I), the changes are massive with log $K_1(NH_3)$ predicted to be 9.8 (relativistic) but only 1.6 (nonrelativistic). One should note that a log $K_1(NH_3)$ value of 1.6 for Au(I) would put it (and also the soft Ag(I) ion) with no RE, chemically in the same league as a metal ion such as Fe(II), with[11] log $K_1(NH_3) = 1.4$. Fe(II) is classified as intermediate in the HSAB classification. The calculations here suggest that without RE, there might be no soft metal ions at all in the HSAB classification, but only very hard and somewhat less hard metal ions.

Statistical Significance of the Correlations. The good *R* values obtained for the least-squares relationships in Figures 3–6 suggest that these can be used to predict the formation constants in aqueous solution with some reliability. Statistical methods can, as suggested by a referee, be used to analyze this in more detail. The LINEST and FDIST functions of EXCEL[38] allow for a ready F-test validation of the relationships, shown in Table 7. In addition, a LOO ("leave-one-out")[39] cross-validation can be applied. In this approach, for a correlation containing *n* points, *n* least-squares fits to the data are carried out omitting a different point each time, to obtain *n* "training sets". The *n* training sets are then used to predict the data point that was left out in each case. The standard error between the predicted and missing data points then indicates how well a point not available in constructing the overall correlation might be predicted. These LOO standard errors are presented for the least-squares correlations in Figures 3–6 in Table 7. Significantly, these indicate that for Figure 3 (eq 3) for M^{2+}

---

(36) Makhmudova, N. K.; Sharipov, Kh. T.; Khodashova, T. S.; Porai-Koshits, M. A.; Parpiev, N. A. *Proc. Natl. Acad. Sci. USSR* **1985**, *280*, 1360.

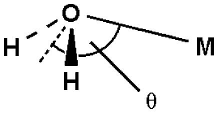
(37) Texter, J.; Hastrelter, J. J.; Hall, J. L. *J. Phys. Chem.* **1983**, *87*, 4690.

(38) Billo, E. J. *EXCEL for Chemists*; Wiley-VCH: New York, 2001.

(39) Rivals, I.; Personnaz, L. *Neural Comput.* **1999**, *11*, 863 and references therein.

ions, which is the only correlation containing exclusively experimental $\Delta G(NH_3)$ values, the LOO standard error is 0.38 kcal mol^{-1}. This means that the value of log $K_1(NH_3)$ could be expected to be predicted for M^{2+} ions at 25 °C by DFT calculation and eq 3 to an accuracy of 0.28 log units. For the M^+ and M^{3+}correlations, the LOO standard errors are higher. This appears to be related to the fact that the log $K_1(NH_3)$ values for many of the M^+ and M^{3+} ions are much larger than for the M^{2+} ions, and therefore, as a percentage deviation, the accuracy remains about the same.

Structures of the Aqua Ions. The structures of the aqua ions generated here show some interesting features. For metal ions with low E'_a/C'_a ratios (roughly soft in the HSAB sense[4,5]), the water molecules coordinate to the metal ion so that the plane containing the water molecule forms an angle (the “wag-angle”, angle θ) with the M−O bond with θ less than 180°. The wag angle for water coordinated to a metal ion is shown below



For metal ions with high E'_a/C'_a ratios (roughly hard), the metal ion lies in the plane of the coordinated water molecule, θ is 180°. The interpretation of this[40,41] is that the bonding of water molecules to metal ions is a balance between two bonding modes. With purely ionic bonding, the metal ion is aligned along the dipole of the water, which minimizes electrostatic repulsion between the positive charge on the metal ion and the protons of the water. With more covalent bonding, overlap between the b_1 molecular orbital of the water molecule (the higher energy lone pair, essentially the $2p_x$ orbital of the oxygen) and the orbitals of the metal ion increases. In the limit, this would have the metal ion coordinated at right angles to the plane of the water molecule ($\theta = 90°$). The transition point between the two bonding modes appears to be an E'_a/C'_a ratio of about 3.5, with higher E'_a/C'_a ratios leading to the planar ionic mode of coordination, while below this point, θ tends to decrease with the decreasing E'_a/C'_a ratio. Thus, θ is, at 132.3°, smallest for Au(I), the softest metal ion. Note that θ is 125.3° for regular tetrahedral coordination around the O atom, assuming two sites to be occupied by lone pairs. Interestingly, θ is small for H^+, which has a moderately high E'_a/C'_a ratio (3.2), suggesting that factors other than covalence contribute to the value of α. As shown in Table 8, θ shows a large increase for Au(I) upon omitting RE corrections, confirming that RE are important for covalence in the Au−L bond and that decreases in covalence will be accompanied by an increase in θ. The increase in θ, upon omitting RE, in the order H(I) < Cu(I) < Ag(I) < Au(I) follows the order of decreasing E'_a/C'_a ratio. Note also the lengthening of the Au−O bond in Table 7 when the RE values are omitted from the calculations of the structure of $[Au(H_2O)_2]^+$.

Table 8. Structural Features of $[M(H_2O)_2]^+$ Aqua Ions Predicted by DFT With and Without Corrections for Relativistic Effects

		Au(I)	Ag(I)	Cu(I)	H(I)
M−O length (Å)	rel[a]	2.084	2.256	1.934	1.220
	nonrel[a]	2.431	2.335	1.960	1.219
angle θ (deg)[b]	rel[a]	132.3	146.4	144.3	141.2
	nonrel[a]	155.7	155.0	147.2	141.8
E'_a/C'_a ratio[c]		−16	−10.6	−1.3	3.3

[a] Rel = calculation with corrections for relativistic effects and nonrel = calculation without corrections for relativistic effects. [b] Angle θ is the angle between the M−O bond and the plane containing the water molecule. [c] The E'_a/C'_a ratio is a measure of covalence in the M−L bond, and relates to the softness of the Lewis acid in the HSAB sense.[4,5] The E'_a and C'_a parameters apply to eq 4. The more positive the E'_a/C'_a ratio, the more ionic the M−L bond.

Conclusions. The work reported here suggests that (1) the DFT-calculated gas-phase ΔG values for the replacement of one H_2O on metal hexa-aqua ions or di-aqua ions by an NH_3 correlate reasonably well with the ΔG values (both experimental and estimated by other approaches) in aqueous solution for the formation of the monoamine complexes. (2) These correlations allow for the prediction of unknown log $K_1(NH_3)$ values for a wide variety of metal ions, which are otherwise experimentally inaccessible. This might be particularly important for transuranic elements that are highly radioactive with short half-lives. (3) The DFT calculations here support the idea[16] that RE are dominant in the chemistry of Au(I), and that soft behavior in the HSAB sense may be largely dependent on such effects. It would be of particular interest to carry out calculations on Uuu(I), which is expected[34] to be in Group 11 of the periodic table with Cu, Ag, and Au. A referee has suggested that the use of a continuum model, such as the one presented by the COSMO feature[20] of DMol3, where the calculations are carried out in a structureless medium of appropriate dielectric constant, might present results closer to actual aqueous solution. This was being done at the time, and surprisingly, the COSMO energies give correlations as in Figures 3−6, very similar to those obtained with simply the ΔG(DFT) energies. Future work will involve complexes of other unidentate ligands, such as F^-, as well as those such as I^-, where solvation effects such as represented by extended versions of eq 4 will be important. It also seems possible that the approach adopted here would work for polydentate ligands such as EDTA where correlations between the ΔG(DFT) for the formation of the EDTA complexes in the gas phase and ΔG(aq) for the EDTA complexes might be expected. Possibly the most promising aspect of the present work is that it may offer a way to create a quantitative approach to HSAB in aqueous solution that also offers insights into factors that govern metal-ion complexation in aqueous solution.

Acknowledgment. The authors thank the University of North Carolina at Wilmington and East Carolina University,

---

(40) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.
(41) Davy, R. D.; Hall, M. B. *Inorg. Chem.* **1988**, *27*, 1417.
(42) Lindqvist-Reis, P.; Muòoz-Páez, A.; Díaz-Moreno, S.; Pattanaik, S.; Persson, I.; Sandström, M. *Inorg. Chem.* **1998**, *37*, 6675.
(43) Beattie, J. K.; Best, S. P. *Coord. Chem. Rev.* **1997**, *166*, 3391.
(44) Glaser, J. *Acta Crystallogr.* **1978**, *A34*, S197.
(45) Ma, G.; Molla-Abbassi, A.; Kritikos, M.; Ilyukhin, A.; Jalilehvand, F.; Kessler, V.; Skripkin, M.; Sandstrom, M.; Glaser, J.; Naslund, J.; Persson, I. *Inorg. Chem.* **2001**, *40*, 6432.
(46) Dutton, P. J.; Fyles, T. M.; Suresh, V. V.; Fronczek, F. R.; Gandour, R. D. *Can. J. Chem.* **1993**, *71*, 239.

as well as NSF Grant No. CHE 01-11131, for generous support for this work.

Note Added in Proof. In reference to the last paragraph in the Ammonia Complexes of Trivalent Metal Ions section, X-ray diffraction studies of Sc^{3+} in aqueous solution have suggested that the aqua ion is the seven-coordinated $[Sc(H_2O)_7]^{3+}$ ion (Yamaguchi, T.; Niihara, M.; Takamuru, T.; Wakita, H.; Kanno, H. *Chem. Phys. Lett.* **1997**, *274*, 485).

Supporting Information Available: The Cartesian coordinates of the refined structures, as well as the energies of the complexes, calculated by DFT here. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050471S