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Prediction of formation constants of metal–ammonia complexes in aqueous solution using density functional theory calculations

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Density functional theory calculation of gas-phase ΔG of replacement of a water molecule by NH_3 on $[M(H_2O)_6]^{n+}(g)$ for 19 different metal ions correlates well with ΔG of formation of mono NH_3 complexes of these ions in water, suggesting this approach will permit prediction of formation constants in aqueous solution, and produce insights into theories of metal complex formation reactions.

Prediction of formation constants of metal ion complexes in aqueous solution[1,2] has been limited to empirical approaches, such as in the Edwards equation,[3] or in a multi-parameter equation[4] (eqn. [1]) based on that of Drago:[5]

$$\log K_1 = E_a'.E_b' + C_a'.C_b' \qquad (1)$$

E and *C* reflect the tendency of the acid (a) or base (b) to undergo ionic or covalent bonding. Eqn. [1] has excellent predictive powers[4] for $\log K_1$ values[6] in aqueous solution. Most metal ions do not form NH_3 complexes in water because these are unstable to hydrolysis, so that $\log K_1(NH_3)$ values are unknown, as found for Bi^{3+}:

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

Eqn. [1] has predicted[4] $\log K_1(NH_3)$ for metal ions such as Bi^{3+}, which appear reasonable from a consideration[7] of the chemistry of Bi^{3+}, but a more theoretical approach to predicting formation constants in aqueous solution would be valuable. The Hard and Soft Acids and Bases (HSAB) principle of Pearson[8] lacks a quantitative basis,[9] which would promote, for example, understanding of the functioning of metalloenzymes.[10] Again, a theoretical approach to predicting formation constants in aqueous solution would provide valuable insights into the theoretical basis of HSAB.

Quantum Chemical prediction of ΔG of reaction for metal ions with bases such as NH_3 in the gas phase is now acceptable.[11] A major difficulty of making predictions of ΔG of complex formation in aqueous solution is clearly that of modeling the complex changes in solvation that occur during complex formation. The approach adopted here was to try to find a correlation between known or estimated log *K* (or equivalently ΔG) values in aqueous solution, and ΔG for the simplest gas-phase complex formation reactions calculated by DFT that would give a reasonable correlation with the aqueous phase results. Reactions involving exchange of an ammonia for a single water molecule on bare metal ions did not here give gas-phase ΔG of complex formation that correlated well with known ΔG ($\equiv \log K_1(NH_3)$) values in water. However, ΔG values calculated for reaction [3] in the gas phase correlated well with ΔG of complex formation in water for metal ions, as shown in Figs. 1 and 2.

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

Electronic structure calculations on reactants and products in eqn. [3] gave reaction free energies. Ground state energies, E_{el}, and optimized geometries were calculated using the density functional[12] software package DMol3.[13–15] The Becke-Tsuneda-Hirao gradient-corrected functional was used for exchange-correlation energy.[16,17] The double numerical plus polarization basis set and Darwin and mass-velocity relativistic effects[18] options were employed. Vibration frequencies (ν_i) for each reactant and product were obtained from a normal mode analysis of the Hessian matrix from DMol3, from which translational and rotational degrees of freedom were projected.[19] These results then gave temperature dependent partition functions needed in the statistical mechanical expression for molecular free energies.[20]

The approach followed here has precedent in calculations of the type where gas-phase basicities of *p*-substituted pyridines obtained from HF type calculations were found[21] to correlate with aqueous phase basicities, but with a slope of 3.5 rather than unity, showing that solvation greatly dampened the electronic effects of the substituents. Inclusion of one water molecule H-bonded to the proton on the N of the pyridine greatly reduces this slope, mimicking in a very simple manner the role of the solvent. In Fig. 1 is plotted ΔG for reaction [3] in the gas-phase against experimental[6] ΔG for formation of NH_3 complexes of M(II) ions in aqueous solution. The correlation should allow prediction of unknown free energies of formation of ammonia complexes in aqueous solution to an accuracy of 0.38 kcal mol^{-1}, or $\log K_1(NH_3)$ to an accuracy of 0.28 log units, based on standard deviations of the line fitted to the data.

It is interesting to note that the slope of the correlation in Fig. 1 is not unity, but has a slope of 2.26, which reflects the dampening effect, as is the case with substituted pyridines,[21] that solvent appears to have on complex formation in this case. The intercept is also not at zero, which again must reflect solvation processes occurring in solution that are not taken into account in the calculations carried out for reaction [3] in the gas phase.

Fig. 2 shows the relationship between ΔG for reaction [3] for M^{3+} ions and ΔG of formation for the NH_3 complexes predicted by eqn. [1]. The Cambridge Structural Database[22] shows that the

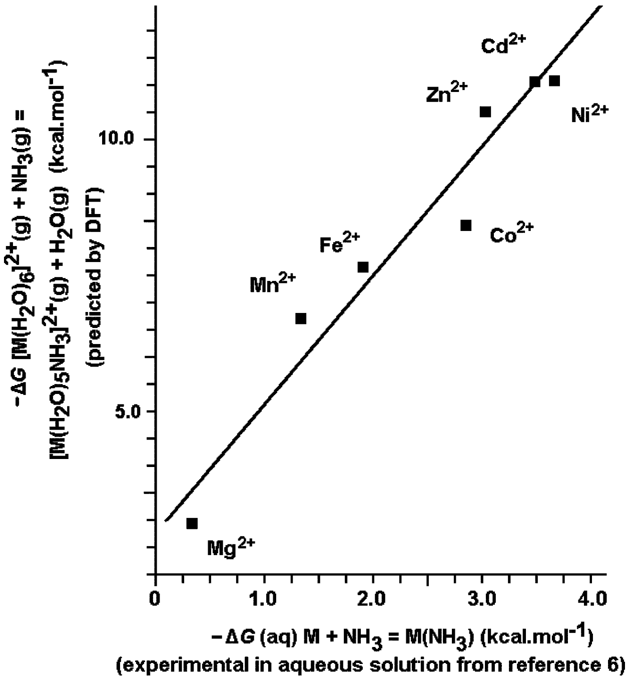

Fig. 1 Relationship between free energies calculated in the gas phase by DFT for reaction [3] in the text, and free energies of formation of the corresponding complexes in aqueous solution for divalent metal ions[6] (all at 25 °C).

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preferred coordination number (C.N.) for all the metal aquo ions in Fig. 1 is 6. Those in Fig. 2 show preferred C.N. values of 9 (○) as well as 6 (●), and two separate correlations occur for these two sets of metal ions. It is interesting that these two correlations run parallel to each other, and have slopes of 1.37, nearer to unity than for divalents. The separate correlations reflect different intercepts, which in turn must reflect different changes in solvation occurring on complex formation for $[M(H_2O)_6]^{3+}$ and $[M(H_2O)_9]^{3+}$ cations. The correlation between the ΔG of formation of metal NH_3 complexes in the gas phase obtained by DFT calculation, and that predicted in aqueous solution by eqn. 1, shows excellent concordance. The correlations enable us to predict log $K_1(NH_3)$ for Rh^{3+} = 8.6, and Ir^{3+} = 9.1, which is much as would be expected from log $K_1(NH_3)$ for Co^{3+} = 7.3. An estimate of log $K_1(NH_3)$ = 1.6 for the inaccessible radioactive metal ion Lr^{3+} has also been made, which is reasonable in comparison with estimates[4] for trivalent 5*f*-block elements such as Am^{3+} = 2.7. The approach involving DFT calculation here augurs well for the prediction of unknown formation constants of complexes of metal ions with unidentate ligands, and may also lead to a quantitative theoretical basis for HSAB.

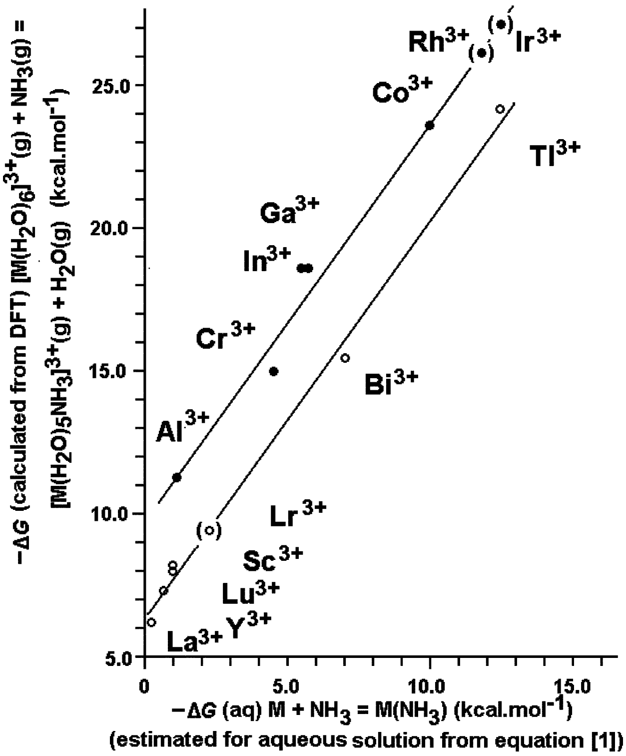

Fig. 2 Relationship between ΔG from DFT calculation for eqn. 3 in the gas phase, and ΔG estimated from eqn. [1] for aqueous solution, all at 25 °C. The points are for metal ions with 6-coordinate (●) and 9-coordinate (○) aquo ions. Points in parentheses are for complexes of metal ions for which no previous estimate of log $K_1(NH_3)$ is available, and are used to predict log $K_1(NH_3)$ Rh^{3+} = 8.6, Ir^{3+} = 9.1, and Lr^{3+} = 1.6.

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