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A DFT study of the affinity of lanthanide and actinide ions for sulfur-donor and nitrogen-donor ligands in aqueous solution

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ABSTRACT

DFT calculations are reported on the affinity of An(III) (An = actinide) and Ln(III) (Ln = lanthanide) ions for ligands with nitrogen-donor and sulfur-donor groups in aqueous solution, aimed at evaluating such donor groups as the basis for separating Am(III) from Ln(III) ions in the processing of nuclear waste. DFT calculations of ΔG(DFT) at 298 K for the gas-phase reactions: $[M(H_2O)_6]^{3+}(g) + L(g) \rightarrow M(H_2O)_5L]^{3+}(g) + H_2O(g)$, where L is NH_3 and M is a variety of Ln(III), An(III) ions, and UO_2^{2+} and NpO_2^{2+} are reported, as well as for the corresponding reactions for the nona-aqua ions for Ln(III) and An(III) ions. Also reported are ΔG(DFT) for the reactions for $L = H_2S$, as representative of thioethers in aqueous solution, for M = Ln(III) and An(III) ions, as well as Al(III), Ga(III), In(III), Tl(III), Bi(III), Fe(III), and Cr(III). ΔG(DFT) for formation of NH_3 complexes in the gas-phase correlates well with $\Delta G(aq)$ values for formation of the corresponding complexes in aqueous solution. The $\log K_1(NH_3)$ values were predicted by the equation: $\log K_1 = E_a \cdot E_b + C_a \cdot C_b$ (R.D. Hancock, A.E. Martell, Chem. Rev. 89 (1989) 1875.), where *E* and *C* are empirical parameters representing the tendencies of the acids (‘a’) and bases (‘b’) towards ionic and covalent bonding respectively. Correlations involving ΔG(DFT) for the reactions for $L = H_2S$ allow for prediction of $\log K_1(R_2S)$ for complexes of thioethers ($R = CH_2CH_2OH$). The importance of predicted $\log K_1(NH_3)$ values lies in the fact that $\log K_1$ for polydentate N-donor ligands correlates with $\log K_1(NH_3)$ for a series of metal ions, so that $\log K_1(NH_3)$ for any metal ion is an important consideration in ligand design. In the case of saturated N-donor ligands, this is a simple linear relationship, which suggests that saturated N-donors could lead to high Am(III)/Ln(III) selectivities. For ligands that contain pyridyl-type donors, such as 1,10-phenanthroline or terpyridyl, the correlation of $\log K_1$ with $\log K_1(NH_3)$ is separated into two linear relations for M(II) and M(III) ions, with M(III) ions having lower affinity for pyridyl donors than do M(II) ions of similar $\log K_1(NH_3)$. The low slope of, for example, $\log K_1$(terpyridyl) versus $\log K_1(NH_3)$ for M(III) ions suggests that ligands based only on pyridyl-type donor groups may not be able to produce large Am(III)/Ln(III) selectivities. The calculations on thioether complexes also suggest that such weakly basic S-donors would produce only weak Am(III)/Ln(III) selectivity, but that more strongly basic thiol-type donors might produce larger selectivities.

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1. Introduction

There has been an ongoing interest in separating actinide (An) ions such as Am(III) and Cm(III) from lanthanide(III) (Ln) ions in the treatment of nuclear waste [1]. Gd, Sm, and Eu have large neutron-capture cross-sections, so that further treatment of recovered Am and Cm in nuclear reactors is inhibited by the presence of these Ln(III) ions. Ac(III) is of interest [2] because of use of the α-emitter ^{225}Ac ($t_{½} = 10.0$ d) in chemotherapy. The ^{225}Ac is attached to an antibody selective for the targeted type of cancer cell via an appropriate ligand, and the cancer cells are destroyed by α-radiation. Potential solvent extractants for separation of An(III) from Ln(III) ions have relied on the somewhat greater covalence [3,4] of An–L (L = ligand) than of Ln–L bonding in selecting potential functional groups. This greater An–L covalence has been exploited largely based on aromatic polypyridyl-type ligands. A selectivity ratio for An(III) over Ln(III) ions of up to about 10^3 has been found for N-donor ligands such as: BTP [5–10], TPEN [11,12] 4,7-diphenyl-phen [13], BTB [14,15], BTphen [16], BTTP [17], TPTZ [18–21], and ODP [22] (see Fig. 1 for key to ligand abbreviations). Sulfur donors as an approach to more covalent M–L bonding to achieve Am(III)/Ln(III) selectivity has mainly involved dithiophosphinic acids [23–29] such as L1 in Fig. 1. Accompanying these developments have been theoretical studies of Am(III) and Ln(III) M–L bonding [15,20,30–33].

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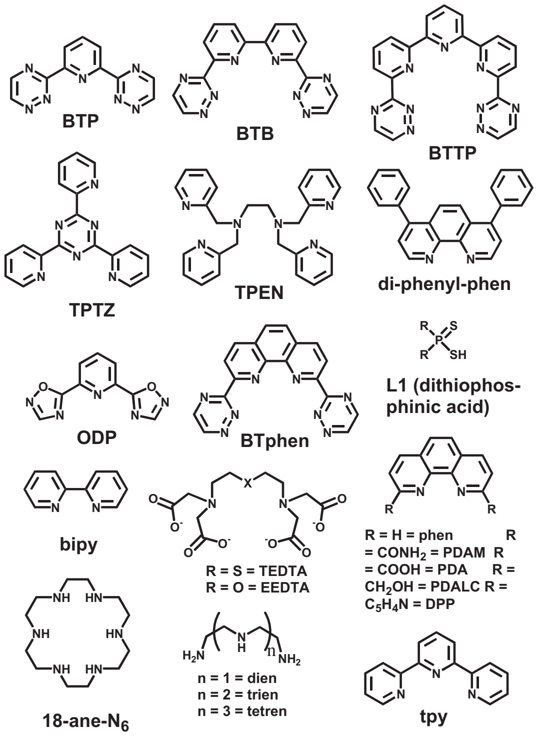

Fig. 1. Ligands discussed in this paper.

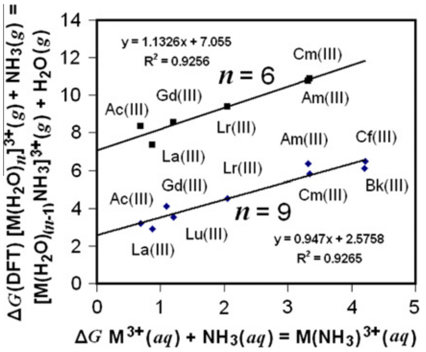

Fig. 2. Correlation between –ΔG values calculated by DFT for the formation of mono-ammine complexes of f-block M(III) ions in the gas-phase as the hexaqua ions ($n = 6$, ■) (equation 1) and nona-aqua ions ($n = 9$, ♦) according to Eq. (2), and $-\Delta G$ values for the corresponding equilibrium in aqueous solution as obtained from Eq. (3). The equations of the least squares best fit lines fitted to the two sets of points are shown on the diagram, as well as R^2, the coefficients of determination.

An approach to predicting the affinity of metal ions for N-donor ligands in aqueous solution [34–37] has been based on DFT calculation of the free energies (ΔG(DFT)) for simple gas-phase reactions of the type:

$$[\mathrm{M(H_2O)_6}]^{n+}(g) + \mathrm{NH_3}(g) \rightarrow [\mathrm{M(H_2O)_5NH_3}]^{n+}(g) + \mathrm{H_2O}(g) \qquad (1)$$

These calculations of ΔG(DFT) for Eq. (1) were carried out for M(II), M(III), and M(IV) ions, which as a simplifying factor were all treated as hexa-aqua ions as in Eq. (1). The ΔG(DFT) energies for Eq. (1) were then plotted against $\Delta G(aq)$ values in aqueous solution, derived from the formation constants, $\log K_1(\mathrm{NH_3})$, for formation of the mono-ammine complexes in aqueous solution [38]. It was found that this approach produced satisfactory correlations of ΔG(DFT) in the gas-phase versus $\Delta G(aq)$ in solution, even when it was probable, as with the Ln(III) and An(III) ions included (Ln = La, Lu, Sc, Y, Am, and Lr) that the coordination numbers (C.N.) were considerably higher than 6. It was found, however, [34–37] that separate correlations of ΔG(DFT) versus $\Delta G(aq)$ were obtained for metal ions that were known to possess C.N. = 6 (e.g. Cr(III), Co(III)), and higher C.N. = 8 or 9 (the Ln(III) and An(III) ions). These ΔG(DFT) values are then plotted against ΔG for the corresponding reaction in aqueous solution ($\Delta G(aq)$), derived from $\log K_1(\mathrm{NH_3})$ values [38], as seen in Fig. 2 for Ln(III) and An(III) ions. The gas-phase reactions do not [34–37] include changes in outer-sphere solvation that must occur in aqueous solution on complex formation, but one assumes that these would be constant with different metal ions of the same charge, or vary systematically with changes in $\Delta G(aq)$. Supporting these assumptions are good LFER (linear free energy relationships) that allow for the prediction of unknown $\log K_1(\mathrm{NH_3})$ values from the calculated ΔG(DFT) values.

Since it is clear that the C.N. values of 6 used previously for the Ln(III) and An(III) ions are too low, it was decided here to repeat the calculations of ΔG(DFT) for the Ln(III) and An(III) ions, with a C.N. of 9. The relationship obtained is included in Fig. 2, for M(III) ions with C.N. = 9, as in Eq. (2):

$$[\mathrm{M(H_2O)_9}]^{n+}(g) + \mathrm{NH_3}(g) \rightarrow [\mathrm{M(H_2O)_8NH_3}]^{n+}(g) + \mathrm{H_2O}(g) \qquad (2)$$

Fig. 2 shows correlations of ΔG for the gas-phase reactions for displacement of a coordinated H_2O molecule by an NH_3, calculated by DFT, versus ΔG derived from the $\log K_1(\mathrm{NH_3})$ values, for both the hexa-aqua and nona-aqua ions of Ln(III) and An(III) ions. The calculations on the nona-aqua ions, are more realistic than those assuming Ln(III) and An(III) ions to be 6-coordinate. Assuming these Ln(III) and An(III) aqua cations to be 6-coordinate [34–37], which is almost certainly not the case in aqueous solution, does not affect the quality of the correlation in Fig. 2.

The $\log K_1(\mathrm{NH_3})$ values used for Ln(III) and An(III) cations in Fig. 2 are not experimental, but predicted [39–41] by Eq. (3), which is based on the '*E* and *C*' equation of Drago [42,43]:

$$\log K_1 = E_a \cdot E_b + C_a \cdot C_b \qquad (3)$$

In Eq. (3), E_a and E_b values were selected to reflect the tendency to ionicity in bond formation of the Lewis acids (a) and bases (b), and the C_a and C_b values have been chosen to reflect covalence [39–41]. It might be thought that in a correlation such as Fig. 2 one is simply plotting ΔG values estimated by one method against ΔG values estimated by another method. Eq. (3) has been discussed at length [41,44], so will not be discussed further here, except to say that one of the present authors (RDH) has made a considerable effort [34–37,41,45–51] to support its predictions. Due to a tendency to hydrolysis [41,44] the NH_3 complexes of most M(III) and M(IV) cations do not exist in appreciable concentrations in aqueous solution, and those that do, such as Co(III), Rh(III), or Cr(III), are kinetically inert, so that $\log K_1(\mathrm{NH_3})$ values can so far only be estimated. The importance of predicted $\log K_1(\mathrm{NH_3})$ values, apart from their intrinsic interest, is that the affinity of metal ions in aqueous solution for polydentate N-donor ligands correlates with the affinity for NH_3. In Fig. 3 $\log K_1$ values for the macrocycle 18-aneN_6 and the polyamine dien are plotted against $\log K_1$ values for NH_3, both experimental [38] and predicted by Eq. (3). Similar results are obtained for other polyamines such as trien and tetren. Complexes of Ln(III) ions with 18-ane-N_6 are stable against hydrolysis in aqueous solution largely because of the stability afforded by the macrocyclic structure of the ligand. These $\log K_1$(18-ane-N_6) values support the predicted [39–41] $\log K_1(\mathrm{NH_3})$ values for the Ln(III) ions. Fig. 3 is typical for correlations involving saturated polyamine ligands, which typically yield R^2 (coefficient of determination) values in excess of 0.9. Eq. (3) can be rearranged to give Eq. (4), which predicts all experimentally known [38] $\log K_1(\mathrm{NH_3})$ values from available [38] $\log K_1$(F-) and $\log K_1(\mathrm{OH^-})$ values to a stan-

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