

Comparative solution chemistry of the 4f and 5f elements

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Abstract

The chemical behaviors of the lanthanide 4f and 5f elements are compared for similarities and differences. The relative stabilities are compared for the II, III, and IV oxidation states and are discussed in terms of the differences in the relative energies of the nf , $(n+1)d$ and $(n+2)p$ orbitals ($n=4$ and 5). Comparisons of the degree of inner sphere hydration and the thermodynamics of hydration as well as the rates of solvolysis and preferential solvation in mixed solvents are discussed. The thermodynamics of complexation of both families are compared and interpreted. A principal focus is the interpretation of such data in terms of relative degrees of covalency in the two families. The validity of the use of appropriate 4f elements as chemical analogs of the 5f elements is reviewed.

Keywords: Chemical behaviour; Thermodynamics; Hydration; Actinides; Lanthanides

1. Introduction

The close chemical similarity of the trivalent lanthanide and actinide elements is often presented as a major success of the periodic table. However, this relationship was not so obvious 50 years ago. Bohr had predicted a 5f series of elements in his Nobel Laureate lecture in 1922, but did not define at which atomic number the series would begin. More than 25 years later Zachariassen argued for a thoride series [1] and Haissinsky, for a uranide series [2]. In 1944, Seaborg proposed that the 5f series had actinium as its predecessor just as the 4f series had lanthanum. This led to the prediction of trivalency for element 95, Am, which was the key to its synthesis and isolation within several months. This actinide hypothesis provided the primary basis for the successful chemical identification of the remaining actinide elements from Cm(f^7) through Lr(f^{14}), even in the case of Md when only five atoms were involved.

However, such faith in the actinide–lanthanide relationship led to a decade-long controversy over the discovery of element 102 (nobelium). The original claim [3] based on a prediction of the elution position of No^{3+} derived by analogy with Yb^{3+} was disputed on several grounds. Not until it was demonstrated that nobelium exists as a divalent ion in solution [4], and, therefore, that its chemistry would not follow that of trivalent ytterbium, was the source of the confusion definitely established.

This problem reflects a significant difference in the chemical behavior of these two families. While the stability of the trivalent oxidation state is a primary characteristic of the lanthanides, it is not the most stable state for the early actinides (Th–Pu), nor as discussed above for nobelium near the end of the series. Fig. 1 shows the correlation of the standard reduction potentials $E_{1/2}^0$ for the 4f and 5f elements for the IV/

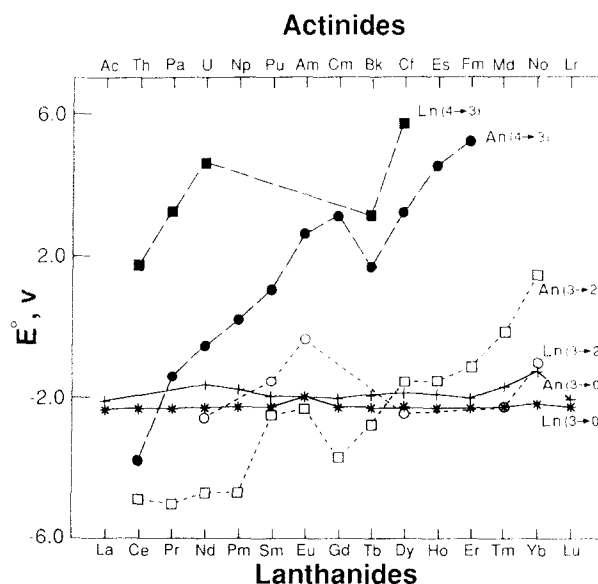


Fig. 1. The variation of the reduction potentials across the 4f and the 5f series for the III \rightarrow 0, III \rightarrow II, and IV \rightarrow III couples from Ref. [5].

III, the III/II and the III/0 couples. The two families have quite similar III/0 potentials but show significant differences for the other oxidation states. The stability of the VI and V states for U through Pu is not shown in this figure as there are no lanthanide analogs for the unique linear dioxo actinyl cations associated with these states in aqueous solution. The differences in the reduction potentials are related to the differences in the relative energies of the nf , $(n+1)d$ and $(n+2)p$ orbitals of the lanthanide ($n=4$) and actinide ($n=5$) elements.

For both series the f orbitals are relatively well shielded from interactions with neighboring atoms or ions. However, it should be noted that the crystal field model was invoked in the 1930s to explain lanthanide spectra since there is a dependence of the spectra on the coordination symmetry of the metal ion. The $5f$ orbitals are more spatially extended and can be expected to experience more interaction with the field of neighboring ions or atoms. This suggests that the actinides may have a greater degree of covalency in their bonding than the analogous lanthanide cations. The evidence is strong for a significant degree of covalency in the bonding between the actinide and the oxygen atoms in the actinyl cations AnO_2^+ and AnO_2^{2+} with both $5f$ and $6d$ orbitals involved. However, the evidence for a difference in covalency in the bonding of the trivalent and tetravalent Ln and An cations is more debated.

2. Evidence for ionic bonding

In both families, the cations are typical hard acids and, in aqueous solution, have chemical behavior that is more similar to the alkali and alkaline earths than to the transition elements. The absence of significant ligand field effects is seen in the parallel regularity of the contraction of the ionic radii with increasing atomic number for both series of M^{3+} and M^{4+} cations [5].

Evidence for a strongly ionic character of f -element bonding with the fluoride anion is shown in Fig. 2. The solid lines represent the value of the free energy of formation of MF calculated by a modified Born equation [6]. The experimental values for hard cations such as Ca^{2+} , Zn^{2+} and Th^{4+} fit the calculations quite well, as is to be expected for interaction with the hard F^- anion. The agreement of the data for the trivalent lanthanides and actinides with the results from the Born equation calculations supports the ionic nature of their bonding with hard fluoride anions.

The linear correlation of the log of the formation constant for MF complexation, $\log \beta_{101}$, for MF formation with the cation charge, as well as a similar constant for acetate complexation, has provided an estimate of the effective charge of the actinides in the linear dioxo cations; i.e. in AnO_2^+ , An(V) has $Z_{eff} \approx$

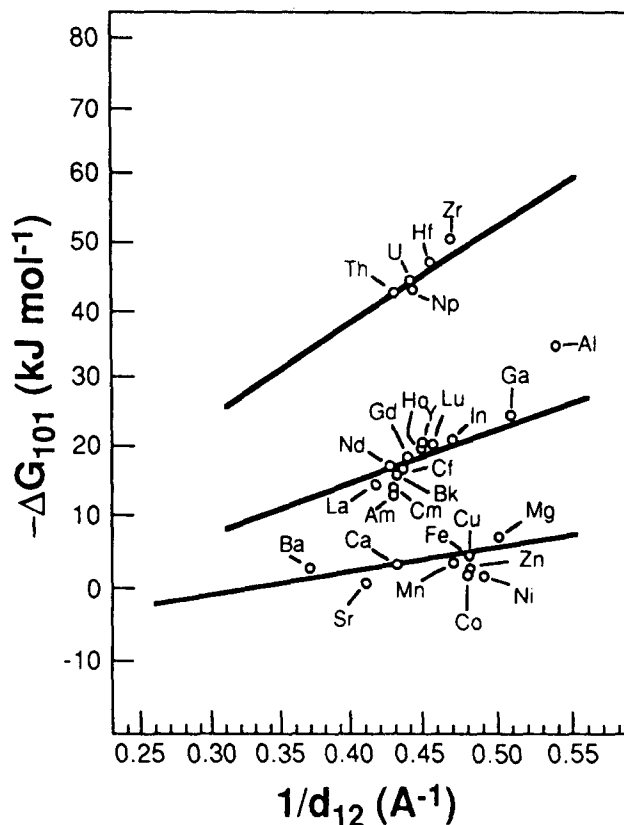


Fig. 2. Plot of $-\Delta G_{101}$ of MF complexation as a function of the reciprocal of the internuclear distance. The solid lines are calculated as described in Ref. [5].

2.2 ± 0.1 ; in AnO_2^{2+} , An(VI) has $Z_{eff} \approx 3.3 \pm 0.2$ [7]. These values also agree with theoretical calculations [8].

The proton is the prototypical hard acid. Since the primary characteristic of hard acid–hard base interactions is their strongly ionic nature, we can expect good correlation of the stability constants for lanthanide–ligand complexation with the acid constants of the ligands. Such a correlation is shown in Fig. 3 of $\log \beta_{101}$ for Sm(III) complexation with both mono and dicarboxylic ligands [9]. Ligands 1–7 and 11 interact via the single carboxylate group while ligands 8–10 form chelates with five-membered rings. As the chelate ring size increases for the linear alkyl dicarboxylate ligands, the complex strength decreases as shown in Fig. 4. The uniformity of decrease for the cations of oxidation states VI through III and for the $4f$ Sm^{3+} and $5f$ Am^{3+} further supports a common mode of ionic interactions in the complexation. This dominance of ionic interaction is reflected in a linear correlation of $\log \beta_{101}$ for UO_2X and $\log \beta_{101}$ for SmX and for ThX for simpler anions in which steric effects do not affect the uranyl complexation [9]. Such correlations using $4f$ data can be useful in predicting the stability constant values for $5f$ cations for which experimental difficulties limit measurements of such constants, e.g. the cations of plutonium.

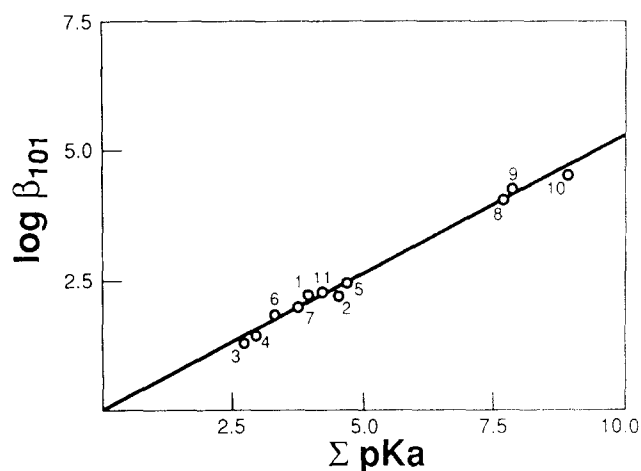


Fig. 3. The correlation of $\log \beta_{101}$ for SmL and the acid constants of the ligands: 1 benzoate; 2 acetate; 3 chloroacetate; 4 iodoacetate; 5 propionate; 6 3-nitrobenzoate; 7 3-fluorobenzoate; 8 phthalate; 9 malonate; 10 diethylmalonate; 11 *p*-methoxybenzoate.

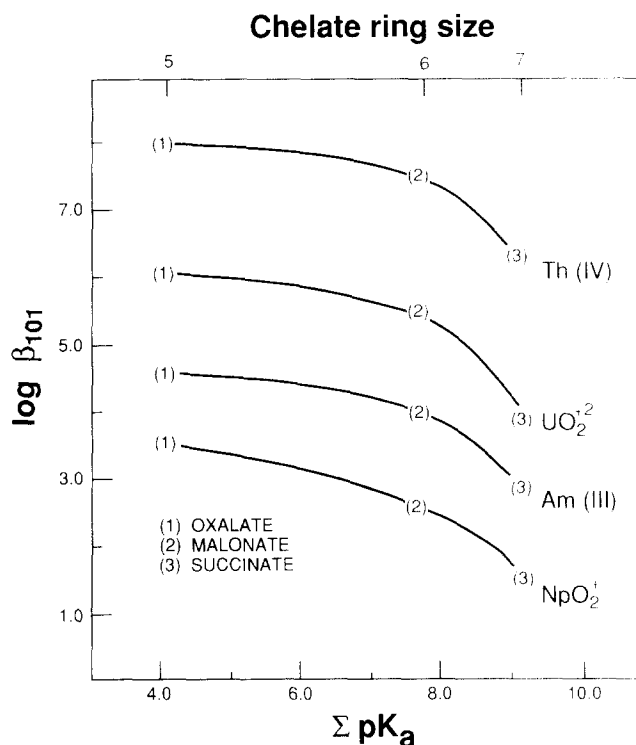


Fig. 4. Dependence of $\log \beta_{101}$ of ML on the size of the chelate ring where L is malonate (1), succinate (2), and glutarate (3).

These correlations also validate the use of oxidation state analogs in modeling. To minimize redox, radiolytic, etc. effects, it may be useful to study such analogs when they are less radioactive and/or more chemically stable (e.g. to redox). For example, Nd^{3+} – Eu^{3+} have quite similar chemical behavior to Pu^{3+} and Am^{3+} , the more redox stable NpO_2^+ is similar to PuO_2^+ , UO_2^{2+} to NpO_2^{2+} and PuO_2^{2+} , and Ce^{4+} or Th^{4+} is similar to Pu^{4+} . Ce^{4+} is relatively sensitive to redox,

which limits its value as a tetravalent analog. The tetravalent analogs do differ slightly from Pu^{4+} and some adjustment is needed in using data from Ce^{4+} or Th^{4+} for Pu^{4+} . However, data for the other oxidation state analogs can be used with little or no adjustment. This useful property is a direct result of the strongly ionic nature of the bonding in both the 4f and 5f elements.

3. Evidence for covalency

As early as 1954, the separation of the trivalent actinides from the lanthanides by elution from cation exchange resin with concentrated hydrochloric acid was interpreted as evidence for enhanced covalency in An–Cl bonding [10]. The evidence is reflected in Fig. 5 where no difference is observed between Eu^{3+} and Am^{3+} in concentrated HClO_4 (ClO_4^- is a strong base which favors ionicity), but is seen in concentrated HCl (Cl^- is a softer donor) [11]. It is likely that such enhanced complexation does reflect a small degree of covalency in the Am–Cl bonds where the covalent interaction involves the 6d and/or 7s orbitals of the actinide cation [12]. Similarly, the elution behavior of actinides and lanthanides from beds of ion exchange resin with solutions of the thiocyanate show even greater differences in the relative complexation [13]. The metal bonds to the nitrogen of the thiocyanate group and the increased strength of the Am–N interaction is consistent with a slightly greater covalency for the Am–N interaction than for the Ln–N interaction. Fig. 6 shows the correlation of $\log \beta_{ML}$ for aminopolycarboxylic acid complexes of Nd^{3+} and Am^{3+} (data from Ref. [14]). These cations were chosen as they have similar radii. As the polydentate character of the ligand increases, a small

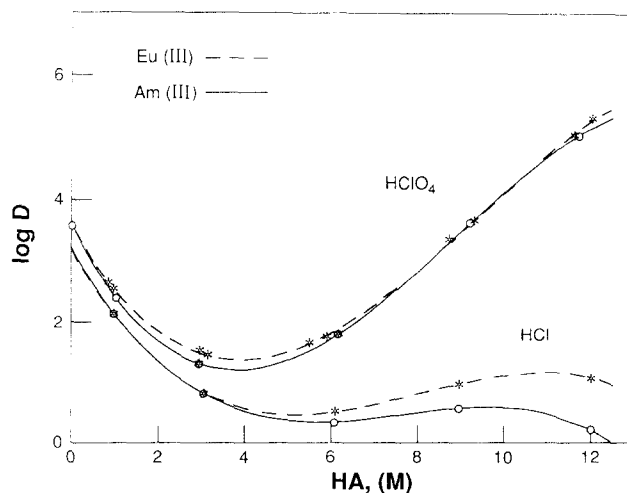


Fig. 5. Variation of $\log D$ (D is the extraction coefficient) of Am^{3+} and Eu^{3+} in a system of HCl or HClO_4 (aqueous phase) and HDEHP in toluene (organic phase).

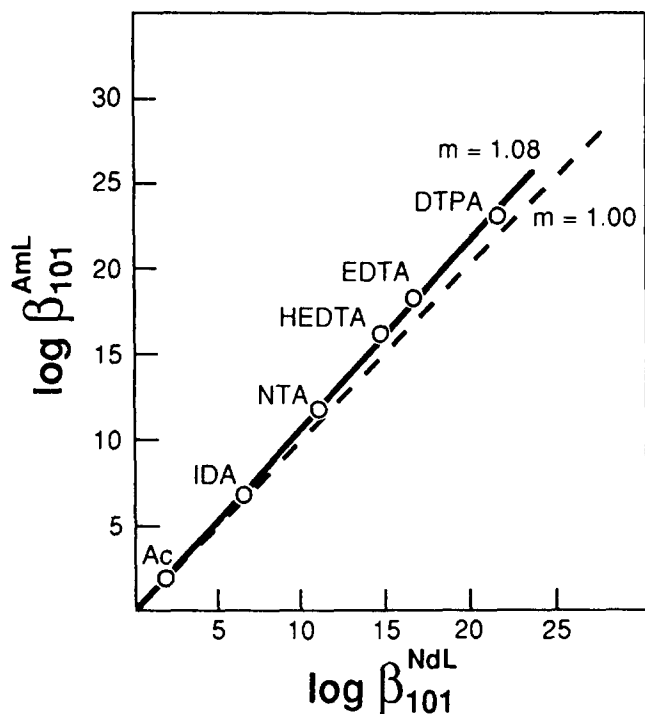


Fig. 6. Correlation of $\log \beta_{101}$ for AmL and NdL with a series of aminopolycarboxylic acids (except Ac which is acetate).

but real increase in the strength of the complexation of AmL compared with NdL is observed. Within the error limits, it is possible that for Am^{3+} the enhancement for the iminodiacetate (IDA) and nitrilotriacetate (NTA) complexes (both with a single M–N bond) is the same while that for the hydroxyethylenediaminetriacetate (HEDTA), and ethylenediaminetetraacetate (EDTA) complexes (both with two M–N bonds) is also similar. This is consistent with the Am–N interaction being slightly stronger than the Nd–N interaction. However, such data are not definite proof for covalency differences owing to the possibility that slight differences in structural, effects such as differences in M–N bond lengths, may be responsible.

If covalency is responsible for the deviation from a slope of unity in Fig. 6, it could be expected to be reflected in the enthalpy change of complexation. Fig. 7 is a plot of ΔH_{101} for Am^{3+} and Cm^{3+} complexation vs. that of Eu^{3+} for a series of ligands [15]. The agreement of the data with a slope of 1.0 fails to support the presence of significant covalent contribution to the enthalpy change. Good linear correlation between ΔH_{101} and ΔS_{101} as well as positive values for both Ln and An complexation has been interpreted as showing that the cation dehydration on complexation is a larger contribution to both ΔH_{101} and ΔS_{101} than the bond formation. However, this effect should not eliminate a decrease in the positive value of ΔH_{101} if covalency were significant.

Proton NMR spectroscopy was used to obtain the equilibrium constants for the reaction in CDCl_3 solvent

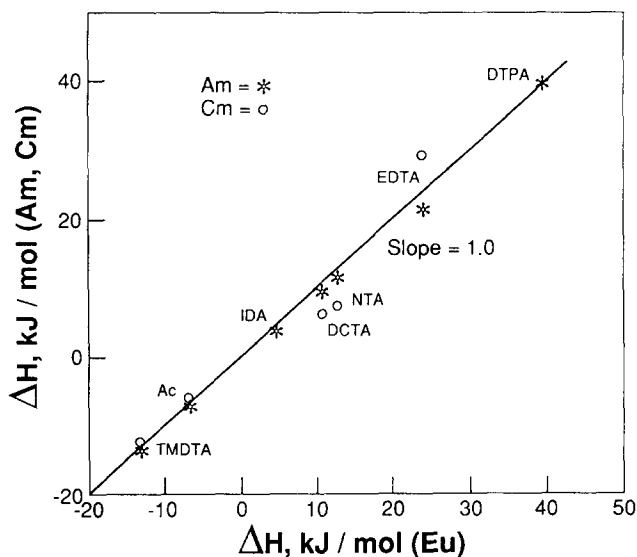


Fig. 7. Correlation of ΔH_{101} of AmL and CmL with ΔH_{101} of EuL for a series of aminopolycarboxylate ligands.

of a series of neutral base adducts with $\text{Nd}[(\text{CF}_3\text{CO})_2\text{CH}]_3$ [16]. The bases have oxygen donors (10 bases) or nitrogen donors (6 bases). The data were analyzed by Drago's E_B and C_B parameters for these bases [17]. In this treatment, the E parameters are associated with the electrostatic part of the acid–base interaction while the C parameters reflect the covalent part. For the oxygen donor bases, a linear fit of $-\Delta G$ and E_B was obtained with a correlation coefficient of 0.86. No correlation between $-\Delta G$ and C_B existed ($R^2=0.35$) for the oxygen donor bases. The situation was reversed for the nitrogen donor bases with a good fit ($R^2=0.966$) between the $-\Delta G$ and C_B values but no fit ($R^2=0.34$) with the E_B values. This pattern of correlations may be reflecting an increased covalency in the Nd–N base interactions relative to that in the Nd–O base interactions.

In summary, there is evidence for some extra covalency in actinide bonds, but obviously the contribution is small. The argument for such extra covalency based on greater 5f spatial extension does not seem to have experimental support. It has been proposed from O-17 NMR studies that 6s and 7s orbitals play the dominant roles in covalency in the bonding of these elements [18]. Involvement of the s orbitals is consistent with the variety of geometric coordination structures observed for both series.

4. Hydration studies

A common feature of the 4f Eu^{3+} and Tb^{3+} and the 5f Cm^{3+} is an inverse relation between the lifetimes of their luminescent decay and the number of water molecules in their primary coordination sphere. This

correlation has been expressed for Eu^{3+} and Tb^{3+} by the equation [19]:

$$n(\text{H}_2\text{O}) = C[(k(\text{H}_2\text{O}) - k(\text{D}_2\text{O}))] \quad (1)$$

where $n(\text{H}_2\text{O})$ is the number of water molecules, $k(\text{H}_2\text{O})$ and $k(\text{D}_2\text{O})$ are the decay constants (reciprocal of mean decay lifetime in H_2O and D_2O), and C is the proportionality constant (1.05 for Eu and 4.2 for Tb). D_2O is used to measure any quenching effects not due to H_2O , as D_2O does not perturb the luminescence. This equation was obtained from luminescence decay measurements of crystalline compounds of Eu and Tb in which the values of $n(\text{H}_2\text{O})$ are well known.

Such a calibration technique is not feasible for Cm^{3+} . However, micro amounts of Cm^{3+} were coprecipitated with La^{3+} compounds of known structure [20]. Since the Cm^{3+} was a very low level impurity, it was assumed it would be forced to have the same coordination structure as that of the bulk La^{3+} which is known. The same procedure was followed for micro amounts of Eu^{3+} . Measurements of the Eu^{3+} decay confirmed the validity of the assumption that the impurity cations would have the known primary hydration as the bulk La^{3+} . Fig. 8 shows the relation between the values of $k(\text{H}_2\text{O})$ and the primary sphere hydration number of the solids. These data gave a value of $C = 0.65$ for Cm^{3+} in Eq. (1).

Table 1 shows the results of a luminescence decay study of some aminopolycarboxylate complexes of Eu^{3+} and Cm^{3+} . The data consistently indicate a greater hydration of Cm^{3+} relative to Eu^{3+} . In the aquated cation, Cm^{3+} seems to have a net hydration number of 9.5 ± 0.5 compared with 8.5 ± 0.5 for Eu^{3+} . It has been proposed from a variety of data that the aquated Eu^{3+} is an equilibrium mixture of $\text{Eu}(\text{H}_2\text{O})_8^{3+}$ and $\text{Eu}(\text{H}_2\text{O})_9^{3+}$. This suggests that aquated Cm^{3+} is prob-

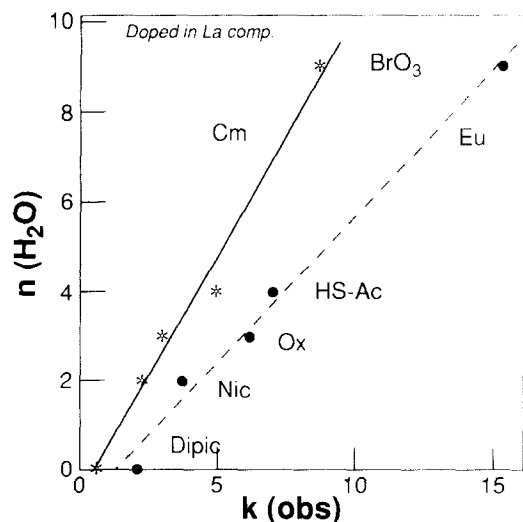


Fig. 8. Relation of $n(\text{H}_2\text{O})$, the number of water molecules bound to La^{3+} , with the luminescence constants k for Eu^{3+} and Cm^{3+} .

Table 1
Cm vs. Eu hydration

Ligand	Cm $n(\text{H}_2\text{O})$	Eu $n(\text{H}_2\text{O})$	Difference	CN_L^a	CN_T^b	CN_T (Eu)
HEDTA	4.2	3.1	1.1	5	9.2	8.1
EDTA	3.7	2.6	1.1	6	9.7	8.6
DCTA	3.5	2.3	1.2	6	9.5	8.3
DTPA	1.5	1.1	0.4	8	9.5	9.1
TTHA	0.2	0.2	0	10	10	?

Eu $n(\text{H}_2\text{O}) = 1.05k(\text{H}_2\text{O} - 0.62)$; Cm $n(\text{H}_2\text{O}) = 0.65k(\text{H}_2\text{O} - 0.88)$.

^a CN_L number of donor groups in the ligand.

^b $\text{CN}_T = \text{CN}_L + n(\text{H}_2\text{O})$.

ably a mixture of $\text{Cm}(\text{H}_2\text{O})_9^{3+}$ and $\text{Cm}(\text{H}_2\text{O})_{10}^{3+}$. However, both ions lose the same number of water molecules in complexation with a common ligand. For example, for EuEDTA formation, the number of water molecules lost is $8.6 - 2.6 = 6$; for CmEDTA it is $9.7 - 3.7 = 6$. This similarity in dehydration explains the linear correlation with a slope of 1.0 in Fig. 7.

5. Summary

In common oxidation states, the chemical behavior of the 4f and 5f element cations is quite similar. This can be used to advantage by employing lanthanides as oxidation state analogs of the 5f elements in studies where the radioactivity of the actinides would perturb the normal chemical behavior. There is evidence for slightly enhanced covalency in actinide bonding to softer donors but, even in these systems, this is a relatively minor perturbation from the pattern of strong chemical similarity.

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