FACTORS IN THE COMPLEXATION OF LANTHANIDES

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When compared with that of the transition metals the coordination chemistry of the lanthanide elements may seem somewhat more limited. Particularly in aqueous solutions, the lanthanides do not form complexes with the wide variety of ligand types that the transition metals do. Nevertheless, the studies of the coordination chemistry of the lanthanide elements do have certain unique features and provide researchers with unique opportunities for studying certain effects. To some extent this is due to the absence in the lanthanides of some of the diversity of the chemistry of the transition elements. The common oxidation state and the progressive decrease of ionic radii over the lanthanides (La-Lu) provide us with a system for studying some of the subtle effects in coordination chemistry.

The lanthanide cations are classified as hard acids. As a result they have a strong preference for hard base ligands and will coordinate much more strongly with oxygen and fluorine donor atoms than with softer base donor species such as nitrogen and sulfur. Complexation involving lanthanides and soft base donor ligands is observed in solids but in aqueous solution complexation almost always involves the replacement of the solvate waters with their metal-oxygen bonds by an oxygen donor ligand forming a new metal-oxygen bond.

Lanthanides and Ionic Models

Inasmuch as the complexation in aqueous solution is associated with differences in lanthanide-oxygen bonding, we can expect relatively small change in the nature of the bonding. Recently it has been suggested that the f→f hypersensitive spectral bands of the lanthanides can be used as a probe for the degree of covalency of the lanthanide bonds.[1,2] However, there is general agreement that the bonding in lanthanide complexes is primarily ionic.[3,4] If this is correct, lanthanide complexation should serve as a good test for the

utility of treatments of electrostatic interactions. If
the bonding is essentially electrostatic we would expect
that the variation of the stability constant should show a
correlation between log β_1 (the stability constant for the
formation of $ML_{(aq)}$) and Z_+Z_-/R_++R_- (Z_i=ionic charge, R_i=
ionic radius). For some ligand systems it has been found
that log β_1 exhibits this behavior. However, in other cases
the variation of the stability constants with the ionic
radius is not linear and the expected relationship is either
absent or obscured by other factors.

Hefter[5] has shown recently that a number of fluoride
complexes of di-, tri-, and tetravalent cations follow the
expected electrostatic relationship between log β_1 and the
cationic charge divided by the sum of the ionic radii. Since
fluoride is a very hard base ligand such a relationship is
not unexpected. To extend the investigation of the appli-
cation of the electrostatic model to lanthanide complexes
we have followed the approach of Munze[6], who has developed
an expression of the free energy of complexation which
involves a coloumbic term, a cratic term, and a term for the
activity coefficients at the experimental ionic strength.
The cratic term takes into account the change in the number
of reacting species upon complexation. Munze has shown that
his expression provided good agreement between experimental
and calculated values for the free energy of formation of
the monoacetate complexes of the trivalent lanthanide cations.
In his calculations the value of 78.5 was used for the
dielectric constant of solution at 25°C.

Since it seems unreasonable that the value of the
dielectric constant of water would be valid in these ionic
solutions, we have modified the approach of Munze and treated
the dielectric constant as a parameter. The equation has the
form:

$$\Delta G = \frac{Ne^2 \, Z_1 Z_2}{(4.187 \times 10^2) D_{eff} \, d_{12}} - RT \, \nu \, \ln \, 55.51 + RT \, \Sigma \, \ln f_{(\mu)} \quad (1)$$

N = Avogadro's Number
e = unit charge; 4.80×10^{-10} esu
Z_1, Z_2 = ionic charge of cation and anion, respectively
D_{eff} = "effective" dielectric constant
d_{12} = $R_+ + R_-$
ν = -1

The value of $\ln f_{(\mu)}$, the activity coefficient term, was cal-
culated by the equation:

$$\Sigma \ln f_{(\mu)} = - \, \Sigma_i z_i^2 \, \frac{0.511 \mu^{1/2}}{1 + B a \mu^{1/2}} - C \mu^{1/2} - D \mu \quad (2)$$

$\Sigma_i z_i^2 = -8$ for $MF^{+3}_{(aq)}$ systems, -6 for $MF^{+2}_{(aq)}$ systems, -4 for $MF^{+1}_{(aq)}$ systems

$B = 0.33; \quad C = 0.75; \quad D = -.015$

$\overset{o}{a} = 4.30 \times 10^{-8} cm; \quad \mu^{1/2} = 1.0$

These values of $\overset{o}{a}$, B, C, and D were obtained by using published values of log β_1 for $ThF^{+3}_{(aq)}$ measured at ionic strengths from 0.01M to 3.0M; the stability constants were all corrected to within experimental error with the listed values of the parameters.[7] With these values we could use equation 2 to calculate $\Sigma lnf_{(\mu)} = 2.4$ for $MF^{+1}_{(aq)}$ complexation, $= 0.67$ for $MF^{+2}_{(aq)}$ complexation, and $= 1.09$ for $MF^{+3}_{(aq)}$ complexation. In order to use equation 1 to calculate values of the free energy of complexation it was necessary to specify the adjustable parameter D_{eff}. This was done by substituting the experimental values of ΔG for $CaF^{+1}_{(aq)}$, $NdF^{+2}_{(aq)}$ and $ThF^{+3}_{(aq)}$ in equation 1 and calculating D_{eff}. The results were:

$D_{eff} = 79.8$ for MF^{+1} systems

$\qquad = 57.0$ for MF^{+2} systems

$\qquad = 40.8$ for MF^{+3} systems

Using these values of D_{eff}, it was possible to calculate the variation of ΔG as a function of d_{12} using equation 1. The results of the calculation are shown as solid lines in Figure 1 while the points in the figure are experimental values. The agreement is quite satisfactory for a large number of complexes involving di-, tri-, and tetravalent cations. In fact, only the AlF^{+2} complexation is in serious disagreement. Of particular interest to us is that the results shown in Figure 1 confirm the ionic nature of the interaction between trivalent lanthanide ions and fluoride anions. We also see that tri- and tetravalent actinide fluoride complexes are satisfactorily correlated with this electrostatic model. The ionic nature of both the lanthanide and actinide fluoride complexes means that neither the 4f nor the 5f orbitals play a significant role in bonding in these complexes.

Compensation and Thermodynamics

In Figure 2 we can see an interesting aspect of the thermodynamics of the formation of lanthanide fluorides. The enthalpy and entropy changes "compensate" each other to produce an almost linear variation in the free energy of complexation. The linearity of the $\Delta H - \Delta S$ correlation of the $LnF^{+2}_{(aq)}$ system as well as the related $AcF^{+2}_{(aq)}$ complexation

is shown in Figure 3. In this figure the slope has a value of 242°†. The slope is expected to be

$$\left(\frac{\partial \Delta H}{\partial \Delta S}\right)_T = \left(\frac{\partial \Delta G}{\partial \Delta S}\right)_T + T \qquad (3)$$

where $T = 298°C$. Only if $(\partial \Delta G / \partial \Delta S)_T = 0$ should the slope equal the experimental temperature of 298°K.

Figure 4 presents the correlation of ΔH and ΔS for formation of the $LnY_{(aq)}$ species for a number of aminocarboxylate ligands.[4] We see there is a segment of each curve for which the slope is equal to T (i.e., ΔG constant). However, for the lightest and the heaviest lanthanides, the slope differs significantly from T.

Many authors. (e.g., 9, 10, 11, 12) have discussed such enthalpy-entropy compensation but there is lacking a definitive analysis from rigorous thermodynamic principles. Following Ives and Marsden, we separate the thermodynamic quantities into hydration and reaction terms where the former relate to solvation changes upon complexation and the latter to the direct interaction between reacting species.

$$\Delta G_h + \Delta G_r = \Delta H_h - T\Delta S_h + \Delta H_r - T\Delta S_r \qquad (4)$$

They further propose that $\Delta G_h \approx 0$, $\Delta H_h \approx T S_h$. The consequence of this is:

$$\Delta G \approx \Delta G_r = \Delta H_r - T\Delta S_r \qquad (5)$$

Such a relation explains the success of the simple ionic model upon which equation 1 is based since the latter ignores specific desolvation effects upon complexation.

The curves in Figure 4 also suggest further interpretations of lanthanide complexing. Generally, for the complexes of the metal cations from Nd(III) through Ho(III), the slope is $\approx 300°$, indicating that hydrational effects are dominant on ΔH and ΔS. Several authors (13, 14, 15) have proposed the existance of an equilibrium of the type

$$Ln(H_2O)_n = Ln(H_2O)_m + (n-m)H_2O \qquad (6)$$

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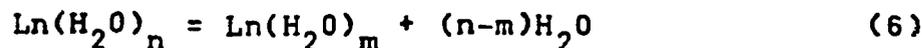
† Norman, et al.[8] have shown that analysis of covariance leads to two linear subsets for $LnF_{(aq)}^2$; La-Gd and Dy to Lu. However, our interest does not require such resolution.

for these cations. Alternately, Anderegg,[16] and others[17,18] have proposed an equilibrium between hydrated complexes for these cations:

$$LnL(H_2O)_x = LnL(H_2O)_y + (x-y)H_2O \qquad (7)$$
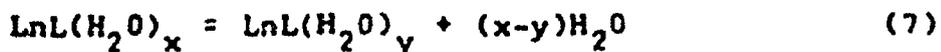
The slope of $\approx 300°$ (=T) would be consistent with a model in which one of these equilibria results in a relatively constant ΔG, possibly due to a relatively constant d_{12}. The variations in ΔH and ΔS are dominated by the ΔH_h and ΔS_h contributions related to reaction (6) or (7). Since both of the equilibria fit this model, we cannot choose between them on this basis.

Additional evidence that a slope with a value of T for the complexes of the elements from Nd to Ho is related to hydration effects is presented in Fig. 5. The formation of the outer sphere complex $EuNO_3^{2}$ [19] and of the inner sphere complex EuF^{+2} [7] was studied in perchlorate solutions of constant ionic strength in which the "inert" cation was variously H^+, Li^+, Na^+ and NH_4^+. The ΔH vs. ΔS data for both complexes fitted a line of slope $\approx 300°$. Moreover, the stability constants of the $EuNO_3^{2}(aq)$ was shown to have a linear correlation with the viscosity B coefficient, reflecting that the variations in ΔG, ΔH and ΔS are related to solvation as a result of the effects of the "inert" cations on the solvent structure.

We may also note from Figure 4, that, except for NTA, the slope for the lightest lanthanides (La-Nd) is approximately $1150°$ (it seems that the slope for the heaviest lanthanides (Er-La) is also $1150°$ but this is not certain). Since $\left(\partial \Delta H / \partial \Delta S\right)_T = 1150 = \left(\partial \Delta G / \partial \Delta S\right)_T + T$, $\left(\partial \Delta G / \partial \Delta S\right)_T = 850°$. In this series of cations, no hydration equilibria are believed to be present. However, a 'normal' compensation[12] can be assumed to be present such that $\Delta H_r = a \Delta S_r$. This arises from the expectation that increased attraction (more negative ΔH) is associated with increased restrictions in freedom of the system (decrease in ΔS) and vice versa. If we take this assumption seriously we can use it and equations (5) and (3) to show that $a = 1450°$. It follows that

$$\Delta H_r = 1.26 \ \Delta G \qquad (8)$$

For $LaEDTA^-_{(aq)}$ we would calculate:

$\Delta H_r = -104$ kJ/m	$\Delta S_r = -72$ kJ/K.m
$\Delta H_h = +89$ kJ/m	$\Delta S_h = +297$ kJ/K.m

Support for this approach is gained from calculation of the ΔS_r values of the lanthanum complexes in Figure 4 as the value of ΔS_r per chelate ring for the complexes is very similar for all the complexes, varying from 1 to 6 chelate rings. The average value of ΔS_r/ring = - 16.1 ± .07 kJ/K.m.

Outer vs. Inner-Sphere Complexation

Another feature of lanthanide complexation which seems promising for more study is the outer-sphere vs. inner-sphere formation. Thermodynamic and kinetic measurements have been used to characterize the nature of complexes but there has been very little progress in understanding the factors which determine which type of complex would be formed for a particular ligand. For example, carboxylic acids formed inner-sphere lanthanide complexes while p-toluenesulfonic acid formed an outer-sphere type. The halides, nitrate, thiocyanate and hexacyanoferrate (III)complexes of the lanthanides are outer-sphere but sulfate and iodate complexes are inner-sphere.[20]

The inorganic ligands studied thus far seem to show a correlation between their basicity and the tendency to inner-sphere formation. From a study of the effect of anion concentration on the spectra of $Nd(III)^{21}$, we can order the tendency to inner sphere formation as

$$ClO_4^- < Cl^- < NO_3^-$$
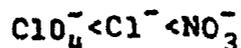
An estimate of about 2 per cent inner-sphere character was given for the lanthanide mononitrate species while for the monothiocyanate species, the estimate of the extent of inner sphere formation was larger, perhaps 20-30 per cent. The order for inner sphere character for the monovalent ligands is

$$\underline{ClO_4^- < Cl^- < NO_3^- < SCN^-} \quad \underline{< IO_3^- < F^-}$$
•   predominantly outer   predominantly inner
    sphere   sphere

If we compare this order with the order of the basicity of the ligand (i.e., the pK_a of the HL species), a direct correspondence is seen. Moreover, it would seem that the changeover from outer to inner-sphere complexation is associated with ligands whose acids have pK_a values of about zero since the pK_a for HSCN is -1.84 while that for HIO_3 is 0.7.

The formation of outer-sphere complexes by p-toulenesulfonate with Am(III) (HpTS has about same acid strength as HCl) and inner-sphere complexes by acetate ($pK_a \sim 4.8$) add further support to this correlation of complex type and basicity of the ligand. Similarly, the basicity of sulfate (i.e., pK_{a2} = 1.9) agrees with the inner-sphere nature of $LnSO_4^+$ whereas the available data on the acidity of $H_3Fe(CN)_6$

$(pK_{a3} < 1)$ would correlate with outer-sphere character for $LnFe(CN)_6$. A systematic study of the complexation of the lanthanides for ligands whose pK_a values vary from -1 to +2 is underway presently.

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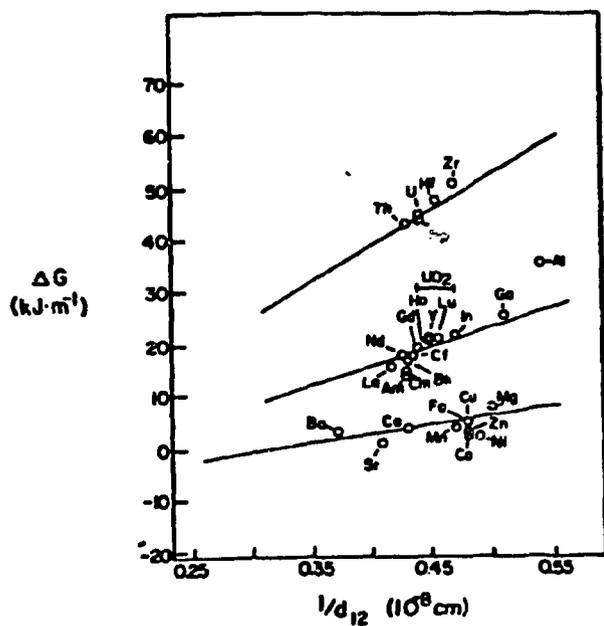21. G.R. Choppin, D.E. Henrie, and K. Buijs, Inorg. Chem., 5, 1743 (1966).

FIGURE 1. CORRELATION OF $\Delta G_{CALCULATED}$ (SOLID LINES) AND ΔG_{EXP}
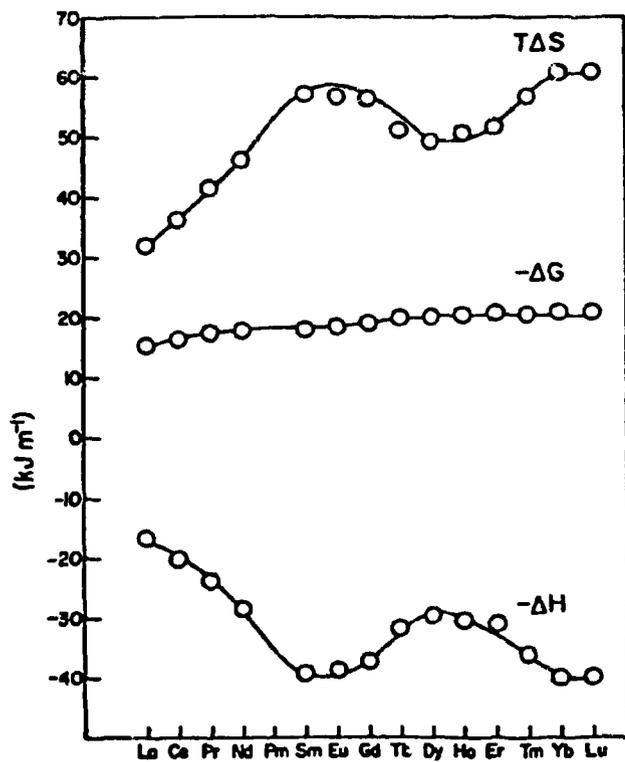AS A FUNCTION OF $1/D_{12}$.

FIGURE 2. THE VARIATION OF THE FREE ENERGY, ENTHALPY AND ENTROPY
OF FORMATION OF $\overline{T}^{+2}_{(AQ)}$ WITH LANTHANIDE ATOMIC NUMBER.
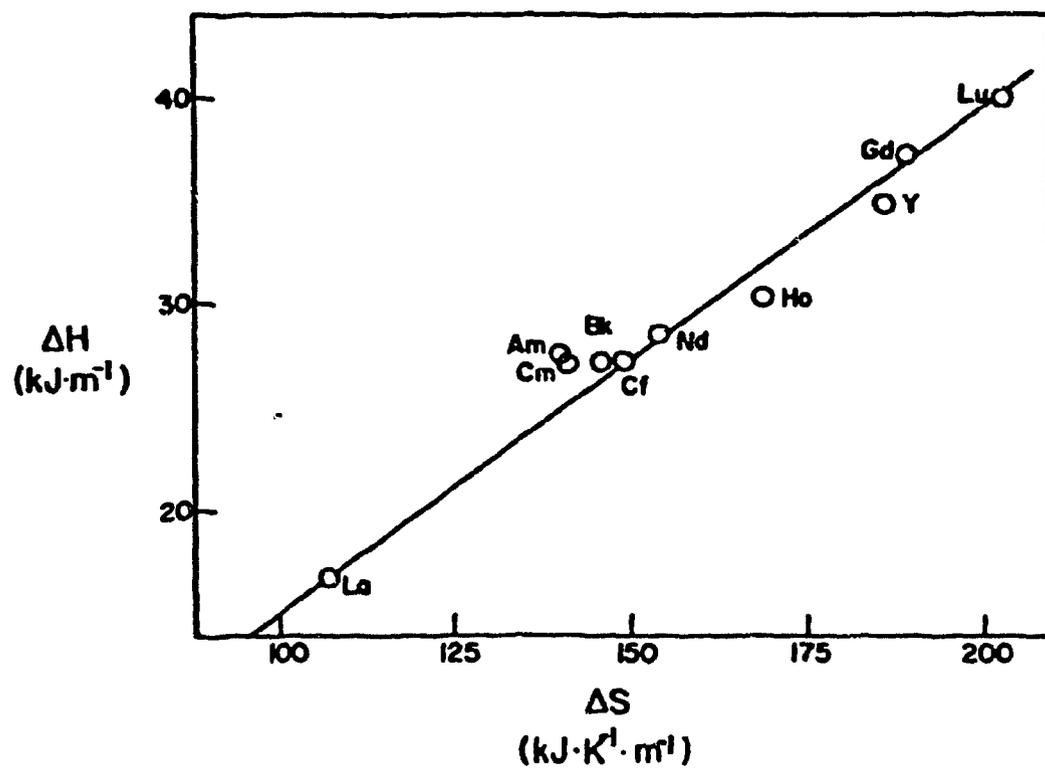
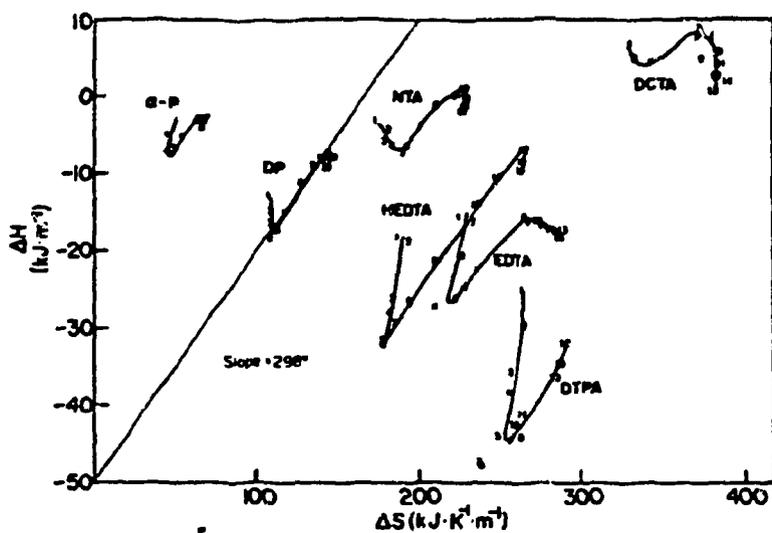FIGURE 3. ENTHALPY VS. ENTROPY CORRELATION FOR THE FORMATION OF THE $MF^{+2}_{(AQ)}$ COMPLEX.

Figure 4. The relationship between the enthalpy and the entropy of formation for lanthanide 1:1 aminocarboxylate (excluding Pm) complexes. The numbers relate to the lanthanides such that La = 1, Lu = 14. α-P = α-picolinate, DP = dipicolinate, NTA = nitrilotriacetate, HEDTA = N-hydroxyethylethylenediaminetriacetate, EDTA = ethylenediaminetetraacetate, DCTA = 1,2-diaminocyclohexanetetraacetate, DTPA = diethylenetriaminepentaacetate.
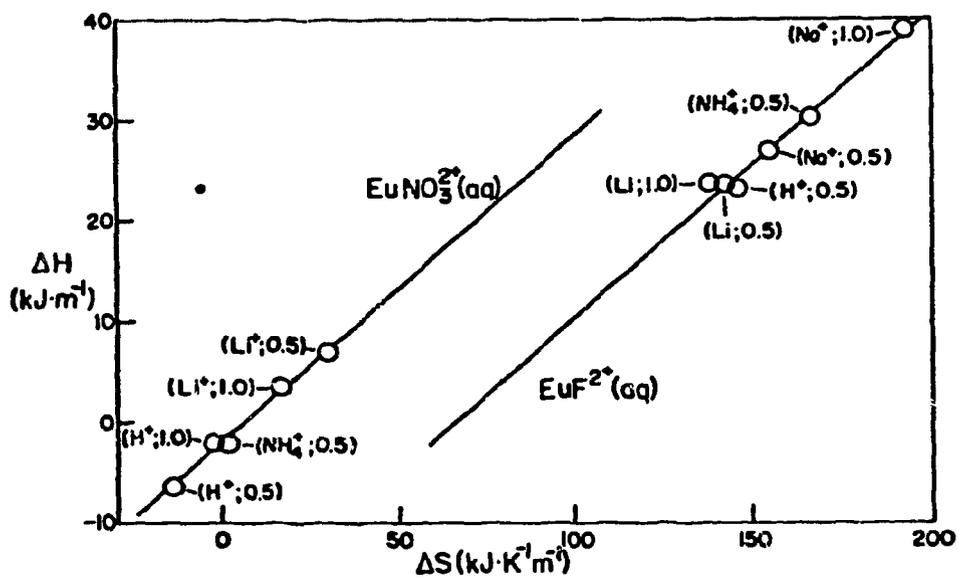

Figure 5. Correlation of the enthalpy and entropy of formation of $EuNO_3^{+2}{}_{(aq)}$ and $EuF^{+2}{}_{(Aq)}$ at u = 0.5M and 1.0 M and different "inert" cations.