

## Modelling thermodynamic properties of lanthanide (LnL)<sup>3+</sup> and actinide (AnL)<sup>3+</sup> complexes with tridentate planar nitrogen ligands (L)

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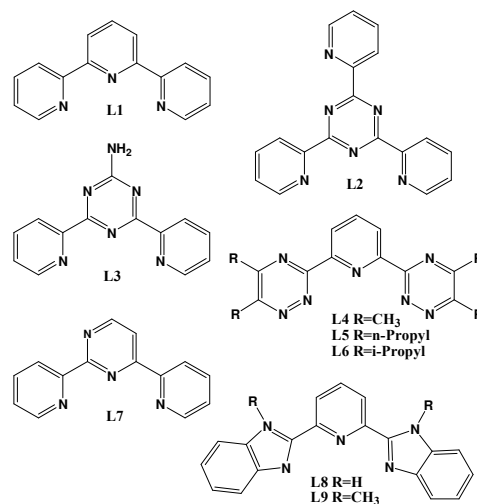
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**Abstract** – We report here the results obtained from a systematic theoretical study on the thermodynamic properties of trivalent lanthanide (Ln) and actinide (An) complexes with chelating nitrogen tridentate ligands. The mechanism of chelation has been investigated and the role of cation desolvation is investigated through a comparison of the thermodynamic properties of solvated cations and complexes. The difference in thermodynamic properties of LnL and AnL complexes is analyzed.

Over the past decade, there has been a considerable interest in the study of trivalent lanthanide complexes with tridentate nitrogen planar ligands. The present paper deals with an important class of tridentate nitrogen planar ligands interacting with trivalent lanthanide (Ln<sup>3+</sup>) and actinide (An<sup>3+</sup>) aqueous cations. The mechanism of interaction has attracted much attention because of the need to separate minor An<sup>3+</sup> from Ln<sup>3+</sup> in acidic effluents in the management of spent nuclear fuels, if one want to achieve the transmutation of the long-lived minor actinide nuclides into short-lived nuclides. The solution to this problem requires a deep understanding of the structural and electronic factors controlling the differences between the thermodynamic properties of trivalent An and Ln complexes with tridentate nitrogen planar ligands, which were found effective for An/Ln partitioning.

An important part of the experimental determinations of the thermodynamic complexation properties of Ln<sup>3+</sup> and An<sup>3+</sup> with various ligands (L1-L9, Scheme 1) is due to research done at the CEA. The most direct information concerning the mechanism of interactions between Ln<sup>3+</sup> cations and tridentate nitrogen planar ligands in a given solvent is obtained when the Gibbs energy  $\Delta G^\circ$  and enthalpy  $\Delta H^\circ$  of complexation are measured with a given ligand across all the lanthanide series [1, 2, 3] as well as with a given cation and various ligands [4]. An important step towards this goal

is the experimental determinations of  $\Delta G^\circ$  and  $\Delta H^\circ$  variations for the formation of the 1:1 complexes: YL3, LnL3, Ln= La-Lu (with the exception of Pm), AnL3, An = Pu, Am and Cm in CH<sub>3</sub>OH(79%)/H<sub>2</sub>O(21%) solution [3]. The stability constants of LnL2 1:1 complexes in aqueous solution have also been measured for all the lanthanides (with the exception of Pm and Ce) and AmL2 [2]. The new experimental and theoretical data concerning the complexation of Ln<sup>3+</sup> with tridentate planar nitrogen ligands, together with the data obtained with mixed oxygen and nitrogen ligands, allow to explain the variation of the stability constants across the lanthanide series.



Scheme 1

We study here: (i) the effect of desolvation of  $\text{Ln}^{3+}(\text{aq})$  and  $\text{An}^{3+}(\text{aq})$  on the thermodynamic stability of  $\text{LnL}$  and  $\text{AnL}$  complexes; (ii) the effect of the presence of a chelating effect in the enthalpy and entropy changes upon complexation; (iii) the comparative stability of  $\text{LnL}$  and  $\text{AnL}$  complexes.

### FREE ENERGY OF COMPLEXATION AND DESOLVATION EFFECTS

We propose that  $|\Delta G^{\circ}_{\text{desolvation}}| > |\Delta G^{\circ}_{\text{complexation}}|$ . If this is the case, it is obvious that a correlation must be found between  $\Delta G^{\circ}_{\text{total}}$  and  $\Delta G^{\circ}_{\text{desolvation}}$ . In order to check our proposition, we use the experimental values of  $\Delta G^{\circ}(\text{ML3})_{\text{MeOH/water}}$  for  $M = \text{Ln}, \text{Pu}, \text{Am}, \text{Cm}$  [3] and the standard energy of formation of aqueous cations  $\Delta G^{\circ}_f(\text{M}^{3+}(\text{aq}))$  from [5]. From the correlation, one can predict the unknown  $\Delta G^{\circ}(\text{ML3})$  values for  $M = \text{Pm}, \text{Cm}, \text{Bk}, \text{Cf}$ . The value of  $\Delta G^{\circ}(\text{CmL3})$  calculated from the correlation is equal to  $-32.2 \text{ kJ}\cdot\text{mol}^{-1}$  whereas the experimental value is  $-33.5 \text{ kJ}\cdot\text{mol}^{-1}$ . Thus, the correlation provides an indication of the significant effect of the desolvation on the complexation. In addition, a more complete picture can be obtained by a more detailed consideration of enthalpy and entropy terms upon complexation.

### CHELATING EFFECTS IN ENTHALPY AND ENTROPY OF COMPLEXATION

In the attempt to quantify the influence of chelation on the enthalpy and entropy variations associated to the complexation of  $\text{Ln}^{3+}$  with tridentate nitrogen planar ligands, we have considered the change of entropy/enthalpy compensation in  $\text{LnL3}$  complexes using the experimental data of complexation obtained by Miguiditchian in  $\text{MeOH}/\text{H}_2\text{O}$  (79%/21%) solution (12). We propose the following relation for  $\Delta H^{\circ}_{\text{total}}$  associated to the complexation reaction:

$$\Delta H^{\circ}_{\text{total}} = \Delta H^{\circ}(\text{LnL3}_{\text{sol}}) - [\Delta H^{\circ}_f(\text{Ln}^{3+}_{\text{sol}}) + \Delta H^{\circ}(\text{L3}_{\text{sol}})]$$

where the first term is the standard enthalpy of formation of  $\text{LnL3}$  complexes, the 2nd and 3rd terms are the standard enthalpy of formation of solvated  $\text{Ln}^{3+}_{\text{sol}}$  cations and ligand  $\text{L3}_{\text{sol}}$ . Thus, the first term depends on the interaction between the cation and the ligand whereas the second and third terms depend on the interactions between

the cation or the ligand and the solvent molecules. We can rewrite  $\Delta H^{\circ}_{\text{total}}$  as:

$$\Delta H^{\circ}_{\text{total}} = \delta\Delta H^{\circ}_{\text{int}} + \omega\Delta H^{\circ}_{\text{ch}} \quad (1)$$

in order to divide the enthalpy contribution into two terms: the first term  $\delta\Delta H^{\circ}_{\text{int}}$  depends on the difference in the interactions between  $\text{Ln}^{3+}\text{-L}$  and  $[(\text{Ln}^{3+}\text{-solvent}) + (\text{L-solvent})]$ , and the second term  $\omega\Delta H^{\circ}_{\text{ch}}$  corresponds to the chelating enthalpy and does not depend on the interaction term. Analogously, the equation for the entropy can be written as:

$$\Delta S^{\circ} = \delta\Delta S^{\circ}_{\text{int}} + (1 - \omega)\Delta S_{\text{ch}} \quad (2)$$

The second terms in equations 1 and 2 can be written as:

$$\Delta H^{\circ}_{\text{ch}} = (n-1)RT \ln M$$

$$\Delta S^{\circ}_{\text{ch}} = (n-1)R \ln M$$

where  $M$  is the molarity of solvent solutions ( $M = 29.0$ ),  $n=3$  is the denticity of the ligand and  $R = 8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Accordingly  $\Delta H^{\circ}_{\text{ch}} = -16.7 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta S^{\circ}_{\text{ch}} = 56 \text{ J}\cdot\text{mol}^{-1}$  or  $T\Delta S^{\circ}_{\text{ch}} = 16.7 \text{ kJ}\cdot\text{mol}^{-1}$

From the analysis of the experimental data determined by Miguiditchian (12) we can conclude that upon the complexation of light lanthanides ( $\text{Ln}^{3+} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$  and  $\text{Gd}$ ) the average enthalpy changes  $\Delta H^{\circ}_{\text{total}} = -18 \pm 4.0 \text{ kJ}\cdot\text{mol}^{-1}$  is close to the calculated value of  $\Delta H^{\circ}_{\text{ch}} = -16.7 \text{ kJ}\cdot\text{mol}^{-1}$ . In the second term of the equation 2, the coefficient  $\omega$  is thus  $\approx 1.0$ . During the complexation, the chelating effect affects more enthalpy than entropy changes: the average complexation entropy of light lanthanides (from  $\text{La}$  to  $\text{Gd}$ ) is equal to  $23 \pm 5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , this value is significantly less than the calculated chelating entropy ( $\Delta S^{\circ}_{\text{ch}} = 56 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ).

The experimental data show that  $\gamma^{\circ}_{\text{exp}} = T\Delta S^{\circ}_{\text{exp}}/\Delta H^{\circ}_{\text{exp}} < 1.0$ . This is unusual for lanthanide complexes with nitrogen and mixed oxygen + nitrogen ligands, for which usually  $\gamma^{\circ} > 1.0$  or even  $\gamma^{\circ} \gg 1.0$ .

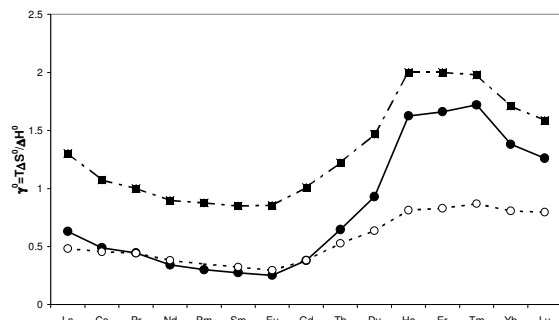


Fig. 1. Entropy/enthalpy compensation effect for LnL3 complexes. Experimental data from ref. 3. (●):  $T\Delta S_{\text{exp}}^0/\Delta H_{\text{exp}}^0$  (■):  $T\Delta S_{\text{ch}}^0/\Delta H_{\text{exp}}^0$  (○):  $T\Delta S_{\text{exp}}^0/\Delta H_{\text{ch}}^0$

Upon the complexation of heavy lanthanides (Ln = Ho, Er, Tm and Lu) the mean entropy changes ( $\Delta S_{\text{total}}^0 = 49 \pm 2 \text{ J.mol}^{-1}\text{K}^{-1}$ ) becomes comparable with the calculated value of  $\Delta S_{\text{ch}}$  ( $56 \text{ J.mol}^{-1}\text{K}^{-1}$ ). In the second term of equation (2) the coefficient  $(1-\omega)$  is thus  $\approx 1.0$ . For the complexes of heavy cations the mechanism of reaction appears to be entropy driven,  $\gamma_{\text{exp}}^0 > 1.0$ . This is characteristic of complexation in aqueous solutions. In Fig. 1, the measured values of the compensation entropy/enthalpy effect ( $\gamma_{\text{exp}}^0 = T\Delta S_{\text{exp}}^0/\Delta H_{\text{exp}}^0$ ) are compared to the values obtained from an entropy mechanism of chelation ( $\gamma_{\text{ch}}^0 = T\Delta S_{\text{ch}}^0/\Delta H_{\text{exp}}^0$ ) or an enthalpy mechanism of chelation ( $\gamma_{\text{ch}}^0 = T\Delta S_{\text{exp}}^0/\Delta H_{\text{ch}}^0$ ). The experimental ratio  $\gamma_{\text{exp}}^0$  is close to  $\gamma_{\text{ch}}^0$  for the complexes of light lanthanides but  $\gamma_{\text{exp}}^0$  is close to  $\gamma_{\text{ch}}^0$  for the complexes of heavy lanthanides.

An analysis of the thermodynamics properties of LnL3 complexes brings the experimental evidence that the origin of chelation, enthalpy or entropy, depends significantly on the size of cations. The largest cations ( $\text{La}^{3+}$ - $\text{Gd}^{3+}$ ) have the highest coordination numbers and interact with the large tridentate ligands with minimum steric strain. The chelation has thus a stronger effect on enthalpy. In the case of the smaller cations ( $\text{Ho}^{3+}$ - $\text{Lu}^{3+}$ ) steric effects become significant and the chelating effect affects the entropy of complexation.

### COMPARISON BETWEEN THE THERMODYNAMICS OF ACTINIDES(III) AND LANTHANIDES(III) COMPLEXATION

Considering the experimental difficulty to obtain thermodynamic data for actinides, one of the aims of the present study is to predict

thermodynamic properties for  $\text{An}^{3+}$  complexation with tridentate nitrogen ligands:  $\Delta G^0(\text{AnL})$ ,  $\Delta H^0(\text{AnL})$  and  $\Delta S^0(\text{AnL})$ . In order to compare lanthanide and actinide properties,  $\Delta H_{\text{f}}^0(\text{Ln}^{3+}(\text{aq}))$ ,  $\Delta H_{\text{f}}^0(\text{An}^{3+}(\text{aq}))$ ,  $\Delta H^0(\text{LnL3})$  and  $\Delta H^0(\text{AnL3})$  values are plotted in Fig. 2.

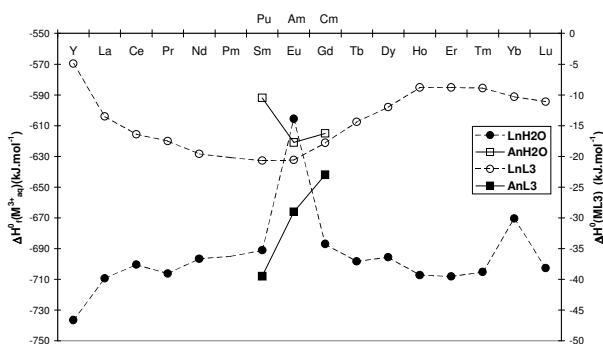


Fig. 2. Trends for the standard enthalpy of formation of ML3 complexes,  $\text{Ln}^{3+}(\text{aq})$  and  $\text{An}^{3+}(\text{aq})$  aquo ions.

The thermodynamics of aqua-cations shows considerable differences in the standard formation Gibbs energy and enthalpy between  $\text{Ln}^{3+}(\text{aq})$  and  $\text{An}^{3+}(\text{aq})$ . Moreover, the trends in variations of  $\Delta H_{\text{f}}^0(\text{Ln}^{3+}(\text{aq}))$  and  $\Delta H_{\text{f}}^0(\text{An}^{3+}(\text{aq}))$  in every half of the lanthanide and actinide series are opposite:

- $\Delta H_{\text{f}}^0(\text{An}^{3+}(\text{aq}))$  decreases with increasing  $Z(\text{An})$  from  $\text{U}^{3+}$  to  $\text{Am}^{3+}$  whereas  $\Delta H_{\text{f}}^0(\text{Ln}^{3+}(\text{aq}))$  increases with increasing  $Z(\text{Ln})$  from Nd to Eu. One expects that the complexation enthalpy of  $\text{An}^{3+}$  by tridentate planar ligands ( $\Delta H^0(\text{AnL})$ ) increases from  $\text{U}^{3+}$  to  $\text{Am}^{3+}$  but that  $\Delta H^0(\text{LnL})$  decreases from La to Sm.
- in the second half of the actinide series, from Am to Cf,  $\Delta H_{\text{f}}^0(\text{An}^{3+}(\text{aq}))$  increases with increasing  $Z(\text{An})$  whereas  $\Delta H_{\text{f}}^0(\text{Ln}^{3+}(\text{aq}))$  decreases with increasing  $Z(\text{Ln})$  from Eu to Ho.
- the variations of  $\Delta H_{\text{f}}^0(\text{An}^{3+}(\text{aq}))$  for light actinides follow the same trend than  $\Delta H_{\text{f}}^0(\text{Ln}^{3+}(\text{aq}))$  for heavy lanthanides; the variations of  $\Delta H_{\text{f}}^0(\text{Ln}^{3+}(\text{aq}))$  for light lanthanides follow the trend of  $\Delta H_{\text{f}}^0(\text{An}^{3+}(\text{aq}))$  for heavy actinides,
- in the case of light actinides, from U to Am, and heavy lanthanides, from Gd to Lu,  $\Delta H_{\text{f}}^0(\text{M}^{3+}(\text{aq}))$  values tend to decrease (become more exothermic). One expects a

linear correlation between  $\Delta H_f^\circ(M^{3+}(aq))$  and  $\Delta H^\circ(ML_3_{solv})$  with  $M = Gd, Tb, Dy, Ho, Er, Tm, Lu, U, Np, Pu, Am, Cm$ ,

- $\Delta H_f^\circ(An^{3+}(aq))$  values are significantly higher (less exothermic) than  $\Delta H_f^\circ(Ln^{3+}(aq))$ . One expects that  $\Delta H^\circ(AnL_3_{solv})$  ( $An = U, Np, Pu$ ) are more exothermic than  $\Delta H^\circ(LnL_3_{solv})$ , ( $Ln = Nd, Pm, Sm$ ).

In the actinide series  $\Delta H_f^\circ(An^{3+}(aq))$  decreases from U to Am and increases from Am to Cf. Am is seen to be the turning element in these trends. One expects that:

$\Delta H^\circ(PuL_3_{solv}) < \Delta H^\circ(CmL_3_{solv}) < \Delta H^\circ(AmL_3_{solv})$   
Finally, the known experimental difficulty to separate  $Am^{3+}$  and  $Cm^{3+}$  from  $Eu^{3+}$  by liquid-liquid extraction by using oxygen-bearing extractants can be attributed to the close values of  $\Delta H_f^\circ(M^{3+}(aq))$  for the three cations,  $-605.6$  (Eu),  $-615$  (Cm) and  $-621.1$  (Am)  $\text{kJ}\cdot\text{mol}^{-1}$  [5].

## CONCLUSION

From the thermodynamic properties of  $(ML)^{3+}$  complexes,  $M = Ln, An$  and  $L = L1-L9$ , that have been accumulated in the last 5 years, it appears that the stability of complexes is largely influenced by solvation effects. We conclude that the difference in enthalpy and entropy of complexation of  $Ln^{3+}$  and  $An^{3+}$  by tridentate planar ligands is significantly influenced by the difference in standard formation enthalpy and entropy of solvated cations.

The thermodynamic properties of complexes 1:1 brings the experimental evidence that the origin of the chelating effect, enthalpic or entropic, depends on the size of the cations. The large cations ( $La^{3+}$ - $Gd^{3+}$ ) have high coordination numbers and are able to accommodate the large tridentate ligands with minimal steric strain. The chelation is thus reflected more in the enthalpy of complexation. In the case of small cations ( $Ho^{3+}$ - $Lu^{3+}$ ) and large ligands the steric strain arises from steric crowding. The chelating effect is more reflected in the entropy of complexation. The softer character of the nitrogen donors in comparison with that of oxygen donors induces larger difference in thermodynamic properties upon complexation of relative  $An^{3+}/Ln^{3+}$  with tridentate planar ligands than with the oxygen donors. This effect has been attributed to the large difference in bond energies between actinides and lanthanides ( $D_o(An-N) - D_o(Ln-N)$ ).

$D_o(An-N)$ ,  $D_o(An-O)$ ,  $D_o(Eu-N)$  and  $D_o(Eu-O)$  bond energies have been calculated in complexes for the coordination numbers equal to 8, 9, 10 and 11.

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