

## Coordination of the Trivalent Lanthanoids in Aqueous Selenate and Perchlorate Solutions

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The nature of complex formation between trivalent lanthanoids and various inorganic ligands has been frequently studied in aqueous solution by measuring macroscopic thermodynamic and transport properties and by the use of spectroscopic methods. A few studies have also been made by direct measurements utilizing X-ray and neutron diffraction. The main questions which have been debated, include the coordination number and its change along the lanthanoid series, and whether the anion is entering the inner (contact) sphere of coordination or remains in the outer (solvent separated) sphere.

For sulfate and selenate solutions no XRD or NRD measurements have been reported, possibly due to the difficulties in obtaining concentrated solutions. On the basis of the basicity of the sulfato ligand, however, Choppin and Bertha<sup>1</sup> have predicted inner sphere complexation in agreement with ultrasonic evidence<sup>2</sup> but thermodynamic and spectroscopic studies have recently been interpreted<sup>3</sup> in favor of a predominantly outer sphere character of the  $[\text{LaSO}_4]^+$  complex. The most recent study on the luminescence lifetimes in a  $\text{Eu}^{3+}-\text{SO}_4^{2-}-\text{H}_2\text{O}$  system favors again the inner sphere complex formation in a wide concentration range.<sup>4</sup> In aqueous perchlorate solution, on the other hand, all reports agree on the outer sphere nature of lanthanoid complexation.

Although direct information on interatomic distances in a solution is obtainable from XRD measurements, the results are often obscured by the simultaneous presence of a large number of both intra and intermolecular interactions all contributing to the same one-dimensional intensity curve. The use of isomorphous substitution offers a possibility to eliminate interactions not involving the substituted metal ion. We have used this method, apparently for the first time for the lanthanoids, to get evidence for inner or outer sphere complex formation. Yttrium, which is chemically closely related to the lanthanoids and has an ionic radius about the same as found for the elements at the end of the lanthanoid series, has been used for this purpose.

In crystal structures lanthanoid selenates and sulfates are often isomorphous; this is the case for the octahydrate series as seen in comparative structural determinations.<sup>5,6</sup> The selenates have been chosen here as they are more favourable for an XRD investigation because of their slightly higher solubilities and the higher atomic number of Se.

Compositions of the solutions investigated are given in Table 1. Diffraction curves were measured with  $\text{MoK}\alpha$  radiation in a  $\theta-\theta$  diffractometer and were corrected and scaled as previously described.<sup>7</sup> They were transformed into radial distribution functions:

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{\max} s \cdot i(s) \cdot \sin(rs) \cdot M(s) ds,$$

with the modification function  $M(s) = f_0^2(0)/f_0^2(s) \cdot \exp(0.01s^2)$ . Here  $f(s)$  are scattering factors and  $s = 4\pi \sin \theta/\lambda$  ( $2\theta =$  scattering angle).

Theoretical peaks,  $p_{pq}$ , for specific pair interactions were obtained by a Fourier transformation of the corresponding intensity contribution, analogous to that used for the experimental curves.<sup>7</sup> After subtracting the contributions from the intramolecular interactions of the  $\text{XO}_4$  groups from the  $D(r)$  functions, the Ln-O distances in the first

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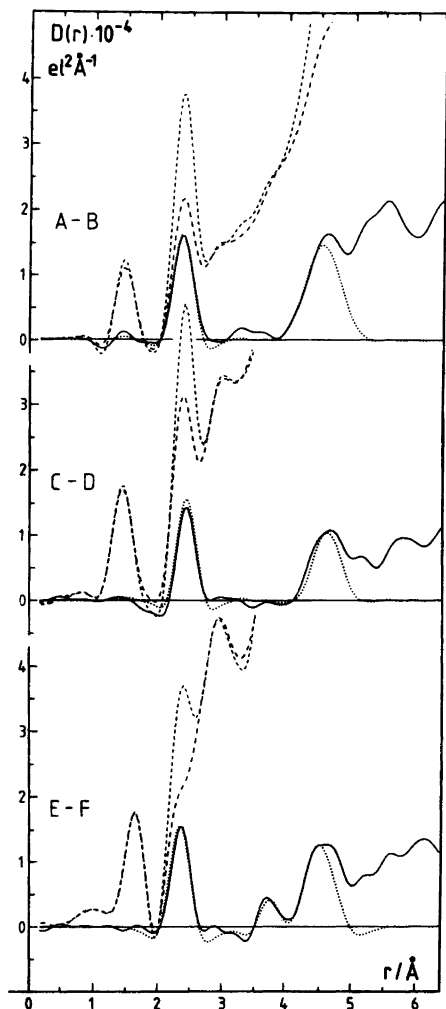


Fig. 1.  $D(r)$  functions (dashed lines) and their differences (solid lines) for the three pairs of solution. Dotted curves indicate theoretical peaks calculated with use of parameters given in Table 1.

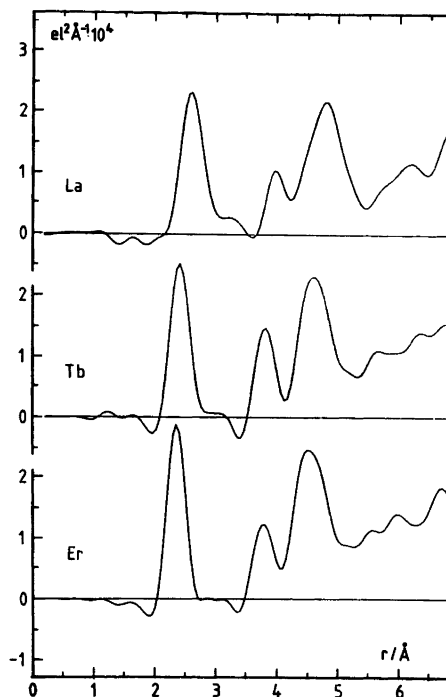


Fig. 2. Radial distribution curves for three lanthanoid selenate solutions after elimination of light atom interactions. The three peaks correspond to Ln-O (1st coord. sphere), Ln-Se (coordinated  $\text{SeO}_4^{2-}$ ) and Ln-O (2nd coord. sphere).

coordination spheres were determined by fitting calculated peaks to the remaining curves. The values obtained are given in Table 1.

The  $D(r)$  functions for the six solutions and the difference for each isomorphous pair of solutions, A-B, C-D and E-F, are shown in Fig. 1. In these difference functions all interactions except those involving the metal ions cancel out and they therefore give an unobscured picture of the surroundings of an average  $\text{Ln}^{3+}$  ion. The first peak at 2.4 Å, corresponding to the first coordination sphere, can be closely reproduced by peaks calculated with the distances in Table 1 assuming a coordination number of 8.0 and an rms variation in the distance of 0.10 Å (Fig. 1). For the perchlorates no other interactions occur up to 4.5 Å, where a peak appears which is rather well defined towards the  $\text{Ln}^{3+}$  ion but is

Table 1. Compositions of solutions (mol dm<sup>-3</sup>) and observed bond lengths (Å).

	[Ln <sup>3+</sup> ]	[XO <sub>4</sub> <sup>2-</sup> ]	X-O	Ln-O 1st coord. sphere	Ln-O 2nd coord. sphere	Ln-Se
A Er(ClO <sub>4</sub> ) <sub>3</sub>	2.96	9.0	1.446	2.36	4.55	
B Y(ClO <sub>4</sub> ) <sub>3</sub>	2.91	8.9	1.450	2.365	4.55	
C Tb(ClO <sub>4</sub> ) <sub>3</sub>	1.093	5.30	1.429	2.40	4.60	
D Y(ClO <sub>4</sub> ) <sub>3</sub>	1.094	5.30	1.429	2.37	4.55	
E Er <sub>2</sub> (SeO <sub>4</sub> ) <sub>3</sub>	0.78	1.55	1.633	2.345	4.47	3.75
F Y <sub>2</sub> (SeO <sub>4</sub> ) <sub>3</sub>	0.77	1.54	1.628	2.33	4.47	3.75

more diffuse towards longer distances. It represents a second coordination sphere around the metal ion. It seems to differ in shape for the different solutions and cannot be fully reproduced by a single interaction peak. The distances used for the theoretical peaks shown in Fig. 1 are listed in Table 1.

For the selenate solution the peak at 3.7 Å defines an Ln-Se interaction and proves the formation of an inner sphere Ln-SeO<sub>4</sub> complex. The theoretical peak is calculated for an average of 0.4 SeO<sub>4</sub><sup>2-</sup> per Er<sup>3+</sup> and an Er-Se distance of 3.75 Å, which corresponds to an Er-O-Se angle of 140°. The next shortest Er-O(SeO<sub>4</sub>) distance will depend on the orientation of the SeO<sub>4</sub><sup>2-</sup> group, but cannot be smaller than 4.0 Å. The bonding of SeO<sub>4</sub><sup>2-</sup> is thus monodentate. The theoretical peak in Fig. 1 has been calculated for this conformation.

Knowing the intramolecular interactions in an yttrium solution we can subtract them from its radial distribution curve and use the remaining curve as an approximation for the light-atom interactions in solutions with other lanthanoid ions. This is exemplified in Fig. 2 for a series of selenate solutions, which are slightly more concentrated than those listed in Table 1. We have then neglected the change in light-atom interactions expected as a result of the increase in ionic radius when going from Er to La. The effect of this will be small, however, and will not affect the main features of the curves, which clearly show the inner sphere complex formation with selenate for all the lanthanoid ions.

The present results on the nature of the complexes formed are in agreement with the crystal structure determinations of the isostructural selenate octahydrates (Pr-Lu),<sup>6</sup> where the coordination number is found to be eight. Also the distances and angles are of the same order of magnitude: in the structure of Yb<sub>2</sub>(SeO<sub>4</sub>)<sub>3</sub> · 8H<sub>2</sub>O the mean Yb-Se distance is 3.71 Å and the mean Yb-O-Se angle is 137°. In crystals of [Ln(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> (Ln=La, Tb, Er) the perchlorate ions are not included in the inner coordination sphere, as is also found here for the solutions, but the octahedral Ln-OH<sub>2</sub> coordination in the crystals differs from that found here for the solutions.<sup>8</sup>

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Received October 30, 1984.