Such $(M + 57)^+$ ions must also be relatively long lived in order for bond-breaking and bond-forming reactions to occur.

Acknowledgment. This work was supported by grants from the National Science Foundation (GP20231), the donors of the Petroleum Research Fund, administered by the American Chemical Society, the University of Delaware Research Foundation, and the Delaware Institute of Medical Education and Research.

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Solute Structuring in Aqueous Lanthanum(III) Chloride Solutions

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Abstract: The structure of the average solute species in four concentrated aqueous $LaCl_3$ solutions, with and without hydrochloric acid, has been measured by X-ray diffraction. In each solution, La^{3+} has 8 ± 0.2 oxygen nearest neighbors with the average La–O distance being ca. 2.48 Å. The ion-pair La ··· Cl distance, ca. 4.7 Å, is easily identified in the atomic radial distribution functions of these solutions, particularly in the solution where the stoichiometric ratio of chloride–lanthanum is 6:1. Models have been proposed which are consistent with the ARDF's obtained.

The coordination chemistry of various lanthanides, particularly in solutions, is one of the frontier areas of chemical research. Studies designed to examine the structural details of various lanthanide complexes have been rather unproductive, to a large extent because the normal spectroscopic tools have not led to a thorough understanding of lanthanide–ligand interactions.

Raman studies of lanthanide complexes[1-3] in solutions have failed to yield direct information concerning lanthanide–ligand interactions. Though for many years visible spectroscopy was not thought to be a useful tool for studying these interactions, it has recently been reported that lanthanide–ligand interactions may be correlated with changes in molar absorptivity[4] and with small changes in the wavelength of maximum absorption.[5]

Stability constant studies have been numerous; but such studies, by their nature, do not provide a detailed knowledge of the coordination of the cation.

Several years ago Brady[6] examined a series of aqueous $ErCl_3$ and ErI_3 solutions with X-ray diffraction methods. He has reported that $Er(H_2O)_6{}^{3+}$ is the predominant species in each solution with the average Er–O distance being ca. 2.2 Å. He also has reported extensive Er ··· Cl ion pairing in these solutions.

We have examined a series of concentrated aqueous solutions of $LaCl_3$, with and without added hydrochloric acid, in an attempt to directly determine the following: (a) the average coordination number and the average coordination geometry of La^{3+} in each solution; (b) the average La–O and/or La–Cl bond distances in each solution; (c) how these parameters are affected by changing solution composition; and (d) the similarity between the coordination of La^{3+} in these solutions and in crystals, where the nearest neighbor coordination of La^{3+} ranges from six to ten.[7-21]

To this end we have examined the solutions described below by X-ray diffraction methods using Mo Kα radiation.

Experimental Section

Solutions were prepared by weight from predried anhydrous $LaCl_3$, 10 *N* hydrochloric acid and/or distilled water. Densities were measured with a specific gravity bulb. Solution compositions are shown in Table I. Each solution was loaded into a Teflon sample holder, which has a window covered by a 1.0-mil Mylar film, and an X-ray diffraction pattern was obtained using the reflection method.[22] Scattered intensities were collected using our θ-θ diffractometer as counts per preset time as a function of the scattering angle from $s = 1.23$ Å^{-1} to $s = 15.09$ Å^{-1} ($s = 4\pi\lambda^{-1} \sin\theta$) at increments in θ of 0.25°. At least three runs over the entire angular range were made for each solution. The average intensity at each scattering point was used in subsequent calculations.

Table I. Solution Compositions

Solution	Molality, mol/kg	Mole fractions				Density, g/ml
		La	Cl	O	H	
A	2.67	0.015	0.045	0.313	0.627	1.53
B	2.10	0.012	0.036	0.317	0.635	1.43
C	1.74	0.010	0.030	0.320	0.640	1.36
D	1.54	0.010	0.060[a]	0.300	0.630	1.40

[a] Excess chloride has been added in the form of hydrochloric acid.

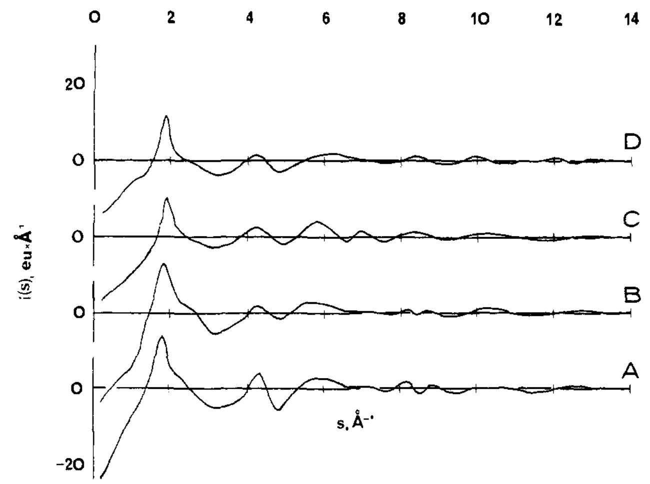

Figure 1. The scaled intensity functions for the solutions. For each solution $i(s) = I_{coh}(s) - \Sigma x_i f_i^2(s)$.

The scattered intensity was corrected for background (*ca.* 5 cpm), for polarization,[23] for sample penetration,[24] for multiple scattering,[25] and, after inclusion of a monochromator discrimination function, for Compton scattering.[26] The corrected intensity, e.g., the coherent intensity curve $I(s)$, was then tentatively computer fitted to $\Sigma x_i f_i^2(s)$[27] according to the methods of Lawrence and Kruh.[28] Final fitting of $I(s)$ to $\Sigma x_i f_i^2(s)$ was performed by a method similar to that used by Konnert and Karle.[29] Atomic radial distribution functions (ARDF's) were calculated at increments in Δr of 0.01 and 0.05 Å by[22,24,30]

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int [si(s)][M(s)][\sin sr] ds$$

With this method $D(r)$ provides a weighted measure of the probability of finding atom pairs in the solution separated by a distance between r and $r + dr$, ρ_0 is the bulk density of the solution, $si(s) = s[I_{coh}(s) - \Sigma x_i f_i^2(s)]$, and

$$M(s) = \{[\Sigma x_i f_i(0)/\Sigma x_i f_i(s)]\}^2 \{\exp(-bs^2)\} \mathrm{USF}$$

USF is a unit step function which terminates the integral at $s_{max} = 15$ Å^{-1}.

Shown in Figure 1 are the $i(s)$ functions for the solutions, and in Figure 2, are the ARDF's obtained with $b = 0.015$. Shown in Figure 3 are the atom-pair correlation functions (e.g., $g(r) = D(r)/4\pi r^2 \rho_0$) obtained for the solutions. Summarized in Table II are the ARDF's.

The area under the first peak in each ARDF was determined via repeated graphical integration so that deviation from the mean area of each first peak was <2% of the peak area.

For each solution the area anticipated for one La–Cl pair ($A_{La\text{-}Cl}$) and that for one La–O pair ($A_{La\text{-}O}$) were calculated by the method of Waser and Schomaker.[31]

Both the position of and the area under the first peak have been utilized to determine the average inner sphere coordination of La^{3+} in each solution by

$$\mathrm{P1} \simeq n_1 d_{La\text{-}O} + n_2 Q d_{La\text{-}Cl}$$

$$\mathrm{P1A} = n_1 A_{La\text{-}O} + n_2 A_{La\text{-}Cl}{}^{32}$$

In these equations n_1 and n_2 are the average number of La–O and La–Cl contacts per La^{3+}, $d_{La\text{-}O}$ and $d_{La\text{-}Cl}$ are the La–O and La–Cl distances as determined in crystals, $Q \simeq A_{La\text{-}Cl}/A_{La\text{-}O}$, P1 is the location of the first peak, and P1A is the area under the peak in each ARDF.

Based upon this method of correlating the primary peak in the ARDF with the average inner-sphere coordination of a cation, the uncertainty in the determination of the coordination number of the cation is not significantly larger than the uncertainty in the area under the primary peak. In several other solutions,[32] the maximum uncertainty in the coordination number of the cation appears to be less than 0.2, and this is consistent with error estimates based on the methods of Konnert and Karle.[29] For these LaCl$_3$ solutions, the maximum uncertainty in the determination of the coordination number of La^{3+} is ca. 0.2.

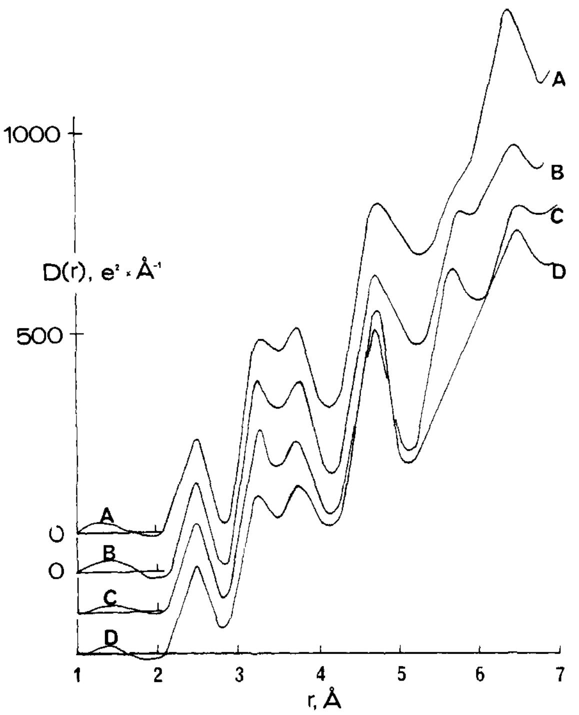

Figure 2. The ARDF's of the solutions with a damping factor of $0.015s^2$.

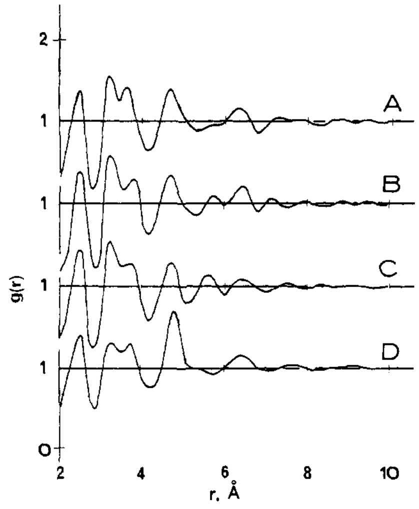

Figure 3. The atom pair correlation functions obtained for the solutions.

Results and Discussion

In each of the ARDF's $D(r) \rightarrow 0$ when $r < 1.9$ Å. Peaks occur in each ARDF at 2.45–2.50 Å (P1), at 3.3 Å (P2), at 3.7 Å (P3), at 4.7 Å (P4), and at 6.4–6.5 Å (P5). In solution A a shoulder appears at 5.4–5.6 Å, and at this distance a peak appears in the ARDF's of solutions B and C. No peak appears at this distance in solution D.

The Primary Peak. In each ARDF the primary peak is well defined and is centered at ca. 2.48 Å. That the area per La as well as the location of P1 is constant in these ARDF's indicates that the ligand environment about the average La^{3+} is the same in these solutions. The location of the pri-

Table II. Summary of the ARDF's

	Solutions			
	A	B	C	D
P1, Å	2.48	2.49	2.48	2.48
P1A, e^2	128	107	85	86
P2, Å	3.3	3.3	3.2	3.3
P3, Å	3.7	3.7	3.7	3.7
P4, Å	4.7	4.7	4.7	4.7
P5, Å	6.5	6.5	6.4	6.5
P6, Å	5.4–5.7[b]	5.5[b]	5.5[b]	[b]
Area per La, e^2 [a]	8.53×10^3	8.56×10^3	8.50×10^3	8.60×10^3

[a] The area per La is P1A/mole fraction of La^{3+} in that solution. [b] The relative intensity of P6 varies dramatically in these solutions. There is no evidence of P6 in the ARDF of solution D, while in solution A P6 is a small shoulder. In the ARDF's of solutions B and C, P6 is a well-defined peak.

mary peak in each ARDF is consistent with La–O bonding, since in crystals La–O bond distances are reported to occur at 2.5–2.6 Å.[11-21] La–Cl contacts occur at significantly larger distances in crystals.[11]

Shown below is the ratio of P1A to A_{La-O} (e.g. n_1) determined for the four solutions examined.

Solution	P1A, e^2	A_{La-O}, e^2	n_1
A	128	15.8	8.1 ± 0.2
B	107	13.4	8.0 ± 0.2
C	83	10.7	8.0 ± 0.2
D	86	10.8	8.0 ± 0.2

Consequently, it is clear that, on the average, La^{3+} has eight oxygen nearest neighbors with the average La–O distance being ca. 2.48 Å.

Unfortunately, inner-sphere O · · · O interactions are not discernible in the ARDF's of these solutions. Consequently it is not possible to determine unequivocally whether the inner-sphere oxygen environment about the La^{3+} is, on the average, cubic or square antiprismatic. Although Brady[6] suggests that Er^{3+} has six oxygen nearest neighbors, Spedding et al.[33] have shown that the coordination number of Er^{3+} is 8 ± 0.1 in aqueous $ErCl_3$ solutions. This latter result in clearly in accord with our findings regarding the inner-coordination sphere about La^{3+} in these solutions.

Secondary Peaks. It is beyond the scope of solution X-ray diffraction methods to unambiguously correlate various solute models with secondary peaks in the ARDF's. However, because of the consistency in location and the unusual sharpness of the remaining peaks in each ARDF, it is possible to speculate about solute models which account for the existence of the remaining peaks in each ARDF.

The existence of P2 in each ARDF is anticipated. In the ARDF's of numerous aqueous metal halide solutions[6,28,32-38] and hydrochloric acid,[39,40] a peak due to hydrogen-bonded Cl–O interactions occurs at 3.2–3.3 Å. The existence of P2 in each ARDF cannot, consequently, be utilized to either support or eliminate any solute model.

Brady[6] proposes that the peak at ca. 4.6 Å in his radial distribution curves may be attributed to ion-paired Er · · · Cl interactions in concentrated aqueous solutions of $ErCl_3$. The ARDF's of these $LaCl_3$ solutions also exhibit a peak in this vicinity, at 4.7 Å. This peak is particularly prominent in the ARDF of solution D, and consequently it has been assigned to La · · · Cl interactions.

Two models have been developed which are consistent with the La–ligand interactions, the cubic inner sphere of oxygens and the La · · · Cl distance being 4.7 Å. These models are shown in Figure 4. In model I the outer-sphere chlorides are assumed to occupy sites adjacent to faces of the cubic $La(H_2O)_8{}^{3+}$, and in model II the chlorides are assumed to occupy sites adjacent to edges of the cubic inner sphere (Table III). An important difference between the models is the distances at which Cl · · · O and Cl · · · Cl interactions occur. With model I Cl · · · O interactions would be anticipated at 3.7 and at 6.5 Å; whereas for model II Cl · · · O interactions would be anticipated at 3.0 Å, at 5.3 Å, and 6.8 Å. Nonbonded Cl · · · Cl interactions would be anticipated at 6.6 Å and at 9.4 Å with model I, or at 4.7 Å, at 6.6 Å, at 8.1 Å, and at 9.4 Å (model II).

Model I accounts for all details of the ARDF of solution D and consequently may be viewed as a plausible description of the average solute species in solution D. Since the stoichometric ratio of chloride–lanthanum is 6:1 in this solution, it is likely that most if not all of the faces of $La(H_2O)_8{}^{3+}$ are occupied by chlorides in the average species. The peak at 3.3 Å, which is not predicted by model I, is attributed to hydrogen-bonded Cl–O interactions, but the peaks at 3.7 Å and at 6.5 Å as well as the major peak at 4.7 Å are consistent with model I.

It appears as if a combination of model I and model II describes the mean solute species in solutions A, B, and C with the contribution of model II increasing as the solute concentration decreases. This supposition is based upon the fact that the peaks at 3.2 and 5.5 Å (predicted by model II)

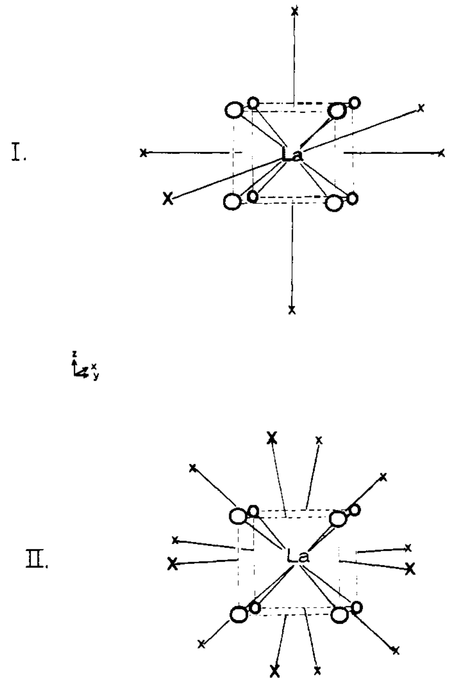

Figure 4. Models which are consistent with the ARDF's. In model I, chlorides are assumed to be located adjacent to some of the faces of cubic $La(H_2O)_8{}^{3+}$. In model II, chlorides are assumed to be located adjacent to some of the edges of cubic $La(H_2O)_8{}^{3+}$. X's denote possible locations of chlorides in the second coordination sphere.

Table III. Plausible Nonbonded Interaction Distances[a]

	Interaction distance, Å	No.
A. Model I (Chlorides Adjacent to Faces of the $La(H_2O)_8{}^{3+}$ Cube)		
1. X···O interactions	3.7	4 per Cl
	6.5	4 per Cl
2. Possible X···X interactions	6.6	*b*
	9.4	*b*
B. Model II (Chlorides Adjacent to Edges of the $La(H_2O)_8{}^{3+}$ Cube)		
X···O interactions	3.0	4 per Cl
	5.3	8 per Cl
	6.8	4 per Cl
2. Possible X···X interactions	4.7	*b*
	6.6	*b*
	8.1	*b*
	9.4	*b*

[a] In both models the La–O distances are 2.48 Å in $La(H_2O)_8{}^{3+}$ and the La–Cl distance is assumed to be 4.7 Å. [b] The number of nonbonded Cl···Cl interactions depends upon the extent to which chlorides occupy the "sites" of the second coordination sphere.

increase in magnitude while the peaks at 3.7 Å and at 6.5 Å (predicted by model I) decrease in magnitude as the solute concentration decreases. Consistent with the ARDF of solution C, model II is at least as important a contributor to the mean species in this solution as is model I.

Several solute models where the $La(H_2O)_8{}^{3+}$ polyhedron has been assumed to be square antiprismatic and where the La · · · Cl distance is 4.7 Å have been considered. However, these models do not account for the ARDF's observed for the $LaCl_3$ solutions, and furthermore the square-antiprismatic model is not consistent with spectra and D_{nh} symmetry observed for similar solutions where Eu^{3+} is the rare earth cation.[41] Consequently, the square-antiprismatic model(s) of $La(H_2O)_8{}^{3+}$ must be disregarded.

Conclusions

In the very concentrated solutions of $LaCl_3$ examined, the inner coordination sphere of La^{3+} is occupied exclusively by oxygens, even when the solvent is 10 *N* hydrochloric acid. The average La-O distance is ca. 2.48 Å and on the average each La^{3+} has eight nearest oxygen nearest neighbors in these solutions. Extensive ion-pair interactions between La^{3+} and Cl^- occur at an average distance of 4.7 Å. It may be concluded that La^{3+} greatly prefers oxygen to chloride as an inner-sphere ligand.

Models which are consistent with these observations and the ARDF's suggest that at high chloride-lanthanum stoichiometric ratios, and/or near saturation, the outer-sphere chlorides lie adjacent to faces of cubic $La(H_2O)_8{}^{3+}$; whereas at lower solute concentrations the chlorides may be adjacent to faces or edges of the cubic inner coordination sphere. However, it is beyond the scope of solution diffraction experiments to unambiguously establish the location(s) of the outer-sphere chlorides, so that these models must be assumed to be speculative.

Acknowledgment. The authors wish to acknowledge research support from Research Corporation (Cottrell Grant) and via a Faculty Research Project Grant from the University.

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