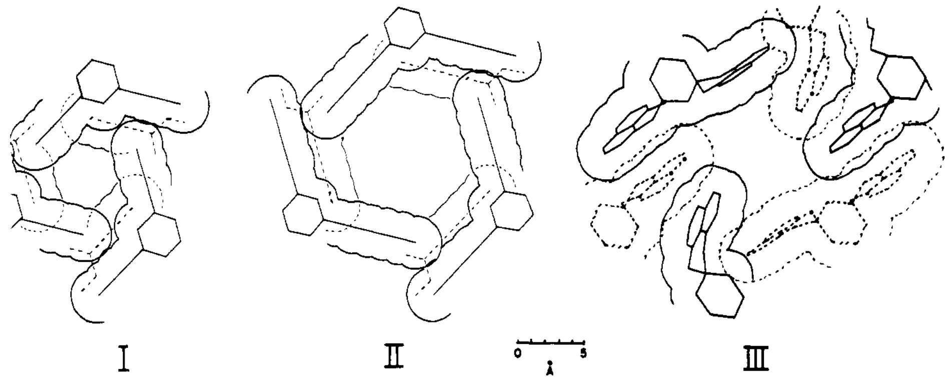

Figure 6. Comparison of the tunnel cross sections of tris(*o*-phenylenedioxy)cyclotriphosphazene (I), tris(2,3-naphthalenedioxy)cyclotriphosphazene (II), and tris(1,8-naphthalenedioxy)cyclotriphosphazene (III).

from the lattice at a temperature of 120–121 °C,[5] and the variable temperature NMR work reported here indicates that *p*-xylene is lost between 100 and 120 °C.

The tunnel diameter in clathrates formed by I is approximately 5 Å. Thus, the tunnel diameter is actually smaller than in III, but the clathrates are, if anything, less stable than those formed by III. Guests, such as benzene and xylene, do not leave the tunnel system of I at 25 °C (760 Torr), but they can be removed slowly at temperatures above 75 °C. Guest molecules in the tunnels formed by I must be capable of broad translational movements since one guest can be replaced by another. Furthermore, the facile interconversion of the triclinic (unclathrated) and hexagonal (clathrated) forms of I undoubtedly facilitates both the release of guest molecules and their reabsorption.

The over-all evidence indicates that clathration in these three systems is a purely mechanical phenomenon, stabilized mainly by van der Waals forces. The binding between host and guest is usually sufficiently weak that the guest molecules can undergo extensive thermal motions within the tunnels. Only when the tunnels are constricted almost into a set of cavities (as in III), or when the guest dimensions are large (as in the adduct of I with triethylbenzene, or II with *p*-xylene), do the guest motions become restricted at ambient temperatures.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Structure factors for benzene and *o*-xylene adducts of I, Tables I and II, respectively, and thermal parameters for benzene and *o*-xylene adducts of I, Tables III and IV, respectively (9 pages). Ordering information is given on any current masthead page.

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A Preliminary Report of the Coordination of Lanthanum(III) in Lanthanum Chloride–Methanol Solutions[1]

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Abstract: Methanolic solutions of $LaCl_3$ were studied by x-ray diffraction and by ^{139}La and ^{35}Cl NMR. An average inner coordination sphere species $LaCl_3(CH_3OH)_5$ is found with La–O and La–Cl distances of 2.48 and 2.95 Å, respectively. Long range interactions in the ARDF were used to propose a dichloro-bridge model, $[LaCl_2(CH_3OH)_5]_2$, for the average solute species.

In an earlier paper,[2] we identified octaquolanthanum(III) as the average coordination species in concentrated aqueous $LaCl_3$ solutions, both with and without added hydrochloric acid. $La(H_2O)_8^{3+}$ has approximately cubic symmetry with an inner-sphere La–O distance of ca. 2.48 Å. In the atomic radial distribution functions (ARDF) of these solutions, the ion-paired La···Cl interactions are easily identified at 4.7 Å. Brady[3] reports the ion-paired Er···Cl distance to be 4.6 Å in aqueous

Table I. Solution Compositions

	Solution A	Solution B
Solvent	Water	Methanol
Density (g/ml)	1.36	1.15
Molality (mol/kg)	1.74	1.95
Viscosity (cP, 32 ± 1 °C)	1.80	2.78
Mole fractions: La	0.010	0.010
Cl	0.030	0.030
O	0.320	0.160
H	0.640	0.640
C	- - -	0.160

solutions of $ErCl_3$, and we have found the ion-paired La···Br distance to be 4.8 Å in aqueous $LaBr_3$ solutions.[4] In these latter solutions, $La(H_2O)_8{}^{3+}$ has also been identified as the mean inner coordination species.

Spedding et al.[5] report an average species of $Ln(H_2O)_x{}^{3+}$ where $x = 8$ or 9 for several aqueous solutions containing various lanthanide ions when the anion is nitrate or perchlorate. However, Raman studies of concentrated $Gd(NO_3)_3$ and $Ce(NO_3)_3$ solutions[6] suggest strong Ln^{3+}–$NO_3{}^-$ interactions, raising some question about Spedding's assignment of the nearest neighbor ligands. NMR studies suggest a coordination number of eight[7a] or nine[7b] for La^{3+} in concentrated aqueous solutions. These NMR studies show strong La^{3+}–$NO_3{}^-$ and La^{3+}–$ClO_4{}^-$ interactions in concentrated aqueous solutions, but La-anion interactions are almost completely absent when the anion is chloride or bromide.

In crystals which contain waters of hydration or oxy-anions, inner-sphere La^{3+}-halide bonding is quite uncommon although dimeric $[La_2Cl_2(H_2O)_{14}]^{4+}$ has recently been reported in $LaCl_3{\cdot}7H_2O$.[8] In this crystal the inner-sphere La–O bond distances range from 2.49 to 2.64 Å, while the inner sphere La–Cl distances are 2.95 and 3.00 Å. In other crystals[9-16] the La–O distances range from 2.45 to 2.60 Å. In all of these crystals La^{3+} is either eight- or nine-coordinated.

In this paper we compare very concentrated methanolic and aqueous $LaCl_3$ solutions to investigate coordination sphere details of the average solute species and to determine whether inner-sphere La–Cl bonding occurs in methanol, a solvent which displays a lower nucleophilicity than water towards metal ions.[17-19]

Experimental Section

Solution Preparation. Solutions were prepared by weight from anhydrous $LaCl_3$ using distilled, deionized water for solution A, and for solution B, methanol which had been "dried" over molecular sieves. Densities were measured with a density bulb and viscosities with an Ostwald viscometer. Measurements were initiated about 4 weeks after the solutions were prepared.

X-Ray Scattering Experiments. Each sample was loaded into a specially designed cylindrical sample holder which had a window covered with 1.0 mil Mylar film. An x-ray diffraction pattern was obtained using the reflection method and Mo Kα radiation from $\theta = 3.00°$ to $\theta = 63.00°$ (or from $s = 0.93$ Å^{-1} to $s = 15.78$ Å^{-1} where $s = 4\pi\lambda^{-1}\sin\theta$) at increments of 0.25° in θ. Two runs over the entire angular range were made to ensure sample and counting consistency. During each run, each of the 240 data points was counted for 30 min. At high scattering angles, where the count rate is lowest, the uncertainty in the count rate[20] was ca. ±0.3% of the total counts at the data point, and the uncertainty diminished to ca. ±0.06% at the most intense peaks. The design of our diffractometer made it impossible to obtain meaningful scattering data at $\theta < 3.0°$ or $\theta > 63.00°$. The average intensity at each scattering point was used in subsequent calculations.

X-Ray Data Treatment. The scattering intensity was corrected for background (ca. 3 cpm), for polarization,[21] for sample penetration,[22] for multiple scattering,[23] and for Compton scattering.[24] The resulting coherent scattering curve, $I(s)$, was fitted to $\Sigma x_i f_i{}^2(s)$[24] utilizing a modification of the Konnert-Karle method described previously.[2]

The atomic radial distribution functions, $D(r)$ and $g(r)$, have been calculated for each solution by the conventional method[25] from $s{\cdot}i(s)^*$, where

$$i(s)^* = [(I(s)/k(s)] - \Sigma x_i f_i{}^2(s)]$$

A scaling function[26] of the form $k(s) = \bar{k}[1 \pm \alpha\cos(\beta s) \pm \gamma\exp(\epsilon s)]$ was used in which α, β, γ, and ϵ were determined by iterative techniques, and $\bar{k}$ is the ratio of $I(s)/\Sigma x_i f_i{}^2(s)$ at high s.

For coordination studies $D(r)$ is the most useful form of the ARDF. $D(r)$ provides a measure of the weighted probability of finding atom-pairs separated from one another by a distance between r and $r + \mathrm{d}r$. The weighting factor is $\Sigma x_i n_{ij} K_i K_j$ where x_i is the mole fraction of atom i, and n_{ij} represents the average number of interactions between atoms i and j. K_i and K_j are the scattering powers of the atoms, and the K_iK_j product may be evaluated by the Waser–Schomaker ideal peak method.[27]

The ideal peak areas anticipated for a La–O atom-pair and a La–Cl atom-pair have been calculated and are shown below:

Solution	$A_{La\text{-}O}$	$A_{La\text{-}Cl}$
A	10.7 e^2	21.6 e^2
B	12.4 e^2	25.0 e^2

For solution B, the area anticipated for one C–O atom-pair per methanol molecule has been calculated to be 18.8 e^2.

The atom-pair correlation function, $g(r)$, for each solution has been calculated by $g(r) = D(r)/4\pi r^2\rho_0$, where ρ_0 is the bulk density of the solution. This function provides a measure of deviation from a uniform atom density and consequently identifies important atom-pair distances in a solution.

NMR Measurements. A conventional wide-line NMR spectrometer (a modified Varian HR-60) operating at 4.2 MHz was used to detect signals of ^{139}La and ^{35}Cl. Suitable precautions were taken to ensure against distortion due to power saturation, overmodulation, etc. All measurements were made at ambient room temperature, 32 ± 1 °C.

Chemical shifts (δ) were determined from zero crossing points, and line widths (ΔH) were measured as peak to peak distances on the first derivative spectrum. Each value reported is the average of at least 15 sweeps. Line shape analysis showed that, to the limits of error imposed by noise, signals were Lorentzian out to at least two line widths distance from the center.

For Lorentzian lines and a spectrometer such as ours, the integrated absorption intensity due to a single NMR species should be proportional to $MA(\Delta H)^{-2}P^{1/2}$, where M is the molar concentration of the species, A is the modulation amplitude, and P is the radio frequency power input to the probe. Taking M as the molar concentration of $LaCl_3$, our data show that for solution B, ^{139}La NMR gives 96 ± 10% and ^{35}Cl NMR gives 90 ± 20% of the intensity observed in solution A; i.e., absorption intensities are about the same in the two solutions.

Results and Discussion

Listed in Table II are the results obtained from the x-ray scattering experiments and the wide-line NMR experiments for these two solutions. The ARDF's for the two solutions are shown in Figure 1 and Figure 2, and an enlarged view of $D(r)$ obtained for solution B is shown in Figure 3. From comparison of the experimental information, it is apparent that the solute species in these two solutions are significantly different.

The ARDF of solution B contains a small peak at 1.48 Å due to the C–O bond of the solvent.[28] The ideal peak area calculated for one C–O bond per methanol (18.8 e^2) compares favorably to the integrated area of this peak. The existence of this peak in solution B, of course, offers no information about the average coordination complex in solution B. No peak occurs at this distance in the ARDF in solution A.

The Inner-Coordination Sphere. The first peak in each ARDF which may be related to La–ligand bonding occurs at ca. 2.48 Å. The peak is due to inner-sphere La–O bonding. P2, which occurs at ca. 2.95 Å in the ARDF of solution B, but which is not present in the ARDF of solution A, may be attributed to inner-sphere La–Cl bonding; this same La–Cl bond distance has been observed in crystals.[8]

Consistent with the resolution of P1 from P2, shown in

Table II. Summary of the Experimental Results

	Solution A[a]	Solution B
	A. Summary of the ARDF's	
PS	[b]	1.48 Å
PSA	[b]	19 e^2
P1	2.48 Å	2.48 Å
P1A	85 e^2	62 e^2
P2	[b]	2.95 Å
P2A	[b]	76 e^2
P3	3.2 Å	3.3 Å
P4	3.7 Å	3.9 Å
P5	4.7 Å	4.6 Å
P6	5.5 Å	5.8 Å
P7	6.4 Å	7.7 Å
	B. NMR Results	
1. ^{139}La NMR ΔH	200 ± 10 Hz	3800 ± 100 Hz
δ	0 ppm[c]	293 ± 5 ppm[d]
2. ^{35}Cl NMR ΔH	70 ± 10 Hz	4640 ± 200 Hz
δ	0 ppm[c]	167 ± 10 ppm[d]

[a] The ARDF of solution A has been previously reported. [b] No peak occurs at this distance in the ARDF of solution A. [c] By definition, solution A is the reference. [d] Downfield from the reference.

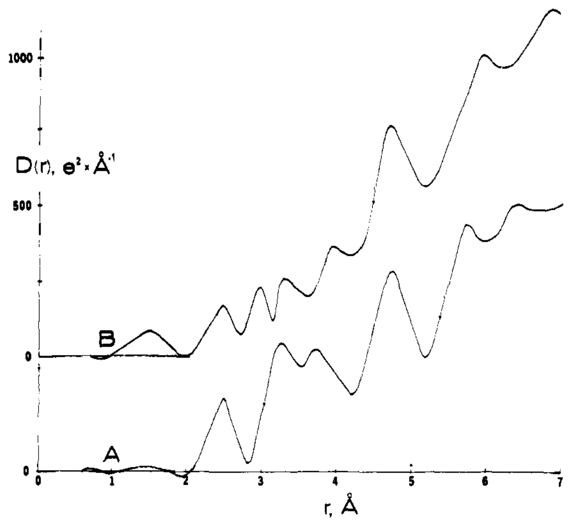

Figure 1. The ARDF's of the two LaCl$_3$ solutions with a damping factor of b = 0.010.

Figure 3, P2A $\simeq$ 76 e^2 and P1A $\simeq$ 62 e^2 for solution B; while P1A $\simeq$ 85 e^2 for solution A.

The average number of La–O and La–Cl interactions per La^{3+} for these two solutions may be evaluated by $n_1 \simeq$ P1A/$A_{\text{La-O}}$, and $n_2 \simeq$ P2A/$A_{\text{La-Cl}}$, where $A_{\text{La-O}}$ and $A_{\text{La-Cl}}$ are the ideal peak areas anticipated for one La–O atom-pair and for one La–Cl atom-pair, and n_1 and n_2 are the average number of La–O and La–Cl atom-pairs per La^{3+} in that solution.[34] Shown below are the values of n_1 and n_2 determined by this method.

Solution	P1A	n_1	P2A	n_2
A	85 e^2	8.0 (±0.2)	0	0.0
B	62 e^2	5.0 (±0.2)	76 e^2	3.0 (±0.1)

Consequently the average inner-sphere solute species are La(H$_2$O)$_8{}^{3+}$ in solution A and ca. LaCl$_3$(CH$_3$OH)$_5$ in solution B.

Hydrogen-Bonded Interactions. The peak at 3.2–3.3 Å in each ARDF is indicative of Cl–O (hydrogen-bonded) interactions, which have been reported in alcoholic[17-19] as well as aqueous solutions of metal chlorides.[30-36] The existence of P3 in each ARDF thus may not be utilized in attempts to determine the ligand arrangement(s) of the eight-coordinated average species in these solutions.

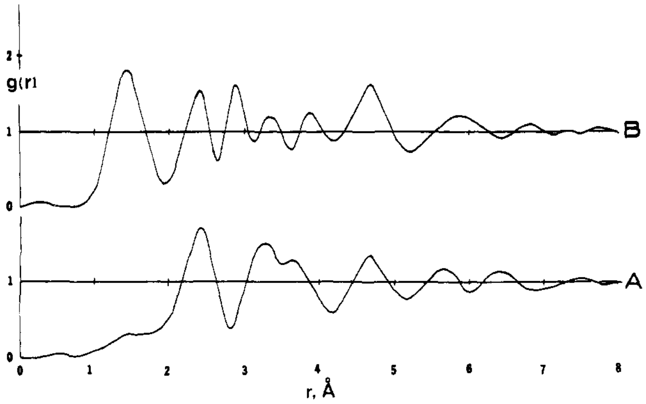

Figure 2. The atom-pair correlation functions of the two solution with b = 0.010.

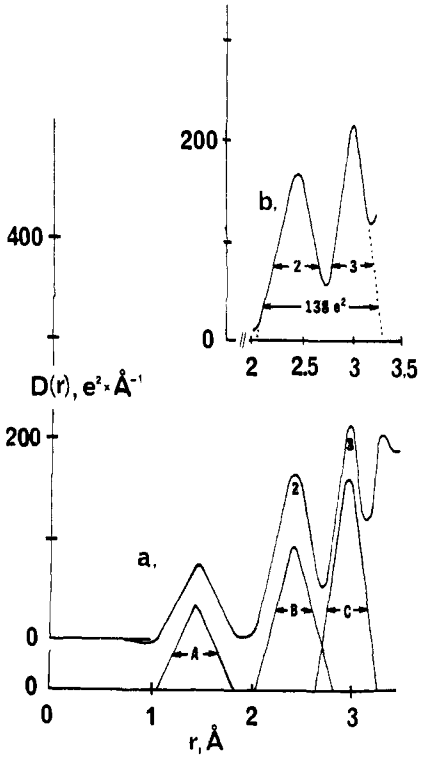

Figure 3. An enlarged view of the ARDF of solution B. The ideal peak for one C–O atom-pair per methanol molecule is indicated by a. The ideal peaks due to five La–O atom-pairs and three La–Cl atom-pairs per La^{3+} are indicated by b and c, respectively. P1 and P2 are indicated, as is the resolution of these two peaks. With this resolution P1A $\simeq$ 62 e^2 and P2A $\simeq$ 76 e^2.

Speculations Concerning Solute Structure(s). Both the ^{35}Cl NMR and the ARDF's indicate that the roles of the chloride ions are entirely different in the two solutions. In the aqueous solution, the chlorides are outer-sphere ligands with La(H$_2$O)$_8{}^{3+}$ being the principal solute species and with the ion-paired La···Cl distance being 4.7 Å. In solution B, each lanthanum has, on the average, three inner-sphere chloride neighbors. Consequently the large peak at 4.7 Å in the ARDF of solution B cannot be attributed to ion-paired La···Cl interactions.

No monomeric model of LaCl$_3$(CH$_3$OH)$_5$ accounts for the large peak at 4.7 Å, though a pseudo-cubic model of the average solute species does account for the remaining peaks observed in the ARDF of solution B. However, a pseudo-cubic dichloro-bridged model of the solute species, similar to the complex ion found in crystalline LaCl$_3$·7H$_2$O,[8] accounts for the peaks observed in the ARDF of this solution. The proposed

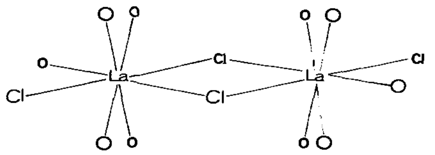

Figure 4. A proposed model of the solute species in solution B.

solution species, $[La_2Cl_4(CH_3OH)_{10}]$, is shown in Figure 4. The peak observed at 3.9 Å may be attributed to La···C, to O···O, and to C···O nonbonded interactions. The large peak at 4.7 Å may be attributed to nonbonded La···La and to Cl···Cl interactions. These interactions are found at 4.8 and at 4.6 Å in crystalline $LaCl_3\cdot7H_2O$.[8] Ion-paired La···Cl interactions are also possible contributors to this peak. The peak at 5.8 Å is likely composed of trans O···Cl and Cl···Cl nonbonded interactions (anticipated at 5.5 and 5.9 Å, respectively), and the peak at 6.7 Å may be attributed to long range La···O, La···Cl, and O···Cl interactions.

This model accounts for the ARDF obtained for solution B—the large peak at 4.7 Å, the inner-sphere of five oxygens and three chlorides, and the remaining, less significant peaks. It is also consistent with the viscosity and NMR data obtained for the solution. To our knowledge no other model is consistent with these experimental results.

NMR Results. Downfield chemical shifts are observed for both ^{139}La and ^{35}Cl in the methanol solution relative to the standard aqueous solution. These shifts are similar in magnitude and direction to results obtained in other ionic solutions.[37] The shifts can be explained either by the formation of partially covalent La–Cl bonds or a short range repulsive force mechanism.[37] An inner-sphere $LaCl_n$ complex, such as the model proposed in Figure 4, is consistent with either explanation.

Since $La(H_2O)_8{}^{3+}$ and outer-sphere chlorides are the only important species in solution A, line shape and intensity data indicate that both ^{139}La and ^{35}Cl are present as single NMR species in solution B. These could be single chemical species, as in solution A, or several chemical species related by rapid exchange reactions (i.e., with lifetime less than 10^{-4} s). The model proposed in Figure 4 contains a single type of La and three chemically different types of chlorides. Rapid exchange of chlorides may be anticipated in this solution since rapid inner-sphere ligand exchange has been reported for aquolanthanum(III) complexes in solutions.[38,39]

The line widths observed in solution B may be explained by a quadrupole relaxation mechanism.[7b] Viscosity data and x-ray data may be used to estimate a correlation time of ca. 3×10^{-10} s for $[La_2Cl_4(CH_3OH)_{10}]$. Assuming that at any instant two-thirds of the chlorides are inner-sphere ligands, the average quadrupole coupling constants are estimated to be ca. 9 MHz for ^{139}La and ca. 15 MHz for ^{35}Cl. In aqueous $La(NO_3)_3$ solutions, where $La-ONO_2$ bonding is known to occur,[40] the ^{139}La quadrupole coupling constant has been estimated to be ca. 9 MHz.[39] Consequently, the ^{139}La quadrupole coupling constant estimated for the $LaCl_3$-CH_3OH solution provides additional evidence of inner-sphere La–Cl interactions.

Conclusions

Whereas in aqueous solutions of $LaCl_3$, octaquolanthanum(III) is the predominant solute species, $LaCl_3(CH_3OH)_5$ describes the average inner coordination sphere when the solvent is methanol. In this latter species the inner-sphere La–O and La–Cl distances are ca. 2.48 and 2.95 Å, respectively. In the aqueous solution, the La–O distance is also 2.48 Å.

NMR data confirm the x-ray evidence for an inner sphere La–Cl complex in methanol solution and also indicate that the complex may undergo rapid exchange reactions.

These results indicate that water is clearly a better nucleophile towards La^{3+} than is chloride or methanol. The latter two potential ligands apparently have about the same nucleophilicity towards La^{3+} in concentrated solutions.

Our preliminary study of the $LaCl_3/CH_3OH$ solution suggests that a pseudo-cubic dichloro-bridged model, $[LaCl_2(CH_3OH)_5]_2$, represents a plausible description of the solute species. A cubic model of $La(H_2O)_8{}^{3+}$ represents a plausible description of the cationic species in the aqueous solution. Both models are consistent with the ARDF's and the NMR measurements obtained. Current experiments in our laboratory are designed to monitor the solute association process(es) and to establish the stereochemistry of the inner- and outer-coordination spheres in the average species present in the $LaCl_3/CH_3OH$ solution.

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