Contribution from the Department of Chemistry,
University of Southern Mississippi, Hattiesburg, Mississippi 39401

Evolving Solute Species in a Very Concentrated Lanthanum Trichloride/Methanol Solution[1]

DAVID L. WERTZ* and S. TERRY FINCH

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The inner-sphere coordination details of La^{3+} change considerably with time in a very concentrated $LaCl_3/CH_3OH$ solution. Initially, the average solute species is $La(CH_3OH)_8{}^{3+}$, whereas about 1 year after preparation of the solution, the average La^{3+} has ca. four chloride and ca. four methanol nearest neighbors, consistent with solute association. The atomic radial distribution function indicates the presence of μ-dichloro bridges between adjacent $LaCl_3$ units in the associated solute species after the solution has aged for 1 year. The presence of μ-dichloro bridge(s) in the highly associated solute species is supported by the large peak at 4.7 Å due to nonbonded La···La and Cl···Cl atom-pair distances across the bridge units. The inner-sphere La–O and La–Cl bond distances are 2.48 and 2.95 Å, respectively, with uncertainties of ca. 0.02 and 0.05 Å. The ion-pair La···Cl distance is ~5.0 Å in the samples of the solution where chlorides are found in the second coordination sphere surrounding the La^{3+}.

Introduction

Solution X-ray diffraction and wide-line NMR measurements of a very concentrated $LaCl_3/CH_3OH$ solution examined approximately 10 months after solution preparation each indicate that extensive La–Cl inner-sphere bonding occurs in the solution.[2] Solute association is consistent with the experimental information obtained from this solution but has not been established with certainty. These results differ from the results of our previous study of concentrated aqueous $LaCl_3$ and $LaBr_3$ solutions, where no inner-sphere La–X bonding is found and where octaaquolanthanum(III) is found to be the solute species.[3]

In an attempt to examine the bonding features in $LaCl_3/CH_3OH$ solutions, we have prepared a nearly saturated stock solution by dissolving anhydrous $LaCl_3$ into predried methanol and have examined samples taken from this stock solution at approximately 3-month time intervals by X-ray diffraction, starting shortly after solution preparation. The density and viscosity of each sample were also measured immediately prior to the X-ray diffraction (XRD) analyses.

The object of these experiments was to determine for each sample (a) the average inner-sphere coordination number of La^{3+}, (b) the identity of the inner-sphere ligands, (c) if either the coordination number or the inner-sphere ligands change as a function of time, and (d) if solute association occurs.

Experimental Section

Solution Preparation. The stock solution was prepared by dissolving anhydrous $LaCl_3$ (Research Organic/Inorganic Chemical Corp.) into predried methanol. The solution was prepared by weight so that the mole fraction of La^{3+} = 0.010. The mole fractions of the remaining species are $X_{Cl^-} = 0.030$, $X_H = 0.640$, and $X_C = X_O = 0.160$, as with our earlier solution.[2]

The stock solution was stored in a tightly sealed, amber glass bottle at ambient temperature. Approximately 40-mL samples were withdrawn from the stock solution at various time intervals over a 1 year period for the X-ray diffraction experiments. Sample deterioration occurred approximately 14 months after solution preparation, terminating the experiments. The time frame of the experiments is given in Table I.

Density and Viscosity. The density of each sample was measured in triplicate with a density bulb immediately prior to the XRD experiments, as was the time required for each sample to transverse a stlagmometer of 25.00-cm length. An estimate of the intrinsic viscosity (Table II) of each sample was calculated from this information by standard methods.[4]

X-ray Scattering Experiments. Each sample taken from the $LaCl_3/CH_3OH$ solution was loaded into a cylindrical sample holder into which was cut a window covered by 1.0-mil Mylar, and an X-ray diffraction pattern was obtained from $\theta = 3.00°$ to $\theta = 48.00°$ with Mo Kα radiation. Counts were accumulated at each of the 226 scattering angles until $\sigma < 0.3\%$ at each angle.[5] The average scattering intensity at each scattering angle was utilized in subsequent calculations. Our X-ray diffractometer, scattering data acquisition, and data treatment have been described previously.[6]

Table I

sample	time lapse,[b] months	sample	time lapse,[b] months
A	0.5	E[a]	10.0
B	3.8	D	12.3
C	6.9	sample deterioration	~14

[a] This sample, discussed in ref 2, was examined by XRD and NMR methods 10 months after its preparation. Its origin is not the stock solution described above but rather another solution, prepared ca. 2 years earlier. The stock solution from which samples A–D were obtained was prepared to the same composition as this previously examined solution. [b] Time between solution preparation and initiation of the experiments.

Table II. Viscosity Values

sample	viscosity, cP	SMD[b]
A	2.41	0.09
B	2.52	0.17
C	2.63	0.07
E[a]	2.78	0.22
D	5.10	0.30

[a] Reference 2. [b] The standard mean deviation based upon three measurements.

The atomic radial distribution functions (ARDF's) were calculated for each sample by the standard method[7] from the coherent interference intensity, $i(s)^*$,[8] and are presented as $D(r)$ and as $g(r)$ where

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

$$g(r) = [D(r)]/4\pi r^2\rho_0 = 1 + (2\pi^2 r\rho_0)^{-1}\int s[i(s)^*][M(s)](\sin sr)\,ds$$

In these equations ρ_0 is the bulk atom density of the sample, $M(s)$ is a function that converts the ARDF's to an atom-pair function, and $s = 4\pi\lambda^{-1}\sin\theta$. In either form, the ARDF provides a convenient measure of atom pairs in the sample for which the product $n_{AB}\sigma_{AB}X_AK_AK_B$ is sufficiently large to be easily discernible. In this expression, n_{AB} is the number of atom pairs per atom A, σ_{AB} is a statistical counting factor (either 1 or 2), X_A is the mole fraction of atom A, and K_AK_B is the scattering power product for the AB atom pair.

$D(r)$ is frequently useful in evaluating the average ligand environment of a metal ion such as La^{3+} if no other atom-pair interactions complicate the ARDF in the vicinity of the metal–ligand peak(s). For such a situation, the area under the peak in $D(r)$ describing this atom pair, A_{AB}, may be related to n_{AB} by $n_{AB} \simeq A_{AB}/IPA_{AB}$, where IPA_{AB} is the ideal peak area[7] anticipated for one AB atom pair.

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Table III. A General Summary of the ARDF's

	location of the peaks,[c] Å				
peak no.	A	B	C	D	E[a]
1	1.49	1.48	1.47	1.49	1.48
2	2.49	2.48	24.9	24.7	24.8
3	*b*	2.91	2.92	2.94	2.95
4	3.1	3.2	3.3	3.4	3.3
5	4.0	4.0	4.0	4.1	3.9
6	4.8	4.8	4.8	4.7	4.6
7	5.1	5.1	5.1	*b*	*b*
8	*b*	5.4	5.5	5.8	5.8
9	6.8	6.8	6.8	6.7	*b*

[a] Reference 2. [b] No peak is discernible in the ARDF of this solution. [c] In the ARDF's of the four samples.

Table IV. Area Analysis of the $D(r)$'s

sample	area,[b,c] e²	sample	area,[b,c] e²
	A. 1.5-Å Region		
A	18.6	E[a]	18.8
B	18.5	D	18.5
C	18.9		
	B. La–Ligand Region (P2 and P3)		
A	98	E[a]	138
B	109	D	151
C	126		

[a] Reference 2. [b] The uncertainty in these peak areas is ca. ±5% since both P1 and the P2–P3 doublet can be easily resolved from one another and from the remainder of $D(r)$ for each sample. [c] For the 1.5-Å region the area is the P1 area, and for the La–ligand region it is the area under the La–ligand peak(s).

Presented as $g(r)$, the ARDF cannot usually be quantitatively interpreted to indicate n_{AB}; though in this form changes in the atom-pair distribution(s) found in the sample may be readily accessed. Popular atom-pair distances, for which $n_{AB}\sigma_{AB}X_AK_AK_B$ is sufficiently large, are indicated by $g(r) > 1$.

Calculation of Ideal Atom-Pair Peaks. The ideal peak shape, $T(\mu)$, anticipated for an atom pair in the ARDF may be calculated by[9]

$$T_{AB}(\mu) = (2\pi^2)^{-1/2}\int [f_A(s)][f_B(s)][M(s)](\cos s\mu)\,d\mu$$

where $f_A(s)$ and $f_B(s)$ are the X-ray scattering factors for atoms A and B, $M(s)$ is the data treatment utilized in calculating the atomic radial distribution function (ARDF) of the sample, $s = 4\pi\lambda^{-1}\sin\theta$, and $\mu = |r - \text{A–B bond distance}|$. The area contribution to the ARDF due to an A–B atom pair may be evaluated by $IPA_{AB} = \int T_{AB}(\mu)\,d\mu$, where IPA_{AB} is termed the ideal peak area due to the A–B atom pair in the sample.

For the $LaCl_3/CH_3OH$ solutions, where C–O, La–O, and La–Cl atom pairs may be anticipated, the calculated ideal peak areas are $IPA_{C-O} = 18.6$ e², $IPA_{La-O} = 12.4$ e², and $IPA_{La-Cl} = 25.0$ e².

Results and Discussion

The ARDF's obtained for the four samples are shown in Figures 1 and 2 and summarized in Table III. The ARDF's contain significant differences, indicating that the average solute species vary with time.

First Peak (P1). This peak is unaffected by solution aging. It appears at 1.48 ± 0.01 Å (Table I) with an area of 18.7 ± 0.2 e² (Table IV) in each $D(r)$. Both the location and the area of P1 are consistent with one C–O atom pair per methanol molecule in liquid methanol[10] and in solutions where methanol is the solvent.[11-13] The area under this peak, at 1.48 Å in our preliminary study of $LaCl_3/CH_3OH$ solutions,[2] was found to be 18.8 e², in good agreement with the P1 areas found for the various samples of this solution.

The consistency of the ARDF's with regard to both the location and the area of P1 suggests an uncertainty of ±0.02 Å and ±5% regarding the locations and peak areas, respectively, for these ARDF's. Previous experiments[14-16] and calculations[8,16,17] are consistent with uncertainties in this range.

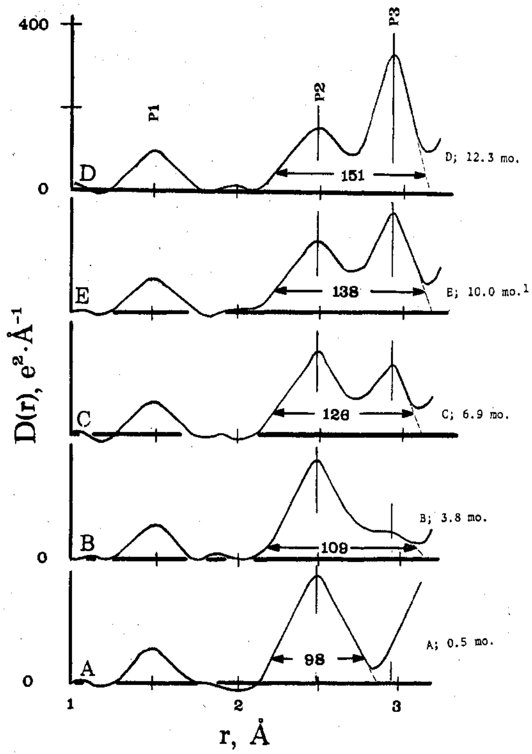

Figure 1. $D(r)$ functions for the samples of the very concentrated $LaCl_3/CH_3OH$ solution. For these $D(r)$'s, a dampening factor of $0.005s^2$ was utilized in calculations with $s_{min} = 0.60$ Å⁻¹ and $s_{max} = 13.00$ Å⁻¹. The area, in e², under the La–ligand peak(s) is indicated. The time laspes (in months) between preparation of the stock solution and the initiation of the XRD experiments with that sample are indicated.

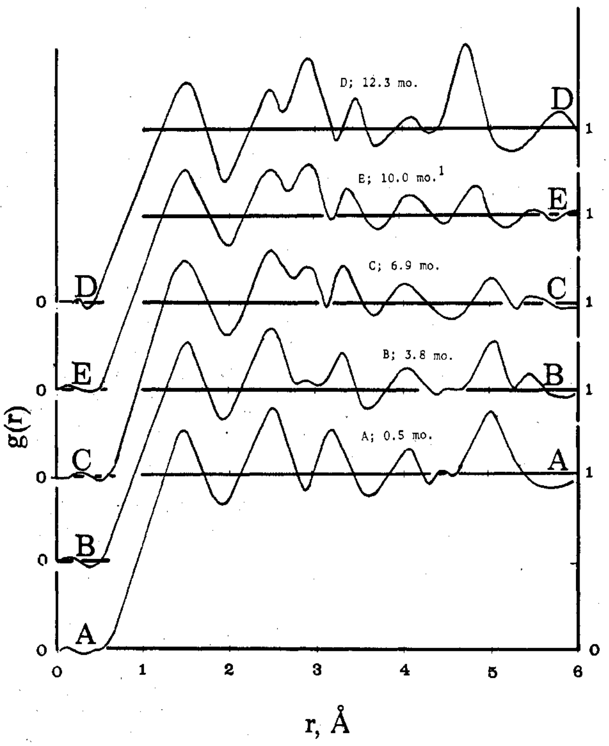

Figure 2. $g(r)$ functions for the samples of the $LaCl_3/CH_3OH$ solution. A dampening factor of $0.005s^2$ with $s_{min} = 0.60$ Å⁻¹ and $s_{max} = 13.00$ Å⁻¹ was utilized in the calculations. The time laspes (in months) between preparation of the stock solution and the initiation of the XRD experiments with that sample are indicated.

Second Peak (P2) and Third Peak (P3). In aqueous $LaCl_3$[3a] and $LaBr_3$[3b] solutions, the average La–O inner-sphere distance

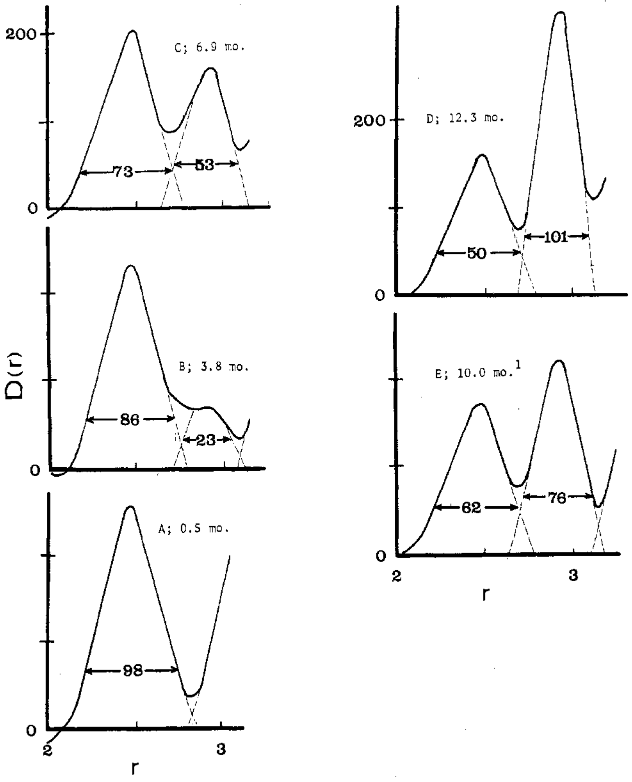

Figure 3. A plausible resolution of the La–O peak (P2) from the La–Cl peak (P3) in each $D(r)$. P2 and P3 areas are indicated in e^2. The time laspes (in months) between preparation of the stock solution and the initiation of the XRD experiments with that sample are indicated.

is 2.49 Å. For that reason P2, at 2.48 ± 0.01 Å in these ARDF's, is assigned to La–O inner-sphere atom pairs. P3, centered at 2.90–2.95 Å, is assigned to La–Cl inner-sphere atom pairs since the inner-sphere La–Cl bond distance is found to be 2.95 Å in crystalline $LaCl_3{\cdot}7H_2O$[18] and since no other atom pairs can account for this peak in a plausible manner. For samples A, E, and D, the two peaks may be readily resolved from one another as well as from the remainder of the $D(r)$'s. P2 and P3 cannot be readily resolved in the $D(r)$'s of samples B and C. Nonetheless, it is clear that P3 increases at the expense of P2; i.e., inner-sphere La–Cl bonding becomes more important while inner-sphere La–O bonding becomes less important, as the solution ages.

Sample A. No peak is discernible in these ARDF's at 2.9 Å. Consequently, inner-sphere La–Cl bonding is minimal in this sample. P2, which is large, symmetrical, and easily resolved from the remainder of $D(r)$, is attributed to La–O inner-sphere interactions. The average number of oxygen (methanol) neighbors per La^{3+} may be estimated from the A_{P2} (98 e^2) by

$$n_{La\text{-}O} \simeq A_{P2}/IPA_{La\text{-}O} \simeq 98.0\ e^2/12.4\ e^2 \simeq 7.9$$

with $n_{La\text{-}Cl} \simeq 0$. Thus in sample A, octakis(methanol)lanthanum(III), i.e., eight nearest oxygen (methanol) neighbors per La^{3+}, represents the average solute species with the La–O inner-sphere distance being ca. 2.48 Å.

Sample D. The ARDF's for sample D are consistent with extensive La–O and La–Cl inner-sphere bonding. A plausible resolution of P2 from P3 (Figure 3) indicates the P2 area to be ca. 50 e^2 and centered at 2.48 Å, while P3, centered at 2.92 Å, has an area of ca. 101 e^2. The areas of the resolved peaks may be utilized to estimate $n_{La\text{-}O}$ and $n_{La\text{-}Cl}$ in sample D by $n_{La\text{-}O} \simeq 50\ e^2/12.4\ e^2 \simeq 4.0$ and $n_{La\text{-}Cl} \simeq 101\ e^2/25.2\ e^2 \simeq 4.0$.

Because of the small uncertainty in resolving P2 from P3 in the $D(r)$ of sample D, it cannot be stated with certainty that the average La^{3+} has exactly four chloride and four oxygen nearest neighbors. It is clear, however, that the average La^{3+} has more than three chloride nearest neighbors in this sample, indicative of chloride sharing between adjacent La^{3+} units.

Table V. Estimate of the Average Number of La–O and La–Cl Inner-Sphere Atom Pairs in Each Sample

A. Resolved P2 and P3 Peaks

sample	r_{P_2}, Å	A_{P_2}, e^2	r_{P_3}, Å	A_{P_3}, e^2
A	2.48	98	*a*	*a*
B	2.47	86	2.92	23
C	2.47	73	2.93	53
E^a	2.48	62	2.95	76
D	2.49	50	2.93	101

B. Estimates of Average Number of La–O and La–Cl Atom Pairs per La^{3+}

sample	$n_{La\text{-}O}$	$n_{La\text{-}Cl}$	$n_{La\text{-}O} + n_{La\text{-}Cl}$
A	7.9	*a*	7.9
B	6.9	0.9	7.8
C	5.9	2.1	8.0
E^a	5.0	3.0	8.0
D	4.0	4.0	8.0

[a] Reference 2.

Table VI

sample	X_{IS}	X_{OS}	sample	X_{IS}	X_{OS}
A	0.0	1.0	E^1	1.0	0.0
B	0.3	0.7	D	1.0	0.0
C	0.7	0.3			

Sample E. Both XRD and NMR analysis of this sample indicated extensive La–Cl inner-sphere bonding.[2] The P2 and P3 areas have been estimated to be about 62 and 76 e^2, respectively, consistent with $n_{La\text{-}O} \simeq 5.0$ and $n_{La\text{-}Cl} \simeq 3.0$.

Samples B and C. Though both P2 and P3 are discernible in the ARDF's of these samples, the resolution of these peaks, requisite for estimation of $n_{La\text{-}O}$ and $n_{La\text{-}Cl}$, can be accomplished only with considerable uncertainty. It is clear, however, that P3 is larger and P2 is smaller in the ARDF's of sample C than in the ARDF's of sample B and that both are intermediate between the values found for samples A and D. Consistent with the peak resolutions shown in Figure 3, $n_{La\text{-}O}$ and $n_{La\text{-}Cl}$ are estimated to be 6.9 and 0.9 for sample B and 5.9 and 2.1 for sample C.

Inner-Sphere Coordination of La^{3+}. The average coordination number of La^{3+} may be calculated for each solution by CN = $(n_{La\text{-}O} + n_{La\text{-}Cl})$. For samples A and D, where P2 is well resolved from P3, $n_{La\text{-}O}$ and $n_{La\text{-}Cl}$ can be accurately evaluated from the P2 and P3 areas found in each ARDF. In each of these samples, the average coordination number of La^{3+} is found to be 8.0 (Table V). The uncertainty in the coordination number is ≤0.2 for each sample. While it is perhaps coincidental that $(n_{La\text{-}O} + n_{La\text{-}Cl}) \simeq 8$ for the remaining samples, where uncertainty in the resolution of P2 and P3 exists, there is no evidence that the average coordination number of La^{3+} $\neq$ 8.0.

Ligand Roles of Chloride. For each sample, the fraction of available chloride which, on the average, is found in the inner coordination sphere of La^{3+} may be calculated by $X_{IS} \simeq n_{La\text{-}Cl}/3.0$. The "outer sphere" chloride fraction may be calculated by $X_{OS} \simeq 1.0 - X_{IS} = (3.0 - n_{La\text{-}Cl})/3.0$. For these samples, X_{IS} and X_{OS} are given in Table VI.

In sample D, where La^{3+} has ca. four chloride nearest neighbors and where the coordination number of La^{3+} is ≃8.0, a chloro-bridged solute species must exist, since the stoichiometric ratio of chloride/lanthanum is 3:1 in the sample.

Speculations Regarding the Remaining Peaks in the ARDF's. The ARDF's obtained for these samples contain a myriad of peaks and are considerably more complicated than the ARDF's of the aqueous $LaCl_3$[3a] and $LaBr_3$[3b] solutions. This complexity is due at least in part to (a) the presence of the methyl groups on the oxo ligands and (b) the dual-ligand role of chlorides. While it is possible to account for all of the peaks in each ARDF via solute modeling, such models are, in this case, highly speculative. The XRD experiments provide insufficient information to allow for unambiguous assignment of all of the ARDF peaks.

The origin of P6, which is large in the ARDF of sample D but quite small in the remaining ARDF's, and P7, which decreases in magnitude as the solution ages, are, however, worthy of brief speculation.

P6, at 4.7 Å in the ARDF of sample D, may be related to the Cl···Cl and La···La distances across a μ-dichloro bridge in the associated solute species projected for this sample. In crystalline $LaCl_3 \cdot 7H_2O$,[18] where such a bridge occurs, the La···La and Cl···Cl distances are reported to be 4.6 and 4.8 Å, respectively. That this peak does not appear in the ARDF's of samples A, B, and C indicates the absence of extensive solute association in these samples.

The magnitude of P7, at 5.0–5.1 Å in the ARDF's of samples A, B, and C, parallels the fraction of non-inner-sphere chloride in each sample. This peak is quite large in the ARDF's of sample A, somewhat smaller in the ARDF's of sample B, and smaller yet in the ARDF's of sample C. The peak is absent in the ARDF's of samples D and E, where all of the chlorides appear to be found in the inner coordination sphere. This peak may be attributed to ion-pair La···Cl interactions, similar to those found in the aqueous $LaCl_3$ solutions at 4.7 Å. The slight increase in the La···Cl ion-pair distance is probably due to the inclusion of the "bulky" methyl group of the inner-sphere methanols in this solution.

Conclusions

In this methanolic $LaCl_3$ solution as well as in the previously investigated aqueous LaX_3 solutions, the solute species initially formed is $La(OHR)_8^{3+}$, where R = H or CH_3, following the highly exothermic dissolution of anhydrous $LaCl_3$ into the solvent. Extensive ion-pair La···Cl interactions occur following dissolution. In this methanolic solution, La–Cl inner-sphere bonding becomes increasingly important as the solution ages, but no similar effect has been found for the aqueous $LaCl_3$ solutions, even when the solvent is 10.0 N hydrochloric acid. Toward La^{3+}, the following ligand preferences have been determined: water >>> chloride > methanol. This trend is probably due to enthalpy differences in the inner-sphere La–ligand bonds, and similar trends in ligand preference for Fe^{3+} and Co^{2+} have also been found.[19]

Chloro bridging of adjacent La^{3+} species, favored by both entropy and enthalpy effects, must be preceded by the formation of chlorolanthanum(III) monomers in the solution, but the specific chlorolanthanum(III) species which are necessary for solute association cannot be identified from the ARDF's.

It is tempting to explain the average solute species found in each sample by the following reactions in the $LaCl_3/CH_3OH$ solution after formation of La^{3+}:[20]

$$La^{3+} + Cl^- \rightleftharpoons LaCl^{2+} \tag{1}$$

$$LaCl^{2+} + Cl^- \rightleftharpoons LaCl_2^+ \tag{2}$$

$$LaCl_2^+ + Cl^- \rightleftharpoons LaCl_3 \tag{3}$$

$$2LaCl_3 \rightleftharpoons Cl_2LaCl_2LaCl_2 \tag{4}$$

$$Cl_2LaCl_2LaCl_2 + nLaCl_3 \rightleftharpoons Cl_2La(Cl_2LaCl_2)_nLaCl_2 \tag{5}$$

While this reaction scheme is not inconsistent with our ARDF's, the existence of any of these specific solute species cannot be verified from the ARDF's and has not been established by other methods. Thus, this reaction scheme, while plausible, is speculative, and the specific solute species which contribute to the average specie in each sample of our stock solution remain unidentified.

While the average species in each sample examined is consistent with eight-coordinated La^{3+}, the presence of actual La^{3+} complexes in the samples with CN $\neq$ 8 cannot be excluded.

Sample deterioration, i.e., the formation of a gelatinous precipitate, is probably due to the $Cl_2La(Cl_2LaCl_2)_nLaCl_2$ achieving a sufficiently high mass to become sparingly soluble in methanol.

References and Notes

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