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^{139}La NMR and Quantitative FT-IR Investigation of the Interaction between Ln(III) Ions and Various Anions in Organic Solvents*

JEAN-CLAUDE G. BÜNZLI**, ANDRÉ E. MERBACH
and ROGER M. NIELSON

Institut de chimie minérale et analytique, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

Understanding the thermodynamic and kinetic properties of metal ion solutions requires knowledge of the composition and structure of the inner-coordination sphere of the metal ion. In the case of Ln(III) ions, this knowledge is difficult to acquire since these ions have high coordination numbers and high kinetic lability. Moreover, it appears from recent reports [1–3] that anion coordination often occurs in organic solvents, even with so-called 'non-coordinating' anions. This problem has been investigated by means of two experimental techniques, ^{139}La NMR and FT-IR.

The ^{139}La NMR Method

The chemical shift of the ^{139}La NMR resonance for solutions of lanthanum compounds is determined by the composition of the inner coordination sphere. A large range of chemical shifts has been observed [4]. Due to rapid exchange processes, the ^{139}La NMR spectrum of a mixture of two different anion coordinated La complexes, LaX^{2+} and LaY^{2+} shows only one resonance with the average chemical shift

$$\delta_{obs} = x\delta_{LaX^{2+}} + (1-x)\delta_{LaY^{2+}}$$

x being the mole fraction of the LaX^{2+} complex. The relative equilibrium constant for 1:1 complexes:

$$LaX^{2+} + Y^- \rightleftharpoons LaY^{2+} + X^-$$

$$K_{Y,X} = [LaY^{2+}][X^-]/[LaX^{2+}][Y^-]$$

can be calculated from the total concentrations $[LaX_3]_t$, $[LaY_3]_t$ and from δ_{obs}:

$$K_{Y,X} = \frac{(1-x)(3[LaX_3]_t - [La]_t x)}{x\{3[LaY_3]_t - [La]_t(1-x)\}}$$

with

$$x = (\delta_{obs} - \delta_{LaY^{2+}})/(\delta_{LaX^{2+}} - \delta_{LaY^{2+}})$$

$$[La]_t = [LaX_3]_t + [LaY_3]_t$$

Absolute stability constants may be estimated from the plots of δ_{obs} *versus* the total concentration in LaX_3:

$$La^{3+} + X^- \rightleftharpoons LaX^{2+} \text{ and } K_X = [LaX^{2+}]/[La^{3+}][X^-]$$

$$\delta_{obs} = (1-x)\delta_{La^{3+}} + x\delta_{LaX^{2+}} \qquad (1)$$

$$[LaX^{2+}] = \tfrac{1}{2}Q - \left(\frac{Q^2}{4} - [LaX_3]_t[X]_t\right)^{1/2} \qquad (2)$$

$$Q = [LaX_3]_t + [X]_t + 1/\gamma_\pm K_X \qquad (3)$$

$$\ln \gamma_\pm = -A|z_+z_-|[I^{1/2}/(1 + rBI^{1/2}) + CI] \qquad (4)$$

(I = ionic strength)

Experimental

Lanthanum salts were prepared from La_2O_3 (99.99%, Research Chemical) and the appropriate acid. They were dried on a vacuum line and the anhydrous solutions in methanol were made by adding a small excess of trimethylorthoformate. The water content was determined by Karl–Fisher titration and was found to be less than 40 ppm.

The ^{139}La NMR spectra were recorded with a Bruker CXP-200 spectrometer operating at 28.252 MHz (15 μs pulse width, 31.25 kHz sweep, 8 K data points, 20 000 to 70 000 pulses). The chemical shifts were referenced to external 0.1 M $La(ClO_4)_3$ in water.

The conditions used in the FT-IR experiments have been previously described [1].

Results

The chemical shifts measured for several LaX_3 methanol solutions are shown in Fig. 1. The large variation of these shifts for the various anions is indicative of the presence of a significant inner-sphere interaction between La(III) and the anions to form complexes of the type $LnX_n^{(3-n)+}$. For all the anions except nitrate the value of n is equal to 1 below 0.5 m. For nitrate it is most probably equal to 2. For the sake of simplicity, however, only $Ln(NO_3)^{2+}$ has been considered for the calculation of the $K_{Y,X}$ values. The constants for nitrate have therefore no intrinsic value; they are only included for the sake of showing the consistency of the data. From Table 1, one sees that the interaction between La(III) and X increases in the order $CF_3SO_3^- \sim ClO_4^- < Br^- < Cl^- < NO_3^-$.

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**Author to whom correspondence should be addressed.

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TABLE I. Relative Stability Constants, [a]Concentrations of Solutions and Chemical Shifts for the Equilibria $LaX^{2+} + Y^- \rightleftharpoons LaY^{2+} + X^-$ in MeOH at 23 °C

X	Y	$[LaX_3]$ (m)	$[LaY_3]$ (m)	δ_X[b] (ppm)	δ_Y[b] (ppm)	δ_{obs} (ppm)	$K_{Y,X}$	$\log K_{Y,X}$	$\log K_{Y,X}$[c]
ClO_4^-	Cl^-	0.247	0.244	−28	272	185	3.82	0.58	0.60
ClO_4^-	Br^-	0.213	0.213	−28	233	113	1.27	0.10	0.07
ClO_4^-	NO_3^-	0.242	0.263	−28	4.5	0.4	13.2	1.12	1.13
Cl^-	NO_3^-	0.236	0.243	272	4.5	85	3.32	0.52	0.53
Br^-	NO_3^-	0.221	0.278	233	4.5	31	11.7	1.07	1.06
$CF_3SO_3^-$	Br^-	0.296	0.238	−31	233	89	1.06	0.02	0.01
$CF_3SO_3^-$	Cl^-	0.260	0.268	−31	272	180	3.26	0.51	0.54

[a]Only LnX^{2+} complexes have been considered, see text. [b]δ_X and δ_Y are the chemical shifts for LaX_3 and LaY_3 (*ca.* 0.5 m) respectively. [c]$\log K_{Y,X}$ is the average of $\log K_{Y,X} = \log K_{Y,Z} + \log K_{Z,X}$, etc.

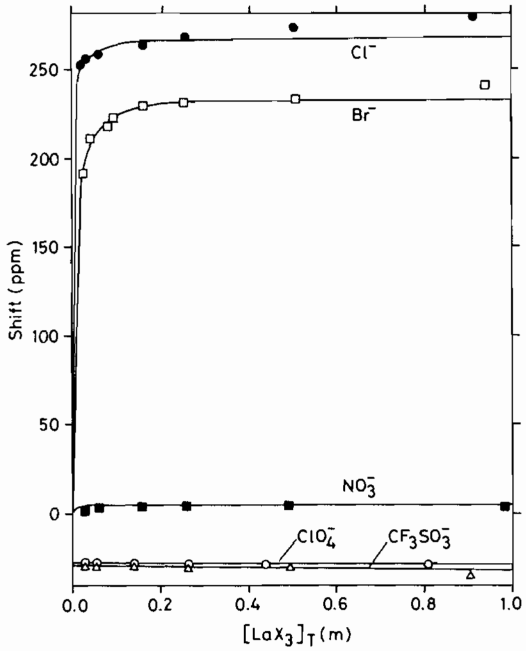

Fig. 1. ^{139}La NMR chemical shifts as a function of LaX_3 concentration in anhydrous methanol at 23 °C. The solid lines drawn through the data points are the results of fitting the data to eqn. (1) to (4).

Attempts have been made to estimate the absolute stability constants K_X by fitting the data to eqns. (1) to (4), using $A = 3.926\ kg^{1/2}\ mol^{1/2}$, $B = 4.542 \times 10^9\ kg^{1/2}\ mol^{1/2}$ [5] and r = La–X distance = 3.07, 3.10 and 2.96 Å for ClO_4^-, Br^-, and Cl^-, respectively. The results are reported in Table II.

Association constants for the formation of $LnClO_4^{2+}$ complexes in anhydrous acetonitrile, as determined by FT-IR spectroscopy [1, 6] are reported in Table III. Although a direct comparison is difficult to make, the two sets of data appear to be consistent.

TABLE II. Estimated Stability Constants for the Equilibria $La^{3+} + X^- \rightleftharpoons LaX^{2+}$ in Methanol at 23 °C

X	K_X	$\log K_X$
ClO_4^-	390 ± 60	2.6 ± 0.2
$CF_3SO_3^-$	450 ± 60	2.7 ± 0.1
Br^-	460 ± 70	2.7 ± 0.2
Cl^-	1500 ± 200	3.2 ± 0.1

TABLE III. Average Number of Associated Perchlorate Ions per Ln(III) Ion and Corresponding Association Constant ($Ln(ClO_4)_3$ Solutions 0.05 M in Anhydrous CH_3CN)

Ln	n (±0.08)	$\log K$ (±0.3)	Ln	n (±0.08)	$\log K$ (±0.3)
La	1.56	[a]	Tb	0.89	1.9
Pr	1.18	[a]	Dy	0.79	1.6
Nd	1.18	[a]	Er	0.93	2.1
Eu	0.87	1.8	Tm	0.87	1.8

[a]$\log K$ for $LnClO_4^{2+}$ is too large to be determined by this technique.

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