Kα radiation were measured by the θ–2θ scan technique.

(7) G. Germain and M. M. Woolson, *Acta Crystallogr., Sect. B*, **24**, 91 (1968).

(8) The ^{13}C NMR spectrum of **3** in C_6D_6 showed resonances at 73.62 and 79.66 ppm, due to the carbon atoms of $=C(SiMe_3)_2$ and $=C(SiPh_2)(C)$, respectively.

(9) Compound **4:** ^1H NMR δ (ppm) 0.02 (Me_3Si, s, 36 H), 7.0–7.9 (Ph, m, 20 H); ^{13}C NMR δ (ppm) 1.95 (q, CH_3Si), 4.80 (q, CH_3Si), 20.13 (s, $C(SiMe_3)_2$), 73.11 (s, $=C(SiMe_3)_2$), 73.70 (s, $=C(SiPh_2)[C(SiMe_3)_2]$), 127.39 (d, Ph), 127.65 (d, Ph), 129.60 (d, Ph), 130.25 (d, Ph), 135.83 (d, Ph), 136.35 (s, Ph), 137.55 (s, Ph), 205.44 (s, $=C=$); ^{29}Si NMR δ (ppm) 4.13 ($SiMe_3$), 2.83 ($SiMe_3$), −0.31 ($SiPh_2$), −4.08 ($SiPh_2$); IR (cm^{-1}) 1870, 1830, 1430, 1255, 1110, 945; mass M^+ 720.

(10) Compound **5:** ^1H NMR δ (ppm) 0.03 (Me_3Si, s, 18 H), 0.06 (Me_3Si, s, 18 H), 7.1–8.0 (Ph, m, 20 H); ^{13}C NMR δ (ppm) 3.98 (q, CH_3Si), 6.06 (q, CH_3Si), 127.56 (d, Ph), 127.66 (d, Ph), 130.22 (d, Ph), 134.11 (s, Ph), 136.26 (d, Ph), 136.31 (d, Ph), 137.06 (s, Ph), 169.92 (s, $=C(SiMe_3)_2$), 183.69 (s, $=C(SiPh_2)(C)$); ^{29}Si NMR δ (ppm) −5.92 ($SiMe_3$), −6.85 ($SiMe_3$), −20.72 ($SiPh_2$); IR (cm^{-1}) 1430, 1270, 1255, 1110, 950; mass M^+ 720.

(11) M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Organomet. Chem.*, **149**, 37 (1978).

(12) M. Ishikawa, K. Nakagawa, M. Ishiguro, F. Ohi, and M. Kumada, *J. Organomet. Chem.*, **152**, 155 (1978).

(13) H. Kwart and J. Slutsky, *J. Am. Chem. Soc.*, **94**, 2515 (1972).

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Lanthanum-139 Nuclear Magnetic Resonance Chemical Shifts

Sir:

Lanthanum-139 with spin, $I = 7/2$ is an abundant nucleus (99.9% natural abundance) with a relatively high NMR sensitivity (300 times that of ^{13}C). However, since it has a quadrupole moment, when ^{139}La is not located in a symmetric electronic environment, rapid quadrupolar relaxation causes extensive line broadening. Several reports have appeared in the literature which utilize relaxation data of ^{139}La to study chemical exchange and coordination of lanthanum(III) in aqueous solution;[1-3] however, no mention was made of ^{139}La chemical shifts.

This communication is the first report of measurements demonstrating that ^{139}La chemical shifts provide a sensitive probe to lanthanide ion complexation. In this initial study the inner (i.e., direct contact) and outer (i.e., solvent separated) sphere complexation of La(III) with acetate and the chloroacetates is examined. Preliminary results on the La/Cl and La/SCN systems are also reported. Introduction of a ligand in the outer sphere should have little effect on the ^{139}La resonance, while inner sphere complexation could be expected to cause a significant change in chemical shift and in line width (due to the resultant asymmetric charge distribution around the metal). The thermodynamic parameters of complexation have been interpreted[4] as reflecting 100% inner sphere formation for $LaAc^{+2}{}_{(aq)}$, 100% outer sphere complex for $La(Cl_3Ac)^{+2}$, and mixtures for $La(ClAc)^{+2}{}_{(aq)}$ and $La(Cl_2Ac)^{+2}{}_{(aq)}$. Consequently, for equal amounts of 1:1 complex formed, acetate is expected to induce the largest change in chemical shift (and line width) and trichloroacetate is expected to induce little or no change.

In a totally outer sphere complex such as $La(ClO_4)_3$, ^{139}La line widths are ~120–150 Hz. Relaxation times ($T_1 = T_2$) are thus always short enough so that several thousand scans (necessary for the dilute solutions studied) can be obtained in 1–10 min, the data acquisition rate being the limiting factor.

Table I. Molar Concentrations, Chemical Shifts, and Line Widths of ^{139}La in Acetate Solutions[a]

$[X]_T$	$[X^-]$	$[LaX^{+2}]$	$[LaX_2{}^+]$	$[La^{+3}]$	^{139}La shift[b]	$\Delta\nu_{1/2}$[c]
0.008	0.0023	0.0046	0.00009	0.055	6.2	204
0.016	0.0047	0.0087	0.0003	0.051	12.0	326
0.024	0.0073	0.012	0.0007	0.047	20	562
0.04	0.013	0.018	0.0019	0.040	30	600
0.06	0.020	0.024	0.0040	0.032	41	670
0.08	0.028	0.027	0.0064	0.026	46	800
0.12	0.047	0.030	0.012	0.018	51	980
0.15	0.063	0.031	0.016	0.013	55	910
0.20	0.091	0.029	0.022	0.009	60	1000
0.30	0.152	0.025	0.031	0.004	74	1100
0.40	0.218	0.020	0.037	0.003	83	1200
0.80	0.495	0.012	0.048	0.0006	108	1300

[a] pH 5.0, $pK_a = 4.6$, $\beta_1 = 36.3$, $\beta_2 = 8.3$, $I = 2.0$ M ($NaClO_4$); other data sets were obtained for the chloroacetates. [b] Chemical shifts downfield from external 0.5 M ($La(ClO_4)_3$). [c] In hertz.

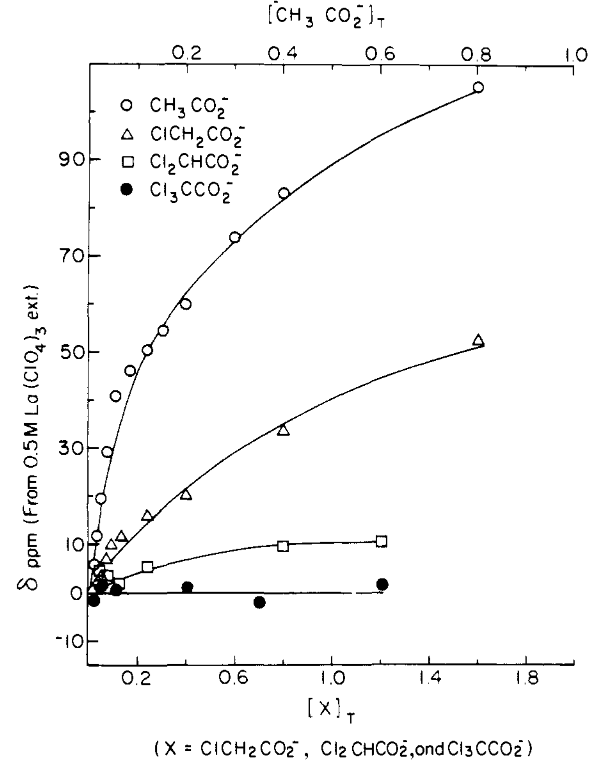

Figure 1. Variation of chemical shift with total added ligand ($Cl_nCH_{3-n}CO_2^-$, $n = 0$–3.

Observed shifts and line widths for the acetate solutions, relative to an external standard of 0.5 M $La(ClO_4)_3$ solution, are presented in Table I.[5,6] The variation in shift for the different ligand systems is shown in Figure 1, with the largest slope for acetate and essentially zero slope for trichloroacetate. Monochloroacetate and dichloroacetate are intermediate in their ability to shift and to broaden ^{139}La resonances. Using reported stability constants,[4] it is possible to calculate a limiting shift for the LaX^{+2} species. These shifts are, respectively, 100, 50, 22, and 0 ppm for acetate, chloroacetate, dichloroacetate, and trichloroacetate, relative to $La^{+3}{}_{(aq)}$. Using the crude approximation that the differences in observed limiting shifts are due solely to the amounts of inner sphere complex formed (i.e., the shifts for all 1:1 inner sphere complexes are the same), an estimate of inner/outer sphere complexation can be obtained. Assuming acetate interacts solely by inner sphere complexation, it is predicted that the portion of inner sphere complexation is ~50% for chloroacetate, 22% for dichloroacetate, and

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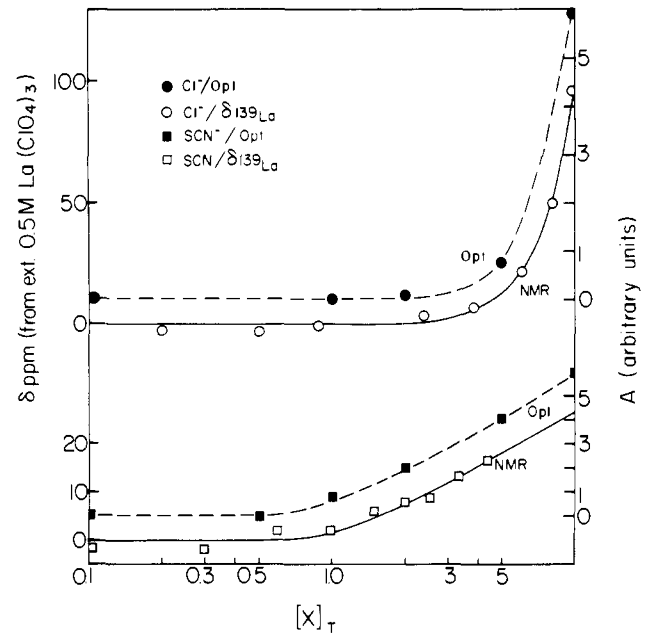

Figure 2. Correlation of the ^{139}La chemical shifts and optical spectra (oscillator strength) of Nd(III) in chloride and thiocyanate solutions. ^{139}La line widths show similar correlations, although not with the same degree of accuracy in the case of the thiocyanate system.

~0% for trichloroacetate. The values for La(ClAc)$^{+2}_{(aq)}$ are somewhat lower than the estimates from entropy data[4] and further work is necessary to evaluate the validity of our assumptions.

While the limiting chemical shifts in the series from LaX^{+2} to LaX$_4^-$ may increase regularly, the line widths may behave differently. Formation of inner sphere LaX^{+2} introduces a large perturbation in the charge symmetry of the lanthanide complex, but formation of higher complexes may lead to species of higher symmetry causing a relative decrease in the line widths. Such is the case in the acetate system where a plot of δ vs. $\Delta\nu_{1/2}$ is linear below the concentration of acetate where La(Ac)$_2^+$ becomes significant. At higher acetate concentration, the line width no longer increases as rapidly as does the chemical shift.

Spectroscopic studies have indicated that both chloride and thiocyanate ions initially form outer sphere complexes with Nd(III).[7] At higher concentrations (1-2 M for SCN$^-$ and 5-6 M for Cl$^-$), inner sphere complexation becomes significant, probably associated with formation of NdX$_3$ or NdX$_4^-$. This change in behavior is easily monitored in ^{139}La NMR studies of the La^{+3}/Cl$^-$ and La^{+3}/SCN$^-$ systems. Both the chemical shift and line width behavior of these systems exhibit no change until concentrations where inner sphere complexation is indicated by the optical spectra (Figure 2). In 10 M HCl the ^{139}La resonance is deshielded by ~100 ppm with a line width of 1300 Hz; in 5 M ammonium thiocyanate the resonance is deshielded by 36 ppm, and the observed line width is 1000 Hz.

In conclusion, chemical shifts of ^{139}La can serve as a valuable probe of the solution behavior of lanthanide ions. While line widths are useful when an equilibrium between two species is being observed, they are difficult to interpret with more complex equilibria, since line widths not only measure the relative amounts of species but also their electronic symmetries. Of course, it is possible in some cases that the spectrum observed may not be the time-averaged resonance of two or more species. Some complexed lanthanum(III) species will be long lived, with resonances obscured by relatively weak intensity and through extensive quadrupolar broadening. Such appears to be the case with certain chelating agents such as EDTA, where two ^{139}La signals are observed with chemical shifts of ~0 and 570 ppm, for uncomplexed and complexed La(III) respectively.

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References and Notes

(1) K. Nakamura and K. Kawamura, *Bull. Chem. Soc. Jpn.*, **44**, 330 (1971).
(2) J. Reuben, *J. Phys. Chem.*, **79**, 2154 (1975).
(3) J. Reuben and Z. Luz, *J. Phys. Chem.*, **80**, 1357 (1976).
(4) D. D. Ensor and G. R. Chopin, unpublished work.
(5) Lanthanum-139 Fourier transform NMR spectra were obtained at 3.52 Tesla on the SEMINOLE spectrometer, operating at 21.18 MHz using quadrature detection. Spectra were recorded using 2K data points with a window of ±7.5 kHz (15 Hz/data point resolution in the transformed spectra obtained without exponential weighting of the free induction decay). Samples were contained in 25-mm tubes with a 0.5 M La(ClO$_4$)$_3$ reference sample in a concentric 5-mm tube.
(6) The SEMINOLE is an in-house design, all-nucleus, high sensitivity FT NMR spectrometer (G. C. Levy et al., Abstracts, 19th Experimental NMR Conference, Blacksburgh, Va., 1978). For ^{139}La, 25-mm sample sensitivity is 120:1 (0.5 M La(ClO$_4$)$_3$, single pulse).
(7) G. R. Choppin, D. E. Henrie, and K. Buijs, *Inorg. Chem.* **5**, 1743 (1966).
(8) Camille and Henry Dreyfus Teacher-Scholar.

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High Resolution ^{13}C NMR Studies of Chemical Exchange Processes in the Solid State Using Magic Angle Spinning

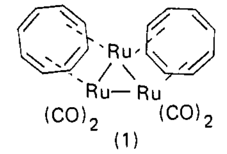
Sir:

Wide-line ^{1}H NMR has been widely used to investigate motional processes in solids, molecular motions partially averaging the proton-proton dipolar interactions and giving rise to line narrowing.[1] However, one cannot deduce *from these NMR measurements alone* whether chemical exchange processes are occurring along with or as part of overall molecular motions.

Techniques have recently been introduced for the measurement of "high-resolution" ^{13}C NMR spectra of solids.[2] In most cases, the measurements involve a combination of high-power decoupling of protons to remove dipolar broadening, cross-polarization schemes for signal enhancement,[3] and spinning of the sample rapidly (several kilohertz) about an axis aligned at an angle of 54° 44′ (the "magic angle") with respect to the dc field[2b] to remove broadening from the chemical shift anisotropy of the carbons. Spectra of moderate resolution are obtained by these techniques; line widths are in the range of 15-100 Hz and separate resolved signals are observed for most magnetically nonequivalent carbons in a molecule.[4-9]

An important feature of the spectra is that the signals observed occur at the isotropic shift values (as in solution) and are characteristic of the environment of the nucleus. As in solution, the observed averaging of signals from magnetically nonequivalent carbon atoms in a molecule should reflect the occurrence of a chemical exchange process. Therefore, high-resolution ^{13}C NMR should provide a direct probe to obtain incisive evidence for the occurrence of chemical exchange processes in the solid state.

To test the above ideas, we have investigated the solid-state behavior of a molecule known to exhibit a fast intramolecular chemical exchange process in solution. The molecule chosen was tetracarbonylbis(cyclooctatetraene)triruthenium(0) (**1**)



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