Lanthanum-139 Nuclear Magnetic Resonance Spectra of Lanthanum Complexes

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Lanthanum-139 n.m.r. spectra are reported for a variety of lanthanum complexes and systems. The ^{139}La linewidths vary greatly and, as expected, an important factor appears to be the symmetry of the environment around the lanthanum. Information concerning complex formation by the La^{3+} ion is obtained from the variations in both the ^{139}La chemical shifts and the linewidths when a ligand is progressively added to anhydrous La[ClO$_4$]$_3$ in MeCN. Slow ligand exchange is found with the [La{P(NMe$_2$)$_3$O}$_6$]$^{3+}$ ion, and with the ethylenediamine and diethylenetriamine complexes.

Lanthanum-139 has an abundance of 99.91%, a magnetic moment of 2.7615 nuclear magnetons, and a spin, $I = \frac{7}{2}$. It has a high receptivity of 336 relative to ^{13}C, but possesses a moderate electric quadrupole moment (Q) of 0.21×10^{-24} cm^2, which can lead to broad resonances as a result of quadrupole relaxation. Systems for which ^{139}La n.m.r. spectra have been reported include aqueous solutions of lanthanum salts with both co-ordinating and non-co-ordinating anions,[1–3] solutions of LaCl$_3$ in methanol [4] and aqueous methanol,[5] and a number of lanthanum hydroxycarboxylate species in aqueous solution.[6]

The present work reports ^{139}La n.m.r. spectra for a variety of lanthanum complexes, with the aim of characterising the species formed in solution, and also of providing a scale of ^{139}La chemical shifts.

For a quadrupolar nucleus, an approximate expression [7] for the linewidth (at half-height), $W_{\frac{1}{2}}$, is that given below

$$W_{\frac{1}{2}} = \frac{3\pi(2I+3)}{10I^2(2I-1)}\,\frac{e^4 q_{zz}{}^2 Q^2}{h^2}\left(1+\tfrac{1}{3}a^2\right)\frac{\eta V f}{kT}$$

where q_{zz} is the largest component of the electric field gradient q at the nucleus, a is the asymmetry parameter for q ($0 < a < 1$), η is the viscosity of the solvent, V is the volume of the molecule or ion, and f is a microviscosity factor which is about 0.16 for pure liquids. Lanthanum-139 linewidths should thus depend, in part, both on the electric field gradients (and hence the symmetry) at the ^{139}La nucleus, and size of the lanthanum complex. Thus, low symmetries and/or large sizes will tend to lead to broad resonances. These features are well illustrated in the present work.

For experimental reasons it was unfortunately not possible to study reliably ^{139}La resonances for which $W_{\frac{1}{2}}$ exceeded about 10 kHz. Nevertheless, the observed values of $W_{\frac{1}{2}}$ can provide useful information.

Acetonitrile was normally used as the solvent since, in addition to possessing a low viscosity, it is also a moderately good ionising solvent, and co-ordinates comparatively weakly to the La^{3+} ion.

Experimental

Preparation of Anhydrous La[ClO$_4$]$_3$ *in* MeCN.—A solution of hydrated La[ClO$_4$]$_3$ in MeCN was refluxed for *ca.* 25 h through a Soxhlet extractor packed with 3A molecular sieves.[8] The water content was estimated from the proton resonance spectra before and after the addition of a known amount of water, and was always less than 0.004 mol dm^{-3}. An additional check on the water content was provided by the width of the ^{139}La resonance (see below). The lanthanum content was determined by titration with ethylenediaminetetra-acetate (edta) at pH 5.8—6.0, using xylenol orange as an indicator.[9]

Acetonitrile was distilled from P$_2$O$_5$ and solutions were prepared and handled under strictly anhydrous conditions. Liquid substrates were (where necessary) freshly distilled, and dried over 3A molecular sieves.

The compounds [NBu$^n_4$]$_3$[LaCl$_6$],[10] [La{P(NMe$_2$)$_3$O}$_6$][CF$_3$SO$_3$]$_3$,[11] [La(pyo)$_8$][ClO$_4$]$_3$ (pyo = pyridine *N*-oxide),[12] [NH$_2$Et$_2$][La{CH(OCCF$_3$)$_2$}$_4$],[13] [NEt$_4$][La(Et$_2$NCS$_2$)$_4$],[14] lutidine *N*-oxide (luto),[15] [NBu$^n_4$][NO$_3$],[16] and LaBr$_3$[17] were prepared by literature procedures, and satisfactory analyses were obtained. [La{P(NMe$_2$)$_3$O}$_4$][CF$_3$SO$_3$]$_3$ was prepared by dissolution of the hexakis complex [11] in acetonitrile and precipitation with dry diethyl ether (Found: C, 24.9; H, 5.75; N, 12.9. C$_{25}$H$_{72}$F$_9$LaN$_{12}$O$_{13}$P$_4$ requires C, 24.9; H, 5.5; N, 12.75%).

[NBu$^n_4$]$_4$[La(NCS)$_7$].—The method in the literature [18] for the preparation of hexakis adducts of the 'rare earths' other than lanthanum consistently yielded the heptakis complex for molar ratios of La[NCS]$_3$: [NBu$^n_4$][NCS] of both 1 : 3 and 1 : 4 (Found, ratio 1 : 3: C, 56.4; H, 9.5; N, 10.2. Found, ratio 1 : 4: C, 56.25; H, 9.65; N, 10.15. C$_{25}$H$_{36}$LaN$_7$S$_7$ requires C, 56.3; H, 9.6; N, 10.15%).

[NBu$^n_4$]$_3$[La(NO$_2$)$_6$].—This was prepared by stirring together an ethanolic solution of [NBu$^n_4$]Cl (1.22 g, 4.4 mmol), LaCl$_3\cdot$7H$_2$O (0.54 g, 1.45 mmol), and NaNO$_2$ (0.68 g, 10 mmol) in the presence of excess triethyl orthoformate (2 cm^3) for 24 h. After filtration (under argon) of the NaCl, the ethanol was removed *in vacuo*. The residue was twice extracted with MeCN, the complex precipitated with dry ethyl acetate, and dried *in vacuo* over P$_2$O$_5$ (Found: C, 50.45; H, 9.55; N, 11.05. C$_{12}$H$_{27}$LaO$_{12}$ requires C, 50.15; H, 9.60; N, 10.6%).

Lanthanum-139 n.m.r. spectra were recorded at 35.3329 MHz on a Bruker WM-250 FT spectrometer, using a pulse rate of 41 ms, 4 K data points, and a sweep width of 50 kHz. For lock purposes a sealed 5 mm n.m.r. tube containing D$_2$O was supported by poly(tetrafluoroethylene) spacers in the 10 mm n.m.r. tubes. Bulk susceptibility corrections are expected to be less than the experimental errors in measuring the ^{139}La chemical shifts. These errors fell in the range 1—10 p.p.m. depending on the linewidth.

Results and Discussion

The observed ^{139}La chemical shifts and linewidths for reasonably well characterised species are collected in the Table.

Octahedral Lanthanum Complexes.—[LaX$_6$]$^{3-}$ (X = Cl *or* Br). The electronic,[19] far-i.r., and Raman spectra [20] of solid

Table. Lanthanum-139 chemical shifts (δ) [a] and linewidths ($W_{\frac{1}{2}}$) for various lanthanum complexes in MeCN solution, at 294 ± 2 K

Complex	Concentration/ mol dm^{-3}	δ/p.p.m.	$W_{\frac{1}{2}}$/Hz
$[La(H_2O)_n]^{3+}$ [b,c]	0.16	(0)	140
$[La(MeCN)_n]^{3+}$ [b]	0.20	−129	380
$[La(luto)_8]^{3+}$ [b]	0.20	−122	2 700
$[La(NO_3)_6]^{3-}$ [d]	0.06	−60	260
$[La(dmf)_8]^{3+}$ [d]	0.21	−39	1 700
$[La(pyo)_8]^{3+}$ [b,e]	0.19	4	2 800
$[La\{CH(OCCF_3)_2\}_4]^-$ [f]	0.15	33	7 000
$[La\{P(NMe_2)_3O\}_6]^{3+}$ [g]	0.20	66	930
$[La(dmso)_8]^{3+}$ [b]	0.21	82	1 800
$[La\{OS(CH_2)_3CH_2\}_8]^{3+}$ [b]	0.21	93	2 600
$[La\{N(CH_2CO_2)_3\}_2]^{3-}$ [c]	0.15	202	7 800
$[La(NO_2)_6]^{3-}$ [d,h]	0.07	342	600
$[La(Et_2NCS_2)_4]^-$ [f,i]	*ca.* 0.19	710	2 100
$[LaCl_6]^{3-}$ [d,j]	0.05	851	200
$[LaCl_6]^{3-}$ [d,j]	0.11	851	270
$[LaBr_6]^{3-}$ [d,k]	0.11	1 090	500
$[La(en)]^{3+}$ [b]	0.20	40	*ca.* 3 800
$[La(en)_4]^{3+}$ [b]	0.20	400	3 800
$[La(dien)]^{3+}$ [b]	0.18	122	7 700
$[La(dien)_3]^{3+}$ [b]	0.18	450	2 400

[a] Positive values to high frequency of $[La(H_2O)_n]^{3+}$ reference. [b] As ClO_4^- salt. [c] In D_2O–H_2O (80 : 20 v/v). [d] As $NBu^n{}_4{}^+$ salt. [e] In the presence of excess ligand. [f] As $NH_2Et_2{}^+$ salt. [g] As $CF_3SO_3{}^-$ salt. [h] In the presence of excess $[NBu^n{}_4][NO_2]$. [i] At 328 K. [j] In the presence of $[NBu^n{}_4]Cl$ (0.45 mol dm^{-3}). [k] Prepared *in situ*: $LaBr_3$ + 5 $[NBu^n{}_4]Br$.

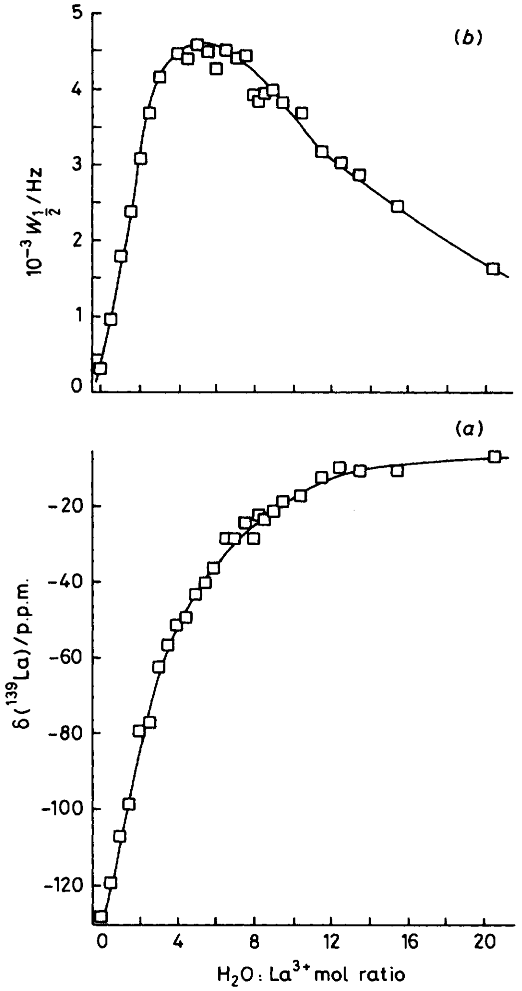

Figure 1. Lanthanum-139 chemical shift (*a*), and width at half-height $W_{\frac{1}{2}}$ (*b*) for the progressive addition of H_2O to $La[ClO_4]_3$ (0.21 mol dm^{-3}) in MeCN at 294 K

species of the type $[PHPh_3]_3[LnX_6]$ and $[NHPh_3]_3[LnX_6]$ (Ln = Pr, Nd, Sm, Dy, Ho, Er, or Tm; X = Cl or Br) indicate that the $[LnX_6]^{3-}$ ions possess rigorous octahedral symmetry. Ryan and Jorgensen [19] have studied the electronic (4*f*–4*f*) spectra of these complexes in succinonitrile–acetonitrile solution. They concluded that, in the presence of excess halide, octahedral $[LnX_6]^{3-}$ ions are present here also. The comparatively narrow ^{139}La resonances observed for solutions of $[NBu^n{}_4]_3[LaX_6]$ in acetonitrile in the presence of excess $[NBu^n{}_4]X$ are in complete agreement with this.

$[La(NO_2)_6]^{3-}$. The nitrite ion forms a series of complexes of the type $A_2B[Ln(NO_2)_6]$ or $A_3[Ln(NO_2)_6]$, where Ln = La—Er and A and B are alkali metals.[21] For $Cs_2Na[La(NO_2)_6]$ the *X*-ray powder pattern [22] and absorption spectrum [23] have been interpreted in terms of an anion of T_d symmetry, with the lanthanum co-ordinated octahedrally by the nitrogen atoms. The narrow ^{139}La resonance for a solution of $[NBu^n{}_4]_3[La(NO_2)_6]$ in MeCN in the presence of excess $[NBu^n{}_4][NO_2]$ indicates that a similar anion is present in solution.

$[La\{P(NMe_2)_3O\}_6]^{3+}$. The maximum number of $P(NMe_2)_3O$ molecules found in lanthanide complexes is six,[24] presumably because of the large size of the ligand. An *X*-ray diffraction study [25] of $[Nd\{P(NMe_2)_3O\}_6][ClO_4]_3$ has shown that the cation is octahedrally co-ordinated.

Complex formation was studied by addition of $P(NMe_2)_3O$ to a solution of $La[ClO_4]_3$ (0.08 mol dm^{-3}) in acetonitrile. The solvation number of the La^{3+} ion in acetonitrile is not known, although the narrow ^{139}La linewidth suggests a fairly symmetric species. Addition of $P(NMe_2)_3O$ up to a molar ratio $P(NMe_2)_3O : La^{3+}$ of 1.5 : 1 causes a small deshielding of the ^{139}La nucleus, and a very rapid increase in $W_{\frac{1}{2}}$ to *ca.* 4 kHz, indicating rapid chemical exchange involving very unsymmetrical species of the type $[La\{P(NMe_2)_3O\}_x(MeCN)_y]^{3+}$. For molar ratios in the region 2—4 : 1 no resonances could be detected, presumably due to excessive linewidths. At a molar ratio of $P(NMe_2)_3O : La^{3+}$ of 5 : 1, however, a comparatively narrow resonance appeared ($W_{\frac{1}{2}}$ *ca.* 1 000 Hz, δ 66 p.p.m.), which merely increased in intensity at molar ratios of 6 : 1 and 7 : 1. With more $P(NMe_2)_3O$, the complex $[La\{P(NMe_2)_3O\}_6][ClO_4]_3$ crystallised out of solution. Similar results were obtained when $P(NMe_2)_3O$ was added to a solution of $[La\{P(NMe_2)_3O\}_4][CF_3SO_3]_3$ (0.21 mol dm^{-3}) in acetonitrile. In this system, when a solution with a molar ratio $P(NMe_2)_3O : La^{3+}$ of 6.0 : 1 was heated to 328 K the signal disappeared. The narrow resonance can be assigned to the $[La\{P(NMe_2)_3O\}_6]^{3+}$ ion which, at 294 K, does not appreciably exchange (on an n.m.r. time-scale) with other La^{3+}–$P(NMe_2)_3O$ species.

'La^{3+}–NCS'. Complexes of the type $[NBu^n{}_4]_3[Ln(NCS)_6]$ have been reported [18,26] for most of the lanthanides, though not for La itself. An *X*-ray study [26] of the Er complex showed the Er^{3+} to be octahedrally surrounded by six almost linear *N*-bonded thiocyanate groups. Our attempts to prepare a similar La complex invariably gave the heptakis adduct $[NBu^n{}_4]_4[La(NCS)_7]$, even when the $NCS^- : La^{3+}$ ratio was 6 : 1 (see Experimental section). This behaviour may be associated with the fact that lanthanum is the largest of the rare earths.

The ^{139}La n.m.r. spectrum of a 0.09 mol dm^{-3} solution of the

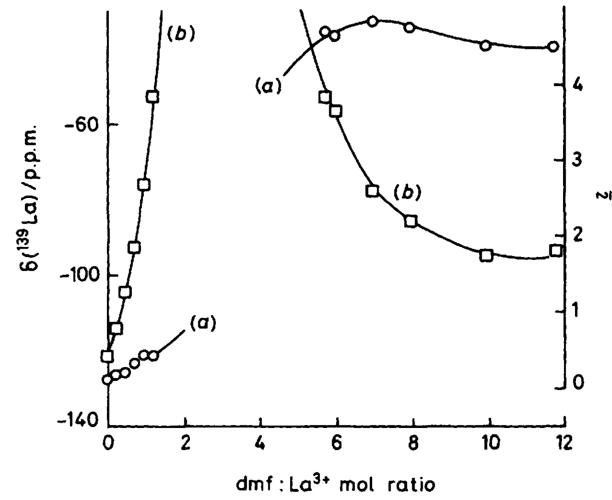

Figure 2. Lanthanum-139 chemical shift (*a*), and width at half-height (*b*), for the progressive addition of dmf to La[ClO$_4$]$_3$ (0.21 mol dm^{-3}) in MeCN at 294 K

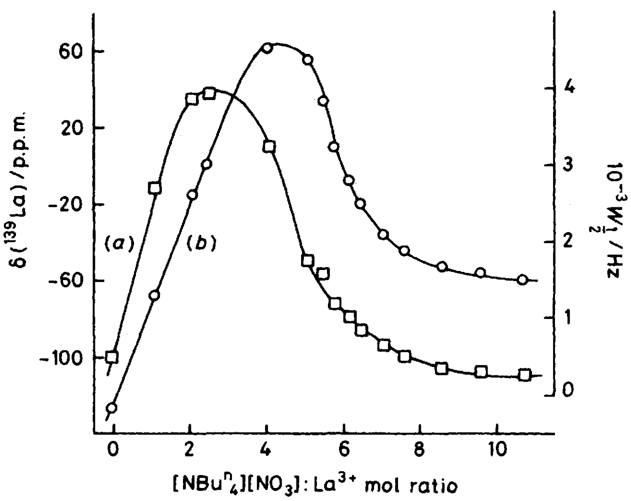

Figure 3. Lanthanum-139 chemical shift (*a*), and width at half-height (*b*), for the progressive addition of [NBu$^n_4$][NO$_3$] to La[ClO$_4$]$_3$ (0.06 mol dm^{-3}) in MeCN at 294 K

heptakis adduct consists of a very broad resonance ($W_{\frac{1}{2}}$ = 4 400 Hz, δ 196 p.p.m.). When La[ClO$_4$]$_3$ in MeCN is added to give a molar ratio NCS$^-$: La^{3+} of 6 : 1, $W_{\frac{1}{2}}$ increases to 5 340 Hz (δ 160 p.p.m.). It seems likely that the unsymmetrical ion [La(NCS)$_7$]$^{4-}$ exists in solution in equilibrium with species containing fewer NCS$^-$ groups. This is consistent with the electronic (*f*–*f*) spectra of acetonitrile solutions of hexathiocyanates of the lighter lanthanides.[26]

Complexes of Higher Co-ordination Number.—La^{3+}–H$_2$O. Figure 1 shows the ^{139}La chemical shifts and linewidths obtained when water is progressively added to a solution of La[ClO$_4$]$_3$ in MeCN. The chemical shifts change monotonically, but the linewidths reach a maximum at a molar ratio H$_2$O : La^{3+} of *ca.* 5 : 1, presumably due to the presence of very asymmetric species of the type [La(H$_2$O)$_x$(MeCN)$_y$]$^{3+}$. The data indicate that complete formation of the aqua-ion {probably [La(H$_2$O)$_9$]$^{3+}$}[27] is not attained even at a H$_2$O : La^{3+} ratio of 20 : 1.

La^{3+}–dmf. Similar plots are shown in Figure 2 for the addition of dimethylformamide (dmf) to La[ClO$_4$]$_3$. In this case the chemical shifts and, in particular, the linewidths reach a constant value at a molar ratio of dmf : La^{3+} of *ca.* 10 : 1 corresponding to the complete formation of [La(dmf)$_n$]$^{3+}$, where *n* is probably eight (La[ClO$_4$]$_3$ is known to form a solid octakis adduct with dmf, which in MeNO$_2$ and dmf behaves as a 1 : 3 electrolyte[28]). The broad linewidths cannot arise from intermediate exchange effects, in view of the comparatively narrow range of chemical shifts, and the fact that the lineshapes were closely Lorentzian.

Similar results were obtained for the La^{3+}–dmso (dimethyl sulphoxide) and La^{3+}–luto systems. In the latter case, due to the close similarity of the ^{139}La chemical shifts of [La(MeCN)$_n$]$^{3+}$ and [La(luto)$_8$]$^{3+}$, the plot of shift against mol fraction of luto was, within experimental error, a horizontal line. The extent of complex formation could, however, be gauged by following the changes in $W_{\frac{1}{2}}$.

La^{3+}–NO$_3^-$. Solid complexes containing the ions [Ln(NO$_3$)$_5$]$^{2-}$ and [Ln(NO$_3$)$_6$]$^{3-}$ are known.[29] *X*-Ray studies of [PPh$_3$Et][Ce(NO$_3$)$_5$][30] and [NO]$_2$[Ho(NO$_3$)$_5$][31] show that the lanthanides are surrounded by 10 oxygen atoms of bidentate nitrate groups, with the D_2 bicapped octahedron as the most appropriate description of the co-ordination polyhedron.*

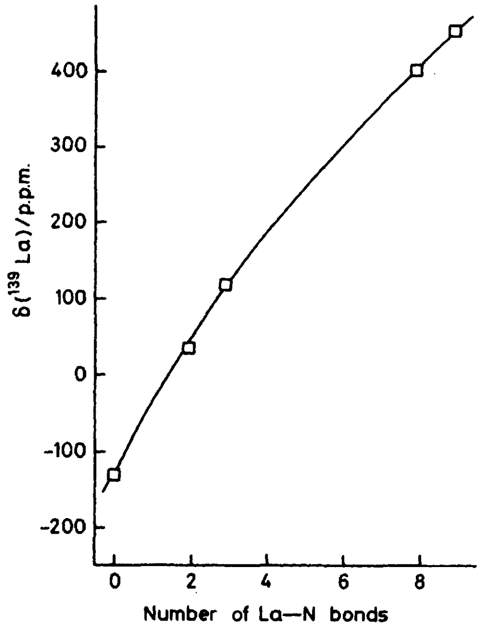

Figure 4. The variation of ^{139}La chemical shift with the number of La–N bonds in complexes of the type [La(en)$_n$]$^{3+}$ (*n* = 1—4) and [La(dien)$_n$]$^{3+}$ (*n* = 1—3) in MeCN solution at 294 K

In both [Ce$_2$Mg$_3$(NO$_3$)$_{12}$]·24H$_2$O[32] and [NH$_4$]$_2$[Ce(NO$_3$)$_6$],[33] on the other hand, the six nitrogen atoms define an octahedron, and the 12 oxygens a (distorted) icosahedron.

Figure 3 presents the ^{139}La chemical shifts and linewidths obtained when [NBu$_4^n$][NO$_3$] is added to La[ClO$_4$]$_3$ in MeCN. The linewidths follow the usual pattern, but the chemical shifts show a pronounced maximum at a molar ratio NO$_3^-$: La^{3+} of *ca.* 4.5 : 1. This may be due to a change in the co-ordination number of the lanthanum, which occurs in this region. The bidentate nitrate group has a very small

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* Alternatively, if each nitrate group is considered to occupy only one co-ordination position, the polyhedron is best described by a trigonal bipyramid.

' bite ' and, as seen above, can give rise to 12-co-ordination. Figure 3 indicates almost complete formation of $[La(NO_3)_n]^{3-n}$ at a molar ratio $NO_3^- : La^{3+}$ of *ca.* 10 : 1. The very narrow linewidth ($W_{\frac{1}{2}}$ *ca.* 275 Hz) suggests that $n = 6$, giving high icosahedral symmetry around the lanthanum.

La^{3+}–en *and* La^{3+}–dien. From measurements of the enthalpy changes when ethylenediamine (en) and diethylenetriamine (dien) are added to $Ln[ClO_4]_3$ in MeCN, Forsberg and co-workers [34] have shown stepwise formation of the complexes $[Ln(en)_n]^{3+}$ (n = 1—4) and $[La(dien)_n]^{3+}$ (n = 1—3).

For en : La^{3+} molar ratios in the region 0.25—1.5 : 1, two separate ^{139}La resonances are found, corresponding to $[La(MeCN)_n]^{3+}$ (δ − 129 p.p.m., $W_{\frac{1}{2}}$ *ca.* 380 Hz) and the 1 : 1 adduct (δ 40 p.p.m., $W_{\frac{1}{2}}$ *ca.* 3 800 Hz). Chemical exchange is therefore slow on the n.m.r. time-scale. The 2 : 1 and 3 : 1 adducts cannot be detected, presumably due to excessive linewidths. However, at molar ratios of en : La^{3+} of 4 : 1 and 4.5 : 1, the ^{139}La resonance of $[La(en)_4]^{3+}$ is observed.

With molar ratios of dien : La^{3+} of 0.75 : 1 and 1.0 : 1, resonances due to $[La(MeCN)_n]^{3+}$ and $[La(dien)]^{3+}$ appeared. The 2 : 1 adduct cannot be detected, but at a molar ratio of 3.5 : 1 the ^{139}La resonance of $[La(dien)_3]^{3+}$ appears.

Factors affecting ^{139}La *Chemical Shifts*.—The range of ^{139}La chemical shifts is quite large (*ca.* 1 200 p.p.m.) and, as with most nuclei, probably results mainly from changes in the ' paramagnetic ' term. The shifts can be roughly correlated with the extent of covalency in the La–ligand bonds, with greater covalency leading to deshielding. This is illustrated by the octahedral complexes studied, and also by a comparison of the eight-co-ordinate ions $[La\{CH(OCCF_3)_2\}_4]$ and $[La(Et_2NCS_2)_4]^-$, with O and S co-ordination respectively.

Lanthanum-139 chemical shifts thus seem to follow the so-called ' inverse order '; that is, increased shielding in the order $I^- < Br^- < Cl^-$.[7] This inverse order is also shown by a few other nuclei including Nb, Tl, the alkali metals, and (possibly) Sc, but it is the reverse of the behaviour pattern of most nuclei. The reasons for these differences are not clear.[7]

It is also not clear what effect changes in co-ordination number have on ^{139}La chemical shifts. However, all the ligands which co-ordinate through oxygen give complexes in which the chemical shifts lie in a fairly narrow region around zero.

For the en and dien complexes, Figure 4 shows that there is a monotonic (though not linear) relationship between δ and the number of ligand N atoms co-ordinated.

Acknowledgements

We wish to thank Mr. R. N. Sheppard and Ms. S. Johnson for measurement of the n.m.r. spectra, and the S.E.R.C. for a postgraduate studentship (to P. H. M.).

References

1 O. Lutz and H. Oehler, *J. Magn. Reson.*, 1980, **37**, 261.
2 J. Reuben, *J. Phys. Chem.*, 1975, **79**, 2154.
3 P. L. Rinaldi, A. K. Shankil, R. C. Gregory, and C. G. Levy, *J. Am. Chem. Soc.*, 1979, **101**, 1350.
4 L. S. Smith, D. C. McCain, and D. L. Wertz, *J. Am. Chem. Soc.*, 1976, **98**, 5125.
5 D. C. McCain, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1185.
6 C. A. M. Vijverberg, J. A. Peters, A. P. G. Kieboom, and H. van Bekkum, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 289.
7 R. K. Harris and B. E. Mann, ' NMR and the Periodic Table,' Academic Press, London, 1979.
8 P. Arthur, W. M. Haynes, and L. P. Varga, *Anal. Chem.*, 1966, **38**, 1630; E. R. Birnbaum and S. Stratton, *Inorg. Chem.*, 1973, **12**, 379.
9 S. J. Lyle and M. M. Rahman, *Talanta*, 1963, **10**, 1177.
10 I. M. Walker, L. Rosenthal, and M. S. Quereshi, *Inorg. Chem.*, 1971, **10**, 2463.
11 L. B. Zinner and G. Vincentini, *J. Inorg. Nucl. Chem.*, 1981, **43**, 193.
12 V. N. Krishnamurthy and S. Soundararajan, *Can. J. Chem.*, 1967, **45**, 189.
13 L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, 1964, **86**, 5117.
14 T. H. Siddall III and W. E. Stewart, *J. Inorg. Nucl. Chem.*, 1970, **32**, 1147.
15 N. Ikekawa and Y. Sato, *Pharm. Bull. Tokyo*, 1954, **2**, 400; N. Rabjohn, ' Organic Synthesis, Collected Volume Four,' Wiley, New York, 1963, p. 828.
16 R. F. Buckles and L. Harris, *J. Am. Chem. Soc.*, 1957, **79**, 886.
17 G. Brauer, ' Handbook of Preparative and Inorganic Chemistry,' Academic Press, New York, 1965, vol. 2; M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, 1962, **24**, 387.
18 J. L. Burmeister, S. D. Patterson, and E. A. Deardorff, *Inorg. Chim. Acta*, 1969, **3**, 105.
19 J. L. Ryan and C. K. Jorgensen, *J. Phys. Chem.*, 1966, **70**, 2845.
20 M. Choca, J. R. Ferraro, and K. Nakamoto, *Coord. Chem. Rev.*, 1974, **12**, 295; *J. Inorg. Nucl. Chem.*, 1975, **37**, 1425.
21 H. C. Goswami and P. H. Sarker, *J. Indian Chem. Soc.*, 1935, **12**, 608; N. K. Dutt, *J. Indian Chem. Soc.*, 1945, **22**, 65.
22 A. Ferrari, L. Cavaka, and M. Nardelli, *Gazz. Chim. Ital.*, 1951, **81**, 1082.
23 J. C. Barnes and R. D. Peacock, *J. Chem. Soc. A*, 1971, 558.
24 K. A. Gsihneidner and L. Eyring, ' Handbook on the Physics and Chemistry of Rare Earths,' North-Holland, Amsterdam, 1978, vol. 3, ch. 25.
25 L. A. Aslapov, V. M. Ionov, A. A. Stepanov, M. A. Porai-Koshits, V. G. Lebedev, B. N. Kulikovskii, O. N. Gilyalov, and T. L. Novoderezhkina, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1975, **11**, 1331.
26 J. L. Martin, L. C. Thompson, L. J. Radonovich, and M. D. Glick, *J. Am. Chem. Soc.*, 1968, **90**, 4493.
27 A. Hąbenschuss and F. H. Spedding, *J. Chem. Phys.*, 1979, **70**, 2797.
28 V. N. Krishnamurthy and S. Soundararajan, *Can. J. Chem.*, 1969, **47**, 995; L. N. Lugina, N. K. Davidenko, and K. B. Yatsimirskii, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1973, **18**, 1453.
29 I. M. Walker and D. H. Weeden, *Inorg. Chem.*, 1973, **12**, 772.
30 A. R. Al-Karaghouli and J. S. Wood, *Chem. Commun.*, 1970, 135; *J. Chem. Soc., Dalton Trans.*, 1973, 2318.
31 G. E. Toogood and C. Chieh, *Can. J. Chem.*, 1975, **53**, 831.
32 A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, 1963, **39**, 2881.
33 T. A. Beineke and J. Dalgaudio, *Inorg. Chem.*, 1968, **7**, 715.
34 J. H. Forsberg and T. Moeller, *Inorg. Chem.*, 1969, **8**, 889; J. H. Forsberg and A. Wathen, *Inorg. Chem.*, 1971, **10**, 1379.

Received 11*th March* 1982; *Paper* 2/432