Complexes of Lanthanoid Salts with the Crown Ether *cis,syn,cis*-2,5,8,15,18,21-Hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane and their Paramagnetically Shifted Nuclear Magnetic Resonance Spectra

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Lanthanoid perchlorates form complexes [M$(ClO_4)_3$(shoth)] with the title crown ether (shoth) whose n.m.r. spectra show shifts which are predominantly dipolar. The magnetic-susceptibility tensors are not axially symmetric.

ALTHOUGH lanthanoid ions complex strongly with those oxygen ligands in which the bonding oxygen atom carries a negative charge, such as $[RCO_2]^-$ or PR_3O, their affinity for ethers is minimal. However, an ether oxygen atom in a multidentate ligand will co-ordinate, as exemplified by $[Nd(O_2CCH_2\overset{*}{O}CH_2CO_2)_3]^{3-}$ where the Nd–$\overset{*}{O}$ distance is 2.52 Å as determined by *X*-ray crystallography.[1] Crown ethers whose ring size is suitable (five or six oxygen atoms) will also co-ordinate, and solid complexes of stoicheiometry $ML(NO_3)_3$, $ML'(NO_3)_3$, and $ML'(NO_3)_3{\cdot}3H_2O{\cdot}Me_2CO$ (L = dibenzo-18-crown-6 and L′ = benzo-15-crown-5) have been isolated.[2]

We now describe lanthanoid complexes of the crown ether *cis,syn,cis*-2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane (shoth),[3,4] with particular reference to their ^{1}H and ^{13}C n.m.r. spectra which, unlike those of the complexes of benzo-crown ethers,[2] have fairly large paramagnetic shifts and individually assignable resonances.

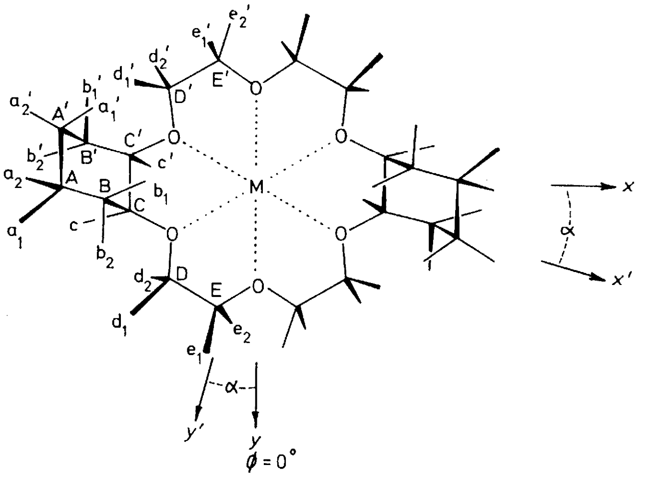

FIGURE 1 General configuration of a complex between shoth and a lanthanoid ion

RESULTS AND DISCUSSION

When lanthanoid nitrates or perchlorates were treated in solution with shoth (1 mol), crystalline products [MX_3(shoth)] (M = a lanthanoid, X = ClO_4 or NO_3) were obtained. Of these, [La$(NO_3)_3$(shoth)] gave crystals of *X*-ray quality and the structure[5] shows the crown ether to be co-ordinated to the lanthanum ion as depicted in Figure 1. Three bidentate nitrate ions, one above and two below the crown ether, are also co-ordinated to the metal.

We have investigated the ^{1}H and ^{13}C n.m.r. spectra of complexes of shoth with praseodymium and other lanthanoid salts in 0.1 or 0.2 mol dm^{-3} CD_3CN–$CDCl_3$ (1 : 1 v/v) solution. There are upfield and downfield shifts in the ligand resonances, the shifted ^{1}H spectra being *ca.* 20 p.p.m. wide (Figure 2). There are nine distinct hydrogen atoms (a_1—e_2) and five distinct carbon atoms (A—E), which are disposed in space in the general manner depicted in Figure 1 when the six oxygen atoms are co-ordinated to the lanthanoid ion. Spectra of praseodymium perchlorate were selected for particular study because of their combination of fairly narrow linewidth and fairly large shifts in directions which facilitate unambiguous assignments.

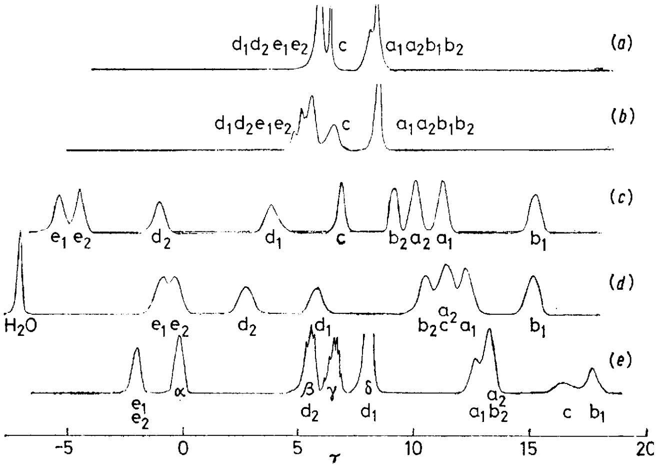

FIGURE 2 Hydrogen-1 n.m.r. spectra at 60 MHz of [M$(ClO_4)_3$(shoth)] [M = La(*a*), Sm(*b*), or Pr (*c*)] and [Pr$(ClO_4)_3$(shoth)] + X [X = 2 H_2O (*d*) or PO(OBu^n)$_3$ (*e*)]. Spectrum amplitudes: (*a*) = (*b*) ≠ (*c*) = (*d*) ≠ (*e*)

Initial experiments showed that metal–ligand exchange was slow on the n.m.r. time scale, sets of resonances from both free and complexed polyether appearing if the molecular concentration of the metal ion was smaller than that of the polyether. Hence a kinetically

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[1] J. Albertsson, *Acta Chem. Scand.*, 1968, **22**, 1563.

[2] R. B. King and P. R. Heckley, *J. Amer. Chem. Soc.*, 1974, **96**, 3118.

[3] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

[4] H. K. Frensdorff, *J. Amer. Chem. Soc.*, 1971, **93**, 4884.

[5] M. E. Harman, F. A. Hart, M. B. Hursthouse, G. P. Moss, and P. R. Raithby, *J.C.S. Chem. Comm.*, 1976, 396.

stable 1 : 1 complex is present in CD_3CN–$CDCl_3$ solution. The spectra are strongly affected by the presence of water, 6 molecular proportions (*ca.* 2 mg) of water producing shifts of up to 10 p.p.m. compared with the water-free solution. Since shifts were independent of the metal : polyether ratio, the individual unshifted origins of the shifted resonances could not be determined from a plot of shift against this ratio, nor from coupling nor from integration differences, all of which were absent. However, assignments of the ^1H spectra were established from the following considerations.

The dipolar shifts of samarium complexes are *ca.* 5—10% of those of similar praseodymium complexes.[6] Hence the samarium system shows the direction and approximate magnitude of the shifts because these slight shifts do not intermingle the resonances originating at τ *ca.* 6.3 (where H is α to oxygen) and at τ 8.6 (where H is β or γ to oxygen). The five resonances in the first group divide into three sections: one proton at 0.2, two protons at −0.8, and two protons at −1.1 p.p.m. compared with the positions of the lanthanum complex. The group at τ 8.6 is shifted slightly upfield by up to 0.4 p.p.m. but is not resolved into individual resonances. This result is interpreted as indicating anisotropy in the plane of the six-oxygen ring, *i.e.* $\chi_x \neq \chi_y$, and the single resonance of the group at τ 6.3 which is shifted upfield is thus c, the two downfield sections being respectively d_1,d_2 and e_1,e_2. Extrapolation to the spectrum of the praseodymium complex then gives the partial assignment: a_1,a_2,b_1,b_2 $\equiv$ τ 9.4, 10.3, 11.5, 15.4; c $\equiv$ 7.0; d_1,d_2 $\equiv$ 4.1, −0.9; e_1,e_2 $\equiv$ −5.9, −5.0, internal permutation within each group being possible.

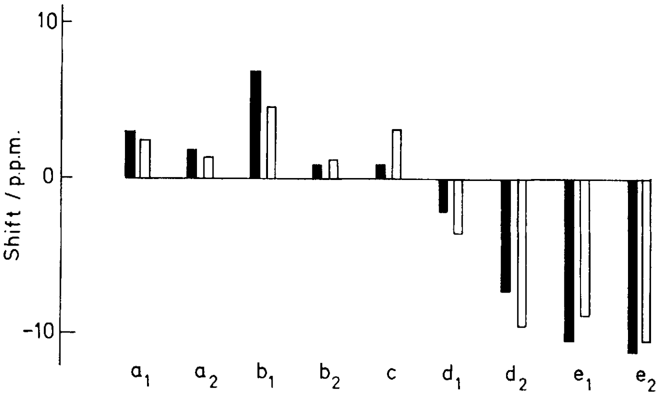

FIGURE 3 Comparison of observed (black) and calculated (white) shifts for $[Pr(ClO_4)_3(shoth)]$

Single-frequency proton-decoupling experiments carried out on the ^{13}C n.m.r. spectrum of the praseodymium complex showed that each member of the following pairs of ^1H resonances arose from a proton bonded to a carbon atom whose chemical shift is given in parentheses: τ 15.4, 9.4 (55.3); 11.5, 10.3 (60.0); 4.1, −0.9 (7.1); −5.9, −5.0 (−3.8 p.p.m. upfield from $CDCl_3$). The ^1H resonance at τ 7.0 was shown to arise from a CH group (^{13}C resonance at 6.6 p.p.m.). A and B, identifiable (as a pair) by their chemical shift, are coupled with the four highest-field proton resonances and C, identifiable as carrying one proton only, is coupled to the fifth.

A distinction between d_1 and d_2 and between e_1 and e_2, enabling a provisional assignment to be made, rests upon the effects of addition of excess of $Pr[ClO_4]_3$ to the solution. It is expected that there will be some association between complexed and uncomplexed Pr^{3+} ions, perhaps by means of perchlorate bridges. This association is expected to be less on the sterically hindered side of the six-oxygen plane but greater on the unhindered side, where c, d_2, and e_2 are located, and the additional Pr^{3+} ion should produce a further shift. It is found that the peaks shown in Figure 2 as c, d_2, and e_2 are shifted to low field by 0.5 p.p.m. while other peaks move only 0—0.2 p.p.m. on addition of a 10% molar excess of $Pr[ClO_4]_3 \cdot 6H_2O$.

Relation between the Susceptibility Tensor and the Molecular Geometry.—On the basis of the *X*-ray structure determination [5] we assume as a trial model that the predominant structure in solution is as in Figure 1 rather than the other conformation of the complex where one of the cyclohexyl rings is in its other chair form. In solution, the Pr^{3+} ion will be co-ordinated in directions above and below the six-oxygen mean plane with perchlorate anions and possibly with acetonitrile molecules. Meaningful conductimetric results, which might have shown the proportion of unco-ordinated perchlorate ions, could not be obtained in the CD_3CN–$CDCl_3$ solvent.

If C_2 molecular symmetry is present in solution, as in solid $[La(NO_3)_3(shoth)]$, the z axis of the tensor will coincide with the C_2 axis but the x axis will in principle be displaced by an angle α as shown in Figure 1. The observed shifts will then be the mean of those produced by this tensor $x'y'z$ and a corresponding tensor associated with the complex in its rapidly interconverting enantiomeric form where both the cyclohexyl rings are in their opposite chair conformations. Thus in the case of proton a_1, for example, the shifts of a_1 and a_1' (Figure 1) were calculated and the mean was taken. The values of α, $(\chi_x - \chi_y)$, and $(\chi_z - \bar{\chi})$ were treated as parameters and were fitted to the observed shift values using values of r, θ, and ϕ for the atomic co-ordinates which were obtained from the *X*-ray structure [5] of solid $[La(NO_3)_3$-$(shoth)]$. The relation $\Delta H/H = (1/2Nr^3)\,[(3\cos^2\theta - 1)(\chi_z - \bar{\chi}) + \sin^2\theta\cos 2\phi\,(\chi_x - \chi_y)]$ was used.

The results (Table) show that, while the agreement between theory and experiment is not exact, the model employed (dipolar shifts and a non-axially symmetric susceptibility tensor) is correct. The error, expressed as $\Sigma|(\text{calculated shift}) - (\text{experimental shift})|/\Sigma|(\text{experimental shift})|$ is *ca.* 0.25. Closer agreement would not be expected because of: (*a*) the possible presence of small contact effects, except perhaps on a_1 and a_2; more importantly, (*b*) possible presence of the C_s form; and (*c*) possible loss of C_2 symmetry because of unsymmetrical

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[6] J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *Chem. Comm.*, 1970, 749.

$[ClO_4]^-$ or CD_3CN co-ordination, so displacing the *z* axis of the tensor from its direction perpendicular to the mean plane of the oxygen atoms of the crown ether. This effect might be more marked in the case of the water and tri-n-butyl phosphate adducts (see below). An attempt to take account of effects (*b*) or (*c*) above would involve the use of seven parameters (two tensor orientations, four anisotropies, and an equilibrium constant) and we believe that the reasonably good agreement we obtain using three parameters is a more valid approach. In particular, it would be unrealistic to perform a computer search to attempt to fix fine details of conformation. In this connection, Dreiding models suggest ready alteration of the dihedral angle between the mean plane of the oxygen atoms of the crown ether and each mean plane of the cyclohexane rings.

TABLE

Table of paramagnetic shifts

(*a*) $[Pr(ClO_4)_3(shoth)]$

$\chi_z - \bar{\chi} = -542$ VVk mol^{-1},* $\chi_x - \chi_y = 927$ VVk, $\alpha = 0°$

	a_1	a_2	b_1	b_2	c	d_1	d_2	e_1	e_2
Obs. shifts (p.p.m.)	2.9	1.8	6.9	0.9	0.8	−2.2	−7.3	−10.5	−11.3
Calc. shifts (p.p.m.)	2.43	1.33	4.58	1.25	3.07	−3.74	−9.57	− 8.85	−10.55

$[\frac{1}{9}(\Sigma^{a_1}_{e_2}E^2)]^{\frac{1}{2}} = 1.56$ p.p.m. [E = (obs. shift − calc. shift)]

$\Sigma^{a_1}_{e_2}E/\Sigma^{a_2}_{e_2}$(obs. shift) = 27.1%

(*b*) $[Pr(ClO_4)_3(shoth)]\cdot 2\,H_2O$

$\chi_z - \bar{\chi} = -144$ VVk mol^{-1}, $\chi_x - \chi_y = 843$ VVk, $\alpha = 0°$

	a_1	a_2	b_1	b_2	c	d_1	d_2	e_1	e_2	H_2O
Obs. shifts (p.p.m.)	3.9	3.0	6.95	2.1	5.1	−0.4	−3.6	−7.15	−6.65	−12.1
Calc. shifts (p.p.m.)	2.03	1.64	3.99	2.26	6.61	−0.8	−4.48	−7.06	−7.02	

E(r.m.s.) = 1.39 p.p.m. Mean E = 24.7%

(*c*) $[Pr(ClO_4)_3(shoth)]\cdot PO(O\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3)_3$

$\chi_2 - \bar{\chi} = 72$ VVk mol^{-1}, $\chi_x - \chi_y = 1\,300$ VVk, $\alpha = -10°$

	a_1	a_2	b_1	b_2	c	d_1	d_2	e_1	e_2
Obs. shifts (p.p.m.)	4.2	4.7	9.3	4.7	10.0	1.4	−1.2	−8.3	−8.2
Calc. shifts (p.p.m.)	2.45	2.68	5.69	5.09	12.02	1.30	−3.12	−8.54	−7.78

E(r.m.s.) = 1.77 p.p.m. Mean E = 24.0%

	α	β	γ	δ
Butyl protons: Obs. shifts (p.p.m.)	−6.0	−2.8	−1.75	−1.0

(*d*) Carbon-13 resonances

	A	B	C	D	E
Calc. shifts (p.p.m.) [a]	2.4	3.4	6.8	−8.7	−16.6
Obs. shifts (p.p.m.) [b]	2.9	2.9	9.5	−3.3	−10.2

* 1 VVk = 10^6 c.g.s. units = 10^{-12} SI units (dimensions m^3).

[a] Obtained by comparison of the spectrum of a solution of $[Pr(ClO_4)_3(shoth)]$ containing 1.2 mol of water with that of a solution of $[La(ClO_4)_3(shoth)]$. Chemical shifts for the lanthanum solution: A, 57.1; B, 52.4; C, −2.9; D, 10.4; E, 6.4 p.p.m. upfield of $CDCl_3$. [b] Calculated using susceptibility values [$(\chi_z - \bar{\chi}) = -409$; $\chi_x - \chi_y = 899$ VVk mol^{-1}] obtained from the ^1H n.m.r. spectrum of the praseodymium solution.

We have also investigated the effects of the addition of water and of $PO(OBu^t)_3$. These ligands are expected to co-ordinate to the lanthanoid ion above or below the crown ether plane and should affect the magnetic anisotropy. When water was added, in steps of 0.2 mol up to a total of 2.0 mol, to solutions of $[Pr(ClO_4)_3(shoth)]$ similar to those used in the previous experiments, the spectra were considerably shifted upfield to an extent proportional to the weight of added water. The individual ^1H peaks could be followed from one spectrum to the next and hence assigned by reference to the spectrum in the absence of water. There is thus rapid water–lanthanoid exchange. A similar procedure was followed using up to 1 mol of $PO(OBu^t)_3$ with similar results. The ^1H peaks of the water and of $PO(OBu^t)_3$ were shifted downfield (Table), the shifts of the strongly co-ordinating $PO(OBu)_3$ being independent of its concentration. Shifts of the water protons varied inversely with water concentration, suggesting that not all the water is co-ordinated. The experimental results were fitted to theory as before. These results show that the added ligands, by co-ordinating in directions above or below the plane of the crown ether ring, increase the ligand field in the *z* direction and hence $(\chi_z - \bar{\chi})$ is increased from −542 for $[Pr(ClO_4)_3(shoth)]$ to −144 for $[Pr(ClO_4)_3(shoth)]\cdot 2H_2O$ and then to 72 VVk mol^{-1} for $[Pr(ClO_4)_3(shoth)]\cdot OP(OBu)_3$. The sign of this change is in accord with theory.[7] The shifts of the protons of the added ligands (Table) indicate that they are located in the area $\phi \simeq 0$ or 180°, $\theta \simeq 60°$, but we present no detailed calculations as there are too many unknown factors.

It remains to consider the origins of the observed anisotropy. The anisotropy $(\chi_z - \bar{\chi})$ follows a trend suggesting that the ligand field of the polyether is larger than that produced in a perpendicular direction to it by the $[ClO_4]^-$ or CD_3CN ligands, but when the latter field

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[7] M. Gerloch and D. J. Mackey, *J.C.S. Dalton*, 1972, 410.

is augmented by water or $PO(OBu)_3$ ligands it becomes approximately equal to the polyether field. The anisotropy $(\chi_x - \chi_y)$ (which was completely unexpected) is probably caused by (*a*) unequal ligand fields from the six polyether oxygen atoms {$[La(NO_3)_3(shoth)]$ has four La–O of *ca.* 2.6 Å and two of *ca.* 2.9 Å; the NaBr complex[8] of the *cis-anti-cis* isomer of this ligand has four Na–O of *ca.* 2.68 Å and two of 2.97 Å} or (*b*) non-axially symmetric co-ordination of ligands situated above the polyether plane, these ligands being influenced sterically by the two cyclohexyl rings so that their overall ligand field deviates from axial symmetry. The lack of effective axial symmetry in these complexes contrasts strongly with lanthanoid shift reagents which always show it, presumably by a time-averaging process. The lanthanoid shift reagents probably owe their function to the contrast between the small ligand field exerted by the substrate (typically an alcohol) and the larger ligand field of the anionic β-diketone donors disposed around the remainder of the periphery of the complex. This is similar in principle to the results of variation of ligand field observed in the present work.

The ^{13}C spectral data were not used to derive values of $(\chi_z - \chi)$ and $(\chi_x - \chi_y)$ because there is evidence[9] that ^{13}C n.m.r. spectra may be considerably affected by contact shifts, especially for carbon atoms α or β to ligand atoms. Instead, the observed ^{13}C shifts were compared with shifts calculated using the $(\chi_z - \chi)$ and $(\chi_x - \chi_y)$ values derived from the ^1H spectra as described above. The comparison (Table) shows that the carbon atoms C, D, and E (the α carbons) have shifts which are 2.7, 5.4, and 6.4 p.p.m. respectively to high field of the calculated positions, while the A and B shifts agree quite well with calculation. It is thus probable that atoms C, D, and E experience contact shifts to high field of *ca.* 3—6 p.p.m.

EXPERIMENTAL

The ligand (shoth) was prepared by hydrogenation of dibenzo-18-crown-6 in n-butanol at 100 atm and 135 °C for 20 h using 5% Ru on Al_2O_3 as catalyst. It was separated from its *anti*-isomer by chromatography on alumina[4] and then had m.p. 62 °C. (There is now a superior method of separation.[10])

(cis,syn,cis-2,5,8,15,18,21-*Hexaoxatricyclo*[20.4.0.0 ^{9,14}]-*hexacosane*)*triperchloratopraseodymium*(III).— $Pr[ClO_4]_3\cdot 6H_2O$ in MeCN solution was treated with shoth (1 mol) in MeCN. The solvents were removed and the product was heated at 65 °C over P_4O_{10} for 14 h at 0.1 mmHg (Found: C, 29.65; H, 4.6; Cl, 13.0. $C_{20}H_{36}Cl_3O_{18}Pr$ requires C, 29.6; H, 4.4; Cl, 13.1%), decomposition point 250—270 °C.

(cis,syn,cis-2,5,8,15,18,21-*Hexaoxatricyclo*[20.4.0.0 ^{9,14}]-*hexacosane*)*trinitratolanthanum*(III).—This complex was prepared from $La[NO_3]_3\cdot 6H_2O$ in a similar way to the preceding complex. Crystallised from ethanol by the addition of diethyl ether, it was characterised by *X*-ray crystallography.[5] The analogous praseodymium complex gave shifted ^1H n.m.r. spectra which, however, were much less suitable for detailed investigation because of coincidental superimposition of resonances.

N.M.R. Spectra.—These were obtained from 0.1 (^1H) or 0.2 mol dm^{-3} (^{13}C) solutions of CD_3CN–$CDCl_3$ (1 : 1 v/v) using Varian EM360 (^1H) or Bruker HFX-13 (^{13}C) instruments. Vacuum-line and glove-box techniques were used in drying solvents and preparing solutions because of the extreme sensitivity of the spectra to the presence of water.

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[8] M. Mercer and M. R. Truter, *J.C.S. Dalton*, 1973, 2215.

[9] R. J. Cushley, D. R. Anderson, and S. R. Lipslay, *J.C.S. Chem. Comm.*, 1972, 636.

[10] R. M. Izat, B. L. Haymore, and J. S. Bradshaw, *Inorg. Chem.*, 1975, **14**, 3132.