Complexes of Lanthanoid Salts with Macrocyclic Ligands. Part 17.[1] Synthesis and Crystal and Molecular Structure of a Hydroxide-bridged Praseodymium Trifluoroacetate Complex with 15-Crown-5 Ether, $[Pr_2(CF_3CO_2)_3(OH)(C_{10}H_{20}O_5)_2][Pr_2(CF_3CO_2)_8]$†

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The reaction of praseodymium trifluoroacetate with 15-crown-5 ether in acetonitrile-methanol (3:1) gave a complex formulated as $[Pr(CF_3CO_2)_3]_2(C_{10}H_{20}O_5)$. This compound was recrystallised and the *X*-ray crystal structure determined by the heavy-atom method and refined by least-squares methods to a final *R* value of 0.075. The recrystallised complex turned out to have a different formula, as indicated in the title. It crystallises in the monoclinic space group $P2_1/m$, with lattice parameters $a = 9.124(1)$, $b = 31.607(4)$, $c = 13.006(2)$ Å, $\beta = 99.55(1)°$, and $Z = 2$. There are two praseodymium sites. One metal ion is nine-co-ordinate and is bonded to the macrocycle [mean Pr–O(crown) 2.58(2) Å], three bridging trifluoroacetate groups [mean Pr–O 2.45(2) Å], and a bridging hydroxide ion [Pr–OH 2.31(1) Å] which lies in the mirror plane $y = \frac{1}{4}$. This gives rise to dimeric cations $[Pr_2(CF_3CO_2)_3(OH)(C_{10}H_{20}O_5)_2]^{2+}$, the co-ordination polyhedron of which may be regarded as arising from distortion of a square antiprism by addition of a ninth ligand. The second praseodymium is eight-co-ordinate with a fairly regular square-antiprismatic co-ordination polyhedron consisting of one bidentate trifluoroacetate and three bridging bidentate trifluoroacetates [mean Pr–O 2.46(2) Å] that give rise to infinite polymeric zigzag chains parallel to *a*.

The study of the interaction between lanthanoid ions and macrocyclic ligands attracts considerable interest. The resulting complexes may be used to study high co-ordination numbers (10, 11, and 12), to stabilise unusual oxidation states, as spectroscopic probes, and in extraction and separation of the lanthanoid ions.[2] The factors influencing the stoicheiometry and the structure of the complexes formed with unsubstituted crown ethers have been reviewed recently.[3] Several crystal structure determinations have been published for complexes with 1:1 and 4:3 metal:ligand ratios. One study also describes the structure of a 2:1 cryptate, $[Sm(NO_3)_3]_2(2,2,2\text{-crypt})\cdot H_2O$ (2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane),[4] which can be represented as $[Sm(NO_3)(2,2,2\text{-crypt})][Sm(NO_3)_5(H_2O)]$. Our research program was mainly devoted to the study of nitrate[5] and perchlorate[6] complexes. In order to determine the influence of the anion on the complex, we have also studied the trifluoroacetates. These form 1:1 and 2:1 complexes with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane) and 2:1 complexes with 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane). Two different structures were postulated for the 2:1 complexes: (*i*) a sandwich type complex with a lanthanoid ion (Ln^{3+}) co-ordinated to each side of the macrocyclic ether and (*ii*) in view of the stability of $[Ln(CF_3CO_2)_4]^-$ ions,[7] a more complex structure formulated as $[Ln(CF_3CO_2)_2(15\text{-crown-}5)][Ln(CF_3CO_2)_4]$. In this paper, we present the results of an *X*-ray crystal structure analysis of a complex formed between praseodymium trifluoroacetate and 15-crown-5 ether.

Experimental

Hydrated praseodymium trifluoroacetate was prepared by dissolving praseodymium oxide in a slight excess of trifluoroacetic acid at 70 °C. The solution was evaporated to dryness and the solid obtained washed with dichloromethane and placed in a vacuum desiccator over KOH for 24 h; the latter procedure was repeated three times to eliminate excess acid. After a further 24 h in a desiccator over P_4O_{10}, $Pr(CF_3CO_2)_3\cdot xH_2O$ ($3 \leqslant x \leqslant 4$) was obtained. A solution of 15-crown-5 ether (5 mmol) in MeCN–MeOH (3:1, 15 cm^3) was added dropwise to a solution of hydrated praseodymium trifluoroacetate (5 mmol) dissolved in MeCN–MeOH (3:1, 15 cm^3). The solution was stirred for 24 h at 60 °C, cooled at room temperature and concentrated to 10—15 cm^3. The precipitated complex, filtered off and dried in a desiccator over P_4O_{10}, contained 2—3 molecules of water per molecule of complex. The completely anhydrous complex was obtained as a pale green powder after drying for 3 d at 60 °C (2×10^{-2} mmHg) {Found: C, 22.4; H, 1.7; Pr, 24.1. Calc. for $[Pr(CF_3CO_2)_3]_2(C_{10}H_{20}O_5)$: C, 22.4; H, 1.7; Pr, 23.9%}. Crystals for this study were obtained by slow recrystallisation from MeCN–MeOH (3:1) at room temperature (approximate dimensions 0.1 × 0.1 × 0.2 mm); they turned out to have a different formula, $Pr_4(CF_3CO_2)_{11}(OH)(C_{10}H_{20}O_5)_2$ (Found: C, 22.7; H, 1.9; Pr, 24.6. Calc. for $C_{42}H_{41}F_{33}O_{33}Pr_4$: C, 22.3; H, 1.8; Pr, 24.9%).

X-Ray Crystallography.—*Crystal data*. $C_{42}H_{41}F_{33}O_{33}Pr_4$, $M = 2\,264.35$, monoclinic, $a = 9.124(1)$, $b = 31.607(4)$, $c = 13.006(2)$ Å, $\beta = 99.55(1)$, $U = 3\,699.1(9)$ Å^3, space group $P2_1/m$, $D_c = 2.03$, $Z = 2$, $D_m = 2.12(8)$ g cm^{-3}, $F(000) = 2\,180$, $\lambda(Cu-K_\alpha) = 1.5418$ Å.

The data for $2\theta = 0$—100° (scan range 2θ about $K_{\alpha 1}$—$K_{\alpha 2}$: ±1°) were collected with a Syntex $P2_1$ four-circle diffractometer using Cu-K_α radiation and a variable scan speed of 2—29.3° min^{-1} depending upon the intensity of a 2-s prescan; background counts of half the scan time were taken before and

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† μ-Hydroxo-tris(μ-trifluoroacetato)-bis[(1,4,7,10,13-pentaoxacyclopentadecane)praseodymium(III)] octakis(trifluoroacetato)dipraseodymate(III).

Supplementary data available (No. SUP 56156, 24 pp.): thermal parameters, least-squares planes, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

after each scan. The background noise and variance of each reflection were calculated with the use of the Lehman–Larsen algorithm.[8] All intensities were corrected for absorption [μ(Cu-K_α) = 20.06 cm^{-1}] by the Gaussian integration method (transmission factors in the range 0.76—0.85 for both crystals). Three standard reflections were monitored every 200 reflections and showed marked deterioration when approximately half the data had been collected. A second crystal was mounted and the data collection completed with this crystal which again showed marked deterioration. The two sets of data were scaled for the observed decomposition and the reflections were corrected for Lorentz and polarisation effects. Of the 7 593 reflections collected (excluding standards) 4 150 were retained after sorting and averaging in Laue class monoclinic $2/m$ and 2 723 were considered observed [$I/\sigma(I) \geqslant 3$] and used in the refinement. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 21 high-angle reflections and were identical within experimental error for both crystals.

The systematic absence $0k0$, $k \neq 2n$, is consistent with space groups $P2_1$ and $P2_1/m$. The Patterson synthesis strongly suggested the latter space group and the positions of two praseodymium atoms were obtained and gave a satisfactory trial solution. Successive structure factor calculations and difference-Fourier syntheses enabled the location of all non-hydrogen atoms and indicated that the compound was $Pr_4(CF_3CO_2)_{11}(OH)(C_{10}H_{20}O_5)_2$ and not $Pr_2(CF_3CO_2)_6(C_{10}H_{20}O_5)$ as originally supposed. Three of the trifluoroacetate groups lay with the two carbon atoms and a fluorine atom in the mirror plane [special position 2(e) (x, $\frac{1}{4}$, z)] as did the hydroxide ion. Successive isotropic and then anisotropic refinement with separate scale factors for the two groups of data converged to $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|] = 0.075$ with a contribution from calculated H atoms (polyether) with a fixed isotropic thermal parameter and application of an empirical weighting scheme based on the analysis of Δ^2 and $w.\Delta^2$ with intervals of $F_{obs.}$ and $\sin\theta$ giving reduced weight to reflections of high $F_{obs.}$ and small $\sin\theta$ and unit weights to most reflections: $w = X.Y$ where $X = 1.0$ or $100/F$ for $F > 100$ and $Y = 1.0$ or $0.25/(\sin\theta/\lambda)$ for $\sin\theta/\lambda > 0.25$. All calculations were carried out using the X-RAY system.[9] Atomic scattering factors for neutral atoms were taken from ref. 10. Dispersion corrections for praseodymium were those calculated by Cromer and Liberman.[11] The most significant peak in the final difference-Fourier synthesis (2.5 e Å^{-3}) was located close to Pr(2) (1.3 Å). The trifluoroacetate groups exhibit some fluxional disorder, as does the polyether, which probably contribute to the rather high R value. As the data were not of the highest quality no attempt was made to resolve these disorders. A refinement based on four independent Pr atoms in space group $P2_1$ was examined and rejected because it did not converge satisfactorily ($R > 0.1$) and bond lengths and angles in the crown ethers were unsatisfactory.

Results

The final atomic positional parameters are given in Table 1. Bond distances and angles are presented in Table 2. The structure contains two different praseodymium sites. One, Pr(1), is bonded on one side to three O atoms of three different trifluoroacetate groups and a hydroxide group, and on the other side to the five O atoms of the macrocycle to give a nine-co-ordinate metal ion. The trifluoroacetate groups lie with two C atoms and one F atom in the mirror plane ($y = \frac{1}{4}$) as does the hydroxide; thus, a mirror-related dimer is formed containing two Pr^{III} ions, as illustrated in Figure 1. The Pr(1)–O distances vary from 2.31 to 2.61 Å, the shortest distance being that to the OH group. The mean Pr(1)–O_2CCF_3 distance is 2.45(2) Å and the longest Pr(1)–O bonds are those to the crown ether [mean 2.58(2) Å]. The distance between mirror-related Pr(1) atoms is 4.158(2) Å.

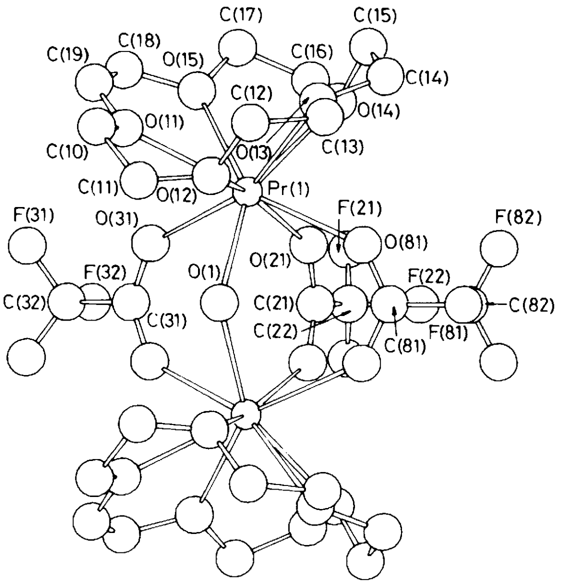

Figure 1. The dimeric cation $[Pr_2(CF_3CO_2)_3(OH)(C_{10}H_{20}O_5)_2]^{2+}$ showing the atomic numbering

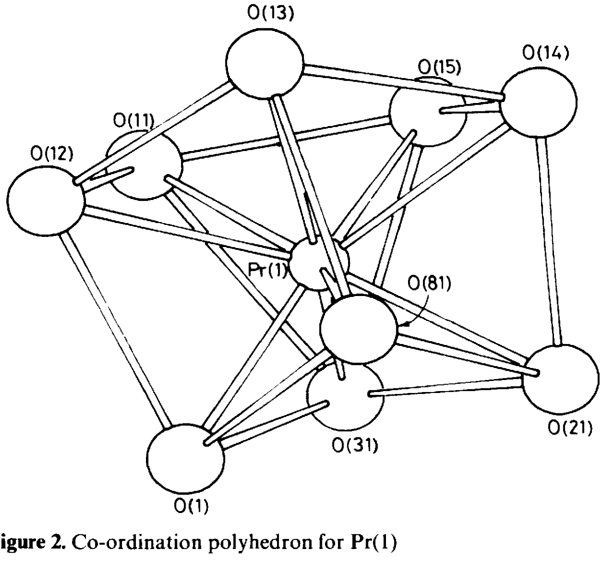

Figure 2. Co-ordination polyhedron for Pr(1)

The co-ordination sphere about Pr(1) does not correspond to one of the usual nine-co-ordinate polyhedra. It is probably best regarded as being derived from the addition of an extra ligand to an eight-co-ordinate square antiprism (Figure 2). Two atoms, O(12) and O(14) of the top face [O(11)O(12)O(14)O(15), σ = 0.025 Å], have been pushed apart by addition of the extra atom, O(13), and one atom of the lower face, O(81), has been pulled upwards. There is almost mirror symmetry about the plane containing Pr(1)O(13)O(31)O(81) (σ = 0.003 Å). (With this latter plane as an equatorial plane, a very distorted tricapped trigonal prism is just discernible.)

The Pr(2) atom is surrounded by eight trifluoroacetate O atoms. However, only one trifluoroacetate group is bidentate to a single Pr^{III} ion. The three others are μ-bidentate; two trifluoroacetate groups bridge to a symmetry related Pr(2) ($1 - x$, $-y$, $1 - z$) to give centrosymmetric dimers; a further $CF_3CO_2^-$ anion bridges to another symmetry related Pr(2)

Table 1. Final atomic co-ordinates (× 10^3) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pr(1)	348.8(2)	184.22(4)	−4.1(1)	O(52)	333(2)	−0.9(6)	417(1)
O(1)	243(3)	250	−44(2)	C(51)	344(3)	−8.0(7)	318(2)
O(11)	113(3)	149.4(8)	43(2)	C(52)	201(4)	−18(1)	253(2)
O(12)	116(3)	174.5(6)	−146(2)	F(51)	185(3)	−13(2)	159(2)
O(13)	353(3)	130.9(5)	−152(1)	F(52)	86(3)	−1(1)	282(2)
O(14)	572(2)	131.7(5)	9(1)	F(53)	160(3)	−57(1)	259(3)
O(15)	374(3)	125.8(6)	136(2)	O(61)	562(2)	66.4(5)	429(1)
C(10)	−22(5)	146(2)	−22(5)	O(62)	441(2)	70.0(4)	564(1)
C(11)	−12(6)	178(1)	−107(4)	C(61)	507(3)	84.6(7)	497(2)
C(12)	115(5)	143.6(9)	−232(2)	C(62)	532(5)	132.5(8)	502(3)
C(13)	269(5)	139.8(8)	−250(2)	F(61)	427(3)	153.5(5)	535(2)
C(14)	497(5)	116.0(9)	−168(2)	F(62)	552(4)	149.6(5)	415(2)
C(15)	565(4)	98.6(8)	−65(3)	F(63)	645(4)	142.3(8)	571(3)
C(16)	620(4)	118.4(9)	116(3)	O(91)	750(2)	−39.2(5)	246(1)
C(17)	495(5)	99.7(9)	158(2)	O(92)	738(2)	29.8(5)	238(1)
C(18)	256(8)	113(2)	182(4)	C(91)	754(3)	−5.1(8)	202(2)
C(19)	127(5)	121(2)	126(4)	C(92)	792(3)	−6.6(9)	90(2)
O(21)	583(3)	214.9(6)	86(2)	F(91)	868(2)	25.6(5)	65(1)
C(21)	629(4)	250	112(3)	F(92)	858(2)	−40.6(5)	69(1)
C(22)	774(7)	250	180(10)	F(93)	662(2)	−5.3(6)	25(1)
F(21)	820(4)	218(1)	223(3)	H(101)	−36	116	−56
F(22)	882(7)	250	120(7)	H(102)	−110	149	16
O(31)	297(3)	215.1(5)	160(1)	H(111)	−113	175	−165
C(31)	291(5)	250(3)	198(3)	H(112)	−34	207	−75
C(32)	255(9)	250(3)	307(3)	H(121)	73	115	−215
F(31)	193(4)	283.0(7)	336(2)	H(122)	46	154	−300
F(32)	383(6)	250	372(3)	H(131)	277	116	−302
O(81)	479(2)	214.9(5)	−136(1)	H(132)	300	167	−279
C(81)	507(6)	250	−169(3)	H(141)	491	93	−224
C(82)	601(9)	250	−257(4)	H(142)	562	139	−189
F(81)	494(7)	250	−347(3)	H(151)	507	74	−45
F(82)	646(4)	283.5(8)	−280(2)	H(152)	672	87	−66
Pr(2)	682.1(2)	−2.29(4)	407.38(9)	H(161)	706	96	118
O(41)	886(2)	42.7(5)	460(1)	H(162)	666	142	160
O(42)	1 122(2)	51.4(5)	529(2)	H(171)	473	70	127
C(41)	998(3)	61.6(6)	479(1)	H(172)	524	95	237
C(42)	999(5)	107(1)	433(3)	H(181)	272	82	202
F(41)	1 009(4)	135.1(6)	502(2)	H(182)	268	129	253
F(42)	1 117(4)	115(1)	395(3)	H(191)	88	91	103
F(43)	900(4)	114.5(7)	357(2)	H(192)	61	130	181
O(51)	446(2)	−7.2(6)	272(1)				

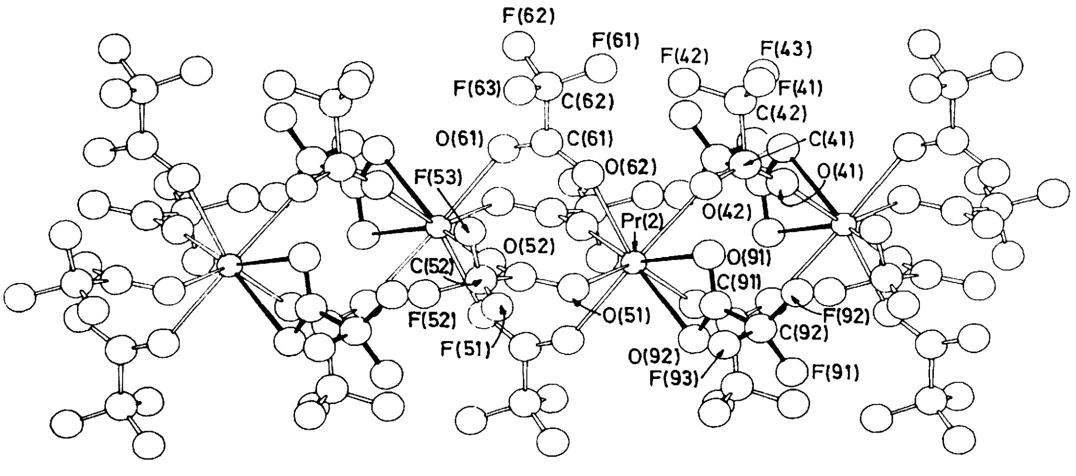

Figure 3. The polymeric anion $[\{Pr(CF_3CO_2)_4\}_n]^{n-}$ showing atomic numbering. Non-bridging $CF_3CO_2^-$ groups are shown using solid bonds

(2 − *x*, −*y*, 1 − *z*) giving rise to further centrosymmetric dimers and, overall, resulting in infinite zigzag chains of Pr(2) atoms parallel to *a* (Figure 3). The Pr(2)–O bond lengths are varied. The bidentate trifluoroacetate is symmetrically attached [Pr(2)–O(91) 2.57(2), Pr(2)–O(92) 2.56(2) Å] as is one of the μ-bridging $CF_3CO_2^-$ ions [Pr(2)–O(61) 2.47(2), Pr(2)–O(62″) 2.48(2) Å]. The two remaining trifluoroacetates are rather unsymmetrically bound. The mean Pr(2)–O distance is 2.46(2) Å,

Table 2. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses *

(*a*) Praseodymium co-ordination polyhedron			
Pr(1)-O(1)	2.31(1)	Pr(2)-O(41)	2.35(2)
Pr(1)-O(11)	2.58(3)	Pr(2)-O(51)	2.55(2)
Pr(1)-O(12)	2.59(2)	Pr(2)-O(61)	2.47(2)
Pr(1)-O(13)	2.57(2)	Pr(2)-O(91)	2.57(2)
Pr(1)-O(14)	2.61(2)	Pr(2)-O(92)	2.56(2)
Pr(1)-O(15)	2.58(2)	Pr(2)-O(42′)	2.41(2)
Pr(1)-O(21)	2.46(2)	Pr(2)-O(52″)	2.32(2)
Pr(1)-O(31)	2.46(2)	Pr(2)-O(62″)	2.48(2)
Pr(1)-O(81)	2.44(2)	Pr(2)-Pr(2′)	5.901(2)
Pr(1)-Pr(1‴)	4.158(2)	Pr(2)-Pr(2″)	4.419(2)
(*b*) Trifluoroacetates			
O(21)-C(21)	1.21(2)	C(21)-C(22)	1.44(8)
O(31)-C(31)	1.21(9)	C(31)-C(32)	1.51(6)
O(81)-C(81)	1.23(3)	C(81)-C(82)	1.54(8)
O(41)-C(41)	1.17(3)	C(41)-C(42)	1.55(4)
O(42)-C(41)	1.25(3)	C(51)-C(52)	1.46(4)
O(51)-C(51)	1.19(4)	C(61)-C(62)	1.53(3)
O(61)-C(61)	1.23(3)	C(91)-C(92)	1.55(3)
O(62)-C(61)	1.23(3)		
O(91)-C(91)	1.22(3)		
O(92)-C(91)	1.21(3)		
O(21)-C(21)-O(21‴)	132(3)	O(21)-C(21)-C(22)	114(2)
O(31)-C(31)-O(31‴)	131(2)	O(31)-C(31)-C(32)	114(7)
O(81)-C(81)-O(81‴)	128(4)	O(81)-C(81)-C(38)	116(2)
O(41)-C(41)-O(42)	131(2)	O(41)-C(41)-C(42)	117(2)
O(51)-C(51)-O(52)	133(2)	O(42)-C(41)-C(42)	112(3)
O(61)-C(61)-O(62)	130(2)	O(51)-C(51)-C(52)	114(2)
O(91)-C(91)-O(92)	127(2)	O(52)-C(51)-C(52)	113(2)
		O(61)-C(61)-C(62)	115(3)
		O(62)-C(61)-C(62)	115(3)
		O(91)-C(91)-C(92)	116(2)
		O(92)-C(91)-C(92)	116(2)
(*c*) Macrocyclic ring			
C(19)-O(11)	1.40(6)	C(14)-C(15)	1.49(4)
O(11)-C(10)	1.38(5)	C(15)-O(14)	1.42(3)
C(10)-C(11)	1.51(8)	O(14)-C(16)	1.44(4)
C(11)-O(12)	1.35(7)	C(16)-C(17)	1.47(6)
O(12)-C(12)	1.48(4)	C(17)-O(15)	1.37(5)
C(12)-C(13)	1.47(6)	O(15)-C(18)	1.38(8)
C(13)-O(13)	1.39(3)	O(18)-C(19)	1.30(8)
O(13)-C(14)	1.44(5)		
C(19)-O(11)-C(10)	113(4)	O(13)-C(14)-C(15)	104(3)
O(11)-C(10)-C(11)	104(4)	C(14)-C(15)-O(14)	108(2)
C(10)-C(11)-O(12)	112(4)	C(15)-O(14)-C(16)	114(2)
C(11)-O(12)-C(12)	116(3)	O(14)-C(16)-C(17)	110(3)
O(12)-C(12)-C(13)	106(3)	C(16)-C(17)-O(15)	109(2)
C(12)-C(13)-O(13)	106(3)	C(17)-O(15)-C(18)	113(3)
C(13)-O(13)-C(14)	108(2)	O(15)-C(18)-C(19)	114(5)
		C(18)-C(19)-O(11)	121(5)

* Key to transformations: prime (2 − *x*, −*y*, 1 − *z*); double prime (1 − *x*, −*y*, 1 − *z*); triple prime (*x*, ½ − *y*, *z*).

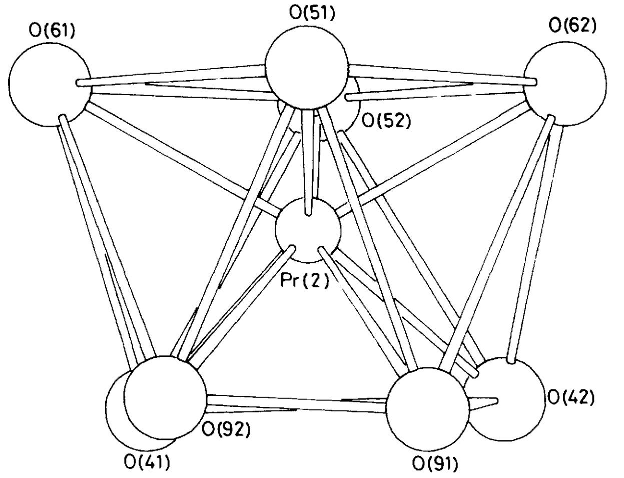

Figure 4. Co-ordination polyhedron for Pr(2)

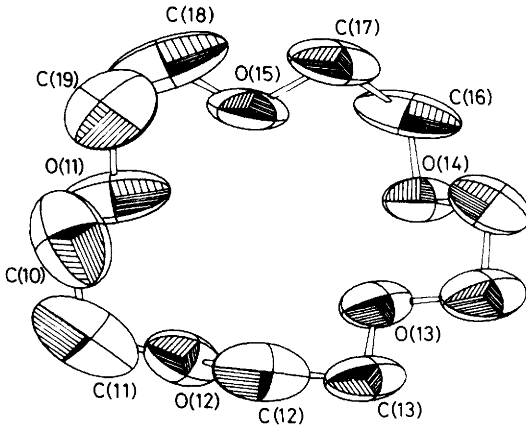

Figure 5. Conformation of the 15-crown-5 ether

which is the same as that of Pr(1) to the trifluoroacetate O atoms. There are two different Pr(2)-Pr(2) distances of 4.419(2) and 5.901(2) Å. The co-ordination polyhedron of Pr(2) is a more or less regular square antiprism approximating to D_{4d} symmetry (Figure 4). The two planes are O(41)O(42′)O(91)O(92) (σ = 0.090 Å) and O(51)O(52″)O(61)O(62″) (σ = 0.004 Å).

The macrocycle (Figure 5) adopts a conformation which tends to equalise all the metal–oxygen bond lengths [2.57(2)—2.61(2); mean 2.58 Å], similar to the situation observed in the complex of 15-crown-5 ether with europium nitrate,[12] although in the latter the mean Eu–O(crown) distance is rather longer (2.63 Å) with a somewhat wider range (2.55—2.69 Å). As a result, some torsion angles do not correspond to an energetically stable conformation: four O–C–C–O torsion angles (Table 3) are nearly synclinal, but the conformation of the fifth is nearly *syn*-periplanar (17°). There are also some deviations from the favoured *trans* arrangement about the C–O bonds, only seven of which can be considered *anti*-periplanar. The mean C–C and C–O distances and mean C–C–O and C–O–C angles are 1.45(6) and 1.40(5) Å and 109(4) and 113(3)° respectively. The rather wide range of individual values reflects some fluxional disorder of the ethylene moieties, notably C(10)–C(11) and C(18)–C(19), which has been previously noted in the structure of $Eu(NO_3)_3$(15-crown-5).[12]

The two components of the present structure, *i.e.* the Pr(1) dimer and Pr(2) polymer, exist as discrete entities with no significant interaction between the two. Figure 6(*a*) and (*b*) shows views of the cell down the *c* and *a* axes respectively. The zigzag chains of Pr(2) atoms are separated by the Pr(1) dimers.

Discussion

The structure of $[Pr_2(CF_3CO_2)_3(OH)(C_{10}H_{20}O_5)][Pr_2(CF_3CO_2)_8]$ contrasts markedly with the previously reported rare-earth metal nitrate crown-ether complexes[12—14] in two ways: first, in displaying lower co-ordination numbers (eight and nine) about the cations compared with 10—12 in the

Table 3. Torsional angles (°) within the macrocyclic ring

O(11)–C(10)–C(11)–O(12)	48	C(13)–O(13)–C(14)–C(15)	168	C(16)–C(17)–O(15)–C(18)	173
C(10)–C(11)–O(12)–C(12)	87	O(13)–C(14)–C(15)–O(14)	59	C(17)–O(15)–C(18)–C(19)	145
C(11)–O(12)–C(12)–O(13)	171	C(14)–C(15)–O(14)–C(16)	173	O(15)–C(18)–C(19)–O(11)	17
O(12)–C(12)–C(13)–O(13)	52	C(15)–O(14)–C(16)–C(17)	81	C(18)–C(19)–O(11)–C(10)	166
C(12)–C(13)–O(13)–C(14)	165	O(14)–C(16)–C(17)–O(15)	48	C(19)–O(11)–C(10)–C(11)	178

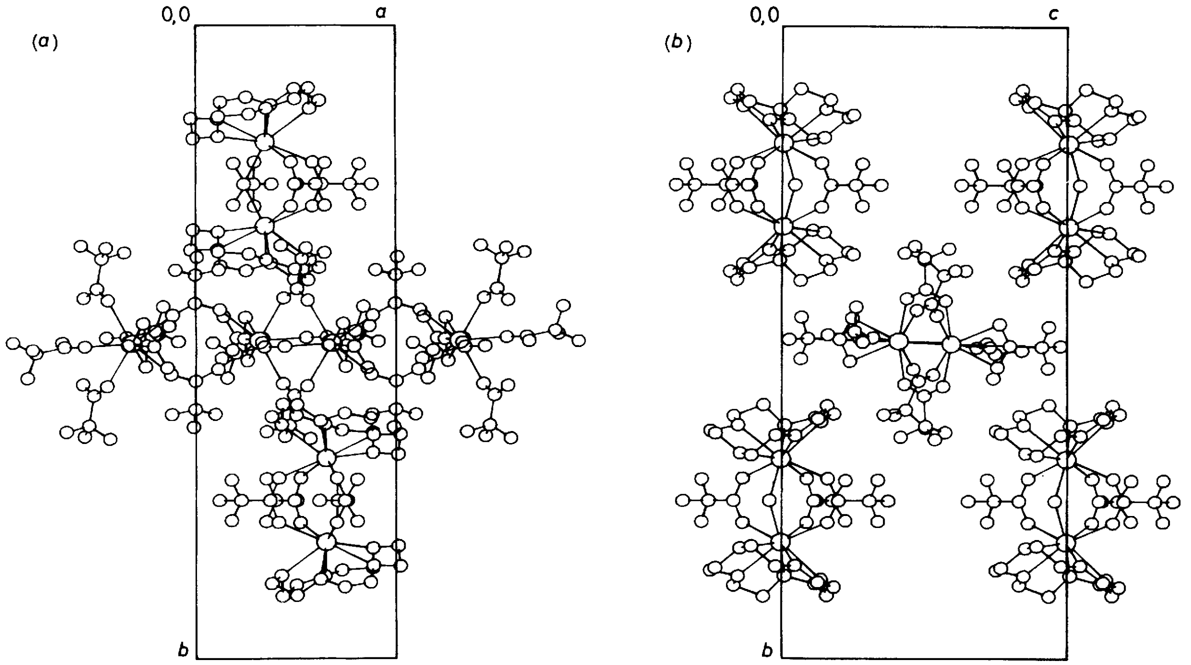

Figure 6. Cell plots; view down (*a*) *c* axis, (*b*) *a* axis

cases of the nitrates, and secondly in the formation of dimeric and polymeric structures rather than discrete complex molecules and ions containing a single cation. In all the macrocyclic complexes so far reported, the nitrate anions behave as bidentate ligands[2] and despite having one free O atom never engage in bridging to neighbouring cations. The relatively small nitrate ion can pack sufficiently close to the rare-earth cation and give a high co-ordination number which effectively blocks the possibility of bridging. In trifluoroacetates, the bulky CF_3 groups greatly increase the steric crowding at each cation to such an extent that, with one exception, the second oxygen of the trifluoroacetate cannot make a sufficiently close approach to the cation and preferentially bonds to another nearby cation. This gives rise to the oligomeric structures observed and overall lower co-ordination numbers in each cation. If this is correct, the complexes of lanthanide acetates with macrocycles if they could be synthesised would probably adopt structures of an intermediate type with possibly some bridging.

A further unusual feature is the presence of the bridging hydroxide group. The Pr(1)–O(1) distance (2.31 Å) is noticeably shorter than those reported in $Pr(OH)_3$[15] (2.54 and 2.52 Å), where each OH is triply bridging. The presence of the hydroxide was rather surprising. The analytical figures of the initial product, before recrystallisation, were consistent with the stoicheiometry $[Pr(CF_3CO_2)_3]_2(C_{10}H_{20}O_5)$. The original complex was therefore hydrolysed during the slow recrystallisation. A freshly prepared sample of the analogous complex of $Ce(CF_3CO_2)_3$ with 15-crown-5 ether showed no i.r. absorption in the region 3 500—3 800 cm^{-1}. However, when two samples were placed (*a*) in a vacuum desiccator over P_4O_{10} and (*b*) at 60 °C over P_4O_{10} *in vacuo*, both showed the presence, after 12 h, of a sharp peak at 3 610 cm^{-1} attributable to OH. After 64 h the intensity of the OH absorption had increased in both cases. Thus it appears that the complexes are slowly hydrolysed, presumably by traces of moisture. Similar hydrolysis has been noted for a samarium nitrate complex of a nitrogen macrocycle, $Sm(C_{18}H_{18}N_6)(NO_3)_3\cdot H_2O$[16] which gave rise to $[Sm(NO_3)(OH)(C_{18}H_{18}N_6)(H_2O)]NO_3\cdot 2MeOH$, and for the uranyl perchlorate complex with 2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane[17] which formed a hydroxyl-bridged complex containing $[(UO_2)_2(OH)_2(H_2O)_6]^{2+}$ when recrystallised from MeCN. In the former, the hydroxide ion is unidentate at a distance of 2.46 Å from the ten-co-ordinate Sm^{III} ion; in the latter complex, two U–OH bonds of 2.27 and 2.31 Å are reported for the bridging OH groups.

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