Crystal Structure of Tetrakis-μ-trifluoroacetato-bis[triaqua(trifluoroacetato)praseodymium(III)]

By **Stephen P. Bone** and **D. Bryan Sowerby,*** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD
Rajendar D. Verma, Department of Chemistry, Panjab University, Chandigarh 160014, India

The structure of the title compound has been determined by three-dimensional *X*-ray diffraction methods. The crystals are monoclinic, space group $P2_1/c$ with unit-cell dimensions $a = 9.30(1)$, $b = 18.94(2)$, $c = 9.88(1)$ Å, $\beta = 114.0(1)°$, and $Z = 4$. The atomic positions have been determined by Patterson and Fourier methods and refined by full-matrix least squares to *R* 0.080 for 2 944 observed reflections. The molecule, which has a dimeric structure, lies on a crystallographic centre and the two praseodymium atoms are linked by four bridging trifluoroacetate groups. The metal atoms have eight-fold co-ordination in the form of a distorted square antiprism, the co-ordination sphere being completed by oxygen atoms from a unidentate trifluoroacetate group and three hydrate water molecules. The non-bonded oxygen atom of the unidentate group participates in both intra- and intermolecular hydrogen bonding. Powder data point to the neodymium and europium analogues being isostructural with the present compound.

LANTHANOID trifluoroacetates can be obtained for a number of the 4*f* elements by crystallization of the solution obtained by dissolving the corresponding oxide or hydroxide in aqueous trifluoroacetic acid.[1] The compounds with La, Pr, Nd, Sm, and Eu have the stoicheiometry $[\mathrm{Ln(O_2CCF_3)_3}]\cdot 3\mathrm{H_2O}$.[2,3]

In common with other 'short-bite' ligands, the trifluoroacetate group can in principle behave as either a uni- or bi-dentate group, or it can bridge between two metal atoms. In contrast to the more extensively investigated nitrate and acetate systems where all three types of co-ordination have been substantiated, trifluoroacetate is known only as a unidentate or bridging group.[4] Vibrational spectroscopy can in principle differentiate between these different possible bonding modes, but generally it is difficult to make a clear distinction between the bidentate and bridging modes. Infrared spectra for the hydrated trifluoroacetates of Pr, Nd, or Eu as Nujol and halogenocarbon oil mulls all show bands at *ca.* 1 710s, *ca.* 1 660s, *ca.* 1 620s, *ca.* 1 460s, and *ca.* 1 300m $\mathrm{cm^{-1}}$, implying that the trifluoroacetate groups are not all equivalent. In addition, spectra in the $>$3 000 $\mathrm{cm^{-1}}$ region show a sharp band at *ca.* 3 660 $\mathrm{cm^{-1}}$ with two broader bands at *ca.* 3 400 and 3 200 $\mathrm{cm^{-1}}$. This series of bands implies that the (three) water molecules are also probably non-equivalent.

To resolve these problems and to determine the co-ordination number of the lanthanoid, a single-crystal *X*-ray structure determination has been carried out on the praseodymium compound.

EXPERIMENTAL

The compound was prepared by adding a slight excess of praseodymium carbonate to an aqueous solution of trifluoroacetic acid. Suitable crystals were obtained by crystallization from this solution {Found: C, 13.4; H, 1.0; F, 32.0; Pr, 26.3. Calc. for $[\mathrm{Pr(O_2CCF_3)_3}]\cdot 3\mathrm{H_2O}$: C, 13.5; H, 1.1; F, 32.0; Pr, 26.4%}.

Crystal Data.—$\mathrm{C_6H_6F_9O_9Pr}$, $M = 533.9$, Monoclinic, $a = 9.30(1)$, $b = 18.94(2)$, $c = 9.88(1)$ Å, $\beta = 114.0(1)°$, $U = 1\,570.8$ Å^3, $D_c = 2.26$ g cm^{-3}, $Z = 4$, $F(000) = 1\,016$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu(\text{Mo-}K_\alpha) = 32.5$ cm^{-1}, space group $P2_1/c$ from systematic absences $h0l$ when $l = 2n + 1$ and $0k0$ when $k = 2n + 1$. Crystal dimensions were *ca.* $0.25 \times 0.15 \times 0.15$ mm.

---

[1] R. Hara and G. H. Cady, *J. Amer. Chem. Soc.*, 1954, **76**, 4285.

[2] J. E. Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 1087.

[3] R. D. Verma and G. H. Cady, unpublished work.

[4] C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 1.

The unit-cell dimensions originally obtained from oscillation and Weissenberg photographs were refined by a least-squares procedure on the positions of 12 strong reflections, accurately measured on a Hilger and Watts four-circle diffractometer. Intensity data were then collected using an ω—2θ scan for 3 770 reflections in the range $0 \leqslant \theta \leqslant 27.5°$, with Mo-$K_\alpha$ radiation. The intensities of the 2 944 reflections for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. Data reduction and subsequent crystallographic calculations used the CRYSTALS programs;[5] atomic scattering factors were taken from ref. 6.

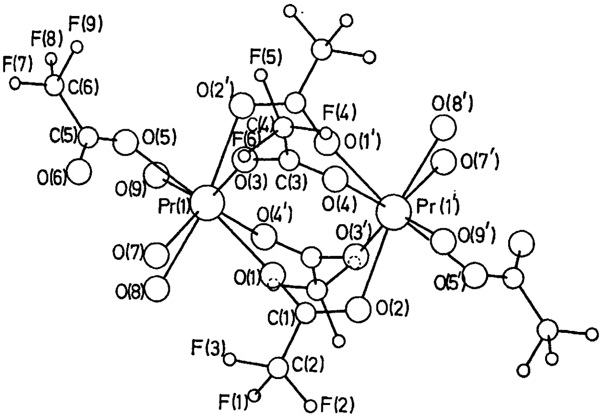

FIGURE 1 Structure of the compound showing the atom-numbering system

A three-dimensional Patterson synthesis showed the expected two double-weight and one single-weight peaks and gave the position of the praseodymium atom. A difference-Fourier synthesis phased on this atom then gave possible positions for all except two of the non-hydrogen atoms. After one cycle of full-matrix least-squares refinement R was reduced to 0.143 and a second difference Fourier revealed the two missing fluorine atoms. Three more cycles of refinement gave convergence with isotropic thermal parameters at R 0.119, and with anisotropic thermal parameters R converged at 0.080 after another three cycles of refinement. The data were not weighted. A final difference-Fourier showed a number of peaks close to the heavy atom and evidence of disorder in the trifluoromethyl groups. Attempts to treat the CF_3 groups as six half-fluorines attached to carbon did not lead to an improvement in the refinement. It was not possible to locate the hydrogen atoms of the water molecules.

Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22334 (29 pp).* Final values for the atomic co-ordinates are listed in Table 1, while bond distances and angles are in Table 2. The atom-numbering scheme is shown in Figure 1.

TABLE 1

Atomic co-ordinates ($\times 10^3$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Pr(1)	298.2(1)	431.5(4)	475.3(1)
O(1)	533.7(14)	420.2(8)	430.4(15)
O(2)	750.7(13)	456.3(6)	413.1(15)
O(3)	513.2(14)	437.3(7)	718.5(12)
O(4)	731.8(14)	489.6(6)	730.7(13)
O(5)	165.2(14)	385.4(6)	624.7(14)
O(6)	241.5(19)	277.3(7)	711.3(18)
O(7)	386.4(13)	306.7(6)	530.9(16)
O(8)	173.5(17)	360.6(8)	245.2(16)
O(9)	13.5(13)	464.9(6)	347.6(13)
C(1)	647(2)	418(1)	396(2)
C(2)	666(4)	339(1)	338(4)
C(3)	654(2)	456(1)	780(2)
C(4)	735(3)	435(2)	945(2)
C(5)	164(3)	332(1)	698(2)
C(6)	68(5)	336(2)	781(4)
F(1)	542(3)	333(1)	197(3)
F(2)	787(2)	331(8)	317(3)
F(3)	626(4)	289(1)	401(3)
F(4)	883(2)	448(2)	1 001(2)
F(5)	655(2)	452(2)	1 021(2)
F(6)	741(4)	365(1)	953(3)
F(7)	38(4)	283(1)	836(5)
F(8)	−36(4)	380(2)	750(4)
F(9)	153(5)	360(3)	915(5)

TABLE 2

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Pr(1)–O(1)	2.41(1)	C(5)–O(5)	1.24(2)
Pr(1)–O(2') *	2.52(1)	C(5)–O(6)	1.25(2)
Pr(1)–O(3)	2.42(1)	C(5)–C(6)	1.44(3)
Pr(1)–O(4')	2.45(1)	C(6)–F(7)	1.22(3)
Pr(1)–O(5)	2.44(1)	C(6)–F(8)	1.22(3)
Pr(1)–O(7)	2.49(1)	C(6)–F(9)	1.32(5)
Pr(1)–O(8)	2.48(1)		
Pr(1)–O(9)	2.51(1)		
C(1)–O(1')	1.24(2)	C(3)–O(3)	1.25(2)
C(1)–O(2')	1.24(2)	C(3)–O(4')	1.21(2)
C(1)–C(2)	1.53(3)	C(3)–C(4)	1.55(3)
C(2)–F(1)	1.40(4)	C(4)–F(4)	1.28(3)
C(2)–F(2)	1.24(3)	C(4)–F(5)	1.30(3)
C(2)–F(3)	1.28(3)	C(4)–F(6)	1.33(3)
O(1)–Pr(1)–O(2')	119.6(4)	O(2')–Pr(1)–O(3)	75.6(4)
O(1)–Pr(1)–O(3)	75.1(5)	O(2')–Pr(1)–O(4')	82.5(4)
O(1)–Pr(1)–O(4')	72.9(4)	O(2')–Pr(1)–O(5)	79.1(4)
O(1)–Pr(1)–O(5)	143.2(4)	O(2')–Pr(1)–O(7)	143.8(5)
O(1)–Pr(1)–O(7)	73.4(4)	O(2')–Pr(1)–O(8)	139.1(4)
O(1)–Pr(1)–O(8)	84.5(5)	O(2')–Pr(1)–O(9)	70.5(4)
O(1)–Pr(1)–O(9)	141.4(4)		
O(3)–Pr(1)–O(4')	124.4(4)	O(4')–Pr(1)–O(5)	143.8(4)
O(3)–Pr(1)–O(5)	80.4(4)	O(4')–Pr(1)–O(7)	132.8(5)
O(3)–Pr(1)–O(7)	76.1(5)	O(4')–Pr(1)–O(8)	73.5(5)
O(3)–Pr(1)–O(8)	145.2(5)	O(4')–Pr(1)–O(9)	71.8(4)
O(3)–Pr(1)–O(9)	139.8(4)		
O(5)–Pr(1)–O(7)	74.3(4)	O(7)–Pr(1)–O(8)	71.2(5)
O(5)–Pr(1)–O(8)	101.4(5)	O(7)–Pr(1)–O(9)	122.4(4)
O(5)–Pr(1)–O(9)	72.7(4)	O(8)–Pr(1)–O(9)	70.9(4)
Pr(1)–O(1)–C(1)	175(1)	Pr(1)–O(3)–C(3)	141(1)
Pr(1')–O(2)–C(1)	111(1)	Pr(1')–O(4)–C(3)	141(1)
O(1)–C(1)–C(2)	118(2)	O(3)–C(3)–C(4)	114(2)
O(2)–C(1)–C(2)	117(2)	O(4)–C(3)–C(4)	116(2)
O(1)–C(1)–O(2)	125(2)	O(3)–C(3)–O(4)	130(2)
C(1)–C(2)–F(1)	106(2)	C(3)–C(4)–F(4)	113(2)
C(1)–C(2)–F(2)	116(2)	C(3)–C(4)–F(5)	113(2)
C(1)–C(2)–F(3)	113(2)	C(3)–C(4)–F(6)	108(2)
Pr(1)–O(5)–C(5)	140(1)	O(5)–C(5)–O(6)	127(2)
O(5)–C(5)–O(6)	127(2)	C(5)–C(6)–F(7)	122(2)
O(5)–C(5)–C(6)	117(2)	C(5)–C(6)–F(8)	120(2)
O(6)–C(5)–C(6)	116(2)	C(5)–C(6)–F(9)	109(3)

* Primed atoms are related to unprimed atoms by the transformation $x,y,z \rightarrow 1 - x, 1 - y, 1 - z$.

---

* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[5] J. R. Carruthers, 'The Oxford Crystallographic Package-CRYSTALS.'

[6] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

DISCUSSION

Description of the Structure.—As shown in Figure 1 the solid-state structure of the compound is a centrosymmetric dimer with four bridging and two unidentate trifluoroacetate groups. Each metal atom is thus co-ordinated to four oxygen atoms from the bridging groups, one oxygen from the unidentate group, and three oxygens from the hydrate water molecules giving a polyhedron best described as a distorted square antiprism. The final state of refinement of the structure is only moderate (*R* 0.080) and this is reflected in the relatively high standard deviations shown for some of the data in Table 2. The trifluoromethyl groups, as is often found, are disordered and thermal parameters for the fluorine atoms are high; in addition high thermal parameters are found for O(6), the non-bonded oxygen of the unidentate trifluoroacetate, and for the carbon atoms [C(2), C(4), find C(6)] of the CF_3 groups. In the O_2CCF_3 groups the mean C–F distance is 1.29 Å (variation between 1.22 and 1.40 Å), the mean C–C–F angle is 113° (variation between 106 and 122°), and the mean F–C–F angle is 104° (variation between 89 and 118°). Within experimental error, the C–O distances in the three independent trifluoroacetate groups are equal (mean 1.24 Å). This is surprising since the unidentate group contains a formal C=O [C(5)–O(6)] grouping. Another anomaly in this group is the short C(5)–C(6) distance (1.44 Å) while the normal C–C distance (1.54 Å) is found for the bridging groups. The O–C–O angles in all the three carboxylate groups are equal (mean 127°) and the angles at each carboxylate carbon atom sum to 360°. The Pr · · · Pr distance is 4.42 Å.

The praseodymium–oxygen distances fall in the range 2.41—2.52 Å (mean 2.47 Å) with those involving the hydrate water being on average slightly longer than those to the trifluoroacetate. The distance between the metal and the non-bonded oxygen [O(6)] of the unidentate trifluoroacetate group is 3.90 Å. The trifluoroacetate group containing O(3) and O(4) forms a symmetrical bridge between the two metal atoms with Pr–O distances of 2.42 and 2.45 Å, and Pr–O–C(3) angles of 141°. The second bridging group is highly unsymmetrical with distances of 2.41 and 2.52 Å to O(1) and O(2) respectively and corresponding Pr–O–C(1) angles of 175 and 111°. It should be noted here that the Pr(1)–O(1′) distance [3.16(2) Å] is too great to be considered as a bonding interaction. The metal–oxygen distance in the unidentate group is 2.44 Å and the Pr–O(5)–C(5) angle is 140°; both values are close to those found in the symmetrical bridging group.

Although it has not been possible to locate the hydrogen atoms of the three water molecules, there are three short O · · · O contacts which also give acceptable angles with atoms attached to each of the oxygen atoms, and the presence of hydrogen bonds can be inferred with some certainty. The formally double-bonded oxygen atom [O(6)] of the unidentate group is involved in two such interactions forming (*a*) an intramolecular hydrogen bond to O(7) (length 2.69 Å) and (*b*) an intermolecular bond to O(8) (length 2.74 Å). The positions of these interactions are indicated in Figure 2, which shows the unit-cell contents projected down the *a* axis. Figure 3 shows a projection down the *c* axis and includes, in addition to the O(6) · · · O(7) hydrogen bond, the position of the intermolecular bonds between O(9) and O(2) (length 2.78 Å). There are two more short O · · · O intramolecular contacts (2.89 Å) between O(8) and O(9) and O(7) and O(8) respectively but the angles to the metal in these cases are *ca.* 55°.

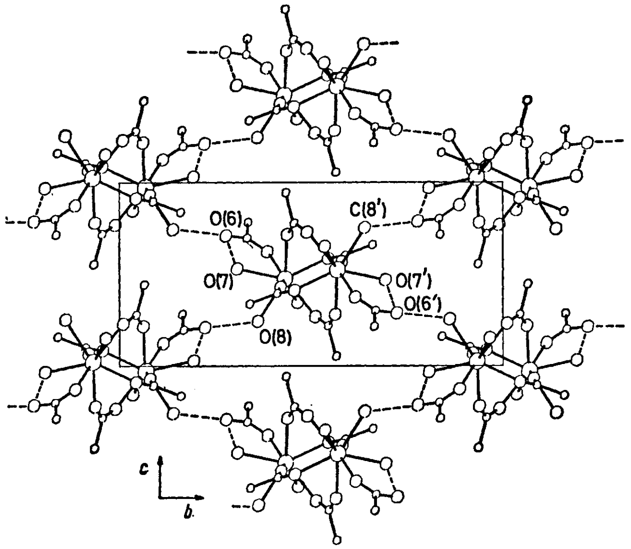

FIGURE 2 Projection of the unit cell down the *a* axis showing the hydrogen bonds to O(6)

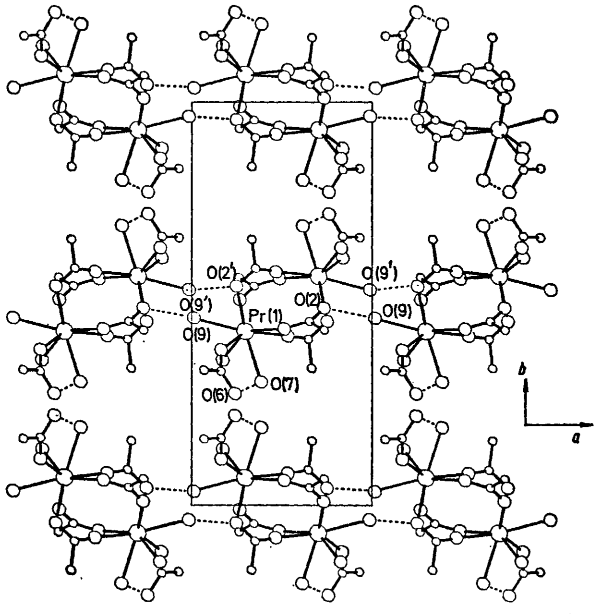

FIGURE 3 Projection of the unit cell down the *c* axis showing the O(6) · · · O(7) and O(2) · · · O(9) hydrogen bonds

Co-ordination about Praseodymium.—Each metal atom in the dimer is considered to be in distorted square-antiprismatic co-ordination. As shown in Figure 4 the oxygen atoms O(1), O(2′), O(3), and O(4′) of the bridging carboxylates form one face, while the second face contains O(5), O(7), O(8), and O(9). The dimensions included in Figure 4 show the extent to which the faces are distorted from the ideal square; this is also shown by the deviations of the atoms from the best plane through the two sets of atoms (see Table 3). For the O(1)–O(4) face the mean deviation is 0.054 Å but for the O(5), O(7)–O(9) face the value is much greater (0.180 Å) probably representing the lower symmetry of the ligand environment. The praseodymium atom is not symmetrically placed with respect to these two planes, the distances being 1.18 and 1.38 Å respectively, but the angle between the two planes is 3.4°, close to the parallelity required for antiprismatic co-ordination. Further confirmation of the presence of this co-ordination polyhedron follows from the dihedral angles given in Table 4.

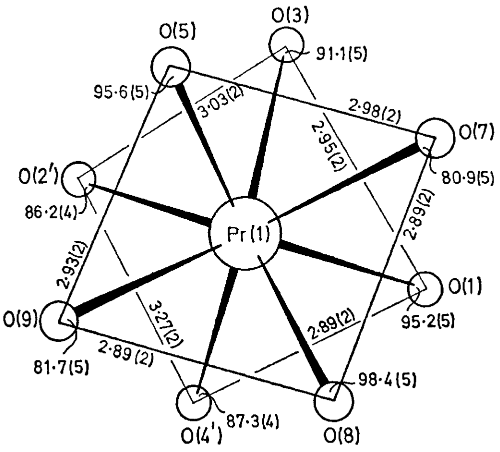

FIGURE 4 Co-ordination polyhedron about Pr^{III}

TABLE 3

Equations of mean planes and distances (Å) of relevant atoms from the plane

Plane (1): O(1)O(2′)O(3)O(4′)

$$-5.808x - 14.364y + 0.837z = -8.717$$

[Pr(1) 1.184, O(1) −0.058, O(2′) −0.050, O(3) 0.056, O(4′) 0.053]

Plane (2): O(5)O(7)O(8)O(9)

$$6.138x + 13.639y - 0.730z = 5.989$$

[Pr(1) 1.380, O(5) −0.175, O(7) 0.178, O(8) −0.184, O(9) 0.181]

Plane (3): O(1)O(2)O(3)O(4)

$$-3.368x + 16.435y - 1.609z = 4.358$$

[Pr(1) 0.058, O(2) −0.052, O(3) −0.055, O(4) 0.048]

Plane (4): O(1′)O(2′)O(3)O(4)

$$1.622x - 8.418y - 8.627z = -9.140$$

[O(1′) 0.101, O(2′) −0.096, O(3) 0.093, O(4) −0.098]

Ideally, the polyhedron described by the eight oxygen atoms of the bridging carboxylate groups between the two praseodymium atoms should be a tetragonal prism, but this is not the case as shown by the dimensions included in Figure 5 and by the appropriate dihedral angles in Table 4. The angles in the polyhedron, which vary between 65.0 and 117.6°, imply skewing of the tetragonal prism along the O(1)–O(2′) diagonal. This allows the angles at O(3) and O(4′) in the resulting parallelepiped to remain close to 90°, and consequently the Pr–O–C angles at O(3) and O(4′) in the bridging carboxylate are both close to 140°. The corresponding angles at O(1) and O(2) (175 and 111°) show the effect of the distortion. It is difficult at first sight to see why the distortion takes place since it seems unconnected with the Pr(1) · · · Pr(1′) distance or with simple electrostatic interactions. Certainly, in the skewed version the oxygen atoms at the eight vertices are removed from the eclipsed positions of the ideal polyhedron, but because the eclipsed atoms are those of a given carboxylate group this effect is likely to be small.

TABLE 4

Dihedral angles between plane (*a*) and plane (*b*)

Plane (*a*)	Plane (*b*)	Dihedral angle (°)
O(1)O(2′)O(3)O(4′)	O(5)O(7)O(8)O(9)	3.4
	O(1)O(2)O(3)O(4)	111.7
	O(1′)O(2′)O(3)O(4)	67.0
	Pr(1)O(1)O(2′)	87.5
	Pr(1)O(3)O(4′)	95.3
	Pr(1)O(5)O(8)	94.4
	Pr(1)O(7)O(9)	86.2
O(5)O(7)O(8)O(9)	O(1)O(2)O(3)O(4)	71.7
	O(1′)O(2′)O(3)O(4)	113.1
	Pr(1)O(1)O(2′)	89.9
	Pr(1)O(3)O(4′)	87.1
	Pr(1)O(5)O(8)	89.0
	Pr(1)O(7)O(9)	93.5
O(1)O(2)O(3)O(4)	O(1′)O(2′)O(3)O(4)	98.7
Pr(1)O(1)O(2′)	Pr(1)O(3)O(4′)	93.2
	Pr(1)O(5)O(8)	46.4
	Pr(1)O(7)O(9)	43.2
Pr(1)O(3)O(4)	Pr(1)O(5)O(8)	40.4
	Pr(1)O(7)O(9)	50.4
Pr(1)O(5)O(8)	Pr(1)O(7)O(9)	90.5

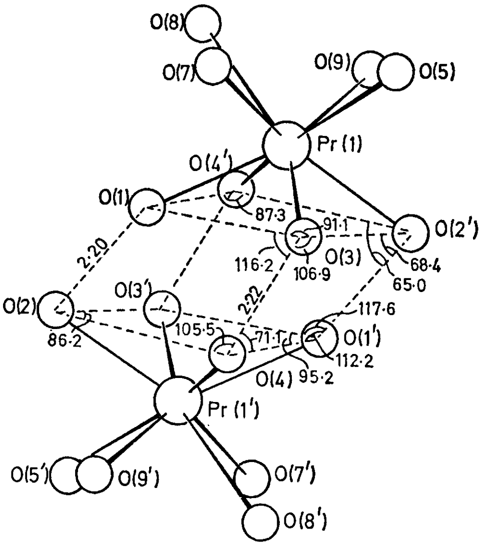

FIGURE 5 Dimensions of the polyhedron between the two metal atoms

In the ideal undistorted state a line through the two praseodymium atoms would be coincident with the $\bar{8}$

axes of the antiprismatic arrangement at each metal atom, and the Pr(1′)–Pr(1)–O angles would be expected to have values close to 58°, *i.e.* that calculated on the hard-sphere model for square-antiprismatic co-ordination.[7]

A simple calculation based on the undistorted structure shows that if the Pr–O–C angles were all 140° and the O–C–O carboxylate angles were allowed to expand to 130°, the maximum reasonable values, the Pr–Pr–O angles would increase to 65°. This is too large to support square-antiprismatic co-ordination at the metal and the only means of lowering this angle toward the 58° ideal value, in the absence of skewing the structure, would be to increase even further the Pr–O–C and O–C–O angles. The observed effects of the distortion of the structure are the reduction of the O(1)–C(1)–O(2) angle to 125° and the reduction of the angles defining the square antiprism, *i.e.* half the requisite O–Pr–O angle, to 60 and 62° for O(1) and O(2′) and O(3) and O(4′) respectively.

Comparison with Other Lanthanoid Carboxylate Structures.—In neutral carboxylate complexes of the trivalent lanthanoid elements the co-ordination number of the central atom is often eight or nine and, because of the ligand potential for chelating and bridging, structures based on monomeric, centrosymmetric dimeric, or chain polymeric units are known. Formally, the compounds most similar to $[Pr(O_2CCF_3)_3]\cdot3H_2O$ for which structures are available are the hydrated acetates $[Er(O_2CMe)_3]\cdot4H_2O$[8] and $[Ce(O_2CMe)_3]\cdot H_2O$.[9] Although the co-ordination number of the metal in each case is nine, the basic unit for the erbium compound is a bridged dimer while in cerium a linear polymer is formed. In the former the metal is co-ordinated to two chelating acetate groups (Er–O 2.30, 2.49 and 2.41, 2.41 Å), one acetate group which is tridentate mixed bridging–chelating (Er–O 2.39, 2.48, and 2.60 Å), and two of the water molecules. For the monohydrate all the three acetate groups are bridging but here two are of the mixed bridging–chelating type. Co-ordination number nine in the form of a monocapped square antiprism is found in bis[diaquatrinicotinatopraseodymium(III)][10] where chelating, bridging, and tridentate groups are found; in the lanthanum and samarium compounds,[11] however, dimeric units are again observed but the lanthanoid is in eight-fold co-ordination to four bridging and one chelating ligand and to two water molecules. In diaquatri-isonicotinatolanthanum(III),[12] although the metal is co-ordinated to eight oxygen atoms the structure is polymeric with alternate metal atoms linked by respectively four and two bridging carboxylate groups. The erbium analogue[13] is similarly polymeric with the metal in eight-fold co-ordination, but here the repeating unit consists of two bridging and one chelating isonicotinate and two water molecules.

The dimeric structure for the hydrated trifluoroacetate reported here is based on four bridging groups and clearly shows a similarity to some of the structures mentioned above. The bridging groups are, however, of the normal type, although one is greatly distorted, and there is no evidence for behaviour as a tridentate bridging–chelating group. The presence of a unidentate carboxylate, with the consequent formation of a trihydrate, is, however, unusual since in all the examples above carboxylate groups which are not involved in bridging are invariably chelating. This is further evidence pointing to the marked reluctance of the trifluoroacetate group to behave as a chelate.

The strong similarities in the i.r. spectra of the hydrated tris(trifluoroacetates) of Y, Pr, Nd, and Eu point to structural similarities which have been confirmed for the last three trifluoroacetates by their identical *X*-ray powder-diffraction patterns.

This work was carried out under the Indo-British Universities Collaboration Scheme. We thank the British Council and the University Grants Commission, Delhi, for support, and Professor T. J. King for help and advice.

[8/261 *Received*, 14*th February*, 1978]

---

[7] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[8] L. A. Aslanov I. K. Abdul'minev M. A. Porai-Koshits, and V. I. Ivanov, *Doklady Chem.*, 1972, **205**, 568.

[9] G. G. Sadikov, G. A. Kukina, and M. A. Porai-Koshits, *J. Struct. Chem.*, 1967, **8**, 492.

[10] L. A. Aslanov, I. K. Abdul'minev, and M. A. Porai-Koshits, *J. Struct. Chem.*, 1972, **13**, 437.

[11] J. W. Moore, M. D. Glick, and W. A. Baker, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 1858.

[12] J. Kay, J. W. Moore, and M. D. Glick, *Inorg. Chem.*, 1972, **11**, 2818.

[13] I. K. Abdul'minev, L. A. Aslanov, M. A. Porai-Koshits, and R. A. Chupakhina, *J. Struct. Chem.*, 1973, **14**, 348.