

## The Crystal and Molecular Structure of the Hydrated Praseodymium Chelate of 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione, $\text{Pr}_2(\text{fod})_6 \cdot 2\text{H}_2\text{O}$

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The crystal structure of the hydrated  $\beta$ -diketonate with empirical formula  $\text{Pr}[\text{CF}_3(\text{CF}_2)_2\text{COCH}\cdot\text{CO}\cdot\text{C}(\text{CH}_3)_3]_3\cdot\text{H}_2\text{O}$  has been determined from 3706 intensities obtained by counter methods at room temperature using  $\text{Mo K}\alpha$  (Zr filter) X-radiation. The crystals are monoclinic with space group  $P2_1/n$  and cell dimensions of  $a=14\cdot280$  (9),  $b=25\cdot589$  (7),  $c=23\cdot182$  (7) Å and  $\beta=100\cdot62^\circ$  (4). The density, measured by flotation, is  $1\cdot65\text{ g}\cdot\text{cm}^{-3}$  and the density calculated for two crystallographically independent formula units, *i.e.* for  $Z=8$ , is  $1\cdot646\text{ g}\cdot\text{cm}^{-3}$ . The intensity of a strong reference reflexion decreased consistently during data collection, because of slight crystal decomposition. The structure was refined by least-squares methods and converged to a conventional  $R$  of 0.085. The two independent formula units were found to constitute a dimer which is formed through bridging across two carbonyl oxygen atoms as well as a molecule of water. The other water molecule was found to be situated between two perfluoro side-chains. The oxygen atom of this water molecule as well as the neighbouring  $-\text{CF}_3$  groups are extremely poorly defined on electron density maps and it appears that the decomposition which occurs on X-irradiation is mainly dehydration in this region. This probably involves the rupture of hydrogen bonds and leads to considerable disorder. All other fluorine atoms are characterized by exceptionally high Debye-Waller factors as is to be expected for a loosely packed volatile diketonate. Both praseodymium atoms are eight-coordinate, but the coordination geometries are different and related to a dodecahedron and a bicapped trigonal prism respectively. The parent octahedra are also different, being *trans* and *cis* respectively.

### Introduction

The  $\beta$ -diketonate  $\text{CF}_3(\text{CF}_2)_2\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}(\text{CH}_3)_3$ , H(fod), forms volatile lanthanide complexes which usually occur as hydrates with empirical formula  $\text{Ln}(\text{fod})_3\cdot\text{H}_2\text{O}$  (Springer, Meek & Sievers, 1967). These authors found that the complexes could be easily dehydrated and concluded that the water was not coordinated to the metal ion. This raised the possibility that the anhydrous materials could be unusual examples of six-coordinate rare-earth chelates. The present study attempts to resolve these surmises crystallographically and to throw more light on the structural aspects of the volatile chelates of the lanthanides.

### Crystal data

The material, kindly supplied by Dr C. S. Springer of Aerospace Research Laboratories, Dayton, Ohio (Now at SUNY at Stony Brook) was recrystallized from *n*-hexane and investigated by conventional oscillation, Weissenberg and precession X-ray methods. The crystals are monoclinic and the cell dimensions, as refined on a four-circle diffractometer using a modified version of the Busing & Levy (1967) least-squares program to refine lattice parameters and determine the orientation matrix, are:

$$a=14\cdot280 \pm 0\cdot009, b=25\cdot589 \pm 0\cdot007, \\ c=23\cdot182 \pm 0\cdot007 \text{ \AA}, \beta=100\cdot62 \pm 0\cdot04^\circ.$$

The reflexion conditions:  $h0l$  for  $h+l=2n$  and  $0k0$  for  $k=2n$  uniquely define space group No. 14 (*International Tables for X-ray Crystallography*, 1965) in the setting  $P2_1/n$ . The density was measured by flotation as  $1\cdot65\text{ g}\cdot\text{cm}^{-3}$  and calculated as  $1\cdot646\text{ g}\cdot\text{cm}^{-3}$  for 8 formula units per unit cell.

### Determination of the structure

Intensity data for the sphere with  $\sin \theta/\lambda \leq 0\cdot4822$  were collected on a Hilger & Watts single-crystal diffractometer using Zr filtered  $\text{Mo K}\alpha$  radiation. An  $\omega$ -scan of

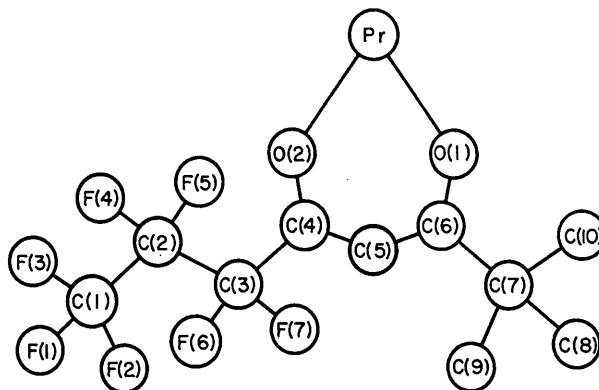


Fig. 1. Schematic drawing of a bidentate ligand chelated to a praseodymium ion. The atoms in each of the six rings in the asymmetric unit are numbered according to the scheme shown here.

sixty  $0.02^\circ$  steps with a counting time of 2 seconds per step was made across each reflexion. Background corrections were applied by measuring the general background as a function of  $\theta$  parallel to a central lattice

row and subtracting appropriately scaled values from the measured integrated intensities. Only the 3706 intensities significantly above the background were used in the analysis after correction for  $L_p$  using a

Table 1. *Fractional atomic coordinates and individual isotropic thermal parameters ( $\text{\AA}^2$ ) with their standard deviations*

The six chelate rings are numbered in Roman numerals and the atoms in each ring according to the scheme of Fig. 1. Parameters of the atoms indicated by asterisks were not refined and  $B$  factors of  $30\text{\AA}^2$  were assigned to these in the final structure factor calculation.

Atom	Ring	x	y	z	B
O(1)	I	0.8543 (14)	0.0230 (8)	0.1879 (9)	6.32 (50)
O(2)	I	0.7569 (14)	0.1105 (8)	0.1419 (9)	5.78 (45)
C(1)	I	0.4500	0.1200	0.0400	*
C(2)	I	0.5523 (48)	0.1168 (29)	0.0728 (31)	15.5 (1.6)
C(3)	I	0.6446 (26)	0.1048 (15)	0.0555 (16)	7.0 (0.8)
C(4)	I	0.7223 (25)	0.0789 (15)	0.1049 (16)	7.2 (0.9)
C(5)	I	0.7400 (24)	0.0283 (14)	0.1017 (15)	7.1 (0.9)
C(6)	I	0.8082 (24)	-0.0001 (13)	0.1438 (15)	6.4 (0.8)
C(7)	I	0.6827 (25)	0.4423 (13)	0.3634 (15)	6.4 (0.8)
C(8)	I	0.7705 (41)	0.4136 (22)	0.3661 (24)	14.8 (1.7)
C(9)	I	0.6492 (35)	0.4323 (19)	0.4191 (22)	12.7 (1.5)
C(10)	I	0.6033 (31)	0.4209 (17)	0.3156 (20)	10.86 (1.2)
F(1)	I	0.5200	0.0450	0.0400	*
F(2)	I	0.4799 (38)	0.1324 (22)	-0.0026 (24)	26.2 (1.7)
F(3)	I	0.3993 (42)	0.1246 (24)	0.0732 (25)	28.6 (1.9)
F(4)	I	0.5221 (32)	0.0723 (20)	0.1133 (21)	21.8 (1.4)
F(5)	I	0.5594 (27)	0.1402 (16)	0.1264 (18)	19.0 (1.2)
F(6)	I	0.6327 (20)	0.0746 (11)	0.0082 (13)	13.4 (0.8)
F(7)	I	0.6754 (16)	0.1498 (10)	0.0393 (10)	10.6 (0.6)
O(1)	II	0.7228 (14)	0.0700 (8)	0.2680 (9)	5.98 (47)
O(2)	II	0.8091 (14)	0.1615 (8)	0.3094 (9)	5.71 (49)
C(1)	II	0.8800	0.2200	0.5000	*
C(2)	II	0.8400	0.2050	0.4400	*
C(3)	II	0.7755 (38)	0.1980 (21)	0.4012 (22)	12.0 (1.3)
C(4)	II	0.7471 (22)	0.1550 (12)	0.3424 (13)	5.1 (0.7)
C(5)	II	0.6871 (23)	0.1162 (13)	0.3471 (14)	6.5 (0.8)
C(6)	II	0.6708 (22)	0.0754 (12)	0.3057 (14)	5.4 (0.7)
C(7)	II	0.6013 (26)	0.0300 (15)	0.3100 (16)	7.2 (0.9)
C(8)	II	0.5068 (42)	0.0528 (22)	0.3181 (24)	14.9 (1.8)
C(9)	II	0.6079 (44)	-0.0140 (26)	0.2776 (28)	17.4 (1.9)
C(10)	II	0.6277 (43)	0.0050 (25)	0.3668 (29)	17.1 (2.0)
F(1)	II	0.8323 (43)	0.2604 (22)	0.4648 (25)	27.1 (1.7)
F(2)	II	0.4415 (38)	0.3134 (20)	0.0156 (22)	24.5 (1.6)
F(3)	II	0.3133 (45)	0.2794 (25)	0.0046 (26)	29.4 (1.9)
F(4)	II	0.8293 (35)	0.1454 (18)	0.4678 (21)	23.0 (1.5)
F(5)	II	0.9130 (36)	0.2069 (21)	0.4128 (22)	25.1 (1.5)
F(6)	II	0.6839 (19)	0.1995 (10)	0.4146 (11)	12.1 (0.7)
F(7)	II	0.7678 (21)	0.2416 (12)	0.3675 (13)	14.0 (0.8)
O(1)	III	0.9401 (14)	0.0495 (8)	0.3120 (9)	6.09 (49)
O(2)	III	0.0261 (14)	0.0944 (7)	0.2212 (8)	4.84 (45)
C(1)	III	0.2350 (43)	0.0141 (26)	0.1099 (27)	13.8 (1.7)
C(2)	III	0.1482 (28)	0.0220 (16)	0.1505 (17)	8.2 (0.9)
C(3)	III	0.1677 (25)	0.0525 (14)	0.2059 (15)	6.6 (0.8)
C(4)	III	0.0849 (21)	0.0573 (12)	0.2412 (13)	4.9 (0.7)
C(5)	III	0.0809 (21)	0.0185 (12)	0.2818 (13)	5.5 (0.7)
C(6)	III	0.0085 (21)	0.0190 (11)	0.3159 (12)	4.6 (0.6)
C(7)	III	0.4877 (25)	0.4769 (14)	0.1361 (16)	7.1 (0.9)
C(8)	III	0.0952 (41)	-0.0125 (22)	0.4117 (25)	15.4 (1.7)
C(9)	III	0.4668 (30)	0.4239 (17)	0.1576 (19)	10.4 (1.1)
C(10)	III	0.5796 (35)	0.4736 (19)	0.1138 (21)	12.6 (1.5)
F(1)	III	0.1902 (25)	-0.0134 (14)	0.0659 (16)	17.4 (1.1)
F(2)	III	0.2132 (21)	0.0650 (13)	0.0864 (13)	14.6 (0.9)
F(3)	III	0.3075 (25)	0.0148 (14)	0.1413 (15)	16.8 (1.0)
F(4)	III	0.0614 (18)	0.0316 (9)	0.1219 (11)	11.2 (0.7)
F(5)	III	0.3588 (16)	0.4707 (10)	0.3330 (10)	11.2 (0.6)
F(6)	III	0.1893 (12)	0.1006 (7)	0.1894 (7)	6.4 (0.4)
F(7)	III	0.2482 (15)	0.0367 (8)	0.2402 (9)	8.5 (0.5)

Table 1 (cont.)

	Ring	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
O(1)	IV	0.0877 (14)	0.2627 (8)	0.2827 (8)	5.65 (45)
O(2)		0.0857 (15)	0.2716 (9)	0.1644 (9)	7.03 (54)
C(1)		0.1150	0.4100	0.0400	*
C(2)		0.0911 (46)	0.3752 (24)	0.1043 (26)	14.9 (1.9)
C(3)		0.1300	0.3550	0.1400	*
C(4)		0.1107 (30)	0.3173 (18)	0.1799 (20)	10.1 (1.1)
C(5)		0.1176 (29)	0.3397 (16)	0.2327 (20)	9.3 (1.1)
C(6)		0.1045 (22)	0.3114 (14)	0.2833 (14)	6.1 (0.8)
C(7)		0.1038 (30)	0.3396 (17)	0.3407 (18)	8.6 (1.0)
C(8)		0.0816 (37)	0.3048 (21)	0.3903 (23)	14.0 (1.6)
C(9)		0.0596 (43)	0.3884 (27)	0.3312 (27)	17.1 (1.9)
C(10)		0.2022 (43)	0.3503 (23)	0.3679 (26)	15.7 (1.8)
F(1)		0.0949 (27)	0.3867 (14)	0.0123 (15)	16.8 (1.0)
F(2)		0.1800	0.4200	0.0360	*
F(3)		0.0286 (28)	0.4353 (15)	0.0278 (17)	18.2 (1.3)
F(4)		0.0134 (23)	0.3955 (13)	0.1285 (14)	15.9 (0.9)
F(5)		0.0108 (22)	0.3385 (12)	0.0767 (13)	14.4 (0.9)
F(6)	0.2016 (28)	0.3921 (16)	0.1527 (17)	18.9 (0.8)	
F(7)	0.1810 (22)	0.3218 (13)	0.0882 (14)	15.1 (0.9)	
O(1)	V	0.2532 (15)	0.2114 (8)	0.2239 (9)	5.81 (49)
O(2)		0.1829 (15)	0.1505 (7)	0.3044 (9)	5.73 (46)
C(1)		0.2440 (42)	0.1016 (22)	0.4993 (25)	12.8 (1.5)
C(2)		0.2259 (29)	0.1403 (16)	0.4338 (17)	8.0 (0.9)
C(3)		0.2872 (28)	0.1272 (16)	0.3902 (17)	8.0 (0.9)
C(4)		0.2730 (23)	0.1587 (12)	0.3335 (14)	5.6 (0.7)
C(5)		0.3430 (22)	0.1854 (13)	0.3164 (14)	6.4 (0.8)
C(6)		0.3303 (24)	0.2115 (13)	0.2610 (15)	6.5 (0.8)
C(7)		0.4195 (30)	0.2411 (17)	0.2423 (19)	8.9 (1.0)
C(8)		0.5035 (41)	0.2040 (23)	0.2517 (25)	15.0 (1.8)
C(9)		0.4361 (36)	0.2835 (21)	0.2793 (23)	13.3 (1.6)
C(10)		0.3966 (39)	0.2559 (22)	0.1803 (26)	14.9 (1.8)
F(1)		0.8197 (23)	0.3568 (13)	0.0196 (13)	15.2 (0.9)
F(2)		0.6790 (24)	0.3691 (13)	0.0206 (14)	15.8 (1.0)
F(3)		0.2784 (26)	0.0689 (14)	0.4914 (16)	17.4 (1.1)
F(4)		0.2174 (19)	0.1908 (12)	0.4363 (11)	13.0 (0.8)
F(5)		0.1376 (17)	0.1214 (9)	0.4089 (10)	10.2 (0.5)
F(6)	0.3812 (17)	0.1351 (9)	0.4186 (10)	10.3 (0.6)	
F(7)	0.2821 (16)	0.0759 (9)	0.3785 (10)	10.0 (0.6)	
O(1)	VI	0.0404 (13)	0.1721 (7)	0.1143 (8)	4.99 (44)
O(2)		0.9120 (13)	0.1877 (7)	0.1903 (8)	4.81 (40)
C(1)		0.7127 (52)	0.3264 (29)	0.1961 (31)	16.1 (2.0)
C(2)		0.8062 (30)	0.2954 (15)	0.1869 (18)	8.2 (0.9)
C(3)		0.7812 (22)	0.2412 (12)	0.1544 (14)	5.5 (0.7)
C(4)		0.8705 (20)	0.2130 (11)	0.1432 (13)	4.7 (0.6)
C(5)		0.8920 (23)	0.2174 (12)	0.0913 (14)	6.0 (0.7)
C(6)		0.9738 (21)	0.1900 (12)	0.0769 (13)	5.4 (0.7)
C(7)		0.9884 (24)	0.1864 (15)	0.0124 (14)	6.7 (0.8)
C(8)		0.4370 (33)	0.2694 (19)	0.4749 (21)	12.0 (1.4)
C(9)		0.4468 (32)	0.3676 (18)	0.4921 (20)	11.5 (1.4)
C(10)		0.0952 (32)	0.1873 (18)	0.0103 (19)	11.0 (1.1)
F(1)		0.7571 (20)	0.3711 (12)	0.2161 (12)	13.7 (0.8)
F(2)		0.6556 (30)	0.3286 (16)	0.1536 (19)	20.5 (1.3)
F(3)		0.6902 (25)	0.3045 (15)	0.2363 (16)	17.7 (1.1)
F(4)		0.8399 (20)	0.3232 (11)	0.1460 (13)	14.2 (0.9)
F(5)		0.8670 (18)	0.2892 (9)	0.2331 (11)	11.1 (0.6)
F(6)	0.7329 (13)	0.2134 (7)	0.1898 (8)	7.3 (0.4)	
F(7)	0.7176 (14)	0.2490 (8)	0.1047 (9)	8.5 (0.5)	
Pr(1)		-0.14088 (12)	0.10732 (7)	0.23547 (8)	4.14 (5)
Pr(2)		0.08931 (12)	0.19077 (7)	0.21902 (8)	4.29 (5)
(H <sub>2</sub> O)(1)		-0.0049 (12)	0.1680 (7)	0.3050 (8)	4.89 (42)
(H <sub>2</sub> O)(2)		0.5008 (63)	0.1779 (37)	0.0554 (40)	36.8 (2.8)

standard computer program. No correction was made for absorption since  $\mu R = 0.26$  for the roughly spherical crystal of radius 0.02 cm. The transmission factor varies from 1.56 at  $\theta = 0$  to 1.55 at  $\theta = 20^\circ$ .

The corrected intensities were used to calculate a three-dimensional Patterson synthesis from which trial coordinates for the two Pr atoms were obtained. Starting from these it was possible to locate most of







apices of a trigonal bipyramid based on oxygen atoms O(III2), O(VI2) and  $\text{H}_2\text{O}(1)$ . Each Pr atom is surrounded by eight oxygen atoms at an average distance of 2.42 Å. Neither of the two distinct polyhedra has crystallographic symmetry or corresponds exactly to any of the regular geometries. In such cases it is often found that descriptions in terms of more than one distorted regular polyhedron could be equally valid (Cunningham, Sands, Wagner & Richardson, 1969). Judging from a three-dimensional model, however, the distortions in the present case appear to be at a minimum if the polyhedra around Pr(1) and Pr(2) are described as a bicapped trigonal prism and a dodecahedron respectively. These geometries are illustrated in Fig. 2 and in Table 3, using the nomenclature suggested by Muettterties & Wright (1967). According to this O(II) and  $\text{H}_2\text{O}(1)$  are the caps on the trigonal prism. The molecular parameters are summarized in Tables 4 and 5 and a stereoscopic view of the binary unit is given in Fig. 3.

Table 3

(a) Numbering of the oxygen atoms in terms of the nomenclature suggested by Muettterties & Wright (1967)

M & W	Dodecahedron	Bicapped trigonal prism
1	$\text{H}_2\text{O}$	O(VI 2)
2	O(V 2)	O(I 2)
3	O(III 2)	O(II 1)
4	O(IV 1)	O(II 2)
5	O(VI 2)	O(I 1)
6	O(V 1)	$\text{H}_2\text{O}$
7	O(VI 1)	O(III 2)
8	O(IV 2)	O(III 1)

This structure is in many respects similar to that of  $\text{Pr}_2(\text{thd})_6$  formed by 2,2,6,6-tetramethyl-3,5-heptanedione (Erasmus & Boeyens, 1970a) except that

Table 3. (cont.)

(b) Geometry of the coordination polyhedra described as interatomic distances using the nomenclature of Table 3(a) and Fig. 2

Dodecahedron		Bicapped trigonal prism	
Approach	Length	Approach	Length
1-2	2.721 Å	1-2	3.024 Å
1-3	2.798	1-4	3.423
1-4	2.853	1-6	2.751
1-5	2.751	1-7	2.904
2-3	3.033	2-3	3.222
2-4	3.176	2-5	2.745
2-6	2.757	2-7	3.965
3-5	2.904	3-4	2.738
3-6	4.404	3-5	3.115
3-7	3.211	3-8	3.127
4-5	3.547	4-6	2.682
4-6	3.217	4-8	3.417
4-8	2.746	5-7	3.043
5-7	2.796	5-8	2.991
5-8	3.417	6-7	2.798
6-7	3.723	6-8	3.144
6-8	2.964	7-8	2.867
7-8	2.824		

$\text{Pr}_2(\text{thd})_6$  has never been observed to occur in the hydrated form. The ease of hydration in the present structure is no doubt due to the presence of the fluorine atoms. This is true for both molecules of water although they are not chemically equivalent in the structure. One of them lies at a typical Pr-O coordination distance from both Pr atoms and is flanked on two sides by perfluoropropyl side-chains. It is in all probability hydrogen bonded to the atoms F(5) of rings II and V which it approaches at distances of 3.112 and 3.090 Å respectively. The angle  $\text{F}-\text{O}-\text{F} = 77.8^\circ$ . The other water molecule does not appear in any of the coordination polyhedra, but lies between the perfluoro chains of rings I and II of neighbouring

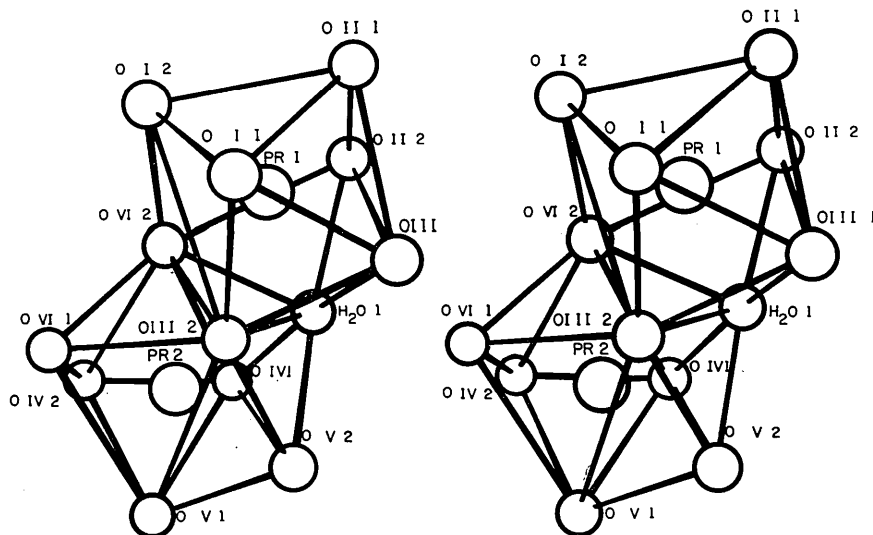


Fig. 2. Stereoscopic drawing of the coordination in the dimer.

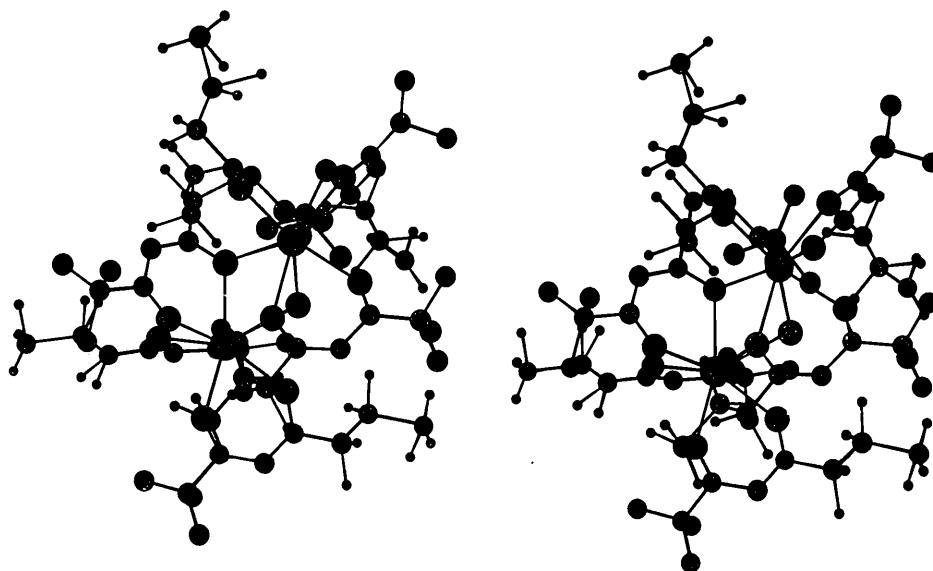


Fig. 3. Stereoscopic drawing of the dimer. The poorly defined water molecule not coordinated to a praseodymium atom is not shown.

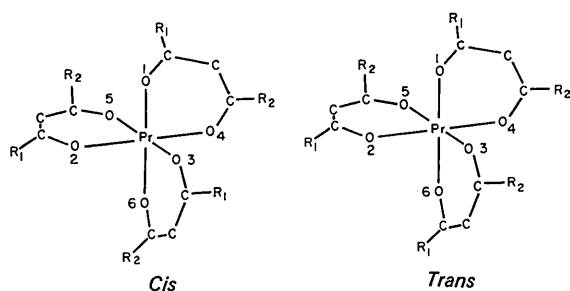


Fig. 4. Schematic drawing to illustrate the configurations of the geometric isomers from which the two parts in the dimer derive.

molecules, probably also hydrogen bonded to fluorine atoms. Because of the disorder in this region the geometry of the arrangement cannot be determined and the 'interatomic distances' are without physical meaning.

### Discussion

In previous studies of lanthanide  $\beta$ -diketonates two types of dimerization leading to the appearance of seven-coordination with the geometry of a monocapped trigonal prism were observed. In  $\text{Pr}_2(\text{thd})_6$  dimerization occurs because of the sharing of two oxygen atoms between coordination polyhedra and in  $\text{Dy}_2(\text{thd})_6$ .

Table 4. Bond lengths ( $\text{\AA}$ ) for the six chelate rings, using the nomenclature of Fig. 1

The term 'bite' refers to  $d(\text{O}-\text{O})$ .

	I	II	III	IV	V	VI	Average	$\sigma$
Pr—O(1)	2.418	2.411	2.433	2.361	2.381	2.446	2.408	} 2.422
Pr—O(2)	2.382	2.413	2.489	2.421	2.406	2.498	2.435	
O(1)—C(6)	1.256	1.255	1.241	1.270	1.267	1.250	1.257	} 1.272
O(2)—C(4)	1.215	1.283	1.296	1.257	1.356	1.313	1.287	
C(4)—C(5)	1.325	1.328	1.377	1.338	1.329	1.301	1.333	0.05
C(5)—C(6)	1.441	1.409	1.412	1.419	1.429	1.453	1.427	0.05
C(1)—C(2)	1.519	1.454	1.701	1.823	1.792	1.600	1.648	0.16
C(2)—C(3)	1.480	1.177	1.486	1.044	1.490	1.586	1.377	0.09
C(3)—C(4)	1.585	1.740	1.561	1.399	1.524	1.529	1.556	0.07
C(6)—C(7)	1.492	1.542	1.540	1.516	1.608	1.550	1.541	0.05
C(7)—C(8)	1.446	1.513	1.490	1.532	1.515	1.529	} 1.479	0.07
C(7)—C(9)	1.480	1.366	1.495	1.397	1.376	1.543		1.536
C(7)—C(10)	1.534	1.451	1.499	1.456	1.464	1.536	} 1.276	0.15
C(1)—F(1)	2.171	1.412	1.307	0.884	1.529	1.348		1.160
C(1)—F(2)	1.190	1.231	1.424	0.991	1.354	1.160	} 1.405	0.15
C(1)—F(3)	1.157	0.978	1.149	1.375	1.004	1.181		1.181
C(2)—F(4)	1.585	1.674	1.316	1.429	1.300	1.343	} 1.387	0.07
C(2)—F(5)	1.365	1.315	1.374	1.528	1.374	1.259		1.366
C(3)—F(6)	1.327	1.401	1.341	1.386	1.395	1.366	} 1.343	0.06
C(3)—F(7)	1.313	1.355	1.334	1.737	1.342	1.343		1.343
Bite	2.745	2.738	2.867	2.746	2.757	2.796	2.775	0.03



Table 5. Bond angles in degrees

	I	II	III	IV	V	VI	Average	$\sigma$
Pr—O(1)—C(6)	139.24	142.17	134.24	138.48	139.22	131.18	137.4	2.6
O(1)—C(6)—C(5)	120.10	120.72	127.76	123.09	123.95	123.93	123.3	3.5
O(1)—C(6)—C(7)	120.85	115.61	114.47	116.46	116.81	115.35	116.6	3.4
C(6)—C(7)—C(8)	114.48	108.46	109.07	114.67	108.17	111.66	110.2	4.0
C(6)—C(7)—C(9)	108.61	118.32	112.11	111.30	104.94	103.52		
C(6)—C(7)—C(10)	109.87	109.09	111.85	107.87	109.98	109.89	108.3	4.5
C(8)—C(7)—C(9)	106.98	122.69	103.44	119.16	111.34	111.89		
C(8)—C(7)—C(10)	111.62	98.41	112.33	95.75	109.30	110.31	119.9	3.7
C(9)—C(7)—C(10)	104.73	95.90	107.77	105.86	112.94	109.37		
C(5)—C(6)—C(7)	118.89	122.91	117.77	120.33	119.18	120.43	121.9	4.1
C(6)—C(5)—C(4)	124.44	121.85	120.26	122.52	122.07	120.53	121.9	4.1
C(5)—C(4)—C(3)	118.84	118.01	115.69	108.66	122.75	117.56	116.9	4.1
C(4)—C(3)—F(6)	108.70	95.68	108.33	124.00	107.09	112.64	108.5	4.2
C(4)—C(3)—F(7)	110.26	94.98	111.40	106.27	110.40	112.24		
C(4)—C(3)—C(2)	115.55	137.07	116.99	136.37	117.72	111.82	122.6	4.2
F(6)—C(3)—C(2)	111.08	117.19	104.60	95.36	106.47	105.32	105.6	5.0
F(7)—C(3)—C(2)	104.93	106.55	111.06	85.63	109.85	109.57		
C(3)—C(2)—C(1)	134.26	152.37	120.02	137.48	116.12	112.11	128.7	5.9
F(4)—C(2)—F(5)	76.09	110.79	102.03	79.16	106.29	112.68	97.8	5.9
F(6)—C(3)—F(7)	105.85	97.16	103.26	95.43	104.36	104.81	101.8	4.0
C(3)—C(2)—F(4)	111.31	92.37	110.27	102.01	108.95	101.92	105.9	6.0
C(3)—C(2)—F(5)	114.60	102.45	105.86	106.07	104.27	110.67		
F(4)—C(2)—C(1)	89.67	85.43	117.33	114.76	120.66	104.38	104.8	5.1
F(5)—C(2)—C(1)	109.64	104.07	97.91	101.31	98.06	114.27		
C(2)—C(1)—F(2)	88.35	103.41	88.43	122.39	90.09	112.60	95.6	6.5
C(2)—C(1)—F(3)	109.51	83.66	108.20	95.81	107.62	103.05		
C(2)—C(1)—F(1)	63.04	65.05	101.17	100.37	81.92	96.65	116.2	10.0
F(2)—C(1)—F(3)	153.02	129.55	109.56	131.92	156.81	116.32		
F(2)—C(1)—F(1)	89.83	156.94	98.69	109.97	89.74	117.57	130.1	2.8
F(3)—C(1)—F(1)	116.04	71.02	139.24	90.46	107.13	108.02		
Pr—O(2)—C(4)	136.08	132.48	128.54	131.91	132.51	119.05	130.5	4.1
O(2)—C(4)—C(5)	129.36	132.25	131.86	129.08	128.92	131.68	130.5	4.1
O(2)—C(4)—C(3)	111.79	107.29	111.91	122.14	108.13	110.76	112.0	3.6
Bite	69.76	69.15	71.24	70.09	70.34	70.94	70.3	0.7

2H<sub>2</sub>O (Erasmus & Boeyens, 1970*b*) coordinated water molecules are hydrogen bonded to oxygen ligand atoms in neighbouring coordination spheres. Both these mechanisms are operative in the present structure, but here the single coordinated water in a dimeric unit is also shared between two metal atoms and is hydrogen bonded to fluorine atoms.

Both Pr atoms are thus eight coordinate although the coordination geometries are different. The polyhedron around Pr(2) is easily recognizable as a dodecahedron whereas the Pr(1) polyhedron is related more to a bicapped trigonal prism, symmetry C<sub>2v</sub> (Muetterties & Wright, 1967). Both these configurations can revert easily, by dehydration, to the monocapped trigonal prism characteristic of the seven-coordinate dimeric chelates (Erasmus & Boeyens, 1970*a, b*).

Table 6

(*a*) Identification of the parent octahedra in terms of the nomenclature of Muetterties & Wright (1967)

M & W	<i>cis</i> (Bicapped prism)	<i>trans</i> (Dodecahedron)
1	O(I 1)	O(VI 1)
2	O(III 1)	O(V 1)
3	O(II 1)	O(IV 2)
4	O(I 2)	O(VI 2)
5	O(III 2)	O(V 2)
6	O(II 2)	O(IV 1)

Table 6 (*cont.*)

According to Fig. 1 each O(1) atom is attached to a C atom with a tertiary butyl side-chain and each O(2) atom to a C atom with a perfluoro propyl side-chain. Note that the corresponding rings II and IV are in different orientation.

(*b*) Interatomic distances illustrating the amount of distortion of the two parent octahedra

Distance	<i>cis</i>	<i>trans</i>
1-2	2.991 Å	3.723 Å
1-3	3.115	2.824
1-4	2.745	2.796
1-5	3.043	4.534
2-3	3.127	2.964
2-5	2.867	2.757
2-6	3.417	3.217
3-4	3.222	3.417
3-6	2.738	2.746
4-5	3.965	4.369
4-6	4.033	3.547
5-6	4.366	3.176

Rupture of the anhydrous dimer can be expected to lead to the formation of octahedral monomers. It is interesting that the two resulting octahedra are not identical, being *cis* and *trans* respectively, as shown in Fig. 4 and in Table 6.

Table 7. Equations to the least-squares planes through the chelate rings and deviations ( $\text{\AA} \times 10^3$ ) of the atoms from these planes

The equations in the form  $lu + mv + nw = d$  are in  $\text{\AA}$  with atomic coordinates expressed in the orthogonal system:  $u \equiv a$ ,  $v \equiv b$  and  $w \equiv c^*$ .

	I	II	III	IV	V	VI
<i>l</i>	0.8456	0.5504	0.3328	0.9665	-0.3056	0.3337
<i>m</i>	0.2195	-0.5504	0.6881	-0.1268	0.8228	0.9426
<i>n</i>	-0.4866	0.6278	0.6448	0.2232	0.4792	0.0127
<i>d</i>	7.605	7.926	9.298	0.682	6.198	4.408
O(1)	79	-27	182	-54	-115	-194
O(2)	70	-143	177	-224	-107	-516
C(3)	-48	176	-91	94	-3	192
C(4)	19	-144	68	-12	29	-50
C(5)	-5	-13	-95	61	76	217
C(6)	40	-61	22	20	4	-37
C(7)	-67	83	-64	-26	10	19
Pr	-89	-130	-200	141	106	370

The chelate rings have a geometry very similar to those in  $\text{Pr}_2(\text{thd})_6$  and those containing oxygen atoms shared between the Pr atoms are also markedly non-planar, as shown in Table 7.

It seems obvious that the structure of anhydrous  $\text{Pr}_2(\text{fod})_6$  will be very similar to that of  $\text{Pr}_2(\text{thd})_6$ . No attempt will therefore be made in this laboratory to determine the structure of the anhydrous complex. It may seem surprising to find coordinated water in this structure, contrary to predictions (Springer, Meek & Sievers, 1967) based on the bulkiness of the perfluoropropyl side chains. In fact, the more hydrophobic tertiary butyl groups in thd provide better protection of the central ion against hydration.

As far as the volatility of its metal chelates are concerned, the disadvantageous hydrophilic character of fod, which allows the uptake of undesirable (Springer, Meek & Sievers, 1967) molecules of water into the coordination sphere, is offset by the higher mutual

repulsion between fluorine atoms. Only one intermolecular F-F contact of less than 3  $\text{\AA}$  has been observed, but since this involves one of the poorly defined fluorine atoms at the end of a chain [F(VI)] little importance can be attached to that. (All intermolecular approaches of less than 3.5  $\text{\AA}$  are listed in Table 8.) In view of the fluorine van der Waals radius of 1.35  $\text{\AA}$  (Evans, 1964) an extremely loose packing illustrated in Fig. 5, is indicated. This ties in well with the observed temperature factors which are reminiscent of the thermal vibrations usually associated only with the gas phase and which render a meaningful crystallographic analysis of the molecular parameters (particularly of the perfluoro side-chains) virtually impossible. Even the slight asymmetry of the chelate rings, caused by the dissimilar side-chains and which appears well established from the present results, must remain doubtful until a structure analysis at low temperature becomes available.

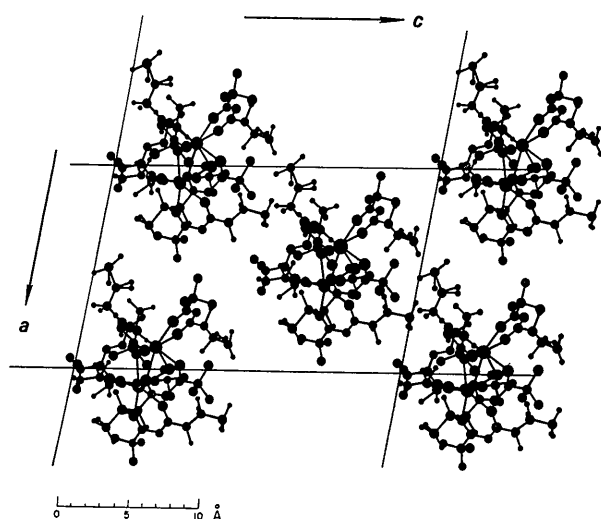


Fig. 5. Projection of half a unit cell along [010]. The other half, left out for the sake of clarity, relates to this part by the action of screw axes.

Table 8. Intermolecular approaches of less than 3.5  $\text{\AA}$ 

Contact	Distance
F(I 2)—C(IV 8)	3.49 $\text{\AA}$
F(I 2)—F(II 1)	3.46
F(I 3)—F(III 2)	3.13
C(II 10)—F(IV 4)	3.46
F(II 3)—F(IV 7)	3.14
F(II 4)—F(IV 2)	3.34
F(IV 1)—F(V 6)	3.45
F(IV 3)—F(V 6)	3.48
F(IV 5)—F(V 1)	2.84
F(V 1)—F(VI 4)	3.02

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## Crystal and Molecular Structure of Fluoromalonic Acid

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The structure of fluoromalonic acid (HOOC-CFH-COOH) has been determined from three-dimensional X-ray data. The accepted space group is *Pnam*. The unit cell, of dimensions  $a=4.606$ ,  $b=8.315$ ,  $c=11.220$  Å, contains four molecules, implying a plane of symmetry in the molecule. The structure has been refined to an *R* index of 0.047 by least-squares methods. The bond lengths (1.251 and 1.245 Å) in the carboxyl group and the C-C-O bond angles (116.7 and 116.9°) have values which differ from those usually observed.

### Introduction

Infrared and X-ray investigations of crystalline tartaric acid indicate that the aliphatic hydroxyl group is not involved in hydrogen bonding (van Eijk, Kanters & Kroon, 1965; Kanters, Kroon, Peerdeman & Vliegthart, 1969). In this structure the molecules form chains by carboxyl group coupling as is frequently observed in dicarboxylic acids. From the lack of hydrogen-bond interaction between these chains it was expected that substitution of the hydroxyl group by a fluorine atom would not essentially change this simple hydrogen bond scheme.

In order to verify this the structure of fluoromalonic acid was determined.

### Experimental

Small prismatic crystals of fluoromalonic acid were obtained by sublimation *in vacuo*. Because of its very hygroscopic character a single crystal of dimensions  $0.2 \times 0.2 \times 0.1$  mm<sup>3</sup> was sealed in a glass tube. The following crystal data were obtained: C<sub>3</sub>O<sub>4</sub>H<sub>3</sub>F;  $a=4.606 \pm 0.001$ ,  $b=8.315 \pm 0.001$ ,  $c=11.220 \pm 0.001$  Å;  $V=430$  Å<sup>3</sup>;  $D_c(Z=4)=1.88$  g.cm<sup>-3</sup>.

The unit-cell dimensions and their standard deviations, calculated by least-squares methods, were determined from the Cu  $K\alpha_1$  component ( $\lambda=1.54051$  Å) of 33 reflexions with  $2\theta > 130^\circ$ , measured on a General Electric diffractometer with a single-crystal orienter and equipped with a scintillation counter.

Intensity data were collected from one single crystal using the apparatus mentioned above. Ninety-five per cent of the independent reflexions within the Cu  $K\alpha$  sphere could be measured. Non-linearity was corrected

for experimentally

$$\left( I_{\text{corrected}} = I_{\text{obs}} \left[ \frac{5.46}{5.46 - 1.1033 \cdot 10^{-5} \cdot I_{\text{obs}}} \right] \right),$$

but absorption was neglected.

From Weissenberg photographs the following extinctions were deduced:  $0kl$ :  $k+l=2n+1$ ;  $h0l$ :  $h=2n+1$ ;  $(h00)$ :  $h=2n+1$ ;  $0k0$ :  $k=2n+1$ ;  $00l$ :  $l=2n+1$ . These extinctions are compatible with both space groups *Pnam* and *Pna2<sub>1</sub>*. As *Pnam* has an eightfold general position and the unit cell contains four molecules, the molecule must have a mirror plane in this space group.

### Structure determination

A strong resemblance between the cell dimensions and  $0kl$  reflexion intensities of tartaric acid ( $a=4.485$ ,  $b=8.813$ ,  $c=10.895$  Å; space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*) and those of fluoromalonic acid led us to accept the tartaric acid coordinates as starting parameters in the least-squares refinement of fluoromalonic acid (Table 1).

Table 1. *Starting parameters*

(*B* overall = 3 Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>
F	-0.1779	+0.0999	+0.2387
O(1)	+0.3797	-0.1403	+0.1101
O(2)	+0.2228	+0.0926	+0.0568
O(3)	+0.2662	+0.1161	+0.4128
O(4)	+0.3809	-0.1283	+0.3775
C(1)	+0.2267	-0.0154	+0.1253
C(2)	+0.0367	-0.0145	+0.2422
C(3)	+0.2433	-0.0011	+0.3545

Refinement in space group *Pna2<sub>1</sub>* of carbon, oxygen and fluorine atoms with isotropic thermal parameters