

## The Crystal Structure of Tetrabutylammonium Tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione)samarium(III), $(C_4H_9)_4N(C_8H_4F_3O_2S)_4Sm(III)$

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### Abstract

The crystal structure of tetrabutylammonium tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione)samarium(III),  $(C_4H_9)_4N(C_8H_4F_3O_2S)_4Sm(III)$ , has been determined using 2425 independent, diffractometer measured intensities and refined by full matrix least squares methods to  $R = 0.080$ ,  $R_w = 0.090$ . The crystals are monoclinic with  $a = 19.181(6)$ ,  $b = 18.076(5)$ ,  $c = 16.595(5)$  Å,  $\beta = 109.40(2)^\circ$ . The space group is  $C2/c$  with  $Z = 4$ , requiring a 2-fold axis in both the cation and anion. The coordination sphere has square antiprismatic geometry with Sm–O bond distances in the range 2.382–2.442 Å. Disorder is found in both independent thienyl rings. The disordered positions are related by  $180^\circ$  rotation about the bond joining the ring to the chelate backbone and have each 1/2 occupancy for one ring and 1/3, 2/3 occupancy for the other ring.

### Introduction

During the past twenty-five years there has been considerable interest in compounds exhibiting eight-fold coordination and comprehensive reviews have been published [1–3]. At Fordham University and Brookhaven National Laboratory crystal structure investigations have been carried out on 8-coordinated lanthanide chelates [4, 5]. For the tetrakis chelates of  $\beta$ -diketones with trivalent lanthanides, the chelate itself is an anion and a monovalent cation is required. In the compound  $NH_4Pr(TTA)_4$  (where  $HTTA = 4,4,4$ -trifluoro-1-(2-thienyl)-1,3-butanedione), a water molecule was found outside the coordination sphere, effectively increasing the size of the small  $NH_4^+$  cation [4]. This suggested that a large cation is necessary for the stability of these structures. Accordingly, using tetrabutylammonium (TBA) as the cation, the serie TBA  $Ln(TTA)_4$  was prepared and crystallized for every lanthanide except promethium; unit cell and space group determinations indicated that only two crystal structures were

present [6]. In the present paper the crystal structure of one isomorph, TBA  $Sm(TTA)_4$ , is described, while corresponding praseodymium compound was selected as a representative of the other, and its crystal structure was also determined [7].

### Experimental

#### Preparation

The compound and crystals were prepared as described previously [6].

#### X-ray Study

The crystals are monoclinic with  $a = 19.181(6)^*$ ,  $b = 18.076(5)$ ,  $c = 16.595(5)$  Å,  $\beta = 109.40(2)^\circ$ . The space group  $C2/c$  with  $Z = 4$ ,  $D_{calc} = 1.568$ ,  $D_{obs} = 1.551$  g cm $^{-3}$  (floatation in  $CCl_4$ – $CHCl_3$  solution at  $25^\circ C$ ). A crystal measuring 0.14 mm  $\times$  0.09 mm  $\times$  0.09 mm was selected for data collection and this was carried out on a computer controlled Picker four circle diffractometer. Graphite monochromated  $Mo K\alpha$  radiation ( $\lambda = 0.7107$  Å) was used with the  $\omega$ – $2\theta$  scanning technique. In the range  $\theta \geq 21.5^\circ$ , 2969 independent reflection intensities were measured in one quadrant of the reciprocal lattice, but data was also collected in a second quadrant. Absorption corrections ( $\mu_{Mo K\alpha} = 13.51$  cm $^{-1}$ ) were calculated for all reflections but since the transmission factors varied only from 0.89 to 0.90 these were not applied. The intensities of the reflections measured in both quadrants were averaged and Lorentz-polarization correction factors applied. The number of reflections included in the final refinement, on the criterion  $F_o/\sigma_F \geq 1.0$ , was 2425.

#### Structure Determination and Refinement

From the systematic absences in the X-ray data the space group could be either  $Cc$  or  $C2/c$ . The latter space group would require that the samarium

\*Here, and throughout this paper, estimated standard deviations, given in parentheses, are right-adjusted to the least significant digit in the preceding number.

and nitrogen atoms lie in special positions. In fact, the dominant vector peak of the Patterson map was on the Harker line  $0, \nu, 1/2$ , indicating that the samarium atom is on a 2-fold axis. The asymmetric unit thus consists of the samarium atom and two of the four ligands of the anion, and the nitrogen atom and two of the four butyl groups of the cation. The choice of the centrosymmetric space group is further justified by the successful refinement.

Successive electron density maps based initially on the phase angles derived from the Sm positions gave the positions of all other non-hydrogen atoms. Full matrix least squares refinement of positional parameters and isotropic thermal parameters for all atoms gave  $R = 0.224$ . However, the final thermal parameters indicated disorder in both thienyl rings due to  $180^\circ$  rotation about the bonds C(4)–C(5) and C(12)–C(13). This was confirmed by the difference electron density maps in which each thienyl ring was subtracted in turn from the structure factor calculations. Accordingly, refinement was carried out as before but adding additional S and C occupancy factors for the atoms S(1), S(2), C(5) and C(13). It was found that the disorder between the S(1) and C(5) sites was almost exactly one half for each configuration, where as between S(2) and C(13) the occupancies were close to 2/3 and 1/3. Refinement was then carried out holding the occupancy factors constant but with anisotropic thermal parameters for all atoms. Due to storage limitations the positional and thermal parameters were refined in alternate cycles until convergence was reached. In the final cycles the hydrogen atoms of the tetrabutylammonium group were added in the calculated positions, with the isotropic thermal parameter of

the carbon atom to which each was bonded. Inclusion of the hydrogen atoms significantly improved the bond distances in the cation as compared to normal values. A final difference electron density map was calculated and showed two peaks of  $2.2 \text{ e } \text{Å}^{-3}$  close to the Sm atom, but no other peaks greater than  $0.8 \text{ e } \text{Å}^{-3}$ .

The function minimized during refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $w$  was obtained from the counting statistics. Unobserved reflections were weighted zero and the final values of  $R$  and  $R_w$  were 0.080 and 0.090, respectively. The atomic scattering factor for Sm was that given by Cromer and Waber [8], while those for the other atoms were taken from the International Tables [9]. Correction for the anomalous scattering of Sm and S was made [10]. Major computing programs used were modifications of ORFLS [11], FORDAP [12], ORFFE [13], PLANET [14] and ORTEP [15]. A table of the final observed and calculated structure factors may be obtained from the Editor.

## Results and Discussion

The refined fractional atomic coordinates are given in Table I and the anisotropic thermal parameters in Table II. The atomic numbering scheme used is shown in Fig. 1, which also includes the bond distances and bond angles. Primed atomic numbers are related to those of the asymmetric unit by a two-fold axis. As illustrated in Fig. 2, a stereoview of the contents of one unit cell, the structure consists of discrete  $\text{Sm}(\text{TTA})_4^-$  anions and tetrabutylammonium cations, and these are held together in the crystal by electrostatic attraction.

TABLE I. Fractional Atomic Coordinates  $\times 10^4$

Atom	x	y	z	Atom	x	y	z
Sm	0(0)	1523(1)	2500(0)	N	5000(0)	1919(9)	2500(0)
O(1)	1141(4)	1059(4)	2430(5)	O(3)	532(4)	2611(4)	2053(5)
O(2)	-254(4)	477(5)	1563(5)	O(4)	-776(4)	1904(4)	1134(5)
S(1)	-1226(3)	-497(3)	381(3)	S(2)	-1788(2)	3139(2)	-846(2)
F(1)	2509(4)	889(5)	2309(6)	F(4)	416(6)	4342(5)	1115(7)
F(2)	2358(5)	-278(5)	2146(7)	F(5)	831(7)	4070(5)	2411(7)
F(3)	2408(5)	244(6)	3315(6)	F(6)	1349(6)	3703(6)	1611(10)
C(1)	2153(8)	311(7)	2502(10)	C(9)	713(9)	3805(8)	1632(11)
C(2)	1334(6)	444(7)	2174(7)	C(10)	239(7)	3099(7)	1523(11)
C(3)	888(6)	-97(6)	1680(8)	C(11)	-401(8)	3071(7)	835(8)
C(4)	115(8)	-22(7)	1359(7)	C(12)	-861(7)	2465(7)	647(7)
C(5)	-337(7)	-578(6)	745(7)	C(13)	-1513(7)	2415(7)	-164(7)
C(6)	-10(4)	-1238(4)	337(4)	C(14)	-1972(5)	1735(6)	-404(6)
C(7)	-752(10)	-1566(8)	-266(9)	C(15)	-2582(7)	1971(9)	-1210(8)
C(8)	-1392(8)	-1214(8)	-245(9)	C(16)	-2530(8)	2655(9)	-1480(8)
C(17)	4762(10)	1415(9)	1709(10)	C(21)	4380(10)	2369(10)	2609(11)
C(18)	5864(9)	881(9)	3374(10)	C(22)	4081(11)	2956(10)	1918(15)
C(19)	6106(12)	578(12)	4268(13)	C(23)	3314(12)	3216(11)	1898(16)
C(20)	6669(13)	8(14)	4442(15)	C(24)	2735(13)	2702(12)	1402(14)

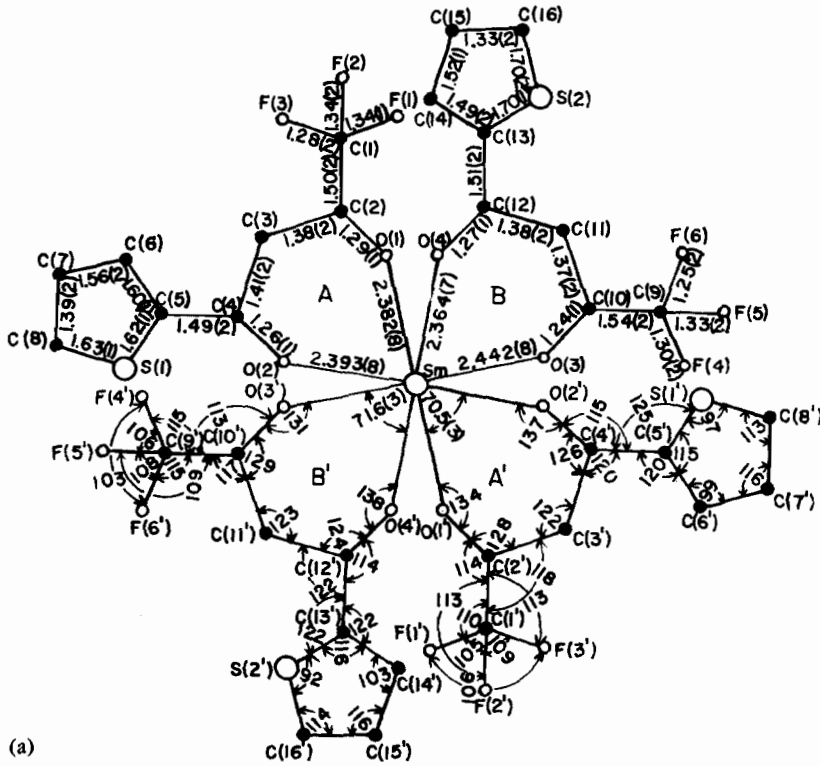
TABLE II. Anisotropic Thermal Parameters  $\times 10^4$  (The temperature factors used were of the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ )

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Sm	26(0)	24(0)	28(1)	0(0)	-3(0)	0(0)
O(1)	24(3)	40(3)	40(4)	3(3)	4(3)	-7(3)
O(2)	23(3)	43(4)	44(5)	-3(5)	-4(3)	-6(4)
S(1)	44(1)	49(2)	52(3)	-6(2)	-2(2)	-13(2)
F(1)	44(3)	62(4)	106(7)	-7(3)	18(4)	1(4)
F(2)	42(4)	58(4)	158(9)	12(3)	7(4)	-29(5)
F(3)	53(4)	91(5)	68(5)	12(4)	-12(4)	22(5)
C(1)	47(7)	28(5)	80(10)	-2(5)	3(7)	-1(6)
C(2)	33(5)	40(5)	34(7)	6(5)	4(5)	0(5)
C(3)	26(5)	32(5)	53(8)	1(4)	-1(5)	1(5)
C(4)	54(7)	31(5)	21(6)	-8(5)	9(5)	7(5)
C(5)	42(6)	27(4)	33(6)	-2(4)	10(5)	-7(5)
C(6)	55(4)	29(3)	43(4)	-7(2)	13(3)	-11(3)
C(7)	75(9)	44(6)	49(8)	-20(6)	22(7)	-7(6)
C(8)	45(7)	43(6)	60(9)	-13(5)	10(6)	-6(6)
O(3)	32(3)	34(3)	42(5)	-4(3)	-2(3)	1(3)
O(4)	37(4)	32(3)	45(5)	6(3)	-8(3)	4(3)
S(2)	47(2)	52(2)	46(3)	10(2)	-1(2)	12(2)
F(4)	85(6)	50(4)	141(9)	-18(4)	-23(6)	42(5)
F(5)	141(8)	59(4)	91(7)	-45(5)	9(6)	-20(5)
F(6)	56(5)	73(6)	259(15)	-16(4)	54(7)	42(7)
C(9)	51(7)	34(6)	82(11)	-6(6)	9(8)	5(7)
C(10)	31(5)	32(5)	43(7)	7(4)	10(5)	2(5)
C(11)	38(6)	32(5)	43(7)	6(5)	0(6)	-2(5)
C(12)	37(6)	38(5)	27(7)	12(5)	-3(5)	-9(5)
C(13)	27(5)	41(5)	34(6)	7(4)	0(5)	-4(5)
C(14)	29(4)	80(7)	39(6)	0(4)	-3(4)	-8(4)
C(15)	34(5)	62(7)	33(7)	10(5)	-4(5)	5(6)
C(16)	46(6)	62(7)	37(8)	10(6)	1(6)	2(6)
C(17)	70(9)	56(7)	56(9)	16(7)	18(7)	-6(7)
C(18)	54(7)	58(7)	67(10)	-5(6)	-5(7)	8(7)
C(19)	79(10)	105(13)	84(13)	-3(10)	0(10)	37(11)
C(20)	90(13)	112(14)	116(17)	-9(12)	-17(12)	25(13)
C(21)	77(9)	57(8)	82(11)	14(7)	42(9)	-6(8)
C(22)	75(10)	60(9)	150(18)	5(8)	53(12)	29(11)
C(23)	70(10)	66(9)	162(20)	2(8)	61(13)	15(11)
C(24)	95(12)	76(11)	136(18)	7(10)	50(13)	-14(11)
N	76(10)	40(7)	53(10)	0(0)	17(8)	0(0)

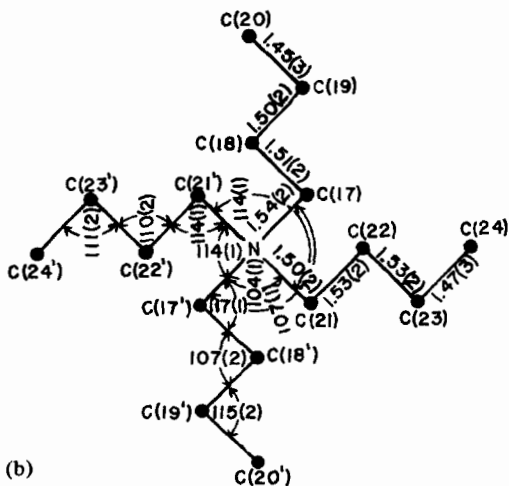
The stereochemistry of the anion is shown in more detail in Fig. 3. The coordination sphere around the samarium atom consists of eight nearly equidistant oxygen atoms (2.382–2.442 Å) located at the vertices of a square (archimedean) antiprism. Figure 4 shows the geometry of an ideal antiprism, which would contain an  $\bar{8}$  axis, together with all independent observed O–O distances. The four bidentate ligands are bound across opposite sides of the squares, and this disposition reduces the symmetry to the  $D_2$  subclass of the square antiprismatic stereoisomers of the type  $M(X_2)_4$  [16]. Further distortions arise due to interactions between the bulky ligands but these appear to be random, rather than significant in the direction of another coordination geometry. The square face of the antiprism is almost planar, with the largest deviation

from the mean plane being 0.055 Å or  $6\sigma$ . The two square faces have a dihedral angle of  $3.5(4)^\circ$ . Using the notation of Hoard and Silverton [16] the antiprism geometry may be described in terms of the average  $l/s$  ratio, where the edges  $l$  and  $s$  are shown in Fig. 4, and the average of  $\theta$ , the angle between a metal–oxygen bond and the (idealized)  $\bar{8}$  axis. For TBA  $\text{Sm}(\text{TTA})_4$   $l/s = 1.066$  and  $\theta = 55.3^\circ$  as compared with the values 1.057 and  $57.3^\circ$  calculate for the 'most favorable' polyhedron [16]. The average dihedral angle between adjacent triangular faces is  $51.3^\circ$ , as compared to the ideal value of  $52.4^\circ$  for the square antiprism and  $29.5^\circ$  for the dodecahedron [17].

Outside the coordination sphere the anion geometry shows features similar to those noted in closely related chelates [4, 5, 18, 19]. The five backbone



(a)



(b)

Fig. 1. The atomic numbering scheme employed with bond distances in Å, and bond angles in degrees for the anion in (a) and the cation in (b). In the anion the e.s.d.s for angles are 1° where these are not given.

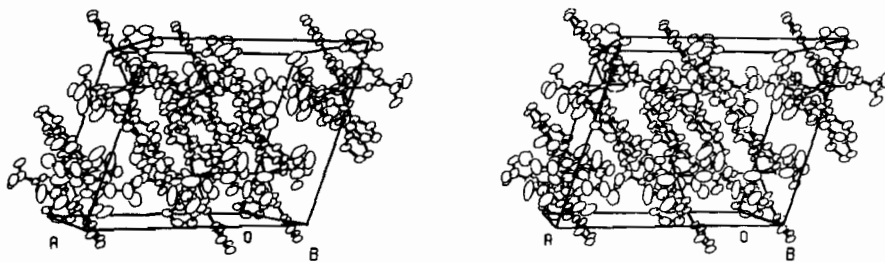


Fig. 2. A stereoview of the contents of one unit cell.

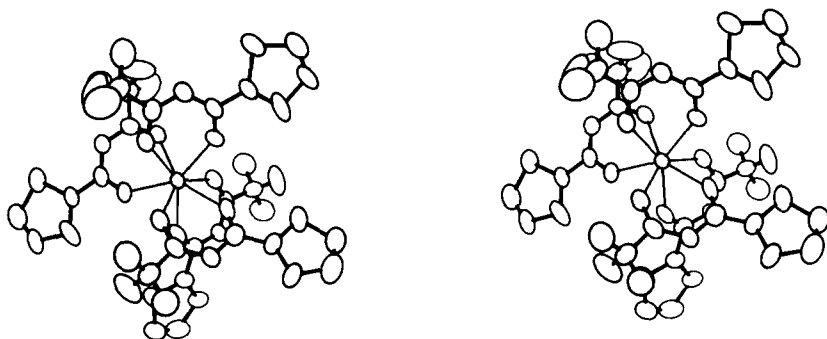


Fig. 3. A stereoview of the  $\text{Sm}(\text{TTA})_4^-$  anion.

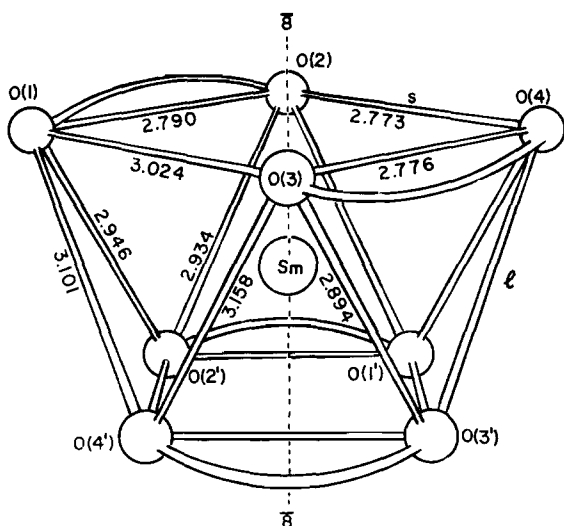


Fig. 4. An ideal square antiprism, showing the ligand attachment and the independent O—O distances.

atoms of each ligand are almost coplanar, with maximum deviations from the least squares mean planes of  $5\sigma$ . However, the six-membered rings formed by the addition of the samarium atom to the other five atoms are far from planar, due to folding about O(1)—O(2) and O(3)—O(4) of  $14.1^\circ$  and  $15.2^\circ$  in ligands A and B, respectively. This folding appears to relieve some interligand strain. The coordinates given for the thienyl ring of ligand B are coplanar within experimental error. In the corresponding ring of ligand A this is not the case, but this result is very probably a consequence of the more severe disorder occurring in this ring. The

bond distance and angles given in Fig. 1 within these rings are also anomalous due to disorder. The thienyl rings make dihedral angles of  $9^\circ$  and  $12^\circ$  with the chelate rings. Although somewhat uncertain because of disorder between S(1) and C(6), the measured S(1)—O(2) distance of 2.83 Å is shorter than the van der Waals' distance. Similar contradictions have been observed in related chelates [4, 5, 18, 19] and a contributory factor may be repulsion between the hydrogen atoms of C(6) and C(3), widening the angle C(4)—C(5)—C(6) and thus 'pushing' S(1) closer to O(2). The fluorine atoms all have high thermal parameters with equivalent isotropic  $B$ s in the range of 8–14 Å<sup>2</sup>. Difference electron density maps computed in the plane of the fluorine atoms in each CF<sub>3</sub> group gave no indication of disorder, and the effect appears to be due to thermal oscillations of the groups about the bonds C(1)—C(2) and C(9)—C(10).

The geometry of the cation is shown in Fig. 5. Two features are immediately evident. First, two of the butyl groups show the preferred zig-zag pattern commonly found in saturated hydrocarbon chains but the other two show deviation in the terminal atom positions. Similar deviations, probably induced by packing, have been found to occur in tetrabutylammonium cations in other crystal structures [20–22]. Second, there is a progressive increase in thermal motion from the nitrogen atom along each chain and the terminal atoms have  $B$ 's of 12 and 14 Å<sup>2</sup>. The anomalously short bonds (Fig. 1(b) involving the terminal atoms are probably due to this high thermal motion for which the distances have not been corrected. Difference electron density maps did not indicate any disorder in these regions.



Fig. 5. A stereoview of the tetrabutylammonium cation.

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