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Synthesis and Crystal Structure of Hexa(μ-trifluoroacetato)tetrakis-(tetramethylenesulfoxide)dilanthanum(III) Polymer and Tetra(μ-trifluoroacetato)-bis(trifluoroacetato)tetrakis(tetramethylenesulfoxide)dineodymium(III)

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Abstract

The structures of the title compounds were determined by three-dimensional X-ray diffraction methods.

$La(CF_3COO)_3 \cdot 2(C_4H_8SO)$: monoclinic $P2_1/c$ (No. 14), $a = 13.666(2)$, $b = 16.887(2)$, $c = 10.706(3)$ Å, $\beta = 108.65(2)°$, $V = 2341(2)$ Å^3, $M = 685.9$, $Z = 4$, $D_c = 1.95$ g cm^{-3}, $\mu = 9.52$ cm^{-1}, $\lambda(MoK\alpha) = 0.71073$ Å, $F(000) = 1324$, $R = 0.093$, 3240 unique reflections, 1446 with $I > 3\sigma(I)$.

$Nd(CF_3COO)_3 \cdot 2(C_4H_8SO)$: monoclinic $P2_1/n$ (No. 14), $a = 11.758(3)$, $b = 15.868(3)$, $c = 12.823(4)$ Å, $\beta = 93.66(2)°$, $V = 2387(2)$ Å^3, $M = 691.2$, $Z = 4$, $D_c = 1.92$ g cm^{-3}, $\mu = 22.9$ cm^{-1}, $\lambda(MoK\alpha) = 0.71073$ Å, $F(000) = 1336$, $R = 0.093$, 4197 unique reflections 2190 with $I > 3\sigma(I)$.

In the La structure the coordination polyhedron is a distorted triangular dodecahedron formed from the oxygen atoms of two C_4H_8SO and six trifluoroacetate groups, these last acting as bridges and giving rise to an infinite chain of identical polyhedra along the direction of the *c*-glide translation.

In the Nd structure the coordination polyhedron is a distorted Archimedean antiprism formed from the oxygen atoms of two C_4H_8SO groups, four trifluoroacetate groups acting as bridges and one acting as a bidentate ligand. The arrangement gives rise to dimers sited on a crystallographic center of symmetry.

Introduction

Lanthanide trifluoroacetates were obtained by the reaction of the corresponding oxides or basic carbonates with a trifluoroacetic acid solution. The thermal properties of the hydrated salts revealed that they exist as a trihydrate. Thermogravimetric studies show that the decomposition proceeds in several stages. The first stage involves a dehydration followed by decomposition of the salt to the respective fluoride [1].

The trifluoroacetate group may behave either as mono or bidentate group, or it can bridge between neighbouring metal ions. Due to its 'short-bite' character, however, it is mostly known as a monodentate or bridging group [2, 3]. Though in principle vibrational spectroscopy may differentiate between these possible modes, it is generally very difficult to distinguish between the bidentate and bridging modes [2]. To resolve this problem and to determine the coordination number and geometry, the crystal structure determination of the title compounds were carried out by three-dimensional X-ray diffraction.

Experimental

Both compounds were prepared by the reaction of the hydrated lanthanide trifluoroacetate with an excess of warm tetramethylenesulfoxide (TMSO). 2,2-dimethoxypropane (dmp) or triethylorthoformate (teof) was added to the solution. The precipitate was collected, washed with dmp or teof and dried *in vacuo* over $CaCl_2$. The complexes were recrystallized by the vapor diffusion method, using ethanol and teof as inner and outer solvents respectively.

Diffraction measurements were carried out on a CAD-4 Enraf-Nonius diffractometer using prismatic crystals of approximate dimensions 0.26 × 0.22 × 0.15 mm and 0.22 × 0.20 × 0.20 mm for La and Nd compounds respectively. Cell dimensions and the orientation matrices were calculated by least-squares from 25 centered reflections. In both crystals, diffraction intensities were measured by the ω–2θ scan technique using a variable scan speed between 2.8–20.0° min^{-1} determined by a pre-scan at 20.0°

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TABLE I. Summary of Data Collection and Crystal Parameters.

Molecular formula	$La(CF_3COO)_3 \cdot 2(C_4H_8SO)$	$Nd(CF_3COO)_3 \cdot 2(C_4H_8SO)$
Molecular weight	685.9	691.2
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Equivalent positions	$x, y, z; \bar{x}, \bar{y}, \bar{z}$	$x, y, z; \bar{x}, \bar{y}, \bar{z}$
	$-x, 1/2 + y, 1/2 - z; x, 1/2 - y, 1/2 + z$	$1/2 - x, 1/2 + y, 1/2 - z; 1/2 + x, 1/2 - y, 1/2 + z$
Cell constants	$a = 13.666(2)$	11.758(3)
	$b = 16.887(2)$	15.868(3)
	$c = 10.706(3)$	12.823(4) Å
	$\beta = 108.65(2)$	93.66(2)°
	$V = 2341(2)$	2387(2) $Å^3$
Complex per cell	4	4
Density (calcd.)	1.95	1.92 g cm^{-3}
Radiation used	$\lambda(MoK\alpha) = 0.71073$	$\lambda(MoK\alpha) = 0.71073$ Å
Absorption coefficient	9.5	22.9 cm^{-1}
Collection range	$0 < \theta < 23°$	$0 < \theta < 25°$
Total data collected	3240	4197
Data with $I > 3\sigma(I)$	1446	2190
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \lvert F_o \rvert$	0.093	0.093

min^{-1}. The intensity of one standard reflection was essentially constant over the duration of both experiments. Data were corrected by Lorentz and polarization effects. A summary of data collection and crystal parameters is given in Table I.

Structure Solution and Refinement

In both cases the heavy atom was readily located from a Patterson synthesis and the rest of the structure was determined by the usual alternate cycles of difference maps and isotropic least-squares. It is remarkable that in spite of their very different packing, both structures show similar positional disorder, giving rise to almost identical behaviour under refinement. All trifluoroacetate groups showed six peaks in an approximate hexagonal arrangement perpendicular to the C–C bond, interpreted as fluorine atoms with occupation site factors 1/2.

Several interatomic distances had to be constrained for the refinement to converge to chemically meaningful results (in the trifluoroacetate groups C–F = 1.31(2) and C–C = 1.51(2) Å; in the TMSO groups C–C = 1.52(2) and C–S = 1.77(2) Å). After choosing the weighting scheme $[\sigma^2(F_o) + CF_o^2]^{-1}$ with $C = 0.008$ and 0.0015 for the La and Nd structures, the isotropic least-squares refinements converged to the same value of 0.093. In both cases three strong reflections suspected of extinction were left out of the calculations (020, 040, 010 and $\bar{1}01$, 101, 011 for the La and Nd structures respectively). No hydrogen atoms were included in the models. Final difference maps showed peaks between 1.3 and −1.2, and 1.4 and −1.2 electrons $Å^{-3}$ for the La and Nd structures.

Complex form factors for the lanthanide ions [4] and complex neutral form factors for the remaining atoms [5, 6] were employed. Most of the calculations were performed on a VAX computer with the SHELX76 system of programs [7]. Final positional parameters and isotropic temperature factors are given in Tables II and III. Structure factor tables have been deposited with the Editor-in-Chief.

TABLE II. Fractional Atomic Coordinates and Isotropic Temperature Factors ($Å^2$) for the Lanthanum Complex.

Atom	x/a	y/b	z/c	B_{iso}
La	0.2013(1)	0.7415(1)	0.3663(1)	3.32(4)
S(1)	0.4811(6)	0.7490(6)	0.423(1)	7.5(2)
O(1)	0.392(2)	0.748(1)	0.478(3)	8.4(6)
C(11)	0.568(3)	0.822(2)	0.515(4)	12(1)
C(12)	0.618(3)	0.792(2)	0.655(4)	10(1)
C(13)	0.620(3)	0.702(2)	0.643(4)	9(1)
C(14)	0.553(3)	0.669(2)	0.512(4)	12(1)
S(2)	0.0482(8)	0.5625(8)	0.360(1)	9.2(3)
O(2)	0.102(2)	0.622(2)	0.287(2)	7.9(5)
C(21)	−0.076(3)	0.534(6)	0.258(8)	24(1)
C(22)	−0.075(4)	0.487(5)	0.139(6)	18(1)
C(23)	0.030(3)	0.456(4)	0.217(5)	13(1)
C(24)	0.123(4)	0.485(4)	0.328(7)	25(1)
O(31)	0.049(1)	0.746(1)	−0.048(2)	5.4(4)
O(32)	0.063(1)	0.773(1)	0.157(2)	5.1(4)
C(31)	0.014(1)	0.755(1)	0.041(2)	3.5(4)
C(32)	−0.102(1)	0.751(1)	0.003(2)	5.9(6)
F(31)	−0.136(2)	0.693(2)	−0.085(4)	6.7(9)
F(32)	−0.151(2)	0.818(2)	−0.042(4)	6.8(9)
F(33)	−0.126(3)	0.743(4)	0.114(3)	8(1)
F(34)	−0.155(3)	0.792(4)	−0.102(4)	11(1)
F(35)	−0.143(6)	0.772(7)	0.094(6)	17(1)
F(36)	−0.147(3)	0.681(2)	−0.018(6)	11(1)
O(41)	0.253(1)	0.855(1)	0.051(2)	5.7(4)
O(42)	0.264(2)	0.854(1)	0.260(2)	6.9(5)
C(41)	0.277(2)	0.879(1)	0.157(2)	3.6(4)
C(42)	0.346(2)	0.951(1)	0.182(2)	6.2(7)
F(41)	0.427(3)	0.954(3)	0.141(5)	10(1)

(continued on facing page)

TABLE II *(continued)*

Atom	x/a	y/b	z/c	B_{iso}
F(42)	0.291(3)	1.017(2)	0.152(5)	11(1)
F(43)	0.400(3)	0.974(3)	0.301(3)	9(1)
F(44)	0.326(3)	1.002(3)	0.265(4)	8(1)
F(45)	0.360(3)	0.979(2)	0.075(3)	6.4(7)
F(46)	0.442(2)	0.935(3)	0.255(5)	9(1)
O(51)	0.229(1)	0.644(1)	0.018(2)	6.2(4)
O(52)	0.288(1)	0.666(1)	0.234(2)	6.6(5)
C(51)	0.282(2)	0.626(1)	0.134(2)	3.7(4)
C(52)	0.331(2)	0.545(2)	0.157(3)	12(1)
F(51)	0.323(4)	0.509(4)	0.046(4)	13(1)
F(52)	0.368(4)	0.527(3)	0.283(3)	8(1)
F(53)	0.431(3)	0.561(3)	0.200(6)	11(1)
F(54)	0.261(3)	0.490(3)	0.117(4)	10(1)
F(55)	0.322(7)	0.503(7)	0.255(7)	23(1)
F(56)	0.396(3)	0.537(3)	0.092(4)	7.7(9)

TABLE III. Fractional Atomic Coordinates and Isotropic Temperature Factors (Å^2) for the Neodymium Complex.

Atom	x/a	y/b	z/c	B_{iso}
Nd	0.0472(1)	0.3771(1)	−0.0583(1)	4.19(4)
S(1)	0.2773(7)	0.2900(5)	0.1152(6)	6.8(2)
O(1)	0.207(2)	0.307(1)	0.013(2)	7.0(4)
C(11)	0.387(2)	0.225(2)	0.070(3)	10(1)
C(12)	0.329(4)	0.140(3)	0.056(4)	15(1)
C(13)	0.245(3)	0.126(2)	0.139(3)	9.3(9)
C(14)	0.202(2)	0.209(1)	0.176(2)	7.2(7)
S(2)	0.290(2)	0.332(1)	−0.217(2)	18.0(6)
O(2)	0.171(2)	0.384(1)	−0.192(2)	8.4(5)
C(21)	0.266(3)	0.264(2)	−0.326(3)	11(1)
C(22)	0.211(4)	0.323(3)	−0.409(4)	16(1)
C(23)	0.277(4)	0.404(3)	−0.386(4)	14(1)
C(24)	0.361(4)	0.408(3)	−0.290(3)	14(1)
O(31)	−0.007(2)	0.258(1)	−0.181(2)	7.0(4)
O(32)	−0.011(2)	0.224(1)	−0.014(2)	6.4(4)
C(31)	−0.016(2)	0.207(2)	−0.106(2)	6.0(6)
C(32)	−0.033(3)	0.116(2)	−0.143(2)	11(1)
F(31)	−0.143(3)	0.098(2)	−0.147(3)	8.5(9)
F(32)	0.001(3)	0.097(2)	−0.236(2)	6.6(7)
F(33)	0.030(3)	0.063(2)	−0.084(3)	8.5(9)
F(34)	−0.052(5)	0.062(3)	−0.069(3)	11(1)
F(35)	0.066(5)	0.095(6)	−0.179(9)	23(1)
F(36)	−0.105(7)	0.095(5)	−0.220(5)	20(1)
O(41)	0.024(1)	0.384(1)	0.130(1)	4.8(3)
O(42)	0.027(1)	0.518(1)	0.189(1)	5.5(4)
C(41)	0.023(2)	0.439(2)	0.199(2)	4.6(5)
C(42)	0.011(2)	0.406(1)	0.309(2)	6.0(6)
F(41)	0.067(4)	0.452(2)	0.382(3)	9(1)
F(42)	0.068(3)	0.334(2)	0.324(3)	6.5(7)
F(43)	−0.101(3)	0.395(3)	0.318(3)	11(1)
F(44)	0.122(3)	0.400(3)	0.338(4)	12(1)
F(45)	−0.008(5)	0.327(2)	0.325(4)	12(1)
F(46)	−0.013(3)	0.464(2)	0.377(2)	6.7(7)
O(51)	0.166(1)	0.631(1)	0.063(1)	6.2(4)
O(52)	0.140(1)	0.504(1)	−0.005(1)	5.9(4)
C(51)	0.202(2)	0.567(1)	0.028(2)	4.3(4)
C(52)	0.331(2)	0.556(2)	0.025(2)	7.1(7)
F(51)	0.389(4)	0.600(3)	0.096(4)	11(1)
F(52)	0.364(3)	0.479(2)	0.045(3)	8.3(9)
F(53)	0.356(3)	0.571(3)	−0.071(2)	8.7(9)
F(54)	0.368(4)	0.530(4)	0.118(3)	12(1)
F(55)	0.390(3)	0.627(2)	0.028(4)	9(1)
F(56)	0.364(3)	0.498(2)	−0.039(3)	8.8(9)

Results and Description of the Structure

Lanthanum Complex

The structure is shown in Fig. 1. For clarity not all the atoms are included in the projection. The La ion is coordinated to six oxygen atoms of six different trifluoroacetate and two TMSO groups, at mean Ln–O distance of 2.49(3) Å. The coordination number is therefore eight and the coordination polyhedron is a somewhat distorted trigonal dodecahedron of point symmetry $\bar{4}2_m$ (D_{2d}). All trifluoroacetate groups act as bridges between neighbour La ions, giving rise to an infinite polymer extending along the direction of c in which two consecutive complexes are directly related by the c-glide operator. Due to the fact that the y coordinate of the La ion is close to 1/2, the La–La interatomic distance is then close to $c/2$ (exactly 5.361(2) Å). All interatomic distances not fixed in the refinement are given in Table IV. The rather low accuracy of these values can be ascribed to the poor quality of the data, due to the occupational disorder of the fluorine atoms and the high values of the apparent temperature factors.

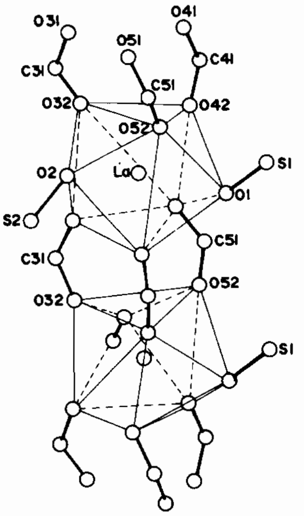

Fig. 1. Structure of Ln Complex.

TABLE IV. Interatomic Bond Distances (Å) in Both Complexes.

	Ln = La	Ln = Nd
Ln–O(1)	2.50(2)	2.32(2)
Ln–O(2)	2.43(3)	2.32(2)
Ln–O(31)	2.54(2)	2.52(2)
Ln–O(32)	2.48(2)	2.60(2)
Ln–O(41)	2.48(2)	2.45(1)
Ln–O(42)	2.50(2)	2.48(2)
Ln–O(51)	2.48(2)	2.51(2)
Ln–O(52)	2.47(2)	2.37(2)
S(1)–O(1)	1.51(3)	1.53(2)
S(2)–O(2)	1.59(3)	1.67(3)
O(31)–C(31)	1.20(3)	1.27(3)
O(32)–C(31)	1.25(3)	1.21(3)
O(41)–C(41)	1.15(3)	1.24(3)
O(42)–C(41)	1.25(3)	1.26(3)
O(51)–C(51)	1.26(3)	1.20(3)
O(52)–C(51)	1.25(3)	1.29(3)

Neodymium Complex

The structure is shown in Fig. 2, where a few atoms have been excluded for the sake of clarity. The Nd ion is coordinated to four oxygen atoms of four trifluoroacetate groups acting as bridges, two oxygen atoms of another trifluoroacetate group acting as a bidentate ligand and the oxygen atoms of the two independent TMSO groups. The coordination number is also eight but the coordination polyhedron, in contrast with the previous case, has an approximate square antiprismatic configuration of point symmetry $\bar{8}2_m$ (D_{4d}). The mean Ln–O distance is of 2.45(10) Å. The arrangement of bridging trifluoroacetate groups gives rise to centrosymmetric dimers of the complexes, as can be appreciated from Fig. 2. These four bridges cause the interatomic Nd–Nd distance to be much shorter (4.347(2) Å) than in the La complex where all ligands bridge between the cations. Interatomic distances not fixed in the refinement are given in Table IV. As in the previous case there is a low accuracy in these values resulting from disorder.

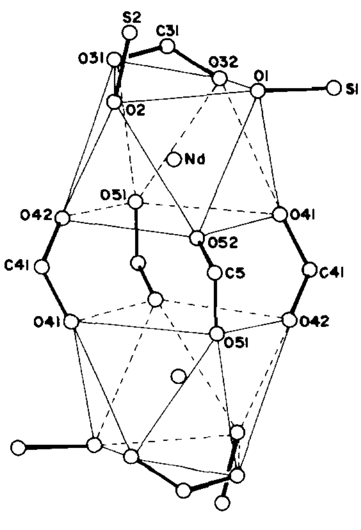

Fig. 2. Structure of Nd complex.

Discussion

Each complex displays one of the two most common types of eight-coordination polyhedra, namely the trigonal dodecahedron (TD) and the Archimedean square antiprism (SA). The occurrence of different coordinations for lanthanide series of identical stoichiometry is a common fact, known to be mainly due to the difference in the ionic radii of the metal ions [8].

The characterization of eight-coordination polyhedra distorted from the ideal models of point symmetry D_{2d} and D_{4d} requires the definition of appropriate criteria. We adopt here the ones proposed by Lippard and Russ [9], based on the observation that the TD may be considered as consisting of two mutually-perpendicular trapezoids [10]. In the SA the best trapezoidal planes make a dihedral angle of 77.4°. In the La complex, these planes are defined by O(1), O(32), O(41), O(42) and O(2), O(31), O(51), O(52); the mean deviations of the atoms from the best least-squares planes through them are 0.16 and 0.08 Å and the dihedral angle is 89°. Also there is not a pair of 'good' parallel square basis. The edges in the TD, labelled according to their type [10], are listed in Table V. In the Nd complex, the best trapezoidal planes are defined by atoms O(2), O(32), O(42), O(51) and O(1), O(31), O(41), O(51), with mean deviation from the least-squares planes through them of 0.01 and 0.13 Å and a dihedral angle of 83°.

This last figure is near the values for the ideal TD and SA polyhedra. However, the planes through atoms O(41), O(42), O(51), O(52) and O(1), O(2), O(31), O(32), with mean deviations 0.04 and 0.14 Å and a dihedral angle of 2°, are characteristic of the square bases in the SA. The edges of the polyhedron, also labelled according to [10], are given in Table V. It can be seen from this table (and even by inspection of Figure 2) that the main distortion of the coordination polyhedron from the ideal SA is the short s-type edge corresponding to the O(31)–O(32) bite. The rise in the configuration energy produced by this distortion is probably threshold high because trifluoroacetate is mostly known as a monodentate or bridging group in lanthanide complexes [3].

The mean values for the different edge types in the complexes are given in Table VI and are compared with the theoretical values for the most favourable polyhedron. It is concluded that in the La complex the coordination polyhedron is closer to the TD, while in the Nd complex it is closer to the SA.

TABLE V. Edge Lengths.

(a) Edge lengths (Å) in the La coordination polyhedron

O(1)–O(42)	3.02(3)a
O(2)–O(31)	3.07(3)a
O(1)–O(41)	2.86(3)m
O(2)–O(52)	2.87(3)m
O(31)–O(51)	2.90(3)m
O(32)–O(42)	2.95(3)m
O(32)–O(51)	4.05(3)b
O(32)–O(52)	3.43(3)b
O(41)–O(51)	3.59(3)b
O(41)–O(52)	3.59(3)b
O(1)–O(51)	3.01(3)s
O(1)–O(52)	2.90(3)s
O(2)–O(32)	2.87(3)s
O(2)–O(41)	2.94(3)s
O(31)–O(32)	3.24(2)s
O(31)–O(41)	3.22(3)s
O(42)–O(51)	2.95(3)s
O(42)–O(52)	3.21(3)s

(b) Edge Lengths (Å) in the Nd coordination polyhedron

O(1)–O(2)	2.91(3)s
O(1)–O(32)	2.88(3)s
O(2)–O(31)	2.90(3)s
O(31)–O(32)	2.21(3)s
O(41)–O(51)	3.24(2)s
O(41)–O(52)	2.96(2)s
O(42)–O(51)	2.97(2)s
O(42)–O(52)	2.99(2)s
O(1)–O(41)	2.96(2)l
O(1)–O(52)	3.23(3)l
O(2)–O(42)	2.80(3)l
O(2)–O(52)	3.10(3)l
O(31)–O(42)	3.56(3)l
O(31)–O(51)	3.04(3)l
O(32)–O(41)	3.15(2)l
O(32)–O(51)	2.98(3)l

TABLE VI. Average Polyhedra Shape Parameters.

	Parameter	Observed	MFP[a]
Dodecahedron (La)	a	1.22	1.22
	m	1.16	1.17
	g	1.22	1.24
	b	1.45	1.49
Antiprism (Nd)	l	1.27	1.26
	s	1.18	1.19
	l/s	1.07	1.06

[a] Most favourable polyhedron [10].

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