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A Bis(2,6-di-*tert*-butyl-4-methylphenolato)samarium(II) Complex, [Sm(OAr)$_2$(thf)$_3$].thf

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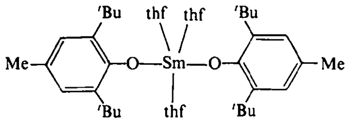
Abstract

The title complex, bis(2,6-di-*tert*-butyl-4-methylphenolato-*O*)tris(tetrahydrofuran-*O*)samarium tetrahydrofuran solvate, [Sm($C_{15}H_{23}O$)$_2$(C_4H_8O)$_3$].C_4H_8O, has distorted trigonal bipyramidal geometry around the Sm^{II} atom. The O(2), O(3) and O(4) atoms of the thf ligands form a plane and the O(1) and O(5) atoms of the aryl groups occupy the apical sites. The Sm—OAr distances Sm—O(1) and Sm—O(5) are 2.318 (7) and 2.290 (9) Å, respectively.

Comment

Divalent samarium complexes are strong reducing agents and structurally defined soluble Sm^{II} complexes are rare (Bel'sky, Gunko, Bulychev, Sizov & Soloveichik, 1990; Evans, Bloom, Hunter & Atwood, 1981; Evans, Drummond, Zhang & Atwood, 1988; Evans, Grate, Choi, Bloom, Hunter & Atwood, 1985). We are interested in the chemical behaviour of Sm^{II} complexes having different ligands. In studying the structures of Sm^{II} complexes with low coordination numbers, the crystal structure of the title compound, (I), obtained from the reaction of (ArO)$_2$SmCl (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) with Na, has been determined. The molecular structure is shown in Fig. 1.



(I)

The title compound consists of one Sm atom, two OAr ligands, three thf ligand molecules and another tetrahydrofuran molecule as a solvent in the unit cell. The coordination number of Sm^{II} is five and, to our knowledge, this is the first X-ray structure determination of a five-coordinate Sm^{II} complex. The coordination polyhedron of the Sm^{II} atom is a distorted trigonal bipyramid. The triangular plane is formed by the thf O(2), O(3) and O(4) atoms; the Sm atom is 0.0046 Å above the plane and the aryloxide O(1) and O(5) atoms occupy the apical sites. This mode of coordination is different from that of the related Yb^{II} compound [Yb(OAr)$_2$(thf)$_3$] (Deacon, Hitchcock, Holmes, Lappert, Mackinnon & Newnham, 1989) which has distorted square-pyramidal coordination. The average Sm—OAr distance is 2.304 (8) Å. The Sm—O(2)(thf) and Sm—O(3)(thf) [2.581 (10) and 2.580 (10) Å, respectively] distances are almost the same, but the Sm—O(4)(thf) distance [2.614 (11) Å] is slightly longer.

The bond angles O(1)—Sm—O(5), O(2)—Sm—O(3), O(2)—Sm—O(4) and O(3)—Sm—O(4) are 156.7 (6), 175.7 (5), 85.7 (5) and 90.0 (4)°, respectively.

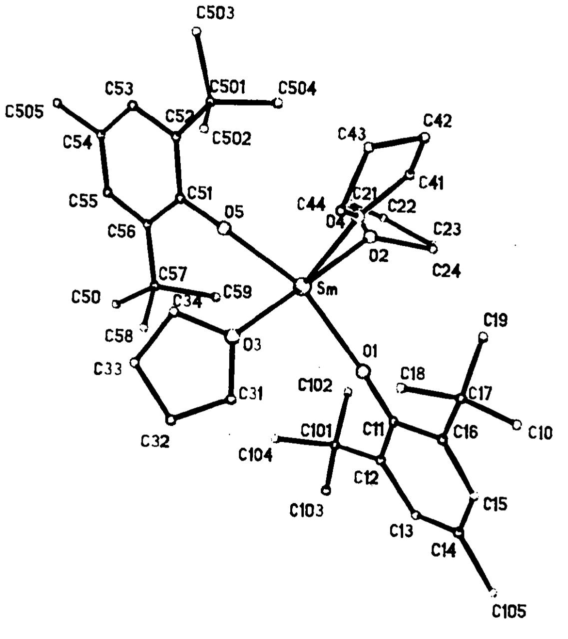


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme.

Experimental

All manipulations were carried out under argon by Schlenk techniques. Crystals were obtained by the reaction of equimolar amounts of (ArO)$_2$SmCl and Na in tetrahydrofuran, followed by crystallization from the toluene–tetrahydrofuran solvent mixture at 268 K. A suitable crystal was sealed in a thin-walled glass capillary for crystal structure determination.

Crystal data

$[Sm(C_{15}H_{23}O)_2(C_4H_8O)_3].C_4H_8O$
$M_r = 877.52$
Monoclinic
$P2_1$
$a = 9.991$ (2) Å
$b = 15.521$ (3) Å
$c = 15.667$ (3) Å
$\beta = 95.67$ (2)°
$V = 2417.4$ (9) Å^3
$Z = 2$
$D_x = 1.21$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 3.19$–13.23°
$\mu = 1.28$ mm^{-1}
$T = 298$ K
Block
0.62 × 0.40 × 0.24 mm
Brown–black

Data collection

Nicolet $R3m/E$ diffractometer
ω scans (6.5° min^{-1})
Absorption correction: empirical
$T_{\min} = 0.303$, $T_{\max} = 0.478$
4081 measured reflections
3992 independent reflections

2735 observed reflections $[F_o > 3\sigma(F_o)]$
$R_{\rm int} = 0.0511$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 19$
$l = -19 \rightarrow 19$
2 standard reflections
frequency: 100 min
intensity variation: <2%

Refinement

Refinement on F
$R = 0.057$
$wR = 0.059$
$S = 0.966$
2735 reflections
452 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F) + 0.0002F^2]$
$(\Delta/\sigma)_{\max} < 0.027$
$\Delta\rho_{\max} = 1.029$ e Å^{-3}
$\Delta\rho_{\min} = -1.617$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Sm	0.00874 (7)	0.5†	0.28145 (4)	0.050 (1)
O(1)	−0.1459 (8)	0.4980 (13)	0.1610 (5)	0.061 (3)
O(2)	−0.1861 (9)	0.4841 (12)	0.3769 (6)	0.078 (6)
O(3)	0.2030 (10)	0.5282 (9)	0.1881 (6)	0.081 (6)
O(4)	0.0039 (10)	0.6636 (7)	0.3205 (7)	0.076 (5)
O(5)	0.1612 (9)	0.4442 (6)	0.3857 (6)	0.057 (4)
C(11)	−0.2232 (13)	0.4906 (16)	0.0903 (8)	0.058 (6)
C(12)	−0.2608 (18)	0.4053 (13)	0.0577 (11)	0.091 (9)
C(13)	−0.3569 (16)	0.3978 (12)	−0.0224 (11)	0.083 (8)
C(14)	−0.4005 (14)	0.4690 (10)	−0.0645 (9)	0.078 (9)
C(15)	−0.3574 (14)	0.5548 (11)	−0.0355 (10)	0.075 (7)
C(16)	−0.2762 (13)	0.5680 (11)	0.0420 (10)	0.057 (6)
C(17)	−0.2413 (15)	0.6559 (14)	0.0728 (12)	0.089 (9)
C(18)	−0.0848 (16)	0.6664 (12)	0.0788 (11)	0.101 (9)
C(19)	−0.2900 (17)	0.6690 (12)	0.1592 (11)	0.091 (9)
C(10)	−0.2975 (18)	0.7296 (14)	0.0137 (14)	0.133 (12)
C(101)	−0.2124 (17)	0.3266 (11)	0.1008 (14)	0.095 (10)
C(102)	−0.2574 (19)	0.3183 (12)	0.1898 (13)	0.106 (10)
C(103)	−0.2560 (20)	0.2430 (13)	0.0544 (15)	0.148 (13)
C(104)	−0.0602 (15)	0.3185 (11)	0.1083 (10)	0.076 (7)
C(105)	−0.4872 (20)	0.4639 (15)	−0.1489 (11)	0.143 (13)
C(21)	−0.1820 (21)	0.4294 (16)	0.4530 (13)	0.140 (12)
C(22)	−0.3087 (20)	0.3904 (19)	0.4545 (12)	0.183 (15)
C(23)	−0.3999 (18)	0.4365 (14)	0.3932 (14)	0.144 (12)
C(24)	−0.3268 (12)	0.5100 (20)	0.3530 (11)	0.099 (8)
C(31)	0.1991 (17)	0.5230 (24)	0.0997 (10)	0.153 (16)
C(32)	0.3203 (19)	0.4920 (29)	0.0743 (10)	0.186 (16)
C(33)	0.4143 (15)	0.5042 (29)	0.1505 (11)	0.192 (15)
C(34)	0.3421 (16)	0.5306 (22)	0.2161 (11)	0.148 (17)
C(41)	−0.0905 (17)	0.7044 (10)	0.3717 (11)	0.090 (8)
C(42)	−0.0470 (22)	0.7915 (12)	0.3834 (16)	0.148 (14)
C(43)	0.0938 (20)	0.7992 (14)	0.3552 (15)	0.127 (12)
C(44)	0.1027 (20)	0.7299 (11)	0.2971 (15)	0.108 (11)
C(51)	0.2402 (15)	0.3991 (10)	0.4484 (10)	0.044 (6)
C(52)	0.2861 (23)	0.4480 (13)	0.5229 (12)	0.048 (7)
C(53)	0.3736 (17)	0.4079 (12)	0.5885 (12)	0.058 (7)
C(54)	0.4000 (14)	0.3185 (10)	0.5797 (9)	0.062 (6)
C(55)	0.3517 (15)	0.2731 (11)	0.5063 (9)	0.065 (6)
C(56)	0.2724 (14)	0.3136 (10)	0.4417 (10)	0.058 (6)
C(57)	0.2182 (15)	0.2631 (11)	0.3622 (11)	0.079 (7)
C(58)	0.2668 (18)	0.2989 (13)	0.2804 (10)	0.096 (9)
C(59)	0.0547 (14)	0.2687 (16)	0.3512 (11)	0.121 (11)
C(50)	0.2604 (21)	0.1690 (11)	0.3664 (14)	0.133 (11)
C(501)	0.2670 (24)	0.5419 (16)	0.5355 (15)	0.086 (11)
C(502)	0.3162 (21)	0.5932 (13)	0.4649 (13)	0.095 (10)
C(503)	0.3300 (17)	0.5849 (12)	0.6206 (11)	0.102 (9)
C(504)	0.1135 (17)	0.5624 (12)	0.5360 (11)	0.098 (9)
C(505)	0.4888 (17)	0.2699 (12)	0.6509 (11)	0.091 (8)
O(6)	1.0888 (31)	0.0392 (21)	0.1734 (22)	0.322 (18)
C(61)	1.0583 (35)	−0.0437 (21)	0.1138 (20)	0.194 (15)
C(62)	0.9419 (34)	−0.0823 (18)	0.1477 (21)	0.166 (12)
C(63)	0.8689 (34)	−0.0046 (34)	0.1733 (25)	0.270 (17)
C(64)	0.9680 (43)	0.0473 (24)	0.2204 (22)	0.234 (18)

† Coordinate fixed to define origin.

Table 2. *Selected geometric parameters* (Å, °)

Sm—O(1)	2.318 (7)	Sm—O(2)	2.581 (10)
Sm—O(3)	2.580 (10)	Sm—O(4)	2.614 (11)
Sm—O(5)	2.290 (9)	O(1)—C(11)	1.292 (15)
O(5)—C(51)	1.388 (17)	O(2)—C(21)	1.460 (26)
O(2)—C(24)	1.475 (18)	C(11)—C(12)	1.455 (31)
C(11)—C(16)	1.488 (27)	C(12)—C(13)	1.507 (23)
C(12)—C(101)	1.455 (26)	C(13)—C(14)	1.339 (23)
C(14)—C(15)	1.458 (23)	C(14)—C(105)	1.509 (22)
C(15)—C(16)	1.406 (20)	C(16)—C(17)	1.478 (27)
C(17)—C(18)	1.565 (22)	C(17)—C(19)	1.497 (26)
C(17)—C(10)	1.542 (29)	C(101)—C(102)	1.511 (30)
C(101)—C(103)	1.530 (28)	C(101)—C(104)	1.519 (22)
C(21)—C(22)	1.405 (31)	C(22)—C(23)	1.445 (31)
C(23)—C(24)	1.525 (33)	O(6)—C(61)	1.60 (5)
O(6)—C(64)	1.48 (5)	C(61)—C(62)	1.45 (5)
C(62)—C(63)	1.49 (6)	C(63)—C(64)	1.42 (6)
O(1)—Sm—O(2)	89.5 (3)	O(1)—Sm—O(3)	91.1 (3)
O(2)—Sm—O(3)	175.7 (5)	O(1)—Sm—O(5)	156.7 (6)
O(2)—Sm—O(5)	92.1 (3)	O(3)—Sm—O(5)	89.1 (3)
O(1)—Sm—O(4)	100.2 (5)	O(2)—Sm—O(4)	85.7 (5)
O(3)—Sm—O(4)	90.0 (4)	O(4)—Sm—O(5)	103.1 (3)
Sm—O(1)—C(11)	173.5 (13)	Sm—O(2)—C(21)	124.6 (11)
Sm—O(2)—C(24)	125.5 (10)	Sm—O(3)—C(34)	126.8 (9)
Sm—O(3)—C(31)	127.5 (10)	Sm—O(4)—C(44)	125.6 (10)
Sm—O(4)—C(41)	125.8 (9)	Sm—O(5)—C(51)	170.9 (9)
O(1)—C(11)—C(16)	121.1 (20)	O(1)—C(11)—C(12)	119.6 (20)
C(11)—C(12)—C(13)	118.9 (16)	C(12)—C(11)—C(16)	119.3 (12)
C(13)—C(12)—C(101)	118.4 (17)	C(11—C(12)—C(101)	122.6 (15)
C(13)—C(14)—C(15)	121.9 (14)	C(12)—C(13)—C(14)	119.7 (16)
C(15)—C(14)—C(105)	116.6 (14)	C(13)—C(14)—C(105)	121.3 (16)
C(11)—C(16)—C(15)	117.9 (15)	C(14)—C(15)—C(16)	122.0 (14)
C(15)—C(16)—C(17)	120.9 (15)	C(11)—C(16)—C(17)	121.2 (13)

Space group $P2_1$ was indicated from systematic absences (hkl, $0k0$, $k = 2n + 1$). Corrections for Lorentz and polarization effects were applied. The main computer program used was *SHELXTL* (Sheldrick, 1983). The structure was solved by the Patterson method and refined by least-squares calculations, initially with isotropic and finally with anisotropic displacement parameters for the non-H atoms. The y coordinate of the Sm atom was fixed to determine the origin and the absolute structure was determined by refinement of a $\Delta f''$ multiplier. H atoms were placed in calculated positions and were assigned common isotropic displacement parameters, $U = 0.08$ Å^2. The H atoms of two of the tetrahydrofuran ligands and also of the tetrahydrofuran solvate molecule were not located.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AL1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Isomorphous Compounds $[Nd(TDTD)_{1.5}(pic)_3]$ and $[Er(TDTD)_{1.5}(pic)_3]$ (pic = Picrate, TDTD = *trans*-1,4-Dithiane *S*,*S*′-Dioxide)

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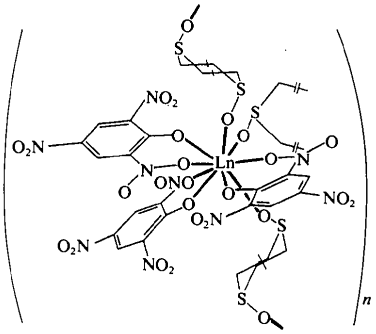
Abstract

The structures of two isomorphous and isostructural lanthanide derivatives, poly[tri(picrato-O^1,O^2)neodymium-μ-(*trans*-1,4-dithione *S*,*S*′-dioxide-*S*:*S*′)$_{1.5}$], $[Nd(C_6H_2N_3O_7)_3(C_4H_8O_2S_2)_{1.5}]$, and poly[tri(picrato-$O^1$,$O^2$)erbium-$\mu$-(*trans*-1,4-dithiane *S*,*S*′-dioxide-*S*:*S*′)$_{1.5}$], $[Er(C_6H_2N_3O_7)_3(C_4H_8O_2S_2)_{1.5}]$, consist of nine-coordinate metal ions, linked to three bidentate picrate ligands, bound *via* the phenoxo O atom and one O atom of an adjacent nitro group, and to three O atoms of three TDTD ligands. The TDTD ligands act as bridges that join three neighbouring lanthanide ions, to give three-dimensional polymers. The coordination polyhedra of the Nd^{III} and Er^{III} ions may best be described as tricapped trigonal prisms.

Comment

We are currently studying the crystal structures and some spectroscopic properties of a series of lanthanide picrates with TDTD as a neutral ligand (Ayala, Zinner, Vicentini, Del Pra & Bombieri, 1993). The title compounds, (I) and (II), have polymeric structures in which the conformations of the picrate (Herbstein & Kaftory, 1976) and TDTD (Shearer, 1959) ligands are unchanged with respect to those of the free ligands. The only feature of note is the shortening of the C—O phenoxo bond [average distance 1.24 (1) Å] with respect to the corresponding distance in picric acid [1.327 (3) Å (Herbstein & Kaftory, 1976)] as has been found in a series of dipicrate derivatives (Nardelli, Pelizzi, Vitali, Bordi, Plazzi & Vitali, 1987) which present a comparable average value of 1.247 (3) Å. This shortening suggests a tendency of the picrate ligand to assume a quinone-like structure.



(I) Ln = Nd
(II) Ln = Er

The structures of the Nd and Er complexes (Figs. 1 and 2) are characterized by similar trends in the Ln—O distances, which can be classified into three types, depending on the nature of the O atom. The shortest distance is Ln—O$_{\rm phenoxo}$ [average Nd—O = 2.348 (5); average Er—O = 2.247 (5) Å], the intermediate distance is Ln—O$_{\rm TDTD}$ [average Nd—O = 2.403 (5); average Er—O = 2.304 (6) Å] and the largest distance is Ln—O$_{\rm nitro}$ [average Nd—O = 2.690 (6); average Er—O = 2.662 (6) Å]. The same trend was observed in the analogous derivatives of the lighter lanthanides, $[Ce(TDTD)_{1.5}(pic)_3].H_2O$ and $[Eu(TDTD)_{1.5}(pic)_3]$ (Ayala *et al.*, 1993).