

Di- μ -phenylthio-bis[bis(η^5 -methylcyclopentadienyl)(tetrahydrofuran)-lanthanum(III)] bis(tetrahydrofuran) solvate

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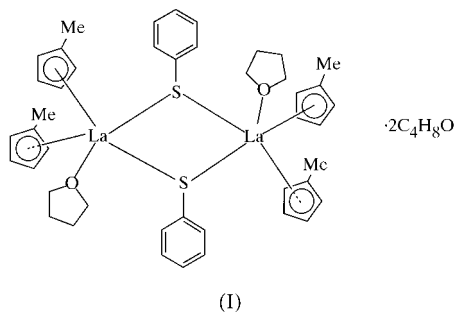
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The title complex, $[\text{La}_2(\text{C}_6\text{H}_7)_4(\text{C}_6\text{H}_5\text{S})_2(\text{C}_4\text{H}_8\text{O})_2] \cdot 2\text{C}_4\text{H}_8\text{O}$, is a centrosymmetric dimer bridged through the S atoms of the benzenethiolate ligands. The bridging La_2S_2 unit is completely planar, while the geometry around the nine-coordinate La atom is that of a distorted trigonal bipyramid. The $\text{La}-\text{S}-\text{La}$ and $\text{S}-\text{La}-\text{S}$ angles are $117.51(4)$ and $62.5(1)^\circ$, respectively, and the average $\text{La}-\text{S}$ bond length is 2.9759 \AA . The crystals contain two tetrahydrofuran solvate molecules for every complex molecule.

Comment

The synthesis of lanthanide–thiolate compounds is of current interest as these compounds are used in organic synthesis (Taniguchi *et al.*, 1994), as rational molecular precursors to materials (Brewer *et al.*, 1994) and as initiators for syndio-specific polymerization of methyl methacrylate (Nakayama *et al.*, 1996). While studying the catalytic properties of organo-lanthanide thiolates, we obtained di- μ -phenylthio-bis[bis(η^5 -methylcyclopentadienyl)(tetrahydrofuran)lanthanum(III)]



bis(tetrahydrofuran) solvate, (I), from the reaction of LaCp'_3 (Cp' is η^5 -methylcyclopentadienyl) with benzenethiol in a 1:1 molar ratio in tetrahydrofuran (THF).

The crystal structure determination of (I) demonstrates that the complex is a centrosymmetric binuclear molecule, with the benzenethiolate ligands as bridging groups. The La atom is coordinated by two Cp' rings, two benzenethiolate S atoms and one THF O atom, forming a distorted trigonal-bipyramid geometry, giving the central metal a formal coordination number of nine if the Cp' group is regarded as occupying three coordination sites.

The two $\text{La}-\text{S}$ distances in (I) are not equal (Table 1) and have an average value of 2.9759 \AA , the average being consistent with that found in the related sulfur-bridged complex $[\text{Ce}(\text{Me}_3\text{CC}_5\text{H}_4)_2(\mu\text{-SCHMe}_2)]_2$ [$2.882(6) \text{ \AA}$; Stults *et al.*, 1990], once the difference in the ionic radii of the metal atoms has been taken into consideration.

The $\text{La}-\text{S}-\text{La}$ angle in (I) [$117.51(4)^\circ$] is larger than that found in the complex $[\text{Yb}(\text{C}_5\text{H}_5)_2(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)]_2$, (II) [$94.43(8)^\circ$; Wu *et al.*, 1996]. However, the $\text{S}-\text{La}-\text{S}$ angle in (I) [$62.5(1)^\circ$] is much smaller than that found in (II) [$85.57(8)^\circ$]. The $\text{Cp}'_{\text{centroid}}-\text{La}$ distances in (I) [$2.565(7)$ and $2.562(6) \text{ \AA}$] are much longer than those observed for the $\text{Cp}'_{\text{centroid}}-\text{Yb}$ distances in (II) (2.315 and 2.412 \AA). These differences may be due to the difference in the ionic radii of the metal atoms in (I) and (II).

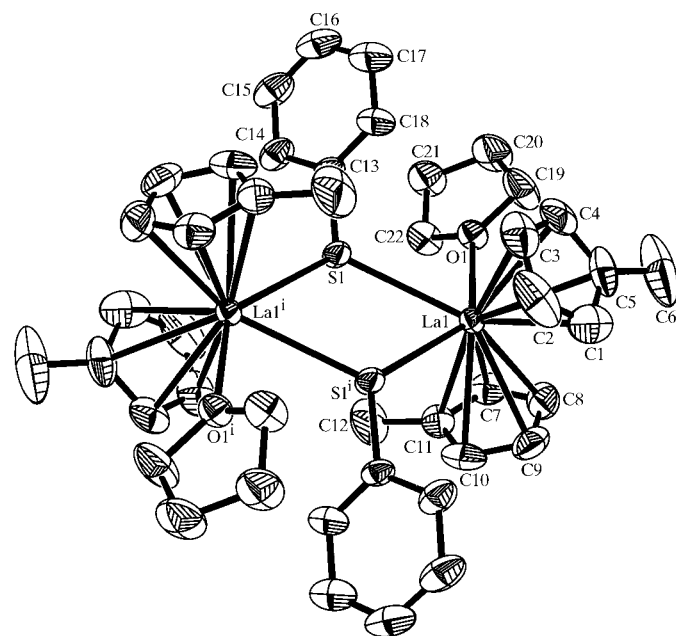


Figure 1

The molecular structure of (I) showing 40% probability displacement ellipsoids and the atom-numbering scheme [symmetry code: (i) $1 - x, -y, -z$]. H atoms have been omitted for clarity.

Experimental

Complex (I) was isolated from the reaction of LaCp'_3 with one equivalent of benzenethiol in THF, followed by crystallization from a toluene–THF solution at 263 K . The complex is very sensitive to air and moisture; therefore, all manipulations were conducted under purified argon using Schlenk techniques. A crystal suitable for analysis was sealed in a thin-walled glass capillary.

Crystal data

[La₂(C₆H₇)₄(C₆H₅S)₂·
(C₄H₈O)₂]·2C₄H₈O
M_r = 1101.07
Monoclinic, P2₁/n
a = 9.1535 (11) Å
b = 17.337 (2) Å
c = 16.637 (2) Å
β = 100.031 (2)°
V = 2599.8 (5) Å³
Z = 2

D_x = 1.406 Mg m⁻³
Mo Kα radiation
Cell parameters from 6888
reflections
θ = 4.7–52.7°
μ = 1.74 mm⁻¹
T = 298 (2) K
Prismatic, colourless
0.70 × 0.45 × 0.40 mm

Data collection

Bruker SMART CCD area-detector
diffractometer
ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)
T_{min} = 0.345, T_{max} = 0.498
10 479 measured reflections
4585 independent reflections

3679 reflections with I > 2σ(I)
R_{int} = 0.025
θ_{max} = 25.0°
h = -10 → 10
k = -16 → 20
l = -16 → 19
Intensity decay: 5.9%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.035
wR(F²) = 0.097
S = 1.07
4585 reflections
272 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0450P)²
+ 3.4381P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.003
Δρ_{max} = 0.63 e Å⁻³
Δρ_{min} = -0.58 e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.0025 (3)

Table 1

Selected bond lengths (Å).

La1—C1	2.799 (7)	La1—C9	2.781 (6)
La1—C2	2.788 (7)	La1—C10	2.817 (6)
La1—C3	2.810 (6)	La1—C11	2.866 (5)
La1—C4	2.829 (6)	La1—O1	2.624 (3)
La1—C5	2.839 (6)	La1—S1	2.9758 (13)
La1—C7	2.834 (6)	S1—La1 ¹	2.9760 (13)
La1—C8	2.772 (6)		

Symmetry code: (i) 1 - x, -y, -z.

H atoms were included in calculated positions (C—H = 0.93–0.98 Å) but not refined.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1111). Services for accessing these data are described at the back of the journal.

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