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Dicyclopentadienyl Complexes of Samarium(III): [Sm(η^5 -C₅H₄SiMe₃)₂(μ -Cl)]₂

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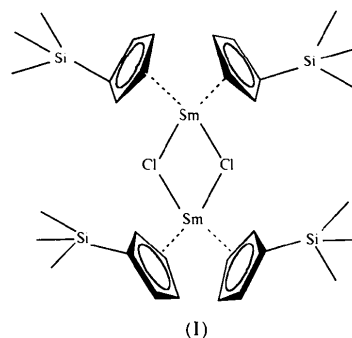
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Abstract

The title compound, di- μ -chloro-bis[(η^5 -trimethylsilylcyclopentadienyl)samarium(III)], [SmCl₂(C₅H₄SiMe₃)₂], which has been characterized by single-crystal X-ray diffraction, is isostructural with its ytterbium analogue. The geometrical parameters of the lanthanide atoms are compared in the two compounds. Results and conclusions reported for [Yb(η^5 -C₅H₄SiMe₃)₂(μ -Cl)]₂ are entirely corroborated by the present structure analysis.

Comment

One important factor affecting the stability of organometallic complexes of the lanthanides is the saturation of the coordination sphere of the metal with bulky ligands in order to sterically block decomposition pathways (Evans, 1982). As the atomic (and ionic) radii decrease when the lanthanide series is traversed from lanthanum to lutetium, it is less difficult to sterically saturate the coordination environment of the elements occurring later in the series. Therefore, Er, Yb and Lu are the most frequently used in synthesis as they form more stable complexes than the larger early members of the lanthanide series. Samarium is a frontier element in terms of obtaining stable organometallic complexes. We reported previously the synthesis and crystal structure analysis of the dimeric complex [Yb(η^5 -C₅H₄SiMe₃)₂(μ -Cl)]₂ (Spirlet & Goffart, 1995). The synthesis of the corresponding samarium derivative, (I), and the growing of single crystals suitable for X-ray diffraction allows a comparison of the coordination geometry in the two complexes which have similar bridged samarium dimers.



The present X-ray structure analysis reveals that the complex [Sm(η^5 -C₅H₄SiMe₃)₂(μ -Cl)]₂ is isostructural with the corresponding Yb derivative (Spirlet & Goffart, 1995). The structural dimeric unit is centrosymmetric with bridging Cl atoms. The pseudo-tetrahedral coordination geometry about the Sm atom, as well as the respective orientation of the ligands in the coordination sphere, are identical in the two compounds. The four centroids of the monosubstituted cyclopentadienyl rings exhibit a square-planar arrangement. The mean bond lengths Sm—Cl [2.754(3) Å] and Sm—C [2.68(1) Å] are, as expected (lanthanide contraction), longer than the corresponding Yb—Cl [2.643(2) Å] and Yb—C [2.599(9) Å] bond distances in [Yb(η^5 -C₅H₄SiMe₃)₂(μ -Cl)]₂. Sm—C distances are in agreement with the values reported for [Sm{C₅H₃(SiMe₃)₂}₂(μ -OH)]₂ (Hitchcock *et al.*, 1991). It has been shown (Evans *et al.*, 1993) that bimetallic tetracyclopentadienylsamarium complexes can adopt either tetrahedral or square-planar geometries for the four ring centroids depending on the size of the bridging ligands and the degree of substitution on the cyclopentadienyl rings. Complexes containing two crowded (C₅Me₅)₂Sm units and small bridging ligands exhibit structures in which the four pentamethylcyclopentadienyl ring centroids define a tetrahedral geometry rather than a square-planar arrangement as in [Sm(C₅Me₅)₂]₂(μ -N₂) (Evans *et al.*, 1988), [Sm(C₅Me₅)₂]₂(μ -O) (Evans *et al.*, 1985), [Sm(C₅Me₅)₂(μ -H)]₂ (Evans *et al.*, 1983) and [Sm(C₅Me₅)₂]₂(μ -HNNH) (Evans *et al.*, 1992). Other complexes which possess less steric congestion favour square-planar arrangements of ring centroids as in [Sm(C₅H₄Me)₂(thf)(μ -Cl)]₂ (Evans *et al.*, 1993), [Sm(C₅H₄Me)₂C≡CC(Me)₃]₂ (Evans *et al.*, 1983), [Sm{C₅H₃(SiMe₃)₂}₂(μ -OH)]₂ (Hitchcock *et al.*, 1991), [Sm(C₅H₃Bu₂)₂(μ -H)]₂ and [Sm(C₅H₃Bu₂)₂(μ -BH₄)]₂ (Gun'ko *et al.*, 1992). The present structure provides further information on how steric effects govern the structures of bimetallic organosamarium complexes. Here, the Sm—Cl—Sm'—Cl' bridging unit is planar like the Sm—O—Sm'—O' unit in the bridged hydroxide, with angles at the lanthanide atom appreciably smaller than at the bridging atom. No unusually short intermolecular contacts are observed.

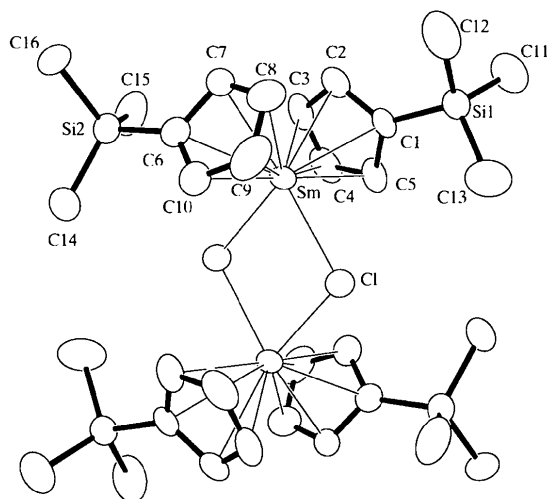


Fig. 1. The molecular structure of (I) showing the atom labelling and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title complex was prepared by reaction of SmCl_3 with $\text{Li}(\text{C}_5\text{H}_4\text{SiMe}_3)$ in THF followed by precipitation with $n\text{-C}_6\text{H}_{14}$. Extraction followed by slow recrystallization from $n\text{-C}_6\text{H}_{14}$ gave prismatic yellow single crystals suitable for X-ray analysis. A selected specimen was sealed in a thin-walled glass capillary. Since the complex is extremely air and moisture sensitive, all manipulations were carried out under nitrogen with strict exclusion of air and water, by use of the Schlenk technique.

Crystal data

$[\text{SmCl}_2(\text{C}_8\text{H}_{13}\text{Si})_4]$

$M_r = 920.70$

Triclinic

$P\bar{1}$

$a = 8.736(2) \text{ \AA}$

$b = 9.909(2) \text{ \AA}$

$c = 12.705(3) \text{ \AA}$

$\alpha = 70.37(3)^\circ$

$\beta = 76.86(3)^\circ$

$\gamma = 88.74(3)^\circ$

$V = 1007.0(4) \text{ \AA}^3$

$Z = 2$

$D_x = 3.036 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Siemens R3m/V-4 diffractometer

$2\theta/\theta$ scans

Absorption correction:

ψ scan (North *et al.*, 1968)

$T_{\min} = 0.107$, $T_{\max} = 0.283$

6028 measured reflections

5675 independent reflections

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 7.0\text{--}45.0^\circ$

$\mu = 6.315 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prism

$0.4 \times 0.3 \times 0.2 \text{ mm}$

Light brown

Cnr1-Sm-Cnr2

$\text{Sm-Cl-Sm}'$

Refinement

Refinement on F

$R = 0.061$

$wR = 0.067$

$S = 2.64$

5017 reflections

181 parameters

H atoms constrained to

parent atoms

$w = 1/[\sigma^2(F_o)]$

$(\Delta/\sigma)_{\max} = 0.010$

$\Delta\rho_{\max} = 1.57 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.74 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cnr1 and *Cnr2* refer to the centroids of rings C1–C5 and C6–C10, respectively.

Sm—C7	2.646 (8)	Si1—C13	1.878 (12)
Sm—C3	2.649 (11)	Si1—C12	1.889 (12)
Sm—C10	2.674 (10)	Si2—C6	1.838 (9)
Sm—C4	2.679 (12)	Si2—C15	1.847 (12)
Sm—C2	2.689 (11)	Si2—C14	1.857 (15)
Sm—C9	2.690 (11)	Si2—C16	1.865 (8)
Sm—C5	2.690 (10)	C1—C2	1.434 (11)
Sm—C8	2.694 (11)	C1—C5	1.474 (14)
Sm—C6	2.707 (8)	C2—C3	1.412 (15)
Sm—C1	2.714 (11)	C3—C4	1.367 (14)
Sm— <i>Cnr1</i>	2.411 (11)	C4—C5	1.373 (13)
Sm— <i>Cnr2</i>	2.401 (11)	C6—C7	1.427 (15)
Sm—Cl	2.745 (2)	C6—C10	1.429 (12)
Sm—Cl'	2.762 (3)	C7—C8	1.392 (14)
Cl—Sm'	2.762 (3)	C8—C9	1.371 (17)
Si1—C1	1.847 (10)	C9—C10	1.379 (17)
Si1—C11	1.854 (15)		
C7—Sm—Cl	134.6 (2)	C1—Si1—C11	108.9 (5)
C3—Sm—Cl	132.2 (2)	C1—Si1—C13	110.0 (6)
C10—Sm—Cl	93.0 (2)	C11—Si1—C13	112.2 (6)
C4—Sm—Cl	103.9 (2)	C1—Si1—C12	109.1 (5)
C2—Sm—Cl	126.6 (2)	C11—Si1—C12	106.4 (6)
C9—Sm—Cl	85.1 (2)	C13—Si1—C12	110.0 (6)
C5—Sm—Cl	83.3 (2)	C6—Si2—C15	110.9 (5)
C8—Sm—Cl	108.1 (2)	C6—Si2—C14	108.6 (5)
C6—Sm—Cl	123.0 (2)	C15—Si2—C14	110.8 (6)
C1—Sm—Cl	95.8 (2)	C6—Si2—C16	108.5 (5)
C7—Sm—Cl'	116.3 (2)	C15—Si2—C16	107.1 (5)
C3—Sm—Cl'	94.5 (3)	C14—Si2—C16	110.9 (5)
C10—Sm—Cl'	89.2 (2)	C2—C1—C5	104.8 (8)
C4—Sm—Cl'	80.6 (3)	C3—C2—C1	108.2 (8)
C2—Sm—Cl'	125.1 (2)	C4—C3—C2	108.6 (8)
C9—Sm—Cl'	116.2 (3)	C3—C4—C5	110.6 (10)
C5—Sm—Cl'	98.4 (2)	C4—C5—C1	107.7 (7)
C8—Sm—Cl'	136.4 (3)	C7—C6—C10	101.7 (8)
C6—Sm—Cl'	87.6 (2)	C8—C7—C6	111.1 (8)
C1—Sm—Cl'	129.0 (2)	C9—C8—C7	107.7 (11)
Cl—Sm—Cl'	81.5 (1)	C8—C9—C10	107.7 (9)
<i>Cnr1</i> —Sm— <i>Cnr2</i>	129.4 (4)	C9—C10—C6	111.7 (10)
Sm—Cl—Sm'	98.5 (1)		

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

H atoms were placed at ideal positions with fixed isotropic displacement parameters ($U_{\text{iso}} = 0.08 \text{ \AA}^2$) and were constrained to ride on the parent atom. The somewhat high S value is related to the use of experimental weights in the refinement.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1990). Program(s) used to refine structure: SHELXTL-Plus (Sheldrick, 1991). Molecular graphics: SHELXTL-Plus. Software used to prepare article for publication: SHELXTL-Plus.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1010). Services for accessing these data are described at the back of the journal.

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Heavy-Metal π Complexes. 13.† Trichloro-(1,2,3-trimethylbenzene)bismuth(III)

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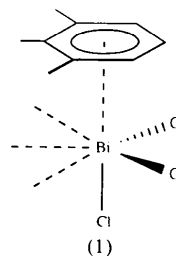
Abstract

The title compound, [BiCl₃(1,2,3-Me₃C₆H₃)], contains quasi-dimeric units of arene-coordinated BiCl₃ fragments that are further associated *via* additional Bi—Cl contacts to form coordination-polymeric layers. The re-

sulting coordination number of Bi is 3 + 3 + 1 (primary + secondary Cl contacts + arene). The Bi–arene bonding is characterized by Bi—C distances in the range 3.168 (7)–3.751 (8) Å.

Comment

The ability of liquid arenes to dissolve BiCl₃ and the isolation of arene solvates from the corresponding solutions was first reported in 1968 (Peyronel *et al.*, 1968). During the last three decades the crystal structures of compounds derived from the most important monocyclic arenes have been elucidated: [BiCl₃(arene)], where arene is C₆H₆ (Frank *et al.*, 1993); MeC₆H₅, 1,2-, 1,3- and 1,4-Me₂C₆H₄ (Müller-Becker *et al.*, 1993); 1,3,5-Me₃C₆H₃ (Schmidbaur, Wallis *et al.*, 1987); [(BiCl₃)₂(C₆Me₆)] (Schmidbaur, Nowak *et al.*, 1987). As part of a systematic study of the dependency of arene basicity on the strength of Bi–arene π bonding, we prepared the hitherto unknown compound [BiCl₃(1,2,3-Me₃C₆H₃)], (1), and determined its solid-state structure at ambient temperature.



In contrast to unsolvated BiCl₃, which has eight Cl atoms in the Bi coordination sphere (Nyburg *et al.*, 1971), the Bi atom in (1) has only six Cl neighbours, suggesting that 1,2,3-trimethylbenzene solvation in a formal sense replaces two weak Bi—Cl interactions. In this respect, 1,2,3-trimethylbenzene behaves like benzene or mesitylene, which both solvate BiCl₃ to give related layer polymers, and unlike the three isomeric xylenes, which all give chain coordination polymers characterized by three strong and two weak Cl contacts and the arene interaction of Bi. With respect to the different strengths of the six Bi—Cl contacts, (1) is best interpreted as a layer coordination compound, built up from quasi-dimeric units of arene-coordinated BiCl₃ fragments.

As documented by the lengths of the three short Bi—Cl bonds [Bi1—Cl1 2.5226 (17), Bi1—Cl2 2.4684 (17) and Bi1—Cl3 2.4680 (14) Å] and the corresponding Cl—Bi—Cl angles [Cl1—Bi1—Cl2 93.13 (6), Cl1—Bi1—Cl3 92.30 (6) and Cl2—Bi1—Cl3 86.24 (6)°], the geometry of the BiCl₃ fragment is closely related to that found in the crystal structure of solid BiCl₃ [Bi—Cl 2.468 (4)–2.518 (7) Å and Cl—Bi—Cl 84.45 (14)–94.9 (3)°]. As shown by the Bi—C distances [Bi—

† Part 12: Frank & Wittmer (1997).