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Tri-μ_2-chloro-tetrachloro-μ_3-oxo-hexakis(tetrahydrofuran-κO)di-titanium(III)samarium(III): a novel trinuclear Sm–Ti mixed species

Claude Villiers,* Pierre Thuéry* and Michel Ephritikhine

CEA/Saclay, DSM/DRECAM/SCM (CNRS URA 331), Bâtiment 125, 91191 Gif-sur-Yvette, France
Correspondence e-mail: villiers@drecam.cea.fr, thuery@drecam.cea.fr

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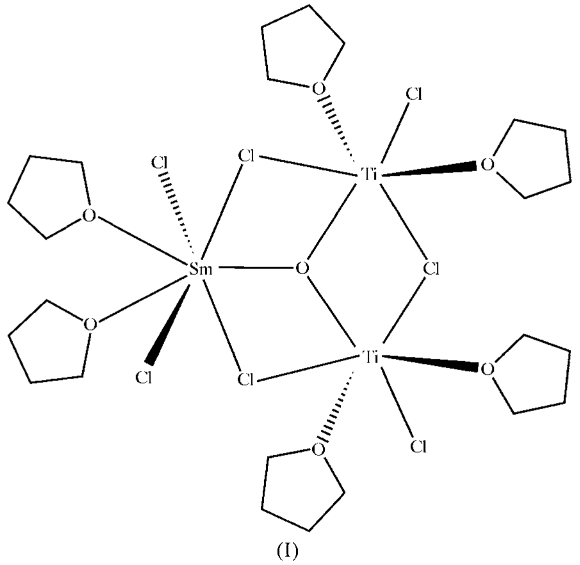
In the title compound, $[SmTi_2Cl_7O(C_4H_8O)_6]$, the metal ions are linked by a central μ_3-oxo ion and by three μ_2-chloro ions, giving a planar moiety containing a binary crystallographic axis. The coordination spheres are completed by terminal chloro ligands and tetrahydrofuran molecules, with resulting pentagonal bipyramidal and octahedral environments for the Sm and Ti atoms, respectively.

Comment

There is increasing interest in the use of the lanthanide metals as electron-transfer reagents in organic transformations, such as the reductive dimerization of carbonyl compounds (Banik, 2002). The dualistic aspect of the latter reaction, including pinacol coupling and olefin reactions, has been extensively investigated in the case of low-valent titanium reagents, produced by $TiCl_4$ or $TiCl_3$ with reducers such as alkali metals, C_8K, $LiAlH_4$, Mg(Hg), Zn or Zn(Cu) (Ephritikhine & Villiers, 2004). On the other hand, the catalytic activity of the $TiCl_4$–Sm system in propylene metathesis has been demonstrated (Imamura *et al.*, 1989). As an extension of our studies on the McMurry reaction with the low-valent titanium reagent system $TiCl_4$–Li(Hg) (Villiers & Ephritikhine, 2001), we have investigated the use of samarium metal instead of lithium amalgam as a reducing agent. In this context, we have isolated the title compound, (I), as the sole species from a tetrahydrofuran (THF) solution of the $TiCl_4$–Sm couple at 333 K, the presence of the oxo ion probably being due to adventitious traces of oxygen and/or water entering the NMR tube during heating. Compound (I) belongs to the family of mixed-metal species uniting lanthanide and transition metal ions. Only one complex with a μ_3-oxo ion bridging two Ti atoms and one Ce atom is reported in the Cambridge Structural Database (CSD; Version 5.25; Allen, 2002), namely a tetranuclear Ce–Ti complex of 1:1 stoichiometry with additional μ,η^2-pinacolate and isopropoxide bridging ligands (Hubert-Pfalzgraf *et al.*, 1999). The only complex in the CSD that comprises both Sm and Ti atoms is the pentanuclear species $[Sm_4Ti(\mu_5\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_6(OR)_6]$, (II), where R denotes isopropyl (Daniele *et al.*, 1994). Compound (I) thus represents a rare example of an Sm–Ti complex and is the first trinuclear one. Whereas alkoxide or oxoalkoxide complexes are frequent occurrences in such lanthanide–3*d* transition mixed-metal compounds, (I) is a unique example of an oxychloride species.



(I)

The asymmetric unit in (I) contains half a molecule, the other half being generated by the binary crystallographic axis containing atoms Sm, O1 and Cl4 (Fig. 1). The three metal ions are bridged by a central trigonal μ_3-oxo ion and by three μ_2-chloro ions, the heptanuclear assemblage thus formed being planar, with an r.m.s. deviation of 0.012 Å. The whole assembly is analogous to one-half of the rhombus-shaped

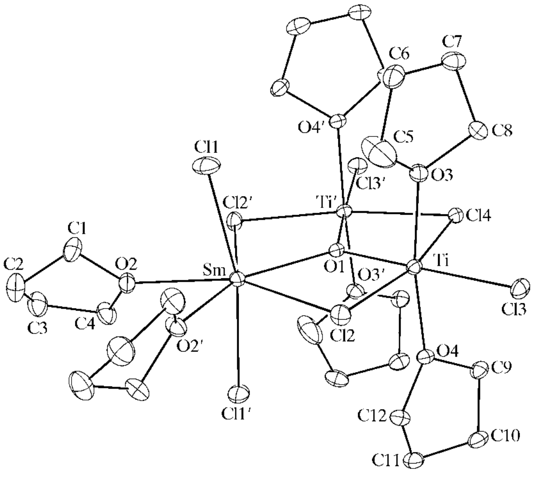


Figure 1
A view of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are at the symmetry position $(-x, y, \frac{3}{2} - z)$.

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assemblage in the di-μ_3-oxo-bridged Ce–Ti tetranuclear complex cited above (Hubert-Pfalzgraf *et al.*, 1999), with atom Cl4 in (I) replacing the second μ_3-oxo ion, and the other chloride ions and the THF moieties in (I) replacing the μ,η^2-pinacolate and isopropoxide ligands.

The Sm atom is bound to four chloride ions, two of them terminal (Cl1 and Cl1′) and the others bridging (Cl2 and Cl2′) [primed atoms are at the symmetry position $(-x, y, \frac{3}{2}-z)$]. The Sm—Cl bond lengths (Table 1) are in reasonable agreement with the Sm^{III}—Cl bond lengths reported in the CSD [2.65 (4) Å for terminal and 2.80 (6) Å for bridging chloride ions]. The Sm—O1 bond length in (I) [2.305 (2) Å] is larger than that in the only other μ_3-oxo–samarium complex reported [2.211 (8) Å; Hosmane *et al.*, 1996], whereas the Sm—O(THF) bond length in (I) [2.4573 (18) Å] agrees with the mean value from the CSD [2.47 (6) Å]. The seven-coordinate Sm atom is in a distorted pentagonal bipyramidal environment, with the terminal Cl atoms in axial positions. In (II), the Sm atoms are six-coordinate.

The two crystallographically equivalent Ti atoms are bound to one terminal and two bridging chloride ions, with Ti—Cl bond lengths of 2.3778 (7) and 2.48 (2) Å (mean value), respectively, both in good agreement with the corresponding mean values for Ti^{III} ions from the CSD [2.35 (4) and 2.49 (6) Å, respectively]. The Ti—O(oxo) bond length [1.9065 (13) Å] is smaller than the mean value [1.968 (6) Å] for the μ_3-oxo–Ti^{III} complexes in the CSD. The Ti atoms are further bound to two THF molecules each, with a mean bond length of 2.131 (6) Å [the mean Ti^{III}—O(THF) bond length from the CSD is 2.16 (7) Å]. The Ti atoms are thus six-coordinate and their environment is distorted octahedral. Each of the three polyhedra associated with the three metal ions shares one edge with each of the two others.

The central μ_3-oxo ion is trigonal, with a difference of only 3.6° between the Sm—O1—Ti and Ti—O1—Ti′ angles, whereas the angles around the two bridging chloride ions differ by about 5°, in keeping with a Ti···Ti′ distance [3.2617 (9) Å] which is smaller than the Sm···Ti distance [3.6745 (5) Å].

Apart from van der Waals interactions, the packing is probably stabilized by a weak C1—H1*A*···Cl1″ hydrogen bond [doubly primed atoms are at the symmetry position $(\frac{1}{2}-x, \frac{1}{2}-y, 2-z)$], which, together with the symmetrical C1″—H″···Cl1 bond, ensures dimerization around a symmetry centre (Table 2).

Crystal data

$[SmTi_2Cl_7O(C_4H_8O)_6]$
$M_r = 942.92$
Monoclinic, $C2/c$
$a = 10.1224$ (4) Å
$b = 34.3476$ (16) Å
$c = 10.9696$ (4) Å
$\beta = 108.435$ (3)°
$V = 3618.2$ (3) Å^3
$Z = 4$
$D_x = 1.731$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 11 856 reflections
$\theta = 2.8$–25.7°
$\mu = 2.59$ mm^{-1}
$T = 100$ (2) K
Irregular, translucent dark pink
0.23 × 0.19 × 0.12 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans
Absorption correction: refined from Δ*F* (*DELABS* in *PLATON*; Spek, 2003)
$T_{min} = 0.472$, $T_{max} = 0.728$
11 856 measured reflections

3384 independent reflections
3155 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 25.7°$
$h = -12 \rightarrow 12$
$k = -41 \rightarrow 41$
$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.054$
$S = 1.06$
3384 reflections
187 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0144P)^2 + 7.993P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.93$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sm—O1	2.305 (2)	Ti—O3	2.1379 (18)
Sm—O2	2.4573 (18)	Ti—O4	2.1250 (18)
Sm—Cl1	2.6437 (7)	Ti—Cl2	2.4599 (7)
Sm—Cl2	2.9045 (7)	Ti—Cl3	2.3778 (7)
Ti—O1	1.9065 (13)	Ti—Cl4	2.5089 (7)
Cl1—Sm—Cl1′	165.84 (3)	O3—Ti—O4	170.97 (7)
Cl2—Sm—O1	68.247 (12)	Sm—Cl2—Ti	86.04 (2)
Cl2—Sm—O2′	74.03 (5)	Ti—Cl4—Ti′	81.09 (3)
O2—Sm—O2′	75.77 (9)	Sm—O1—Ti	121.19 (6)
Cl2—Ti—Cl4	165.12 (3)	Ti—O1—Ti′	117.61 (12)
Cl3—Ti—O1	177.10 (6)		

Symmetry code: (′) $-x, y, \frac{3}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*A*···Cl1″	0.97	2.82	3.651 (3)	144

Symmetry code: (″) $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$.

Experimental

An NMR tube was charged with Sm (6.0 mg, 0.040 mmol) and anhydrous THF (0.6 ml) in a glove-box. $TiCl_4$ (8.8 µl, 0.080 mmol) was then introduced *via* a microsyringe. The colour of the solution immediately became yellow, indicating formation of the Ti^{IV} chloride–tetrahydrofuran complex. The solution was stirred for 15 min and then thermostated at 333 K in a sand bath. After 12 h, dark-pink single crystals suitable for X-ray analysis were recovered as the sole crystalline product from the clear brown solution (8 mg, 20% yield).

H atoms of the tetrahydrofuran ligands were introduced in calculated positions as riding atoms, with C—H distances of 0.97 Å and U_{iso}(H) values of $1.2U_{eq}$(C).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1036). Services for accessing these data are described at the back of the journal.

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