

Bis{ μ -N-[2-(η^5 -cyclopentadienyl)-ethyl]-4-toluenesulfonamido-N,O:O'}-bis[bis(trifluoromethanesulfonato-O)-titanium(II)] bis(dichloromethane) solvate

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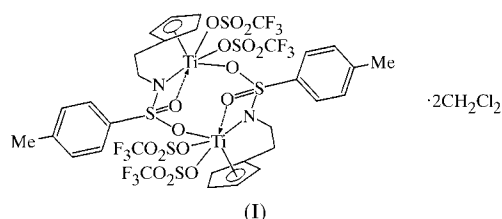
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The title compound, $[\text{Ti}_2(\text{CF}_3\text{O}_3\text{S})_4(\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S})_2] \cdot 2\text{CH}_2\text{Cl}_2$, consists of unique centrosymmetric dimers, with an eight-membered ring derived from the monomer subunits by formation of two Ti–(N,O)–S–O head-to-tail sequences around a crystallographic inversion centre, and two ordered dichloromethane solvate molecules. The Ti ion has distorted octahedral coordination, through the N atom and one O atom of one *p*-toluenesulfonamido group linked by an ethyl group to the bound cyclopentadiene moiety, one O atom from the other *p*-toluenesulfonamido group and two singly bound trifluoromethanesulfonates moieties which are coordinated in pseudo-*cis* positions. Both Ti–O(sulfonamido) bond lengths [2.149 (3) and 2.388 (3) Å] are considered bonding interactions.

Comment

The title compound, (I), was prepared as part of an extensive study of titanium compounds with potential as homogeneous catalysts for stereoregular polymerizations (Lensink *et al.*, 2001). The coordination of interest involved the N-[2-(cyclopentadienyl)ethyl]-*p*-toluenesulfonamido ligand, which is capable of coordinating *via* the cyclopentadiene and the N atom only (Sinnema *et al.*, 1997; Lensink, 1998) or, by analogy with bis(isopropoxy)[1,2-bis(*p*-tolylsulfonamido)cyclohexane]-titanium (Pritchett *et al.*, 1998), *via* the N and O atoms of the



sulfonamido group, or *via* all three donors (Lensink *et al.*, 2001). In the case of (I), two sulfonamido ligands utilize all the

N and O atoms to bridge the two Ti atoms, forming a centrosymmetric dimer.

The crystal structure of (I) consists of independent dimers (Fig. 1), with no significant intermolecular contacts to the solvate or to other dimers; the closest intermolecular contact is C7–H7B···F4A($\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$) at 2.511 (2) Å, compared with the closest intramolecular contact, C12–H12···O8A($1 - x, -y, -z$) of 2.350 (2) Å. The unique eight-membered dimer ring is derived from the monomer subunits by formation of two Ti–(N,O)–S–O head-to-tail sequences around a crystallographic inversion centre. There are several reported bridged systems containing $M\text{--}O\text{--}S\text{--}O\text{--}M'$, for example, with $M = \text{Rh}$ (Clegg *et al.*, 1984) or $M = \text{Co}$ (Jiang *et al.*, 1995), and four $M\text{--}N\text{--}S\text{--}O\text{--}M'$ systems, with $M = \text{Al}$ (Corey *et al.*, 1992), $M = \text{In}$ (Blaschette *et al.*, 1991) and $M = \text{Ag}$ (Jones *et al.*, 1994; Weitze *et al.*, 1997). However, most have a further O atom bound to the sulfur which is not coordinated to a metal. The closest related compound is therefore a yttrium compound, namely bis{[μ -*trans*-1,2-bis(2,4,6-triisopropylbenzenesulfonamidato)cyclohexane-*N,N',O,O',O''*]}bis(dimethylsilyl)(amido)yttrium(III)}, hereafter QABGIJ (Gorlitzer *et al.*, 1998), which has a similar centrosymmetric Y–(N,O)–S–O sequence but different other ligands.

The Ti ion in (I) has distorted octahedral coordination through the N and one O atom of the sulfonamide which is linked to the bound cyclopentadiene *via* an ethyl group [Ti–O1 2.388 (3) and Ti–N5 2.004 (4) Å], the cyclopentadiene [Ti–C_g 2.040 (5) Å, where C_g is the centre of the cyclopentadiene ring], one O atom from the adjacent sulfonamide [Ti–O2 2.149 (3) Å] and two trifluoromethanesulfonates [Ti–O 2.051 (3) and 2.066 (3) Å]. The trifluoromethanesulfonates are coordinated in pseudo-*cis* positions, bent away from the cyclopentadiene [*e.g.* O6–Ti–O1 82.4 (1)° and C_g–Ti–O6 114.6 (2)°].

The longer Ti–O1(sulfonamide) distance of 2.388 (3) Å is considered to be a significant, though weak, bond based on the

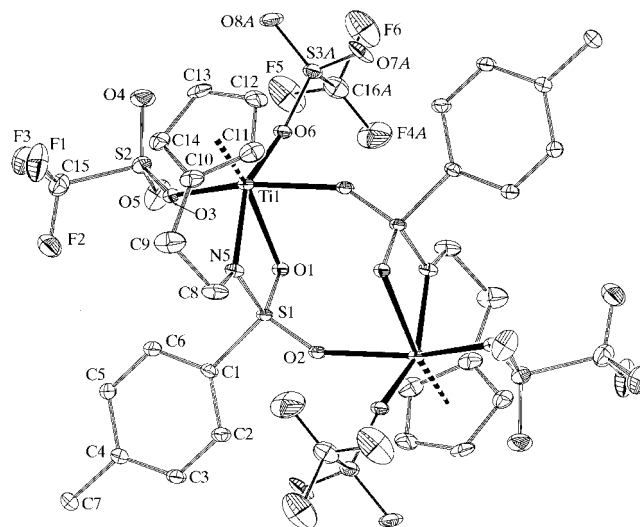


Figure 1

The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and the minor conformation of one trifluoromethanesulfonate moiety have been excluded for clarity.

stereochemistry and the identical S=O bond lengths [1.466 (3) Å], in agreement with the analysis presented in our previous paper (Lensink *et al.*, 2001). The comparable values in QABGIJ are S=O of 1.463 and 1.482 Å, and Y–O of 2.234 and 2.599 Å, compared with values of 2.20 and 2.44 Å calculated by us on the basis of different ionic radii (0.05 Å).

The trifluoromethanesulfonate geometries are similar to that of the singly bound ligand in [2,3-bis(dimethylamino)-phenyl](isopropoxy)(trifluoromethylsulfonyloxy-*O*)(trifluoromethylsulfonyloxy-*O,O'*)titanium(IV) (Donkervoort *et al.*, 1997), where Ti–O is 2.093 Å, compared with 2.051 (3) and 2.066 (3) Å in (I).

The crystallization geometry of the dichloromethane solvent is normal (Spence *et al.*, 1998). Although the molecule is not disordered, as in some other crystals (Carmalt *et al.*, 1998), it appears to have no crystal-binding function.

Cambridge Structural Database searches were performed using *CONQUEST* (Version 1.0; Cambridge Structural Database, 2000).

Experimental

The air-sensitive title compound was prepared from the reaction of dichloro[*N*-[2-(η^5 -cyclopentadienyl)ethyl]-*p*-toluenesulfonamido]-titanium with a stoichiometric amount of AgSO₃CF₃ in dichloromethane. Crystals of (I) were obtained from dichloromethane-pentane; details and spectroscopic data will be reported elsewhere.

Crystal data

[Ti ₂ (CF ₃ O ₃ S) ₄ (C ₁₄ H ₁₅ NO ₂ S) ₂] \cdot 2CH ₂ Cl ₂	$D_x = 1.739 \text{ Mg m}^{-3}$
$M_r = 1384.6$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 5304 reflections
$a = 11.551 (4) \text{ \AA}$	$\theta = 2.2\text{--}25.2^\circ$
$b = 15.068 (5) \text{ \AA}$	$\mu = 0.848 \text{ mm}^{-1}$
$c = 15.218 (5) \text{ \AA}$	$T = 173 (2) \text{ K}$
$\beta = 93.233 (5)^\circ$	Block, orange
$V = 2644.4 (16) \text{ \AA}^3$	$0.36 \times 0.28 \times 0.24 \text{ mm}$
$Z = 2$	

Data collection

Siemens SMART CCD area-detector diffractometer	5361 independent reflections
φ and ω scans	3085 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.091$
$T_{\text{min}} = 0.736$, $T_{\text{max}} = 0.816$	$\theta_{\text{max}} = 26.39^\circ$
31 967 measured reflections	$h = -14 \rightarrow 11$
	$k = -18 \rightarrow 18$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 7.19P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.139$	$(\Delta\sigma)_{\text{max}} = 0.003$
$S = 1.053$	$\Delta\rho_{\text{max}} = 1.08 \text{ e \AA}^{-3}$
5361 reflections	$\Delta\rho_{\text{min}} = -0.63 \text{ e \AA}^{-3}$
355 parameters	
H-atom parameters constrained	

Part of one of the trifluoromethylsulfonates was disordered between two conformations, labelled *A* and *B*, which refined to occupancies of 0.633 (4) and 0.367 (4), respectively. One fluorine (F6) is common to both conformations. Atom C16*B* was refined with an isotropic displacement parameter. H atoms were refined as riding, with isotropic displacement parameters 1.2 (phenyl, methylene and cyclopentadienyl) and 1.5 (methyl) times U_{eq} of their parent atoms, and C–H distances of 0.95, 0.99, 1.00 and 0.98 Å, respectively.

Table 1

Selected geometric parameters (Å, °).

Ti1–N5	2.004 (4)	Ti1–C12	2.350 (5)
Ti1–O6	2.051 (3)	Ti1–C14	2.360 (5)
Ti1–O3	2.066 (3)	Ti1–C11	2.372 (5)
Ti1–O2 ⁱ	2.149 (3)	Ti1–C10	2.381 (5)
Ti1–C13	2.349 (5)	Ti1–O1	2.388 (3)
N5–Ti1–O6	146.02 (15)	O3–Ti1–O2 ⁱ	151.16 (14)
N5–Ti1–O3	92.00 (14)	N5–Ti1–O1	63.80 (13)
O6–Ti1–O3	83.59 (13)	O6–Ti1–O1	82.39 (12)
N5–Ti1–O2 ⁱ	90.67 (14)	O3–Ti1–O1	77.77 (11)
O6–Ti1–O2 ⁱ	78.31 (12)	O2 ⁱ –Ti1–O1	77.73 (11)
O2–S1–O1–Ti1	–118.67 (17)	N5–S1–O2–Ti1 ⁱ	–84.2 (4)
N5–S1–O1–Ti1	3.65 (18)	C1–S1–O2–Ti1 ⁱ	155.1 (4)
C1–S1–O1–Ti1	120.85 (19)	O1–S1–N5–C8	–173.8 (4)
O1–S1–O2–Ti1 ⁱ	31.0 (5)	Ti1–N5–C8–C9	32.9 (7)

Symmetry code: (i) $2 - x, -y, -z$.

Data collection and cell refinement: *SMART* (Siemens, 1996); data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990) and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1309). Services for accessing these data are described at the back of the journal.

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