

## {*N*-[2-( $\eta^5$ -Cyclopentadienyl)ethyl]-4-toluenesulfonamido-*N,O*}(tetrahydrofuran-*O*)bis(trifluoromethanesulfonato-*O*)titanium(II)

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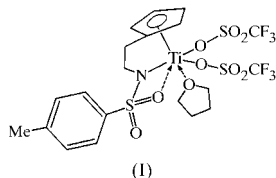
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The title compound, [Ti(CF<sub>3</sub>O<sub>3</sub>S)<sub>2</sub>(C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub>S)(C<sub>4</sub>H<sub>8</sub>O)], contains a unique ligand system in which the Ti ion is bound to the N and O atoms of a 2-*p*-toluenesulfonamide ligand, which is linked by an ethyl group to a coordinated cyclopentadiene moiety. The distorted octahedral geometry about the Ti ion is completed by two trifluoromethanesulfonate ligands and a tetrahydrofuran molecule. Comparison with related compounds shows that both the Ti–N and Ti–O bonds of the sulfonamide, although longer than normal values, indicate significant 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. The coordination of interest involved the *N*-[2-(cyclopentadienyl)ethyl]-*p*-toluenesulfonamide ligand, which is capable of coordinating *via* the cyclopentadiene and the N atom only (Sinnema *et al.*, 1997; Lensink, 1998; see comments below), 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. In the unique present case, cyclopentadiene, nitrogen and oxygen are all found to be coordinated.



The crystal structure of (I) consists of independent molecules (Fig. 1) with no significant intermolecular contacts; the closest contact is H18B...O4(−*x*, *y* − 1/2, 1/2 − *z*) at 2.48 (1) Å. The Ti ion has distorted octahedral coordination through the N atom and one O atom of the sulfonamide, the cyclopentadiene, which is linked *via* the ethyl group to the N atom, the tetrahydrofuran (THF) and the two trifluoromethane-

sulfonate ligands. The Ti ion is 0.546 (1) Å toward the cyclopentadiene above the plane through N1, O3, O6 and O9 [the average out-of-plane deviation is 0.026 (1) Å]. The trifluoromethanesulfonates are coordinated in pseudo-*trans* positions, bent away from the cyclopentadiene [*e.g.* O3–Ti–O2 75.86 (9)° and C<sub>g</sub>–Ti–O3 104.8 (1)°, where C<sub>g</sub> is the centroid of the cyclopentadiene ring].

The Ti–C<sub>g</sub> distance varies over the narrow range 2.008–2.081 Å in structures in which Ti is bound to a cyclopentadiene linked to a bound N atom by an ethyl group (Beckhaus *et al.*, 1997; Sinnema *et al.*, 1997; Lensink, 1998; Yanlong *et al.*, 1997; Herrman *et al.*, 1995) or by a propyl group (Sinnema *et al.*, 1997). In complete contrast, the Ti–N distances in such compounds range from the expected amido distance of 1.864 Å [as noted by Pritchett *et al.* (1997) and found in the two structures studied by Sinnema *et al.* (1997)] to 2.437 Å in ( $\eta^5$ -cyclopentadienyl){[ $\eta^5$ -(dimethylamino)ethyl]tetramethylcyclopentadienyl}chlorotitanium (Beckhaus *et al.*, 1997). Ti–C<sub>g</sub> bond distances for six- and seven-coordinate Ti to cyclopentadiene without any additional links are in the range 2.037–2.122 Å (mean 2.07 Å). The Ti–N value in (I) is 1.993 (3) Å, slightly longer than the value of 1.963 (2) Å in dichloro{*N*-[2-( $\eta^5$ -cyclopentadienyl)ethyl]-*p*-toluenesulfonamido}titanium (Lensink, 1998).

Normal  $\sigma$ -covalent Ti–O bond lengths have been predicted to be in the range 1.99–2.05 Å (Kim *et al.*, 1997). There is self-consistent evidence that Ti–O(sulfonamide) interactions as long as 2.45 Å represent intramolecular dative interactions (Pritchett *et al.*, 1997). Some measure of this interaction is also reflected in the S–O bond distances in such compounds; the coordinated S–O bonds are always longer than the unbound S=O bonds [in (I), S–O2 is 1.479 (2) Å, compared with 1.431 (2) Å for S–O1]. The S=O bond length in the free ligand *N*-[2-(1-3*H*-indenyl)ethyl]-*p*-toluenesulfonamide is 1.433 (2) Å (Gainsford & Lensink, 1996). From a series of structures which contain sulfonylamido ligands (–N–SO<sub>2</sub>–) bound to Ti, it can be deduced that when one S–O bond length exceeds 1.465 Å, there will be a significant bonding interaction between that O atom and the Ti ion, with Ti–O distances ranging from 2.219 (Pritchett *et al.*, 1997) to 2.448 Å (Pritchett *et al.*, 1998). In the case of (I), Ti–O2 is 2.289 (2) Å. In summary, it is apparent that the binding of this unusual ligand is tighter around the Ti ion in (I) than it is in dichloro{*N*-[2-( $\eta^5$ -cyclopentadienyl)ethyl]-*p*-toluenesulfonamido}titanium (Lensink, 1998). We note that, in this latter case, the Ti–O2 and S–O2 distances of 2.556 (2) and 1.454 (2) Å, respectively, and the stereochemistry, suggest that there is a weak interaction between the Ti ion and one sulfonyl O atom.

The trifluoromethanesulfonate geometries in (I) are self-consistent and 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), which has a Ti–O distance of 2.093 Å, compared with values of 2.086 (2) and 2.093 (2) Å in (I). Ti–O(THF) bonds can vary in the range 2.07–2.21 Å in Ti compounds with bound cyclopentadiene; in (I), the ring

dimensions and the Ti—O length [2.156 (2) Å] are similar to those found in bis( $\eta^5$ -cyclopentadienyl)(trifluoromethanesulfonato-*O*)(tetrahydrofuran)titanium(III) (Berhalter & Thewalt, 1991), where the ring is in an envelope conformation. The tetrahydrofuran ring in (I) is similar, though best described as in a twist conformation puckered at C16—C17, with puckering parameters (Cremer & Pople, 1975) of  $Q_2 = 0.355$  (5) Å and  $\varphi = 264$  (1)°.

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

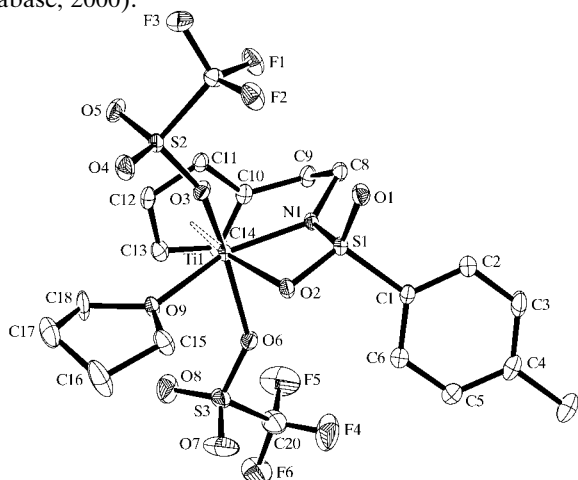


Figure 1

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

## Experimental

The air-sensitive title compound was prepared from the reaction of dichloro[*N*-[2-( $\eta^5$ -cyclopentadienyl)ethyl]-*p*-toluenesulfonamido]-titanium with a stoichiometric amount of  $\text{AgSO}_3\text{CF}_3$  in THF. Crystals of (I) were obtained from a solution in THF; details and spectroscopic data will be reported elsewhere.

### Crystal data

$[\text{Ti}(\text{CF}_3\text{O}_3\text{S})_2(\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S})\text{C}_4\text{H}_8\text{O}]$

$M_r = 679.47$

Monoclinic,  $P2_1/c$

$a = 20.674$  (7) Å

$b = 7.653$  (2) Å

$c = 19.211$  (6) Å

$\beta = 116.939$  (4)°

$V = 2709.6$  (15) Å<sup>3</sup>

$Z = 4$

### Data collection

Siemens SMART CCD area-detector diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (Blessing, 1995)

$T_{\min} = 0.465$ ,  $T_{\max} = 0.775$

33 169 measured reflections

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.120$

$S = 0.964$

5499 reflections

362 parameters

$D_x = 1.666$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

Cell parameters from 8118

reflections

$\theta = 2.54$ – $26.20$ °

$\mu = 0.638$  mm<sup>-1</sup>

$T = 168$  (2) K

Block, yellow

$0.60 \times 0.46 \times 0.40$  mm

5499 independent reflections

3496 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.089$

$\theta_{\text{max}} = 26.38$ °

$h = -25 \rightarrow 25$

$k = -6 \rightarrow 9$

$l = -23 \rightarrow 23$

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.006$

$\Delta\rho_{\text{max}} = 0.56$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.61$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Ti1—N1	1.993 (3)	Ti1—C11	2.373 (3)
Ti1—O3	2.086 (2)	Ti1—C13	2.375 (3)
Ti1—O6	2.093 (2)	Ti1—C12	2.378 (3)
Ti1—O9	2.156 (2)	Ti1—C14	2.379 (3)
Ti1—O2	2.289 (2)	Ti1—C10	2.385 (3)
N1—Ti1—O3	89.99 (10)	O6—Ti1—O2	77.56 (9)
N1—Ti1—O6	94.31 (10)	O9—Ti1—O2	82.82 (8)
O3—Ti1—O6	148.26 (9)	S1—O2—Ti1	93.84 (11)
N1—Ti1—O9	147.83 (10)	S2—O3—Ti1	151.67 (14)
O3—Ti1—O9	79.42 (9)	S3—O6—Ti1	140.03 (14)
O6—Ti1—O9	80.35 (9)	C15—O9—Ti1	120.49 (18)
N1—Ti1—O2	65.09 (9)	C8—N1—Ti1	132.0 (2)
O3—Ti1—O2	75.86 (9)	S1—N1—Ti1	102.35 (13)
N1—S1—O2—Ti1	−8.07 (12)	O2—S1—N1—Ti1	9.48 (14)
C1—S1—O2—Ti1	−121.85 (13)	Ti1—N1—C8—C9	−37.6 (4)
C20—S3—O6—Ti1	148.9 (3)		

All H atoms were treated as riding (C—H distances of 0.99, 0.95 and 0.98 Å for methylene, cyclopentadienyl and methyl H atoms, respectively), with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of their parent atom, except those on C7, for which the ratio factor was 1.5.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999) and *ORTEP-3* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1308). Services for accessing these data are described at the back of the journal.

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