Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

μ-Oxo-bis[trichlorobis(dimethylsulfane)-titanium(IV)]

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Received 21 July 2003
Accepted 23 July 2003
Online 31 July 2003

Key indicators

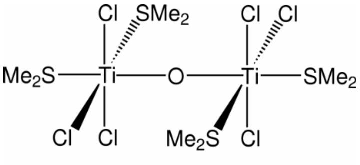
Single-crystal X-ray study
T = 140 K
Mean σ(S–C) = 0.004 Å
Disorder in main residue
R factor = 0.029
wR factor = 0.077
Data-to-parameter ratio = 20.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of $[Ti_2Cl_6O(Me_2S)_4]$ shows a distorted octahedral arrangement around the Ti atom. The molecule does not possess an inversion centre at the O atom.

Comment

Thio- and selenoether adducts, as well as alkanethiol adducts of titanium tetrachloride have been used as single-source precursors for chemical vapour deposition (CVD) of TiS_2 (Winter *et al.*, 1993) and $TiSe_2$ (McKarns *et al.*, 1997) layers. The quality of these films was found to be as high as those obtained from the corresponding two-component processes. Along with the CVD studies, the properties of thio and seleno ethers have been investigated (Levason *et al.*, 2000; Wilson *et al.*, 2003; Zeltner *et al.*, 1999). The X-ray structure determination of $[(Me_2S)_2Cl_3Ti]_2(\mu\text{-O})$, (I), is reported here.



(I)

Compound (I) crystallizes in the orthorhombic space group $Pna2_1$ with four molecules per unit cell. The titanium metal centres exhibit distorted octahedral arrangements. The thioether ligands are mutually *cis*, with one *trans* to the bridging O atom. The chloride and thioether ligands bend away from the oxo ligand [O—Ti—Cl = 95.71 (8)–99.64 (8)°; O—Ti—S = 93.69 (8) and 96.64 (8)°]. An almost identical arrangement can be found in $[(MeS(CH_2)_2SMe)Cl_3Ti]_2(\mu\text{-O})$ (Levason *et al.*, 2000); here an inversion centre situated at the bridging O ligand links the two distorted octahedral titanium(IV) centres. However, compound (I) does not possess an inversion centre [Ti—O = 1.778 (2) and 1.812 (2) Å, and Ti—O—Ti = 171.86 (14)°]. Related oxo-bridged homodinuclear titanium species are known, both with $\{[(\eta^5C_5H_5)TiCl_2]_2(\mu\text{-O})$; Thewalt & Schomburg, 1977} and without $\{[THF_2Cl_3Ti]_2(\mu\text{-O})$; Streltsova *et al.*, 1988; Mahrwald *et al.*, 2001} an inversion centre in the oxo bridge.

Experimental

Compound (I) was formed from the hydrolysis product $Cl_3Ti(\mu\text{-O})TiCl_3$ contaminating the starting material $TiCl_4$; a thioether adduct was formed. The title compound was isolated after crystallization from petroleum ether at 253 K as orange blocks.

Crystal data

$[Ti_2Cl_6O(C_2H_6S)_4]$
$M_r = 573.01$
Orthorhombic, $Pna2_1$
$a = 25.311\ (5)$ Å
$b = 9.801\ (2)$ Å
$c = 9.4720\ (19)$ Å
$V = 2349.7\ (8)$ Å^3
$Z = 4$
$D_x = 1.620$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 221 reflections
$\theta = 1.6–22.7°$
$\mu = 1.71$ mm^{-1}
$T = 140\ (1)$ K
Block, orange
0.40 × 0.35 × 0.30 mm

Data collection

Rigaku R-AXIS-IIc diffractometer
φ scans
Absorption correction: none
11796 measured reflections
4350 independent reflections

4021 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.4°$
$h = -30 \rightarrow 30$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.077$
$S = 1.06$
4153 reflections
201 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.4789P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Absolute structure: Flack (1983), 1846 Friedel pairs
Flack parameter = 0.45 (3)

The disordered methyl group C42 was modelled in two positions and their ratio of occupancy was refined to 59:41 (7). H atoms were included in idealized positions (C—H 0.960 Å) and their U_{iso} values were set at 1.5 times U_{eq} of the parent C atom. Compound (I) crystallizes as a twin, and the Flack parameter represents the contribution of the second polar axis component.

Data collection: *R-AXIS Control Software* (Molecular Structure Corporation, 1994); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO* and SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XL* in *SHELXTL*.

This work was supported by the European Commission (contract No. HPRN-CT2000-00004).

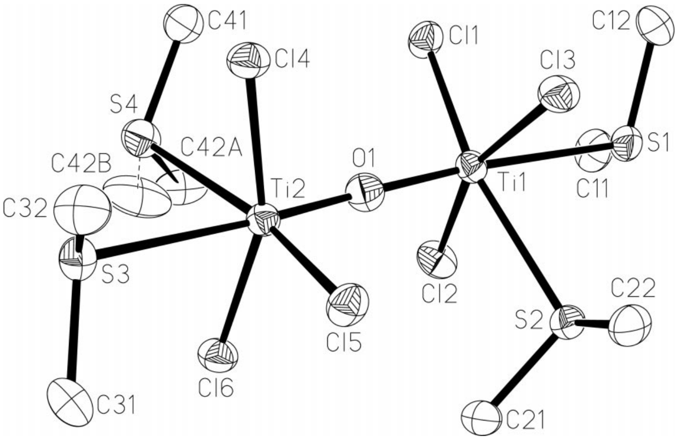


Figure 1
A view of (I), with displacement ellipsoids drawn at the 40% probability level. Hydrogen atoms have been omitted. Both disorder components are shown.

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