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Titanium(IV) chloride at 150 K

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(Ti–Cl) = 0.001 Å
R factor = 0.020
wR factor = 0.080
Data-to-parameter ratio = 28.6

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

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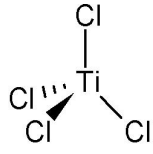
Titanium(IV) chloride, $TiCl_4$, is an air-sensitive liquid under ambient conditions. The crystal structure consists of tetrahedral molecules weakly associated in pairs, and is isostructural with tin(IV) bromide.

Comment

Titanium(IV) chloride is an important chemical in the commercial production of titanium metal and titanium dioxide. Under ambient conditions of temperature and pressure, titanium(IV) chloride is an air-sensitive liquid which freezes at 248 K. Of the remaining titanium(IV) halides, TiF_4 (Bialowons *et al.*, 1995) and TiI_4 (Troyanov, 1993) are polymeric, high-melting compounds (557 K and 423 K respectively), and $TiBr_4$ is monomeric (Brand & Schmidt, 1966; Troyanov *et al.*, 1990), with a correspondingly low melting point (312 K). Here we report the structure of titanium(IV) chloride, (I), at 150 K.



(I)

The low-temperature solid-state structure of titanium(IV) chloride is composed of tetrahedral molecules (Fig. 1). The molecules form loose dimers (Fig. 2), with intermolecular Ti···Cl contacts of 3.994 (1) Å. This separation is significantly shorter than the other Ti···Cl separations, with the next shortest contact over 0.4 Å longer at 4.407 (1) Å. The structure can be considered to be based on hexagonal close packing of the chlorine atoms.

The structure is isostructural with tin(IV) bromide, consistent with the observations of Brand & Sackmann (1963). Titanium(IV) bromide has also been refined in the $SnBr_4$ structure (Brand & Schmidt, 1966). In common with $TiBr_4$, the Ti—halogen bond is short, with a mean value of 2.1646 (6) Å. A search of the CSD (Allen & Kennard, 1993) for four-coordinate titanium compounds containing Ti—Cl bonds gave a mean value for the Ti—Cl bond of 2.24 (4) Å for 49 fragments.

Experimental

Titanium(IV) chloride was purchased from Aldrich and used as received. A crystal of titanium(IV) chloride was grown *in situ* in a capillary, using the laser method of Boese & Nussbaumer (1994), at a temperature of 244.2 K. Data were collected at 150 K.

Crystal data

Cl_4Ti	D_x = 2.127 Mg m^{-3}
M_r = 189.71	Mo Kα radiation
Monoclinic, $P2_1/c$	Cell parameters from 3737 reflections
a = 9.670 (2) Å	θ = 3–29°
b = 6.4737 (15) Å	μ = 3.09 mm^{-1}
c = 9.682 (2) Å	T = 150 K
β = 102.168 (4)°	Cylinder, colourless
V = 592.5 (2) Å^3	0.41 × 1.00 (length) mm
Z = 4	

Data collection

Bruker SMART APEX diffractometer equipped with an Oxford Cryosystems low-temperature device and an OHCD laser-assisted crystallization device (Scientific Consulting, Essen, Germany)	2765 measured reflections 1345 independent reflections 1228 reflections with $I > 2\sigma(I)$ R_{int} = 0.04 θ_{max} = 28.5° $h = -12 \rightarrow 9$ $k = -8 \rightarrow 6$ $l = -12 \rightarrow 12$
φ and ω scans	
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2002) T_{min} = 0.08, T_{max} = 0.28	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.020	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$wR(F^2)$ = 0.080	$\Delta\rho_{min}$ = −0.48 e Å^{-3}
S = 0.99	Extinction correction: Larson (1970) eq. 22
1343 reflections	Extinction coefficient: 134.8 (84)
47 parameters	
Weighting scheme: see text	

Table 1
Selected geometric parameters (Å, °).

Ti1—Cl2	2.1652 (6)	Ti1—Cl4	2.1634 (6)
Ti1—Cl3	2.1647 (6)	Ti1—Cl5	2.1651 (5)
Cl2—Ti1—Cl3	109.62 (2)	Cl2—Ti1—Cl5	109.66 (2)
Cl2—Ti1—Cl4	109.88 (2)	Cl3—Ti1—Cl5	108.86 (2)
Cl3—Ti1—Cl4	109.71 (3)	Cl4—Ti1—Cl5	109.10 (2)

Indexing of this crystal using *GEMINI* (Sparks, 1999) indicated that the crystal was not single, with two major (indexable) components. The data set was integrated using both orientation matrices. Data corresponding to the second crystal were used for structure solution and refinement; inclusion of the first component gave significantly worse refinement statistics, possibly because of contamination by reflections from further small, unindexed crystals.

The possibility of higher (*C*-centred orthorhombic) symmetry in the structure was noted during space-group determination. This was rejected on the basis of merging statistics: R_{int} for primitive monoclinic was 0.022 compared with 0.341 for orthorhombic *C*-centred (*XPREP*, Sheldrick, 2001). Structure solution and refinement in this higher symmetry was unacceptable.

A robust-resistant Tukey and Prince weighting scheme was used (Carruthers & Watkin, 1979), where weight = $[w][1-(\Delta F/6\sigma F)^2]^2$ and $[w]$ is given by a three-term Chebychev polynomial with coefficients 77.2, 33.7, 8.14.

Data collection: *SMART* (Bruker–Nonius, 2001); cell refinement: *SAINT* (Bruker–Nonius, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

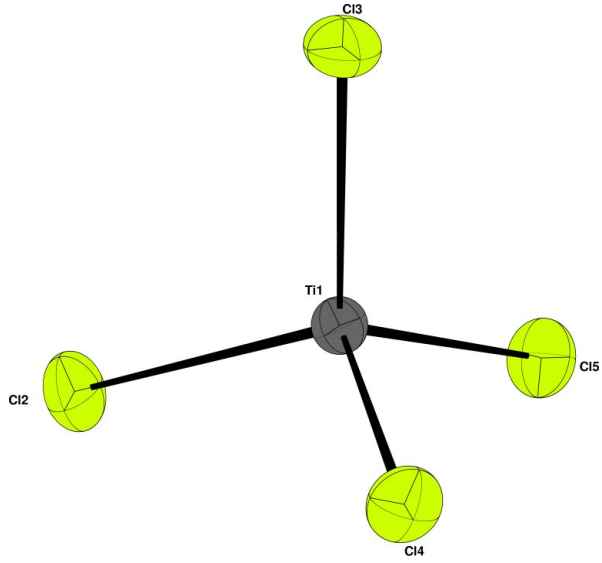


Figure 1
The molecular structure of titanium(IV) chloride, shown with 50% probability displacement ellipsoids

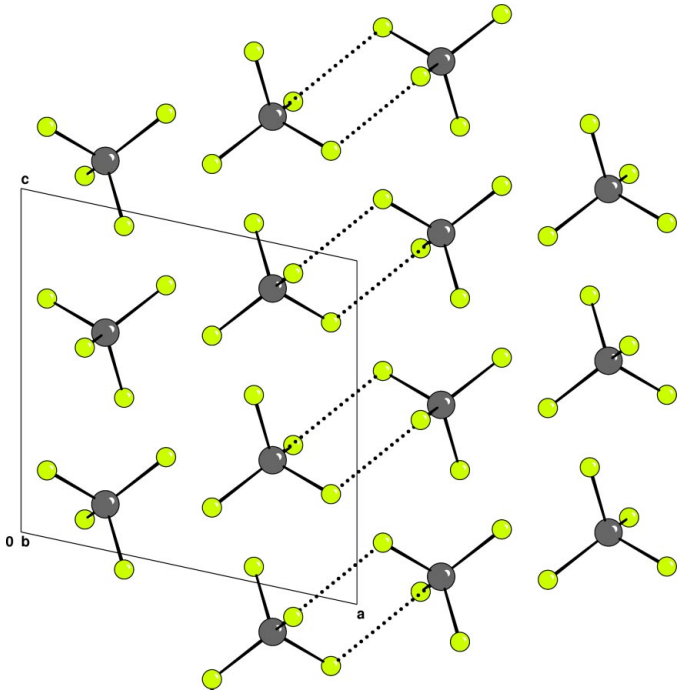


Figure 2
Packing of titanium(IV) chloride, viewed down *b*. The dotted lines indicate the closest Ti—Cl contacts.

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