

Tetrabromo(2,6-dimethylpyridine-*N*)-titanium(IV), a twinned crystal structure

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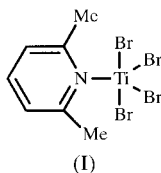
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The reaction of 2,6-dimethylpyridine with TiBr_4 affords the title compound, $[\text{TiBr}_4(\text{C}_7\text{H}_9\text{N})]$, which is the first example of a neutral TiBr_4L complex (L is a singly bonded ligand). The environment around the Ti atom can be described as a somewhat distorted trigonal bipyramid, with the nitrogen base occupying an equatorial position. The crystal was a non-merohedral twin.

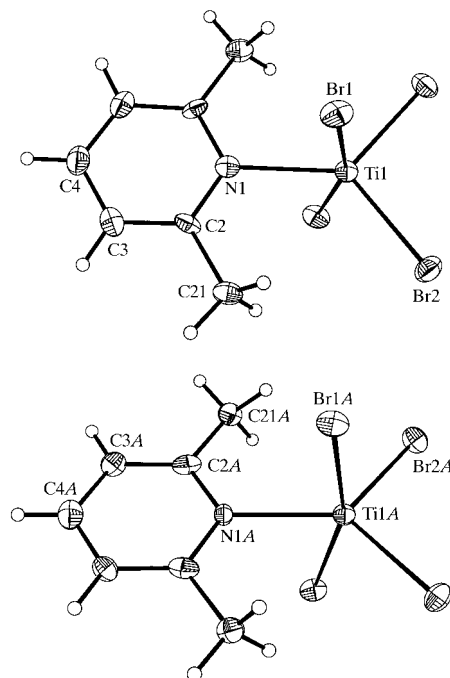
Comment

Titanium tetrahalides are strong Lewis acids and form Lewis acid–base adducts with electron-pair donors. These reactions have been of scientific interest for a long time (Emeléus & Rao, 1958; Rao, 1960; Hensen, Pickel *et al.*, 1997). Two representative examples of such adducts are the structures of $\text{TiCl}_4(\text{pyridine})_2$ (Mazo *et al.*, 1987) and di- μ -chloro-hexachlorobis(*N*-trimethylsilylimidazol-3-yl)ditanium (Hensen, Lemke & Näther, 1997). However, no neutral penta-coordinated TiX_4L complexes (X is a halogen atom and L is a singly bonded ligand) have yet been described. We present here the first example of such a complex, (I), with $X = \text{Br}$ and $L = 2,6$ -dimethylpyridine.

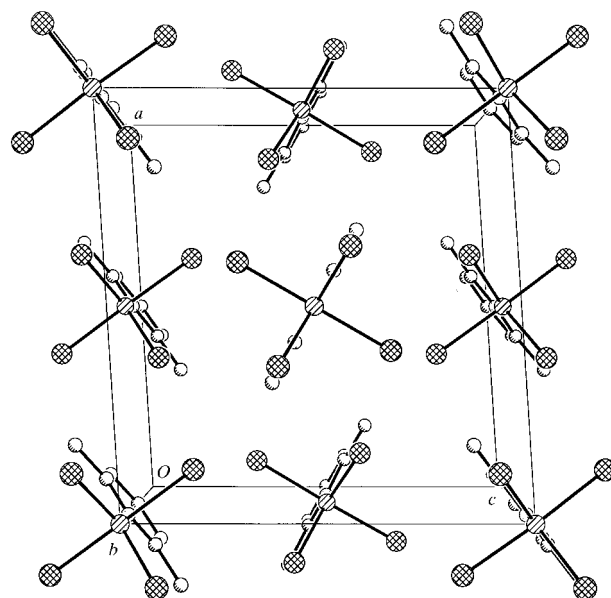


The asymmetric unit of (I) consists of two half molecules, in which the Ti1, N1 and C4 atoms of molecule 1 and the Ti1A, N1A and C4A atoms of molecule 2 are located on a special position of site symmetry 2. The two molecules (Fig. 1) are nearly identical; a least-squares fit of all non-H atoms gives an r.m.s. deviation of 0.026 Å. The environment of the titanium centres can be described as trigonal bipyramidal, with the nitrogen base occupying an equatorial position. According to the valence-shell electron-pair repulsion (VSEPR) model

(Haaland, 1989; Gillespie & Robinson, 1996), an axial position of the base ligand should be expected. However, steric effects force this residue into the equatorial plane. The methyl groups of the pyridine ligands cause the equatorial N–Ti–Br angles to be widened, whereas the equatorial Br–Ti–Br angles are decreased (Table 1). The angles between the two axial Br ligands (Br1 and its symmetry equivalent) show that these


Figure 1

Perspective view (not the relative orientation in the crystal) of the independent molecules of (I) with the atom-numbering scheme; only symmetry independent atoms are labelled. Displacement ellipsoids are shown at the 50% probability level.


Figure 2

Packing diagram of (I) viewed in the ac plane.

atoms are displaced from the ideal linear arrangement in the direction of the aromatic ring. In contrast, the equatorial Br atoms lie nearly exactly in the plane of the aromatic ring and the axial Br—Ti bonds are almost perpendicular to the plane of the aromatic ring. The structure displays an interesting packing motif (Fig. 2); the two symmetry independent molecules lie on different parallel lines in a head-to-tail manner. One line is located on the twofold rotation axis coinciding with the *b* axis (0, *y*, 0), whereas the other one is situated on the twofold rotation axis with coordinates 0, *y*, $\frac{1}{2}$. The displacement between the two molecules in the direction of the *b* axis (as defined by the difference in the *y* coordinates of the equivalent atoms) is approximately 0.46. The angle between the pyridyl rings of the two symmetry independent molecules is 66.6 (2)°.

Experimental

Because of the extreme susceptibility of the titanium halides to hydrolysis, all operations were carried out under an inert gas atmosphere. 2,6-Dimethylpyridine (9.45 mmol, 1.1 ml) was added to a solution of TiBr₄ (0.96 ml, 9.11 mmol) in hexane (30 ml). The red precipitate was washed with hexane and dried. Sublimation at 353 K yielded suitable crystals after approximately two weeks.

Crystal data

[TiBr ₄ (C ₇ H ₉ N)]	$D_x = 2.462 \text{ Mg m}^{-3}$
$M_r = 474.69$	Mo $K\alpha$ radiation
Monoclinic, <i>C</i> 2	Cell parameters from 8192 reflections
$a = 11.6811(2) \text{ \AA}$	$\theta = 1\text{--}25^\circ$
$b = 9.8679(2) \text{ \AA}$	$\mu = 13.109 \text{ mm}^{-1}$
$c = 11.1300(2) \text{ \AA}$	$T = 133(2) \text{ K}$
$\beta = 93.4820(10)^\circ$	Plate, red
$V = 1280.56(4) \text{ \AA}^3$	$0.40 \times 0.20 \times 0.05 \text{ mm}$
$Z = 4$	

Data collection

Siemens CCD three-circle diffractometer	$R_{\text{int}} = 0.073$
ω scans	$\theta_{\text{max}} = 26.50^\circ$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$h = -14 \rightarrow 14$
$T_{\text{min}} = 0.077$, $T_{\text{max}} = 0.560$	$k = -12 \rightarrow 12$
10 417 measured reflections	$l = 0 \rightarrow 13$
2002 independent reflections	145 standard reflections
1798 reflections with $I > 2\sigma(I)$	frequency: 1200 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.002$	$\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$
2002 reflections	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
124 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.03 (2)

Using all reflections initially found on the first frames for determination of a preliminary cell, it turned out that several reflections with systematic deviations from integral indices did not fit the derived cell; this was a strong indication of twinning. However, these reflections could be indexed when the orientation matrix was transformed using the matrix $(\bar{1}00/0\bar{1}0/0.11,0,1)$. Thus, the transformation for the reflection indices of the two twin components is: $h_{\text{twin}} = -h$, $k_{\text{twin}} = -k$, $l_{\text{twin}} = l + h/9$. This means that most of the reflections are suffi-

Table 1

Selected geometric parameters (Å, °).

Ti1—N1	2.181 (8)	Ti1A—N1A	2.176 (9)
Ti1—Br2	2.3585 (14)	Ti1A—Br2A	2.3564 (14)
Ti1—Br1	2.4326 (8)	Ti1A—Br1A	2.4372 (8)
N1—Ti1—Br2	128.60 (4)	N1A—Ti1A—Br2A	128.54 (4)
Br2—Ti1—Br2 ⁱ	102.81 (8)	Br2A ⁱⁱ —Ti1A—Br2A	102.92 (8)
N1—Ti1—Br1	80.92 (5)	N1A—Ti1A—Br1A	80.69 (5)
Br2—Ti1—Br1	96.07 (3)	Br2A—Ti1A—Br1A	96.59 (4)
Br1 ⁱ —Ti1—Br1	161.84 (9)	Br1A ⁱⁱ —Ti1A—Br1A	161.38 (9)
Br2—Ti1—N1—C2	−0.2 (4)	Br2A—Ti1A—N1A—C2A	−2.1 (4)
Br1—Ti1—N1—C2	−90.7 (4)	Br1A ⁱⁱ —Ti1A—N1A—C2A	−91.1 (4)

Symmetry codes: (i) 1 − *x*, *y*, 2 − *z*; (ii) 1 − *x*, *y*, 1 − *z*.

ciently separated for a satisfactory data collection, but exact overlap occurred for the reflections with $h = 9m$ (with m being an integer). Since the reflections with $|h| = 1, 8, 10$ showed only partial overlap and their correct intensity could not be derived, they were discarded from the refinement process. For refinement, the data were read in *via* *HKLF5* and an additional variable was introduced (using the *BASF* command) describing the fractional contributions of the two twin components for the reflections with $h = 9m$; the ratio refined to 0.202 (3)/0.798 (3). All H atoms were located by difference Fourier synthesis and were refined with fixed individual displacement parameters [$U(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$ or $U(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$] using a riding model with C—H(aromatic) = 0.95 Å or C—H(methyl) = 0.98 Å. The methyl groups were allowed to rotate about their local threefold axes.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Siemens, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1419). Services for accessing these data are described at the back of the journal.

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