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Tetrabromo(2-methylpyridine-*N*)-titanate(IV)

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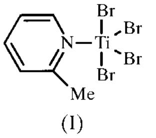
The reaction of 2-methylpyridine with $TiBr_4$ affords tetrabromo(2-methylpyridine-*N*)titanate(IV), $C_6H_7Br_4NTi$. The environment around the Ti atom can be described as a slightly distorted trigonal bipyramid, with the nitrogen base occupying an equatorial position. The crystal structure of the title compound is isomorphous with tetrachloro(2-methylpyridine-*N*)titanate(IV).

Comment

Titanium tetrahalides are strong Lewis acids and form Lewis acid–Lewis base adducts with electron-pair donors. These reactions have been of scientific interest over a long period of time (Emeléus & Rao, 1958; Rao, 1960; Hensen, Pickel *et al.*, 1997). Ti^{IV} affords adducts with different ligands. Two representative examples are the structures of $TiCl_4(pyridine)_2$ (Mazo *et al.*, 1987) and bis(μ-dichloro)hexachlorobis(*N*-trimethylsilylimidazol-3-yl)dititanium (Hensen, Lemke & Nather, 1997). However, neutral pentacoordinated TiX_4L complexes (X = halogen atom, L = single-bonded ligand) have just recently been described (Hensen *et al.*, 2000*a*,*b*). We present in this work another example, (I), of this kind of compound.



(I)

The environment of the titanium centre can be described as a trigonal bipyramid 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 ligands should be expected. However, steric reasons force these residues into the equatorial plane.

The two axial Ti—Br bonds display nearly the same lengths and are significantly longer than the equatorial Ti—Br bonds. The methyl group shows two steric effects: the first one is that the equatorial Ti—Br bond adjacent to the methyl group is markedly longer than the other equatorial Ti—Br bond. The second effect is that the equatorial N—Ti—Br angle is widened whereas the equatorial Br—Ti—Br angle is decreased (Table 1). The angles involving the two axial Br ligands show that these atoms are displaced from the ideal linear arrangement in the direction of the aromatic ring. On the other hand, 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 is isomorphous with tetrachloro(2-methylpyridine-*N*)titanate(IV) (Hensen *et al.*, 2000*b*). A least-squares fit of the two molecules excluding the halogen and H atoms gives an r.m.s.d. of 0.036 Å and the bond lengths and angles involving the halogen substituents show the same geometric features as in the title compound [$Ti—Cl_{ax}$ 2.289 (1) and 2.297 (1) Å, $Ti—Cl_{eq}$ 2.211 (1) Å, $Ti—Cl_{eq}$(adjacent to CH_3) 2.253 (1) Å]. The Ti—N bond length is a little shorter than in the three comparable compounds: 2.185 (3) Å in tetrachloro(2-methylpyridine-*N*)titanate(IV), 2.190 (2) Å in tetrachloro(2,6-dimethylpyridine-*N*)titanate(IV) (Hensen *et al.*, 2000*b*), and 2.179 (7) and 2.199 (8) Å in the two molecules in the asymmetric unit of tetrabromo(2,6-dimethylpyridine-*N*)titanate(IV) (Hensen *et al.*, 2000*a*).

Experimental

Due to the extreme susceptibility to hydrolysis of titanium halides, all operations were carried out under an inert gas atmosphere. To a solution of $TiBr_4$ (0.96 ml, 9.11 mmol) in hexane (30 ml), 2-methylpyridine (1.1 ml, 9.45 mmol) was added. The red precipitate was washed with hexane and dried. Sublimation at 353 K yielded suitable crystals after approximately two weeks.

Crystal data

$C_6H_7Br_4NTi$
$M_r = 460.67$
Monoclinic, $P2_1/n$
$a = 6.7416$ (1) Å
$b = 9.8984$ (2) Å
$c = 17.3338$ (3) Å
$\beta = 91.820$ (1)°
$V = 1156.12$ (4) Å^3
$Z = 4$

$D_x = 2.647$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6306 reflections
$\theta = 1$–25°
$\mu = 14.515$ mm^{-1}
$T = 173$ K
Block, red
0.25 × 0.20 × 0.20 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*: Sheldrick, 1997)
$T_{min} = 0.026$, $T_{max} = 0.055$
15 542 measured reflections
2159 independent reflections
1587 reflections with $I > 2\sigma(I)$

$R_{int} = 0.086$
$\theta_{max} = 26.21°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -21 \rightarrow 20$
131 standard reflections
frequency: 1000 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.106$
$S = 1.088$
2159 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 4.5123P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.98$ e Å^{-3}
$\Delta\rho_{\min} = -0.92$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ti1—N1	2.145 (7)	Ti1—Br3	2.4129 (17)
Ti1—Br2	2.3245 (17)	Ti1—Br4	2.4202 (17)
Ti1—Br1	2.3502 (17)		
N1—Ti1—Br2	115.5 (2)	Br2—Ti1—Br4	97.98 (6)
N1—Ti1—Br1	136.3 (2)	Br1—Ti1—Br4	92.75 (6)
Br2—Ti1—Br1	108.17 (7)	Br3—Ti1—Br4	160.36 (7)
N1—Ti1—Br3	81.74 (19)	C2—N1—C6	119.8 (7)
Br2—Ti1—Br3	97.47 (6)	C2—N1—Ti1	122.6 (6)
Br1—Ti1—Br3	93.88 (6)	C6—N1—Ti1	117.6 (6)
N1—Ti1—Br4	80.69 (19)		
Br2—Ti1—N1—C2	−176.9 (6)	Br3—Ti1—N1—C2	−82.5 (6)
Br1—Ti1—N1—C2	4.4 (8)	Br4—Ti1—N1—C2	88.6 (6)

All H atoms were located by difference Fourier synthesis refined with fixed individual displacement parameters [U(H) = 1.5$U_{\rm eq}$($C_{\rm methyl}$) or U(H) = 1.2$U_{\rm eq}$($C_{\rm aromatic}$)] using a riding model with aromatic C—H = 0.95 Å or methyl C—H = 0.98 Å. The methyl group was allowed to rotate about its local threefold axis.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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