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Structure of Monomeric $[\text{TiCl}_4(\text{hexamethylphosphoric triamide})_2]$

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Abstract

trans-Tetrachlorobis(*N,N,N',N',N'',N''*-hexamethylphosphoric triamide-*O*)titanium, $[\text{TiCl}_4(\text{hmpa})_2]$, where hmpa is $\text{C}_6\text{H}_{18}\text{N}_3\text{OP}$, is monomeric and octahedral about the metal centre with the hmpa ligands occupying a *trans* position relative to one another. Both hmpa groups bind to the Ti via their O atoms.

Comment

Hexamethylphosphoric triamide (hmpa) is a well known monodentate donor compound that has been used widely in alkali-metal synthetic (Wakefield, 1990) and structural (Mulvey, 1991; Gregory, Schleyer & Snaith, 1991) chemistry. The use of this compound as a donor ligand in peroxo complexes of titanium has been recorded also (Mimoun, Postel, Casabianca, Fischer & Mitschler, 1982; Postel, Casabianca, Gauffreteau & Fischer, 1986). We report here the molecular structure of the complex formed between TiCl_4 and two hmpa ligands. By adopting a *trans* orientation with respect to the hmpa ligands, the six-coordinate Ti atom assumes an almost perfect octahedral environment, *cis* bond angles around the Ti being within 1.1° of 90° . The corresponding *cis* structure would be sterically crowded because of the bulk of the hmpa ligand, so to minimize van der Waals repulsions a *trans* structure is adopted. The Ti atom lies on a crystallographic centre of symmetry.

The complex formed between TiCl_4 and the hmpa relative POCl_3 , $[(\text{TiCl}_4.\text{POCl}_3)_2]$, has been characterized previously (Brändén & Lindqvist, 1960). However, this compound adopts a dimeric arrangement with two Cl bridges and the POCl_3 ligands sitting *trans* to one another; the phosphoryl O—Ti bond length is $2.10(1) \text{ \AA}$, in contrast to the shorter $1.945(3) \text{ \AA}$ in the monomeric hmpa complex. As the Ti centre in each of these complexes is six-coordinate, the critical factor here must be the stronger donating nature of the hmpa ligand. Mean Ti—Cl bond

distances in the dimer are 2.49 \AA (bridging) and 2.23 \AA (terminal). The hmpa adduct has a mean Ti—Cl bond length (2.328 \AA) lying between these values. The POCl_3 ligand does not coordinate linearly to Ti, having a bond angle Ti—O—P of $151.8(13)^\circ$; the hmpa complex has a slightly wider angle of $158.7(2)^\circ$.

Recently, a study of the reactions between phosphate esters and titanium compounds appeared in the literature (Thorn & Harlow, 1992). Another relative of hmpa, namely $\text{OP}(\text{OSiMe}_3)_2$, gave the elimination product $[\text{Ti}_2\text{Cl}_7\{\text{O}_2\text{P}(\text{OSiMe}_3)_2\}\{\text{OP}(\text{OSiMe}_3)_3\}]$ in direct reaction with TiCl_4 . The structure is dimeric with two chloro bridges and one $\text{O}_2\text{P}(\text{OSiMe}_3)_2$ bridge. Five terminal Cl atoms and a terminal $\text{OP}(\text{OSiMe}_3)_3$ group make each Ti six-coordinate. Bond lengths and angles involving the Ti centre in this structure are similar to those discussed previously for $[(\text{TiCl}_4.\text{OPCl}_3)_2]$. Elimination of ClSiMe_3 occurs in this case as a result of the good leaving ability of the SiMe_3 substituent.

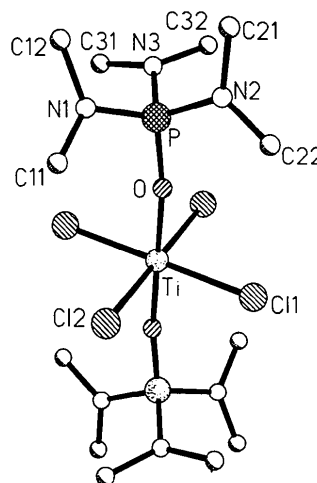


Fig. 1. Molecular structure of $[\text{TiCl}_4(\text{hmpa})_2]$.

Experimental

Crystal data

$[\text{TiCl}_4(\text{C}_6\text{H}_{18}\text{N}_3\text{OP})_2]$

$M_r = 548.11$

Monoclinic

$P2_1/n$

$a = 8.737(3) \text{ \AA}$

$b = 10.096(4) \text{ \AA}$

$c = 14.093(6) \text{ \AA}$

$\beta = 96.05(3)^\circ$

$V = 1236.2(8) \text{ \AA}^3$

$Z = 2$

$D_x = 1.473 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54184 \text{ \AA}$

Cell parameters from 32

reflections

$\theta = 11.28\text{--}19.86^\circ$

$\mu = 8.311 \text{ mm}^{-1}$

$T = 240(1) \text{ K}$

Block

$0.84 \times 0.58 \times 0.35 \text{ mm}$

Orange

Data collection

Stoe Siemens diffractometer
 ω/θ scans

$R_{\text{int}} = 0.118$ (on F^2)

$\theta_{\text{max}} = 65.07^\circ$

Absorption correction: $h = -10 \rightarrow 9$
 empirical $k = -10 \rightarrow 11$
 $T_{\min} = 0.005$, $T_{\max} = 1$ $l = -15 \rightarrow 16$
 0.107 3 standard reflections
 2627 measured reflections frequency: 60 min
 2072 independent reflections intensity variation: 5%
 1846 observed reflections
 $[I > 2\sigma(I)]$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} < 0.001$
 $R(F) = 0.0800$ [$F^2 > 2\sigma(F^2)$] $\Delta\rho_{\max} = 1.490 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.2260$ $\Delta\rho_{\min} = -0.704 \text{ e } \text{\AA}^{-3}$
 $S = 1.12$ Extinction correction: none
 2071 reflections Atomic scattering factors
 124 parameters from *International Tables*
 Calculated weights for *Crystallography* (1992),
 $w = 1/[\sigma^2(F_o^2) + (0.1455P)^2]$ Vol. C, Tables 4.2.6.8,
 $+ 0.7706P]$ 6.1.1.4)
 where $P = (F_o^2 + 2F_c^2)/3$

H atoms were constrained to give C—H = 0.97 Å, H—C—H = 109.5°, staggered conformations and $U(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1992). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ti	0			0.0544 (4)
P	0.26521 (12)	0.74208 (10)	0.55322 (7)	0.0502 (4)
Cl1	0.1591 (2)	0.32056 (12)	0.54216 (10)	0.0770 (5)
Cl2	-0.0921 (2)	0.49041 (13)	0.64936 (8)	0.0711 (5)
O	0.1628 (3)	0.6213 (3)	0.5485 (2)	0.0526 (7)
N1	0.1918 (5)	0.8505 (4)	0.6222 (3)	0.0597 (9)
N2	0.4386 (4)	0.6924 (4)	0.5898 (3)	0.0622 (10)
N3	0.2807 (5)	0.8222 (4)	0.4542 (3)	0.0604 (9)
C11	0.1087 (8)	0.8063 (5)	0.6997 (4)	0.080 (2)
C12	0.2559 (7)	0.9829 (5)	0.6354 (4)	0.0717 (14)
C21	0.5628 (7)	0.7893 (7)	0.6130 (5)	0.087 (2)
C22	0.4735 (9)	0.5646 (8)	0.6242 (7)	0.129 (3)
C31	0.1538 (7)	0.8986 (6)	0.4084 (4)	0.0791 (15)
C32	0.3861 (7)	0.7784 (6)	0.3867 (3)	0.0731 (14)

Table 2. Geometric parameters (\AA , °)

Ti—O	1.945 (3)	N1—C11	1.445 (7)
Ti—Cl1	2.3224 (14)	N1—C12	1.454 (6)
Ti—Cl2	2.333 (2)	N2—C22	1.400 (7)
P—O	1.510 (3)	N2—C21	1.472 (7)
P—N2	1.627 (4)	N3—C31	1.446 (7)
P—N3	1.631 (4)	N3—C32	1.460 (7)
P—N1	1.639 (4)		
O—Ti—Cl1	90.31 (10)	C11—N1—C12	113.9 (4)
O—Ti—Cl2	91.04 (9)	C11—N1—P	120.1 (3)
Cl1—Ti—Cl2	89.48 (6)	C12—N1—P	121.3 (4)
O—P—N2	107.0 (2)	C22—N2—C21	114.0 (5)
O—P—N3	117.7 (2)	C22—N2—P	123.7 (4)
N2—P—N3	105.4 (2)	C21—N2—P	120.4 (4)
O—P—N1	107.4 (2)	C31—N3—C32	112.2 (4)
N2—P—N1	115.3 (2)	C31—N3—P	121.1 (3)
N3—P—N1	104.4 (2)	C32—N3—P	121.5 (4)
P—O—Ti	158.7 (2)		

The title compound was prepared by the addition of excess hmpa (40 mmol) to a solution of TiCl_4 (10 mmol) in toluene. A sparingly soluble solid was deposited and removed by filtration. Good quality orange crystals were grown from the remaining dilute mother liquor. As a result of the air- and moisture-sensitive nature of this work, Schlenk and vacuum techniques were employed and the crystals were sealed inside Lindemann capillary tubes in an argon-filled glove box prior to data collection.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71467 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1061]

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Dilithium Zinc Crotonate, a Mixed-Metal Sheet Polymeric Structure

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Abstract

The structure of dilithium zinc tetra-*trans*-2-butenate, $[\text{Li}_2\text{Zn}(\text{C}_4\text{H}_5\text{O}_2)_4]$, is made up of polymeric sheets. Each crotonate anion bridges three metal ions, with one O atom