

## THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS-DIMETHYL-AMINOTITANIUM DIFLUORIDE TETRAMER

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### Summary

The crystal structure of  $[(\text{Me}_2\text{N})_2\text{TiF}_2]_4$  has been determined by single-crystal X-ray diffraction. The crystals are tetragonal,  $I\bar{4}$ ,  $a = b = 11.313(5)$ ,  $c = 12.862(4)$  Å,  $Z = 2$ . The titanium atoms display a distorted octahedral coordination and are linked by Ti—F—Ti and Ti—NMe<sub>2</sub>—Ti bridges to form a tetramer, which possesses a crystallographic inverse tetrad axis at its centre. One fluorine and one dimethylamino group do not participate in the bridging. The principal bond lengths are Ti—F(bridging) 2.00(2) and 2.06(2), Ti—F (terminal) 1.77(2), Ti—N(bridging) 2.14(3) and 2.19(3), Ti—N(terminal) 1.99(3) Å. The structure has been refined to  $R = 0.077$  for 231 visually estimated unique reflections.

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### Introduction

The hitherto unknown dialkylaminotitanium fluorides  $(\text{R}_2\text{N})_n\text{TiF}_{4-n}$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$  (Me, Et);  $n = 1 - 3$ ) have recently been synthesised [1]. The structural significance of these molecules is indicated by a comparison of the anomalous polymeric nature of  $\text{TiF}_4$  with the monomeric  $\text{TiCl}_4$ ,  $\text{TiBr}_4$  and  $\text{TiI}_4$  [2]. It is to be anticipated, for instance, that the tendency towards association observed for the dialkylaminotitanium chlorides through chlorine bridging [3 - 5] should be even more marked when fluorine is involved.  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectral measurements on  $(\text{Et}_2\text{N})_2\text{TiF}_2$  suggested not only the presence of Ti—F—Ti but also Ti—NR<sub>2</sub>—Ti bridging, a phenomenon not previously observed for titanium(IV) but postulated, however, for  $\text{Ti}^{\text{III}}$  compounds [6]. Owing to insolubility, NMR and molecular weight investigations for the dimethylamino derivatives  $\text{Me}_2\text{NTiF}_3$  and  $(\text{Me}_2\text{N})_2\text{TiF}_2$  proved not to be feasible, although IR measurements supported the assumption of —NMe<sub>2</sub>— bridging in the former compound. In view of the diverse structural interpretations available, a crystal-structure determination was undertaken in order to characterise the nature of the association in  $(\text{Me}_2\text{N})_2\text{TiF}_2$ .

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## Experimental

Orange crystals of  $(\text{Me}_2\text{N})_2\text{TiF}_2$  were obtained from the reaction of  $\text{TiF}_4$  with  $\text{Ti}(\text{NMe}_2)_4$  [1]. A suitable tetragonal-bipyramidal shaped crystal ( $0.25 \times 0.25 \times 0.35$  mm) was sealed into a Lindemann glass capillary tube and intensities estimated visually from equi-inclination Weissenberg photographs (layers  $0kl-7kl$  inclusive) taken with Ni-filtered  $\text{Cu-K}\alpha$  radiation. Lorentz, polarisation and approximate absorption corrections ( $\mu = 88.7 \text{ cm}^{-1}$ ) were applied and the data placed on a self-consistent scale using the linear least-squares method of Rae and Blake [7]. Accurate unit-cell dimensions were obtained from measurements of 18  $0kl$  reflections on a zero-layer Weissenberg photograph calibrated with tungsten ( $a = 3.1653 \text{ \AA}$ ), using a least-squares routine which corrected for potential systematic eccentricity errors.

### Crystal data

$\text{C}_{16}\text{H}_{48}\text{N}_8\text{F}_8\text{Ti}_4$ , mol. wt. 706.2, tetragonal, Laue group  $4/m$ ,  $a = b = 11.313(5)$ ,  $c = 12.862(4) \text{ \AA}$ ,  $U = 1646.3(11) \text{ \AA}^3$ ,  $d_c = 1.42$  for  $Z = 2$ . The observed systematic absences ( $hkl$  with  $h + k + l = 2n$ ) are consistent with either of the space groups  $I4$  or  $I4$ .

### Structure solution and refinement

A three-dimensional Patterson synthesis was interpreted to give a set of coordinates for the titanium atom which was consistent with either of the space groups  $I4$  or  $I4$ . The remaining atoms, except for hydrogen, were located from a difference electron-density synthesis, which also indicated that  $I4$  was the appropriate space group. This conclusion was confirmed by the subsequent full-matrix least-squares refinement of the structure. In the final cycles of this refinement a total of 52 parameters were varied simultaneously, consisting of 27 positional parameters, 18 anisotropic temperature-factor components for the titanium and fluorine atoms, six isotropic temperature factors for the nitrogen and carbon atoms, and an overall scale factor. The introduction of anisotropic refinement for the nitrogen or carbon temperature factors was felt to be unjustified, in view of the fact that the observed data was limited to 231 unique reflections. Likewise, no attempt was made to locate and refine the hydrogen-atom positions. Complex neutral-atom scattering factors [8,9] were employed for all atoms. The weighting scheme adopted was  $w = (16.95 + |F_o| + 0.00869F_o^2)^{-1}$ , which has been converted to an absolute scale of  $F_o$ . The final value of  $R_w = \Sigma w^{1/2}(|F_o| - |F_c|) / \Sigma w^{1/2}F_o$  was 0.083 and the corresponding unweighted index  $R = 0.077$ . Observed and calculated structure factors are given in Table 1. The results from the final least-squares cycle are summarised in Tables 2 and 3; these results, together with the full covariance matrix were used to calculate the bond lengths and angles, and their estimated standard deviations presented in Table 4. The shortest non-bonded distances are summarised in Table 5.

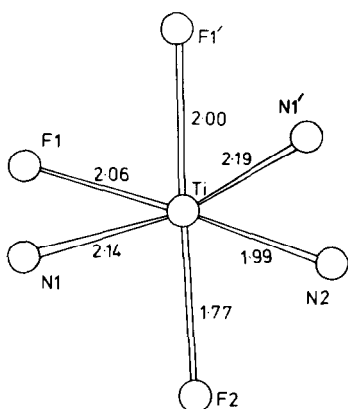


Fig. 1. The coordination at titanium. (All bond lengths in Å units.)

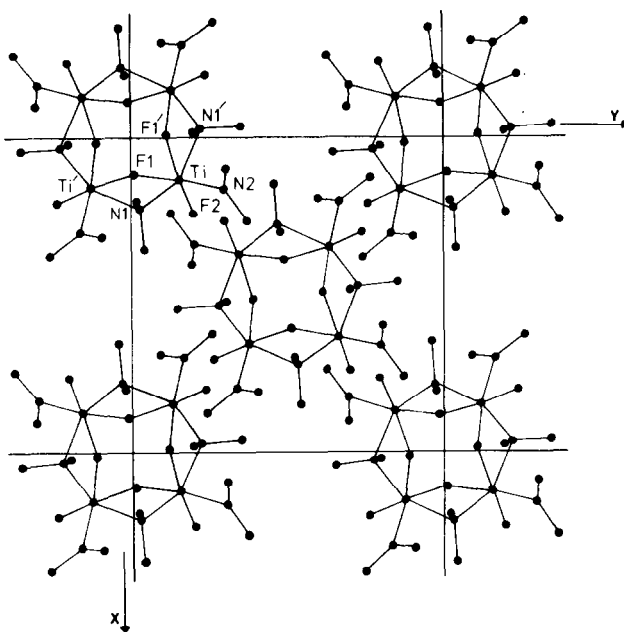


Fig. 2. Projection of the crystal structure perpendicular to the  $c$ -axis.

Figure 1 depicts the nature of the coordination around titanium and Figure 2 the unit-cell contents, together with the numbering system, shown perpendicular to  $[001]$ .

## Discussion

The crystal-structure determination demonstrates that  $(\text{Me}_2\text{N})_2\text{TiF}_2$  is tetrameric in the solid phase. The titanium achieves 6-coordination through



TABLE 3

Atom coordinates and anisotropic vibrational amplitudes ( $\text{\AA}^2 \times 10^3$ )<sup>a</sup> with estimated standard deviations

Atom	x/a	y/b	z/c	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Ti	0.1306(4)	0.1575(5)	-0.0004(7)	75(4)	86(4)	87(4)	10(5)	6(5)	3(3)
F(1)	0.1148(13)	0.0079(10)	0.0893(13)	87(11)	51(9)	95(13)	- 3(9)	-10(11)	11(9)
F(2)	0.2414(16)	0.2001(16)	0.0889(18)	107(13)	129(15)	109(18)	- 1(15)	-34(14)	-11(12)

<sup>a</sup> The anisotropic temperature factor takes the form:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}hb^*c^* + 2U_{31}hc^*a^* + 2U_{12}hka^*b^*)]$

TABLE 4

Interatomic distances (Å) and bond angles (degrees)

Ti—F(1)	2.06(2)	Ti—F(1')	2.00(2)
Ti—F(2)	1.77(2)	Ti—N(2)	1.99(3)
Ti—N(1)	2.14(3)	Ti—N(1')	2.19(3)
N(1)—C(11)	1.55(3)	N(1)—C(12)	1.45(4)
N(2)—C(21)	1.45(4)	N(2)—C(22)	1.51(4)
F(1)—Ti—N(1)	75.7(8)	F(1)—Ti—F(1')	93.1(5)
F(1)—Ti—N(1')	84.2(5)	F(1)—Ti—F(2)	85.5(8)
F(1')—Ti—N(1')	75.7(8)	F(1')—Ti—N(2)	89.8(8)
F(1')—Ti—N(1)	83.7(7)	N(1)—Ti—N(2)	98.7(10)
N(1)—Ti—F(2)	102.0(10)	N(1')—Ti—N(2)	102.3(7)
N(1')—Ti—F(2)	98.0(8)	F(2)—Ti—N(2)	92.2(9)
Ti'—F(1)—Ti	107.7(8)	Ti'—N(1)—Ti	98.1(11)
C(11)—N(1)—Ti	108(2)	C(12)—N(1)—Ti	120(2)
C(11)—N(1)—Ti'	107(2)	C(12)—N(1)—Ti'	116(2)
C(11)—N(1)—C(12)	106(3)	C(21)—N(2)—Ti	120(2)
C(22)—N(2)—Ti	120(2)	C(21)—N(2)—C(22)	120(3)

membered TiFTiN rings showing the most marked degree of distortion (75.7°). The terminal Ti—F bond length of 1.77(2) Å is much shorter than the mean values of 1.86 and 1.88 Å observed in the octahedrally-coordinated  $\text{TiF}_6^{2-}$  anion in  $\text{CuTiF}_6 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{CuTiF}_7 \cdot 4\text{H}_2\text{O}$  respectively [10,11], in which the fluorine atoms are, however, also involved in hydrogen bonding. The terminal Ti—N bond length of 1.99(3) Å is not significantly different from the value of 1.96 Å which may be estimated for a theoretical  $\sigma$  bond. This contrasts markedly with the value of 1.852(4) Å observed [5] in  $\text{Et}_2\text{NTiCl}_3$ , the shortness of which was attributed to the presence of  $(p \rightarrow d)\pi$  bonding, as inferred from the  $sp^2$  hybridisation observed at nitrogen. However, the sum of the bond angles at the terminal nitrogen in  $[(\text{Me}_2\text{N})_2\text{TiF}_2]_4$  is also 360°, which would indicate that the nitrogen lone pair displays p character in this case as well, a conclusion which conflicts strongly with the observation of an exceptionally long Ti—N bond length.

The bridging Ti—F distances are 2.00(2) and 2.06(2) Å and the bridging Ti—N distances 2.14(3) and 2.19(3) Å. The relatively high standard deviations in these bond lengths are, at least in part, due to the high degree of thermal motion observed in the molecule, a fact which is reflected in the small number of unique reflections which could be estimated. It is interesting to note that, in contrast to  $\text{Et}_2\text{NTiCl}_3$ , there would appear to be no evidence that the bond lengths to titanium are influenced by the nature of the bond in the *trans* position within the coordination octahedron. For example, the two bridging Ti—F bond distances are not significantly different, although one (the shorter) is opposite a terminal Ti—F and the other a terminal Ti—N bond.

The F...F non-bonded distance across the tetramer is particularly short at 2.60 Å. There are no particularly short intermolecular non-bonded distances.

TABLE 5

Non-bonded distances (Å) under 3.5 Å

<i>(a) Intramolecular distances with adjacent unit (y, -x, -z)</i>			
Ti—Ti	3.27	Ti—C(11)	3.04
Ti—C(12)	3.12	F(1)—F(1)	2.94
F(1)—N(1)	2.85	F(1)—C(12)	3.03
F(2)—N(1)	3.00	F(2)—C(12)	3.25
N(2)—C(11)	3.14		
<i>(b) Intramolecular distances with adjacent unit (-y, x, -z)</i>			
F(1)—N(1)	2.76	F(1)—N(2)	2.82
F(1)—C(12)	3.00	F(1)—C(21)	2.82
N(1)—N(2)	3.26		
<i>(c) Intramolecular distances across the tetramer (-x, -y, z)</i>			
F(1)—F(1)	2.60		
<i>(d) Intermolecular distances</i>			
F(2)—C(21)	3.38		

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