catena-Di-μ-chloro-bis-μ-(trimethylsilylamino)-di[chlorotitanium(IV)]: Preparation, Properties, and Crystal Structure

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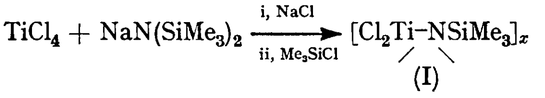
The preparation of the title compound is reported from the slow reaction of $TiCl_4$ and $N(SiMe_3)_3$, and its crystal structure has been determined by direct methods from diffractometer data (1 298 reflections, R 0·090). Crystals are monoclinic, space group $P2_1/c$, $a = 17.74$, $b = 18.52$, $c = 11.46$ Å, $\beta = 102.71°$, $Z = 8$. It contains planar four-membered $(Ti–N)_2$ rings with planar geometry at N apparently with considerable π-bonding in the rings. These are linked by Cl-bridges to give five-co-ordinate Ti atoms in approximately trigonal bipyramidal geometry. Depending on the donor nature or otherwise of the solvent, this polymeric structure breaks down in solution to give discrete $(Ti–N)_2$ units in which the metal atoms are either four- or six-co-ordinate. As an example of the latter a 1 : 2 adduct with pyridine is described.

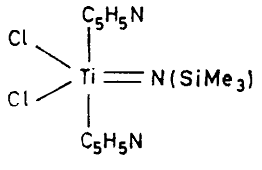
AT face value the reaction of titanium(IV) chloride and sodium bis(trimethylsilyl)amide represents a convenient route to the cyclic (Ti–N) system (I) following the energetically favourable salt elimination and release of trimethylchlorosilane (b.p. 332 K) [equation (1)]. With



$$\mathrm{TiCl_4 + NaN(SiMe_3)_2 \xrightarrow[\text{ii, Me}_3\text{SiCl}]{\text{i, NaCl}} [Cl_2Ti{-}NSiMe_3]_x} \qquad (1)$$

(I)

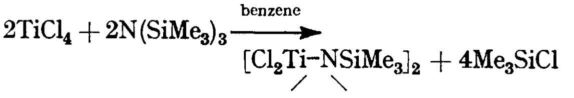
the reported formation of $Cl_3Ti–N(SiMe_3)_2$ (II) and, rather surprisingly, Na_2TiCl_6 as reaction products, however, the sequence evidently only proceeds to half-completion at the expense of step (ii). Subsequent treatment with pyridine induces elimination of trimethylchlorosilane from (II), but instead of (I) as product, the adduct $Cl_2Ti–NSiMe_3·2py$ (III) with a postulated titanium–imide linkage was obtained.[1]



(III)

Geometry of $Cl_2TiNSiMe_3·2C_5H_5N$, (III), as suggested by Bürger and Wannagat (ref. 1)

As an alternative approach to formation of (I) and one that inherently avoids complications arising from complex ion [hexachlorometallate(IV)] formation, we have studied the reaction of titanium(IV) chloride with the tertiary amine tris(trimethylsilyl)amine.[2] Although extremely slow, the reaction proceeds with release of trimethylchlorosilane according to equation (2), and the



$$\mathrm{2TiCl_4 + 2N(SiMe_3)_3 \xrightarrow{\text{benzene}} [Cl_2Ti{-}NSiMe_3]_2 + 4Me_3SiCl} \qquad (2)$$

resulting titanazane formation conforms to the general reaction pattern of silylamine chemistry where ready Si–N cleavage on reaction with covalent halides $\geqslant$M–X has led to the synthesis of a wide variety of linear and

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[1] H. Bürger and U. Wannagat, *Monatsh. Chem.*, 1963, **94**, 761.

[2] Preliminary report, M. Pierce-Butler and G. R. Willey, *J. Organometallic Chem.*, 1973, **54**, C19.

cyclic $\geqslant$M-N derivatives.[3] Although a tetrameric (Ti_4-N_4) structure was originally favoured for the orange crystalline product (I) a crystallographic study has revealed the novel dimeric (Ti_2N_2) heterocycle.[4] The only other possible representatives of such a Group IVA *N*-bonded cyclic system are the suggested four-membered ring compounds $[Ti(NMe_2)_2(NBu^t)]_2$ and $[Ti(NMe_2)(NBu^t)(NHBu^t)]_2$ formed during the ammonolysis (Bu^tNH_2) of the titanium amides $Ti(NR_2)_4$ (R = Me or Et).[5]

EXPERIMENTAL

As a necessary precaution against air-moisture hydrolysis, all materials were handled under dry oxygen-free nitrogen. Organic solvents were normally stored over calcium hydride and/or phosphoric oxide and distilled before use. Tris(trimethylsilyl)amine was prepared by the method of Lehn.[6] Titanium tetrachloride (Hopkin and Williams) was stored over copper powder and distilled *in vacuo* as required.

I.r. spectra (4 000—200) cm^{-1} were recorded, on a Perkin-Elmer 621 spectrophotometer, with samples as Nujol or Fluorolube mulls held between caesium iodide plates, or in solution with potassium bromide windowed cells. ^1H n.m.r. spectra (60 MHz) were recorded on a Perkin-Elmer R12 spectrophotometer, and electronic spectra on a Cary 14 spectrophotometer, using solutions held in sealed 1 cm silica cells.

Elemental microanalyses were obtained professionally, chlorine was determined by the Volhard method, and titanium was determined by the method of Tribalat and Caldero.[7]

Preparation of catena-*Di-μ-chloro-bis-μ-(trimethylsilylamino)-di[chlorotitanium*(IV)] [I].—Titanium(IV) chloride (3 cm^3, 0.03 mol) was distilled *in vacuo* into a glass reaction vessel containing tris(trimethylsilyl)amine (2.33 g, 0.01 mol) and benzene (*ca.* 30 cm^3). On sealing and allowing the vessel to warm to 293 K, a yellow solution was apparent which gradually deepened over a few days to red. As reaction proceeded over a period of 3 months, orange needle crystals of (I) separated from solution. These were washed with n-hexane and sealed under nitrogen into glass ampoules (1.33 g, 65%), suitable specimens being selected for *X*-ray structural analysis. Fractional distillation of the filtrate gave the expected trimethylchlorosilane, b.p. 332—333 K/760 mmHg (1.9 g, 90%) (Found: C, 17.5; H, 4.4; Cl, 34.3; N, 6.7; Ti, 23.1. Calc. for $[C_3H_9NSiTiCl_2]_x$: C, 17.5; H, 4.4; Cl, 34.4; N, 6.8; Si, 13.6; Ti, 23.3%); m.p. (decomp.) > 415 K.

Reaction of (I) *with Pyridine*.—A mixture of (I) (2 g), excess of pyridine (*ca.* 10 cm^3), and benzene (*ca.* 20 cm^3) was sealed in an evacuated glass vessel to give an orange-red solution. After several days mechanical shaking, an orange semi-crystalline solid was deposited. Careful filtration and evaporation, followed by several washings with n-hexane, gave the orange product bis-μ-(trimethylsilylamino)-tetrachlorotetra(pyridine)dititanium(IV) (3.2 g, 88%) (Found: C, 42.6; H, 5.0; Cl, 19.6; N, 11.5; Ti, 13.0. Calc. for $[C_{13}H_{19}N_3SiTiCl_2]_x$: C, 42.9; H, 5.3; Cl, 19.5; N, 11.5; Si, 7.7; Ti, 13.2%). M.p. (decomp.) >393 K. This product appears to be identical with compound (III) isolated by Bürger and Wannagat.[1]

Crystal Data.—$C_6H_{18}Cl_4N_2Si_2Ti_2$, Monoclinic, $a = 17.74(2)$, $b = 18.52(2)$, $c = 11.46(1)$ Å, $\beta = 102.71(5)°$, $U = 3671$ Å^3, $D_c = 1.504$, $Z = 8$, $D_m = 1.505(5)$, Mo-K_α *X*-radiation, $\lambda = 0.710\ 69$ Å; μ(Mo-K_α) = 23.8 cm^{-1}, $F(000) = 832$. Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$ indicate space group $P2_1/c$. There are also marked pseudo-absences, such that almost all observed reflections in the $h0l$ and $hk0$ zones satisfy the conditions $h0l$, $h = 2n$; $hk0$, $k = 2n$, and $h = k/2 = 2n$. The needle-shaped crystals were very moisture sensitive and one was mounted in a Lindemann capillary in a dry box. D_m was measured by flotation in benzene–methylene iodide, the manipulations being performed in a dry box. Data were collected on a Stoe Weissenberg diffractometer, for layers $hk0$—8 ($2\theta_{max.} - 60°$). Of 4 955 reflections examined, 1 298 were considered observed, having $I/\sigma(I) \geqslant 3.5$. Unit-cell constants were determined from the reflecting positions of high-angle reflections and their errors estimated from the accuracy of the observations. No absorption corrections were made.

Structure solution was initially attempted unsuccessfully by Patterson synthesis and by the PHASER direct methods program of the *X*-Ray system.[8] Inequalities and the Sayre relationship were then applied by hand to the centred ($b' = b/2$) sub-cell of the $hk0$ projection to give phases for 27 reflections. A Fourier synthesis showed six 'atoms' (presumed to be the two Ti and four Cl expected in the sub-cell) and refinement and the inclusion of further atoms gave R 0.128 for the 102 reflections. A similar approach to the $h0l$ projection (as its sub-cell, $a' = a/2$, $c' = c/2$) also gave a solution, with fairly good agreement in the common x co-ordinates.

These projections apparently showed four molecules in the cell, centred around ($0,0,0$; $0,\frac{1}{2},0$) and ($\frac{1}{2},\frac{1}{4},0$; $\frac{1}{2},\frac{3}{4},0$). However, on the presumption that these were each eight-membered rings (Ti_4N_4), the space group could not be $P2_1/c$; this would relate two halves of one ring by a centre of symmetry but the halves of the other by a glide plane with a 5.3 Å translation. The only space group not imposing similar relationships is $P2$ but all attempts failed to generate a three-dimensional structure in $P2$ by combining the two-dimensional co-ordinates (in numerous permutations). Further progress came with three-dimensional direct methods and the MULTAN sequence of programs.[9] The calculation of E values immediately revealed large differences in mean intensity between parity groups (*eee* : *ooo* ratio of 2.65 : 1), and the groups were therefore separately

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[3] See *e.g.* H. Bürger and H-J Neese, *Chimia* (*Switz.*), 1970, **24**, 209; O. J. Scherer and P. Klusmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 752; R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat, and L. Stobbs, *J.C.S. Dalton*, 1973, 1414; N. G. Klyuchnikov, F. I. Karabadzhak and V. B. Losev, *J. Gen. Chem.* (*U.S.S.R.*), 1971, **41**, 166; H. Nöth, D. Reiner, and W. Storch, *Chem. Ber.*, 1973, **106**, 1508; W. Lehr, *Z. anorg. Chem.*, 1969, **371**, 225; W. Wolfsberger and H. H. Pickel, *J. Organometallic Chem.*, 1973, **54**, C8; N. Wiberg and G. Schwenk, *Angew. Chem. Internat. Edn.*, 1969, **8**, 755; J. S. Harman, M. E. McCartney, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1971, 1547; G. Czieslik, G. Flaskerud, R. Höfer, and O. Glemser, *Chem. Ber.*, 1973, **106**, 399. For a general review of the chemistry of the Si–N bond, see U. Wannagat, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 265.

[4] Preliminary report, N. W. Alcock, M. Pierce-Butler, and G. R. Willey, *J.C.S. Chem. Comm.*, 1974, 627.

[5] D. C. Bradley and E. G. Torrible, *Canad. J. Chem.*, 1963, **41**, 134.

[6] W. L. Lehn, *J. Amer. Chem. Soc.*, 1964, **86**, 305.

[7] S. Tribalat and J. M. Caldero, *Bull. Soc. chim. France*, 1964, 3187.

[8] J. M. Stewart in 'Crystollagraphic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 71.

[9] G. German and M. M. Woolfson, *Acta Cryst.*, 1968, **B24**, 91.

normalized.* The intensity statistics after this strongly supported a centrosymmetric space group, and phasing was therefore attempted first in $P2_1/c$. Encouragingly, of the seven first phase sets, the one with the best MULTAN figure-of-merit gave an electron-density map agreeing closely in projection with the previously obtained *hk*0 map. It showed clearly that a tetrameric structure could not be fitted to the located peaks, but much of the Fourier map could be explained in terms of dimeric $(Ti–N)_2$ units centred around (0,0,0), (0,0,½), (0,½,0), and (0,½,½). Based on this an *R* value of 0.240 was reached. The other two ' molecules ' were still confused and the complete solution came with the recognition of disorder in these, involving the titanium atoms and half the chlorine atoms. When allowance had been made for this, and the temperature factors of the titanium atoms, the chlorine atoms, the nitrogen atoms of the ordered molecule, and the silicon atoms of the disordered molecule had been allowed to refine anisotropically, *R* reached a final value of 0.090. Unit weights were used and were found to be satisfactory. A final difference synthesis showed no significant features. Scattering factors were

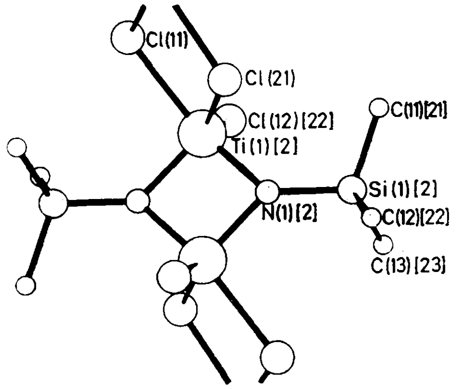

FIGURE 1 One unit of the ordered chain around (0,0,0) showing the atom numbering; the numbering for the identical unit around (0,0,½) is given in square brackets. Each has an inversion centre at the centre of the ring

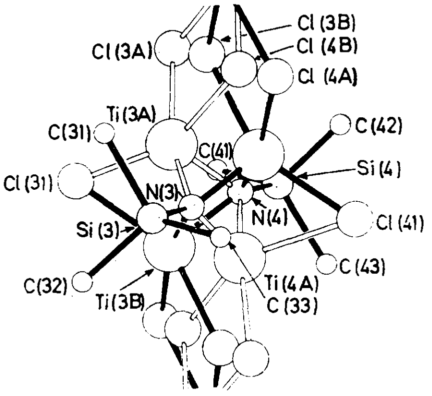

FIGURE 2 The independent atoms of the disordered chain, showing the atom numbering. One molecule is shown linked with closed bonds, the other with open (apart from the $SiMe_3$ group which is common to both)

TABLE 1

Atomic co-ordinates (× 10^4), isotropic and anisotropic ‡ temperature factors (× 10) with standard deviations in parentheses

Atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ti(1)	−383(3)	277(3)	3 930(5)	25(2)	14(2)	6(3)	0(2)	1(2)	1(2)
Ti(2)	387(3)	308(3)	−772(5)	37(3)	19(2)	3(3)	4(2)	3(2)	−2(2)
Ti(3A) †	4 710(7)	2 831(7)	709(16)	27(6)	33(7)	92(12)	−4(7)	15(6)	3(5)
Ti(3B) †	4 714(9)	2 724(8)	−1 136(17)	58(9)	68(10)	79(12)	13(8)	24(7)	3(7)
Ti(4A) †	5 498(7)	2 200(7)	−854(14)	35(6)	38(7)	69(10)	2(6)	23(6)	8(5)
Ti(4B) †	5 506(9)	2 192(8)	1 022(18)	49(8)	49(8)	107(13)	6(8)	21(7)	−3(6)
Cl(11)	−1 309(5)	−71(5)	2 036(8)	36(4)	41(4)	20(5)	3(3)	1(3)	−7(3)
Cl(12)	−1 124(5)	1 203(5)	4 154(10)	46(5)	31(4)	62(7)	−1(4)	19(4)	11(3)
Cl(21)	−506(4)	37(5)	−2 676(8)	30(4)	40(4)	6(5)	−5(3)	7(3)	7(3)
Cl(22)	1 106(5)	1 233(5)	48(9)	45(5)	31(4)	54(7)	−13(4)	3(4)	−13(3)
Cl(31)	3 898(8)	3 669(7)	−528(15)	81(8)	61(7)	138(13)	31(7)	28(7)	36(6)
Cl(3A) †	3 774(9)	2 562(12)	2 010(18)	28(7)	74(12)	42(13)	21(10)	7(7)	10(8)
Cl(3B) †	4 629(9)	2 484(14)	−2 720(20)	24(8)	88(14)	65(14)	26(12)	11(7)	22(10)
Cl(41)	6 275(7)	1 328(7)	455(16)	55(7)	62(7)	172(14)	−13(8)	25(7)	27(6)
Cl(4A) †	6 390(9)	2 483(12)	2 888(19)	26(7)	65(11)	49(13)	−15(10)	16(7)	−1(8)
Cl(4B) †	5 576(11)	2 564(15)	2 618(23)	39(9)	98(16)	78(17)	13(14)	19(9)	−10(11)
Si(3)	3 955(7)	1 252(8)	−449(14)	49(7)	73(8)	98(11)	−19(7)	28(6)	−16(6)
Si(4)	6 165(8)	3 801(7)	343(14)	89(9)	36(2)	83(10)	7(6)	12(7)	−29(6)
N(1)	594(18)	425(18)	5 060(29)	78(20)	56(23)	47(27)	0(18)	15(16)	20(16)
N(2)	−573(20)	405(19)	−162(30)	81(23)	60(21)	66(26)	33(17)	10(16)	−35(16)

Atom	*X*	*Y*	*Z*	*B*	Atom	*X*	*Y*	*Z*	*B*
Si(1)	1 187(4)	1 210(4)	5 209(8)	20(2)	C(22)	−964(15)	1 748(15)	−1 789(28)	20(6)
Si(2)	−1 210(5)	1 212(5)	−482(9)	29(2)	C(23)	−1 171(21)	1 732(20)	863(37)	45(8)
N(3)	4 570(9)	1 976(10)	−220(18)	4(4)	C(31)	4 234(40)	628(39)	−1 498(63)	123(20)
N(4)	5 523(11)	3 030(11)	159(20)	15(4)	C(32)	4 155(25)	704(25)	986(42)	66(11)
C(11)	2 165(26)	721(26)	5 374(45)	71(12)	C(33)	2 867(25)	1 615(24)	−854(44)	61(11)
C(12)	990(20)	1 815(19)	6 513(36)	40(8)	C(41)	5 908(27)	4 384(27)	1 425(46)	78(12)
C(13)	998(19)	1 691(19)	3 747(34)	40(8)	C(42)	7 199(16)	3 460(16)	758(29)	23(6)
C(21)	−2 117(32)	675(33)	−1 111(53)	96(16)	C(43)	5 898(24)	4 334(25)	−1 114(41)	65(11)

‡ In the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}klb^*c^* + 2B_{13}hla^*c^* + 2B_{12}hka^*b^*)]$.

† These atoms have half-occupancy.

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* This explains the earlier failure with PHASER, whose normalization program does not allow separate treatment of parity groups.

from ref. 10, and further computing was with the programs of Dr. D. Russell on an ICL 4130 computer.

Figures 1 and 2 show the atomic numbering for the ordered and disordered units; Tables 1 and 2 contain atomic parameters, bond lengths, and angles. It is considered that these are substantially more reliable for the ordered molecule, and in the following discussion only these are used. Final structure factors are listed in Supplementary Publication No. SUP 21584 (10 pp., 1 microfiche).†

TABLE 2

Internuclear distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances

(i) Ordered chain

Ti(1)–Cl(11)	2.501(10)	Ti(2)–N(2)′	1.69(3)
Ti(1)–Cl(12)	2.209(10)	Si(1)–N(1)	1.78(3)
Ti(1)–Cl(21)	2.427(9)	Si(2)–N(2)	1.86(4)
Ti(1)–N(1)	1.94(3)	Si(1)–C(11)	1.93(5)
Ti(1)–N(1)′	1.83(3)	Si(1)–C(12)	1.96(4)
Ti(2)–Cl(11)	2.452(11)	Si(1)–C(13)	1.86(4)
Ti(2)–Cl(21)	2.449(10)	Si(2)–C(21)	1.89(6)
Ti(2)–Cl(22)	2.217(10)	Si(2)–C(22)	1.93(3)
Ti(2)–N(2)	1.99(4)	Si(2)–C(23)	1.81(4)

(ii) Disordered chain

Ti(3A)–Cl(31)	2.37(2)	Ti(4B)–Cl(4A)	2.42(3)
Ti(3A)–Cl(3A)	2.53(2)	Ti(4B)–N(3)	1.98(2)
Ti(3A)–Cl(4B)	2.43(3)	Ti(4B)–N(4)	1.84(3)
Ti(3A)–N(3)	1.90(2)	Si(3)–N(3)	1.71(2)
Ti(3A)–N(4)	1.74(2)	Si(4)–N(4)	1.81(2)
Ti(3B)–Cl(31)	2.47(2)	Si(3)–C(31)	1.81(7)
Ti(4A)–Cl(41)	2.41(2)	Si(3)–C(32)	1.90(5)
Ti(4A)–Cl(3B)	2.41(3)	Si(3)–C(33)	2.00(5)
Ti(4A)–N(3)	1.98(2)	Si(4)–C(41)	1.78(5)
Ti(4A)–N(4)	1.91(3)	Si(4)–C(42)	1.90(3)
Ti(4B)–Cl(41)	2.29(2)	Si(4)–C(43)	1.91(5)

(*b*) Angles

(i) Ordered chain

Cl(11)–Ti(1)–Cl(12)	90.4(4)	Ti(2)–N(2)–Si(2)	122(2)
Cl(12)–Ti(1)–Cl(21)	137.3(4)	Ti(2)–N(2)–Si(2)	141(2)
Cl(11)–Ti(1)–Cl(21)	79.2(3)	Ti(2)–N(2)–Ti(2)	95(2)
Cl(12)–Ti(1)–N(1)	106.3(10)	N(1)–Si(1)–C(11)	97(2)
Cl(11)–Ti(1)–N(1)	159.2(10)	N(1)–Si(1)–C(12)	110(2)
Cl(21)–Ti(1)–N(1)	80.1(10)	N(1)–Si(1)–C(13)	109(2)
N(1)–Ti(1)–N(1)	88(2)	N(2)–Si(2)–C(21)	95(2)
Cl(11)–Ti(2)–Cl(22)	89.6(4)	N(2)–Si(2)–C(22)	110(1)
Cl(21)–Ti(2)–Cl(22)	137.3(4)	N(2)–Si(2)–C(23)	111(2)
Cl(11)–Ti(2)–Cl(21)	78.8(3)	C(11)–Si(1)–C(12)	120(2)
Cl(22)–Ti(2)–N(2)	103.8(1)	C(11)–Si(1)–C(13)	107(2)
Cl(11)–Ti(2)–N(2)	163.7(10)	C(12)–Si(1)–C(13)	113(2)
Cl(21)–Ti(2)–N(2)	84.0(10)	C(21)–Si(2)–C(22)	107(2)
N(2)–Ti(2)–N(2)	85(3)	C(21)–Si(2)–C(23)	118(2)
Ti(1)–N(1)–Si(1)	127(2)	C(22)–Si(2)–C(23)	115(2)
Ti(1)–N(1)–Ti(1)	93(2)		

(ii) Disordered chain

Cl(3A)–Ti(3A)–Cl(31)	95.2(7)	Ti(3A)–N(3)–Ti(4A)	90.6(9)
Cl(31)–Ti(3A)–Cl(4B)	148.6(10)	Ti(3B)–N(3)–Ti(4B)	93.4(11)
Cl(3A)–Ti(3A)–Cl(4B)	78.2(8)	Ti(3A)–N(3)–Si(3)	138(1)
Cl(31)–Ti(3A)–N(3)	103.0(9)	Ti(3B)–N(3)–Si(3)	133(1)
Cl(31)–Ti(3A)–N(4)	95.1(10)	Ti(4A)–N(3)–Si(3)	132(1)
Cl(3A)–Ti(3A)–N(3)	93.3(9)	Ti(4B)–N(3)–Si(3)	133(1)
Cl(3A)–Ti(3A)–N(4)	165.4(12)	Ti(3A)–N(4)–Ti(4A)	97.8(11)
Cl(4B)–Ti(3A)–N(3)	108.3(10)	Ti(3B)–N(4)–Ti(4B)	94.0(12)
Cl(4B)–Ti(3A)–N(4)	87.7(10)	Ti(3A)–N(4)–Si(4)	133(1)
N(3)–Ti(3A)–N(4)	89.4(1)	Ti(3B)–N(4)–Si(4)	132(1)
Cl(41)–Ti(4A)–Cl(3B)	149.6(9)	Ti(4A)–N(4)–Si(4)	129(1)
Cl(41)–Ti(4A)–N(3)	92.5(8)	Ti(4B)–N(4)–Si(4)	133(1)
Cl(41)–Ti(4A)–N(4)	103.4(10)	N(3)–Si(3)–C(31)	110(2)
Cl(3B)–Ti(4A)–N(3)	87.1(8)	N(3)–Si(3)–C(32)	107(2)
Cl(3B)–Ti(4A)–N(4)	106.6(10)	N(3)–Si(3)–C(33)	109(2)
N(3)–Ti(4A)–N(4)	82.1(10)	N(4)–Si(4)–C(41)	108(2)
Cl(31)–Ti(3B)–N(3)	102.4(10)	N(4)–Si(4)–C(42)	108(1)
Cl(31)–Ti(3B)–N(4)	87.5(10)	N(4)–Si(4)–C(43)	106(2)
N(3)–Ti(3B)–N(4)	87.4(12)	C(31)–Si(3)–C(32)	102(3)
Cl(41)–Ti(4B)–Cl(4A)	95.5(8)	C(31)–Si(3)–C(33)	117(3)
Cl(41)–Ti(4B)–N(3)	96.5(10)	C(32)–Si(3)–C(33)	111(2)
Cl(41)–Ti(4B)–N(4)	110.8(11)	C(41)–Si(4)–C(42)	114(2)
Cl(4A)–Ti(4B)–N(3)	163.9(11)	C(41)–Si(4)–C(43)	104(2)
Cl(4A)–Ti(4B)–N(4)	101.7(11)	C(42)–Si(4)–C(43)	116(2)
N(3)–Ti(4B)–N(4)	84.0(11)		

DISCUSSION

Structure.—The titanium atoms adopt the unusual co-ordination number of five by polymerising *via* intermolecular chlorine bridges, parallel to the *c* axis. (Figure 2.) The ordered chain consists of two independent sets of rings, each centrosymmetric, and each ring is inclined by *ca.* 45° from the chain axis, alternately up and down so that titanium atoms on adjacent rings approach close enough for double chlorine bridges to be formed between them. The stacking of the rings is such as to align the trimethylsilyl and terminal chlorine groups parallel to *c* at a spacing of 5.73 Å. Apart from the disorder itself (see later), the disordered chains are identical to the ordered ones, except that there are no symmetry elements at the centre of the $\mathrm{Ti_2N_2}$ rings. Although a few dimensions appear to differ significantly from those of the ordered chain, we consider these differences are unlikely to be physically meaningful for the reason noted earlier.

The most notable features of the structure are the four-membered rings which are planar, rigorously so for two of the four independent examples. The geometry about titanium is best described as trigonal bipyramidal with one nitrogen atom and one of the bridging chlorine atoms axial [angles 159(1) and 164(1)°]. The remaining nitrogen, bridging chlorine, and terminal chlorine all lie in the equatorial plane; the largest equatorial angle is 137.3(4)° between the two chlorine atoms. This is similar to the geometry of $[\mathrm{TiCl_2(OX)_2}]_2$ ($X = \mathrm{Et}$ or Ph) with oxygen bridges,[11] which may also be described as trigonal bipyramidal with an axial distortion very similar to that of the cyclotitanazane [mean axial angles 159.5 ($X = \mathrm{Et}$) and 167° ($X = \mathrm{Ph}$)].

The titanium–nitrogen bond distances differ markedly between the axial and equatorial positions [means 1.96(4) and 1.76(3) Å]. This may be partly due to the non-equivalence of the trigonal bipyramidal hybrid orbitals. A similar difference (0.15 Å) is found in a four-membered phosphorus–nitrogen ring $(\mathrm{Cl_3PNCH_3})_2$ in which the phosphorus atom adopts an approximately trigonal bipyramidal geometry with one axial and one equatorial nitrogen atom.[12] The five co-ordinate alkoxytitanium(IV) species already mentioned also shows titanium–oxygen distances, with bond lengths of 1.96 (axial) and 1.77 Å (equatorial).

The Ti–N bond length in (diethylamino)titanium(IV) trichloride is 1.852 Å, and some degree of multiple bonding

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† See notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[10] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[11] H. Hoppe and W. Haase, *Acta Cryst*, 1968, **B24**, 281; K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, 1966, **5**, 1782.

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is suggested, as this is considerably shorter than the hypothetical value of 1.96 Å for a pure Ti–N single bond.[13] The extremely short alternate Ti–N bonds of 1.76 Å found in the cyclotitanazane, together with the planarity of the ring, indicate considerable interaction between the p_π orbitals on nitrogen and the d_π orbitals on titanium (see later).

The mean internal ring angles are 86(2)° at titanium and 94(2)° at nitrogen. The deviation from the 90° predicted on the Dewar *et al.* model (see later)[14] may be to allow the larger titanium atoms greater separation. Across the ring Ti ··· Ti is 2.72(2) Å, and N ··· N is 2.50(10) Å.

The terminal chlorine–titanium bonds are 2.217(10) and 2.209(10) Å, slightly longer than the value (2.185 Å) reported for titanium tetrachloride.[15] This may be due to the increase from four- to five-co-ordination, since the bond lengths are similar to those in the five-co-ordinate species $[Cl_2Ti(OPh)_2]_2$ (2.219 and 2.209 Å). The bridging chlorine–titanium distance varies between 2.427(10) and 2.501(10) Å, similar to values (2.419 and 2.509 Å) in $[Cl_3Ti(C_5H_7O_2)]_2$, and (2.456 and 2.496 Å) in $Cl_3Ti-NEt_2$.[13,16]

The nitrogen environment is planar, despite the strain caused by the small internal ring-angle, thus indicating at least some multiple bonding in the silicon–nitrogen bond. The extent of π interaction is, however, in doubt since the Si–N bond lengths vary considerably [in the ordered molecule 1.728(34) and 1.862(38), and in the disordered molecule 1.712 and 1.809(35) Å]. None differs by $>3\sigma$ from the mean (1.791 Å), but because of the individual variations this distance cannot be used as a reliable guide to the extent of the multiple bonding. The trimethylsilyl group appears to be essentially normal, with mean Si–C 1.89(5) Å (standard distance 1.875 Å).

Five-co-ordination.—This novel titanium–nitrogen ring compound (I) provides an example of five-co-ordinate titanium(IV), a generally elusive co-ordination for which few of the postulated examples have been authenticated. In the vast majority of titanium(IV) compounds, if the metal is not tetrahedral, it achieves octahedral geometry *via* bridging atoms: *e.g.* chlorine-bridged species diethylaminotitanium(IV) trichloride [13] and di-μ-chloro-hexachlorobis(ethylcyanoformate-*N*)dititanium(IV).[17] However, the occurrence of a few five-co-ordinate species suggests that it is not energetically unfavourable in itself. In (I) possible reasons for the five-co-ordination can be suggested. The planar ring (itself the result of π interaction) produces ring angles of 90° and these would severely distort a tetrahedral titanium atom. Octahedral geometry with *cis*-nitrogen atoms would be a better arrangement, but for this both chlorine atoms would be required to form intermolecular bridges (implying a three-dimensional polymeric structure) and this would clearly be sterically very crowded. The five-co-ordinate trigonal bipyramidal structure allows *ca.* 90° ring angles, with one axial and one equatorial nitrogen atom, with less crowding. The bridging link is easily broken to allow two pyridine molecules to attach to each titanium, which thus achieves the normal co-ordination number of six, when there is less overcrowding.

A puckered trimeric structure would more easily accommodate the tetrahedral geometry of the titanium, but the dimeric (planar) structure favours ring π bonding.

π Bonding.—The planarity of the solid-state structure implies considerable π interaction and this is confirmed by the shortened bond lengths. The structure may be compared to that of the dimeric cyclosilazane $(Me_2SiN-SiMe_3)_2$ which is also strictly planar.[18] In this molecule the bond lengths indicate substantial d_π–p_π bonding both in the ring and in the *N*-silyl group.

Multiple bonding between nitrogen and silicon is found to be much greater than with the heavier Group IVB elements.[19] This is attributable to the relative compactness of the 3*d* relative to the 4*d* and 5*d* orbitals, which thus allows more effective overlap with a π-donor orbital. Titanium(IV) is similar to silicon in the availability of vacant 3*d* orbitals which can act as π-acceptors. In titanium the 3*d* orbitals may be slightly lower in energy than in silicon because of the increase in atomic number; *d* orbitals are known to be more sensitive to changes in effective nuclear charge than are *s* or *p* orbitals.[20] The presence of electronegative substituents such as chlorine will increase the effective nuclear charge, which should cause some contraction of the 3*d* orbitals; this should bring the *d* orbital and the nitrogen lone-pair energies closer together and enhance the π-bonding.

The best description of the π-bonding around the ring skeleton is probably in terms of the three-centre ' island ' delocalisation of Dewar *et al.*[14] The d_{xz} and d_{yz} orbitals are combined to give equivalent orbitals directed along the Ti–N bonds, d_π^a on Ti(1), and d_π^b on Ti(2). These then

$$d_\pi^a = (1/\sqrt{2})(d_{xz} + d_{zy})$$
$$d_\pi^b = (1/\sqrt{2})(d_{xz} - d_{yz})$$

combine with p_z on N(1) to give the three-centre π system, occupied by the lone pair originally localized in the p_z orbital. In the particular case of (1), there is also involvement of an Si orbital (say d_{xz}) with these three orbitals. Optimum bonding requires internal ring angles of 90° and d_{xz} and d_{yz} orbitals of equal energies. If the energies of these orbitals differ (as is expected in a trigonal bipyramidal structure) the π-bonding is expected to be concentrated in alternate bonds. Although orbital energies for trigonal bipyramidal titanium(IV) have not been calculated, the observed lengths are consistent with this alternation.

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Packing.—Figure 3 shows the arrangement of chains parallel to *c*, and the pseudosymmetry this produces in the *hk*0 projection. The rings of the ordered chains are centrosymmetric, but in the disordered chain (Figure 2) the *c* glide relates the atoms of one ring, *e.g.* those with closed bonds, to the atoms in the next ring in the other chain, *i.e.* with open bonds; thus the glide plane is only present statistically. The packing of the chains is clearly controlled exclusively by interactions between the outward pointing groups $SiMe_3$ and Cl. The two arrangements in the disordered chain have these atoms in common, and only differ in having their Ti_2N_2 rings tipped up or down. Thus, there are no packing preferences at all for one orientation or the other and both occur equally.

Spectra and Reactivity.—The orange crystals of (I) are extremely sensitive to air-moisture hydrolysis *via* Ti–Cl cleavage, and decompose without melting >415 K to a brown amorphous solid. The ^1H n.m.r. spectrum (Table 3) confirms the presence of equivalent Me_3Si groups, the expected singlet peak being slightly downfield from that of the parent tertiary amine. Except for subtle differences in the metal–halogen stretching frequency location, both solid and solution i.r. spectra are identical, and band assignments are given in Table 4. For tetrahedral titanium(IV) compounds $\nu(TiCl)_{terminal}$ vibrations occur in the region 470—490 cm^{-1}, whereas similar absorptions for octahedral species are normally found[21] between 370 and 400 cm^{-1}. Thus the strong band at 427 cm^{-1}, observed in the solid-phase spectrum and assigned to a $\nu(TiCl)_{terminal}$ mode, is consistent with five-co-ordination. The lower-frequency band at 231 cm^{-1} is assigned to a $\nu(TiCl)$ mode associated with halogen-bridge bonding. In the solution spectrum the latter disappears and the dominant $\nu(TiCl)_{terminal}$ vibration has shifted to 470 cm^{-1}, indicating a decrease in the co-ordination number of the metal atom; the species in solution would therefore appear to be discrete $(Ti{-}N)_2$ rings based on four-co-ordinate titanium(IV). The intense absorption at 45 660 cm^{-1} in the solution electronic spectrum (Table 3) attributable to a $Si(3d){\leftarrow}N(n)$ rather than a $Ti(3d){\leftarrow}Cl(\pi)$ transition[22] appears 4 240 cm^{-1} to lower energy than in the initial amine. Assuming partial delocalization in the form of 'isolated' Ti–N(Si)–Ti chromophores, this shift is in line with (i) a decrease in double-bond character and (ii) a change in nitrogen geometry in the solution dimer towards tetrahedral, accompanying the two-step silyl replacement: $NSi_3{\rightarrow}NSiTi_2$. Interestingly, vacuum sublimation of (I) gives two components: a yellow amorphous powder (A) which sublimes slowly at 363—373 K/5 × 10^{-4} mmHg, and an orange microcrystalline solid (B) which collects at >373 K/5 × 10^{-4} mmHg. Elemental analyses and solution spectra (i.r., ^1H n.m.r., and electronic) confirm (A) and (B) as being polymorphs

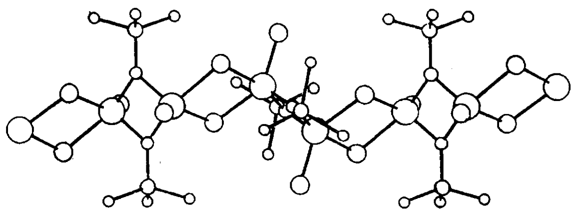

FIGURE 3 The ordered chain

TABLE 3

Spectral data for $[Cl_2Ti{\cdot}NSiMe_3]_2$ (I)

Complex	Electronic Absorption max./cm^{-1} [a]	^1H n.m.r. Absorption max./τ [b,c]
(I)	45 660 (4 100), 44 250sh, 40 800sh, 33 500sh, 25 510 (995)	9.46
$N(SiMe_3)_3$	Rising absorption to 49 900	9.72

[a] Cyclohexane solution; $\varepsilon_{max.}$ values in parentheses. [b] Dichloromethane solution. [c] Tetramethylsilane as internal reference standard.

TABLE 4

I.r. spectral data for (I) and its pyridine addition complex (IV)

(I) [a]		Sublimate (A)		(IV)	Mode [d]
Solid [b]	Sol. [c]	Solid [b]	Sol.	Solid [b]	
				3 102w *	
				3 062w *	
				3 042w *	
2 848w	2 965w	2 978w	2 965w	2 848m	$\nu_{as}(Me)$
2 819sh				2 820sh	
2 785w	2 910w	2 920w	2 910w	2 787w	$\nu_s(Me)$
				2 746w	
				1 603s *	
				1 482w *	
				1 442w *	
1 403w	1 410m	1 406m	1 410m		$\delta_{as}(Me)$
	1 265sh	1 265sh	1 265sh	1 250m *	
1 244s	1 252s	1 252s	1 252s	1 239m	$\delta_s(Me)$
				1 212m *	
				1 151m *	
1 014w	1 070w	1 012w	1 070w	1 069m *	
	986w		986w	1 041m *	
886m	896s	894m	896s	946s	$\nu_{as}(SiN)$
844vs	847s	845vs	847s	833s	$\rho_{as}(Me)$
827s	826s	826s	826s		
756s	759s	758s	759s	753s *	$\nu_s(SiC)$
698m	698m	698m	698s *	692s *	$\rho_s(Me)$
670m	670m	670m	670m	670w	$\nu_{as}(SiC_3)$
				654w *	
640s	641s	643s	641s	636s	$\nu(TiN)$
624m	624m	624m	624m	620sh	$\nu_s(SiC_3)$
				428m *	
427s	468s	470s	468s	371s	$\nu(TiCl)$(term.)
356m	356m	352m	356m	350s	
276m		276m		258m	$\delta(SiN)$
231w					$\nu(TiCl)$(br.)

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder;

* Due to co-ordinated pyridine (see ref. 25).

[a] Sublimate (B) and (I) have identical [$\pm$1 cm]$^{-1}$ spectra both in solution and solid phase. [b] Nujol and Fluorolube mulls. [c] Dichloromethane solution. [d] Bands have been assigned on the basis of previously reported data for $N(SiMe_3)_3$ (ref. 26), $(Cl_3{-}Ti)NMe_2$ (ref. 27), $Ti(NR_2)_4$ (ref. 28), and $TiCl_4{\cdot}2L$ (ref. 29) derivatives.

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of (I), yet the non-appearance of a $\nu(\mathrm{TiCl})_{\mathrm{terminal}}$ band at 470 $\mathrm{cm^{-1}}$ for (A) contrasts with the ν(TiCl) spectral profile of (B) which is identical with that of (I) (Table 4). Even allowing for a contribution from a loss of crystallinity[23] these variations are clear indication of a loss of intermolecular halogen bridge bonding in (A) and reversal towards a four-co-ordinate metal species reminiscent of that in solution.

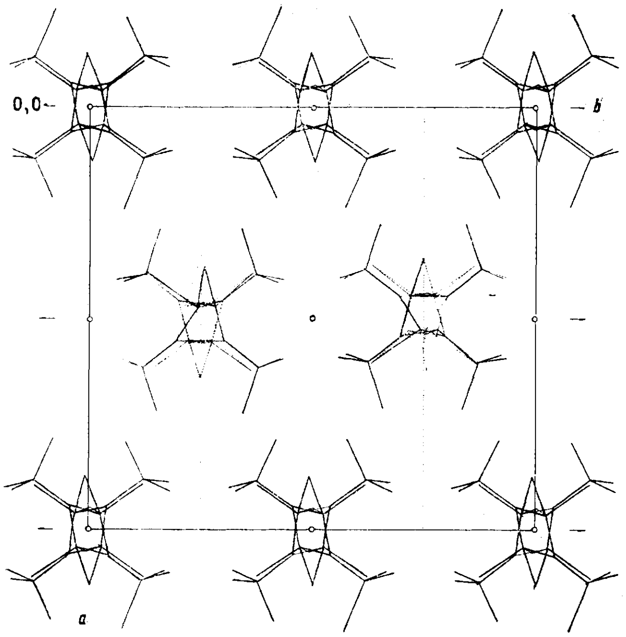
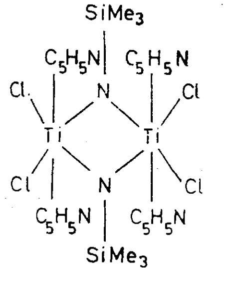


FIGURE 4 Crystal structure projected down *c*. The bonds between one set of disordered atoms are shown as dashed lines

Finally, and as a direct comparison with the behaviour of (II) under similar circumstances, (I) was treated with an excess of pyridine. No reduction was apparent (*cf.* the $\mathrm{TiCl_4}$–pyridine system[24]) and the orange microcrystalline product (IV) gave analyses corresponding to $\mathrm{C_{13}H_{19}Cl_2N_3SiTi}$, which is consistent with a bispyridine addition complex formulation. Limited solubility in the common organic solvents as in the case of (I) prevented molecular-weight evaluation, and the air-moisture hydrolysis of (IV) is rapid. The solid-phase i.r. spectrum (Table 4) shows all the bands expected for co-ordinated pyridine,[25] and also the majority of the bands diagnostic of the ring skeleton. However, the low-energy band at *ca.* 230 $\mathrm{cm^{-1}}$, associated with a bridge $\nu(\mathrm{TiCl})_{\mathrm{terminal}}$ vibration in (I), is conspicuously missing; also the strong $\nu(\mathrm{TiCl})_{\mathrm{terminal}}$ vibration at 371 $\mathrm{cm^{-1}}$ lies well within the region associated with octahedral titanium(IV) species. The ^{1}H n.m.r. spectrum (dichloromethane solution) shows a complex multiplet (τ *ca.* 1.0) of integrated intensity 10.0 and a sharp singlet (τ 9.52) of integrated intensity 9.0 in accord with the formulation of (IV) as a bispyridine addition complex.

In view of this spectral evidence for the integrity of the ring skeleton during addition complex formation (I)→(IV) and the existence of (I) as discrete $(\mathrm{Ti{-}N})_2$ rings in solution, (IV), which is clearly identical to the Bürger and Wannagat product (III), is assigned a dimeric structure *i.e.* bis-μ-(trimethylsilylamino)-tetrachlorotetra(pyridine)-dititanium(IV) in preference to their original monomeric titanium imide formulation.



(IV)

Schematic representation of the suggested dimer structure of (IV), $[(\mathrm{Cl_2Ti})\underset{/\ \backslash}{\mathrm{N}}\mathrm{SiMe_3}]_2\cdot 2\mathrm{py}$

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