Planar Ti_2N_2 Rings with Five-co-ordinate Titanium(IV): *X*-Ray Structure of *catena*-Di-μ-chloro-bis-μ-(trimethylsilylamino)-di-[chlorotitanium(IV)]

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Summary The crystal structure of the title compound has been determined; it contains planar four-membered $(Ti–N)_2$ rings with planar geometry at N which are linked by Cl-bridges, giving five-co-ordinate Ti atoms in approximately trigonal bipyramidal geometry.

THE title compound[1] was prepared by the reaction of tris(trimethylsilyl)amine with titanium(IV) chloride. It has now been examined by single crystal *X*-ray methods, revealing the first cyclic (Ti–N) structure.

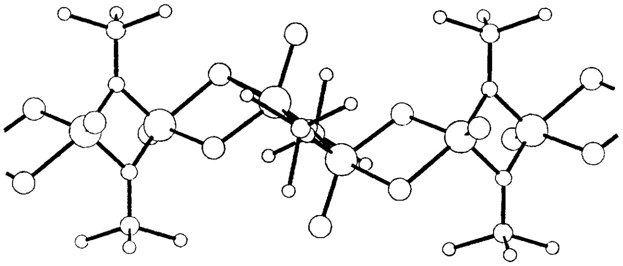

FIGURE. The ordered chain of $[Me_3SiNTiCl_2]_n$. Each ring has an inversion centre at its centre. The circles are, in decreasing order of size, Ti, Cl, Si, N, and C.

Crystal data: monoclinic, $a = 17{\cdot}74$, $b = 18{\cdot}52$, $c = 11{\cdot}46$ Å, $\beta = 102{\cdot}71°$, $Z = 8$; space group $P2_1/c$. 1298 observed reflections were collected on a STOE 2-circle diffractometer. The structure was solved by direct methods (MULTAN) and refined to a current R of 0·010, with anisotropic temperature factors for Ti and Cl (ordered).

The most notable features of the structure are the four-membered $(Ti–N)_2$ rings which are planar (rigorously so for two of the four independent examples); the Si atoms also lie in the ring planes. This suggests considerable π-interaction between *p*-orbitals on N and *d*-orbitals on Ti and perhaps on Si as well (contrary to predictions based on the electronic spectrum).[1] The rings are polymerized through Cl-bridges into chains parallel to *c*, with four chains in each unit cell (two affected by inversion disorder) (Figure).†

Each ring is tipped by about 45° from the chain axis, alternately up and down so that Ti atoms on adjacent rings approach close enough for double Cl-bridges to be formed between each pair of Ti atoms. The Ti atoms are thus five-co-ordinate. Their geometry is best described as distorted trigonal bipyramidal (angles: axial ∠ N–Ti–Cl of 158 and 165°; maximum equatorial ∠ Cl–Ti–Cl of 137°).

Five-co-ordination is extremely rare for Ti^{IV} apparently because it is normally capable of forming octahedral complexes [*e.g.* by Cl-bridges in diethylaminotitanium(IV) trichloride[2] and di-μ-chloro-bis(dichloroacetonylacetone)-titanium(IV)].[3] It does occur in $[TiCl_2(OX)_2]_2$ (X = Et[4] or Ph[5]) with oxygen bridges, whose geometry can also be described as trigonal bipyramidal (∠ O–Ti–O of 156 and 167° respectively). We would suggest that in these compounds and that examined here, steric hindrance by Et, Ph, or $SiMe_3$ prevents the formation of further bridges.

In the title compound, Ti–N distances average 1·89 Å, terminal Ti–Cl average 2·21 Å, and bridge Ti–Cl range between 2·43 and 2·51 Å. Distances in the $-NSiMe_3$ groups are normal.

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† Distances and angles are the well defined values from the ordered chains.

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