value of 1·17 (1) Å, found in the isostructural $[Rh_2Cl_2(CO)_4]$ compound (Dahl, Martell & Wampler, 1961).

The Pd^{II} atom lies in an approximate distorted square-planar environment. The angles C(1)—Pd—C(2), C(2)—Pd—Cl and Cl—Pd—Cl(*A*) are close to 90° at 89·8 (5), 93·1 (4) and 85·5 (1)°, respectively. The dihedral angle between $PdCl(CO)_2$ groups is 121·9 (4)° in agreement with the dihedral angle (124°) reported for the isostructural $[Rh_2Cl_2(CO_4)]$ compound.

The packing of the dimeric molecules in the unit cell is shown in Fig. 2. The discrete dimeric molecules are held in the crystal by van der Waals and packing forces. There is only one Pd—Pd intermolecular contact of 3·317 (2) Å (0·5 – *x*, *y*, 0·75 – *z*).

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Structure of $[Ti_8O_{12}(H_2O)_{24}]Cl_8.HCl.7H_2O$

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Abstract. $M_r = 1453·75$, monoclinic, *C*2/*c*, *a* = 20·3058 (20), *b* = 11·7172 (18), *c* = 25·3984 (15) Å, β = 117·201 (6)°, *V* = 5375 (2) Å³, *Z* = 4, D_x = 1·80 g cm⁻³, λ(Mo *K*α) = 0·71073 Å, μ = 16·60 cm⁻¹, *F*(000) = 2944, *T* = 298 K, *R* = 0·0328 for 2921 observed reflections. The reaction of $TiCl_4$ with water vapor produced colorless crystals that have been found to contain Ti atoms coordinated by water and oxide to form a cubic octamer. The average O—Ti—O bond angle is 99·55° [range 97·51 (8)–102·35 (9)°] and the average Ti—O bond distance is 1·820 Å [1·791 (2)–1·859 (2) Å]. The average Ti—O—Ti angle is 154·60° [153·10 (11)–156·03 (11)°]. The average Ti—OH_2 bond distance is 2·129 Å [2·081 (2)–2·179 (2) Å] and the average H_2O—Ti—OH_2 bond angle is 79·52° [78·51 (7)–80·95 (8)°]. The average axial octahedral H_2O—Ti—O angle is 164·57° [162·25 (8)–166·23 (8)°].

Introduction. A titanium hydroxychloride produced from the reaction of $TiCl_4$ with H_2O has been examined previously and the powder X-ray diffraction pattern reported (Walter-Levy & Ferey, 1968). The empirical formula was determined by elemental analysis to be $TiCl(OH)_3.2H_2O$ (Walter-Levy & Ferey, 1966; Golub, Tischenko & Kikot, 1970). We have isolated single crystals from this reaction and have characterized them as $[Ti_8O_{12}(H_2O)_{24}]Cl_8.HCl.7H_2O$. The powder XRD pattern of these crystals matches that previously reported for '$TiCl(OH)_3.2H_2O$'.

Experimental. Small irregular colorless crystals were discovered in the center of clumps of powder obtained by reaction of $TiCl_4$ with moist air. Fragments were selected by optical examination and mounted on glass fibers using polycyanoacrylate cement. They were then coated with this cement to prevent further reaction with the air.

X-ray data were obtained with an Enraf–Nonius CAD-4 diffractometer. The approximate dimensions of the crystal were 0·19 × 0·20 × 0·30 mm. The 2θ range was 2 < 2θ < 45°, +*h*(0,21), +*k*(0,12), ±*l*(−27,27),

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θ–2θ scan [$\Delta\theta = (0{\cdot}5 + 0{\cdot}35\tan\theta)°$] with θ speeds 0·6–6·7° $\min^{-1}$. Intensity standards were measured after every hour of X-ray exposure time. Over the data-collection period a 2·3% decrease in intensity was observed. The data were corrected for this decay. No correction for absorption was needed. 4251 reflections were collected and 3506 of these were unique.

The structure was solved using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) in space group $C2/c$ and refined to convergence *via* standard least-squares and Fourier techniques. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, with $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (pF^2)^2]$; p was set to 0·03 throughout the refinement. For 289 variables refined against the 2921 data for which $F^2 > 3\sigma(F^2)$, $R = 0{\cdot}0328$, $wR = 0{\cdot}0518$ and $S = 2{\cdot}429$. For all 3506 data $R = 0{\cdot}0457$. Determination of the stoichiometry of the compound was based on the observed electron density of Fourier peaks and on the calculated interatomic distances and angles. In a difference Fourier map calculated following refinement of all non-hydrogen atoms, peaks were found corresponding to most of the positions for H atoms expected on the basis of potential hydrogen bonding. H-atom parameters were included in structure-factor calculations but not refined. Towards the end of refinement indications of severe secondary-extinction effects were found on a few reflections and a secondary-extinction parameter (Zachariasen, 1963) was refined in the final cycles. The maximum electron density in the final difference Fourier map was 0·42 e $Å^{-3}$. Scattering factors were obtained from *International Tables for X-ray Crystallography* (1974). Table 1 gives the positional parameters for the non-hydrogen atoms.*

Table 1. *Positional parameters and their estimated standard deviations*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Ti(1)	0·43117 (3)	0·13469 (6)	0·06600 (3)	1·57 (1)
Ti(2)	0·62210 (3)	0·13241 (6)	0·10288 (3)	1·67 (2)
Ti(3)	0·57379 (3)	0·16435 (6)	−0·05191 (3)	1·72 (2)
Ti(4)	0·38356 (3)	0·16683 (6)	−0·08646 (3)	1·58 (1)
Cl(1)	0·25683 (5)	−0·0226 (1)	0·11441 (4)	3·02 (2)
Cl(2)	0·6556 (1)	0·5643 (1)	0·23482 (7)	8·31 (6)
Cl(3)	0·500	0·3333 (1)	0·250	3·43 (4)
Cl(4)	0·79674 (5)	−0·00866 (9)	0·05931 (4)	2·84 (2)
Cl(5)	0·500	−0·577 (2)	0·250	4·64 (5)
Cl(6)	0·4921 (1)	0·4679 (2)	0·4746 (1)	3·33 (5)*
O(1)	0·5261 (1)	0·1652 (2)	0·0817 (1)	2·21 (6)
O(2)	0·6195 (1)	0·1358 (3)	0·0291 (1)	2·58 (7)
O(3)	0·4818 (1)	0·1961 (2)	−0·0616 (1)	2·27 (6)
O(4)	0·3878 (1)	0·1389 (2)	−0·0142 (1)	2·32 (6)
O(5)	0·4354 (1)	−0·0197 (2)	0·0771 (1)	2·11 (6)
O(6)	0·6225 (1)	−0·0215 (2)	0·1108 (1)	2·05 (6)
O(7)	0·3186 (1)	0·1469 (2)	0·0538 (1)	2·51 (6)
O(8)	0·4217 (1)	0·3120 (2)	0·0769 (1)	2·78 (7)
O(9)	0·4511 (2)	0·1423 (2)	0·1561 (1)	3·06 (7)
O(10)	0·6530 (2)	0·1414 (2)	0·1930 (1)	2·96 (7)
O(11)	0·6406 (1)	0·3098 (2)	0·1163 (1)	3·10 (7)
O(12)	0·7403 (1)	0·1395 (3)	0·1364 (1)	2·90 (7)
O(13)	0·5530 (2)	0·2181 (3)	−0·1369 (1)	3·17 (7)
O(14)	0·5974 (1)	0·3430 (2)	−0·0353 (1)	2·81 (7)
O(15)	0·6863 (1)	0·1732 (3)	−0·0415 (1)	2·78 (7)
O(16)	0·2670 (1)	0·1841 (2)	−0·1175 (1)	2·37 (6)
O(17)	0·3502 (2)	0·2133 (2)	−0·1744 (1)	2·84 (7)
O(18)	0·3731 (1)	0·3471 (2)	−0·0794 (1)	2·75 (7)
O(21)	0·6650 (2)	−0·0514 (3)	0·2501 (1)	5·4 (1)
O(22)	0·6626 (2)	0·3138 (3)	0·2664 (1)	3·26 (7)
O(23)	0·5370 (3)	0·4579 (6)	0·1153 (3)	4·7 (2)*
O(24*A*)	0·5027 (8)	0·413 (1)	−0·1882 (6)	5·5 (4)†
O(24*B*)	0·5559 (7)	0·398 (1)	−0·1916 (6)	4·7 (3)†
O(24*C*)	0·5107 (6)	0·443 (1)	−0·1603 (5)	3·1 (2)†
O(24*D*)	0·5433 (7)	0·424 (1)	−0·1757 (6)	4·7 (3)†

* Occupancy at site is 0·50 (determined empirically).

† Occupancy at site is 0·25 (determined empirically); atoms refined with isotropic thermal parameters.

Discussion. The discovered stoichiometry of the crystal is $[Ti_8O_{12}(H_2O)_{24}]Cl_8.HCl.7H_2O$. The structure consists of a cubic titanium octamer of basic form $[Ti_8O_{12}(H_2O)_{24}]^{8+}$ linked to interstitial chloride ions and water molecules by a complex net of hydrogen bonds. The cubic cation forming the core of the structure is shown in Fig. 1. The cation has a crystallographic inversion center and further exhibits a good approximation to mmm (D_{2h}) symmetry. The average O—Ti—O bond angle is 99·55° [range 97·51 (8)–102·35 (9)°] and the average Ti—O bond distance is 1·820 Å [1·791 (2)–1·859 (2) Å]. The average Ti—O—Ti angle is 154·60° [153·10 (11)–156·03 (11)°]. The average Ti—OH_2 bond distance is 2·129 Å [2·081 (2)–2·179 (2) Å] and the average H_2O—Ti—OH_2 bond angle is 79·52° [78·51 (7)–80·95 (8)°]. The average axial octahedral H_2O—Ti—O angle is 164·57° [162·25 (8)–166·23 (8)°]. The indicated Ti—O and Ti—OH_2 bond distances are consistent with previously reported values for titanium organometallic complexes (Griffith, 1970; McCarthy & Richardson, 1983). Outside the cubic cation, hydrogen bonds link the entire structure into a complex three-dimensional network. There is no obvious layer structure or other higher-level organization.

The title compound is unstable and decomposes on oxidation, heating, or upon dissolution in water. In the bulk phase, anatase is formed regardless of the method of decomposition. In contrast, oxidation of SiO_2-supported $[Ti_8O_{12}(H_2O)_{24}]Cl_8.HCl.7H_2O$ produces primarily the $TiO_2(B)$ phase of titania (Reichmann & Bell, 1986). It is interesting to note that $TiO_2(B)$ retains the cubic octamer unit of $[Ti_8O_{12}(H_2O)_{24}]$-$Cl_8.HCl.7H_2O$ whereas anatase does not.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43959 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

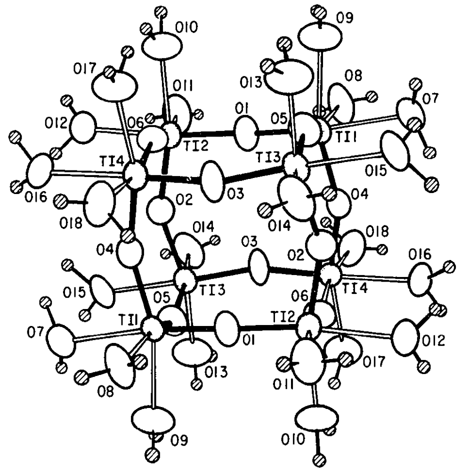

Fig. 1. The octameric cation complex, $[Ti_8O_{12}(H_2O)_{24}]^{8+}$. The ellipsoids are drawn at the 70% probability level.

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Structure of Germyl Chloride at 97 K

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Abstract. GeH_3Cl, $M_r = 111\cdot07$, orthorhombic, $Cmc2_1$, $a = 7\cdot146\,(3)$, $b = 5\cdot5587\,(21)$, $c = 8\cdot383\,(14)$ Å, $V = 333\cdot0$ Å^3, $Z = 4$, $D_x = 2\cdot215$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71069$ Å, $\mu = 9\cdot58$ mm^{-1}, $F(000) = 208$, $T = 97$ K, $R = 0\cdot0422$ for 500 observed reflections. The structure contains zigzag chains of molecules formed by close [3·3760 (16) Å] Cl···Ge intermolecular contacts: these chains are approximately linear at Ge and have an angle of 96·85 (5)° at Cl. At 2·2220 (16) Å, the Ge—Cl bond is considerably longer than the value of 2·14947 (5) Å found in the gas phase. Low-temperature X-ray powder diffraction shows SiH_3Cl and GeH_3Cl to be isostructural; it is perhaps more surprising that these compounds are isostructural with CH_3Cl.

Introduction. We have for some time been interested in the structures of the simple silyl halides SiH_3X (X = F, Cl, Br, I) and pseudohalides (*e.g.* SiH_3CN). Part of this interest stems from the observation that in the vibrational spectra large shifts occur in the ν(Si—X) or ν(Si—C) frequencies on going from the gas to the solid phase, suggesting significant intermolecular interactions in the crystal (Ball, Buttler & McKean, 1965; Cradock, personal communication). Single-crystal X-ray studies at low temperature have elucidated the structures of SiH_3CN (Barrow, Ebsworth & Harding, 1987), SiH_3F (Blake, Ebsworth, Henderson & Welch, 1985) and SiH_3I (Blake, Ebsworth, Henderson & Welch, 1987), confirming the presence of important secondary contacts. In the case of SiH_3Cl and SiH_3Br, however, our attempts to grow single crystals have been frustrated by the occurrence of phase transformations below the freezing points of these compounds. We have therefore turned our attention to the analogous germyl series and here we report the crystal structure of GeH_3Cl, where ν(Ge—Cl) drops from 423 to 371 cm^{-1} on going from the vapour to the solid phase (Freeman, Rhee & Wilson, 1963).

Experimental. Colourless cylindrical crystal, 0·04 × 0·04 × 0·05 cm, grown *in situ* on Weissenberg camera

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