Controlled Hydrolysis Reactions of Solvated [TiCl$_n$]$^{(4-n)+}$ Species. Crystal and Molecular Structures of [Mg(MeCN)$_6$][{TiCl$_4$(MeCN)}$_2$(μ-O)]·4MeCN and [{TiCl$_2$(MeCN)$_2$(μ-O)}$_4$]·2MeCN†

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Partial hydrolysis reactions of the solvated [TiCl$_5$(MeCN)]$^-$ anion and of the adduct TiCl$_4$·2MeCN gave the μ-oxo-dititanium anion [{TiCl$_4$(MeCN)}$_2$(μ-O)]$^{2-}$ and the neutral tetranuclear μ-oxo compound [{TiCl$_2$(MeCN)$_2$(μ-O)}$_4$], respectively, as established by X-ray crystallographic studies. Crystals of [Mg(MeCN)$_6$][{TiCl$_4$(MeCN)}$_2$(μ-O)]·4MeCN **1** are monoclinic, space group $P2_1/n$, a = 14.777(6), b = 14.603(6), c = 21.214(10) Å, β = 105.3(1)°. The structure contains discrete octahedral [Mg(MeCN)$_6$]$^{2+}$ cations, [{TiCl$_4$(MeCN)}$_2$(μ-O)]$^{2-}$ anions and solvent (MeCN) molecules. Crystals of [{TiCl$_2$(MeCN)$_2$(μ-O)}$_4$]·2MeCN **2** are orthorhombic, space group $P2_12_12_1$, a = 12.165(6), b = 12.367(6), c = 27.927(11) Å. The structure contains discrete [{TiCl$_2$(MeCN)$_2$(μ-O)}$_4$] units and solvent (MeCN) molecules. In **1** both titanium atoms have an octahedral environment. The Ti–O–Ti bridge is approximately linear [174.7(3)°] with equivalent Ti–O distances of 1.783(4) and 1.764(4) Å. By contrast in **2** there are four Ti–O–Ti bridges but in each case the two Ti–O distances are significantly different with mean values of 1.668, 1.954 Å.

Controlled hydrolysis of Ti–X (X = halogen) bonds is a convenient route to titanoxanes involving either oxo-bridged linkages Ti$_n$(μ-O)$_m$ or the terminal bonded titanyl Ti=O unit. For the former, dinuclear (n = 2) complexes with single (m = 1) or double (m = 2) bridging oxygen atoms are, perhaps, the more familiar, particularly where the metal carries an extremely bulky ancillary ligand such as C$_5$H$_5$,[1] C$_5$H$_2$(SiMe$_3$)$_3$,[2] crown ether[3] or 1,4,7-triazacyclononane ([9]aneN$_3$),[4] but multinuclear (n > 2) titanium complexes in the form of cages and/or rings are also well documented.[5] Examples of titanyl compounds are limited to just a handful, *viz.* [NEt$_4$]$_2$[Ti(O)Cl$_4$],[6] [Ti(O)(oep)][7] (oep = 2,3,7,8,12,13,17,18-octaethylporphinato dianion) [Ti(O)(dmoep)][8] (dmoep = 5,15-dihydro-5,15-dimethyl-2,3,7,8,12,13,17,18-octaethylporphinato dianion), [Ti(O)(pc)][9] (pc = C$_{32}$H$_{16}$N$_8$$^{2-}$ the phthalocyaninato dianion) and, more recently, [Ti(O)L][10] (H$_2$L = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine. In all these hydrolysis reactions the stoichiometry of reactants and the experimental conditions employed, in particular the manner of addition of the relatively small amounts of H$_2$O involved, appear to be critical with respect to the number and type(s) of product obtained.

In 1963 Feltz[11] reported that partial hydrolysis of [TiCl$_4$(MeCN)$_2$] using acetonitrile as bulk solvent leads to the addition compounds Ti$_2$Cl$_6$O·4MeCN and Ti$_2$Cl$_6$O·6.5MeCN. Furthermore, direct treatment of Ti$_2$Cl$_6$O·4MeCN and dioxane (diox) yielded an adduct which was formulated as Cl$_3$Ti(O)-TiCl$_3$·4diox. Intrigued by these results we decided to take a closer look at hydrolysis reactions of simple chlorotitanium(IV) species, [TiCl$_n$]$^{(4-n)+}$, with the objective of X-ray structural characterisation of the product(s). Herein we describe the results obtained from studies of the controlled hydrolysis of (a) the neutral adduct [TiCl$_4$(MeCN)$_2$] as a repeat of the Feltz study (n = 4) and (b) the solvated pentachloro anion [TiCl$_5$(MeCN)]$^-$ (n = 5), which was obtained as the magnesium salt from the reaction system 2TiCl$_4$–MgCl$_2$–MeCN $\longrightarrow$ [Mg(MeCN)$_6$][TiCl$_5$(MeCN)]$_2$.

Experimental

All manipulations were carried out using Schlenk and high-vacuum line techniques in conjunction with a standard dinitrogen atmosphere glove-box. Solvents were stored over CaH$_2$ and sodium–potassium amalgam and distilled under a dinitrogen atmosphere prior to use. The IR spectra were recorded on a Perkin-Elmer 580B instrument with samples as Nujol mulls placed between CsI discs. Elemental analyses were carried out by Medac, Uxbridge, Middlesex.

Preparation of the Complexes.—*Solution* A. The addition of water for the controlled hydrolysis reactions was effected by syringe injection of the appropriate amount of a standard H$_2$O–MeCN solution (0.0406 g cm^{-3}); the latter was prepared by careful addition of H$_2$O (2.030 g) to acetonitrile in a calibrated 50 cm^3 volumetric flask.

[Mg(MeCN)$_6$][{TiCl$_4$(MeCN)}$_2$(μ-O)]·4MeCN **1**. A solution of TiCl$_4$ (2.13 g, 11.229 mmol) in MeCN (25 cm^3) was added dropwise to a suspension of MgCl$_2$ (0.535 g, 5.615 mmol) in MeCN (50 cm^3). The mixture was warmed (50 °C) and stirred for 5 h to give a clear yellow solution. On cooling this solution to room temperature hydrolysis was induced by the dropwise addition of solution A (2.50 cm^3, 5.634 mmol) and the resulting deep yellow solution was stirred for a further 24 h. Slow removal of solvent, to approximately one quarter of the original volume, resulted in the deposition of yellow needle crystals. Yield 1.98 g, 38.6% (Found: C, 31.40; H, 3.80; Cl, 29.95; N, 18.20. Calc. for C$_{24}$H$_{36}$Cl$_8$MgN$_{12}$OTi$_2$: C, 31.60; H, 4.00; Cl, 31.10; N, 18.40%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 2313, 2286 [ν(C≡N)], 786 [ν$_{asym}$(Ti–O–Ti)], 495s, 428s, 405w, 390w, 345vs (br) [ν(Ti–Cl)], 280vs (sh).

[{TiCl$_2$(MeCN)$_2$(μ-O)}$_4$]·2MeCN **2**. The standard solution A (2.00 cm^3, 4.507 mmol) was added dropwise to a chilled (0 °C) solution of TiCl$_4$ (1.710 g, 9.014 mmol) in MeCN (30 cm^3) and the resulting deep yellow solution was stirred at room

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

temperature for 24 h. Following slow removal of solvent, to approximately one quarter of the original volume, the concentrated solution was placed in the refrigerator when light yellow needle crystals deposited. Yield 0.89 g, 41.5% (Found: C, 25.00; H, 3.00; Cl, 29.65; N, 14.30. Calc. for $C_{20}H_{30}Cl_8N_{10}O_4Ti_4$: C, 25.30; H, 3.20; Cl, 29.85; N, 14.75%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2310, 2279 [ν(CN)], 780 [ν_{asym}(Ti–O–Ti)], 492w, 402 (sh), 380vs (br) [ν(TiCl)], 330 (sh), 274s.

X-Ray Crystallography.—Crystal data are given in Table 1, together with refinement details. Data for both crystals were collected with Mo-Kα radiation using the MAR research image plate system. The crystals were positioned at 75 mm from the X-ray source. 90 Frames were measured at 2° intervals with a counting time of 5 min. Data analysis was carried out with the XDS program.[12] Both structures were solved using direct methods with SHELX86.[13] In both structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the MeCN groups were included as rigid groups each with a common thermal parameter. Both structures were then refined using SHELXL.[14] All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading. The final atomic coordinates for **1** and **2** are given in Tables 2 and 3 and important dimensions in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Hydrolysis of $[TiCl_5]^-$.—Sobota *et al.*[15] have shown that the reaction of $MgCl_2$ and $TiCl_4$ in tetrahydrofuran (thf) can provide three separate products depending on the ratio of reactants (Mg:Ti) used. Specifically, with a 1:2 stoichiometry the salt $[Mg(thf)_6][TiCl_5(thf)]_2$ is formed following chloride transfer to titanium(IV) acting as a Lewis acid. We have used this route to the desired pentachloro anion but with acetonitrile as solvent; the subsequent hydrolysis reaction was induced by careful introduction of 1 equivalent of water [equation (1)].

$$MgCl_2 + 2TiCl_4 \xrightarrow{MeCN} [Mg(MeCN)_6][TiCl_5(MeCN)]_2$$

$$\Big\downarrow H_2O$$

$$\underset{\mathbf{1}}{[Mg(MeCN)_6][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]} + 2HCl \quad (1)$$

Compound **1** was isolated (39% yield) as yellow air- and moisture-sensitive needle crystals; the HCl eliminated was not monitored. Microanalytical and spectroscopic data of **1** are consistent with the proposed formulation. The IR spectrum contains a strong band at 786 cm^{-1} [ν_{asym}(Ti–O–Ti)] indicative of a linear μ-oxo linkage of two titanium groups[2,16] and a sharp doublet at 2313, 2286 cm^{-1} [ν(CN)] characteristic of coordinated acetonitrile. The broad intense asymmetric band at 345 cm^{-1} [ν(TiCl)] most likely incorporates a contribution from the Mg–N stretching mode of $[Mg(MeCN)_6]^{2+}$ (ν_{14} 330 cm^{-1}).[17]

The structure of **1** consists of a discrete $[Mg(MeCN)_6]^{2+}$ cation, a $[\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]^{2-}$ anion and four solvent (MeCN) molecules as depicted in Fig. 1. The structure of the anion is shown in Fig. 2 together with the atom numbering scheme. It contains no crystallographic symmetry; each of the approximately octahedral titanium atoms is bonded to four chlorine atoms in an equatorial plane and a mutually *trans* MeCN ligand and bridging oxygen atom (D_{4h}). The two Ti–O bond distances are approximately equivalent at 1.783(4), 1.764(4) Å, with a Ti–O–Ti angle of 174.7(3)°. The Ti–N bond distances are 2.273(5) and 2.278(5) Å and the Ti–Cl bond distances range from 2.296(2) to 2.323(2) Å. The two $TiCl_4$ moieties are approximately eclipsed with Cl–Ti···Ti–Cl torsion angles of < 2.0°. These dimensions compare favourably with those found in the isomeric form reported by Krug and Muller,[18] as an inadvertent hydrolysis product from the $TiCl_4$–$Se(SiMe_3)_2$–PPh_4Cl reaction system. Here each acetonitrile ligand is in a *cis* location with respect to the bridging oxygen atom (C_{2h}) (see Table 6). The $[Mg(MeCN)_6]^{2+}$ cation has expected dimensions[21] with Mg–N bond distances ranging between 2.129(6) and 2.184(7) Å. The four solvent (MeCN) molecules show no close contacts to either cation or anion.

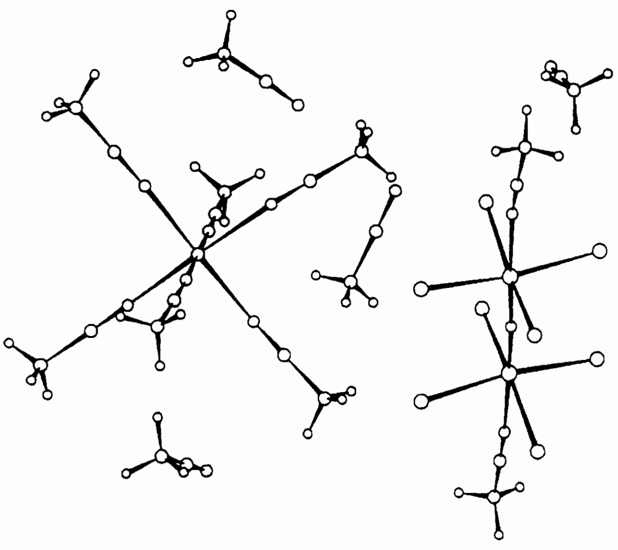


Fig. 1 Structure of **1** showing the octahedral $[Mg(MeCN)_6]^{2+}$ cation, the $[\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]^{2-}$ anion and the four solvent MeCN molecules

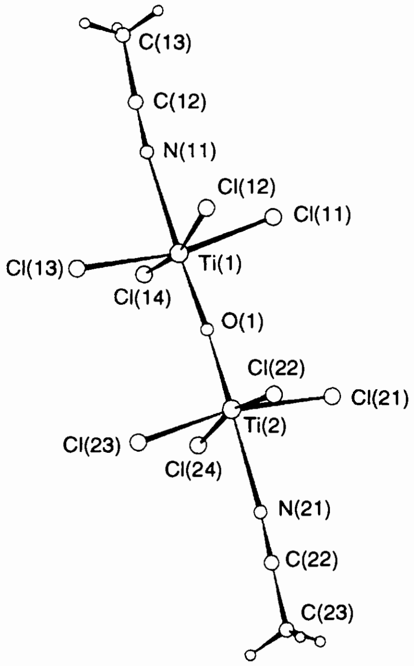
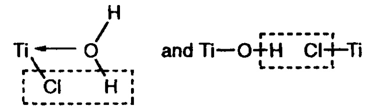


Fig. 2 Structure of the $[\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]^{2-}$ anion of **1** showing the atomic numbering scheme

Hydrolysis of *in situ* $[TiCl_5(MeCN)]^-$ anions is seen to involve ligand exchange ($H_2O \longleftrightarrow$ MeCN), hydrogen chloride elimination (**I**) and condensation (**II**) reactions leading directly to the formation of **1**. As mentioned earlier, stabilisation of the single Ti–O–Ti unit normally derives from

Table 1 Crystal data and structure refinement for $[Mg(MeCN)_6][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]\cdot4MeCN$ **1** and $[\{TiCl_2(MeCN)_2(\mu\text{-}O)\}_4]\cdot2MeCN$ **2**

	1	2
Empirical formula	$C_{24}H_{36}Cl_8MgN_{12}OTi_2$	$C_{20}H_{30}C_{18}N_{10}O_4Ti_4$
M	912.36	949.69
T/K	293	293
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	14.777(6)	12.165(6)
b/Å	14.603(6)	12.367(6)
c/Å	21.214(10)	27.927(11)
β/°	105.3(1)	
U/Å^3	4415	4 202
Z	4	8
D_c/Mg m^{-3}	1.373	1.492
λ(Mo-Kα)/Å	0.710 71	0.710 71
μ/mm^{-1}	0.895	1.279
F(000)	1856	1 880
Crystal size/mm	0.2 × 0.2 × 0.2	0.3 × 0.2 × 0.1
θ range/°	1.99–24.83	2.20–25.00
Index ranges	$-15 < h < 15, 0 < k < 17, -24 < l < 24$	$0 < h < 14, -14 < k < 14, -33 < l < 33$
Reflections collected	12 765	13 094
Independent reflections	6814 [R(int) 0.0237]	7185 [R(int) 0.056 9]
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/parameters	6814/466	7185/401
Goodness-of-fit on F^2	0.940	0.767
Final R indices [$I > 3\sigma(I)$]	0.050 (4806 reflections)	0.055 (4284 reflections)
R indices (all data) $R1$	0.110 8	0.126 0
$wR2$	0.306 6	0.340 9
Max., min. electron density/e Å^{-3}	0.524, −1.219	0.577, −0.706



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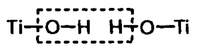


II

the presence of large bulky substituents on the metal which can act as a steric control against subsequent hydrolysis reactions. What is surprising in the present instance is that with such a high density of chlorine atoms around each metal centre further hydrolysis, perhaps involving 'stray' water molecules from solvent impurity, to give a double $Ti_2(\mu\text{-}O)_2$ or ring oxo-bridged system was not observed. Presumably the overall negative charge of these anion species effectively minimises nucleophilic attack at the metal.

Hydrolysis of $TiCl_4$.—Treatment of titanium(IV) chloride (1 mol) (as the bis-adduct species $TiCl_4\cdot2MeCN$ formed *in situ*) with water (0.5 mol) in acetonitrile provided light yellow needle crystals of the neutral tetranuclear titanoxane $[\{TiCl_2(MeCN)_2(\mu\text{-}O)\}_4]$ **2**. The IR spectrum shows characteristic bands at 780 [ν_{asym}(Ti–O–Ti)], 380 [ν(TiCl)] and a doublet at 2310, 2279 cm^{-1} [ν(CN)] characteristic of co-ordinated acetonitrile. The structure of **2**, shown in Fig. 3 with the atom labelling used, consists of discrete molecules of the tetramer $[\{TiCl_2(MeCN)_2(\mu\text{-}O)\}_4]$ together with two solvent MeCN molecules. The Ti_4O_4 moiety is significantly distorted from planarity: the four oxygen atoms are planar to within 0.06 Å but the titanium atoms are *ca.* 0.28 Å alternately above and below this plane. The four Ti–O–Ti angles range from 166.8(6) to 172.6(5)°. Within the tetrameric unit the four titanium atoms have equivalent geometries being bonded to two mutually *cis* terminal chlorine atoms, two mutually *cis* terminal MeCN ligands and two mutually *cis* bridging oxygen atoms. The two Ti–O bond distances differ somewhat, with those *trans* to MeCN (mean value 1.668 Å) shorter than those *trans* to chlorine (mean value 1.954 Å). This situation is atypical since in the majority of Ti–O–Ti moieties the individual Ti–O bonds are broadly equivalent. The Ti–N bond distances *trans* to the shorter Ti–O bond are longer at *ca.* 2.320 Å compared to those *trans* to the chlorine atoms at *ca.* 2.184 Å. The Ti–Cl bond distances follow a similar pattern in that those *trans* to oxygen, albeit the less strongly bound oxygen, are significantly longer at 2.323(4), 2.329(4), 2.341(4), 2.334(4) Å than those *trans* to nitrogen (MeCN) at 2.287(5), 2.295(5), 2.285(4), 2.280(5) Å. Condensed titanoxanes containing a Ti_4O_4 skeletonal unit are known, *e.g.* $[\{Ti(\eta^5\text{-}C_5H_5)Cl(\mu\text{-}O)\}_4]$, planar [Ti–O–Ti 159.7(4), 164.8(5)°];[5a] $[\{Ti(\eta^5\text{-}C_5H_5)(OC_9H_{11})(\mu\text{-}O)\}_4]$ (OC_9H_{11} = 2,4,6-trimethylphenoxo), planar [Ti–O–Ti 153.8(2), 165.6(3)°];[5b] $[\{Ti(\eta^5\text{-}C_5HMe_4)Br(\mu\text{-}O)\}_4]$, planar [Ti–O–Ti 149.3(5), 175.7(5)°];[5c] $[\{Ti(\eta^5\text{-}C_5H_4SiMe_3)(NCS)(\mu\text{-}O)\}_4]$, planar [Ti–O–Ti 148.8(6), 171.2(6), 146.7(4), 177.6(7)°];[5d] $[\{(TiCl)_2(\mu\text{-}O)[\mu\text{-}\eta^5:\eta^5\text{-}(C_5H_4)_2SiMe_2]\}_2(\mu\text{-}O)_2]$, non-planar

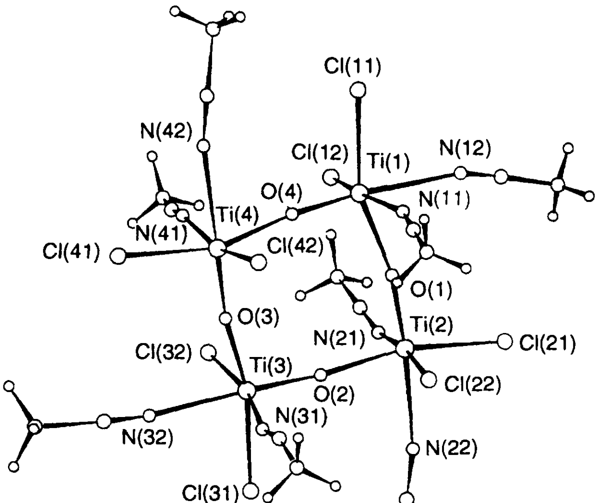


Fig. 3 Structure of the $[\{TiCl_2(MeCN)_2(\mu\text{-}O)\}_4]$ tetramer in **2** showing the atomic numbering scheme

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Ti(1)	7 789(1)	7 574(1)	1 584(1)
Cl(11)	7 967(1)	6 000(1)	1 681(1)
Cl(12)	9 187(1)	7 705(1)	1 310(1)
Cl(13)	7 770(1)	9 150(1)	1 709(1)
Cl(14)	6 576(1)	7 483(1)	2 089(1)
Ti(2)	6 476(1)	7 525(1)	−75(1)
Cl(21)	6 559(1)	5 956(1)	−199(1)
Cl(22)	7 751(1)	7 702(1)	−499(1)
Cl(23)	6 224(1)	9 092(1)	−172(1)
Cl(24)	5 002(1)	7 346(1)	95(1)
Mg(3)	7 924(2)	2 660(2)	−774(1)
O(1)	7 080(3)	7 556(3)	761(2)
N(11)	8 722(4)	7 573(4)	2 625(2)
C(12)	9 176(5)	7 532(4)	3 126(3)
C(13)	9 802(7)	7 491(6)	3 778(4)
N(21)	5 628(4)	7 515(4)	−1 141(2)
C(22)	5 182(5)	7 561(5)	−1 641(4)
C(23)	4 565(7)	7 647(8)	−2 304(4)
N(31)	8 279(4)	2 077(4)	−1 597(3)
C(32)	8 565(5)	1 732(5)	−1 974(3)
C(33)	8 930(6)	1 313(6)	−2 465(4)
N(41)	6 577(4)	1 993(4)	−1 069(3)
C(42)	5 941(5)	1 541(5)	−1 129(3)
C(43)	5 138(5)	938(5)	−1 207(4)
N(51)	7 508(5)	3 259(4)	22(3)
C(52)	7 189(5)	3 591(5)	384(3)
C(53)	6 775(7)	4 035(6)	849(4)
N(61)	9 272(5)	3 298(4)	−455(3)
C(62)	9 962(5)	3 663(5)	−347(3)
C(63)	10 853(5)	4 140(5)	−209(4)
N(71)	7 435(5)	3 917(4)	−1 314(3)
C(72)	7 317(5)	4 633(5)	−1 503(3)
C(73)	7 175(6)	5 574(6)	−1 736(4)
N(81)	8 419(5)	1 438(4)	−210(3)
C(82)	8 576(5)	754(5)	28(3)
C(83)	8 782(6)	−133(6)	350(4)
N(84)	4 654(10)	5 297(10)	−2 202(6)
C(85)	4 757(7)	4 870(8)	−1 748(5)
C(86)	4 882(7)	4 312(7)	−1 193(4)
N(87)	7 591(10)	2 016(8)	1 625(6)
C(88)	7 092(8)	1 562(7)	1 286(5)
C(89)	6 471(8)	979(7)	851(7)
N(91)	9 631(7)	5 325(6)	−1 477(5)
C(92)	9 574(6)	4 826(6)	−1 879(5)
C(93)	9 474(8)	4 168(7)	−2 379(6)
N(94)	9 025(7)	9 617(6)	−1 325(5)
C(95)	8 247(8)	9 536(5)	−1 492(4)
C(96)	7 258(7)	9 434(8)	−1 704(4)

Table 3 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Ti(1)	6 178(2)	6 352(2)	1 787(1)
Cl(11)	5 045(3)	4 959(4)	2 048(2)
Cl(12)	6 600(4)	6 974(4)	2 536(2)
Ti(2)	7 153(2)	8 763(2)	1 195(1)
Cl(21)	5 556(3)	9 802(3)	1 192(2)
Cl(22)	6 995(4)	8 259(4)	407(2)
Ti(3)	9 913(2)	7 700(2)	1 250(1)
Cl(31)	11 033(3)	9 114(3)	981(1)
Cl(32)	10 395(4)	7 875(4)	2 037(1)
Ti(4)	8 725(2)	5 066(2)	1 461(1)
Cl(41)	10 248(3)	3 921(3)	1 429(2)
Cl(42)	8 133(3)	4 690(4)	704(2)
O(1)	6 606(6)	7 674(8)	1 466(4)
O(2)	8 703(8)	8 341(7)	1 241(4)
O(3)	9 351(7)	6 228(7)	1 355(3)
O(4)	7 309(7)	5 642(7)	1 670(3)
N(11)	5 590(10)	6 006(10)	1 071(5)
C(111)	5 641(14)	5 687(15)	719(7)
C(112)	5 620(19)	5 302(21)	204(8)
N(12)	4 543(10)	7 370(12)	1 823(6)
C(121)	3 964(13)	8 031(13)	1 865(6)
C(122)	3 229(13)	8 947(15)	1 905(8)
N(21)	7 505(11)	9 534(10)	1 875(4)
C(211)	7 738(16)	9 671(16)	2 252(6)
C(212)	7 847(22)	10 073(33)	2 742(10)
N(22)	7 987(10)	10 324(10)	927(6)
C(221)	8 470(13)	11 008(13)	804(6)
C(222)	9 183(21)	11 925(17)	639(11)
N(31)	9 698(11)	7 235(11)	493(4)
C(311)	9 331(12)	6 992(13)	131(6)
C(312)	8 880(21)	6 680(20)	−312(8)
N(32)	11 478(11)	6 673(12)	1 127(6)
C(321)	12 047(15)	6 016(16)	1 077(8)
C(322)	12 856(14)	5 095(20)	965(12)
N(41)	9 091(9)	5 235(11)	2 225(5)
C(411)	9 241(13)	5 602(14)	2 586(7)
C(412)	9 438(25)	6 043(21)	3 064(7)
N(42)	7 793(11)	3 514(9)	1 711(6)
C(421)	7 075(17)	2 971(12)	1 753(8)
C(422)	6 159(18)	2 245(18)	1 833(10)
C(100)	686(25)	4 254(25)	38(12)
C(101)	1 272(33)	3 323(33)	51(15)
N(102)	1 693(36)	2 494(39)	105(16)
N(103)	4 297(30)	3 041(34)	709(15)
C(104)	3 726(46)	2 305(43)	831(20)
C(105)	3 128(38)	1 712(39)	1 126(19)

[Ti–O–Ti 176.2(1), 144.5(1)°];[5e] [{Ti(η^5-C_5H_4Me)Cl(μ-O)}$_4$], planar [Ti–O–Ti 157.2(2), 169.1(1)°],[5f] but all of these are based on a four-co-ordinate (tetrahedral) metal geometry. The present structure **2** is the first example of a Ti_4O_4 core unit with μ-oxo bridging between six-co-ordinate metal centres. A related hydrolysis product of titanium(IV) chloride of empirical formula $TiCl(OH)_3{\cdot}2H_2O$ contains the cubic octameric titanium cation $[Ti_8O_{12}(H_2O)_{24}]^{8+}$ **3** in which each octahedral metal centre is bonded to three water molecules and three separate μ-O bridging atoms {Ti–O(mean) 1.820 Å [1.791(2)–1.859(2) Å], Ti–O–Ti(mean) 154.6° [153.10(11)–156.03(11)°]}.[22]

Interestingly although the 'expected' Feltz compound [{$TiCl_3(MeCN)_2$}$_2$(μ-O)] was not isolated in this present study, the thf (solvate) analogue [{$TiCl_3(thf)_2$}$_2$(μ-O)] has been reported by Strel'tsova *et al.*[19] and identified by X-ray crystallography as the C_2 symmetry isomer. Here the two solvent molecules at each metal site are mutually *cis* with one occupying a *trans* position with respect to the bridging oxygen atom (see Table 6). In comparison the lower valence counterpart [{$TiBr_2(py)_3$}$_2$(μ-O)] (py = pyridine) based on Ti^{III} adopts the highly symmetric D_{2h} structure with a *trans*-*trans*-eclipsed arrangement of the co-ordinated pyridine ligands (see Table 6).[20]

Allowing for the different nature of the surrounding ligands there is no obvious correlation between Ti–O bond distances in the Ti–O–Ti linkages as a reflection of the overall charge. Thus, anionic: [{$TiCl_4$(MeCN)}$_2$(μ-O)]$^{2-}$, Ti–O 1.804 Å (ref. 18) and (mean) 1.774 Å (this work); neutral: [{$TiCl_3(thf)_2$}$_2$(μ-O)], Ti–O 1.787 Å (ref. 19); [{$TiCl_2(MeCN)_2$(μ-O)}$_4$], Ti–O (mean) 1.668, 1.954 Å (this work); cationic: [{Ti(η^5-C_5H_5)$_2$(H_2O)}$_2$-(μ-O)]$^{2+}$, Ti–O 1.829 Å (ref. 23); [{Ti(L)}$_2$(μ-O)]$^{2+}$ (H_2L = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine), Ti–O 1.806, 1.830 Å [ref. 10(*c*)]. When compared with the formal titanyl Ti=O linkage, however, there is a clear differential of some 0.2 Å as a result of increased multiple (π) bonding in the latter, *viz.* [Ti(O)L], Ti–O 1.653 Å [ref. 10(*a*)], [Ti(O)(oep)] (oep = 2,3,7,8,12,13,17,18-octaethylporphinato dianion), Ti–O 1.613 Å [ref. (7)].

In simple terms the formation of compound **2** can be regarded as the result of further hydrolysis of the 'expected' Feltz compound [{$TiCl_3(MeCN)_2$}$_2$(μ-O)] leading to the tetranuclear titanoxane as a dimeric structure. By extrapolation further hydrolysis of **2** could lead in principle (dimerisation) to a cubic octameric derivative [$Ti_8O_{12}(MeCN)_{16}Cl_8$] as the direct analogue of the titanium cation **3** with corner metal atoms co-ordinated by two acetonitrile molecules, one chlorine atom and three separate bridging oxygen atoms. It should be noted that controlled hydrolysis of the tin(IV) chloride solvate $SnCl_4$·2thf gives the dinuclear derivative [{$SnCl_3$(thf)}$_2$(μ-OH)$_2$][24] in which two μ-hydroxy groups are preferred to a single μ-oxo linkage.

Provided there is strict adherence to a 2 : 1 stoichiometry, we can write a general equation for the controlled hydrolysis of six-co-ordinate solvated chlorotitanium(IV) species leading to the generic dititanoxane series, equation (2).

$$2[TiCl_nL_{6-n}]^{(4-n)+} + H_2O \xrightarrow{L} [(TiCl_{n-1}L_{6-n})_2(\mu\text{-}O)]^{(8-2n)+} + 2HCl \quad (2)$$

Currently we are still pursuing the dinuclear Feltz (n = 4) compound and investigating the controlled hydrolysis of the [$TiCl_3(MeCN)_3$]$^+$ cation (n = 3) as a possible route to the dinuclear dication [{$TiCl_2(MeCN)_3$}$_2$(μ-O)]$^{2+}$.

Table 4 Selected bond lengths (Å) and angles (°) in the anion of **1**

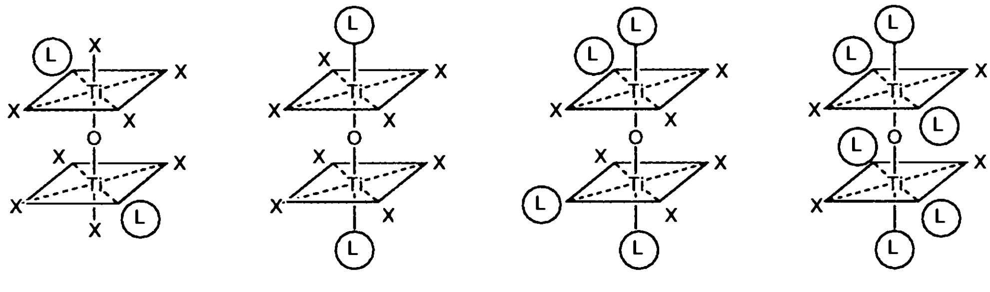
Ti(1)–O(1)	1.783(4)	Ti(2)–O(1)	1.764(4)
Ti(1)–N(11)	2.273(5)	Ti(2)–N(21)	2.278(5)
Ti(1)–Cl(11)	2.316(2)	Ti(2)–Cl(21)	2.314(2)
Ti(1)–Cl(12)	2.296(2)	Ti(2)–Cl(22)	2.306(2)
Ti(1)–Cl(13)	2.318(2)	Ti(2)–Cl(23)	2.318(2)
Ti(1)–Cl(14)	2.323(2)	Ti(2)–Cl(24)	2.316(2)
O(1)–Ti(1)–N(11)	178.5(2)	O(1)–Ti(2)–N(21)	177.0(2)
O(1)–Ti(1)–Cl(12)	95.08(14)	O(1)–Ti(2)–Cl(22)	98.1(2)
N(11)–Ti(1)–Cl(12)	83.7(2)	N(21)–Ti(2)–Cl(22)	84.5(2)
O(1)–Ti(1)–Cl(11)	95.54(13)	O(1)–Ti(2)–Cl(21)	96.43(14)
N(11)–Ti(1)–Cl(11)	83.54(14)	N(21)–Ti(2)–Cl(21)	85.0(2)
Cl(12)–Ti(1)–Cl(11)	90.93(8)	Cl(22)–Ti(2)–Cl(21)	89.62(7)
O(1)–Ti(1)–Cl(13)	96.00(14)	O(1)–Ti(2)–Cl(24)	95.3(2)
N(11)–Ti(1)–Cl(13)	84.95(14)	N(21)–Ti(2)–Cl(24)	82.0(2)
Cl(12)–Ti(1)–Cl(13)	89.17(7)	Cl(22)–Ti(2)–Cl(24)	166.54(9)
Cl(11)–Ti(1)–Cl(13)	168.41(8)	Cl(21)–Ti(2)–Cl(24)	89.19(7)
O(1)–Ti(1)–Cl(14)	97.2(2)	O(1)–Ti(2)–Cl(23)	95.19(14)
N(11)–Ti(1)–Cl(14)	84.0(2)	N(21)–Ti(2)–Cl(23)	83.4(2)
Cl(12)–Ti(1)–Cl(14)	167.62(9)	Cl(22)–Ti(2)–Cl(23)	89.08(7)
Cl(11)–Ti(1)–Cl(14)	89.18(7)	Cl(21)–Ti(2)–Cl(23)	168.37(8)
Cl(13)–Ti(1)–Cl(14)	88.25(7)	Cl(24)–Ti(2)–Cl(23)	89.40(8)
		Ti(2)–O(1)–Ti(1)	174.7(3)

Table 5 Selected bond lengths (Å) and angles (°) for compound **2**

Ti(1)–O(4)	1.664(10)	Ti(3)–O(2)	1.672(10)
Ti(1)–O(1)	1.936(10)	Ti(3)–O(3)	1.967(9)
Ti(1)–N(11)	2.166(14)	Ti(3)–N(31)	2.207(13)
Ti(1)–Cl(12)	2.287(5)	Ti(3)–Cl(32)	2.285(4)
Ti(1)–Cl(11)	2.323(4)	Ti(3)–N(32)	2.314(14)
Ti(1)–N(12)	2.356(13)	Ti(3)–Cl(31)	2.341(4)
Ti(2)–O(1)	1.683(10)	Ti(4)–O(3)	1.653(9)
Ti(2)–O(2)	1.960(10)	Ti(4)–O(4)	1.954(10)
Ti(2)–N(21)	2.168(12)	Ti(4)–N(41)	2.191(14)
Ti(2)–N(22)	2.305(12)	Ti(4)–Cl(42)	2.280(5)
Ti(2)–Cl(22)	2.295(5)	Ti(4)–Cl(41)	2.334(4)
Ti(2)–Cl(21)	2.329(4)	Ti(4)–N(42)	2.336(12)
O(4)–Ti(1)–O(1)	97.6(4)	O(3)–Ti(3)–N(31)	82.0(4)
O(4)–Ti(1)–N(11)	89.3(5)	O(2)–Ti(3)–Cl(32)	101.3(4)
O(1)–Ti(1)–N(11)	80.1(5)	O(3)–Ti(3)–Cl(32)	91.9(3)
O(4)–Ti(1)–Cl(12)	99.9(4)	N(31)–Ti(3)–Cl(32)	167.6(4)
O(1)–Ti(1)–Cl(12)	94.5(4)	O(2)–Ti(3)–N(32)	169.1(5)
N(11)–Ti(1)–Cl(12)	170.0(4)	O(3)–Ti(3)–N(32)	78.5(4)
O(4)–Ti(1)–Cl(11)	99.2(3)	N(31)–Ti(3)–N(32)	79.2(5)
O(1)–Ti(1)–Cl(11)	158.6(3)	Cl(32)–Ti(3)–N(32)	89.1(4)
N(11)–Ti(1)–Cl(11)	87.0(4)	O(2)–Ti(3)–Cl(31)	98.8(3)
Cl(12)–Ti(1)–Cl(11)	95.5(2)	O(3)–Ti(3)–Cl(31)	160.3(3)
O(4)–Ti(1)–N(12)	171.2(5)	N(31)–Ti(3)–Cl(31)	87.4(3)
O(1)–Ti(1)–N(12)	78.2(4)	Cl(32)–Ti(3)–Cl(31)	95.1(2)
N(11)–Ti(1)–N(12)	82.3(5)	N(32)–Ti(3)–Cl(31)	83.3(4)
Cl(12)–Ti(1)–N(12)	88.3(4)	O(4)–Ti(4)–O(3)	98.2(4)
Cl(11)–Ti(1)–N(12)	83.2(4)	O(3)–Ti(4)–N(41)	89.8(5)
O(1)–Ti(2)–O(2)	97.9(4)	O(4)–Ti(4)–N(41)	81.5(4)
O(1)–Ti(2)–N(21)	92.0(5)	O(3)–Ti(4)–Cl(42)	99.1(4)
O(2)–Ti(2)–N(21)	82.5(4)	O(4)–Ti(4)–Cl(42)	94.2(3)
O(1)–Ti(2)–N(22)	172.0(5)	N(41)–Ti(4)–Cl(42)	170.6(4)
O(2)–Ti(2)–N(22)	79.7(4)	O(3)–Ti(4)–Cl(41)	98.9(3)
N(22)–Ti(2)–N(21)	80.1(5)	O(4)–Ti(4)–Cl(41)	158.9(3)
O(1)–Ti(2)–Cl(22)	100.5(4)	N(41)–Ti(4)–Cl(41)	86.2(3)
O(2)–Ti(2)–Cl(22)	94.1(3)	Cl(42)–Ti(4)–Cl(41)	95.3(2)
N(21)–Ti(2)–Cl(22)	167.4(4)	O(3)–Ti(4)–N(42)	172.4(5)
N(22)–Tl(2)–Cl(22)	87.3(4)	O(4)–Ti(4)–N(42)	77.4(4)
O(1)–Ti(2)–Cl(21)	96.5(3)	N(41)–Ti(4)–N(42)	83.4(5)
O(2)–Ti(2)–Cl(21)	161.6(3)	Cl(42)–Ti(4)–N(42)	87.5(4)
N(21)–Ti(2)–Cl(21)	85.7(4)	Cl(41)–Ti(4)–N(42)	84.2(3)
N(22)–Ti(2)–Cl(21)	84.5(3)	Ti(2)–O(1)–Ti(1)	172.3(5)
Cl(22)–Ti(2)–Cl(21)	94.4(2)	Ti(3)–O(2)–Ti(2)	166.8(6)
O(2)–Ti(3)–O(3)	97.8(4)	Ti(4)–O(3)–Ti(3)	172.6(5)
O(2)–Ti(3)–N(31)	90.2(5)	Ti(1)–O(4)–Ti(4)	168.5(6)

Table 6 Molecular geometry and dimensions of [$L_{5-n}X_nTi$–O–TiX_nL_{5-n}] compounds

[$Ti_2X_8(O)L_2$]$^{2-}$ [$Ti_2X_6(O)L_4$] [$Ti_2X_4(O)L_6$]



X	Cl	Cl	Cl	Br
L	MeCN	MeCN	thf	Pyridine
Symmetry	C_{2h}	D_{4h}	C_2	D_{2h}
Ref.	18	This work	19	20
Ti–X (Å)	2.287–2.420; (mean) 2.343	2.296–2.323; (mean) 2.313	2.279–2.314; (mean) 2.302	2.609–2.657; (mean) 2.633
Ti–L (Å)	2.254	2.273, 2.278	2.131–2.171; (mean) 2.151	2.236–2.319; (mean) 2.267
Ti–O (Å)	1.804	1.764, 1.783	1.787	1.799, 1.794
Ti–O–Ti (°)	180.0	174.7	176.7	180.0

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