Crown Ether Complexation of Titanium: Synthesis and Structural Characterisation of a Cationic Oxygen-bridged Titanium(IV) Dimer*

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1,4,7,10-Tetraoxacyclododecane (12-crown-4) reacts with $[TiCl_3(MeCN)_3][SbCl_6]$ in MeCN to form a complex which provides the crown ether titanoxane $[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2\cdot 2CH_2Cl_2$ **1** following inadvertent hydrolysis. The structure of **1** contains a discrete di-μ-oxo-dititanium cation placed on a crystallographic centre of inversion, two regular (O_h) $SbCl_6^-$ anions and two molecules of CH_2Cl_2 as lattice solvate. The complex crystallises in the space group $P2_1/n$ with cell dimensions $a = 8.337(4)$, $b = 21.307(10)$, $c = 13.626(8)$ Å, $\beta = 107.13(4)°$, with $Z = 2$; $R = 0.038$ for 3271 observed reflections $[I/\sigma(I) \geqslant 2.0]$. The core Ti_2O_2 ring is planar with dimensions Ti–O 1.823(4) and 1.811(3) Å and O–Ti–O 79.7(2) and Ti–O–Ti 100.3(2)°. In addition to the two bridging oxygen atoms each titanium atom is bonded to one chlorine [Ti–Cl 2.277(2) Å] and all four oxygen atoms of a crown macrocycle [Ti–O 2.121(4)–2.237(4), mean 2.242 Å].

A dominant theme in the chemistry of titanium is the facile formation of multicomponent Ti–O bonds. The wide variety of metal halide (and related) complexes incorporating *O*-donor ligands,[1] homonuclear (Ti–O–Ti) and heteronuclear (Ti–O–M) oxo-bridged compounds[2] and, more recently, terminal bonded (Ti=O) complexes[3] provides ample demonstration of the rapacious Lewis-acid characteristics of the metal. Against this background, crown ethers such as 12-crown-4 (1,4,7,10-tetraoxacyclododecane), 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane), and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) represent an 'obvious' set of potential multidentate *O*-donor ligands as a probe to high-co-ordination metal geometry. Surprisingly we can find only two structures reported in the literature of crown ether complexation with titanium, *viz.* $TiCl_4\cdot$18-crown-6[4] in which only two oxygen atoms of the crown are involved in bonding to the metal and $TiCl_3(H_2O)\cdot$18-crown-6$\cdot CH_2Cl_2$[5] (deep blue) where, again, a bidentate bonding mode is involved. For the non-hydrated complex $TiCl_3\cdot$18-crown-6 (yellow), IR evidence indicates crown complexation *via* a terdentate bonding mode.[5] Evidently the titanium-(IV) and -(III) centres retain their preferred six-co-ordinate geometries at the expense of reduced ligand denticity in these particular cases. For the analogous $ZrCl_4$–18-crown-6 system, ring opening of the crown macrocycle occurs and the product isolated is $[ZrCl_2\{(OCH_2CH_2)_5OCH_2CH_2Cl\}][ZrCl_5(thf)]$.[6]

The use of titanium cations with their high oxophilicity offers an alternative approach to titanium–crown ether complexes. Herein we report the isolation and X-ray characterisation of a novel crown ether titanoxane $[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2\cdot 2CH_2Cl_2$ **1** obtained by hydrolysis of the initial product from the reaction of $[TiCl_3(MeCN)_3][SbCl_6]$ and 12-crown-4. In distinction to the two 18-crown-6 complexes this is the first authentic example of a crown macrocycle completely chelated to titanium.

Experimental

Manipulations of materials were carried out using a standard Schlenk system and/or a dinitrogen glove-box. The salt $[TiCl_3(MeCN)_3][SbCl_6]$ was prepared as described previously.[7] The 12-crown-4 (Aldrich) was stored over preheated (250 °C) molecular sieves under an atmosphere of dinitrogen. Dichloromethane and pentane were refluxed with and distilled from CaH_2 under an atmosphere of dinitrogen. Acetonitrile was purified following the procedure of Walter and Ramaley.[8]

Preparation of Complex **1**.—The 12-crown-4 (0.37 g, 2.10 mmol) in MeCN (25 cm^3) was added dropwise to a cold (solid CO_2–acetone) solution of $[TiCl_3(MeCN)_3][SbCl_6]$ (1.30 g, 2.12 mmol) in MeCN (30 cm^3). The resulting yellow solution was allowed to warm to room temperature and stirred for 24 h. Removal of solvent gave a pale yellow solid which was washed with pentane (3 × 25 cm^3) and pumped dry *in vacuo*. The crude product was dissolved in the minimum volume of MeCN (*ca* 20 cm^3) and layered with an equal volume of CH_2Cl_2. The large colourless block crystals which formed within 3 h were collected by filtration and pumped dry *in vacuo*. Yield 0.56 g, 39.7% (Found: C, 15.65; H, 2.80; Cl, 45.80; Ti, 6.60. Calc. for $C_{18}H_{36}Cl_{18}O_{10}Sb_2Ti_2$: C, 15.55; H, 2.60; Cl, 45.90; Ti, 6.90%). ν_{max} 1259m, 1255w, 1250w, 1128m, 1065s, 1030m, 950m, 920w, 875m, 815w, 785m and 345vs (br) cm^{-1} (Nujol). $\delta(CD_3CN)$ 3.70 (16 H, s, CH_2 of crown). λ_{max}(MeCN) 38 100 cm^{-1}.

X-Ray Structure Determination.—*Crystal data.* $[C_{16}H_{32}Cl_2O_{10}Ti_2]^{2+}2[SbCl_6]^-\cdot 2CH_2Cl_2$ **1**, $M = 1389.93$, monoclinic, space group $P2_1/n$, $a = 8.337(4)$, $b = 21.307(10)$, $c = 13.626(8)$ Å, $\beta = 107.13(4)°$, $U = 2313$ Å^3, $Z = 2$, $D_c = 1.90$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\,69$ Å, μ(Mo-Kα) = 2.57 mm^{-1}, $T = 290$ K.

A large colourless block crystal was mounted in a Lindemann tube to prevent hydrolysis. Data were collected with a Siemens R3m four-circle diffractometer in ω–2θ mode. Maximum 2θ was 50° with scan range ±0.65°(ω) around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 3–15°(ω) min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The *hkl* ranges were 0–9, 0–23, −15 to 15.

Three standard reflections were monitored every 200 reflections, and showed a slight decrease (2%) during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit of 15 reflections (28 < 2θ < 30°). Reflections were processed using

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

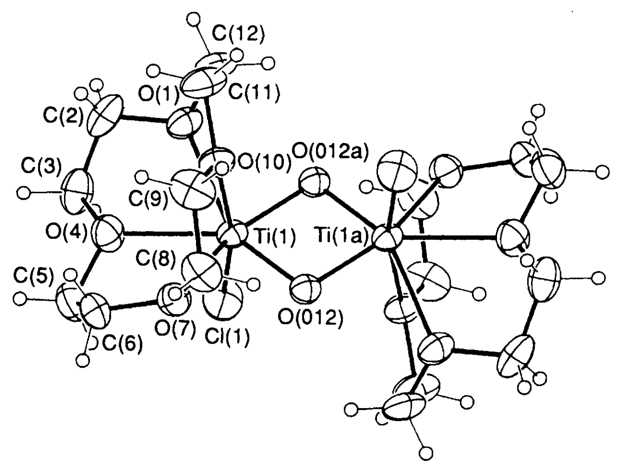


Fig. 1 Side view of the $[\{\mathrm{TiCl}(\mu\text{-O})(12\text{-crown-}4)\}_2]^{2+}$ cation with atom numbering

Table 1 Atom coordinates (× 10⁴) for complex 1

Atom	*x*	*y*	*z*
Sb(1)	−3576.1(5)	3413.0(2)	6124.4(3)
Cl(11)	−859.2(22)	3227.2(10)	5956.3(15)
Cl(12)	−6278.9(21)	3571.9(10)	6310.9(14)
Cl(13)	−4770.2(22)	2797.6(8)	4645.2(12)
Cl(14)	−3872.0(27)	4302.6(8)	5088.0(14)
Cl(15)	−2392.3(23)	4003.9(10)	7614.6(13)
Cl(16)	−3273.6(28)	2497.9(9)	7149.3(15)
Ti(1)	369.0(10)	628.1(4)	5256.7(6)
Cl(1)	3142.3(17)	608.0(7)	5353.9(13)
O(012)	−346(4)	132(2)	4133(2)
O(1)	646(4)	869(2)	6948(3)
C(2)	1117(8)	1499(3)	7321(5)
C(3)	1986(8)	1779(3)	6631(5)
O(4)	924(5)	1643(2)	5627(3)
C(5)	1087(7)	2021(3)	4774(5)
C(6)	−595(8)	1954(3)	4012(5)
O(7)	−960(5)	1295(2)	3938(3)
C(8)	−2711(7)	1144(3)	3652(4)
C(9)	−3293(7)	1151(3)	4605(5)
O(10)	−2048(4)	825(2)	5397(3)
C(11)	−2357(7)	858(3)	6399(5)
C(12)	−796(7)	627(3)	7177(4)
Cl(01)	6018.2(28)	1309.0(11)	8535.0(16)
Cl(02)	4197.5(39)	146.6(12)	8466.1(19)
C(01)	5749(11)	618(4)	9159(7)

profile analysis to give 4083 unique reflections ($R_{\mathrm{int}} = 0.038$), of which 3271 were considered observed [$I/\sigma(I) \geqslant 2.0$]. These were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.35 and 0.60. Crystal dimensions were 0.94 × 0.60 × 0.71 mm. Systematic reflection conditions: $h0l$, $h + l = 2n$; $0k0$, $k = 2n$ indicate space group $P2_1/n$.

Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found by E-map expansion and successive Fourier syntheses. The cation was found to consist of an O-bridged dimer placed on a crystallographic centre of inversion, and the crystals also include one molecule of solvent CH_2Cl_2 in each asymmetric unit. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.08$ Å². They were inserted at calculated positions and not refined. Final refinement was on F by least-squares methods refining 226 parameters. Largest positive and negative peaks on a final Fourier difference synthesis were of height ± 0.5 e Å⁻³.

A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0024$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.038$, $R' = 0.061$, $S = 1.02$. Maximum shift/error in final cycle 0.01. Computing with SHELXTL PLUS[9] on a DEC MicroVax-II computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 10. Final atomic coordinates are given in Table 1, and selected bond lengths in Table 2.

Table 2 Selected bond lengths (Å) and bond angles (°) for complex 1

Ti(1)–Cl(1)	2.277(2)	Ti(1)–O(012)	1.811(3)
Ti(1)–O(1)	2.306(4)	Ti(1)–O(4)	2.237(4)
Ti(1)–O(7)	2.303(4)	Ti(1)–O(10)	2.121(4)
Ti(1) • • • Ti(1a)	2.789(2)	Ti(1)–O(012a)	1.823(4)
O(012)–Ti(1a)	1.823(4)	O(1)–C(2)	1.448(7)
O(1)–C(12)	1.424(8)	C(2)–C(3)	1.472(10)
C(3)–O(4)	1.423(7)	O(4)–C(5)	1.453(8)
C(5)–C(6)	1.486(8)	C(6)–O(7)	1.433(7)
O(7)–C(8)	1.433(7)	C(8)–C(9)	1.513(10)
C(9)–O(10)	1.436(6)	O(10)–C(11)	1.464(8)
C(11)–C(12)	1.498(7)		
Cl(1)–Ti(1)–O(1)	98.3(1)	O(012)–Ti(1)–O(1)	152.4(2)
Cl(1)–Ti(1)–O(4)	82.3(1)	O(012)–Ti(1)–O(4)	138.6(2)
O(1)–Ti(1)–O(4)	66.8(1)	Cl(1)–Ti(1)–O(7)	107.7(1)
O(012)–Ti(1)–O(7)	74.8(1)	O(1)–Ti(1)–O(7)	121.8(1)
O(4)–Ti(1)–O(7)	66.4(1)	Cl(1)–Ti(1)–O(10)	166.8(1)
O(012)–Ti(1)–O(10)	96.1(1)	O(1)–Ti(1)–O(10)	71.6(1)
O(4)–Ti(1)–O(10)	85.8(2)	O(7)–Ti(1)–O(10)	72.3(1)
Cl(1)–Ti(1)–O(012a)	95.9(1)	O(012)–Ti(1)–O(012a)	79.7(2)
O(1)–Ti(1)–O(012a)	75.7(1)	O(4)–Ti(1)–O(012a)	141.7(1)
O(7)–Ti(1)–O(012a)	146.8(1)	O(10)–Ti(1)–O(012a)	89.8(2)
C(2)–O(1)–C(12)	114.7(5)	Ti(1)–O(012)–Ti(1a)	100.3(2)
C(6)–O(7)–C(8)	114.7(4)	C(3)–O(4)–C(5)	118.5(4)
Cl(1)–Ti(1)–O(012)	96.5(1)	C(9)–O(10)–C(11)	113.0(4)

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

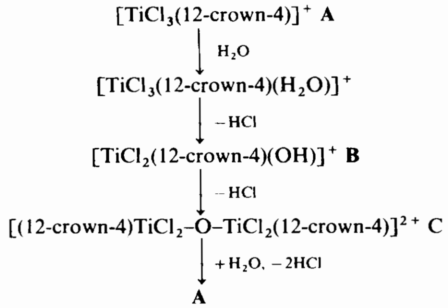
Results and Discussion

The structure of $[\{\mathrm{TiCl}(\mu\text{-O})(12\text{-crown-}4)\}_2][\mathrm{SbCl}_6]_2\cdot 2\mathrm{CH}_2\mathrm{Cl}_2$ **1** consists of a discrete dinuclear oxo-bridged titanium(IV) cation, two octahedral $SbCl_6^-$ counter anions and two molecules of CH_2Cl_2 trapped as lattice solvate. Fig. 1 shows the structure of the cation $[\{\mathrm{TiCl}(\mu\text{-O})(12\text{-crown-}4)\}_2]^{2+}$ with the atom labelling used. Relevant bond lengths and angles are listed in Table 2. The essential features are a planar Ti_2O_2 core unit with tetradentate O chelation of a crown ether macrocycle to each of the titanium atoms. Each metal centre is seven-coordinate and the Ti • • • Ti separation distance is 2.789(2) Å. The $\mathrm{Ti{-}O_{crown}}$ distances range between 2.121(4) and 2.237(4) Å, mean 2.242 (Å), *cf.* 2.102(4) and 2.138(4) Å in $\mathrm{TiCl_4}\cdot$18-crown-6[4] and 2.123(8) and 2.154(9) Å in $\mathrm{TiCl_3(H_2O)}\cdot$18-crown-6$\cdot\mathrm{CH_2Cl_2}$,[5] whereas the $\mathrm{Ti{-}O_{core}}$ distances 1.823(4) and 1.811(3) Å, mean 1.817 Å, are significantly shorter as a reflection of multiple-bond formation with the anionic bridging oxygen atoms (formally O^{2-}). There are relatively few examples of complexes which feature a discrete core $\mathrm{Ti_2(\mu\text{-}O)_2}$ unit, *viz.*, $[\{\mathrm{Ti(acac)_2(\mu\text{-}O)}\}_2]$ **2** (acac = acetylacetonate),[11] $\mathrm{K_4[Ti(O_2C_6H_4)_2(\mu\text{-}O)]_2\cdot 9H_2O}$ **3**,[12] $[\{\mathrm{Ti(OC_6H_3Pr^i{}_2\text{-}2,6)_2(NC_5H_4NC_4H_8\text{-}4)(\mu\text{-}O)}\}_2]$ **4**,[13] $[\{\mathrm{TiCl[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4](\mu\text{-}O)}\}_2]$ **5**,[14] $[\{\mathrm{TiCl(\sigma{:}\eta^5\text{-}C_5H_4CMe_2C_5H_4N)(\mu\text{-}O)}\}_2]\cdot 2\mathrm{CH_2Cl_2}$ **6**[15] and $[\{\mathrm{Ti(\eta^5\text{-}C_5Me_5)}\}_2(\mu\text{-O})_2(\sigma{:}\eta^5\text{-}\mathrm{C_5Me_4CH_2})]$ **7**.[16] The bond distances and angles of the $\mathrm{Ti_2(\mu\text{-}O)_2}$ core units in these compounds are listed in Table 3.

In compounds **1**–**5** the central Ti_2O_2 unit is exactly planar [in **1** this coplanarity is extended to include an oxygen atom O(4) and O(4a) in each crown] and there is only a very small distortion from a perfect square array. The remarkable similarity in these dimensions, despite the variation in co-ordination number of $\mathrm{Ti^{IV}}$ from four in **5** to seven in **1**, not only

Table 3 Dimensions of the core $Ti_2(\mu\text{-}O)_2$ unit in complexes **1**–**7**

Compound	Metal co-ordination number	Ti–O (Å)	Ti • • • Ti (Å)	O–Ti–O (°)	Ti–O–Ti (°)	Ref.
1 (planar)	7	1.823(4) 1.811(3)	2.789(2)	79.7(2)	100.3(2)	This work
2 (planar)	6	1.824(4) 1.831(3)	2.729(1)	83.4(8)	96.6(2)	11
3 (planar)	6	1.859(1) 1.876(1)	2.819(1)	82.0(1)	98.0(1)	12
4 (planar)	5	1.865(2) 1.829(2)	2.796(1)	81.6(1)	98.4(1)	13
5 (planar)	4	1.814(1) 1.835(1)	2.707(0)	84.23(3)	95.78(3)	14
6 (non-planar)	5	1.791(3) 1.910(2)	2.801(1)			15
7 (non-planar)	4	1.961(3) 1.787(3)	2.724(1)	79.9(2)	93.1(1)	16



$$\begin{array}{c} [TiCl_3(12\text{-crown-}4)]^+\ \mathbf{A} \\ \downarrow{\scriptstyle H_2O} \\ [TiCl_3(12\text{-crown-}4)(H_2O)]^+ \\ \downarrow{\scriptstyle -HCl} \\ [TiCl_2(12\text{-crown-}4)(OH)]^+\ \mathbf{B} \\ \downarrow{\scriptstyle -HCl} \\ [(12\text{-crown-}4)TiCl_2\text{–}O\text{–}TiCl_2(12\text{-crown-}4)]^{2+}\ \mathbf{C} \\ \downarrow{\scriptstyle +H_2O,\ -2HCl} \\ \mathbf{A} \end{array}$$

Scheme 1

demonstrates the underlying rigidity of such a unit but also provides a standard geometry, *viz.* Ti–O 1.81–1.88 Å, OTiO 80–84° and TiOTi 96–100°. The non-planar and unsymmetrical arrangement of the Ti_2O_2 unit in **7** is most likely induced by the supporting methylenic $\sigma:\eta^5\text{-}C_5Me_4CH_2$ bridging ligand. Although the observed metal–metal distances in these d^0 systems **1**–**5**, mean 2.768 Å, are within the 'bonding distance' criterion of a Ti–Ti single bond, *cf.* 2.764–2.954,[17] they must be non-bonded interactions resulting from the constraints imposed by the rigid Ti_2O_2 ring.

The co-ordination geometry of the titanium atoms in complex **1** is best viewed as a 4:3 arrangement[18] involving the four oxygen atoms of the crown and the chlorine plus two bridging oxygen atoms respectively. A least-squares plane through the four oxygen atoms of the oxacrown shows a regular zig-zag puckering of the ring with deviations O(1) −0.2434, O(4) +0.2595, O(7) −0.2430 and O(10) +0.2268 Å (mean 0.2432 Å). The titanium atom is located at a distance of 1.3520 Å from this plane and at 1.1092 Å from the plane defined by Cl(1), O(012), O(012a). The dihedral angle is 7.2°. The conformation adopted by the crown ether results in quite severe staggering of the methylene hydrogens as witnessed by the torsion angles about the C–C bonds (41.2, −44.5, −49.1, 47.8°). The same 4:3 metal geometry is observed in the half-sandwich structures $MCl_3\cdot 12$-crown-4 (M = As, Sb or Bi) but here the four oxygen atoms of the crown are precisely coplanar; typically for M = Bi the four C–C torsion angles are 50.0, 39.2, 43.1, 45.0°.[19] The $SbCl_6^-$ anions are unexceptional with regular octahedral co-ordination around Sb atoms, Sb–Cl 2.333(2)–2.376(2), mean 2.359 Å, ClSbCl mean 90.0 and 178.7°.

Formation of complex **1** from the reaction of $[TiCl_3(MeCN)_3][SbCl_6]$ and 12-crown-4 can be rationalised in terms of a hydrolysis sequence starting from an (assumed) initial adduct $[TiCl_3(12\text{-crown-}4)][SbCl_6]$ (Scheme 1). Despite our rigorous drying procedures, partial contamination of solvents must be regarded as the most likely source of trace amounts of water. Why the dinuclear complex **C** was not obtained is unclear especially since the linear $Ti_2(\mu\text{-}O)$ unit is a common product in titanoxane chemistry particularly where the titanium atoms carry at least one bulky substituent such as the pentamethylcyclopentadienyl (and related) groups.[20] As a case in point, Okuda and Herdtweck[14] report that controlled hydrolysis of $[TiCl_3R]$ provides both $[RCl_2Ti(\mu\text{-}O)TiCl_2R]$ and $[RClTi(\mu\text{-}O)_2TiClR]$ for the extremely bulky ligands R = $\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4$ and $\eta^5\text{-}C_5H_2Bu^n(SiMe_3)_2\text{-}1,2,4$. On the other hand the complex $TiCl_3(H_2O)\cdot 18$-crown-$6\cdot CH_2Cl_2$ (bidentate mode) actually crystallises with a stray molecule of water co-ordinated to the Ti^{III}. The fact that this water molecule is involved in auxiliary weak hydrogen bonding to three of the remaining oxygen atoms of the 18-crown-6 when taken in conjunction with the decreased reactivity (polarity) of a Ti^{III}–Cl *vs.* a Ti^{IV}–Cl bond evidently inhibits HCl expulsion. Presumably, in our case, the cationic nature of the titanium(IV) centres in **C** enhances further nucleophilic (H_2O) attack which, in the presence of a limited (critical) amount of water, leads directly to complex **1**. The possibility that yet further controlled hydrolysis of **1** could open up a route to condensed oxacrown titanoxanes incorporating multi-component $Ti_n(\mu\text{-}O)_m$ units, *cf.* $[\{Ti(\eta^5\text{-}C_5Me_5)Br(\mu\text{-}O)\}_3]$,[21] $[\{Ti(\eta^5\text{-}C_5H_5)Cl(\mu\text{-}O)\}_4]$,[22] $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu\text{-}O)_6]$,[23] *etc.*, has been investigated but forms only hydrated titanium oxide and other intractable residues.

Acknowledgements

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