

Crown ether complexes of titanium(IV) chloride and bromide and the structures of the hydrolysis products $[\text{Ti}_2\text{Cl}_6(\mu\text{-O})(18\text{-crown-6})_2]$ and $[\text{Ti}_4\text{Cl}_8(\mu\text{-O})_4(15\text{-crown-5})_4]$

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Received 11th October 2002, Accepted 26th November 2002

First published as an Advance Article on the web 6th January 2003

The titanium(IV) complexes of 12-crown-4, 15-crown-5 and 18-crown-6 and of 1,4-dithia-7,10,13-trioxacyclopentadecane (L') of type $[\text{TiX}_4(\eta^2\text{-L})]$ ($X = \text{Cl}$ or Br , $L = 15\text{-crown-5}$ or 18-crown-6 ; $X = \text{Br}$, $L = 12\text{-crown-4}$) and $[\text{TiCl}_4(L')]$ have been prepared from TiX_4 and the ligands in anhydrous toluene, and characterised by analysis, IR, UV-visible and ^1H NMR spectroscopy. Complexes with TiI_4 do not form under similar conditions. The $[\text{TiCl}_4(L')]$ complex contains the thia-oxa-crown coordinated *via* sulfur to the titanium. The complexes are extremely readily hydrolysed and examples of the first two stages of the hydrolysis have been characterised by X-ray crystallography. These are the dimer $[(18\text{-crown-6})\text{Cl}_3\text{Ti}(\mu\text{-O})\text{TiCl}_3(18\text{-crown-6})]$ which contains a single non-linear oxo-bridge linking two six-coordinate titanium centres also coordinated η^2 to 18-crown-6 and to three (*mer*) chlorines. The second product is the tetrameric $[\{\text{TiOCl}_2(15\text{-crown-5})\}_4]$ in which there is an eight-membered ring composed of alternating Ti and O, each titanium also coordinated η^2 to 15-crown-5 and two terminal (*cis*) chlorines.

Introduction

Crown ether ligands form stable complexes with many hard metal ions, the best known examples being with alkali and alkaline earth metals. However, there are also examples with oxophilic metal centres such as early transition metals in medium and high oxidation states.¹ Few titanium complexes have been characterised, but these include: $[\text{Ti}^{\text{IV}}\text{Cl}_3(15\text{-crown-5})(\text{MeCN})][\text{SbCl}_6]$ (six-coordinate Ti with a Cl_3NO_2 donor set);² $[\text{Ti}^{\text{III}}\text{Cl}_3(\text{H}_2\text{O})(18\text{-crown-6})]$ (six-coordinate Ti; Cl_3O_3);³ and $[\text{Ti}^{\text{IV}}\text{Cl}_4(18\text{-crown-6})]$ (six-coordinate Ti; Cl_4O_2);⁴ and the hydrolysis product $[\{\text{Ti}^{\text{IV}}\text{ClO}(12\text{-crown-4})\}_2][\text{SbCl}_6]_2$ [seven-coordinate Ti; $\text{ClO}_4(\mu\text{-O})_2$].⁵

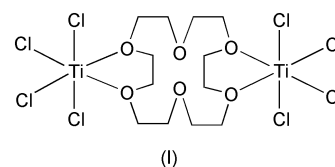
Here we report the synthesis and characterisation of complexes of TiCl_4 and TiBr_4 with the three crown ethers, 12-crown-4, 15-crown-5 and 18-crown-6, and one thia-oxa-crown [15]ane S_2O_3 (1,4-dithia-7,10,13-trioxacyclopentadecane), and the structures of two products representing different stages of hydrolysis.

Results and discussion

Tetrahalotitanium(IV) complexes

The reaction of TiCl_4 with 18-crown-6 or 15-crown-5 in a 1 : 1 mol ratio in toluene under rigorously anhydrous conditions produced yellow $[\text{TiCl}_4(\text{crown})]$. Anhydrous hexane can also be used as solvent, but the poor solubility of both the crowns and the products makes it more difficult to obtain pure complexes from this solvent. The structure of $[\text{TiCl}_4(\eta^2\text{-18-crown-6})]$ was reported by Bott *et al.*⁴ and shown to contain a distorted octahedral titanium centre with the crown ether coordinated *via* two neighbouring oxygens. No other data were given, but we have confirmed that we obtained the same compound by comparing the PXRD pattern of our product with a simulated pattern calculated from the single crystal X-ray data. The far-IR spectra of the complexes show very strong broad bands in the region $400\text{--}380\text{ cm}^{-1}$ assigned to terminal $\nu(\text{Ti}\text{--}\text{Cl})$ modes (theory $4: 2a_1 + b_1 + b_2$).^{6,7} In anhydrous CD_2Cl_2 the ^1H NMR spectra at 300 K (Experimental section) show overlapping multiplets at δ 4.23–5.00 which can be assigned to the CH_2 groups next to the coordinated ether oxygens, and several features at lower frequencies due to CH_2 groups adjacent to the uncoordinated ether functions. The spectra are unchanged on

cooling to 220 K, showing that neither dissociation nor fast exchange between “free” and coordinated ether groups is occurring. Wet solvents discharge the yellow colour immediately, producing a white precipitate and the supernatant solution has a singlet at δ 3.6 in the ^1H NMR spectrum, typical of the “free” crown. Addition of TiCl_4 to a solution of $[\text{TiCl}_4(\eta^2\text{-18-crown-6})]$ in CD_2Cl_2 results in precipitation of a bright yellow solid of composition $[\text{Ti}_2\text{Cl}_8(18\text{-crown-6})]$, which shows terminal $\nu(\text{Ti}\text{--}\text{Cl})$ modes at 383 and 397 cm^{-1} . The complex is poorly soluble in CH_2Cl_2 but the ^1H NMR spectrum is simpler than that of the 1 : 1 complex, showing only three CH_2 regions with patterns of equal intensities, consistent with the structure (I).



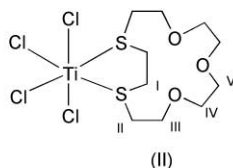
The yellow colours are derived from a broad feature in the UV/visible spectrum (diffuse reflectance, DR) at *ca.* 28000 cm^{-1} assigned as $\pi(\text{Cl}) \rightarrow t_{2g}(\text{Ti})$.⁶ Similar reactions of TiBr_4 with 18-crown-6, 15-crown-5 or 12-crown-4 in a 1 : 1 ratio in toluene produced orange $[\text{TiBr}_4(\text{crown})]$ which are analogous to the chloride complexes with $\nu(\text{Ti}\text{--}\text{Br})$ at $320\text{--}280\text{ cm}^{-1}$ and $\pi(\text{Br}) \rightarrow t_{2g}(\text{Ti})$ at *ca.* 22000 cm^{-1} .⁶ The bromides differ in that in CD_2Cl_2 solution the ^1H NMR spectra at 300 K show broad CH_2 resonances to high frequency of those in the free crown indicative of rapid exchange processes, and even at 220 K little change in the spectra was evident. Attempts to prepare crown ether adducts of TiI_4 by a similar method were unsuccessful.

The yellow $[\text{TiCl}_4([\text{15}]ane\text{S}_2\text{O}_3)]$ was made from the constituents in toluene and was generally similar in properties to the 15-crown-5 analogue. The chief point of interest was whether the [15]ane S_2O_3 was coordinated to the titanium *via* O or S. We have been unable to grow X-ray quality crystals of this poorly soluble complex, but the UV/visible spectrum of the solid shows features at 27500 and 22000 cm^{-1} which are readily assigned as $\pi(\text{Cl}) \rightarrow t_{2g}(\text{Ti})$ and $\pi(\text{S}) \rightarrow t_{2g}(\text{Ti})$ by comparison with the spectrum of $[\text{TiCl}_4(\text{MeSCH}_2\text{CH}_2\text{SMe})]$.⁷ This clearly shows that S–Ti bonds are present and hence either S,S or S,O coordination of the [15]ane S_2O_3 . The ^1H NMR spectrum of

Table 1 Selected bond lengths (Å) and angles (°) for [Ti₂Cl₆(μ-O)(18-crown-6)₂]^{1/2}C₇H₈

Ti(1)–O(13)	1.7993(12)	Ti(1)–O(1)	2.1860(13)
Ti(1)–O(2)	2.1004(12)	Ti(1)–Cl(1)	2.2893(5)
Ti(1)–Cl(2)	2.2582(5)	Ti(1)–Cl(3)	2.3329(5)
Ti(2)–O(13)	1.7948(12)	Ti(2)–O(7)	2.1334(13)
Ti(2)–O(8)	2.1856(12)	Ti(2)–Cl(4)	2.2551(5)
Ti(2)–Cl(5)	2.3077(5)	Ti(2)–Cl(6)	2.3199(5)
Ti(1)–O(13)–Ti(2)	167.75(8)	O(13)–Ti(1)–O(2)	94.50(5)
O(13)–Ti(1)–O(1)	168.28(5)	O(1)–Ti(1)–O(2)	73.95(5)
O(13)–Ti(1)–Cl(2)	99.32(4)	O(13)–Ti(1)–Cl(1)	95.55(4)
O(13)–Ti(1)–Cl(3)	93.49(4)	O(2)–Ti(1)–Cl(2)	166.18(4)
O(1)–Ti(1)–Cl(2)	92.23(4)	O(1)–Ti(1)–Cl(1)	85.78(4)
O(2)–Ti(1)–Cl(3)	85.26(4)	Cl(2)–Ti(1)–Cl(1)	92.78(2)
O(1)–Ti(1)–Cl(3)	83.78(4)	Cl(2)–Ti(1)–Cl(3)	93.54(2)
Cl(1)–Ti(1)–Cl(3)	167.99(2)	O(13)–Ti(2)–O(7)	95.70(5)
O(13)–Ti(2)–O(8)	170.17(5)	O(7)–Ti(2)–O(8)	74.54(5)
O(13)–Ti(2)–Cl(4)	99.98(4)	O(7)–Ti(2)–Cl(4)	164.30(4)
O(8)–Ti(2)–Cl(4)	89.80(4)	O(13)–Ti(2)–Cl(5)	93.85(4)
O(7)–Ti(2)–Cl(5)	83.81(4)	O(8)–Ti(2)–Cl(5)	86.34(4)
Cl(4)–Ti(2)–Cl(5)	94.24(2)	O(13)–Ti(2)–Cl(6)	92.21(4)
O(7)–Ti(2)–Cl(6)	84.68(4)	O(8)–Ti(2)–Cl(6)	85.83(4)
Cl(4)–Ti(2)–Cl(6)	95.50(2)	Cl(5)–Ti(2)–Cl(6)	167.46(2)

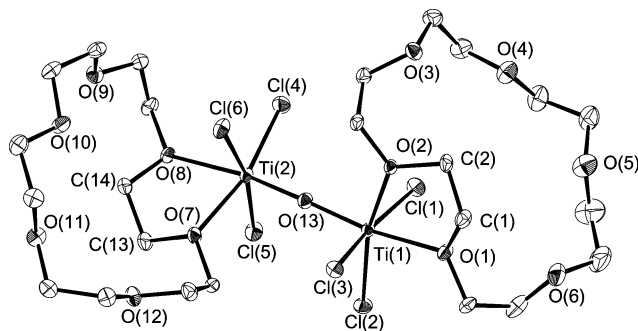
[TiCl₄([15]aneS₂O₃)] shows the CH₂S resonances in the “free” ligand at δ 2.72 and 2.90 have shifted to 2.98 and 3.20 in the complex and overall five distinct CH₂ groups are present, indicating S,S coordination (structure II).



Although Ti(IV) is usually classed as a hard acid, it complexes readily with phosphorus, arsenic,⁶ sulfur and selenium⁷ ligands. The case of [15]aneS₂O₃ is particularly interesting since the titanium is given the choice of O versus S in identical environments, and evidently prefers S.

Hydrolysis products

The [TiX₄(crown)] complexes are hydrolytically very unstable, even traces of water in organic solvents or brief exposure to the atmosphere is sufficient to cause hydrolysis. During an attempt to obtain a crystal of [TiCl₄(18-crown-6)] from toluene solution by slow evaporation in a glove-box, a few pale yellow crystals were obtained which proved to be [(18-crown-6)Cl₃Ti(μ-O)TiCl₃(18-crown-6)]^{1/2}C₇H₈. The structure is shown in Fig. 1 with selected bond lengths and angles in Table 1. The structure consists of a discrete species containing two titaniums linked by a single, non-linear oxygen bridge, with each titanium also coordinated to an η²-bound 18-crown-6 and three chlorines in a

**Fig. 1** View of the structure of [(18-crown-6)Cl₃Ti(μ-O)TiCl₃(18-crown-6)] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity.**Table 2** Selected bond lengths (Å) and angles (°) for [Ti₄Cl₈(μ-O)₄(15-crown-5)₄]^{1/2}·4C₇H₈·2H₂O

Ti(1)–O(6)	1.690(5)	Ti(1)–O(6*)	2.001(5)
Ti(1)–O(1)	2.244(5)	Ti(1)–O(5)	2.117(5)
Ti(1)–Cl(1)	2.351(2)	Ti(1)–Cl(2)	2.312(2)
Ti(1)–O(6)–Ti(1*)	169.2(3)	O(6)–Ti(1)–O(6*)	94.3(3)
O(5)–Ti(1)–O(6)	96.4(2)	O(5)–Ti(1)–O(6*)	83.9(2)
O(6)–Ti(1)–O(1)	169.1(2)	O(6*)–Ti(1)–O(1)	82.3(2)
O(5)–Ti(1)–O(1)	73.0(2)	O(6)–Ti(1)–Cl(2)	102.7(2)
O(6*)–Ti(1)–Cl(2)	91.1(2)	O(5)–Ti(1)–Cl(2)	160.6(2)
O(1)–Ti(1)–Cl(2)	87.7(2)	O(6)–Ti(1)–Cl(1)	95.6(2)
O(6*)–Ti(1)–Cl(1)	168.4(2)	O(5)–Ti(1)–Cl(1)	89.1(2)
O(1)–Ti(1)–Cl(1)	86.9(2)	Cl(1)–Ti(1)–Cl(2)	92.6(1)

Symmetry operation: * = 1 – y, x – 1/2, –z.

mer arrangement. The Ti–O–Ti linkage is well established in Ti(IV) chemistry.^{8–13} The *d*(Ti–O) and Ti–O–Ti angle in the present case [1.7993(12), 1.7948(12) Å; 167.75(8)°] may be compared with those in [(thf)₂Cl₃Ti(μ-O)TiCl₃(thf)₂]¹³ (1.787 Å and 176.7°), [(MeSCH₂CH₂SMc)Cl₃Ti(μ-O)TiCl₃(MeSCH₂CH₂SMc)]⁶ [1.788(1) Å and 180.0°], or two isomers of [TiCl₄(MeCN)₂(μ-O)]^{2–9,12} [1.774 (av.), 1.804(1) Å; 174.7(3), 180.0°]. The *d*(Ti–O_{crown}) are longer [2.1004(12)–2.1860(13) Å] than the *d*(Ti–O_{Ti}) suggesting that the latter may have some degree of multiple bond character. The *d*(Ti–Cl_{trans-Cl}) [2.2893(5)–2.3329(5) Å] are significantly longer than *d*[Ti–Cl_{trans-O(crown)}] [2.2582(5), 2.2551(5) Å], a pattern also found in [TiCl₄(18-crown-6)].⁴ The geometry at the titanium is distorted octahedral with ∠Cl–Ti–Cl somewhat greater than 90° and within the five-membered chelate rings ∠O–Ti–O much smaller [73.95(5), 74.54(5)°].

We were able to obtain a bulk sample of the dimer complex from the prolonged reaction (48 h) of TiCl₄ and 18-crown-6 in toluene (short reaction times normally yields [TiCl₄(18-crown-6)] above). The spectroscopic properties of the oxo-bridged dimer are generally similar to those of [TiCl₄(18-crown-6)], among the few notable differences for the former are the ν(Ti–Cl) at 394 and 366 cm⁻¹. Attempts to identify the ν(Ti–O–Ti) vibrations were complicated by vibrations of the crown ether occurring in the same region. The Ti–O–Ti angle (168°) means that ν_{sym} will be very weak in the infrared, but ν_{asym} is tentatively assigned as the medium intensity feature at 775 cm⁻¹, which compares with 762 cm⁻¹ in [η⁵-C₅H₂(SiMe₃)₃]₂Ti₂Cl₄(μ-O),⁸ and 786 cm⁻¹ in [TiCl₄(MeCN)₂(μ-O)]^{2–9}.

Adventitious hydrolysis of [TiCl₄(15-crown-5)], when a solution in toluene was allowed to evaporate in a glove box, proceeded a stage further, producing crystals of the tetramer [TiOCl₂(15-crown-5)]₄. We were not able to obtain a bulk sample of this material. The molecule (Table 2, Fig. 2) which has S₄ symmetry, consists of a near planar eight-membered ring of alternating Ti and O atoms. The titaniums are at the corners of a square with single asymmetric, non-linear (169°) oxygen bridges. The geometry at the titanium is close to octahedral, composed of two *cis* chlorines, a chelating crown ether and two bridging oxygens. The *d*(Ti–O_{Ti}) are markedly different; Ti–O(6) which is *trans* to an ether oxygen is short [1.690(5) Å] whilst Ti–O(6*) which is *trans* to a chlorine is much longer [2.001(5) Å], indicating the strong *trans* influence of chlorine in these systems. As observed in the dimer described above, the *d*(Ti–O_{crown}) distances are longer again [Ti–O_{trans-O} = 2.244(5), Ti–O_{trans-Cl} = 2.117(5) Å]. These data clearly show that the *trans* influence of the various donors on Ti(IV) is O(oxide) > Cl > O(ether). The disparate *d*(Ti–O) distances in the bridge are atypical of Ti–O–Ti linkages in general^{9–12} which in the majority of cases are broadly symmetrical, but was observed in [TiOCl₂(MeCN)₂]₄⁹ which has a similar structure with MeCN replacing the crown ether oxygens.

Repeated attempts to isolate a TiCl₄ complex with 12-crown-4 were unsuccessful; initial precipitation of a yellow solid

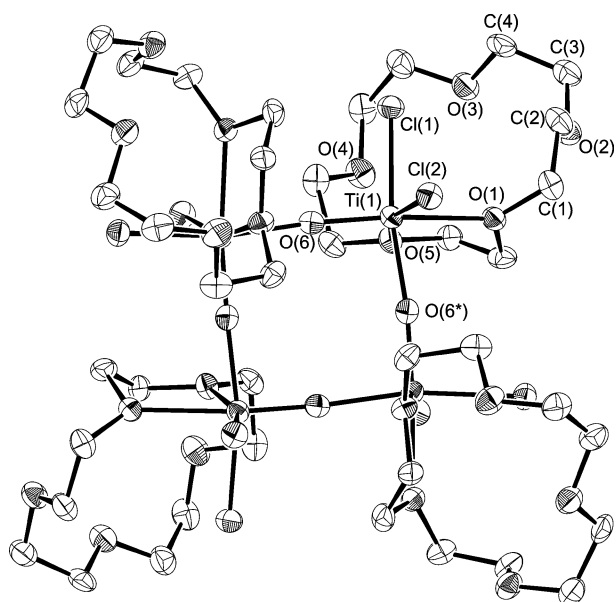


Fig. 2 View of the structure of the tetrameric $[\text{Ti}_4\text{Cl}_8(\mu\text{-O})_4(15\text{-crown-5})_4]$ with numbering scheme adopted. Ellipsoids are shown at the 40% probability level and H atoms are omitted for clarity. Symmetry operation: $* = 1 - y, x - 1/2, -z$.

occurred but this turned white rapidly on standing in the mother liquor or during drying *in vacuo*. Several samples of this material were prepared and analyses suggested the composition was probably $[\text{Ti}_2\text{Cl}_6\text{O}(12\text{-crown-4})_2]$. It is unclear why the $\text{TiCl}_4/12\text{-crown-4}$ system is so prone to hydrolysis, particularly as $[\text{TiBr}_4(12\text{-crown-4})]$ was isolated without problems. A complex $\{[\text{TiCl}(\mu\text{-O})(12\text{-crown-4})]_2[\text{SbCl}_6]_2\}$ has been obtained by hydrolysis of a mixture of $[\text{TiCl}_3(\text{MeCN})_3][\text{SbCl}_6]$ and 12-crown-4 in MeCN and contains a planar Ti–O–Ti–O ring with each titanium bonded to all four oxygens of a 12-crown-4 ligand.⁵

Conclusions

We have shown that the initial products of reaction of TiX_4 ($X = \text{Cl}$ or Br) with simple crowns are six-coordinate $[\text{TiX}_4(\eta^2\text{-crown})]$. These are very sensitive to hydrolysis, and the two structures reported show the first and second stage hydrolysis products. Replacement of one chlorine/Ti results in the oxo-bridged dimer $[(18\text{-crown-6})\text{Cl}_3\text{Ti}(\mu\text{-O})\text{TiCl}_3(18\text{-crown-6})]$, whilst the replacement of two chlorines/Ti affords a tetramer $[\{\text{TiOCl}_2(15\text{-crown-5})\}_4]$, the common structural motif being the titaniums linked by oxo-bridges and the remaining coordination sites filled by terminal chlorines and bidentate crown ethers. The further stage of hydrolysis would be of stoichiometry $\text{Ti}_2\text{Cl}_2(\mu\text{-O})_3(\text{crown})_2$ and, to retain the “linear” Ti–O–Ti connectivity, may be octa-nuclear with titanium situated at the corners of a cube. A precedent is the $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]^{8+}$,¹⁴ a hydrolysis product of TiCl_4 . It is also notable that the hydrolysis proceeds by O/Cl replacement, whereas for the preceding element scandium, we find¹⁵ that in the hydrolysis of $[\text{Sc}(\text{crown})\text{Cl}_3]^{(3-x)+}$ water displaces the crown to produce $[\text{ScCl}_3(\text{H}_2\text{O})_3]$, the displaced crown being hydrogen bonded (secondary coordination) to the scandium-bound water. The major difference may be that the highly polarising Ti(IV) prefers the oxo-group coordination with its possibility for π -interaction, whereas the larger and less highly charged scandium is compatible with aquo-ligands

Experimental

Titanium halides were obtained from Aldrich and used as received. The crown ethers were obtained commercially and dried *in vacuo* or by treatment with SOCl_2 before use. The

$[\text{15}] \text{aneS}_2\text{O}_3$ was made by the literature method.¹⁶ Physical measurements were made as described previously.^{6,7} All syntheses were carried out in freshly distilled solvents, previously dried by refluxing over sodium (toluene, hexane) or CaH_2 (CH_2Cl_2), under a dinitrogen atmosphere using Schlenk and vacuum line techniques. Solid samples were handled and stored in a glove box (< 5 ppm H_2O).

Synthesis

$[\text{TiCl}_4(18\text{-crown-6})]$. A stirred solution of 18-crown-6 (0.26 g, 1.0 mmol) in toluene (10 cm^3) was treated dropwise with TiCl_4 (0.19 g, 1.0 mmol) resulting in a yellow precipitate. The mixture was stirred for 30 min, filtered, and the yellow solid washed with *n*-hexane (10 cm^3). The solid was dried *in vacuo*. Yield 0.095 g (42%). IR (Nujol)/ cm^{-1} : 1303w, 1261w, 1208w, 1168m, 1144s, 1134m, 1073m, 1037s, 972m, 932m, 901m, 842m, 804m, 733m, 566w, 467w, 377br,s. UV/Vis. DR(BaSO_4)/ cm^{-1} : 28000. ^1H NMR (CD_2Cl_2) 300 K: δ 3.60, 3.76 (overlapping) [12H], 4.00 [4H], 4.23–4.60 [8H]; 220 K: no change.

$[(\text{TiCl}_4)_2(18\text{-crown-6})]$. Was made similarly to the above using a 2 : 1 mol. ratio of TiCl_4 : 18-crown-6 in CH_2Cl_2 . Yield 70%. (Found: C, 20.4; H, 4.0. Calc. for $\text{C}_{12}\text{H}_{24}\text{Cl}_8\text{O}_6\text{Ti}_2$: C, 21.7; H, 3.6%). IR (Nujol)/ cm^{-1} : 1300m, 1272w, 1249w, 1169w, 1144s, 1131m, 1068s, 1033s, 932m, 918m, 839m, 804m, 781m, 565w, 397vs, 383br,vs. UV/Vis. DR(BaSO_4)/ cm^{-1} : 28000. ^1H NMR (CD_2Cl_2) 300 K: δ 3.70 [8H], 4.00 [8H], 4.52 [8H]; 200 K: 3.3–4.5 very complex pattern.

$[\text{Ti}_2\text{Cl}_6(\text{O})(18\text{-crown-6})_2]$. Was made essentially as described for $[\text{TiCl}_4(18\text{-crown-6})]$ except that the reaction mixture was stirred under nitrogen for 48 h, resulting in adventitious hydrolysis. Yield 60%. (Found: C, 33.3; H, 5.8. Calc. for $\text{C}_{24}\text{H}_{48}\text{Cl}_6\text{O}_{13}\text{Ti}_2$: C, 33.8; H, 5.6%). IR (Nujol)/ cm^{-1} : 1303w, 1260w, 1250w, 1142, 1121w, 1098m, 1081s, 1037m, 1020s, 942s, 917m, 894m, 851m, 828w, 775m, 540m, 439w, 394s, 366s, 307m. UV/Vis. DR(BaSO_4)/ cm^{-1} : 28600. ^1H NMR (CD_2Cl_2) 300 K: δ 3.60, 3.65 (overlapping) [12H], 3.99 [4H], 4.43–4.70 [8H]; 200 K: 3.42, 3.49, 3.77, 4.50, 4.53.

$[\text{TiBr}_4(18\text{-crown-6})]$. A solution of TiBr_4 (0.19 g, 0.5 mmol) in toluene (10 cm^3) was treated with 18-crown-6 (0.13 g, 0.5 mmol) in toluene (10 cm^3) producing a red-brown precipitate. The solid was filtered off, rinsed with toluene (5 cm^3) and dried *in vacuo*. Yield 60%. (Found: C, 22.6; H, 4.0. Calc. for $\text{C}_{12}\text{H}_{24}\text{Br}_4\text{O}_6\text{Ti}$: C, 22.8; H, 3.8%). IR (Nujol)/ cm^{-1} : 1302m, 1258w, 1168w, 1150m, 1081s, 1039s, 953s, 921w, 891w, 836w, 803w, 770w, 562w, 467sh, 334s, 321s, 312m, 300m. UV/Vis. DR(BaSO_4)/ cm^{-1} : 21000. ^1H NMR (CD_2Cl_2) 300 K: δ 3.72; unchanged at 220 K.

$[\text{TiCl}_4(15\text{-crown-5})]$. Was made similarly to the 18-crown-6 analogue as a yellow powder. Yield 40%. (Found: C, 29.5; H, 5.2. Calc. for $\text{C}_{10}\text{H}_{20}\text{Cl}_4\text{O}_5\text{Ti}$: C, 29.3; H, 4.9%). IR (Nujol)/ cm^{-1} : 1305s, 1261w, 1168w, 1130s, 1062s, 1020w, 978s, 930m, 907m, 848s, 827m, 769w, 565w, 546w, 519w, 430m, 394s, 363s, 339s, 321m. UV/Vis. DR(BaSO_4)/ cm^{-1} : 28,000. ^1H NMR (CD_2Cl_2) 300 K: 3.60 (br) [8H], 4.33 [4H], 4.60[4H], 5.00 [4H]; 220 K: little change on cooling.

$[\text{TiBr}_4(15\text{-crown-5})]$. Was isolated as a brown solid from reaction of the constituents in dry toluene following the method for $[\text{TiBr}_4(18\text{-crown-6})]$. Yield 50%. (Found: C, 20.3; H, 3.6. Calc. for $\text{C}_{10}\text{H}_{20}\text{Br}_4\text{O}_5\text{Ti}$: C, 20.4; H, 3.4%). IR (Nujol)/ cm^{-1} : 1305m, 1260w, 1169m, 1150s, 1138s, 1119s, 1104m, 1013m, 975s, 951s, 921s, 904m, 845s, 821m, 767w, 565w, 544w, 438w, 320s, 282vs. UV/Vis. DR(BaSO_4)/ cm^{-1} : 22,000. ^1H NMR (CD_2Cl_2) 300 K: δ 3.64 (br) [12H], 4.65–5.00 (overlapping) [8H]; 220 K: no change.

Table 3 Crystallographic data

	[Ti ₂ Cl ₆ (μ-O)(18-crown-6) ₂] ^{1/2} C ₇ H ₈	[Ti ₄ Cl ₈ (μ-O) ₄ (15-crown-5) ₄] ^{1/2} C ₇ H ₈ ·2H ₂ O
Formula	C _{27.5} H ₅₂ Cl ₆ O ₁₃ Ti ₂	C ₆₈ H ₁₁₆ Cl ₈ O ₂₆ Ti ₄
<i>M</i>	899.19	1824.8
Crystal system	Triclinic	Tetragonal
Space group	<i>P</i> 1̄ (no. 2)	<i>P</i> 4/n (no. 85)
<i>a</i> /Å	10.2483(5)	20.353(3)
<i>b</i> /Å	13.835(1)	20.353(3)
<i>c</i> /Å	14.721(1)	10.739(2)
<i>α</i> ^o	84.669(3)	90
<i>β</i> ^o	81.909(3)	90
<i>γ</i> ^o	79.892(3)	90
<i>U</i> /Å ³	2029.3(2)	4448.6(12)
<i>Z</i>	2	2
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.844	0.655
Unique reflections	9239	3883
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	8071	1722
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0346	0.0733
<i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0873	0.1671

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$$

[TiCl₄([15]aneS₂O₃)]. A solution of [15]aneS₂O₃ (0.25 g, 1.0 mmol) in toluene (10 cm³) was treated dropwise with TiCl₄ (0.19 g, 1.0 mmol) producing an orange precipitate, which was filtered off, washed with toluene (5 cm³) and dried *in vacuo*. Yield 70%. (Found: C, 26.8; H, 4.8. Calc. for C₁₀H₂₀Cl₄O₃S₂Ti: C, 27.2; H, 4.6%). IR (Nujol)/cm⁻¹: 1303s, 1255w, 1169w, 1155w, 1080m, 1021w, 968m, 933m, 918m, 889s, 848m, 805m, 770m, 566w, 482s, 472m, 409s, 385s, 377s, 353sh. UV/Vis. DR(BaSO₄)/cm⁻¹: 27500, 22000. ¹H NMR (CD₂Cl₂) 300 K: δ 2.98 [4H], 3.20 [4H], 3.61, 3.73 [8H], 3.87 [4H]; 220 K: little change on cooling.

[TiBr₄(12-crown-4)]. Was made as a brown solid following the method described for [TiBr₄(18-crown-6)]. Yield 60%. (Found: C, 17.6; H, 2.8. Calc. for C₈H₁₆Br₄O₄Ti: C, 17.7; H, 3.0%). IR (Nujol)/cm⁻¹: 1303m, 1261w, 1169s, 1151m, 1092m, 1021m, 973s, 936m, 919w, 846m, 821m, 803m, 562w, 416w, 394w, 348w, 321m, 275s, 242m. UV/Vis. DR(BaSO₄)/cm⁻¹: 21700, 25000. ¹H NMR (CD₂Cl₂) 300 K: δ 3.66 (br); 220 K: no change.

X-Ray crystallography

Brief details of the crystallographic data collection and refinement parameters are given in Table 3. Data collection used a Nonius kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) with the crystal held at 120 K. Structure solution and refinement were routine.¹⁷⁻¹⁹ During refinement of the data for [(18-crown-6)-Cl₃Ti(μ-O)TiCl₃(18-crown-6)] a 50% occupied toluene solvent molecule was identified in the asymmetric unit. This is related by a centre of symmetry to another 50% occupied toluene such that the Me carbon on one molecule is essentially superimposed onto a ring carbon of the crystallographically related toluene. Hence only six C atoms were refined, five with occupancies of 1/2, the sixth with an occupancy of 1. One fully occupied toluene solvent molecule (albeit with slightly high thermal parameters) and one 50% occupied H₂O solvent molecule were also identified per Ti centre in the tetrameric [(TiOCl₂(15-crown-5))₄]. Selected bond lengths and angles are presented in Tables 1 and 2.

CCDC reference numbers 195314 (dimer) and 195315 (tetramer).

See <http://www.rsc.org/suppdata/dt/b2/b210012f/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC for support, Dr A. L. Hector for measuring the PXRD data and N. J. Hill for collecting the X-ray data.

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