DALTON
FULL PAPER

Some crown ether chemistry of Ti, Zr and Hf derived from liquid clathrate media

Abbas Alvanipour,[a] Jerry L. Atwood,*[,a] Simon G. Bott,[a] Peter C. Junk,*[,†,b] Ulrich H. Kynast[c] and Horst Prinz[a]

[a] *Department of Chemistry, University of Missouri-Columbia, Columbia, MO, 65211, USA*
[b] *Department of Chemistry, James Cook University of North Queensland, Townsville, Qld, 4811, Australia*
[c] *Fachhochschule Meunster, Abt. Steinfurt, FB Chemieingenieurwesen, 48565, Steinfurt, Germany*

The reaction of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ with HCl(g) in the presence of 18-crown-6 formed the oxonium ion-containing complex $[H_3O^+\cdot\text{18-crown-6}][TiCl_5(H_2O)^-]$ **1**. Its crystal structure shows the oxonium ion resides within the crown ether and has a pyramidal structure. Treatment of $[Ti(\eta\text{-}C_5H_5)Cl_3]$ with $AlMe_3$ in the presence of 18-crown-6 resulted in the formation of the titanium(III) complex $[Ti(\eta\text{-}C_5H_5)Cl^+\cdot\text{18-crown-6}][AlCl_2Me_2]$ **2**. The structure of **2** reveals a cation with a five-co-ordinate Ti where the centroid of the C_5H_5 ring occupies the apex of a square pyramid. The crown ether 18-crown-6 underwent C–O bond scission by treatment with $ZrCl_4$ in the presence of thf (tetrahydrofuran) to form the ring-opened zirconium(IV) co-ordination complex $[ZrCl_2\cdot(OCH_2CH_2)_5OCH_2CH_2Cl^+][ZrCl_5(thf)^-]$ **3**. The structure of **3** shows the formation of a zirconium alkoxide species formed by the ring-opening reaction. The seven-co-ordinate zirconium center has pentagonal-bipyramidal geometry with two chloride atoms in the axial positions. In an analogous reaction, but in the presence of NaCl, $HfCl_4$ formed the ionic complex $[Na^+\cdot\text{18-crown-6}][HfCl_5(thf)^-]$ **4**, which has a structure similar to that of **1**.

Ziegler–Natta catalysts have been a topic of active research for well over 30 years.[1] Indeed, the $AlEt_3 + TiCl_4$ system is still studied, even though it was initiated many years ago. It is known that the generation of the catalytically active species involves both an alkylation and reduction step at the Group IV metal center. In order to gain understanding of well used catalytic systems and to generate new ones the addition of a third component, often an electron donor, has become popular.[2]

Our group has been investigating compounds related to Ziegler–Natta type catalysts in which a Group IV metal species is treated with an alkylaluminium reagent in the presence of a crown ether. Typically, these compounds form liquid clathrate species, and it would be attractive to incorporate a catalytically active complex into a two-phase system for separation purposes. We have gained some interesting results in these systems[3–6] and this prompted us to further investigate the components obtained prior to the reduction step. The compounds obtained may act as models in the hunt for intermediates in the formation of Ziegler–Natta type catalysts and may shed light onto some of the complex chemistry involved in these systems.

As part of our study of liquid clathrate systems[7–9] and more recently of the Group IV–$H_3O^+\cdot$18-crown-6 system,[10–13] we have now investigated the formation of complexes obtained by the interaction between a Group IV halide or organohalide compound and 18-crown-6, typically under rather forcing conditions. Different reaction conditions have been employed and the identity of some of the reaction products has been revealed.

Herein we report the syntheses and crystal structures of the oxonium ion–crown ether-containing complex $[H_3O^+\cdot\text{18-crown-6}][TiCl_5(H_2O)^-]$ **1**, the reduced titanium species $[Ti(\eta\text{-}C_5H_5)Cl^+\cdot\text{18-crown-6}][AlCl_2Me_2^-]$ **2**, the ring-opened complex $[ZrCl_2\cdot(OCH_2CH_2)_5OCH_2CH_2Cl^+][ZrCl_5(thf)^-]$ **3**, and the sodium ion–crown ether-containing complex $[Na^+\cdot\text{18-crown-6}][HfCl_5(thf)^-]$ **4**, which were all isolated from aromatic media. We have previously reported a preliminary account of the structure of compound **2**, where the 18-crown-6 molecule undergoes an interesting ring-opening reaction upon treatment with $ZrCl_4$.[4]

Experimental

The compounds $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$, $[Ti(\eta\text{-}C_5H_5)Cl_3]$, $ZrCl_4$, $HfCl_4$ and 18-crown-6 were obtained from Aldrich Chemical Co. while HCl gas was from Atlas Co. Complex **1** was prepared exposed to air, prior to the reaction mixture being sealed in an air-tight screw-top tube; **2** to **4** were prepared under an inert atmosphere using standard Schlenk techniques. Repeated attempts at obtaining consistent microanalytical data for all compounds were foiled by either their high affinity for moisture and/or loss of solvent.

Preparations

$[H_3O^+\cdot$18-crown-6$][TiCl_5(H_2O)^-]$ 1. To a sample of 18-crown-6 (1.0 g, 3.8 mmol) in toluene was added water (0.072 g, 4.0 mmol) and $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ (1.00 g, 4.0 mmol) and stirred rapidly for 15 min. Hydrogen chloride gas was then rapidly bubbled through the mixture for *ca.* 1 h during UV irradiation. After this time a red liquid clathrate layer separated with a crown : toluene composition of 1 : 2.1 (as determined by ^1H NMR spectroscopy). Bright yellow crystals of complex **1** grew from the liquid clathrate layer after *ca.* 72 h in *ca.* 45% yield, m.p. 130 °C (decomp.).

$[Ti(\eta\text{-}C_5H_5)Cl^+\cdot$18-crown-6$][AlCl_2Me_2^-]$ 2. To a solution of $[Ti(\eta\text{-}C_5H_5)Cl_3]$ (1.1 g, 5.0 mmol) and 18-crown-6 (1.32 g, 5 mmol) in toluene (*ca.* 30 cm^3), was added trimethylaluminum (0.072 g, 1 mmol). An exothermic reaction commenced immediately resulting in a green solution. Colorless crystals of $[AlMe_2^+\cdot\text{18-crown-6}][AlCl_2Me_2^-]$ deposited overnight. These were filtered off, the solution concentrated *in vacuo*, and on standing at 5 °C for 48 h blue crystals of complex **2** were obtained, m.p. 102–104 °C (decomposes above 130 °C).

---

† E-Mail: peter.junk@jcu.edu.au

[$ZrCl_2$·(OCH_2CH_2)$_5OCH_2CH_2Cl^+$][$ZrCl_5$(thf)$^-$] 3. A solution of 18-crown-6 (1.59 g, 6.0 mmol) in toluene was added to a suspension of $ZrCl_4$ (1.40 g, 6.0 mmol) in toluene. Tetrahydrofuran was added up to 15% by volume, and the tube was sealed and heated to 100 °C for 24 h. Upon cooling to room temperature, colorless, air-sensitive crystals of compound **3** formed in *ca.* 25% yield. IR (Nujol mull): 1385m, 1375 (sh), 1355w (crown, thf), 1310m (crown, thf), 1280w (thf), 1255m (crown, thf), 1250 (sh), (crown, thf), 1175w (thf), 1145w (crown), 1120w, 1090m (crown, thf), 1050s (crown), 1010m (thf), 995m (crown), 960m (crown), 940m (crown), 925m (crown), 885w, 840m (crown, thf), 750s (Zr–O–R), 680w (thf), 420w ($ZrCl_2^+$, ν_s) and 300s cm^{-1} (Zr–Cl, anion, ν_s).

[Na^+·18-crown-6][$HfCl_5$(thf)$^-$] 4. A solution of 18-crown-6 (1.59 g, 6.0 mmol) in toluene was added to a suspension of $HfCl_4$ (1.40 g, 6.0 mmol) and NaCl (0.35 g, 6 mmol) in toluene. Tetrahydrofuran (15% by volume) was added, and the tube was sealed and heated to 100 °C for 24 h. Upon cooling to room temperature, colorless, air-sensitive crystals of compound **4** formed in *ca.* 60% yield.

Crystallography

Single crystals of compounds **1** to **4** were sealed in thin-walled glass capillaries. Final lattice parameters as determined from the least-squares refinement of the angular settings of 24 high-angle reflections (2θ > 30°) accurately centered on an Enraf-Nonius CAD4 diffractometer are given in Table 1. A summary of data collection parameters is also given. An empirical absorption correction based on ψ-scan data was performed. Calculations were carried out using the SHELX system of computer programs.[14]

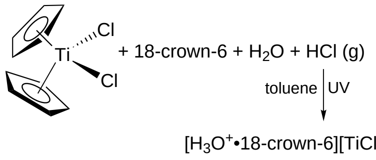
Positions of heavy atoms in all compounds were determined from a three-dimensional Patterson function. All other non-hydrogen atoms were located from a Fourier-difference synthesis. For complex **1** all non-hydrogen atoms were refined with anisotropic thermal parameters. The protons of the H_3O^+ ion and the water molecule were located on the difference map, assigned isotropic thermal parameters and their positions refined. All other hydrogen atoms were placed at calculated positions and their parameters were not refined. For **2** all non-hydrogen atoms, except those of the 18-crown-6 molecule, were refined anisotropically due to limited data. All hydrogen atoms were placed at calculated positions and their parameters were not refined. For **3** all non-hydrogen atoms, except the carbon atoms of the 18-crown-6 and thf molecules (due to limited data and high thermal motion), were refined anisotropically. All hydrogen atoms were placed at calculated positions and their parameters were not refined. For **4** all non-hydrogen atoms, except the carbon atoms of the 18-crown-6 molecule (due to limited data and high thermal motion), were refined anisotropically. All hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinements converged with $R = 0.049$ for 2620 observed reflections for **1**, $R = 0.070$ for 1224 observed reflections for **2**, $R = 0.068$ for 1751 observed reflections for **3** and $R = 0.049$ for 2386 observed reflections for **4**.

CCDC reference number 186/863.

Results

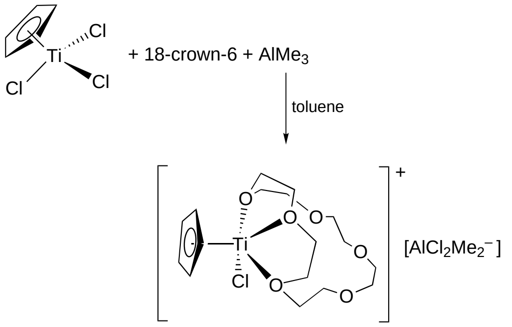
Preparation of complexes

The complexes studied were prepared according to various synthetic procedures represented in Schemes 1 to 3. All the reaction mixtures yielded two phases corresponding to liquid clathrate species. The upper layer was neat toluene, while the metal complexes formed were completely dissolved within the clathrate layer. For **1** the reaction was performed in contact with air, followed by sealing the reaction vessel from aerial contact. For **2**–**4**, the reactions were performed with exclusion of oxygen and moisture using standard Schlenk techniques. Reaction conditions throughout were optimized to yield liquid clathrates and X-ray-quality crystals. To identify the species present in the liquid clathrate layers, all the compounds investigated were structurally authenticated using X-ray crystallography. The complexes were obtained in moderate yields, and no attempts were made to maximize these.



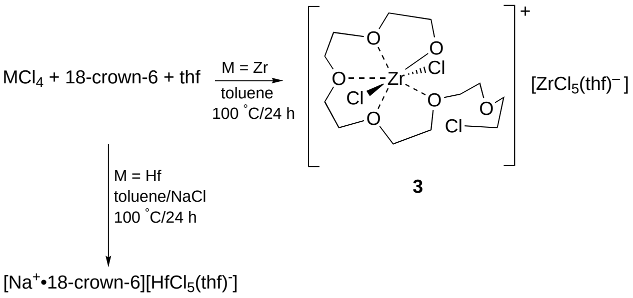
1

Scheme 1



2

Scheme 2



3

4

Scheme 3

Structural results

Selected bond distances and angles for complexes **1**–**4** are shown in Tables 2–5, torsion angles in Table 6.

[H_3O^+·18-crown-6][$TiCl_5(H_2O)^-$] 1. This complex does not crystallize as discrete anions and cations. There are several observable hydrogen-bonded contacts between the water ligand on the titanium atom and either oxygen atoms of the crown ether or chloride ligands of the anion (see Fig. 1).

In the cation the H_3O^+ ion resides close to the center of the macrocyclic ligand and has O (oxonium)···O (crown) distances of 2.68(1) to 2.94(1) Å. The distances from O (oxonium) to the oxygen atoms to which it is hydrogen bonded [O(2), O(4) and O(6)] are slightly shorter than those to which it is not bound [2.68(1) to 2.69(1) Å compared with 2.72(1) to 2.94(1) Å]. The O (oxonium) atom resides 0.51 Å out of the plane defined by O(2), O(4) and O(6), implying a pyramidal conformation for the oxonium ion. It is bound to three protons at distances of 0.87(1), 0.83(1) and 0.76(1) Å respectively and these protons are bound to O(2), O(4) and O(6) at 1.81(1), 2.10(1) and 1.93(1) Å respectively. The O (oxonium)–H–O(2),

Table 1 Crystal data and summary of data collection for complexes **1**–**4** *

	$[H_3O^+\cdot$18-crown-6]-$[TiCl_5(H_2O)^-]$ **1**	$[Ti(\eta$-$C_5H_5)Cl^+\cdot$18-crown-6]-$[AlCl_2Me_2^-]$ **2**	$[ZrCl_2\cdot(OCH_2CH_2)_5OCH_2$-$CH_2Cl^+][ZrCl_5(thf)^-]$ **3**	$[Na^+\cdot$18-crown-6]-$[HfCl_5(thf)^-]$ **4**
Formula	$C_{12}H_{29}Cl_5O_8Ti$	$C_{19}H_{35}AlCl_3O_6Ti$	$C_{16}H_{32}Cl_8O_7Zr_2$	$C_{16}H_{32}Cl_5HfNaO_7$
M	526.5	537.8	802.5	715.2
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	10.217(1)	8.543(5)	7.238(7)	11.003(6)
b/Å	21.978(3)	19.405(9)	13.754(6)	23.482(9)
c/Å	10.511(2)	16.340(9)	16.378(9)	10.739(4)
α/°	—	—	105.52(4)	—
β/°	104.76(1)	101.34(9)	91.17(4)	92.43(8)
γ/°	—	—	98.17(4)	—
U/Å^3	2282	2656	1555	2772
Z	4	4	2	4
D_c/g cm^{-3}	1.538	1.350	1.720	1.720
μ/cm^{-1}	9.96	6.77	13.89	42.77
Scan width/°	0.80 + 0.20 tan θ	0.85 + 0.20 tan θ	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
2θ Range/°	2–50	2–40	2–50	2–44
No. reflections collected	4358	2838	3365	3817
No. observed reflections	2620	1224	1751	2386
No. parameters varied	250	181	218	211
R	0.049	0.070	0.068	0.049
R′	0.051	0.068	0.074	0.053

* Details in common: Mo-Kα radiation (λ = 0.710 73 Å); 3σ cut-off; unit weights; 295 K.

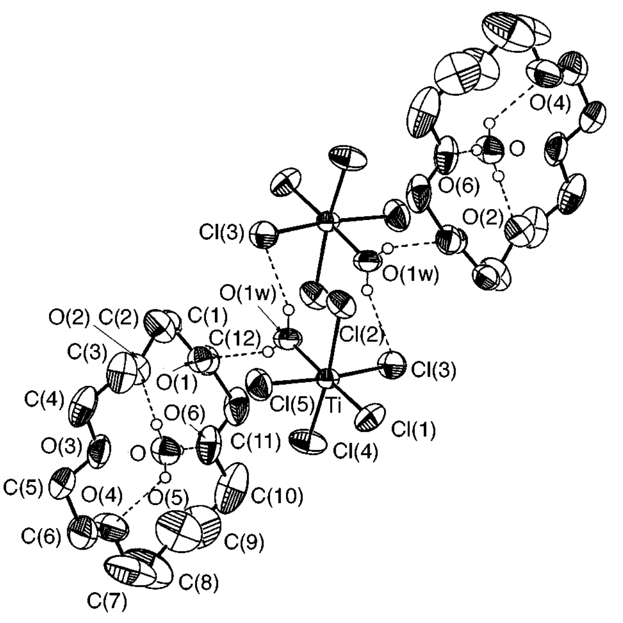


Fig. 1 Structure of $[H_3O^+\cdot$18-crown-6]$[TiCl_5(H_2O)^-]$ **1**, showing the hydrogen bonding between anions and cations. The O (crown) to O(2), O(4) and O(6) distances range from 2.68(1) to 2.69(1) Å. The internuclear hydrogen-bonding contacts are Cl(3) to O(1w) 3.17 and O(1) to O(1w) 2.82(2) Å

Table 2 Selected bond distances (Å) and angles (°) for $[H_3O^+\cdot$18-crown-6]$[TiCl_5(H_2O)^-]$ **1**

Ti–O(1w)	2.138(4)	Ti–Cl(1)	2.205(2)
Ti–Cl(2)	2.337(2)	Ti–Cl(3)	2.366(2)
Ti–Cl(4)	2.280(2)	Ti–Cl(5)	2.299(2)
O···O(2)	2.68(1)	O···O(4)	2.68(1)
O···O(6)	2.69(1)		
O(1w)–Ti–Cl(1)	178.4(1)	Cl(1)–Ti–Cl(2)	95.15(6)
O(1w)–Ti–Cl(2)	83.5(1)	Cl(1)–Ti–Cl(3)	93.61(7)
Cl(2)–Ti–Cl(3)	88.13(6)	O(1w)–Ti–Cl(3)	85.5(2)
Cl(1)–Ti–Cl(4)	96.80(7)	Cl(2)–Ti–Cl(4)	167.83(7)
Cl(3)–Ti–Cl(4)	88.85(7)	O(1w)–Ti–Cl(4)	84.6(1)
Cl(1)–Ti–Cl(5)	94.83(7)	Cl(2)–Ti–Cl(5)	90.31(7)
Cl(3)–Ti–Cl(5)	171.52(7)	Cl(4)–Ti–Cl(5)	90.95(7)
O(1w)–Ti–Cl(5)	86.0(2)		

O (oxonium)–H–O(4) and O (oxonium)–H–O(6) angles are 176.8(1), 128.0(1) and 176.1(1)° respectively.

The average Ti–Cl (equatorial) lengths in the anion are 2.32(3) Å, while Ti–Cl(1), which is the Cl ligand *trans* to the water ligand, is shorter at a distance of 2.205(2) Å. The Ti–O (water) distance is 2.138(4) Å and the Cl(1)–Ti–Cl(2), Cl(1)–Ti–Cl(3), Cl(1)–Ti–Cl(4) and Cl(1)–Ti–Cl(5) angles which average 95(1)° reflect the distortion from regular octahedral stereochemistry, where the equatorial Cl ligands are bent down and away from the axial Cl ligand. The water ligand on the anion also forms a hydrogen bond to O(1) of the crown ether [2.82(1) Å], and there is a relatively weak contact between the water ligand and Cl(3) of an adjacent $[TiCl_5(H_2O)^-]$ anion, where the distance is 3.17(1) Å (see Fig. 1).

$[Ti(\eta$-$C_5H_5)Cl^+\cdot$18-crown-6]$[AlCl_2Me_2^-]$ 2. This complex crystallizes as discrete anions and cations. There are no contacts of less than 3.5 Å between the anions and cations. The five-coordinate $[Ti(\eta$-$C_5H_5)Cl^+\cdot$18-crown-6] cation exists as a square pyramid (or a four-legged piano-stool), where Cl(1), O(1), O(2) and O(3) make up the base of the pyramid and the centroid of the cyclopentadienyl ligand represents the apex (see Fig. 2). The Ti–Cl(1), Ti–O(1), Ti–O(2) and Ti–O(3) distances are 2.340(4), 2.09(1), 2.154(9) and 2.14(1) Å respectively, and these four atoms are coplanar to within 0.04 Å, with the Ti residing 0.87 Å out of the plane. The angle between the planes derived by the four atoms at the base of the pyramid and that of the C_5H_5 ligand is 0.8°, indicating near coplanarity. The cyclopentadienyl centroid–titanium distance is 2.04(1) Å, and centroid–Ti–Cl(1), centroid–Ti–O(1), centroid–Ti–O(2) and centroid–Ti–O(3) angles are 115(1), 113(1), 113(1) and 113(1)° respectively. The 18-crown-6 molecule has been highly distorted to accommodate the rather bulky $Ti(\eta$-$C_5H_5)Cl^+$ fragment (see torsion angles in Table 6).

In the $[AlCl_2Me_2]^-$ anion the geometry around the Al is very close to a regular tetrahedron. The Al–Cl and Al–Me bond lengths average 2.206(5) and 2.01(2) Å respectively and the angles about the Al range from 101.7(3) to 117.5(8)°.

$[ZrCl_2\cdot(OCH_2CH_2)_5OCH_2CH_2Cl^+][ZrCl_5(thf)^-]$ 3. This complex crystallizes as distinct cations and anions with no significantly short distances representing any interionic contacts. The pentagonal-bipyramidal zirconium-containing cation is shown in Scheme 3 (the crystal structure was published previously[4]). The ring-opened crown ether macrocyclic ligand

Table 3 Selected bond distances (Å) and angles (°) for [Ti(η-C_5H_5)$^+$·18-crown-6][$AlCl_2Me_2^-$] **2**

Ti–Cl(1)	2.340(4)	Ti–O(1)	2.09(1)
Ti–O(2)	2.154(9)	Ti–O(3)	2.14(1)
Ti–Centroid	2.04(1)		
Cl(1)–Ti–O(1)	87.2(3)	Cl(1)–Ti–O(2)	132.3(3)
O(1)–Ti–O(2)	73.1(4)	Cl(1)–Ti–O(3)	89.1(3)
O(1)–Ti–O(3)	131.3(4)	O(2)–Ti–O(3)	74.1(4)
Centroid–Ti–Cl(1)	115(1)	Centroid–Ti–O(1)	113(1)
Centroid–Ti–O(2)	113(1)	Centroid–Ti–O(3)	113(1)

Table 4 Selected bond distances (Å) and angles (°) for [$ZrCl_2$·(OCH_2CH_2)$_5$$OCH_2CH_2Cl^+$][$ZrCl_5(thf)^-$] **3**

Zr(1)–Cl(1)	2.431(8)	Zr(1)–Cl(2)	2.438(7)
Zr(1)–O(1)	1.93(2)	Zr(1)–O(2)	2.24(1)
Zr(1)–O(3)	2.25(1)	Zr(1)–O(4)	2.33(2)
Zr(1)–O(5)	2.24(1)	Zr(2)–Cl(4)	2.452(7)
Zr(2)–Cl(5)	2.449(8)	Zr(2)–Cl(6)	2.45(1)
Zr(2)–O(7)	2.24(2)	Cl(3)–C(12)	1.71(5)
Cl(1)–Zr(1)–Cl(2)	165.8(3)	Cl(1)–Zr(1)–O(1)	97.6(5)
Cl(2)–Zr(1)–O(1)	96.6(5)	Cl(1)–Zr(1)–O(2)	93.0(5)
Cl(2)–Zr(1)–O(2)	91.8(5)	O(1)–Zr(1)–O(2)	73.0(5)
Cl(1)–Zr(1)–O(3)	84.9(4)	Cl(2)–Zr(1)–O(3)	84.5(4)
O(1)–Zr(1)–O(3)	140.8(5)	O(2)–Zr(1)–O(3)	67.8(5)
Cl(1)–Zr(1)–O(4)	82.1(5)	Cl(2)–Zr(1)–O(4)	85.2(4)
O(1)–Zr(1)–O(4)	151.3(5)	O(2)–Zr(1)–O(4)	135.7(5)
O(3)–Zr(1)–O(4)	67.9(5)	Cl(1)–Zr(1)–O(5)	95.0(5)
Cl(2)–Zr(1)–O(5)	86.6(5)	O(1)–Zr(1)–O(5)	80.8(6)
O(2)–Zr(1)–O(5)	153.4(6)	O(3)–Zr(1)–O(5)	138.1(6)
O(4)–Zr(1)–O(5)	70.6(5)	Cl(4)–Zr((2)–Cl(5)	88.0(3)
Cl(4)–Zr(2)–Cl(6)	89.3(3)	Cl(5)–Zr(2)–Cl(6)	169.1(3)
Cl(4)–Zr(2)–Cl(7)	174.1(3)	Cl(5)–Zr(2)–Cl(7)	89.9(3)
Cl(6)–Zr(2)–Cl(7)	91.7(3)	Cl(4)–Zr(2)–Cl(8)	92.8(3)
Cl(5)–Zr(2)–Cl(8)	94.0(3)	Cl(6)–Zr(2)–Cl(8)	96.6(3)
Cl(7)–Zr(2)–Cl(8)	92.8(3)	Cl(4)–Zr(2)–O(7)	88.5(4)
Cl(5)–Zr(2)–O(7)	85.4(5)	Cl(6)–Zr(2)–O(7)	84.0(6)
Cl(7)–Zr(2)–Cl(7)	85.8(4)	Cl(8)–Zr(2)–O(7)	178.6(5)

Table 5 Selected bond distances (Å) and angles (°) for [Na^+·18-crown-6][$HfCl_5$(thf)$^-$] **4**

Hf(1)–Cl(1)	2.431(4)	Hf(1)–Cl(2)	2.420(4)
Hf(1)–Cl(3)	2.382(4)	Hf(1)–Cl(4)	2.414(4)
Hf(1)–Cl(5)	2.427(4)	Hf(1)–O(7)	2.21(1)
Cl(1)–Hf(1)–Cl(2)	173.1(2)	Cl(1)–Hf(1)–Cl(3)	93.8(2)
Cl(2)–Hf(1)–Cl(3)	93.0(2)	Cl(1)–Hf(1)–Cl(4)	88.1(2)
Cl(2)–Hf(1)–Cl(4)	90.3(2)	Cl(3)–Hf(1)–Cl(4)	94.7(2)
Cl(1)–Hf(1)–Cl(5)	89.3(2)	Cl(2)–Hf(1)–Cl(5)	91.1(2)
Cl(3)–Hf(1)–Cl(5)	94.6(2)	Cl(4)–Hf(1)–Cl(5)	170.5(2)
Cl(1)–Hf(1)–O(7)	87.6(3)	Cl(2)–Hf(1)–O(7)	85.6(3)
Cl(3)–Hf(1)–O(7)	178.3(3)	Cl(4)–Hf(1)–O(7)	86.3(3)
Cl(5)–Hf(1)–O(7)	84.5(3)		

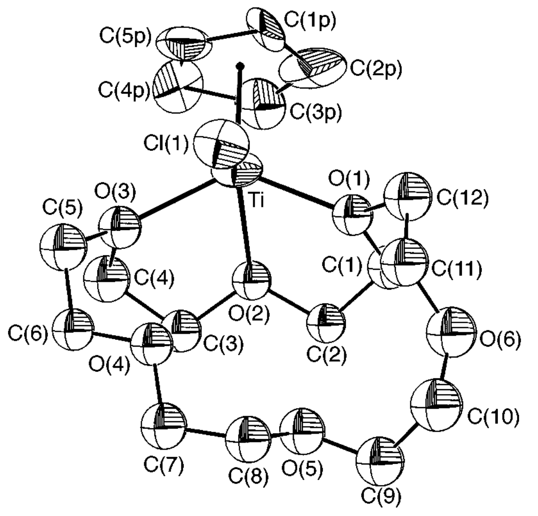


Fig. 2 Structure of four-legged piano-stool cation [Ti(η-C_5H_5)Cl^+·18-crown-6] in complex **2**

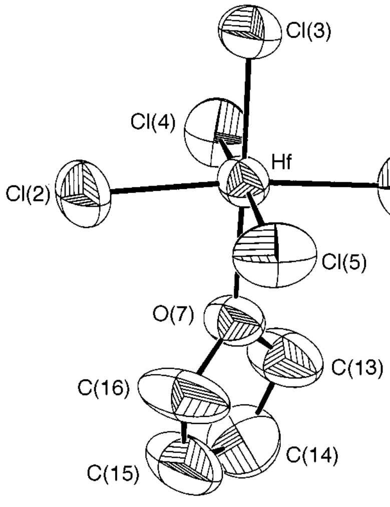


Fig. 3 Structure of the [$HfCl_5$(thf)]$^-$ anion in complex **4**. The [$ZrCl_5$(thf)]$^-$ anion in **3** is isostructural

occupies the five equatorial sites, with the two chloride ligands in the axial sites, completing the seven-co-ordination. The Zr(1)–O(1) distance of 1.93(2) Å represents a full covalent interaction, whereas the remaining Zr–O lengths are much longer [2.24(1)–2.33(2) Å], being more reminiscent of donor–acceptor bonds. The five zirconium-bonded oxygen atoms are coplanar to within 0.08 Å, and the zirconium atom resides 0.03 Å out of this plane. The Zr–Cl distances are 2.431(8) and 2.438(7) Å. Atom Cl(3), which has migrated from the zirconium atom to the hydrocarbon chain, is bound to C(12) at a distance of 1.71(5) Å which represents a typical covalent interaction.

The [$ZrCl_5$(thf)]$^-$ anion in this complex displays nearly perfect octahedral geometry about the zirconium, and is isostructural to the hafnium analogue (see Fig. 3 and discussion in the following section). The Zr–Cl bonding distances range from 2.388(8) to 2.452(7) Å, and the O atom of the thf molecule is bound to the zirconium at a distance of 2.24(2) Å.

[Na^+·18-crown-6][$HfCl_5$(thf)$^-$] 4. As with the zirconium complex above, this complex crystallizes as distinct cations and anions with no interionic interactions. The cation exists in a similar morphology to that in complex **1**, where the oxonium ion has been replaced with a sodium ion. The sodium ion resides very close to the center of the macrocyclic ring, and has Na–O distances ranging from 2.61(2) to 2.84(2) Å. It is interesting here that, as in the oxonium cation in complex **1**, there are three long and three short Na–O distances. The Na to O(1), O(3) and O(5) distances range from 2.82(2) to 2.84(2) Å, while the Na to O(2), O(4) and O(6) distances are slightly shorter at 2.61(2) to 2.76(2) Å.

The [$HfCl_5$(thf)]$^-$ anion which is isostructural to the zirconium analogue above is shown in Fig. 3. The Hf to Cl distances range from 2.382(4) to 2.431(4) Å, and the Hf to O (thf) distance is 2.21(1) Å.

Discussion

The four complexes discussed herein were prepared by the synthetic procedures outlined in Schemes 1 to 3, and all reaction mixtures exhibited a liquid clathrate or two-phase effect. Complex **1** was prepared according to Scheme 1 and involved the treatment of [Ti(η-C_5H_5)$_2$$Cl_2$] with HCl(g) in the presence of

Table 6 Torsion angles (°) for compounds **1** to **4**

Atoms	**1**	**2**	**3**	**4**
O(1)–C(2)–C(3)–O(2)	65	43	−40	46
O(2)–C(3)–C(4)–O(4)	−63	−47	49	−64
O(3)–C(5)–C(6)–O(4)	−83	55	−54	71
O(4)–C(7)–C(8)–O(5)	−58	−66	57	−51
O(5)–C(9)–C(10)–O(6)	−10	−60	−60	57
O(6)–C(11)–C(12)–O(1)	98	79	149*	−15
C(1)–C(2)–O(2)–C(3)	175	−170	−174	−178
C(2)–O(2)–C(3)–C(4)	−158	172	173	−164
C(3)–C(4)–O(3)–C(5)	173	−111	169	163
C(4)–O(3)–C(5)–C(6)	−28	64	−168	179
C(5)–C(6)–O(4)–C(7)	−128	−176	−179	175
C(6)–O(4)–C(7)–C(8)	−62	−179	174	−175
C(7)–C(8)–O(5)–C(9)	43	−167	137	171
C(8)–O(5)–C(9)–C(10)	−175	−81	81	177
C(9)–C(10)–O(6)–C(11)	−154	98	176	168
C(10)–O(6)–C(11)–C(12)	176	−163	−150	175
C(11)–C(12)–O(1)–C(1)	63	−87	—	173
C(12)–O(1)–C(1)–C(2)	−175	141	—	158

* Refers to the O(6)–C(11)–C(12)–Cl(3) angle.

18-crown-6 and water while irradiating with UV light in toluene. These reaction conditions have been used previously by us in the formation of oxonium ion–crown ether complexes of the Group VI metals, and we were interested to investigate the nature of species we could obtain from these oxonium ion–crown ether complexes of the Group IV metals.[10–13] In this case the severe reaction conditions resulted in dealkylation of the titanium center where the two C_5H_5 ligands were substituted by chloride ligands, and the co-ordination number of titanium was increased from four (if the centroid of the C_5H_5 ligand is considered as occupying one co-ordination site) to six with further halide attack on the metal. A water molecule completes the octahedral geometry of titanium. An attempt to prepare complex **1** from $TiCl_4$, 18-crown-6, HCl(g) and stoichiometric quantities of water was hampered by the formation of white insoluble material, presumably TiO_2, and was not pursued. The synthesis of **1** was much smoother using the air- and moisture-stable $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$. In related syntheses, $TiCl_4$ reacts with 18-crown-6 to form a 1:1 adduct,[15] and treatment of a $TiCl_3$–18-crown-6 mixture with moist hexane gives $[18\text{-crown-}6\cdot TiCl_3(H_2O)]$.[6] In both cases the macrocycle acts as a bidentate ligand towards titanium in simple 1:1 adduct species.

The formation of an oxonium ion, and subsequent trapping of it by co-ordination within the cavity of the 18-crown-6 molecule, is typical in reactions of this type.[10–13,16–26] We have shown that the 18-crown-6 macrocycle is selective for the isolation of the H_3O^+ oxonium ion with a large number of anions, for example, $[Cl{-}H{-}Cl]^-$, Br_3^-, I_7^-, $[MCl_4]^{n-}$ ($n = 1$, M = Fe; $n = 2$, M = Co), $[MoOCl_4(H_2O)]^-$, $[W(CO)_5Cl]^-$, $[W(CO)_4Cl_3]^-$, $[WOCl_4(H_2O)]^-$ and $[WOBr_4(H_2O)]^-$.[10–13,16,17]

Complex **2** was formed by the reduction of $[Ti(\eta\text{-}C_5H_5)Cl_3]$ by $AlMe_3$ in the presence of 18-crown-6. In the absence of $AlMe_3$, $[Ti(\eta\text{-}C_5H_5)Cl_3]$ does not react with 18-crown-6 at room temperature, but when $AlMe_3$ is added the reaction becomes vigorous. A green solution results from which colorless, crystalline $[AlMe_2\cdot 18\text{-crown-}6][AlMe_2Cl_2]$[27] precipitates. Upon cooling and concentrating, pale blue air-sensitive crystals of compound **2** are isolated. Most examples of alkylaluminium–transition metal complexes involve bridging moieties such as carbonyl, alkyls or hydrides,[28] and the implied intermediate in the formation of **2** is most probably a similar species.

The reduction of Ti^{IV} to Ti^{III} is well known, especially in the presence of alkylaluminium reagents.[1] Many efforts have centered on this type of research due to these complexes being industrially important as Zieger–Natta catalysts in the polymerization of olefins. While the Ziegler–Natta process has been known for many years, the composition of the catalytically active species is not well understood, although it is generally thought that a titanium(III) species is responsible.

Complex **3** was formed by the reaction of 18-crown-6 with $ZrCl_4$ in toluene–thf (15% thf by volume). The isolation of this ring-opened species came as somewhat of a surprise because in an analogous reaction $TiCl_4$ in the presence of 18-crown-6 forms the $TiCl_4\cdot 18\text{-crown-}6$ adduct, in which the crown ether functions as a bidentate ligand.[15] This ring-opening reaction is of vital importance to researchers in the zirconium chemistry field and calls for extra caution in the interpretation of experimental data. The transfer of a halide from an early transition metal to a hydrocarbon has precedent in the pyrolysis of diethyl ether complexes of $NbCl_5$ and $TaCl_5$ where ethyl chloride and metal oxide trihalides are generated.[29] With this information, and with the known propensity of $ZrCl_4$ to cleave C–O bonds in donor complexes because of the strength of the Zr–O bond,‡ a mechanism has been postulated.[4] It is significant that the ring-opening reaction involves the 18-crown-6 molecule and not thf, a cyclic ether which other metals are known to cleave.[30,31]

Complex **4** was formed under analogous conditions to those used in the formation of **3** above, except in this case NaCl was added to the reaction mixture. The latter addition allows the formation of discrete cations and anions in an aromatic medium, conditions which are favorable for liquid clathrate formation. The complexation of the Na^+ ion by 18-crown-6 is well known[32] and is obviously more facile than complexation of the $HfCl_4$ molecule, where an $HfCl_4\cdot 18\text{-crown-}6$ adduct would be formed as with titanium and zirconium. This preference for the Na^+ ion over $HfCl_4$ most probably inhibits the ring-opening reaction which the $ZrCl_4\cdot 18\text{-crown-}6$ adduct undergoes. The stabilization of an $Na^+\cdot 18\text{-crown-}6$ cation inhibits attack by the Lewis acid.

Compounds **1** to **4**, in particular **2**, are related in nature to known Ziegler–Natta type catalysts and efforts will be centered on the catalytic activity of these complexes with respect to the polymerization of olefins. The potential of catalytic complexes in liquid clathrate media, where two phases exist, is extremely promising. These two-phase systems have been demonstrated to be of great importance in separation science and coal-liquefaction technology.[7–9]

The crystal structures of the four complexes prepared herein revealed some interesting features. The anions in **1**, **3** and **4** are all similar, and are all close to regular octahedral geometry. These types of species are not common, and there are few structural reports on related species such as $[ZrCl_5]^-$ and $[TiCl_5(thf)]^-$.[33,34]

The $[H_3O^+\cdot 18\text{-crown-}6]$ cation in complex **1** is similar in geometry to other established cations of this type. To our knowledge this is the first complex with an oxonium ion–crown ether cation with a Ti-bearing anion. The H_3O^+ ion forms three hydrogen bonds with the oxygen atoms of the crown ether, and resides 0.51 Å out of the plane of these three heteroatoms. There has been much discussion in the literature concerning the geometry of the H_3O^+ oxonium ion, particularly when encapsulated in a hydrogen-bonded fashion within a macrocycle.[13,18,19] In such cases, the O (oxonium) has been found to reside between 0.03 and 0.90 Å but out of the plane of the crown atoms to which it is hydrogen bonded.[18,19] In the present case the more favored pyramidal geometry around the O (oxonium) is found.

The square-pyramidal (or four-legged piano-stool) cation in complex **2**, $[Ti(\eta\text{-}C_5H_5)Cl^+\cdot 18\text{-crown-}6]$, is a rare example of an isolated mixed-metal complex containing a titanium-bearing cation and an aluminium-bearing anion, some related species being $[Ti^{III}Cl_2\cdot 15\text{-crown-}5][AlCl_4]$[35] and $[Ti^{III}Cl_2(MeCN)_4][AlCl_4]$.[36] In addition, the isolation of cationic titanium(III)

---

‡ Early transition metals are known to be involved in the cleavage of the C–O bond in thf.[30]

species, and their co-ordination by crown ether molecules, is also rare.

The zirconium atom in complex **3** is seven-co-ordinate with the opened macrocycle filling the five equatorial sites. The Zr–O(1) interaction is a full covalent bond at 1.93(2) Å,[37] while the remaining Zr–O lengths [2.24(1) to 2.33(2) Å] are typical for donor–acceptor interactions. These donor–acceptor interactions compare favorably with the Zr–O distance in the anion of 2.24(2) Å. The opened macrocycle appears to be similar to 15-crown-5 in its ability to co-ordinate the metal.§ The O···O separations, 2.49(1) to 2.65(1) Å, are close to those found in complexes of the crown ether with the exception of O(1)···O(5) at 2.72(1) Å. Atom O(6) is not required to fill out the co-ordination sphere of the zirconium, and it does not interact with the metal. The terminal chlorine atom exhibits high thermal motion, but the C–Cl bond length of 1.71(5) Å is near the ideal value (the high e.s.d. notwithstanding).

The cation in complex **4** is similar to established [Na^+·18-crown-6] ions where the Na^+ ion resides close to the center of the macrocycle, albeit with three short and three longer Na–O distances (see structural section).[32]

This chemistry highlights the conformational mobility of the 18-crown-6 macrocycle. The torsion angles of the respective crown ethers in compounds **1** to **4** (Table 6) display the ability of the 18-crown-6 molecule to adopt a conformation suitable for its environment. In the cases where there is an ion available for the crown ether to act as a macrocyclic ligand, *i.e.* complexes **1** and **4**, the ion was completely engulfed by the ligand. For compound **2**, where the cation is too large to be completely encapsulated by the crown, the ligand adopts a distorted conformation to co-ordinate to the metallic center and complete the electronic requirements of the metal. In **3** the crown initially co-ordinates to the Lewis acid, $ZrCl_4$ molecule, most probably distorting the crown, but then reacts with the $ZrCl_4$, opening the crown ether. Only after ring opening has occurred the crown ether is able to chelate about the zirconium center.

Conclusion

We have established some interesting structural chemistry of crown ether complexes of titanium, zirconium and hafnium. Mainly by X-ray crystallography, it was shown that the 18-crown-6 molecule will adopt a variety of conformations depending on the nature of the species being complexed and that ring-opening reactions are possible.

Acknowledgements

We are grateful to the National Science Foundation for support. We also acknowledge the Chemistry Department at the University of Alabama for collection of the X-ray data.

---

§ Although there is no related complex between 15-crown-5 and $ZrCl_2^{2+}$, comparisons can be made with regard to 15-crown-5·$AlCl_2^+$ (ref. 3) and ref. 38.

References

1 G. W. Parshall, *Homogeneous Catalysis*, Wiley, New York, 1980; J. Boor, jun., *Ziegler-Natta Catalysis and Polymerizations*, Academic Press, New York, 1979.

2 R. F. Jordan, R. E. LaPointe, C. S. Bajgur, S. F. Echols and R. Willett, *J. Am. Chem. Soc.*, 1987, **109**, 4111.

3 S. G. Bott, H. Elgamal and J. L. Atwood, *J. Am. Chem. Soc.*, 1985, **107**, 1796.

4 H. Prinz, S. G. Bott and J. L. Atwood, *J. Am. Chem. Soc.*, 1986, **108**, 2113.

5 J. A. Ewen, L. Haspeslagh, J. L. Atwood and H. Zhang, *J. Am. Chem. Soc.*, 1987, **109**, 6544.

6 S. G. Bott, U. Kynast and J. L. Atwood, *J. Incl. Phenom.*, 1986, **4**, 241.

7 J. L. Atwood, in *Inclusion Compounds*, eds. J. L. Atwood, J. D. Davies and D. D. MacNicol, Academic Press, London, 1984, vol. 1, pp. 375–405.

8 J. L. Atwood, in *Chemical Separations*, eds. C. J. King, J. D. Navratil. Litarvan, Denver, 1986, pp. 335–354.

9 J. L. Atwood, in *Separation Technology*, eds. N. N. Li and H. Strathmann, United Engineering Trustees, New York, 1988, pp. 46–56.

10 P. C. Junk and J. L. Atwood, *J. Chem. Crystallogr.*, 1994, **24**, 243.

11 J. L. Atwood, S. G. Bott, P. C. Junk and M. T. May, *J. Organomet. Chem.*, 1995, **487**, 7.

12 P. C. Junk, L. R. MacGillivray, M. T. May, K. D. Robinson and J. L. Atwood, *Inorg. Chem.*, 1994, **34**, 5395.

13 J. L. Atwood, S. G. Bott, P. C. Junk and M. T. May, *J. Coord. Chem.*, 1996, **37**, 89.

14 G. M. Sheldrick, SHELX 76, A System of Computer Programs for X-Ray Structure Determination, University of Cambridge, 1976.

15 S. G. Bott, H. Prinz, A. Alvanipour and J. L. Atwood, *J. Coord. Chem.*, 1987, **16**, 303.

16 J. L. Atwood, S. G. Bott, A. W. Coleman, K. D. Robinson, S. B. Whetstone and C. M. Means, *J. Am. Chem. Soc.*, 1987, **109**, 8100; J. L. Atwood, S. G. Bott, C. M. Means, A. W. Coleman, H. Zhang and M. T. May, *Inorg. Chem.*, 1990, **29**, 467.

17 J. L. Atwood, P. C. Jumk, M. T. May and K. D. Robinson, *J. Chem. Crystallogr.*, 1994, **24**, 243.

18 C. B. Shoemaker, L. V. McAfree, D. P. Shoemaker and C. W. DeKock, *Acta Crystallogr., Sect. C*, 1986, **42**, 1310.

19 J.-P. Behr, P. Dumas and D. Moras, *J. Am. Chem. Soc.*, 1982, **104**, 4540.

20 R. D. Rogers, A. H. Bond, W. G. Hipple, A. N. Rollins and R. F. Henry, *Inorg. Chem.*, 1991, **30**, 2671.

21 R. Chenevert, D. Chamberland, M. Simard and F. Brisse, *Can. J. Chem.*, 1989, **67**, 32.

22 R. Chenevert, D. Chamberland, M. Simard and F. Brisse, *Can. J. Chem.*, 1990, **68**, 797.

23 V. S. Sergienko, L. Kh. Minacheva, N. Kh. Ashurova, M. A. Porai-Koshits, K. G. Yakubov and V. G. Sakharova, *Russ. J. Inorg. Chem.*, 1991, **36**, 212.

24 V. S. Sergienko, L. Kh. Minacheva, G. G. Sadikov, N. Kh. Ashurova, V. V. Minin, K. G. Yakubov and V. M. Sherbakov, *Russ. J. Inorg. Chem.*, 1992, **37**, 164.

25 J. L. Atwood, S. G. Bott, K. D. Robinson, E. J. Bishop and M. T. May, *J. Crystallogr. Spectrosc. Res.*, 1991, **21**, 459.

26 W. Ming, W. Boyi, Z. Peiju, W. Wenji and L. Jie, *Acta Crystallogr., Sect. C*, 1988, **44**, 1913.

27 S. G. Bott, A. Alvanipour, S. D. Morley, D. A. Atwood, C. M. Means, A. W. Coleman and J. L. Atwood, *Angew. Chem.*, 1987, **26**, 485.

28 D. F. Shriver and A. Alich, *Coord. Chem. Rev.*, 1972, **8**, 15; A. T. T. Hsieh, *Inorg. Chim. Acta*, 1975, **14**, 87; R. D. Rogers, W. J. Cook and J. L. Atwood, *Inorg. Chem.*, 1979, **18**, 279.

29 A. Cowley, F. Fairbrother and N. Scott, *J. Chem. Soc.*, 1958, 3133.

30 E. Bartmann, *J. Organomet. Chem.*, 1985, **284**, 149.

31 C. Jones, L. M. Engelhardt, P. C. Junk, D. S. Hutchings, W. C. Patalinghug, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1991, 1560.

32 D. E. Fenton, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, p. 37.

33 A. F. Demiray and W. Brockner, *Monatsh. Chem.*, 1980, **111**, 21.

34 P. Sobota, J. Utko and T. Lis, *J. Chem. Soc., Dalton Trans.*, 1984, 2077.

35 V. K. Bel'skii, B. M. Bulychev and N. R. Strel'tsova, *Zh. Neorg. Khim.*, 1992, **37**, 1531.

36 B. I. Kharisov, V. B. Rybakov and S. I. Troyanov, *Koord. Khim.*, 1994, **20**, 597.

37 J. L. Atwood, R. D. Rogers and R. V. Bynum, *Acta Crystallogr., Sect. C*, 1984, **40**, 1812 and refs. therein.

38 J. L. Atwood, H. Elgamal, G. H. Robinson, S. G. Bott, J. A. Weeks and W. E. Hunter, *J. Incl. Phenom.*, 1985, **2**, 367.

Received 24*th October* 1997; *Paper* 7/07684C