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Synthesis and crystal structures of oxonium ion complexes of 21-crown-7 and dibenzo-30-crown-10

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The reactions of $[W(CO)_6]$ with 21-crown-7 (1,4,7,10,13,16,19-heptaoxacyclohenicosane) or dibenzo-30-crown-10 (6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo[*b*,*q*][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontine) in the presence of water and HCl(g) in toluene have been explored. They were promoted by the use of UV radiation and formed liquid clathrates almost immediately. In each case, oxidation of the tungsten center from either 0 to +2, +5 or +6 occurred. In the reaction of 21-crown-7 with $[W(CO)_6]$ structural data suggest that the $H_5O_2^+$ ion is selectively co-ordinated through hydrogen bonds to the 21-crown ether, in the tungsten(VI) complex, $[H_5O_2^+\cdot$21-crown-7$][WOCl_5^-]$ **1**, which crystallized from the liquid clathrate layer. For the reaction of dibenzo-30-crown-10 with $[W(CO)_6]$ initially the tungsten(II) complex $[2H_3O^+\cdot$dibenzo-30-crown-10$][W(CO)_4Cl_3^-]_2\cdot 2C_6H_5Me$ **2** formed. Upon exposure of **2** to the atmosphere for *ca.* 30 min the tungsten(V) complex $[2H_3O^+\cdot$dibenzo-30-crown-10$][WOCl_4(H_2O)^-]_2$ **3** was produced. The structures of each of these complexes were established by X-ray crystallography.

Our group[1–8] and others[9–19] have established that the 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) macrocyclic ligand is selective at stabilizing the H_3O^+ oxonium ion. The size of the cavity of the ligand appears to be sufficient just to accommodate H_3O^+ and a number of crystal structures have verified the existence of the oxonium ion snugly bound in the crown.[1–8,10,13–19] Furthermore, we have isolated a number of complexes from liquid clathrate systems in which we are able to stabilize H_3O^+ and $H_5O_2^+$ in aromatic media (*e.g.* Scheme 1[1–3]).[1–8] In an extension to this work we have used these cations to prepare liquid clathrates in which simple transition-metal species act as counter ions.[5,6]

As part of our study of liquid clathrate systems,[20–22] we now turn our attention to the reactions of $[W(CO)_6]$ with 21-crown-7 (1,4,7,10,13,16,19-heptaoxacyclohenicosane) and dibenzo-30-crown-10 (6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo[*b*,*q*][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontine). In moving to these larger crown ethers there exists the potential for selectively isolating higher oligomers in the oxonium ion series, $nH_2O\cdot H^+$. The structural chemistry of 21-crown-7 is also very limited, there being only one crystal structure of the unsubstituted macrocycle.[23] In established structures of dibenzo-30-crown-10 the crown shows remarkable conformational mobility,[24–35] and therefore appeared to be a perfect candidate for isolating interesting oxonium ion–crown ether complexes.

Herein we report the synthesis and crystal structures of $[H_5O_2^+\cdot$21-crown-7$][WOCl_5^-]$ **1**, $[2H_3O^+\cdot$dibenzo-30-crown-10$][W(CO)_4Cl_3^-]_2\cdot 2C_6H_5Me$ **2** and $[2H_3O^+\cdot$dibenzo-30-crown-10$][WOCl_4(H_2O)^-]_2$ **3**, which were all isolated from aromatic media. In complex **1** we have isolated a complex where the 21-crown-7 molecule adopts an unusual bowlic structure selectively to complex an $H_5O_2^+$ ion in its unusual *cis* conformation. In **2** and **3**, H_3O^+ oxonium ions were selectively isolated within the cavity of the dibenzo-30-crown-10 molecules. Complex **1** was the subject of a preliminary communication[36] and we present the full account of this compound herein.

Experimental

$$\begin{tikzcd}
\text{18-crown-6} + H_2O + HCl(g) \arrow[r, "\text{toluene}"] & {[H_3O^+\cdot\text{18-crown-6}][Cl{-}H{-}Cl]} \arrow[d, "2\,H_2O"] \\
 & {[H_3O^+\cdot\text{18-crown-6}][H_5O_2^+]Cl_2}
\end{tikzcd}$$

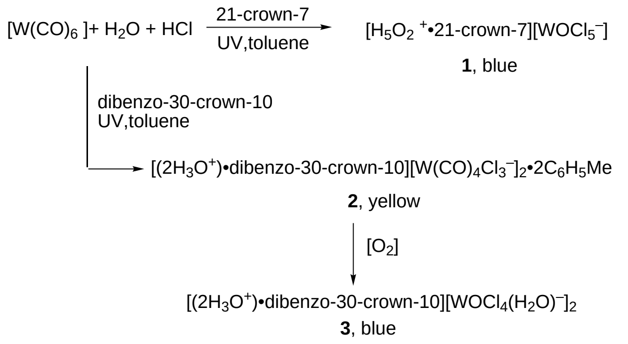
Scheme 1

The compounds $[W(CO)_6]$ and dibenzo-30-crown-10 were obtained from Aldrich Chemical Co., 21-crown-7 from Parish Chemical Co., and HCl gas from Atlas Co. Complexes **1** and **2** were prepared exposed to air, prior to the reaction mixture being sealed in an air-tight screw-top tube. Proton NMR chemical shifts were similar for all complexes, δ 1.95 and 6.85 (toluene), *ca.* 3.6 (crown ethers) and 9.4 (oxonium ions).

Preparations

$[H_5O_2^+\cdot$21-crown-7$][WOCl_5^-]$ 1. To a sample of 21-crown-7 (0.25 g, 0.81 mmol) in toluene (*ca.* 30 cm^3), was added water (0.015 g, 0.81 mmol) and $[W(CO)_6]$ (0.30 g, 0.85 mmol) and stirred rapidly for 15 min. Hydrogen chloride gas was then rapidly bubbled through the mixture for *ca.* 1 h while irradiating with UV radiation. During this time a yellow liquid clathrate separated from the solvent. The composition of the liquid clathrate layer was not conclusive, but the oxonium ion–crown cation : toluene ratio of 1 : 1.2 was determined by ^{1}H NMR spectroscopy. Deep blue crystals of complex **1** deposited from the clathrate layer after *ca.* 24 h.

$[2H_3O^+\cdot$dibenzo-30-crown-10$][W(CO)_4Cl_3^-]_2\cdot 2C_6H_5Me$ 2. To a sample of dibenzo-30-crown-10 (0.17 g, 0.32 mmol) in toluene (*ca.* 50 cm^3) was added water (0.006 g, 0.32 mmol) and $[W(CO)_6]$ (0.11 g, 0.32 mmol) and stirred rapidly for 15 min. Hydrogen chloride gas was then rapidly bubbled through the mixture for *ca.* 1 h while irradiating with UV radiation. During this time a yellow liquid clathrate separated from the toluene layer. The composition of the liquid clathrate, as determined by ^{1}H NMR spectroscopy, was $[2H_3O^+\cdot$dibenzo-30-crown-10$][W(CO)_4Cl_3^-]_2\cdot 2C_6H_5Me$. Bright yellow crystals of complex **2** deposited from the liquid clathrate layer after *ca.* 30 h.



Scheme 2

[$2H_3O^+$·dibenzo-30-crown-10][$WOCl_4(H_2O)^-$]$_2$ 3. After crystals of complex **3** had been isolated from the reaction mixture above, the solution was left exposed to air for *ca.* 30 min. After several days bright blue crystals of complex **3** deposited from solution.

Crystallography

Single crystals of complexes **1**, **2** and **3** were sealed in thin-walled glass capillaries under an atmosphere of toluene. Final lattice parameters as determined from the least-squares refinement of the angular settings of 24 high-angle reflections ($2\theta > 30°$) 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 for compounds **1** and **2** were carried out using the SHELX system of computer programs,[37] while those for **3** were performed using the NRCVAX system.[38]

Positions of heavy atoms were determined from a three-dimensional Patterson function. All other non-hydrogen atoms were located from a Fourier-difference synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the water molecules and oxonium ions were not located on the difference map. All other hydrogen atoms were placed at calculated positions and their parameters were not refined. Complex **2** suffered from severe absorption, and upon anisotropic refinement the carbonyl carbon, C(d), had high thermal motion, and was located much closer to the tungsten atom than would generally be expected. Refinements converged with $R = 0.082$ for 3874 observed reflections for **1**, $R = 0.035$ for 2032 observed reflections for **2**, and $R = 0.044$ for 2648 observed reflections for **3**.

CCDC reference number 186/720.

Results

Preparation of complexes

Complexes **1**–**3** were prepared according to the novel reaction conditions presented in Scheme 2. In the formation of **1** and **2** the mixture rapidly separated into two phases yielding liquid clathrate species. The upper layer in these reactions was neat toluene (as determined by ^1H NMR spectroscopy), while the complexes formed were completely dissolved within the clathrate layer. Reactions were performed in contact with air, followed by sealing the reaction vessel from aerial contact. Promotion of CO removal was aided by irradiating the reaction mixtures with UV light. In all reactions oxidation of the metal center occurred, from 0 to +6 for **1**, 0 to +2 for **2**, and +2 to +5 for **3**. It is suggested that oxidation occurs from contact with air. In other reactions where we have performed the experiment in the total exclusion of oxygen no oxidation of the metal center takes place. Instead, complexes of the type $[M(CO)_5Cl]^-$ are readily formed for chromium and tungsten.[6]

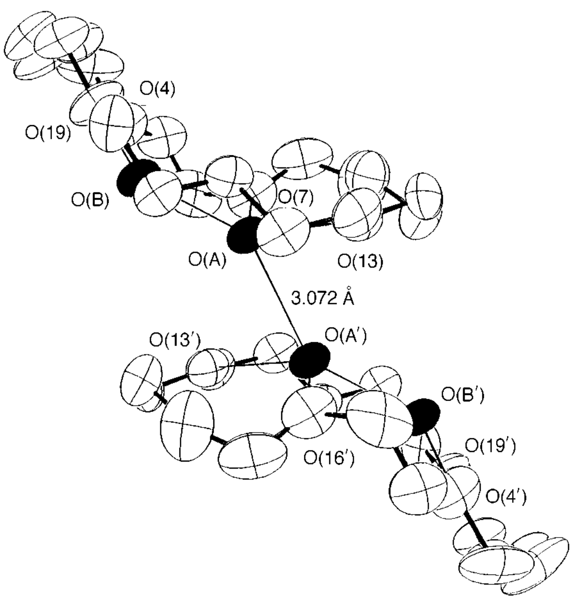


Fig. 1 The cation–cation separation in [$H_5O_2^+$·21-crown-7][$WOCl_5^-$] showing a possible interaction between adjacent $H_5O_2^+$ ions

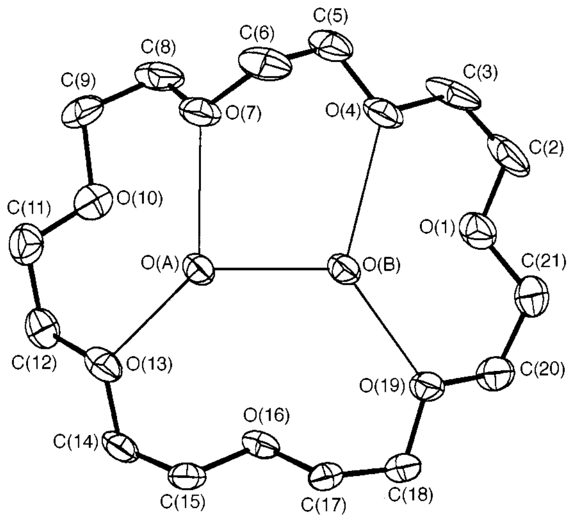


Fig. 2 Structure of the [$H_5O_2^+$·21-crown-7] cation viewed perpendicular to the 21-crown-7 macrocycle. Hydrogen-bonding distances are O(A)···O(B) 2.41(3), average O ($H_5O_2^+$)···O (crown) 2.66(3) Å

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 the yields.

Crystal structures

Selected bond distances and angles for complexes **1**–**3** are shown in Tables 2–4. Torsion angles for **1** and deviations of the crown oxygen atoms from their least-squares plane are given in Tables 5 and 6 respectively. Torsion angles for **2** and **3** are given in Table 7.

[$H_5O_2^+$·21-crown-7][$WOCl_5^-$] 1. This complex crystallizes in discrete layers of anions and cations. There are no cation to anion contacts less than 3.5 Å, but there is one rather surprising cation to cation contact of 3.072 Å which appears to be a weak hydrogen bond linking adjacent $H_5O_2^+$ ions (Fig. 1).

The structure of the [$H_5O_2^+$·21-crown-7] cation is shown in Fig. 2. The $H_5O_2^+$ ion fits snugly within the cavity of the

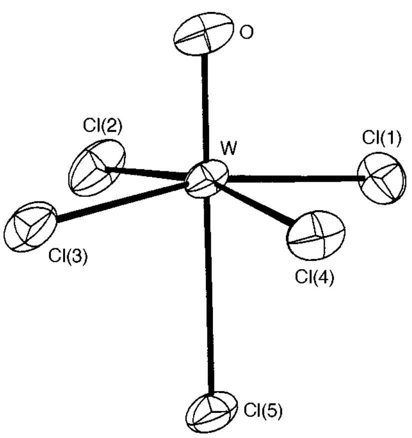


Fig. 3 Structure of the $[WOCl_5]^-$ anion; W–Cl (equatorial) 2.366(5) (average), O–W–Cl (equatorial) 96.5(6)°

macrocycle (Fig. 2) and adopts the *cis* arrangement rigidly to bind through hydrogen bonds to O(4), O(19), O(7) and O(13) of the crown. These distances of 2.63(2) to 2.70(3) Å are significantly shorter than the O(A)···O(10) and O(B)···O(1) distances of 2.85(4) and 2.97(3) Å respectively, and even though the protons on the $H_5O_2^+$ ion were not located the hydrogen-bonding pattern is evident. The O(A)···O(B) distance in the $H_5O_2^+$ oxonium ion [2.41(3) Å] is typical of this ion.[39,40] There is one other surprising intermolecular contact which the $H_5O_2^+$ ion displays (Fig. 1). The angles about the $H_5O_2^+$ oxonium ion displaying the hydrogen-bonding contacts are as follows; O(B)–O(A)–O(A′) 139, O(A)–O(B)–O(19) 123, O(A)–O(B)–O(4) 104, O(B)–O(A)–O(13) 125, O(B)–O(A)–O(7) 89, O(A′)–O(A)–O(7) 80, O(A′)–O(A)–O(13) 93, O(7)–O(A)–O(13) 121 and O(4)–O(B)–O(19) 119°. The 21-crown-7 molecules adopts a bowlic shape where the O(A) and O(B) atoms of the $H_5O_2^+$ ion reside 1.48 and 1.01 Å respectively out of the least-squares plane of the crown oxygen atoms. The crown oxygen atoms also deviate significantly from the least-squares plane derived from these atoms (see Table 6).

The structure of the $[WOCl_5]^-$ anion is shown in Fig. 3, and adopts a highly distorted octahedral stereochemistry, where the axial Cl(5) ligand is bound at a distance of 2.666(5) Å, compared with an average 2.366(7) Å for the other four chloride ligands. The W–O distance is 1.67(1) Å and the Cl ligands are bent down and away from the oxide ligand at an average of 96.5(6)°. The O–W–Cl(5) angle [178.8(4)°] is close to linear. There are no interionic distances between anions and cations or anions and anions less than 3.5 Å.

$[2H_3O^+\cdot$dibenzo-30-crown-10$][W(CO)_4Cl_3^-]_2\cdot 2C_6H_5Me$ 2. This complex crystallizes as discrete anions and cations with no significant interionic contacts. Also included in the crystal lattice are two molecules of toluene per ionic complex. This solvent molecule appears only to serve to fill voids in the crystal, since there are no close contacts between the toluene and other molecules.

The structure of the $[2H_3O^+\cdot$dibenzo-30-crown-10] cation, which resides on an inversion center, is shown in Fig. 4. The macrocycle adopts a relatively flat-stepped conformation, and is pinched at the center of the crown between where the two H_3O^+ oxonium ions reside. The protons on the oxonium ion were not located, but the hydrogen bonding within the macrocycle is easy to assign. The O (oxonium)···O (crown) distances of O···O(1) 2.77, O···O(2) 2.73, O···O(3) 2.82, O···O(4) 2.59 and O···O(5′) 2.54 Å indicate the oxonium ion is bound to O(2), O(4) and O(5′). The O (oxonium) ion atoms reside out of the plane of the O (crown) atoms to which they are bound by 0.37 Å, indicating the H_3O^+ ion adopts pyramidal geometry. They also reside on opposite sides of the macrocycle [Fig. 4(*b*)]. The O (oxonium)···O′ (oxonium) ion distance of 5.09(1) Å precludes any ion–ion interaction.

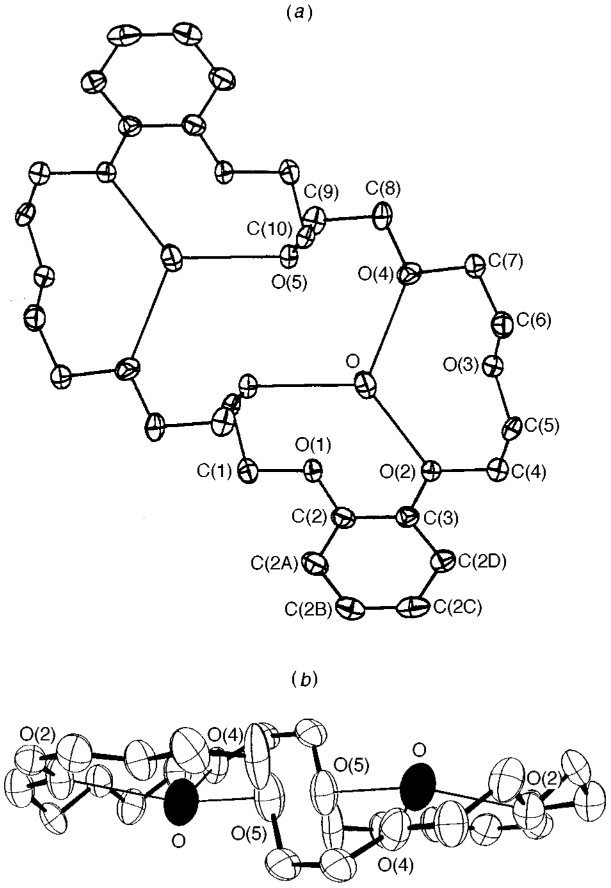


Fig. 4 (*a*) Structure of the $[2H_3O^+\cdot$dibenzo-30-crown-10] cation in complex **2** (the cation in **3** is similar) which resides on a crystallographic center of inversion. The average O (H_3O^+)···O (crown) hydrogen-bonding distance in **2** is 2.62(1) (the value for **3** is 2.60 Å). The O···O′ distances are 5.09(1) Å in **2** and 4.69(1) Å in **3**. (*b*) Structure of the $[2H_3O^+\cdot$dibenzo-30-crown-10] cation in complexes **2** and **3**, showing the position of the H_3O^+ ions relative to the plane of the crown ether oxygen atoms. The O (oxonium) ions reside *ca.* 0.3 Å out of the plane of the oxygen atoms to which they are bound. The carbons of the phenyl rings have been omitted for clarity

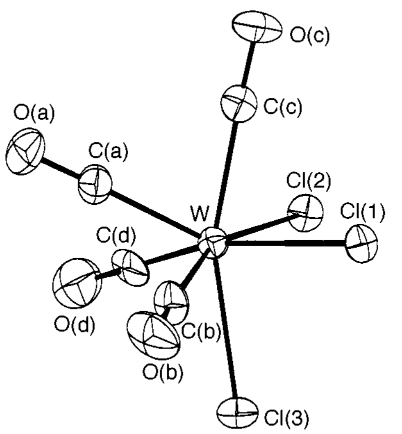


Fig. 5 Structure of the seven-co-ordinate $[W(CO)_4Cl_3]^-$ anion in complex **2**, displaying the 4 : 3 piano stool geometry

The anion in this complex exists as a seven-co-ordinate tungsten(II) species giving the anion capped trigonal-anti-prismatic geometry (or 4 : 3 piano stool) (see Fig. 5). The average W–Cl, W–C (carbonyl) and C–O bond distances are 2.493(5), 2.01(3) and 1.13(1) Å respectively. There were no obvious intermolecular contacts of this ion with others in the complex. The compound did suffer from an absorption

Table 1 Crystal data and summary of data collection for complexes **1**–**3***

	$[H_5O_2^+\cdot$21-crown-7][$WOCl_5^-$] **1**	[$2H_3O^+\cdot$dibenzo-30-crown-10]-[$W(CO)_4Cl_3^-]_2\cdot 2C_6H_5Me$ **2**	[$2H_3O^+\cdot$dibenzo-30-crown-10]-[$WOCl_4(H_2O)^-]_2$ **3**
M	722.5	1563.5	1294.0
Crystal symmetry	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	8.328(2)	10.558(3)	9.711(3)
b/Å	13.129(2)	13.211(4)	24.679(3)
c/Å	13.779(1)	13.360(4)	9.714(2)
α/°	103.30(1)	110.02(4)	90
β/°	98.50(1)	101.78(3)	109.81(1)
γ/°	104.34(1)	111.05(3)	90
U/Å^3	1387(2)	1516(8)	2190(1)
Z	2	1	2
D_c/g cm^{-3}	1.736	1.719	1.970
μ/cm^{-1}	47.95	42.2	59.4
Scan width/°	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ	0.80 + 0.35 tan θ
No. reflections collected	4336	2511	4091
No. observed reflections [$I > 3\sigma(I)$]	3874	2032	2648
No. parameters varied	271	346	244
R	0.082	0.035	0.044
R'	0.097	0.039	0.055

* Details in common: Mo-Kα radiation (λ = 0.710 69 Å); 2θ range 2–50°; unit weights; 296 K.

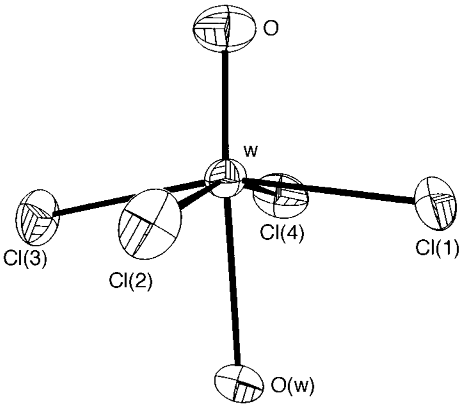


Fig. 6 Structure of the distorted octahedral [$WOCl_4(H_2O)]^-$ anion in complex **3**

problem, and upon anisotropic refinement C(d) refined much closer to the tungsten atom than would have been expected, presumably due to extraneous electron density around the tungsten atom.

[$2H_3O^+\cdot$dibenzo-30-crown-10][$WOCl_4(H_2O)^-]_2$ 3. This complex crystallizes in a similar fashion to that of complex **2**. The only significant differences are the anion, and one torsion angle [O(2)–C(4)–C(5)–O(3)], which has an angle of 63° compared with −64° in compound **2**. In this complex there is also a hydrogen-bonding contact binding the anions to the cations.

In the cation, the O (oxonium)···O (crown) distances of O···O(1) 2.80, O···O(2) 2.72, O···O(3) 2.85, O···O(4) 2.56 and O···O(5′) 2.51 Å indicate the oxonium ion is bound to O(2), O(4) and O(5′) (Fig. 4). The O (oxonium) ion atoms reside out of the plane of the O (crown) atoms to which they are bound by 0.31 Å, again indicating the H_3O^+ ion adopts pyramidal geometry. They also reside on opposite sides of the macrocycle (Fig. 6). The O (oxonium)···O′ (oxonium) ion distance is much shorter than in compound **2** [4.69(1) Å] but again indicates no $H_3O^+\cdots H_3O^+$ interaction.

The [$WOCl_4(H_2O)]^-$ anion which exists as a highly distorted octahedron is shown in Fig. 6. The W–O (water) bond, which is *trans* to the oxide ligand is appreciably lengthened due to the *trans* effect [W–O(w) 2.320(7), W–O 1.661(8) Å]. The W–Cl bonding distances average 2.368(9) Å, and are bent down and away from the oxide ligand at an average of 98(2)°, reflecting the distortion away from a regular octahedron. The water ligand in the anion forms a hydrogen bond to an oxygen atom of the macrocycle in the cation and to a chloride ligand in an adjacent anion, forming a hydrogen-bonded network [O(w)···O(5) 2.80(1), O(w)···Cl(2) 3.22(1) Å].

Discussion

Complexes **1**–**3** have been prepared by a novel approach which we have shown to be a general method for the preparation of other oxonium ion–crown ether complexes of transition-metal co-ordination compounds.[5,6] In these reactions a metal in its 0 oxidation state is treated with HCl gas in the presence of 21-crown-7 or dibenzo-30-crown-10, while being irradiated with UV light. A liquid clathrate species rapidly forms, and from this medium self-assembly of the product of lowest energy occurs, and indeed it has often been found that the lowest-energy species which exist in liquid clathrate media are simple co-ordination complexes or unusual oxonium ion species.[5,6,8] We have previously demonstrated that oxidation of the metal center from 0 to +6 for **1**, 0 to +2 for **2** and 0 to +5 for **3** occurs on performing the reaction in contact with air. In the absence of air, anions of the type [$M^0(CO)_5Cl]^-$ are isolated.[6]

The cation in complex **1** displays only the second crystal structure of the 21-crown-7 molecule. The overall structure of the macrocycle adopts a shallow bowlic-type conformation (Fig. 2), which it most likely adopts to contain the higher energy[41] *cis* conformation of the $H_5O_2^+$ ion. This conformation is significantly different from the only previous structure determination of an unsubstituted 21-crown-7, where the macrocycle adopted a much flatter form.[23] It has been established that 18-crown-6 is of sufficient size selectively to isolate H_3O^+, and many crystal structures have now been determined on this cation.[1–8,10,13–19] In moving to the larger 21-crown-7 macrocycle the diameter of the crown is just large enough to accommodate $H_5O_2^+$ in its *cis* conformation, and further work should highlight the complexing ability of this crown ether for $H_5O_2^+$ ion over other oxonium ions.

An interesting and surprising aspect of compound **1** is the short intermolecular contact between an $H_5O_2^+$ ion and its symmetry equivalent of 3.07 Å. While this distance may be relatively long for a typical O–H···O bonding distance, it cannot be ignored, and may arise due to packing forces. For this to be a genuine hydrogen bond there would have to be some disorder of the H atoms of the $H_5O_2^+$, and the hydrogen bonding

Table 2 Selected bond distances (Å) and angles (°) for $[H_5O_2^+{\cdot}21\text{-crown-}7][WOCl_5^-]$ **1**

W–O	1.67(1)	W–Cl(1)	2.366(5)
W–Cl(2)	2.371(5)	W–Cl(3)	2.354(6)
W–Cl(4)	2.372(5)	W–Cl(5)	2.666(5)
O(A)–O(B)	2.411		
O–W–Cl(1)	97.0(5)	O–W–Cl(2)	97.0(5)
O–W–Cl(3)	96.2(5)	O–W–Cl(4)	95.6(5)
O–W–Cl(5)	178.8(4)	Cl(1)–W–Cl(2)	88.4(2)
Cl(1)–W–Cl(3)	166.8(2)	Cl(1)–W–Cl(4)	90.4(2)
Cl(1)–W–Cl(5)	83.3(2)	Cl(2)–W–Cl(3)	89.6(2)
Cl(2)–W–Cl(4)	167.4(2)	Cl(2)–W–Cl(5)	84.2(2)
Cl(3)–W–Cl(4)	88.7(2)	Cl(3)–W–Cl(5)	83.5(2)
Cl(4)–W–Cl(5)	83.2(2)		

Table 3 Selected bond distances (Å) and angles (°) for $[2H_3O^+{\cdot}\text{dibenzo-30-crown-10}][W(CO)_4Cl_3^-]_2{\cdot}2C_6H_5Me$ **2**

W–C(a)	1.97(1)	C(a)–O(a)	1.14(1)
W–C(b)	2.02(1)	C(b)–O(b)	1.11(2)
W–C(c)	2.04(1)	C(c)–O(c)	1.14(2)
W–C(d)	1.67(5)	C(d)–O(d)	1.28(6)
W–Cl(1)	2.497(4)	W–Cl(2)	2.497(3)
W–Cl(3)	2.486(3)	O···O(1)	2.77
O···O(2)	2.73	O···O(3)	2.82
O···O(4)	2.59	O···O(5′)	2.54
C(a)–W–C(b)	71.8(6)	C(a)–W–C(c)	73.2(5)
C(a)–W–C(d)	71(1)	C(a)–W–Cl(1)	125.6(7)
C(a)–W–Cl(2)	128.0(5)	C(a)–W–Cl(3)	125.8(4)
C(b)–W–C(c)	112.9(7)	C(b)–W–C(d)	106(1)
C(b)–W–Cl(1)	78.3(5)	C(b)–W–Cl(2)	160.0(4)
C(b)–W–Cl(3)	76.8(5)	C(c)–W–C(d)	114(1)
C(c)–W–Cl(1)	78.3(5)	C(c)–W–Cl(2)	79.4(4)
C(c)–W–Cl(3)	161.0(3)	C(d)–W–Cl(1)	163.0(8)
C(d)–W–Cl(2)	81(1)	C(d)–W–Cl(3)	77.0(7)
Cl(1)–W–Cl(2)	89.4(1)	Cl(1)–W–Cl(3)	88.3(1)
Cl(2)–W–Cl(3)	87.2(1)		

Table 4 Bond distances (Å) and angles (°) for $[2H_3O^+{\cdot}\text{dibenzo-30-crown-10}][WOCl_4(H_2O)^-]_2$ **3**

W–Cl(1)	2.373(3)	O(3)–C(6)	1.44(1)
W–Cl(2)	2.376(3)	O(3)–C(5)	1.42(1)
W–Cl(3)	2.351(3)	C(4)–C(5)	1.49(2)
W–Cl(4)	2.371(3)	C(3)–C(2d)	1.39(2)
W–O	1.661(8)	C(3)–C(2)	1.39(2)
W–O(w)	2.320(7)	C(2d)–C(2c)	1.39(2)
O(2)–C(4)	1.43(2)	C(2c)–C(2b)	1.35(2)
O(2)–C(3)	1.38(1)	C(2b)–C(2a)	1.41(2)
O(1)–C(2)	1.38(2)	C(2a)–C(2)	1.40(1)
O(1)–C(1)	1.43(1)	C(1)–C(10)	1.50(2)
O(5)–C(10)	1.44(2)	C(9)–C(8)	1.47(2)
O(5)–C(9)	1.43(1)	C(7)–C(6)	1.49(2)
O(4)–C(8)	1.43(2)		
O(4)–C(7)	1.45(1)		
Cl(1)–W–Cl(2)	89.0(1)	C(6)–O(3)–C(5)	110.9(8)
Cl(1)–W–Cl(3)	162.3(1)	O(2)–O(4)–C(5)	108.8(9)
Cl(1)–W–Cl(4)	89.9(1)	O(2)–O(3)–C(2d)	124.6(9)
Cl(1)–W–O	97.0(3)	O(2)–C(3)–C(2)	115.7(8)
Cl(2)–W–Cl(3)	87.3(1)	C(2d)–C(3)–C(2)	119.7(9)
Cl(2)–W–Cl(4)	163.8(1)	C(3)–C(2d)–C(2c)	119.0(9)
Cl(2)–W–O	100.3(3)	C(2d)–C(2c)–C(2b)	121.7(9)
Cl(3)–W–Cl(4)	88.9(1)	C(2c)–C(2b)–C(2a)	120.5(9)
Cl(3)–W–O	100.7(3)	C(2b)–C(2a)–C(2)	117.9(9)
Cl(4)–W–O	95.8(3)	O(1)–C(2)–C(3)	115.6(8)
Cl(1)–W–O(w)	80.5(1)	O(1)–C(2)–C(2a)	123.3(9)
Cl(2)–W–O(w)	82.6(1)	C(3)–C(2)–C(2a)	121.1(9)
Cl(3)–W–O(w)	81.9(1)	O(1)–C(1)–C(10)	107.1(8)
Cl(4)–W–O(w)	81.4(1)	O(5)–C(10)–C(1)	113.9(9)
O–W–O(w)	176.2(3)	O(5)–C(9)–C(8)	113.7(9)
C(4)–O(2)–C(3)	116.1(8)	O(4)–C(8)–C(9)	110.4(9)
C(2)–O(1)–C(1)	117.5(8)	O(4)–C(7)–C(6)	107.8(8)
C(10)–O(5)–C(9)	117.2(9)	O(3)–C(6)–C(7)	107.6(8)
C(8)–O(4)–C(7)	113.5(9)	O(3)–C(5)–C(4)	109.6(8)

Table 5 Torsion angles (°) for compound **1**

Angle	Compound **1**	$[MeOC_6H_4N_2{\cdot}21\text{-crown-}7][BF_4]$[23]
O(1)–C(2)–C(3)–O(4)	66	67.4
C(2)–C(3)–O(4)–C(5)	175	158.0
C(3)–O(4)–C(5)–C(6)	161	173.3
O(4)–C(5)–C(6)–O(7)	−161	−66.3
C(5)–C(6)–O(7)–C(8)	50	−165.9
C(6)–O(7)–C(8)–C(9)	146	−172.1
O(7)–C(8)–C(9)–O(10)	−62	74.0
C(8)–C(9)–O(10)–C(11)	163	−175.8
C(9)–O(10)–C(11)–C(12)	174	−159.5
O(10)–C(11)–C(12)–O(13)	66	−60.9
C(11)–C(12)–O(13)–C(14)	174	177.8
C(12)–O(13)–C(14)–C(15)	174	−169.6
O(13)–C(14)–C(15)–O(16)	−73	−58.1
C(14)–C(15)–O(16)–C(17)	−177	−167.9
C(15)–O(16)–C(17)–C(18)	159	−165.2
O(16)–C(17)–C(18)–O(19)	71	72.3
C(17)–C(18)–O(19)–C(20)	−174	177.6
C(18)–O(19)–C(20)–C(21)	−161	−156.3
O(19)–C(20)–C(21)–O(1)	−59	−68.0
C(20)–C(21)–O(1)–C(2)	168	173.9
C(21)–O(1)–C(2)–C(3)	−175	173.2

Table 6 Deviations (Å) from the least-squares plane for the crown oxygen atoms in compound **1**

Atom*	Compound **1**	$[MeOC_6H_4N_2{\cdot}21\text{-crown-}7][BF_4]$[23]
O(1)	0.36	−0.48
O(4)	1.92	0.44
O(7)	1.36	0.09
O(10)	−1.03	−0.30
O(13)	−1.36	−0.07
O(16)	−1.09	0.33
O(19)	−0.16	−0.02

* Atoms O(A) and O(B) of the $H_5O_2^+$ ions reside 1.48 and 1.01 Å respectively out of the least-squares plane of the oxygen atoms of the crown.

Table 7 Torsion angles (°) for compounds **2** and **3**

	Compound		Dibenzo-30-crown-10[24]
	2	**3**	
C(1)–O(1)–C(2)–C(3)	178	166	154
O(1)–C(2)–C(3)–O(2)	6	−2	2
C(2)–C(3)–O(2)–C(4)	177	177	174
C(3)–O(2)–C(4)–C(5)	−167	175	−165
O(2)–C(4)–C(5)–O(3)	−64	63	−63
C(4)–C(5)–O(3)–C(6)	177	−178	−177
C(5)–O(3)–C(6)–C(7)	−173	−167	175
O(3)–C(6)–C(7)–O(4)	61	67	72
C(6)–C(7)–O(4)–C(8)	174	162	−177
C(7)–O(4)–C(8)–C(9)	−174	−177	180
O(4)–C(8)–C(9)–O(5)	51	47	70
C(8)–C(9)–O(5)–C(10)	53	50	169
C(9)–O(5)–C(10)–C(1′)	68	65	−95
O(5)–C(10)–C(1′)–O(1′)	49	54	67
C(10)–C(1′)–O(1′)–C(2′)	175	179	−148

of this ion appears to be explained by the close contacts it has with the 21-crown-7 oxygen atoms. However, the geometry of these two adjacent $H_5O_2^+$ ions is reminiscent of the linear chain conformation observed in a crystal structure of an $H_9O_4^+$ ion.[18] The angles about the linear chain are also similar to those in $H_9O_4^+$.[18] However, in the present case, the identity and charge of the oxonium ions is clearly defined by the 1− charge of the metal-containing anion. The O(A)–O(B) distance of 2.41(3) Å is typical for an $H_5O_2^+$ ion,[39,40] and is further evidence for this type of oxonium ion.

The first crystal structural determination of the $[WOCl_5]^-$ anion occurred in compound **1**. The significant lengthening observed for the Cl(5) ligand [2.666(5) Å] compared with the four equatorial Cl ligands [2.366(7) Å] is typical of the *trans* effect where ligands *trans* to oxo ligands are appreciably lengthened. Other similarly distorted octahedral tungsten structures have been observed, although the tungsten is in the +5 oxidation state.[42–44] The structure of this tungsten(VI) anion is very similar to the tungsten(V) analogue $[WOCl_4(H_2O)]^-$ we have observed in related crown ether–oxonium ion chemistry and also in complex **3**, where the loosely bound terminal Cl ligand is replaced by a H_2O molecule.[8]

By increasing the size of the crown ether further from 21-crown-7 to dibenzo-30-crown-10 the potential for complexation of higher oligomers of oxonium ions should increase. The 30-crown-10 molecule has a high conformational mobility, so it should be possible for the macrocycle to fold, and encapsulate $H_5O_2^+$ or even $H_7O_3^+$, as in potassium ion complexes of dibenzo-30-crown-10, where the K^+ ion is co-ordinated by all ten O (crown) atoms.[24,27] We find, however, that the dibenzo-30-crown-10 ligand preferentially complexes two H_3O^+ oxonium ions, and adopts a much flatter conformation than in the potassium complex. The cations obtained in complexes **2** and **3** are the first compounds showing the selective complexation of H_3O^+ by dibenzo-30-crown-10. Indeed, they are also the first to exhibit a crown ether in which two oxonium ions are co-ordinated to the interior of the macrocycle. The crown ether adopts a relatively flat conformation with an H_3O^+ oxonium ion bound toward either end of the interior of the crown ether. The oxonium ions reside *ca.* 0.3 Å out of the plane defined by the O (crown) atoms, defining approximately pyramidal geometry for the H_3O^+ ions. This type of geometry is the lowest-energy conformation for the H_3O^+ ion, and is typically found in complexes where 18-crown-6 has been used selectively to isolate H_3O^+, although there is some conjecture as to whether some of these complexes contain planar H_3O^+ ions.[1–8,10,13–19]

The anions isolated in compounds **2** and **3** are similar to others we have isolated using the synthetic procedure employed in Scheme 1, where the cations were oxonium ion complexes of other crown ethers.[6,8] These types of ions have also been previously reported.[17,19,45] In complex **2** the anion shows capped trigonal-antiprismatic (or 4:3 piano stool) geometry, similar to other structures of this ion and also the analogous $[W(CO)_4Br_3]^-$ ion.[46,47] The anion in complex **3** exists with highly distorted octahedral stereochemistry, reminiscent of the *trans* effect, where the oxo and water ligands are in *trans* positions, and is similar to other $[MOX_4(H_2O)]^-$ ions we have previously isolated.[8]

Conclusion

We have shown in this contribution that, by using the novel synthetic approach that we have established for producing transition-metal-containing liquid clathrates, we can isolate interesting and unusual compounds using the 21-crown-7 and dibenzo-30-crown-10 macrocycles. Crystallographic studies have shown the 21-crown-7 molecule is of sufficient size to stabilize the $H_5O_2^+$ ion, by complexation through hydrogen bonds to the crown ether, over other oxonium ions from the liquid clathrate medium. This is only the second crystal structure determination of the 21-crown-7 molecule, and the conformation of the crown is significantly different from that in the previous structure, highlighting the conformational mobility of this crown. The first crystal structure of the $[WOCl_5]^-$ ion also appears in this complex. We have also shown that the dibenzo-30-crown-10 molecule appears preferentially to complex two H_3O^+ oxonium ions within the macrocycle, where the oxonium ions adopt pyramidal geometry.

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