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Use of metal carbonyls in the formation of $[H_5O_2^+ \cdot 15\text{-crown-5}][MOCl_4(H_2O)^-]$, (M = Mo, W), and a second sphere coordination complex in $[mer\text{-}CrCl_3(H_2O)_3 \cdot 15\text{-crown-5}]$[1]

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Abstract

The reactions of $M(CO)_6$ (M = Mo, W) with $HCl_{(g)}$ in the presence of 15-crown-5 and H_2O in toluene have been explored. These reactions were promoted with the use of UV radiation and formed liquid clathrates almost immediately upon reaction. For each metal species, oxidation of the metal center from either [0] to [+ 3] in the case of Cr or from [0] to [+ 5] in the case of both Mo and W occurred. For chromium, a new isomer of $CrCl_3(H_2O)_3$ was generated in the second-sphere coordination complex, $[mer\text{-}CrCl_3(H_2O)_3 \cdot 15\text{-crown-5}]$ (**1**), which crystallized from the liquid clathrate layer in the reaction mixture. For molybdenum and tungsten the isostructural complexes, $[H_5O_2^+ \cdot 15\text{-crown-5}][MOCl_4(H_2O)^-]$, (M = Mo (**2**), M = W, (**3**)) rapidly formed where the $H_5O_2^+$ oxonium ion was stabilized within the liquid clathrate layer. The structures of each of these complexes were established by X-ray crystallography. Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.261(3)$, $b = 16.182(3)$, $c = 12.899(5)$ Å, $\beta = 107.87(1)°$, $V = 1839$ Å^3 and $D_{calc.} = 1.568$ g cm^{-3} for $Z = 4$. Refinement based on 3217 observed reflections led to a final R value of 0.085. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.840(3)$, $b = 12.053(1)$, $c = 13.290(2)$ Å, $\beta = 94.26(3)°$, $V = 2051$ Å^3 and $D_{calc.} = 1.720$ g cm^{-3} for $Z = 4$. Refinement based on 3208 observed reflections led to a final R value of 0.051. Complex **3** is isostructural with **2** with $a = 12.805(2)$, $b = 12.024(1)$, $c = 13.293(2)$ Å, $\beta = 94.25(1)°$, $V = 2041$ Å^3 and $D_{calc.} = 2.015$ g cm^{-3} for $Z = 4$. Refinement based on 2543 observed reflections led to a final R value of 0.045.

Keywords: Carbonyls; 15-Crown-5; Second sphere coordination

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1. Introduction

The carbonyls and halocarbonyls of the Group VI elements have been widely explored, particularly as starting materials for various adducts of these transition metals [1]. $[M^0(CO)_5X]^-$ anions are well known, and can be easily prepared from $M(CO)_6$ and $NR_4^+X^-$ [2]. The M^{II} species $[M^{II}(CO)_4X_2]$ is typically prepared by halogen oxidation of $M(CO)_6$ (M = Mo, W but not Cr) [3]. The M^{II} complex can then be used in the synthesis of $[M^{II}(CO)_4X_3]^-$ and $[M^{II}(CO)_3L_2X_2]$ [3]. All these complexes are useful for further reaction, for example, where CO undergoes ligand substitution reactions or where further oxidation of the metal center is desired. We have been using metal carbonyls as useful starting materials for the synthesis of either halocarbonyl- or oxohalo-metal anions which stabilize oxonium ion/crown ether cations in liquid clathrate media [4]. Furthermore our studies of transition metal complexes existing within liquid clathrate media, displays the potential for catalytically active species being formed within these systems.

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[1] Dedicated to Professor Michael Bruce on the occasion of his 60th birthday.

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Our group [4–9] and others [10–20] have established that the 18-crown-6 macrocyclic ligand is selective at stabilizing the H_3O^+ oxonium ion. The size of the cavity of the ligand appears to be of sufficient size to just accommodate H_3O^+ and a number of structures have verified the existence of the oxonium ion snugly bound in the crown [4–9,11,14–20]. Furthermore, we have isolated a number of complexes from liquid clathrate systems in which we are able to stabilize H_3O^+ in aromatic media [4–9]. In novel reactions, we have been able to generate simple transition metal species which act as counterions to $[H_3O^+ \cdot 18\text{-crown-6}]$ cations, by the addition of metal carbonyls [e.g. $M(CO)_6$ (M = Cr, Mo, W)] to the reaction mixture ([4]a,b,g). In moving to the larger crown ethers 21-crown-7 and dibenzo-30-crown-10 we found that the cavities within the crown ether were sufficiently large to accommodate an $H_5O_2^+$ ion in the former and two H_3O^+ ions in the latter ([4]c,d). In analogous reactions for 15-crown-5 and the first row transition metals, manganese, iron and cobalt, we found that the metal competed with oxonium ions for coordination within the crown ([4]e,f). Here, the ratio of the metal ion diameter to the crown cavity diameter dictated that the metal would reside within the crown.

We now present a study of similar systems with 15-crown-5 and the Group VI metals, chromium, molybdenum and tungsten. In moving to these transition metal ions where the metal center is not suitable for complete complexation by the crown, oxonium ions can compete for coordination sites of the crown ether. We therefore felt that an investigation, where this competition does not occur, would open up new chemistry and possibly lead to the oxonium ion selectivity for 15-crown-5.

As part of our study of liquid clathrate systems [21–23], particularly of the $[H_3O^+ \cdot 18\text{-crown-6}]$ ion, we have now investigated the formation of chromium, molybdenum and tungsten complexes of the $[(H_2O)_nH^+ \cdot 15\text{-crown-5}]$ system. Herein we report the synthesis and crystal structures of [*mer*-$CrCl_3(H_2O)_3 \cdot 15$-crown-5] (**1**), and $[H_5O_2^+ \cdot 15\text{-crown-5}][MOCl_4(H_2O)^-]$, (M = Mo, **2** and M = W, **3**), which were all isolated from aromatic media. In complex **1**, we have established a new structural isomer for the $CrCl_3(H_2O)_3$ system, where the species also exhibits second-sphere coordination to a 15-crown-5 molecule. In complexes **2** and **3**, $H_5O_2^+$ oxonium ions were selectively isolated and were involved in H-bonded polymeric strands linking successive 15-crown-5 molecules. The anions obtained in compounds **2** and **3** are similar to those we have previously obtained in these novel reactions.

2. Experimental section

$Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ were obtained from Aldrich and HCl gas was purchased from Atlas. Complexes **1–3** were prepared exposed to air, prior to the reaction mixture being sealed in an air-tight screw-top tube. Attempts to ascertain the complex:toluene ratio present in the liquid clathrate layer by ^{1}H-NMR, were hampered by the paramagnetic nature of the metal species in each complex. Repeated attempts at obtaining microanalytical data were foiled by decomposition of the crystalline material in the absence of solvent.

2.1. Preparation of [mer-$CrCl_3(H_2O)_3 \cdot$ 15-crown-5], ***1***

To a sample of 15-crown-5 (0.80 g, 3.62 mmol) in toluene (ca. 100 ml), was added H_2O (0.065 g, 3.62 mmol) and $Cr(CO)_6$ (0.80 g, 3.62 mmol) and stirred rapidly for 15 mins. $HCl_{(g)}$ was then rapidly bubbled through the mixture for ca. 1 h while irradiating with UV radiation. A violet-colored liquid clathrate separated from the solvent during the addition of $HCl_{(g)}$. Deep violet-colored crystals of the title complex deposited from the liquid clathrate layer after ca. 72 h.

2.2. Preparation of $[H_5O_2^+ \cdot$ 15-crown-5]$[MoOCl_4(H_2O)^-]$, ***2***

To a sample of 15-crown-5 (0.80 g, 3.62 mmol) in toluene (ca. 100 ml), was added H_2O (0.065 g, 3.62 mmol) and $Mo(CO)_6$ (1.0 g, 3.62 mmol) and stirred rapidly for 15 min. $HCl_{(g)}$ was then rapidly bubbled through the mixture for ca. 1 h while irradiating with UV radiation. During this time a red-colored liquid clathrate separated from the toluene layer. Bright green crystals of the title complex deposited from the liquid clathrate layer after ca. 30 h.

2.3. Preparation of $[H_5O_2^+ \cdot$ 15-crown-5]$[WOCl_4(H_2O)^-]$, ***3***

A sample of 15-crown-5 (0.80 g, 3.62 mmol) was moistened with distilled water (0.065 ml, 3.62 mmol) and ca. 100 ml of toluene added. A sample of $W(CO)_6$ (1.27g, 3.62 mmol) was then added and $HCl_{(g)}$ was rapidly bubbled through the mixture for ca. 1 h while irradiating with UV light. After this time, a bright yellow liquid clathrate separated from the solvent. Bright blue crystals of the title complex deposited from the clathrate layer after ca. 24 h.

2.4. Collection of X-ray diffraction data, and solution and refinement of the structures

Single crystals of **1**, **2** and **3** were sealed in thin walled glass capillaries under an atmosphere of

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

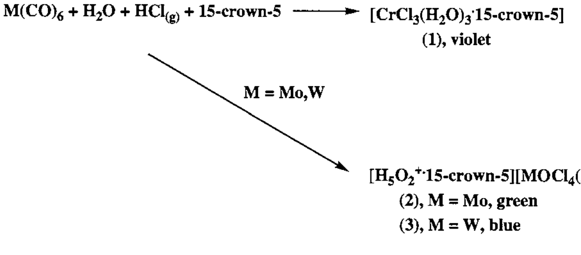
Compound	[*mer*-$CrCl_3(H_2O)_3 \cdot$ 15-crown-5] (**1**)	[$H_5O_2^+ \cdot$ 15-crown-5][$MoOCl_4(H_2O)^-$] (**2**)	[$H_5O_2^+ \cdot$ 15-crown-5][$WOCl_4(H_2O)^-$] (**3**)
Molecular weight	432.7	529.1	617.0
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Cell constants			
a (Å)	9.261(3)	12.840(3)	12.805(2)
b (Å)	16.182(3)	12.053(1)	12.024(1)
c (Å)	12.899(5)	13.290(2)	13.293(2)
α (°)	90	90	90
β (°)	107.87(3)	94.26(3)	94.25(1)
γ (°)	90	90	90
V (Å^3)	1839(2)	2051(8)	2041(2)
Z	4	4	4
$D_{calc.}$ (g cm^{-3})	1.568	1.720	2.015
Crystal dimensions (mm)	$0.28 \times 0.32 \times 0.18$	$0.44 \times 0.24 \times 0.22$	$0.40 \times 0.36 \times 0.24$
μ (cm^{-1})	10.8	11.9	63.1
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$	Mo–K$_\alpha$
Scan width (°)	$0.80 + 0.20 \tan\theta$	$0.80 + 0.20 \tan\theta$	$0.80 + 0.20 \tan\theta$
2θ range (°)	2–50	2–50	2–50
No. reflections collected	3450	3963	3390
No. reflections observed	3217	3208	2543
No. parameters varied	317	217	217
Sigma cutoff	3σ	3σ	3σ
T (K)	296	296	296
R	0.085	0.051	0.045
R_w	0.052	0.067	0.059

toluene due to crystals decomposing in the absence of solvent. 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 in Table 1. An empirical absorption correction based on psi scan data was performed on all three compounds. Intensity standards of all three compounds showed insignificant deviation or decay during data collection, therefore a decay correction was not applied. Calculations were carried out using the SHELX system of computer programs [24].

Positions of heavy atoms were determined from a 3-D Patterson function. All other non-H atoms were located from a difference-Fourier synthesis. All non-H atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the water molecules and oxonium ions in **1, 2** and **3**, were not located on the difference map. All other hydrogen atoms were placed at calculated positions and their parameters were not refined. The 15-crown-5 molecule in complex **1** was disordered over two sites. The disorder of this molecule was successfully modeled, with C1, 2 being refined with full occupancies and C3 to C10 being refined with half occupancies. All O atoms of the 15-crown-5 molecule were refined with half occupancies. Refinements converged with $R = 0.085$ for 3217 observed reflections for **1**, $R = 0.051$ for 3208 observed reflections for **2** and $R = 0.045$ for 2543 observed reflections for **3**.

2.5. Preparation of complexes

Complexes **1**–**3** were prepared according to the novel reaction conditions presented in Scheme 1. In each reaction the mixture rapidly separated into two phases yielding liquid clathrate species. The upper layer in these reactions was neat toluene (as determined by ^{1}H-NMR), 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 [+3] for **1** and [0] to



Scheme 1. Preparation of complexes **1**–**3**.

Table 2
Selected bond distances (Å) and angles (°) for [*mer*-$CrCl_3(H_2O)_3\cdot$15-crown-5], **1**

Bond distances (Å)			
Cr–Cl(1)	2.312(2)	Cr–O(1w)	1.987(2)
Cr–Cl(2)	2.325(2)	Cr–O(2w)	2.046(3)
Cr–Cl(3)	2.269(1)	Cr–O(3w)	2.024(3)
Bond angles (°)			
Cl(1)–Cr–Cl(2)	174.20(5)	Cl(2)–Cr–O(3w)	88.4(1)
Cl(1)–Cr–Cl(3)	92.74(5)	Cl(3)–Cr–O(1w)	92.46(8)
Cl(1)–Cr–O(1w)	89.06(9)	Cl(3)–Cr–O(2w)	177.66(9)
Cl(1)–Cr–O(2w)	85.6(1)	Cl(3)–Cr–O(3w)	89.20(9)
Cl(1)–Cr–O(3w)	93.5(1)	O(1w)–Cr–O(2w)	89.2(1)
Cl(2)–Cr–Cl(3)	92.78(5)	O(1w)–Cr–O(3w)	176.9(1)
Cl(2)–Cr–O(1w)	88.90(9)	O(2w)–Cr–O(3w)	89.2(1)
Cl(2)–Cr–O(2w)	88.9(1)		

[+5], for **2** and **3**. 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 ([4]b).

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.

2.6. Structural results

Selected bond distances and angles for complexes **1–3** are shown in Tables 2–4. Details for the diffraction experiments are given in Section 2.4.

2.6.1. [mer-$CrCl_3(H_2O)_3\cdot$15-crown-5], **1**

This complex does not crystallize as discrete anions and cations, but rather as a neutral Cr^{III} species where the Cr has three Cl^- and three H_2O ligands. The coordination compound is then coordinated in a second-sphere fashion by two 15-crown-5 molecules which are hydrogen bonded to the three water ligands which generates a polymeric array (see Fig. 1).

Table 3
Selected bond distances (Å) and angles (°) for [$H_5O_2^+\cdot$15-crown-5][$MoOCl_4(H_2O)^-$] (**2**)

Bond distances (Å)			
Mo–Oxo	1.66(5)	Mo–Wat	2.345(5)
Mo–Cl(1)	2.370(2)	Mo–Cl(2)	2.370(2)
Mo–Cl(3)	2.386(2)	Mo–Cl(4)	2.373(2)
		O(A)–O(B)	2.399(2)
Bond angles (°)			
Wat–Mo–Oxo	178.1(2)	Oxo–Mo–Cl(1)	100.0(2)
Wat–Mo–Cl(1)	81.9(1)	Cl(1)–Mo–Cl(2)	89.21(8)
Oxo–Mo–Cl(2)	98.6(3)	Wat–Mo–Cl(2)	81.5(2)
Cl(1)–Mo–Cl(3)	163.23(8)	Cl(2)–Mo–Cl(3)	88.93(8)
Oxo–Mo–Cl(3)	96.7(2)	Wat–Mo–Cl(3)	81.4(1)
Cl(1)–Mo–Cl(4)	88.43(8)	Cl(2)–Mo–Cl(4)	162.45(8)
Cl(3)–Mo–Cl(4)	88.34(7)	Oxo–Mo–Cl(4)	98.9(3)
Wat–Mo–Cl(4)	80.9(2)		

Table 4
Selected bond distances (Å) and angles (°) for [$H_5O_2^+\cdot$15-crown-5][$WOCl_4(H_2O)^-$] (**3**)

Bond distances (Å)			
W–Oxo	1.67(1)	W–Wat	2.321(9)
W–Cl(1)	2.363(4)	W–Cl(2)	2.369(4)
W–Cl(3)	2.377(4)	W–Cl(4)	2.375(4)
		O(A)–O(B)	2.383(2)
Bond angles (°)			
Wat–W–Oxo	178.3(4)	Oxo–W–Cl(1)	99.4(4)
Wat–W–Cl(1)	82.3(3)	Cl(1)–W–Cl(2)	89.4(1)
Oxo–W–Cl(2)	99.6(4)	Wat–W–Cl(2)	80.9(3)
Cl(1)–W–Cl(3)	163.6(1)	Cl(2)–W–Cl(3)	89.0(1)
Oxo–W–Cl(3)	96.9(4)	Wat–W–Cl(3)	81.4(2)
Cl(1)–W–Cl(4)	87.9(1)	Cl(2)–W–Cl(4)	162.5(1)
Cl(3)–W–Cl(4)	88.7(1)	Oxo–W–Cl(4)	97.9(3)
Wat–W–Cl(4)	81.6(2)		

The six-coordinate metal complex adopts close to regular octahedral stereochemistry where the Cl and water ligands reside in *meridional* sites around the metal center (Fig. 1). The Cr–O(H_2O) lengths are 2.02(2) (av, average) Å, while the average Cr–Cl distances are 2.30(2) Å. The angles about the octahedral metal center range from 85.6(1) to 93.5(1)° and reflect the slight distortion from regular octahedral stereochemistry.

The 15-crown-5 molecules in this complex are H-bonded through the heteroatoms of the crown to the water ligands on the metal center in a second-sphere fashion. The 15-crown-5 molecules bridge successive [*mer*-$CrCl_3(H_2O)_3$] molecules through this second-sphere H-bonded framework. The H-bonding distances are as follows: O(1w)···O(2) 2.83, O(1w)···O(5) 2.63, O(2w)···O(1) 2.98, O(2w)···O(3) 2.85 and O(3w)···O(4) 2.68 Å. The 15-crown-5 molecules are disordered over the two sites, where the crown is rotated by ca. 36° so that in the model, ten O sites were located at half occupancy and eight of the ten C atoms were located with half occupancy, with the remaining two C being modeled with full occupancy (relatively high thermal motion is observed for the C atoms).

2.6.2. [$H_5O_2^+\cdot$15-crown-5][$MoOCl_4(H_2O)^-$], **2** *and [$H_5O_2^+\cdot$15-crown-5][$WOCl_4(H_2O)^-$],* **3**

Both the molybdenum and tungsten analogues (compounds **2** and **3**) are isostructural. These complexes crystallize with discrete [$MOCl_4(H_2O)^-$] (M = Mo, W) anions which reside in cavities between the [$H_5O_2^+\cdot$15-crown-5] cations which are hydrogen bonded in strands throughout the crystal. The $H_5O_2^+$ oxonium ions link together the 15-crown-5 molecules in cationic strands through a 1-D H-bonded array (Fig. 2).

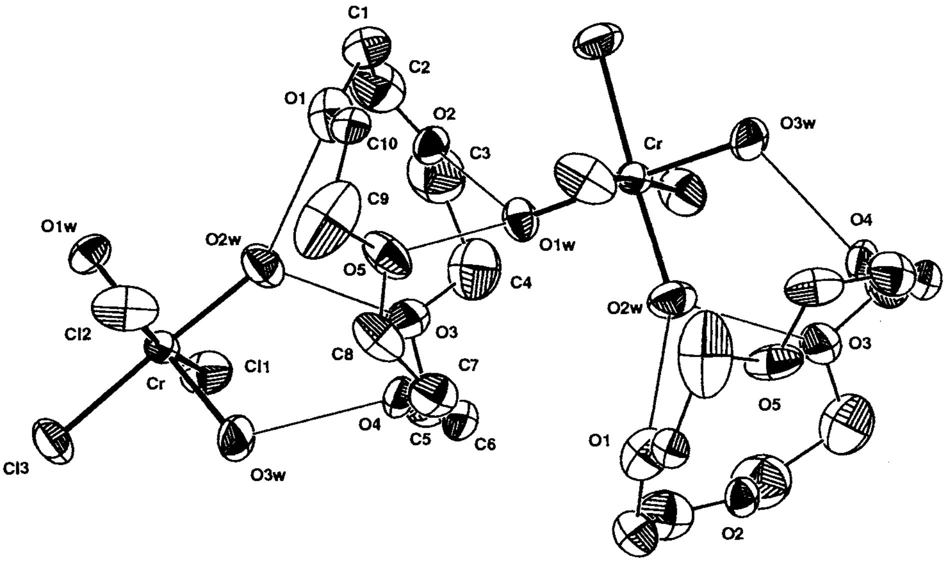


Fig. 1. Structure of the [*mer*-$CrCl_3(H_2O)_3 \cdot$15-crown-5] (**1**), showing the second-sphere coordination by the 15-crown-5 molecule about the chromium center.

In the [$H_5O_2^+ \cdot$15-crown-5] cation, the geometry around the $H_5O_2^+$ center is the lower energy staggered conformation [25]. Although the H atoms on these ions were not located, the staggered arrangement is evident (see Fig. 2). The $H_5O_2^+$ oxonium ions link together successive 15-crown-5 molecules, forming one dimensional polymeric strands. The Oa···Ob distances of 2.399(2) Å for compound **2**, and 2.383(2) Å for compound **3** in the $H_5O_2^+$ ion are slightly shorter than is typically found in these ions [26,27], but is within the range of distances observed, where distances as short as 2.327(8) Å have been established ([4]e). The oxonium ion to crown distances for compound **2** are as follows: Oa···O(4) 2.625, Oa···O(13) 2.630, Ob···O(1) 2.728 and Ob···O(10) 2.783 Å. Those for compound **3** are: Oa···O(4) 2.623, Oa···O(13) 2.624, Ob···O(1) 2.706 and Ob···O(10) 3.085 Å.

It is also possible that there is potential disorder in structures **2** and **3**. It is evident that it is possible that O(b) binds to O(7) in both the molybdenum and tungsten structure, where the distances are 3.099 and 2.738 Å, respectively. If this is the case, the conformation around the $H_5O_2^+$ ion does not significantly change, and the lower energy staggered arrangement still exists. The high thermal parameters on C(8) and C(9) in compounds **2** and **3** indicate there is possible disorder in these ethylene bridges, but this was not modeled.

The [$MOCl_4(H_2O)^-$] (M = Mo, compound **2**, W, compound **3**) anions exist as discrete ions in voids formed between the cationic, polymeric strands. There are no interionic distances shorter than 3.5 Å. The anion exists as a highly distorted octahedron where the M–O(wat) bonds, which are *trans* to the Oxo ligand are appreciably lengthened due to the *trans* effect (Mo–Wat 2.345(5), Mo–Oxo 1.661(5), W–Wat 2.321(9) and W–Oxo 1.67(1) Å). The M–Cl bonding distances average 2.375(6) Å in **2** and 2.371(5) Å in **3**, and are bent down and away from the Oxo ligand at 99(1)° in **2** and 98(1)° in **3**, and reflect the distortion away from a regular octahedron.

3. 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 coordination compounds [4]. In these reactions a metal carbonyl in its [0] oxidation state is treated with HCl gas ion the presence of 15-crown-5, 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 unusual coordination complexes or oxonium ion species ([4]g). In a number of these reactions, ^{13}C-NMR spectroscopy of the liquid clathrate layer immediately following completion of the reaction indicated the presence of a large number of carbonyl resonances. This indicates that either (i) the reaction is incomplete and a number of intermediates are present or (ii) that there are a large number of species present in the liquid clathrate layer in a complex equilibrium which is shifted as the lowest energy product is deposited from solution. We have previously demonstrated that oxidation of the metal center from [0] to [+3] for **1** and [0] to [+5] for **2** and **3**, occurs from

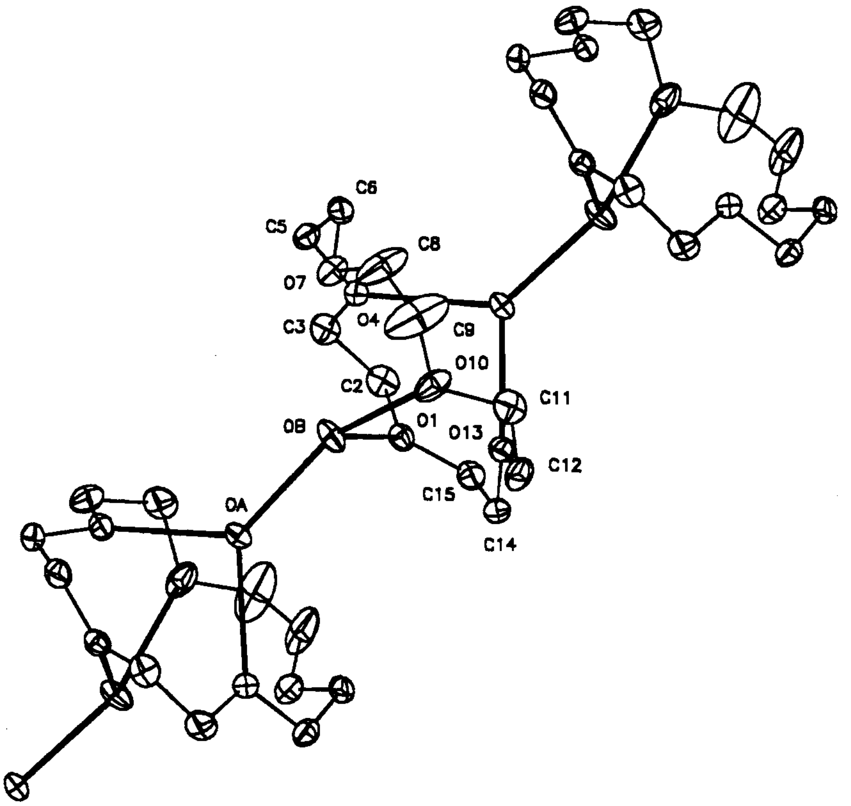


Fig. 2. Structure of the cationic polymeric [$H_5O_2^+ \cdot$15-crown-5], strands in the isostructural complexes **2** and **3**. The hydrogen bonding contacts for compound **2** are as follows (distances for compound **3** are in parentheses); Oa$\cdots$Ob 2.399(2), (2.383(2)), Oa$\cdots$O(4) 2.625, (2.623), Oa$\cdots$O(13) 2.630, (2.624), Ob$\cdots$O(1) 2.728, (2.706) and Ob$\cdots$O(10) 2.783 Å, (3.085 Å).

performing the reaction in contact with air. In the absence of air, anions of the type [$M^0(CO)_5Cl^-$] are isolated ([4]b).

In most other reactions employing the synthetic approach used herein, we have isolated oxonium ions either coordinated within the macro cycle or linking crown ether molecules together in hydrogen bonded arrays. The factor which dictates whether or not, coordination of the oxonium ion occurs is the diameter of the crown ether cavity. For 18-crown-6, the cavity is of sufficient size (diameter, 2.6–3.2 Å [28]) to selectively coordinate the H_3O^+ oxonium ion. In moving to 15-crown-5, the diameter of the crown is significantly diminished (diameter, 1.7–2.2 Å [29]), so coordination of an oxonium ion within the macrocycle is not expected, and indeed in all three species isolated, no *endo* complexation occurs. Possible competition for coordination within the crown ether could come from the metal ion itself. However, in looking at the metal ion diameter/crown ether cavity diameter ratios of 0.56–0.72 for Cr^{3+}, 0.55–0.72 for Mo^{5+} and 0.56–0.0.73 for W^{5+}, it is not surprising that we have isolated no complexes with the transition metal coordinated within the macrocycle. It has been established that ratios of 0.75–0.90 are favorable for direct ion/crown ether bonding in alkali metals [30]. For the first-row transition metals Mn, Fe and Co, we have shown that this guideline holds true for liquid clathrate species ([4]e,f).

For complex **1** no oxonium ions were isolated, instead the second sphere coordination complex [*mer*-$CrCl_3(H_2O)_3$15-crown-5] deposited from the liquid clathrate layer. This complex contains three water molecules and three chloride ligands in a *meridional* arrangement and represents a new isomeric form for the well known species $CrCl_3(H_2O)_3$. Previously, three isomeric forms for $CrCl_3(H_2O)_3$ have been established, viz, the violet hexaaqua ion, $[Cr(H_2O)_6]Cl_3$, the dark green *trans*-$[CrCl_2(H_2O)_4]Cl \cdot$2H2O, which is the commercially available salt, and the pale green $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ [31,32]. Complex **1** is closely related however, to the tetrahydrofuranate salt [*mer*-$CrCl_3(THF)_3$], where the average bonding parameters compare well with compound **1** ($Cr-Cl_{av}$ 2.30(1), $Cr-O_{av}$ 2.03(3) Å for [*mer*-$CrCl_3(THF)_3$] and $Cr-Cl_{av}$ 2.30(2), $Cr-O_{av}$ 2.02(2) Å for compound **1**) [33]. The stabilization of this new form of $CrCl_3(H_2O)_3$ may be due to either of two factors. Firstly, the conditions the species encounters in the liquid clathrate medium, i.e. a highly ionic, ordered aromatic medium, are extremely different to aqueous media where the other three isomers are observed. Energy levels for the existence of certain species in this media are almost certainly vastly different, allowing the isolation of new species. Secondly, the formation of a second-sphere coordination complex, where a 15-crown-5 molecule is hydrogen bonded to the water ligands, may sufficiently stabilize the compound where the *meridional* stereochemistry is observed.

For the isostructural complexes, **2** and **3**, $[H_5O_2^+ \cdot 15\text{-crown-5}][MOCl_4(H_2O)^-]$ (M = Mo, **2**, M = W, **3**) oxonium ions were isolated. Due to the size of the metal in question, the crown ether is of insufficient size for metal ion complexation, and the $[MOCl_4(H_2O)^-]$ anions, which we have typically observed in these reactions are isolated [16,18,27].

The oxonium ion isolated in compounds **2** and **3** was the $H_5O_2^+$ species, where it successively bridges 15-crown-5 molecules to form polymeric H-bonded strands. It is encouraging that in both complexes, the $H_5O_2^+$ ion was isolated, and further chemistry may define the selectivity of 15-crown-5 for $H_5O_2^+$ in these types of systems. Of course if there is competition for complexes of lower energy to self assemble, as in the case of [*mer*-$CrCl_3(H_2O)_3 \cdot$15-crown-5] **1**, above, then it may not be possible to establish a general selectivity pattern.

The $H_5O_2^+$ oxonium ions are of the lowest energy staggered type, typically encountered [25]. The $Oa \cdots Ob$ distances of 2.399(2) and 2.383(2) Å are slightly shorter than is typically observed (2.41–2.45 Å) [26,27] and may arise due to the sandwiching of the ion between the successive 15-crown-5 molecules. As in complexes where we observe the $[H_3O^+ \cdot 18\text{-crown-6}]$ ion, we only observe H-bonding contacts between the crown ether and the oxonium ions. No interionic distances < 3.5 Å were observed. However, in the $[H_3O^+ \cdot 18\text{-crown-6}]$ case, the ions were isolated as discrete cations, while in the present case, the $[H_5O_2^+ \cdot 15\text{-crown-5}]$ ions form polymeric strands of oxonium ions and 15-crown-5 molecules, which is similar to several oxonium ion/12-crown-4 complexes we have isolated ([4]e,f). This prompts further questions as to what type of molecular building blocks, where there are H-bond donors and acceptors, can be utilized in engineering molecular architectures.

The anions isolated in compounds **2** and **3** are similar to others we have isolated using the synthetic procedure employed in Scheme 1 ([4]c,g). These types of ions have also been previously been reported [18,20,34]. They exist with highly distorted octahedral stereochemistry, being reminiscent of the *trans* effect, where the oxo and water ligands are in *trans* positions.

4. Conclusions

We have highlighted in this paper that using $M(CO)_6$ (M = Cr, Mo, W) as convenient starting materials, transition metal containing liquid clathrates that also involve the 15-crown-5 macrocycle can be isolated. A new isomeric form of $CrCl_3(H_2O)_3$ has been isolated from the liquid clathrate medium and further shows that within this medium, different and exciting new chemistry can be observed. In reactions involving molybdenum and tungsten, we have stabilized and isolated the oxonium ion/crown ether species $[H_5O_2^+ \cdot 15\text{-crown-5}]$, where the cation forms hydrogen bonded polymeric strands. Further chemistry involving 15-crown-5 will be pursued to explore the selectivity of the macrocycle for the $H_5O_2^+$ oxonium ion.

5. Supplementary material available

Lists of anisotropic thermal parameters, complete bond lengths and angles tables and listings of observed and calculated structure factors are available from the author. Ordering information is on any current masthead page.

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