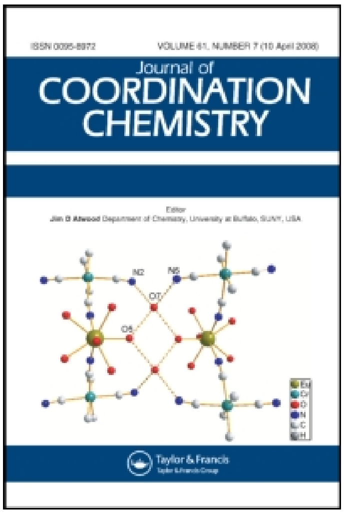

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SYNTHESES AND X-RAY CRYSTAL STRUCTURES OF NOVEL OXONIUM ION-12-CROWN-4 COMPLEXES ISOLATED FROM LIQUID CLATHRATE MEDIA

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The reactions of $Mo(CO)_6$ and $W(CO)_6$ with $HCl_{(g)}$ in the presence of 12-crown-4 and H_2O have been investigated in toluene. For both reactions, two products were isolated, depending on the oxidation of the metal center. For molybdenum, the Mo^{III} species, $[H_3O^+ \cdot 12\text{-crown-4}]_3[Mo_2Cl_9{}^{3-}]$, **1**, was obtained from the liquid clathrate layer in the reaction mixture. Upon air oxidation of the reaction mixture, the Mo^V complex, $[H_7O_3^+ \cdot H_5O_2^+ \cdot (12\text{-crown-4})_2][MoOCl_4(H_2O)^-]_2$, **2**, rapidly formed. For tungsten, the W^{II} species, $[(H_5O_2^+)_2 \cdot 12\text{-crown-4}][W(CO)_4Cl_3^-]_2$, **3**, deposited from the liquid clathrate layer which upon oxidation formed the W^V complex, $[H_3O^+ \cdot 12\text{-crown-4}][WOCl_4(H_2O)^-]$, **4**. These reactions were promoted by UV radiation and formed liquid clathrates almost immediately upon reaction. X-ray crystal structures were performed on each compound. Complexes **1** and **4** have H_3O^+ oxonium ions involved in complex hydrogen bonded arrays with the 12-crown-4 acceptor molecules. The $H_5O_2^+$ oxonium ions in **2** and **3** contain extremely short $O \cdots O$ separations, equivalent to the shortest $O{-}H \cdots O$ bonds known. Also isolated in complex **2** was the $H_7O_3^+$ oxonium ion which contains an unusual *linear* $O \cdots O \cdots O$ core.

Keywords: Liquid clathrate; crown ether; molybdenum carbonyl; tungsten carbonyl; crystal structure

INTRODUCTION

We have recently been interested in the stabilization of transition metal anionic complexes in liquid clathrate media by utilizing the lipophilic cation,

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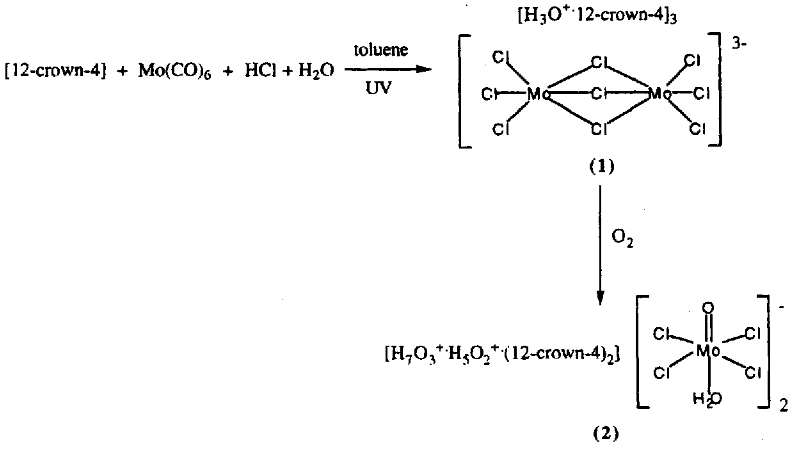
$[H_3O^+ \cdot 18\text{-crown-6}]$.[1-3] The cavity of the 18-crown-6 ligand is of sufficient size to accommodate the H_3O^+ oxonium ion in either a planar or pyramidal geometry.[4,5] In moving to smaller crown ethers *e.g.*, 15-crown-5 and 12-crown-4, however, the cavities of these macrocyclic ligands are not large enough for the oxonium ion to reside inside the cyclic ether. Here, the Na^+ and Li^+ ions respectively, are of a suitable size for incorporation into the ring, whereas for larger cations, the crown ethers must adopt higher energy, distorted conformations.[6] It was of interest to us to determine if this is also the case for the oxonium ions and therefore a structural investigation into the species obtained in the solid state with 12-crown-4 appeared warranted. The existence of higher oligomers of the $[(H_2O)_n \cdot H^+]$ species in these complexes was probable, in order for a well defined hydrogen bonded framework to exist. A prior investigation into the species obtained when 12-crown-4 exists in acidic media, found the existence of an inorganic uranium network held together by hydrogen bonds between water and 12-crown-4 (no oxonium ions were found).[7] This reaction was carried out in aqueous acetic acid media, whereas we have been investigating the species obtained when performing these reactions in aromatic media.

In our ongoing study of liquid clathrate systems,[8-10] particularly of the $[H_3O^+ \cdot 18\text{-crown-6}]$ ion, we have now investigated the formation of anionic molybdenum and tungsten complexes of the $[(H_2O)_nH^+ \cdot 12\text{-crown-4}]$ system. Incorporation of transition metal complexes into liquid clathrate media should promote the possibility of catalytic reactions in these highly ionic localized systems.

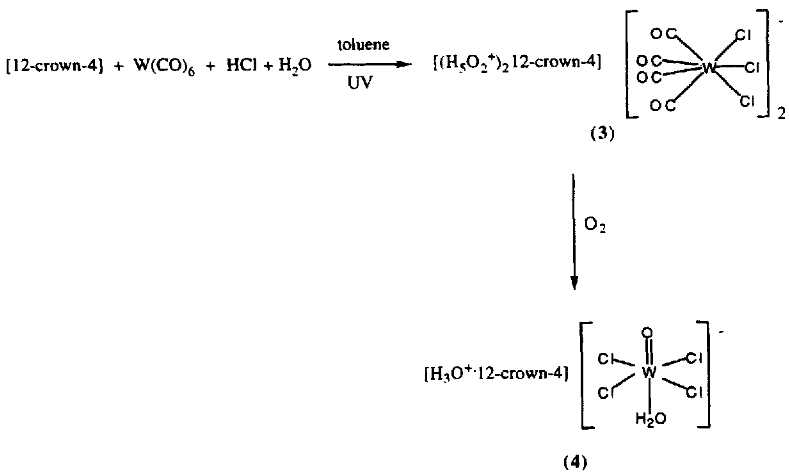
Herein we report the synthesis and crystal structures of $[H_3O^+ \cdot 12\text{-crown-4}]_3[Mo_2Cl_9{}^{3-}]$, **1**, $[H_7O_3^+ \cdot H_5O_2^+ \cdot (12\text{-crown-4})_2][MoOCl_4(H_2O)^-]_2$, **2**, $[(H_5O_2^+)_2 \cdot 12\text{-crown-4}][W(CO)_4Cl_3{}^-]_2$, **3**, and $[H_3O^+ \cdot 12\text{-crown-4})][WOCl_4(H_2O)^-]$, **4**, which were all isolated from aromatic media. Complex **2** is the first report of a compound containing *both* the $H_5O_2^+$ and $H_7O_3^+$ ions in the same complex and indeed the first time $H_7O_3^+$ has been identified in aromatic media. The $H_5O_2^+$ oxonium ions isolated in complexes **2** and **3** contain $O \cdots O$ separations which are equivalent to the shortest $O-H \cdots O$ hydrogen bonds reported. The $H_7O_3^+$ ion found in complex **2** contains a linear and symmetrical $O \cdots O \cdots O$ framework, which is the first evidence of this type of conformation for the $H_7O_3^+$ species.

PREPARATION OF COMPLEXES

Complexes studied in this investigation were prepared according to Schemes 1 and 2. In both reactions the reaction mixture quickly separated



SCHEME 1



SCHEME 2

into two phases yielding colored liquid clathrate species. The upper layer in these reactions was neat toluene, while the metal 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 (for **1** and **3**). Promotion of CO removal was aided by irradiating the reaction mixtures with UV light. In both reactions only partial oxidation of the metal center, from [0] to [3+], for **1** and [0] to [2+], for **3**, occurred.

Further exposure of reaction mixtures from **1** and **3** to air led to further oxidation of the metal centers from [3+] to [5+] for **2**, and from [2+] to [5+] for **4**. In other reactions where we have performed the experiment in the total exclusion of oxygen, no oxidation of the metal center takes place. Instead, we form complexes of the type $[M(CO)_5Cl^-]$.[2] In these reactions an assortment of cations of 12-crown-4 with different oligomers of $[(H_2O)_n \cdot H^+]$ in coexistence were isolated. The degree of oligomerization most probably depends on a number of factors including the size of the cation and the array of hydrogen bonding within the network of the crystalline material.

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 optimize these yields.

STRUCTURAL RESULTS

Details for the diffraction experiments are given in the Experimental section and in Table I. Fractional coordinates and bond distances and angles for complexes **1**–**4** are shown in Tables II–IX.

$[H_3O^+ \cdot 12\text{-crown-4}]_3[Mo_2Cl_9{}^{3-}]$, 1

This complex does not crystallize as discrete anions and cations, but rather as a framework held together by a hydrogen bonding network between the $[H_3O^+ \cdot 12\text{-crown-4}]$ moieties and the $[Mo_2Cl_9]^{3-}$ anion.

The anion resides on a mirror plane (through Mo(1), Mo(2), Cl(2), Cl(4) and Cl(6)) and consists of two octahedral $MoCl_6$ centers, which share three bridging chlorides. The average Mo–Cl(terminal) lengths are 2.41(1) Å, while the average Mo–Cl(bridging) distances are slightly longer at 2.46(1) Å. The Mo(1)–Mo(2) distance of 2.732(1) Å is similar to that in other $[Mo_2Cl_9{}^{3-}]$ type anions, *e.g.*, 2.727(6) Å in $[H_3O^+ \cdot 18\text{-crown-6}]_2[H_5O_2^+ \cdot Mo_2Cl_9{}^{3-}]$, and reflects negligible metal–metal interaction.[2d] Cl–Mo–Cl angles indicate the geometry around the metal centers is very close to a regular octahedron.

Two of the $[H_3O^+ \cdot 12\text{-crown-4}]$ cations were fully refined, the third was disordered over two sites. In the first two, the cation sits on the mirror plane (through O(oxonium) and O(1) and O(7)), and the O(oxonium) resides out of the plane defined by the heteroatoms of the crowns; 1.962 Å for cation A

TABLE I Crystal data and summary of data collection for complexes 1–4

Compound	$[H_3O^+ \cdot 12\text{-crown-4}]_3$ $[Mo_2Cl_9{}^{3-}]$ **1**	$[H_7O_3{}^+ \cdot H_5O_2{}^+ \cdot (12\text{-crown-4})_2]$ $[MoOCl_4(H_2O)^-]_2$ **2**	$[(H_5O_2^+)_2 \cdot 12\text{-crown-4}]$ $[W(CO)_4Cl_3{}^-]_2$ **3**	$[H_3O^+ \cdot 12\text{-crown-4}]$ $[WOCl_4(H_2O)^-]$ **4**
Molecular Formula	$C_{24}H_{57}Cl_9Mo_2O_{15}$	$C_{16}H_{51}Cl_8Mo_2O_{17}$	$C_{16}H_{26}Cl_6O_{16}W_2$	$C_8H_{21}Cl_4O_7W$
Molecular Weight	1096.7	991.1	1054.8	554.9
Space group	Pnma	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	23.874(3)	8.158(2)	8.035(1)	11.383(2)
b, Å	12.217(2)	11.370(4)	8.653(1)	11.889(2)
c, Å	15.229(1)	20.007(5)	12.904(1)	12.549(2)
α, (°)	90	90	100.08(1)	90
β, (°)	90	92.93(3)	107.83(1)	93.12(1)
γ, (°)	90	90	102.22(1)	90
V, Å^3	4442(1)	1853(3)	806(5)	1696(1)
Molecules/unit cell, *Z*	4	2	1	4
D_c, g cm^{-3}	1.640	1.656	2.382	2.154
μ, cm^{-1}	11.62	13.04	76.97	74.64
Radiation	MoKα	MoKα	MoKα	MoKα
2θ range, (°)	2–50	2–50	2–50	2–48
No. reflections collected	4087	3487	2590	2630
No. of observed reflections	3078	2700	2409	2147
No. of parameters varied	255	197	181	181
Sigma cutoff	2σ	2σ	2σ	2σ
Weighting scheme	Unit weights	Unit weights	Unit weights	Unit weights
Temp. of data colln. (°)	23	23	296	296
*R*1	0.059	0.075	0.060	0.087
R (all data)	0.069	0.081	0.062	0.091

TABLE II Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $[H_3O^+ \cdot 12\text{-crown-}4]_3[Mo_2Cl_9{}^{3-}]$ (1). *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
Mo(1)	644(1)	2500	1745(1)	33(1)
Mo(2)	1491(1)	2500	2951(1)	34(1)
Cl(1)	473(1)	1138(1)	625(1)	48(1)
Cl(2)	−316(1)	2500	2185(2)	50(1)
Cl(3)	807(1)	1017(1)	2802(1)	46(1)
Cl(4)	1653(1)	2500	1354(1)	45(1)
Cl(5)	2207(1)	1114(2)	3148(1)	57(1)
Cl(6)	1306(1)	2500	4514(1)	53(1)
OA	7462(3)	2500	9663(4)	49(2)
O(1A)	8592(3)	2500	10546(4)	51(2)
C(2A)	8865(3)	1511(8)	10302(5)	70(2)
C(3A)	8436(4)	626(7)	10231(5)	66(2)
O(4A)	8050(2)	826(4)	9537(3)	55(1)
C(5A)	8279(4)	603(7)	8671(5)	64(2)
C(6A)	8133(4)	1519(7)	8064(5)	66(2)
O(7A)	8378(3)	2500	8392(4)	51(2)
OB	1104(3)	2500	9085(4)	64(2)
O(1B)	1530(3)	2500	7307(5)	56(2)
C(2B)	1392(3)	3469(7)	6858(5)	61(2)
C(3B)	1352(4)	4368(7)	7511(6)	69(2)
O(4B)	918(2)	4176(4)	8156(3)	62(1)
C(5B)	365(4)	4377(8)	7844(7)	80(3)
C(6B)	−16(3)	3485(8)	8125(6)	75(3)
O(7B)	174(3)	2500	7733(5)	62(2)
OC	8338(4)	2128(8)	2268(6)	73(3)
O(1C)	9726(14)	2500	4730(20)	183(12)
C(2C)	4386(10)	3590(20)	353(16)	109(7)
C(3C)	9168(13)	4210(20)	5279(19)	139(9)
O(4C)	8691(10)	4326(18)	5408(15)	99(6)
C(5C)	8373(7)	3376(15)	5628(11)	82(4)
C(6C)	7767(7)	3301(15)	5475(12)	85(4)
O(7C)	7850(20)	2500	4820(40)	270(20)
OD	8458(8)	2992(16)	3692(12)	94(6)
O(1D)	3690(20)	2500	1330(40)	148(19)
C(2D)	4578(14)	3210(30)	−270(20)	116(10)
C(3D)	4098(12)	3710(20)	359(17)	76(7)
O(4D)	3428(15)	4380(30)	40(20)	166(12)
C(5D)	3049(15)	4290(30)	230(20)	107(9)
C(6D)	2892(8)	3446(17)	243(13)	58(4)
O(7D)	2640(20)	2500	−520(30)	171(17)

and 1.998 Å for cation B, see (Figure 1(a) and (b)). The O(oxonium) is hydrogen bonded to O(4) and O(4′) of the crown at a distance of 2.488(5) and 2.531(5) Å for cations A and B, respectively. The O(A)(oxonium) center is also hydrogen bonded to Cl(6) of the anion at a distance of 3.015(6) Å and the O(B)(oxonium) center may have an extended interaction with Cl(1) of the anion, at a distance of 3.252(6) Å. All these hydrogen bonding distances

TABLE III Selected bond distances (Å) and angles (°) for $[H_3O^+ \cdot 12\text{-crown-4}]_3[Mo_2Cl_9{}^{3-}]$ (**1**)

Atoms	*Distance*	*Atoms*	*Distance*
Mo(1)–Cl(2)	2.389(2)	Mo(2)–Cl(6)	2.421(2)
Mo(1)–Cl(1)	2.4180(16)	Mo(2)–Cl(5)#1	2.4230(17)
Mo(1)–Cl(1)#1	2.4180(16)	Mo(2)–Cl(5)	2.4230(17)
Mo(1)–Cl(3)#1	2.4547(16)	Mo(2)–Cl(3)	2.4499(16)
Mo(1)–Cl(3)	2.4547(16)	Mo(2)–Cl(3)#1	2.4499(16)
Mo(1)–Cl(4)	2.479(2)	Mo(2)–Cl(4)	2.462(2)
Mo(1)–Mo(2)	2.7323(10)		
Atoms	*Angle*	*Atoms*	*Angle*
Cl(2)–Mo(1)–Cl(1)	92.08(6)	Cl(5)#1–Mo(2)–Cl(5)	88.64(9)
Cl(2)–Mo(1)–Cl(1)#1	92.08(6)	Cl(6)–Mo(2)–Cl(3)	88.27(6)
Cl(1)–Mo(1)–Cl(1)#1	87.00(9)	Cl(5)#1–Mo(2)–Cl(3)	176.35(6)
Cl(2)–Mo(1)–Cl(3)#1	88.16(6)	Cl(5)–Mo(2)–Cl(3)	87.97(6)
Cl(1)–Mo(1)–Cl(3)#1	175.93(6)	Cl(6)–Mo(2)–Cl(3)#1	88.27(6)
Cl(1)#1–Mo(1)–Cl(3)#1	88.93(6)	Cl(5)#1–Mo(2)–Cl(3)#1	87.97(6)
Cl(2)–Mo(1)–Cl(3)	88.16(6)	Cl(5)–Mo(2)–Cl(3)#1	176.35(6)
Cl(1)–Mo(1)–Cl(3)	88.93(6)	Cl(3)–Mo(2)–Cl(3)#1	95.39(8)
Cl(1)#1–Mo(1)–Cl(3)	175.93(6)	Cl(6)–Mo(2)–Cl(4)	178.47(8)
Cl(3)#1–Mo(1)–Cl(3)	95.15(8)	Cl(5)#1–Mo(2)–Cl(4)	90.69(6)
Cl(2)–Mo(1)–Cl(4)	177.56(8)	Cl(5)–Mo(2)–Cl(4)	90.69(6)
Cl(1)–Mo(1)–Cl(4)	89.69(6)	Cl(3)–Mo(2)–Cl(4)	90.71(5)
Cl(1)#1–Mo(1)–Cl(4)	89.69(6)	Cl(3)#1–Mo(2)–Cl(4)	90.71(5)
Cl(3)#1–Mo(1)–Cl(4)	90.20(5)	Mo(2)–Cl(3)–Mo(1)	67.71(4)
Cl(3)–Mo(1)–Cl(4)	90.20(5)	Mo(2)–Cl(4)–Mo(1)	67.14(6)
Cl(6)–Mo(2)–Cl(5)#1	90.41(6)		
Cl(6)–Mo(2)–Cl(5)	90.41(6)		

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1/2, z$.

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $[H_7O_3^+ \cdot H_5O_2^+ \cdot (12\text{-crown-4})_2][MoOCl_4(H_2O)^-]_2$ (**2**). U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
Mo(1)	5817(1)	9749(1)	8525(1)	33(1)
Cl(2)	6504(3)	8492(2)	9467(1)	61(1)
Cl(3)	5195(3)	11339(2)	7810(1)	60(1)
Cl(1)	8650(2)	10236(2)	8473(1)	53(1)
Cl(4)	3065(2)	9697(2)	8829(1)	58(1)
Owat	5955(6)	11183(5)	9349(2)	48(1)
Ooxo	5781(8)	8690(5)	7968(3)	65(2)
O(1)	1283(7)	8409(5)	3967(2)	52(1)
O(2)	−1661(7)	9632(6)	3549(3)	64(2)
O(3)	279(7)	11674(5)	3837(2)	57(1)
O(4)	3271(8)	10449(7)	4216(3)	71(2)
C(1)	−90(20)	7996(9)	3519(6)	118(5)
C(2)	−1026(13)	8711(16)	3189(6)	115(6)
C(3)	−1803(15)	10829(18)	3222(7)	142(8)
C(4)	−470(20)	11532(10)	3223(6)	123(6)
C(5)	2020(20)	12079(9)	3790(9)	128(6)
C(6)	3230(17)	11306(18)	3752(8)	140(8)
C(7)	3792(14)	9282(19)	3989(7)	133(7)
C(8)	2713(18)	8554(10)	3669(9)	117(6)
O(1A)	1090(7)	7864(5)	130(3)	58(1)
O(1B)	0	5000	5000	110(4)
O(1C)	1339(10)	4756(9)	180(3)	104(3)

TABLE V Selected bond distances (Å) and angles (°) for $[H_7O_3^+ \cdot H_5O_2^+ \cdot (12\text{-crown-}4)_2]\,[MoOCl_4(H_2O)^-]_2$ (2)

Atoms	*Distance*
Mo(1)–Ooxo	1.639(5)
Mo(1)–Owat	2.317(5)
Mo(1)–Cl(3)	2.3444(18)
Mo(1)–Cl(4)	2.3569(19)
Mo(1)–Cl(1)	2.3844(18)
Mo(1)–Cl(2)	2.4094(18)
Atoms	*Angle*
Ooxo–Mo(1)–Owat	176.9(3)
Ooxo–Mo(1)–Cl(3)	99.0(2)
Owat–Mo(1)–Cl(3)	83.85(15)
Ooxo–Mo(1)–Cl(4)	100.0(2)
Owat–Mo(1)–Cl(4)	81.15(13)
Cl(3)–Mo(1)–Cl(4)	89.88(8)
Ooxo–Mo(1)–Cl(1)	97.1(2)
Owat–Mo(1)–Cl(1)	81.70(12)
Cl(3)–Mo(1)–Cl(1)	88.54(8)
Cl(4)–Mo(1)–Cl(1)	162.84(8)
Ooxo–Mo(1)–Cl(2)	95.2(2)
Owat–Mo(1)–Cl(2)	81.92(15)
Cl(3)–Mo(1)–Cl(2)	165.76(8)
Cl(4)–Mo(1)–Cl(2)	88.26(8)
Cl(1)–Mo(1)–Cl(2)	89.09(7)

TABLE VI Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $[(H_5O_2^+)_2 \cdot 12\text{-crown-}4][W(CO)_4Cl_3^-]_2$ (3). U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
W	2422(1)	1785(1)	3633(1)	33(1)
Cl(1)	2892(4)	4579(3)	3312(2)	47(1)
Cl(2)	2774(4)	862(4)	1795(2)	54(1)
Cl(3)	−845(4)	1213(4)	2500(3)	60(1)
CA	5166(12)	2523(13)	4035(10)	44(2)
OA	6657(11)	2901(13)	4220(9)	69(3)
CB	1618(19)	−616(18)	3437(12)	57(3)
OB	1151(17)	−2039(12)	3283(12)	95(4)
CC	3523(15)	1399(14)	5124(10)	51(3)
OC	4223(13)	1074(13)	5944(7)	65(2)
CD	1503(16)	2960(18)	4763(12)	57(3)
OD	984(13)	3619(14)	5379(8)	70(3)
OX	897(13)	2246(12)	9297(9)	74(3)
OY	535(11)	3924(12)	847(7)	59(2)
O(1)	−3827(9)	6755(10)	1215(7)	47(2)
C(2)	−4263(18)	5379(16)	1641(10)	54(3)
C(3)	−2847(15)	4484(17)	1753(10)	53(3)
O(4)	−2702(8)	3847(9)	689(6)	42(2)
C(5)	−4020(18)	2279(16)	64(12)	56(3)
C(6)	−5083(16)	7763(16)	1114(11)	57(3)

TABLE VII Selected bond distances (Å) and angles (°) for $[(H_5O_2^+)_2 \cdot \text{12-crown-4}]$ $[W(CO)_4Cl_3^-]_2$ (3)

Atoms	*Distance*
W-CC	1.976(11)
W-CA	2.032(9)
W-CB	1.986(15)
W-CD	2.041(13)
W-Cl(3)	2.474(3)
W-Cl(2)	2.488(3)
W-Cl(1)	2.494(3)
CA-OA	1.109(12)
CB-OB	1.171(18)
CC-OC	1.149(14)
CD-OD	1.129(16)

Atoms	*Angle*	*Atoms*	*Angle*
CC-W-CA	73.4(5)	Cl(3)-W-Cl(2)	85.19(11)
CC-W-CB	73.5(5)	CC-W-Cl(1)	122.4(3)
CA-W-CB	109.3(5)	CA-W-Cl(1)	78.3(3)
CC-W-CD	70.4(6)	CB-W-Cl(1)	164.0(4)
CA-W-CD	114.5(4)	CD-W-Cl(1)	77.9(4)
CB-W-CD	110.0(6)	Cl(3)-W-Cl(1)	88.00(10)
CC-W-Cl(3)	128.4(3)	Cl(2)-W-Cl(1)	86.93(10)
CA-W-Cl(3)	158.2(4)	OA-CA-W	177.7(10)
CB-W-Cl(3)	80.3(4)	OB-CB-W	177.6(15)
CD-W-Cl(3)	78.3(4)	OC-CC-W	173.8(11)
CC-W-Cl(2)	131.7(4)	OD-CD-W	179.1(14)
CA-W-Cl(2)	77.3(3)		
CB-W-Cl(2)	81.3(4)		
CD-W-Cl(2)	157.9(5)		

TABLE VIII Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $[H_3O^+ \cdot \text{12-crown-4}]$ $[WOCl_4(H_2O)^-]$ (4). U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
W	1888(1)	2296(1)	2237(1)	25(1)
Cl(1)	217(4)	2270(3)	1043(3)	40(1)
Cl(2)	3103(4)	2699(4)	814(4)	45(1)
Cl(3)	3395(4)	2919(4)	3445(3)	45(1)
Cl(4)	569(4)	2347(4)	3669(4)	43(1)
WAT	1462(9)	4147(8)	2136(9)	36(2)
OXO	2112(10)	913(10)	2301(10)	50(3)
O	1842(8)	6831(10)	7226(8)	40(3)
O(1)	727(9)	4822(9)	8034(9)	41(3)
C(2)	732(17)	3999(18)	7216(16)	58(5)
C(3)	477(18)	4550(19)	6175(17)	64(5)
O(4)	1447(12)	5279(12)	5927(9)	56(3)
C(5)	2460(20)	4790(20)	5501(17)	82(8)
C(6)	3538(19)	5280(20)	6029(14)	70(7)
O(7)	3524(9)	4966(10)	7172(9)	42(3)
C(8)	4278(16)	5575(17)	7881(17)	56(5)
C(9)	3827(16)	5470(20)	8939(15)	62(6)
O(10)	2677(9)	5992(10)	8959(9)	46(3)
C(11)	1862(16)	5470(20)	9579(12)	57(5)
C(12)	1335(15)	4482(19)	9001(15)	57(6)

TABLE IX Selected bond distances (Å) and angles (°) for [$H_3O^+ \cdot$ 12-crown-4] [$WOCl_4(H_2O)^-$] (4)

Atoms	*Distance*
W-OXO	1.665(12)
W-WAT	2.256(10)
W-Cl(3)	2.346(4)
W-Cl(1)	2.356(4)
W-Cl(2)	2.366(4)
W-Cl(4)	2.404(4)

Atoms	*Angle*	*Atoms*	*Angle*
OXO-W-WAT	176.4(4)	Cl(3)-W-Cl(2)	89.27(16)
OXO-W-Cl(3)	100.1(5)	Cl(1)-W-Cl(2)	90.43(17)
WAT-W-Cl(3)	82.9(3)	OXO-W-Cl(4)	95.1(4)
OXO-W-Cl(1)	97.7(4)	WAT-W-Cl(4)	82.9(3)
WAT-W-Cl(1)	79.3(3)	Cl(3)-W-Cl(4)	88.47(16)
Cl(3)-W-Cl(1)	162.03(14)	Cl(1)-W-Cl(4)	87.70(16)
OXO-W-Cl(2)	98.2(4)	Cl(2)-W-Cl(4)	166.70(17)
WAT-W-Cl(2)	83.8(3)		

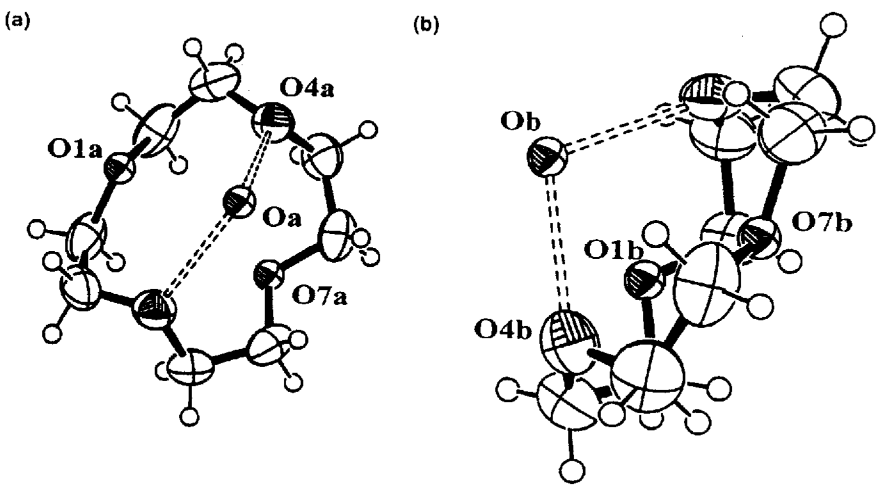


FIGURE 1 Two projections (a and b) of the [$H_3O^+ \cdot$ 12-crown-4] cations in **1** and **4**. The anions are omitted for clarity, but are involved in hydrogen bonding with the cations (see text).

are within established limits for this mode of interaction.[11] The third cation also lies on a mirror plane (through O(1) and O(7)), but in this case, the O(oxonium) ion is disordered and does not reside on the crystallographically imposed mirror plane.

$[H_7O_3^+ \cdot H_5O_2^+ \cdot (12\text{-crown-}4)_2][MoOCl_4(H_2O)^-]_2$, 2

In this complex the $[H_7O_3^+ \cdot H_5O_2^+ \cdot (12\text{-crown-}4)_2]$ cations form polymeric hydrogen bonded strands, where $[(H_5O_2^+) \cdot (12\text{-crown-}4)_2]$ subunits are linked by $H_7O_3^+$ units (Figure 2). The anions sit in cavities between the polymeric strands of the cation.

In the anion, the geometry around the Mo center is a distorted octahedron. The average bonding parameters are Mo–Cl = 2.37(2) Å, Mo–Oxo = 1.639(5) Å, and Mo–Wat = 2.317(5) Å. The Cl ligands are bent down and away from the oxo group (ave. O(oxo)–Mo–Cl = 98(2)°). The distance between Cl(1) and Ob($H_7O_3^+$) of 3.206(9) Å may indicate some interaction between the cations and anions.

The cation resides on an inversion center through Oc, the central oxygen of the $H_7O_3^+$ unit (see Figure 2). This implies that the three oxygens of this unit are linear. The $H_7O_3^+$ spans four 12-crown-4 moieties, and the terminal oxygens (Oa) of the $H_7O_3^+$ unit are hydrogen bonded to O(4) and O(10) of these crowns at distances of 2.756(8) and 2.757(8) Å, respectively. The Oa ··· Oc distance is 2.594(9) Å. Sandwiched between the two 12-crown-4 molecules is an $H_5O_2^+$ unit, in which each oxygen is hydrogen bonded to O(1) and O(7) of the crown at distances of 2.535(8) and 2.580(8) Å, respectively. Hydrogen bonding separations found here are within the accepted limits for this mode of interaction.[11] The oxygens of the $H_5O_2^+$ unit are separated at a distance of 2.327(8) Å, which is very short for this type of oxonium ion. The $H_7O_3^+$ oxonium ion links together the $[H_5O_2^+ \cdot (12\text{-crown-}4)_2]$ in a linear polymeric array.

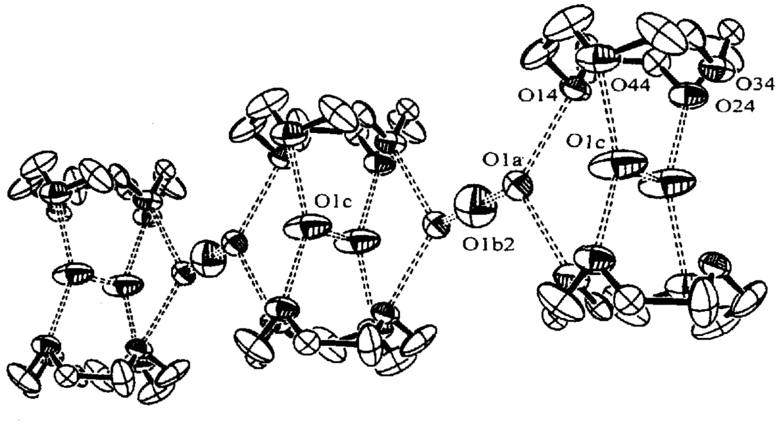


FIGURE 2 Structure of hydrogen bonded polymer in **2**, showing the linking of $[H_5O_2^+ \cdot (12\text{-crown-}4)_2]$ groups by linear $H_7O_3^+$ ions. The $MoOCl_4H_2O$-anions have been omitted for clarity, but are involved in hydrogen bonding with O1b through Cl(1).

[$(H_5O_2^+)_2 \cdot$ 12-crown-4][$W(CO)_4Cl_3^-$]$_2$, 3

In this complex two $H_5O_2^+$ oxonium ions span consecutive 12-crown-4 molecules, in a stepwise polymeric array (Figure 3). Each $H_5O_2^+$ is also hydogen bonded to a chlorine atom of the [$W(CO)_4Cl_3^-$] anion. The anion in this complex exists as a seven-coordinate tungsten(II) species giving the anion capped trigonal antiprismatic geometry (or 4:3 piano stool). The average W–Cl, W–C(carbonyl) and C–O bond distances are 2.49(1), 2.01(5) and 1.14(3) Å, respectively. Cl(1) of the anion is hydrogen bonded to Oy of the $H_5O_2^+$ cation at a distance of 3.026(7) Å, and there is a possible longer range contact from Cl(2) to Ox of 3.272(7) Å.

The cation resides on a center of inversion where half of each $H_5O_2^+$ oxonium ion resides in the asymmetric unit (see Figure 3). The Ox of the $H_5O_2^+$ unit hydrogen bonds to O(1) of the crown at a distance of 2.681(4) Å and has possible long range interactions with O(4) and Cl(2) of the anion

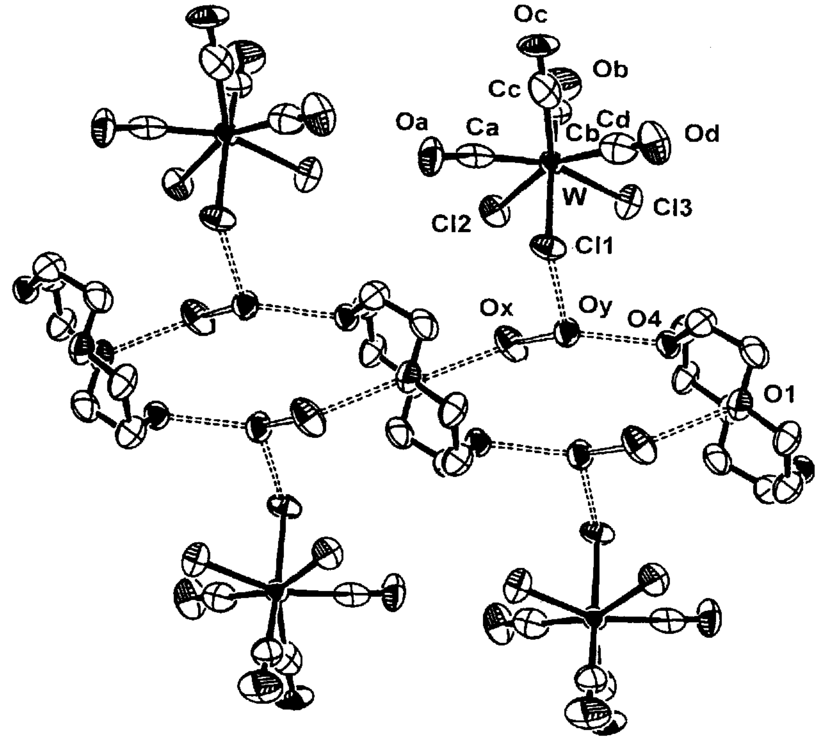


FIGURE 3 Polymeric structure of [$(H_5O_2^+)_2 \cdot$ 12-crown-4][$W(CO)_4Cl_3^-$],3. The $H_5O_2^+$ ions both reside on a center of inversion.

discussed above. Oy of the $H_5O_2^+$ unit hydrogen bonds to O(4) of the crown and Cl(1) of the anion at separations of 2.569(7) and 3.026(7) Å, respectively. The Ox···Oy separation of 2.387(8) Å for this cation is again very short for this type of oxonium ion. Two $H_5O_2^+$ oxonium ions on either side of the 12-crown-4 molecules extend the polymeric array of the cation throughout the structure. There is no interaction between the two $H_5O_2^+$ ions, being separated by more than 3.5 Å.

$[H_3O^+ \cdot$ 12-crown-4)][$WOCl_4(H_2O)^-$], 4

This complex crystallizes in a hydrogen bonded array, where there is close interaction between the anion and cation, as well as an infinite polymeric array of hydrogen bonded anions (see Figure 4).

The anion exists in a distorted octahedral geometry. The W–Cl(ave), W–oxo and W–wat separations are 2.37(2), 1.66(1) and 2.26(1) Å, respectively. The Cl ligands adopt equatorial geometry and are bent down and away from the oxo ligand at an average of 98(3)°. The oxo–W–wat angle is 176.4(4)°. The axial water ligand hydrogen bonds to O(1) of the 12-crown-4 molecule and also to the oxo ligand on another anion at separations of 2.790(9) and 2.732(8) Å, respectively. Cl(4) of the anion hydrogen bonds to the O-(oxonium) ion at a distance of 3.067(7) Å.

The cation exists in a similar morphology to that in complex **1**, where the O-(oxonium) ion resides above the face (least squares plane derived from the O atoms of the crown) of the 12-crown-4 molecule at a distance of 1.93 Å

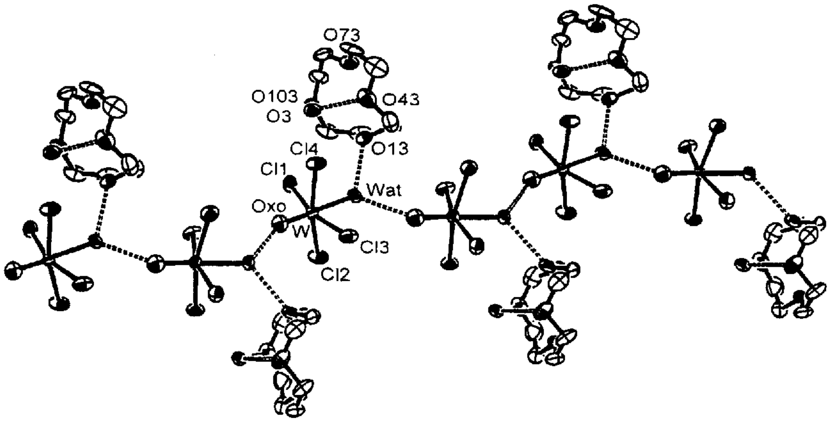


FIGURE 4 Structure of $[H_3O^+ \cdot$ 12-crown-4][$WOCl_4(H_2O)^-$], **4**, showing the close interaction between the anions and cations.

(see Figure 1(a) and (b)). The O-(oxonium) ion binds strongly to O(4) and O(10) of the 12-crown-4 molecule at separations of 2.493(6) and 2.504(6) Å, respectively. As noted above, O(1) of the crown also hydrogen bonds to the water ligand of the anion, albeit much more weakly.

DISCUSSION

The formation of all complexes reported herein is novel. We have shown that the $[Mo_2Cl_9]^{3-}$, $[MoOCl_4(H_2O)]^-$, $[W(CO)_4Cl_3]^-$ and $[WOCl_4(H_2O)]^-$ anions can be prepared in liquid clathrate media with $[H_3O^+ \cdot 18\text{-crown-6}]$ cations.[2] The same complexes have also been prepared here with oxonium complexes of 12-crown-4. The formation involves irradiating $M(CO)_6$ in toluene with UV light in the presence of moisture and an excess of $HCl_{(g)}$. In this and future publications we show that these and other unusual cations can be generally prepared in liquid clathrate media in this manner.

In light of the size of the cavity in 12-crown-4 *vs.* the size of the H_3O^+ oxonium ion, which snugly fits within 18-crown-6,[1,2,12–15] we had hoped to isolate species of higher oligomers of the oxonium ion $[(H_2O)_nH^+]$. In the complexes formed, we found a range of such oligomers ranging from H_3O^+, through $H_5O_2^+$ to $H_7O_3^+$. It appears that the higher oligomers form so that the 12-crown-4 molecules are sufficiently separated in the crystal to allow space for the large cations to reside. The oxonium ions then form linking units between the 12-crown-4 molecule to form polymeric hydrogen bonded arrays.

For complexes **1** and **4** where H_3O^+ was the only oxonium species isolated, the O center sits nearly 2.0 Å out of the face of the crown, with which it forms two hydrogen bonds. The H_3O^+ also forms $O\text{–}H \cdots Cl$ hydrogen bonds with the $[Mo_2Cl_9]^{3-}$ anion in **1** and $[WOCl_4(H_2O)]^-$ in **4**.

The range of $O\text{–}H \cdots O$ hydrogen bonding we find in these $[H_3O^+ \cdot 12\text{-crown-4}]$ complexes ranges from 2.488(5) to 2.531(5) Å. The typical O(oxonium)$\cdots$O(crown) distances observed are 2.7–2.8 Å, for example in $[H_3O^+ \cdot 18\text{-crown-6}]$ complexes.[1,2,12–15] Shorter $O\text{–}H \cdots O$ distances are seen in $[H_3O^+][NO_3^-]$, $[H_3O^+][HSO_4^-]$ and $[H_3O^+]_2[SO_4^{2-}]$ where the $O \cdots O$ separations are of the order 2.52–2.66 Å.[16] The sum of the van der Waals radii for O (1.40 Å), leads to a van der Waals separation of 2.80 Å.[17] According to Emsley, a hydrogen bond of > 0.3 Å less than the van der Waals radii is classified a strong hydrogen bond.[18] The reason for the formation of strong hydrogen bonds between the H_3O^+ oxonium ion and the 12-crown-4 oxygens is unknown. A possible reason is that the oxonium tends to bind more strongly to the O-centers of the crown in preference to the chloride ligands of the anion, to which they are also hydrogen bonded. These O···Cl distances (3.015(6) and 3.067(7) Å) are typical of O–H···Cl hydrogen bonding distances.[11] Packing forces in the crystal may contribute to the observed hydrogen bond shortening.

The structure of **2** exhibits the first example of a complex containing *both* $H_5O_2^+$ and $H_7O_3^+$ in the same compound, and indeed it is the first example of $H_7O_3^+$ being isolated from aromatic media. The $H_7O_3^+$ oxonium ion lies on a crystallographic center of inversion which forms a *linear*, *symmetrical* array of oxygen atoms, with an O···O separation of 2.594(9) Å. The hydrogen atoms of the central H_3O^+ of the $H_7O_3^+$ unit were not located and are presumably disordered. Disorder of this ion is a requirement for the central H_3O^+ to reside on an inversion center. This is the first example of this type of conformation for the $H_7O_3^+$ ion. Previous examples have regarded it as a pyramidal H_3O^+ unit to which two H_2O molecules are hydrogen bonded, resulting in an O···O···O angle of approx 115°.[19] They also typically contain non-symmetrical O···O distances of 2.45 and 2.55 Å.[19] In a crystal structure of the related $H_9O_4^+$ oxonium ion, the O–O–O–O unit formed a Z-shaped structure.[7] The $H_7O_3^+$ spans four 12-crown-4 moieties, and the terminal oxygens (Oa) of the $H_7O_3^+$ unit are hydrogen bonded to O(4) and O(10) of these crowns at distances of 2.756(8) and 2.757(8) Å respectively. Formation of the linear $H_7O_3^+$ ion must be a consequence of the unit being forced into this conformation by the restraints imposed by the packing of the anions and cations in the crystal. Theoretical calculations on $H_7O_3^+$ ions have not considered the linear array. The energy of this conformation is presumably significantly higher than the lowest energy structures considered. A theoretical consideration of the first solvation shell for H_3O^+ contained four H_2O molecules spatially arranged around the oxonium ion. Three of these H_2O molecules are very close to linear, and it is possible that other atoms in the structure may force this array, by causing hydrogen bond distortion and mobility.[20,21]

The $H_5O_2^+$ oxonium ions in **2** and **3** have O···O separations of 2.327(8) and 2.387(8) Å. These separations are extremely short and are equivalent to some of the shortest O–H···O bonding distances known. Typical O–H···O distances in $H_5O_2^+$ species are in the range 2.40–2.45 Å,[16] with the previous shortest distance being 2.34(1) Å in $[NEt_4^+]_3[H_5O_2^+][Mo_2Cl_8H^{3-}][MoOCl_4(H_2O)^-]$.[22] The shortest known O–H···H hydrogen bonds observed were in a dimeric copper complex where the O–H···O distances were 2.31(1) and 2.33(1) Å,[23] and in the $H_5O_2^+$ core of the $H_{13}O_6^+$ oxonium ion where the O···O separation was 2.29 Å.[24] The reason for the very short

O···O separation in **2** is unsure, but it may be due to the compression of the $H_5O_2^+$ unit by the sandwiching of the unit by the 12-crown-4 molecules. Further compression may be due to the pinching together of the two 12-crown-4 molecules by the $H_7O_3^+$ oxonium ion. The O(oxonium)···O(crown) distances in **2** are also relatively short indicating very strong hydrogen bonding between the units. Compression of the sandwich by the $H_7O_3^+$ ion may also be the cause of these very short O–H···O hydrogen bonds. In complex **3** there are two $H_5O_2^+$ units linking 12-crown-4 molecules in a stepwise polymeric array. The distance between adjacent oxygens of different $H_5O_2^+$ units exceeds 3.5 Å indicating there is no bonding interaction.

The anions obtained in complexes **1–4** are similar to those we have observed in [H_3O^+ · 18-crown-6] complexes of these anions.[2,3] Differences do occur in this case however, due to the hydrogen bonding interactions between cations and anions. For the complexes obtained with [H_3O^+ · 18-crown-6], the H_3O^+ oxonium ion is completely encapsulated by the 18-crown-6 molecule, and therefore eliminates the possibility of hydrogen bonding between anions and cations. Because of this, only discrete anions and cations were observed for 18-crown-6 complexes.

The tungsten(II) complex in complex **3** retains four carbonyl ligands while the molybdenum(III) species in complex **1** loses all its original carbonyls. This is probably a reflection of the relative bond strengths established for $M(CO)_6$ species where the order is W > Cr > Mo.[25] In our investigations of these species, we have identified both chromium and tungsten complexes which retain carbonyls, while molybdenum has, without exception, undergone ligand exchange in the harsh liquid clathrate environment.

EXPERIMENTAL SECTION

$Mo(CO)_6$ and $W(CO)_6$ were obtained from Aldrich Chemical Co. and HCl gas was purchased from Atlas Co. Complexes **1–4** were prepared exposed to air, prior to the reaction mixture being sealed in an air-tight screw-top tube. ^1H NMR spectra on the liquid clathrates were recorded as neat solutions on a Varian EM360L 60 MHz Spectrometer. ^1H NMR chemical shifts for all complexes were similar, and shifts were in the ranges as follows: δ 1.95 and 6.85 ppm (toluene), δ 3.6 ppm (12-crown-4), $\delta > 9.0$ ppm (oxonium ions).

Preparation of [$H_3O^+ \cdot$ 12-crown-4]$_3$[$Mo_2Cl_9^{3-}$], 1

To a sample of 12-crown-4 (0.64 g, 3.62 mmol) in toluene, was added H_2O (0.065 g, 3.62 mmol) and $Mo(CO)_6$ (1.00 g, 3.62 mmol) and stirred rapidly for 15 min. $HCl_{(g)}$ was then rapidly bubbled through the mixture for approx. 1 h while irradiating with UV radiation. After this time, a red liquid clathrate separated from the solvent with a toluene : complex ratio of 1.7 : 1 as determined by ^1H NMR. Deep red crystals of the title complex deposited from the clathrate layer after approx. 72 h.

Preparation of $[H_7O_3^+ \cdot H_5O_2^+ \cdot (12\text{-crown-}4)_2][MoOCl_4(H_2O)^-]_2$, 2

The reaction mixture from **1** above was exposed to air for approx. 1 h whereupon the vessel was once again sealed from the atmosphere. After 2 days, the liquid clathrate had turned bright green. The liquid clathrate had the same toluene : complex ratio as complex **1**. Bright green crystals of the title complex deposited from the clathrate layer after 24 h.

Preparation of $[(H_5O_2^+)_2 \cdot 12\text{-crown-}4][W(CO)_4Cl_3^-]$, 3

A sample of 12-crown-4 (0.64 g, 3.62 mmol) was moistened with distilled water (0.065 mL, 3.62 mmol) and approx. 100 mL of toluene added. $W(CO)_6$ (1.27 g, 3.62 mmol) was then added and $HCl_{(g)}$ was rapidly bubbled through the mixture for approx. 1 h while irradiating with UV radiation. After this time, an orange/yellow liquid clathrate separated from the solvent with a toluene : complex ratio of 2.3 : 1 as determined by ^1H NMR. Yellow crystals of the title complex deposited from the clathrate layer after approx. 72 h.

Preparation of $[H_3O^+ \cdot 12\text{-crown-}4)][WOCl_4(H_2O)^-]$, 4

The reaction mixture from **3** above was exposed to the air for approx. 1 h whereupon the vessel was once again sealed from the atmosphere. The liquid clathrate maintained its orange/yellow color and had the same toluene : complex ratio as complex **3**. Bright blue crystals of the title complex deposited from the clathrate layer after 24 h.

Collection of X-ray Diffraction Data, and Solution and Refinement of the Structures

Single crystals of **1**–**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 ($2\theta > 30°$) accurately centered on an Enraf-Nonius CAD4 diffractometer are given in Table I. A summary of data collection parameters is also given in Table I. An empirical absorption correction based on ψ scan data was performed. Calculations were carried out using the SHELXL97 system of computer programs.[26]

Positions of heavy atoms were determined from a three-dimensional Patterson function. All other non-hydrogen atoms were located from a difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinements converged with $R = 0.059$ for 4087 observed reflections for **1**, $R = 0.075$ for 3253 observed reflections for **2**, $R = 0.060$ for 2590 observed reflections for **3**, $R = 0.087$ for 2630 observed reflections for **4**.

Acknowledgments

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