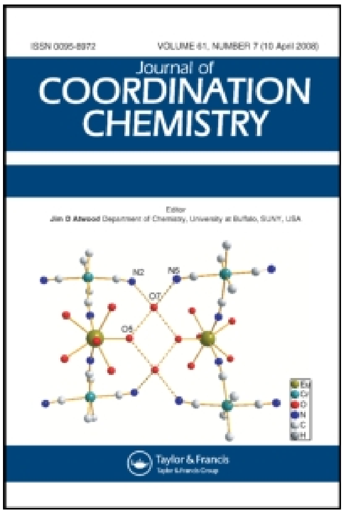

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ANIONIC COORDINATION COMPLEXES OF Mo AND W WHICH CRYSTALLIZE FROM LIQUID CLATHRATE MEDIA WITH OXONIUM ION-CROWN ETHER CATIONS[‡]

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The complexes $[H_3O^+\cdot 18\text{-crown-6}][MoOCl_4(H_2O)^-]$, 1, and $[H_2O\cdot$*aza*-$18\text{-crown-6}\cdot(H^+)]$ $[MoOCl_4(H_2O)^-]$, 3, were synthesized from a mixture of $Mo(CO)_6$, HCl(g), H_2O and either 18-crown-6 for 1 or mono-*aza*-18-crown-6 for 3, in toluene. For complex 4, $[H_2O\cdot$*aza*-$18\text{-crown-6}\cdot(H^+)]_2[WOCl_4(H_2O)^-][Cl^-]$, reaction conditions were as for 3 except $W(CO)_6$ was used in place of $Mo(CO)_6$. Similarly, for complex 2, $[H_3O^+\cdot 18\text{-crown-6}][WOBr_4(H_2O)^-]$, $W(CO)_6$ and HBr were used in the reaction mixture. These reactions were promoted by UV radiation and formed liquid clathrates almost immediately upon reaction. X-ray crystal structures were performed on each compound. Complex 1 crystallizes in the triclinic space group $P\bar{1}$ with a = 10.206(1), b = 10.486(1), c = 11.701(1) Å, α = 71.11(1), β = 74.60(1), γ = 75.08(1)°, and D_c = 1.649 g cm^{-3} for Z = 2. Refinement based on 3925 observed reflections led to a final R value of 0.078. Complex 2 crystallizes in the monoclinic space group $P2_1/c$ with a = 9.710(1), b = 19.824(1), c = 12.399(1) Å, β = 104.58 (1)°, and D_c = 2.369 g cm^{-3} for Z = 4. Refinement based on 2008 observed reflections led to a final R value of 0.090. Complex 3 crystallizes in the orthorhombic space group Pnmn with a = 16.927(1), b = 12.226(1), c = 11.167(1) Å, and D_c = 1.598 g cm^{-3} for Z = 4. Refinement based on 1486 observed reflections led to a final R value of 0.040. Complex 4 crystallizes in the monoclinic space group $C2/m$ with a = 11.761(2), b = 12.096(2), c = 14.966(1) Å, β = 132.91(1)°, and D_c = 1.502 g cm^{-3} for Z = 4. Refinement based on 2021 observed reflections led to a final R value of 0.051. In all cases the metal coordination sphere was essentially octahedral with the water ligand *trans* to the oxo species.

KEYWORDS: liquid clathrate, oxonium ion, crown ether, molybdenum, tungsten

INTRODUCTION

Recently, attention has been focused on forming a number of simple transition metal coordination compounds in liquid clathrate media.[1-6] With the $[H_3O^+\cdot 18\text{-crown-6}]$ cation, liquid clathrates have been formed paired with simple anions, *e.g.* $[Cl\text{-}H\text{-}Cl^-]$,[7,8] and with transition metal-containing anions.[1,2]

Much discussion has centered on the structure of the $[H_3O^+\cdot 18\text{-crown-6}]$ cation, where arguments have revolved around *planar vs. pyramidal* geometry for the

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[‡] Dedicated to Toshi Iwamoto, friend and colleague in the field for these many years.

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oxonium ion. Species have been identified where the O(oxonium) atom sits within 0.1 Å of the plane of the crown ether oxygen atoms,[9] while others have been found to reside greater than 0.5 Å out of this plane.[10]

As part of our investigations of liquid clathrate systems,[11-13] involving the stabilized oxonium ion, $[H_3O^+ \cdot 18\text{-crown-6}]$,[14,15] we now report the interaction of $M(CO)_6$ (M = Mo, W) with the 18-crown-6/H_2O/HX (X = Cl, Br) system in toluene. Generally, anions of the type $[MOX_4(H_2O)^-]$ were obtained with either $[H_3O^+ \cdot 18\text{-crown-6}]$ or protonated *aza*-crown cations. A discussion of the geometry of the $[H_3O^+ \cdot 18\text{-crown-6}]$ cation is also presented.

EXPERIMENTAL

$Mo(CO)_6$ and $W(CO)_6$ were obtained from Aldrich Chemical Co. and HCl gas was purchased from Atlas. Complexes **1–4** were prepared in air before the reaction mixture was 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 were in the ranges: δ1.95 and 6.85 ppm (toluene), δ 3.00–4.00 ppm (crown ethers), δ 9.40 ppm (H_3O^+).

Preparation of $[H_3O^+ \cdot 18\text{-crown-6}][MoOCl_4(H_2O)^-]$, **1**[16]

To a sample of 18-crown-6 (1.0 g, 3.7 mmol) in toluene, was added H_2O (0.067 g, 3.7 mmol) and $Mo(CO)_6$ (1.0 g, 3.7 mmol) with rapid stirring for 15 min. HCl(g) was then rapidly bubbled through the mixture for approximately 1 h, while irradiating with UV light. The UV radiation was used to facilitate the breaking of the Mo-CO bonds; the reaction occurs, but at a slower rate in the absence of UV radiation. After this time, a red liquid clathrate separated from the solvent with a toluene: complex ratio of 1.9:1 as determined by ^1H NMR integration. From the liquid clathrate, red crystals of $[H_3O^+ \cdot 18\text{-crown-6}]_2[Mo_2Cl_9(H_5O_2^+)^{2-}]$ deposited.[4] Exposure of this reaction mixture to air for *ca.* 1h, followed by resealing the tube from the atmosphere, resulted in the deposition of bright green crystals of the title compound from the liquid clathrate layer.

Preparation of $[H_3O^+ \cdot 18\text{-crown-6}][WOBr_4(H_2O)^-]$, **2**

A sample of 18-crown-6 (0.66 g, 2.5 mmol) was moistened with distilled water (0.045 mL, 2.5 mmol) and approximately 50 mL of toluene added. $W(CO)_6$ (0.87 g, 2.5 mmol) was then added with rapid stirring for *ca.* 15 min. HBr(g) was then rapidly bubbled through the solution for *ca.* 40 min while irradiating the mixture with UV light. An orange colored liquid clathrate resulted after 20 min with the composition $[H_3O^+ \cdot 18\text{-crown-6}][WOBr_4(H_2O)^-] \cdot 3C_7H_8$. Orange crystals deposited from the liquid clathrate layer over a 72 h period.

Preparation of $[H_2O \cdot \text{aza-18-crown-6} \cdot (H^+)][MoOCl_4(H_2O)^-]$, **3**

A sample of mono-*aza*-18-crown-6 (0.53 g, 2.0 mmol) was moistened with distilled water (0.036 mL, 2.0 mmol) and approximately 100 mL of toluene added. $Mo(CO)_6$

(0.53 g, 2.0 mmol) was then added and HCl(g) was rapidly bubbled through the mixture for approximately 1 h while irradiating with UV light. After this time, a brown/yellow liquid clathrate resulted, which turned bright red overnight. The liquid clathrate had composition $[H_2O \cdot$ *aza*-18-crown-6 $\cdot (H^+)][MoOCl_4(H_2O)^-] \cdot 1.9C_7H_8$. Bright green crystals of the title complex deposited from the liquid clathrate layer after approximately 1 week.

Preparation of $[H_2O \cdot$ *aza*-18-crown-6 $\cdot (H^+)]_2[WOCl_4(H_2O)^-][Cl^-]$, **4**

A sample of mono-*aza*-18-crown-6 (0.65 g, 2.5 mmol) was moistened with distilled water (0.045 mL, 2.5 mmol) and approximately 30 mL of toluene added. $W(CO)_6$ (0.87 g, 2.5 mmol) was then added and HCl(g) was rapidly bubbled through the mixture for approximately 1 h while irradiating with UV light. After this time, a light yellow liquid clathrate resulted with a toluene: complex ratio of 2.1:1, as determined by ^1H nmr integration. Bright blue crystals of the title complex deposited from the liquid clathrate layer over approximately 2 days.

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

Single crystals of **1**, **2**, **3**, and **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 1. A summary of data collection parameters is also given in Table 1. An empirical absorption correction based on psi scan data was performed. Calculations were carried out using the SHELX system of computer programs.[17]

In each case, the position of the heavy atom was 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. Hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinement converged with $R = 0.078$ for 2973 observed reflections for **1**, $R = 0.090$ for 2008 observed reflections for **2**, $R = 0.040$ for 1486 observed reflections for **3**, $R = 0.051$ for 2021 observed reflections for **4**. Fractional coordinates and bond distances and angles for complexes **1–4** are shown in Tables 2–9.

RESULTS

Preparation of Complexes

The title compounds were prepared according to Scheme 1. In all cases the reaction mixture quickly separated into two phases yielding liquid clathrate species. The upper layer in these reactions was neat toluene, while the metal complexes formed were completely dissolved within the liquid clathrate layer. In all cases the reaction was performed in contact with air, followed by sealing the reaction vessel from contact with air. In each case an oxidation of the metal species from [0] to [+5] occurred.

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

Compound	$[H_3O^+ \cdot 18\text{-crown-}6]$ $[MoOCl_4(H_2O)^-]$, 1	$[H_3O^+ \cdot 18\text{-crown-}6]$ $[WOBr_4(H_2O)^-]$, 2
Mol Wt.	555.1	820.9
Space group	$P\bar{1}$	$P2_1/c$
cell constants		
a, Å	10.206(1)	9.710(1)
b, Å	10.486(1)	19.824(1)
c, Å	11.701(1)	12.399(1)
α, deg	71.11(1)	90
β, deg	74.60(1)	104.58(1)
γ, deg	75.08(1)	90
V, $Å^3$	1122(3)	2310(1)
molecules/unit cell	2	4
D_c, g cm^{-3}	1.649	2.369
μ, cm^{-1}	10.9	120.4
radiation	Mo Kα	Mo Kα
scan width, deg	0.80 + 0.20 tan θ	0.85 + 0.20 tan θ
2θ range, deg	2–50	2–50
no. reflcns collcd	3925	4218
no. of obsd reflcns	2973	2008
no. of params varied	237	235
sigma cutoff	3σ	3σ
weighting scheme	unit weights	unit weights
temp of data colln, deg	23	23
R	0.078	0.090
R_w	0.096	0.106

Compound	$[H_2O \cdot$ *aza*-18-crown-6 $\cdot H^+]$ $[MoOCl_4(H_2O)^-]$, 3	$[H_2O \cdot$ *aza*-18-crown $\cdot 6 \cdot (H^+)]_2$ $[WOCl_4(H_2O)^-][Cl^-]$, 4
Mol.Wt.	554.1	899.3
Space group	Pnmn*	C2/m
cell constants		
a, Å	16.927(1)	11.761(2)
b, Å	12.226(1)	12.096(2)
c, Å	11.167(1)	14.966(1)
α, deg	90	90
β, deg	90	132.91(1)
γ, deg	90	90
V, $Å^3$	2311(1)	3994(5)
molecules/unit cell	4	4
D_c, g cm^{-3}	1.598	1.502
μ, cm^{-1}	10.6	80.3
radiation	Mo Kα	Mo Kα
scan width, deg	0.80–0.20 tan θ	0.80–0.20 tan θ
2θ range, deg	2–50	2–50
no. reflcns collcd	2338	2214
no. of obsd reflcns	1486	2021
no. of params varied	130	220
sigma cutoff	3σ	3σ
weighting scheme	unit weights	unit weights
temp of data colln, deg	23	23
R	0.040	0.051
R_w	0.043	0.063

* alternative setting to Pnnm #58

Table 2 Final fractional coordinates for [$H_3O^+ \cdot$18-crown-6] [$MoOCl_4(H_2O)^-$], **1**.

Atom	x/a	y/b	z/c
Mo	-.0311(1)	.0197(1)	.2376(1)
Cl(1)	.1862(4)	.0136(4)	.2849(4)
Cl(4)	-.0427(5)	-.1965(4)	.3891(4)
Cl(2)	-.0488(5)	.2570(4)	.1444(4)
Cl(3)	-.2699(5)	.0486(5)	.2404(4)
Oxo	.034(1)	-.042(1)	.1168(9)
Wat	-.116(1)	.096(1)	.4151(8)
O	.560(1)	.471(1)	.2383(9)
O(1)	-.328(1)	.320(1)	.460(1)
O(4)	-.242(1)	.560(2)	.295(2)
O(7)	-.333(2)	.702(2)	.072(2)
O(10)	-.613(2)	.678(2)	.119(1)
O(13)	-.676(1)	.424(2)	.206(1)
O(16)	-.572(1)	.289(1)	.412(1)
C(2)	-.268(3)	.401(3)	.496(2)
C(3)	-.168(2)	.460(2)	.393(3)
C(5)	-.161(3)	.640(3)	.187(3)
C(6)	-.252(4)	.753(3)	.129(3)
C(8)	-.436(4)	.809(4)	.025(5)
C(9)	-.553(5)	.784(3)	.045(4)
C(11)	-.697(6)	.640(5)	.069(5)
C(12)	-.759(3)	.550(3)	.135(3)
C(14)	-.750(2)	.337(2)	.303(2)
C(15)	-.648(2)	.231(2)	.363(3)
C(17)	-.495(2)	.191(2)	.506(2)
C(18)	-.432(2)	.265(2)	.556(2)

Table 3 Selected bond distances (Å) and angles (°) for **1**.

Atoms		Distance	Atoms		Distance
Mo	--Oxo	1.65(1)	Mo	--Wat	2.339(9)
Mo	--Cl(1)	2.405(4)	Mo	--Cl(2)	2.352(4)
Mo	--Cl(3)	2.371(4)	Mo	--Cl(4)	2.392(4)

Atoms			Angle	Atoms			Angle
Wat	-Mo	-Oxo	176.9(4)	Oxo	-Mo	-Cl(1)	96.8(4)
Wat	-Mo	-Cl(1)	81.4(3)	Cl(1)	-Mo	-Cl(2)	89.4(2)
Oxo	-Mo	-Cl(2)	101.3(4)	Wat	-Mo	-Cl(2)	81.3(3)
Cl(1)	-Mo	-Cl(3)	164.0(2)	Cl(2)	-Mo	-Cl(3)	87.9(2)
Oxo	-Mo	-Cl(3)	99.2(4)	Wat	-Mo	-Cl(3)	82.6(3)
Cl(1)	-Mo	-Cl(4)	88.5(1)	Cl(2)	-Mo	-Cl(4)	161.9(2)
Cl(3)	-Mo	-Cl(4)	89.3(2)	Oxo	-Mo	-Cl(4)	96.8(4)
Wat	-Mo	-Cl(4)	80.6(3)				

Table 4 Final fractional coordinates for [$H_3O^+ \cdot$ 18-crown-6] [$WOBr_4(H_2O)^-$], **2**.

Atom	x/a	y/b	z/c
W	.1164(2)	.2719(1)	.6013(1)
Br(1)	.0945(5)	.3972(2)	.5721(4)
Br(2)	.1538(5)	.1557(2)	.6841(5)
Br(3)	.3834(4)	.2850(3)	.6356(4)
Br(4)	-.1350(4)	.2658(3)	.6228(3)
O(1)	.600(3)	.119(2)	.401(2)
O(4)	.317(3)	.088(2)	.405(2)
O(7)	.244(3)	-.035(2)	.296(2)
O(10)	.362(3)	-.094(2)	.131(2)
O(13)	.618(3)	-.034(2)	.146(2)
O(16)	.796(3)	.050(2)	.305(2)
C(2)	.520(5)	.160(3)	.453(4)
C(3)	.421(5)	.117(3)	.498(3)
C(5)	.232(4)	.041(3)	.444(3)
C(6)	.151(5)	.002(3)	.341(3)
C(8)	.160(4)	-.079(3)	.203(4)
C(9)	.266(6)	-.128(3)	.177(4)
C(11)	.477(5)	-.134(3)	.118(4)
C(12)	.577(5)	-.0.91(2)	.072(4)
C(14)	.743(5)	-.004(2)	.126(5)
C(15)	.765(4)	.063(3)	.188(4)
C(17)	.833(4)	.110(2)	.371(4)
C(18)	.709(4)	.158(3)	.361(4)
Wat	.164(3)	.305(2)	.786(2)
Oxo	.084(4)	.249(2)	.464(2)
O	.478(3)	.021(2)	.271(3)

Table 5 Selected bond distances (Å) and angles (°) for **2**.

Atoms		Distance	Atoms		Distance
W	--Br(1)	2.511(5)	W	-- Br(2)	2.511(5)
W	--Br(3)	2.533(5)	W	-- Br(4)	2.524(4)
W	--Wat	2.31(2)	W	-- Oxo	1.71(3)

Atoms			Angle	Atoms			Angle
Br(1)	-W	-Wat	81.4(8)	Br(2)	-W	-Wat	83.3(8)
Br(3)	-W	-Wat	82.1(7)	Br(4)	-W	-Wat	82.4(7)
Br(1)	-W	-Br(2)	164.7(2)	Br(1)	-W	-Oxo	97(1)
Br(2)	-W	-Oxo	98(1)	Br(3)	-W	-Oxo	97(1)
Br(4)	-W	-Oxo	99(1)	Wat	-W	-Oxo	178(1)
Br(1)	-W	-Br(3)	88.2(2)	Br(2)	-W	-Br(3)	89.3(2)
Br(1)	-W	-Br(4)	90.8(2)	Br(2)	-W	-Br(4)	87.5(2)
Br(3)	-W	-Br(4)	164.5(2)				

Table 6 Final fractional coordinates for $[H_2O\cdot$*aza*-18-crown-6$\cdot(H^+)][MoOCl_4(H_2O)^-]$, **3**.

Atom	x/a	y/b	z/c
Mo(1)	.13863(5)	.0000	.23063(7)
Cl(1)	.1596(2)	.0000	.4417(2)
Cl(2)	.1576(1)	.1932(1)	.2293(2)
Cl(3)	.1575(2)	.0000	.0207(2)
Wat	.2741(4)	.0000	.2312(5)
Oxo	.0415(4)	.0000	.2322(7)
O	.9763(4)	.5000	.2803(6)
N(1)	.8701(6)	.5000	.0640(6)
C(2)	.8756(6)	.4036(7)	-.0064(7)
C(3)	.8566(6)	.3071(7)	.0717(7)
O(4)	.9073(3)	.2999(4)	.1650(5)
C(5)	.8924(5)	.2037(6)	.2323(7)
C(6)	.4485(4)	.2902(6)	.1563(6)
O(7)	.4334(3)	.1944(4)	.0843(4)
C(8)	.3564(4)	.1924(5)	.0253(6)
C(9)	.3520(4)	.0965(6)	-.0587(5)
C(10)	.3576(4)	.0000	.0118(5)

Table 7 Selected bond distances (Å) and angles (°) for **3**.

Atoms		Distance	Atoms		Distance
Mo(1)	-- Wat	2.291(5)	Mo(1)	-- Oxo	1.644(6)
Mo(1)	-- Cl(1)	2.385(2)	Mo(1)	-- Cl(2)	2.384(1)
Mo(1)	-- Cl(3)	2.366(2)			

Atoms			Angle	Atoms			Angle
Oxo	-Mo(1)	-Wat	179.2(3)	Wat	-Mo(1)	-Cl(1)	81.3(2)
Oxo	-Mo(1)	-Cl(1)	97.9(2)	Cl(1)	-Mo(1)	-Cl(2)	89.22(5)
Wat	-Mo(1)	-Cl(2)	82.29(4)	Oxo	-Mo(1)	-Cl(2)	97.72(4)
Cl(1)	-Mo(1)	-Cl(3)	163.64(9)	Cl(2)	-Mo(1)	-Cl(3)	88.59(4)
Wat	-Mo(1)	-Cl(3)	82.4(1)	Oxo	-Mo(1)	-Cl(3)	98.4(2)

Table 8 Final fractional coordinates for $[H_2O\cdot aza\text{-}18\text{-crown-}6\cdot(H^+)]_2[WOCl_4(H_2O)^-][Cl^-]$, 4.

Atom	x/a	y/b	z/c
W	.5000	.28622(3)	.5000
Cl(1)	.4044(2)	.3001(1)	.2640(3)
Cl(2)	.3671(2)	.3026(1)	.4670(3)
Cl(3)	.1120(3)	.0000	.4938(4)
O(4)	.5901(5)	.3744(3)	.1676(7)
O(7)	.7567(5)	.3801(3)	.2314(8)
O(10)	.8211(8)	.5000	.211(1)
N(1)	.5373(7)	.5000	.206(1)
C(2)	.4799(7)	.4398(6)	.145(1)
C(3)	.5409(8)	.3774(5)	.207(1)
C(5)	.6480(8)	.3199(5)	.217(1)
C(6)	.7005(8)	.3232(5)	.177(1)
C(8)	.8119(9)	.3827(6)	.203(2)
C(9)	.8750(9)	.4436(6)	.275(2)
O(14)	−.0770(6)	.3768(4)	.7231(9)
O(17)	.1061(5)	.3798(4)	.9645(7)
O(20)	.172(1)	.5000	1.114(1)
N(11)	−.150(1)	.5000	.576(2)
C(12)	−.190(1)	.4391(7)	.533(1)
C(13)	−.150(1)	.3828(7)	.586(2)
C(15)	−.0177(7)	.3279(5)	.763(1)
C(16)	.0563(8)	.3232(5)	.909(1)
C(18)	.1713(9)	.3799(6)	1.105(1)
C(19)	.224(1)	.4410(7)	1.151(1)
Ow	.5000	.3979(4)	.5000
O(100)	.6636(7)	.5000	.185(1)
O(200)	−.013(1)	.5000	.854(1)
O	.5000	.2021(4)	.5000

Table 9 Selected bond distances (Å) and angles (°) for **4**.

Atoms		Distance	Atoms		Distance
W	– Cl(1)	2.384(3)	W	– Cl(2)	2.374(3)
W	– O	1.703(7)	W	– Ow	2.262(9)

Atoms			Angle	Atoms			Angle
Cl(1)'	-W	-Cl(1)	166.5(1)	Cl(1)	-W	-O	96.76(7)
Cl(2)	-W	-O	98.02(7)	Cl(1)	-W	-Cl(2)	88.1(1)
Cl(1)	-W	-Cl(2)'	90.0(1)	Cl(2)'	-W	-Cl(2)	164.0(1)
Cl(1)	-W	-Ow	83.24(7)	Cl(2)	-W	-Ow	81.98(7)
O	-W	-Ow	179.937				

$$\mathrm{M(CO)_6 + H_2O + HX \xrightarrow{\text{toluene/UV}} [H_3O^+\cdot 18\text{-crown-6}][MOX_4(H_2O)^-]}$$

(1) M = Mo, X = Cl,
(2) M = W, X = Br

$$\xrightarrow{\text{toluene/UV}} \mathrm{[H_2O\cdot \mathit{aza}\text{-}18\text{-crown-6}(H^+)]_n[MOCl_4(H_2O)^-][Cl^-)_m}$$

(3) M = Mo, n = 1, m = 0,
(4) M = W, n = 2, m = 1

Scheme 1

The novel synthetic method represents a general route to Group VI coordination complexes in the +5 and other oxidation states.[2,4,5] In these reactions, a sample of the metal [0] hexacarbonyl undergoes air oxidation to the +5 state under rather forcing conditions, namely rapid bubbling of HCl(g) through the mixture while irradiating with UV light.

Structural Results

To identify the species present in the liquid clathrates, all the compounds investigated were structurally authenticated using X-ray crystallographic techniques. During the course of these studies, all attempts were aimed at obtaining X-ray quality crystals, not at maximizing yields.

$[H_3O^+\cdot 18\text{-crown-6}][MoOCl_4(H_2O)]^-$, **1**. This complex crystallizes as discrete anions and cations; there are no interionic contacts less than 3.5 Å.

The structure of the anion in **1** is shown in Figure 1. The geometry is that of a distorted octahedron, where the equatorial Cl ligands are forced down and away from the axial oxo ligand (O = Mo-Cl angles range from 96.8(4) to 101.3(4)°). A water molecule fills the coordination sphere of the molybdenum center, being weakly held *trans* to the oxo ligand at a distance of 2.339(9) Å. The Mo = O distance is 1.65(1) Å and the Cl ligands are bound at an average of 2.38(2) Å from the Mo center.

The structure of the $[H_3O^+\cdot 18\text{-crown-6}]$ cation in **1** is shown in Figure 2. The hydrogen atoms of the H_3O^+ ion could not be located from the difference electron density map. The average O(oxonium) ... O(crown) distance is 2.75(9) Å, which is well within the limits for O-H ... O hydrogen bonding.[18] However, there are three O ... O(crown) contacts of 2.648(5) to 2.72(2) Å and three of 2.72(1) to 2.925(6) Å, at alternating O(crown) sites around the macrocycle. This suggests that the H_3O^+ is more strongly bound to O4, O10, and O16. The O(oxonium) atom resides 0.65 Å out of the plane defined by the O4, O10, and O16(crown) atoms.

$[H_3O^+\cdot 18\text{-crown-6}][WOBr_4(H_2O)^-]$, **2**. In this complex, the anions exhibit hydrogen-bonding contacts between the axial water and oxo ligands of 2.74 Å, forming head-to-tail hydrogen-bonded polymeric strands of anions throughout the structure (see Figure 3). There is also a short distance between the axial water molecule on the anion and O4 of the $[H_3O^+\cdot 18\text{-crown-6}]$ cation, 2.79 Å, indicating a hydrogen bonding contact.

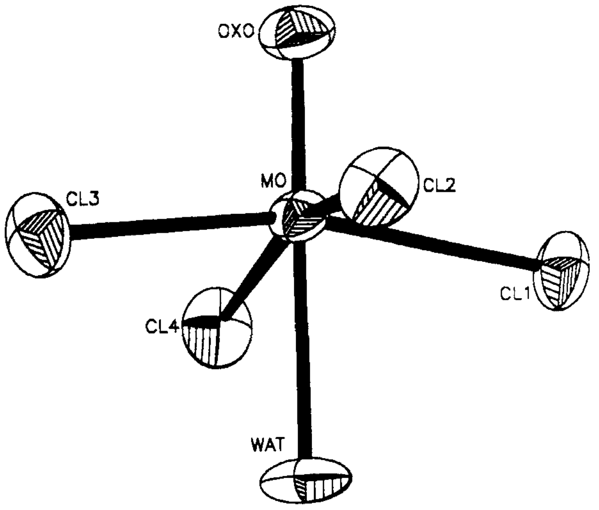

Figure 1 Structure of the $[MoOCl_4(H_2O)]^-$ anion in **1** and **3**. In **3**, the Mo, O(water), Oxo and two Cl atoms reside on a mirror plane. The Oxo-Mo-Cl angles range 96.8(4)–101.3(4)° and 97.72(4)–98.4(2)° in **1** and **3**, respectively. Mo-Oxo and Mo-O(water) distances are 1.65(1) and 2.339(9) Å in **1** and 1.644(6) and 2.291(5) Å in **3**.

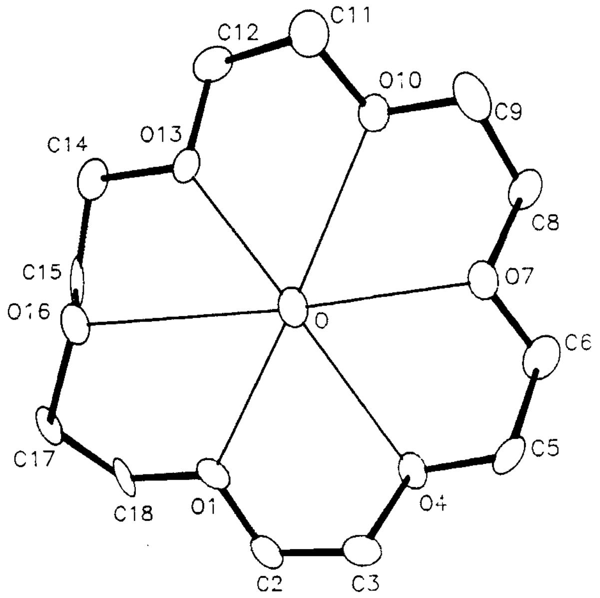

Figure 2 Structure of the $[H_3O^+ \cdot 18\text{-crown-}6]$ cation in **1** and **2**. In **1** the H_3O^+ binds to O4, O10, and O16 at 2.72(2), 2.67(1), and 2.65(1) Å, and has H_3O^+ to O1, O7 and O13 distances of 2.93(1), 2.82(2), and 2.72(2) Å. In **2** the H_3O^+ binds to O1, O7, and O13 at 2.60(1), 2.62(1), and 2.55(2) Å, and has H_3O^+ to O4, O10, and O16 distances of 2.88(2), 2.91(2), and 3.06(1) Å.

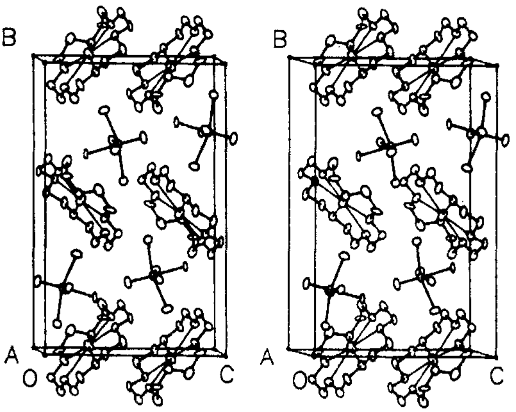

Figure 3 Stereoview of the unit cell packing in [$H_3O^+ \cdot$18-crown-6][$WOBr_4(H_2O^-$], **2**. There are head-to-tail hydrogen bonding contacts between the axial oxo and water ligands of 2.74 Å in the anions.

The structure of the anion in **2**, Figure 4, is similar to the distorted octahedral geometry seen in the anion of **1**. The W = O, W-O(wat), and average W-Br bond distances are 1.71(3), 2.31(2), and 2.520(9) Å, respectively. The O = W-Br angles range from 97(1) to 99(1)°.

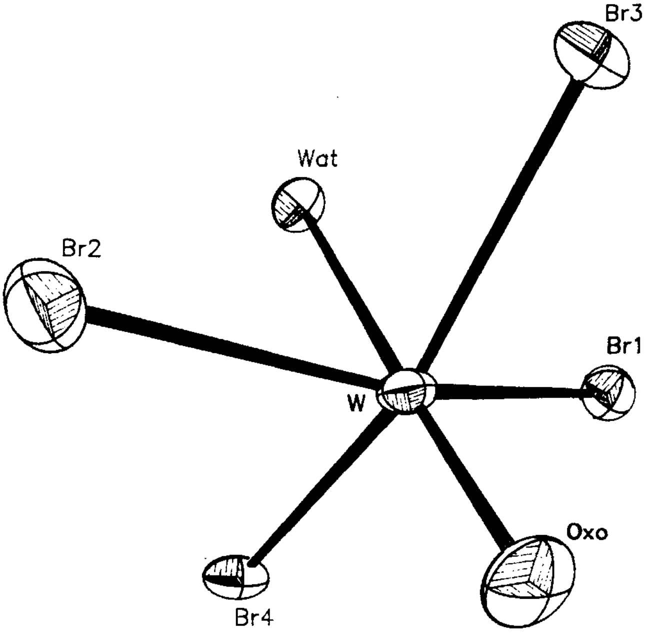

Figure 4 Structure of the [$WOCl_4(H_2O)]^-$ anion in **4**, which resides on a 2-fold axis. The Oxo-W-Cl angles range from 96.76(7)–98.02(7)°. The W-Oxo and W-O(water) distances are 1.703(7) and 2.262(9) Å, respectively.

The structure of the [$H_3O^+ \cdot$ 18-crown-6] cation in **2**, Figure 2, is similar to that in compound **1**. Again, hydrogen atoms of the H_3O^+ ion could not be located from the difference electron density map. The O(oxonium) atom resides close to the center of the macrocyclic ligand and has three short and three long O(oxonium) . . . O(crown) separations. The short distances are to O1 (2.60 Å), O7 (2.62 Å), and O16 (2.55 Å), while the longer distances are to O4 (2.88 Å), O10 (2.91 Å), and O16 (3.06 Å). This suggests that the H_3O^+ is more strongly bound to O1, O7 and O13. The O(oxonium) atom resides 0.17 Å out of the plane defined by the O(crown) atoms.

[$H_2O \cdot$ *aza*-18-crown-6 $\cdot (H^+)$][$MoOCl_4(H_2O)^-$], **3**. This complex crystallizes with intermolecular hydrogen bonding contacts between the cation and anion. The water molecule in the cation is completely bound within the macrocycle and has no other hydrogen-bonding contacts. The water molecule in the axial position on the anion is hydrogen bonded through a proton on the N atom of the macrocycle at a distance of 2.81 Å, and also to O10 of the crown ether at 2.83 Å, through a water hydrogen atom.

The structure of the anion is that of a distorted octahedron and is similar to the anion in complex **1**. A mirror plane contains the axial oxo, the water ligands, the central Mo atom and two of the equatorial Cl ligands. The Mo = O, Mo-O(wat), and average Mo-Cl bond distances are 1.644(6), 2.291(5) and 2.375(9) Å, respectively. The O = Mo-Cl angles range from 97.72(4) to 98.4(2)°.

The structure of the cation in compound **3** is shown in Figure 5. The macrocycle resides on a crystallographic mirror plane (through N1, O10, and O(wat)). The protons on the water molecule and on N1 could not be located from the X-ray study. The cation is best viewed as an N-protonated *aza*-crown ether with an encapsulated water molecule. The O(water) atom resides closest to two O(crown)

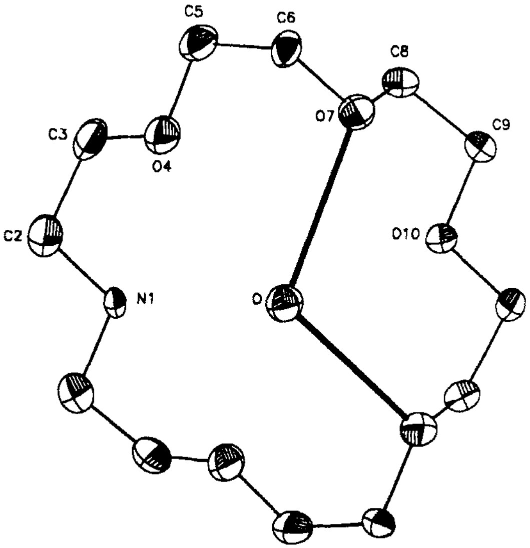

Figure 5 Structure of the [$H_2O \cdot$ axa-18-crown-6(H^+)] cation in **3** which resides on a crystallographic mirror plane. The protons on the water molecule were not located. O to crown heteroatom distances are as follows: O . . . N3, 3.011 Å; O . . . O4, 3.002 Å; O . . . O7, 2.909 Å; O . . . O10 3.070 Å.

atoms with the N and three other O(crown) atoms at longer distances. The O . . . O7 distance of 2.91 Å is within the limits for O-H . . . O hydrogen bonding. Distances of O to O4, N1, and O10 (3.00, 3.01, and 3.07 Å) are slightly longer and indicate that the water molecule is most strongly bound to the two O7 atoms. The water molecule resides 1.41 Å out of the plane defined by the heteroatoms of the crown, although the heteroatoms are not strictly planar (out-of-plane distances being N1, 0.41; O4, -0.49; O7, -0.46; O10, 0.54 Å).

$[H_2O \cdot$ *aza*-18-crown-6$\cdot (H^+)]_2[WOCl_4(H_2O)^-]$, 4. This complex crystallizes as discrete anions and cations, Figure 6, with no interionic distances of less than 3.5 Å.

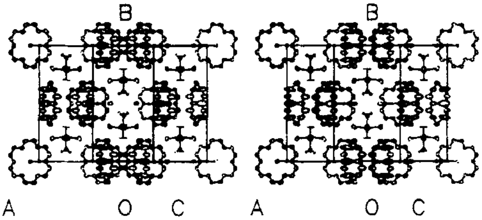

Figure 6 Stereoview of the unit cell packing in $[H_2O \cdot \text{aza-18-crown-6}(H^+)][WOCl_4(H_2O)^-][Cl^-]$, 4. The complex crystallizes as discrete anions and cations. There are no intermolecular distances of less than 3.5 Å.

The anion in compound 4, which resides on a two-fold axis, has distorted octahedral geometry (see Figure 7), and is similar to those of the other three

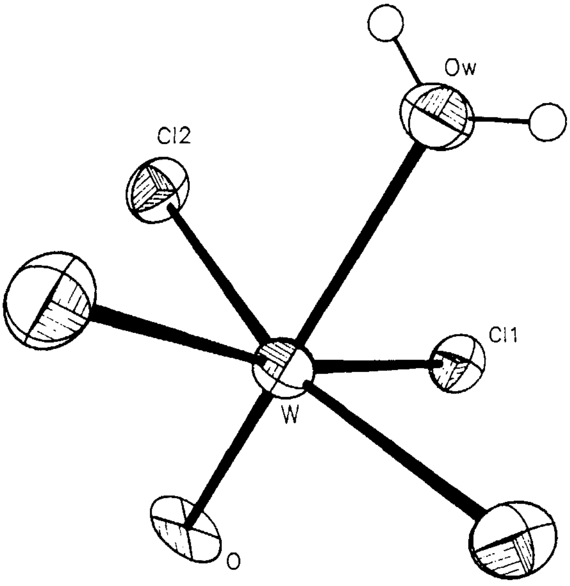

Figure 7 Structure of the $[WOCl_4(H_2O)^-]$ anion in **4**, which resides on a two-fold axis. The Oxo-W-Cl angles range from 97.76(7) to 98.02(7)°. The W-Oxo and W-O(water) distances are 1.703(7) and 2.262(9) Å, respectively.

complexes. The W = O, W-O(wat), and average W-Cl bond distances are 1.703(7), 2.262(9), and 2.379(5) Å, respectively. The O = W-Cl angles range from 96.76(7) to 98.02(7)°.

There are two crystallographically distinct cations in compound **4**. One of these, which resides on a mirror plane through N1, O10, and the water oxygen atom, is shown in Figure 8. Here, the N-O(water) distance is 2.71 (2.77) Å. The other O(water) to crown heteroatom distances are O100 . . . O4, 2.86 (2.81), O100 . . . O7, 2.85 (2.99), O100 . . . O10, 2.89 (2.88)Å, indicating the water molecule is also hydrogen bonded in a disordered fashion to the other appropriate atoms. The hydrogen atom on the amine is located 1.65 Å from the water oxygen atom and 1.08 Å from the nitrogen atom, indicating the oxygen atom is more likely part of a water molecule than an oxonium ion. In these cations the O(water) atom resides 0.24 and 0.57 Å out of the plane defined by the respective heteroatoms of the crown.

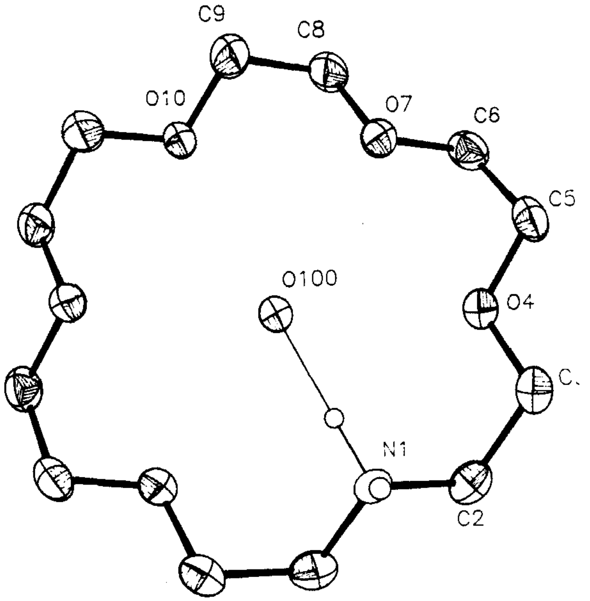

Figure 8 Structure of one of the crystallographically distinct [H_2O·aza-18-crown-6(H^+)] cations in **4**, which resides on a mirror plane. The O100 to crown heteroatom distances are as follows (with the second ion values in parentheses): O100 . . . N1, 2.71 (2.77) Å; O100 . . . O4, 2.86 (2.81) Å; O100 . . . O7, 2.85 (2.99) Å; O100 . . . O10, 2.89 (2.88) Å. The proton forming the hydrogen bond between O100 and N1 was located at 1.65 Å from O100 and 1.08 Å from N1.

DISCUSSION

Formation of the [$MOX_4(H_2O)^-$] anions directly from $M(CO)_6$ has proven to be a general mode of synthesis.[2,4,5]. It is noteworthy that it is essential to perform these reactions in contact with external oxygen for oxidation of the meal from [0] to [+5]. Under an inert atmosphere, anions of the type [$M(CO)_5X^-$] are formed, where no oxidation of the metal occurs.[2] Where reactions were performed in the absence of

UV radiation, it typically took several weeks for complex formation to reach completion, although liquid clathrates were observed almost immediately.

There is considerable literature concerning the structure of the [$H_3O^+ \cdot$ 18-crown-6] cation.[1,2,4,7-10,14-16,19-25] Discussions center on the geometry of the oxonium ion, H_3O^+. Arguments have favored both (i) planar conformations, where the O(oxonium) atom resides within 0.1 Å of the plane of the O(crown) atoms,[9] and (ii) pyramidal conformations, where the O(oxonium) atom sits at distances of up to 0.93 Å out of the plane of the crown oxygen atoms.[19] Table 10 presents the out-of-plane distances for a range of [$H_3O^+ \cdot$ 18-crown-6] complexes with various anions.[1,2,4,7-10,14-16,19-24] The compounds reported herein, **1** (0.17 Å) and **2** (0.65 Å), fall within the ranges reported in the literature. Clearly, there is not a discrete leap from planar to pyramidal, rather a gradual change. In a number of these complexes, the protons on the oxonium ion were not located and the structures may involve bifurcated interactions between O(oxonium) and O(crown), or those with crystallographic disorder. In these types of compounds the O(oxonium) atom may reside within the plane of the crown oxygens but still be pyramidal Although the conformation adopted is most probably due to the

Table 10 Geometry of Oxonium Ions Coordinated Within 18-crown-6 Macrocycles

Compound	Distance out of plane of crown heteroatoms (Å)	Geometry	Reference
[$H_3O^+ \cdot$ 18-crown-6$(COOH)_4$]	0.61	pyramidal	10
[$H_2O \cdot$ 2,6-pyrido-18-crown-6 $\cdot H^+$] [ClO_4^-]	0.93	pyramidal	19
$H_2O \cdot$ 2,6-pyrido-18-crown-6 $\cdot H^+$] [picrate]	0.64	pyramidal	19
[$H_3O^+ \cdot$ 18-crown-6]$_2$[$Mo_6O_{19}^{2-}$]	0.10	planar[a]	9
[$H^3O^+ \cdot$ 18-crown-6][Cl-H-Cl^-]	0.29[b]	planar/pyramidal	7
[$H_3O^+ \cdot$ dicyclohexano-18-crown-6] [$Th(NO_3)_6$]	0.04	planar	20
[$H_3O^+ \cdot$ 18-crown-6]$_2$[$Pd_2Cl_6^{2-}$]	0.16	pyramidal	21
[$H_3O^+ \cdot$ 18-crown-6]$_2$[$ZnCl_4^{2-}$]	0.33(0.19)	pyramidal	22
[$H_3O^+ \cdot$ 18-crown-6]$_2$[$MnCl_4^{2-}$]	0.45(0.88)	pyramidal	22
[$H_3O^+ \cdot$ 18-crown-6][Br-H-Br^-]	0.29	planar/pyramidal	8
[$H_3O^+ \cdot$ 18-crown-6][$(H_5O_2^+)(Cl)_2^-$]	0.41	pyramidal	23
[$H_3O^+ \cdot$ 18-crown-6]$_2$ [$(UO^2(NO_3)_2C_2O_4$]	0.005[c]	planar	24
[$H_3O^+ \cdot$ 18-crown-6][$MoOCl_4(H_2O)^-$]	0.84	pyramidal	16
[$H_3O^+ \cdot$ 18-crown-6][$ReOCl_4(H_2O)^-$]	0.87	pyramidal	16
[$H_3O^+ \cdot$ 18-crown-6]$_2$[$FeCl_4^-$]	0.32	planar/pyramidal	1
[$H_3O^+ \cdot$ 18-crown-6][Br_3]	0.092	planar	14
[$H_3O^+ \cdot$ 18-crown-6][I_7^-]	0.09	planar	15
[$H_3O^+ \cdot$ 18-crown-6][$CrCl_4(H_2O)_2^-$]	0.60	pyramidal	4
[$H_3O^+ \cdot$ 18-crown-6][$(H_5O_2^+)Mo_2Clg^{3-}$]	0.05(0.50)	planar(pyramidal)	4
[$H_3O^+ \cdot$ 18-crown-6][$WOCl_4(H_2O)^-$]	0.32	planar/pyramidal	4
[$H_3O^+ \cdot$ 18-crown-6][$W(CO)_5Cl^-$]	0.40	pyramidal	2
[$H_3O^+ \cdot$ 18-crown-6][$W(CO)_4Cl_3^-$]	0.007	planar	2
[$H_3O^+ \cdot$ 18-crown-6][$MoOCl_4(H_2O)^-$]	0.65	pyramidal	This Work
[$H_3O^+ \cdot$ 18-crown-6][$WOBr_4(H_2O)^-$]	0.17	planar	This Work

[a] The O(oxonium) atom had large thermal motion and the H atoms were not located. The authors stated they could not rule out pyramidal geometry for the H_3O^+ ion. [b] The O(oxonium) atom resides 0.09 Å out of the plane of its three closest O(crown) atoms and could therefore be classified as almost planar. [c] The O(oxonium) atom resides 0.005 Å out of the plane of its closest three O(crown) atoms, and 0.40 Å out of the plane of the other three O(crown) atoms.

crystal packing requirements of the anions and cations, low temperature X-ray or neutron diffraction studies are needed.

The cations in **3** and **4** are properly considered as protonated amino macrocycles which contain a bonded water molecule. In these ions, the water molecule is more tightly bound to two O(crown) atoms through hydrogen bonding than through the proton on the amine. This situation has been previously seen in cations formally described as [$H_3O^+ \cdot$*aza*-18-crown-6], where the proton resides much closer to the N than O atoms.[19,26] However, there is an example of a [$H_3O^+ \cdot$*aza*-18-crown-6] cation in which the proton is equally shared by the N and O(water) atoms.[27]

The anions isolated all had similar geometries, viz., distorted octahedra in which the equatorial halide ligands are bent down and away from the axial oxo ligand, typically at around 98°. In all cases a water molecule is weakly bound to the metal center, *trans* to the oxo ligand. The long distances obtained for the M-O(wat) separations of *ca.* 2.30 Å are typical of the *trans* effect. These geometries are characteristic of [$MOX_4(H_2O)^-$] anions.[4,5,16,28,29]

Acknowledgements

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