Liquid clathrate media containing transition metal halocarbonyl anions; formation and crystal structures of [K$^+$· 18-crown-6][Cr(CO)$_5$Cl], [H$_3$O$^+$· 18-crown-6][W(CO)$_5$Cl], [H$_3$O$^+$· 18-crown-6][W(CO)$_4$Cl$_3$], and [H$_2$O · bis-aza-18-crown-6 · (H$^+$)$_2$][W(CO)$_4$Cl$_3$]$_2$

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Abstract

The complexes [H$_3$O$^+$· 18-crown-6][W(CO)$_5$Cl], (2) [H$_3$O$^+$· 18-crown-6][W(CO)$_4$Cl$_3$], (3) and [H$_2$O · bis-aza-18-crown-6 · (H$^+$)$_2$][W(CO)$_4$Cl$_3$]$_2$, (4) were synthesized from a mixture of W(CO)$_6$, HCl$_{(g)}$, H$_2$O and either 18-crown-6 for 2 and 3 or bis-aza-18-crown-6 for 4, in toluene. Reaction conditions for [K$^+$· 18-crown-6][Cr(CO)$_5$Cl], (1) were similar except that Cr(CO)$_6$ and KCl were used in place of W(CO)$_6$ and H$_2$O, respectively. These reactions were promoted with the use of UV radiation and liquid clathrates were formed almost immediately upon reaction. X-ray crystal structures were deduced for each compound. Complex 1 crystallizes in the orthorhombic space group $Pbnm$ with $a = 7.432(1)$, $b = 16.521(3)$, $c = 19.508(2)$ Å, and $D_c = 1.48$ g cm^{-3} for $Z = 4$. Refinement based on 1277 observed reflections led to a final R value of 0.078. Complex 2 crystallizes in the rhombohedral space group $R\bar{3}$ with $a = 13.458(1)$, $c = 10.769(1)$ Å, and $D_c = 1.77$ g cm^{-3} for $Z = 3$. Refinement based on 715 observed reflections led to a final R value of 0.014. Complex 3 crystallizes in the monoclinic space group $C2/c$ with $a = 22.411(2)$, $b = 11.018(1)$, $c = 16.340(2)$ Å, $\beta = 114.34(1)°$, and $D_c = 1.24$ g cm^{-3} for $Z = 4$. Refinement based on 1966 observed reflections led to a final R value of 0.068. Complex 4 crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.761(1)$, $b = 12.096(1)$, $c = 14.966(1)$ Å, $\alpha = 107.88(1)$, $\beta = 91.19(1)$, $\gamma = 117.44(1)°$, and $D_c = 2.03$ g cm^{-3} for $Z = 2$. Refinement based on 3065 observed reflections led to a final R value of 0.054.

1. Introduction

The 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)$_5$X]$^-$ 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)$_4$X$_2$] 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)$_4$X$_3$]$^-$ and [M^{II}(CO)$_3$L$_2$X$_2$] [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.

Structural and other aspects of the [M^0(CO)$_5$X]$^-$ anion have been previously discussed. The complex typically exists in a monomeric octahedral array [4-6].

Seven-coordinate complexes of tungsten(II) are not uncommon [7]. However, for mononuclear, monodentate species the number is rather diminished. Several structures have been determined and three geometries have been recognized for this coordination number: (i) the capped octahedron [8], (ii) the capped trigonal prism [9], and (iii) the 4:3 piano stool [10]. The capped octahedron dominates these morphologies [7]. The [W(CO)$_4$Br$_3$]$^-$ anion has been described as both a capped octahedron [8] and a capped trigonal antiprism [9].

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

Compound	[K⁺· 18-crown-6] [Cr(CO)₅Cl⁻] (1)	[H₃O⁺· 18-crown-6] [W(CO)₅Cl⁻] (2)	[H₃O⁺· 18-crown-6] [W(CO)₄Cl₃⁻] (3)	[H₂O · bis-aza-18-crown-6 · (H⁺)₂] [W(CO)₄Cl₃⁻]₂ (4)
Mol. Wt.	530.92	642.74	685.59	1087.00
Space group	Pbnm ᵃ	R3̄	C2/c	P1̄
Cell constants				
a, Å	7.432(1)	13.948(1)	22.411(2)	11.761(1)
b, Å	16.521(3)	13.948(1)	11.018(1)	12.096(1)
c, Å	19.508(2)	10.769(1)	16.340(2)	14.966(1)
α, deg	90	90	90	107.88(1)
β, deg	90	90	114.34(1)	91.19(1)
γ, deg	90	120	90	117.44(1)
V, Å³	2395(1)	1814(1)	3676(15)	1765(9)
Molecules/unit cell	4	3	4	2
D_c, g cm⁻³	1.48	1.77	1.24	2.05
μ, cm⁻¹	8.04	50.61	34.66	71.94
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Scan width, deg	0.80 + 0.20 tan θ	0.85 + 0.35 tan θ	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
2θ range, deg	2-45	2-50	2-45	2-45
No. reflcns collcd	2185	1705	3159	4306
No. of obsd reflcns	1277	715	1966	3065
No. of params varied	156	61	147	388
Sigma cutoff	3σ	3σ	3σ	3σ
Weighting scheme	unit weights	unit weights	unit weights	unit weights
Temp. of data colln, deg	23	23	23	23
R	0.078	0.014	0.068	0.054
R_w	0.076	0.016	0.076	0.063

ᵃ Alternative setting of Pnma, No. 62.

Much discussion has centered on the structure of H₃O⁺, as well as the [H₃O⁺· 18-crown-6] cation [11,12], where arguments have focused on planar versus pyramidal geometry around the oxonium ion center. Species have been identified where the O(oxonium) atom sits

Table 2
Final fractional coordinates for [K⁺·18-crown-6] [Cr(CO)₅Cl⁻] (1)

Atom	x	y	z
Cr(1)	0.1365(3)	0.1129(1)	0.2500
Cl	0.1337(9)	0.1240(4)	0.3796(4)
Cax	0.138(3)	0.105(1)	0.343(1)
Oax	0.142(3)	0.093(1)	0.107(1)
Ca	0.367(2)	0.1615(9)	0.2500
Oa	0.507(2)	0.1914(8)	0.2500
Cb	0.244(2)	0.005(1)	0.2500
Ob	0.302(2)	−0.0552(7)	0.2500
Cc	−0.096(2)	0.0650(9)	0.2500
Oc	−0.239(1)	0.0379(8)	0.2500
Cd	0.027(3)	0.214(1)	0.2500
Od	−0.037(2)	0.2801(8)	0.2500
K	0.0000	0.0000	0.5000
O(1)	−0.2593(8)	−0.0192(4)	0.4014(3)
C(2)	−0.287(1)	−0.0975(6)	0.3785(5)
C(3)	−0.118(1)	−0.1373(7)	0.3624(5)
O(4)	−0.0134(9)	−0.1436(4)	0.4226(3)
C(5)	0.160(1)	−0.1770(6)	0.4121(5)
C(6)	0.253(1)	−0.1850(6)	0.4806(5)
O(7)	0.2929(8)	−0.1088(4)	0.5051(3)
C(8)	0.368(1)	−0.1147(6)	0.5713(5)
C(9)	−0.418(1)	0.0262(6)	0.4052(5)

within 0.1 Å of the plane of the crown ether oxygen atoms [13], while others have been found to reside further than 0.5 Å out of this plane [14].

As part of our investigations of liquid clathrate systems [15-17], involving the stabilized oxonium ion, [H₃O⁺· 18-crown-6] [18-22], we now report the interaction of W(CO)₆ with the 18-crown-6/HCl/H₂O system in toluene. Several species have been identified using this novel synthetic approach, depending on the oxidation state of the metal. A discussion of the geometry of the [H₃O⁺· 18-crown-6] cation is also presented, since this is a rare species not only in aromatic solvents but also paired with organometallic anions. Also included is the interaction of Cr(CO)₆ with 18-crown-6/KCl/HCl in toluene in the absence of moisture.

2. Experimental section

Cr(CO)₆ and W(CO)₆ were obtained from Aldrich Chemical Co. and HCl gas was purchased from Atlas-Airco. Complexes 1 and 2 were prepared under an inert atmosphere, while complexes 3 and 4 were prepared while 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 spectrom-

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

Bond distances						
Oax	–Cax		0.98(3)	Oa	–Ca	1.15(2)
Ob	–Cb		1.09(2)	Oc	–Cc	1.15(2)
Od	–Cd		1.19(2)	K	–O(1)	2.740(6)
K	–O(4)		2.814(6)	K	–O(7)	2.823(6)
Cr(1)	–Cl		2.534(7)	Cr(1)	–Cax	1.83(2)
Cr(1)	–Oax		2.81(2)	Cr(1)	–Ca	1.89(2)
Cr(1)	–Cb		1.95(2)	Cr(1)	–Cc	1.90(2)
Cr(1)	–Cd		1.86(2)			
Bond angles						
Oax	–Cax	–Cr(1)	173 (3)	Oa	–Ca	–Cr(1)	179.8(4)
Ob	–Cb	–Cr(1)	179 (1)	Oc	–Cc	–Cr(1)	178 (1)
Od	–Cd	–Cr(1)	178 (2)	Cax	–Cr(1)	–Cl	179.8(2)
Oax	–Cr(1)	–Cl	177.4(5)	Ca	–Cr(1)	–Cl	88.7(2)
Ca	–Cr(1)	–Cax	91.4(7)	Ca	–Cr(1)	–Oax	92.1(4)
Cb	–Cr(1)	–Cl	94.0(2)	Cb	–Cr(1)	–Cax	85.9(8)
Cb	–Cr(1)	–Oax	83.5(4)	Cb	–Cr(1)	–Ca	91.0(6)
Cc	–Cr(1)	–Cl	91.3(2)	Cc	–Cr(1)	–Cax	88.6(7)
Cc	–Cr(1)	–Oax	87.9(4)	Cc	–Cr(1)	–Ca	179.4(6)
Cc	–Cr(1)	–Cb	89.6(6)	Cd	–Cr(1)	–Cl	86.1(2)
Cd	–Cr(1)	–Cax	94.1(8)	Cd	–Cr(1)	–Oax	96.4(4)
Cd	–Cr(1)	–Ca	90.6(7)	Cd	–Cr(1)	–Cb	178.4(7)
Cd	–Cr(1)	–Cc	88.8(7)				

eter. ^{1}H 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 3.00–4.00 ppm (crown ethers), δ 9.40 ppm (H_3O^+).

2.1. Preparation of [K$^+$· 18-crown-6][Cr(CO)$_5$Cl] (1)

To a sample of 18-crown-6 (1.0 g, 3.62 mmol) in toluene was added KCl (0.27 g, 3.62 mmol) and Cr(CO)$_6$ (0.80 g, 3.62 mmol) and stirred rapidly for 15 min. HCl(g) was then rapidly bubbled through the mixture for approximately 1 h while irradiating with UV radiation. After this time, a light yellow liquid clathrate separated from the solvent with a toluene:complex ratio of 1.7:1 as determined by ^{1}H NMR. Yellow crystals of the title complex deposited from the liquid clathrate layer after 48 h.

2.2. Preparation of [H$_3$O$^+$· 18-crown-6][W(CO)$_5$Cl] (2)

A sample of 18-crown-6 (0.66 g, 2.50 mmol) was moistened with distilled water (0.045 ml, 2.50 mmol) and approximately 50 ml of toluene added. W(CO)$_6$ (0.87 g, 2.50 mmol) was then added and HCl(g) was rapidly bubbled through the mixture for approximately 1 h while irradiating with UV radiation. After this time, a slightly yellow liquid clathrate separated from the solvent with a toluene:complex ratio of 3.1:1 as determined by ^{1}H NMR. Yellow prism shaped crystals of the title complex deposited from the liquid clathrate layer after five days.

2.3. Preparation of [H$_3$O$^+$· 18-crown-6][W(CO)$_4$Cl$_3$](3)

A sample of 18-crown-6 (1.0 g, 3.62 mmol) was moistened with distilled water (0.065 ml, 3.62 mmol) and approximately 100 ml of toluene added. W(CO)$_6$

Table 4
Final fractional coordinates for [H$_3$O$^+$·18-crown-6] [W(CO)$_5$Cl$^-$] (2)

Atom	x	y	z
W	.0000	.0000	.0000
O(1)	.2224(2)	.1566(2)	.5173(2)
C(1)	.2980(3)	.1211(3)	.4824(3)
C(2)	.2495(3)	.2599(3)	.4625(3)
O [a]	.2063(6)	.1007(7)	.1731(7)
C [a]	.1350(5)	.0672(5)	.1111(7)
Cl [a]	.188(1)	.096(1)	.131(1)
O(2)	.0000	.0000	.4634(6)

[a] C and O refined with occupancies = 5/6, Cl with occupancy = 1/6

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

Bond distances						
W	–Cl		2.68(1)	W	–C	2.023(6)
O	–C		1.090(9)			
Bond angles						
Cl	–W	–Cl'	94.7(7)	C	–W	–C″	88.6(5)
C	–W	–C*	180.0(5)	Cl'	–W	–C	92.3(6)
Cl″	–W	–C	91.2(6)	Cl*	–W	–C	175.5(6)
W	–C	–O	177.9(8)				

Symmetry codes: ' (x, y, z) → (-y, x-y, z); ″ (y-x,-x, z); * (-x,-y,-z).

Table 6
Final fractional coordinates for [H₃O⁺·18-crown-6] [W(CO)₄Cl₃⁻] (3)

Atom	x	y	z
W	0.28412(5)	0.2875(1)	0.34433(7)
Cl(1)	0.3472(4)	0.2993(8)	0.5103(4)
Cl(2)	0.3751(4)	0.1598(9)	0.3426(6)
Cl(3)	0.3464(4)	0.4688(8)	0.3318(6)
Ca	0.186(1)	0.265(3)	0.274(2)
Oa	0.1342(9)	0.253(2)	0.237(2)
Cb	0.265(1)	0.278(3)	0.207(2)
Ob	0.256(1)	0.277(3)	0.137(1)
Cc	0.240(2)	0.427(4)	0.372(3)
Oc	0.212(2)	0.505(3)	0.390(2)
Cd	0.263(2)	0.123(3)	0.383(2)
Od	0.253(1)	0.036(2)	0.406(2)
O	0.0000	0.306(4)	0.7500
O(1)	0.0000	0.080(4)	0.7500
C(2)	0.047(2)	0.007(4)	0.812(3)
C(3)	0.094(2)	0.086(3)	0.869(2)
O(4)	0.071(2)	0.179(3)	0.910(2)
C(5)	0.129(4)	0.250(7)	0.975(5)
C(6)	0.089(3)	0.360(6)	0.974(4)
O(7)	0.048(2)	0.436(3)	0.900(2)
C(8)	0.006(4)	0.536(7)	0.909(6)
C(9)	0.022(3)	0.594(6)	0.850(4)
O(10)	0.0000	0.569(6)	0.7500

(1.27 g, 3.62 mmol) was then added and HCl(g) was rapidly bubbled through the mixture for approximately 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. Orange crystals of the title complex deposited from the liquid clathrate layer after three days.

2.4. Preparation of [H₂O · biz-aza-18-crown-6 · (H⁺)₂]-[W(CO)₄Cl₃]₂ (4)

A sample of bis-aza-18-crown-6 (0.2 g, 0.76 mmol) was moistened with distilled water (0.02 ml, 0.80 mmol) and approximately 30 ml of toluene added. W(CO)₆ (0.27 g, 0.76 mmol) was then added and HCl(g) was rapidly bubbled through the mixture for approximately 1 h while irradiating with UV radiation. After this time, a light yellow liquid clathrate separated from the solvent with a toluene:complex ratio of 2.2 : 1 as determined by ¹H NMR. Orange crystals of the title complex deposited from the liquid clathrate layer after three days.

2.5. 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 25 high angle reflections $(2\theta > 30°)$ accurately centered on an Enraf-Nonius CAD4 diffractometer are given in Table 1 with a summary of data collection parameters. An empirical absorption correction based on psi scan data was performed. Calculations were carried out using the SHELX system of computer programs [23].

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, except the Cl and

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

Bond distances							
W	–Ca		2.03(3)	Oa	–Ca		1.08(3)
W	–Cb		2.11(3)	Ob	–Cb		1.07(3)
W	–Cc		1.98(6)	Oc	–Cc		1.19(6)
W	–Cd		2.04(5)	Od	–Cd		1.08(3)
W	–Cl(1)		2.491(4)	W	–Cl(2)		2.488(8)
W	–Cl(3)		2.492(8)				
Bond angles							
Cb	–W	–Ca	72 (1)	Cc	–W	–Ca	73 (1)
Cc	–W	–Cb	112 (1)	Cd	–W	–Ca	74 (1)
Cd	–W	–Cb	108 (1)	Cd	–W	–Cc	115 (2)
Oa	–Ca	–W	179 (2)	Ob	–Cb	–W	178 (3)
Oc	–Cc	–W	176 (4)	Od	–Cd	–W	177 (3)
Ca	–W	–Cl(1)	128.5(7)	Cb	–W	–Cl(1)	–159.6(8)
Cc	–W	–Cl(1)	80 (1)	Cd	–W	–Cl(1)	79.2(9)
Cl(1)	–W	–Cl(2)	86.7(3)	Ca	–W	–Cl(2)	128.5(8)
Cb	–W	–Cl(2)	76.6(9)	Cc	–W	–Cl(2)	159 (1)
Cd	–W	–Cl(2)	78 (1)	Cl(1)	–W	–Cl(3)	87.8(3)
Cl(2)	–W	–Cl(3)	87.9(3)	Ca	–W	–Cl(3)	124.1(8)
Cb	–W	–Cl(3)	80.0(9)	Cc	–W	–Cl(3)	75 (1)
Cd	–W	–Cl(3)	161.5(9)				

Table 8
Final fractional coordinates for [H₂O · bis-aza-18-crown-6 · (H⁺)₂][W(CO)₄Cl₃⁻]₂ (4)

Atom	x	y	z
W(1)	0.47662(9)	0.8904(1)	0.16268(7)
Cl(11)	0.3847(4)	−0.2653(5)	−0.0132(3)
Cl(21)	0.6165(5)	−0.2166(5)	0.1690(4)
Cl(31)	0.3044(5)	−0.2874(5)	0.2131(4)
Ca(1)	0.534(3)	0.084(3)	0.210(2)
Oa(1)	0.434(2)	−0.194(2)	0.762(2)
Cb(1)	0.539(2)	−0.037(2)	0.310(2)
Ob(1)	0.560(2)	−0.006(3)	0.389(1)
Cc(1)	0.313(3)	−0.096(2)	0.133(2)
Oc(2)	0.781(2)	0.095(2)	0.880(1)
Cd(1)	0.618(3)	−0.031(2)	0.090(2)
Od(1)	0.299(2)	−0.017(2)	0.949(2)
W(2)	0.03140(9)	0.0528(1)	0.30857(7)
Cl(12)	1.1252(5)	0.2138(6)	0.4783(4)
Cl(22)	1.2365(6)	0.2063(6)	0.2632(5)
Cl(32)	0.9232(5)	0.1853(5)	0.2860(4)
Ca(2)	0.942(2)	−0.134(2)	0.262(2)
Oa(2)	0.883(2)	−0.259(2)	0.233(1)
Cb(2)	0.975(3)	−0.013(3)	0.164(2)
Ob(2)	−0.048(2)	−0.044(2)	0.086(1)
Cc(2)	0.872(3)	−0.009(3)	0.378(2)
Oc(2)	0.790(2)	−0.039(2)	0.415(1)
Cd(2)	1.170(3)	0.007(3)	0.349(2)
Od(2)	1.242(2)	−0.017(2)	0.369(2)
O	0.195(1)	0.452(1)	0.289(1)
O(1)	0.428(2)	0.490(2)	0.179(1)
C(2)	0.375(2)	0.384(3)	0.080(2)
C(3)	0.271(2)	0.393(3)	0.029(2)
O(4)	0.169(1)	0.359(2)	0.076(1)
C(5)	0.067(3)	0.377(3)	0.039(2)
C(6)	−0.040(3)	0.343(3)	0.095(2)
N(7)	0.013(1)	0.445(2)	0.187(1)
C(8)	−0.087(3)	0.462(3)	0.235(2)
C(9)	−0.023(3)	0.584(3)	0.319(2)
O(10)	0.045(2)	0.558(2)	0.382(1)
C(11)	0.124(3)	0.675(4)	0.465(2)
C(12)	0.203(3)	0.641(4)	0.517(2)
O(13)	0.293(2)	0.621(2)	0.462(1)
C(14)	0.389(3)	0.612(4)	0.512(2)
C(15)	0.508(3)	0.646(3)	0.464(2)
N(16)	0.481(1)	0.557(2)	0.376(1)
C(17)	0.585(3)	0.588(2)	0.327(2)
C(18)	0.538(2)	0.488(3)	0.229(2)

axial CO ligand in **1**, which were 50:50 disordered. Hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinements converged with $R = 0.078$ for 1277 observed reflections for **1**, $R = 0.014$ for 715 observed reflections for **2**, $R = 0.068$ for 1966 observed reflections for **3**, $R = 0.054$ for 3065 observed reflections for **4**. Fractional coordinates and bond distances and angles for complexes **1–4** are shown in Tables 2–9.

3. Results and discussion

The title compounds were prepared according to Schemes 1 and 2. In all cases the reaction mixture

$$Cr(CO)_6 + 18\text{-crown-6} + KCl + HCl_{(g)}$$

$$\xrightarrow[\text{UV}]{\text{toluene}} [K^+ \cdot 18\text{-crown-6}]$$

$$[Cr(CO)_5Cl]$$

(1)

Scheme 1.

quickly separated into two phases yielding light yellow liquid clathrates. The upper layer in these reactions was neat toluene, while the metal complexes formed were completely dissolved within the liquid clathrate layer. In the cases where the reaction was carried out under an inert atmosphere (for **1** and **2**), no oxidation of the metal center occurred. Here, reaction was complete after monosubstitution at the metal center had taken place. Where the reaction was performed in contact with air, followed by sealing the reaction vessel from aerial contact (for **3** and **4**), partial oxidation of the metal center, from [0] to [2 +], occurred.

The formation of [Cr(CO)₅Cl]⁻ in **1** is similar to that of other [M(CO)₅X]⁻ anions in the literature [2], where typical syntheses are from M(CO)₆ and species such as NR₄⁺Cl⁻. The formation of the [W(CO)₅Cl]⁻ in **2** via the route in Scheme 2 is novel, where halogenation from HCl₍g₎ occurs. It should be noted that in both cases oxidation of the metal center does not occur.

The formation of the [W(CO)₄Cl₃]⁻ anion in **3** and **4** is a new route to these species. Typical preparations involve the halogen oxidation of W(CO)₆ to yield [W(CO)₄Cl₂], followed by treatment with [NH₄Cl] yielding [NH₄][W(CO)₄Cl₃] [24]. This anion has also been found in a mixture of products obtained from the reaction of W(CO)₅Cl⁻, WCl₆ and Cl⁻ [25]. In the present study, both reactions were carried out with contact to air. The partial oxidation of the metal center from [0] to [2 +] in both cases is, therefore, presumably due to aerial oxygen.

To identify the species present in the liquid clathrate

$$W(CO)_6 + H_2O + HCl \xrightarrow{(i)} [H_3O^+ \cdot 18\text{-crown-6}][W(CO)_5Cl]$$

(2)

$$\xrightarrow{(ii)} [H_3O^+ \cdot 18\text{-crown-6}][W(CO)_4Cl_3]$$

(3)

$$\xrightarrow{(iii)} [H_2O \cdot \text{bis-}aza\text{-18-crown-6} \cdot (H^+)_2][W(CO)_4Cl_3]_2$$

(4)

Reagents and conditions: (i) 18-crown-6, UV, inert atmosphere; (ii) 18-crown-6, toluene, UV; (iii) bis-aza-18-crown-6, toluene, UV.

Scheme 2.

layers, all the compounds investigated were structurally authenticated using X-ray crystallographic techniques.

The first structure of the chloropentacarbonylchromium(0) anion (1) is shown in Fig. 1. The Cr and the four equatorial CO ligands reside on a mirror plane, and there is 50:50 disorder along the Cl–Cr–CO_{ax} axis. The structure exists as a distorted octahedron. Cr–C(carbonyl)$_{eq}$ bond lengths (av. = 1.90(3) Å), and the Cr–C(carbonyl)$_{ax}$ bond length (1.83(2) Å) are similar to the related $[Cr(CO)_5I]^-$ anion in $[N_4P_4Me_8^+][Cr(CO)_5I^-]$ [6]. The Cr–Cl distance, 2.534(7) Å, is midway between the the two different Cr–Cl lengths in $[NMeH_3]_2[CrCl_4]$: 2.41 and 2.82 Å [26].

The structure of the anion in 2 is shown in Fig. 2. There was disorder among the CO_{ax} and Cl_{ax} ligands, so these atoms were refined with 5/6 and 1/6 occupancies, respectively. The tungsten atom resides in a regular octahedron with CO_{eq}–W–CO_{eq} angles very close to 90° and a CO_{ax}–W–Cl_{ax} angle of 175.5(6)°.

W–C(carbonyl) bond lengths, 2.023(6) Å, are typical and the W–Cl distance, 2.68(1) Å, is long (cf. 2.560(3) Å in $[N(PPh_3)_2][W(CO)_5Cl]$ [27] and 2.566(2) Å in $[NMe_4][W(CO)_5Cl]$ [28]).

The structure of the $[W(CO)_4Cl_3]^-$ anion in 3 (Fig. 3) and 4 is that of a capped trigonal antiprism (or, if the two ligand types are considered, a 4:3 piano stool), similar to the geometry found in the two structures of $[W(CO)_4Br_3]^-$ [8,9]. The W–C(carbonyl) bond lengths are similar for the three anions in 3 and 4 (av. = 2.04(5) Å for 3 and 2.03(7) Å for 4), and are close to those in $[W(CO)_4Br_3]^-$ (1.99(4) Å [8] and 2.01(3) Å [9]) and $W(CO)_6$ (2.05–2.07 Å) [29]. W–Cl bond lengths for 3 (av. = 2.490(2) Å) are slightly shorter than for 4 (av. = 2.54(2) Å). These are longer than typical W–Cl bond distances, for example, 2.386(1) Å in $[C_{10}H_{13}O_2]$$[WO_2Cl_2(acac)]$ [30]. They are, however, midway between the two different W–Cl lengths in $[WSCl_4]$: 2.30(4) and 3.05(1) Å [31].

The structure of the cation in 1 is shown in Fig. 4.

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

| Bond distances							
W(1)	–Ca(1)		1.99(3)	W(2)	–Ca(2)		1.87(2)
W(1)	–Cb(1)		2.09(2)	W(2)	–Cb(2)		2.04(2)
W(1)	–Cc(1)		2.05(3)	W(2)	–Cc(2)		2.10(3)
W(1)	–Cd(1)		2.03(3)	W(2)	–Cd(2)		2.08(3)
W(1)	–Cl(11)		2.570(4)	W(2)	–Cl(12)		2.516(5)
W(1)	–Cl(21)		2.534(5)	W(2)	–Cl(22)		2.538(5)
W(1)	–Cl(31)		2.518(5)	W(2)	–Cl(32)		2.548(5)
Ca(1)	–Oa(1)		1.12(3)	Ca(2)	–Oa(2)		1.26(3)
Cb(1)	–Ob(1)		1.10(2)	Cb(2)	–Ob(2)		1.10(2)
Cc(1)	–Oc(1)		1.12(3)	Cc(2)	–Oc(2)		1.09(3)
Cd(1)	–Od(1)		1.16(3)	Cd(2)	–Od(2)		1.08(3)
Bond angles							
Cb(1)	–W(1)	–Ca(1)	73.0(9)	Cc(1)	–W(1)	–Ca(1)	74.1(9)
Cc(1)	–W(1)	–Cb(1)	109.4(8)	Cd(1)	–W(1)	–Ca(1)	75(1)
Cd(1)	–W(1)	–Cb(1)	114.3(9)	Cd(1)	–W(1)	–Cc(1)	114.3(9)
Oa(1)	–Ca(1)	–W(1)	178(2)	Ob(1)	–Cb(1)	–W(1)	173(2)
Oc(1)	–Cc(1)	–W(1)	175(2)	Od(1)	–Cd(1)	–W(1)	178(2)
Ca(1)	–W(1)	–Cl(11)	124.4(7)	Cb(1)	–W(1)	–Cl(11)	162.6(6)
Cc(1)	–W(1)	–Cl(11)	78.8(6)	Cd(1)	–W(1)	–Cl(11)	74.6(7)
Cl(11)	–W(1)	–Cl(21)	87.4(1)	Ca(1)	–W(1)	–Cl(21)	127.1(7)
Cb(1)	–W(1)	–Cl(21)	80.8(6)	Cc(1)	–W(1)	–Cl(21)	158.7(6)
Cd(1)	–W(1)	–Cl(21)	75.7(7)	Cl(11)	–W(1)	–Cl(31)	89.7(2)
Cl(21)	–W(1)	–Cl(31)	87.4(2)	Ca(1)	–W(1)	–Cl(31)	128.0(8)
Cb(1)	–W(1)	–Cl(31)	77.8(6)	Cc(1)	–W(1)	–Cl(31)	77.3(5)
Cd(1)	–W(1)	–Cl(31)	157.2(7)	Cb(2)	–W(2)	–Ca(2)	71.5(9)
Cc(2)	–W(2)	–Ca(2)	73(1)	Cc(2)	–W(2)	–Cb(2)	112.4(9)
Cd(2)	–W(2)	–Ca(2)	77(1)	Cd(2)	–W(2)	–Cb(2)	113.0(8)
Cd(2)	–W(2)	–Cc(2)	111.8(9)	Oa(2)	–Ca(2)	–W(2)	178(2)
Ob(2)	–Cb(2)	–W(2)	176(3)	Oc(2)	–Cc(2)	–W(2)	179(2)
Od(2)	–Cd(2)	–W(2)	180.0(5)	Ca(2)	–W(2)	–Cl(12)	129.4(6)
Cb(2)	–W(2)	–Cl(12)	158.9(7)	Cc(2)	–W(2)	–Cl(12)	76.7(6)
Cd(2)	–W(2)	–Cl(12)	78.6(6)	Cl(12)	–W(2)	–Cl(22)	87.4(2)
Ca(2)	–W(2)	–Cl(22)	127.4(8)	Cb(2)	–W(2)	–Cl(22)	78.8(8)
Cc(2)	–W(2)	–Cl(22)	159.9(7)	Cd(2)	–W(2)	–Cl(22)	76.3(8)
Cl(12)	–W(2)	–Cl(32)	88.1(2)	Cl(22)	–W(2)	–Cl(32)	90.3(2)
Ca(2)	–W(2)	–Cl(32)	121.8(6)	Cb(2)	–W(2)	–Cl(32)	76.2(6)
Cc(2)	–W(2)	–Cl(32)	77.1(7)	Cd(2)	–W(2)	–Cl(32)	161.4(7)
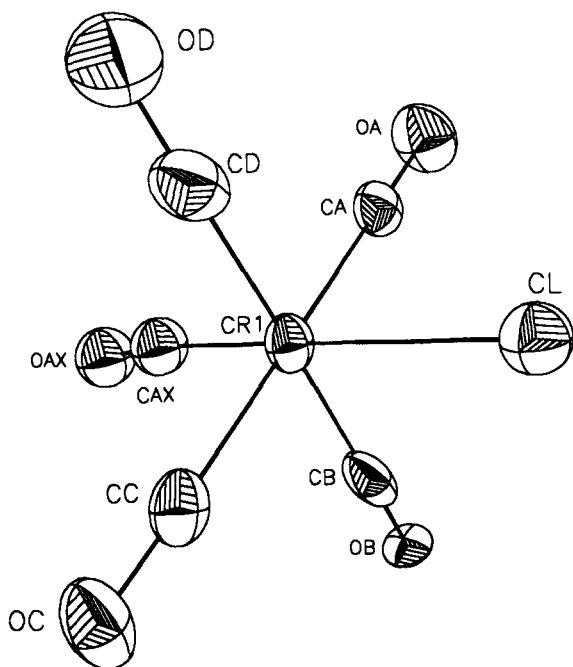
Fig. 1. Structure of the [Cr(CO)₅Cl]⁻ anion in 1. The Cr atom and four equatorial CO ligands reside on a mirror plane. There is 50:50 disorder between the axial Cl and CO ligands.

The potassium ion resides on a center of inversion and has an average K–O(crown) distance of 2.78(5) Å. It also sits 0.006 Å out of the plane defined by the six O-(crown) centers. The geometry is similar to that established in [K⁺· 18-crown-6][NCS⁻] [32].
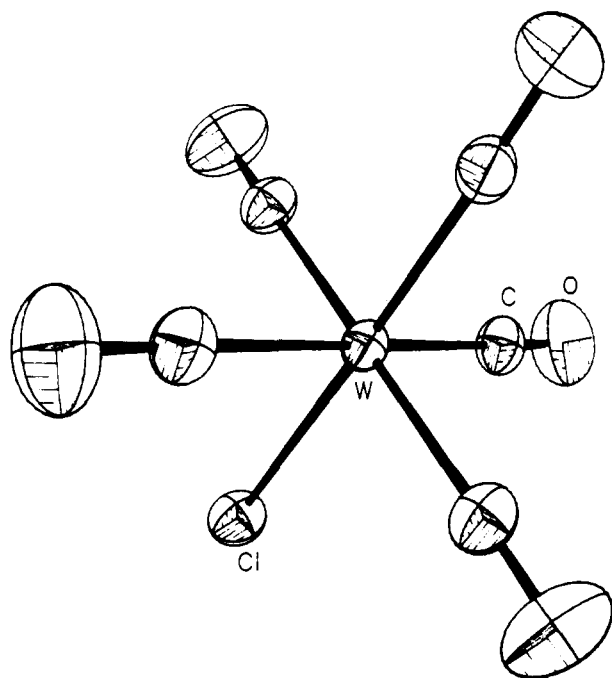

Fig. 2. Structure of the [W(CO)₅Cl]⁻ anion in 2, which resides on a 3̄ symmetry site.
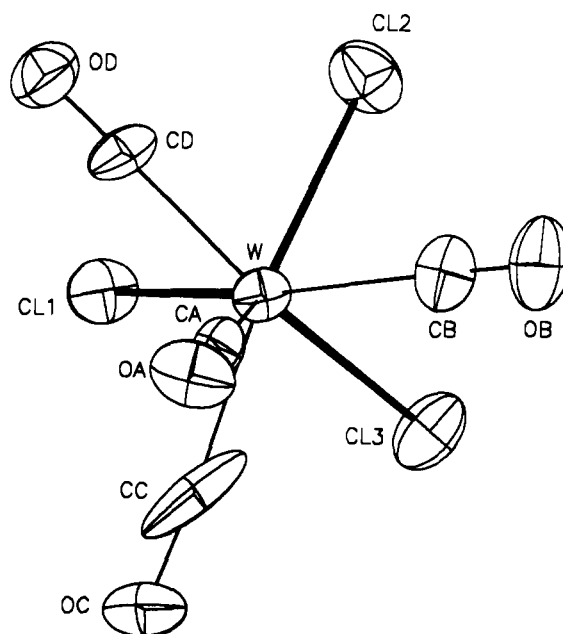
Fig. 3. Structure of the [W(CO)₄Cl₃]⁻ anion in complex 3. The same structure is also found for the two independent anions in 4.

The structure of the [H₃O⁺· 18-crown-6] cation in 2 is shown in Fig. 5. In both 2 and 3 the hydrogen atoms of the H₃O⁺ ion could not be located. In 2, the average O(oxonium)··· O(crown) distance is 2.82(1) Å, and for 3, there are three contacts of 2.55(5) to 2.63(4) Å and three of 2.81(6) to 2.84(5) Å. In both cases the distances are well within the range defined for hydrogen bonding between oxygen centers [33]. For 2, the O(oxonium)··· O(crown) distances are similar,
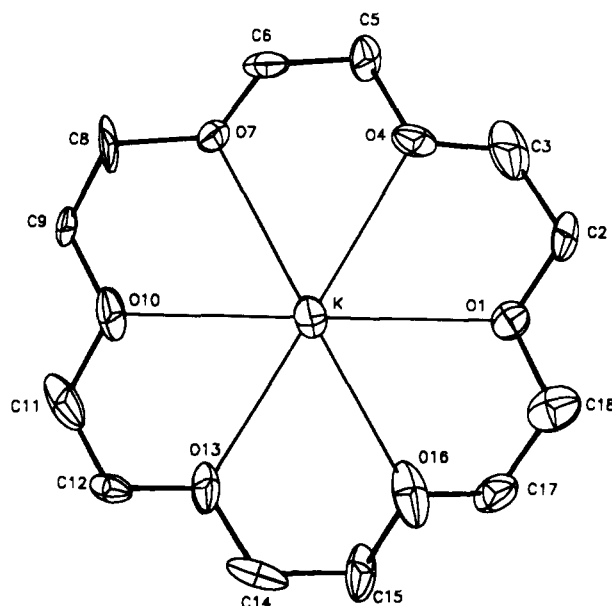
Fig. 4. Structure of the [K⁺·18-crown-6] cation in 1 which resides on an inversion center. The average K ··· O distance is 2.78(5) Å.

implying that the hydrogen atoms of the H_3O^+ ion are probably disordered over two positions. In **3**, the alternating long (av. = 2.83(1) Å) and short (av. = 2.60(4) Å) hydrogen bonds imply that the H_3O^+ is secured by the more tightly bound atoms: O1, O7, and O13. For **2**, the O(oxonium) center resides at 0.40 Å above the plane of the crown oxygen atoms, while in **3**, the O(oxonium) atom resides in the plane (0.007 Å). Structures of the $[H_3O^+ \cdot$ 18-crown-6] ion in several other compounds have shown that the H_3O^+ ion lies within the extremes of 0.092 Å in $[H_3O^+ \cdot$ 18-crown-6][Br_3^-]) [22] to 0.61 Å in $[H_3O^+ \cdot$ 18-crown-6(COOH)$_4$][Cl$^-$] [14] from the crown oxygen atom plane. In these complexes the question of planar versus pyramidal H_3O^+ has been argued.

The first structure of the $[H_2O \cdot$ bis-*aza*-18-crown-6 $\cdot (H^+)_2]$ cation is shown in complex **4** (see Fig. 6). The hydrogen atoms in this ion could not be located on the difference map. The bis-*aza* crown has been diprotonated, and O(water) to hetero-crown distances suggest that the structure exists as a diprotonated diamino crown, with a water molecule hydrogen bonded to N7 and O13 within the crown. O(water) $\cdots$ N7 and $\cdots$ O13 distances (2.55(3) and 2.58(2) Å, respectively) are much shorter than other O(oxonium) to hetero-crown distances: 2.79(3) to 3.15(2) Å. Since the protons on the cation were not located it is possible that there is an oxonium ion and protonation of one *aza*-nitrogen

Fig. 6. Structure of the diprotonated [$H_2O \cdot$ bis*aza*-18-crown-6· $(H^+)_2$] cation in **4**. The hydrogen atoms on the water molecule were not located. O(water)$\cdots$N7 and O(water)$\cdots$O13 distances are 2.55(3) and 2.58(2) Å, respectively. If a third hydrogen bond exists within the cation, O1 is the geometrical site. The O(water)$\cdots$O1 distance is 3.15(2) Å. The other non-bonded contacts are shorter: O$\cdots$O10 = 2.79(3) Å; O$\cdots$N16 = 3.08(2) Å; O$\cdots$O4 = 2.99(1) Å.

has occurred. There is however, no indication of further hydrogen bonding around the oxonium ion, as is typically the case [13,14,18–22]. Evidence of a water molecule hydrogen bonded to the protonated amine in a tungsten complex with the $[H_2O \cdot aza$-18-crown-6 $\cdot$ $H^+]$ ion has been presented [34]. The O(water) atom resides 0.63 Å out of the plane defined by the hetero-crown atoms.

4. Conclusions

We have shown that by using novel synthetic approaches (see Schemes 1 and 2), we can isolate liquid clathrate species which deposit halometalcarbonyl complexes of oxonium ion/crown ether cations. The anions we have isolated are of the type [$M^0(CO)_5Cl^-$] or [$W^{II}(CO)_4Cl_3^-$] depending on reaction conditions. The cations contained either K^+, H_3O^+ or H_2O bound within the macrocyclic crown ether. X-ray crystal structures revealed slightly distorted octahedral structures for the six-coordinate metal [0] complexes, and capped trigonal antiprismatic (or 4:3 piano stool) geometry for the seven-coordinate metal [II] complexes.

Fig. 5. Structure of the [$H_3O^+ \cdot$ 18-crown-6] cation in complexes **2** and **3**. The three hydrogen atoms on the oxonium ion were not located in either complex and are disordered to produce the two equivalent hydrogen bonding patterns. The O(oxonium) resides 0.40 Å above the plane of the crown oxygens in **2** and to within 0.007 Å of the O(crown) plane in **3**.
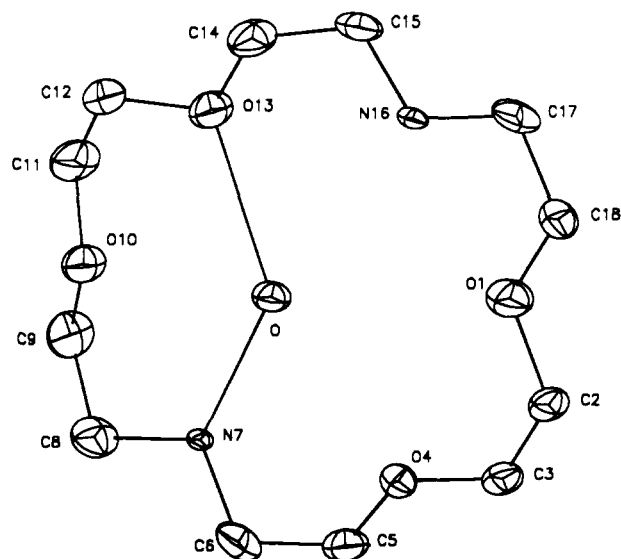
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