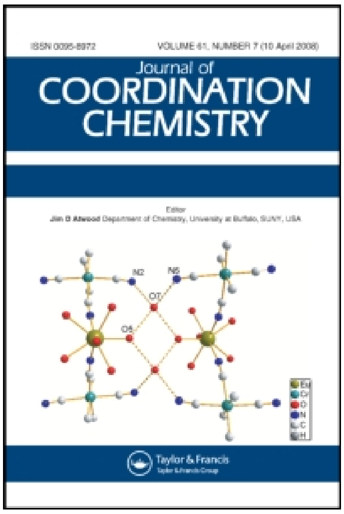

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NEW, SIMPLE COORDINATION COMPOUNDS OF Cr, Mo, AND W FROM LIQUID CLATHRATE MEDIA

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NEW, SIMPLE COORDINATION COMPOUNDS OF Cr, Mo, AND W FROM LIQUID CLATHRATE MEDIA

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The reactions of $M(CO)_6$ (M = Cr, Mo, W) with 18-crown-6 in the presence of H_2O and HCl(g) in toluene have been explored. In each case, a liquid clathrate formed almost immediately upon reaction, from which new and unusual coordination complexes of Cr, Mo and W were isolated. The structures of $[H_3O^+\cdot 18\text{-crown-6}]\,[Cr^{III}Cl_4(H_2O)_2^-]$, $[H_3O^+\cdot 18\text{-crown-6}]_2\,[H_5O_2\cdot Mo^{III}{}_2Cl_9{}^{2-}]$ and $[H_3O^+\cdot 18\text{-crown-6}][W^{V}OCl_4(H_2O)^-]$ were established by X-ray crystallography.

Keywords: liquid clathrates; coordination compounds; group 6 metals

The existence of the $[H_3O^+\cdot 18\text{-crown-6}][Cl—H—Cl]$ moiety in aromatic media is now well established, as is the reaction of this compound with several alkali/alkaline earth salts.[1–2] The interaction of transition and main group metal salts, aqueous hydrochloric acid, and 18-crown-6 has also been studied.[3–4] In this communication we report related systems where the $[H_3O^+\cdot 18\text{-crown-6}]$ cation in a liquid clathrate system[5] affords a variety of new coordination compounds of Cr, Mo, and W. The importance of this communication lies in the discovery of simple, new compounds of these metals after extensive investigation of the chemistry of these elements over the past many years.

Our interest in the interaction of salts with aromatic media prompted investigation of the chemistry leading to the generation of $[H_3O^+\cdot 18\text{-crown-6}]$ in the presence of $M(CO)_6$ (M = Cr, Mo, W). The reaction of 18-crown-6, H_2O, $M(CO)_6$, and excess HCl(g) in toluene, in the presence of air, affords yellow-colored liquid clathrates in all cases. Upon prolonged standing (*ca.* two weeks) these liquid clathrates deposit highly colored (for M = Cr, purple; M = Mo, red; M = W, blue) crystalline products. To promote the formation of these products in subsequent reactions the mixture

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was irradiated with a UV lamp (450 watt, immersion type). This accelerated deposition of compounds 1–3 in 2–3 days.

In the case of chromium, oxidation of the metal from Cr(0) to Cr(III) occurs with concurrent loss of the CO ligands and replacement with Cl and H_2O, forming $[H_3O^+ \cdot$ 18-crown-6$][CrCl_4(H_2O)_2^-]$. Resistance to formation of an oxo (Cr = 0) species is presumably due to the inherent stability of the Cr(III) species.[6] For an oxo species to form, an oxidation state higher than 3+ would probably result. The $[CrCl_4(H_2O)_2]^-$ anion is a new species. Anions such as $[CrCl_5(H_2O)]^{2-}$ exist in aqueous media, while $[CrCl_4]^-$ can be obtained from anhydrous acetonitrile,[7] and $[CrCl_4(H_2O_2]^{2-}$ can be prepared from $CrCl_2$ and MCl (M = alkali metal) in aqueous media.[8] The formation of **1** is presumably stabilized by the liquid clathrate environment in which the Cr complex exists.

The anion of compound **1** (Figure 1) consists of a distorted octahedral array around the Cr center, with the H_2O molecules lying *cis* to one another.[9] The Cr—Cl and Cr—$O(H_2O)$ bond lengths are typical (av = 2.32(2) Å and av = 2.046(6) Å, respectively). The $[H_3O^+ \cdot$18-crown-6] cation has an unusual geometry, being in a slightly puckered arrangement with the H_3O^+ ion sitting within the puckered cavity. The origin of this structural effect is not clear at this time, but may be due to crystal packing forces.

For molybdenum, the liquid clathrate formed during the reaction deposited red crystals of compound **2** over several days.[10] Compound **2** was found to be the

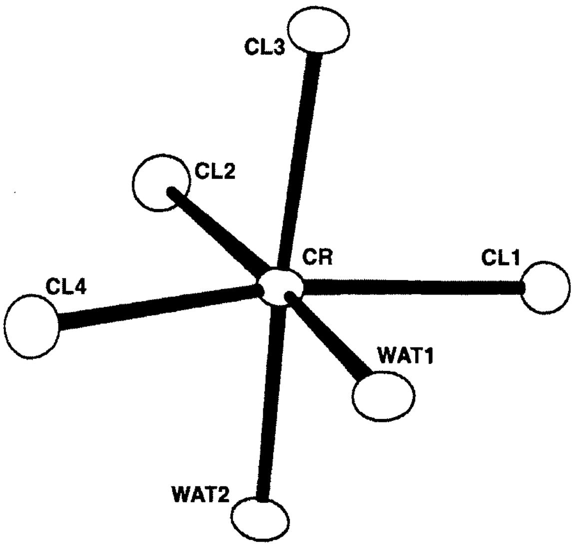

FIGURE1 Structure of the [CrC14(H4O)] anion (WAT = water oxygen atom).

triply chloro-bridged molybdenum dimer, $[H_3O^+\cdot 18\text{-crown-}6]_2[H_5O_2^+][Mo_2Cl_9^{3-}]$, which exhibits the $H_5O_2^+$ unit hydrogen bonded between layers of the $Mo_2Cl_9^{3-}$ anions (Figure 2). The existence of the $Mo_2Cl_9^{3-}$ species has been previously reported,[12] but the structure herein contains the unusually hydrogen bonded $H_5O_2^+$ as part of the anionic unit creating a $[H_5O_2^+\cdot Mo_2Cl_9^{3-}]$ anion. The structure of the dianion in compound **2** contains two confacial distorted octahedral molybdenum centers and is similar to the $[Mo_2Cl_9]^{3-}$ anion with Mo-Mo distances of 2.727(6) and 2.655(6) Å, respectively.[12] The $H_5O_2^+$ group is hydrogen bonded to the Cl ligands at distances of 2.91(1) to 3.26(1) Å. The O···O separation of 2.425(6) Å is typical.[13]

Exposure of compound **2** to air affords the green Mo^V species $[H_3O^+\cdot 18\text{-crown-}6][MoOCl_4(H_2O)^-]$. This compound has been previously prepared and its structure characterized.[14] The species formed from aromatic solution herein crystallizes in a different manner. These differences will be discussed in a full paper.

For tungsten, a single compound deposits from the liquid clathrate overnight: the bright blue $[18\text{-crown-}6\cdot H_3O^+][WOCl_4(H_2O)]$, **3**.[15] This is the first crystallographic determination of this type of species for tungsten. It is seen from the X-ray crystallographic characterization that the anion (Figure 3) contains a distorted octahedral tungsten center with the oxo and aquo ligands *trans* to one another. The H_2O molecule is rather weakly held to the tungsten center at a distance of 2.280(9) Å. This position is the site of binding of the tungsten center to another oxo center at a distance of 2.2 Å in the polymeric complex $[WOCl_4]$.

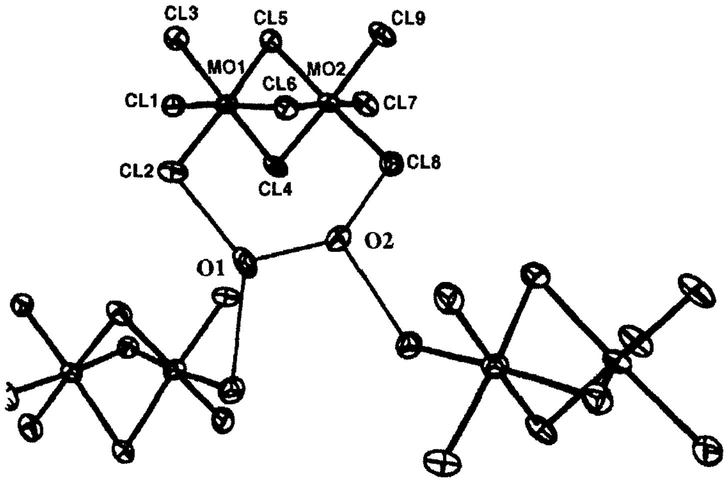

FIGURE 2 Structure of the $[H_5O_2^+\cdot Mo_2Cl_9^{9-}]$ anion (O1 and O2 are the oxygen atoms of the $H_5O_2^+$ ion).

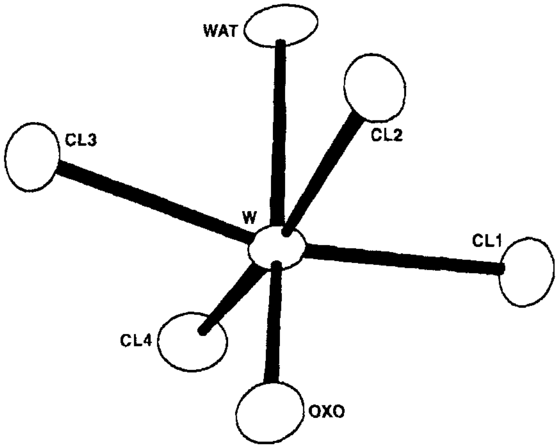

FIGURE 3 Structure of the [$WOCl_4(H_2O)^-$] anion (WAT = water oxygen atom).

The W-O(oxo), 1.71(1) Å, and W-Cl, av = 2.36(2) Å, distances are similar to those in literature complexes, *e.g.* [$WOCl_4$] (1.80 and 2.29 Å, respectively).[16]

If the reaction in the tungsten system is carried out in the absence of air and UV irradiation, the W(0) species [18-crown-6·H_3O^+][$W(CO)_5Cl$] is obtained.[17] This establishes that oxygen from air is responsible for oxidation of the metal center in the compounds described in the preceding paragraphs. The anion obtained here, [$W(CO)_5Cl$]$^-$, is rather common,[18] and will be reported in later publications on our further investigations of these systems.

The chemistry demonstrated in this communication highlights the wealth of chemistry available in liquid clathrate systems. The fact that simple new coordination species of Cr, Mo, and W can be stabilized by these systems opens a large sphere of chemistry for other transition metals. We will show in future publications that the syntheses used herein provide a general pathway to exciting new compounds.

Acknowledgments

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[9] ^1H NMR chemical shifts for all complexes were similar, and shifts were in ranges as follows; δ 1.95 and 6.85 ppm (toluene), δ 3.6 ppm (18-crown-6), δ 9.3 ppm (oxonium ions).

Preparation of $[H_3O^+\cdot 18\text{-crown-6}][CrCl_4(H_2O)_2^-]$, (1). To a sample of 18-crown-6(1.00g, 3.62 mmol) in toluene, was added H_2O (0.065g, 3.62 mmol) and $Cr(CO)_6$ (0.80g, 3.62 mmol) and the solution was stirred rapidly for 15 min. HCl(g) was then vigorously bubbled through the mixture for approx. 1h while irradiating with UV radiation. After this time, an orange/yellow liquid clathrate separated from the solvent with a toluene:complex ratio of 1.67:1 as determined by ^1H NMR. Purple crystals of the title complex deposited from the liquid clathrate layer after approx. 72h.

Crystal Data; Compound 1. $[H_3O^+\cdot 18\text{-crown-6}][CrCl_4(H_2O)_2^-]$. $C_{12}H_{31}Cl_4O_4Cr$, monoclinic $P2_1/n$, $a = 8.508(1)$, $b = 10.223(2)$, $c = 25.168(4)$ Å, $\beta = 94.55(1)°$, $V = 2182(2)$ Å^3, and $D_c = 1.568$ g cm^{-3} for $Z = 4$. Of 4336 data collected (CAD4, $2\theta_{max} = 50°$, MoKα), 3094 were observed at $3\sigma F_o$. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinement converged with R = 0.062 and $R_w = 0.068$.

[10] **Preparation of $[H_3O^+\cdot 18\text{-crown-6}]_2[H_5O_2^+\cdot Mo_2Cl_9^{3-}]$**, (2). This complex was prepared as for compound **1** except $Mo(CO)_6$ was used as the metal source. The toluene:complex ratio found was 1.90:1, as determined by ^1H NMR. Deep red crystals of **2** deposited from the liquid clathrate layer over a 24 h period.

Crystal Data; Compound **2**. $[H_3O^+\cdot 18\text{-crown-6}]_2[H_5O_2^{+\cdot}\ Mo_2Cl_9^{2\cdot}]$ $C_{24}H_{59}Cl_9O_{16}Mo_2$, monoclinic, $P2^1/n$, $a = 9.333(1)$, $b = 29.642(5)$, $c = 16.407(2)$, $\beta = 90.68(1)°$, $V = 4538$ Å^3, and $D_c = 1.638$ g cm^{-3} for $Z = 4$. Of 8647 data collected (CAD4, $2\theta max = 50°$, MoKα), 3143 were observed at $3\sigma F_o$. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinement converged with R = 0.085 and $R_w = 0.093$.

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[15] **Preparation of $[H_3O^+\cdot 18\text{-crown-6}][WOCl_4(H_2O)^-]$, (3).** This complex was prepared as for compound **1** except $W(CO)_6$ was used as the metal source. The toluene:complex ratio found was 2.30:1, as determined by ^1H NMR. Bright blue crystals of **3** deposited from the liquid clathrate layer.

Crystal Data; Compound 3. $[H_3O^+\cdot 18\text{-crown-6}][WOCl_4(H_2O)^-]$. $C_{12}H_{29}Cl_4O_9W$, monoclinic, $P2_1/c$, $a = 9.600(1)$, $b = 19.356(2)$, $c = 12.164$ (4), $\beta = 104.84(1)°$, $V = 2184(3)$ Å^3, and $D_c = 1.962$ g cm^{-3} for $Z = 4$. Of 3753 data collected (CAD4, $2\theta max = 50°$, MoKα), 2617 were observed at $3\sigma F_o$. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinement converged with R = 0.039 and $R_w = 0.058$.

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