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Structure of the Triaquatricarbonylrhenium(I) Cation and Its Conjugate Base

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The crystal structure of the $Re(CO)_3(H_2O)_3^+$ cation has been determined from crystals obtained by evaporation of an aqueous solution of $[Re(CO)_3(H_2O)_3]Br$. The bromide ion is incorporated in the $Re_2(CO)_9(\mu_3\text{-}Br)_3^-$ anion. A second structure was obtained by removal of bromide as AgBr and precipitation of the $Re(CO)_3(H_2O)_3^+$ cation with PF_6^-. In the latter structure the conjugate base, $Re(CO)_3(OH)(H_2O)_2$ is cocrystallized in the structure. Each structure along with the previously known cubane $[Re(CO)_3(\mu_3\text{-}OH)]_4{\cdot}4H_2O$ was obtained multiple times during crystallization studies. The use of other anions to generate crystalline products was unsuccessful.

Introduction

The discoveries of the $Re(CO)_3(H_2O)_3^+$ cation **1**$^+$ and its technetium congener[1,2] sparked intense interest in recent years for their potential as reagents in aqueous organometallic chemistry. One focal point is the search for viable d^6 $M(CO)_3L^+$ ($M = {}^{186/188}Re$, ${}^{99m}Tc$) compounds for use as therapeutic and imaging agents, respectively, in nuclear medicine.[3,4] Kinetic and thermodynamic details of water exchange and ligand substitution for these aquacarbonyl ions have been reported[5,6] and many syntheses utilizing these important synthons have been published.[7–11] Several crystal structures have been solved that formally result from the deprotonation of **1**$^+$ in aqueous solution and subsequent aggregation.[12] Although the preparation and isolation of [**1**]Br have been described[13] and attempts to grow crystals of this cation have been reported,[12] its structure has not appeared. There are, in fact, only a limited number of elucidated structures of aquacarbonyl complexes in the chemical literature, and only four structures with exclusively water and carbon monoxide as ligands.[14–17] We have discovered that crystals containing **1**$^+$ are surprisingly easy to prepare. We now report the first crystal structures of salts of **1**$^+$ and the formal appearance of its conjugate base, $Re(CO)_3(OH)(H_2O)_2$ **2** in a crystal structure.[18]

Results and Discussion

Our initial attempt at growing crystals containing **1**$^+$ consisted of dissolving [**1**]Br in distilled water in air and allowing the water to evaporate. Crystals in two separate morphologies were obtained along with some non-crystalline material. The majority of the product was in the form of small colorless rods, with a smaller fraction of large colorless, crystalline blocks. X-ray crystallographic analysis of the blocks showed the presence of the known cubane structure $[Re(CO)_3(\mu_3\text{-}OH)]_4{\cdot}4H_2O$ (**3**)[13] which had not previously been crystallized from aqueous solution. Crystallographic characterization of the rods showed the presence of the desired cation in the salt [**1**]$[Re_2(CO)_6(\mu_2\text{-}Br)_3]{\cdot}6H_2O$.[19]

Figure 1 shows the structure of [**1**]$[Re_2(CO)_6(\mu_2\text{-}Br)_3]{\cdot}6H_2O$. The cation has the expected octahedral geometry with a facial disposition of both carbon monoxide and water ligands. The identity of the anion was unexpected, but it is supposed that the bromide ion competes as a ligand with water molecules when the solvent evaporates as shown in Equation (1). The dimeric anion $Re_2(CO)_6(\mu_2\text{-}Br)_3^-$ has

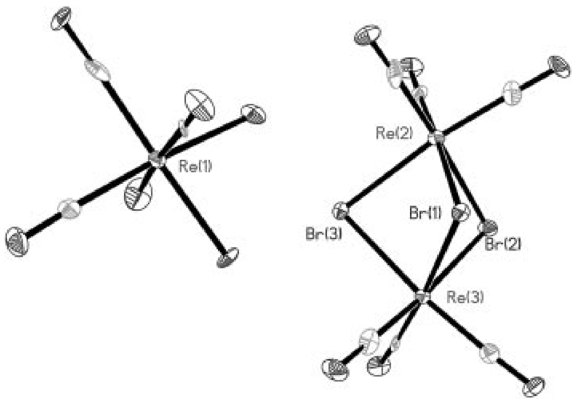

Figure 1. Structure of [**1**]$[Re_2(CO)_6(\mu_2\text{-}Br)_3]{\cdot}6H_2O$ with 50% thermal ellipsoids. Solvent water and hydrogen atoms have been omitted.

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been seen before and has the expected D_{3h} geometry.[20,21] The IR spectrum of [**1**][$Re_2(CO)_6(\mu_2\text{-}Br)_3$]·6$H_2O$ shows two sets of tricarbonyl bands as predicted.

$$3\ \mathbf{1}^+ + 3\ Br^- \rightarrow [\mathbf{1}][Re_2(CO)_6(\mu_2\text{-}Br)_3]\cdot 6H_2O \qquad (1)$$

We were interested in seeing if $\mathbf{1}^+$ could be crystallized with other anions in the hope of increasing the yield of the cation by preventing formation of the $Re_2(CO)_6(\mu_2\text{-}Br)_3^-$ anion and minimizing formation of **3**. A variety of bromide-free crystallization experiments were set up with different non-coordinating anions, PF_6^-, $CF_3SO_2^-$ or NO_3^-, at various pH values adjusted by the appropriate acid. Only the PF_6^- trials produced crystals. Crystals grown with PF_6^- as the counterion at acidic pH (ca. 1.5–4) produced primarily a single crystalline form of product. These needles were analyzed and can be formally represented as **2**·[**1**][PF_6]·H_2O,[22] corresponding to the co-crystallization of **2** with [**1**][PF_6]. In distilled water, pH = 5.6, with the PF_6^- anion, crystals of **3** formed along with **2**·[**1**][PF_6]·H_2O. Figure 2 shows the structure of **2**·[**1**][PF_6]·H_2O.

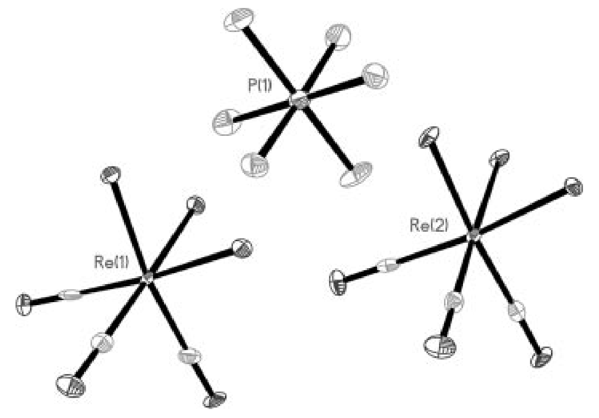

Figure 2. Structure of **2**·[**1**][PF_6]·H_2O with 50% thermal ellipsoids. See text for explanation of the assignments of $\mathbf{1}^+$ and **2**. Solvent water and hydrogen atoms have been omitted.

Because the hydrogen atoms were not observed directly by the difference map, the assignments of $\mathbf{1}^+$ and **2** are problematic. Table 1 lists the average distances for the structures. Each monomeric rhenium species in the two structures shows a slight elongation of the octahedral geometry along the C_3 axis as observed for $Ru(CO)_3(H_2O)_3^{2+}$.[15] The average Re–C distance of $\mathbf{1}^+$ in [**1**][$Re_2(CO)_6(\mu_2\text{-}Br)_3$]·6$H_2O$ is 0.03 Å longer than it is in either rhenium unit in **2**·[**1**][PF_6]·H_2O. This difference may be due in part to a decrease in hydrogen bonding in **2**·[**1**][PF_6]·H_2O vs. [**1**][$Re_2(CO)_6(\mu_2\text{-}Br)_3$]·6$H_2O$. The average Re–O distance in $\mathbf{1}^+$ in the first structure and in Re(1) in **2**·[**1**][PF_6]·H_2O are nearly identical. The corresponding value for Re(2) in **2**·[**1**][PF_6]·H_2O is about 0.02 Å shorter. At issue is whether the differences in these two average Re–O bond lengths are meaningful with regard to protonation state.

Table 1. Comparison of selected average bond lengths and angles[a] for compounds reported.

	$\mathbf{1}^+$ [b]	Re(1)[c]	Re(2)[d]	**4**[e]
Re–C [Å]	1.912(12)	1.887(8)	1.887(14)	1.908(4)
Re–O [Å]	2.201(14)	2.195(10)	2.178(10)	2.132(3)
C–Re–O [°]	96.1(8)	96.2(21)	96.8(14)	–

[a] Errors cover the range of observed values. [b] Average values for the cation from [**1**][$Re_2(CO)_6(\mu_2\text{-}Br)_3$]·6$H_2O$. [c] Average values associated with Re(1) in **2**·[**1**][PF_6]·H_2O. [d] Average values associated with Re(2) in **2**·[**1**][PF_6]·H_2O. [e] From ref.[23].

The sixteen structurally characterized Re^I compounds that have a CO *trans* to a water ligand, including $Re(CO)_5(H_2O)^+$,[17] were analyzed to compare bond lengths. In these compounds the Re–C bond lengths span the range 1.80–1.92 Å, while the Re–O distances vary from 2.17–2.26 Å. There is only one characterized rhenium compound, Re(dmbpy)$(CO)_3$(OH) **4** (dmbpy = 4,4′-dimethyl-2,2′-bipyridine), with a terminal hydroxide *trans* to a carbon monoxide ligand.[23] In this compound, the Re–C(*trans*) bond length measures 1.908(4) Å and the Re–O bond length is 2.132(3) Å.[24] From the structural data for **2**·[**1**][PF_6]·H_2O the evidence is not conclusive as to whether the hydroxide is disordered over the three possible positions [making Re(1) the center of $\mathbf{1}^+$ and Re(2) the center of **2**] or over the six possible positions of the two rhenium species (meaning that the identity of $\mathbf{1}^+$ and **2** is ambiguous). However, the IR spectrum of crystals of **2**·[**1**][PF_6]·H_2O shows a single tricarbonyl pattern suggesting that rapid proton exchange involving water ligands on both tricarbonyl species is likely.

Previous compounds crystallized from aqueous solutions of $\mathbf{1}^+$ include [NEt_4][$Re_2(CO)_6(\mu_2\text{-}OH)_3$] (**5**) and [$NEt_4$][$Re_3(CO)_9(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)$] (**6**).[1] Both of these were separately prepared by addition of a stoichiometric amount of NaOH and allowing the solutions to stand. The structure of the tetranuclear cluster associated with **3** has been reported previously with other solvates but typically it was prepared from wet organic solvents and not from water directly.[12,13] Compound **2** has also been observed in solution previously, but was proposed to be an intermediate which promptly produced dimers, trimers and tetramers.[12] In all of our crystallization trials the only rhenium-containing crystalline products we observed were [**1**][$Re_2(CO)_6(\mu_2\text{-}Br)_3$]·6$H_2O$, **2**·[**1**][$PF_6$]·$H_2O$ and **3**. Each was observed multiple times indicating that despite expectations $\mathbf{1}^+$ is a stable crystallizable species.

Conclusions

This work has shown that it is possible to crystallize the rhenium(I)triaquatricarbonyl cation under specific conditions and with specific anions. Work is in progress to crystallize other Group 7 aqua carbonyl complexes.

Experimental Section

[1][$Re_2(CO)_6(\mu_2\text{-}Br)_3$]·6$H_2O$: [**1**]Br[13] (50 mg) was dissolved in distilled water (3 mL). Slow evaporation gave a solid that consisted of large colorless blocks of **3**, small colorless rods of [**1**][$Re_2(CO)_6(\mu_2$-$Br)_3$]·$6H_2O$ and a non-crystalline solid. The rods were the major component of the solid. IR of separated crystals: $\tilde{\nu}$ = 2021, 2028, 1920, 1888 cm^{-1}.

2·[1][PF$_6$]·H$_2$O: 100 mg (0.22 mmol) of [**1**]Br was dissolved in 3 mL of distilled water. Addition of 55 mg (0.22 mmol) of $AgPF_6$, produced copious precipitation which was removed by centrifugation. The solution was allowed to evaporate. Large colorless blocks of **3**, rods consisting of **2**·[**1**][PF_6]·H_2O and non-crystalline material were found. IR of separated crystals: $\tilde{\nu}$ = 2036, 1905 cm^{-1}.

Other attempts to grow crystals: Aqueous solutions of [**1**][PF_6] were created with pH values between 1.5 and 4. The solutions were allowed to slowly evaporate. In each case crystals of **2**·[**1**][PF_6]·H_2O were obtained along with non-crystalline material. **3** was also observed in one trial due to incomplete precipitation of bromide.

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[19] Crystallographic data was collected at 100 K (Bruker KRYOFLEX) with a Bruker SMART APEX CCD-based X-ray diffractometer (Mo-K_α radiation, λ = 0.71073 Å). The structures were refined using the Bruker SHELXTL Software Package (Version 6.10) and were solved until the final anisotropic full-matrix, least-squares refinement of F^2 converged. Crystal data for [**1**][$Re_2(CO)_6(\mu_2$-$Br)_3$]·$6H_2O$: $C_9Br_3O_{17}Re_3H_{16}$, M_r = 1193.66, crystal size 0.10 mm × 0.10 mm × 0.05 mm, monoclinic, $P2_1/c$, a = 9.264(2), b = 10.075(2), c = 27.121(6) Å, β = 94.870(4)°, V = 2522.1(10) Å^3, Z = 4, ρ = 3.103 mg m^{-3}. A total of 18827 reflections was collected (4954 independent reflections). $F(000)$ = 2080, R_1 = 0.0472, wR_2 = 0.1024 [for 4954 I_o, $I_o > 2\sigma(I_o)$].

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