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Ammonium Salts of the Aquapentachloro- and Aquapentabromomolybdenum(III) Ions. Crystal Structures and Magnetic Susceptibilities

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The $[\text{MoCl}_5(\text{H}_2\text{O})]^{2-}$ and $[\text{MoBr}_5(\text{H}_2\text{O})]^{2-}$ ions have long been known, but their structures have not been determined by crystallography. The crystal structures and magnetic susceptibilities of ammonium salts of these two ions have been determined. The ammonium salts are isomorphous, orthorhombic, with space group *Pnma* and $Z = 4$. The crystallographic properties of the salts are as follows. $(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$ (1): $a = 13.860$ (2), $b = 9.944$ (2), $c = 7.133$ (1) Å; $V = 938.1$ (2) Å³. $(\text{NH}_4)_2[\text{MoBr}_5(\text{H}_2\text{O})]$ (2): $a = 14.423$ (1), $b = 10.373$ (1), $c = 7.516$ (1) Å; $V = 1124.3$ (1) Å³. The structures were refined by full-matrix least-squares techniques to R and R_w factors of 0.022 and 0.035, respectively, for 1 and 0.033 and 0.043 for 2. The coordination geometry for both anions is essentially octahedral. The structural details of the ions are as follows. For 1: Mo-O, 2.155 Å; Mo-Cl (trans to O), 2.415 Å; girdle of Mo-Cl, 2.428-2.437 Å. For 2: Mo-O, 2.185 Å; Mo-Br (trans to O), 2.560 Å; girdle of Mo-Br, 2.573-2.597 Å. The H atoms on the coordinated H₂O molecule in 1 were observed. The temperature-dependent magnetic susceptibilities of the two compounds were found to obey the Curie-Weiss law and to be field independent. Effective magnetic moments were found to be $\mu = 3.83$ (± 0.02) μ_B for 1 and $\mu = 3.60$ (± 0.02) μ_B for 2.

Introduction

The $[\text{MoCl}_5(\text{H}_2\text{O})]^{2-}$ anion has been known for some time,^{2,3} but no crystallographic structural information is available for this species or its bromo analogue.

Aqueous halide acid solutions of Mo(III) have been used to prepare dimers of Mo(III)⁴ and Mo(II).⁵ Although spectroscopic evidence indicates a monomeric species in dilute solution,⁶ a Mo-Mo interaction clearly occurs in very concentrated solutions^{4,5} by means of a complex process. Herein we report accurate crystal structures of ammonium salts of the $[\text{MoX}_5(\text{H}_2\text{O})]^{2-}$ anions (X = Cl, Br) that may be precursors of the dimeric Mo(III) species.

Experimental Section

Preparations. $(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$ (1). Ammonium molybdate (85% molybdic acid; 12.0 g) was dissolved in 100 mL of 12 M HCl. The resultant Mo(VI) solution was reduced electrolytically with a current of 0.5 A in the cathode compartment of an electrochemical cell^{2,3} with a stream of nitrogen bubbled through the cathode compartment. A platinum-gauze cathode and a carbon anode were used. The anode compartment contained 12 M HCl and was separated by a glass frit from the cathode compartment. Passage of current was continued well past the theoretical time to achieve complete reduction to Mo(III). The resultant orange solution was allowed to evaporate to near dryness in a shallow vessel in a fume hood. Well-formed crystals appeared over 2-3 days. The crystals were washed with small aliquots of 12 M HCl and then ethanol and allowed to dry in air. Anal. Calcd for $(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$: Cl, 54.2; H, 3.1; N, 8.6. Found: Cl, 54.2; H, 3.1; N, 8.7.

$(\text{NH}_4)_2[\text{MoBr}_5(\text{H}_2\text{O})]$ (2). The preparation was analogous to the preparation of the complex chloride except that 9 M HBr was substituted for 12 M HCl. Dark red crystals were obtained. Anal. Calcd for $(\text{NH}_4)_2[\text{MoBr}_5(\text{H}_2\text{O})]$: Br, 72.7; H, 1.8; N, 5.1. Found: Br, 72.4; H, 1.82; N, 5.08. Crystals of both salts appear to be indefinitely stable in the normal laboratory atmosphere.

Crystallographic Measurements. Weissenberg and precession photographs (Cu K α) showed that crystals of 1 and 2 both belong to the orthorhombic system. From the systematic absences of reflections ($k + l = 2n + 1$ for $0kl$ and $h = 2n + 1$ for $h k 0$) the space group was determined to be either *Pnma* or *Pna*₂₁. Data for 1 were

Table I. Crystallographic Data

	1	2
formula	$(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$	$(\text{NH}_4)_2[\text{MoBr}_5(\text{H}_2\text{O})]$
space group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> , Å	13.860 (2)	14.423 (1)
<i>b</i> , Å	9.944 (2)	10.373 (1)
<i>c</i> , Å	7.133 (1)	7.516 (1)
<i>V</i> , Å ³	938.15	1124.3
d_c , g/cm ³	2.211	3.246
d_o , g/cm ³	2.214	>2.8
<i>Z</i>	4	4
cryst size, mm	0.10 × 0.22 × 0.08	0.15 × 0.29 × 0.14
X-ray radiation	Mo K α	Cu K α
range of 2θ , deg	1-50	1-156
μ , cm ⁻¹	26.19	332.7
no. of unique data	1186	1251
data with $F_o^2 > 3\sigma(F_o^2)$	948	1022
R_1	0.022	0.033
R_2	0.035	0.043

collected on an Enraf-Nonius CAD4 automated diffractometer in the Structure Determination Laboratory at the University of Alberta using Mo ($\lambda = 0.71073$ Å) radiation with a graphite-crystal monochromator in the incident beam. The crystal-to-detector distance was 205 mm. Data for 2 were collected on an Enraf-Nonius CAD4 automated diffractometer in the Biochemistry Department at the University of Saskatchewan using Cu ($\lambda = 1.5418$ Å) radiation with a Ni filter in the incident beam. The crystal-to-detector distance was 368 mm. Scans of several strong reflections in each case indicated that the crystals were of satisfactory quality. The unit cell dimensions were obtained by a least-squares fit of 25 reflections for both crystals (range $13^\circ < 2\theta < 34^\circ$ for 1 and range $28^\circ < 2\theta < 148^\circ$ for 2). Data were collected at $20 \pm 3^\circ$ by using the ω - 2θ scan technique with a variable scan rate (1.3-10.1°/min for 1 and 1.0-5.0°/min for 2). Backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range to give a peak to background counting time ratio of 2:1. Three standard reflections were monitored every 60 reflections, and no apparent decay of intensity was detected.

Crystallographic data and other pertinent information are given in Table I. For both crystals, Lorentz and polarization corrections were applied and intensity data were corrected for absorption by using the Gaussian integration method.⁷ The maximum and minimum transmission coefficients were 0.8211 and 0.7375, respectively, for 1 and 0.2234 and 0.0695, respectively, for 2. These corrections were deemed necessary because of the size and shape of the crystals and the exceptionally large absorption coefficient for 2.

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Solution and Refinement of the Structures.⁸ The structure **1** was solved by using a three-dimensional Patterson synthesis, which gave positional parameters for the Mo and two Cl atoms. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis. The structure was refined in space group *Pnma* to convergence by using anisotropic thermal parameters for all non-hydrogen atoms and full-matrix least-squares techniques on F , minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weighting factor w is given by $w = 4F_o^2 / (T + (pI)^2 + t^2B)$, where I is the net peak count, T is the total peak count, B is the total background count, t is the ratio of peak-scan time to total background counting time ($t = 2$ for these studies), and p is a factor to down-weight intense reflections (chosen as 0.040 for **1**). The neutral-atom scattering factors were calculated from the analytical expressions for the scattering factor curves.⁹ The f' and f'' components of anomalous dispersion¹⁰ were included in the calculations for all non-hydrogen atoms.

A difference Fourier revealed the presence of the independent H atom of the coordinated water molecule but failed to give positions for the H atoms of the ammonium cation. Consequently, the H atom of the water was included and successfully refined, but the remaining four H atoms were not included in the subsequent calculations. The discrepancy indices (eq 1) are listed in Table I. The highest peak in the final difference Fourier was $0.63 \text{ e}/\text{\AA}^3$.

$$R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o| \quad (1)$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

Because **1** and **2** were apparently isomorphous, the positions of all non-hydrogen atoms of **2** were taken from the corresponding positions in **1**. Refinement was carried out in a manner analogous to the refinement of **1** with the additional inclusion of an extinction coefficient in the least-squares refinement.^{11,12} The factor p in the weighting function was given a value of 0.010 for the refinement of the structure of **2**. The final value of the extinction coefficient was 1.950. A difference Fourier after the last anisotropic refinement cycle did not show the presence of any H atoms on either the O or N atoms. The highest peak in the final difference Fourier was $1.4 \text{ e}/\text{\AA}^3$.

Lists of all observed and calculated structure factors and positional and thermal parameters for both structures are available as supplementary material.

Magnetic Susceptibility Measurements. Data for compounds **1** and **2** were obtained over the temperature range 95–295 K with a Faraday balance described previously.¹³ The various field strengths were calibrated by using $\text{HgCo}(\text{SCN})_4$ as a standard.¹⁴ All of the measured susceptibilities were corrected for diamagnetism. From Pascal's constants¹⁵ for the constituents of the substances (in units of $10^{-6}/\text{mol}$: NH_4^+ , -13.3 ; H_2O , -13.0 ; Cl^- , -23.4 ; Br^- , -34.6 ; Mo^{3+} , -23) the molar diamagnetic susceptibilities of **1** and **2** were calculated to be $-179.6 \times 10^{-6}/\text{mol}$ and $-235.6 \times 10^{-6}/\text{mol}$, respectively. The full data are given in the supplementary material and a summary is given Table III.

Results

Compounds of similar stoichiometry such as K_2MoOCl_5 ¹⁶ are isomorphous with **1** and **2**, but other compounds of similar stoichiometry exhibit different structures; e.g., $\text{K}_2[\text{TcCl}_5(\text{OH})]$ was assigned to the (cubic) *Fm3m* space group¹⁷ on the basis

- (8) For **1** all crystallographic computing was done on a PDP 11/34A computer in the Structure Determination Laboratory at the University of Alberta using the Enraf-Nonius Structure determination package. For **2** all crystallographic computing was done on a DEC 2060 computer at the University of Saskatchewan using the XRAY76 program package.
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Table II. Bond Distances (Å) and Bond Angles (deg) for $(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$ (**1**) and $(\text{NH}_4)_2[\text{MoBr}_5(\text{H}_2\text{O})]$ (**2**)^a

1		2	
Bond Distances			
Mo-Cl(1)	2.437 (1)	Mo-Br(1)	2.583 (1)
Mo-Cl(2)	2.448 (1)	Mo-Br(2)	2.597 (2)
Mo-Cl(3)	2.428 (1)	Mo-Br(3)	2.573 (2)
Mo-Cl(4)	2.415 (1)	Mo-Br(4)	2.560 (2)
Mo-O	2.155 (3)	Mo-O	2.18 (1)
O-H(1)	0.73 (4)		
O-H(1)'	0.73 (4)		
Bond Angles			
Cl(1)-Mo-Cl(1)'	175.63 (4)	Br(1)-Mo-Br(1)'	175.02 (5)
Cl(1)-Mo-Cl(2)	89.65 (2)	Br(1)-Mo-Br(2)	89.55 (3)
Cl(1)-Mo-Cl(3)	90.37 (2)	Br(1)-Mo-Br(3)	90.45 (3)
Cl(1)-Mo-Cl(4)	92.16 (2)	Br(1)-Mo-Br(4)	92.45 (3)
Cl(2)-Mo-Cl(3)	179.32 (4)	Br(2)-Mo-Br(3)	180.00 (7)
Cl(2)-Mo-Cl(4)	89.75 (4)	Br(2)-Mo-Br(4)	89.87 (5)
Cl(3)-Mo-Cl(4)	89.57 (4)	Br(3)-Mo-Br(4)	90.14 (5)
Cl(1)-Mo-O	87.85 (2)	Br(1)-Mo-O	87.55 (3)
Cl(2)-Mo-O	90.8 (1)	Br(2)-Mo-O	90.2 (3)
Cl(3)-Mo-O	89.9 (1)	Br(3)-Mo-O	89.8 (3)
Cl(4)-Mo-O	179.5 (1)	Br(4)-Mo-O	180.0 (2)
Mo-O-H(1)	135.0 (1.0)		
H(1)-O-H(1)'	88.0 (1.0)		

^a The primed atoms are related to the unprimed atoms by the space group mirror plane.

Table III. Magnetic Susceptibility Data

compd	temp range, K	μ, μ_B	Weiss const (θ), °C	ref
$(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$ (1)	95–295	3.83 (2)	-6.7 ± 2.0	this work
$(\text{NH}_4)_2[\text{MoBr}_5(\text{H}_2\text{O})]$ (2)	98–294	3.60 (2)	-2.6 ± 2.1	this work
$(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$	rt ^a	3.78		28
$(\text{NH}_4)_3\text{MoCl}_6$	15–300	3.59	-5	27
$(\text{NH}_4)_3\text{MoCl}_6$	4–15	anomalous		27

^a Room temperature.

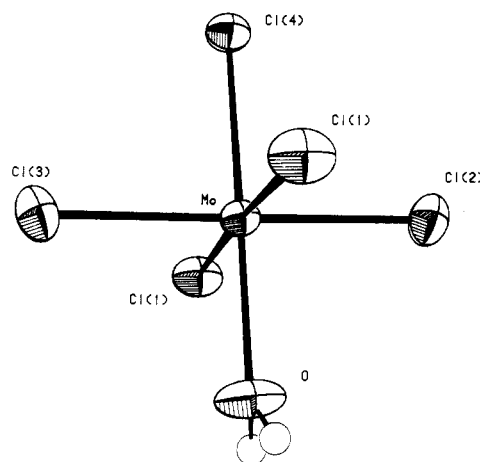


Figure 1. The $[\text{MoCl}_5(\text{H}_2\text{O})]^{2-}$ ion showing the atom-numbering scheme. The non-H atoms are represented as 50% thermal ellipsoids, while the H atoms are represented at an arbitrary size.

of limited single-crystal data and on the assumption of random replacement of Cl by OH. Analogues of **1** and **2** but with larger cations such as Cs^+ exhibit different crystal structures; e.g., both $\text{Cs}_2[\text{RhCl}_5(\text{H}_2\text{O})]$ and $\text{Cs}_2[\text{RuCl}_5(\text{H}_2\text{O})]$ belong to the (orthorhombic) *Amam* space group.^{18,19} Powder data for

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Cs[MoOCl₅] were analyzed on the basis of a cubic space group *Fm3m* if random replacement of Cl by O is assumed.²⁰ Note that the Cs⁺ salt of MoOCl₅²⁻ has a different structure from that of the K⁺ salt. Few detailed single-crystal analyses have however been done on these systems, most of the available data having been obtained from powder diffraction or visual intensity analysis of film data obtained on a single crystal (e.g., ref 17).

In **1** and **2** all atoms of the anion except X(1) and H(1) lie in the crystallographic mirror plane. Table II lists all of the bond distances and angles in these structures. Figure 1 depicts the [MoCl₅(H₂O)]²⁻ ion and defines the atomic numbering scheme.

The magnetic susceptibility data and some results from other workers are summarized in Table III. The temperature-dependent magnetic susceptibilities of the two compounds were found to obey the Curie-Weiss law and to be field independent. Effective magnetic moments were found to be $\mu = 3.83 (\pm 0.02) \mu_B$ for **1** and $\mu = 3.60 (\pm 0.02) \mu_B$ for **2**.

Discussion

A surprising observation during this study was the air stability of **1** and **2** and the fact that these compounds could be crystallized by evaporation of 12 M HCl and 9 M HBr, respectively, from an open vessel. This is in contrast to the air oxidation of Mo₂(O₂CCH₃)₄ to Mo(V) observed by Bino and Cotton.^{21,22} The major difference in their preparation was an initial heating of the solutions to 70–80 °C. Either the Mo(II) in Mo₂(O₂CCH₃)₄ does not go through a Mo(III) monomer state during the oxidation process or the major part of the oxidation occurs at the elevated temperatures used in part of the process. Another possibility is that the large cations used by Bino and Cotton stabilize the Mo(V) oxidation state in some way.

An unusual result of this structural study was the observation of the hydrogen atoms of the water molecule coordinated to the Mo in compound **1**. Within experimental error this water molecule is symmetrically coordinated, with both H's, both Cl(1)'s, Mo, and Cl(4) all lying in a plane. This is an unexpected coordination geometry and must be stabilized by hydrogen bonding to nearby chloride ions on the same or adjacent anions and/or by the nature of the orbitals involved in bonding the Mo to the oxygen. Previous studies of the analogues RhCl₅(H₂O)²⁻¹⁸ and RuCl₅(H₂O)²⁻¹⁹ did not reveal hydrogen atoms although hydrogen-bonding interactions were indicated as one of the possible sources of the distortions observed in the geometry.

The water hydrogens were not observed in compound **2**, apparently due to the high scattering power of the nearby

bromide ions and the lower quality of the data due to the very large absorption correction.

In **1**, the chloride ions closest to the hydrogen on the water moiety are Cl(1) and Cl(4) of different adjacent [MoCl₅(H₂O)]²⁻ ions at 2.45 (4) and 3.08 (4) Å, respectively. The shorter of these two distances is well below the sum of the van der Waals radii and indicates significant intermolecular bonding. In addition, Cl(1), in the same molecular unit as H, is at a distance of 3.22 (4) Å. Although this distance is at the limit of possible interaction, there is a distortion in the octahedral geometry of the complex ion consistent with a long-range attraction. The angle Cl(1)–Mo–O is 2–3° less than the other two Cl–Mo–O angles. An analogous distortion is also observed in the structure of **2**.

The long Mo–O bond and the observed geometry of the coordinated water molecule in **1** are consistent with the expectation that H₂O does not form very strong adduct σ bonds and is a π donor.²³ The Mo–O bond length of 2.155 Å in **1** and 2.185 Å in **2** is substantially longer than the molybdenyl Mo=O "double bonds" that are characteristically about 1.65 Å,²⁴ but the present Mo–OH₂ bond lengths are shorter than that observed²⁵ for the hexavalent complex K₂[Mo₂O₅(C₂O₄)₂(H₂O)₂] (2.33 Å), wherein the water molecules are trans to Mo=O functions.

The magnetic susceptibility data show, as expected, similarity to those of K₃MoCl₆^{26,27} and are consistent with an isolated d³ species in both cases.

From the structural data on **1** and **2**, there is no evidence of any dimer units as precursors to the formation of the Mo₂X₉³⁻ ions. It is possible that such evidence may be found in salts of the same anions with larger cations.

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Registry No. **1**, 13820-59-2; **2**, 13815-02-6.

Supplementary Material Available: Tables of 10F₀ and 10F_c, anisotropic thermal parameters, and details of the temperature-dependent magnetic susceptibility measurements (*T* (K) vs. χ_M^{cor}); three field strengths for the chloride salt and two for the bromide salt) for each compound (15 pages). Ordering information is given on any current masthead page.

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