in the powder spectra (see Figure 2). However, it can be noted that while the low-field region of powder spectra resembles the usual tetragonal copper(II) spectra, the high-field region is more spread out in the case of the intermediate five-coordinate complexes, as a consequence of both the anisotropy in the g values and the relatively large values of A.

Registry No. CuSalMe, 19031-10-8; ZnSalMe, 16457-01-5; CuSalMeDPT, 15378-53-7; ZnSalMeDPT, 15412-50-7.

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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Studies on Metal Carboxylates. 14.[1] Reactions of Molybdenum(II) and Rhenium(III) Carboxylates with the Gaseous Hydrogen Halides in Alcoholic Media. Synthesis, Characterization, and Reactivity of the New Haloanions of Molybdenum and Rhenium, $Mo_2Br_6^-$, $Mo_4I_{11}^{2-}$, and $Re_2I_8^{2-}$

H. D. GLICKSMAN and R. A. WALTON*

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The reactions of the molybdenum(II) and rhenium(III) carboxylates with hydrogen bromide and hydrogen iodide in alcoholic media are quite different from those previously encountered in the analogous reactions of these complexes with the gaseous hydrogen halides. The salts $(Bu_4N)Mo_2Br_6$ and $(Bu_4N)_2Mo_4I_{11}$ are produced when HBr and HI are reacted with methanol solutions containing $Mo_2(O_2CCH_3)_4$ and the appropriate tetra-*n*-butylammonium halide. While the paramagnetic iodide salt ($\mu_{eff} = 1.95$ μ_B and $g_{av} = 2.03$ at room temperature) is known to contain a tetrahedral Mo_4 cluster, the detailed structure of $(Bu_4N)Mo_2Br_6$ is unknown at present although it almost certainly contains, as its most dominant structural feature, pairs of molybdenum atoms bound together by a very strong metal–metal bond. A discrete $Mo_2Br_6^-$ anion with an "ethane-like" structure would possess a $\sigma^2\pi^4(\pi^*)^1$ ground-state electronic configuration and a metal–metal bond order of 2.5. $(Bu_4N)Mo_2Br_6$ is paramagnetic ($\mu_{eff} = 1.5$ μ_B and $g_{av} = 1.98$ at room temperature) and reacts with pyridine and tertiary phosphines (PEt_3, P-*n*-Pr_3, $Ph_2PCH_2CH_2PPh_2$, and $Ph_2PCH_2CH_2AsPh_2$) to afford the molybdenum(II) dimers $Mo_2Br_4L_4$ and $Mo_2Br_4(LL)_2$. These reactivity patterns are quite different from those displayed by $(Bu_4N)_2Mo_4I_{11}$ toward these same ligands. The treatment of mixtures of $Re_2(O_2CC_6H_5)_4Cl_2$ and Bu_4NX with HX (X = Cl, Br, or I) in methanol or ethanol affords the salts $(Bu_4N)_2Re_2X_8$. This is the first reported synthesis of the octaiododirhenate(III) anion, a species which upon reaction with tertiary phosphines produces the rhenium(II) dimers $Re_2I_4(PR_3)_4$, where R = Et, *n*-Pr, or *n*-Bu, and $Re_2I_4(LL)_2$, where LL = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2AsPh_2$. The reaction of $(Bu_4N)_2Re_2I_8$ with acetic and pivalic acids leads to the carboxylate-bridged dimers $Re_2(O_2CR)_4I_2$. When a methanol solution of $Re_2(O_2CC_6H_5)_4Cl_2$ is reacted with HCl in the absence of Bu_4N^+, the green methyl benzoate complex $Re_2Cl_6(C_6H_5CO_2CH_3)$ is formed. This species is probably the final reaction intermediate prior to the formation of $(Bu_4N)_2Re_2Cl_8$ when an excess of Bu_4N^+ is added.

Introduction

The reactions of crystalline molybdenum(II) acetate with *gaseous* hydrogen chloride, bromide, and iodide at ca. 300 °C produces the molybdenum(II) halides, β-MoX_2,[1-4] which are the parent halides of the haloanions $Mo_2X_8^{4-}$ [5-7] and, accordingly, are best formulated as $[Mo_2X_4]_n$.[1,4] The analogous metal–metal bonded rhenium(III) acetate, $Re_2(O_2CCH_3)_4Cl_2$, also reacts upon treatment with the gaseous hydrogen halides but, in this instance, a trinuclear halide cluster Re_3X_9, where X = Cl, Br, or I, is produced.[1,4] Since $Mo_2(O_2CCH_3)_4$ and $Re_2(O_2CCH_3)_4Cl_2$ are converted to salts of the $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$ anions upon treatment with concentrated hydrochloric acid,[5,8,9] the course of the reactions between these dimeric metal–metal bonded acetates and HX is clearly dependent upon the reaction conditions. The possibility that the reactions in aqueous media could differ significantly from those which might occur when a nonaqueous solvent system was used prompted us to explore the reactions of $Mo_2(O_2CCH_3)_4$ and $Re_2(O_2CC_6H_5)_4Cl_2$ with the hydrogen halides in alcoholic media (methanol and ethanol). This study has led, among other things, to the isolation of salts of the new $Mo_2Br_6^-$, $Mo_4I_{11}^{2-}$, and $Re_2I_8^{2-}$ anions. In the present article we describe details of their synthesis, characterization, and reactivity.

Experimental Section

Starting Materials. The following compounds were prepared by standard literature procedures: $Mo_2(O_2CCH_3)_4$,[2,10] $Re_2(O_2CCH_3)_4Cl_2$,[4,11] and $Re_2(O_2CC_6H_5)_4Cl_2$.[12] Reagent grade solvents and gases were obtained from commercial sources. All solvents were

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deoxygenated by purging with nitrogen gas for at least 1 h prior to use.

Synthetic Procedures. A. Reactions of $Mo_2(O_2CCH_3)_4$ with Hydrogen Halides. (i) Hydrogen Bromide. Freshly prepared $Mo_2(O_2CCH_3)_4$ (0.5 g) and Bu_4NBr (1.7 g) were added to 30 mL of dry, deoxygenated methanol, and nitrogen gas was then bubbled into the solution for 15 min. The nitrogen gas was then replaced by hydrogen bromide and the solution heated. Hydrogen bromide was continuously bubbled into the solution and the solution refluxed until all of the $Mo_2(O_2CCH_3)_4$ had reacted (~2 h). After cooling of the solution and flushing out of the remaining hydrogen bromide with nitrogen gas, the reaction mixture was filtered to remove any insoluble residue. The reaction filtrate was then evaporated to a small volume, and the resulting brown crystals of $(Bu_4N)Mo_2Br_6$ (0.42 g) were filtered off, washed with ethanol and diethyl ether, and then dried under vacuum. Anal. Calcd for $C_{16}H_{36}Br_6Mo_2N$: C, 21.01; H, 3.94; Br, 52.52. Found (for separate preparative samples): C, 21.86, 21.29; H, 4.05, 3.75; Br, 52.40, 51.80; yield >40%. This complex was soluble in acetone, acetonitrile, and tetrahydrofuran.

(ii) Hydrogen Iodide. Nitrogen gas was bubbled through a suspension of freshly prepared $Mo_2(O_2CCH_3)_4$ (0.28 g) in 35 mL of dry deoxygenated methanol for 15 min. The solution was then heated while hydrogen iodide was bubbled through. After the $Mo_2(O_2CCH_3)_4$ had reacted (~1 h), the reaction system was cooled and flushed with nitrogen gas, and the supernatant carefully decanted into a methanol solution (5 mL) of Bu_4NI (0.24 g). Black crystals of $(Bu_4N)_2Mo_4I_{11}$ (0.39 g) immediately precipitated and these were then collected, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $C_{32}H_{72}I_{11}Mo_4N_2$: C, 16.95; H, 3.17; I, 61.68; Mo, 16.95. Found: C, 17.05; H, 3.13; I, 62.02; Mo, 16.85; yield >50%. $(Bu_4N)_2Mo_4I_{11}$ was found to be soluble in acetone, acetonitrile, and tetrahydrofuran.

B. Reactions of $(Bu_4N)Mo_2Br_6$ and $(Bu_4N)_2Mo_4I_{11}$ with Tertiary Phosphines and Heterocyclic Amines. (i) $Mo_2Br_4(PEt_3)_4$. $(Bu_4N)Mo_2Br_6$ (0.32 g) was added to 15 mL of dry, deoxygenated acetone, followed by 1.0 mL of triethylphosphine, and the solution refluxed for 3 days. The solution was then filtered, the filtrate was evaporated to near dryness, and the resulting blue crystals of $Mo_2Br_4(PEt_3)_4$ (0.04 g) were washed with ethanol and dried under vacuum. Anal. Calcd for $C_{24}H_{60}Br_4Mo_2P_4$: C, 29.27; H, 6.10. Found: C, 29.23; H, 5.91; yield 13%. The spectral properties of this product were identical with those of the complex of this same stoichiometry which is isolated by the reaction of PEt_3 with β-$MoBr_2$.[4]

(ii) $Mo_2Br_4(P\text{-}n\text{-}Pr_3)_4$. $(Bu_4N)Mo_2Br_6$ (0.39 g) was added to 15 mL of dry, deoxygenated acetone. Tri-*n*-propylphosphine (0.6 mL) was then added and the solution refluxed for 2 days. The resulting blue crystals of $Mo_2Br_4(P\text{-}n\text{-}Pr_3)_4$ (0.1 g) were filtered off, washed with ethanol and diethyl ether, and dried in vacuum; yield ~22%. The identity of this complex was confirmed by a comparison of its spectral properties with those reported in the literature.[4]

(iii) $Mo_2Br_4(dppe)_2$. $(Bu_4N)Mo_2Br_6$ (0.23 g) and 1,2-bis(diphenylphosphino)ethane (0.23 g) were added to 15 mL of acetone, and the solution was heated for 3 h. After the solution was allowed to cool, the red-brown crystals of $Mo_2Br_4(dppe)_2$ (0.08 g) were collected, washed with ethanol, acetone, and diethyl ether, and dried in vacuo. Anal. Calcd for $C_{52}H_{48}Br_4Mo_2P_4$: C, 47.70; H, 3.67. Found: C, 46.65; H, 3.80; yield 24%.

(iv) $Mo_2Br_4(arphos)_2$. $(Bu_4N)Mo_2Br_6$ (0.44 g) and 1-diphenylphosphino-2-diphenylarsinoethane (0.39 g) were added to 20 mL of acetone, and the solution was refluxed for 20 h. The reaction mixture was then cooled to room temperature; the resulting dark red crystals of $Mo_2Br_4(arphos)_2$ (0.16 g) were filtered off, washed with ethanol, benzene, acetone, and diethyl ether, and dried in vacuo; yield 24%. Anal. Calcd for $C_{52}H_{48}As_2Br_4Mo_2P_2$: C, 44.70; H, 3.44; Br, 22.92. Found: C, 44.62; H, 3.56; Br, 23.16.

(v) $Mo_2Br_4(py)_4$. $(Bu_4N)Mo_2Br_6$ was added to 15 mL of dry, deoxygenated acetone, followed by the addition of 1.0 mL of pyridine, and the resulting solution stirred for 45 min. Filtration of this reaction mixture afforded the green complex $Mo_2Br_4(py)_4$ (0.1 g), which was washed with ethanol and diethyl ether and dried in vacuo. Anal. Calcd for $C_{20}H_{20}Br_4Mo_2N_4$: C, 28.99; H, 2.44. Found: C, 28.93; H, 2.64; yield 45%.

(vi) $Mo_2I_4(bpy)_2$. $(Bu_4N)_2Mo_4I_{11}$ (0.46 g) and 2,2′-bipyridyl (0.2 g) were added to 15 mL of dry, deoxygenated acetonitrile, and the solution was refluxed for 4 days. The solution was filtered when cold and the brown complex $Mo_2I_4(bpy)_2$ (0.11 g) collected, washed with acetone and diethyl ether, and dried in vacuo. Anal. Calcd for $C_{20}H_{16}I_4Mo_2N_4$: C, 23.72; H, 1.58; I, 50.20. Found: C, 23.54; H, 2.06; I, 49.41; yield 54%.

(vii) $Mo_4I_6(dppe)_2$. $(Bu_4N)_2Mo_4I_{11}$ (0.34 g) and 1,2-bis(diphenylphosphino)ethane (0.3 g) were added to 15 mL of dry, deoxygenated acetonitrile, and the solution was refluxed for 3 days. After the solution was allowed to cool, it was filtered and the insoluble brown product (0.13 g) collected, washed with ethanol, benzene, and diethyl ether, and dried in vacuo. Its microanalytical data were in accord with its formulation as $Mo_4I_6(dppe)_2$. Anal. Calcd for $C_{52}H_{48}I_6Mo_4P_4$: C, 32.13; H, 2.47; I, 39.24; Mo, 19.77. Found: C, 32.40; H, 2.76; I, 39.03; Mo, 19.27; yield 45%.

C. Reactions of $Re_2(O_2CC_6H_5)_4Cl_2$ with Hydrogen Halides. (i) Hydrogen Chloride. A mixture of $Re_2(O_2CC_6H_5)_4Cl_2$ (0.1 g) and Bu_4NBr (0.15 g) was added to 25 mL of methanol and the system flushed with nitrogen gas for 5 min. A slow stream of dry hydrogen chloride was then passed into the solution while it refluxed for 2 h. By the end of this period, the reaction mixture had become blue. It was cooled to room temperature and filtered, and the filtrate was concentrated to about one-third of its original volume. The resulting blue complex $(Bu_4N)_2Re_2Cl_8$ (0.065 g) was filtered off, washed with ethanol, and dried in vacuo; yield 48%. The identity of this product was confirmed by a comparison of its properties with those reported for authentic samples of this complex.[8,13,14] In a similar fashion, use of Ph_4AsCl in place of Bu_4NBr produced $(Ph_4As)_2Re_2Cl_8$ (58% yield) when ethanol was used as the reaction solvent.

When this reaction was carried out in the *absence* of Bu_4NBr or Ph_4AsCl, a different product was obtained. Dry, deoxygenated methanol (40 mL) was added to $Re_2(O_2CC_6H_5)_4Cl_2$ (1.33 g) and the reaction system flushed with nitrogen gas. A slow stream of dry hydrogen chloride was then bubbled into the solution while it refluxed for approximately 3 h. By this time, the solution had become blue-green, all of the $Re_2(O_2CC_6H_5)_4Cl_2$ had reacted, and a green solid was present. This mixture was cooled, flushed with nitrogen gas, and filtered. The green insoluble complex (0.66 g), which had a stoichiometry close to that of the rhenium(III) complex of methyl benzoate, $Re_2Cl_6(C_6H_5CO_2CH_3)$, was then collected, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $C_8H_8Cl_6O_2Re_2$: C, 13.32; H, 1.12; Cl, 29.50. Found: C, 13.25; H, 1.02; Cl, 28.89; yield 62%.

(ii) Hydrogen Bromide. The reaction between $Re_2(O_2CC_6H_5)_4Cl_2$, Bu_4NBr, and hydrogen bromide in methanol was carried out using a similar procedure to that described in C(i). The resulting crystals of $(Bu_4N)_2Re_2Br_8$ were filtered off and dried.

(iii) Hydrogen Iodide. A mixture of $Re_2(O_2CC_6H_5)_4Cl_2$ (1.0 g) and 40 mL of dry, deoxygenated ethanol was flushed with nitrogen gas for 5 min. A slow stream of hydrogen iodide was then bubbled into the solution while it refluxed. Heating was continued until the solution became dark brown and $Re_2(O_2CC_6H_5)_4Cl_2$ was no longer present at the bottom of the flask (approximately 2 h). The solution was cooled, the excess hydrogen iodide flushed out with nitrogen gas, and any residue filtered off. A quantity of Bu_4NI (0.9 g), dissolved in 5 mL of ethanol, was then added to the filtrate and the solution refrigerated overnight. The solution was then filtered, and the black crystals of $(Bu_4N)_2Re_2I_8$ (0.4 g) were washed with ethanol and diethyl ether and dried in vacuo. Anal. Calcd for $C_{32}H_{72}I_8N_2Re_2$: C, 20.57; H, 3.89; I, 54.27. Found: C, 20.51; H, 3.85; I, 54.51; yield 20%.

If the solution obtained after adding the Bu_4NI is evaporated to low volume, some $(Bu_4N)_2Re_2I_8$ can still be obtained. However, the major problem associated with this modification of the procedure is that the salt $(Bu_4N)I_3$ may also begin to precipitate, thereby contaminating the $(Bu_4N)_2Re_2I_8$.

D. Reactions of $(Bu_4N)_2Re_2I_8$ with Carboxylic Acids and Tertiary Phosphines. (i) $Re_2(O_2CCH_3)_4I_2$. $(Bu_4N)_2Re_2I_8$ (0.25 g) was added to a 4:1 mixture of deoxygenated acetic acid/acetic anhydride and the resultant solution refluxed for 5 days. After cooling of the solution, the red-brown complex $Re_2(O_2CCH_3)_4I_2$ (0.11 g) was then collected, washed with ethanol, acetone, and diethyl ether, and dried. Anal. Calcd for $C_8H_{12}I_2O_8Re_2$: I, 29.47. Found: I, 29.75; yield 95%.

(ii) $Re_2[O_2CC(CH_3)_3]_4I_2$. $(Bu_4N)_2Re_2I_8$ (0.57 g) was placed in a dry round-bottom flask and flushed with nitrogen gas. Trimethylacetic acid (10 mL) and trimethylacetic anhydride (5 mL) were then added, and the solution was refluxed for 5 days. The reaction mixture was cooled and filtered, and the red-brown crystals of $Re_2[O_2CC(CH_3)_3]_4I_2$ (0.17 g) were collected, washed with a small volume of benzene, and dried in vacuo. Anal. Calcd for $C_{20}H_{36}I_2O_8Re_2$: I, 24.66. Found: I, 24.88; yield 54%.

(iii) $Re_2I_4(PEt_3)_4$. $(Bu_4N)_2Re_2I_8$ (0.6 g) was dissolved in 10 mL of acetone and 0.6 mL of triethylphosphine added. Immediately, the dark gray complex $Re_2I_4(PEt_3)_4$ (0.3 g) precipitated. It was then collected, washed with acetone, and dried in vacuo. Anal. Calcd for $C_{24}H_{60}I_4P_4Re_2$: C, 21.30; H, 4.44; I, 37.57. Found: C, 21.49; H, 3.73; I, 37.38; yield 70%.

(iv) $Re_2I_4(P\text{-}n\text{-}Pr_3)_4$. $(Bu_4N)_2Re_2I_8$ (0.27 g) was dissolved in 15 mL of acetone to which 0.5 mL of tri-*n*-propylphosphine was added. The dark gray $Re_2I_4(P\text{-}n\text{-}Pr_3)_4$ (0.07 g) which then precipitated was collected, washed with acetone, and dried in vacuo. Anal. Calcd for $C_{36}H_{84}I_4P_4Re_2$: C, 28.42; H, 5.53; I, 33.42. Found: C, 27.76; H, 5.4; I, 33.55; yield 34%.

(v) $ReI_4(P\text{-}n\text{-}Bu_3)_4$. $(Bu_4N)_2Re_2I_8$ (0.45 g) was dissolved in 15 mL of acetone, and 1.0 mL of tri-*n*-butylphosphine was added. After agitation of the reaction flask for 5 min, the dark green $Re_2I_4(P\text{-}n\text{-}Bu_3)_4$ (0.2 g) was collected, washed with acetone, and dried in vacuo. Anal. Calcd for $C_{48}H_{108}I_4P_4Re_2$: C, 34.12; H, 6.40; I, 30.1. Found: C, 34.34; H, 6.23; I, 30.1; yield 49%.

(vi) $Re_2I_4(dppe)_2\cdot(CH_3)_2CO$. $(Bu_4N)_2Re_2I_8$ (0.16 g) and 0.12 g of 1,2-bis(diphenylphosphino)ethane (dppe) were dissolved in 15 mL of acetone. The solution was heated for 30 min by which time a dark green solid had precipitated. The solution was cooled and filtered, and the resulting complex $Re_2I_4(dppe)_2$ (0.09 g), which was obtained as its acetone solvate, was washed with ethanol, benzene, ethanol, and diethyl ether and dried in vacuo. Anal. Calcd for $C_{55}H_{54}I_4OP_4Re_2$: C, 38.06; H, 3.11; I, 29.30. Found: C, 38.11; H, 3.00; I, 30.10; yield 60%.

(vii) $Re_2I_4(arphos)_2\cdot(CH_3)_2CO$. Employing a similar procedure to that used in D(vi), but with 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos) in place of dppe, we obtained the dark green complex $Re_2I_4(arphos)_2\cdot(CH_3)_2CO$. Anal. Calcd for $C_{55}H_{54}As_2I_4OP_2Re_2$: C, 36.22; H, 2.96; I, 27.88. Found: C, 36.02; H, 2.97; I, 28.06; yield 30%.

Physical Measurements. These were carried out as described previously[4] with the exception of ^1H NMR spectra which were recorded using a Perkin-Elmer R32 (90 MHz) instrument.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

(a) Reactions of $Mo_2(O_2CCH_3)_4$ with the Hydrogen Halides. The reactions of mixtures of $Mo_2(O_2CCH_3)_4$ and Bu_4NCl with hydrogen chloride in methanol or ethanol were very exothermic and produced solids ranging in color from brown to light green. Unfortunately, these reaction products were not reproducible except for the isolation of a beautiful light green material which was determined to be the molybdenum(V) complex $(Bu_4N)MoOCl_4$. It contains the molybdenyl cation MoO^{3+} and is the same, in terms of microanalysis and physical and spectroscopic properties, as other salts containing the $MoOCl_4^-$ anion which have been prepared from molybdenum(V) chloride.[15] Accordingly, this system was not investigated further.

In contrast to our failure to isolate any new species from the reaction between $Mo_2(O_2CCH_3)_4$ and hydrogen chloride, the analogous reactions of this acetate with hydrogen bromide and hydrogen iodide in the presence of the appropriate tetra-*n*-butylammonium halide produced low oxidation state molybdenum halide complexes which we formulate as $(Bu_4N)Mo_2Br_6$ and $(Bu_4N)_2Mo_4I_{11}$,[16] possessing higher metal oxidation states than the parent acetate $Mo_2(O_2CCH_3)_4$. They are fairly stable in the solid state, although they will slowly oxidize if not kept under a nitrogen atmosphere and refrigerated. The X-ray diffraction powder patterns of these complexes confirm that they are not isomorphous.

The electronic absorption spectral data for $(Bu_4N)Mo_2Br_6$ and $(Bu_4N)_2Mo_4I_{11}$ are presented in Table I. In each case, the similarity of the solution spectrum in acetone to that displayed for the solid complex indicates that there is no structural change upon their dissolution in this solvent. Indeed, both complexes can be recrystallized from acetone.

Although there are no previous reports on the isolation of molybdenum halide complexes of the type $(Bu_4N)Mo_2X_6$, the bromide salt may bear a fairly close structural relationship to the well-characterized metal–metal bonded dimers of molybdenum(III) which possess a Mo_2L_6 "ethane-like" structure (for example, $Mo_2[CH_2Si(CH_3)_3]_6$[17] and $Mo_2[N(CH_3)_2]_6$[18]). Complexes of the latter type possess a metal–metal triple bond and, accordingly a $\sigma^2\pi^4$ ground-state electronic configuration.[19] It is possible that $Mo_2Br_6^-$ is structurally similar but with a formal molybdenum oxidation state of +2.5 and a metal–metal bond order of 2.5 rather than 3. Evidence in support of this postulate is provided by the magnetic properties of this complex. Its paramagnetic nature ($\chi_g = 0.55 \times 10^{-6}$ cgsu, $\mu_{eff} = 1.5\ \mu_B$) is in accord with its possessing a $\sigma^2\pi^4(\pi^*)^1$ ground-state configuration. The ESR spectrum of a powdered sample of this complex displayed a fairly broad symmetric absorption (peak to peak separation of 105 G) with a g_{av} value of 1.98. ESR spectra on several different "glassy" solutions (methanol and dichloromethane) were also recorded but revealed no additional information.

McCarley and co-workers[20] had previously reported the isolation of the salt $(Bu_4N)_2Mo_4I_{10}Cl$, a complex which is generated by the thermal decomposition of $(Bu_4N)Mo(CO)_4I_3$, followed by its extraction and recrystallization from 1,2-dichloromethane (it is this solvent which provides the source of the Cl atom which is incorporated into the anion).[20] The molybdenum cluster complex prepared by McCarley[20] is paramagnetic ($\mu_{eff} = 1.75\ \mu_B$ from magnetic susceptibility measurements and $g_{av} = 2.027$ from the ESR spectrum of a powdered sample),[20] which agrees quite well with the comparable data we have obtained for our sample of $(Bu_4N)_2Mo_4I_{11}$, namely, $\mu_{eff} = 1.9\ \mu_B$ and $g_{av} = 2.03$.

Since we began the present study, Professor McCarley has kindly informed[21] us that he has now succeeded in isolating the iodo complex $(Bu_4N)_2Mo_4I_{11}$ by the thermal decomposition of $(Bu_4N)Mo(CO)_4I_3$. Preliminary details of the crystal structure of this salt reveal[21] that the four molybdenum atoms form a distorted tetrahedron with three different kinds of iodine environments being present. This structural information agrees well with the I 3d binding energy spectrum of $(Bu_4N)_2Mo_4I_{11}$ which we have investigated.[22] The similarity of the samples of $(Bu_4N)_2Mo_4I_{11}$ prepared by ourselves, via the reaction of $Mo_2(O_2CCH_3)_4$ with hydrogen iodide in methanol, and by McCarley[21] is substantiated by a comparison of their electronic absorption spectra in acetonitrile. Measurements on our samples reveal absorptions at 630, ~490, and 350 nm, in good agreement with the comparable data communicated to us[21] by Professor McCarley (i.e., 625, 490, and 355 nm).

The X-ray photoelectron spectra of $(Bu_4N)Mo_2Br_6$ and $(Bu_4N)_2Mo_4I_{11}$ were recorded and the appropriate Mo 3d binding energies are listed in Table I. In both complexes only one type of molybdenum is seen. Compared to $Mo_2Br_6^-$, the Mo $3d_{5/2}$ binding energy of $Mo_4I_{11}^{2-}$ is quite low (229.2 eV vs. 230.1 eV) which is most likely a reflection of the greater charge density at the metal center due to the lower electronegativity of iodine, as well as the slightly lower formal oxidation state of molybdenum in $(Bu_4N)_2Mo_4I_{11}$. These binding energies are in the range expected for molybdenum halide complexes having formal oxidation states between Mo(II) and Mo(III).[23]

(b) Reactions of $(Bu_4N)Mo_2Br_6$ and $(Bu_4N)_2Mo_4I_{11}$ with Tertiary Phosphines and Pyridine. The reactions of $(Bu_4N)Mo_2Br_6$ with pyridine and the tertiary phosphines PEt_3 and $P\text{-}n\text{-}Pr_3$ afford the molybdenum(II) complexes $Mo_2Br_4L_4$,[24] where L = py or PR_3, which are identical with the products of this same stoichiometry obtained from reactions of β-$MoBr_2$[4] and $Cs_3Mo_2Br_8H$[25] with these ligands. Their infrared spectra in the 400–4000-cm^{-1} region indicate that the ligand is coordinated, that Bu_4N^+ is no longer present, and

Table I. Spectroscopic Properties of New Halide Complexes of Molybdenum and Rhenium

				XPS,[c] eV			
				Mo (Re)		Br (I)	
complex	medium[a]	electronic absorption maxima, nm	infrared spectra,[b] cm^{-1} (400-200 cm^{-1})	$3d_{3/2}$ ($4f_{5/2}$)	$3d_{5/2}$ ($4f_{7/2}$)	$3p_{1/2}$ ($3d_{3/2}$)	$3p_{3/2}$ ($3d_{5/2}$)
$(Bu_4N)Mo_2Br_6$	DR	720 m, br, 475 sh, 420 s	244 m-s, 225 s	233.2	230.1 (1.1)	189.3	182.7 (2.7)
	$(CH_3)_2CO$	~750 m-w, br, 480 m-w, 420 vs					
$(Bu_4N)_2Mo_4I_{11}$	NM	665 m, 530 m, 360 s	~200 w	232.5	229.2 (1.1)	*d*	*d*
	$(CH_3)_2CO$	~775 vw, 652 s, 535 s, ~490 sh, 358 vs					
$Mo_2Br_4(arphos)_2$	DR	815 s, ~575 sh, 505 s	310 m, 270 m-w				
	NM	815 s, ~575 sh, 500 s, 375 vs					
$Mo_2I_4(bpy)_2$	DR	615 s	*f*	231.6	228.8 (1.2)	630.6	619.2 (1.3)
	NM	~650 m, br					
$Mo_4I_6(dppe)_2$	NM	~380 s, br[e]	*f*	232.5	229.3 (1.5)	631.0	619.6 (2.0)
$Re_2Cl_6(C_6H_5CO_2CH_3)$	DR	820 w, 640 s, 550 w, sh, 440 sh	371 s, 337 s, br, 281 sh, 235 w	46.0	43.6 (1.2)		
	CH_3OH	810 w, 650 s, 550 w, 440 sh					
$(Bu_4N)_2Re_2I_8$	DR	~900 sh, 775 s, 675 s, ~620 sh, 520 s, 400 s	*f*	45.5	43.2 (1.5)	630.3	618.8 (2.0)
	NM	~900 sh, 780 s, 683 s, 605 w, 520 s, 400 sh					
$Re_2(O_2CCH_3)_4I_2$	NM	600 sh, 505 m, 380 s	390 m, 354 m, 262 w, 229 w	45.8	43.4 (2.0)	630.6	619.2 (1.8)
$Re_2[O_2CC(CH_3)_3]_4I_2$	NM	625 sh, 490 m, 405 s					
$Re_2I_4(PEt_3)_4$	NM	~700 m, br, 540 m	312 w	43.8	41.3 (1.0)	631.5	620.0 (1.5)
	CH_2Cl_2	695 m, br, 535 m, 475 m					
$Re_2I_4(P\text{-}n\text{-}Pr_3)_4$	DR	705 m, 530 m, 475 sh?	375 w, 310 w				
	NM	~700 m, br, 515 sh, 460 sh					
$Re_2I_4(P\text{-}n\text{-}Bu_3)_4$	NM	690 m, 540 m, 460 sh	398 w, ~360 vw, 310 w	43.6	41.1 (1.3)	631.3	619.9 (1.6)
	CH_2Cl_2	690 m, 535 m-s, 480 m-w					
$Re_2I_4(dppe)_2\cdot(CH_3)_2CO$	NM[g]	638 m, 550 sh, 475 sh	356 m-w, 342 w	43.9	41.4 (1.1)	631.1	619.8 (1.2)
	CH_2Cl_2[g]	615 sh, 525 sh, 455 sh					
$Re_2I_4(arphos)_2\cdot(CH_3)_2CO$	DR	610 m	312 m	43.9	41.5 (1.0)	631.2	619.8 (1.1)
	CH_2Cl_2	610 m					

[a] DR = diffuse reflectance; NM = Nujol mull. [b] All spectra recorded as Nujol mulls. [c] All X-ray photoelectron spectra are referenced to a C 1s binding energy of 285.0 eV for the organic ligands; full-width half-maximum values (fwhm) are given in parentheses. [d] Details of the I 3d binding energy spectrum of $(Bu_4N)_2Mo_4I_{11}$ will be reported elsewhere. [e] This absorption band has a broad low-energy tail which extends well into the visible region. [f] No prominent absorption bands in the 400-200-cm^{-1} region. [g] These spectra also revealed a relatively weak absorption band at 960-890 nm which was not present in the related electronic absorption spectra of the arphos complex and, accordingly, may be due to a contaminant.

that there are no oxomolybdenum contaminants present in the complexes. In addition, $(Bu_4N)Mo_2Br_6$ reacts with the bidentate ligands $Ph_2PCH_2CH_2PPh_2$(dppe) and $Ph_2PCH_2CH_2AsPh_2$(arphos) to produce $Mo_2Br_4(LL)_2$. Previously, only the dppe complex, prepared by a ligand-exchange reaction from $Mo_2Br_4(PEt_3)_4$,[26] had been isolated. From a comparison of the electronic absorption spectrum of $Mo_2Br_4(dppe)_2$, details of which have been described elsewhere,[26] with that reported in Table I for $Mo_2Br_4(arphos)_2$, it is clear that a close structural similarity exists between these two complexes. This in turn implies that $Mo_2Br_4(arphos)_2$, like most other complexes of the type $Mo_2X_4(LL)_2$, where X = Cl or Br and LL = dppe or arpos,[26] possesses a staggered noncentrosymmetric structure, in which the arphos ligands bridge the molybdenum atoms *within* the dimer.[26,27]

While the preceding observations concerning the reactivity of $(Bu_4N)Mo_2Br_6$ do not prove the structure of the $Mo_2Br_6^-$ anion, the ease with which metal–metal bonded dimers of molybdenum(II) are produced with a wide variety of ligands certainly lends credence to the belief that a Mo_2 unit is retained in this complex and that it most likely contains a metal–metal bond of high order.

The reactivity patterns of $(Bu_4N)Mo_2Br_6$ contrast quite strikingly with those we observed for the iodide salt $(Bu_4N)_2Mo_4I_{11}$. In particular, the failure of $(Bu_4N)_2Mo_4I_{11}$ to afford $Mo_2I_4L_4$ upon reaction with pyridine and monodentate tertiary phosphines[28] is support for the existence of a major structural difference between these anions. Only in two instances did we reproducibly obtain products from the reactions of the iodide complex.

The reaction between $(Bu_4N)_2Mo_4I_{11}$ and 2,2′-bipyridyl produced a complex of stoichiometry $Mo_2I_4(bpy)_2$, which demonstrates that the $Mo_4I_{11}^{2-}$ cluster can, in certain circumstances, be disrupted to afford molybenum(II) dimers. Although Brencic et al.[29] have reported preparing $Mo_2I_4(bpy)_2$ from $(picH)_2Mo_2I_6(H_2O)_2$, very few details of its spectroscopic properties were described, thereby making any comparisons (see Table I) rather inconclusive. The infrared spectrum of $Mo_2I_4(bpy)_2$ matches that reported for $Mo_2X_4(bpy)_2$ (X = Cl or Br)[25] and the Mo 3d binding energies (Table I) are those expected[23] for a molybdenum(II) halide complex of the type $Mo_2X_4L_4$ or $Mo_2X_4(LL)_2$. The Mo $3d_{3/2,5/2}$ energies agree very closely with those previously reported[1] for $Mo_2I_4(P\text{-}n\text{-}Pr_3)_4$ (231.7 and 228.6 eV). The diffuse reflectance electronic absorption spectrum of $Mo_2I_4(bpy)_2$ exhibits its lowest energy absorption at ~625 nm. The position of this band is characteristic of dinuclear molybdenum(II) complexes[25] and is in keeping with the trend set by $Mo_2Cl_4(bpy)_2$ and $Mo_2Br_4(bpy)_2$ which have the corresponding absorption at 530 and 575 nm, respectively.[25]

Unlike the reaction with 2,2′-bipyridyl, the reaction of $(Bu_4N)_2Mo_4I_{11}$ and dppe gives a product that reinforces the theory that $Mo_4I_{11}^{2-}$ has a quite different structure from that of $Mo_2Br_6^-$. From elemental analyses, the best formulation of this product is $Mo_4I_6(dppe)_2$. This brown material is virtually insoluble in all common organic solvents. Its solid-state electronic absorption spectrum was devoid of any dominant absorption maxima in the visible and near-infrared regions and clearly did not resemble the spectra of either $Mo_2I_4(bpy)_2$ or $Mo_2X_4(dppe)_2$ (X = Cl or Br).[26] $Mo_4I_6(dppe)_2$ is paramagnetic, with a measured magnetic susceptibility $\chi_g = 1.31 \times 10^{-6}$ cgsu ($\mu_{eff} = 1.9\ \mu_B$ assuming $Mo_4I_6(dppe)_2$), and a single peak is seen in the ESR spectrum of a powdered sample of this material at a g_{av} value of 2.079. While the X-ray photoelectron spectrum of $Mo_4I_6(dppe)_2$ displays similar Mo 3d binding energies to the XPS of $(Bu_4N)_2Mo_4I_{11}$ (Table I), the I 3d peaks are not split (unlike the I 3d spectrum of $(Bu_4N)_2Mo_4I_{11}$)[22] thereby implying[30] that the iodine atoms may possess similar structural environments. However, these I 3d peaks (Table I) are rather broad (fwhm ~2.0 eV), a phenomenon which may reflect either partial sample decomposition or the existence of differential surface charging. Note that the complexes in Table I which have the broadest I 3d peaks also have the broadest metal peaks ($Mo_4I_6(dppe)_2$, $(Bu_4N)_2Re_2I_8$, and $Re_2(O_2CCH_3)_4I_2$), an observation which is consistent with either of these interpretations.

(c) Reactions of $Re_2(O_2CC_6H_5)_4Cl_2$ with the Hydrogen Halides. In view of the insolubility of the rhenium(III) acetate $Re_2(O_2CCH_3)_4Cl_2$ in most organic solvents and its failure to react with the hydrogen halides when suspended in methanol and ethanol, we chose to use the related benzoate complex instead. It is prepared[12] from the acetate by a carboxylate exchange reaction. Treatment of a methanol or ethanol solution of this complex (in the presence of an excess of tetra-*n*-butylammonium bromide or iodide) with the appropriate hydrogen halide (HCl, HBr, or HI) produces the crystalline salts $(Bu_4N)_2Re_2X_8$. Of particular note is the isolation, for the first time, of the iodide salt. The related isoelectronic species $Mo_2I_8^{4-}$ is still unknown, although the 4-methylpyridinium salt $(picH)_2Mo_2I_6(H_2O)_2$ has been isolated,[29] thereby hinting that, with a careful choice of reaction conditions, salts of the $Mo_2I_8^{4-}$ anion might be isolated.

The use of a nonaqueous solvent for the preparation of $(Bu_4N)_2Re_2I_8$ is clearly essential since it has already been demonstrated that treatment of rhenium(III) carboxylates with 55% aqueous HI produces $Re_2(O_2CR)_4I_2$ and/or $Re_2(O_2CR)_2I_4$[12,31] but not $Re_2I_8^{2-}$. Bratton and Cotton[31] have noted, from a consideration of the likely bonded and nonbonded Re–Re, Re–I, and I–I contacts for $Re_2I_8^{2-}$, that "it appears that the $Re_2I_8^{2-}$ ion may be sterically feasible." Our work confirms this prediction.

The properties of $(Bu_4N)_2Re_2X_8$ (X = Cl or Br) prepared by this method are identical with those reported previously[8,13,14] for these salts and, accordingly, these reaction products will not be considered further. In the reaction between $Re_2(O_2CC_6H_5)_4Cl_2$ and hydrogen chloride in methanol, a green complex of stoichiometry $Re_2Cl_6(C_6H_5CO_2CH_3)$ could be isolated when Bu_4N^+ salts were not added to the reaction mixture. This complex is of interest because it represents the closest we have yet come to the isolation of the parent chloride $[Re_2Cl_6]_n$ of the $Re_2Cl_8^{2-}$ anion. Its formulation is supported by spectroscopic characterizations, several details of which are presented in Table I. First, its infrared spectrum reveals the absence of any ν(O–H) vibrations thereby ruling out the presence of benzoic acid and methanol in the product. In the low-frequency region (400–200 cm^{-1}), the ν(Re–Cl) absorptions at 371 and 337 cm^{-1}, while slightly higher in frequency than those characteristic of complexes of the type $Re_2Cl_6L_2$ (where L = PR_3 for example),[32] are nonetheless in accord with such a structural formation. The ^1H NMR spectrum of a solution of this complex in Me_2SO-d_6 exhibited resonances at δ 3.44 (methyl) and δ 7.76 and 8.08 (phenyl) due to the coordinated methyl benzoate and, furthermore, confirmed the absence of methanol. The electronic absorption spectrum of this complex (Table I) displays a very similar spectral profile to that of the $Re_2Cl_8^{2-}$ anion[8,14,33] and the tertiary phosphine complexes $Re_2Cl_6(PR_3)_2$,[32] with the $\delta \rightarrow \delta^*$ transition[14,33] being assigned to the intense, sharp absorption band at ~650 nm. The origin of the weak absorption at ~820 nm is unknown since it does not appear in the spectra of other derivatives of the Re_2^{6+} core. The rhenium core electron binding energies (Re $4f_{5/2}$ and $4f_{7/2}$ in Table I) closely resemble those of $Re_2Cl_6(PR_3)_2$[34] when the same binding energy standard is used,[35] and a single set of Cl 2p energies at 200.7 ($2p_{1/2}$) and 199.1 ($2p_{3/2}$) eV indicate[30] that only one type of chlorine environment is present in this complex.

$Re_2Cl_6(C_6H_5CO_2CH_3)$ is probably the final reaction intermediate prior to the formation of $(Bu_4N)_2Re_2Cl_8$ when an excess of Bu_4N^+ is added to the system. The presence of methyl benzoate is hardly surprising bearing in mind that the formation of this ester from benzoic acid and methanol will be catalyzed by the HCl which is present.

The pertinent spectral data for the diamagnetic complex $(Bu_4N)_2Re_2I_8$ are presented in Table I. As expected, the infrared-active ν(Re–I) modes occur below the range of our measurements (<200 cm^{-1}) and, with the exception of proving the absence of Re═O and O—H contaminants, the infrared spectrum of this complex provides little additional information. The Re 4f binding energies of $(Bu_4N)_2Re_2I_8$ (Table I) closely resemble those reported previously for $(Bu_4N)_2Re_2X_8$ (X = Cl or Br),[36] and its electronic absorption spectrum shows the expected shift of the absorption maxima to lower energies relative to $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$.[8,14,33] The interpretation of this spectrum may be complicated by the appearance of halogen → metal charge-transfer transitions (e.g., $I(\pi) \rightarrow Re(\delta^*)$) in the visible region which will likely mask certain of the weaker, metal-based transitions.[14] It is possible that the lowest energy band at ~780 nm is assignable to the $\delta \rightarrow \delta^*$ transition.[33]

(d) Reactions of $(Bu_4N)_2Re_2I_8$ with Carboxylic Acids and Tertiary Phosphines. The octaiododirhenate(III) anion resembles the related $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ anions in many of its reactions and thereby provides the most direct route available for the synthesis of dimeric rhenium iodide complexes containing strong metal–metal bonds. The acetate and pivalate complexes of the type $Re_2(O_2CR)_4I_2$, for example, were prepared in good yield by this method. Their spectroscopic properties (Table I) closely resemble those of the related chloride and bromide derivatives.[12,13,37]

In contrast to the reactions of $(Bu_4N)_2Re_2X_8$, where X = Cl or Br, with tertiary phosphines, whereupon either unreduced or reduced complexes of the types $Re_2X_6L_2$, $Re_2X_5L_3$, or $Re_2X_4L_4$ can be produced (depending upon the choice of reaction conditions), the related iodide salt $(Bu_4N)_2Re_2I_8$ produces only derivatives of rhenium(II), namely, $Re_2I_4(PR_3)_4$, where R = Et, *n*-Pr, or *n*-Bu, and $Re_2I_4(LL)_2$, where LL = dppe or arphos. The more rapid reduction of $Re_2I_8^{2-}$ to rhenium(II) derivatives is in accord with the known redox chemistry of other metal halides in which the tendency for reduction increases in the order Cl < Br < I.[38] The similarity of the spectroscopic properties of these new complexes (Table I) to those of their chloride and bromide analogues suggests[32,39] that they possess similar molecular and electronic structures, details of which have been elucidated previously by single-crystal X-ray structure analyses of $Re_2Cl_4(PEt_3)_4$[40] and $Re_2Cl_4(dppe)_2$[41] and SCF-Xα-SW calculations on $Re_2Cl_4(PH_3)_4$.[42] These conclusions are further supported by electrochemical studies on $Re_2X_4(PR_3)_4$ and $Re_2X_4(LL)_2$, where X = Cl, Br, or I. Within the two series of complexes, cyclic voltammetric measurements have revealed[43-45] very similar $E_{1/2}$ values for the oxidations of these species to $[Re_2X_4(PR_3)_4]^{n+}$ and $[Re_2X_4(LL)_2]^{n+}$, where n = 1 or 2. The electronic absorption spectra of $Re_2I_4(PR_3)_4$, like those of $Re_2Cl_4(PR_3)_4$ and $Re_2Br_4(PR_3)_4$, often display a broad, intense absorption in the 1400–1600-nm region due to contamination by the species $Re_2I_4(PPr_3)_4^+$ or $Re_2I_5(PR_3)_3$ which are produced by the O_2 oxidation of the neutral dimers.[32,44,46]

The isolation of the dppe and arphos complexes as acetone solvates is supported by microanalytical data and the presence of a sharp ν(C=O) absorption at 1720 cm^{-1} in their infrared spectra.

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Registry No. $(Bu_4N)Mo_2Br_6$, 68024-66-8; $(Bu_4N)_2Mo_4I_{11}$, 68024-65-7; $Mo_2Br_4(arphos)_2$, 67815-31-0; $Mo_2I_4(bpy)_2$, 59646-63-8; $Mo_4I_6(dppe)_2$, 67951-62-6; $Re_2Cl_6(C_6H_5CO_2CH_3)$, 67891-13-8; $(Bu_4N)_2Re_2I_8$, 67815-33-2; $Re_2(O_2CCH_3)_4I_2$, 67815-34-3; $Re_2[O_2CC(CH_3)_3]_4I_2$, 67815-35-4; $Re_2I_4(PEt_3)_4$, 65805-11-0; $Re_2I_4(PPr_3)_4$, 64508-27-6; $Re_2I_4(PBu_3)_4$, 65805-14-3; $Re_2I_4(dppe)_2$, 67662-28-6; $Re_2I_4(arphos)_2$, 67815-36-5; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Mo_2Br_4(PEt_3)_4$, 59752-94-2; $Mo_2Br_4(PPr_3)_4$, 59752-95-3; $Mo_2Br_4(dppe)_4$, 64508-29-8; $Mo_2Br_4(py)_4$, 53850-66-1; $Re_2(O_2CC_6H_5)_4Cl_2$, 33614-57-2; HBr, 10035-10-6; HI, 10034-85-2; HCl, 7647-01-0.

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