

Such a difference has previously been envisaged for CrOH^{2+} and Cr^{3+} substitution processes.

The comparison made between analogous CrSH_2^{3+} and Cr^{3+} reactions and those of CrSH^{2+} and CrOH^{2+} shows that the Cr-S bond is more labile than the Cr-O bond. In addition the Cr-S bond exercises a quite dramatic effect on other replaceable aquo ligands.

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Registry No. $[\text{Cr}(\text{H}_2\text{O})_5\text{SH}]\text{SO}_4$, 58342-01-1; NCS^- , 302-04-5; $[\text{Cr}(\text{H}_2\text{O})_4(\text{NCS})\text{SH}]^+$, 58281-49-5.

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Complex Halides of the Transition Metals. XXI.¹ Evidence for the Existence of Tertiary Phosphine Derivatives of the New $[\text{Mo}_6\text{Cl}_8]^{2+}$ Cluster Cation

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A novel reduction of the $[\text{Mo}_6\text{Cl}_8]^{4+}$ cluster has been discovered. Triethyl-, tri-*n*-propyl-, and diethylphenylphosphine react with $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ and salts of the $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ anions, where X = Cl, Br, or I, to afford complexes of stoichiometry $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PR}_3)_3$. The less basic triphenylphosphine and diphenylethylphosphine do not reduce this cluster and only adducts of the type $\text{Mo}_6\text{Cl}_{12}(\text{PR}_3)_2$ can be isolated. On the basis of magnetic susceptibility and spectral measurements, these reduced phases are formulated as ionic $[(\text{Mo}_6\text{Cl}_8)(\text{PR}_3)_6]^{2+}[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$, in which the cation is a derivative of the previously unknown $[\text{Mo}_6\text{Cl}_8]^{2+}$ cluster, obtained by the two-electron reduction of $[\text{Mo}_6\text{Cl}_8]^{4+}$.

Introduction

Although niobium and tantalum halide clusters of the type $[\text{M}_6\text{X}_{12}]^{n+}$ undergo one-electron redox reactions within the series for $n = 2-4$,² without accompanying changes in the gross molecular structure of these species, the same has invariably not been found in the case of the molybdenum(II) and tungsten(II) halides which contain the $[\text{M}_6\text{X}_8]^{4+}$ cluster. The only exception involves the bromine oxidation of $[\text{W}_6\text{Br}_8]\text{Br}_4$, which leads to derivatives of the $[\text{W}_6\text{Br}_8]^{6+}$ ion.^{3,4} In contrast to this, the chlorine oxidation of $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ and $[\text{W}_6\text{Cl}_8]\text{Cl}_4$ leads to the phases $[\text{Mo}_6\text{Cl}_{12}]\text{Cl}_3$ and $[\text{W}_6\text{Cl}_{12}]\text{Cl}_6$, respectively, in which the original $[\text{M}_6\text{Cl}_8]$ cores are no longer present.^{5,6} With these exceptions, previous studies of the chemistry of the molybdenum and tungsten halide clusters $[\text{M}_6\text{X}_8]\text{X}_4^{2b,7}$ have not revealed any redox behavior in which a cluster structure is preserved. We have now discovered a novel redox chemistry for $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ in its reactions with certain tertiary phosphines in which derivatives of the unknown $[\text{Mo}_6\text{Cl}_8]^{2+}$ cluster are formed. This is the first instance where reduction of a metal halide $[\text{M}_6\text{X}_8]^{4+}$ cluster has been achieved.

Experimental Section

Molybdenum(II) chloride was prepared by the method of Sheldon, as modified by Jolly.⁸ Samples of the complexes $(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ and $[(n\text{-Bu})_4\text{N}]_2[(\text{Mo}_6\text{Cl}_8)\text{X}_6]$, where X = Br or I, were prepared using the procedures described by Cotton et al.⁹ All tertiary phosphines and solvents were obtained from commercial

sources. Solvents were deoxygenated by purging with N_2 gas for several hours and all reactions were carried out in a nitrogen atmosphere.

(a) **Triethylphosphine.** (i) $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ (0.1 g) was dissolved in 20 ml of ethanol, 0.2 ml of triethylphosphine syringed into this solution, and the reaction mixture refluxed for 5 min. The resulting yellow precipitate (0.12 g) was filtered off, washed with petroleum ether and diethyl ether, and then dried in vacuo. Microanalytical data showed that this product was the complex $\text{Mo}_6\text{Cl}_{12}(\text{PET}_3)_2$ (Table I); yield 98%.

(ii) The reaction between $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ (0.11 g) and triethylphosphine (0.5 ml) was repeated but with a reflux time of 14 days. During this period, the initial yellow product slowly turned orange. This complex (0.125 g) was filtered off, washed with ethanol (40 ml), petroleum ether (20 ml), and diethyl ether (20 ml), and finally dried in vacuo. Microanalytical data for this complex were consistent with the stoichiometry $\text{Mo}_6\text{Cl}_{11}(\text{PET}_3)_3$ (Table I); yield 86%.

(iii) When the salt $(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ (0.21 g) was used in place of $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ in the reaction with triethylphosphine (1.4 ml), a much shorter reflux time (7 days) was necessary to produce the reduced species $\text{Mo}_6\text{Cl}_{11}(\text{PET}_3)_3$ (0.18 g); yield 86%.

The related reactions between $(\text{Bu}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{X}_6]$, where X = Br or I, and triethylphosphine in ethanol produced the insoluble orange complexes of stoichiometry $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PET}_3)_3$ (Table I) after a reflux time of only 1 day. Workup procedures were the same as those described in section a(ii); yields 79% (X = Br) and 72% (X = I).

(b) **Tri-*n*-propylphosphine.** The orange complexes of stoichiometry $\text{Mo}_6\text{Cl}_8\text{X}_3[\text{P}(n\text{-Pr})_3]_3$, where X = Cl or I, were prepared from $(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ and $(\text{Bu}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{I}_6]$ using procedures similar to those described in section a(iii). Reflux times of 18 days

Table I. Products of the Reactions of $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ and $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) with Tertiary Phosphines

No.	Complex stoichiometry	Starting material	% C		% H		% Cl		% Br or I	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
I	$\text{Mo}_6\text{Cl}_{12}(\text{PET}_3)_2$	$[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$	11.65	12.0	2.45	2.5	34.5	34.2		
II	$\text{Mo}_6\text{Cl}_{11}(\text{PET}_3)_3^a$	$[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$	16.4	16.6	3.45	3.6	29.55	29.5		
		$(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$	16.4	16.5	3.45	3.4				
III	$\text{Mo}_6\text{Cl}_8\text{Br}_3(\text{PET}_3)_3$	$[(n\text{-Bu})_4\text{N}]_2[(\text{Mo}_6\text{Cl}_8)\text{Br}_6]$	14.9	14.7	3.1	3.05	19.5	19.4	16.5	16.5
IV	$\text{Mo}_6\text{Cl}_8\text{I}_3(\text{PET}_3)_3$	$[(n\text{-Bu})_4\text{N}]_2[(\text{Mo}_6\text{Cl}_8)\text{I}_6]$	13.55	13.7	2.8	2.6	17.8	17.85	23.9	23.95
V	$\text{Mo}_6\text{Cl}_{11}[\text{P}(n\text{-Pr})_3]_3$	$(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$	22.5	22.1	4.4	4.6	27.0	26.8		
VI	$\text{Mo}_6\text{Cl}_8\text{I}_3[\text{P}(n\text{-Pr})_3]_3$	$[(n\text{-Bu})_4\text{N}]_2[(\text{Mo}_6\text{Cl}_8)\text{I}_6]$	19.5	19.8	3.8	3.8				
VII	$\text{Mo}_6\text{Cl}_{11}(\text{PET}_2\text{Ph})_3$	$[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$	24.6	25.7 ^b	3.1	3.3				
VIII	$\text{Mo}_6\text{Cl}_{12}(\text{PET}_2\text{Ph})_2$	$[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$	23.5	23.3	2.1	2.1	28.8	29.8		

^a Molybdenum analysis: calcd, 43.6%; found, 43.4%. ^b This carbon microanalysis was high for duplicate preparative samples of this complex. While this may arise from the presence of a small amount of contaminant, the analytical data are still sufficient to distinguish this product from one having the alternative stoichiometry $\text{Mo}_6\text{Cl}_{12}(\text{PET}_2\text{Ph})_2$.

and 2 days, respectively, were used. In the reaction between $(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ and tri-*n*-propylphosphine, the orange crystals of $\text{Mo}_6\text{Cl}_{11}[\text{P}(n\text{-Pr})_3]_3$ were contaminated with a yellow powder and accordingly were separated by hand; yield 31%.

(c) **Diethylphenylphosphine.** The reaction of $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ (0.10 g) with diethylphenylphosphine (1.0 ml) in 15 ml of 1-propanol afforded a red-orange solution after 4 weeks of reflux. The reaction was then cooled to room temperature and after 2 days a small quantity of the orange complex $\text{Mo}_6\text{Cl}_{11}(\text{PET}_2\text{Ph})_3$ (0.05 g) precipitated. This was filtered off, washed with small quantities of 1-propanol and diethyl ether, and dried in vacuo; yield 34%.

(d) **Ethylidiphenylphosphine.** (i) The yellow unreduced complex $\text{Mo}_6\text{Cl}_{12}(\text{PETPh}_2)_2$ (0.10 g) was isolated when $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ (0.08 g) was refluxed with 1 ml of ethylidiphenylphosphine in 1-propanol (20 ml) for 6 days; yield 86%.

(ii) There was no apparent reaction between $(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ and ethylidiphenylphosphine in 1-propanol even when the reaction mixture was refluxed for 21 days. Infrared spectroscopy confirmed the recovery of unreacted $(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$.

(e) **Reaction of $\text{Mo}_6\text{Cl}_{11}(\text{PET}_3)_3$ with Methanol-HCl.** A suspension of $\text{Mo}_6\text{Cl}_{11}(\text{PET}_3)_3$ (0.03 g) in 5 ml of concentrated hydrochloric acid and 5 ml of deoxygenated methanol was refluxed for 10 min to produce a cloudy yellow solution. After refrigerating the solution overnight, it was filtered into a solution containing Ph_4AsCl (0.10 g) in 3 ml of methanol. The yellow precipitate (0.03 g), which formed immediately, was filtered off, washed with methanol and diethyl ether, and dried for several hours; yield 73%. Anal. Calcd for $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Mo}_6\text{Cl}_{14}$: C, 31.4; H, 2.2. Found: C, 31.5; H, 2.6.

Physical Measurements. Magnetic susceptibility and infrared and electronic spectral measurements were carried out as described previously.^{1,10} Raman spectra were recorded using a Jarrel-Ash Raman system, Model 25-300, equipped with a He-Ne laser. X-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminum $K\alpha_{1,2}$ line (1486.6 eV) was used as the excitation source. Sample preparation and full details of the experimental procedure are described fully elsewhere.^{11,12}

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory or by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

(a) **Synthesis and Preliminary Characterization.** The only previous report of tertiary phosphine complexes of $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ described the isolation and characterization of the unreduced triphenylphosphine and 1,2-bis(diphenylphosphino)ethane adducts $\text{Mo}_6\text{Cl}_{12}(\text{PPh}_3)_2$ and $\text{Mo}_6\text{Cl}_{12}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$.¹³ In contrast to this behavior, we find that triethylphosphine slowly reacts with $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ in refluxing ethanol to afford the orange complex $\text{Mo}_6\text{Cl}_{11}(\text{PET}_3)_3$, via the intermediate unreduced yellow species $\text{Mo}_6\text{Cl}_{12}(\text{PET}_3)_2$. X-ray powder measurements showed that the reduced phase was free of any contamination by $\text{Mo}_6\text{Cl}_{12}(\text{PET}_3)_2$.¹⁴ This same complex was obtained in a much shorter time (7 rather than 14 days) from the reaction of the salt $(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$, with excess triethylphosphine. Similarly, when the related mixed-halide salts $(\text{Bu}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{X}_6]$, where $\text{X} = \text{Br}$ or I , were used, the orange complexes $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PET}_3)_3$ were produced. Use

of tri-*n*-propylphosphine or diethylphenylphosphine in place of triethylphosphine afforded reduced complexes of this same stoichiometry. On the other hand, the reaction of ethylidiphenylphosphine with $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ gave only yellow $\text{Mo}_6\text{Cl}_{12}(\text{PETPh}_2)_2$ and there was no evidence for reduction. The tendency for reduction decreased with increasing phenyl substitution of the phosphine, a trend which parallels the results we have recently obtained¹⁰ on the reduction of the octahalodirhenate anions by tertiary phosphines. The new complexes prepared in the present study, together with their microanalytical data, are listed in Table I. In all instances, the infrared spectra of these complexes in the 4000–600- cm^{-1} region were typical of coordinated phosphine and showed the absence of $\text{Mo}=\text{O}$ and $\text{Mo}-\text{OH}$ contaminants.

The yields of the tri-*n*-propylphosphine and diethylphenylphosphine complexes were significantly lower (<40%) than for $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PET}_3)_3$ (ca. 70–90%), an apparent reflection on the greater solubility of the former complexes in the preparative reaction media. The complexes were insoluble in nonpolar solvents, and although they exhibited very limited solubilities in certain polar solvents in the absence of added phosphine, they could not be recovered unchanged from these solutions (see later).

Treatment of $\text{Mo}_6\text{Cl}_{11}(\text{PET}_3)_3$ with methanol-HCl resulted in oxidation to $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ (isolated as its crystalline tetraphenylarsonium salt), a reaction which is reminiscent of those in which the reduced rhenium(II) phases $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ and $[\text{Re}_3\text{Cl}_6(\text{py})_3]_n$ are oxidized to $\text{Re}_2\text{Cl}_6(\text{PET}_3)_2$ and $(\text{pyH})_2\text{Re}_3\text{Cl}_{11}$, respectively, by this same reagent.^{10,15} Hydrogen gas was not released during this reaction. In addition, no $\nu(\text{Mo}-\text{H})$ frequencies were detected in the infrared spectra of any of the reduced molybdenum phases and thus we have no evidence to support their being hydride derivatives.

(b) **Magnetic and Spectral Studies.** Magnetic susceptibility measurements on the complexes $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PET}_3)_3$, where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$, showed that they are diamagnetic at room temperature,¹⁶ a result which is inconsistent with their being derivatives of the $[\text{Mo}_6\text{Cl}_8]^{3+}$ cluster, since this species should be paramagnetic with 25 electrons available for metal-metal bonding.¹⁷ The susceptibilities are readily understood if these complexes in fact possess the ionic structure $[(\text{Mo}_6\text{Cl}_8)(\text{PR}_3)_6]^{2+}[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$, where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$, in which phosphine derivatives of the new $[\text{Mo}_6\text{Cl}_8]^{2+}$ cluster, obtained by the two-electron reduction of $[\text{Mo}_6\text{Cl}_8]^{4+}$, are stabilized in salts with the unreduced and well-characterized $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ counterions.

Evidence in support of the above structure is as follows. The $[\text{Mo}_6\text{Cl}_8]^{2+}$ cluster and its derivatives would have 26 electrons available for metal-metal bonding¹⁷ and could well be expected to be diamagnetic, as we have observed. Also, a careful examination of the low-frequency infrared spectra of all of the complexes of the type $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PR}_3)_3$ in the region 400–200 cm^{-1} (Table II) showed the presence of an intense band at 334

Table II. Low-Frequency Infrared Spectra (400–200 cm^{-1}) of Complexes of the Type $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PR}_3)_3$ and Salts of the $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ Anions

Complex	Absorption max (cm^{-1}) and rel intens			
$\text{Mo}_6\text{Cl}_{11}(\text{PEt}_3)_3$	336 vs ^b	~300 w, br	248 m	222 m
$\text{Mo}_6\text{Cl}_{11}[\text{P}(n\text{-Pr})_3]_3$	334 vs ^b	~300 sh, br	247 m-s	222 m
$\text{Mo}_6\text{Cl}_{11}(\text{PEt}_2\text{Ph})_3$	334 vs ^b	~300 vw, sh?	248 m	~225 w
$(\text{Et}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$	332 vs	302 vw	248 s	221 m
$\text{Mo}_6\text{Cl}_8\text{Br}_3(\text{PEt}_3)_3$	361 m	334 vs ^b	311 vs	235 m-w
$(\text{Bu}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Br}_6]^{2-}$	363 m		311 vs	234 m
$\text{Mo}_6\text{Cl}_8\text{I}_3(\text{PEt}_3)_3$	359 m	334 vs ^b	303 s	~228 w, br
$\text{Mo}_6\text{Cl}_8\text{I}_3[\text{P}(n\text{-Pr})_3]_3$	360 m	333 s ^b	303 s	~230 w, br?
$(\text{Bu}_4\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{I}_6]^{2-}$	362 m		303 s	232 w

^a Our data are in excellent agreement with those reported previously in the literature: F. A. Cotton, R. M. Wing, and R. A. Zimmerman, *Inorg. Chem.*, 6, 11 (1967). ^b This frequency is assigned to a vibration involving the $[(\text{Mo}_6\text{Cl}_8)(\text{PR}_3)_6]^{2+}$ cation. In the case of the chloro complexes $\text{Mo}_6\text{Cl}_8(\text{PR}_3)_3$, it is fortuitously coincident with a band at this same frequency which arises from a vibration of the $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ anion.

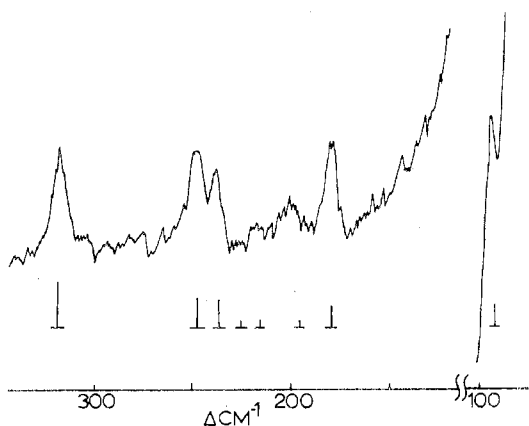


Figure 1. Raman spectrum of solid $\text{Mo}_6\text{Cl}_{11}[\text{P}(n\text{-Pr})_3]_3$. The appropriate Raman frequencies of the $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ anion are shown below the spectral trace; the heights of these lines are an approximate measure of relative intensities (see ref 18).

$\pm 2 \text{ cm}^{-1}$. This is consistent with the presence of a common absorbing species such as $[(\text{Mo}_6\text{Cl}_8)(\text{PR}_3)_6]^{2+}$. The only other absorption bands of significant intensity in this spectral region were those which showed a striking resemblance in both frequency and relative intensity to those exhibited by salts of the $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ anions (Table II). Other infrared absorption bands associated with the $[(\text{Mo}_6\text{Cl}_8)(\text{PR}_3)_6]^{2+}$ cations either may be obscured by anion absorptions or may occur at frequencies below the limit of our measurements (200 cm^{-1}). The low-frequency Raman spectra of $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PR}_3)_3$ apparently confirm the presence of the $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ anions (Table III and Figure 1). These spectra are all dominated by intense lines at 315 ± 4 and $246 \pm 2 \text{ cm}^{-1}$. These frequencies are found in the Raman spectra of the $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ anions at 318 and $248 \pm 1 \text{ cm}^{-1}$, respectively.¹⁸ Additional coincidences between the Raman data for $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PR}_3)_3$ and that reported in the literature for $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$ further support the above conclusions. For example, fairly intense Raman lines in the regions 236–230, 178–173, and $96\text{--}92 \text{ cm}^{-1}$ for the derivatives $\text{Mo}_6\text{Cl}_{11}(\text{PR}_3)_3$ are also present in the spectra of $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ at 236, 179, and 92 cm^{-1} . Several of the weaker lines observed in the Raman spectra of these complexes are most likely due to vibrations of the $[(\text{Mo}_6\text{Cl}_8)(\text{PR}_3)_6]^{2+}$ cation. The observation

Table III. Raman Spectra of Complexes of the Type $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PR}_3)_3$

Complex	$\Delta\nu, \text{cm}^{-1}$
$\text{Mo}_6\text{Cl}_{11}(\text{PEt}_3)_3$	312 s, br, 303 m-w, 243 m, br, ~230 m, br, 218 w, br, ~208 w, br, 198 w, 173 m, 160 w?, 152 s, ~140 m-w, br, 126 w?, 113 m, 105 m, 95 m
$\text{Mo}_6\text{Cl}_{11}[\text{P}(n\text{-Pr})_3]_3$	315 s, 303 vw?, 248 s, 236 m-s, 217 w?, 198 m-w, 178 s, 158 w?, 144 w, 132 w?, 92 m-s
$\text{Mo}_6\text{Cl}_8\text{Br}_3(\text{PEt}_3)_3$	312 s, br, 280 w?, 261 w, br?, 244 vs, br, ~192 w, br?, 175 w, ~157 w, ~128 w, ~93 m-w, 88 s
$\text{Mo}_6\text{Cl}_8\text{I}_3(\text{PEt}_3)_3$	320 m, 313 s, ~280 w?, 248 m-s, 195 m-w, 180 m-w, 161 m-w, 154 m-w, ~140 sh, br, ~112 sh, br
$\text{Mo}_6\text{Cl}_8\text{I}_3[\text{P}(n\text{-Pr})_3]_3$	315 s, ~282 vw, br, 250 s, ~200 w, vbr, 175 w, 160 w?, 155 m-w, 142 m-w, ~118 sh

Table IV. Molybdenum 3d and Chlorine 2p Binding Energies (eV) of the Complexes $\text{Mo}_6\text{Cl}_{12}(\text{PEt}_3)_2$ and $\text{Mo}_6\text{Cl}_8\text{X}_3(\text{PR}_3)_3$ ^{a, b}

Complex	Mo		Cl		
	3d _{3/2}	3d _{5/2}	2p _{1/2,3/2}		
$\text{Mo}_6\text{Cl}_{12}(\text{PEt}_3)_2$	232.4	229.2	202.0	200.4	197.9
$\text{Mo}_6\text{Cl}_{11}(\text{PEt}_3)_3$	232.0	228.8	201.8	200.3	198.0
$\text{Mo}_6\text{Cl}_{11}[\text{P}(n\text{-Pr})_3]_3$	232.1	228.9	201.6	200.0	197.7
$\text{Mo}_6\text{Cl}_8\text{Br}_3(\text{PEt}_3)_3$	231.6	228.4	200.9		199.5
$\text{Mo}_6\text{Cl}_8\text{I}_3(\text{PEt}_3)_3$	231.9	228.7	201.5		199.8
$\text{Mo}_6\text{Cl}_8\text{I}_3[\text{P}(n\text{-Pr})_3]_3$	231.5	228.4	200.9		199.5

^a These binding energies were located with a precision of $\pm 0.1 \text{ eV}$ and are considered accurate to at least $\pm 0.2 \text{ eV}$, relative to a carbon 1s binding energy of 284.0 eV for the carbon atoms of the phosphine ligands. ^b Fwhm values are as follows: Mo 3d, $1.6 \pm 0.1 \text{ eV}$; Cl 2p, $1.4 \pm 0.1 \text{ eV}$.

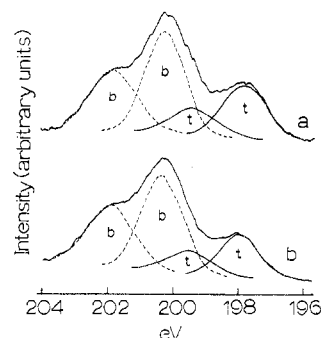


Figure 2. Chlorine 2p binding energy spectra of (a) $\text{Mo}_6\text{Cl}_{12}(\text{PEt}_3)_2$ and (b) $\text{Mo}_6\text{Cl}_{11}(\text{PEt}_3)_3$ showing deconvolution into two Cl 2p_{1/2,3/2} doublets; Cl_b and Cl_t components are distinguished by the labels b and t. Deconvolutions were carried out within limits for $I[\text{Cl}(2p_{3/2})]:\text{Cl}(2p_{1/2})]$ of 1.9 ± 0.2 and $E_b[\text{Cl}(2p_{3/2})]-\text{Cl}(2p_{1/2})]$ of $1.5 \pm 0.1 \text{ eV}$ (see ref 11).

that the 334-cm^{-1} infrared frequency is not Raman active is consistent with the $[(\text{Mo}_6\text{Cl}_8)(\text{PR}_3)_6]^{2+}$ cation being a centrosymmetric species, unless intensities of Raman lines other than this have been resonance enhanced, a point we are not able to check on account of the insolubility of these complexes.

The x-ray photoelectron spectra of these complexes conform exactly to that expected for such a structural formulation. The chlorine 2p binding energy spectrum of $\text{Mo}_6\text{Cl}_{11}(\text{PR}_3)_3$ resembled those of $\text{Mo}_6\text{Cl}_{12}(\text{PEt}_3)_2$ and similar complexes derived from $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$,¹¹ in exhibiting three peaks (Table IV and Figure 2) arising from overlap between two Cl 2p_{1/2,3/2} spin-orbit doublets. The higher energy doublet is due to the intracluster bridging chlorine atoms (Cl_b) and the lower energy doublet to chlorine atoms (Cl_t) in terminal Mo–Cl bonds.¹¹ Deconvolution of the $\text{Mo}_6\text{Cl}_{11}(\text{PEt}_3)_3$ spectrum, using the

procedure described previously,¹¹ yielded a Cl_b:Cl_t intensity ratio of 2.4:1.0, close to that expected (2.67:1.0) for the structure [(Mo₆Cl₈)(PR₃)₆][(Mo₆Cl₈)Cl₆].¹⁹ A related deconvolution of the chlorine 2p spectrum of unreduced Mo₆Cl₁₂(PEt₃)₂ showed a Cl_b:Cl_t intensity ratio of 1.9:1.0. Further support for this assignment comes from related binding energy measurements on the bromo and iodo derivatives [(Mo₆Cl₈)(PR₃)₆][(Mo₆Cl₈)X₆], for which the lower energy chlorine 2p doublet is now absent, consistent with the replacement of chlorine in the six terminal Mo-X bonds of the anion by bromine or iodine.

(c) Structural Considerations. So far, we have been unable to grow single crystals of sufficient quality to pursue an x-ray structure analysis on any of these derivatives. Consequently, while the magnetic and spectral data support our suggestion that the complexes have the ionic structure [(Mo₆Cl₈)(PR₃)₆][(Mo₆Cl₈)X₆], where X = Cl, Br, or I, in the solid state, these conclusions can only be regarded as tentative at the present time. Studies on the solution properties of these complexes were thwarted either by their low solubility or by rapid decomposition in the solvents of choice. Thus, although a freshly prepared solution of Mo₆Cl₁₁(PEt₃)₃ in warm pyridine (0.92 × 10⁻³ M) exhibited a conductivity (Λ_m = 33 ohm⁻¹ cm²) which was consistent with the proposed ionic structure, this complex could not be recovered unchanged from this solution. A variety of ion-exchange reactions were also attempted²⁰ but a suitable solvent could not be found which would both dissolve the reagents and not decompose the reduced molybdenum phase.

In conclusion, we note that the existence of cationic molybdenum cluster species of the type [(Mo₆Cl₈)L₆]ⁿ⁺, as we have proposed are present in these reduced phases, is not without precedent since Cotton and Curtis²¹ have previously isolated the molybdenum(II) perchlorate salts [(Mo₆Cl₈)L₆](ClO₄)₄, where L = dimethyl sulfoxide or dimethylformamide.

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Registry No. I, 58485-78-2; II, 58561-02-7; III, 58561-01-6; IV, 58569-39-4; V, 58569-37-2; VI, 58569-38-3; VII, 58581-87-6; VIII, 58485-77-1; [(C₆H₅)₄As]₂Mo₆Cl₁₄, 12367-68-9; [Mo₆Cl₈]Cl₄, 11062-51-4; (Et₄N)₂[(Mo₆Cl₈)Cl₆], 51056-19-0; [(n-Bu)₄N]₂[(Mo₆Cl₈)Br₆], 12367-10-1; [(n-Bu)₄N]₂[(Mo₆Cl₈)I₆], 12367-11-2; HCl, 7647-01-0; PEt₃, 554-70-1; P(n-Pr)₃, 2234-97-1; PEt₂Ph, 1605-53-4.

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