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46

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Advances in
INORGANIC CHEMISTRY

Including Bioinorganic Studies

EDITED BY

A. G. Sykes

*Department of Chemistry
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THE OCTAHEDRAL M_6Y_8 AND M_6Y_{12} CLUSTERS OF GROUP 4 AND 5 TRANSITION METALS

NICHOLAS PROKOPIUK and D. F. SHRIVER

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

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I. Introduction

The early transition metal halide clusters $\{M_6Y_8\}^{n+}$ ($M = Mo, W$; $Y = Cl, Br, I$; $M = Nb$; $Y = I$) and $\{M_6Y_{12}\}^{n+}$ ($M = Nb, Ta$; $Y = Cl, Br$) are the basis for a diverse solid-state chemistry in which cluster fragments are interconnected by halide bridges. Discrete clusters containing the $\{M_6Y_8\}^{n+}$ and $\{M_6Y_{12}\}^{n+}$ units are obtained from these materials by addition of ligands that disrupt the halide bridges. Control of the coordination environment about the metal octahedron in the soluble clusters provides control of the chemical and physical properties

of the cluster. In addition, the discrete clusters provide building blocks for the construction of new types of extended cluster arrays and cluster based materials.

Octahedral clusters of the electropositive metals, groups 3 to 7, are stabilized by π -donor ligands such as halides, chalcogenides, and alkoxides, but the majority accessible to solution chemistry are the halide complexes. These highly symmetric and aesthetically pleasing $\{M_6Y_8\}^{n+}$ and $\{M_6Y_{12}\}^{n+}$ clusters contain a robust core of six metal atoms and either 8 face-capping $\{M_6Y_8\}^{n+}$ or 12 edge-bridging $\{M_6Y_{12}\}^{n+}$ halide ligands Y. An additional 6 ligands X are terminally bound, one to each metal center, completing the structures $[M_6Y_8X_6]^{n-6z}$ and $[M_6Y_{12}X_6]^{n-6z}$ (Fig. 1). In the present discussion it is convenient to refer to the charge of only the $\{M_6Y_8\}^{n+}$ or $\{M_6Y_{12}\}^{n+}$ unit instead of referring to the entire cluster and its full complement of axial ligands. This notation is especially useful when there is ambiguity as to the type and charge of the ligands occupying the axial sites or when the properties of the cluster core are independent of the axial ligands. Nomenclature developed by Schäfer and von Schnering (1) denotes the bridging ligands as inner (superscript i) and the terminal ligands outer (from *ausser*) or axial (superscript a); thus, $[Mo_6Cl_{14}]^{2-}$ is noted $[Mo_6Cl_8^iCl_6^a]^{2-}$. Soluble octahedral clusters $\{M_6Y_8\}^{n+}$ and $\{M_6Y_{12}\}^{n+}$ with inner halide ligands have been reported for Nb, Ta, Mo, and W. Molybdenum and tungsten are observed predominately in the $\{M_6Y_8\}^{n+}$ geometry, and the group 5 metals are found with the $\{M_6Y_{12}\}^{n+}$ arrangement. One notable exception is the niobium iodide clusters such as $[Nb_6I_8(NH_2CH_3)_6]$ in which the iodide ligands occupy face-capping sites on the Nb_6 octahedron (2).

Solid compounds with $\{M_6Y_8\}^{n+}$ or $\{M_6Y_{12}\}^{n+}$ units and halide ligands have been observed for other metals, including those of the rare earth

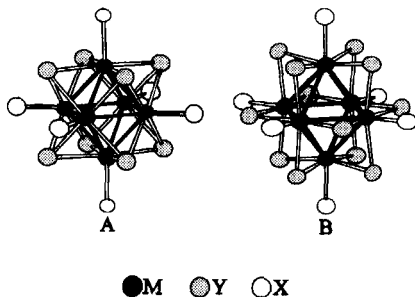


FIG. 1. Structures of $[M_6Y_8X_6]^{n-6z}$ A and $[M_6Y_{12}X_6]^{n-6z}$ B.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn				
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd				
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg				
Ac													
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

FIG. 2. Periodic table of metals (shaded) found in $\{M_6Y_8\}^{n+}$ or $\{M_6Y_{12}\}^{n+}$ geometry.

and late d-block elements (Fig. 2). Extensive intercluster bridging has confined the chemistry of the majority of these compounds to the condensed phases. By contrast, the weak intercluster bridging in the group 5 and 6 derivatives provides solid-state materials that are easily dissolved into molecular cluster species. Subsequent solution chemistry has revealed rich photophysical and redox properties for these compounds. The relationship between the ligation of the group 5 and 6 metal halide clusters and their chemical and physical properties, as well as the subsequent materials chemistry that has evolved from this association, is the subject of this review. The solid-state and solution chemistry of the related zirconium halide clusters $\{Zr_6Y_{12}\}^{n+}$, which occur with interstitial atoms occupying the center of the metal octahedron or hydrides ligands bridging the octahedron faces, is relatively new and has been the subject of a number of reviews (3, 4).

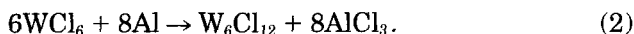
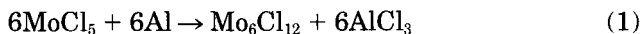
II. Group 6

Recent interest in halide clusters containing the $\{M_6Y_8\}^{n+}$ unit stems in part from its structural relationship to the superconducting Chevrel phases $PbMo_6Q_8$ ($Q = S, Se, Te$) in which eight chalcogenide ligands Q occupy the face-capping positions (5, 6). Early development of the ligand substitution chemistry of the group 6 clusters had led to recent applications of these compounds to catalysis and materials

chemistry. Molybdenum(II) chloride was discovered over 100 years ago (7), and the related cluster $\text{Mo}_6\text{Cl}_8(\text{OH})_4(\text{H}_2\text{O})_2$ was one of the first complexes characterized by X-ray diffraction (8). Renewed interest in the substitution chemistry of the inner ligands arises from the promise of generating $\{\text{Mo}_6\text{Q}_6\}^{2-}$ ($\text{Q} = \text{S}, \text{Se}, \text{Te}$) units in solution, which are potential precursors to Chevrel phases. Also of current interest is the discovery of the long-lived excited state exhibited by the molybdenum and tungsten clusters (9, 10).

A. SYNTHESIS OF GROUP 6 CLUSTERS

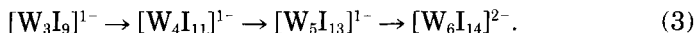
Early synthetic procedures for the group 6 metal halide clusters relied on disproportionation reactions of the intermediate halides, MoCl_3 , MoBr_3 , WCl_4 , and WBr_4 , at elevated temperatures to produce the clusters M_6X_{12} (11, 12). These reactions suffered from inherently poor yields and the need to synthesize and isolate the reactive intermediate metal halide. McCarley and co-workers (13) introduced the use of sodium tetrahaloaluminate melts to reduce the halides MoX_5 and WX_6 ($\text{X} = \text{Cl}, \text{Br}$) with aluminum at lower temperatures:



Near quantitative yields are achieved for the molybdenum halides, but substantially lower yields (50%) are obtained in the synthesis of the tungsten clusters, which require higher temperatures and the use of Vycor reaction vessels. A higher yield low-temperature synthesis was devised by McCarley and co-workers for W_6Cl_{12} using iron as the reducing agent (14).

The chemical reduction of the higher Mo and W halides provides good yields of the octahedral clusters, but the mechanism is obscure. By contrast, chemical oxidation of zero-valent Mo and W leads to the bromo and iodo cluster species in poor yields but provides considerable insight into the formation of these cluster compounds. The reaction of the hexacarbonyls $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ with I_2 at moderately low temperatures produces a mixture of metal halide phases (15, 16). In the reaction $\text{W}(\text{CO})_6$ with I_2 , lower nuclearity clusters have been isolated as reaction intermediates that lead to W_6 species. The tri-, tetra-, and pentanuclear tungsten iodide species are obtained from $\text{W}(\text{CO})_6$ and I_2 by varying reaction times and temperatures, and the

following reaction sequence was proposed by Franolic, Long, and Holm:



The lower nuclearity clusters $[\text{Mo}_5\text{Cl}_{13}]^{2-}$ were isolated from MoCl_5 in $\text{AlCl}_3/\text{KCl}/\text{BiCl}_3/\text{Bi}$ melts that led to the hexanuclear species (17). This is the only intermediate isolated from reaction mixture that produces the $\{\text{Mo}_6\text{Cl}_8\}^{4+}$ core. Solution chemistry has yielded Mo_2 , Mo_3 , and Mo_4 halide species from mononuclear molybdenum complexes, suggesting that a nucleation process similar to that proposed for the tungsten systems may take place during the formation of hexanuclear molybdenum clusters (18–22).

Extraction of the cluster from the products of the solid-state reactions with HX yields the hydronium salts of the molecular species $(\text{H}_3\text{O})_2(\text{M}_6\text{X}_8\text{X}_6) \cdot 6\text{H}_2\text{O}$, which are converted into the polymeric material $\text{M}_6\text{X}_8\text{X}_2\text{X}_{4/2}^a$ under vacuum at 200°C (12, 23). The structure of $\text{M}_6\text{X}_8\text{X}_2\text{X}_{4/2}^a$, also designated M_6X_{12} , consists of a $\{\text{M}_6\text{X}_8\}^{4+}$ core with two terminal axial ligands X_2^a and four axial ligands bridged to neighboring clusters $\text{X}_{4/2}^a$ (11) (Fig. 3). Both M_6X_{12} and $(\text{H}_3\text{O})_2(\text{M}_6\text{X}_8\text{X}_6) \cdot 6\text{H}_2\text{O}$ may serve as precursors to new molecular species containing the metal halide cluster core $\{\text{M}_6\text{X}_8\}^{4+}$.

B. AXIAL LIGAND CHEMISTRY

The ligand substitution chemistry of the axial ligands of the group 6 clusters is considerably more developed than the substitution chem-

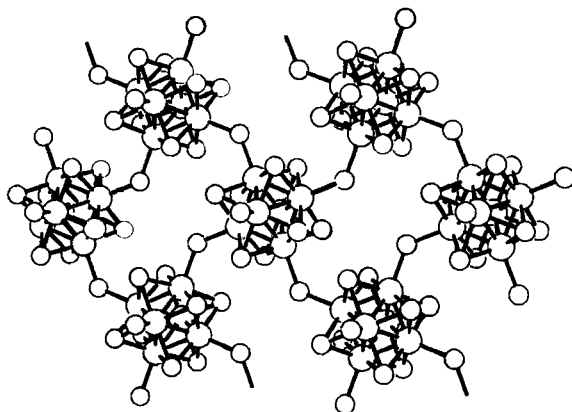


FIG. 3. Structure of $\text{Mo}_6\text{Cl}_8\text{Cl}_2\text{Cl}_{4/2}$. Reprinted with permission from Ref. (130).

istry of the inner ligands. This is due largely to the robust nature of the $\{M_6Y_8\}^{4+}$ core, which requires substantially harsher conditions to displace the inner ligands. The increased lability of the axial ligands enables the coordination environment about the $\{M_6Y_8\}^{4+}$ framework to be altered without disrupting the metal octahedron on the Y_8 cube.

1. Mechanism of Ligand Exchange

Kinetic studies of the ligand exchange reaction



were performed by Sheldon with ^{36}Cl -labeled $[Mo_6Cl_8Cl_6]^{2-}$ in aqueous solutions. The rate-determining step was found to be first order with respect to the molybdenum cluster and independent of halide concentration, and hence the aquation step

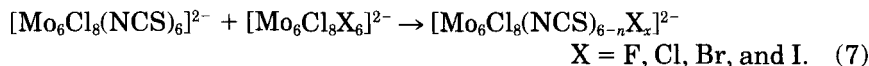


was proposed as rate limiting (24). Schäfer found similar results with the exchange reactions of $[Mo_6Cl_8Cl_6]^{2-}$ and $[W_6Cl_8Cl_6]^{2-}$ with Br^- and I^- (25). Two significant findings from Schäfer's work are the equivalency of the six axial positions and the rate dependence on the metal itself, which show that reactions of molybdenum clusters proceed faster than those of the analogous tungsten complexes.

Pretz substantiated the equivalency of the axial positions for the ligands F^- , Cl^- , Br^- , I^- , and NCS^- by monitoring the ^{19}F and ^{15}N and ^{95}Mo NMR spectra of the ligand exchange reactions



and

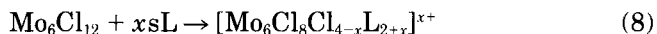


Reaction rates were found to increase with the series $X = Cl < Br < I < SCN < F$, equilibration of the thiocyanate cluster was achieved in 10 h, and 2–3 days were required for the formation of the fluoride cluster at room temperature (26, 27). All the clusters $[Mo_6Cl_8F_{6-n}X_n]^{2-}$ and $[Mo_6Cl_8(NCS)_{6-n}X_n]^{2-}$ including structural isomers (i.e., *mer* or *fac* of $[Mo_6Cl_8F_3X_3]^{2-}$) were identified by NMR. In all cases a statistical

distribution of all possible compounds, inclusive of the ratios for the structural isomers, was obtained. Importantly, no evidence of isomer-steering electronic effects was observed.

2. Synthesis of Molecular $\{M_6Y_8\}$ Clusters

Various types of neutral ligands, including nitrogen donors (12, 23, 28, 29), oxygen donors (12, 28, 30, 31), phosphines (28, 32, 33), and solvent molecules (28, 34, 35), disrupt the extended Mo_6Cl_{12} and W_6Cl_{12} solid structure. Under harsher conditions terminal chloride ligands of Mo_6Cl_{12} are displaced by neutral donor ligand, L:



For instance, addition of PPh_3 to Mo_6Cl_{12} yields $Mo_6Cl_8Cl_4(PPh_3)_2$ at room temperature, but it is necessary to reflux Mo_6Cl_{12} with an excess of PPh_3 in tetrahydrofuran to produce the triphosphine cluster $[Mo_6Cl_8Cl_3(PPh_3)_3]Cl$ (28). Similar experiments by Walton and co-workers with PEt_3 and Mo_6Cl_{12} in refluxing ethanol resulted in the reduced cluster $Mo_6Cl_8Cl_3(PEt_3)_3$, which contains a $\{Mo_6Cl_8\}^{3+}$ core. Magnetic susceptibility measurements conducted on $Mo_6Cl_8Cl_3(PEt_3)_3$ indicate that the cluster is diamagnetic, a result inconsistent with the expected odd number of electrons in the $\{Mo_6Cl_8\}^{3+}$ core. The compound was subsequently reformulated as the reduced species $[Mo_6Cl_8(PEt_3)_6]^{2+}$, which crystallizes with the counteranion $[Mo_6Cl_8Cl_6]^{2-}$ (32). The introduction of two triphenyl phosphine ligands increases the lability of the remaining chloride ligand in the biphosphine cluster $Mo_6Cl_8Cl_4(PPh_3)_2$. Both ethanol and pyridine dissolve Mo_6Cl_{12} , forming the solvent complexes $Mo_6Cl_8Cl_4(solvent)_2$, but dissolution of the biphosphine cluster $Mo_6Cl_8Cl_4(PPh_3)_2$ in these solvents leads to the species $[Mo_6Cl_8Cl_2(PPh_3)_2(HOEt)_2]^{2+}$ and $[Mo_6Cl_8Cl_2(PPh_3)_2(py)_2]^{2+}$ (28).

Neutral clusters with the formula $Mo_6Cl_8Cl_4L_2$ can exist as *cis* or *trans* isomers. Differences in polarity of the *cis* and *trans* structures were employed by Saito and co-workers to separate the isomers of $[Mo_6Cl_8Cl_4(P(n-C_3H_7)_3)_2]$ by chromatography to produce 3 and 15% yields of the *cis* and *trans* respectively (33). The less polar *trans* isomers of $Mo_6Cl_8Cl_4(PR_3)_2$ ($R = n-C_4H_9, n-C_5H_{11}$) have also been isolated in greater than 40% yields (Fig. 4). Shifts in the ^{31}P NMR spectra reveal a preference for the formation of the all-*trans* isomer. DiSalvo and co-workers effected the isomerization of *trans*- $Mo_6Cl_8Cl_4[P(n-C_5H_{11})_3]_2$ into *cis*- $Mo_6Cl_8Cl_4[P(C_2H_5)_3]_2$ by immersing the *trans*- $P(n-C_4H_{11})_3$ cluster in a THF solution of $P(C_2H_5)_3$ (Fig. 5). A 95% conversion

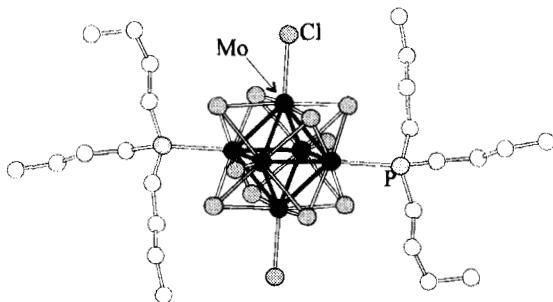


FIG. 4. Structure of *trans*- $\text{Mo}_6\text{Cl}_8\text{Cl}_4[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$.

to the *cis* isomer was obtained (36). Alkylation of the *trans* phosphine clusters $\text{Mo}_6\text{Cl}_8\text{Cl}_4(\text{PR}_3)_2$ with trialkylaluminum reagents AlR'_3 ($\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, \text{and } n\text{-C}_6\text{H}_{13}$) leads to the replacement of two axial chloride ligands with R groups, $\text{Mo}_6\text{Cl}_8\text{Cl}_2(\text{PR}_3)_2(\text{R}')_2$ (Fig. 6). Additional AlR'_3 reacts with $\text{Mo}_6\text{Cl}_8\text{Cl}_2(\text{PR}_3)_2(\text{R}')_2$ producing the trialkyl $\text{Mo}_6\text{Cl}_8\text{Cl}(\text{PR}_3)_2(\text{R}')_3$, and both *mer* and *fac* isomers were shown to be present by ^{31}P NMR. These organometallic derivatives are the only examples in which carbon atoms are directly bound to the metal atoms of the $\{\text{Mo}_6\text{Cl}_8\}^{4+}$ framework.

Addition of two equivalents of sodium methoxide to $\text{Mo}_6\text{Cl}_{12}$ in methanol leads to $[\text{Mo}_6\text{Cl}_8\text{Cl}_4(\text{OCH}_3)_2]^{2-}$ (37). Single-crystal X-ray diffraction reveals that the methoxide ligands occupy axial positions in a *trans* geometry (Fig. 7). However, it is not clear whether the *trans*

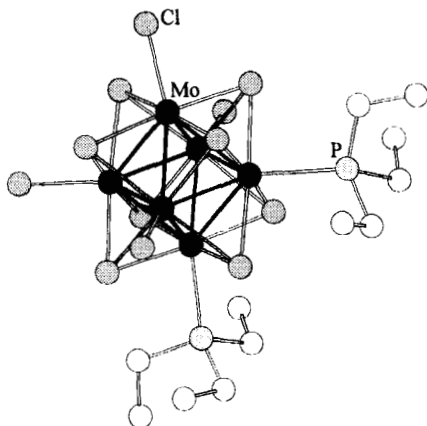


FIG. 5. Structure of *cis*- $\text{Mo}_6\text{Cl}_8\text{Cl}_4[\text{P}(\text{C}_2\text{H}_5)_3]_2$.

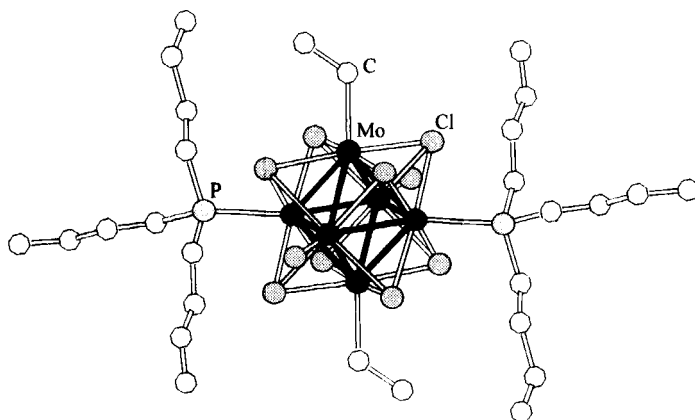


FIG. 6. Structure of all-*trans*- $\text{Mo}_6\text{Cl}_8\text{Cl}_2(\text{C}_2\text{H}_5)_2[\text{P}(\text{C}_2\text{H}_5)_3]_2$.

isomer is formed exclusively or only crystallizes preferentially because neither solution NMR nor X-ray powder pattern data on the bulk material was reported. In contrast to the bisphosphine clusters $\text{Mo}_6\text{Cl}_8\text{Cl}_4(\text{PR}_3)_2$, in which both electronic and steric factors may affect the *cis/trans* ratio of the products, only electronic effects are likely to influence the formation of the *trans* isomer of $[\text{Mo}_6\text{Cl}_8\text{Cl}_4(\text{OCH}_3)_2]^{2-}$. The *trans* isomer of $[\text{Mo}_6\text{Cl}_8\text{Cl}_4\text{Br}_2]^{2-}$ was prepared from crystalline $\text{Mo}_6\text{Cl}_8\text{Cl}_4(\text{H}_2\text{O})_2$ in a heterogeneous reaction with Br^- . Homogeneous mixtures of $\text{Mo}_6\text{Cl}_8\text{Cl}_4(\text{H}_2\text{O})_2$ and $\text{LiBr}/[(\text{C}_6\text{H}_5)_4\text{As}]\text{Br}$ lead to bromide-rich clusters $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Mo}_6\text{Cl}_8\text{Cl}_{1.2}\text{Br}_{4.8}]$ after only 30 min (35).

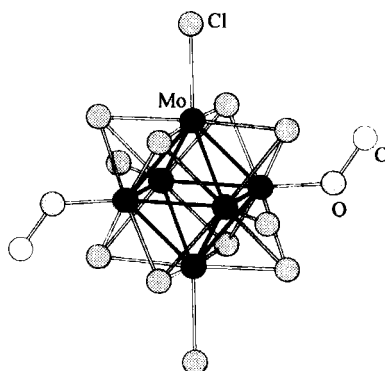
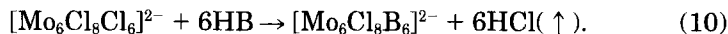
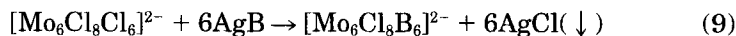


FIG. 7. Structure of *trans*- $[\text{Mo}_6\text{Cl}_8\text{Cl}_4(\text{OCH}_3)_2]^{2-}$.

Mixed halo clusters $(\text{H}_3\text{O})_2\text{M}_6\text{Cl}_8\text{Y}_6$ ($\text{M} = \text{Mo}, \text{W}; \text{Y} = \text{F}, \text{Br}, \text{I}$) have been prepared from the aqueous acids HY and $\text{Mo}_6\text{Cl}_{12}$ (12, 27, 32, 35). It is likely the substitution results from an excess of the acid, HX , rather than the relative affinities of the $\{\text{Mo}_6\text{Cl}_8\}^{4+}$ core for the halide, X^- , ions. Dehydration of $(\text{H}_3\text{O})_2[\text{Mo}_6\text{Cl}_8\text{Y}_6]$ leads to the mixed ligand bridged systems $\text{Mo}_6\text{Cl}_8\text{Y}_2\text{Y}_{4/2}$, which are analogous in structure and reactivity to $\text{Mo}_6\text{Cl}_{12}$ in that addition of 2L produces $\text{Mo}_6\text{Cl}_8\text{Y}_4\text{L}_2$. One of the first comparative studies of the mixed halide clusters $\text{Mo}_6\text{Cl}_8\text{Y}_2\text{Y}_{4/2}$ ($\text{Y} = \text{Cl}, \text{Br}, \text{and I}$) revealed that the axial iodide ligands of $\text{Mo}_6\text{Cl}_8\text{I}_2\text{I}_{4/2}$ are more susceptible to displacement by nitrobenzene than the terminal bromide or chloride ligands of $\text{Mo}_6\text{Cl}_8\text{Y}_2\text{Y}_{4/2}$ ($\text{Y} = \text{Cl}, \text{Br}$) (23). Dissolution of $\text{Mo}_6\text{Cl}_8\text{I}_2\text{I}_{4/2}$ in nitrobenzene produces $[\text{Mo}_6\text{Cl}_8\text{I}_3(\text{NO}_2\text{C}_6\text{H}_5)_3]\text{I}$, and the bromo and chloro derivatives yield bis-nitrobenzene complexes $\text{Mo}_6\text{Cl}_8\text{Y}_4(\text{NO}_2\text{C}_6\text{H}_5)_2$.

Strongly basic anions such as hydroxide and alkoxide easily displace the axial chloride ligands of $[\text{Mo}_6\text{Cl}_8\text{Cl}_6]^{2-}$; thus, titration of $[\text{Mo}_6\text{Cl}_8\text{Cl}_6]^{2-}$ with OH^- initially precipitates the tetrahydroxo cluster $\text{Mo}_6\text{Cl}_8(\text{OH})_4(\text{H}_2\text{O}) \cdot 14\text{H}_2\text{O}$, which redissolves as the hexahydroxo cluster $[\text{Mo}_6\text{Cl}_8(\text{OH})_6]^{2-}$ with increasing pH (23). Similarly, when $\text{Mo}_6\text{Cl}_{12}$ is refluxed with sodium alkoxides in alcohol solution, the alkoxide substitutes for all of the axial chloride ligands (35, 39). Methoxide, ethoxide, and pentafluorophenoxide clusters $[\text{Mo}_6\text{Cl}_8(\text{OR})_6]^{2-}$ have also been generated by this method (35, 38).

Increased lability of the axial positions has been achieved by introducing weakly coordinating ligands such as triflate (trifluoromethanesulfonate) (40, 41), tetrafluoroborate (26, 42–45), nitrate (43, 46, 47) tosylate (40), trifluoroacetate (40, 48), and perchlorate (34). (*Caution: perchlorate complexes are hazardously explosive.*) Reactions of the chloro cluster $[\text{Mo}_6\text{Cl}_8\text{Cl}_6]^{2-}$ with the silver salt or the protonated form of the weakly coordinating base B^- generate the reactive species $[\text{Mo}_6\text{Cl}_8\text{B}_6]^{2-}$:



Only the axial chloride ligands were abstracted by the silver salts or acids, leaving the inner ligands and the $\{\text{Mo}_6\text{Cl}_8\}^{4+}$ core intact. The weakly coordinating ligands are easily displaced by anionic, X^- , or neutral ligands, L , generating the hexasubstituted clusters $[\text{Mo}_6\text{Cl}_8\text{X}_6]^{2-}$ or $[\text{Mo}_6\text{Cl}_8\text{L}_6]^{4+}$. Cotton and Curtis first employed this strategy with AgClO_4 to prepare the first tetracationic clusters with

the $\{\text{Mo}_6\text{Cl}_8\}^{4+}$ unit, $[\text{Mo}_6\text{Cl}_8(\text{solvent})_6](\text{ClO}_4)_4$ (solvent = DMF or DMSO) (34). These compounds demonstrate the utility of using weakly coordinating ions to alter the coordination environments about the $\{\text{Mo}_6\text{Cl}_8\}^{4+}$ core, but they are potentially explosive.

The triflate derivative $[\text{Mo}_6\text{Cl}_8(\text{OSO}_2\text{CF}_3)_6]^{2-}$ (Fig. 8), has been used extensively in our laboratory to prepare new cluster derivatives with neutral ligands not previously observed to bind to the $\{\text{Mo}_6\text{Cl}_8\}^{4+}$ core in all six axial positions. Limits of the substitutional lability of the triflate ligand of $[\text{Mo}_6\text{Cl}_8(\text{OSO}_2\text{CF}_3)_6]^{2-}$ have been explored with ^{19}F NMR (49). Diagnostic shifts in the ^{19}F NMR signal of coordinated and uncoordinated (free) $\text{OSO}_2\text{CF}_3^-$ may be employed to monitor the displacement reactions. As expected, only one peak is observed in the ^{19}F NMR spectrum of $[\text{Mo}_6\text{Cl}_8(\text{OSO}_2\text{CF}_3)_6]^{2-}$ in noncoordinating methylene chloride. Two peaks are observed with THF, acetonitrile, and acetone, suggesting incomplete substitution of the triflate ligand by solvent molecules. A single peak is observed for $[\text{Mo}_6\text{Cl}_8(\text{OSO}_2\text{CF}_3)_6]^{2-}$ in both DMSO and methanol, indicating that the triflate ligands are completely displaced in these solvents (49). Titration of $[\text{Mo}_6\text{Cl}_8(\text{OSO}_2\text{Cl}_8)]^{2-}$ in methylene chloride with phosphine ligands PR_3 (R = Et, *t*-butyl, Ph) generates all possible species $[\text{Mo}_6\text{Cl}_8(\text{OSO}_2\text{CF}_3)_{6-x}(\text{PR}_3)_x]^{2-x-}$ ($0 \leq x \leq 6$) as determined by ^{31}P NMR. Unlike the ligand exchange reactions between $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ and $[\text{Mo}_6\text{Cl}_8\text{Y}_6]^{2-}$ (Y = Cl, Br, I, and NCS), in which a statistical distribution of products was formed (26, 27), the $x = 2$ species is disfavored in the phosphine titration reactions. This may be due in part to the polar CH_2Cl_2 solvent, which may disfavor the neutral species. Interestingly species

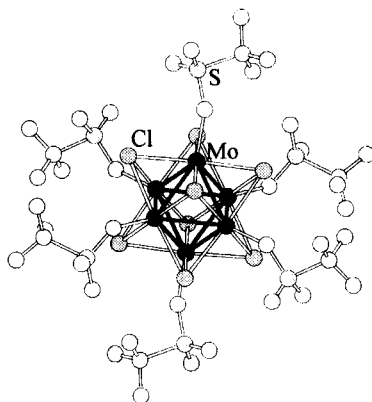


FIG. 8. Structure of $[\text{Mo}_6\text{Cl}_8(\text{OSO}_2\text{CF}_3)_6]^{2-}$.