Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Tables of hydrogen atom positions and thermal displacement parameters for $Cr_2(O_2CCPh_3)_4 \cdot {}^3/_2C_6H_4F_2$ and for $Cr_2(O_2CCPh_3)_4 \cdot C_6H_4Me_2 \cdot C_6H_{14}$ and bond distances and angles for the (disordered) lattice hexane molecule in $Cr_2(O_2CCPh_3)_4 \cdot C_6H_4Me_2 \cdot C_6H_{14}$ (7 pages); tables of observed and calculated structure factors for both compounds (10 pages). Ordering information is given on any current masthead page.

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Preparation of Bis(tetrabutylammonium) Octa(μ_3-chloro)hexakis(trifluoromethanesulfonato)-*octahedro*-hexamolybdate(2–), $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$: A Versatile Starting Material for Substituted Mo(II) Clusters Containing the $[Mo_6Cl^i_8]^{4+}$ Core

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The useful starting material $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$, was synthesized in high yield by the reaction of $(Bu_4N)_2[Mo_6Cl^i_8Cl^a_6]$ with $AgCF_3SO_3$ in CH_2Cl_2. The crystal structure of the benzyltrimethylammonium salt of this cluster reveals an average Mo–Mo distance of 2.593 (4) Å, an average Mo–Cl distance of 2.465 (4) Å, and an average Mo–O distance of 2.126 (9) Å. The triflate ligands, $CF_3SO_3^-$, are readily substituted by other ligands. Convenient routes are reported for the preparation of the clusters $[Mo_6Cl^i_8X^a_6]^{2-}$, X = Cl^-, Br^-, I^-, SCN^-, OMe^-, $CH_3CO_2^-$, $CH_3C_6H_4SO_3^-$, and $CF_3CO_2^-$; the latter three are new. These anionic clusters were characterized by IR, UV–vis and fast atom bombardment mass spectrometry. Solution IR data of the title compound in dimethylformamide are consistent with the complete displacement of the triflate ligands by the solvent, only partial displacement is observed in acetone, and the cluster retains all $CF_3SO_3^-$ ligands in CH_2Cl_2. The isolation of the new cationic clusters, $[Mo_6Cl^i_8L^a_6]$,$^{4+}$ with L = C_5H_5NO, $(C_6H_5CH_2)_2SO$, and $(C_6H_5)_3PO$, as triflate salts is also described. Crystal data for $(BzMe_3N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ are as follows: triclinic space group, $P\bar{1}$ (No. 2); a = 11.036 (2) Å, b = 11.553 (3) Å, c = 12.010 (2) Å; α = 79.05 (2)°, β = 78.06 (1)°, γ = 86.58 (2)°; V = 1471 (1) Å^3; Z = 1.

Introduction

The early d-block halide clusters of group 6, such as $[Mo_6Cl_{14}]^{2-}$ and $[W_6Cl_{14}]^{2-}$, were the first metal clusters to be structurally characterized.[1] Their ligand substitution chemistry has been extensively explored,[2] and metal–metal bonding in these systems has been investigated theoretically.[3] Recently these compounds have been shown to exhibit interesting redox chemistry and photophysical properties.[4] The existence of related groups 4 and 5 clusters[5] and the superconducting Chevrel phases, e.g. $PbMo_6S_8$,[6] adds further interest to the octahedral clusters containing π-donor ligands.

The Mo(II) chloride cluster consists of a substitution resistant core of $[Mo_6Cl_8]^{4+}$ with eight face-bridging inner ligands (labeled i)[7] and six semilabile terminal outer ligands (labeled a).[7] For example, anionic clusters such as $[Mo_6Cl^i_8X^a_6]^{2-}$ (where X = Cl^-, Br^-, I^-, or OH^-) are known as well as neutral compounds of the type $[Mo_6Cl^i_8Cl^a_4L^a_2]$ (where L = a neutral ligand).[2] Many compounds with four outer chlorides and two other outer ligands have been reported, but the replacement of all six chlorides is difficult unless the substituting ligand is another halide or pseudo-halide.[2e,j] Moreover, the synthetic procedures for these compounds are specific for a given class of compounds and occasionally require long reaction times. More labile terminal ligands than chloride are needed to extend and facilitate the preparative chemistry of these interesting clusters. Although the perchlorate ligand has been explored in this context, the explosive nature of this cluster complex greatly decreases the synthetic utility of $[Mo_6Cl^i_8(dmf)^a_6][ClO_4]_4$.[8]

We report the preparation of a new Mo(II) cluster compound having easily replaceable ligands and the crystal structure of the bis(benzyltrimethylammonium) salt and demonstrate the use of $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ in the preparation under mild conditions of other clusters containing anionic and neutral ligands. The salt compound $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ is soluble in the poorly coordinating solvent CH_2Cl_2, which minimizes competition with ligands.

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Experimental Section

The Mo(II) cluster $(H_3O)_2[Mo_6Cl^i_8Cl^a_6]\cdot 6H_2O$ was prepared by the method of Dorman and McCarley.[9] It was converted to the tetrabutylammonium (Bu_4N^+) salt by addition of excess Bu_4NCl to an ethanol solution of the cluster.[4b] The precipitated $(Bu_4N)_2[Mo_6Cl^i_8Cl^a_6]$ was recrystallized by slow evaporation of an acetone solution. The benzyltrimethylammonium and bis(triphenylphosphine)iminium (PPN^+) salts were also prepared by this method. Silver trifluoromethanesulfonate, silver *p*-toluenesulfonate, silver trifluoroacetate, benzyltrimethylammonium chloride, tetrabutylammonium chloride, tetrabutylammonium iodide, potassium iodide, tetrabutylammonium hydroxide, triphenylphosphine oxide, sodium methoxide, and dibenzyl sulfoxide were used as received from Aldrich. Bis(triphenylphosphine)iminium chloride was used as received from Alfa. Reagent grade pyridine *N*-oxide, potassium thiocyanate, and sodium bromide were used without further purification. Tetrabutylammonium acetate was prepared from acetic acid and tetrabutylammonium hydroxide.

The following procedures were carried out in a dry nitrogen atmosphere using standard Schlenk and syringe techniques unless otherwise stated. All solvents, dichloromethane, tetrahydrofuran (THF), acetone, diethyl ether, ethanol, and methanol, were dried and freshly distilled before use. The replacement of the six inert, terminal chloride ligands with more labile ligands (triflate, trifluoroacetate and tosylate) was accomplished by addition of the appropriate silver salt in CH_2Cl_2 to $(Bu_4N)_2[Mo_6Cl^i_8Cl^a_6]$. The other clusters were prepared by the substitution of triflate ligands in $[Mo_6Cl^i_8(CF_3SO_3)^a_6]^{2-}$ with the Bu_4N^+ salt of the desired anion or the neutral ligand in CH_2Cl_2. In other syntheses, the appropriate alkali-metal salt of the desired anion in methanol was employed. The solubility of the starting substances and the separation of the desired cluster from byproducts determined the choice of procedure.

Synthesis of $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$, $(Bu_4N)_2[Mo_6Cl^i_8(CF_3CO_2)^a_6]$, and $(Bu_4N)_2[Mo_6Cl^i_8(CH_3C_6H_4SO_3)^a_6]$. A slurry of 1.0 g (0.64 mmol) of $(Bu_4N)_2[Mo_6Cl^i_8Cl^a_6]$ and 1.1 g (4.3 mmol) of $Ag(CF_3SO_3)$ in 15 mL of CH_2Cl_2 was stirred overnight in the absence of light. The precipitated AgCl was removed by filtration through a medium-porosity glass frit containing Celite as a filter aid. The volume of the filtrate was reduced to 3–5 mL under vacuum at room temperature and 20 mL of diethyl ether was layered onto the CH_2Cl_2. The large, lemon yellow crystals were collected by vacuum filtration and washed with two portions (5 mL) of ether to yield 1.3 g (93%) of product. The benzyltrimethylammonium or the bis(triphenylphosphine)iminium (PPN^+) salts of the chloride cluster, $[Mo_6Cl^i_8Cl^a_6]^{2-}$, were used to obtain crystals of the corresponding salts of $[Mo_6Cl^i_8(CF_3SO_3)^a_6]^{2-}$ in high yield. In solution the triflate ligands are readily replaced by water and the solid is slightly hygroscopic; therefore, the solid was stored in a dry N_2 atmosphere. Anal. Calcd for $C_{38}H_{72}N_2Mo_6Cl_8F_{18}S_6O_{18}$: C, 20.38; H, 3.24; N, 1.25. Found: C, 20.29; H, 3.21; N, 1.35.

The same synthetic procedure was used with $Ag(CF_3CO_2)$ or $Ag(CH_3C_6H_4SO_3)$ in place of $Ag(CF_3SO_3)$. Anal. Calcd for $(Bu_4N)_2[Mo_6Cl^i_8(CF_3CO_2)^a_6]$, $C_{44}H_{72}N_2Mo_6Cl_8F_{18}O_{12}$: C, 26.11; H, 3.58; N, 1.38. Found: C, 26.14; H, 3.57; N, 1.33.

Anal. Calcd for $(Bu_4N)_2[Mo_6Cl^i_8(CH_3C_6H_4SO_3)^a_6]$, $C_{74}H_{114}N_2Mo_6Cl_8O_{18}S_6$: C, 37.48; H, 4.85; N, 1.18. Found: C, 37.53; H, 4.68; N, 1.19.

General Synthesis of $(Bu_4N)_2[Mo_6Cl^i_8X^a_6]$ ($X = Cl^-, Br^-, I^-, CH_3CO_2^-$). A solution of $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ (0.200 g, 0.089 mmol) in 5 mL of CH_2Cl_2 was added dropwise to an excess (approximately 0.60 mmol) of the tetrabutylammonium salt of the anion in 3 mL of CH_2Cl_2. Anhydrous diethyl ether was layered over the CH_2Cl_2 solution and crystals of the Bu_4N^+ salt of the $[Mo_6Cl^i_8L^a_6]^{2-}$ cluster formed. Yield: for $X = Cl^-$, 68% recrystallized from CH_2Cl_2; for $X = Br^-$, 66%, recrystallized from THF; for $X = I^-$, 93%, not recrystallized. In the case where $X = CH_3CO_2^-$, an oil was initially obtained in the precipitation from CH_2Cl_2/ether. The solution was decanted and the oil was extracted 3 times with 10 mL of anhydrous ether. Recrystallization from CH_2Cl_2 produced yellow crystals of $(Bu_4N)_2[Mo_6Cl^i_8(CH_3CO_2)^a_6]$. Yield: 0.10 g (67%). Anal. Calcd for $C_{44}H_{90}N_2Mo_6Cl_8O_{12}$: C, 31.10; H, 5.34; N, 1.65. Found: C, 31.03; H, 5.38; N, 1.62.

Alternative Synthesis for $(Bu_4N)_2[Mo_6Cl^i_8X^a_6]$ ($X = Br^-, I^-, SCN^-$). Solid $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ (0.10 g, 0.045 mmol) and 0.30 mmol of the alkali-metal salt were combined in 5 mL of methanol and stirred. The product was generally insoluble in methanol. The methanol was removed under vacuum and CH_2Cl_2 was added to dissolve the Bu_4N^+ salt of the cluster (in the case of I^-, 25 mL of CH_2Cl_2 per 0.1 g of cluster). The solution was filtered to remove the excess alkali-metal salt and the triflate byproduct. The filtrate was reduced in volume and diethyl ether was added to precipitate the crystalline product. The yield for $X = Br^-$ was 79% (starting with NaBr), $X = I^-$ was 79% (starting with KI), and $X = SCN^-$ was 93% (starting with KSCN).

Synthesis of $Na_2[Mo_6Cl^i_8(OMe)^a_6]$. This procedure is similar to that described as the "alternative" synthesis for the halide and pseudo-halide derivatives. $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ (0.200 g, 0.089 mmol) and $NaOCH_3$ (0.050 g, 0.925 mmol) were each dissolved in 10 mL of MeOH. The cluster solution was added to the $NaOCH_3$ solution dropwise with stirring. The volume of the yellow solution was reduced to ca. 2 mL. Addition of 30 mL of Et_2O precipitated bright yellow microcrystals which were dried in vacuo. Yield (OCH_3): 0.075 g (75%). Anal. Calcd for $C_6H_{18}Mo_6Cl_8Na_2O_6$: C, 6.60; H, 1.66. Found: C, 6.88; H, 1.53. NMR (MeOD, 300 MHz): $\delta_{OCH_3} = 3.81$ ppm, singlet.

Synthesis of $[Mo_6Cl^i_8(C_5H_5NO)^a_6](CF_3SO_3)_4$. A CH_2Cl_2 solution of 0.10 g (0.045 mmol) of $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ was added dropwise to a solution of 0.10 g (1.05 mmol) of pyridine *N*-oxide in 20 mL of CH_2Cl_2. The flask containing the cluster was rinsed with 5 mL of CH_2Cl_2 and this was added to the reaction flask. After approximately 1 min the solution became cloudy and the stirring was ceased. The very fine crystals which formed were collected by vacuum filtration. The cluster was only slightly soluble in CH_2Cl_2 but very soluble in acetone. However, recrystallization from acetone was not successful, either an amorphous solid or an oil was formed. Yield: 0.06 g (66%). Anal. Calcd for $C_{34}H_{30}N_6Mo_6Cl_8O_{18}F_{12}S_4$: C, 20.14; H, 1.54; N, 4.15. Found: C, 20.06; H, 1.44; N, 4.11.

Synthesis of $[Mo_6Cl^i_8((C_6H_5)_3PO)^a_6](CF_3SO_3)_4$. A solution of 0.200 g (0.089 mmol) of $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ in 10 mL of CH_2Cl_2 was added slowly to a solution of 0.150 g (0.539 mmol) of triphenylphosphine oxide in 10 mL of CH_2Cl_2. The light yellow solution was stirred for 10 min and the volume was reduced to ca. 2 mL. Dropwise addition of 4 mL of Et_2O resulted in the slow precipitation of light yellow crystals. Excess Et_2O leads to coprecipitation of $(Bu_4N)CF_3SO_3$. Yield: 0.200 g (72%). Anal. Calcd for $C_{112}H_{90}P_6Mo_6Cl_8F_{12}O_{18}S_4$: C, 43.04; H, 2.90; P, 5.95. Found: C, 42.41; H, 2.92; P, 6.01.

Synthesis of $[Mo_6Cl^i_8(DBSO)^a_6](CF_3SO_3)_4$ (DBSO = Dibenzyl Sulfoxide). A CH_2Cl_2 solution of 0.100 g (0.035 mmol) of $(PPN)_2[Mo_6Cl^i_6(CF_3SO_3)^a_6]$ was added dropwise to a solution of excess dibenzyl sulfoxide in 10 mL of CH_2Cl_2. A pale yellow precipitate formed immediately upon addition of the cluster solution. The solid was isolated by filtration, washed with 5 mL of Et_2O, and dried in vacuo. Yield: 0.080 g (80%). Anal. Calcd for $C_{88}H_{84}S_{10}Mo_6Cl_8F_{12}O_{18}$: C, 37.25; H, 2.98; S, 11.30. Found, C, 37.78; H, 2.83; S, 11.67.

Instrumentation. The infrared spectra for all compounds were measured at 2 cm^{-1} resolution using a Bomem MB-100 FT-IR equipped with a DTGS detector. Mull spectra were collected using Nujol between KBr plates.

In situ solution spectra were measured using an Axiom Analytical DPR-111 FT-IR deep immersion probe[10] coupled to a Bomem MB-120 spectrometer equipped with an MCT detector. The UV-vis measurements were made using a Perkin-Elmer Model 330 spectrophotometer. The 1.00-cm cell was designed so that the solution could be kept under an inert atmosphere. The liquid secondary ion (colloquially FAB) mass spectra were run on a VG-70 SE double-focusing high-resolution mass spectrometer. Cesium iodide were used as the primary ion source, and *m*-nitrobenzyl alcohol was used as the matrix. The primary source current was 1 μA, and 30 kV of ion beam was used to sputter the liquid sample surface. Negative ion detection was used to collect all of the mass spectral data.

Crystal Structure. Yellow crystals of $(BzMe_3N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of the cluster. A crystal measuring 0.34 × 0.33 × 0.13 mm was mounted on a glass fiber and transferred to the N_2 cold stream (−120 °C) of an Enraf-Nonius CAD-4 diffractometer. All measurements were made using graphite monochromated Mo $K\alpha$ radiation. A set of 25 reflections were used to generate a least-squares refined reduced unit cell corresponding to the triclinic group. The cell dimensions were verified by axial photographs. The space group $P\bar{1}$ (No. 2) was confirmed by the average values of the normalized structure factors and the successful solution and refinement of the structure. The data were collected ($-h, \pm k, \pm l$), using the ω/θ scan technique to a maximum 2θ value of 51.9°. This gave 6073 total reflections, 5753 unique reflections, and 4832 observed ($I > 3.00\sigma$) reflections. A summary of the crystallographic data is given in Table V. The intensities of three standard reflections were monitored at 90-min intervals and no appreciable decay was observed. The data were corrected for absorption, secondary extinction, Lorentz, and polarization effects. Analytical absorption corrections were applied resulting in transmission factors ranging from 0.58 to 0.80.

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Table I. Infrared Spectra of Solid $NaCF_3SO_3$ and of $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ in Nujol and Three Different Solvents[a]

assignment[b]	$NaCF_3SO_3$[b]	$(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$			
		Nujol	CH_2Cl_2	DMF	acetone
$\nu_{as}(SO_3)$[c]	1280	1343	1349	1275	1274
		1199, 1181 (sh)	1205		1341
					1199
$\nu_s(CF_3)$	1232	1234	1237	1223	1240
$\nu_{as}(CF_3)$	1168	1162	1167	1152	1166
					1151
$\nu_s(SO_3)$	1036	990	994	1034	1034
					989

[a] All values have the unit cm^{-1}. [b] Data from: Miles, M. G.; Doyle, G.; Cooney, R. P.; Tobias, R. S. *Spectrochim. Acta* **1969**, *25*, 1515. Assignments from: Buerger, H.; Burczyk, K.; Blaschette, A. *Monatsh. Chem.* **1970**, *101*, 102. [c] This degenerate stretching mode is split for coordinated CF_3SO_3.

Table II. Characteristic Infrared Bands for Ligands Coordinated to $[Mo_6Cl^i_8]^{4+}$ [a]

compound	infrared band, cm^{-1}	assignment
$(Bu_4N)_2[Mo_6Cl^i_8(SCN)^a_6]$	2019	$\nu(C{\equiv}N)$[b]
	2041	$\nu(C{\equiv}N)$
$(Bu_4N)_2[Mo_6Cl^i_8(CH_3CO_2)^a_6]$	1628	$\nu(C{=}O)$[c]
	1360	$\nu(C{-}O)$
$(Bu_4N)_2[Mo_6Cl^i_8(CF_3CO_2)^a_6]$	1704	$\nu(C{=}O)$[c]
	1403	$\nu(C{-}O)$
$(Bu_4N)_2[Mo_6Cl^i_8CH_3C_6H_4SO_3)^a_6]$	956	$\nu_s(SO_3)$[d]
$Na_2[Mo_6Cl^i_8(OCH_3)^a_6]$	1047	$\nu(C{-}O)$[e]
$[Mo_6Cl^i_8(C_5H_5NO)^a_6](CF_3SO_3)_4$	1193	$\nu(N{=}O)$[f]
$[Mo_6Cl^i_8(Ph_3PO)^a_6](CF_3SO_3)_4$	1062	$\nu(P{=}O)$[g]
$[Mo_6Cl^i_8(DBSO)^a_6](CF_3SO_3)_4$	936	$\nu(S{=}O)$[h]

[a] All spectra were taken as Nujol mulls. [b] By comparison to values reported in ref 2j. [c] Baillie, M. J.; Brown, D. H.; Moss, K. C.; Sharp, D. W. A. *J. Chem. Soc. A* **1968**, 3110. [d] By comparison to spectrum obtained for $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$. [e] By comparison to values reported in ref 2h. [f] Garvey, R. G.; Nelson, J. H.; Ragsdale, R. O. *Coord. Chem. Rev.* **1968**, *3*, 375. [g] By comparison to values reported in ref 2d. [h] By comparison to values reported in ref 8.

All calculations were performed using the TEXSAN7 crystallographic software package. The structure was solved by direct methods. Atomic scattering factors[11] and anomalous dispersion terms[12,13] were taken from the literature. All non-hydrogen atoms were refined anisotropically. Initial solution and refinement suggested that one of the three crystallographically unique triflate groups is disordered over two different sites. The occupancy of the two sites, A and B, was refined resulting in populations of 0.65 and 0.34, respectively. Final full matrix least-squares refinement converged to a final R value of 0.024 (R_w = 0.033). The largest peak in the final difference map was 0.70 e/Å^3.

Results

Synthesis. Two methods were developed for preparing Mo(II) chloride clusters with different terminal ligands, $[Mo_6Cl^i_8X^a_6]^n$, where $n = +4$ or -2. In the first, metathesis with a silver salt, AgX (X = $CF_3SO_3^-$, $CF_3CO_2^-$, $CH_3C_6H_5SO_3^-$) was used. When X = $CH_3C_6H_4SO_3^-$ or $CH_3CO_2^-$, this method produced an amorphous solid. In the second method, the triflate ligands on $[Mo_6Cl^i_8(CF_3SO_3)^a_6]^{2-}$ were substituted by the desired ligand in either CH_2Cl_2 or methanol.

IR. The IR bands of the triflate ion as a ligand in the cluster and as an uncoordinated anion in sodium triflate are listed in Table I. The results of the attenuated total reflectance (ATR) IR study of $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$ in DMF, acetone, and CH_2Cl_2 are also listed in Table I. Ligand IR bands that are sensitive to coordination are listed in Table II.

Table III. UV–vis Spectra of $[Mo_6Cl^i_8L^a_6]^n$, $n = +4$ or -2[a]

L	λ_{max}, nm	$10^{-4}\epsilon$, L mol^{-1} cm^{-1}	ref
$CH_3CO_2^-$	285	0.43	this work
$CF_3CO_2^-$	288	0.39	this work
$CF_3SO_3^-$	296	0.33	this work
Cl^-	313	0.319	2j
	313	0.32	this work
Br^-	350	0.38	this work
	240	15.7[b]	
I^-	282	22	this work
SCN^-	283	14.9	2j
$(C_6H_5)_3PO$	295	0.64	this work
	264	3.0	
	260 sh	2.9	

[a] All spectra taken in dichloromethane. [b] Peak on the edge of the solvent absorption.

Table IV. FAB Mass Spectrometry Data and Analysis for the Tetrabutylammonium Molybdenum(II) Halide Clusters and Their Derivatives

species	mass (highest intensity)		rel intens	R, %
	calcd	obsd		
$\{(Bu_4N)[Mo_6Cl^i_8Cl^a_6]^-\}$	1315	1315	0.52	1.24
$\{[Mo_6Cl^i_8Cl^a_6]^-\}$	1073	1072	0.45	1.93
$\{[Mo_6Cl^i_8Cl^a_5]^-\}$	1036	1035	1.00	1.82
$\{(Bu_4N)[Mo_6Cl^i_8Br^a_6]^-\}$	1581	1582	0.46	5.24
$\{[Mo_6Cl^i_8Br^a_6]^-\}$	1339	1338	0.31	1.79
$\{[Mo_6Cl^i_8Br^a_5]^-\}$	1260	1260	1.00	1.69
$\{(Bu_4N)[Mo_6Cl^i_8I^a_6]^-\}$	1863	1864	0.50	1.77
$\{[Mo_6Cl^i_8I^a_5]^-\}$	1494	1494	1.00	1.35
$\{(Bu_4N)[Mo_6Cl^i_8(SCN)^a_6]^-\}$	1450	1451	1.00	1.73
$\{[Mo_6Cl^i_8(SCN)^a_5]^-\}$	1149	1149	0.56	2.13
$\{(Bu_4N)[Mo_6Cl^i_8(CF_3SO_3)^a_6]^-\}$	1997	1997	0.76	3.22
$\{[Mo_6Cl^i_8(CF_3SO_3)^a_5]^-\}$	1604	1605	1.00	4.71
$\{[Mo_6Cl^i_8(CF_3SO_3)^a_4(O)^a]^-\}$	1471	1473	0.42	6.89
$\{(Bu_4N)[Mo_6Cl^i_8(tosyl)^a_6]^-\}$	2130	2128	1.00	2.53
$\{[Mo_6Cl^i_8(tosyl)^a_5]^-\}$	1715	1717	0.36	4.60

UV–Visible. The absorption peaks and their molar absorptivities for the clusters are listed in Table III. Most of the clusters have a broad peak between 280 and 350 nm with a molar absorptivity of 3000–7000 M^{-1} cm^{-1}. The clusters with terminal iodide and thiocyanate ligands have sharper, more intense absorptions in this region.

Mass Spectrometry. FAB-MS was used to characterize the anionic clusters, $(Bu_4N)_2[Mo_6Cl^i_8X^a_6]$ (X = Cl^-, Br^-, I^-, SCN^-, $CF_3SO_3^-$, $CH_3C_6H_4SO_3^-$) (see Table IV). The three highest mass envelopes correspond to the parent anion paired with one cation, the parent anion with a single negative charge, and the parent anion minus one ligand. For each envelope, the individual masses correspond to the expected isotopic distribution.

The mass distributions in the FAB mass spectra are quite broad because molybdenum has seven naturally occurring isotopes. Each envelope of peaks was compared to the theoretical mass distribution for the assigned species. An R factor (analogous to a crystallographic R factor) was calculated to provide a quantitative measure of the fit. Peaks 10 mass units on either side of the most intense peak in the observed spectrum were used in this calculation. Previous workers[14] have determined that the mass spectral assignments are satisfactory when the values of R are roughly similar to those in acceptable crystal structure determinations; i.e., a value less than 5% represents an excellent fit. According to this criterion, the mass envelopes are convincingly assigned.

Crystal Structure. An ORTEP diagram of the anion is shown in Figure 1, which displays the disordered triflate ligand only in the position with higher occupancy. For clarity, only the crystallographically unique molybdenum and chlorine atoms are la-

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(11) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(12) Ibers, J. A.; Hamilton, W. C. *Acta. Crystallogr.* **1974**, *17*, 781.

(13) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(14) Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 1556.

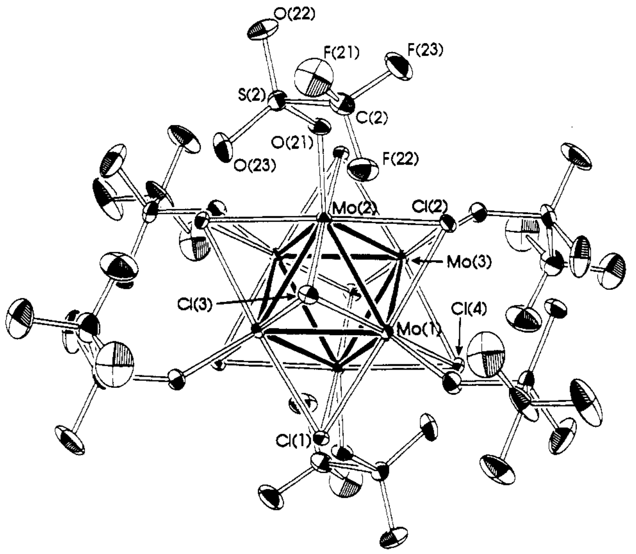

Figure 1. ORTEP diagram for the anion of $(BzMe_3N)_2[Mo_6Cl^i{}_8(CF_3SO_3)^a{}_6]$. Thermal ellipsoids are drawn at 35% probability. See text for description of labeling scheme.

Table V. Crystallographic Data for $(BzMe_3N)_2[Mo_6Cl^i{}_8(CF_3SO_3)^a{}_6]$

empirical formula	$[Mo_6Cl_8S_6F_{18}O_{18}N_2C_{26}H_{32}]$
formula weight	2054.14
space group	$P\bar{1}$ (No. 2)
a, Å	11.036 (2)
b, Å	11.553 (3)
c, Å	12.010 (2)
α, deg	79.05 (2)
β, deg	78.06 (1)
γ, deg	86.58 (2)
V, Å^3	1471 (1)
Z	1
ρ_{calcd}, g/cm^3	2.319
μ, cm^{-1} (Mo Kα)	19.01
transmission coeff	0.58–0.80
radiation	Mo Kα (λ = 0.71069 Å)
T, °C	−120
$R(F)^a$	0.024
$R_w(F)^b$	0.033

$^a R(F) = [\sum|(|F_o| - |F_c|)|/\sum|F_o|]$. $^b R_w(F) = [(\sum w(|F_o| - |F_c|)^2)/\sum wF_o{}^2]^{1/2}$. $w = 4F_o{}^2/\sigma^2(F_o{}^2)$.

beled in the ORTEP diagram. The numbering scheme for the triflate atoms is as follows: The first digit specifies the molybdenum atom to which the triflate is bound. The second digit, if present, indicates consecutive atoms of the same type within a single triflate group. The oxygen labeled O(X1) (where X = 1, 2, 3) is always the oxygen bound to the molybdenum labeled Mo(X). The two positions of the disordered triflate [bound to Mo(2)] are labeled A and B, with position A having the higher occupancy (0.65). A summary of the crystal data is given in Table V. The final positional parameters for the anion are listed in Table VI. A list of selected bond length and bond angles is given in Table VII.

Table VI. Positional Parameters and B_{eqv} for $(BzMe_3N)_2[Mo_6Cl^i{}_8(CF_3SO_3)^a{}_6]$

atom	x	y	z	$B_{eqv}{}^a$
Mo(1)	0.02443 (2)	0.84906 (2)	1.07421 (2)	1.17 (1)
Mo(2)	0.14282 (2)	1.04437 (2)	1.03453 (2)	1.15 (1)
Mo(3)	0.08839 (2)	0.96289 (2)	0.86401 (2)	1.12 (1)
Cl(1)	−0.19724 (6)	0.84992 (6)	1.16750 (6)	1.47 (4)
Cl(2)	0.24284 (6)	0.86334 (6)	0.97365 (6)	1.67 (4)
Cl(3)	0.07419 (7)	0.93323 (7)	1.23231 (6)	1.70 (4)
Cl(4)	−0.02878 (7)	0.77925 (6)	0.90923 (6)	1.70 (4)
S(1A)	0.1187 (1)	0.5668 (1)	1.1448 (1)	2.20 (8)
S(1B)	0.1678 (2)	0.6066 (2)	1.1849 (2)	2.1 (1)
S(2)	0.35160 (7)	1.13249 (7)	1.16530 (7)	2.08 (4)
S(3)	0.23853 (8)	0.83570 (9)	0.64131 (8)	2.62 (5)
F(11A)	0.030 (1)	0.474 (1)	1.356 (1)	5.9 (6)
F(11B)	0.046 (2)	0.496 (2)	1.373 (2)	8 (1)
F(12A)	0.208 (1)	0.408 (1)	1.2878 (8)	6.8 (6)
F(12B)	0.021 (1)	0.437 (1)	1.198 (1)	8 (1)
F(13A)	0.2013 (6)	0.5768 (7)	1.3267 (5)	6.9 (5)
F(13B)	0.188 (3)	0.390 (2)	1.267 (2)	9 (1)
F(21)	0.4818 (3)	1.0199 (3)	1.3096 (2)	5.6 (2)
F(22)	0.3589 (2)	0.9100 (2)	1.2606 (2)	4.1 (1)
F(23)	0.5250 (2)	0.9695 (2)	1.1432 (2)	4.6 (2)
F(31)	0.0128 (2)	0.8140 (3)	0.6181 (3)	6.1 (2)
F(32)	0.1521 (3)	0.7465 (3)	0.4920 (3)	6.5 (2)
F(33)	0.1217 (3)	0.9330 (3)	0.4807 (2)	6.4 (2)
O(11)	0.0479 (2)	0.6743 (2)	1.1656 (2)	2.5 (1)
O(12A)	0.0497 (7)	0.4856 (5)	1.1111 (7)	5.8 (5)
O(12B)	0.2262 (8)	0.6507 (9)	1.266 (1)	4.0 (6)
O(13A)	0.252 (1)	0.593 (1)	1.080 (2)	2.7 (5)
O(13B)	0.222 (3)	0.577 (3)	1.079 (3)	3 (1)
O(21)	0.3123 (2)	1.0953 (2)	1.0666 (2)	2.1 (1)
O(22)	0.4438 (3)	1.2197 (2)	1.1253 (2)	3.6 (2)
O(23)	0.2502 (2)	1.1491 (2)	1.2563 (2)	3.3 (2)
O(31)	0.1904 (2)	0.9338 (2)	0.7014 (2)	2.3 (1)
O(32)	0.2292 (4)	0.7249 (3)	0.7192 (3)	5.4 (2)
O(33)	0.3499 (3)	0.8628 (4)	0.5613 (3)	6.2 (3)
N(1)	0.4065 (3)	0.4603 (2)	0.7983 (3)	2.3 (2)
C(1A)	0.1407 (9)	0.503 (1)	1.2869 (7)	4.7 (6)
C(1B)	0.087 (2)	0.469 (2)	1.252 (3)	7 (2)
C(2)	0.4337 (3)	1.0001 (3)	1.2231 (3)	2.9 (2)
C(3)	0.1235 (4)	0.8315 (4)	0.5528 (4)	3.7 (3)

$^a B_{eqv} = 8\pi^2/3\sum^3{}_{i=1}\sum^3{}_{j=1}U_{ij}a^*{}_ia^*{}_j\vec{a}_i\cdot\vec{a}_j$.

Table VII. Selected Interatomic Distances (Å) and Bond Angles (deg) for $(BzMe_3N)_2[Mo_6Cl^i{}_8(CF_3SO_3)^a{}_6]^a$

Mo(1)–Mo(2)	2.5906 (7)	Mo(2)–Cl(2)	2.470 (1)
Mo(1)–Mo(2*)	2.5969 (6)	Mo(2)–Cl(3)	2.4652 (9)
Mo(1)–Mo(3)	2.5910 (7)	Mo(2)–Cl(4*)	2.4612 (7)
Mo(1)–Mo(3*)	2.5938 (7)	Mo(3)–Cl(1*)	2.4646 (7)
Mo(2)–Mo(3)	2.5981 (6)	Mo(3)–Cl(2)	2.4661 (9)
Mo(2)–Mo(3*)	2.5889 (5)	Mo(3)–Cl(3*)	2.4641 (5)
Mo(1)–Cl(1)	2.4713 (8)	Mo(3)–Cl(4)	2.463 (1)
Mo(1)–Cl(2)	2.4623 (8)	Mo(1)–O(11)	2.136 (2)
Mo(1)–Cl(3)	2.459 (1)	Mo(2)–O(21)	2.123 (2)
Mo(1)–Cl(4)	2.4630 (9)	Mo(3)–O(31)	2.119 (2)
Mo(2)–Cl(1*)	2.4695 (6)		
Mo(1)–O(11)–S(1A)	138.1 (2)	Mo(2)–O(21)–S(2)	135.3 (1)
Mo(1)–O(11)–S(1B)	129.1 (2)	Mo(3)–O(31)–S(3)	139.9 (1)

^{a} Atoms labeled with an asterisk indicate atoms related by the center of inversion.

Discussion

Complexes containing the triflate ligand, $CF_3SO_3^-$, have the desirable properties of high stability in the solid state and solubility in noncoordinating solvents. As with many mononuclear coordination compounds,[15] the $CF_3SO_3^-$ ligand is readily displaced from $[Mo_6Cl^i{}_8(CF_3SO_3)^a{}_6]^{2-}$ to produce a variety of complexes.

The strong sulfur–oxygen IR stretching bands of the triflate ligand provide a method of monitoring the displacement of triflate by other ligands. The IR bands of the coordinated triflate ligand in the cluster and of sodium triflate (noncoordinating triflate ion) are listed in Table I. The formation of a SO–Mo linkage drops the symmetry of $CF_3SO_3^-$ from C_{3v} to C_s, so the degenerate (E symmetry) SO_3 stretch at 1280 cm^{-1} in $NaCF_3SO_3$ correlates with two IR features at 1349 and 1205 cm^{-1} for $[Mo_6Cl^i{}_8(CF_3SO_3)^a{}_6]^{2-}$ in CH_2Cl_2 solution. Additional bands observed in the IR spectrum of the solid presumably are due to different environments of the triflate ligands. An additional influence of coordination is to lower the symmetric SO_3 stretch by about 40 cm^{-1} (from 1036 cm^{-1} in $NaCF_3SO_3$ to 994 cm^{-1} in $[Mo_6Cl^i{}_8(CF_3SO_3)^a{}_6]^{2-}$). The IR spectra of $[Mo_6Cl^i{}_8(CF_3SO_3)^a{}_6]^{2-}$ salts in a KBr pellet reveal bands for both coordinated and uncoordinated triflate, indicating partial substitution of triflate ligands by Br$^-$. Therefore, KBr pellets were not used in the IR studies of these clusters.

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[15] (a) Shreeve, J. M., Ed. *Inorg. Synth.* **1986**, *24*, 243–306. (b) Lawrence, G. A. *Chem. Rev.* **1986**, *86*, 17–33.

Many of the ligands used to replace triflate on the $[Mo_6Cl^i_8]^{4+}$ cluster also have IR bands which change upon coordination (see Table II). The ν(CN) for the thiocyanate-coordinate cluster is lowered in frequency from free thiocyanate and has been assigned by Weissenhorn[2j] to correspond to N-bonded coordination. For the cluster with acetate or trifluoroacetate ligands, the difference between bands due to the CO_2 stretch indicates that acetate is attached through a single oxygen.[16] The *p*-toluenesulfonate ligand has a very intense band at 956 cm^{-1}, which is most likely the symmetric SO_3 stretch. Other bands could not be definitively assigned due to overlapping ring-bending modes. The strong IR band at 1047 cm^{-1} for the methoxide-substituted cluster was observed and assigned by Nannelli and Block[2h] as the methoxide C–O stretch.

The pyridine *N*-oxide N═O stretch is shifted to 1193 cm^{-1} (from 1245 cm^{-1} for free C_5H_5NO) which is within the 30–70-cm^{-1} shift previously observed for metal complexes of pyridine *N*-oxide.[16] The IR band for the P═O stretch of the coordinated triphenylphosphine oxide, 1062 cm^{-1}, is shifted significantly from 1193 cm^{-1} for the free ligand. Sheldon[2d] observed the same band at 1060 cm^{-1} for $[Mo_6Cl^i_8Cl^a_4(OPPh_3)^a_2]$. The strong sulfur–oxygen stretch at 936 cm^{-1} for the dibenzyl sulfoxide-coordinated cluster agrees well with the S═O stretch observed[8] for the DMSO-coordinated cluster. For the pyridine *N*-oxide, phosphine oxide, and dibenzyl sulfoxide complexes, the triflate $\nu_s(SO_3)$ band at 1030 cm^{-1} and absence of any band at 994 cm^{-1} indicates that the triflate is not coordinated to the cluster.

An ATR-IR immersible probe provided a convenient method to monitor the substitution of solvent molecules for the triflate ligands in $(Bu_4N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$. The IR bands of the cluster in dimethylformamide, acetone, and dichloromethane are compared in Table I with IR bands for the mull spectra of the cluster and sodium triflate. The absence of an absorption at 1030 cm^{-1} for the cluster in CH_2Cl_2 indicates that the triflate ligands remain completely coordinated. When the cluster is dissolved in DMF, the appearance of the 1030-cm^{-1} peak and the complete disappearance of the 994-cm^{-1} band indicate that all triflate anions are replaced by DMF. The IR spectrum of the cluster in acetone contains bands at 989 and 1034 cm^{-1}, indicating only partial substitution of $CF_3SO_3^-$ by the solvent. In an attempt to isolate the acetone-coordinated cluster, ether was added to the acetone solution; an oil formed which, upon standing, turned into a solid. The IR spectrum of this solid is identical to that of the cluster with six-coordinated triflate ligands. Apparently, coordinated acetone is lost upon crystallization. No attempt was made to isolate the cluster with DMF ligands since that cluster complex has already been reported as a perchlorate salt.[8]

The UV–vis spectra (Table III) of the clusters with the terminal ligands X = Br^- or Cl^- or an oxygen donor ligand consist of a broad band which has a maximum between 280 and 350 nm. This maximum appears to be slightly dependent upon the identity of the terminal ligand. A more intense peak at shorter wavelengths was observed for X = Br^-. For clusters with X = SCN^- and I^-, only one very intense peak is in the 270–280-nm region. An attempt was made to determine the electronic spectrum of $[Mo_6Cl^i_8(H_2O)^a_6]^{4+}$ by allowing water vapor to diffuse into a CH_2Cl_2 solution of $[Mo_6Cl^i_8(CF_3SO_3)^a_6]^{2-}$. However, the solution became cloudy and a spectrum could not be obtained.

FAB mass spectroscopy proved to be very useful for the characterization of the anionic clusters. The fragmentation patterns differ for each cluster; however, in the case of the all-halide-substituted clusters, the most intense peak always corresponded to the cluster (no cations) with loss of one halide, i.e., $[Mo_6Cl^i_8X^a_5]^-$. The triflate-substituted cluster shows one envelope corresponding to complete loss of one triflate ligand, plus another envelope of isotopomers corresponding to loss of (SO_2CF_3) with retention of an oxygen by the cluster.

The structure (geometry, bond distances, bond angles) of the $[Mo_6Cl^i_8]^{4+}$ core is essentially identical to previously characterized examples.[1,2n,2o] The average molybdenum to oxygen distance of 2.126 (9) Å is within the expected range for a triflate ligand bound to a transition metal through a single oxygen.[15b] The molybdenum–oxygen–sulfur bond angles vary from 129.1 (2) to 139.9 (1)°. This is also within the range previously observed for covalent transition-metal triflate complexes (see ref 15b and references therein). The relative positions of the disordered triflate group may be described primarily in terms of a simple rotation about both the Mo(1)–O(11) bond (52°) and the O(11)–S(1A, 1B) bond (ca. 35°).

In summary, the cluster, $[Mo_6Cl^i_8(CF_3SO_3)^a_6]^{2-}$, is a very useful starting material for the preparation of the clusters with the $[Mo_6Cl_8]^{4+}$ core attached to a variety of terminal ligands. Preliminary results show that the present method may be used to prepare labile triflate complexes of $[Mo_6Br_8]^{4+}$, $[Mo_6I_8]^{4+}$, and $[W_6Cl_8]^{4+}$, and its extension to many other d-block halide clusters seems promising.

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Supplementary Material Available: Tables of X-ray crystallographic data for $(BzMe_3N)_2[Mo_6Cl^i_8(CF_3SO_3)^a_6]$, including complete refined atomic coordinates, anisotropic thermal parameters, bond distances, and bond angles and ORTEP drawings (17 pages); calculated and observed structure factors (33 pages). Ordering information is given on any current masthead page.

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(16) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986; pp 191–371.