Preparation and Structure of [Mo₆Cl₈(CH₃CN)₆](SbCl₆)₄·2EtOH

**Grant M. Ehrlich,† Christopher J. Warren,†
Robert C. Haushalter,*,‡ and Francis J. DiSalvo*,†**

Department of Chemistry, Cornell University,
Ithaca, New York 14853-1301, and NEC Research Institute,
4 Independence Way, Princeton, New Jersey 08540

Introduction

Recently Johnston et al. reported the preparation of a versatile starting material for the preparation of $Mo_6Cl_8^{4+}$ cluster compounds, $(Bu_4N)_2Mo_6Cl_8(CF_3SO_3)_6$.[1] The $Mo_6Cl_8^{4+}$ structural unit is a common moiety, and the structures of many Mo_6-Cl_8 cluster compounds have been determined recently. For example, Preetz et al. reported the structures of the series $(Bu_4N)_2Mo_6Cl_8X_6$ (X = halide),[2] and an interesting derivative of $(Bu_4N)_2[Mo_6Cl_8(CF_3SO_3)_6]$, $(PPN)_2[Mo_6Cl_8\{(\mu\text{-NC})Mn(CO)_2$-$Cp\}_6]$, was prepared by Johnston et al.[3] Saito et al. has also made hexanuclear molybdenum, tantalum, and niobium chloride cluster compounds coordinated with trialkylphosphorus ligands.[4] Presented herein are the preparation and structure determination of $[Mo_6Cl_8(CH_3CN)_6](SbCl_6)_4\cdot 2EtOH$ (**1**), a derivative of $(Bu_4N)_2$-$Mo_6Cl_8(CF_3SO_3)_6$.

While Johnston et al.[1,3] showed that the triflate anion is weakly coordinated to molybdenum and can be replaced by many other stronger neutral or anionic Lewis bases, it was found that the acetonitrile ligand is at least as weak a donor to the molybdenum acceptors as triflate, since in acetonitrile solution only approximately half of the triflate ligands are displaced.[5] Since we are interested in producing an even wider variety of ligated and linked clusters with potentially weak donors such as pyrazine, we have been investigating reactions in which donors weaker than triflate can be bound to the $Mo_6Cl_8^{4+}$ cluster.

Experimental Section

General Procedures. All manipulations were carried out either in an Ar atmosphere or in vacuo unless explicitly stated. The starting cluster for the preparation of $[Mo_6Cl_8(CH_3CN)_6](SbCl_6)_4\cdot 2EtOH$ (**1**) was $(Bu_4N)_2Mo_6Cl_8(CF_3SO_3)_6$. It was prepared according to the method of Johnston et al.[1] by the reaction of $(Bu_4N)_2Mo_6Cl_{14}$ and $AgCF_3SO_3$. KSH was prepared by the reaction of KOEt and H_2S (Matheson, CP grade, dried over P_2O_5) in a method similar to Eibeck's preparation of $NaSH$.[6] $SbCl_5$ (Aldrich) was distilled before use. Ethanol was dried with 3 Å molecular sieves which had been heated to 400 °C in vacuo. The Raman spectra were taken on a Dilor XY100 spectrometer with a He–Ne laser. EDAX measurements were made on a JEOL 733 Superprobe using the vendor-supplied SSQ or SQ software packages for standardless semiquantitative elemental analysis.

Synthesis of $[Mo_6Cl_8(CH_3CN)_6](SbCl_6)_4\cdot 2EtOH$. The synthesis of $[Mo_6Cl_8(CH_3CN)_6](SbCl_6)_4\cdot 2EtOH$ (**1**) was accomplished in a one-neck
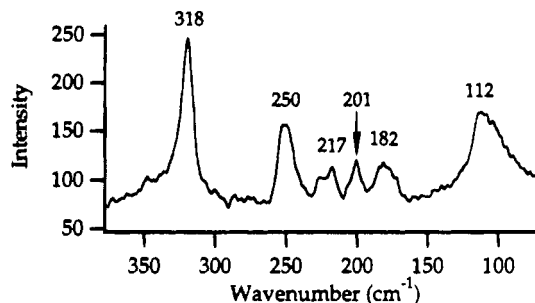
Figure 1. Raman spectrum of the yellow crystals of [Mo₆Cl₈(CH₃-CN)₆](SbCl₆)₄·2EtOH (**1**).

100 mL flask which was loaded with $(Bu_4N)_2Mo_6Cl_8(CF_3SO_3)_6$ (200 mg, 0.089 mmol), KSH (42.3 mg, 0.586 mmol), and ethanol (25 mL) [which was condensed directly into the flask]. The stirred mixture was maintained at 70 °C overnight, allowed to cool to room temperature, and filtered at 5 °C to yield an orange-brown powder (40.1 mg, yield calculated for $(Bu_4N)_2Mo_6Cl_8(SH)_6$ 29%), which was washed once with EtOH. A 50 mL two-neck flask was fitted with a connecting adapter and a solids addition funnel. The 50 mL flask was loaded with 10 mg of the orange-brown powder, and the solids addition funnel was loaded with $SbCl_5$ (1.63 mg, 5.45 μmol). CH_3CN (20 mL) was condensed directly into the flask, and CH_3CN (5 mL) was condensed into the solids addition funnel. The $SbCl_5$ solution was added to the suspension in the flask. After 1 day, the solution was decanted. Three weeks later, the resulting mixture was filtered to yield yellow hexagonal crystals in low yield (less than 5%). EDAX analysis of the yellow crystals showed peaks at 2.3, 2.6, 3.6, and 3.9 keV, consistent with the presence of Mo, Cl, and Sb. The Raman spectrum of the yellow crystals (Figure 1), showed peaks at 112, 182, 201, 217, 250, and 318 cm⁻¹. The absorptions at 182, 201, 217, 250, and 318 cm⁻¹ are characteristic for a Mo_6Cl_8 cluster, similar to the absorptions observed in the Raman spectrum of $(Bu_4N)_2Mo_6Cl_{14}$ which occur at 181, 201, 219, 251, and 320 cm⁻¹.[2]

Crystallography. A yellow hexagonal-shaped crystal of approximate dimensions 0.12 × 0.05 × 0.01 mm was mounted in a glass capillary tube in a drybox. X-ray and intensity data were collected on a Rigaku AFC7R automatic four-circle diffractometer with Mo Kα radiation and a RU300 18 kW rotating-anode generator. Cell constants and an orientation matrix for data collection were obtained from the setting angles of 18 carefully centered reflections in the range 6.91° ≤ 2θ ≤ 15.45° and corresponded to a primitive orthorhombic cell with the unit cell dimensions given in Table 1. The systematic absences of $0kl$ ($k \neq 2n$), $h0l$ ($l \neq 2n$), and $hk0$ ($h \neq 2n$) uniquely determined the space group to be $Pbca$ (No. 61).

The data collection consisted of scans of $(0.73 + 0.35 \tan \theta)°$ in the range 5° ≤ 2θ ≤ 40° which were made using the ω-2θ scan technique at a speed of 8°/min (in ω). The weak reflections [$I < 20\sigma(I)$] were rescanned a maximum of four times, and the counts were accumulated to ensure good counting statistics. The intensities of 3 standard reflections were measured after every 150 reflections and, over the course of data collection, decreased in intensity by 13%. A polynomial correction factor was applied to the data to account for this presumed decomposition in the X-ray beam. An empirical absorption correction using the program DIFABS[7] was applied, resulting in transmission factors ranging from 0.74 to 1.01. The data were also corrected for Lorentz and polarization effects.

The structure was solved by direct methods and refined on F by full-matrix least-squares using the teXsan crystallographic software package of Molecular Structure Corp.[8] Due to the paucity of data, only the Sb, Mo, and Cl atoms were refined with aniostropic displacement parameters, while the C and N atoms were refined isotropically. Hydrogen atoms were not included in the refinements. The final least-squares refinement was based on 1719 unique reflections [$I < 3.0\sigma(I)$] and 178 variable parameters and converged with R (R_w)

† Cornell University.
‡ NEC Research Institute.
(1) Johnston, D. H.; Gaswick, D. C.; Lonergan, M. C.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1992**, *31*, 1869.
(2) Preetz, W.; Harder, K.; Schnering, H. G.; Kliche, G.; Peters, K. *J. Alloys Compounds* **1992**, *183*, 413.
(3) Johnston, D. H.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1993**, *32*, 5170.
(4) (a) Saito, T.; Nishida, M.; Yamagata, T.; Yamagata, Y.; Yamaguchi, Y. *Inorg. Chem.* **1986**, *25*, 1111. (b) Imoto, H.; Hayakawa, S.; Morita, N.; Saito, T. *Inorg. Chem.* **1990**, *29*, 2007.
(5) Johnston, D. H. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1993.
(6) Eibeck, R. E. *Inorg. Synth.* **1963**, *7*, 128ff.

(7) Walker, N.; Stuart, D. *Acta. Crystallogr.* **1983**, *A39*, 158.
(8) *teXsan Single Crystal Structure Analysis Software Package*, version 1.6; Molecular Structure Corp.: The Woodlands, TX 77381, 1992.

Table 1. Crystallographic Data for
[Mo₆Cl₈(CH₃CN)₆](SbCl₆)₄·2EtOH (**1**)

chem formula Sb₄Cl₃₂Mo₆C₁₆H₃₀N₆O₂	fw 2535.59
$a = 25.043(8)$ Å	space group *Pbca* (No. 61)
$b = 21.253(7)$ Å	$T = 25$ °C
$c = 13.188(6)$ Å	$\lambda = 0.710\ 69$ Å
$V = 7018(3)$ Å³	$\varrho_{calcd} = 2.399$ g cm⁻³
$Z = 4$	$\mu = 73.88$ cm⁻¹
	$R = 0.066$
	$R_w = 0.067$

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|,\ R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}.$

Table 2. Atomic Coordinates and Equivalent Isotropic
Displacement Parameters (Å²) for the Non-Hydrogen Atoms of
[Mo₆Cl₈(CH₃CN)₆](SbCl₆)₄·2EtOH (**1**)

atom	x	y	z	$B(eq)^a$
Sb(1)	0.2394(1)	0.3900(1)	0.3219(3)	6.54(9)
Sb(2)	−0.0404(1)	0.3329(1)	0.4779(2)	4.88(8)
Mo(1)	0.0373(1)	0.0178(1)	0.3843(2)	3.07(8)
Mo(2)	0.0312(1)	0.0674(1)	0.5631(2)	3.11(8)
Mo(3)	−0.0546(1)	0.0511(1)	0.4569(2)	3.01(8)
Cl(1)	0.1163(3)	0.0316(4)	0.4916(8)	4.4(3)
Cl(2)	0.0140(3)	0.1285(4)	0.4080(7)	3.8(2)
Cl(3)	−0.0576(4)	0.0948(4)	0.6299(7)	3.9(2)
Cl(4)	0.0454(4)	−0.0015(4)	0.7088(6)	3.9(2)
Cl(5)	0.2822(7)	0.4660(8)	0.229(1)	15.3(6)
Cl(6)	0.2585(5)	0.4459(6)	0.470(1)	8.8(3)
Cl(7)	0.1590(6)	0.4426(7)	0.310(1)	12.1(5)
Cl(8)	0.1958(6)	0.3133(7)	0.424(1)	12.3(5)
Cl(9)	0.2187(6)	0.3332(6)	0.174(1)	11.1(4)
Cl(10)	0.3175(6)	0.3312(7)	0.344(1)	12.6(5)
Cl(11)	−0.0041(5)	0.4219(6)	0.402(1)	8.9(4)
Cl(12)	−0.0289(5)	0.3790(6)	0.636(1)	10.1(4)
Cl(13)	−0.1240(6)	0.3723(6)	0.459(1)	10.8(4)
Cl(14)	−0.0731(4)	0.2427(5)	0.558(1)	7.3(3)
Cl(15)	−0.0483(5)	0.2820(5)	0.3203(9)	7.4(3)
Cl(16)	0.0485(5)	0.2912(5)	0.4902(9)	7.9(3)
O(1)	0.180(2)	0.136(2)	0.298(4)	17(1)
N(1)	0.080(1)	0.034(1)	0.246(3)	4.7(7)
N(2)	0.066(1)	0.148(1)	0.639(2)	4.0(7)
N(3)	−0.116(1)	0.112(1)	0.403(2)	4.9(8)
C(1)	0.098(1)	0.045(2)	0.168(3)	4.7(9)
C(2)	0.122(1)	0.054(2)	0.067(3)	5.3(9)
C(3)	0.077(1)	0.193(2)	0.683(3)	4.4(8)
C(4)	0.094(1)	0.249(2)	0.737(3)	5.8(10)
C(5)	−0.145(2)	0.146(2)	0.386(3)	6(1)
C(6)	−0.185(2)	0.202(2)	0.367(3)	8(1)
C(7)	0.259(3)	0.124(3)	0.410(5)	13(1)
C(8)	0.217(3)	0.131(4)	0.370(7)	17(1)

$^a B(eq) = {}^8/_3\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*$
$\cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha].$

= 0.066 (0.067). Further details of the X-ray structural analysis are given in Table 1. The final positional and equivalent isotropic displacement parameters are given in Table 2, a list of selected bond distances and angles is given in Table 3.

Discussion

The structure of [Mo₆Cl₈(CH₃CN)₆](SbCl₆)₄·2EtOH (**1**) consists of a substitution-resistant core of Mo₆Cl₈⁴⁺, with eight face-bridging chlorine ligands and six terminal acetonitrile ligands, which is surrounded in the solid state by four SbCl₆⁻ counter-anions. The structure of the Mo₆Cl₈⁴⁺ cluster unit consists of six molybdenum atoms in an almost regular octahedral arrangement with Mo−Mo single-bond distances ranging from 2.588-(4) to 2.598(4) Å and all Mo−Mo−Mo angles very near either 60 or 90°. Eight chlorine atoms cap the Mo₃ faces of the Mo₆ octahedron, making a cube of Cl atoms with Mo−μ₃-Cl distances ranging from 2.433(9) to 2.466(9) Å. The coordination environment of each molybdenum atom is completed by a single acetonitrile ligand in the exo position (perpendicular to
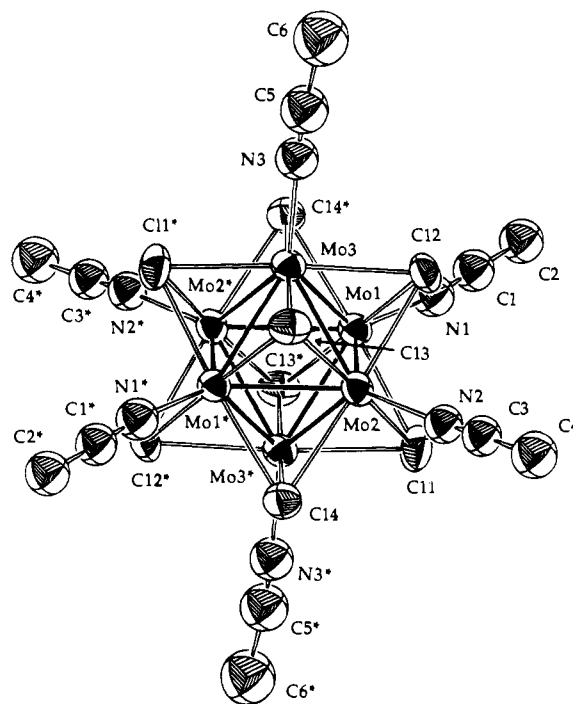
Figure 2. View of the Mo₆Cl₈(CH₃CN)₆⁴⁺ cluster compound with 50% probability thermal ellipsoids and atomic numbering scheme.

Table III. Selected Bond Distances (Å) and Angles (deg) in
[Mo₆Cl₈(CH₃CN)₆](SbCl₆)₄·2EtOH (**1**)

Bond Distances			
Mo(1)−Mo(2)	2.588(4)	Mo(2)−Cl(2)	2.462(9)
Mo(1)−Mo(2*)	2.590(4)	Mo(2)−Cl(3*)	2.461(10)
Mo(1)−Mo(3)	2.593(4)	Mo(2)−Cl(4)	2.442(9)
Mo(1)−Mo(3*)	2.590(4)	Mo(3)−Cl(1*)	2.435(9)
Mo(2)−Mo(3)	2.589(4)	Mo(3)−Cl(2)	2.466(9)
Mo(2)−Mo(3*)	2.598(4)	Mo(3)−Cl(3*)	2.464(10)
Mo(1)−Cl(1)	2.448(10)	Mo(3)−Cl(4*)	2.437(9)
Mo(1)−Cl(2)	2.445(9)	Mo(1)−N(1)	2.14(3)
Mo(1)−Cl(3*)	2.453(9)	Mo(2)−N(2)	2.17(3)
Mo(1)−Cl(4*)	2.433(9)	Mo(3)−N(3)	2.12(3)
Mo(2)−Cl(1)	2.450(9)		

Bond Angles			
Mo(2)−Mo(1)−Mo(2*)	90.1(1)	Mo(2)−Mo(1)−Cl(2)	58.5(2)
Mo(3)−Mo(1)−Mo(3*)	90.2(1)	Mo(2)−Mo(1)−Cl(3*)	118.6(3)
Mo(1)−Mo(2)−Mo(1*)	89.9(1)	Mo(2)−Mo(1)−Cl(4*)	117.9(2)
Mo(3)−Mo(2)−Mo(3*)	90.1(1)	Mo(2)−Mo(1)−N(1)	138.1(8)
Mo(1)−Mo(3)−Mo(1*)	89.8(1)	Mo(2*)−Mo(1)−Cl(1)	117.7(2)
Mo(2)−Mo(3)−Mo(2*)	89.9(1)	Mo(2)−Mo(1*)−Cl(2*)	118.7(2)
Mo(2)−Mo(1)−Mo(3)	60.0(1)	Mo(2)−Mo(1*)−Cl(3)	58.4(2)
Mo(2)−Mo(1)−Mo(3*)	60.2(1)	Mo(2)−Mo(1*)−Cl(4)	58.1(2)
Mo(2*)−Mo(1*)−Mo(3)	60.2(1)	Mo(2)−Mo(1*)−N(1*)	131.8(8)
Mo(2*)−Mo(1)−Mo(3)	60.0(1)	Mo(3)−Mo(1)−Cl(2)	58.5(2)
Mo(1)−Mo(2)−Mo(3)	60.1(1)	Mo(3)−Mo(1)−Cl(3*)	118.5(3)
Mo(1)−Mo(2)−Mo(3*)	59.9(1)	Mo(3)−Mo(1)−Cl(4*)	57.9(2)
Mo(1)−Mo(2*)−Mo(3)	60.0(1)	Mo(3)−Mo(1)−N(1)	135.5(8)
Mo(1*)−Mo(2)−Mo(3)	60.0(1)	Mo(3)−Mo(1*)−Cl(1*)	57.7(2)
Mo(1)−Mo(3)−Mo(2)	59.9(1)	Mo(3)−Mo(1*)−Cl(2*)	118.7(3)
Mo(1)−Mo(3)−Mo(2*)	59.8(1)	Mo(3)−Mo(1)−Cl(3*)	58.4(2)
Mo(1)−Mo(3*)−Mo(2)	60.0(1)	Mo(3)−Mo(1)−Cl(4*)	118.0(2)
Mo(1*)−Mo(3)−Mo(2)	59.8(1)	Mo(3)−Mo(1)−N(1)	134.1(8)
Mo(2)−Mo(1)−Cl(1)	58.1(2)		

the cube face). The two ethanol molecules in the structure do not interact with the Mo₆Cl₈(CH₃CN)₆⁴⁺ cluster compound or the SbCl₆⁻ counteranions and are merely present as solvates of crystallization. These solvates were presumably present in the solid before the SbCl₅/CH₃CN solution was added.

The title compound was prepared in a reaction that was designed to produce a different product[9] and is not suggested as an optimal route to that compound. For example, a simpler

and potentially higher yield reaction might be that of $MoCl_2$ (which structurally is better represented as the cluster compound $[Mo_6Cl^i_8]Cl^a_4$) with $SbCl_5$ in acetonitrile. Alternatively, the sodium salt $Na_2Mo_6Cl_{14}$ may also be of use in making the acetonitrile-ligated cluster in polar media. Finally, Johnston showed in his thesis that an acetonitrile-ligated cluster could be prepared by oxidizing the azide derivative $(Bu_4N)_2Mo_6Cl_8$-$(N_3)_6$ with $NO[PF_6]$ in acetonitrile.[5]

In conclusion, the reaction of $(Bu_4N)_2Mo_6Cl_8(CF_3SO_3)_6$ and KSH in ethanol, followed by the extraction of the resulting

product with $SbCl_5$ in acetonitrile, yields single crystals of the molybdenum chloride cluster $[Mo_6Cl_8(CH_3CN)_6](SbCl_6)_4 \cdot 2EtOH$ (**1**). The synthesis, which involves the replacement of a strongly bound ligand (Cl^-) with a more weakly bound one (CH_3CN) via a metathesis reaction using the strong Lewis acid $SbCl_5$, should be a useful route to other cluster compounds with even more weakly bound ligands.

Supporting Information Available: Text presenting the crystallographic procedures and complete tables of experimental crystallographic details, bond distances and angles, torsion angles, nonbonded contacts, and anisotropic displacement parameters for **1** (25 pages). Ordering information is given on any current masthead page.

---

(9) We were initially hoping that the SH^- ligands might migrate to the capping positions on the Mo_6 octahedron and replace the Cl^- ligands, which would now be terminal. The Cl^- ligands could then have been easily removed in a metathesis reaction with the $SbCl_5/CH_3CN$ solution, leaving a molybdenum sulfide cluster with labile CH_3CN ligands.

IC9414810