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Synthesis, Crystal Structure, and Spectroscopic Characterization of a Series of Cubane-like Mo−Sb Clusters Containing a $[Mo_3SbOS_3]^{7+}$ Core

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By using $[Mo_3OS_3(\mu\text{-OAc})(dtp)_3(py)]$ and $[Mo_3OS_3(\mu\text{-OAc})_2(dtp)_2(py)]$ as the starting materials, a series of Mo−Sb clusters containing a $[Mo_3SbOS_3]^{7+}$ core, i.e., $[Mo_3(SbCl_3)OS_3(\mu\text{-OAc})(dtp)_3(py)]$ (**1**), $[Mo_3(SbBr_3)OS_3(\mu\text{-OAc})(dtp)_3(py)][(CH_3)_2CO]$ (**2**), $[Mo_3(SbI_3)OS_3(\mu\text{-OAc})(dtp)_3(py)][(CH_3)_2CO]$ (**3**), and $[Mo_3(SbBr_3)OS_3(\mu\text{-OAc})_2(dtp)_2(py)][0.5(C_2H_5OH)]$ (**5**), have been obtained for the first time (OAc = $OOCCH_3^-$, dtp = $S_2P(OC_2H_5)_2^-$, py = C_5H_5N). Among them, the cluster type of $[Mo_3(SbX_3)OS_3(\mu\text{-OAc})_2(dtp)_2(py)]$ (X = Cl, Br, I) is an unprecedented species. It is shown from the results of the crystal structure analysis and IR, Raman, UV−vis, and ^{95}Mo NMR spectra that the addition of SbX_3 may cause an enhancement of Mo−Mo bonds and exerts a significant influence on the electronic structure. As the halogen atoms are softer in Cl, Br, I order. The energies of the electron transfer gradually decrease leading to a red shift of UV−vis peaks. The ^{95}Mo NMR spectra indicate an "inverse halogen dependence". Crystal data: **1**, triclinic, *P*-1, $a = 11.746(4)$ Å, $b = 12.462(3)$ Å, $c = 17.851(6)$ Å, $\alpha = 73.54(2)°$, $\beta = 75.06(3)°$, $\gamma = 88.11(3)°$, $V = 2419(3)$ Å^3, $Z = 2$, 4253 reflections, $R = 0.055$; **2**, triclinic, *P*-1, $a = 12.76(1)$ Å, $b = 17.86(1)$ Å, $c = 11.882(4)$ Å, $\alpha = 75.05(4)°$, $\beta = 88.15(7)°$, $\gamma = 73.24(4)°$, $V = 2502(6)$ Å^3, $Z = 2$, 1849 reflections, $R = 0.086$; **3**, triclinic, *P*-1, $a = 11.727(4)$ Å, $b = 12.951(3)$ Å, $c = 17.957(4)$ Å, $\alpha = 73.52(3)°$, $\beta = 76.22(3)°$, $\gamma = 89.00(2)°$, $V = 2536(3)$ Å^3, $Z = 2$, 6306 reflections, $R = 0.053$; **5**, triclinic, *P*-1, $a = 13.261(4)$ Å, $b = 13.529(4)$ Å, $c = 12.535(8)$ Å, $\alpha = 101.54(3)°$, $\beta = 105.13(4)°$, $\gamma = 93.20(2)°$, $V = 2113(2)$ Å^3, $Z = 2$, 4104 reflections, $R = 0.060$.

Introduction

The first example of the hybrid transition metal−main group Mo−Sb−S single cubane-like cluster $[Mo_3(SbCl_3)S_4(\mu\text{-dtp})(dtp)_3(L)]$ (dtp = $S_2P(OC_2H_5)_2^-$, L = C_2H_5OH, C_3H_3ON) was reported by us in 1987.[1] Subsequently, based on the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with a main group metal, the single cubane $[Mo_3MS_4]$ (M = In[2], Sn[3], Ga[4]) and sandwich cubane $[(H_2O)_9Mo_3S_4MS_4Mo_3(H_2O)_9]$ (M = Hg,[5] Sn,[6] Sb[7]) were reported by Shibahara et al. In addition, the Pb−Mo and Bi−Mo clusters were also investigated.[8−10] All of these cluster compounds mentioned above possess a $[Mo_3MS_4]$ single cubane-type cluster core; however, as far as the structures of $[Mo_3MOS_3]$ single cubane-type clusters are concerned, only the $[Mo_3(SnBr_3)OS_3]$ cluster was reported so far.[11] In this paper, the synthesis and structure characterization of four hybrid Mo−Sb clusters containing a $[Mo_3SbOS_3]$ core, i.e., $[Mo_3(SbCl_3)OS_3(\mu\text{-OAc})(dtp)_3(py)]$ (**1**), $[Mo_3(SbBr_3)OS_3(\mu\text{-OAc})(dtp)_3(py)][(CH_3)_2CO]$ (**2**), $[Mo_3(SbI_3)OS_3(\mu\text{-OAc})(dtp)_3(py)][(CH_3)_2CO]$ (**3**), and $[Mo_3(SbBr_3)OS_3(\mu\text{-OAc})_2(dtp)_2(py)][0.5(C_2H_5OH)]$ (**5**), prepared by the addition reaction of $[Mo_3OS_3]$ type clusters with SbX_3 (X =Cl, Br, I), are reported. The effect of the addition of SbX_3 to the {Mo_3} cluster upon the structure is discussed.

Experimental Section

General Procedures. All reactions and manipulations were performed in air. CP and SP grade reagents and solvents were used. The elemental analyses of Mo and Sb were carried out with an inductively coupled plasma-atomic emission spectrometer (ICP-AES) and by atomic absorption on a Perkin-Elmer 306 Spectrophotometer. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer as KBr disk (4000−600 cm^{-1}) and CsI disk (600−100 cm^{-1}). The Raman spectra were collected with a 910 Laser Raman FT spectrometer with SP grade KBr as the diluent for the sample. A Varian Unit 500 spectrometer operating at 32.616 MHz was used to obtained ^{95}Mo NMR spectra at room temperature. The samples were dissolved in CH_2Cl_2 as a saturated solution, and 2 M solution of Na_2MoO_4 in D_2O was used as the external reference. The UV−vis spectra were measured with a Shimadzu UV-3000 spectrometer.

Synthesis. (a) $[Mo_3(SbCl_3)YS_3(\mu\text{-OAc})(dtp)_3(py)]$ (1) ($Y = 90\%$ O + 10% S). Starting compound $[Mo_3OS_3(\mu\text{-OAc})(dtp)_3(py)]$ (240 mg, 0.22 mmol),[12] $SbCl_3$ (46 mg, 0.2 mmol), CH_2Cl_2 (10 mL), and acetone (10 mL) were mixed and stirred at room temperature for 30 min. After filtering, the brown-red filtrate was left standing to allow crystallization by volatilization. On 2 weeks of standing, the mother

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Table 1. Crystal Data and Experimental Parameters for the Intensity Data Collection

	formula			
	$C_{19}H_{38}Cl_3Mo_3NO_{8.9}P_3S_{9.1}Sb$	$C_{22}H_{44}Br_3Mo_3NO_{10}P_3S_9Sb$	$C_{22}H_{44}I_3Mo_3NO_{10}P_3S_9Sb$	$C_{18}H_{32.5}Br_3Mo_3NO_{9.5}P_2S_7Sb$
formula wt	1323.51	1513.25	1654.34	1351.61
space group	*P*-1 (No. 2)	*P*-1 (No. 2)	*P*-1 (No. 2)	*P*-1 (No. 2)
a, Å	11.746(4)	12.758(14)	11.727(5)	13.261(4)
b, Å	12.462(3)	17.859(13)	12.951(3)	15.529(4)
c, Å	17.851(6)	11.882(4)	17.957(4)	12.535(8)
α, deg	73.54(2)	75.05(4)	73.52(3)	101.54(3)
β, deg	75.06(3)	88.15(7)	76.22(3)	105.13(4)
γ, deg	88.11(3)	73.24(7)	89.00(3)	93.20(2)
V, Å^3	2419(3)	2502(6)	2536(3)	2113(2)
Z	2	2	2	2
D_{calcd}, g cm^{-3}	1.82	2.01	2.17	2.12
μ, cm^{-1}	19.79	41.26	35.38	47.44
$R(F)^a$	0.055	0.086	0.053	0.060
$R_w(F)^a$	0.065	0.099	0.065	0.076

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

liquor was removed. The solid product was separated and then washed with C_2H_5OH/petroleum ether and dried to yield 60 mg (21%) black crystals.

(b) $[Mo_3(SbBr_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)][(CH_3)_2CO]$ (2). The procedure of the synthesis was similar to that for cluster **1**, except that $SbBr_3$ (72 mg, 0.2 mmol) was used instead of $SbCl_3$. After 2 weeks standing, a crystalline black product (80 mg, 24%) was obtained. Anal. Calcd for $C_{22}H_{44}Br_3Mo_3NO_{10}P_3S_9Sb$: Mo, 18.85; Sb, 7.97. Found: Mo, 19.10; Sb, 7.94 (atomic absorption method).

(c) $[Mo_3(SbI_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)][(CH_3)_2CO]$ (3). The procedure similar to that for cluster **1** was conducted, except that SbI_3 (104 mg, 0.2 mmol) was used rather than $SbCl_3$. After 6 days of standing, 60 mg (17%) of black crystals was isolated. Anal. Calcd for $C_{22}H_{44}I_3Mo_3NO_{10}P_3S_9Sb$: Mo, 17.40; Sb, 7.4. Found: Mo, 17.50; Sb, 7.49 (atomic absorption method).

(d) $[Mo_3(SbBr_3)OS_3(\mu\text{-}OAc)_2(dtp)_2(py)][0.5(C_2H_5OH)]$ (5). Starting compound $[Mo_3OS_3(\mu\text{-}OAc)_2(dtp)_2(py)]^{13}$ (150 mg, 0.15 mmol), $SbBr_3$ (54 mg, 0.15 mmol), CH_2Cl_2 (10 mL), and acetone (15 mL) were mixed, and the reaction mixture was stirred for 30 min and then filtered. The solid product separated the next day was filtered and washed with C_2H_5OH/petroleum ether. The mixture of the washing solution, and the mother liquor was stood continuously. After 2 weeks, 30 mg (15%) of the black crystal suitable for X-ray analysis work was obtained.

Crystal Structure Determination. All of the crystals are stable in air and were mounted at the end of glass fiber using epoxy glue. The intensity data were collected on a CAD4 four-circle diffractometer for cluster **1** and **3** or Rigaku AFC5R for cluster **2** and **5** using graphite-monochromated Mo Kα radiation. A summary of the pertinent crystallographic data and experimental details for all four crystals are listed in Table 1. The structures were solved by the combination of Patterson and direct method which revealed the position of Mo, Sb, and halogen atoms (Cl, Br, I). The remaining atoms were located in succeeding difference Fourier synthesis. The refinement was carried out by full-matrix least-squares method. The scattering contributions of hydrogen atoms were added to the structure factor calculations but their positions were not refined. All calculations were performed on a VAX computer by using the TEXSAN program system.[14]

It is worthwhile to note that for cluster **1**, when the triply bridging atom Y which binds three Mo atoms was involved into the calculations as oxygen, an unusual small thermal parameter for this atom and the slight longer Mo−O distances than those of normal $[Mo_3OS_3]$ core occurred. For this reason, the atomic position was ultimately modeled as 90% O and 10% S. This assignment was confirmed reasonable by the further refinement. $Y = 90\%O + 10\%S$ was thought to be caused by a little impurity (i.e., $[Mo_3(\mu_3\text{-}S)S_3(\mu\text{-}OAc)(dtp)_3(py)]$) mixed in the starting material $[Mo_3(\mu_3\text{-}O)S_3(\mu\text{-}OAc)(dtp)_3(py)]$. Moreover, several ethyl groups of (dtp) were disordered: the distribution ratio of two C(22) sites and two C(33) sites were of 0.7 to 0.3 statistically. For cluster **2**, on account of the limited amount of data, only the atoms of $[Mo_3(SbBr_3)OS_3]$ core were refined with anisotropic thermal parameters, whereas the remaining nonhydrogen atoms refined only by using isotropic. For cluster **3**, since the solvent molecule acetone was found to be distributed disorderly, two atoms O(40) and C(41) were not strictly O or C but (0.5O + 0.5C). For cluster **5**, the temperature factors of the atoms belonging to the solvent molecule C_2H_5OH were relatively high, thus indicating a position disorder. The values of the associated C−O, C−C bond lengths and angles were anomalous. These atoms were refined isotropically.

All the nonhydrogen atom coordinates and the equivalent isotropic thermal parameters for the four clusters **1**, **2**, **3**, and **5** have been deposited as the Supporting Information.

Results and Discussion

1. Synthetic Reaction. As the synthesis of $[Mo_3(SbCl_3)S_4(\mu\text{-}dtp)(dtp)_3(L)]$ (dtp = $S_2P(OC_2H_5)_2$-, L = C_2H_5OH, C_3H_3ON) by the reaction of $[Mo_3S_4(\mu\text{-}dtp)(dtp)_3(H_2O)]$ with $SbCl_3$ has been successful, it is natural for us first to consider to start with a similar addition reaction for analogous $[Mo_3OS_3]$-type clusters. It is already known from the previous experimental work that the $[Mo_3OS_3]$ core is easy to be converted to $[Mo_3S_4]$ core in the presence of some source of S^{2-}.[15] However, this conversion can be avoided by the substitution of (μ-dtp) by (μ-OAc) owing to the strengthening of the Mo−(μ_3-O) bonding. Therefore $[Mo_3OS_3(\mu\text{-}OAc)(dtp)_3(py)]$ and $[Mo_3OS_3(\mu\text{-}OAc)_2(dtp)_2(py)]$ were chosen as the starting materials in which the lone pair electrons of the three (μ-S) can also be coordinated to SbX_3 (X = Cl, Br, I) to form $[Mo_3SbOS_3]$ core via three Sb−S bonds as in the $[Mo_3S_4]$ core. The reaction schemes are as follows:

$Mo_3OS_3(\mu\text{-}OAc)(dtp)_3(py) + SbX_3 \rightarrow Mo_3(SbX_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)$

$Mo_3OS_3(\mu\text{-}OAc)_2(dtp)_2(py) + SbX_3 \rightarrow Mo_3(SbX_3)OS_3(\mu\text{-}OAc)_2(dtp)_2(py)^{16}$ (X = Cl, Br, I)

2. Structural Feature. The molecular configuration of clusters **1**, **2**, **3**, and **5** are shown in Figures 1, 2, 3, and 4, respectively, with hydrogen atoms omitted for clarity. All of the four compounds contain a mixed S/O triple bridging $[Mo_3SbOS_3]$ cluster core. These structures can further be divided

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(16) $[Mo_3(SbBr_3)OS_3(\mu\text{-}OAc)_2(dtp)_2(py)]$: triclinc, *P*-1, $a = 13.839(7)$ Å, $b = 14.014(5)$ Å, $c = 11.760(5)$ Å, $\alpha = 102.75(3)°$, $\beta = 103.15(4)°$, $\gamma = 95.64(4)°$, $V = 2139(2)$ Å^3, $Z = 2$, $R = 0.12$ (unpublished result).

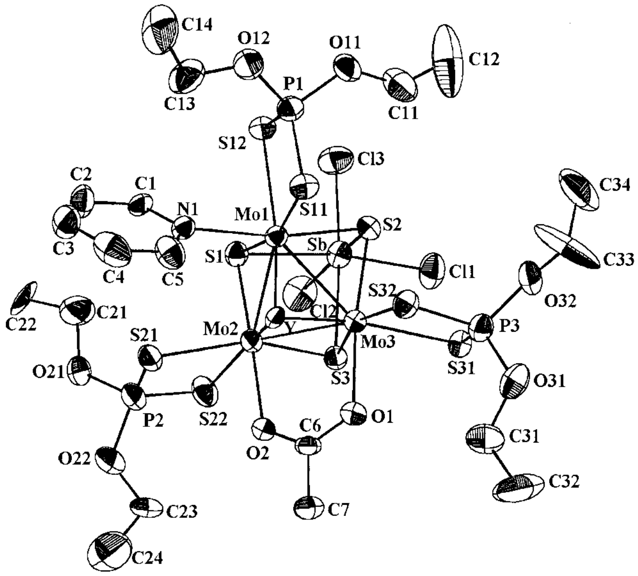

Figure 1. An ORTEP diagram of $[Mo_3(SbCl_3)YS_3(\mu\text{-}OAc)(dtp)_3(py)]$ (**1**) ($Y = 90\%O + 10\%S$) showing 30% probability thermal ellipsoids.

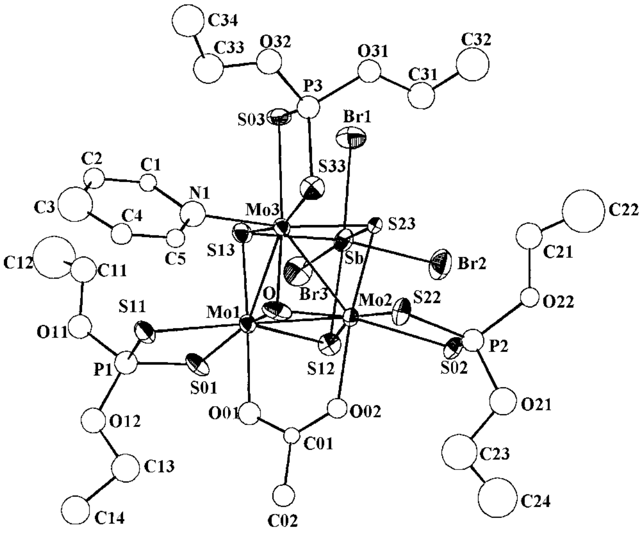

Figure 2. An ORTEP diagram of $[Mo_3(SbBr_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)]$ (**2**) showing 30% probability thermal ellipsoids.

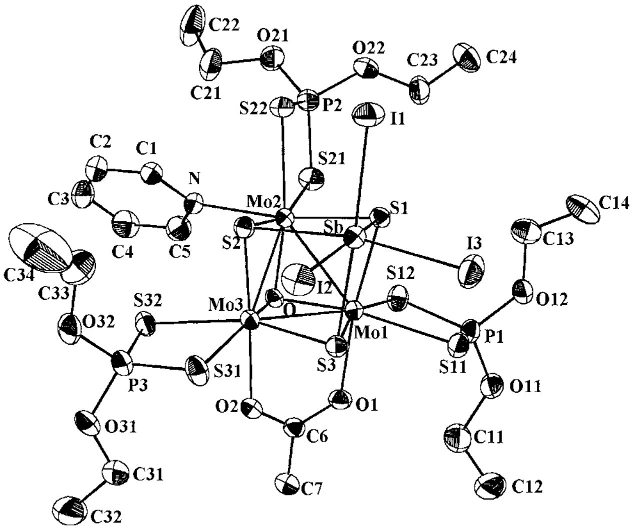

Figure 3. An ORTEP diagram of $[Mo_3(SbI_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)]$ (**3**) showing 30% probability thermal ellipsoids.

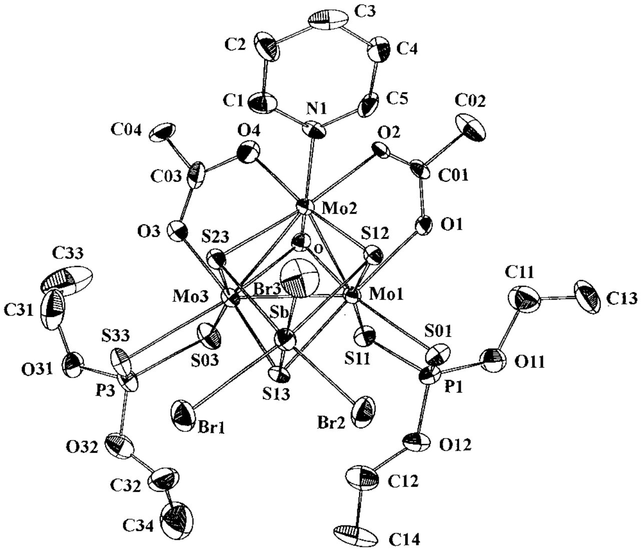

Figure 4. An ORTEP diagram of $[Mo_3(SbBr_3)OS_3(\mu\text{-}OAc)_2(dtp)_2(py)]$ (**5**) showing 30% probability thermal ellipsoids.

into two types pursuant to their coordinated environment around the metal atoms. The first one, SC_1, (SC stands for single cubane while the subscript is used to designate the number of bridging (OAc) groups) is generically formulated as $Mo_3(SbX_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)$ (X = Cl, Br, I). Clusters **1**−**3** belong to this type. The overall cluster symmetry is C_1. Each Mo atom is coordinated by one (μ_3-O), two (μ_3-S) (the S atom triply bridging two Mo atoms and one Sb atom), two S atoms from one terminal (dtp) group, and one oxygen atom of the bridging (OAc) or N atom of (py) group to complete a distorted octahedral coordination geometry. Three Mo atoms form an isosceles triangle with two long and one short edges, of which the short edge corresponds to the (μ-OAc) bridged Mo−Mo bond. On the other hand, cluster **5** belongs to the second type (SC_2) in which two bridging (OAc) ligands are coordinated to the cluster core in a symmetric style making the structure of C_s symmetry with a pseudo-mirror plane through Mo(2), Sb (μ_3-O), Br(3), and S(13). This is an unprecedented configuration and is obtained only by starting from the trimolybdenum clusters containing $[Mo_3OS_3]$ core. No example of this configuration has resulted so far by the reaction of the $[Mo_3S_4]$ core. In this type, two Mo atoms have the same octahedral coordination environments: each is coordinated to one (μ_3-O), two (μ_3-S), two S atoms of a terminal (dtp) ligand, and one oxygen atom of the bridging (OAc). By comparison, the third Mo atom has a slight different octahedral coordination sphere consisting of one (μ_3-O),two (μ_3-S), two oxygen atoms belonging to two respective (OAc) groups, and a terminal pyridine ligand. The $\{Mo_3\}$ framework is approximately an isosceles triangle in which there are two relatively short Mo−Mo distances bridged by (OAc) ligand and one slightly longer Mo−Mo bond. It is noted that Mo−Mo bond distances of 2.571(2)−2.638(2) Å and the average Mo−(μ_3-O)bond length of 2.00(1) Å are shorter than those found in clusters **1**−**3** of the type SC_1.

The Sb exhibits an irregular staggered triangular prismoidal geometry bonded to three (μ_3-S) atoms and three halogen atoms (Cl, Br, or I). The distances between Mo−Sb ranging from 3.788(2) to 3.859(6) Å are too long to contain any significant bonding.

A comparison of the main bond lengths for four clusters **1**−**3** and **5** with their starting trinuclear clusters **4** and **6** is given in Table 2. It can be seen from these data that the most striking change does exist in Mo−(μ-S) bond distances owing to the

Table 2. Selected Bond Distances (Å)

cluster^a	Mo−Mo (av)	Mo−(μ_3-O) (av)	Mo−(μ-S) or Mo−(μ_3-S) (av)	Mo−O$_{(OAc)}$ (av)	Mo−N$_{(py)}$	Sb−(μ_3-S) (av)	Sb-X (av)	Sb−X^c	Mo···Sb (av)
1	2.609(2)^b 2.637(2) 2.643(2) (2.630)	2.093(9) 2.111(8) 2.107(7) (2.100)	2.313(4) 2.323(3) 2.324(4) 2.332(4) 2.319(4) 2.325(4) (2.323)	2.16(1) 2.18(1) (2.17)	2.31(1)	2.768(4) 2.781(4) 2.825(4) (2.791)	2.364(5) 2.378(5) 2.379(5) (2.373)	2.36	3.828(2) 3.824(2) 3.850(2) (3.834)
2	2.598(6)^b 2.635(6) 2.628(6) (2.620)	2.06(3) 1.95(3) 2.08(3) (2.03)	2.34(1) 2.35(1) 2.32(1) 2.34(1) 2.31(1) 2.34(1) (2.33)	2.18(3) 2.17(3) (2.18)	2.27(4)	2.76(1) 2.78(1) 2.81(1) (2.78)	2.535(7) 2.540(7) 2.554(7) (2.543)	2.50	3.835(6) 3.835(6) 3.859(6) (3.843)
3	2.605(2)^b 2.629(2) 2.642(2) (2.625)	2.064(7) 2.051(7) 2.077(7) (2.064)	2.320(3) 2.324(3) 2.322(3) 2.325(3) 2.323(3) 2.328(3) (2.324)	2.147(7) 2.150(7) (2.149)	2.301(9)	2.764(3) 2.785(3) 2.815(3) (2.788)	2.775(1) 2.776(2) 2.759(1) (2.770)	2.719	3.842(1) 3.842(1) 3.845(1) (3.843)
4	2.589(2)^b 2.642(2) 2.627(2) (2.625)	2.05(1) 2.04(1) 2.04(1) (2.04)	2.289(5) 2.297(5) 2.286(5) 2.286(5) 2.280(5) 2.281(5) (2.287)	2.20(1) 2.20(1) (2.20)	2.30(1)				
5	2.575(2)^b 2.571(2)^b 2.638(2) (2.595)	2.014(9) 1.99(1) 2.001(9) (2.00)	2.326(4) 2.331(4) 2.337(4) 2.347(4) 2.321(4) 2.333(4) (2.333)	2.18(1) 2.11(1) 2.13(1) 2.17(1) (2.15)	2.25(1)	2.753(4) 2.770(4) 2.804(4) (2.776)	2.537(2) 2.540(2) 2.553(3) (2.543)	2.50	3.788(2) 3.826(2) 3.847(2) (3.820)
6	2.584(4)^b 2.587(4)^b 2.657(3) (2.609)	2.00(2) 1.96(2) 1.98(2) (1.98)	2.31(1) 2.32(1) 2.30(1) 2.30(1) 2.29(1) 2.30(1) (2.30)	2.11(2) 2.13(2) 2.24(2) 2.17(2) (2.16)	2.27(2)				

[a] $[Mo_3(SbCl_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)]$ (**1**), $[Mo_3(SbBr_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)][(CH_3)_2CO]$ (**2**), $[Mo_3(SbI_3)OS_3(\mu\text{-}OAc)(dtp)_3(py)][(CH_3)_2CO]$ (**3**), $[Mo_3OS_3(\mu\text{-}OAc)(dtp)_3(py)]$ (**4**), $[Mo_3(SbBr_3)OS_3(\mu\text{-}OAc)_2(dtp)_2(py)][0.5(C_2H_5OH)]$ (**5**), and $[Mo_3OS_3(\mu\text{-}OAc)_2(dtp)_2(py)]$ (**6**). [b] Mo−Mo bond bridged by OAc. [c] In SbX_3 complex.

addition of SbX_3. Obviously, the double bridging (μ-S) atoms of clusters **4** and **6** have been converted to triple bridging (μ_3-S) linking two Mo atoms and one Sb atom for clusters **1**−**3** and **5**. Mo−S bond distances are lengthened by about 0.030−0.037 Å (from 2.287(5) Å of **4** to 2.324(3) Å for type SC_1, from 2.303(1) Å of **6** to 2.333(4) Å for type SC_2). Three Sb−S bond lengths lie within the range of 2.753(4)−2.825(4) Å. As for the Mo−Mo bonds, the addition of SbX_3 has only a very slight effect on the shortening of the Mo−Mo distances. Furthermore, the comparison of the structure characteristics of clusters **1**, **2**, and **3** (their addition complexes are $SbCl_3$, $SbBr_3$ and SbI_3, respectively) indicates that although their structures are very similar to each other, Sb−S bond lengths of clusters **2** and **3** are shorter than that of cluster **1**. Besides, it is clear that all lengths of Sb−X are significantly longer than those of free SbX_3 compound,[17] about 0.013 Å for Sb−Cl, 0.043 Å for Sb−Br, and 0.051 Å for Sb−I. As expected, the lengthening effect of Sb−X bond distances follows the order of Sb−Cl < Sb−Br < Sb−I.

3. Spectroscopic Characterization. Table 3 lists the spectroscopic data of the IR, Raman, UV−vis, and ^{95}Mo NMR.

IR and Raman. In addition to the vibration peaks of dtp, OAc, and py,[18−20] the important absorption bands are experimentally assigned. From Table 3, first, the ν(Mo−(μ-S)) band positions of clusters **1**, **2**, **3**, and **5** (453.2, 454.2, 454.2, and 450.0 cm^{-1}, respectively) are lower by 5−10 cm^{-1} with respect to that of starting {Mo$_3$} cluster **4** (459.0 cm^{-1}). Besides, the values of νSb−X (being 306.0, 210.2, and 167.8 cm^{-1} for (Sb−Cl) of **1**, (Sb−Br) of **2**, (Sb−I) of **3**, respectively) are lower by 20−70 cm^{-1} than those of the free SbX_3 compounds (380.7, 256.0, and 186.5 cm^{-1} for $SbCl_3$, $SbBr_3$, and SbI_3, respectively[19,21]). Second, the vibrational spectra of type SC_1 and SC_2

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Table 3. The Spectroscopic Data

	cluster^a				
	1	**2**	**3**	**5**	**4**
	IR (cm^{-1})				
ν Mo−(μ_3-O)	694.3	696.2	694.3	717.4	694.3
ν Mo−(μ_3-S)	453.2	454	454	450	459.0
ν Mo−O(OAc)	676.9, 530.3	676.9, 532.3	676.9, 532.3	676.9, 530.3	675.0
ν Mo−N(py)	636.4, 499.5	634.5, 497.6	634.5, 495.6	638.3	642.2
ν Mo−S(dtp)	310−300	310−300	310−300	310−300	
ν Sb−(μ_3-S)	258−239	258−239.1	258.4, 239.1	258.4−239.1	
ν Sb−X	306 (315.6)^b	210.2 (209.5)^b	167.8 (163.2)^b	210.2 (211.4)^b	
ν Mo−Mo (Raman)	213.4	213.4	213.4	230	∼200
	UV−Vis				
λ (nm (ϵ M^{-1} cm^{-1}))					
λ_1	465(8.58×10^3)	500(7.98×10^3)	570(1.01×10^4)	500(9.51×10^3)	
λ_2	405(1.37×10^4)	415(1.47×10^4)	425(1.30×10^4)	400(1.55×10^4)	
λ_3	310(1.23×10^4)	325(1.00×10^4)	330(1.14×10^4)	317(8.03×10^4)	
λ_4	238(4.74×10^4)	238(4.88×10^4)	245(4.82×10^4)	235(3.80×10^4)	
^{95}Mo NMR (ppm)	1:1:1	1:1:1	1:1:1		
(the line width is given in paratheses, Hz)	1442(528)	1493(865)	1598(656)		
	1245(671)	1289(754)	1378(747)		
	1176(477)	1218(551)	1319(655)		

[a] $[Mo_3(SbCl_3)OS_3(\mu\text{-OAc})(dtp)_3(py)]$ (**1**), $[Mo_3(SbBr_3)OS_3(\mu\text{-OAc})(dtp)_3(py)][(CH_3)_2CO]$ (**2**), $[Mo_3(SbI_3)OS_3(\mu\text{-OAc})(dtp)_3(py)][(CH_3)_2CO]$ (**3**), $[Mo_3OS_3(\mu\text{-OAc})(dtp)_3(py)]$ (**4**), and $[Mo_3(SbBr_3)OS_3(\mu\text{-OAc})_2(dtp)_2(py)][0.5(C_2H_5OH)]$ (**5**). [b] In Raman spectra.

have also been compared. For type SC_2 (cluster **5**), ν Mo−(μ_3-O) band at 717.4 cm^{-1} is ca. 23 cm^{-1} higher than that of type SC_1 (about 694 cm^{-1}). As for the Raman spectra, according to some related literature,[22] the relatively strong band at 213 and 230 cm^{-1} for types SC_1 and SC_2, respectively, may be assigned to Mo−Mo vibration. These values are higher than those of pre-addition $\{Mo_3\}$ clusters $[Mo_3OS_3(\mu\text{-OOCR})(dtp)_3L]$ (∼200 cm^{-1}),[23] and this difference can reflect the strengthening of Mo−Mo bonds. All of these changes are consistent with the results from the X-ray structure analysis.

UV−Vis. From Table 3, it can be seen that the red shifts of UV−vis peaks are observed in Cl, Br, I order for clusters **1**−**3**. Therefore, the softer X atoms lead to the smaller energies of electron transfer ΔE. Concerning the comparison between clusters **2** and **5**, all of them use $SbBr_3$ as the addition complex but possess different structures. The peak positions and the ϵ values of UV−vis spectra are also considerably different.

^{95}Mo NMR. The ^{95}Mo NMR of clusters **1**−**3** in CH_2Cl_2 together with their chemical shifts and line widths are given in Table 3. It is apparent that the chemical shifts increase with Cl, Br, I order. That is to say, the shielding order I < Br < Cl gives an “inverse halogen dependence”. Perhaps the valence shell electron configuration of less than half-filled of Mo(IV) is responsible for this effect.[24]

Conclusion

In contrast with the $[Mo_3SbS_4]$ clusters reported previously, the studied series of $[Mo_3SbOS_3]$ cubane-type clusters containing mixed O/S bridges is reported for the first time. The successful syntheses of these compounds show that, starting from $[Mo_3OS_3]$-type clusters with (OAc) as bridging ligand, the addition reaction of SbX_3 can preserve the presence of (μ_3-O) to construct $[Mo_3(SbX_3)OS_3]$-type clusters. Their structures can be viewed as the simple combination of responding trimolybdenum cluster with respective halide complex via the formation of three S−Sb bonds. The trimolybdenum parts of the cubane-like clusters almost remain their original structures. Actually, the addition of SbX_3 has much greater influences on the electronic structure than on the geometrical configurations of the starting trimolybdenum clusters.

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Supporting Information Available: Raman and IR spectra, UV−vis spectra for complexes $[Mo_3(SbCl_3)OS_3(\mu\text{-OAc})(dtp)_3(py)]$ **1**, $[Mo_3(SbBr_3)OS_3(\mu\text{-OAc})(dtp)_3(py)][(CH_3)_2CO]$ **2**, $[Mo_3(SbI_3)OS_3(\mu\text{-OAc})(dtp)_3(py)][(CH_3)_2CO]$ **3**, and $[Mo_3(SbBr_3)OS_3(\mu\text{-OAc})_2(dtp)_2(py)][0.5(C_2H_5OH)]$ **5**, and ^{95}Mo NMR spectra for clusters **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org. An X-ray crystallographic file in CIF format for these compounds is available on the Internet only.

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