Synthesis and Characterization of Three Tetranuclear Clusters Containing a $[Mo_3OS_3Sn]^{6+}$ Cubane-like Core

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Three heterometallic cubane-like clusters, $[Mo_3(\mu_3\text{-O})(\mu_3\text{-S})_3(SnCl_3)(dtp)_3(py)_3]$ (dtp = $S_2P(OC_2H_5)_2^-$, py = C_5H_5N) (**1**), (PPN)$[Mo_3(\mu_3\text{-O})(\mu_3\text{-S})_3(SnCl_3)(dtp)_3(\mu\text{-OAc})(py)]$ (OAc = CH_3COO^-, PPN = $(C_6H_5)_3PNP(C_6H_5)_3^+$) (**2**), and $(Et_4N)[Mo_3(\mu_3\text{-O})(\mu_3\text{-S})_3(SnCl_3)(dtp)_2(\mu\text{-OAc})_2(py)]$ (**3**) have been prepared by the reaction of $[Mo_3(\mu_3\text{-O})(\mu\text{-S})_3(dtp)_4(H_2O)]$ (**4**), $[Mo_3(\mu_3\text{-O})(\mu\text{-S})_3(dtp)_3(OAc)\ (py)]$ (**5**), and $[Mo_3(\mu_3\text{-O})(\mu\text{-S})_3(dtp)_2(OAc)_2\ (py)]$ (**6**) with $SnCl_2$, respectively. They have been characterized by IR, UV−vis, ^{31}P NMR, ^{95}Mo NMR, and X-ray structure analysis. All of these heterometallic clusters have a $[Mo_3OS_3Sn]^{6+}$ core but contain a different arrangement of peripheral ligands. As far as the neutral cluster **1** is concerned, there is no bridging OAc ligand, while only one bridging OAc ligand is observed for cluster **2** and two are for cluster **3**. The Mo−Mo distances are about 0.03−0.04 Å shorter than those of the starting trimolybdenum clusters. This indicates that the incorporation of $SnCl_3^-$ fragment into $\{Mo_3\}$ clusters makes the Mo−Mo bonding enhanced. Crystal data for **1**: triclinic, space group P-1, $a = 10.7423(2)$ Å, $b = 14.0357(1)$ Å, $c = 16.9346(2)$ Å, $\alpha = 84.054(1)°$, $\beta = 87.095(1)°$, $\gamma = 84.517(1)°$, $V = 2525.82(6)$ Å^3, $Z = 2$, $R = 0.038$ for 5584 reflections ($I > 2.0\sigma(I)$). Crystal data for **2**: triclinic, space group P-1, $a = 12.9529(1)$ Å, $b = 15.6324(2)$ Å, $c = 19.6355(1)$ Å, $\alpha = 92.083(1)°$, $\beta = 97.908(1)°$, $\gamma = 110.337(1)°$, $V = 3677.41(6)$ Å^3, $Z = 2$, $R = 0.034$ for 8665 reflections ($I > 2.0\sigma(I)$). Crystal data for **3**: monoclinic, space group $P2_1/n$, $a = 14.0852(5)$ Å, $b = 15.1324(5)$ Å, $c = 23.2691(7)$ Å, $\beta = 97.371(1)°$, $V = 4918.7(3)$ Å^3, $Z = 4$, $R = 0.049$ for 4970 reflections ($I > 2.0\sigma(I)$).

Introduction

In our systematical study on the hybrid Mo(W)−main group metal clusters containing sulfur bridges, the halide complexes of groups 14 and 15 metals are found to be important reaction materials.[1−3] Among them, SnX_3^- (X = Cl, Br, I) can be considered as an effective reagent to react with $[M_3S_3]$ (M = Mo, W) cluster ring to form Mo−Sn−S compounds on account of the advantage of lone pair electrons of Sn^{2+}. Based on this supposition, several $M_3S_4(SnX_3)(dtp)_3(py)_3$ (M = Mo, W; X = Cl, Br, I; dtp = $S_2P(OC_2H_5)_2^-$) hybrid metallic clusters have been synthesized.[4] Similar Mo−Sn−S clusters reported so far include $[Mo_3S_4Sn(H_2O)_9]^{6+}$,[5] $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9]^{8+}$,[5] $(Me_2NH_2)_6[Mo_3S_4(SnCl_3)(NCS)_9]0.5H_2O$,[6] $[Me_2NH_2]_6[(SCN)_9W_3S_4SnCl_3]0.5H_2O$,[7] and $Mo_3S_4Sn\ (S_2PEt_2)_6$.[8] All of the clusters mentioned above are synthesized by the reaction of $[Mo_3(\mu_3\text{-S})(\mu\text{-S})_3]^{4+}$ core with either Sn metal or Sn^{2+} complex. As an analogue of $[Mo_3(\mu_3\text{-S})(\mu\text{-S})_3]^{4+}$ cluster, the $[Mo_3(\mu_3\text{-O})(\mu\text{-S})_3]^{4+}$ cluster was once thought difficult to be available due to the size incompatibility of the μ_3-O atoms to the μ-S atoms.[9] In our reaction system, however, we are fortunate to synthesize a series of clusters containing a $[Mo_3(\mu_3\text{-O})(\mu\text{-S})_3]^{4+}$ core through the control of acidity of the reaction medium.[10] There is no doubt that the investigation of the reaction of $[Mo_3(\mu_3\text{-O})(\mu\text{-S})_3]^{4+}$ with main-group metal complexes such as $SnCl_3^-$ and a further comparison with that of $[Mo_3(\mu_3\text{-S})(\mu\text{-S})_3]^{4+}$ on this basis will be of significance in the structural chemistry. Up to now, clusters $[Mo_3(\mu_3\text{-O})(\mu_3\text{-S})_3(SnBr_3)(dtp)_3(py)_3]$,[11] $[Mo_3(\mu_3\text{-O})(\mu_3\text{-S})_3(SbX_3)\ (dtp)_3(OAc)(py)]$ (X = Cl, Br, I),[12] $\{Mo_3OS_3(BiI_3)(OAc)_2(py)_3(\mu\text{-O})\}_2$,[13] and $\{Mo_3OS_3Pb(dtp)_2(OAc)_2(py)_3(\mu\text{-O})\}_2$[14] are the few structures reported in this species. Herein, the synthesis and the structural characterization of three new mixed O/S bridging cubane-type Mo−Sn clusters $[Mo_3(\mu_3\text{-O})(\mu_3\text{-S})_3(SnCl_3)(dtp)_3(py)_3]$ (**1**), (PPN)$[Mo_3(\mu_3\text{-O})(\mu_3\text{-S})_3(SnCl_3)(dtp)_3(\mu\text{-OAc})(py)]$ (**2**), and $(Et_4N)[Mo_3(\mu_3\text{-O})(\mu_3\text{-S})_3$-

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(1) Lu, S. F.; Huang, J. Q. 214th ACS National Meeting, Book of Abstracts, 1997, INORG 069.

(2) Lu, S. F.; Huang, J. Q.; Wu, Q. J.; Huang, X. Y.; Yu, R. M.; Wu. D. X.; *Inorg. Chim. Acta* **1997**, *261*, 201−209.

(3) Lu, S. F.; Huang, J. Q.; Huang, X. Y.; Wu, Q. J.; Yu, R. M. *Acta Chim. Sinica* **1998**, *56*, 905−913 (in Chinese).

(4) Lu, S. F.; Huang, J. Q. *Acad. Periodical Abstr. China* **1998**, *4* (11), 1431−1432.

(5) Shibahara, T.; Akashi, H. *Inorg. Chem.* **1989**, *28*, 2906−2907.

(6) Varey, J. E.; Lamprecht, G. J.; Fedin, V. P.; Holder, A.; Clegg, W.; Elsegood, M. R. J.; Sykes, A. G. *Inorg. Chem.* **1996**, *35*, 5525−5530.

(7) Müller, A.; Fedin, V. P.; Dimann, E.; Bögge, H.; Krickemeyer, E.; Sölter, D.; Giuliani, A. M.; Barbieri, R.; Adler, P. *Inorg. Chem.* **1994**, *33*, 2243−2247.

(8) Keck, H.; Kruse, A.; Kuchen, W.; Mootz, D.; Wiskeman, R.; Wunderlich, H. *Naturforsch* **1989**, *45b*, 461−464.

(9) Martinez, M.; Ooi, B. L.; Sykes, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4615−4619.

(10) Huang, J. Q.; Huang, J. L.; Shang, M. Y.; Lu, S. F.; Lin, X. T.; Lin, Y. H.; Wu, D. M.; Zhuang, H. H.; Lu, J. X. *Pure Appl. Chem.* **1988**, *60*, 1185−1192.

(11) Huang, J. Q.; Lu, S. F.; Huang, X. Y.; Wu, Q. J.; Yu, R. M. *J. Cluster Sci.* **1997**, *8* (1), 47−57.

(12) Lu, S. F.; Huang, J. Q.; Huang, X. Y.; Wu, Q. J.; Yu, R. M. *Inorg. Chem.* **1999**, *38*, 3801−3805.

(13) Lu, S. F.; Huang. J. Q.; Wu, Q. J.; H. X. Y.; Wu, D. X.; Zheng, Y.; Yu, R. M. *Polyhedron* **1998**, *18*, 281−287.

(14) Yu, R. M.; Lu, S. F.; Huang, X. Y.; Wu, Q. J.; Huang, J. Q. *Inorg. Chem.* **1999**, *38*, 3313−3315.

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Table 1. Crystallographic Data for Compounds **1**−**3**

	chemical formula		
	$C_{27}H_{45}Cl_3Mo_3N_3O_7P_3S_9Sn$	$C_{55}H_{67}Cl_3Mo_3N_2O_9P_5S_9Sn$	$C_{25}H_{51}Cl_3Mo_3N_2O_9P_2S_7Sn$
formula weight	1417.97	1856.36	1322.90
space group	P-1 (No. 2)	P-1(No. 2)	$P2_1/n$ (No. 14)
a (Å)	10.7423(2)	12.5929(1)	14.0852(5)
b (Å)	14.0357(1)	15.6324(2)	15.1324(5)
c (Å)	16.9346(2)	19.6355(1)	23.2691(7)
α (deg)	84.054(1)	92.083(1)	90
β (deg)	87.095(1)	97.908(1)	97.371(1)
γ (deg)	84.517(1)	110.337(1)	90
V (Å^3)	2525.82(6)	3677.41(6)	4918.7(3)
Z	2	2	4
T (°C)	23	23	23
λ (Å)	0.71073	0.71073	0.71073
ρ_{calcd}, g·cm^{-3}	1.864	1.676	1.786
μ, cm^{-1}	18.83	13.59	18.17
R (F_o^2)[a]	0.038	0.034	0.049
wR (F_o^2)[b]	0.093	0.077	0.120

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $\mathrm{wR} = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, $P = (2F_c^2 + F_o^2)/3$.

$(SnCl_3)(dtp)_2(\mu\text{-}OAc)_2(py)]$ (**3**) are reported. Their structural features provide a different reactive behavior and coordination of $[Mo_3OS_3]$ and $[Mo_3S_4]$ in the metal addition reaction.

Experimental Section

General Procedures. All of the reactions and manipulations were carried out in air. Commercially available reagents were used as received. Compounds$[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(dtp)_4(H_2O)]$ (**4**), $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(dtp)_3(OAc)(py)]$ (**5**), and $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(dtp)_2(OAc)_2(py)]$ (**6**) were prepared according to the literature.[15−17]

Elemental analyses were performed by Italy Elemental Analyzer EO1106. IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer as KBr pellets (4000−400 cm^{-1}). ^{31}P and ^{95}Mo NMR were carried out at 202.358 and 32.616 MHz, respectively, on a Variant Unity 550 spectrometer. Chemical shifts were measured with respect to H_3PO_4 (^{31}P) or Na_2MoO_4 (^{95}Mo) in D_2O as external standard. UV−vis spectra were recorded on a Shimadzu UV-3000 spectrometer.

Preparation of $[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_3(py)_3]$ (1). Compound **4** (360 mg, 0.31 mmol), $SnCl_2{\cdot}2H_2O$(90 mg, 0.40 mmol) and PPNCl (180 mg, 0.31 mmol) were dissolved in 10 mL of CH_2Cl_2 and 5 mL of C_2H_5OH. Pyridine (0.06 mL) was added to the solution. The mixture was stirred for 30 min and then filtered. The green filtrate was evaporated in air. A lot of green powder was obtained the next day. The green powder then was dissolved in acetone to recrystallize; 250 mg of black crystals suitable for X-ray diffraction work were obtained (a yield of 57%). Anal. Calcd for $C_{27}H_{45}Cl_3Mo_3N_3O_7P_3S_9Sn$: C, 22.87; H, 3.17; N, 2.96. Found: C, 22.78; H, 3.11; N, 2.86. IR (cm^{-1}) (KBr): 2983.4(m), 2935.2(w), 2865.7(w), 1602.6(s), 1484.9(w), 1475.3(w), 1444.4(vs), 1388.5(m), 1353.8(w), 1290.2(w), 1236.2(w), 1218.8(s), 1162.9(m), 1095.4(w), 1066.5(s), 1031.7(vs), 1010.5(vs), 956.5(vs), 871.7(w), 811.9(m), 792.6(s), 769.5(s), 696.2(s), 655.7(m), 648.0(m), 634.5(w), 549.6(w), 536.1(w), 501.4(w), 439.7(w), 428.1(w).

Preparation of $(PPN)[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_3(\mu\text{-}OAc)(py)]$ (2). Solid $SnCl_2{\cdot}2H_2O$ (70 mg, 0.31 mmol), PPNCl (250 mg, 0.53 mmol), and pyridine (0.06 mL) were added to the brown solution of compound **5** (360 mg, 0.33 mmol) in 10 mL of acetone and 5 mL of C_2H_5OH. The color turns to green immediately. After 30 min of stirring, the mixture was filtered. The filtrate was kept openly in air at room temperature. On standing for 4 days, 450 mg of black crystals were isolated, washed with absolute alcohol and petroleum ether, and then dried in air (a yield of 73%). Anal. Calcd for $C_{55}H_{67}Cl_3Mo_3N_2O_9P_5S_9Sn$: C, 33.54; H, 3.60; N, 1.51. Found: C, 33.28; H, 3.49; N, 1.47. IR (cm^{-1}) (KBr): 3054.7(m), 2975.7(s), 2933.2(m), 2896.6(m), 1602.6(w), 1587.1(w), 1573.6(w), 1531.2(m), 1483.0(m), 1475.3(m), 1438.7(vs), 1388.5(m), 1348.0(w), 1292.1(s), 1267.0(vs), 1220.7(m), 1186.0(m), 1162.9(m), 1114.7(vs), 1012.5(vs), 958.5(vs), 850.5(w), 813.8(s), 792.6(s), 771.4(s), 761.8(m), 744.4(m), 725.1(vs), 690.4(vs), 675.0(s), 659.5(m), 644.1(s), 545.8(vs), 536.1(vs), 526.5(s), 503.3(s), 457.1(w), 452.3(w), 439.7(w), 418.5(w).

Preparation of $(Et_4N)[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_2(\mu\text{-}OAc)_2(py)]$ (3). Method 1, from Compound 6. Compound $SnCl_2{\cdot}2H_2O$ (100 mg, 0.44 mmol), $Et_4NCl{\cdot}H_2O$ (100 mg, 0.37 mmol), and pyridine (0.06 mL) were added into the brown solution of compound **6** (360 mg, 0.37 mmol) in 25 mL of acetone and 5 mL of C_2H_5OH. The color turns to green immediately. After 1 h of stirring, the mixture was filtered. The filtrate was kept openly in air to crystallize by vaporization at room temperature. On standing for half a month, 350 mg of black crystals were isolated, washed with absolute alcohol and petroleum ether, and then dried in air (a yield of 72%). Anal. Calcd for $C_{25}H_{51}Cl_3Mo_3N_2O_9P_2S_7Sn$: C, 22.70; H, 3.86; N, 2.12. Found: C, 22.56; H, 3.79; N, 2.15.

Method 2, from Compound 4. To the solution of compound **4** (360 mg, 0.31 mmol) in 25 mL of acetone were added $SnCl_2{\cdot}2H_2O$ (100 mg, 0.44 mmol), $Et_4NCl{\cdot}H_2O$ (100 mg, 0.37 mmol), acetic acid (0.5 mL), and pyridine (0.10 mL). The green mixture was refluxed for about 2 h and then filtered. The filtrate was allowed to stand in air to crystallize at room temperature. Days later, 260 mg of black crystalline product was isolated from the filtrate, washed with absolute alcohol and petroleum ether, and then dried in air (a yield of 64%). The product was confirmed to be compound **3** by its IR spectra. IR (cm^{-1}): 3116.4(w), 3077.9(w), 3050.9(w), 2977.6(s), 2927.4(m), 2900.5(m), 2867.7(w), 1606.4(m), 1525.4(vs), 1481.1(s), 1444.4(vs), 1419.4(vs), 1392.4(s), 1365.4(m), 1348.0(s), 1297.9(m), 1220.7(m), 1182.2(w), 1166.7(s), 1095.4(m), 1045.2(s), 1008.6(vs), 950.7(vs), 817.7(vs), 784.9(vs), 765.6(vs), 717.4(s), 696.2(s), 675.0(vs), 657.6(s), 644.1(s), 621.0(w), 526.5(m), 439.7(w), 416.6(m), 403.1(w).

X-ray Structure Determination. A summary of the crystal data and parameters for data collection are presented in Table 1. Data collections were performed on a Siemens SMART CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K. The structures were solved by direct methods and subsequent Fourier difference techniques. All nonhydrogen atoms were refined anisotropically by full matrix least squares based on F^2 value with weighting scheme $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants adjusted by the program. The idealized positions of the hydrogen atoms were located by using a riding model. The scattering contributions of hydrogen atoms were added to the structure factor calculations but their positions were not refined. All calculations were carried out on a

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(15) Lu, S. F.; Shang, M. Y.; Huang, J. Q.; Huang, J. L.; Lu, J. X. *Scientia Sinica Ser. B* **1988**, *31* (2), 147−160.

(16) Lu, S. F.; Huang, J. Q.; Huang, M. D.; Huang, J. L. *Acta Chim. Sinica Engl. Ed.* **1989**, *1*, 24−36.

(17) Lu, S. F.; Huang, J. Q.; Huang, Z. X.; Zhang, B.; Huang, J. L. *Chin. J. Chem.* **1992**, *10* (6), 500−507.

computer with SHELXS-86 (Sheldrick, 1990) program for structure solution and SHELXL-93 (Sheldrick, 1993) program for structure refinement.[18]

Results and Discussion

Synthesis Reaction. The reaction schemes of the present three clusters as well as their products are as follows.

$$[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu\text{-}\mathrm{S})_3(\mathrm{dtp})_4(\mathrm{H_2O})]\ (\mathbf{4}) + \mathrm{PPNCl} + \mathrm{SnCl_2} + \mathrm{py} \rightarrow [\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_3(\mathrm{py})_3]\ (\mathbf{1}) + \mathrm{PPNdtp} + \mathrm{H_2O} \quad (1)$$

$$[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu\text{-}\mathrm{S})_3(\mathrm{dtp})_3(\mathrm{OAc})(\mathrm{py})]\ (\mathbf{5}) + \mathrm{PPNCl} + \mathrm{SnCl_2} \rightarrow (\mathrm{PPN})[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_3(\mu\text{-}\mathrm{OAc})(\mathrm{py})]\ (\mathbf{2}) \quad (2)$$

$$[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu\text{-}\mathrm{S})_3(\mathrm{dtp})_2(\mathrm{OAc})_2(\mathrm{py})]\ (\mathbf{6}) + \mathrm{SnCl_2} + \mathrm{Et_4NCl} \rightarrow (\mathrm{Et_4N})[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_2(\mu\text{-}\mathrm{OAc})_2(\mathrm{py})]\ (\mathbf{3}) \quad (3)$$

It can be seen from these reactions that the difference between the starting {$\mathrm{Mo_3}$} clusters **4** and **5** lies in the bidentate bridging ligand and "loose coordination ligand",[10] i.e., (μ-dtp) and ($\mathrm{H_2O}$) for **4** while (μ-OAc) and (py) for **5**. After the reactions, the (μ-dtp) ligand and ($\mathrm{H_2O}$) in cluster **4** drop off whereas the (μ-OAc) ligand of cluster **5** remains during the reaction 2. This is indicates that the Mo−(μ-OAc) bonds are stronger than the Mo−(μ-dtp) bonds. Moreover, reaction 1 cannot be regarded as a simple [3 + 1] combination, but the combination of $\mathrm{SnCl_3}^-$ accompanies simultaneously the replacement of dtp^- and $\mathrm{H_2O}$ by three py ligands.

As is indicated in our experiment, the reaction of compound **1** or **2** with acetic acid can also be adopted to synthesize compound **3** (see reactions 4 and 5).

$$[\mathrm{Mo_3}\ (\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_3(\mathrm{py})_3]\ (\mathbf{1}) + \mathrm{HOAc} \rightarrow [\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_2(\mu\text{-}\mathrm{OAc})_2(\mathrm{py})]^-\ (\mathbf{3}) + \mathrm{Hdtp} + \mathrm{py} + \mathrm{H}^+ \quad (4)$$

$$[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_3(\mu\text{-}\mathrm{OAc})(\mathrm{py})]^-\ (\mathbf{2}) + \mathrm{HOAc} \rightarrow [\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_2(\mu\text{-}\mathrm{OAc})_2(\mathrm{py})]^-\ (\mathbf{3}) + \mathrm{Hdtp} \quad (5)$$

Reactions 4 and 5 involve the substitution of some terminal dtp ligand and the rearrangement of the peripheral ligands, which demonstrate the liability of the terminal dtp ligands and the stability of the $[\mathrm{Mo_3OS_3Sn}]^{6+}$ core.

Structure Features. The selected bond lengths of three heterometallic tetranuclear clusters **1**−**3** and three related trimolybdenum clusters **5**−**7** are listed in Table 2. The clusters **7**, **5**, and **6** are regarded as the structure units of clusters **1**, **2**, and **3** before the addition of $\mathrm{SnCl_3}^-$, respectively. The spectroscopic data of clusters **1**−**3** are given in Table 3. In the following, the structure features of three clusters will be described separately.

Compound $[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_3(\mathrm{py})_3]$ (1). This is a neutral cluster. The ORTEP plot of the structure is shown in Figure 1. Although the molecule has no crystallographic symmetry in a strict sense, it can be seen from the Figure 1 that the cluster molecule as a whole can be taken as close to a C_{3v} symmetry with a pseudo-3-fold axis passing through the Sn and (μ_3-O) atoms. The molecule can also be regarded as the linking of $[\mathrm{Mo_3OS_3(dtp)_3(py)_3}]^+$ trinuclear unit and $\mathrm{SnCl_3}^-$ via three Sn−(μ_3-S) bonds. This trinuclear unit is just like the cluster cation of the compound $[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu\text{-}\mathrm{S})_3(\mathrm{dtp})_3(\mathrm{py})_3][\mathrm{CdI(dtp)_2}]$ (**7**).[19] In the $[\mathrm{Mo_3OS_3Sn}]^{6+}$ core, three Mo atoms form approximately an equilateral triangle and the Mo−Mo bond distances between them are 2.6015(7), 2.6103(7), and 2.6141(8) Å, respectively. In addition, they have completely the same octahedral coordination environment and three terminal ligands dtp of them are also equivalent chemically. Therefore, in ^{95}Mo NMR spectrum, there appears only a peak at 1317 ppm, and in ^{31}P NMR spectrum, only a unique singlet is observed at 105.0 ppm (see Table 3).

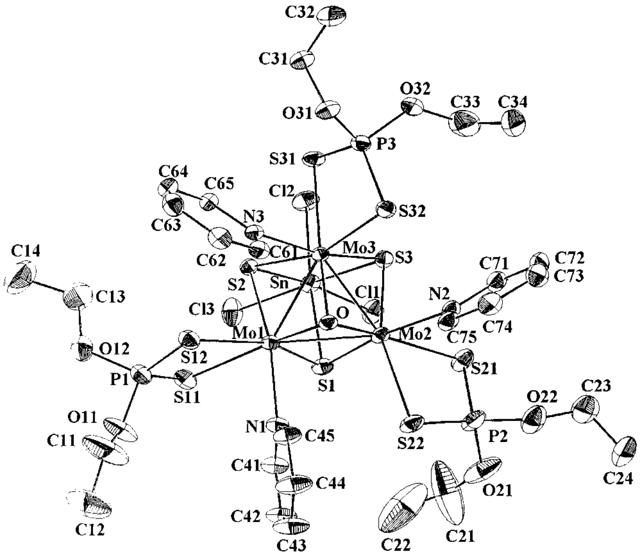

Figure 1. ORTEP diagram of compound **1** showing at 20% thermal ellipsoids.

Compound $(\mathrm{PPN})[\mathrm{Mo_3}(\mu_3\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{S})_3(\mathrm{SnCl_3})(\mathrm{dtp})_3(\mu\text{-}\mathrm{OAc})(\mathrm{py})]$ (2). The compound is an ionic cluster, and the tetranuclear Mo−Sn cluster unit is a cluster anion. Its structure is shown in Figure 2. The overall symmetry of the cluster unit belongs to the lowest C_1 group. It can be regarded as the simple combination of compound **5** with $\mathrm{SnCl_3}^-$. In the $[\mathrm{Mo_3OS_3Sn}]^{6+}$ core, three Mo atoms form an approximate isosceles triangle with two relatively longer Mo−Mo edges of 2.6088(3) and 2.6111(3) Å, respectively, and one shorter Mo−Mo edge of 2.5644(2) Å. The latter one is bridged by an OAc ligand. In this unit, although their coordination geometry is of a distorted octahedron, the coordination environment of the three Mo atoms are different and nonequivalent chemically. Therefore, in ^{95}Mo NMR spectrum, three peaks appear in the ratio of 1:1:1 at 1517, 1324, and 1264 ppm, respectively, of which the latter two peaks are assigned to the resonances of two Mo atoms bridged by (μ-OAc) whereas the 1517 ppm is due to the resonance of Mo atom coordinated by py. The ^{31}P NMR spectrum of cluster **2** reveals four resonances, as shown in Figure 3, of which three peaks centered at 106.7, 106.0, and 105.0 ppm, respectively, are assigned to the p atoms of three nonequivalent dtp ligands while 21.70 ppm is due to the resonance of p atoms in the cation PPN. It is worth noting that, of the three peaks due to p atoms in dtp, two are doublets with a coupling constant of ca. 5.3 Hz, which is estimated to be due to the ^{31}P−^{31}P long-range coupling in the cluster unit. It is calculated from the crystal structure analysis that the distances between three P atoms belonging to

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[18] Sheldrick, G. M. SHELXL 93, University of Gottingen, 1993.

[19] Lu, S.-F.; Huang, J.-Q.; Huang, X.-Y.; Wu, Q.-J. *Chin. J. Chem.* **1997**, *15*, 296−303.

Table 2. A Comparison between Compounds **1**−**3** and Trimolybedum Clusters **5**−**7**[a]

cluster	Mo−Mo (av.)	Mo−(μ_3-O) (av.)	Mo−(μ-S) or Mo−(μ_3-S) (av.)	Mo−$O_{(OAc)}$ (av.)	Mo−$N_{(py)}$ (av.)	Sn−(μ_3-S) (av.)	Sn−X (av.)	Mo···Sn	ref
1	2.6141(8)	2.031(4)	2.328(2)		2.303(5)	2.686(2)	2.413(2)	3.8096(7)	this work
	2.6103(7)	2.028(4)	2.331(2)		2.274(5)	2.706(2)	2.413(2)	3.8420(7)	
	2.6015(7)	2.030(4)	2.335(2)		2.286(5)	2.746(2)	2.402(2)	3.8486(7)	
	(2.6086)	(2.030)	2.315(2)		(2.287)	(2.713)	(2.409)	(3.8334)	
			2.316(2)						
			2.334(2)						
			(2.326)						
2	2.5644(2)	2.018(3)	2.3359(12)	2.185(3)	2.275(4)	2.6892(12)	2.4160(14)	3.8132(3)	this work
	2.6088(3)	2.019(3)	2.3434(12)	2.182(3)		2.6988(12)	2.4202(13)	3.7836(3)	
	2.6111(3)	2.012(3)	2.3296(12)	(2.184)		2.6484(12)	2.4260(13)	3.7703(3)	
	(2.5948)	(2.016)	2.3445(12)			(2.675)	(2.420)	(3.7890)	
			2.3348(12)						
			2.3357(12)						
			(2.338)						
3	2.6089(9)	2.002(5)	2.361(2)	2.136(5)	2.244(6)	2.669(2)	2.411(3)	3.8008(9)	this work
	2.5517(9)	1.996(5)	2.349(2)	2.129(5)		2.664(2)	2.404(3)	3.7751(9)	
	2.5478(10)	1.995(5)	2.337(2)	2.201(5)		2.656(2)	2.428(2)	3.7772(9)	
	(2.5695)	(1.998)	2.351(2)	2.188(5)		(2.653)	(2.401)	(3.7844)	
			2.338(2)	(2.163)					
			2.348(2)						
			(2.347)						
5	2.589(2)	2.05(1)	2.289(5)	2.20(1)	2.30(1)				15
	2.642(2)	2.04(1)	2.297(5)	2.20(1)					
	2.627(2)	2.04(1)	2.286(5)	(2.20)					
	(2.625)	(2.04)	2.286(5)						
			2.280(5)						
			2.281(5)						
			(2.285)						
6	2.584(4)	2.00(2)	2.31(1)	2.11(2)	2.27(2)				16
	2.587(4)	1.96(2)	2.32(1)	2.13(2)					
	2.657(3)	1.98(2)	2.30(1)	2.24(2)					
	(2.609)	(1.98)	2.30(1)	2.17(2)					
			2.29(1)	(2.16)					
			2.30(1)						
			(2.30)						
7	2.651(1)	2.080(4)	2.283(2)		2.306(2)				17
	2.652(1)	2.079(4)	2.284(2)		2.328(2)				
	2.652(1)	2.072(4)	2.285(2)		2.302(2)				
	(2.652)	(2.077)	2.290(2)		(2.302)				
			2.284(2)						
			2.290(2)						
			(2.286)						

[a] **1**, $[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_3(py)_3]$; **2**, $(PPN)[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_3(\mu\text{-}OAc)(py)]$; **3**, $(Et_4N)[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_2(\mu\text{-}OAc)_2(py)]$; **5**, $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(dtp)_3(OAc)(py)]$; **6**, $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(dtp)_2(OAc)_2(py)]$; **7**, $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(dtp)_3(py)_3][CdI(dtp)_2]$.

Table 3. Spectroscopic Data for the Clusters **1**−**3**

	1	**2**	**3**
IR (cm^{-1})			
νMo−(μ_3-O)	655	675	717
νMo−(μ_3-S)	439	418	416
νMo−N(py)	648	659	675
^{95}Mo NMR (ppm) (the line width, Hz)	1317(539)	1:1:1	2:1
		1517(1047)	1515(1010)
		1324(1000)	1445(786)
		1264(1010)	
^{31}P NMR (ppm) (the line width, Hz)	105.0(7.8)	106.7(2.2)	104.51(3.6)
		106.0(d, J_{p-p} 5.3 Hz) (3.0)	
		105.0(d, J_{p-p} 5.3 Hz) (2.6)	
UV−vis nm (ϵ, M^{-1} cm^{-1}))	246 (4.82×10^4)	242 (4.96×10^4)	306(1.09×10^4)
	380 (1.44×10^4)	276 (4.46×10^4)	315(1.29×10^4)
	418 (9.14×10^3)	370(1.36×10^4)	374(1.66×10^4)
		420 (8.3×10^3)	412(8.8×10^3)

three dtp ligands are P1−P2 8.73 Å, P1−P3 7.22 Å, and P2−P3 6.32 Å, respectively. Therefore, the $^{31}P-^{31}P$ coupling exists possibly between P2 and P3.

Compound $(Et_4N)[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_2(\mu\text{-}OAc)_2(py)]$ (3). The Mo−Sn cluster unit in the structure is also a cluster anion composed of compound **6** and $SnCl_3^-$ via the formation of three Sn−S bonds as shown in Figure 4. The cluster unit has an overall symmetry of C_s. In the $[Mo_3OS_3Sn]^{6+}$ core, three Mo atoms form an approximate isosceles triangle with two relatively shorter Mo−Mo edges of 2.5478(10) and 2.5517(9) Å and one long Mo−Mo edge of 2.6089(9) Å. The two shorter bonds correspond to two Mo−Mo bonds bridged by (μ-OAc) ligands. Obviously, two of the Mo atoms have the same coordinated geometry and two terminal dtp ligands are

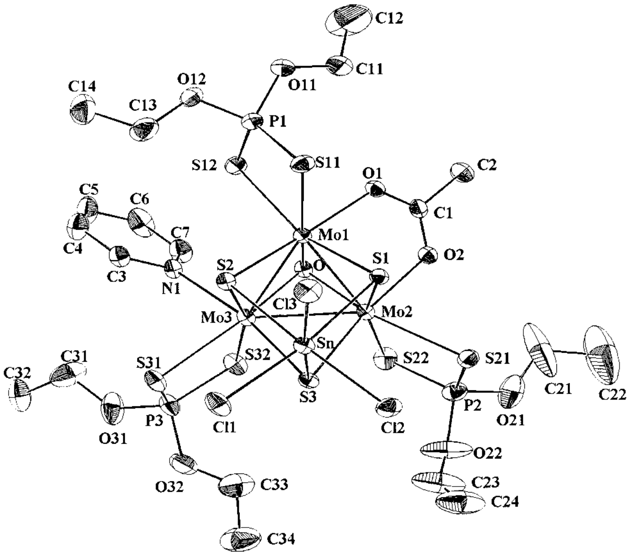

Figure 2. ORTEP diagram of the cluster anion of compound **2** showing at 20% thermal ellipsoids.

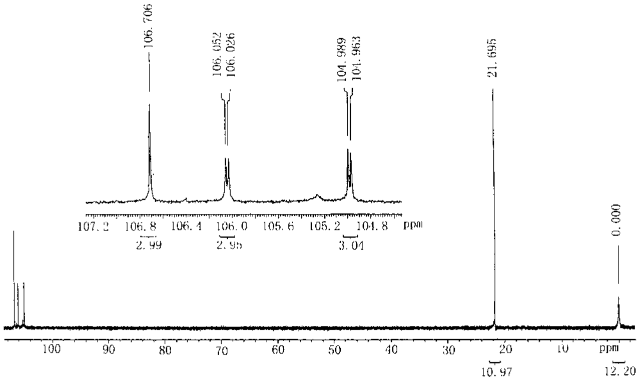

Figure 3. The ^{31}P NMR spectrum of compound **2**.

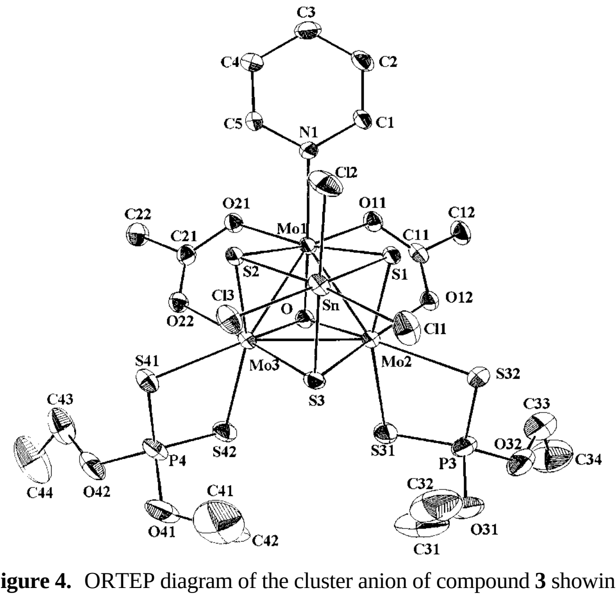

Figure 4. ORTEP diagram of the cluster anion of compound **3** showing at 20% thermal ellipsoids.

also equivalent chemically. Thus, in ^{95}Mo NMR spectrum of compound **3**, there are two resonances at 1515 and 1446 ppm in a ratio of 2:1, of which the peak at 1446 ppm is assigned to the Mo atom coordinated by py ligand while the peak at 1515 ppm is assigned to two equivalent Mo atoms. The ^{31}P NMR spectrum shows a singlet at 104.5 ppm in consistence with the complete equivalence of two terminal dtp. It is worthwhile to note that the average Mo$-$(μ_3-O) bond length of 1.998 Å is evidently shorter than those of compound **1** (2.030 Å) and **2** (2.017 Å). Moreover, its IR spectra exhibit a characteristic νMo$-$(μ_3-O) stretching vibration at 717 cm^{-1}.

In the three clusters mentioned above, the coordination geometry of Sn atoms is a distorted octahedron formed by three μ_3-S and three Cl atoms. All of the Mo$-$Sn distances are more than 3.7 Å indicating that there is no direct metal$-$metal bond between Mo and Sn atoms.

Summary. As is mentioned above, the major difference between the structures of the present three cluster units lies in the number of OAc ligands around the [Mo_3OS_3Sn]$^{6+}$ core. There is no OAc ligand in cluster **1**, while only one in cluster **2** and two in cluster **3**. It can be seen from Table 2 that with the increase of the number of bridging OAc ligands, the average Mo$-$Mo, Mo$-$(μ_3-O), and Mo$-$N(py) bond distances are gradually shortened while that of the Mo$-$(μ_3-S) lengthened. The variety of the corresponding stretching vibration frequencies in IR spectra is exactly in accordance with the varying tendency of the bond lengths (see Table 3). It can also be seen from the ^{95}Mo NMR that the chemical shifts increase (to a lower field region) with increasing OAc bridging ligands. As far as the UV$-$vis spectra is concerned, since the spectra of clusters **1**$-$**3** are very similar at a region over 350 nm, it can thus be taken that the absorptions at ca. 370$-$380 nm and 400$-$418 nm are likely to be the characteristic peaks of the cuboidal [Mo_3OS_3-Sn] core.

The Effect of $SnCl_3^-$ Incorporation with the [Mo_3OS_3] Clusters. To investigate the effect of $SnCl_3^-$ incorporation on the important bonding distances of the {Mo_3} clusters, the comparison of that parameters for clusters **1** and **7**, **2** and **5**, and **3** and **6** is made in Table 2. It is obvious that the average Mo$-$(μ-S) bond length is lengthened by ca. 0.040$-$0.053 Å due to the formation of Sn$-$S bonds. It is more important that the average Mo$-$Mo bond lengths of 2.652, 2.625, and 2.609 Å in clusters **7**, **5**, and **6** are reduced to a value of 2.609, 2.595, and 2.570 Å for clusters **1**, **2**, and **3**, respectively. There the maximal shortening would reach a value of 0.043 Å. That means by way of Sn$-$S bonding, Sn^{2+} offers the lone pair electrons to the [Mo_3OS_3] core and thus enhances the Mo$-$Mo bonding, and Sn^{2+} seems to be oxidized formally. This result is in consistence with the analysis of the bonding of [Mo_3S_4M'] reported by Bahn.[20]

Conclusion

By the addition reaction of [Mo_3OS_3] clusters with $SnCl_2$, three new Mo$-$Sn heterometallic and heterobridging clusters with a [Mo_3OS_3Sn] core have been synthesized successfully. It is shown from the structure analysis and spectroscopic characterization that the OAc ligands are advantageous to the stabilization of (μ_3-O) and the strengthening of Mo$-$(μ_3-O) bonds. As in [Mo_3S_4Sn], the addition of $SnCl_3^-$ causes the electron transfer from Sn^{2+} to [Mo_3OS_3] core resulting in an enhancement of the Mo$-$Mo bonding. The configuration of cluster **1** is very similar to that of [$Mo_3S_4(SnCl_3)(dtp)_3(py)_3$] while on the other hand, the two novel adducts clusters **2** and **3** have not been formed so far in the reaction of [Mo_3S_4] with SnX_2. The study on the reaction of [Mo_3OS_3] type clusters with other main-group metals is still in progress.

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(20) Bahn, C. S.; Tan, A.; Harris, S. *Inorg. Chem.* **1998**, *37*, 2770$-$2778.

IR and UV−vis spectra. Thanks are also due to the National Natural Science foundation of China (29733090 and 29673046), NSF of Fujian Province, and State Key Laboratory of Structural Chemistry for their support.

Supporting Information Available: IR, UV−vis, and ^{95}Mo NMR spectra of complexes [$Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_3(py)_3$] (**1**), (PPN)[$Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_3(\mu\text{-}OAc)(py)$] (**2**), and ($Et_4N$)[$Mo_3(\mu_3\text{-}O)(\mu_3\text{-}S)_3(SnCl_3)(dtp)_2(\mu\text{-}OAc)_2(py)$] (**3**), ^{31}P NMR of compounds **1** and **3** and X-ray crystallographic files in CIF format for the structures of complexes **1**, **2**, and **3** are available. These materials are available free of charge via the Internet at http://pubs.acs.org.

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