CHEMISTRY LETTERS, pp. 2025-2028, 1987.

Synthesis and Crystal Structures of Trinuclear Molybdenum Chloro Sulfido Clusters Coordinated with Triethylphosphine and Methanol

Taro SAITO,* Naohiro YAMAMOTO, Tsuneaki YAMAGATA, and Hideo IMOTO
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

Two triethylphosphine complexes of trinuclear molybdenum chlorosulfido clusters have been synthesized. Determination of the crystal structures have shown that they can be formulated as $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_n(MeOH)_{5-n}]$ (n = 3, 4).

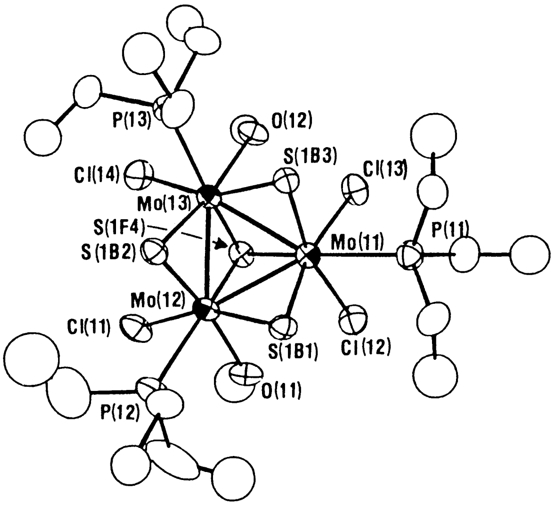
The $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3]^{4+}$ clusters with a variety of ligands have been prepared[1)] and they serve also as the building blocks of larger clusters. This is exemplified by the recent syntheses of the cubane and double-cubane type complexes from the trinuclear molybdenum clusters capable of coordinating to a mononuclear metal center through the edge-bridging sulfur ligands.[2-4)] As we have demonstrated in our previous papers,[5,6)] trialkylphosphines are versatile ligands to improve the solubility of transition metal cluster complexes in organic solvents and to stabilize the M-C bonding. We have now prepared trialkylphosphine derivatives of the trinuclear molybdenum chloro sulfido complexes by two different preparative methods and determined their structures.

In the first method, a green aqueous solution of the $[Mo_3S_4]^{4+}$ ion prepared from $Mo(CO)_6$[1c)] was used as the starting material. Water was evaporated from the solution to give a dark green residue. The solid (0.13 g) was dissolved in methanol (5.0 cm^3) and treated with triethylphosphine (0.22 cm^3) for 12 h at room temperature. Methanol and excess triethylphosphine were removed under reduced pressure and the residue was washed with diethyl ether. The product was recrystallized from methanol to afford dark green crystals with the empirical formula $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$ (**1**). The complex is soluble in common organic solvents and has absorption maxima at 371 nm(ε 6.4×10^3 $mol^{-1}dm^3cm^{-1}$) and 666 nm (ε 3.1×10^2 $mol^{-1}dm^3cm^{-1}$) in a visible spectrum.

In order to obtain the complex **1** in quantity at a time, we used another reaction similar to that described briefly for the preparation of $[Mo_3S_4Cl_4(PPh_3)_2]$.[10)] It has turned out that the reaction of the solid state chloride sulfide $Mo_3S_7Cl_4$ (= $(Mo_3S(S_2)_3Cl_2Cl_{4/2})_\infty$) with triethylphosphine gives two kinds of the Mo_3S_4 complexes, both of which are coordinated with five neutral ligands in contrast to the reported complex with two triphenylphosphine ligands. Thus $Mo_3S_7Cl_2Cl_{4/2}$ (1.0 g)[11)] was treated with triethylphosphine (3.4 cm^3, 23 mmol) in THF (5.0 cm^3) at room temperature for 5 h. The solvent and excess triethylphosphine were removed under reduced pressure and the residue was washed with ether (3 x 5 cm^3) to give brown solid. The product was dissolved in methanol (5 cm^3), filtered and the filtrate was left at room temperature to form dark green crystals. Yield; 0.36 g (24%). From the elemental analysis, infrared and ^1H NMR spectra, and the space group and the cell constants of the single crystals, this complex was identified as **1**.

Another complex **2** was separated from the same reaction but with slightly different workup. Namely the residue after the removal of the solvent and excess triethylphosphine was dissolved in methanol, filtered, concentrated and ether was slowly added to the solution to form dark green crystals. Yield; 0.7 g (46%). The elemental analysis and ^1H NMR spectrum agree with the formula $[Mo_3S_4Cl_4(PEt_3)_4(MeOH)]$.

The structure of **1** prepared by the first method was solved by a single crystal X-ray structure determination.7) There are two kinds of independent molecules in a unit cell. As their structures are almost identical except the conformation of the carbon chains of triethylphosphines, the molecular structure of one of them is illustrated in Fig. 1. The Mo_3 core bound by a face-bridging and three edge-bridging sulfur atoms is an isosceles triangle with the ca. 0.04 Å shorter Mo(12)-Mo(13) distance than the other two edges. Four terminal chloro, three triethylphosphine and two methanol ligands are coordinated to the cluster framework. The triethylphosphine and the edge-bridging sulfido ligands are on one side of the Mo_3 triangle and the chloro, methanol and the face-bridging sulfido ligands are on the other. The Mo-Mo, Mo-μ_3-S, and Mo-μ-S bond distances are similar to those of the reported Mo_3S_4 clusters (Mo-Mo, 2.738 - 2.812 Å; Mo-μ_3-S, 2.33 - 2.36 Å; Mo-μ-S, 2.28 - 2.31 Å).1) The Mo-P distances are within the range of those of molybdenum chloride clusters coordinated with trialkylphosphines.5,6,8,9)

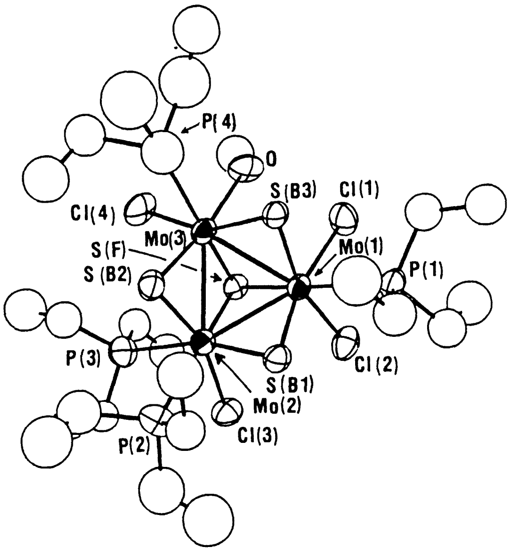


Selected Bond Distances

Mo(11)-Mo(12)	2.780(1)	Mo(11)-Mo(13)	2.779(1)
Mo(12)-Mo(13)	2.738(1)	Mo(11)-S(1F4)	2.356(3)
Mo(12)-S(1F4)	2.351(3)	Mo(13)-S(1F4)	2.359(3)
Mo(11)-S(1B1)	2.285(3)	Mo(11)-S(1B3)	2.287(3)
Mo(12)-S(1B1)	2.308(3)	Mo(12)-S(1B2)	2.275(3)
Mo(13)-S(1B2)	2.281(3)	Mo(13)-S(1B3)	2.292(3)
Mo(11)-Cl(12)	2.533(3)	Mo(11)-Cl(13)	2.541(3)
Mo(12)-Cl(11)	2.416(3)	Mo(13)-Cl(14)	2.428(3)
Mo(11)-P(11)	2.606(3)	Mo(12)-P(12)	2.596(4)
Mo(13)-P(13)	2.596(3)	Mo(12)-O(11)	2.326(8)
Mo(13)-O(12)	2.337(7)	P-C	1.83(1)-1.90(2)
O-C	1.45(2)-1.58(2)	C-C	1.30(3)-1.55(2)

Fig. 1. ORTEP drawing of $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$.

The structure of **2** has also been determined12) and is shown in Fig. 2. A face-bridging and three edge-bridging sulfurs are bonded to the Mo_3 cluster core with two chlorine and a triethylphosphine bonded to Mo(1); a chlorine and two triethylphosphines at Mo(2); and a chlorine, a triethylphosphine and a methanol at Mo(3). The structure of **2** can be derived from the complex **1** by replacing one of the methanol ligands with a triethylphosphine and changing the coordination environment at Mo(2).



Selected Bond Distances

Mo(1)-Mo(2)	2.795(1)	Mo(1)-Mo(3)	2.790(1)
Mo(2)-Mo(3)	2.785(1)	Mo(1)-S(F)	2.354(3)
Mo(2)-S(F)	2.368(3)	Mo(3)-S(F)	2.356(3)
Mo(1)-S(B1)	2.262(3)	Mo(2)-S(B1)	2.300(3)
Mo(2)-S(B2)	2.305(3)	Mo(3)-S(B2)	2.264(3)
Mo(1)-S(B3)	2.320(3)	Mo(3)-S(B3)	2.284(3)
Mo(1)-Cl(1)	2.570(3)	Mo(1)-Cl(2)	2.464(3)
Mo(2)-Cl(3)	2.457(3)	Mo(3)-Cl(4)	2.447(4)
Mo(1)-P(1)	2.616(3)	Mo(2)-P(2)	2.629(4)
Mo(2)-P(3)	2.690(4)	Mo(3)-P(4)	2.583(4)
Mo(3)-O	2.324(8)	O-C	1.44(2)
P-C	1.79(2)-1.90(1)	C-C	1.27(3)-1.55(2)

Fig. 2. Structure of $[Mo_3S_4Cl_4(PEt_3)_4(MeOH)]$.

The ^{31}P NMR spectra have exhibited a remarkable temperature dependence indicating fluxionality of the triethylphosphine ligands in the complexes **1** and **2**.[13] This may be related to the formation of the two clusters with different triethylphosphine content by the slight change of the workup conditions.

The present complexes are the rare examples of the trinuclear molybdenum sulfido complexes with tertiary phosphine and terminal chloro ligands and will be useful as the starting compounds to other derivatives.

The financial support from the Ministry of Education, Science, and Culture (No 61125007) is gratefully acknowledged. Triethylphosphine is a generous gift from Nihon Kagaku Kogyo Ltd.

References

1) a) F. A. Cotton, Polyhedron, 5, 3 (1986); b) S. P. Gubin, Russian Chem. Rev., 54, 305 (1985); c) F. A. Cotton, Z. Dori, R. Llusar, and W. Schwotzer, J. Am. Chem. Soc., 107, 6734 (1985); d) T. Shibahara and H. Kuroya, Polyhedron, 5, 357 (1986).

2) T. Shibahara, H. Akashi, and H. Kuroya, J. Am. Chem. Soc., 108, 1342 (1986).

3) T. Shibahara, T. Yamamoto, H. Kanadani, and H. Kuroya, J. Am. Chem. Soc., 109, 3495 (1987).

4) F. A. Cotton, Z. Dori, R. Llusar, and W. Schwotzer, Inorg. Chem., 25, 3654 (1986).

5) T. Saito, M. Nishida, T. Yamagata, Y. Yamagata, and Y. Yamaguchi, Inorg. Chem., 25, 1111 (1986).

6) T. Saito, H. Manabe, T. Yamagata, and H. Imoto, Inorg. Chem., 26, 1362 (1987).

7) Crystal data for **1**: $C_{20}H_{53}Cl_4Mo_3O_2P_3S_4$, fw = 976.46, monoclinic, space group $P2_1$, a = 17.627(3), b = 19.082(4), c = 11.689(1) Å, β = 99.79(1)°, V = 3875(1) Å^3, Z = 4, D_c, D_m = 1.674, 1.673(2) g cm^{-3}, μ(Mo Kα) = 14.54 cm^{-1}. Data were collected on a Rigaku AFC-4 diffractometer over the range $0° < 2\theta < 50°$ at 293 K (θ-2θ scan) at Crystallographic Research Center of Institute for Protein Research of Osaka University. Lorentz, polarization and absorption corrections (φ scan method) were applied. 5087 [$F_o > 6\sigma(F_o)$] reflections were used to solve the structure by direct methods (MULTAN 78) and Fourier difference techniques (UNICS) to the final residuals R = 0.0359 and R_w = 0.0358 ($w=1/\sigma(F_o)^2$).

8) R. N. McGinnis, T. R. Ryan, and R. E. McCarley, J. Am. Chem. Soc., 100, 7900 (1978).

9) F. A. Cotton and G. L. Powell, Inorg. Chem., 22, 871 (1983).

10) V. E. Fedorov, A. V. Mishchenko, and V. P. Fedin, Russian Chem. Rev., 54, 408 (1985).

11) A. A. Opalovskii, V. E. Federov, and K. A. Khaldoyanidi, Dokl. Akad. Nauk SSSR, 182, 1095 (1968).

12) Crystal data for **2**: $C_{25}H_{64}Cl_4Mo_3OP_4S_4$, fw = 1062.57, monoclinic, space group $P2_1/n$, a = 19.866(5), b = 18.410(5), c = 11.790(3) Å, β = 90.66(2)°, V = 4312(2) Å^3, Z = 4, D_c, D_m = 1.637, 1.642 g cm^{-3}, μ(Mo Kα) = 14.40 cm^{-1}. Data were collected ($0° < 2\theta < 40°$) as above for **1** and 2897 [$F_o > 3\sigma(F_o)$] reflections were used to solve the structure by direct methods (MULTAN 78) and Fourier difference techniques (UNICS) to the final residuals R = 0.0499 and R_w = 0.0417 ($w=1/\sigma(F_o)^2$).

13) T. Saito, to be published.

(Received July 27, 1987)