CHEMISTRY LETTERS, pp. 2117-2118, 1994.

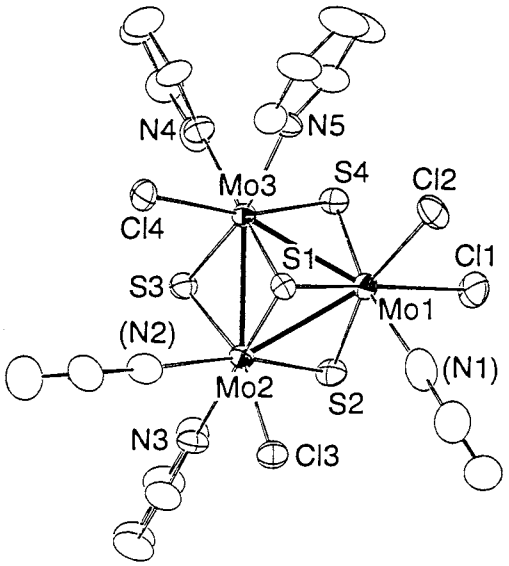
Synthesis and Structure of a Pyridine Complex of Trinuclear Molybdenum Cluster $[Mo_3S_4Cl_4(py)_5]$

Jun MIZUTANI, Hideo IMOTO, and Taro SAITO*
Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113

A pyridine complex of trinuclear molybdenum chloro sulfido cluster $[Mo_3S_4Cl_4(py)_5]$ has been synthesized by the excision reaction of a solid state cluster compound $Mo_3S_7Cl_4$ with pyridine and triphenylphosphine. The structure has been determined by the single crystal X-ray structure analysis.

Many incomplete-cubane type $[Mo_3S_4]^{4+}$ clusters have been obtained by various methods.[1] Tertiary phosphine complexes, $[Mo_3S_4Cl_4(PR_3)_xL_{5-x}]$, (R = Et, L = MeOH, x = 3, 4;[2] R = Et, Ph, L = H_2O, x = 3[3]) (**1**) have been synthesized by the excision reaction of a solid state cluster compound $Mo_3S_7Cl_4$[4] (**2**) with tertiary phosphines in tetrahydrofuran. Meanwhile, a combination of sulfur abstraction by triphenylphosphine and ligand substitution has been applied to $[Mo_3S_7Br_6]^{2-}$ for the preparation of various $[Mo_3S_4]^{4+}$ cluster complexes.[5] In the present study, we used triphenylphosphine and pyridine in the excision reaction of **2**, and obtained a new trinuclear cluster complex with pyridine ligands, $[Mo_3S_4Cl_4(py)_5]$ (**3**).

All manipulations were carried out under an inert atmosphere. A mixture of 0.25 g of **2**, 0.37 g of triphenylphosphine, and 12 mL of pyridine was stirred under reflux for 3 h to give a green suspension. Pyridine was removed under reduced pressure and the residue was washed with hexane. The resulting powder was recrystallized from dichloromethane to afford green crystals in 33% yield.



Mo1-Mo2	2.789(1)	Mo2-S3	2.284(2)
Mo1-Mo3	2.785(1)	Mo2-N2	2.326(5)
Mo2-Mo3	2.783(1)	Mo2-N3	2.318(5)
Mo1-S1	2.335(2)	Mo2-Cl3	2.484(2)
Mo1-S2	2.283(2)	Mo3-S1	2.329(2)
Mo1-S4	2.275(2)	Mo3-S3	2.279(2)
Mo1-N1	2.327(5)	Mo3-S4	2.286(2)
Mo1-Cl1	2.499(2)	Mo3-N4	2.291(5)
Mo1-Cl2	2.468(2)	Mo3-N5	2.333(5)
Mo2-S1	2.339(2)	Mo3-Cl4	2.479(2)
Mo2-S2	2.279(2)		

Fig. 1. ORTEP drawing and selected bond distances (Å) for $[Mo_3S_4Cl_4(py)_5] \cdot CH_2Cl_2$.

The UV-visible spectrum shows absorption maxima at 664 nm ($\varepsilon = 2.8\times10^2$ $M^{-1}cm^{-1}$) and 397 nm ($\varepsilon = 4.6\times10^3$ $M^{-1}cm^{-1}$).

The single crystal X-ray structure analysis of **3**[6] has shown that the crystal contains 1 mol of dichloromethane as a crystallization solvent. The ORTEP drawing and the selected bond distances are shown in Fig. 1. The Mo_3 core bound with one μ_3-S and three μ_2-S ligands is a regular triangle. The Mo-Mo bond distances are near those in **1** (2.758-2.790 Å).[2,3] Four chloro and five pyridine ligands are coordinated to the cluster core in an asymmetric manner. The pyridine rings are almost perpendicular to the Mo_3 triangle to minimize the steric hindrance between them. The oxidation state of molybdenum is +4, and the skeletal electron count is 6.

Both **1** and **3** have five coordination sites for neutral ligands, which are absent in the starting compound **2**. Three of the sites are generated by the abstraction of a sulfur atom from each μ_2-S_2 ligand by tertiary phosphines. Other two sites are generated by the cleavage of chloro bridges connecting the cluster units. In the formation of **1**, tertiary phosphines act also as the reagent for the cleavage, and coordinate to the cluster unit.[3] However, in the formation of **3**, the resulting ligands are only pyridine, and triphenylphosphine does not coordinate. Thus, if we assume the reagents which cleave the bridges remain as the ligands, the reagent for the cleavage is pyridine. If this is the case, pyridine and triphenylphosphine play different roles in the excision reaction.

The financial support from the Ministry of Education, Science, and Culture (No.04241102) is gratefully acknowledged.

References

1) Some of the reviews published recently: T.Shibahara, *Adv.Inorg.Chem.*, **37**, 143 (1991); T.Shibahara, *Coord.Chem.Rev.*, **123**, 73 (1993).
2) T.Saito, N.Yamamoto, T.Yamagata, and H.Imoto, *Chem.Lett.*, **1987**, 2025.
3) F.A.Cotton, P.A.Kibala, M.Matusz, C.S.McCaleb, and R.B.W.Sandor, *Inorg.Chem.*, **28**, 2623 (1989); F.A.Cotton, P.A.Kibala, and C.S.Miertschin, *ibid.*, **30**, 548 (1991).
4) A.A.Opalovskii, V.E.Fedorov, and K.A.Khaldoyanidi, *Dokl.Akad.Nauk SSSR*, **182**, 1095 (1968); J.Marcoll, A.Rabenau, D.Mootz, and H.Wunderlich, *Rev.Chim.Miner.*, **11**, 607 (1974).
5) M.D.Meienberger, K.Hegetschweiler, H.Rüegger, and V.Gramlich, *Inorg.Chim.Acta*, **213**, 157 (1993).
6) Crystallographic data for **3**·CH_2Cl_2: formula $C_{26}H_{27}Cl_6Mo_3N_5S_4$, fw = 1038.3, triclinic, $P\bar{1}$, a = 11.660(3), b = 15.616(5), c = 11.265(4) Å, α = 99.36(3), β = 99.13(3), γ = 109.45(2)°, U = 1857.7(10) Å^3, Z = 2, $D_{calcd.}$ = 1.856 g cm^{-3}, μ(Mo Kα) = 14.74 cm^{-1}, crystal size 0.7 × 0.3 × 0.2mm, diffractometer Rigaku AFC-5R, temperature of data collection 297 K, measured reflections 8955 ($5° \leq 2\theta \leq 55°$), observed reflections 5780 ($|F_o| > 3\sigma(|F_o|)$), refined parameters 398 (All non-hydrogen atoms are refined anisotropically, and hydrogen atoms are located at calculated positions.), R = 0.055, R_w = 0.034 ($w = 1/\sigma(|F_o|)^2$), S = 1.531, highest residual density 1.01 Å^{-3}.

(Received August 11, 1994)