Syntheses and Structures of Trinuclear Molybdenum Cluster Complexes $[Mo_3S_4Cl_4(C_5H_5N)_5]$ and $[Mo_3S_4Cl_3(C_5H_5N)_6]I$

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A trinuclear molybdenum chloro sulfido cluster complex $[Mo_3S_4Cl_4(C_5H_5N)_5]$ (**1**) was synthesized by the excision of a nonmolecular cluster compound $Mo_3S_7Cl_4$ with triphenylphosphine and pyridine. Three molybdenum atoms and four sulfur atoms form an incomplete cubane-type cluster core, which is coordinated by four chloro and five pyridine ligands. By the reaction of **1** with I_2 in pyridine, $[Mo_3S_4Cl_3(C_5H_5N)_6]I$ (**2**) was synthesized. Three μ-S in the cluster cation and the iodine anion have short contacts, within the sum of the van der Waals radii of sulfur and iodine.

The excision reaction, which is the extrusion of a cluster core from a nonmolecular cluster compound using ligands, is one of the important methods for the syntheses of molecular metal cluster complexes.[1—6] The advantage of using an excision reaction is the predictability of the structure of the cluster core in the product. The reaction of a nonmolecular cluster compound $Mo_3S_7Cl_4$ with triethylphosphine, followed by recrystallization from methanol, gives trinuclear molybdenum cluster complexes, $[Mo_3S_4Cl_4(PEt_3)_n(MeOH)_{5-n}]$ (n=3, 4),[7] whose cluster core is useful as a building block for the fragment condensation reactions giving an octahedral[8] and a raft-type[9] hexanuclear cluster complexes. In this excision reaction, triethylphosphine is considered to participate in both abstraction of a sulfur atom from each μ-S_2 ligand and cleavage of the chlorine bridges connecting adjacent trinuclear units. In this article, for the purpose of clarifying the excision process of $Mo_3S_7Cl_4$, we studied the excision reactions of $Mo_3S_7Cl_4$ using the combinations of tertiary phosphines having affinity to sulfur, and N-donor ligands without sulfur-abstraction ability. We obtained a new molybdenum cluster complex $[Mo_3S_4Cl_4(C_5H_5N)_5]$ (**1**) containing the $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cluster core when triphenylphosphine and pyridine are used. By the reaction of **1** with I_2, an ionic cluster complex $[Mo_3S_4Cl_3(C_5H_5N)_6]I$ (**2**) was synthesized, and the short contacts of the μ-S ligands and iodide anion were found. A part of the preliminary results has been published elsewhere.[10]

Experimental

$Mo_3S_7X_4$ (X = Cl,[11] Br,[12] I,[13]) were prepared according to the literature methods. Pyridine, β-picoline, γ-picoline, butylamine, and triethylamine were dried with KOH and distilled from molecular sieves 4 A, and dichloromethane was dried with $CaCl_2$ and distilled from CaH_2 under argon. Triphenylphosphine, tributylphosphine, and tris(dimethylamino)phosphine were purchased from Tokyo Kasei, trimethylphosphine, 2,2′-bipyridine, and 4,4′-bipyridine from Aldrich, triethylphosphine from Kanto Kagaku, and iodine, piperidine, and imidazole from Wako Chemicals. All were used as received. Triisopropylphosphine was prepared by the reaction of PCl_3 with isopropyl magnesium bromide. All manipulations were performed under inert atmosphere using standard Schlenk techniques. Ultraviolet-visible spectra were measured with a Hitachi U-3500 spectrometer. Elemental analyses were carried out by the elemental analysis center of our department.

Synthesis of $[Mo_3S_4Cl_4(C_5H_5N)_5]$ (1). Treatment of 1.0 g (1.53 mmol) of $Mo_3S_7Cl_4$ and 1.50 g (5.72 mmol) of triphenylphosphine in 30 cm^3 of pyridine for 18 h under the refluxing condition gave a green suspension. The supernatant was removed by filtration, and the resulting green powder was extracted with 240 cm^3 of dichloromethane. After the volume was reduced to ca. 30 cm^3, the solution was left at −20 °C for 10 d to give green crystals of **1**·CH_2Cl_2. Yield: 0.87 g (55%). Found: C, 30.5 ; H, 2.7; N, 6.6; S, 12.2; Cl, 19.3%. Calcd for $C_{26}H_{27}Cl_6Mo_3N_5S_4$: C, 30.1; H, 2.6; N, 6.7; S, 12.4; Cl, 20.5%. UV-vis (CH_2Cl_2) λ_{max}/nm ($\varepsilon/10^3$ M^{-1} cm^{-1}) 395 (4.6), 665 (0.28) (1 M = 1 mol dm^{-3}).

Synthesis of $[Mo_3S_4Cl_3(C_5H_5N)_6]I$ (2). Treatment of 0.10 g (0.105 mmol) of **1** and 0.20 g (0.788 mmol) of iodine in 30 cm^3 of pyridine for 5 h under the refluxing condition gave brown solution. Standing the solution at room temperature for 10 d yielded brown crystals of **2**·0.5 C_5H_5N. Yield: 0.037 g (33%). Found: C, 33.5; H, 3.0; N, 7.9; S, 10.7; Cl, 8.8%. Calcd for $C_{32.5}H_{32.5}Cl_3IMo_3N_{6.5}S_4$: C, 33.6; H, 2.8; N, 7.8; S, 11.0; Cl, 9.1%. UV-vis (CH_2Cl_2) λ_{max}/nm ($\varepsilon/10^3$ M^{-1} cm^{-1}) 370 (5.5), 400 (sh), 490 (4.2), 620 (sh).

X-Ray Crystallographic Studies. Single crystals were sealed in glass capillaries under argon and mounted on a Rigaku AFC-5R diffractometer equipped with a Rotaflex rotating anode X-ray generator. The radiation used was Mo $K\alpha$ monochromatized with graphite (λ = 0.7107 Å). Intensity data were collected with ω–2θ scans in the range $5° < 2\theta < 55°$ at room temperatures. Three standard reflections were monitored every 150 reflections and no decays in intensities were observed. Atomic scattering factors were taken from a standard source.[14] Crystallographic parameters are shown in Table 1. Details of the crystallographic studies have been deposited at the Cambridge Crystallographic Database Centre. The

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Table 1. Crystallographic Parameters for $[Mo_3S_4Cl_4(C_5H_5N)_5]\cdot CH_2Cl_2$ (**1·CH_2Cl_2**) and $[Mo_3S_4Cl_3(C_5H_5N)_6]I\cdot 0.5\ C_5H_5N$ (**2·0.5C_5H_5N**)

	1·CH_2Cl_2	**2·0.5C_5H_5N**
Formula	$C_{26}H_{27}Cl_6Mo_3N_5S_4$	$C_{32.5}H_{32.5}Cl_3IMo_3N_{6.5}S_4$
Fw	1038.3	1163.5
Crystal size /mm	$0.7\times0.3\times0.2$	$0.5\times0.3\times0.3$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a / Å	11.660(3)	27.989(5)
b / Å	15.616(5)	15.261(8)
c / Å	11.265(4)	25.939(5)
α / °	99.36(3)	
β / °	99.13(3)	112.75(1)
γ / °	109.45(2)	
V / Å^{-3}	1857.7(10)	10217(4)
Z	2	8
D_{calcd} / g cm^{-3}	1.856	1.513
μ(Mo $K\alpha$) / cm^{-1}	14.74	16.75
No. observations[a]	5780 ($I>1.5\ \sigma(I)$)	5082 ($I>3.0\ \sigma(I)$)
No. variables	398	448
R, R_w[b]	0.055, 0.034	0.078, 0.098
$\Delta\rho$ / e$^-$Å^{-3} [c]	1.01	1.43

a) The criterions for the observations are shown in parentheses. b) $w=1/\sigma^2(F_o)$. c) Maximum residual electron densities in the final difference Fourier maps.

F_o-F_c data have been deposited as Document No. 71011 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Structure Determination of 1·CH_2Cl_2. Cell parameters were determined from 25 reflections in the range $26°<2\theta<30°$. An empirical absorption correction was applied with ψ-scans.[15] The crystal system required a space group such as $P1$ or $P\bar{1}$, and the structure was successfully solved under $P\bar{1}$. Heavy atoms were located by direct method using SHELXS86,[16] and the structure was expanded by successive application of least-squares refinements and difference Fourier syntheses using ANYBLK[17] and SHELX76.[18] One dichloromethane solvent molecule was located. Chlorine atoms in the solvent molecule (C15A–C16C) had a site occupancy factor of 1/3 due to disorder. All the non-hydrogen atoms in the solvent molecule were refined isotropically, and those in the cluster molecule were refined anisotropically. Hydrogen atoms in the cluster molecule were fixed on the calculated positions, and those in the solvent molecule were not included in the calculation.

Structure Determination of 2·0.5 C_5H_5N. Cell parameters were determined with 24 diffractions in the range of $21°<2\theta<30°$. Empirical absorption correction was applied using DIFABS.[19] Systematic absences required the space group to be Cc or $C2/c$, and the structure was successfully solved under $C2/c$. Heavy atoms were located by direct method using SIR92,[20] and the structure was expanded by successive application of least-squares refinements and difference Fourier syntheses using ORFLS.[21] One pyridine solvent molecule was located. All the atoms in the solvent molecule (N7, C31—C35) had a site occupancy factor of 1/2 evaluated from the elemental analysis, and were refined isotropically. Non-hydrogen atoms in the cluster cation and the iodine atom were refined anisotropically.

Results and Discussion

Synthesis and Structure of $[Mo_3S_4Cl_4(C_5H_5N)_5]$ (1). Treatment of the orange mixture of $Mo_3S_7Cl_4$ and triphenylphosphine in pyridine under refluxing conditions gave green powder which was soluble in dichloromethane. The ultraviolet-visible spectrum of the product showed two characteristic absorption maxima centered on 395 and 665 nm which were almost identical to those of $[Mo_3S_4Cl_4(PEt_3)_n(MeOH)_{5-n}]$.[7] From the elemental analysis, the product was identified as a trinuclear cluster complex coordinated by pyridine, $[Mo_3S_4Cl_4(C_5H_5N)_5]$. The formal oxidation state of the molybdenum is +4 and the number of cluster valence electrons is six, which is common among the reported $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cluster complexes[2] and is consistent with three Mo–Mo single bonds.

The structure of **1** was determined with the single crystal X-ray structure analysis using a crystal obtained by recrystallization from dichloromethane. The atomic parameters and the selected geometric parameters are shown in Tables 2 and 3, respectively. The structural drawing of **1** is shown in Fig. 1. Three molybdenum atoms form an Mo_3 triangle, one μ_3-S ligand caps one side of the Mo_3 triangle, and three μ-S ligands bridge the Mo–Mo bonds, which form an incomplete cubane-type $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cluster core. Mo1 is coordinated by two chloro and one pyridine ligands, and Mo2 and Mo3 are coordinated by one chloro and two pyridine ligands, leading the environment of each molybdenum atom to distorted octahedral six-coordination if all the Mo–Mo bonds are neglected. The cluster molecule has no symmetry element due to the asymmetric coordination of the five pyridine ligands around the cluster core and all the pyridine rings are vertical to the Mo_3 triangle. Considering the steric repulsions between geminal pyridine ligands and those between ligands coordinating to adjacent molybdenum atoms, we found that the observed coordination mode was

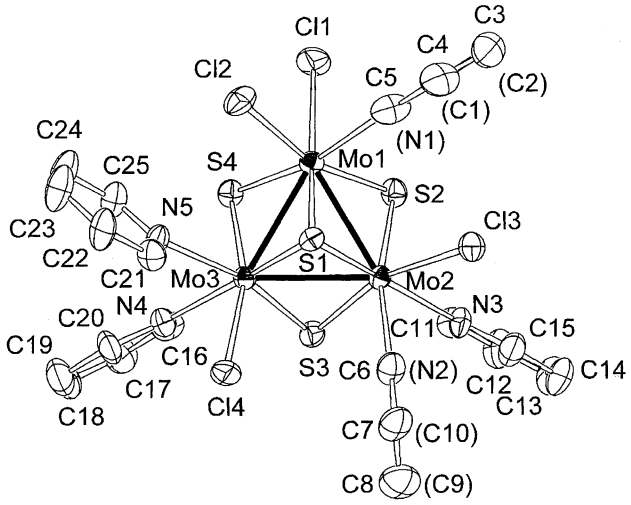

Fig. 1. Drawing of $[Mo_3S_4Cl_4(C_5H_5N)_5]$ (**1**) with probability level of 50% viewed through the axis perpendicular to the Mo_3 plane. Hydrogen atoms are not shown. Labels of the hidden atoms are shown with parentheses.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $[Mo_3S_4Cl_4(C_5H_5N)_5]\cdot CH_2Cl_2$ (**1·CH$_2$Cl$_2$**)

Atom	x/a	y/b	z/c	U_{eq}[a)]
Mo1	0.58663(4)	0.33157(3)	0.44972(4)	0.0242(2)
Mo2	0.42540(4)	0.28856(3)	0.21903(4)	0.0227(2)
Mo3	0.33484(4)	0.22237(3)	0.41384(4)	0.0227(2)
S1	0.48029(12)	0.18332(8)	0.31964(12)	0.0242(5)
S2	0.56156(14)	0.43189(9)	0.33044(13)	0.0315(6)
S3	0.25301(13)	0.29638(10)	0.28499(13)	0.0306(6)
S4	0.45172(13)	0.35263(9)	0.56649(12)	0.0287(6)
N1	0.7585(4)	0.3351(3)	0.3673(4)	0.039(2)
N2	0.2887(4)	0.1610(3)	0.0647(4)	0.034(2)
N3	0.3734(4)	0.3727(3)	0.0820(4)	0.034(2)
N4	0.1776(4)	0.2256(3)	0.5111(4)	0.033(2)
N5	0.3702(4)	0.1338(3)	0.5535(4)	0.031(2)
Cl1	0.74480(15)	0.47564(10)	0.59597(13)	0.0482(7)
Cl2	0.67791(14)	0.25180(11)	0.58775(13)	0.0427(7)
Cl3	0.56928(13)	0.27032(9)	0.08474(12)	0.0358(6)
Cl4	0.17777(14)	0.06854(9)	0.29624(13)	0.0401(6)
C1	0.8338(5)	0.4145(4)	0.3463(6)	0.048(3)
C2	0.9338(6)	0.4213(5)	0.2922(6)	0.059(4)
C3	0.9567(6)	0.3397(6)	0.2577(6)	0.064(4)
C4	0.8832(6)	0.2595(5)	0.2788(6)	0.057(3)
C5	0.7835(6)	0.2564(4)	0.3332(5)	0.048(3)
C6	0.3171(6)	0.0838(4)	0.0331(5)	0.041(3)
C7	0.2351(6)	0.0052(4)	−0.0558(5)	0.052(3)
C8	0.1224(7)	0.0056(5)	−0.1132(6)	0.065(4)
C9	0.0919(6)	0.0815(4)	−0.0818(5)	0.054(3)
C10	0.1768(5)	0.1588(4)	0.0069(5)	0.041(3)
C11	0.3432(5)	0.4480(4)	0.1260(5)	0.041(3)
C12	0.3115(6)	0.5009(4)	0.0489(6)	0.053(3)
C13	0.3091(6)	0.4774(5)	−0.0731(6)	0.059(4)
C14	0.3385(6)	0.4019(5)	−0.1185(6)	0.057(3)
C15	0.3700(6)	0.3504(4)	−0.0378(5)	0.047(3)
C16	0.1488(5)	0.3022(4)	0.5336(5)	0.040(3)
C17	0.0498(6)	0.3047(5)	0.5857(6)	0.052(3)
C18	−0.0213(6)	0.2254(5)	0.6187(6)	0.061(4)
C19	0.0092(6)	0.1458(5)	0.6002(6)	0.057(3)
C20	0.1079(6)	0.1490(4)	0.5457(5)	0.044(3)
C21	0.3629(5)	0.0443(4)	0.5109(5)	0.038(3)
C22	0.3915(6)	−0.0083(4)	0.5923(6)	0.051(3)
C23	0.4267(7)	0.0294(5)	0.7162(6)	0.061(4)
C24	0.4326(7)	0.1201(4)	0.7609(5)	0.060(4)
C25	0.4032(6)	0.1682(4)	0.6748(5)	0.044(3)
Cl5A	0.2085(11)	0.8277(8)	0.1095(10)	0.086(3)
Cl5B	0.2141(8)	0.8543(5)	0.1530(7)	0.073(2)
Cl5C	0.1538(9)	0.8107(7)	0.0947(10)	0.109(4)
Cl6A	0.0301(14)	0.6319(11)	0.0680(13)	0.096(4)
Cl6B	0.0184(10)	0.6668(6)	0.0604(9)	0.104(4)
Cl6C	0.0612(14)	0.6233(12)	0.0692(15)	0.148(7)
C26	0.1884(7)	0.7151(6)	0.0906(7)	0.083(3)

a) $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 3. Selected Geometric Parameters (Å, °) for $[Mo_3S_4Cl_4(C_5H_5N)_5]\cdot CH_2Cl_2$ (**1·CH$_2$Cl$_2$**)

Mo1–Mo2	2.789(1)	Mo1–Mo3	2.785(1)
Mo1–S1	2.335(2)	Mo1–S2	2.283(2)
Mo1–S4	2.275(2)	Mo1–N1	2.327(5)
Mo1–Cl1	2.499(2)	Mo1–Cl2	2.468(2)
Mo2–Mo3	2.783(1)	Mo2–S1	2.339(2)
Mo2–S2	2.279(2)	Mo2–S3	2.284(2)
Mo2–N2	2.326(5)	Mo2–N3	2.318(5)
Mo2–Cl3	2.484(2)	Mo3–S1	2.329(2)
Mo3–S3	2.279(2)	Mo3–S4	2.286(2)
Mo3–N4	2.291(5)	Mo3–N5	2.333(5)
Mo3–Cl4	2.479(2)		
Mo2–Mo1–Mo3	59.91(2)	Mo1–Mo2–Mo3	59.97(2)
Mo1–Mo3–Mo2	60.12(2)	S1–Mo1–S2	104.55(6)
S1–Mo1–S4	104.71(6)	S1–Mo1–N1	87.22(13)
S1–Mo1–Cl2	85.68(6)	S2–Mo1–S4	95.28(6)
S2–Mo1–N1	86.31(13)	S2–Mo1–Cl1	84.26(6)
S4–Mo1–Cl1	85.57(6)	S4–Mo1–Cl2	94.68(6)
N1–Mo1–Cl1	81.82(13)	N1–Mo1–Cl2	81.07(13)
Cl1–Mo1–Cl2	83.29(6)	S1–Mo2–S2	104.54(6)
S1–Mo2–S3	104.18(6)	S1–Mo2–N2	87.88(13)
S1–Mo2–Cl3	86.98(5)	S2–Mo2–S3	97.00(6)
S2–Mo2–N3	83.45(13)	S2–Mo2–Cl3	93.21(6)
S3–Mo2–N2	86.68(13)	S3–Mo2–N3	83.64(13)
N2–Mo2–N3	83.2(2)	N2–Mo2–Cl3	80.08(13)
N3–Mo2–Cl3	83.31(13)	S1–Mo3–S3	104.66(6)
S1–Mo3–S4	104.56(6)	S1–Mo3–N5	86.82(13)
S1–Mo3–Cl4	87.50(5)	S3–Mo3–S4	96.52(6)
S3–Mo3–N4	84.64(13)	S3–Mo3–Cl4	91.07(6)
S4–Mo3–N4	83.48(13)	S4–Mo3–N5	87.68(13)
N4–Mo3–N5	82.8(2)	N4–Mo3–Cl4	82.70(13)
N5–Mo3–Cl4	81.74(13)	Mo1–S1–Mo2	73.27(5)
Mo1–S1–Mo3	73.33(5)	Mo2–S1–Mo3	73.20(5)
Mo1–S2–Mo2	75.39(5)	Mo2–S3–Mo3	75.18(5)
Mo1–S4–Mo3	75.28(5)		

the most favorable among alternatives. The average value of the interatomic distances between the molybdenum atoms is 2.786 Å, which is in the range of those found in the reported $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cluster complexes having six cluster valence electrons.[2] The average distance of Mo–(μ_3-S) is 2.334 Å and that of Mo–(μ-S) is 2.281 Å, both of which are normal values for a $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cluster complex.[2] Two of the μ-S ligands (S2 and S4) are close to those in another cluster molecule related with a symmetrical inversion center with a distance of 3.439 Å, which is considerably shorter than the sum of the van der Waals radii of two sulfur atoms (3.70 Å).[22] These short contacts result in the formation of the cluster dimer in the crystal lattice (see Fig. 2). The S3 atom does not participate in the short contact because the S3 atom lies between two *cis* pyridine ligands and cannot approach to another molecule due to the steric requirement. Similar short contacts are found for several $Mo_3(\mu_3\text{-}E)(\mu\text{-}E)_3$ and $Mo_3(\mu_3\text{-}E)(\mu\text{-}E_2)_3$ (E = chalcogens) cluster complexes.[23] Especially, a tungsten sulfido cluster complex $(CH_3C_6H_4SO_3)_4[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]$ has the same arrangement of two contacts of the two μ-S ligands with the distances of 3.36 Å.[23,24]

The starting compound $Mo_3S_7Cl_4$ contains triangular $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cluster cores connected to each other by Mo–(μ-Cl)–Mo bridges, forming infinite chains.[25] Several excision reactions of $Mo_3S_7Cl_4$ using tertiary phosphines have been reported so far. The reaction of $Mo_3S_7Cl_4$ with two equivalents of triphenylphosphine in nitriles gives $[Mo_3S_7Cl_4(PPh_3)_2]$,[26] while that

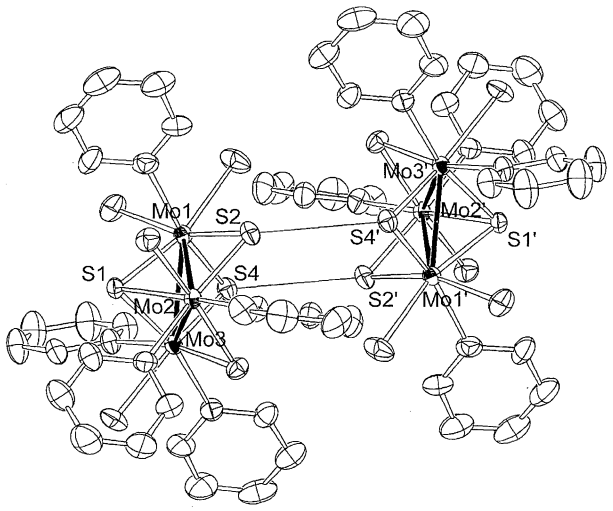

Fig. 2. Short contacts of **1** in the crystal lattice. Labels with primes indicate the atoms generated by a crystallographic inversion center.

with excess triphenylphosphine in tetrahydrofuran yields $[Mo_3S_4Cl_4(PPh_3)_2(H_2O)_2]$.[27] In the former reaction, one of the bonds in the Mo–(μ-Cl)–Mo bridge connecting two cluster cores is cleaved, and triphenylphosphine coordinates to the resulting vacant coordination site on the molybdenum atom. The μ-S_2 ligands in $Mo_3S_7Cl_4$ are unchanged in the course of the excision process. In the latter reaction, triphenylphosphine abstracts also one sulfur atom from each μ-S_2 ligand, affording a $Mo_3(\mu_3\text{-S})(\mu\text{-S})_3$ cluster core. Compared with these examples, the present excision reaction giving **1** is participated in by both triphenylphosphine and pyridine. The abstraction of a sulfur atom from the μ-S_2 ligands is effected by triphenylphosphine, because pyridine has no ability of abstracting sulfur atoms, and triphenylphosphine sulfide was generated as a byproduct in the reaction. The cleavage of the μ-Cl bridges is apparently induced by the coordination of pyridine, because of the larger coordination ability of pyridine as compared with that of triphenylphosphine. This presumption is supported by the fact that the cluster complex coordinated by triphenylphosphine was not obtained even when an excess amount of triphenylphosphine was used. Furthermore, the additional supporting result is that the reactions using three equivalents of other tertiary phosphines (trimethylphosphine, triethylphosphine, triisopropylphosphine, tributylphosphine, and tris(dimethylamino)phosphine) instead of triphenylphosphine invariably gave **1** and the corresponding tertiary phosphine sulfides. The excision reactions using these trialkylphosphines occurred even at room temperature, in contrast with the refluxing conditions for triphenylphosphine, which suggests that sulfur-abstracting abilities of these trialkylphosphines are greater than that of triphenylphosphine. It is worth mentioning that the reaction of $[Mo_3S_7Br_6]^{2-}$, triphenylphosphine, and η^3-N-donor ligands (triaminoinositol derivatives = L) gives $[Mo_3S_4L_3]^{4-}$.[28] In this reaction, a sulfur atom is abstracted from each μ-S_2 ligand by triphenylphosphine, and bromo ligands are substituted by the N-donor ligands. This combination of the abstraction of sulfur atoms and the substitution of bromo ligands is similar to the present excision reaction of $Mo_3S_7Cl_4$ with triphenylphosphine and pyridine, where the substitution of bromo ligands corresponds to the cleavage of the μ-Cl bridges by the coordination of pyridine.

Excision Reactions Using Other Reagents. To investigate the general applicability of this excision reaction, we carried out the reactions of the combinations of $Mo_3S_7X_4$ (X = Cl, Br, I), tertiary phosphines (trimethylphosphine, triethylphosphine, tributylphosphine, and triphenylphosphine), and N-donor ligands (pyridine, β-picoline, γ-picoline, 2,2′-bipyridine, 4,4′-bipyridine, NEt_3, $^nBuNH_2$, piperidine, and imidazole). Because $Mo_3S_7X_4$ are insoluble in any solvents, the occurrence of the excision reaction was judged by the generation of soluble compounds whose colors were between green and brown. Coordination of the N-donor ligands in the products was confirmed by the shifts of the infrared absorptions of the ligands from those of free ligand molecules. The bromide $Mo_3S_7Br_4$ was reacted with all the tertiary phosphines listed above in pyridine, affording brown powders whose elemental analyses were consistent with the calculated values for the formula $[Mo_3S_4Br_4(C_5H_5N)_5]$. The reaction temperature required for each tertiary phosphine was same as that of the reaction of $Mo_3S_7Cl_4$ (room temperature for trimethylphosphine, triethylphosphine, and tributylphosphine; refluxing condition for triphenylphosphine). In contrast, $Mo_3S_7I_4$ did not react with any tertiary phosphines in pyridine, and the starting compound was recovered. These results show that the reactivity of $Mo_3S_7Br_4$ is similar to $Mo_3S_7Cl_4$, and that of $Mo_3S_7I_4$ is much lower than the chloride and the bromide. Among the treatments of $Mo_3S_7Cl_4$ with triphenylphosphine and the N-donor ligands, only $^nBuNH_2$ reacted at room temperature; β-picoline, γ-picoline, 2,2′-bipyridine, 4,4′-bipyridine, and piperidine reacted at higher temperatures, and NEt_3 and imidazole did not react. The differences of the reactivities may be related to the coordination abilities of the ligands. From the similarities of the UV-visible spectra of these products with that of **1**, they probably contain the same trinuclear cluster core as **1**.

Synthesis and Structure of $[Mo_3S_4Cl_3(C_5H_5N)_6]I$ (2). By the reflux of the pyridine solution of **1** and I_2, the color of the solution changed from green brown to red brown. Cooling the solution to room temperature gave brown crystals of $[Mo_3S_4Cl_3(C_5H_5N)_6]I$ (**2**). The structure of **2** was determined with a single crystal X-ray structure analysis. The atomic parameters and some selected geometric parameters are shown in Tables 4 and 5, respectively. A structural drawing of **2** is shown in Fig. 3. The $Mo_3(\mu_3\text{-S})(\mu\text{-S})_3$ cluster unit is retained from **1**, and one chloro ligand in **1** is substituted by a pyridine ligand, leading to the coordination of each molybdenum atom by one chloro and two pyridine ligands. The ligands coordinate in such a symmetrical manner around the cluster core as to lead to the virtual C_3 symmetry of the cluster cation. The formal oxidation state of molybdenum (+4) is unchanged from **1**. Mo–Mo(2.780 Å), Mo–(μ_3-S)(2.331 Å), and Mo–(μ-S) distances (2.286 Å) are almost identical with those in **1**. The iodide anion is close to the three μ-S li-

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $[Mo_3S_4Cl_3(C_5H_5N)_6]\cdot 0.5\ C_5H_5N$ (**2·0.5 C_5H_5N**)

Atom	x/a	y/b	z/c	U_{eq}[a)]
I	0.12842(5)	0.0244(1)	−0.11043(5)	0.0611(4)
Mo1	0.24471(5)	0.0268(1)	0.08486(5)	0.0395(4)
Mo2	0.14695(5)	0.0679(1)	0.08151(5)	0.0395(4)
Mo3	0.17287(5)	−0.1057(1)	0.07291(5)	0.0378(3)
Cl1	0.3238(2)	−0.0525(3)	0.1443(2)	0.056(1)
Cl2	0.1706(2)	0.1932(3)	0.1465(2)	0.057(1)
Cl3	0.1260(2)	−0.1753(3)	0.1257(2)	0.055(1)
S1	0.2105(2)	−0.0134(3)	0.1501(2)	0.045(1)
S2	0.1008(2)	−0.0317(3)	0.0156(2)	0.041(1)
S3	0.2199(2)	−0.0813(3)	0.0189(2)	0.042(1)
S4	0.1877(2)	0.1282(3)	0.0289(2)	0.044(1)
N1	0.2971(5)	0.074(1)	0.0414(6)	0.059(4)
N2	0.2852(5)	0.1393(9)	0.1453(6)	0.046(4)
N3	0.0795(5)	0.1595(9)	0.0349(6)	0.048(4)
N4	0.0951(5)	0.037(1)	0.1300(5)	0.048(4)
N5	0.1398(5)	−0.2208(10)	0.0139(6)	0.048(4)
N6	0.2335(5)	−0.2085(10)	0.1193(5)	0.048(4)
C1	0.2779(7)	0.081(1)	−0.0156(7)	0.060(6)
C2	0.3078(8)	0.116(1)	−0.0455(8)	0.073(6)
C3	0.3596(8)	0.142(2)	−0.0130(9)	0.074(7)
C4	0.3789(7)	0.133(2)	0.0458(9)	0.074(7)
C5	0.3468(7)	0.100(1)	0.0718(8)	0.065(6)
C6	0.3053(7)	0.122(1)	0.2031(7)	0.061(6)
C7	0.3250(8)	0.196(2)	0.2401(8)	0.070 (7)
C8	0.3288(8)	0.278(2)	0.2239(8)	0.079(7)
C9	0.3073(8)	0.292(2)	0.163(1)	0.086(8)
C10	0.2863(7)	0.219(1)	0.1259(8)	0.065(6)
C11	0.0536(7)	0.204(1)	0.0587(7)	0.056(5)
C12	0.0103(7)	0.257(1)	0.0302(10)	0.077(7)
C13	−0.0081(7)	0.260(1)	−0.0275(9)	0.071(7)
C14	0.0155(7)	0.215(1)	−0.0547(8)	0.061(6)
C15	0.0598(7)	0.166(1)	−0.0229(8)	0.056(5)
C16	0.1163(7)	0.038(1)	0.1864(7)	0.064(6)
C17	0.0849(9)	0.010(2)	0.2167(8)	0.081(7)
C18	0.0324(8)	−0.006(2)	0.1892(8)	0.096(8)
C19	0.0108(8)	−0.006(2)	0.1272(9)	0.099(8)
C20	0.0448(6)	0.013(1)	0.1002(7)	0.065(6)
C21	0.1250(7)	−0.211(1)	−0.0436(7)	0.054(5)
C22	0.1093(9)	−0.279(1)	−0.0777(9)	0.081(7)
C23	0.1098(8)	−0.360(2)	−0.0586(10)	0.089(8)
C24	0.1250(8)	−0.377(2)	0.0003(10)	0.085(8)
C25	0.1394(7)	−0.304(1)	0.0335(7)	0.056(5)
C26	0.2571(7)	−0.257(1)	0.0945(7)	0.055(5)
C27	0.2933(8)	−0.325(1)	0.1182(8)	0.076(7)
C28	0.3061(10)	−0.336(2)	0.178(1)	0.116(10)
C29	0.2831(9)	−0.284(2)	0.2056(8)	0.091(8)
C30	0.2468(7)	−0.222(1)	0.1766(7)	0.064(6)
N7	0.640(2)	0.043(4)	0.134(2)	0.15(2)
C31	0.686(3)	0.050(5)	0.149(3)	0.15(3)
C32	0.719(3)	−0.042(7)	0.183(4)	0.20(3)
C33	0.674(2)	−0.076(5)	0.189(2)	0.12(2)
C34	0.629(3)	−0.076(6)	0.173(3)	0.17(3)
C35	0.594(4)	−0.015(7)	0.115(4)	0.22(3)

a) $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 5. Selected Geometric Parameters (Å, °) for $[Mo_3S_4Cl_3(C_5H_5N)_6]I\cdot 0.5\ C_5H_5N$ (**2·0.5 C_5H_5N**)

Mo1–Mo2	2.776(2)	Mo1–Mo3	2.783(2)
Mo1–Cl1	2.470(4)	Mo1–S1	2.325(4)
Mo1–S3	2.282(4)	Mo1–S4	2.291(4)
Mo1–N1	2.28(1)	Mo1–N2	2.30(1)
Mo2–Mo3	2.780(2)	Mo2–Cl2	2.463(5)
Mo2–S1	2.329(4)	Mo2–S2	2.279(4)
Mo2–S4	2.283(5)	Mo2–N3	2.28(1)
Mo2–N4	2.31(1)	Mo3–Cl3	2.472(5)
Mo3–S1	2.339(4)	Mo3–S2	2.288(4)
Mo3–S3	2.293(4)	Mo3–N5	2.28(1)
Mo3–N6	2.28(1)		
I···S2	3.740(4)	I···S3	3.710(4)
I···S4	3.701(4)		
Mo2–Mo1–Mo3	60.00(5)	Mo1–Mo2–Mo3	60.13(5)
Mo1–Mo3–Mo2	59.87(5)	Cl1–Mo1–S1	86.4(2)
Cl1–Mo1–S3	93.1(2)	Cl1–Mo1–N1	82.6(4)
Cl1–Mo1–N2	81.6(4)	S1–Mol–S3	105.3(2)
S1–Mo1–S4	104.9(2)	S1–Mo1–N2	86.2(4)
S3–Mo1–S4	94.5(2)	S3–Mo1–N1	85.6(4)
S4–Mo1–N1	84.2(4)	S4–Mo1–N2	88.1(4)
N1–Mo1–N2	82.0(5)	Cl2–Mo2–S1	88.1(2)
Cl2–Mo2–S4	91.8(2)	Cl2–Mo2–N3	80.6(4)
Cl2–Mo2–N4	81.0(4)	S1–Mo2–S2	105.1(2)
S1–Mo2–S4	105.0(2)	S1–Mo2–N4	86.1(3)
S2–Mo2–S4	95.2(2)	S2–Mo2–N3	84.2(4)
S2–Mo2–N4	88.8(4)	S4–Mo2–N3	86.5(4)
N3–Mo2–N4	81.2(5)	Cl3–Mo3–S1	86.9(2)
Cl3–Mo3–S2	92.7(2)	Cl3–Mo3–N5	82.9(4)
Cl3–Mo3–N6	81.9(4)	S1–Mo3–S2	104.5(2)
S1–Mo3–S3	104.4(2)	S1–Mo3–N6	88.0(4)
S2–Mo3–S3	95.4(2)	S2–Mo3–N5	85.2(4)
S3–Mo3–N5	84.0(4)	S3–Mo3–N6	87.0(4)
N5–Mo3–N6	81.4(5)	Mo1–S1–Mo2	73.2(1)
Mo1–S1–Mo3	73.3(1)	Mo2–S1–Mo3	73.1(1)
Mo2–S2–Mo3	75.0(1)	Mo1–S3–Mo3	74.9(1)
Mo1–S4–Mo2	74.7(1)		

gands in the cluster cation, with the average distance of 3.713 Å, which is considerably shorter than the sum of the van der Waals radii of iodine and sulfur (4.00 Å).[22] Several examples of short contacts between $Mo_3(\mu_3\text{-}E)(\mu\text{-}E_2)_3$ (E=chalcogens) cluster cores and various anions are known,[23,29,30] but those between $Mo_3(\mu_3\text{-}E)(\mu\text{-}E)_3$ cluster cores and anions have not been reported so far. By the reported molecular orbital calculation for a $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3^{4+}$ cluster unit, the μ-S atoms have some cationic character,[31—33] which may explain the short contacts of the three μ-S and the iodide anion. UV-visible spectrum of **2** shows two new absorption maxima at 370 and 490 nm, which are absent in that of **1**. Because the electronic structure of the cluster core in **2** is thought to be essentially the same as that in **1**, these new bands may originate from the charge-transfer between the cluster cation and the iodide anion.

The reaction of **1** with iodine did not lead to the oxidation of the cluster core or substitution of chloro to iodo ligand. Instead, a pyridine molecule substituted for a chloro ligand

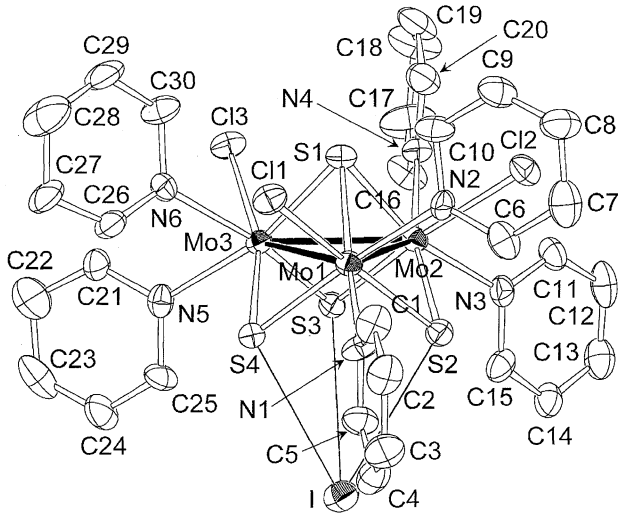

Fig. 3. Drawing of $[Mo_3S_4Cl_3(C_5H_5N)_6]I$ (**2**) with probability levels of 40%.

and an iodide anion positioned in outer sphere near the three μ-S in the cluster cation, which may be due to the greater affinity of the softer iodide anion to sulfur. We carried out the reaction of **1** with KI in pyridine under reflux, and found that **2** was formed, judging from the UV-visible spectrum. This result shows that **2** can also be formed by the application of I^- to **1**. It indicates that no oxidation process is involved in the reaction of **1** with I_2, suggesting that the redox potential of I_2 is not high enough to oxidize the Mo_3S_4 cluster.

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References

1) S. C. Lee and R. H. Holm, *Angew. Chem., Int. Ed. Engl.*, **29**, 840 (1990).
2) T. Shibahara, *Adv. Inorg. Chem.*, **37**, 143 (1991).
3) T. Shibahara, *Coord. Chem. Rev.*, **123**, 73 (1993).
4) I. Dance and K. Fisher, *Prog. Inorg. Chem.*, **41**, 637 (1994).
5) T. Saito, in "Early Transition Metal Clusters with π-Donor Ligands," ed by M. H. Chisholm, VCH, New York (1995), pp. 63—164.
6) T. Saito, H. Imoto, K. Tsuge, S. Mita, J. Mizutani, S. Yamada, and H. Fujita, in "Transition Metal Sulfur Chemistry: Biological and Industrial Significance," ACS Symposium Series, Vol. 653, ed by E. I. Stiefel and K. Matsumoto, American Chemical Society, Washington, D.C. (1996), pp. 240—250.
7) T. Saito, N. Yamamoto, T. Yamagata, and H. Imoto, *Chem. Lett.*, **1987**, 2025.
8) T. Saito, N. Yamamoto, T. Nagase, T. Tsuboi, K. Kobayashi, T. Yamagata, H. Imoto, and K. Unoura, *Inorg. Chem.*, **29**, 764 (1990).
9) J. Mizutani, S. Yamada, H. Imoto, and T. Saito, *Inorg. Chem.*, **35**, 244 (1996).
10) J. Mizutani, H. Imoto, and T. Saito, *Chem. Lett.*, **1994**, 2117.
11) A. A. Opalovskii, V. E. Fedorov, and K. A. Khaldoyanidi, *Dokl. Akad. Nauk SSSR*, **182**, 1095 (1968).
12) V. E. Fedorov, Yu. V. Mironov, O. A. Kuz'mina, and V. P. Fedin, *Zh. Neorg. Khim.*, **31**, 2476 (1986); *Russ. J. Inorg. Chem.*, **31**, 1429 (1986).
13) V. E. Fedorov, A. P. Mazhara, V. K. Evstaf'ev, and S. D. Kirik, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **1978**, 56.
14) D. T. Cromer and J. T. Waber, in "International Tables for X-Ray Crystallography," ed by T. Hahn, Kynoch Press, Brimingham, England (1974), Vol. IV, Table 2.2A.
15) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **A24**, 351 (1968).
16) G. M. Sheldrick, "SHELXS86, a program for crystal structure determination," University of Göttingen, Federal Republic of Germany (1986).
17) H. Imoto, S. Hayakawa, N. Morita, and T. Saito, *Inorg. Chem.*, **29**, 2007 (1990).
18) G. M. Sheldrick, "SHELX76, a program for crystal structure determination," University of Cambridge, U. K. (1976).
19) N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, **A39**, 158 (1983). An empirical absorption correction program.
20) A. Altomare, G. Cascarano, C. Giacovazzo, and A. Guagliardi, *J. Appl. Crystallogr.*, **26**, 343 (1993).
21) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A FORTRAN Crystallographic Least Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1962).
22) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, New York (1960), p. 260.
23) A. V. Virovetz and N. V. Podberezskaya, *Zh. Struct. Khim.*, **34**, 150 (1993); *J. Struct. Chem.*, **34**, 306 (1993).
24) T. Shibahara, A. Takeuchi, A. Ohtsuji, K. Kohda, and H. Kuroya, *Inorg. Chim. Acta*, **127**, L45 (1987).
25) J. Marcoll, A. Rabenau, D. Mootz, and H. Wunderlich, *Rev. Chim. Miner.*, **11**, 607 (1974).
26) V. P. Fedin, S. P. Gubin, A. V. Mishchenko, and V. E. Fedorov, *Koord. Khim.*, **10**, 901 (1984); *Sov. J. Coord. Chem.*, **10**, 501 (1984).
27) F. A. Cotton, P. A. Kibala, M. Matusz, C. S. McCaleb, and R. B. W. Sandor, *Inorg. Chem.*, **28**, 2623 (1989).
28) M. D. Meienberger, K. Hegetschweiler, H. Rüegger, and V. Gramlich, *Inorg. Chim. Acta*, **213**, 157 (1993).
29) V. P. Fedin, H. Imoto, and T. Saito, *J. Chem. Soc., Chem. Commun.*, **1995**, 1559.
30) V. P. Fedin, H. Imoto, T. Saito, W. McFarlane, and A. G. Sykes, *Inorg. Chem.*, **34**, 5097 (1995).
31) Z. D. Chen, J. X. Lu, C. W. Liu, and Q. E. Zhang, *Polyhedron*, **10**, 2799 (1991).
32) J. Li, C. W. Liu, and J. X. Lu, *Polyhedron*, **13**, 1841 (1994).
33) J. Li, C. W. Liu, and J. X. Lu, *J. Chem. Soc., Faraday Trans.*, **90**, 39 (1994).