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Cubane-Type Mixed-Metal Clusters with Mo_3NiS_4 Cores. Syntheses, Characterization, and X-ray Structures of $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4 \cdot 7H_2O$ and $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl] \cdot 14H_2O$

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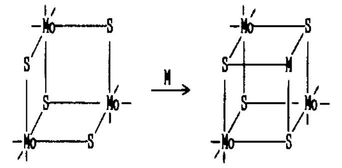
Reaction of the incomplete cubane-type aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$ (A) with nickel metal gives a novel cubane-type mixed-metal cluster $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (B′) in high yields (75%), which is further converted to $[Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-}$ (C′; H_3nta = nitrilotriacetic acid). The cluster B′ is fairly stable toward air oxidation. Driving forces for the formation of the cubane-type mixed-metal clusters are discussed. The crystallographic results obtained are as follows. $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4 \cdot 7H_2O$ (B): triclinic, $P\bar{1}$, $a = 17.889$ (6) Å, $b = 19.601$ (8) Å, $c = 8.969$ (4) Å, $\alpha = 102.83$ (4)°, $\beta = 103.78$ (3)°, $\gamma = 63.45$ (3)°, $V = 2707.7$ (19) Å^3, $Z = 2$, 7153 unique data ($|F_o| \geq 3\sigma|F_o|$), $R = 7.28\%$. $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl] \cdot 14H_2O$ (C), triclinic, $P\bar{1}$, $a = 11.939$ (5) Å, $b = 18.379$ (6) Å, $c = 11.666$ (3) Å, $\alpha = 103.60$ (3)°, $\beta = 106.13$ (3)°, $\gamma = 85.97$ (3)°, $V = 2390.1$ (15) Å^3, $Z = 2$, 7675 unique data ($|F_o| \geq 3\sigma|F_o|$), $R = 4.99\%$. If the Mo–Mo and Mo–Ni bonds are not counted, each molybdenum atom is octahedrally coordinated in B and C, and the nickel atom has fairly regular tetrahedral geometry in B and C. The magnetic moment of B is very low, indicating the presence of strong interaction between molybdenum and nickel atoms. The following stoichiometry was determined: $Mo_3NiS_4^{4+}(aq) + 2Fe^{3+}(aq) \rightarrow Mo_3S_4^{4+}(aq) + Ni^{2+}(aq) + 2Fe^{2+}(aq)$. No intermediate such as $Mo_3NiS_4^{5+}(aq)$ appeared. The electronic spectrum of the aqua ion B in 2 M HPTS has peaks at 680 nm ($\epsilon = 610$ M^{-1} cm^{-1}) and 500 nm ($\epsilon = 200$). The peaks of B in 2 M HCl are at 800_{sh} nm ($\epsilon = 360$), 688 nm ($\epsilon = 488$), and 498 nm ($\epsilon = 366$). The peaks of C in water are at 703 nm ($\epsilon = 683$ M^{-1} cm^{-1}) and 500_{sh} nm ($\epsilon = 280$), while those of C in 2 M $CaCl_2$ are at 810_{sh} nm ($\epsilon = 455$), 700 nm ($\epsilon = 535$), and 502 nm ($\epsilon = 439$). Coordination of chloride ion to nickel atom was observed; the formation constant K for the following equilibrium was determined to be 15 M^{-1}: $[Mo_3NiS_4(Hnta)(nta)_2(H_2O)]^{4-} + Cl^- \rightleftharpoons [Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-} + H_2O$. There exist three kinds of cubane-type cores: single cubane type (Mo_3MS_4), double cubane type ($Mo_3S_4MMS_4Mo_3$), and sandwich cubane type ($Mo_3S_4MS_4Mo_3$). The relationship between Mo–M distance and formal charge of the cores are discussed.

Mixed-metal cluster compounds have been studied extensively.[1] Above all, much interest has been focused on (incomplete) cubane-type clusters.[2,3] We have reported preliminary results that the incomplete cubane-type aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$ (A)[4] reacted with metals (Fe,[5] Co,[6] Ni,[7] Cu,[8] Sn,[9] Hg[10]) or metal ion (Sn^{2+})[9] to give mixed metal cubane-type aqua cluster ions with Mo_3MS_4 cores as shown in Scheme I. The reaction of the aqua ion A with divalent metal ions in reducing conditions to give the clusters with Mo_3MS_4 cores has also been reported[11] recently. Without the use of the aqua ion A, mixed-metal clusters with Mo_3MS_4 cores can also be synthesized (a) by the reaction of $[Mo_3S_4(dtp)_4(L)]$ (L = H_2O, C_3H_3ON; dtp = $S_2P(OC_2H_5)_2$) with $SbCl_3$ or CuI[12-14] or (b) by the reaction of $[Mo_3S_4(Et_2PS_2)_4]$ with $[W(CO)_3(CH_3CN)_3]$.[15]

Scheme I. Formation of Cubane-Type Mixed-Metal Clusters



We describe here syntheses, characterization, and X-ray structures of two cubane-type mixed-metal clusters with Mo_3NiS_4 cores, $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4 \cdot 7H_2O$ (B) and $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl] \cdot 14H_2O$ (C; H_3nta = nitrilotriacetic acid). Reports on molybdenum–nickel–sulfur clusters are very rare, and no clusters with the cubane-type Mo_3NiS_4 cores have been reported so far. The compound $[Mo_2Ni_2S_4Cp_2(CO)_2]$ is the only other compound reported to have a cubane-type Mo–Ni–S core,[3c] and another interesting compound, $[Mo_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}CO)Cp_4]$, is known to have a bicapped-trigonal-bipyramid core.[18]

Experimental Section

Syntheses of Compounds. All the procedures were performed in air unless otherwise stated.

$[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4 \cdot 7H_2O$ (B). A solution of the incomplete cubane-type aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$ (A) was obtained by the published procedure.[4a] A like volume (10 mL) of concentrated HCl was added to the solution of A in 2 M HCl (0.080 M per trimer, 10 mL; λ_{max} = 620 nm, $\epsilon = 351$ M^{-1} cm^{-1}). Several pieces of nickel plates (1.25 g, Ni/A = ca. 25), the surface of which had been washed with concentrated HCl, were introduced to a conical flask containing the aqua ion A, and the mixture was allowed to stand for 5 days with stirring under a dinitrogen atmosphere at 50–55 °C in a water bath. The color of the solution turned from green to dark brown. The solution was filtered and the remaining nickel plates were removed. After the filtrate was diluted

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Table I. Crystallographic Data for $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ and $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl]\cdot 14H_2O$

formula	$Mo_3NiS_8O_{29}C_{28}H_{62}$	$Mo_3NiCa_{2.5}ClS_4O_{32}N_3C_{18}H_{47}$
fw	1465.82	1427.97
space group	$P\bar{1}$	$P\bar{1}$
a, Å	17.889 (6)	11.939 (5)
b, Å	19.601 (8)	18.379 (6)
c, Å	8.969 (4)	11.666 (3)
α, deg	102.83 (4)	103.60 (3)
β, deg	103.78 (3)	106.13 (3)
γ, deg	63.45 (3)	85.97 (3)
V, Å^3	2707.7 (19)	2390.1 (15)
Z	2	2
T, °C	18	18
λ(Mo Kα), Å	0.71073	0.71073
d_{obsd}, g/cm^3	1.80	1.98
d_{calcd}, g/cm^3	1.798	1.984
μ, cm^{-1}	13.8	17.2
R, %	7.28	4.99
R_w, %	8.60	6.91

to 20 times its original volume with water, Dowex 50W-X2 column chromatography was applied (2.5 cm × 45 cm). The first band containing the Ni^{2+} ion was eluted with 0.5 M HCl, and the second band (deep green) containing the mixed-metal aqua cluster $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (B′) was collected by use of 1 M HCl: yield, ca. 75%. The third band contains a small amount of the starting material, A. Brown bands remain on the upper part of the column.

In order to obtain crystals of $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ (B), the solution of B′ in 1 M HCl from the second band was absorbed on a short cation exchanger, Dowex 50W-X2. The resin was washed with 0.1 M HPTS (*p*-toluenesulfonic acid) to remove chloride ion, and slow elution with 4 M HPTS gave a bluish green solution. The concentrated part of the solution was stored in a refrigerator. After several days, green crystals deposited, which were collected by filtration, washed with ethyl acetate, and air-dried: yield, ca. 50% based on the solution in 1 M HCl. Anal. Found (calcd): C, 23.13 (22.94); H, 4.21 (4.26).

$Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl]\cdot 14H_2O$ (C). Nitrilotriacetic acid (0.22 g, H_3nta/B' = 3.6) dissolved in a minimum amount of 10 M KOH was added to a solution of the mixed-metal aqua ion B′ in 1 M HCl (0.0063 M, 50 mL) with stirring, the pH was adjusted to 1.2 with 10 M KOH, and the resultant solution was allowed to stand overnight at room temperature. The solution was diluted to 5 times its original volume with water and absorbed on an anion exchanger, Dowex 1-X2 (1.7 cm × 5 cm). The resin was washed with 0.1 M $CaCl_2$, and the green band was eluted with 3 M $CaCl_2$. The pH of the eluate was adjusted to 1.2 by the addition of 1 M HCl. Addition of a small amount of methanol to the solution and allowing the solution to stand overnight gave green plate crystals: yield, 0.23 g (50%). Anal. Found (calcd): Ca, 6.75 (7.01); Mo, 20.48 (20.15); N, 2.92 (2.94); C, 14.85 (15.14); H, 3.40 (3.31).

Structure Determinations of $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ (B) and $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl]\cdot 14H_2O$ (C). A green plate crystal (dimensions 0.20 × 0.10 × 0.03 mm) of B was mounted in a glass capillary and a green plate crystal (dimensions 0.30 × 0.27 × 0.20 mm) of C was mounted on a glass fiber with an adhesive. The crystallographic data for B and C are given in Table I and in the supplementary material (Tables SI and SII). Cell constants and orientation matrixes for both crystals were obtained form least-squares refinement, by using setting angles of 24 reflections in the range of 20° < 2θ < 30° measured on a RIGAKU AFC-6A diffractometer by use of Mo Kα radiation (λ = 0.71073 Å). Intensities were corrected for polarization and Lorentz factors but not for absorption. The intensities of standard reflections monitored after every 150 reflections for both crystals did not show any appreciable decay.

The coordinates of Mo, Ni, and S atoms that composed the cores were determined by means of MULTAN[16a] for B and by SHELXS-86[16b] for C, and the remaining non-hydrogen atoms were located from difference maps. No attempt was made to locate hydrogen atoms for both crystals. The refinement of the structures was performed by the block-diagonal least-squares method. No chemically significant peaks were observed on the final difference Fourier maps for B and C. Computations were performed on a FACOM M380 computer at the Okayama University of Science using the programs in the UNICS[17a] system and the program ORTEP.[17b] Atomic scattering factors for Mo^0, Ni^0, Ca^{2+}, Cl^-, S, O, N, and C were taken from ref 18. The atomic coordinates and thermal parameters for B are listed in Table II and those for C in Table III.

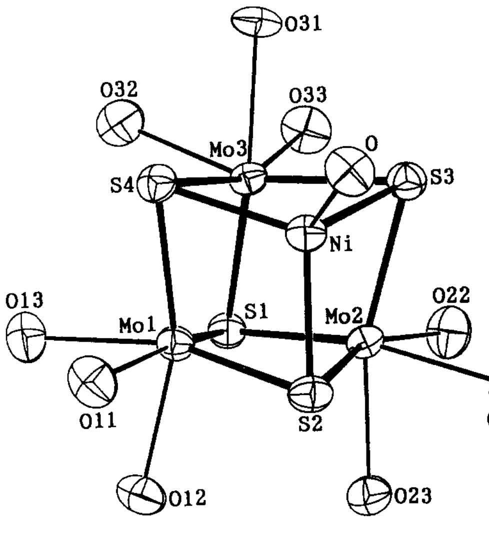

Figure 1. Perspective view of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$.

Oxidation of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (B′) by Fe^{3+}(aq). Three milliliters of B (1.564 mM in 2 M HCl, 4.69 × 10^{-3} mmol) was put into an absorption cell, to which a very small amount (0.020 mL) of iron alum, $Fe(NH_4)(SO_4)_2\cdot 12H_2O$, (0.0500 M in 2 M HCl) was added, the absorption was measured, and this procedure was repeated till the value Fe^{3+}/B reached ca. 3.

Determination of Formation Constant. Sodium chloride was used to vary the concentration of chloride ion (0.03–0.25 M), which was much higher than the total concentration of C (8.70 × 10^{-4} M). The ionic strength was adjusted to 1.0 M by the use of $NaClO_4$. Measurements of the absorbances were done at room temperature (ca. 20 °C).

Elemental Analyses. Analyses of carbon, hydrogen, and nitrogen were as described earlier.[19] Molybdenum and calcium were determined by ICP emission spectrometry by the use of a SHIMADZU ICPS-500 instrument.

Other Physical Measurements. UV, visible, and near-infrared spectra were recorded on Hitachi U-2000, 320, or 330 spectrophotometers.

Results and Discussion

Syntheses and Properties of $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ (B) and $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl]\cdot 14H_2O$ (C). The incomplete cubane-type aqua ion A in 7 M HCl reacts at 50–55 °C in 5 days with nickel metal to give the cubane-type mixed-metal aqua ion B′ in high yield (ca. 75%). At room temperature, the reaction in 7 M HCl will take more than 2 weeks to complete. The reaction is slower in more diluted HCl (e.g., 2 M HCl). The reason why the reaction rate depends on acidity is not clear at present.

Isolation of the crystals B is successful when 4 M HPTS is used. It is important to thoroughly remove chloride ion from the solution by use of a cation exchanger: addition of solid HPTS to make 4 M HPTS to the HCl solution containing B′ did not give crystals. The color of the cluster changes slightly by the change of solvent (deep green in 1 M HCl; bluish green in 4 M HPTS). The crystals of B dissolve in some organic solvents (e.g. acetonitrile, acetone, and *N,N*-dimethylformamide).

In order to see whether the one-electron-oxidation product of the aqua ion B′, $Mo_3NiS_4^{5+}$(aq), can be detected or not, iron alum

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Table II. Atomic Coordinates and Equivalent Isotropic Temperature Factors for $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4 \cdot 7H_2O^a$

atom	x	y	z	$B_{eq}/Å^2$
Mo1	1.0668 (1)	0.6803 (1)	0.5513 (1)	1.99 (3)
Mo2	0.9458 (1)	0.8288 (1)	0.5812 (1)	1.96 (3)
Mo3	1.0551 (1)	0.7671 (1)	0.8397 (1)	1.87 (3)
Ni	1.1087 (1)	0.7984 (1)	0.6254 (2)	2.22 (5)
S1	0.9527 (2)	0.7262 (2)	0.6871 (3)	2.0 (1)
S2	1.0381 (2)	0.7739 (2)	0.3982 (3)	2.5 (1)
S3	1.0194 (2)	0.8877 (2)	0.7732 (3)	2.3 (1)
S4	1.1783 (2)	0.6919 (2)	0.7352 (3)	2.3 (1)
O11	1.1653 (5)	0.6062 (5)	0.407 (1)	3.6 (3)
O12	0.9954 (5)	0.6286 (5)	0.368 (1)	3.2 (3)
O13	1.1013 (5)	0.5668 (4)	0.620 (1)	3.2 (3)
O21	0.8942 (5)	0.9325 (4)	0.4641 (9)	3.1 (3)
O22	0.8311 (5)	0.8985 (5)	0.689 (1)	3.3 (3)
O23	0.8490 (5)	0.8067 (4)	0.3998 (9)	3.0 (3)
O31	1.1380 (5)	0.7999 (5)	1.0386 (9)	2.9 (3)
O32	1.0915 (5)	0.6790 (5)	0.990 (1)	3.4 (3)
O33	0.9674 (5)	0.8231 (5)	1.0082 (9)	3.1 (3)
O	1.1886 (5)	0.8400 (5)	0.615 (1)	3.2 (3)
SP1	1.2239 (2)	0.4733 (2)	1.0101 (4)	3.5 (1)
SP2	1.3045 (2)	0.6927 (2)	0.3313 (4)	3.5 (1)
SP3	1.2392 (2)	0.9325 (2)	1.0098 (4)	3.6 (1)
SP4	0.7076 (2)	0.7927 (2)	0.6615 (5)	4.4 (1)
OP11	1.1855 (6)	0.4984 (6)	1.149 (1)	4.9 (4)
OP12	1.2011 (6)	0.5357 (5)	0.921 (1)	5.2 (4)
OP13	1.2043 (6)	0.4113 (5)	0.913 (1)	4.6 (4)
OP21	1.2815 (6)	0.7725 (6)	0.398 (1)	5.1 (4)
OP22	1.2691 (6)	0.6856 (6)	0.169 (1)	5.2 (4)
OP23	1.2832 (6)	0.6530 (7)	0.419 (1)	5.6 (5)
OP31	1.2072 (6)	0.9586 (6)	1.156 (1)	6.1 (5)
OP32	1.2310 (6)	0.8626 (6)	0.940 (1)	5.6 (5)
OP33	1.2028 (7)	0.9884 (8)	0.907 (2)	8.7 (7)
OP41	0.7395 (6)	0.8382 (6)	0.774 (1)	6.3 (5)
OP42	0.7339 (6)	0.7161 (6)	0.690 (2)	7.4 (6)
OP43	0.7311 (7)	0.7870 (8)	0.504 (2)	8.1 (6)
CP11	1.3349 (8)	0.4352 (7)	1.064 (1)	3.3 (5)
CP12	1.379 (1)	0.3572 (9)	1.091 (2)	5.5 (6)
CP13	1.4669 (9)	0.332 (1)	1.128 (2)	5.6 (6)
CP14	1.5099 (9)	0.375 (1)	1.140 (2)	5.5 (7)
CP15	1.4652 (9)	0.449 (1)	1.121 (2)	5.3 (7)
CP16	1.3756 (9)	0.4825 (9)	1.083 (2)	4.5 (6)
CP17	1.607 (1)	0.343 (1)	1.177 (2)	9. (1)
CP21	1.4156 (7)	0.6500 (7)	0.347 (1)	2.7 (4)
CP22	1.4540 (9)	0.6675 (9)	0.251 (2)	4.5 (6)
CP23	1.5416 (8)	0.6379 (8)	0.270 (2)	4.1 (5)
CP24	1.5902 (8)	0.5890 (8)	0.380 (2)	4.4 (6)
CP25	1.5531 (9)	0.5703 (9)	0.473 (2)	5.1 (6)
CP26	1.4634 (9)	0.6015 (9)	0.456 (2)	4.3 (6)
CP27	1.6902 (9)	0.555 (1)	0.402 (2)	7.3 (8)
CP31	1.3481 (7)	0.9103 (7)	1.057 (1)	2.7 (4)
CP32	1.3845 (9)	0.9338 (9)	0.971 (2)	4.9 (7)
CP33	1.4740 (9)	0.910 (1)	1.002 (2)	6.0 (7)
CP34	1.5219 (8)	0.8668 (9)	1.115 (2)	5.2 (6)
CP35	1.4839 (9)	0.843 (1)	1.204 (2)	6.3 (7)
CP36	1.3979 (9)	0.8643 (9)	1.173 (2)	5.0 (6)
CP37	1.619 (1)	0.841 (1)	1.144 (2)	7.6 (9)
CP41	0.5957 (8)	0.8383 (8)	0.641 (2)	3.9 (5)
CP42	0.5570 (9)	0.9170 (9)	0.646 (2)	4.9 (6)
CP43	0.4666 (9)	0.9541 (8)	0.614 (2)	5.0 (6)
CP44	0.4209 (9)	0.908 (1)	0.588 (2)	5.8 (7)
CP45	0.4617 (9)	0.8273 (9)	0.583 (2)	5.0 (6)
CP46	0.5477 (9)	0.7935 (8)	0.608 (2)	4.5 (6)
CP47	0.3220 (9)	0.951 (1)	0.554 (2)	7.3 (8)
OW1	0.8717 (5)	1.0668 (5)	0.653 (1)	4.3 (4)
OW2	0.9667 (6)	0.9384 (5)	0.238 (1)	3.7 (3)
OW3	0.8442 (7)	0.6367 (7)	0.388 (1)	6.6 (5)
OW4	0.9786 (8)	0.6456 (9)	0.068 (1)	7.7 (7)
OW5	0.8140 (7)	0.8568 (7)	0.113 (1)	6.6 (6)
OW6	0.8131 (9)	0.7049 (9)	0.993 (2)	10.5 (8)
OW7	0.881 (1)	0.5496 (9)	0.632 (2)	14 (1)

[a] Equivalent isotropic temperature factors ($B_{eq} = {}^4/_3\{\sum\sum B_{ij}a_ia_j\}$).

Table III. Atomic Coordinates and Equivalent Isotropic Temperature Factors for $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl] \cdot 14H_2O^a$

atom	x	y	z	$B_{eq}/Å^2$
Mo1	0.22126 (4)	0.20922 (3)	0.00331 (4)	1.45 (1)
Mo2	0.35410 (4)	0.29954 (3)	0.21716 (4)	1.31 (1)
Mo3	0.14014 (4)	0.24657 (3)	0.21088 (4)	1.35 (1)
Ni	0.3231 (1)	0.15501 (4)	0.2005 (1)	1.60 (2)
S1	0.1709 (1)	0.3296 (1)	0.0974 (1)	1.67 (4)
S2	0.4215 (1)	0.1962 (1)	0.0930 (1)	1.67 (4)
S3	0.3155 (1)	0.2438 (1)	0.3627 (1)	1.54 (4)
S4	0.1429 (1)	0.1270 (1)	0.0858 (1)	1.71 (4)
Cl	0.4111 (2)	0.0563 (1)	0.2707 (2)	3.5 (1)
O11	0.2584 (4)	0.2581 (2)	−0.1327 (4)	2.8 (1)
O12	0.0541 (4)	0.2086 (2)	−0.1290 (4)	2.7 (1)
O13	0.3033 (6)	0.2378 (3)	−0.3089 (5)	4.2 (2)
O14	−0.0796 (4)	0.1383 (3)	−0.2771 (5)	4.0 (2)
O15	0.2659 (4)	−0.0310 (3)	−0.3161 (4)	3.2 (1)
O16	0.3340 (5)	−0.0895 (3)	−0.1682 (5)	3.6 (2)
O21	0.3454 (4)	0.4057 (2)	0.3397 (4)	2.1 (1)
O22	0.4233 (4)	0.3728 (2)	0.1387 (4)	2.4 (1)
O23	0.4008 (4)	0.4590 (3)	0.5383 (4)	3.0 (1)
O24	0.5734 (5)	0.4398 (4)	0.1495 (6)	5.5 (2)
O25	0.7784 (4)	0.3228 (2)	0.4931 (4)	2.9 (1)
O26	0.7646 (4)	0.2071 (3)	0.5132 (5)	3.3 (1)
O31	−0.0410 (4)	0.2575 (2)	0.1258 (4)	2.3 (1)
O32	0.0902 (4)	0.3416 (2)	0.3337 (4)	2.0 (1)
O33	−0.2212 (4)	0.2412 (3)	0.1287 (6)	4.5 (2)
O34	0.0349 (4)	0.3839 (2)	0.5039 (4)	3.0 (1)
O35	−0.0265 (4)	0.1092 (3)	0.4622 (5)	3.5 (2)
O36	0.1233 (4)	0.0319 (3)	0.4648 (5)	3.3 (2)
N1	0.2331 (4)	0.1069 (3)	−0.1531 (4)	1.9 (1)
N2	0.5418 (4)	0.3195 (2)	0.3453 (4)	1.5 (1)
N3	0.0527 (4)	0.1947 (3)	0.3262 (4)	1.5 (1)
C11	0.2835 (6)	0.2161 (4)	−0.2252 (6)	2.7 (2)
C12	0.0224 (6)	0.1487 (4)	−0.2102 (6)	2.7 (2)
C13	0.2947 (6)	0.1315 (4)	−0.2323 (6)	2.8 (2)
C14	0.1080 (5)	0.0848 (3)	−0.2226 (6)	2.5 (2)
C15	0.2964 (6)	0.0410 (3)	−0.1084 (6)	2.3 (2)
C16	0.2975 (5)	−0.0290 (3)	−0.2069 (6)	2.3 (2)
C21	0.4176 (5)	0.4148 (3)	0.4468 (6)	2.0 (2)
C22	0.5292 (6)	0.3936 (4)	0.1846 (7)	2.8 (2)
C23	0.5281 (5)	0.3690 (3)	0.4615 (6)	2.2 (2)
C24	0.6071 (6)	0.3586 (4)	0.2835 (6)	2.6 (2)
C25	0.6075 (5)	0.2500 (3)	0.3728 (6)	2.2 (2)
C26	0.7258 (5)	0.2625 (3)	0.4675 (6)	1.9 (2)
C31	−0.1161 (5)	0.2303 (4)	0.1641 (6)	2.5 (2)
C32	0.0588 (5)	0.3315 (3)	0.4257 (6)	1.9 (2)
C33	−0.0713 (5)	0.1790 (4)	0.2512 (6)	2.7 (2)
C34	0.0562 (6)	0.2525 (3)	0.4409 (6)	2.3 (2)
C35	0.1139 (5)	0.1248 (3)	0.3565 (6)	2.2 (2)
C36	0.0649 (5)	0.0859 (3)	0.4340 (6)	2.0 (2)
Ca1	−0.1850 (1)	0.0865 (1)	−0.4761 (1)	1.56 (3)
Ca2	−0.0832 (1)	0.4066 (1)	0.6411 (1)	2.25 (4)
Ca3	0.4952 (4)	0.4544 (2)	−0.0663 (4)	5.7 (1)^b
OW1	0.8282 (4)	0.4860 (3)	0.4977 (5)	3.3 (2)
OW2	0.7696 (6)	0.4683 (3)	−0.2673 (6)	5.3 (2)
OW3	0.9886 (7)	0.4752 (3)	0.2672 (8)	8.1 (3)
OW4	0.6115 (8)	0.0814 (4)	−0.0637 (7)	7.6 (3)
OW5	0.1049 (6)	0.3819 (5)	0.7807 (8)	7.7 (3)
OW6	−0.1091 (8)	0.3084 (4)	0.7386 (7)	8.0 (3)
OW7	−0.3433 (7)	0.0664 (4)	−0.407 (1)	8.5 (4)
OW8	0.350 (1)	0.3893 (5)	−0.278 (1)	12.4 (6)
OW9	0.460 (1)	0.1449 (9)	−0.427 (1)	17.3 (8)
OW10A	0.648 (1)	0.5482 (8)	0.042 (1)	7.4 (3)^b
OW10B	0.687 (2)	0.517 (1)	0.004 (2)	7.2 (5)^b
OW11A	0.730 (1)	0.1938 (9)	−0.131 (2)	9.6 (4)^b
OW11B	0.587 (3)	0.255 (2)	−0.308 (3)	12.3 (9)^b
OW12A	0.523 (2)	0.313 (2)	−0.088 (3)	17.9 (9)^b
OW12B	0.0	0.5	0.0	18 (1)^b
OW13A	0.641 (2)	0.397 (1)	−0.162 (2)	14.3 (7)^b
OW13B	0.573 (3)	0.427 (2)	−0.230 (3)	11.8 (8)^b
OW14A	0.803 (2)	0.400 (1)	0.096 (2)	9.9 (5)^b
OW14B	0.869 (2)	0.372 (1)	0.001 (2)	11.5 (6)^b

[a] Equivalent isotropic temperature factors ($B_{eq} = 4/3\{\sum\sum B_{ij}a_ia_j\}$).
[b] Isotropic temperature factors were used. The following occupancy factors were used for the disordered atoms: Ca3, 0.5; OW10A, 0.6; OW10B, 0.4; OW11A, 0.6; OW11B, 0.4; OW12A, 0.6; OW12B, 0.4; OW13A, 0.6; OW13B, 0.4; OW14A, 0.5; OW14B, 0.5.

solution was added little by little to B′ in 2 M HCl. The absorption changes with retention of isosbestic points, and the final spectrum corresponds to that of A in 2 M HCl. Absorption at 700 nm was plotted against the value $Fe(aq)^{3+}/B'$, and a break was observed

Table IV. Selected Interatomic Distances (Å) and Angles (deg) in $[Mo_3NiS_4(H_2O)_{10}]^{4+}$

Mo1–Mo2	2.743 (1)	Mo3–S4	2.320 (3)
Mo1–Mo3	2.760 (2)	mean	2.333 [8]
Mo2–Mo3	2.762 (2)	Ni–S2	2.204 (3)
mean	2.755 [10]	Ni–S3	2.202 (3)
Mo1–Ni	2.644 (2)	Ni–S4	2.210 (3)
Mo2–Ni	2.647 (2)	mean	2.205 [4]
Mo3–Ni	2.630 (2)	Mo1–O11	2.201 (9)
mean	2.640 [9]	Mo1–O12	2.186 (9)
Mo1–S1	2.349 (3)	Mo1–O13	2.216 (9)
Mo2–S1	2.351 (4)	Mo2–O21	2.213 (9)
Mo3–S1	2.346 (3)	Mo2–O22	2.203 (8)
mean	2.349 [3]	Mo2–O23	2.202 (8)
Mo1–S2	2.336 (4)	Mo3–O31	2.209 (8)
Mo1–S4	2.329 (3)	Mo3–O32	2.196 (10)
Mo2–S2	2.345 (3)	Mo3–O33	2.192 (9)
Mo2–S3	2.331 (3)	mean	2.202 [10]
Mo3–S3	2.334 (4)	Ni–O	1.964 (11)
Mo2–Mo1–Mo3	60.24 (3)	S2–Ni–O	113.8 (3)
Mo1–Mo2–Mo3	60.18 (4)	S3–Ni–O	105.2 (2)
Mo1–Mo3–Mo2	59.58 (4)	S4–Ni–O	109.1 (2)
mean	60.00 [36]	mean	109.4 [43]
Mo2–Mo1–Ni	58.8 (1)	O11–Mo1–O12	79.8 (3)
Mo3–Mo1–Ni	58.2 (1)	O11–Mo1–O13	79.9 (4)
Mo1–Mo2–Ni	58.7 (1)	O21–Mo2–O22	80.4 (3)
Mo3–Mo2–Ni	58.2 (1)	O21–Mo2–O23	79.6 (3)
Mo1–Mo3–Ni	58.7 (1)	O31–Mo3–O32	77.7 (3)
Mo2–Mo3–Ni	58.7 (1)	O31–Mo3–O33	80.1 (3)
mean	58.6 [3]	mean	79.6 [10]
Mo1–Ni–Mo2	62.5 (1)	O12–Mo1–O13	75.7 (3)
Mo1–Ni–Mo3	63.1 (1)	O22–Mo2–O23	79.1 (3)
Mo2–Ni–Mo3	63.1 (1)	O32–Mo3–O33	76.0 (3)
mean	62.9 [3]	mean	76.9 [19]
S1–Mo1–S2	106.9 (1)	Mo1–S1–Mo2	71.4 (1)
S1–Mo1–S4	105.2 (1)	Mo1–S1–Mo3	72.0 (1)
S1–Mo2–S2	106.5 (1)	Mo2–S1–Mo3	72.0 (1)
S1–Mo2–S3	105.6 (1)	mean	71.8 [3]
S1–Mo3–S3	105.6 (1)	Mo1–S2–Mo2	71.7 (1)
S1–Mo3–S4	105.6 (1)	Mo2–S3–Mo3	72.6 (1)
mean	105.9 [7]	Mo1–S4–Mo3	72.8 (1)
S2–Mo1–S4	101.0 (1)	mean	72.4 [6]
S2–Mo2–S3	100.6 (1)	Mo1–S2–Ni	71.2 (1)
S3–Mo3–S4	101.9 (1)	Mo2–S2–Ni	71.1 (1)
mean	101.2 [7]	Mo2–S3–Ni	71.4 (1)
S2–Ni–S3	109.5 (1)	Mo3–S3–Ni	70.8 (1)
S2–Ni–S4	109.3 (1)	Mo1–S4–Ni	71.2 (1)
S3–Ni–S4	109.9 (1)	Mo3–S4–Ni	70.9 (1)
mean	109.6 [3]	mean	71.1 [2]

at $Fe(aq)^{3+}/B' = 2$. From this, no intermediate could be observed for

$$Mo_3NiS_4^{4+}(aq) + 2Fe^{3+}(aq) \rightarrow Mo_3S_4^{4+}(aq) + Ni^{2+}(aq) + 2Fe^{2+}(aq)$$

The cluster B′ in diluted HCl or HPTS is fairly stable toward air oxidation and can be handled in the air; however, if the solution is stored for a long time, it is recommended that it be stored under a dinitrogen atmosphere: the solution in 2 M HPTS is air-oxidized by only ca. 15% in a month.

By a replacement reaction of the aqua ion B′, the nitrilotriacetato cluster C was obtained in a rather good yield (50%). Cluster C can also be handled in the air.

Structures of $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4{\cdot}7H_2O$ (B) and $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl]{\cdot}14H_2O$ (C). The structure of the cation $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ is shown in Figure 1, and the selected interatomic distances and angles are collected in Table IV. An additional water of crystallization was discovered compared with the preliminary result,[7] giving in total seven waters of crystallization. The structure is isomorphous with the Mo–Fe–S cluster $[Mo_3FeS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4{\cdot}7H_2O$.[20] The structure of the anion $[Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-}$ is shown in Figure 2, and selected interatomic distances and angles are collected in Table V. Both the cluster cation and anion have an approximate symmetry of C_{3v} and contain the same type of a cubane-type core as Mo_3NiS_4. In both ORTEP figures, metal–metal bond are not drawn for clarity. If the Mo–Mo and Mo–Ni bonds are not counted, each molybdenum atom is octahedrally coordinated by three sulfur and three oxygen atoms in B, and by three sulfur atoms, two oxygen atoms, and one nitrogen atom in C, respectively. The nickel atom has a fairly regular tetrahedral geometry in B and C, where the nickel atom is surrounded by three sulfur and one oxygen atoms in B and by three sulfur and one chlorine atoms in C, respectively: the S–Ni–S, S–Ni–O, and S–Ni–Cl angles are close to 109° (see Tables IV and V). Although the nickel atom is tetrahedrally coordinated,[21] the magnetic moment of B is very low (e.g., 0.11 μ_B BM at 2.0 K and 1.26 μ_B at 260.7 K),[22] which can be explained by a strong interaction between three molybdenum atoms and one nickel atom.

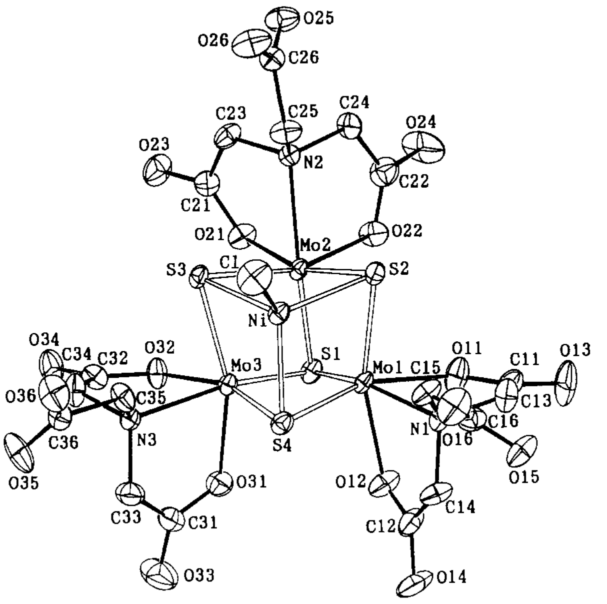

Figure 2. Perspective view of $[Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-}$.

Mean values of bond distances and angles in the pts^- anion are collected in Table VI.

The presence of one $Hnta^{2-}$ and two nta^{3-} ligands in C is deduced by comparison of C–O distances in the CO_2 groups. Among the three uncoordinated CO_2 groups, the C16–O16 distance (1.298 (8) Å) is far longer than C16–O15 (1.216 (8) Å), while C26–O25, C26–O26, C36–O35, and C36–O36 are not very different from each other, and coordination of a hydrogen ion to O16 is most probable.

The Mo–Mo and Mo–metal distances of compounds with Mo_3MS_4, $Mo_3S_4MMS_4Mo_3$, or $Mo_3S_4MS_4Mo_3$ cores are described in Table VII together with the Mo–Mo distance in $[Mo_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4{\cdot}9H_2O$ (**16**)[23] for comparison. Some clusters have slightly longer and others have a slightly shorter Mo–Mo distances than that of **16**, and no definite tendency of elongation or contraction of the Mo–Mo distance could be observed on the formation of the mixed-metal clusters. On the other hand, the Mo–M distances show some tendencies. In single cubane-type clusters (**1**–**9**), the higher the charge of the core is, the longer the Mo–M distance. Compounds **8** and **9** have very long Mo–M distances. As for the double cubane-type clusters, the Mo–Co distance in compound **10** is similar to those of Mo–M (M = Fe,

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(20) $[Mo_3FeS_4(H_2O)_{10}](CH_3{\cdot}C_6H_4{\cdot}SO_3)_4{\cdot}7H_2O$: Akashi, H.; Shibahara, T. *Abstracts of Papers*; The 39th Symposium on Coordination Chemistry of Japan, Mito, Japan; Japan Society of Coordination Chemistry: Okazaki, Japan, 1989; Abstract 1BP06.

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(23) Akashi, H.; Shibahara, T.; Kuroya, H. *Polyhedron* **1990**, *9*, 1671–1676.

Table V. Selected Interatomic Distances (Å) and Angles (deg) in $[Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-}$

Mo1–Mo2	2.778 (1)	O31–C31	1.282 (9)
Mo1–Mo3	2.775 (1)	O32–C32	1.286 (9)
Mo2–Mo3	2.773 (1)	mean	1.278 [8]
mean	2.775 [3]	O13–C11	1.221 (10)
Mo1–Ni	2.668 (1)	O14–C12	1.251 (8)
Mo2–Ni	2.662 (1)	O23–C21	1.236 (8)
Mo3–Ni	2.674 (1)	O24–C22	1.230 (11)
mean	2.668 [6]	O33–C31	1.224 (8)
Mo1–S1	2.345 (2)	O34–C32	1.239 (7)
Mo2–S1	2.352 (2)	mean	1.234 [11]
Mo3–S1	2.348 (2)	O15–C16	1.216 (8)
mean	2.348 [4]	O16–C16	1.298 (8)
Mo1–S2	2.349 (2)	O25–C26	1.244 (7)
Mo1–S4	2.338 (2)	O26–C26	1.259 (8)
Mo2–S2	2.343 (2)	O35–C36	1.245 (9)
Mo2–S3	2.337 (2)	O36–C36	1.239 (8)
Mo3–S3	2.344 (2)	mean	1.247 [9]
Mo3–S4	2.338 (2)	N1–C13	1.491 (11)
mean	2.342 [5]	N1–C14	1.520 (7)
Ni–S2	2.219 (2)	N1–C15	1.503 (8)
Ni–S3	2.208 (2)	N2–C23	1.489 (8)
Ni–S4	2.217 (2)	N2–C24	1.508 (10)
mean	2.215 [6]	N2–C25	1.504 (8)
Ni–Cl	2.240 (2)	N3–C33	1.505 (7)
Mo1–O11	2.154 (6)	N3–C34	1.493 (7)
Mo1–O12	2.156 (4)	N3–C35	1.498 (8)
Mo2–O21	2.145 (4)	mean	1.501 [10]
Mo2–O22	2.120 (5)	C11–C13	1.536 (10)
Mo3–O31	2.131 (4)	C12–C14	1.509 (9)
Mo3–O32	2.148 (4)	C15–C16	1.513 (8)
mean	2.142 [14]	C21–C23	1.504 (8)
Mo1–N1	2.320 (5)	C22–C24	1.511 (10)
Mo2–N2	2.321 (4)	C25–C26	1.526 (8)
Mo3–N3	2.309 (6)	C31–C33	1.513 (11)
mean	2.317 [7]	C32–C34	1.508 (9)
O11–C11	1.267 (8)	C35–C36	1.525 (11)
O12–C12	1.273 (7)	mean	1.516 [10]
O21–C21	1.287 (7)		
O22–C22	1.275 (8)		
Mo2–Mo1–Mo3	59.92 (3)	S2–Ni–Cl	111.8 (1)
Mo1–Mo2–Mo3	59.98 (3)	S3–Ni–Cl	106.6 (1)
Mo1–Mo3–Mo2	60.10 (3)	S4–Ni–Cl	111.0 (1)
mean	60.00 [9]	mean	109.8 [28]
Mo2–Mo1–Ni	58.48 (3)	O11–Mo1–O12	76.8 (2)
Mo3–Mo1–Ni	58.81 (3)	O21–Mo2–O22	77.9 (2)
Mo1–Mo2–Ni	58.69 (3)	O31–Mo3–O32	77.6 (2)
Mo3–Mo2–Ni	58.90 (3)	mean	77.4 [6]
Mo1–Mo3–Ni	58.60 (3)	O11–Mo1–N1	76.2 (2)
Mo2–Mo3–Ni	58.48 (3)	O12–Mo1–N1	76.3 (2)
mean	58.66 [17]	O21–Mo2–N2	75.2 (2)
Mo1–Ni–Mo2	62.83 (4)	O22–Mo2–N2	77.7 (2)
Mo1–Ni–Mo3	62.59 (3)	O31–Mo3–N3	77.1 (2)
Mo2–Ni–Mo3	62.62 (4)	O32–Mo3–N3	76.0 (2)
mean	62.68 [13]	mean	76.4 [9]
S1–Mo1–S2	105.5 (1)	Mo1–S1–Mo2	72.5 (1)
S1–Mo1–S4	105.5 (1)	Mo1–S1–Mo3	72.5 (1)
S1–Mo2–S2	105.4 (1)	Mo2–S1–Mo3	72.3 (1)
S1–Mo2–S3	105.8 (1)	mean	72.4 [1]
S1–Mo3–S3	105.7 (1)	Mo1–S2–Mo2	72.6 (1)
S1–Mo3–S4	105.4 (1)	Mo2–S3–Mo3	72.7 (1)
mean	105.6 [2]	Mo1–S4–Mo3	72.8 (1)
S2–Mo1–S4	101.0 (1)	mean	72.7 [1]
S2–Mo2–S3	100.9 (1)	Mo1–S2–Ni	71.4 (1)
S3–Mo3–S4	100.5 (1)	Mo2–S2–Ni	71.3 (1)
mean	100.8 [3]	Mo2–S3–Ni	71.6 (1)
S2–Ni–S3	109.3 (1)	Mo3–S3–Ni	71.9 (1)
S2–Ni–S4	109.3 (1)	Mo1–S4–Ni	71.7 (1)
S3–Ni–S4	108.9 (1)	Mo3–S4–Ni	71.8 (1)
mean	109.2 [2]	mean	71.6 [2]

Table VI. Mean Values of Bond Distances (Å) and Angles (deg) in $CH_3C_6H_4SO_3^-$

S–O	1.444 [35]	C–C[a]	1.392 [28]
S–C	1.764 [16]	C–C[b]	1.561 [21]
O–S–C	107.2 [9]	C–C–C[a]	120.0 [21]
O–S–O	111.6 [25]	C–C–C[b]	119.8 [19]
S–C–C	119.3 [7]		

[a] Carbon atoms in a phenylene group. [b] Carbon atoms in methyl and phenylene groups.

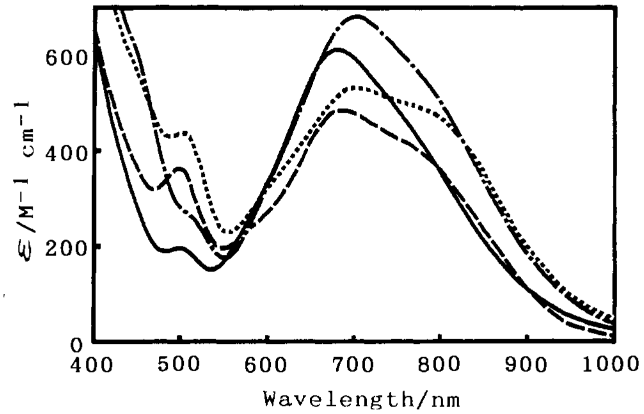


Figure 3. Electronic spectra: (a, —) $[Mo_3NiS_4(H_2O)_{10}](CH_3C_6H_4SO_3)_4 \cdot 7H_2O$ dissolved in 2 M HPTS; (b, – –) $[Mo_3NiS_4(H_2O)_{10}](CH_3 \cdot C_6H_4 \cdot SO_3)_4 \cdot 7H_2O$ dissolved in 2 M HCl ($[Mo_3NiS_4(H_2O)_9Cl]^{3+}$ exists predominantly); (c, – · –) $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl] \cdot 14H_2O$ dissolved in water ($[Mo_3NiS_4(Hnta)(nta)_2(H_2O)]^{4-}$ exists predominantly); (d, ‐‐) $Ca_{2.5}[Mo_3NiS_4(Hnta)(nta)_2Cl] \cdot 14H_2O$ dissolved in 2 M $CaCl_2$.

Ni) in **1–4**. The Mo–Cu distance in **11** is a little longer than those of Mo–M (M = Fe, Ni) in **1–4** and similar to that of **5**, which contains a Cu atom. The Mo–M distances of the sandwich cubane-type clusters **12**, **13**, and **15** are longer than those of single cubane-type clusters with core charge of 4+, though the values have a wide range.

The Mo–Ni distances in **3** and **4** are shorter than those found in a cubane-type cluster, $[Mo_2Ni_2S_4Cp_2(CO)_2]$ (Mo–Ni = 2.720–2.724 Å)[3c] and similar to that in a bicapped-trigonal-bipyramid cluster, $[Mo_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}CO)Cp_4]$ (Mo–Ni = 2.680 Å).[1g]

Electronic Spectra. Electronic spectra of B and C in different media are shown in Figure 3. No peaks were observed in the near-infrared region for all four spectra in contrast to the case of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$.[5] The electronic spectrum of the aqua ion B in 2 M HPTS has peaks at 680 nm (ϵ = 610 M^{-1} cm^{-1}) and 500 nm (ϵ = 200). The peaks of B in 2 M HCl are at 800_{sh} nm (ϵ = 360), 686 nm (ϵ = 488), and 498 nm (ϵ = 366). The peaks of C in water are at 703 nm (ϵ = 683) and 500_{sh} nm (ϵ = 280), while those of C in 2 M $CaCl_2$ are at 810_{sh} nm (ϵ = 455), 700 nm (ϵ = 535), and 502 nm (ϵ = 439).

Spectra for both complexes in media containing chloride ion show a distinct shoulder at around 800 nm (Figure 3b,d) contrary to the those for the complexes in media without chloride ion (Figure 3a,c). This means that coordination of chloride ion to nickel atom causes the appearance of the shoulders. In compound C, $Hnta^{2-}$ and nta^{3-} ligands cover molybdenum atoms, and coordination of chloride ion is probable only to the nickel atom. Although, in the case of B, the coordination of chloride ion is also possible to molybdenum atoms as well as to the nickel atom, the degree of coordination of chloride ion to molybdenum atom(s) seems to be less than that to the nickel atom: the change of the spectrum of B through the change of the medium from HPTS to HCl is similar to the case of C, where the medium is changed from water to 2 M $CaCl_2$.

Dissociation of Cl^- from $[Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-}$. From the spectral change of C through the change of concentration of

Table VII. Cubane-Type Mixed-Metal Clusters with Mo_3MS_4, $Mo_3S_4MMS_4Mo_3$, and $Mo_3S_4MS_4Mo_3$ Cores

compound					
no.	formula	Mo–Mo, Å	Mo–M, Å	charge[a]	ref
1	$[Mo_3FeS_4(H_2O)_{10}]^{4+}$	2.767 [5]	2.673 [12]	4+	5, 20
2	$[Mo_3FeS_4(NH_3)_9(H_2O)]^{4+}$	2.794 [18]	2.683 [10]	4+	5
3	$[Mo_3NiS_4(H_2O)_{10}]^{4+}$	2.755 [10]	2.640 [9]	4+	*h*
4	$[Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-}$	2.775 [3]	2.668 [6]	4+	*h*
5	$[Mo_3CuS_4(dtp)_3(CH_3COO)(I)(dmf)]$[b]	2.733 [48]	2.849 [39]	5+	14
6	$[Mo_3CuS_4(dtp)_3(CH_3COO)(I)(H_2O)]$[b]	2.741 [43]		5+	13
7	$[Mo_3WS_4(Et_2PS_2)_6]$[c]	2.857 [148]		6+	15
8	$[Mo_3SbS_4(dtp)_4(Cl_3)(EtOH)]$[d]	2.735 [12]	3.822 [9]	7+	12, 13
9	$[Mo_3SbS_4(dtp)_4(Cl_3)(oxazole)]$[d]	2.741 [12]	3.825 [19]	7+	12, 13
10	$[(H_2O)_9Mo_3S_4CoCoS_4Mo_3(H_2O)_9]^{8+}$[e]	2.744 [10]	2.643 [24]	8+	6
11	$[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$[f]	2.730 [8]	2.886 [93]	8+	8
12	$[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9]^{8+}$	2.689 [7]	3.712 [37]	8+	9
13	$[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9]^{8+}$	2.713 [9]	3.833 [93]	8+	10
14	$Mo_3SnS_4{}^{6+}(aq)$			6+	9
15	$[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$	2.770 [4]	3.046 [18][g]	8+	24
16	$[Mo_3S_4(H_2O)_9]^{4+}$	2.735 [8]		4+	23

[a] Formal charge of Mo_3MS_4, $Mo_3S_4MMS_4Mo_3$, $Mo_3S_4MS_4Mo_3$, and Mo_3S_4 cores, respectively. [b] An acetate ligand bridges the two Mo's in the compounds **5** and **6**. [c] Three Mo and one W atoms are statistically disordered, and a bridging $Et_2PS_2^-$ exists between two metals in **7**. [d] Three terminal and one bridging dtp ligands exist in compounds **8** and **9**. [e] Co–Co′ = 2.498 (10) Å. [f] Cu–Cu′ = 2.424 (3) Å. [g] One of the Mo's resides at the center of the cluster. [h] This work.

chloride ion, the formation constant *K* for the following equilibrium can be determined:

$$[Mo_3NiS_4(Hnta)(nta)_2(H_2O)]^{4-} + Cl^- \rightleftharpoons [Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-} + H_2O \quad (1)$$

$$K = [C']/([D'][Cl^-]) \quad (2)$$

where C′ and D′ denote $[Mo_3NiS_4(Hnta)(nta)_2Cl]^{5-}$ (C′) and $[Mo_3NiS_4(Hnta)(nta)_2(H_2O)]^{4-}$ (D′), respectively. Absorption of the solution can be expressed by

$$Abs = \epsilon_{C'}[C'_0](1 - \alpha)L + \epsilon_{D'}[C'_0]\alpha L \quad (3)$$

where $[C'_0]$ is the total concentration of C′ and D′ and α is the degree of dissociation of chloride ion from C′. Dependency of absorption on $[Cl^-]$ was measured at 700 nm at constant ionic strength (1.0 M, $NaClO_4$). From the eqs 1–3, eq 4 is deduced.

$$K = \{\epsilon_{D'} - Abs/([C'_0]L)\}/\{Abs/([Cl'_0]L) - \epsilon_{C'}\}\{1/[Cl^-]\} \quad (4)$$

The value *K* becomes fairly constant against the change of $[Cl^-]$, when $\epsilon_{C'} = 565\ M^{-1}\ cm^{-1}$ is employed, where $\epsilon_{D'} = 698\ M^{-1}\ cm^{-1}$ at 700 nm is used. The *K* value thus obtained is 15 M^{-1}.

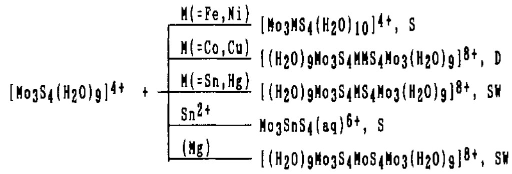
Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ (A) with Metals and Metal Ion. Reaction of A with metals (Fe,[5,20] Co,[6] Ni,[7] Cu,[8] Sn,[9] Hg[10]) and metal ion (Sn^{2+})[9] to give mixed-metal aqua ions is summarized in Scheme II. The reaction product of A with magnesium[24] is also included. All the structures but that of $Mo_3SnS_4{}^{6+}(aq)$ have been determined as *p*-toluenesulfonates by single-crystal X-ray crystallography. There exist three kinds of cubane-type cores as shown in Chart I: single cubane type (Mo_3MS_4, S), double cubane type ($Mo_3S_4MMS_4Mo_3$, D), and sandwich cubane type ($Mo_3S_4MS_4Mo_3$, SW). We note that in HPTS solution the single cubane-type and double cubane-type clusters come up alternatively in the order of the atomic number of the incorporated metals (Mo_3FeS_4, $Mo_3S_4CoCoS_4Mo_3$, Mo_3NiS_4, and $Mo_3S_4CuCuS_4Mo_3$).

We can think of two kinds of driving forces for the formation of the cubane-type mixed-metal clusters from the incomplete cubane-type aqua ion A and metals. One factor is the reducing ability of the metal, and another is the affinity of the metal for the bridging sulfur atoms. Both factors seem responsible for the formation of the clusters containing the following atoms: Fe, Co, Ni, Sn. In these cases, the reactions can be regarded as *reductive addition* of metals or metal ion to the $Mo_3{}^{IV}S_4$ core:

$$Mo_3{}^{IV} + M \rightarrow Mo^{IV}Mo_2{}^{III}M^{II}$$

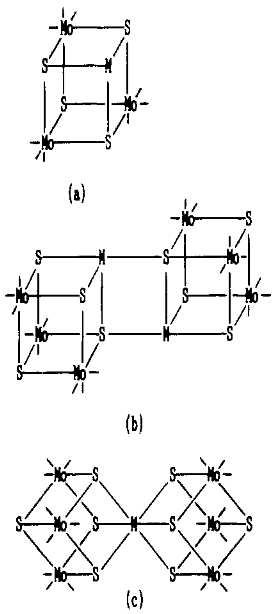
$$Mo_3{}^{IV} + Sn^{2+} \rightarrow Mo^{IV}Mo_2{}^{III}Sn^{IV}$$

Scheme II. Formation of Three Kinds of Cubane-Type Mixed-Metal Clusters by the Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Metals and a Metal Ion[a]



[a] Key: S, single cubane-type; D, double cubane-type; SW, sandwich cubane-type.

Chart I. Three Kinds of Cubane-Type Mixed-Metal Cores: (a) Single Cubane Type; (b) Double Cubane Type; (c) Sandwich Cubane Type



The factor of affinity will play a major role in the formation of the clusters with the Cu or the Hg atom, though the role of the reducing factor could not be negligible in the case of the Cu cluster. If a metal having strong reducing power and little affinity to sulfur is mixed with the aqua ion A, the Mo_3S_4 core in A is broken and a novel sandwich cubane-type cluster without the metal is constructed (Chart I): magnesium metal has little tendency to make a chemical bond to sulfur, and aluminum metal reacts similarly

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(24) Shibahara, T.; Yamamoto, T.; Kanadani, H.; Kuroya, H. *J. Am. Chem. Soc.* **1987**, *109*, 3495–3496.

with A to give the same sandwich cluster as the reaction of A with magnesium does.

Recently Sykes and colleagues reported the following reaction to give mixed-metal aqua complexes with Mo_3MS_4 cores:[11]

$$Mo_3S_4(aq)^{4+} + M^{2+} + 2e \rightarrow Mo_3MS_4^{4+}$$

Generation of $[Mo_4S_4(H_2O)_{12}]^{5+}$ from A and $[Mo(H_2O)_6]^{3+}$ in the presence of $NaBH_4$ is also described.

By the addition of $SbCl_3$ or CuI to incomplete cubane-type clusters $[Mo_3S_4(dtp)_4(L)]$ ($L = H_2O, C_3H_3ON$), new mixed-metal clusters with Mo_3MS_4 cores (M = Sb, Cu) have been synthesized: Lu et al.[12] and Huang et al.[13] reported the syntheses, characterization and structures of $[Mo_3SbS_4(dtp)_4(Cl_3)(L)]$ (L = EtOH, oxazole); Wu et al.[14] described the synthesis and structure of $[Mo_3CuS_4(dtp)_3(CH_3COO)(I)(dmf)]$; the structure of $[Mo_3CuS_4(dtp)_3(CH_3COO)(I)(H_2O)]$ has also been determined.[13]

Kuchen and co-workers synthesized $[Mo_3WS_4(Et_2PS_2)_6]$ by the reaction of equimolar quantities of $[Mo_3S_4(Et_2PS_2)_4]$, $[W(CO)_3(CH_3CN)_3]$, and $(Et_2P(S))_2S_2$.[15]

Except for compound **7** (Table VII), the formal charges of the cores of the mixed-metal compounds are addition of the formal charges of the Mo_3S_4 core (=+4) and the metals or metal ions: 4 + 0 for **1**–**4**; 4 + 1 for **5** and **6**; 4 + 3 for **8** and **9**; 2 × 4 + 2 × 0 for **10** and **11**; 2 × 4 + 0 for **12** and **13**; 4 + 2 for **14**. In compound **7**, oxidative addition of the ligand $(Et_2P(S))_2S_2$ occurs: 4 + 0 (from $[W(CO)_3(CH_3CN)_3]$) + 2 (from the ligand).

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Supplementary Material Available: Listings of crystallographic and machine parameters, thermal parameters, bond distances and angles, and short contacts (Tables SI–SVIII) and plots of absorption changes by the addition of Fe^{3+} to B′ (Figure S1), absorption at 700 nm vs Fe^{3+}/B' (Figure S2), and determination of the formation constant (Figure S3) (25 pages); tables of F_o and F_c values for compounds B and C (27 pages). Ordering information is given on any current masthead page.

Notes

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Reactions of Polycyano Compounds with Chlorine Fluoride

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Introduction

N,N-Dihaloperfluoroalkylamines continue to be of interest as isolable intermediates. Straightforward, high-yield syntheses of chlorofluoroamines have made these compounds readily available in useful quantities. *N,N*-Dichloroperfluoroalkylamines are commonly used for generation of perfluoroalkyldiazenes via photolytic or thermal processes.[3,4]

We have sought to produce new *N,N*-dichloroperfluoro(polyfluoro)alkylamines by the reaction of ClF with compounds possessing two or more cyano groups. In this way, new compounds with multiple $-NCl_2$ functionalities should result that could lead to new heterocycles or possibly azo polymers. Compounds that contain two $-NCl_2$ groups are known; e.g., with ClF, cyanogen gives $Cl_2NCF_2CF_2NCl_2$. However, H_2NCN was observed to lose NCl_3 upon reaction with an excess of ClF, which suggests that $Cl_2NCF_2NCl_2$ was an intermediate.[5] Perfluoromalononitrile, also gives a bis-NCl_2 derivative.[6]

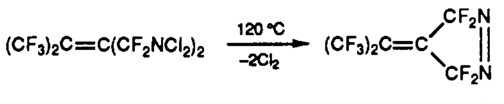
Compounds with two or more cyano groups undergo rapid reaction to produce the respective derivatives in nearly quantitative yields. Reactants that contain carbon–carbon double bonds give products that are also unsaturated. In this paper, we report the reactions of $(NC)_2C{=}C(CN)_2$ (TCNE), $H_2C(CN)_2$, $KC(CN)_3$, and $(CF_3)_2C{=}C(CN)_2$ with ClF and the subsequent attempts to prepare diazenes. In addition, an improved, one-step synthesis of CF_3NCl_2, a precursor of hexafluoroazomethane, from ClCN and ClF over CsF is given.

Results and Discussion

In general, the controlled addition of ClF to polycyano compounds leads to interesting new products. The product obtained from the reaction of $(CF_3)_2C{=}C(CN)_2$ with ClF (1:5) exhibits a weak carbon–carbon double bond at 1635 cm^{-1} in the infrared spectrum. Only 80% of the chlorine fluoride is consumed, which also indicates that the reaction is one of saturation of the cyano groups only

$$(CF_3)_2C{=}C(CN)_2 + ClF(excess) \rightarrow \underset{95\%}{(CF_3)_2C{=}C(CF_2NCl_2)_2}$$

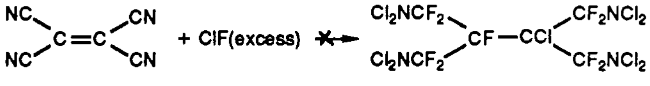
Although a molecule ion is not observed in the mass spectrum, with ($M^+ - Cl_2F$) being the highest *m/e* seen, when $(CF_3)_2C{=}C(CF_2NCl_2)_2$ is thermolyzed at 120 °C, loss of chlorine occurs to give the cyclic diazene



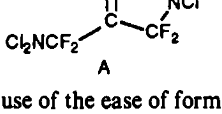
No molecule ion is observed in the mass spectrum, where the highest *m/e* seen is at *m/e* 262 ($M^+ - N_2$), but excellent elemental analyses support the proposed structure.

Because of the low thermal stability of $H_2C(CF_2NCl_2)_2$ [$H_2C(CN)_2$ + ClF], dimerization via thermolysis or photolysis was not attempted. However, since HF elimination was observed, several attempts were made in order to isolate a new olefin. With KF or CsF, there was a violent reaction but no new compounds were isolated.

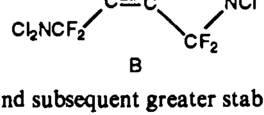
When study of these systems was initiated, it was supposed that an excess of ClF would saturate all of the multiple bonds in TCNE



Because stoichiometric elimination of N_2 and Cl_2 was observed and only two groups of structurally equivalent fluorine atoms were found in the ^{19}F NMR spectrum, two structures seem likely



A



B

Because of the ease of formation and subsequent greater stability of a five-membered ring, structure A is more likely. The intensity of the C=C bond stretching frequency at 1685 cm^{-1} in the infrared spectrum is very weak, but the band is definitely present. This suggests little polarization in the molecule. Structure B would be expected to have a much more intense C=C stretching band

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