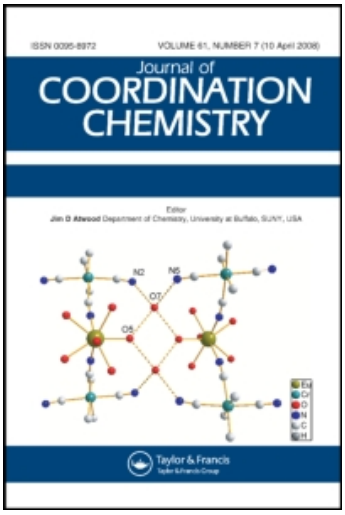

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Preparation and X-Ray Structure of Cubane-Type Mixed Metal Aqua Ion, $[Mo_3NiS_4(H_2O)_{10}]^{4}$

Takashi Shibahara[a]; Hisao Kuroya[a]
[a] Department of Chemistry, Okayama University of Science, Okayama, Japan

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PREPARATION AND X-RAY STRUCTURE OF CUBANE-TYPE MIXED METAL AQUA ION, $[Mo_3NiS_4(H_2O)_{10}]^{4+}$

TAKASHI SHIBAHARA* and HISAO KUROYA
Department of Chemistry, Okayama University of Science, Okayama 700, Japan

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We have recently reported that the incomplete cubane-type aqua ion, $[Mo_3S_4(H_2O)_9]^{4+}$ (**A**), reacts with metals (Fe,[1] Cu,[2], and Hg[3]) to give cubane-type mixed metal aqua ions, the core structures of which have been verified by the X-ray structure analyses of the complexes derived from the aqua ions. In addition, it was found that the reaction of **A** with metallic magnesium gave a double cubane-type aqua ion.[4] We now present the preparation, properties, and X-ray structure of a new cubane-type molybdenum-nickel-sulfur mixed metal cluster compound, $[Mo_3NiS_4(H_2O)_{10}](CH_3.C_6H_4.SO_3)_4.6H_2O$ (**B**), prepared from the aqua ion **A** and metallic nickel. $Mo_2Ni_2Cp_2(CO)_2$ is the only compound so far reported to have the cubane-type Mo-Ni-S core.[5]

A nickel plate (0.5 g) was introduced to a conical flask containing the aqua ion **A** (0.2 M in 20 mL of 6 M HCl), which was allowed to stand for two weeks under a dinitrogen atmosphere. A green solution, the spectrum of which has absorption peaks at 500 and 690 nm, was obtained by the successive application of Sephadex G-15 (1 M HCl) and Dowex 50W-X2 cation exchanger (0.5 M HCl) column chromatography. The solution was absorbed on the cation exchanger again and eluted with 4 M Hpts (p-toluenesulfonic acid). Green crystals of **B** were obtained from the eluate in a few days. Anal. Found

(calcd): C, 23.13 (23.22); H, 4.21 (4.17)%.

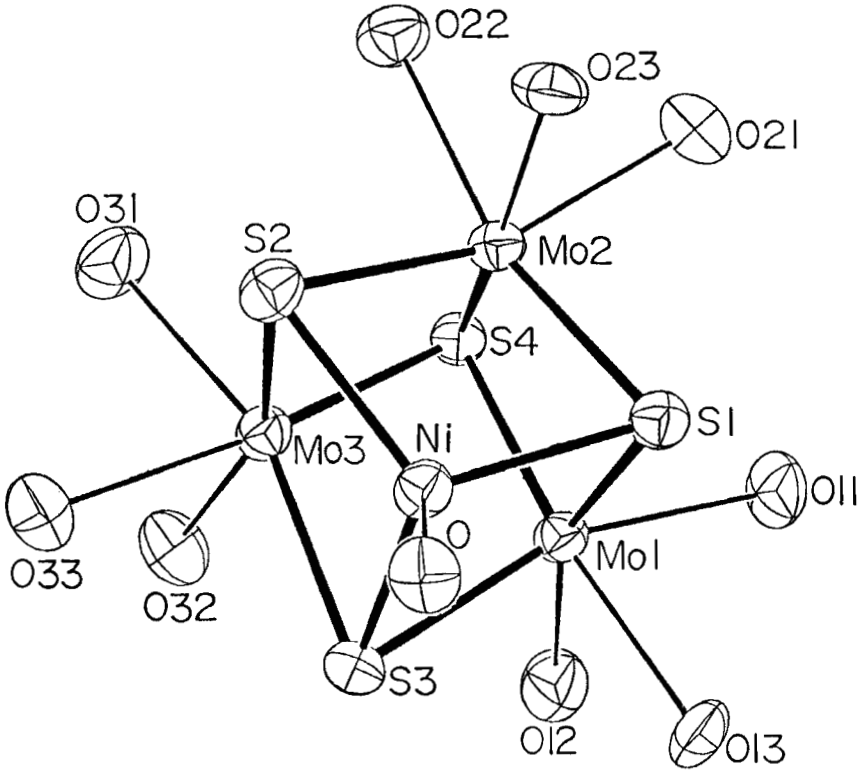

FIGURE 1. Perspective view of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$. Selected bond distances/Å: Mo1-Mo2, 2.761(2); Mo1-Mo3, 2.761(2); Mo2-Mo3, 2.744(2); Mo1-Ni, 2.630(2); Mo2-Ni, 2.646(2); Mo3-Ni, 2.646(2); Mo1-S1, 2.334(4); Mo1-S3, 2.323(4); Mo1-S4, 2.352(4); Mo2-S1, 2.331(4); Mo2-S2, 2.340(4); Mo2-S4, 2.353(4); Mo3-S2, 2.336(4); Mo3-S3, 2.329(4); Mo3-S4, 2.349(4); Ni-S1, 2.203(4); Ni-S2, 2.200(4); Ni-S3, 2.210(4); Mo-OH_2, 2.21[1]; Ni-OH_2, 1.97(1)

The compound **B** crystallizes in triclinic system, space group $P\bar{1}$ with cell dimensions a = 17.889(6) Å, b = 19.601(8) Å, c = 8.969(4) Å, α = 102.83(4)°, β = 103.78(3)°, γ = 63.45(3)°, V = 2707.9(19) Å^3, Z = 2, D_c = 1.775 g cm^{-3}. Intensity data ($2\theta \leq 50°$) were collected on a RIGAKU AFC-6A four-circle diffractometer by use of graphite-monochromated Mo Kα radiation. The structure was solved by the direct method (MULTAN) and refined by least squares to a current R value of 0.0556 for 5233 reflections ($F_o \geq 8\sigma(F_o)$). The presence of a cubane-type Mo_3NiS_4 core is verified (Figure 1). The bond distances are similar to the corresponding ones observed for the Mo_3FeS_4 core.[1]

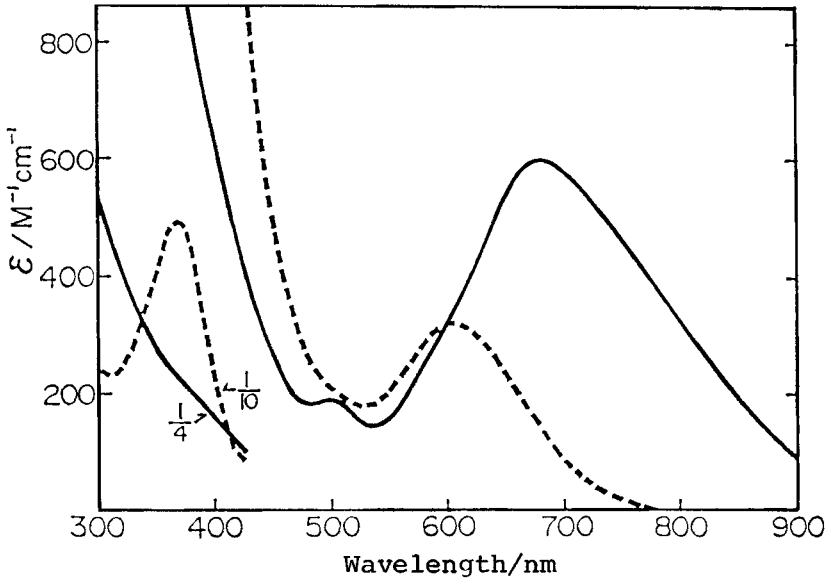

FIGURE 2. Electronic spectra in 1 M HPTS:
——— $[Mo_3NiS_4(H_2O)_{10}]^{4+}$
— — — — — $[Mo_3S_4(H_2O)_9]^{4+}$

The electronic spectrum of the aqua ion **B**, which is shown in Figure 2 together with that of **A**, has peaks at 678 (ε = 601 M^{-1} cm^{-1}) and 500 nm (ε 195), having no peaks in the near-infra-red region in contrast to the case of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$. Compound **B** is fairly resistant toward air oxidation. The absorbance of solution of **B** changes only a few percent in a day.

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Supplementary Material. A list of atomic coordinates, thermal parameters, bond distances, and bond angles can be obtained from the author (T. S.) on request.

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