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Sulfur-Bridged Double Cubane-Type Tungsten-Nickel Mixed-Metal Cluster. Synthesis and X-Ray Structure of $[\{W_3NiS_4(H_2O)_9\}_2](CH_3C_6H_4SO_3)_8 \cdot 20H_2O$

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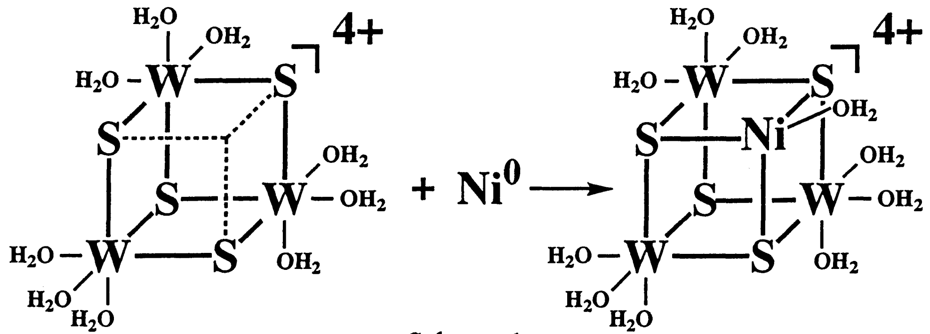
Reaction of a sulfur-bridged incomplete cubane-type tungsten cluster $[W_3S_4(H_2O)_9]^{4+}$ with nickel metal afforded a cubane-type mixed-metal cluster $[W_3NiS_4(H_2O)_{10}]^{4+}$, whose structure was determined by the X-ray structure analysis of $[\{W_3NiS_4(H_2O)_9\}_2](CH_3C_6H_4SO_3)_8 \cdot 20H_2O$. The reactivity difference between $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and $[W_3NiS_4(H_2O)_{10}]^{4+}$ with ethylene can be explained by the difference in the binding energies of nickel ($2p_{3/2}$) obtained from XPS spectra of the clusters.

Metal-incorporation reactions of the incomplete cubane-type sulfur-bridged molybdenum aqua cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (A) to give mixed-metal clusters with Mo_3MS_4 cores (M = metals: e.g. Fe, Ni, Cu, Sn, and In) have been reported by the authors1) and by other groups.2) Other routes to the Mo_3MS_4 core clusters have also been reported.3) However, very little is known about the reactivity of the corresponding tungsten aqua cluster $[W_3S_4(H_2O)_9]^{4+}$ (B).4) Only the reaction of the aqua ion B with Sn (or Sn^{2+}) has been reported so far.5) Other routes to the clusters with W_3MS_4 cores (M=metal) are also limited and clusters with W_3CuS_4 cores are only reported .6)

We report here the reaction of tungsten cluster B with nickel metal to afford a cubane-type mixed-metal cluster $[W_3NiS_4(H_2O)_{10}]^{4+}$ (C) as shown in Scheme 1. The structure was determined by the X-ray structural analysis of $[\{W_3NiS_4(H_2O)_9\}_2](pts)_8 \cdot 20H_2O$ (C'; Hpts = p-toluenesulfonic acid).7) No report on clusters with W_3NiS_4 cores has appeared so far.



Scheme 1.

The cluster C was synthesized under a dinitrogen atmosphere. Nickel plate (3.38 g) was added to the violet aqua ion B (0.038 M per trimer, 50 mL; Ni/B = ca.30) in 7 M HCl, which was stirred for 17 hours above 90 °C in a water bath. The color of the solution turned from violet to green. The solution was filtered and the remaining nickel plates were removed. After the filtrate was diluted to 35 times its original volume, Dowex 50W-X2 column chromatography was applied (2.1 cm x 10 cm). The first band containing the Ni^{2+} ion was eluted with 0.5 M HCl, and the second band (green) containing the mixed-metal aqua cluster C was collected using 1 M HCl: yield, ca. 86% based on B.$^{8)}$ Unreacted B was eluted after C using 1 M HCl. In order to obtain crystals of C', the solution of C in 1 M HCl from the second band was absorbed on a short cation exchanger, Dowex 50W-X2 (2.1 cm x 1.8 cm). The resin was washed with 0.1 M Hpts to remove chloride ion, and slow elution with 4 M Hpts gave a bluish green solution. Cooling of the solution in a freezer for several days gave green crystals: yield, ca. 64% based on the solution of C in 1 M HCl. Anal. Found: C, 19.18; H, 3.74%. Calcd for $W_6Ni_2S_{16}O_{62}C_{56}H_{132}$: C, 19.05; H, 3.77%. The cluster C in solution is more air-sensitive than the corresponding molybdenum-nickel cluster $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (D).$^{9)}$

The X-ray analysis$^{10)}$ of C' revealed the existence of a double cubane-type core of $(W_3NiS_4)_2$ as shown in Fig. 1.

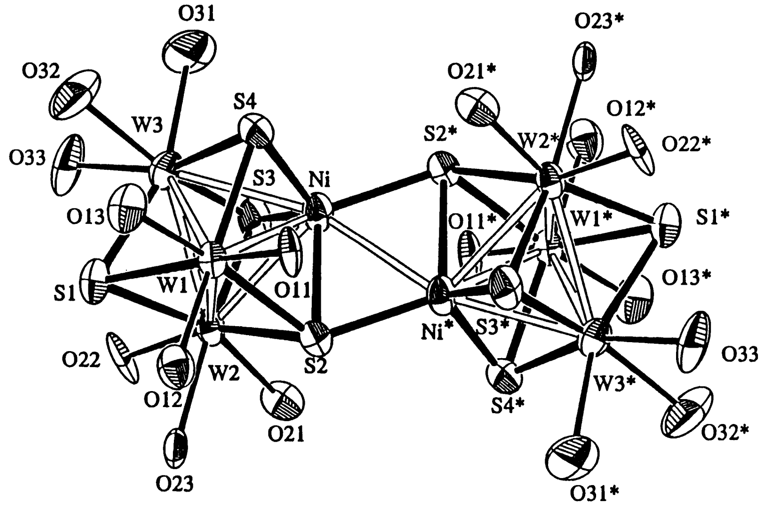


Fig. 1. Perspective view of $[\{W_3NiS_4(H_2O)_9\}_2]^{8+}$ cation with selected interatomic distances (Å) and angles (deg): W1-W2, 2.746(1); W1-W3, 2.737(1); W2-W3, 2.725(1); W1-Ni, 2.681(3); W2-Ni, 2.698(3); W3-Ni, 2.610(3); W1-S1, 2.348(6); W1-S2, 2.351(5); W1-S4, 2.318(6); W2-S1, 2.352(6); W2-S2, 2.353(5); W2-S3, 2.327(6); W3-S1, 2.360(6); W3-S3, 2.335(6); W3-S4, 2.331(6); Ni-S2, 2.296(6); Ni-S3, 2.195(6); Ni-S4, 2.181(7); Ni-Ni*, 2.561(5); Ni-S2*, 2.260(6); W-O(H_2O), 2.17[3]; W3-W1-W2, 59.59(4); W3-W2-W1, 60.03(4); W2-W3-W1, 60.38(4). (The asterisked atoms are related to the unasterisked ones by a center of symmetry.)

A center of symmetry resides on the midpoint of the two nickel atoms which are bridged by two sulfur atoms. The Ni-Ni distance (2.561(5) Å) is close to that in metallic nickel (2.55 Å). If possible W-Ni and Ni-Ni bonds are ignored, the nickel atom has a distorted tetrahedral geometry. The structure is close to that of the molybdenum-copper double cubane-type cluster $[\{Mo_3CuS_4(H_2O)_9\}_2]^{8+}$.$^{1\text{-}c)}$ It is interesting that while the tungsten-nickel cluster C' is the double cubane-type, the molybdenum-nickel cluster crystallizes out of solution as a single cubane-type cluster $[Mo_3NiS_4(H_2O)_{10}](pts)_4 \cdot 7H_2O$ ($\underline{D'}$). The introduction of a nickel atom to the W_3S_4 core changes slightly the dimensions of $\underline{B}$ in $[W_3S_4(H_2O)_9](pts)_4 \cdot 9H_2O$ ($\underline{B'}$): The W-W distance is elongated ($\underline{B'}$, 2.708[5] Å; $\underline{C'}$, 2.736[11] Å), as is the Mo-Mo distance ($[Mo_3S_4(H_2O)_9](pts)_4 \cdot 9H_2O$ ($\underline{A'}$), 2.735[8];[11] $\underline{D'}$, 2.755[10]). The W_3 triangle in $\underline{C'}$ remains equilateral approximately.

Although the X-ray analysis of $\underline{C'}$ revealed the existence of the double cubane-type core structure, *in solution* the double cubane-type cluster $[\{W_3NiS_4(H_2O)_9\}_2]^{8+}$ dissociates to give two $\underline{C}$ clusters of single cubane-type, which was evident from the behavior of $\underline{C}$ on the Dowex 50W-X2 column: Using 1 M HCl the cluster $\underline{C}$ was eluted earlier than the cluster $\underline{B}$ having the charge of 4+ as noted above, and the charge of $\underline{C}$ can not be 8+; furthermore, a mixture of $\underline{C}$ and $\underline{D}$ was inseparable from each other by elution with 2 M Hpts on Dowex 50W-X2 column chromatography, which indicates that the charge of $\underline{C}$ is 4+. Electronic spectra of $\underline{B}$ and $\underline{C}$ in 2 M Hpts are shown in Fig. 2. The spectra in 1 M HCl and in 2 M Hpts differ little from each other in the 300-1100 nm region.

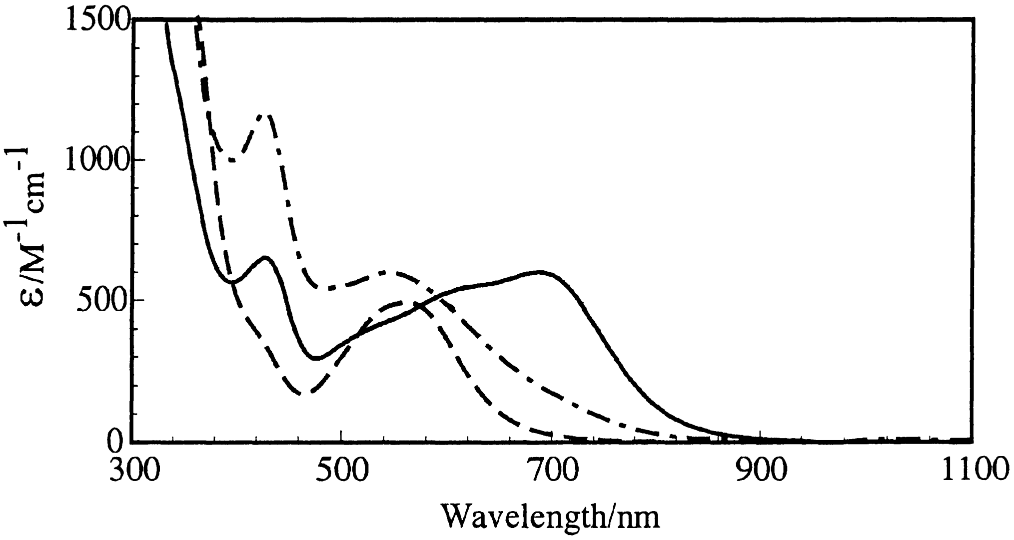


Fig. 2. Electronic Spectra: (———) $[W_3NiS_4(H_2O)_{10}]^{4+}$ ($\underline{C}$) in 2 M Hpts; (- - - - - -) $[W_3S_4(H_2O)_9]^{4+}$ ($\underline{B}$) in 2 M Hpts; (— - — - — -) $[W_3NiS_4(C_2H_4)(H_2O)_9]^{4+}$ obtained by passing ethylene through $\underline{C}$ in 2 M Hpts.

The cluster $\underline{C}$ reacts reversibly with ethylene in 2 M Hpts to give $[W_3NiS_4(C_2H_4)(H_2O)_9]^{4+}$ (see Fig. 2),[12] while the formation constant of the reaction of corresponding molybdenum-nickel cluster $\underline{D}$ with ethylene is rather low; application of pressurized ethylene is necessary in 2 M Hpts to get large electronic spectral change. Binding energies of nickel ($2p_{3/2}$) obtained from XPS spectra of the clusters ($\underline{C'}$, 854.5 eV; $\underline{D'}$, 854.7 eV) indicate that the nickel atom in $\underline{C'}$ is slightly richer in electron density than that in $\underline{D'}$, which corresponds well to the above experimental results.

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12) A cluster including ethylene $[W_3NiS_4(C_2H_4)(H_2O)_9](Hpts)_{0.5}(pts)_4{\cdot}6H_2O$ (E') has been isolated. Anal. Found: C, 22.47; H, 3.77%. Calcd for $W_3NiS_8O_{29}C_{34}H_{66.5}$: C, 22.26; H, 3.68%. X-ray analysis of E' has revealed the existence of the cluster cation $[W_3NiS_4(C_2H_4)(H_2O)_9]^{4+}$; T. Yamamoto, T. Watase, and T. Shibahara, 66th National Meeting of the Chemical Society of Japan, Nishinomiya, September 1993, Abstr., No. 3C2 17. Details will be published elsewhere.

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