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Uptake of Carbon Monoxide by a Sulfur-Bridged Molybdenum-Nickel Cluster. Synthesis and Structure of $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$

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The molybdenum-nickel cubane-type cluster $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ uptakes carbon monoxide in dilute HCl to give a new cluster $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$. The X-ray structure analysis verified that the nickel atom has a tetrahedral configuration surrounded by one CO and three S's neglecting three Ni-Mo bonds.

Carbon monoxide is one of the most important resources in C_1 chemistry, and much attention has been paid to the chemistry and uses of carbon monoxide, and many processes such as Fischer-Tropsch synthesis have been reported for the activation of carbon monoxide.[1-3] The water-gas-shift reaction and some of Reppe reactions also concern carbon monoxide.[2,4]

We have recently developed a new type of reaction that the incomplete cubane-type sulfur-bridged molybdenum cluster $[Mo_3S_4(H_2O)_9]^{4+}$ (**A**) takes in metals to give cubane-type mixed-metal clusters with Mo_3MS_4 cores (M = Fe, Co, Ni, Cu, In, Sn, Sb, Hg, etc.).[5-13] The reaction of **A** with palladium was also reported recently.[14] Here we report that the molybdenum-nickel cluster $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (**B**) uptakes carbon monoxide to give a new cluster $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ (**C**) with a remarkable color change (from green for **B** to red-purple for **C**).

The molybdenum-nickel cluster **B** uptakes carbon monoxide in dilute HCl as well as in organic solvents such as methanol, and two methods are effective for the synthesis of **C**. Method A: CO gas was passed through the green solution containing **B** in 1 M HCl. The resultant red-purple solution was allowed to stand overnight and was absorbed on Dowex 50W-X2 cation exchanger. Washing of the resin with 0.1 M HPTS (p-toluenesulphonic acid) to remove Cl^- ion, and elution with 4 M HPTS gave a red-purple solution. Cooling of the eluted solution in a refrigerator for a week gave red-purple crystals of $[Mo_3NiS_4(CO)(H_2O)_9](CH_3 \cdot C_6H_4 \cdot SO_3)_4 \cdot 7H_2O$ (**C'**). Method B: A green solution of **B** in 2 M HCl was dried up to a powder, which was dissolved in methanol and CO gas was passed through the solution. Then, the same procedure as the Method A was applied to give the crystals of **C'**. In agreement with the color change, the peak of **B** at 686 nm in UV-visible spectrum decreases and new intense peaks appear at 472 and 525 nm as shown in Fig. 1. The infra-red spectrum of **C'** shows a single intense absorption peak at 2060 cm^{-1} due to CO stretching. The cluster **C** has remarkable stability toward air oxidation and can be handled in the air.

The X-ray structure analysis of **C'** has verified that one CO molecule combined with the nickel atom in the cluster.[15] The nickel atom in **C** has a tetrahedral configuration surrounded by one CO and three S's neglecting three Ni-Mo bonds as shown in Fig. 2, and can be compared with that in the tetrahedral $Ni(CO)_4$.[16,17]

A molecular orbital calculation of **C** by DV-Xα method[18] indicates overlapping of atomic orbitals between C-Ni, Ni-S, and Ni-Mo as shown in Fig. 3.[19] The existence of the Ni-S and Ni-Mo bonds will give much influence on the reactivity of the CO attached to the Ni atom in the novel mixed-metal cluster **C**.

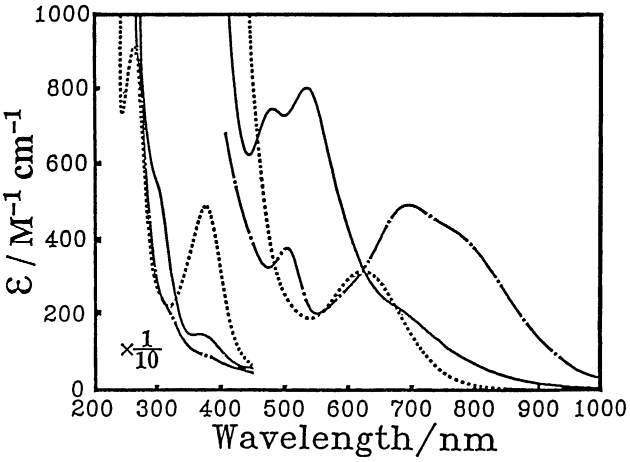


Fig. 1. UV-visible spectra in 1 M HCl.
--------- $[Mo_3S_4(H_2O)_9]^{4+}$
—— - —— $[Mo_3NiS_4(H_2O)_{10}]^{4+}$
———— $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$

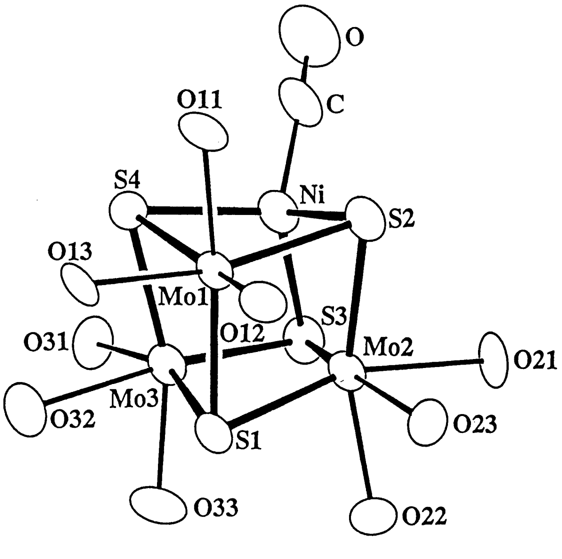


Fig. 2. Perspective view of $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ cation. Bond distances (Å) and angles (°): Ni-C, 1.874(12); C-O, 1.095(16); Mo-Mo(av.), 2.744[8]; Mo-Ni(av.), 2.678[7]; Mo-S1(av.), 2.342[2]; Mo-S (S2,S3,S4;av.), 2.327[9]; Mo-O(av.), 2.196[8]; Ni-C-O, 176.9(12); S-Ni-S(av.), 108.4[6]; Mo-Mo-Mo(av.), 60.00[29]; Mo-Ni-Mo(av.), 61.64[20].

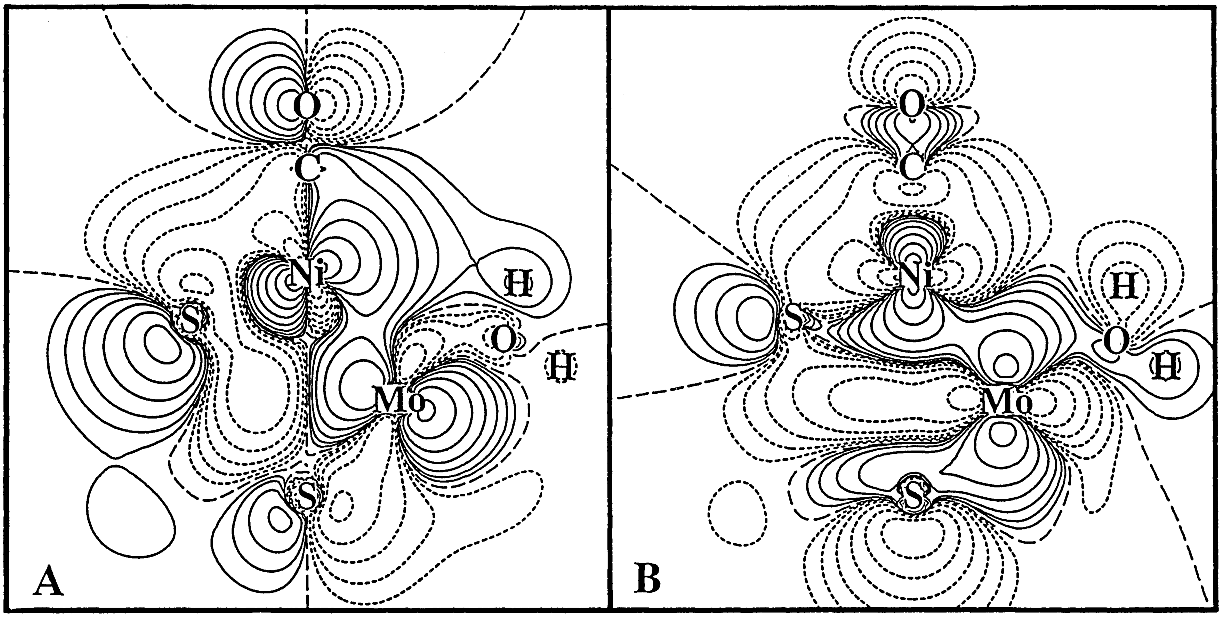
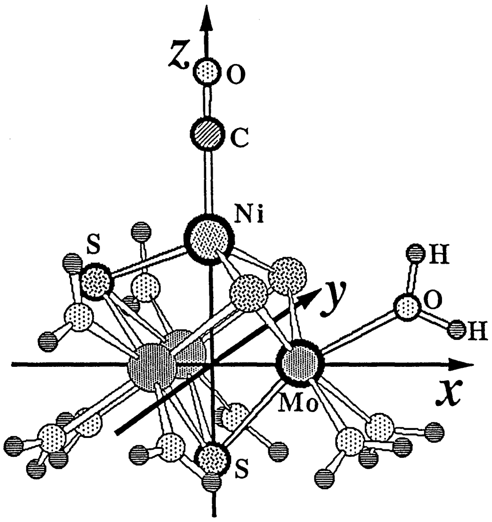


Fig. 3. Contour maps of "HOMO" (a) and "next to HOMO" (b) of $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ (C) in zx plane. The atoms in zx plane are indicated by bold-faced circles. The three molybdenum atoms are in the xy plane. Solid, dotted, and dashed lines indicate positive, negative, and zero contour lines, respectively.



We are investigating the reactivity of CO in the cluster **C** as well as the reactivity of **B** with other small molecules.

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15)Crystal data: triclinic system, space group $P\bar{1}$, a = 10.286(2) Å, b = 31.714(5) Å, c = 8.626(2) Å, α = 94.88(2)°, β = 100.90(2)°, γ = 82.71(2)°, V = 2735.3(10) $Å^3$, Z = 2, D_c = 1.792 g cm^{-3}, D_m = 1.77 g cm^{-3}, R = 8.11%. Supplementary Material Available: Tables of crystallographic data, atomic coordinates, thermal parameters, bond distances, and bond angles.

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