aldehyde (0.5 mmol) in 0.5 mL of dimethyl ether in total darkness. After 4 h of reaction, the ether solvent was evaporated and the analysis of the resulting white precipitate showed ~6% dideuterioformaldehyde. Again no evidence was obtained for the formation of dideuterioethylene oxide.

These results show that formaldehyde *O*-methylide **4** is formed by the reaction of dideuteriodiazomethane with monomeric formaldehyde under both photochemical and thermal conditions (latter involving oxadiazoline **5**[2]).

The symmetrical nature of formaldehyde *O*-methylide has been probed theoretically by Borden and co-workers.[6] Results of ab initio MCSCF and CI calculations indicate that the formaldehyde *O*-methylide shows strong preference for equal C–O bond lengths, indicating an allyl type resonance interaction (**3a** ↔ **3b**). Our experimental work seems to support the theoretical prediction.

In conclusion we have shown that formaldehyde *O*-methylide is indeed an intermediate in the reaction of diazomethane with monomeric formaldehyde under both photochemical and thermal conditions.

Acknowledgment. Support of our work by National Science Foundation is gratefully acknowledged.

Cubane-Type $Mo_3FeS_4^{4+}$ Aqua Ion and X-ray Structure of $[Mo_3FeS_4(NH_3)_9(H_2O)]Cl_4$

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We have recently reported on the preparation and properties of $Mo_3S_4^{4+}$ aqua ion (I).[1] A sequence of incomplete cubane-type aqua ions of $Mo_3O_4^{4+}$,[2] $Mo_3O_3S^{4+}$,[3] $Mo_3O_2S_2^{4+}$,[4] and $Mo_3OS_3^{4+}$,[5] are known;[6] the second to fourth aqua ions have μ_3-S and the presence of the isomeric forms having μ_3-O has also been reported.[7] Actually, four types of triangular molybdenum(IV) complexes have been reported.[8] However, as far as aqua ions are concerned, only the incomplete cubane-type is known so far.

We describe here the reaction of the aqua ion I with metallic iron as follows:

$$Mo_3S_4^{4+} + Fe \rightarrow Mo_3FeS_4^{4+}$$

This is the first example of a reaction in which the missing corner of the incomplete cubane-type core is filled with another metal.

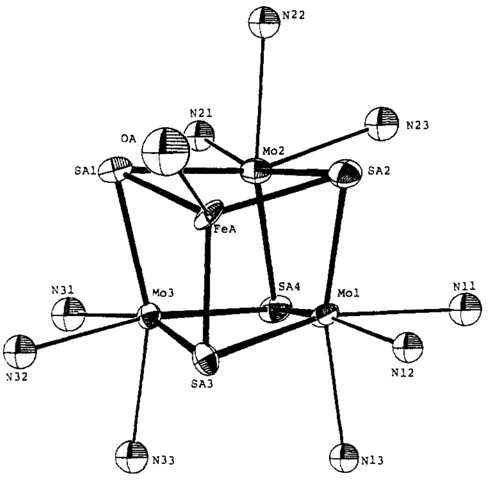

Figure 1. Perspective view of $[Mo_3FeS_4(NH_3)_9(H_2O)]^{4+}$ cation. Bond distances (Å): Mo1–Mo2, 2.766 (8); Mo1–Mo3, 2.783 (3); Mo2–Mo3, 2.830 (8); Mo1–FeA, 2.684 (13); Mo2–FeA, 2.675 (15); Mo3–FeA, 2.691 (13); Mo1–SA2, 2.34 (1); Mo1–SA3, 2.38 (3); Mo1–SA4, 2.30 (3); Mo2–SA1, 2.33 (1); Mo2–SA2, 2.39 (1); Mo2–SA4, 2.36 (3); Mo3–SA1, 2.37 (1); Mo3–SA3, 2.35 (3); Mo3–SA4, 2.42 (3); FeA–SA1, 2.26 (2); FeA–SA2, 2.25 (2); FeA–SA3, 2.25 (3); Mo–N (av), 2.29 (5); FeA–OA, 2.04 (4).

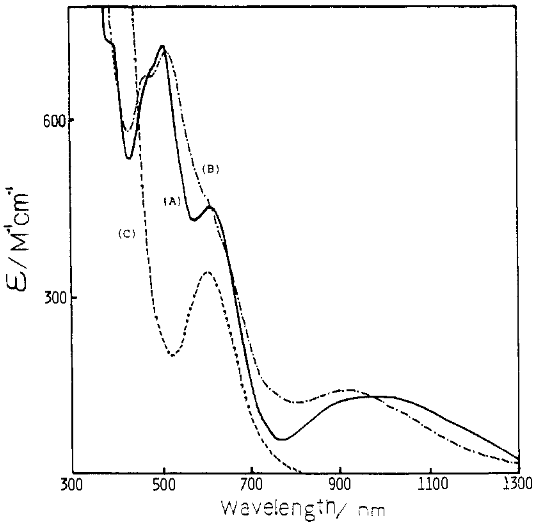

Figure 2. Electronic spectra. (A) $Mo_3FeS_4^{4+}$ in 2 M HPTS; (B) $[Mo_3FeS_4(NH_3)_9(H_2O)]^{4+}$ in concentrated aqueous ammonia (In order to avoid the strong light absorption of ammonia, dilute aqueous ammonia solution (1 M) was used in 800–1300-nm region, although the spectrum is gradually changeable.); (C) $Mo_3S_4^{4+}$ in 2 M HPTS.

There are many clusters with a core like, but none the same as, Mo_3FeS_4; cubane-type clusters of Mo_4S_4,[9] $Mo_2Fe_2S_4$,[10] $MoFe_3$-

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(6) Strictly speaking, the term aqua ion cannot be used for ions containing sulfur atom(s). The term aqua ion, however, will be used here for species in which bridging sulfur atom(s) exist and other ligands are only water.

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S_4,[11,12] and Fe_4S_4[12,13] have been found.

All the experiments were carried out under a dinitrogen atmosphere. An iron wire (3 g) was introduced to a conical flask containing the aqua ion I (0.05 M, 25 mL) in 2 M HCl. The color of the solution turned from green to red-purple in a few hours. After the remaining iron was removed, the resultant solution was purified by the use of the ion exchange technique. The solution was absorbed on a Dowex 50W-X2 cation exchanger. Ferrous ion was eluted with 0.5 M HCl and red-purple eluent was obtained by the use of 1 M HCl.[14] This was analyzed to give Mo/Fe = 2.93 ± 0.15 (three determinations). An HPTS (*p*-toluenesulfonic acid) solution of the ion was obtained by the absorption of the ion on the cation exchanger from the HCl solution followed by the elution of it with 2 M HPTS. The analytical result of Mo/Fe ≈ 3 and the behavior of the aqua ion on the cation exchanger are indicative of the presence of heterometal $Mo_3FeS_4^{4+}$ aqua ion (II). This is in remarkable contrast to the case[15] of reaction of the $Mo_3O_4^{4+}$ aqua ion (III) with iron, the reaction product being simply the reduced form[16] of III with no addition of an iron atom. Exposure of II to the air gives the starting material, i.e., I together with ferrous ion.

Preparation of $[Mo_3FeS_4(NH_3)_9(H_2O)]Cl_4$ (IV) is as follows. The red-purple solution obtained from the mixture of I and an iron wire was introduced into an ice-cold flask containing concentrated aqueous ammonia. Black-purple crystals deposited in a few days.[17]

X-ray crystal structural analysis[18] revealed the existence of a heterometal cubane-type $Mo_3FeS_4^{4+}$ core in IV. The unit cell has two independent chemical units, but no significant structural difference can be seen between the two units. One of the cluster cation is shown in the Figure 1 together with selected bond distances and angles.[19]

There is no clear structural evidence for localized bonding in the $Mo_3FeS_4^{4+}$ core. Therefore if the oxidation state of iron is assumed to be 2+, a mean $Mo^{3.33+}$ state or a formal oxidation state of Mo(IV) + 2Mo(III) is assigned. Each molybdenum is approximately octahedrally coordinated (three μ_3-S and three ammonia molecules, the Mo–Mo and Mo–Fe bonds being ignored), while the iron is tetrahedrally coordinated (three μ_3-S and one water molecule). Electronic spectrum of II, which is shown in Figure 2, together with those of I and IV has peaks at 955 (ϵ 130 (M^{-1} cm^{-1})/mol), 602 (ϵ 454), 505 (ϵ 726), and 470 nm, sh (ϵ 669). The spectrum of II is similar to that of IV. This similarity and the X-ray structure analysis support the presence of heterometal cubane-type $Mo_3FeS_4^{4+}$ aqua ion (probably $[Mo_3FeS_4(H_2O)_{10}]^{4+}$) in solution.

The reaction of I with other metals (e.g., Cu or Hg) is under investigation.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and the perspective view of the other $[Mo_3FeS_4(NH_3)_9(H_2O)]^{4+}$ cation (3 pages). Ordering information is given on any current masthead page.

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[17] Anal. Found (Calcd): NH_3, 19.49 (19.54)%; H, 3.96 (3.73)%; Cl, 17.76 (18.06)%.

[18] Crystal data: monoclinic system, space group $P2_1$, a = 18.662 (3) Å, b = 14.959 (3) Å, c = 9.208 (2) Å, β = 119.54 (1)°, V = 2236.7 (7) $Å^3$, Z = 4. The structure was solved by direct method (MULTAN) and refined by least squares to a current R value of 0.078 for 3913 reflections ($F_o \geq 2\sigma(F_o)$).

[19] The X-ray structural analysis could not discriminate unequivocally oxygen from nitrogen, a water molecule is tentatively coordinated to the iron atom, and all the coordination sites of the three molybdenum atoms were occupied by ammonia molecules.

X-ray Structure Analysis of the Pentagonal Dodecahedrane Hydrocarbon $(CH)_{20}$

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It has been stated that "the dodecahedrane geometry is exquisite in its perfection".[1] A significant part of the fascination surrounding this almost spherical $(CH)_{20}$ hydrocarbon arises from its exceptional I_h symmetry,[2] regular polyhedral nature, and aesthetically appealing topology. These features, in combination with occlusion by the structural cage of a cavity incapable of solvation, have fostered many innovative theoretical treatments of dodecahedrane's molecular properties. These include assessments of its vibrational frequencies,[3] ordering of orbital energies,[4,5] ionization potential,[6] formation of inclusion compounds,[5,7,8] NMR spin–spin coupling constants,[7a,9] and heat of formation.[10] Following the successful synthetic elaboration of dodecahedrane (**1**) by Paquette and co-workers,[11] some of the unusual physical characteristics of the hydrocarbon were elucidated experimentally.

A matter of continuing interest has been definition of the three-dimensional structure of dodecahedrane by X-ray crystal structure analysis. Precise measurement of bond lengths and bond angles, together with detailed knowledge of the dimensions of the cavity, would provide, inter alia, a reliable foundation for future theoretical work.[12] As a direct result of dodecahedrane's unique shape, however, it has been widely anticipated that the molecule would not crystallize in any preferred orientation. We find instead that the molecule not only adopts a preferred orientation, but takes advantage of the highest crystallographic symmetry available to it.

The X-ray structure determination was achieved with data from a clear, colorless, twinned crystal grown from benzene solution.

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