

quency is very similar to the plasmon frequency¹¹ of 520 nm of colloidal Au particles with an average diameter of approximately 200 Å^{12,13} (Figure 1, curve b). Is such similarity an indication of the beginning of the collective phenomenon characteristic of the bulk?

To help shed light on the question, we also prepared aqueous bimetallic colloidal Au_{1-x}Ag_x alloy solutions of 200–400 Å via standard methods¹⁴ and obtained their absorption spectra. The optical spectrum of the Au_{0.22}Ag_{0.78} colloidal solution is depicted in Figure 1, curve c. We found that the frequency of the absorption maximum is highly composition dependent. It varies monotonically from 520 nm (2.4 eV) in Au particles to 400 nm (3.1 eV) in Ag particles as shown in Figure 1, inset, solid curve. The fact that we did not observe two distinct absorption maxima at 520 and 400 nm for the bimetallic (Au_{1-x}Ag_x) colloidal solutions argues strongly against segregated Au and Ag particles.¹⁵

As indicated by the arrow in Figure 1, inset, solid curve, the optical absorption of cluster **1** at 2.5 eV with Ag mole fraction of 0.53 virtually coincides with that of Au bimetallic colloidal particles. This is a strong indication that the 495-nm absorption observed in **1** can be interpreted as a plasmon frequency similar to that of colloidal particles. We believe that, even at the level of a few dozen metal atoms, a cluster, under appropriate ligand environment and suitable molecular architecture and symmetry, may already exhibit collective electronic behavior characteristic of that of the bulk.¹⁶

To further our understanding of the optical behavior of the colloidal Au_{1-x}Ag_x particles, we performed a semiquantitative computer simulation of the composition dependence of plasmon frequency (Figure 1, inset, dashed curve). Following Mie's theory,¹⁷ the frequency of the absorption peak is proportional to $\epsilon_2/[(\epsilon_1 + 2\epsilon_0)^2 + \epsilon_2^2]$ where ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric constant and ϵ_0 is the dielectric constant of the medium. Here we take ϵ_1 and ϵ_2 to be the composition-weighted averages¹⁸ of the bulk dielectric constants of Au and Ag (viz., $\epsilon_i = (1-x)\epsilon_i^{\text{Au}} + x\epsilon_i^{\text{Ag}}$ for $i = 1, 2$) and ϵ_0 to be the dielectric constant of water (1.333²). While the theory predicts quite satisfactorily the general trend of the composition dependence of the plasmon frequency, quantitative agreement is lacking. We believe that the discrepancy is largely due to (1) the inappropriateness of using bulk dielectric constants for these small particles and (2) the neglect of the effect caused by the smallness of the particle size compared with the electron mean free path λ . We note that these particles (15 Å for **1** and 200–400 Å for the colloidal particles) are of dimensions less than λ (~500 Å) which in turn is less than the wavelength of light (~5000 Å). In other words, the electron mean free path of either the molecular or the colloidal systems discussed here is limited by the small size of the cluster or particle.

We conclude that the observation of the plasmon frequency of the 38-atom cluster **1** of approximate 15 Å in diameter (metal

core only) is a strong indication that the cluster possesses the free electron quasi-band structure behavior characteristic of bulk metal (viz., entering the quantum-size regime).¹⁹ In other words, the ensemble of the electrons, responsible for the optical absorption, can be considered collectively as a whole in much the same way as in the metal. Further experimental and theoretical studies are in progress.²⁰

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(19) To what extent electrons in a metal cluster are localized (or delocalized) is difficult to assess. In view of the similar interatomic distance between the metal atoms in **1** as compared to that in bulk Au or Ag, we believe that electrons are delocalized.

(20) Conduction electron spin resonance (CESR) can be a useful means of providing information on the collective behavior of the electrons in metal-cluster systems. The line width of CESR will decrease because the spin-relaxation rates may be limited due to the discreteness of electronic states (thereby making CESR easier to be observed in small particles than in the bulk). However, such a change in line width is complicated by several factors, e.g., spin-orbit coupling, electron-phonon interaction, surface scattering, etc. The line-width variation as a function of particle size, for instance, depends on the strength of spin-orbit coupling. Moreover, when the particle size falls below 30 Å, the number of conduction electrons in a cluster may be so low as to make CESR difficult to observe.

Double-Cubane-Type Molybdenum-Sulfur Cluster Aqua Ion, [(H₂O)₉Mo₃S₄MoS₄Mo₃(H₂O)₉]⁸⁺

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We have recently reported that the reaction of the incomplete cubane-type Mo₃S₄⁴⁺ aqua ion (**1**) with metallic iron gives the cubane-type Mo₃FeS₄⁴⁺ aqua ion, the core structure of which has been verified by the X-ray structure analysis of [Mo₃FeS₄(N-H₃)₉(H₂O)]Cl₄ derived from the aqua ion and ammonia water.¹

We will describe here the preparation, properties, and X-ray structure analysis of a double-cubane-type cluster compound, [(H₂O)₉Mo₃S₄MoS₄Mo₃(H₂O)₉](CH₃-C₆H₄-SO₃)₈·18H₂O, prepared from the aqua ion **1** and metallic magnesium.

Magnesium foil (5 g) was put into a conical flask containing the aqua ion **1** (0.2 M in 50 mL of 6 M HCl) placed in an ice bath. The color of the solution turned rapidly from green to brown. After 1 day, HCl (1 M, 400 mL) was added to the brown solution, which was allowed to stand for several days. Then the solution was filtered and Sephadex G-10 column chromatography was applied (1 M HCl). The second² band (dark brown) from the column was absorbed on a Dowex 50W-X2 cation exchanger, which was washed with 1 M HCl. Then the purple solution obtained by use of 2 M HCl³ was absorbed on the cation exchanger again and eluted with 4 M HPTS (*p*-toluenesulfonic acid). The resultant purple solution was kept in a refrigerator. Black-purple crystals were obtained in a week.⁴

(1) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342-1343.

(2) The first band contains Mo₃S₄⁵⁺ aqua ion. (The yield was ca. 45% based on the starting aqua ion **1**.)

(3) Elution with 6 M HCl gives a brown solution which is converted to a purple solution containing **2** by passing air through it.

(4) Anal. Found (Calcd): Mo, 22.68 (22.79); C, 23.68 (22.83); H, 4.05 (4.37). The yield was ca. 15% based on the starting aqua ion **1**.

(11) See, for example: Kittel, C. *Introduction to Solid State Physics*, 3rd ed.; Wiley: New York, 1968.

(12) (a) Kreibig, U.; Zacharias, P. *Z. Phys.* **1970**, *231*, 128. (b) Kreibig, U. *J. Phys. F: Met. Phys.* **1974**, *4*, 999. (c) Kreibig, U.; Fragstein, C. V. *Z. Phys.* **1969**, *224*, 307.

(13) (a) Doremus, R. H. *J. Chem. Phys.* **1964**, *40*, 2389. (b) Steubing, W. *Ann. Phys.* **1908**, *26*, 329.

(14) The colloidal Au_{1-x}Ag_x solutions where $x = 0-1$ were prepared by the citrate method (Turkevich, J.; Stevenson, P.; Hillier, J. *Discuss. Faraday Soc.* **1951**, *11*, 55). Silver was introduced as AgNO₃.

(15) The penetration depth is much greater than the size of the particles. If the metallic components in the particles indeed segregate, either on the surface or inside the particle, there should be two distinct absorption peaks. Our observation of a single peak thus gives a strong indication of homogeneously organized clusters.

(16) While such a connection between "large" metal cluster compounds containing $\leq 10^2$ atoms and "small" metal particles containing $\geq 10^6$ atoms is rather striking, we note that the similar conclusion that the magnetic behavior of metal clusters containing $\leq 10^2$ atoms and reaching a certain size and shape begins to resemble that of colloidal particles or the bulk have also been reported recently.^{2,3}

(17) Mie, G. *Ann. Phys.* **1908**, *25*, 377.

(18) Fukutani, H.; Sueoka, O. In *Optical Properties and Electronic Structure of Metals and Alloys*; Abeles, F., Ed.; Wiley: New York, 1966; p 565.

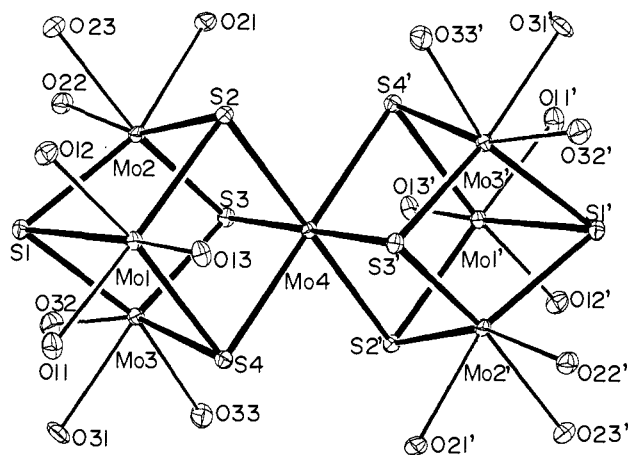


Figure 1. Perspective view of $[(\text{H}_2\text{O})_9\text{Mo}_3\text{S}_4\text{MoS}_4\text{Mo}_3(\text{H}_2\text{O})_9]^{8+}$ aqua ion. Bond distances (\AA): Mo1-Mo2, 2.773 (2); Mo1-Mo3, 2.766 (2); Mo2-Mo3, 2.770 (2); Mo1-Mo4, 3.026 (1); Mo2-Mo4, 3.051 (1); Mo3-Mo4, 3.060 (1); Mo1-S1, 2.351 (3); Mo1-S2, 2.327 (3); Mo1-S4, 2.331 (3); Mo2-S1, 2.354 (3); Mo2-S2, 2.321 (3); Mo2-S3, 2.325 (3); Mo3-S1, 2.346 (3); Mo3-S3, 2.325 (3); Mo3-S4, 2.323 (3); Mo4-S2, 2.446 (3); Mo4-S3, 2.462 (3); Mo4-S4, 2.447 (3); Mo-O(H_2O), 2.18 [2]. (The primed atoms are related to the unprimed ones by a center of symmetry.)

X-ray structure analysis⁵ of the crystal revealed the existence of a double-cubane-type cluster aqua ion $[(\text{H}_2\text{O})_9\text{Mo}_3\text{S}_4\text{MoS}_4\text{Mo}_3(\text{H}_2\text{O})_9]^{8+}$ (**2**) (Figure 1). Two incomplete cubane-type cores, Mo_3S_4 's, are bridged by a molybdenum atom (Mo4) which lies on a center of symmetry. The Mo4-Moi ($i = 1, 2, 3$) bond distances are distinctly longer than Mo1-Mo2, Mo1-Mo3, and Mo2-Mo3. Although many cubane-type cluster compounds with Mo_3S_4 cores are known,⁶ no double-cubane-type cluster with an $\text{Mo}_3\text{S}_4\text{MoS}_4\text{Mo}_3$ core has been reported. It seems that the triangular core of **1** is broken by the reaction with magnesium which is a stronger reducing agent than iron and that the novel double-cubane-type core is constructed by way of some intermediate(s). It should be noted that different double-cubane-type molybdenum-iron-sulfur clusters (e.g., $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SR})_9]^{3-7}$ and $[\text{Mo}_2\text{Fe}_7\text{S}_8(\text{SR})_{12}]^{3-8}$) have been prepared, and their properties (electronic spectra, electrochemical behavior, and catalytic activity⁹) had been investigated in detail.

The electronic spectrum of **2**, which is depicted in Figure 2, together with that of **1**, shows λ_{max} 's at 950 nm (ϵ 606 ($\text{M}^{-1}\text{cm}^{-1}$)/Mo), 635 (1266), 518 (1469), 480 (sh, 1295), 416 (1027), and 360 (770). These ϵ values in the visible and near-infrared region are very large compared to those of **1**. In **2**, as described above, are present two, structurally different types of Mo's whose mean oxidation number is 3.43,¹⁰ whereas in **1** there are three

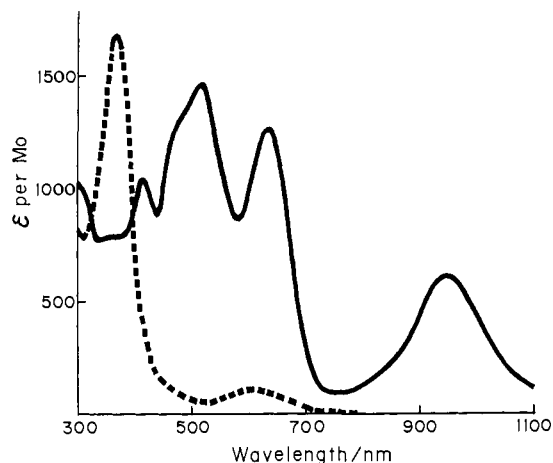


Figure 2. Electronic spectra in 1 M HPTS: (—) $[(\text{H}_2\text{O})_9\text{Mo}_3\text{S}_4\text{MoS}_4\text{Mo}_3(\text{H}_2\text{O})_9]^{8+}$; (---) $\text{Mo}_3\text{S}_4^{4+}$

equal Mo atoms, each in the oxidation state of 4.00. On the other hand, the Mo_3S_4 cubane-type compounds composed of structurally equivalent Mo atoms do not have such a large ϵ value, even though some of them have fractional oxidation numbers.¹¹ Thus, a charge-transfer transition might be responsible for the strong absorption of **2**.

Compound **2** is fairly resistant toward air oxidation, not only in the solid state but also in solution. The absorbance of a solution of **2** changes by less than few percent in a day.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles (3 pages). Ordering information is given on any current masthead page.

(10) Compound **2** is diamagnetic at room temperature: we have no conclusive explanation of this at present.

(11) For example, ref 6g.

2,3-Methano-2,4-didehydroadamantane: A [4.1.1]Propellane Possessing Two Unequivalent Inverted Carbons

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We report the first synthesis and reactivity studies of 2,3-methano-2,4-didehydroadamantane (**2**), a [4.1.1]propellane derivative containing the *trans*-bicyclo[4.1.0]heptane unit.¹ This is the smallest carbocyclic propellane system possessing two

(1) Certain cyclosteroids also contain this unit.^{2a} Recently, a few other derivatives of *trans*-bicyclo[4.1.0]heptane have been prepared.^{2b} Its lower homologue, *trans*-bicyclo[3.1.0]hexane, still remains an illusive target.

(2) (a) Cf.: Dauben, W. G.; Wipke, W. T. *Pure Appl. Chem.* **1964**, *9*, 539-553. Dauben, W. G.; Willey, F. G. *Tetrahedron Lett.* **1962**, 893-899. Just, G.; DiTullio, V. *Can. J. Chem.* **1964**, *42*, 2153-2160. Gassman, P. G.; Hymans, W. E. *J. Chem. Soc., Chem. Commun.* **1967**, 795-796. Gassman, P. G. *Ibid.* **1967**, 793-795. (b) Gassman, P. G.; Bonser, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 667-669. Gassman, P. G.; Mlinarić-Majerski, K. *J. Org. Chem.* **1986**, *51*, 2397-2398.

(5) Crystal data: triclinic system, space group $P\bar{1}$, $a = 15.816$ (4) \AA , $b = 16.589$ (4) \AA , $c = 11.722$ (3) \AA , $\alpha = 97.29$ (2) $^\circ$, $\beta = 108.91$ (2) $^\circ$, $\gamma = 72.47$ (2) $^\circ$, $V = 2772.6$ (12) \AA^3 , $Z = 1$. The structure was solved by direct method (MULTAN) and refined by least squares to a current R value of 0.058 for 5131 reflections ($F_o > 5\sigma(F_o)$).

(6) References cited in ref 1 and: (a) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322-329. (b) Vandenberg, J. M.; Brasen, D. *J. Solid State Chem.* **1975**, *14*, 203-208. (c) Muller, A.; Eltzner, W.; Clegg, W.; Sheldrick, G. M. *Angew. Chem.* **1982**, *94*, 555-556. (d) Brunner, H.; Kauermann, H.; Wachter, J. *J. Organomet. Chem.* **1984**, *265*, 189-198. (e) Muller, A.; Jostes, R.; Eltzner, W.; Nie, C.-S.; Diemann, E.; Bogge, H.; Zimmermann, M.; Dartmann, M.; Reinsch-Vogel, U.; Che, S.; Cyvin, S. *J. Inorg. Chem.* **1985**, *24*, 2872-2884. (f) Cotton, F. A.; Diebold, M. P.; Dori, Z.; Llusar, R.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 6735-6736. (g) Shibahara, T.; Kuroya, H.; Matsumoto, K.; Ooi, S. *Inorg. Chim. Acta* **1986**, *116*, L25-L27. (h) Shibahara, T.; Kawano, E.; Okano, M.; Nishi, M.; Kuroya, H. *Chem. Lett.* **1986**, 827-828.

(7) For example: Wolff, T. E.; Berg, J. M.; Hodgson, K. O.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 4140-4150. Simulation of the EXAFS of the unsynthesized double-cubane structure $\text{Fe}_3\text{S}_4\text{MoS}_4\text{Fe}_3$ is included in this paper.

(8) For example: Palermo, R. E.; Power, P. P.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 173-181.

(9) For example: Tanaka, K.; Nakamoto, M.; Tashiro, Y.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 316-321.