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# Magnetism and Electronic Structure of a Cubane-Type $Mo_4S_4$ Cluster

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(Received September 30, 1987)

**Synopsis.** The static magnetic susceptibilities of the stable cubane-type compounds of $[Mo_4S_4]^{m+}$ with a set of consecutive oxidation numbers have been measured in the temperature range from 2 to 300 K at the field strength of 0.5 T. $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ ($m$=5) has been found to be paramagnetic with $S=1/2$, whereas $Mg_2[Mo_4S_4(edta)_2]\cdot 22H_2O$ ($m$=4) and $Mg[Mo_4S_4(edta)_2]\cdot 12H_2O$ ($m$=6) to be diamagnetic. The electronic structure of the $[Mo_4S_4]^{m+}$ clusters is discussed on the basis of the MO theory from the magnetic properties of these compounds.

The cubane-type $[Mo_4S_4]^{m+}$ clusters have recently been synthesized and found to be stable for a set of consecutive oxidation numbers, $m$=4, 5, and 6.[1-3] A comparative investigation of $[Mo_4S_4]^{m+}$ clusters will lead to understanding the electronic structure of the clusters. We report herein the temperature dependence of static magnetic susceptibilities of the compounds including $[Mo_4S_4(edta)_2]^{n-}$ anions[4] in the three oxidation states over the range from 2 to 300 K. From the results, we discuss the electronic structure of the clusters.

## Experimental

$Mg_2[Mo_4S_4(edta)_2]\cdot 22H_2O$ ($m$=4), $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ ($m$=5), and $Mg[Mo_4S_4(edta)_2]\cdot 12H_2O$ ($m$=6) were prepared by the methods described elsewhere.[1,2] These chemical compositions, particularly the contents of water, were determined by the X-ray crystallographical analyses[1,2] on referring to the results of the elemental analyses.[5] The magnetic susceptibility $\chi$ was measured by means of a Faraday-type magnetic balance[6] under the field at 0.5 T. To avoid loss of water of crystallization during the susceptibility measurements, we used the polycrystalline sample in the form of a compressed pellet immersed in liquid paraffin. The spin susceptibilities $\chi_s$ of the three compounds were obtained by subtracting the diamagnetic contribution $\chi_d$ from $\chi$ after correction for liquid paraffin. The diamagnetic susceptibility was determined experimentally from a $\chi-T^{-1}$ plot.

## Results and Discussion

The spin susceptibilities of all the compounds, plotted as a function of temperature in Fig. 1, can be fitted to the Curie-Weiss law $\chi=C/(T-\theta)$ over the whole temperature range examined. The Curie constant $C$ and the Weiss constant $\theta$ for the $[Mo_4S_4]^{m+}$ clusters are summarized in Table 1 together with the

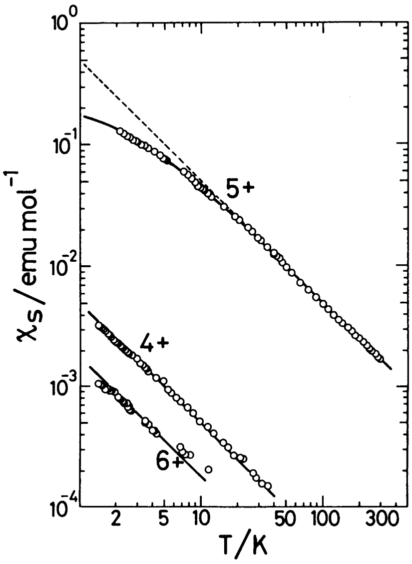

Fig. 1. Temperature dependence of spin susceptibilities of molybdenum compounds consisting of a cubane-type $Mo_4S_4$ cluster. Open circles represent experimental data. The susceptibilities calculated using Curie–Weiss law are shown by solid lines. The notations 4+, 5+, and 6+ stand for the compounds including $[Mo_4S_4]^{4+}$, $[Mo_4S_4]^{5+}$, and $[Mo_4S_4]^{6+}$ clusters, respectively.

Table 1. Curie Constant $C$, Weiss Constant $\theta$, and Diamagnetic Susceptibility $\chi_d$ for the Molybdenum Compounds Including $[Mo_4S_4]^{m+}$ Clusters[a]

| Compound | $10^3C$ | $\theta$ | $10^6\chi_d$ |
|---|---|---|---|
| | emu K mol$^{-1}$ | K | emu mol$^{-1}$ |
| $Mg_2[Mo_4S_4(edta)_2]\cdot 22H_2O$ ($m$=4) | 4.9±0.3 | 0.0±0.2 | −1000±20 |
| $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ ($m$=5) | 525±20 | −2.0±0.2 | −300±20 |
| $Mg[Mo_4S_4(edta)_2]\cdot 12H_2O$ ($m$=6) | 1.7±0.3 | 0.0±0.2 | −410±20 |

a) 1 emu K mol$^{-1}$=4$\pi$ cm$^3$ K mol$^{-1}$; 1 emu mol$^{-1}$=4$\pi$ cm$^3$ mol$^{-1}$.

diamagnetic susceptibility $\chi_d$. The Curie constant for $[Mo_4S_4]^{5+}$ is significantly large and is consistent with the presence of an $S=1/2$ moment per cluster with $g=2.32\pm0.02$; the $g$-factor being determined by the electron paramagnetic resonance measurements at room temperature. In contrast, the Curie constants for the other compounds are very small. There is a moment with $S=1/2$ per about 100 clusters for $[Mo_4S_4]^{4+}$ and a moment per about 300 clusters for $[Mo_4S_4]^{6+}$. The very small Curie constants observed in $[Mo_4S_4]^{4+}$ and $[Mo_4S_4]^{6+}$ are probably ascribed to extrinsic origin such as chemical impurities. Thus it is concluded that $[Mo_4S_4]^{4+}$ and $[Mo_4S_4]^{6+}$ are essentially diamagnetic, whereas $[Mo_4S_4]^{5+}$ is in the paramagnetic $S=1/2$ ground state.

X-Ray crystal structure analyses of the compounds consisting of $[Mo_4S_4(edta)_2]^{n-}$ ($n$=2, 3, 4) anions have revealed that the structures of the anions are very similar to each other except for a slight difference in the mean Mo–Mo bond distance and the volume of the cubane core.[2] Since the four Mo–Mo distances are almost completely identical in each compound, Mo tetramer can approximately be regarded as belonging to the $T_d$ symmetry. Under this symmetry 4d electrons from the four Mo atoms could occupy six bonding orbitals ($a_1+e+t_2$) which have mainly Mo 4d character.[7–9] Energy difference between the bonding and antibonding orbitals would be on the order of magnitude of 25000 $cm^{-1}$, since the lowest energy transition is observed near 400 nm in $[Mo_4S_4]^{4+}$ as a weak absorption band.[2]

The magnetism of the cubane-type clusters consisting of four transition-metal atoms and four chalcogen atoms has been commonly explained by assuming different values of antiferromagnetic interactions between the magnetic moments localized on the metal atoms.[10,11] This approach seems to be quite natural for those compounds having appreciable difference among the metal-metal distances and among the angles of chalcogen-metal-chalcogen bridges. However, the same approach would not be applicable for the molybdenum cluster compounds, because such appreciable difference in bond length and angle is not observed, although the magnetism changes quite drastically. It seems to be unnatural to assume significantly different values of the antiferromagnetic interactions for the series of compounds having approximately identical mean Mo–Mo distances and quite different magnetic properties.

For the reasons mentioned above, we here adopt the approach based on the MO theory to explain the magnetism of the molybdenum compounds. All the bonding orbitals are fully occupied by the twelve electrons in the case of $m$=4 and hence the $Mo_4S_4$ cluster has to be diamagnetic as actually observed in $Mg_2[Mo_4S_4(edta)_2]\cdot22H_2O$. Removal of one electron from the orbitals yields an unpaired electron whether HOMO is degenerate or not. Therefore, $[Mo_4S_4]^{5+}$ is expected to be in a paramagnetic ground state with $S=1/2$. This is also consistent with the result observed in $Na_3[Mo_4S_4(edta)_2]\cdot10H_2O$. Removal of two electrons from the orbitals of the $m$=4 state yields different situations depending on the energy sequence of the bonding orbitals. If HOMO of the $[Mo_4S_4]^{4+}$ cluster is not degenerate (i.e., $a_1$), it becomes empty by removal of two electrons and consequently $[Mo_4S_4]^{6+}$ is diamagnetic. If HOMO is degenerate (i.e., e or $t_2$), the ground state should be paramagnetic with $S=1$ because of Hund's rule. The experimental result that $Mg[Mo_4S_4(edta)_2]\cdot12H_2O$ is diamagnetic is favorable for the former situation. Although tetragonal distortion from the idealized symmetry ($T_d\rightarrow D_{2d}$) also results in diamagnetic state, there has been no evidence for large distortion in the $[Mo_4S_4]^{6+}$ cluster.[2] Therefore, it is most probable that the HOMO of $[Mo_4S_4]^{4+}$ belongs to the $a_1$ representation.

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4) edta: ethylenediaminetetraacetic acid.

5) Anal. Found: C, 16.02; H, 3.72; N, 3.72. Calcd for $Mg_2Mo_4S_4C_{20}H_{68}N_4O_{38}$: C, 15.66; H, 4.46; N, 3.65; although the results of the analysis were more close to the values calculated for $Mg_2[Mo_4S_4(edta)_2]\cdot20H_2O$, we here calculated for $Mg_2[Mo_4S_4(edta)_2]\cdot22H_2O$, which was given by the crystal structure analysis. Found: C, 17.92; H, 2.97; N, 4.19; Na, 5.00. Calcd for $Na_3Mo_4S_4C_{20}H_{44}N_4O_{26}$: C, 17.95; H, 3.31; N, 4.18; Na, 5.15. Found: C, 17.87; H, 2.97; N, 4.20. Calcd for $MgMo_4S_4C_{20}H_{48}N_4O_{28}$: C, 18.07; H, 3.64; N, 4.21.

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