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EPR Studies of the Mixed-Metal Cubane-Type Complex Having a $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ Core

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The mixed-metal single-cubane-type complex $[Mo_3CuS_4(H_2O)_{10}]^{4+}$, which was generated by disintegration of the double-cubane-type complex $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$, was studied by EPR spectroscopy and EHMO calculations. The hyperfine coupling constants of the molybdenum and copper nuclei were determined from frozen solution EPR spectra for the ^{95}Mo-enriched and -unenriched complexes. EPR analyses show that the single-cubane-type complex $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ is a paramagnetic of $S = {}^1/_2$ and the paramagnetic center is mainly situated on one of the three molybdenum ions; the three molybdenum ions are not equivalent to each other, but they are formally close to Mo(III), Mo(IV), and Mo(IV), respectively. It is also shown that there is little spin density on copper, which may be close to Cu(I) rather than Cu(II), and that the paramagnetic site, Mo(III), is jumping among the three molybdenum ions at such a rate as to cause a line width broadening effect on the molybdenum hyperfine components of the EPR spectrum.

Introduction

Metal−sulfur clusters are biologically important molecular units which are found in enzymes such as nitrogenases having Fe−S and Mo−Fe−S clusters in their active sites. A lot of model compounds have been examined in order to understand these functional groups.[2] The metal−sulfur cubane-type clusters have interested inorganic chemists by their unique structures and chemical properties. The "soft" character of sulfur allows for a variety of complexes with transition metals or metal ions.[3]

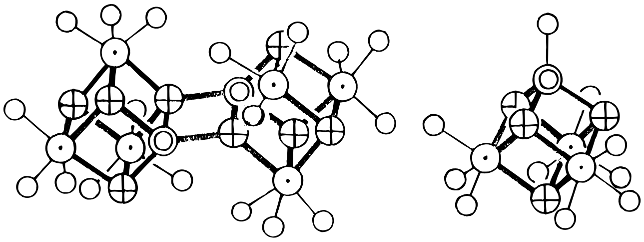

Figure 1. Structures of $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$ (left) and $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ (right): ⊙, Mo; concentric rings, Cu; ⊕, S; ○, O.

Shibahara's group[4−6] and others[7,8] reported that the incomplete cubane-type complex ion $[Mo_3S_4(H_2O)_9]^{4+}$ reacts with some metals to give mixed-metal cubane-type complexes. The reactuion of $[Mo_3S_4(H_2O)_9]^{4+}$ ion with copper, for example, gives the single-cubane-type complex, $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ (**1**), which crystallizes from 4 M HPTS (*p*-toluenesulfonic acid) solution as a double-cubane-type complex $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9](CH_3{\cdot}C_6H_4SO_3)_8{\cdot}20H_2O$ (**2**).[5,6,8] It is shown that the complex **2** is completely disintegrated to the single-cubane-type complex in HCl solution (Figure 1). It is interesting to clarify the structures of these complexes and their physicochemical properties. In the previous paper, Shibahara et al. examined them by X-ray crystallographic analysis, XPS analysis, electronic absorption spectroscopy, and magnetic susceptibility measurements.[5]

In the present work, we applied EPR spectroscopy to structural studies of the complexes. EPR measurements were performed for neat crystal powders and the frozen HCl solution of **2**. Recently, Nasreldin et al.[8] also observed EPR spectra for frozen solutions of **1** in 2 M HCl and in 2 M HPTS. For the

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EPR measurements they used the reaction product solution of $[Mo_3S_4(H_2O)_9]^{4+}$ with copper turnings in 2 M HCl and the solution obtained by elution of **1** with 2 M HPTS from a Dowex 50W-X2 cation exchange column loaded by the reaction products. They, however, did not report detailed analyses of the EPR spectra. In the present work, we observed EPR spectra from the HCl solution of **2**, which can be assigned to the single-cubane-type complex **1** formed by disintegration of **2**. We examined also PR of the ^{95}Mo-enriched complex for obtaining information of the molybdenum hyperfine couplings. In this paper, we present analyses of the EPR spectra and discuss the electronic structure of the single-cubane-type complex **1** based on EPR analyses and Hückel MO calculations.[9]

Experimental Section

Preparation of Complexes. The double-cubane-type complex **2** was synthesized under nitrogen gas atmosphere according to the previous paper.[5] For EPR analyses, 95% ^{95}Mo enriched complex, **2′**, was also synthesized.

EPR Measurements. EPR measurements were performed for neat crystal powders of **2** and 1 M HCl frozen solutions of **2** and **2′**. The crystal powders and the 1 M HCl solutions were sealed in EPR tubes under nitrogen gas atmosphere. EPR spectra were recorded with a JEOL JES-FE2XG X-band spectrometer at 77 K to room temperature and with a Varian E 112 X-band spectrometer at 10−77 K. The temperatures were controlled with an Oxford ESR 9 helium gas flow cryostat for measurements at 10−77 K and with a nitrogen gas flow variable temperature accessory for measurements at 100 K to room temperature. The measurements at 77 K were performed by using a liquid nitrogen dewar. The HCl solution was frozen as fast as possible but carefully to make a glass by liquid nitrogen before insertion into the cold cryostat. The spin concentration responsible for the EPR signal was measured by comparing the integrated intensity of the observed spectrum with that for a known amount of $CuSO_4{\cdot}5H_2O$ crystal powders, which were freshly obtained by recrystallization, to confirm whether the EPR signal really comes from the disintegrated species of **2** or not.

Extended Hückel MO Calculations. Extend Hückel MO (EHMO) calculations were executed for model complexes of **1**. Atomic integral parameters needed for the calculations were taken from literature.[10] As there are no X-ray crystallographic data on **1**, the MO calculations were executed for different core structures with reference to the X-ray crystallographic data on the double-cubane-type complex **2**.[5]

Results

Any EPR spectrum attributable to the complex **2** could not be detected for neat crystal powders of **2** at temperatures from room temperature to 77 K. On the other hand, EPR spectra were observed for the frozen 1 M HCl solutions of **2** and of ^{95}Mo-enriched complex **2′** as shown in Figure 2. The spectrum observed for **2** in 1 M HCl accompanies weak satellites, while the spectrum for **2′** in HCl shows a complicated hyperfine structure which can be attributed to additional splittings by a hyperfine coupling with the enriched ^{95}Mo. No appreciable changes in the hyperfine pattern with temperature were found for the frozen HCl solution of **2** and **2′** except for line width changes. The spin concentration of the sample solution determined from the integrated spectral intensity was in the range of 160−210% of the concentration of **2** in solution, which corresponds to the concentration expected for the species produced by disintegration of **2**.

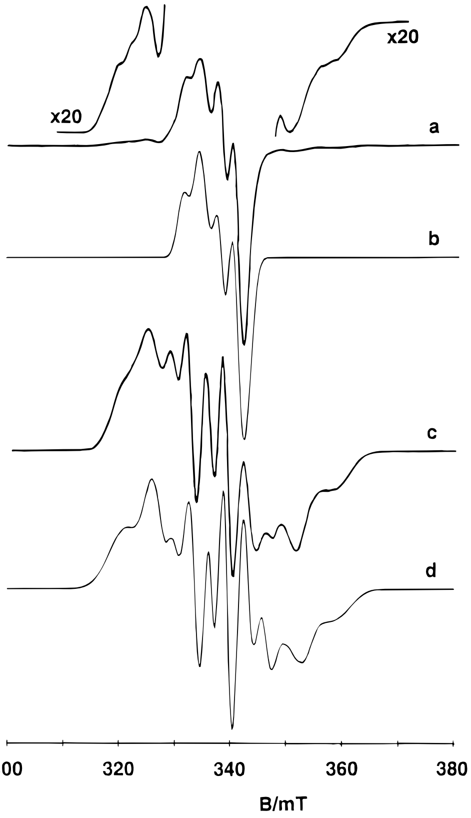

Figure 2. X-band EPR spectra of (a) the complex **1** and (c) the ^{95}Mo-enriched comples **1′** and their computer simulation (b and d, respectively). The used parameters for the computer simulation are listed in Table 1. Spectrum a: microwave frequency, 9.1638 GHz; microwave power, 5 mW; field modulation, 100 kHz and 5 G; temperature, 77 K. Spectrum c: microwave frequency, 9.1727 GHz; microwave power, 0.05 mW; field modulation, 100 kHz and 10 G; temperature, 14.8 K.

Discussion

Identification of the Observed Paramagnetic Species. It has been shown that $[Mo_3S_4(H_2O)_9]^{4+}$ reacts with some metals or metal ions to form heterometallic incorporated adducts with Mo_3MS_4 cores. Reactions of $[Mo_3S_4(H_2O)_9]^{4+}$ with copper in 1 M HCl give a mixed-metal complex ion. On the basis of elution behavior of the complex ion from the cation exchange resin Dowex 50W-X2, UX−visible absorption spectroscopy, and stoichiometric analyses, the complex ion was assigned to $[Mo_3CuS_4(H_2O)_{10}]^{4+}$. This mixed-metal complex ion crystallizes from 4 M HPTS solution as a double-cubane-type complex **2**.[5,6,8]

On the other hand, the double-cubane-type complex **2** dissolved in HCl or in HPTS shows UV−visible absorption spectra having almost the same spectral pattern as those observed for **1** in the respective solvents. The complex **2** shows also the same elution behavior as that observed for **1** when **2** is eluted with HCl; the elution occurs earlier than that for $[Mo_3S_4(H_2O)_9]^{4+}$. Though the charge of a metal ion cannot be solely determined by its ion exchange behavior, definite distinction may be possible between 4+ and 8+ charges of a transition metal ion by comparing its elution behavior with that for related ions of known charges. The elution behavior of **2** in HCl strongly suggests disintegration of the double-cubane-type complex with an 8+ charge to the single-cubane-type complex with some Cl^- complexing.

The EPR spectral pattern observed for the complex **2** in HCl in the present work is the same as that attributed to **1** by

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Table 1. EPR Parameters for $[Mo_3CuS_4]^{4+\,a}$

	principal values		
	x	y	z
g	1.923	1.940	1.948
A(Cu)/MHz	48	51	87
$A(Mo_1)$/MHz[b]	195	90	80

[a] The parameters were determined by computer simulation of the spectra under the assumption that all the parameters are coaxial. In the calculation, the line width broadening effects expressed by the $\Gamma = \Gamma_a + \Gamma_b m_I + \Gamma_c m_I^2$ were taken into account. The values of Γ_a, Γ_b, and Γ_c were determined to be 32, 8, and 12 kHz, respectively, in the process of simulation calculation. [b] Only one molybdenum nucleus is contributing to the hyperfine splittings.

Narseldin et al.,[8] except for the satellite signals which are clearly observed in the present work. The satellite signals can be assigned to the hyperfine couplings with the magnetic nuclei ^{95}Mo ($I = {}^5/_2$, $\mu(^{95}\mathrm{Mo}) = -0.9134\ \mu_N$) and ^{97}Mo ($I = {}^5/_2$, $\mu(^{97}\mathrm{Mo}) = -0.9326\ \mu_N$) contained in natural abundance (^{95}Mo, 15.8%; ^{97}Mo, 9.5%). The spin concentration responsible for the EPR spectrum in the present system is nearly the same as that expected for the disintegrated species from **2** in solution. These facts apparently indicate that the EPR spectra observed in this work can be assigned to the single-cubane-type complex **1** which is generated by disintegration of the double-cubane-type complex **2**.

Analyses of EPR Spectra. The four-line EPR pattern for **1** (Figure 2a) is explained by the hyperfine splitting by interaction with a nuclear spin of $I = {}^3/_2$, i.e., the interaction with copper. The ^{95}Mo-enriched complex of **1** shows a more complicated hyperfine pattern, and it can be analyzed by hyperfine interactions with both ^{95}Mo and copper. The satellite signals observed for the spectrum with the four-line pattern for **1** are attributed to the signals arising from the complex containing the magnetic nucleus ^{95}Mo or ^{97}Mo. EPR parameters were determined by computer simulation of the spectra of the ^{95}Mo-enriched and -unenriched complexes (Figure 2), and they are listed in Table 1. It should be noted that the molybdenum hyperfine splittings are not due to interactions with the three molybdenum nuclei but due to interaction with only one molybdenum nucleus. The observed EPR spectra and the calculated ones overlap relatively well. It is also noticed that the satisfactory overlap could be attained only when a line width broadening effect which is dependent on the magnetic quantum number of ^{95}Mo was taken into account (vide infra). The EPR spectral data including the g values indicate that the $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ core is paramagnetic with $S = {}^1/_2$. On the other hand, the double-cubane-type complex **2** was EPR silent, indicating that there may be an antiferromagnetic exchange interaction between the two $[Mo_3CuS_4(H_2O)_9]^{4+}$ cores through the bonds in **2**.[11]

As Table 1 shows, the observed copper hyperfine coupling is much smaller than that of ordinary copper(II) complexes; it is about ${}^1/_4$–${}^1/_6$ of that of ordinary copper(II) complexes. Such a small copper hyperfine coupling indicates that there is little unpaired electron density on copper, i.e., the copper ion may be close to Cu(I) rather than Cu(II). The XPS data of **2** indicate that copper in the double-cubane-type complex has a d^{10} electronic configuration,[5] indicating that the situation of copper in the double-cubane-type complex **2** is conserved for disintegration of **2** into the single-cubane-type complex **1**; the disintegration would occur by dissociation of the Cu–S bonds connecting between the two cubane cores without changes in the valence states of copper and sulfur, followed by complexing of H_2O or Cl^- to the dissociation sites. The EPR spectra for the 2 M HCl solution of **1** observed in the present work and by Narseldin et al.[8] are almost coincident with the spectrum in 2 M HPTS, indicating that replacement of some of the coordinating water molecules to the chloride ions would not affect the EPR spectrum so much; the complexing of the chloride ion does not appreciably affect the spin state in the complex core.

The EPR spectral pattern at both the high-field and the low-field edges for the ^{95}Mo-enriched complex (Figure 2c) is nearly the same as that of the satellite signals (Figure 2a) due to the hyperfine interactions with the ^{95,97}Mo nuclei in natural abundance. Since the natural abundance of ^{95}Mo and ^{97}Mo is 15.4% and 7.6%, respectively, the observed satellite signals for the ^{95}Mo-unenriched sample can be assigned to those coming from the species containing a single ^{95}Mo or ^{97}Mo nucleus. Therefore, the coincidence of the satellite pattern with the hyperfine structure of the ^{95}Mo-enriched complex means that the molybdenum hyperfine splitting in the ^{95}Mo-enriched complex comes from the interaction with a single molybdenum nucleus among the three molybdenum nuclei. This is well consistent with the result for the spectral simulation mentioned above. These indicate that the unpaired electron is not delocalized over the three molybdenum ions but mainly populated on a specific molybdenum ion; the three molybdenum ions in $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ are not equivalent to each other. The three molybdenum ions do not have an average charge of +3.67, but they must be close to the states of Mo(III), Mo(IV), and Mo(IV), respectively, the paramagnetic site being on Mo(III).

Spin-Coupling Schemes. It has been shown above that the copper ion is close to Cu(I) rather than Cu(II), i.e., it has a d^{10} diamagnetic configuration. However, there is no information about the spin state of the molybdenum ions in such cluster systems, though some Mo(IV) complexes are known to be diamagnetic. In this section we consider the spin-coupling schemes in **1** to give a total spin of $S = {}^1/_2$ and to show the hyperfine coupling due to a single molybdenum nucleus based on the so-called spin vector model.

According to the spin vector model under an assumption of no hopping of spins among the metal sites,[12] the hyperfine coupling of the ith molybdenum ion and the g value are expressed as

$$A^{\mathrm{exp}}(\mathrm{Mo}_i) = K(\mathrm{Mo}_i)\, d_{\mathrm{B}}(\mathrm{Mo}_i)\, a(\mathrm{Mo}_i) \tag{1}$$

$$g = \sum_i K(\mathrm{Mo}_i) g_i \tag{2}$$

In the equations, $K(\mathrm{Mo}_i)$ is a spin projection factor, given by eq 3; $d_{\mathrm{B}}(\mathrm{Mo}_i)$ a covalency factor relating to spin delocalization from the paramagnetic center (molybdenum ion) to the ligands; $a(\mathrm{Mo}_i)$ the intrinsic hyperfine coupling constant of the ith molybdenum ion; and g_i the contribution of the ith molybdenum ion to the observed g factor, respectively

$$K(\mathrm{Mo}_i) = \langle \mathbf{S}(\mathrm{Mo}_i)\cdot\mathbf{S}_t \rangle / [S_t(S_t + 1)] \tag{3}$$

In view of the fact that wo Mo(IV) ions are considered to be in the same structural circumstance, which would be conserved

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(11) The μ_{eff} value reported in ref 4 should be revised as 0.48 μ_B, which was newly obtained. Correction of the diamagnetic contribution to the experimental magnetic susceptibility data was made by Pascal's rule (Gupta, R. R. In *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, New Series II/**16**; Hellewege, K.-H., Hellewege, A. M., Eds.; Springer-Verlag, Berlin, 1986).

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from that of **2**, it is likely to consider that they must be in the same spin state. In the following, we pick up only the cases where the two Mo(IV) ions are equivalent to each other. Firstly (case 1), one assumes that Mo(III) is in $S_1 = {}^3/_2$ and two $Mo_{2,3}$(IV) are in $S_2 = S_3 = 1$. The two $Mo_{2,3}$(IV) ions constitute a pair, and they ferromagnetically couple with each other. The pair further couples antiferromagnetically with Mo_1(III) to give $S_t = {}^1/_2$. Secondly (case 2), one assumes that Mo_1(III) is in $S_1 = {}^1/_2$, while two $Mo_{2,3}$(IV) are in $S_2 = S_3 = 1$, which antiferromagnetically couple with each other to give $S_{2+3} = 0$. The total spin S_t hence becomes ${}^1/_2$. Thirdly (case 3), two $Mo_{2,3}$(IV) are in the low-spin state $S_2 = S_3 = 0$ and Mo_1(III) is in $S_1 = {}^1/_2$, giving $S_t = {}^1/_2$.

In these spin-coupled schemes, case 1 gives $K(Mo_1(III)) = -1$ and $K(Mo_2(IV)) = K(Mo_3(IV)) = 1$, and cases 2 and 3 give $K(Mo_1(III)) = 1$ and $K(Mo_2(IV)) = K(Mo_3(IV)) = 0$. Hence, in case 1 the three molybdenum ions should contribute to the hyperfine splittings, while in cases 2 and 3 only Mo(III) contributes to the hyperfine splittings. Case 1 is apparently inconsistent with the experimental observation showing the hyperfine splitting due to a single molybdenum nucleus. Cases 2 and 3 are consistent with the experimental results. However, there is no information from EPR to distinguish cases 2 and 3, but we can say at least on the spin state that the two Mo(IV) ions must be $S_{2+3} = 0$ as a pair and only the Mo(III) ion contributes to the hyperfine splitting.

Spin Density on the Molybdenum Ion and *g* Factor. In the spin vector model, the spin density on the *i*th molybdenum ion is given by $K(Mo_i)\ d_B(Mo_i)$ in eq 1. We have shown above that the spin projection factor must be $K(Mo_1(III)) = 1$ and $K(Mo_2(IV)) = K(Mo_3(IV)) = 0$. We attempt to estimate the delocalization factor d_B for Mo(III) as well as spin distributions on the Mo(III) d and s orbitals. We divide the observed molybdenum hyperfine coupling constants to anisotropic and isotropic parts as $A(Mo)_{aniso1} = 73$ MHz and $A(Mo)_{iso} = 122$ MHz. Since the anisotropic and the isotropic parts can be regarded as coming from hyperfine interactions with the spin on the molybdenum 4d and 5s orbitals, respectively, spin densities on the molybdenum 4d and 5s orbitals are evaluated to be 73/86.1 = 0.85 and 122/1984 = 0.061, respectively, by using the intrinsic coupling parameters, a(Mo,4d) = 86.1 MHz and a(Mo,5s) = 1984 MHz, taken from literature.[13] Hence, the total spin density on Mo(III) and the delocalization factor d_B for Mo(III) become 0.91. If taking into account the fact that the spin is delocalized onto copper and others as is shown by the copper hyperfine splitting, this spin density on Mo(III) may be a little high, but for a more reliable evaluation of the spin population, some elaborate corrections such as a correction for changes of the intrinsic coupling constants by formal charges may be needed.

It is clear from the $K(Mo_i)$ values that the observed g values are mainly contributed from the Mo(III) ion. Since the Mo(III) ion has d orbitals of which more than half are unoccupied, spin excitation rather than hole excitation must make dominant contribution to the g shift. The observed negative g shift from the free spin value (2.0023) (Table 1) is, therefore, consistent with the fact that the Mo(III) ion is making a main contribution to the g factor in $[Mo_3Cu_4(H_2O)_{10}]^{4+}$. Such negative g shifts have also been observed for many single nuclear molybdenum complexes.[14]

EHMO Calculations for the Complex 1. The spin vector model used for the above discussion is based on the valence-bond-like description. In the actual case, however, the spins are expected to be delocalized on the neighbor ligand atoms or further to the other metal sites by overlaps of their orbital functions. In the extreme case, the spins on the molybdenum ions delocalize well over the cluster core according to the molecular orbital functions by the large orbital overlaps. In this case each metal ion contributes to the hyperfine splittings according to the molecular orbital function for the unpaired electron orbital. In this section we consider the electronic state of **1** in reference to the EHMO calculation.

The EHMO approximation is not necessarily powerful for systems where spin correlation or configuration interactions are important. However, this method will still be useful to get some insights on the electronic properties including nature of the molecular orbital functions or spin delocalization in the cluster. It is interesting to see the experimental data from the point of view of the MO theory.

Prior to showing the calculated result, we briefly present the MO scheme for the $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ core under the EHMO approximation.[15] Under the localized site symmetry at each metal nucleus, the nine valence orbitals are constructed from five molybdenum 4d, one 5s, and three 5p basis functions for each molybdenum. Three of the nine localized molybdenum valence orbitals are used for the bonding with the three sulfurs, the next three are for the bonding with the three water molecules, and the remaining three participate in the metal−metal bondings. The water molecules and sulfurs with a −2 charge have a closed-shell electronic configuration. The copper atom also has a closed-shell electronic configuration as discussed above. Then, three of the four localized copper valence orbitals constructed from one copper 4s and three copper 4p orbitals are used for bonding with the three sulfur atoms, and the remaining one is for the bonding with one water molecule. After all, the nine valence orbitals and the seven valence electrons from the three molybdenum ions participate in the metal−metal bonding in the $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ core, and hence, one electron remains as an unpaired spin to give the paramagnetic properties of $S_t = {}^1/_2$.

The coordinates for the $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ core used in the calculations are constructed by referring to the X-ray analysis data for the double-cubane-type complex **2**.[5] The calculations have been made for four cases. In cases 1 and 2, all the Mo−Mo bonds were taken to have an equal distance, but in case 1 (denoted as FC in Figure 3), different atomic integral parameters were assigned to Mo(III) and Mo(IV), while in case 2 (denoted as C_{3v}), three molybdenum ions were treated as equivalent. In cases 3 and 4, the Mo(IV)−Mo(IV) bond was taken to be shorter (denoted as A) or longer (denoted as O) than the Mo(III)−Mo(IV) bonds in order to reflect the different valence states for one molybdenum from the other two.

The calculated results show that there are three closely situated orbitals as candidates for the highest occupied level. Their orbital functions are schematically drawn in Figure 4. The small changes of the cluster structure cause changes of the ordering among the three orbital levels. In cases 1 and 3, the MO function of type e(a′) becomes the half-filled orbital, and it results in the hyperfine structure to which one molybdenum ion (Mo(III)) largely contributes. These are consistent with the experimental observations. The structure used for case 3 seems to be reasonable from the viewpoint of the spin configuration of the scheme (2) in the vector model where the spins on the two Mo(IV) ions form a pair antiferromagnetically coupling. It may also be reasonable from the viewpoint that Mo(IV) has a shorter radius than that for Mo(III). The C_{3v} structure, in which

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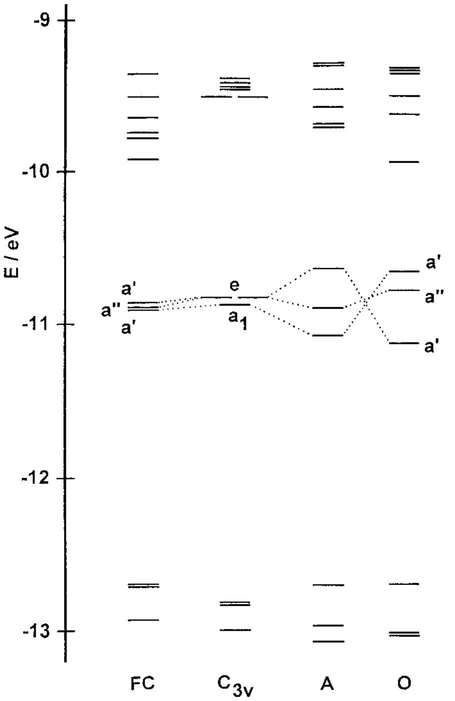

Figure 3. Orbital energy level diagram of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ core. FC: all Mo–Mo distances are taken to be equal, but three molybdenum ions have III, IV, and IV formal valence charges, respectively. C_{3v}: All Mo–Mo distances are taken to be equal and all molybdenum ions are treated as equivalent. A: The core structure is distorted so that three Mo atoms make an acute triangle. O: Three Mo atoms make an obtuse triangle.

the three molybdenum ions are equivalent, makes the e-symmetry orbitals the highest occupied orbitals, resulting in a degenerate ground state. It would lead to the Jahn–Teller distortion of the molecule. The calculation for case 4 using an obtuse triangle for the three-molybdenum framework gives the highest occupied level the $a_1(a')$ type orbital. This orbital has a large spin distribution on copper, and it is inconsistent with the observation. It is likely, therefore, that the cluster molecule is distorted such that the Mo(IV)–Mo(IV) bond is shorter than the Mo(III)–Mo(IV) bonds, as in case 3.

The features described by the MO method are common to those given by the spin vector model discussed in the previous section, and they are also consistent with the experimental observations. The calculated result by the MO method explains well that the unpaired spin responsible for the molybdenum hyperfine splitting is mainly localized on Mo(III) and the other two molybdenum ions do not contribute to the hyperfine couplings. Further, it explains that there is little unpaired spin density on copper.

Dynamics of the Unpaired Spin Site, Mo(III). It has been shown above that the unpaired spin site, Mo(III), is localized on one of the molybdenum atoms. If the spin site was rapidly jumping among the three molybdenum sites in the so-called EPR time scale, the EPR spectrum would show the hyperfine splittings due to the three molybdenum nuclei. However, presence of the observed line width broadening effect, which is dependent on the molybdenum nuclear quantum numbers, indicates that the Mo(III) site is not fixed at a specific position but it is moving among the three molybdenum ions at such a rate as to cause the so-called exchange-broadening effect on the molybdenum hyperfine components, i.e., at a rate of the order of 10^7 s^{-1}. It may accompany fluctuation of the cluster structure.

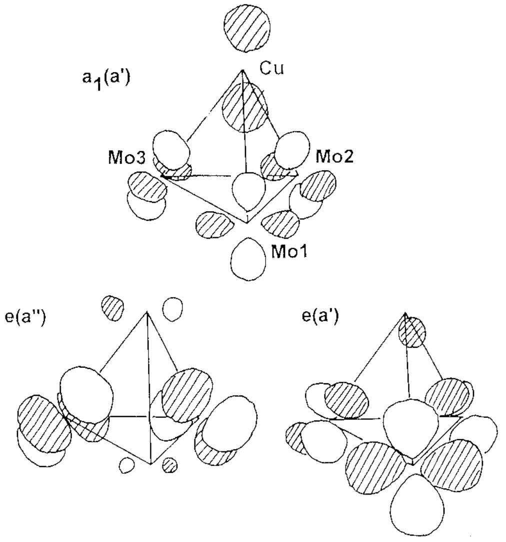

Figure 4. Schematic drawings of illustration of molecular orbitals of e (a′ and a″) and a_1(a′) under the C_{3v} symmetry.

Concluding Remark

On the basis of EPR analyses for ^{95}Mo-enriched and -unenriched complexes the electronic structure of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$, which is obtained by disintegration of the double-cubane-type complex $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9](CH_3{\cdot}C_6H_4SO_3)_8{\cdot}20H_2O$, was discussed. It was found that $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ is a paramagnetic species of $S = {}^1/_2$, and the single molybdenum ion, assigned to Mo(III), contributes to the hyperfine splitting. The Mo(III) site is jumping among the three molybdenum sites at such a rate as to cause the line width broadening in the molybdenum hyperfine components of the EPR spectrum. On the other hand, the copper ion is close to Cu(I) rather than Cu(II), and there is little spin density on it.

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