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Magnetic Properties of [μ-(Ethylenediaminetetraacetato)-di-μ-sulfido-bis{oxomolybdate(V)}]$^{2-}$ and [μ-(Ethylenediaminetetraacetato)-di-μ-oxo-bis{oxomolybdate(V)}]$^{2-}$ Ions

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Sodium [μ-(ethylenediaminetetraacetato)-di-μ-sulfido-bis{oxomolybdate(V)}]·n-hydrates, $n=2$ and 3, are antiferromagnetic dimers with an exchange interaction within a pair of Mo(V) ions of about $-140\,k$ having an averaged g-value of about 2 for each Mo(V) ion. In these salts, magnetic moments of only about 0.5 Bohr magneton are localized at Mo(V) sites, though Mo(V) has one electron in the 4d orbital. Here a π-bonding looped structure is considered to have a contribution to the diamagnetic susceptibilities of about -5.0×10^{-5} (CGSemu). Sodium [μ-(ethylenediaminetetraacetato)-di-μ-oxo-bis{oxomolybdate(V)}]·n-hydrates, $n=3$, 4, and 6, are the antiferromagnetic dimers with an exchange interaction within a pair of Mo(V) ions of about $-150\,k$ and an averaged g-value of 1.91. The magnetic moments of only about 0.5 Bohr magneton are localized at Mo(V) sites. In these salts, too, a π-bonding structure in each dimer is considered to make a contribution to the diamagnetic susceptibility of about -4.0×10^{-5} (CGSemu). A broad minimum of the molar magnetic susceptibility of [μ-(ethylenediaminetetraacetato)-di-μ-oxo-bis{oxomolybdate(V)}] salts was considered due to the conformation interconversion.

Polynuclear coordination complex compounds of early transition metals with bridges of sulfur between metal ions sometimes show unstable magnetic behaviours. Some compounds among them, for example, Xanthine Oxidase, are well known to have activities as enzymes.[1)]

$Na_2[Mo_2O_2S_2(cysteine)_2]\cdot4H_2O$[2)] and $Na_2[Mo_2O_2S_2(histidine)_2]\cdot H_2O$,[2)] which are Mo(V) dimers with disulfido bridges, and $[Mo_2O\{O_2(C_2H_5OCS_2)_2\}_2]$,[3)] which is a Mo(V) dimer with an oxygen bridge, have been reported to be diamagnetic in solid phase.

$(PyH)_4[Mo_2O_4(NCS)_4]$ has been reported to be paramagnetic with Bohr magneton numbers of 0.59 at 293 K and of 0.39 at 120 K. $Na_2[Mo_2O_4(edta)]\cdot4H_2O$ is also known to be paramagnetic at 293 K. Such paramagnetism with small Bohr magneton numbers was observed by Mitchell and Williams.[4)]

In the present paper, the magnetic properties of $Na_2[Mo_2O_2S_2(edta)]\cdot nH_2O$ ($n=2$ and 3) and $Na_2[Mo_2O_4(edta)]\cdot nH_2O$ ($n=3$, 4, and 6) are investigated as a first step to elucidate the complex activities of Mo(V) dimer structure in the many enzymes.[2)] The sexadentate ethylenediaminetetraacetate salts were chosen as the most strongly constructed dimers. The edta ligand coordinates to each molybdenum atom through two carboxylates and with one nitrogen. Mo(V) was chosen because it is in the simplest 4d^1 state.

Experimental

Chemicals. $Na_2[Mo_2O_2S_2(edta)]\cdot nH_2O$ ($n=2$ and 3) and $Na_2[Mo_2O_4(edta)]\cdot nH_2O$ ($n=3$, 4, and 6) were synthesized following Ott *et al.*,[5)] Spivack and Dori,[6)] and Pecsok and Sawyer.[7)] Numbers of crystalline waters were determined from the results of chemical analysis on C, H, and N, as shown in Table 1.

Measurements. The magnetic susceptibilities were measured by the Faraday method balance (Shimadzu MB-2) under about 6000 G** of applied field using the full scale 2 dyn range. An airtight sample cell was made of Teflon. As the measured amount of susceptibility was very small, the measurements of the empty cell were carefully done to assure the calibrations. As a standard of the magnetic susceptibility, $[Cr(NH_3)_6]Cl_3$ or NaCl was used.

Electron paramagnetic resonances were observed on powder samples by a JEOL PE-3X with a microwave oscillator ES-SCXA. Signals were found with 128 min/2000 G scanning under 10 G modulation at amplitude magnified by 1000. When the resonance was observed at low temperatures, DPPH packed in a thin Teflon tubing was put in the sample as reference.

Measurements of X-ray powder patterns and differential scanning calorimetry were made by usual methods.

Results and Discussion

Molar magnetic susceptibilities of $Na_2[Mo_2O_2S_2(edta)]\cdot nH_2O$, $n=2$ and 3, which were corrected for atomic diamagnetism using Pascal's law and did not need to be corrected for the temperature independent paramagnetism in view of the absence of absorption in the near infrared region, were less than 1.0×10^{-4} cm^3 (CGSemu) or 1.3×10^{-9} m^3 (SI) and showed a very broad maximum between liquid N_2 temperature and room temperature. The atomic diamagnetic susceptibilities of these salts are about -3×10^{-4} cm^3 (CGSemu) or -4×10^{-9} m^3 (SI) as shown in Table 2; therefore the magnetic susceptibilities characteristic of the magnetic dimers with antiferromagnetic mutual exchange interactions are submerged beneath the sea of the diamagnetism. But at room temperature, namely at higher temperature than that showing the broad maximum of the susceptibilities, electron paramagnetic resonances (X-band) were observed in each salt around 3000 G of the applied field: widths were 600—800 G, showing rapid spin lattice relaxations. Figure 1a shows the experimental molar magnetic susceptibility of $Na_2[Mo_2O_2S_2(edta)]\cdot2H_2O$ as a function of temperature. This curve is already corrected for atomic diamagnetic susceptibility of -2.99×10^{-4} cm^3

** 1 G$=10^{-4}$ T.

TABLE 1. ANALYTICAL DATA

Compound	Found(%)			Calcd(%)		
	C	H	N	C	H	N
$Na_2[Mo_2O_2S_2(edta)]\cdot 2H_2O$	17.95	2.52	4.38	18.2	2.45	4.26
$Na_2[Mo_2O_2S_2(edta)]\cdot 3H_2O$	17.59	2.60	4.19	17.8	2.68	4.14
$Na_2[Mo_2O_4(edta)]\cdot 3H_2O$	18.02	3.28	4.35	18.65	2.82	4.35
$Na_2[Mo_2O_4(edta)]\cdot 4H_2O$	17.71	3.14	4.21	18.14	3.04	4.23
$Ba[Mo_2O_4(edta)]\cdot 6H_2O$	15.79	2.62	3.69	15.86	3.19	3.70

TABLE 2. MOLAR MAGNETIC SUSCEPTIBILITIES, g-VALUES AND LATTICE CONSTANTS

	$Na_2[Mo_2O_2S_2$-(edta)]$\cdot 2H_2O$	$Na_2[Mo_2O_2S_2$-(edta)]$\cdot 3H_2O$	$Na_2[Mo_2O_4$-(edta)]$\cdot 3H_2O$	$Na_2[Mo_2O_4$-(edta)]$\cdot 4H_2O$	$Ba[Mo_2O_4$-(edta)]$\cdot 6H_2O$
χ'_M[a)] at 273.15 K/cm^3 (CGSemu)	8.4×10^{-5}	9.4×10^{-5}	1.8×10^{-5}	8.6×10^{-5}	6.4×10^{-5}
$\chi_{dia.\ atom.}$/cm^3 (CGSemu)	-29.9×10^{-5}	-31.2×10^{-5}	-26.0×10^{-5}	-27.3×10^{-5}	-31.3×10^{-5}
$\chi_{looped\text{-}bonding}$/cm^3 (CGSemu)	-5.0×10^{-5}	-5.0×10^{-5}	-4.0×10^{-5}	-4.0×10^{-5}	-4.0×10^{-5}
χ_M[b)] at 273.15 K/cm^3 (CGSemu)	13.4×10^{-5}	14.4×10^{-5}	5.8×10^{-5}	12.6×10^{-5}	10.4×10^{-5}
χ_M[b)] at 273.15 K/m^3 (SI)	1.68×10^{-9}	1.81×10^{-9}	7.29×10^{-10}	1.58×10^{-9}	1.31×10^{-9}
g-Values	$g_{av}=2$	$g_{av}=2$	$g_1=1.8700$ $g_2=1.9184$ $g_3=1.9328$	$g_1=1.8780$ $g_2=1.9170$ $g_3=1.9330$	
Orthorhombic lattice constants/Å	$a=27.838$ $b=6.948$ $c=22.668$	$a=27.534$ $b=6.905$ $c=23.264$	$a=12.815$ $b=6.130$ $c=19.478$	$a=12.834$ $b=6.109$ $c=19.288$	$a=14.129$ $b=6.497$ $c=23.860$

a) χ'_M: Experimental molar magnetic susceptibility which is corrected for atomic diamagnetism. b) χ_M: Molar magnetic susceptibility which is corrected for atomic diamagnetism and looped π-bonding diamagnetism.

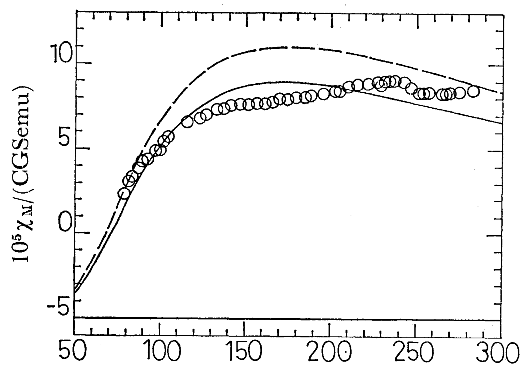
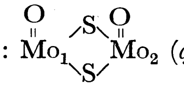


Fig. 1a. The molar magnetic susceptibility of $Na_2[Mo_2O_2S_2(edta)]\cdot 2H_2O$. ○: χ'_M that is the experimental molar magnetic susceptibility corrected for only atomic diamagnetism. ----: The calculated molar magnetic susceptibility of a dimer with $J_{12}=-140k$, $g=2$ and the effective Bohr magneton number $\mu_{eff}=0.56$ at 273.15 K. A base line of this curve is taken at -5.0×10^{-5} (CGSemu). ——: The calculated molar magnetic susceptibility of a dimer with $J_{12}=-140k$, $g=2$, and $\mu_{eff}=0.52$ at 273.15 K. Its base line is at -5.0×10^{-5} (CGSemu).

(CGSemu) or -3.76×10^{-9} m^3 (SI) following Pascal's law. A π-bonding looped structure may have an anisotropic diamagnetic susceptibility because the π-electrons can move along the looped structure when a magnetic field is applied. Lonsdale[8)] showed that the aromatic rings give rise to anisotropic diamagnetic susceptibilities. Namely, a looped π-bonding structure with an effective radius r has an anisotropic diamagnetic susceptibility of $\chi_{ring}=(-Ne^2/4mc^2)\sum_p r^2$, where N is the Avogadro number, p is the number of π-electrons in the π-bonding linkage and other symbols have the usual meanings. The unit of e is CGSesu and r is taken in Å. Following her method, the projections of the area of π-bonding looped structure of the Mo(V) dimers on the planes perpendicular to the external magnetic field directions were calculated in order to estimate the anisotropic diamagnetic susceptibilities. The following linkage was considered to be effective in the dimer:  $\overset{O}{\overset{\|}{Mo_1}}\overset{S}{\underset{S}{\rangle\langle}}\overset{O}{\overset{\|}{Mo_2}}$ (*cf.* Fig. 6. In the places of the oxygen double bridges in the figure, $[Mo_2O_2S_2(edta)]$ salts have double bridges of sulfur.) with effective area 4.96 Å^2 [6)] and 22 movable π-electrons, that is, three 4p electrons from each Mo(V)

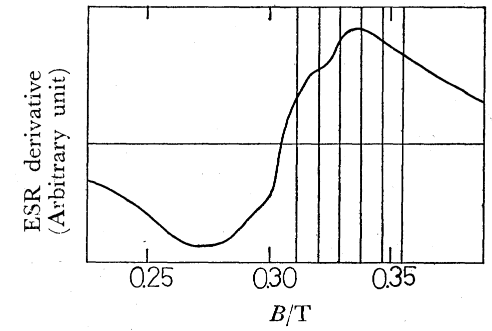


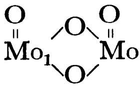
Fig. 1b. The ESR derivative curve of $Na_2[Mo_2O_2S_2(edta)]\cdot 2H_2O$ on powder. The ordinate is in an arbitrary unit. Six lines parallel to the ordinate show the hyperfine splittings of a Mn(II) salt.

ion whose ligands are a terminal O^{2-} ion, two s^{2-} ions, two O^- ions and a N atom, three 3p electrons from each bridging S^{2-}, and five 2p electrons from terminal O^{2-} ions were accounted for. The diamagnetic susceptibility estimated in this way is about $-5.0\times10^{-5}\,\mathrm{cm^3}$ (CGSemu) or $-6.3\times10^{-10}\,\mathrm{m^3}$ (SI). Setting this value as a new base line, a fit of the experimental magnetic susceptibility to the theoretical susceptibility of the dimer was investigated. If $\vec{S}_1$ and $\vec{S}_2$ denote the spin vectors of the two Mo(V) ions within a dimer and J_{12} the mutual exchange interaction between $\vec{S}_1$ and $\vec{S}_2$, the Hamiltonian $H=-2J_{12}\times(\vec{S}_1\cdot\vec{S}_2)^{9)}$ is taken to calculate the magnetic susceptibility. For the Mo(V) dimer, the molar magnetic susceptibility[1)] is

$$\chi_M=\frac{2N\beta^2}{kT}\frac{4}{3+\exp\left(\frac{-2J_{12}}{kT}\right)},\qquad(1)$$

where $g=2$ is used. β is the Bohr magneton, k is Boltzmann's constant and T is absolute temperature. In Fig. 1b an ESR derivative curve of $\mathrm{Na_2[Mo_2O_2S_2(edta)]\cdot 2H_2O}$ is shown to indicate $g_{av}=2$. The very broad absorption is characteristic of di-μ-sulfido ligands. A tolerable fit of the magnetic susceptibility was obtained if magnetic moments of 0.52 Bohr magneton are assumed to be localized at the Mo sites at 273.15 K, with $J_{12}=-140k$. If one 4d electron of $S=1/2$ is localized at each Mo(V) ion site, the effective Bohr magneton number at 273.15 K is about 0.94.

The molar magnetic susceptibility and ESR of $\mathrm{Na_2[Mo_2O_2S_2(edta)]\cdot 3H_2O}$ were similar to those of $\mathrm{Na_2[Mo_2O_2S_2(edta)]\cdot 2H_2O}$ but not completely the same. Therefore X-ray powder patterns were checked for both of $\mathrm{Na_2[Mo_2O_2S_2(edta)]}\cdot n\mathrm{H_2O}$, $n=2$ and 3. These could be assigned to the orthorhombic symmetry, like that of $\mathrm{Cs_2[Mo_2O_2S_2(edta)]\cdot 2H_2O}$ at room temperature. The lattice constants are shown in Table 2, which are near each other but not completely the same, corresponding to the experimental results of the magnetic susceptibilities and ESR.

The experimental molar magnetic susceptibilities of $\mathrm{Na_2[Mo_2O_4(edta)]}\cdot n\mathrm{H_2O}$ ($n=3$, 4, and 6) corrected for the atomic diamagnetism also were smaller than $1.0\times10^{-4}\,\mathrm{cm^3}$ (CGSemu) or $1.3\times10^{-9}\,\mathrm{m^3}$ (SI). The atomic diamagnetic susceptibilities are about $-3\times10^{-4}\,\mathrm{cm^3}$ (CGSemu) or $-4\times10^{-9}\,\mathrm{m^3}$ (SI); therefore, $\mathrm{Na_2[Mo_2O_4(edta)]}\cdot n\mathrm{H_2O}$ salts are seemingly diamagnetic. The molar magnetic susceptibility of $\mathrm{Na_2[Mo_2O_4(edta)]\cdot 4H_2O}$ is plotted in Fig. 2a. Between liquid N_2 temperature and room temperature, the susceptibility shows two broad maxima accompanied by a very broad minimum centerd about 180 K. As in the case of $\mathrm{Na_2[Mo_2O_2S_2(edta)]}\cdot n\mathrm{H_2O}$ salts, the diamagnetism due to the π-bonding looped structure in the Mo(V) dimer ion was estimated to be about $-4.0\times10^{-5}\,\mathrm{cm^3}$ (CGSemu) or $-5.0\times10^{-10}\,\mathrm{m^3}$ (SI), namely,  $\mathrm{O{=}Mo_1(\mu\text{-}O)_2Mo_2{=}O}$ (*cf.* Fig. 5) has an effective area of 3.71 Å^2 [10)] and the 22 π-electrons consist of three 4p electrons from each $\mathrm{Mo^{5+}}$ ion, three 2p electrons from each bridging O^{2-}, and five 2p electrons from each terminal O^{2-} ion. In Fig. 2b, the ESR of $\mathrm{Na_2[Mo_2O_4(edta)]\cdot 4H_2O}$ is shown. The signal was obtained by 64 min/1000 G scanning with amplitude magnified 1600 times. The best fit of the g-values to the experimental signals was a set of $g_1=1.8780$, $g_2=1.9170$, and $g_3=1.9330$, with a width of 8 G, neglecting the hyperfine structure which is seen in the ESR but is too weak to analyse by a simulation. It is certain that the spin-lattice relaxation times of di-μ-oxo-bis{oxomolybdate}salts are longer than those of di-μ-sulfido-bis-{oxomolybdate}salts. In Fig. 2a, the dashed line shows the curve of the theoretical magnetic susceptibility with $J_{12}=-150k$, $g_{av}=1.91$ and localized spins of about 0.53 Bohr magneton at 273.15 K and the solid line shows the curve with $J_{12}=-150k$, $g_{av}=1.91$ and localized magnetic moments of 0.51 Bohr magneton at 273.15 K. The base line of the theoretical curve is taken at $-4.0\times10^{-5}\,\mathrm{cm^3}$ (CGSemu) or $-5.0\times10^{-10}\,\mathrm{m^3}$ (SI). To see what is the anomalous temperature dependence of the magnetic susceptibility of this Mo(V) dimer, namely the broad minimum of the susceptibility ceterd at about 180 K, the temperature dependence of ESR was observed. As is shown in Fig. 3, no decrease of the ESR signal between 210 K and 150 K was observed. Therefore this anomalous temperature dependence of the magnetic susceptibility

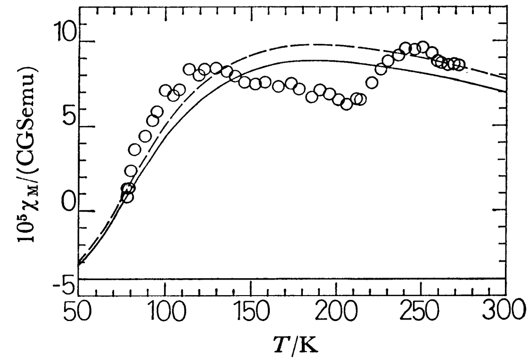


Fig. 2a. The molar magnetic susceptibility of $\mathrm{Na_2[Mo_2O_4(edta)]\cdot 4H_2O}$. ○: χ'_M, namely, the experimental molar magnetic susceptibility which is corrected for only atomic diamagnetism. ----: The calculated molar magnetic susceptibility of a dimer with $J_{12}=-150k$, $g=1.91$, and $\mu_{eff}=0.53$ at 273.15 K. ——: A dimer with $J_{12}=-150k$, $g=1.91$, and $\mu_{eff}=0.51$ at 273.15 K. The base line of the calculated curves is taken at -4.0×10^{-5} (CGSemu).

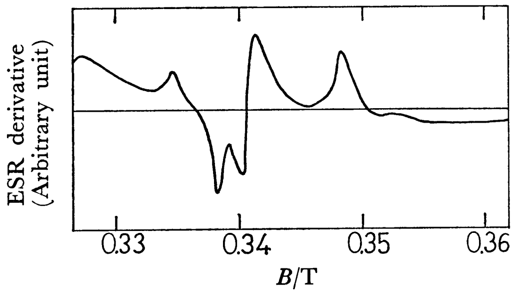


Fig. 2b. The ESR derivative curve of $\mathrm{Na_2[Mo_2O_4(edta)]\cdot 4H_2O}$ on powder. The ordinate is in an arbitrary unit.

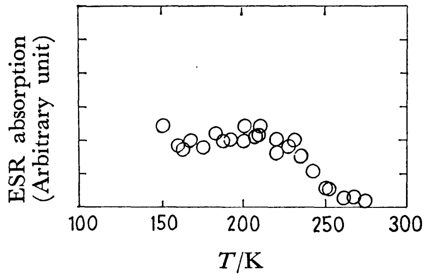


Fig. 3. The temperature dependence of the ESR absorption of $Na_2[Mo_2O_4(edta)]\cdot 4H_2O$ on powder.

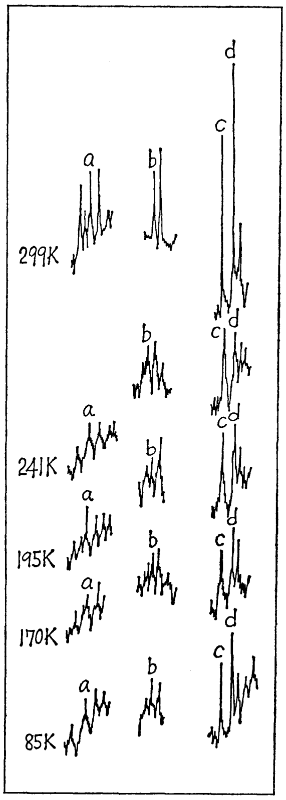


Fig. 4. Temperature dependence of some X-ray diffaction powder patterns. a: Atomic plane distance 3.789 Å, b: 4.822 Å, c: 5.724 Å, and d: 5.946 Å. All the signals were measured by same conditions. In the figure, patterns of each temperature are drawn from the same base line.

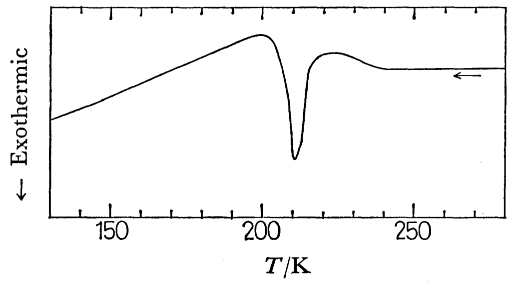


Fig. 5. The differential scanning calorimetry curve of $Na_2[Mo_2O_4(edta)]\cdot 3H_2O$. The graph shows that the sample releases heat in the region between 230 K and 190 K on cooling from room temperature to 130 K.

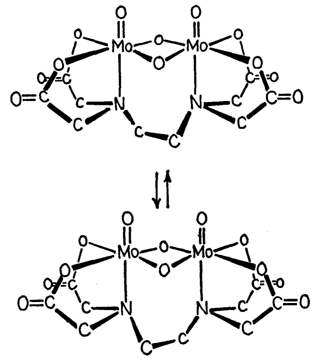


Fig. 6. The interconversion between two isomeric conformations of $[Mo_2O_4(edta)]$ anion.

is not due to the paramagnetic spins. Then the temperature dependence of the powder X-ray pattern was checked on $Na_2[Mo_2O_4(edta)]\cdot 3H_2O$. When the temperature was changed from 85 K to 299 K, the atomic plane distances did not change but widths and intensities of some lines changed, that is, the widths of the lines of atomic plane distances of 5.946 Å, 5.724 Å, 4.822 Å, and 3.789 Å were broader around 190 K than those of lower and higher temperatures, as shown in Fig. 4. The temperature dependence of the X-ray diffraction intensities was considered due to dynamic vibrations of a conformation, as will be shown below. Differential scanning calorimetries were observed for $Na_2[Mo_2O_4(edta)]\cdot 3H_2O$ and $Na_2[Mo_2O_2S_2(edta)]\cdot 2H_2O$. The former (Fig. 5) showed an exothermic signal at temperatures between 190 K and 230 K in the measurement on cooling from room temperature to 130 K, but the latter showed nothing. It is known from the measurement of ^{13}C NMR[11] that $[Mo_2O_4(edta)]^{2-}$ ion in the aqueous solution has a conformation interconversion. According to Blackmer *et al.*, the ethylene diamine backbone of edta chelate has an interconversion between the two isomeric forms, seen in Fig. 6, which is too rapid at 310 K to split the ^{13}C NMR of about 60 MHz, but at 273 K, the absorption line splits into two, that is, the relaxation time of each conformation becomes long enough to give the line splitting. They assigned a value of 0.5 to the transition coefficient k, since the ethylenediamine backbone of edta complex has an equal probability of returning to its original isomeric conformation or continuing the conversion process to achieve the other isomeric conformational form after reaching a planar intermediate. In the solid state of $[Mo_2O_4(edta)]^{2-}$ complex in a pressed cell, the interconversion has been considered to happen over a broad temperature region from 190 K to 230 K, centerd about 210 K. It is said by X-ray analysis[6] that at room temperature, $[Mo_2O_4(edta)]$ salts have two isomeric conformations with equal probability of the ethylenediamine backbone of edta. The crystal would transform from a higher temperature state to a preferred lower temperature form of the ethylenediamine by the interconversion in the broad temperature region. The interconversion of edta is considered to produce a change of the diamagnetic susceptibility due to the π-bonding

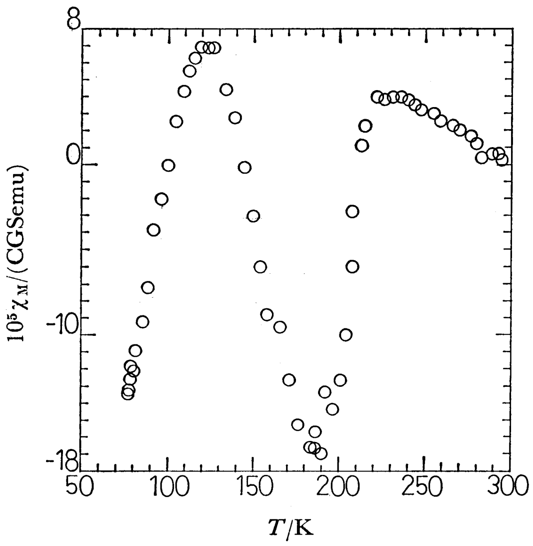
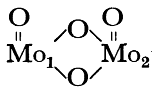


Fig. 7. The molar magnetic susceptibility of $Na_2[Mo_2O_4(edta)]\cdot 3H_2O$ corrected for only atomic diamagnetism as a function of temperature.

looped  structure, though it is not elucidated yet that the change of the diamagnetic susceptibility is caused by the change of the number of the movable electrons or the change of the effective area of the π-bonding looped structure. Now, though we explained the magnetic susceptibility data of $Na_2[Mo_2O_2S_2(edta)]\cdot nH_2O$ by a simple dimer model, the fit with the theoretical curve was never satisfactory. There may be an interconversion between the two forms of the ethylenediamine of edta in di-μ-sulfido-bis{oxomolybdate(V)} ion and it would make the fit poor. But much less energy would be needed for the interconversion because the distances between two Mo(V) ions and two N atoms in the edta in di-μ-sulfido-bis{oxomolybdate} ion are longer than those of di-μ-oxo-bis{oxomolybdate} ion. Thus the difference of the two forms of the ethylenediamine is so small that the DSC signal could not be observed.

We would like to remark on a datum of the molar magnetic susceptibility of $Na_2[Mo_2O_4(edta)]\cdot 3H_2O$, which showed a much smaller magnetic susceptibility, as shown in Fig. 7, than those of $Na_2[Mo_2O_4(edta)]\cdot 4H_2O$ and $Ba[Mo_2O_4(edta)]\cdot 6H_2O$ though its temperature dependence is similar to them. This phenomenon suggests this salt may be trapping some extra even number of electrons in the π-bonding looped structure.

The experimental results show that the complete determination of the diamagnetic susceptibility on a molecule with π-bonding looped structure is necessary. Of course, the molecular orbitals of many polycyclic aromatic hydrocarbon compounds have been calculated and from their energy under an applied magnetic field anisotropic diamagnetic susceptibilities are obtained. But the molecular orbital calculations at present are possible to molecules with 40 atoms and 127 orbitals, therefore the complete calculation of the diamagnetic susceptibilities for molecules containing 4d transition metals with π-bonding looped structure which have more than 200 orbitals may not be possible in the near future. We are going to elucidate the diamagnetic susceptibilities of 4d transition metal coordination compounds with π-bonding looped structures by the observation of the non-magnetic 4d transition metal coordination compound molecules with π-bonding looped structures.

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References

1) E. I. Stiefel, "Proceedings of the Inorganic Chemistry," An Interscience Publication, John Wiley and Sons, New York (1977), Vol. 22.

2) B. Spivack and Z. Dori, *J. Chem. Soc., D*, **1970**, 1716.

3) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).

4) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, **1962**, 4570.

5) V. R. Ott, D. S. Swieter, and F. A. Schultz, *Inorg. Chem.*, **16**, 2538 (1977).

6) B. Spivack and Z. Dori, *J. Chem. Soc., Dalton Trans.*, **1973**, 1173.

7) R. L. Pecsok and D. T. Sawyer, *J. Am. Chem. Soc.*, **78**, 5496 (1956)

8) K. Lonsdale, *Proc. R. Soc. London, Ser. A*, **159**, 149 (1936).

9) K. Kambe, *J. Phys. Soc. Jpn.*, **5**, 48 (1950).

10) F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, **4**, 1377 (1965).

11) G. L. Blackmer, K. J. Johnson, and R. L. Roberts, *Inorg. Chem.*, **15**, 596 (1976).