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Magnetic Properties of Molybdenum(IV) Trinuclear Coordination Compounds, Ba[$Mo_3O_3S(Hnta)_3$]·$10H_2O$ and $Ca_{1.5}$[$Mo_3S_4(Hnta)_2(nta)$]·$12H_2O$

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The magnetic susceptibilities of two molybdenum(IV) trinuclear coordination compounds with cores [$Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3$] and [$Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$] were measured in the temperature region from liquid He to room temperature. They had some extra diamagnetic susceptibilities in addition to the calculated values which have been discussed in anticipation of mesoscopic electronic devices.

Diamagnetism of capped and edge-bridged triangular trinuclear clusters of molybdenum(IV) are discussed in relation to Ba[$Mo_3O_3S(Hnta)_3$]·$10H_2O$(H_3nta: nitrilotriacetic acid)(**1**) and $Ca_{1.5}$[$Mo_3S_4(Hnta)_2(nta)$]·$12H_2O$ (**2**), which are incomplete cubane-type clusters. Sample **1** has a core of [$Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3$]$^{4+}$ and **2** that of [$Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$]$^{4+}$. These coordination compounds, which have no magnetic ions, have some characteristics common to the superatom,[1] which is one of the mesoscopic systems.[2]

Experimental

Sample **1**[3] was prepared from Mg[$Mo_2O_3S(edta)$]·$6H_2O$ (edta: ethylenediaminetetraacetate(4−) anion),[4] which was a dimer of molybdenum(V) with a core of [$Mo_2(\mu\text{-}O)(\mu\text{-}S)$]. Sample **2**[5] was synthesized from Na_2[$Mo_2O_2S_2(cys)_2$]·$4H_2O$ (cys:cysteine(2−) anion),[4] which was also a dimer of molybdenum(V) with a core of [$Mo_2(\mu\text{-}S)_2$]. The complex anions of **1** and **2** are compared in Figs. 1 and 2 (quoted from Refs. 5 and 3).

The magnetic susceptibilities of powder samples of **1** and **2** were measured in the temperature region from about 2 K to room temperature by a magnetic balance (Oxford Instruments) while using the Faraday method,[6,7] at the Institute for Solid State Physics, the University of Tokyo. In this method a magnetic field of constant strength of 5000 Oe is applied with a homogeneous gradient of 500 Oe cm^{-1}. The powder sample was put into a quartz cell together with a minimum amount of liquid paraffin of special grade, sufficient to cover the powder sample in order to prevent the water content from changing. A thermometer was fixed to the cryostat wall. Its indication was corrected by the magnetic susceptibilities of a paramagnetic [$Cr(NH_3)_6$]Cl_3 measured in the same temperature range during measurements of the samples. For each measurement the sample cell site in the cryostat was checked, as well as the pressure of the heat exchange He gas and the time schedules of the temperature variation to get precise magnetic susceptibilities. Electron spin resonance attempted on powder samples **1** and **2** at room temperature gave no signal of paramagnetic complex ions. The absorption spectra of samples **1** and **2** showed no absorption peak near the infrared region.

In the description of the present work, units of CGSemu nonrationalized system are used, which are listed in Ref. 8 with their conversions.

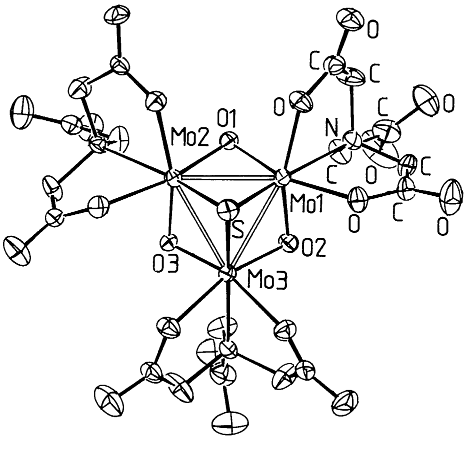

Fig. 1. [$Mo_3O_3S(Hnta)_3$]$^{2-}$ ion of sample **1** (Ref. 5). H atoms are not shown.

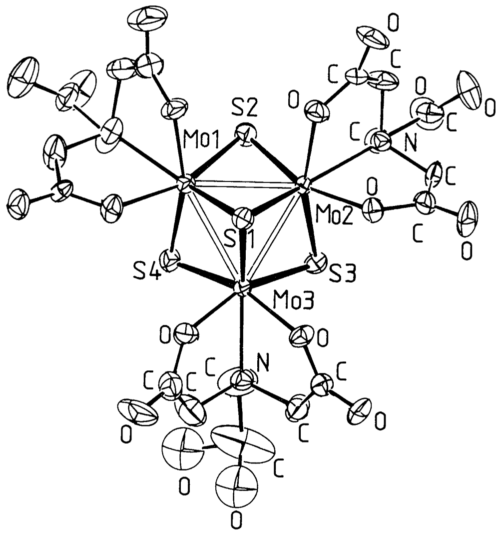

Fig. 2. [$Mo_3S_4(Hnta)_2(nta)$]$^{2-}$ ion of sample **2** (Ref. 3). H atoms are not shown. Oxygen atoms of the nta ligand coordinated to Mo3 are disordered.

Results and Discussion

The results of the magnetic susceptibilities are shown in Figs. 3 and 4, where no correction for diamagnetic susceptibilities has been applied. The main part of the data is in the diamagnetic region, except for data at very low temperatures, where the susceptibilities increased to the paramagnetic region. Since the molybdenum ions were chemically determined to be Mo(IV), samples **1** and **2** were considered to be diamagnetic salts containing some paramagnetic impurities. Fittings of the data to $\chi_M=(C/T)+\alpha$ gave for **1**, $\alpha=-0.578\times10^{-3}$ cm^3 and for **2**, $\alpha=-0.657\times10^{-3}$ cm^3. C of **1** was <0.00179 cm^3 K and C of **2** was <0.00115 cm^3 K. If the paramagnetic impurities are assumed to have $S=1/2$ and $g=2$, every 200 molecules of sample **1** and about 300 molecules of sample **2** carry one impurity. The molecular diamagnetic susceptibilities calculated by the Pascal–Pacault–Hoarau method[9] are -0.5119×10^{-3} cm^3 for **1** and -0.5856×10^{-3} cm^3 for **2**.

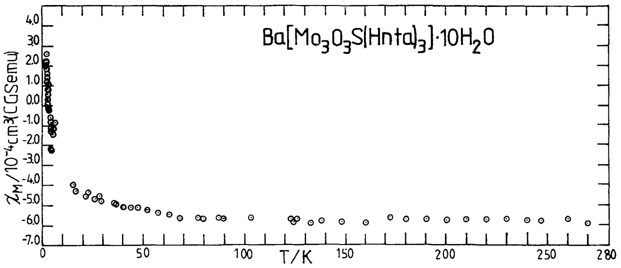

Fig. 3. Molar magnetic susceptibility of sample **1**, Ba[$Mo_3O_3S(Hnta)_3$]·$10H_2O$ as a function of temperature.

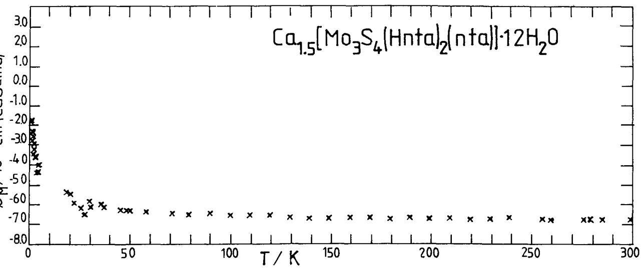

Fig. 4. Molar magnetic susceptibility of sample **2**, $Ca_{1.5}$[$Mo_3S_4(Hnta)_2(nta)$]·$12H_2O$ as a function of temperature.

The molybdenum(IV) ion has a temperature-independent paramagnetic susceptibility, χ_{TIP}, due to spin-orbit coupling, if it takes the $^3T_{1g}$ term. MoO_2, which is considered to be an oxide of Mo(IV), has a χ_{TIP} of 0.33×10^{-6} CGSemu per gram (0.0422×10^{-3} cm^3 per mole).[10] The Mo ion in the MoO_2 forms an MoO_6 octahedra, but in the chain of the MoO_6's Mo ions are alternately nearer to and farther from each other. The dimeric state, in which the nearer Mo–Mo distance is 2.50 Å and farther distance is 3.10 Å, indicates the presence of a direct bond between the Mo atoms, a situation that is very similar to the metal–metal bonds in samples **1** and **2**. Using this value of the temperature-independent paramagnetic susceptibility for samples **1** and **2**, their χ_{TIP} of 0.127×10^{-3} cm^3 was assumed. Then, sample **1** has an extra molar diamagnetic susceptibility of -0.193×10^{-3} cm^3 and **2** has that of -0.198×10^{-3} cm^3. Sample **1** shows absorptions at ca. 530 nm ($\varepsilon=352$ M^{-1} cm^{-1}) and ca. 330 nm ($\varepsilon=1830$ M^{-1} cm^{-1}), and **2** at ca. 620 nm ($\varepsilon=350$ M^{-1} cm^{-1}) and 370 nm ($\varepsilon=5200$ M^{-1} cm^{-1}), respectively. If these are assumed to be due to spin-orbit interactions and the parameters obtained from the lowest absorptions, 18870 cm^{-1} and 16130 cm^{-1}, are used into Figgis's formula[11] for the magnetic susceptibility of the d^2 configuration in $^3T_{1g}$, the temperature-independent parts of the magnetic susceptibilities become 0.114×10^{-3} cm^3 and 0.129×10^{-3} cm^3, respectively, which are near to the χ_{TIP} obtained from

Table 1. Some Averaged Interatomic Distances in the Capped and Edge-Bridged Triangular Trinuclear Complex Ions of Molybdenum

Complex ions	Mo-Mo	Mo-(μ_3-L)	[L]	Mo-(μ-L)	[L]	Ref.
	Å	Å		Å		
a) [$Mo_3O_4(C_2O_4)_3(H_2O)_3$]$^{2-}$	2.486	2.019	O	1.921	O	12
b) [$Mo_3O_4\{(O_2CCH_2)_2NCH_3\}_3$]$^{2-}$	2.495	2.043	O	1.918	O	13
c) [$Mo_3O_4F_9$]$^{5-}$	2.505	2.032	O	1.920	O	14
d) [$Mo_6O_8(EDTA)_3$]$^{4-}$	2.504	2.038	O	1.926	O	15
	2.508	2.045	O	1.915	O	
e) [$Mo_3O_3S(Hnta)_3$]$^{2-}$	2.589	2.360	S	1.917	O	3
f) [$Mo_3S_4(Hnta)_2(nta)$]$^{3-}$	2.750	2.332	S	2.286	S	5
g) [$Mo_3S_4\{HN(CH_2CO_2)_2\}_3$]$^{2-}$	2.754	2.349	S	2.295	S	16
h) [$Mo_3S_4(CN)_9$]$^{5-}$	2.765	2.363	S	2.312	S	17
i) [$Mo_3S_4(CN)_9$]$^{5-}$	2.773	2.361	S	2.322	S	18
j) [$Mo_3S_4(SCH_2CH_2S)_3$]$^{2-}$	2.783	2.345	S	2.293	S	19
k) [$Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2$]	2.766	2.355	S	2.288	S	20
l) [$Mo_3S_4Cl_4(PEt_3)_4(MeOH)$]	2.790	2.359	S	2.289	S	20
m) [$Mo_3S_4(h\text{-}C_5H_5)_3$]$^{+}$	2.812	2.314	S	2.293	S	21

MoO_2.

In Table 1, the interatomic distances in the capped and edge-bridged triangular trinuclear complex ions of Mo(IV) with cores of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3]$, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3]$, and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3]$ are shown. Müller et al.[22] gave a metal–metal bond length of 2.47—2.524 Å for Mo_3 clusters with a six-electron configuration with a coordination number 6 of simple donor ligands of each Mo ion. The averaged Mo–Mo interatomic distances of a), b), c), and d) of Table 1 is 2.500 Å, which is within the lengths given by Müller. Half of 2.500 Å is considered to be the radius of the Mo(IV) ion in the complex ions given in Table 1; then, the length of Mo–(μ-O) is the sum of the radii of a Mo(IV) ion and a $\mu\text{-}O^{2-}$ ion, the length of Mo–(μ_3-O) is the sum of the radii of a Mo(IV) ion and a $\mu_3\text{-}O^{2-}$ ion, the length of Mo–(μ-S) is the sum of the radii of a Mo(IV) ion and a $\mu\text{-}S^{2-}$ ion and the length of Mo–(μ_3-S) is the sum of the radii of a Mo(IV) ion and a $\mu_3\text{-}S^{2-}$ ion. The averaged values of radii were 1.25 Å for the Mo(IV) ion, 0.67 Å for the $\mu\text{-}O^{2-}$ ion, 0.79 Å for the $\mu_3\text{-}O^{2-}$ ion, 1.05 Å for the $\mu\text{-}S^{2-}$ ion, and 1.10 Å for the $\mu_3\text{-}S^{2-}$ ion, respectively, which are very near to the bond lengths of covalent or metallic bonds of each ion.[23] Using these radii, the cores of **1**, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3]^{4+}$, and **2**, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3]^{4+}$, are given in Figs. 5 and 6. Sample **1** has a ligand of three Hnta, where six oxygen atoms of the three Hnta take sites on the same side, with the capped sulfur ion to the plane made by three molybdenum ions; the three nitrogen atoms of the three Hnta take sites on the same side with the bridged oxygen ions to the plane made by the three molybdenum ions. Sample **2** has ligands of two Hnta and one nta. Their coordination to the molybdenum ions are similar to sample **1**.

Bursten et al.[24] observed the photoelectron spectra of triangular trinuclear coordination compounds Re_3Cl_9 and Re_3Br_9 and analized the spectra on the basis of the results of SCF-X-SW and Fenske–Hall molecular orbital calculations. Of course, these compounds are much different from samples **1** and **2** in the present paper, but Re_3Cl_9 and Re_3Br_9 have σ-type bonding between the Re metal ions of $5d^4$. Some figures of the

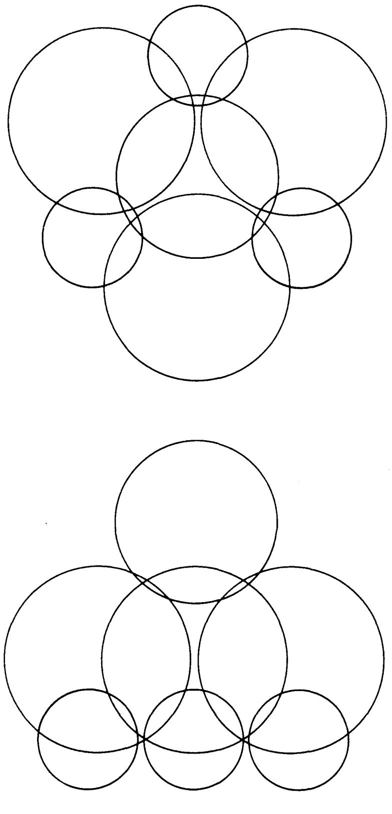

Fig. 5. $[Mo_3O_3S]^{4+}$ core of sample **1**, $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$. The upper figure is a projection to the Mo triangular plane and the lower one is drawn along an axis perpendicular to the Mo triangular plane. The largest circles are Mo^{4+} ions, the middle one is the $\mu_3\text{-}S^{2-}$ ion and the smallest ones are $\mu\text{-}O^{2-}$ ions. Radii are shown in the text.

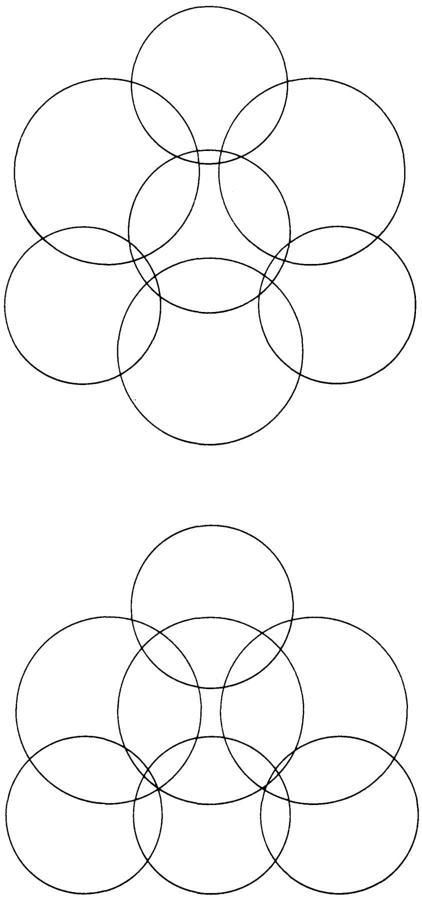

Fig. 6. $[Mo_3S_4]^{4+}$ core of sample **2**, $Ca_{1.5}[Mo_3S_4(Hnta)_2(nta)]\cdot 12H_2O$. The upper figure is a projection to the Mo triangular plane and the lower one is drawn along an axis perpendicular to the Mo triangular plane. The largest circles are Mo^{4+} ions, the middle one is $\mu_3\text{-}S^{2-}$ ion and the smallest ones are $\mu\text{-}S^{2-}$ ions. Radii are shown in the text.

electron density distribution in the planes made with triangle of three Re atoms show some linked electron contour distributions without using any node points of the wave functions. A similar electron distribution linked in each contour is shown in the case of $Ru_3(CO)_{12}$ by Delley et al.[25] These results cause us to imagine that when a magnetic field is applied in a direction perpendicular to the plane of a triangle, there will be a diamagnetic susceptibility due to the Larmor rotations of the electrons of each contour linked. Bursten et al.[26] examined the bondings in several structures of triangular trinuclear molybdenum(IV) cluster compounds. They proceeded considerations from the $[Mo_3]^{12+}$ core to a $[Mo_3O_2]^{8+}$ core, then to a $[Mo_3O_6]$ core. The first one is a "naked" triangle of three Mo^{4+} ions. The second one is a triangle of three Mo^{4+} ions with capped O^{2-} ions at both sides of the triangle plane. The third one is the triangle of three Mo^{4+} ions doubly bridged by O^{2-} ions between two Mo^{4+} ions. In the first one of D_{3h} symmetry, one 4dγ orbital and one 4dε orbital of each Mo^{4+} make bondings which link three Mo ions together into a triangle and six valence electrons are expected to occupy these orbitals resulting in a bond order of one between each pair of Mo ions. In the second one, the metal triangle framework was not significantly influenced by the capped ligands. The 4dγ orbitals, which were directed to the centre of the triangle in the first one, were strongly bonded with 2p orbitals of capped O^{2-} ions. The highest occupied Mo of the second one is not the antibonding orbital but, rather, the bonding which makes the bonding tight. Bursten et al. concluded that the capping oxygen atoms in $[Mo_3O_2]^{3+}$ were bound primarily through Mo–O covalent σ-interaction and only in a secondary was by π-donation from the oxygen atoms into empty metal–metal orbitals. In the third one, the presence of edge-bridging oxygen atoms did not cause the metal–metal bonding to rehybridize; however, strong covalent Mo–O bondings were found, as in second one. Then, Bursten et al. examined a $[Mo_3O_4]^{4+}$ core that comprised triangular three Mo^{4+} with a capped O^{2-} and three edge-bridged O^{2-}, compared with the abovementioned cores. The results are shown in the table of the Mulliken populations. Electron densities within the capped and bridged triangle were not significantly changed by other ligands. On the other hand the lower symmetry C_{3v} of $[Mo_3O_4]^{4+}$ than D_{3h}, which $[Mo_3O_2]^{8+}$ and $[Mo_3O_6]$ have, has brought strong mixing of edge bridging dε-type orbitals and increased the electron population to the capped oxygen orbitals of Mo ions. Let us return to Fig. 5. Sample **1** has a core of $[Mo_3O_3S]^{4+}$, which may be considered to be analogous to the $[Mo_3O_4]^{4+}$. Figure 5 makes us imagine the three Mo ions of the $[Mo_3O_3S]^{4+}$ would have a distribution of 4d electrons linked without any node within the triangular area and the capped S ion would supply more electrons to the linkage. The bridged three oxygens are tightly bonded to the Mo ions. They could have a linked electron distribution along the triangle, together with the Mo ions. In the core $[Mo_3S_4]^{4+}$ of sample **2** (Fig. 6) the bridged S ions seem to make the Mo–Mo direct bondings weaker than those in $[Mo_3O_3S]^{4+}$. The density of the electrons distributed in the parallel planes to the triangle may be smaller than that of the $[Mo_3O_3S]^{4+}$ core. If a magnetic field is applied in a direction perpendicular to the Mo triangle plane, those electrons making links without a node point will begin Larmor rotations and show some diamagnetism. As in the case of $[Mo_3O_4]^{4+}$, where there are strong bondings between the Mo ions, the capped ion and Mo ions and bridged ions and Mo ions, some electrons will be brought into the Larmor rotations. Following the results of Bursten et al., some electrons from the MO in Table IV of Ref. 26 could contribute to this extra diamagnetism. This anisotropic diamagnetism could be approximated by a magnetic susceptibility formula given by Lonsdale[27] for the aromatic rings, namely, $\chi_{\text{ring}}=(-Ne^2/4\,mC^2)\sum_p r^2$, where N is the Avogadro number, m is the electron mass (g), p is the number of rotating electrons, r is the distance of an electron from the centre of the molecule in cm and other symbols have their usual meanings. If in Fig. 5, a circular area with a diameter of about 2.2 Å (the diameter of the capped S^{2-} ion) is assumed to be an orbital area sufficient to produce an extra diamagnetic susceptibility of -0.193×10^{-3} cm^3 for **1**, the number of electrons participating in the Larmor rotations is about 9.4. If a similar consideration is made regarding sample **2**, the number of electrons participating in the Larmor rotations on a ring of diameter of about 2.2 Å, is about 9.6. Until the real number of electrons participating in the Larmor rotations could be known, the number of electrons which contribute to the extra diamagnetism caused by the Larmor rotations are only estimated numbers. This extra diamagnetism due to the Larmor rotations would mainly have arisen from the direct metal-metal bondings, which are remarkable in triangle 4d metal coordinated compounds with single-atom bridges.

Some magnetic polynuclear coordination compounds have been used as catalyzers[28] because they have more magnetic moments than monomer magnetic ions. Though the present trinuclear compounds are not magnetic, if they are compared with the mesoscopic superatoms, the capped ion size would determine the superatom's core diameter and number of electrons brought into the Larmor rotation would correspond to the number of donors modulation-doped into the superatoms. Diamagnetic polynuclaer coordination compounds can be designed in a manner similar to a superatom. Their crystal lattices would construct arrays of linked electron densities which would provide a step to using diamagnetic polynuclear coordination compounds in electronic devices, since they can rotate more electrons along the overlapped molecular orbitals without a node potential than a single ion of the same size.

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References

1) T. Inoshita, S. Ohnishi, and A. Oshiyama, *Phys. Rev. Lett.*, **57**, 2560 (1986).

2) B. Schwarzschild, *Phys. Today,* **39**, 17 (1986).

3) T. Shibahara, H. Hattori, and H. Kuroya, *J. Am. Chem. Soc.*, **106**, 2710 (1984).

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

5) T. Shibahara and H. Kuroya, 5th International Conf. of the Chem. and Uses of Molybdenum, Newcastle upon Tyne, England, July 1985, p. 59. The used sample **2** has been newly prepared. The results of chemical analysis and X-ray analysis were: $Ca_{1.5}[Mo_3S_4(Hnta)_2(nta)]\cdot 12H_2O$, *M*: 2517.46, Found: Ca, 4.81; C, 16.98; H, 3.25; N, 3.30. Calcd for $Ca_{1.5}Mo_3C_{18}H_{44}N_3O_{30}S_4$: Ca, 4.77; C, 17.17; H, 3.52; N, 3.33. Space group $P\ \bar{1}$, Lattice parameters: a=11.992(3), b=16.067(5), c=11.538(3) Å, α=101.52(3), β=103.69(3), γ=90.59 (2), V=2112(1) Å^3, Z=2, number of reflections 4792: 3σ cut, $2\theta_{max}$=45°, D_x=1.979, D_m=1.96 g cm^{-3}, R=5.33%, R_w=7.70%.

6) M. Takahashi, T. Sugano, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **57**, 26 (1984).

7) K. Kimura and S. Bandow, *Kotai Butsuri*, **19**, 31 (1984).

8) List of units and their conversions.

	SI unit	CGSemu non-rationalized system of unit
B: Magnetic flux density	T=Wb m^{-2}	G
H: Strength of magnetic field	A m^{-1}	Oe
M: Magnetization	A m^{-1}	
χ_M: Molar magnetic susceptibility	m^3	cm^3

3.336×10^{-10}/coulomb=1/e.s.u. of elec. charge
$10^{-4}/T=1/G$
$10^3\times4\pi/Am^{-1}=1/Oe$
$(\chi_M \text{ in SI})/m^3=4\pi\times10^{-6}\ (\chi_M \text{ in CGSemu})/cm^3$

9) R. R. Gupta, "Landolt-Börnstein, Numerical data and functional relationships in science and technology," New series II, Vol. 16, Diamagnetic susceptibility, Editors: K.-H. Hellwege and A. M. Hellwege.

10) E. Pøst, *J. Am. Chem. Soc.*, **81**, 3843 (1959).

11) B. N. Figgis, "Introduction to Ligand Fields," ed by Interscience Publishers, a division of John Wiley & Sons, New York, London, Sydney (1964).

12) A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, **100**, 5252 (1978).

13) S. F. Gheller, T. W. Hambley, R. T. C. Brownlee, M. J. O'Connor, M. R. Snow, and A. G. Wedd, *J. Am. Chem. Soc.*, **105**, 1527 (1983).

14) A. Müller, A. Ruck, M. Dartmann, and U. Reinsch-Vogell, *Angew. Chem., Int. Ed. Engl.*, **20**, 483 (1981).

15) A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, **101**, 3842 (1979).

16) T. Shibahara and H. Kuroya, *Polyhedron,* **5**, 1/2,357 (1986).

17) A. Müller and U. Reinsch, *Angew. Chem., Int. Ed. Engl.*, **19**, 72 (1980); N. C. Howlader, G. P. Haight, Jr., T. W. Hambley, G. A. Lawrance, K. M. Rahmoeller, and M. R. Snow, *Aust. J. Chem.*, **36**, 377 (1983).

18) A. Müller, R. Jostes, W. Eltzner, Chong-Shi Nie, E. Diemann, H. Bögge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, Shun Che, S. J. Cyvin, and B. N. Cyvin, *Inorg. Chem.*, **24**, 2872 (1985).

19) T. R. Halbert, K. McGauley, W.-H. Pan, P. S. Czernuszewicz, and E. I. Stiefel, *J. Am. Chem. Soc.*, **106**, 1849 (1984).

20) T. Saito, N. Yamamoto, T. Yamagata, and H. Imoto, *Chem. Lett.*, **1987**, 2025.

21) P. J. Vergamini, H. Vahrenkamo, and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 6327 (1971).

22) A. Müller, R. Jostes, and F. A. Cotton, *Angew. Chem., Int. Ed. Engl.*, **19**, 875 (1980).

23) "The Nature of the Chemical Bond and the Structure of Molecules and Crystals," L. Pauling, 3rd ed, Cornell Univ. Press, Ithaca New York (1960).

24) B. E. Bursten, F. A. Cotton, J. C. Green, E. A. Seddon, and G. G. Stanley, *J. Am. Chem. Soc.*, **102**, 955 (1980).

25) B. Delley, M. C. Manning, D. E. Ellis, J. Berkowitz, and W. C. Trogler, *Inorg. Chem.*, **21**, 2247 (1982).

26) B. E. Bursten, F. A. Cotton, M. B. Hall, and R. C. Najjar, *Inorg. Chem.*, **21**, 302 (1982).

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

28) For example, M. Castiglioni, R. Giordano, E. Sappa, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, **1986**, 23.