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Linear Tetranuclear Copper(II) Complexes with Bridging Methoxide and a Schiff-Base Ligand: The Preparation and Magnetic Study of the [Cu(salpd-μ-*O,O'*)(μ-L)Cu(μ-CH_3O)$_2$Cu(μ-L)(sapd-μ-*O,O'*)Cu] Complexes (and L=Acetate or Formate Ions) and the Structure Determination of the Complex with L=Acetate

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The title complexes have been synthesized in quantitative yield from [Cu(salpd)] and copper(II) acetate or copper(II) formate , where H_2salpd represents *N,N'*-disalicylidene-1,3-propanediamine. [Cu(salpd-μ-*O,O'*)(μ-L)Cu(μ-CH_3O)$_2$Cu(μ-L)(salpd-μ-*O,O'*)Cu] crystallizes in the monoclinic space group $P2_1/n$ with formula=$Cu_4C_{40}H_{44}N_4O_{10}$, F.W.=995.0, a=11.826(2) Å, b=17.192(4) Å, c=9.836(2) Å, β=94.08(2)°, V=1994.8(7) Å^3 and Z=2 (R=3.83%), where L=CH_3COO. The complex forms a centrosymmetric molecule made up of two units of [Cu(salpd-μ-*O,O'*)(μ-CH_3COO)Cu] bound by a pair of methoxo bridges; each terminal copper(II) ion forms four short bonds with N and O atoms of salpd and a slightly longer (2.235(4) Å) axial bond with one of the oxygens of the acetato group, whereas each inner copper(II) ion is also pyramidally coordinated by two methoxo oxygens, one of the acetato oxygens, and one of the bridging salpd oxygens, the distant axial position being occupied (Cu-O=2.323(3) Å) by the remaining bridging salpd oxygen. The magnetic susceptibilities of the complexes in the 86.8—299.0 K range have been analyzed on the basis of a four-spin model for the linear copper(II) complexes, and the values of g and J_{ij}, based on the Heisenberg-type Hamiltonian $H=-2\sum J_{ij}S_i\cdot S_j$, have been estimated as g (average)=2.13, $J_{12}=-390$ cm^{-1}, $J_{13}=67$ cm^{-1} and $J_{14}=J_{34}=0$ cm^{-1} in the complex with acetate bridges, and as g (average)=2.20, $J_{12}=-263$ cm^{-1}, and $J_{13}=39$ cm^{-1} and $J_{14}=J_{34}=0$ cm^{-1} in the complex with formate bridges, where the numbering refers to the 3-1-2-4 arrangement of the Cu^{2+} ions.

Intramolecular exchange interaction in multinuclear transition metal complexes has a long history of research work by an enormous number of investigators, yet there remain many unsettled problems. Although a large number of polynuclear complexes with the antiferromagnetic property have been reported, only a limited number of multinuclear complexes with the ferromagnetic property are known.[1-8] In recent years, the present authors have prepared a series of trinuclear Schiff-base complexes in which the central metal ion is different from the terminal ones in its oxidation state or elemental species.[9,10] In the course of a study of the preparation of trinuclear complexes with Schiff-base copper(II) terminal units, new compounds were obtained and were proved to be novel type of tetranuclear copper(II) complexes in which copper ions are linearly linked with methoxide, phenolate, and acetate ions. In this paper we wish to report on the synthesis, structure, and magnetism of these tetranuclear complexes, [Cu(salpd-μ-*O,O'*)(μ-L)Cu(μ-CH_3O)$_2$Cu(μ-L)(salpd-μ-*O,O'*)Cu]. Here, when L=CH_3COO, and HCOO, the compounds are designated by **1** and **2** respectively. The temperature dependence of the magnetic susceptibility showed that the ferromagnetic and antiferromagnetic interactions operate simultaneously in these complexes.

Experimental

Syntheses: 1. Nitrogen gas was bubbled through a methanol solution (60 cm^3) containing copper(II) acetate monohydrate (0.57g, 0.0029 mol) for 10 min. To this solution we added [Cu(salpd)] (1 g, 0.0029 mol) and then triethylamine (0.58 g, 0.0057 mol). The mixed solution was then stirred at room temperature for ca. 36 h. The light green product thus deposited was collected on a sintered-glass filter and washed with methanol and diethyl ether. The product was dried at 60 °C under reduced pressure for 40 min. Yield, 1.45 g (100%). Found: C, 47.91; H, 4.39; N, 5.63; Cu, 26.00%. Calcd for $Cu_4C_{40}H_{44}N_4O_{10}$: C,48.29; H, 4.46; N, 5.63; Cu, 25.55%.

The Preparation of a Single Crystal of 1. The copper(II) acetate monohydrate (0.11 g, 0.00057 mol) and [Cu(salpd)] (0.2 g, 0.00058 mol) were dissolved in methanol (60 cm^3) by using a shaker. When the dark-green solution was allowed to stand in the dark for 5 days, well-formed dark-green prisms were separated. Found: C, 48.10; H, 4.38; N, 5.55%. Calcd. for $Cu_4C_{40}H_4N_4O_{10}$: C, 48.29; H, 4.46; N, 5.63%.

2. Nitrogen gas was bubbled into a suspension containing copper(II) formate tetrahydrate (0.65 g, 0.0029 mol) in methanol (50 cm^3) for 15 to 20 min at room temperature. In to this suspension we then stirred triethylamine (0.59 g, 0.0058 mol) and subsequently [Cu(salpd)] (1 g, 0.0029 mol). The reaction mixture was stirred further at room temperature for ca. 65 h. The green product thus deposited was treated in the same manner as in the case of Complex **1** described above. Yield, 1.34 g (97.1%). Found: C, 46.82; H, 4.20; N, 5.75; Cu, 25.73%. Calcd for $Cu_4C_{38}H_{41}N_4O_{10}$: C, 46.77; H, 4.23; N, 5.74; Cu, 26.04%.

Physical Measurements. The IR spectra were measured with a Hitachi-Perkin-Elmer 225 grating IR spectrometer on KBr disks. The magnetic susceptiblities were measured by the Faraday method in the range of 80—300 K using a Cahn 2000 electric balance. The apparatus was calibrated using Hg[Co(NCS)$_4$]. Diamagnetic corrections were carried out using Pascal's constants. The molar effective magnetic moment was calculated by the use of the equation: $\mu_{\mathrm{eff}}=2.828\sqrt{X_{\mathrm{A}}\cdot T}$.

X-Ray Crystallography. The diffraction data of a single crystal of **1** were obtained on a Rigaku AFC-5 four-circle diffractometer at the Faculty of Science, Kyushu University, using graphite-monochromatized Mo*Kα* radiation at 24±1 °C. The scan mode was θ-2θ, with the scan speed of 6 min^{-1}, $2\theta_{\max}=52°$, the scan width of $(1.0+0.35\tan\theta)°$, and the octant measured as $+h$, $\pm k$, and $\pm l$. The intensities of the monitored standard reflections showed no changes during data collection. The unit cell dimensions and standard deviations were obtained by the least-squares fit of 25 reflections ($20°<2\theta<30°$).

The reflections were corrected for the Lorentz-polarization effect, but not for absorption.

Crystal Data: Formula=$Cu_4C_{40}H_{44}N_4O_{10}$, F.W.=995.0, monoclinic system, space group $P2_1/n$. a=11.826(2) Å, b=17.192(4) Å, c=9.836(2) Å, β=94.08(2)°, and V=1994.8(7) Å^3, D_{calcd}=1.657 g cm^{-3}, Z=2. μ(Mo *Kα*)=21.71 cm^{-1}, crystal dimensions 0.4×0.5×0.3 mm, 2999 reflections with $|F_o|>3\sigma(|F_c|)$.

The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method, in which the function minimized was $\sum\omega(|F_o|-|F_c|)^2$; the equal weight of $\omega=1$ was adopted for all the reflections. The hydrogen atoms were located on the difference Fourier map and refined. The positions of the non-hydrogen atoms were refined by the use of anisotropic thermal parameters, while those of the hydrogen atoms were refined by the use of the isotropic thermal parameters, giving R=3.83%, and R_w=4.22%. The final difference Fourier synthesis was featureless, where the heighest peak was 0.4 e Å^{-3}. The atomic parameters of the hydrogen atoms, the thermal parameters of non-hydrogen atoms, and the F_o-F_c tables are deposited as Document No. 8902 at the Office of the Editor of Bull. Chem. Soc. Jpn. The caculations were carried out by the use of the UNICS III computer program system[11] on a FACOM M 780 computer at the Computer Center of Kyushu University. The atomic scattering factors were taken from Ref. 12. The final positional parameters are given in Table 1.

Table 1. Atomic Coordinates for [Cu(salpd-μ-*O,O′*)(μ-CH$_3$COO)Cu(μ-CH$_3$O)$_2$Cu(μCH$_3$COO)(salpd-μ-*O,O′*)Cu][a)]

Atom	*X*	*Y*	*Z*	B_{EQV}/Å^2
Cu(1)	178.2(0.5)	699.2(0.3)	4104.5(0.5)	2.67(1)
Cu(2)	−510.0(0.5)	2409.6(0.3)	3362.5(0.6)	2.90(1)
O(1)	−898.2(2.7)	1333.9(1.6)	2850.7(2.9)	2.95(7)
O(2)	−132.8(3.1)	1904.1(1.7)	5079.9(3.1)	3.46(8)
O(3)	1504.8(2.8)	1029.4(1.9)	3232.6(3.5)	3.68(9)
O(4)	1167.1(3.1)	2236.0(1.9)	2491.6(3.9)	4.18(9)
OM	987.8(2.7)	−124.5(1.7)	5080.6(3.4)	3.43(8)
CM	2063.0(4.5)	−419.1(3.2)	4901.5(5.8)	4.20(14)
N(1)	−1384.6(3.9)	2813.2(2.3)	1723.6(4.7)	4.29(12)
N(2)	−51.5(4.0)	3448.4(2.1)	4110.3(4.5)	4.11(12)
C(1)	−1254.4(4.0)	1069.2(2.6)	1632.9(4.4)	2.96(11)
C(2)	−1251.1(6.8)	287.5(3.2)	1363.7(6.4)	6.60(21)
C(3)	−1610.4(8.0)	−5.8(4.0)	121.4(7.5)	8.51(27)
C(4)	−1974.7(6.5)	466.9(4.1)	−935.2(6.0)	6.34(20)
C(5)	−2024.5(5.2)	1241.3(3.7)	−687.0(5.1)	4.82(16)
C(6)	−1663.6(4.3)	1565.5(2.8)	573.9(4.6)	3.36(12)
C(7)	−1752.8(5.0)	2392.7(3.0)	731.7(5.5)	4.51(14)
C(8)	−1628.0(7.2)	3661.5(3.3)	1598.7(10.0)	8.95(29)
C(9)	−519.5(8.8)	4100.9(4.0)	1895.8(9.0)	9.53(32)
C(10)	−125.1(8.1)	4158.5(3.7)	3265.6(8.4)	8.79(28)
C(11)	414.7(4.6)	3545.6(2.7)	5312.2(5.5)	3.89(13)
C(12)	572.6(4.2)	2992.2(2.7)	6390.4(4.9)	3.34(12)
C(13)	1010.4(5.1)	3263.7(3.4)	7675.2(6.0)	4.83(16)
C(14)	1081.3(6.1)	2795.1(4.1)	8786.9(5.9)	6.01(20)
C(15)	734.6(5.8)	2025.5(4.1)	8663.3(5.9)	5.61(18)
C(16)	338.5(5.0)	1736.1(3.3)	7417.0(5.3)	4.40(15)
C(17)	256.2(4.2)	2203.0(2.7)	6239.9(4.7)	3.18(11)
C(18)	1752.4(4.1)	1642.9(2.7)	2615.6(4.5)	3.10(11)
C(19)	2885.1(4.8)	1645.4(3.4)	2019.2(6.1)	4.58(15)

a) Aomic parameters are multiplied by 10^4. Thermal parameters are given by the equivalent temperature factors.

Results and Discussion

Formation of the Acetate-, Methoxide-, and Phenolate-Bridged Tetranuclear Complex. The formation of the tetranuclear copper(II) complex with methoxo bridges, for example, can be represented by this equation:

$$2\,[\mathrm{Cu(salpd)}]+2\,\mathrm{Cu(L)_2}+2\,\mathrm{CH_3OH}\rightarrow$$
$$[\mathrm{Cu(salpd}\text{-}\mu\text{-}O,O')(\mu\text{-L})\mathrm{Cu}(\mu\text{-CH_3O})_2\mathrm{Cu}(\mu\text{-L})\text{-}$$
$$(\mathrm{salpd}\text{-}\mu\text{-}O,O')\mathrm{Cu}]+2\,\mathrm{LH}$$

where L=HCOO or CH$_3$COO. This reaction, accompanied by methoxide-bridging, takes place even without the addition of a base, although the addition of triethylamine makes the reaction quantitative. However, attempts to obtain the tetranuclear copper(II) complex with bridging ethoxide ions instead of methoxide ions were unsuccessful under similar conditions.

Structure of 1. The molecular structure, with its atomic numbering, is shown in Fig. 1, while the bond lengths and bond angles are given in Table 2. The complex is tetranuclear and has a center of inversion. The zigzag-chain structure of the copper(II) ions in the complex is made up of four units of a square pyramid. Each salpd ligand occupies the four equatorial positions of the terminal copper(II) ion, with the bond distances of 1.963(3)—1.978(5) Å, while the apical position is occupied by one of the oxygens of the acetate ion with the bond distance of 2.235(4) Å. Each basal plane of the inner two copper(II) ions is formed by the two bridging methoxide oxygens (1.917(3) Å, 1.927(3) Å), one of the phenolate oxygens (2.027(3) Å) and one of the acetate oxygens (1.926(3) Å). The apical position is occupied by another phenolate oxygen of salpd (Cu(1)-O(2)=2.323(3) Å). It is noteworthy that one of the oxygen atoms of the bridging acetate ion coordinates to Cu(2) at the apical position, while the other oxygen atom coordinates to Cu(1) at an equatorial position.

The Cu(1), OM, Cu(1′), and OM* atoms make a

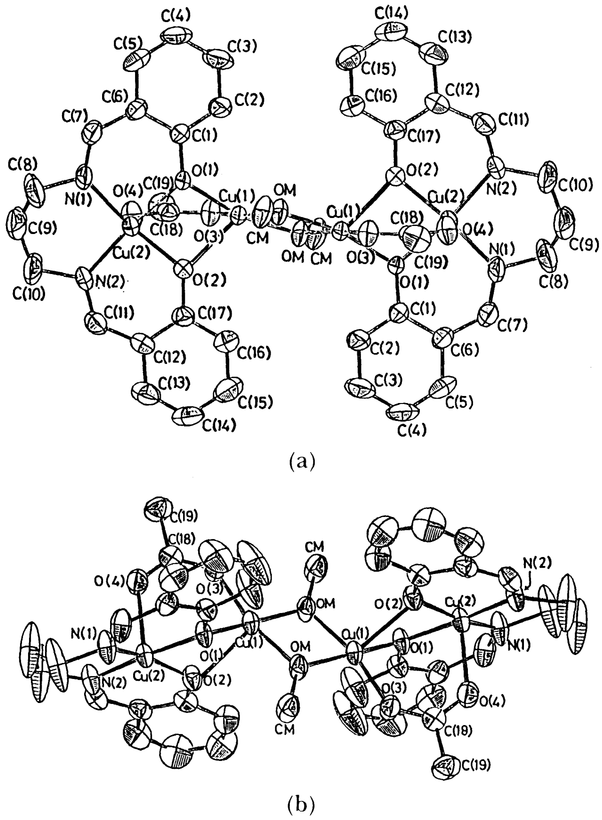


Fig. 1. Molecular structure of [Cu(salpd-μ-*O,O'*)(μ-CH_3COO)Cu(μ-CH_3O)$_2$Cu(μ-CH_3COO)(salpd-μ-*O,O'*)Cu] (a) and the side view (b) drawn by ORTEP.[17)]

Table 2. Interatomic Distances (l/Å) and Bond Angles (ϕ/°) of the Coordination Sphere for [Cu(salpd-μ-*O,O'*)(μ-CH_3COO)Cu(μ-CH_3O)$_2$Cu(μ-CH_3COO)(salpd-μ-*O,O'*)Cu] with Estimated Standard Deviations in Parentheses

Distance (l/Å)		Angle (ϕ/°)	
Cu(1)-Cu(1')	3.027(1)	Cu(1)-OM-Cu(1')	103.9(2)
Cu(1)-Cu(2)	3.123(1)	Cu(1)-OM-CM	129.1(3)
Cu(1)-OM	1.927(3)	Cu(1')-OM-CM	123.8(3)
Cu(1)-OM*	1.917(3)	Cu(1)-O(3)-C(18)	133.2(3)
OM-CM	1.392(7)	Cu(2)-O(4)-C(18)	129.4(3)
Cu(1)-O(1)	2.027(3)	O(3)-C(18)-O(4)	126.2(5)
Cu(2)-O(2)	2.323(3)	O(3)-C(18)-C(19)	115.8(4)
Cu(1)-0(3)	1.926(3)	O(4)-C(18)-C(19)	118.0(5)
Cu(2)-O(1)	1.963(3)	O(1)-Cu(1)-O(2)	70.1(1)
Cu(2)-O(2)	1.924(4)	O(1)-Cu(1)-O(3)	93.8(1)
Cu(2)-O(4)	2.235(4)	O(1)-Cu(1)-OM*	95.3(1)
Cu(2)-N(1)	1.978(5)	O(3)-Cu(1)-OM	92.7(1)
Cu(2)-N(2)	1.992(5)	OM-Cu(1)-OM*	76.1(1)
O(3)-C(18)	1.262(6)	O(1)-Cu(2)-O(2)	80.5(2)
O(4)-C(18)	1.234(6)	O(1)-Cu(2)-N(1)	91.2(2)
C(18)-C(19)	1.500(8)	N(1)-Cu(2)-N(2)	95.7(2)
		Cu(1)-O(1)-Cu(2)	103.0(2)
		Cu(1)-O(2)-Cu(2)	94.2(1)

Table 3. IR Data of Tetranuclear Copper(II) Complexes (cm^{-1})

Complex	Skeletal	ν_{C-O}		ν_{M-OCH_3}	
		ν(as)	ν(s)	ν_{C-O}	ν_{M-O}
1	1538vs 1550vs	1578vs	1390vs	1062vs	535s
2	1540vs 1550vs	1590vs	1346vs	1063vs	530s

The skeletal vibration of [Cu(salpd)] is found at 1538 cm^{-1}.

perfect plane, as required by the crystallographic symmetry.

The most prominent feature of the structure is that the basal planes of the inner copper atoms (Cu(1) and Cu(1')) are nearly perpendicular to those of the terminal copper atoms (Cu(2) and Cu(2')), the dihedral angle between the mean basal planes of Cu(1) and Cu(2') being 108.4°. The basal atoms of terminal copper are slightly distorted toward a tetrahedron, the dihedral angle formed by the Cu(2), O(2), N(2), and Cu(2), O(1), N(1) planes being 163.6°. Cu(2) is lifted by 0.11 Å toward the acetate oxyen.

Infrared Spectra. Some frequencies of the selected bands of the complexes are listed in Table 3. The two bands at 1550 and 1540 cm^{-1} may be assigned to the skeletal vibrations related to the phenolic oxygen of the Schiff-base ligand.[13–15)] A similar band was observed at 1538 cm^{-1} for the mononuclear complex [Cu(salpd)]. Since it is known that the phenoxide band shifts to a higher frequency when a singly coordinated phenoxide oxygen further coordinates to another metal ion, the band at 1550 cm^{-1} should be assigned to the vibration related to O(1), which strongly binds to both coppers (Cu(1) and Cu(2)), while the lower-frequency band seems to be due to the vibration related O(2), which is only weakly bound to Cu(1).

Magnetic Properties. Figure 2 represents the temperature variation in the magnetic susceptibilities (χ_A) and the magnetic moment (μ_{eff}) of the tetranuclear complexes in the temperature range of 77.4—296.0 K. The magnetic moments gradually decrease with the lowering of the temperature, as is shown in Fig. 2. This suggests that there is antiferromagnetic interaction between copper(II) ions. Hatfield and Inman proposed the interaction Hamiltonian for a four spin model with superexchange interaction to account for the unusual magnetic properties of the complex, [4-(*o*-hydroxyphenylimino)-2-pentanonato]-copper(II), as given below.[16)]

$$H=-2J_{12}S_1S_2-2J_{13}(S_1S_3+S_2S_4)-2J_{14}(S_1S_4+S_2S_3)-2J_{34}S_3S_4 \quad (1)$$

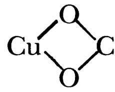
Here the numbering both on the exchange integrals J_{ij} and on the spin vectors **S** refers to the 3-1-2-4 arrangement of the Cu(II) ions. The present study has shown that the magnetic susceptibility expression for this sort of system may be given in an explicit form as follows:

$$\chi_A = Ng^2\beta^2/kT \cdot A/B + TIP \tag{2}$$

$$\begin{aligned}A={}&10\exp[(K/2+N)/(kT)]+2\exp[(K/2-N)/(kT)]\\&+2\exp[(-K/2+\sqrt{M^2+L^2})/(kT)]\\&+2\exp[(-K/2-\sqrt{M^2+L^2})/(kT)]\end{aligned}$$

$$\begin{aligned}B={}&5\exp[(K/2+N)/(kT)]+3\exp[(K/2-N)/(kT)]\\&+3\exp[(-K/2+\sqrt{M^2+L^2})/(kT)]\\&+3\exp[(-K/2-\sqrt{M^2+L^2})/(kT)]\\&+\exp[(-K/2-N-\sqrt{(K-N)^2+3L^2})/(kT)]\\&+\exp[(-K/2-N+\sqrt{(K-N)^2+3L^2})/(kT)]\end{aligned}$$

where $K=J_{12}+J_{34}$, $L=J_{14}-J_{13}$, $M=J_{12}-J_{34}$, and $N=J_{14}+J_{13}$, β is is the Bohr magneton; N, Avogadro's number; k, the Boltzmann constant, and g, the Lande g factor over copper(II) ions. The magnetic susceptibility data were, therefore, fit to Eq. 2 by using the best-fit method, assuming $J_{14}=J_{34}=0$ and $TIP=60\times10^{-6}$ c.g.s. u. per gram-atom copper; the coupling constants J_{12}, and J_{13} were varied systematically until the standard deviation of the value for Lande g factor reached a minimum in the range of 77.4—296.0 K. The calculation yielded g (average)=2.13, $J_{12}=-390$ cm^{-1}, $J_{13}=67$ cm^{-1} in Complex **1**, and g (average)=2.20, $J_{12}=-263$ cm^{-1}, $J_{13}=39$ cm^{-1} in Complex **2**. The solid curves in Fig. 2 represent the theoretical curves of the best fit of the data to Eq. 2 with the parameters specified above. The magnetic coupling constants in both complexes **1** and **2** indicate the existence of a strong antiferromagnetic superexchange interaction between the inner copper pair and a weak ferromagnetic superexchange interaction between the outer adjacent copper pairs.§

During the last two decades structural factors determining spin exchange coupling in dialkoxo-bridged dicopper(II) complexes have been the subject of continuing discussions by many researchers.[18–26] Among the many structural factors, the Cu-O-Cu angle or the coplanarity of the two coordination planes has been pointed out as the major factor by many workers. These two factors are not independent, but are linked to each other so that each factor may be used for the diagnosis of spin-exchange interaction.[26] In view of this, the strong antiferromagnetic interaction between the inner copper pair observed for the present complexes seems quite natural, since the  bridging system is perfectly coplanar and the Cu-O-Cu angle (103.6°) is fairly large.[20] As for the outer copper (Cu(1), Cu(2)) pair, the geometry of the bridging system is very complicated, as has been described in the preceding section, so that it is not easy to predict the extent of spin coupling in a straightforward manner. However, in many cases of such bridging systems with a very distorted geometry, as is the present complex, only a weak spin coupling has been reported.[27] Thus, the weak ferromagnetism found in this study is not a surprising result.

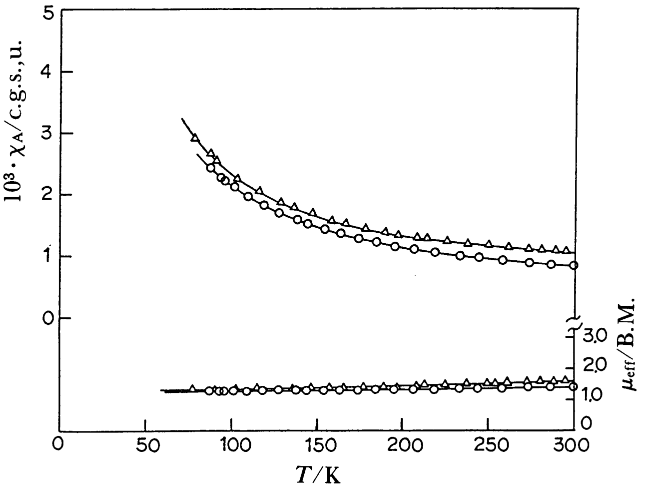


Fig. 2. Temperature variation of the atomic susceptibility (χ_A) and magnetic moment (μ_{eff}) for the tetranuclear complexes: **1** (○) and **2** (△). The solid lines were drawn on the basis of the values of χ_A and μ_{eff} obtained from Eq. 2, when $J_{12}=-390$ cm^{-1}, $J_{23}=67$ cm^{-1}, $J_{14}=J_{34}=0$ cm^{-1}, and g=2.13 for complex **1**, and $J_{12}=-263$ cm^{-1}, $J_{13}=39$ cm^{-1}, $J_{14}=J_{34}=0$ cm^{-1}, and g=2.20 for complex **2**.

Judging from the qualitative similarity of the magnetic parameters, the principal configuration of Complex **2** is likely to be similar to that of **1**.

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§ It is possible to obtain a tolerable agreement between the experimental data and the theoretical χ-T curve by using a value from a considerably wide range (±30 cm^{-1}) for J_{13}, with a slight adjustment of the J_{12} value. However, we have confirmed that a much less satisfactory agreement be obtained by using a negative J_{13} value.

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