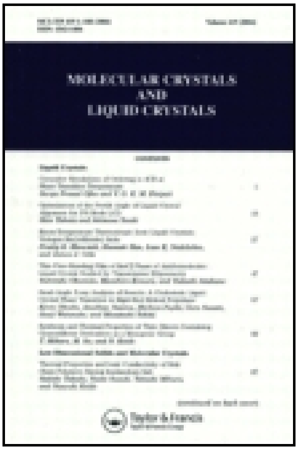

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MAGNETIC INTERACTIONS BETWEEN COPPER(II) CENTERS THROUGH $[MO_4]^{2-}$ (M = Cr(VI) AND Mo(VI)) BRIDGES

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Abstract The reaction of $[Cu(acpa)]^+$ with $[MO_4]^{2-}$ (Hacpa = N-(1-acetyl-2-propyridene)(2-pyridylmethyl)amine and M= Cr and Mo) in water-methanol or water-acetonitrile solution affords dinuclear copper(II) complexes with metalate bridges, $[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]\cdot 4CH_3OH\cdot 4H_2O$ (**1**) and $[\{Cu(acpa)\}_2(\mu\text{-}MoO_4)]\cdot 4H_2O$ (**2**), respectively. The crystal structures and the magnetic properties have been studied. Complexes **1** and **2** are isomorphous and the structures are made up of discrete dimers in which two copper(II) ions are bridged by the $[MO_4]^{2-}$ anion. The coordination geometry about the copper(II) ions is square planar with a N_2O chelate group from acpa and an oxygen atom from $[MO_4]^{2-}$. Magnetic susceptibility measurements for **1** revealed that a ferromagnetic interaction between copper(II) ions is propagated through the $[CrO_4]^{2-}$ bridge and the coupling constant ($2J$) was evaluated to be 14.6(1) cm^{-1} ($H = -2JS_1 \cdot S_2$). In **2**, two copper(II) ions bridged by $[MoO_4]^{2-}$ anion are antiferromagnetically coupled with the $2J$ value of -5.1(4) cm^{-1}. The ferromagnetic interaction in **1** is explained by means of the orbital topology of frontier orbitals.

INTRODUCTION

Magnetochemistry of multinuclear metal complexes has been a subject of current interest. The bridging ligands between paramagnetic metal ions usually mediate antiferromagnetic interactions due to the magnetic orbital overlap through the bridge. Ferromagnetic interactions, however, can be achieved, if the magnetic orbitals are (accidentally) orthogonal to each other.[1] For example, the orthogonality of $d\sigma$ and $d\pi$ spins in Cu^{II}-V^{IV}=O and Ni^{II}-Cr^{III} complexes leads to the ferromagnetic interaction.[2,3] This approach has also been applied to metal complexes with organic radicals, in which the central metal ions are diamagnetic. In Ti^{IV} and Ga^{III}-semiquinone complexes,[4] coordinated semiquinones are orthogonally arranged and the intramolecular ferromagnetic interactions -56 cm^{-1} ($H = JS_1 \cdot S_2$) and 7.8 cm^{-1} ($H = -2JS_i \cdot S_j$) between semiquinones have been observed, respectively. In $[Cu^I(immepy)_2](PF_6)$ (immepy = bidentate iminonitroxide), a tetrahedral coordination geometry of the copper(I) ion gives an orthogonal arrangement of the iminonitroxides, which have ferromagnetic coupling with $2J$ value of 103 cm^{-1} ($H = -2JS_1 \cdot S_2$).[5] On the other hand, tetraoxo anions such as phosphate, arsenate, vanadate, and molybdate have been known to bridge metal ions. Diiron(III) complexes as models for purple acid phosphatases have been the subject of study from structural, electronic, and vibrational view points.[6] However, magnetic interactions mediated through tetraoxo anions remain unclear. We report herein the structures and magnetic properties of dinuclear copper(II) complexes bridged by tetraoxometalate, $[CrO_4]^{2-}$ and $[MoO_4]^{2-}$. The magnetic interaction through the metalate will be discussed by means of orbital symmetry of the frontier orbitals.

EXPERIMENTAL

Syntheses

$[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]\cdot 4CH_3OH\cdot 4H_2O$ (**1**). To a methanol solution (10 ml) of $Cu(BF_4)_2\cdot 4H_2O$ (310 mg, 1 mmol) and Hacpa (190 mg, 1 mmol) was added an aqueous solution (3 ml) of triethylamine (200 mg, 2 mmol) and K_2CrO_4 (97 mg, 0.5 mmol). The solution was stirred at room temperature for 1 h, yielding a dark green solution. Upon standing in a refrigerator for 2 days, the mixture deposited dark green tablets. These were filtered and one of these was subjected to the X-ray analysis. Some water and methanol molecules were lost upon drying.

$[\{Cu(acpa)\}_2(\mu\text{-}MoO_4)]\cdot 4H_2O$ (**2**). **2** was obtained similarly to **1** from water-acetonitrile solution by using K_2MoO_4 (129 mg, 0.5 mmol) instead of K_2CrO_4. Some water and acetonitrile molecules were also lost upon drying. One of the dark blue tablets was subjected to the X-ray analysis.

RESULTS AND DISCUSSION

Description of the Structure.

$[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]\cdot 4CH_3OH\cdot 4H_2O$ (**1**) and $[\{Cu(acpa)\}_2(\mu\text{-}MoO_4)]\cdot 4H_2O$ (**2**) crystallize in the monoclinic system with space group $P2_1/m$. An ORTEP view of **1** is presented in Figure 1 with the atom numbering scheme. The numbering system for **2** is the same as that used in **1** except for the Mo atom. The complex molecules of **1** and **2** are located on a crystallographic mirror plane, thus the asymmetric unit consists of a half molecule. Copper(II) ions in each asymmetric unit are bridged by the O1-M-O1* unit of $[MO_4]^{2-}$ (M= Cr or Mo) with separations of 6.443(1) and 6.703(2) Å, respectively. The coordination geometry about the copper(II) ions is square planar, in which the four coordination sites are occupied with N_2O chelate groups from acpa and an oxygen atom from the $[MO_4]^{2-}$ anion. The copper(II) ions in **1** and **2** stay 0.03(1) Å above the mean plane of N1-N2-O1-O4 and bond distances between the copper(II) and coordinated atoms are 1.903(4) - 1.984(5) Å, which implies the magnetic orbital of the copper(II) ion to being $d_{x^2-y^2}$. Two square planar coordination planes of the copper(II) ions bridged by the $[CrO_4]^{2-}$ and $[MoO_4]^{2-}$ unit make the angles of 10.6(1)° and 4.8(2)°, respectively. The coordination geometries around the Cr and Mo atoms are pseudo-tetrahedral, where M-O (M = Cr and Mo) bond lengths are in the range of 1.606(6) - 1.679(4) Å and 1.730(9) - 1.782(6) Å and O-M-O bond angles of 108.6(2) - 110.7(2)° and 108.7(2) - 111.2(3)°, respectively. The bond length of Cr or Mo with the O1 atoms coordinated to the copper(II) ion is the longest among the M-O bonds and the bond angles (Cr-O1-Cu and Mo-O1-Cu) about the bridging O1 atom are 141.3(2)° and 149.0(4)°, respectively.

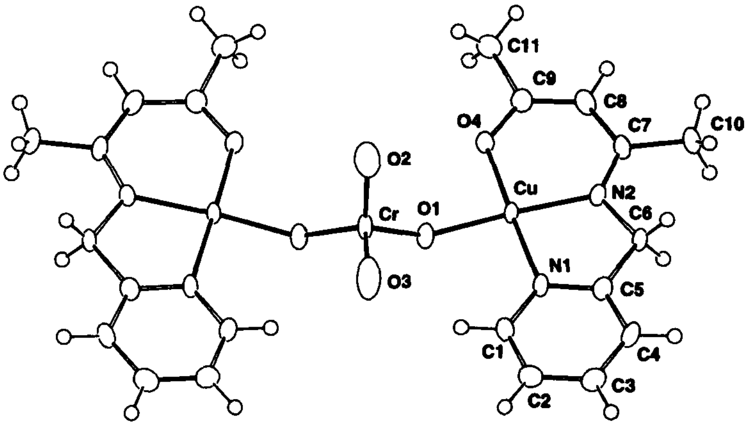


FIGURE 1. $[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]$ (**1**).

Magnetic Properties

Temperature dependent magnetic susceptibilities for the complexes have been measured down to 2.0 K and $\chi_m T$ values vs. temperature for **1** and **2** are plotted together in Figure 2, where χ_m is the molar magnetic susceptibility per dinuclear unit.

For **1**, the $\chi_m T$ value at 300 K is 0.89 emu mol^{-1} K, which would be expected for the uncorrelated spins. On lowering the temperature, $\chi_m T$ for **1** increases and exhibits a maximum at 10 K ($\chi_m T$ = 1.00 emu mol^{-1} K) and then decreases. The magnetic behavior for **1** suggests that a ferromagnetic interaction between the copper(II) ions is

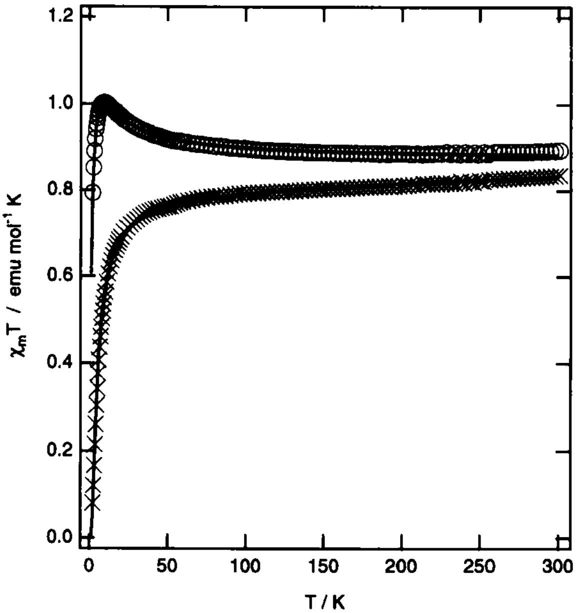


FIGURE 2. Plots of χ_mT *vs* T for (O) $[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]\cdot 4CH_3OH\text{-}4H_2O$ (**1**) and (x) $[\{Cu(acpa)\}_2(\mu\text{-}MoO_4)]\cdot 4H_2O$ (**2**). Solid lines correspond to the best fit curves by using the parameters given in the text.

predominant at intermediate temperature and then a weaker antiferromagnetic coupling is involved at lower temperature. The magnetic susceptibility data were analyzed by the Bleaney-Bowers equation ($H = -2JS_1 \cdot S_2$) as[7]

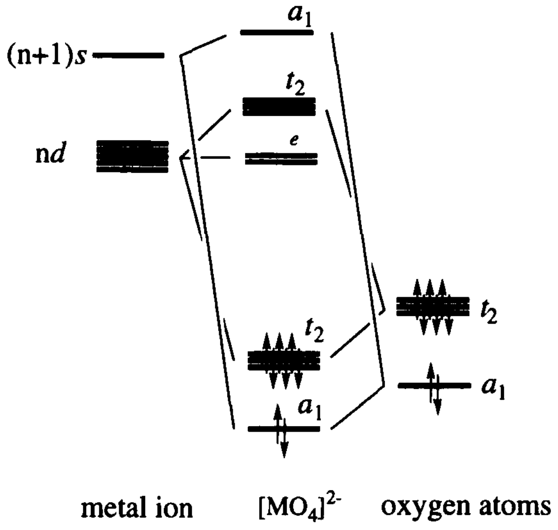
$$\chi_m = \frac{Ng^2\beta^2}{k(T-\theta)}\left[\frac{2}{3+exp\,(-2J/kT)}\right] + N\alpha \qquad (1)$$

where the contribution of the intermolecular antiferromagnetic interaction (θ) and temperature independent term ($N\alpha$: $60\text{x}10^{-6}$ emu/Cu) were included in the calculations. The symbols have their usual meaning. The best fit parameters were $2J = +14.6(1)$ cm^{-1}, $g = 2.12(1)$, and $\theta = -0.8(1)$ K. In contrast to **1**, the χ_mT values for **2** show gradual decrease as the temperature was lowered, and this behavior is characteristic of antiferromagnetically coupled copper(II) ions. The least squares fitting of the experimental data with the equation (1) led to $2J = -5.1(4)$ cm^{-1}, $g = 2.07(1)$, and θ = -1.2(1) K. Epr measurement for **1** showed no signal at 77 K, which might be due to a rapid spin relaxation. On the other hand, **2** showed an axially symmetric epr pattern ($g_{//}$

= 2.195 and g = 2.079) at 77 K, which is characteristic of magnetically isolated copper(II) ions with the square planar coordination.

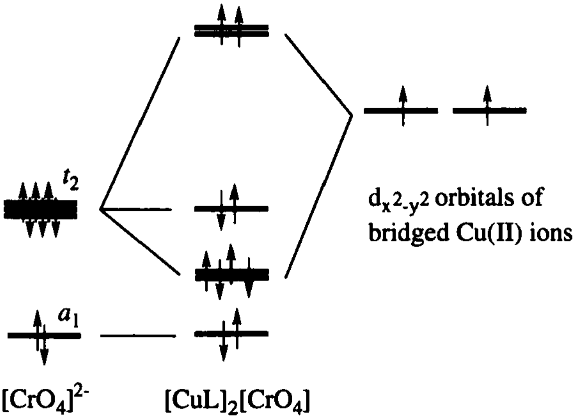
When two magnetic orbitals, each having one electron, are sufficiently close to interact, either a ferromagnetic or an antiferromagnetic interaction is propagated. The magnetic interaction can be expressed as the sum of *K* (exchange integral) and $2\beta S$ (β: transfer integral and *S*: overlap integral) which favor the ferromagnetic and antiferromagnetic interactions, respectively.[1] When two magnetic orbitals overlap each other, the $2\beta S$ term is much larger than the *K* term, and thus the antiferromagnetic interaction is predominant. On the other hand, in the case of the two magnetic orbitals orthogonal to each other (strict orthogonality), or the $2\beta S$ term being small enough compared with *K* term, the ferromagnetic interaction can be obtained. It should be noted that bridging ligands are responsible for the ferromagnetic contribution and that magnetic properties can be understood by orbital symmetry of the bridging ligand and magnetic orbitals.

Scheme I



If we assume that the ions $[CrO_4]^{2-}$ and $[MoO_4]^{2-}$ have tetrahedral geometry, where the X-ray crystallographic analyses for **1** and **2** revealed the two ions to have pseudo-tetrahedral symmetry, we expect the metal d-orbitals are split into e and t_2 type orbitals. The e pair of the d-orbitals has no matching combination of oxygen orbitals, hence these orbitals remain nonbonding. The t_2 type orbitals of the metal ion, however, have the same symmetry as combinations of the coordinated oxygen orbitals and these orbitals form triply degenerate bonding and antibonding orbitals. Orbital mixing of the metal d and oxygen p-orbitals depends on the orbital energy of the metal ions. Six electrons form the oxygen p-orbitals occupy the t_2-type bonding orbitals (Scheme I). When the $[CrO_4]^{2-}$ anion bridges copper(II) ions along the equatorial directions, two of the t_2 type molecular orbitals of the $[CrO_4]^{2-}$ anion form two sets of σ-type bonding and antibonding orbitals with $d_{x^2-y^2}$ orbitals of the copper(II) ions, and the remainder of the t_2 type orbitals remains nonbonding. The two unpaired electrons from the copper(II) ions occupy the antibonding orbitals (Scheme II).

Scheme II



In **1**, the complex molecule has only mirror symmetry, hence the molecular geometry of the complex is C_s. It should be noted that there are no degenerate orbitals under the C_s symmetry. The magnetic susceptibility measurements of **1**, however, do show the ferromagnetic interaction between the copper(II) ions. Therefore, the two antibonding MOs must be energetically close enough to have a large exchange integral *K* overcoming the stabilization of the singlet state, or they must be nearly degenerate. In contrast to **1**, **2** showed only a weak antiferromagnetic interaction through the $[MoO_4]^{2-}$ ion. The lack of the substantial magnetic interaction in **2** can be understood by orbital energy mismatch of the Mo and O atoms. Figure 3 shows uv-visible spectra of K_2CrO_4 and K_2MoO_4 in water. K_2CrO_4 shows strong absorption bands at 370 ($\varepsilon = 3900$ M^{-1} cm^{-1}) and 270 nm ($\varepsilon = 3200$ M^{-1} cm^{-1}) which are assigned to LMCT bands from O to Cr atom,[8] while the corresponding CT bands for K_2MoO_4 appear in the high energy region (226 nm with $\varepsilon =$ 5000 M^{-1} cm^{-1} and 207 nm with $\varepsilon = 9800$ M^{-1} cm^{-1}).[9] The uv-visible spectra suggest that in the $[CrO_4]^{2-}$ ion the t_2 type orbitals undergo substantial mixing of the chromium d- and oxygen p-orbitals, while such orbital mixing for $[MoO_4]^{2-}$ is energetically inaccessible. In **1** and **2**, the oxygen atoms of the metalate ions coordinate to the

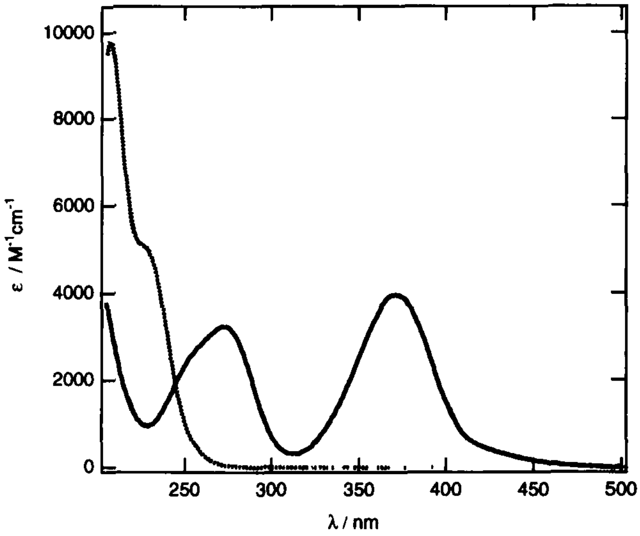


FIGURE 3. Uv-visible spectra of (——) K_2CrO_4 and (-----) K_2MoO_4 in water.

copper(II) ions from their equatorial plane ($d_{x^2-y^2}$ orbital) and the spin of the copper(II) ions is considered to be delocalized onto the coordinated oxygen atoms of the metalate ions. In the $[MoO_4]^{2-}$ bridged complex, however, the magnetic interaction between two delocalized spins on the oxygen atoms are disconnected by the Mo atom due to the energy mismatching of the molybdenum d- and oxygen p-orbitals. Hence, the fairly weak antiferromagnetic interaction observed in **2** does not occur through $[MoO_4]^{2-}$ unit but results from the magnetic dipole-dipole interaction.

CONCLUSION

One of the purposes of this paper was to verify the validity of the $[CrO_4]^{2-}$ bridging unit to link paramagnetic species with ferromagnetic interactions. The chromate bridged dicopper system studied here does show the ferromagnetic interaction due to the accidental degeneracy of the σ-type frontier orbitals. Some multinuclear complexes with $[CrO_4]^{2-}$ as the bridging ligand have been magnetically and structurally characterized.[10] For example, $[LFe^{III}(\mu\text{-}CrO_4)_3Fe^{III}L]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) has shown the antiferromagnetic interaction ($2J = -15$ cm^{-1}) between the high-spin iron(III) centers through the three chromate bridges.[11] The antiferromagnetic interaction in the iron(III) complexes might be understood by an extra π-orbital overlap between $[CrO_4]^{2-}$ and Fe^{III} ions leading to the non-degenerate frontier orbitals of the $[Fe^{III}{}_2(\mu\text{-}CrO_4)_3]$ chromophore.

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