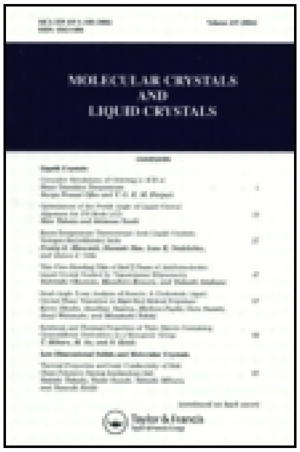

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Magnetic Interactions in $[MO_4]^{2-}$ (M = Cr(VI), Mo(VI) and W(VI)) Bridged Copper(II) and Nickel(II) Complexes

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MAGNETIC INTERACTIONS IN $[MO_4]^{2-}$ (M = Cr(VI), Mo(VI) AND W(VI)) BRIDGED COPPER(II) AND NICKEL(II) COMPLEXES

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Abstract Tetraoxometalate $[MO_4]^{2-}$ bridges Cu(II) and Ni(II) ions to form dinuclear, trinuclear, and one-dimensional complexes. The crystal structures and magnetic properties of $[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]\cdot 4CH_3OH\cdot 4H_2O$ **1** and $[\{Cu(acpa)\}_2(\mu\text{-}MoO_4)]\cdot 4H_2O$ **2**, (Hacpa = *N*-(1-acetyl-2-propyridene)(2-pyridylmethyl)amine), *catena*-$(\mu\text{-}CrO_4\text{-}O,O')[Ni(cyclam)]\cdot 2H_2O$ **3**, $[\{Ni(cyclam)\}_3(\mu\text{-}MoO_4)_2\text{-}(H_2O)_2](ClO_4)_2$ **4**, and $[\{Ni(cyclam)\}_3(\mu\text{-}WO_4)_2(H_2O)_2](ClO_4)_2$ **5** were presented. 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. In **3**, Ni(II) ions are bridged by the chromate ion to form one dimensional chain, while in **4** and **5** two metalate ions bridge three Ni(II) ions to form trinuclear complexes. Magnetic susceptibility measurements for **1** and **3** revealed that ferromagnetic interactions between Cu(II) and Ni(II) ions are propagated through the $[CrO_4]^{2-}$ bridges and the coupling constants (J) were evaluated to be 7.3(1) cm^{-1} ($H = -2JS_1\cdot S_2$) for **1** and 0.6(1) cm^{-1} for **3**. In **2**, **4**, and **5**, paramagnetic metal centers are antiferromagnetically coupled with J values of -2.5(4), -1.7(1), -0.9(1) cm^{-1}, respectively. The ferromagnetic interactions in **1** and **3** are explained by means of the orbital topology of frontier orbitals.

INTRODUCTION

The 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 $Cu^{II}\text{-}V^{IV}{=}O$ and $Ni^{II}\text{-}Cr^{III}$ 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), one-dimensional Ni(II) and trinuclear Ni(II) complexes, bridged by tetraoxo-metalate, $[CrO_4]^{2-}$, $[MoO_4]^{2-}$, and $[WO_4]^{2-}$ The magnetic interactions 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** and $[\{Cu(acpa)\}_2(\mu\text{-}MoO_4)]\cdot 4H_2O$ **2**. To a methanol solution of $Cu(BF_4)_2\cdot 4H_2O$ and Hacpa (190 mg, 1 mmol) was added an aqueous solution of triethylamine and K_2CrO_4 or K_2MoO_4 . 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.

catena-$(\mu\text{-}CrO_4)[Ni(cyclam)]\cdot 2H_2O$ **3**, $[\{Ni(cyclam)\}_3(\mu\text{-}MoO_4)_2(H_2O)_2](ClO_4)_2$ **4**, and $[\{Ni(cyclam)\}_3(\mu\text{-}WO_4)_2(H_2O)_2](ClO_4)_2$ **5**.

A reaction mixture of $[Ni(cyclam)](ClO_4)_2$, K_2MO_4 (M = Cr, Mo , and W), and triethylamine in water was stirred for 1 hr. After standing for 1 week, dark red tablets of **3** and purple tublets of **4** and **5** were obtained.

RESULTS

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**.

Complexes **1** and **2** are isomorphous to each other and an ORTEP view of **1** is presented in Figure 1. The complex molecules of **1** and **2** are located on a crystallographic mirror plane, thus the asymmetric unit consists of a half molecule. Cu(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 bond distances between the copper(II) and coordinated atoms are in the range of 1.903(4) - 1.984(5) Å, which implies the magnetic orbital of the Cu(II) ion to a $d_{x^2-y^2}$ orbital 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.

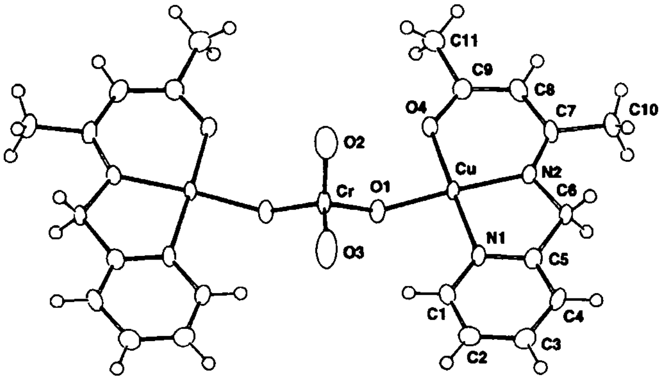


FIGURE 1. ORTEP diagram of $[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]$ **1**.

catena-$(\mu\text{-}CrO_4)[Ni(cyclam)]\cdot 2H_2O$ **3**, $[\{Ni(cyclam)\}_3(\mu\text{-}MoO_4)_2(H_2O)_2](ClO_4)_2$ **4**, and $[\{Ni\text{-}(cyclam)\}_3(\mu\text{-}WO_4)_2(H_2O)_2](ClO_4)_2$ **5**.

In **3**, the dark red crystal consists of a $[CrO_4]^{2-}$ anion and two kinds of crystallographically independent $[Ni(cyclam)]^{2+}$ cations, where both of the $[Ni(cyclam)]^{2+}$ cations locate on the center of inversion and coordination geometry about the Ni^{II} ions are close each other. The equatorial coordination sites of the Ni^{II} ions are occupied by four nitrogen atoms from cyclam (Ni-N = 2.061(2) - 2.076(2) Å) and the axial sites are completed by two oxygen atoms from $[CrO_4]^{2-}$ anion (Ni-O = 2.083(2) - 2.092(1) Å). The $[CrO_4]^{2-}$ anions bridge the Ni^{II} ions and form a one-dimensional structure with a Ni-Ni separation of 6.5954(9) Å (Figure 2a). Complexes **4** and **5** are isomorphous and complex molecules consist of three $[Ni(cyclam)]^{2+}$ cations bridged by$[CrO_4]^{2-}$ (Figure 2b). The coordination geometries about the Ni(II) ions are almost the same as that of **3** except that the axial coordination sites of the terminal Ni(II) ions are capped by coordinated water molecules. The bond distances of Ni(II) ions and equatorial nitrogen atoms are in the range of 2.052(8) - 2.08(1) for both complexes, while bond distances of Ni(II) ions with axial oxygen atoms are rather long (2.081(5) - 2.131(5)Å).

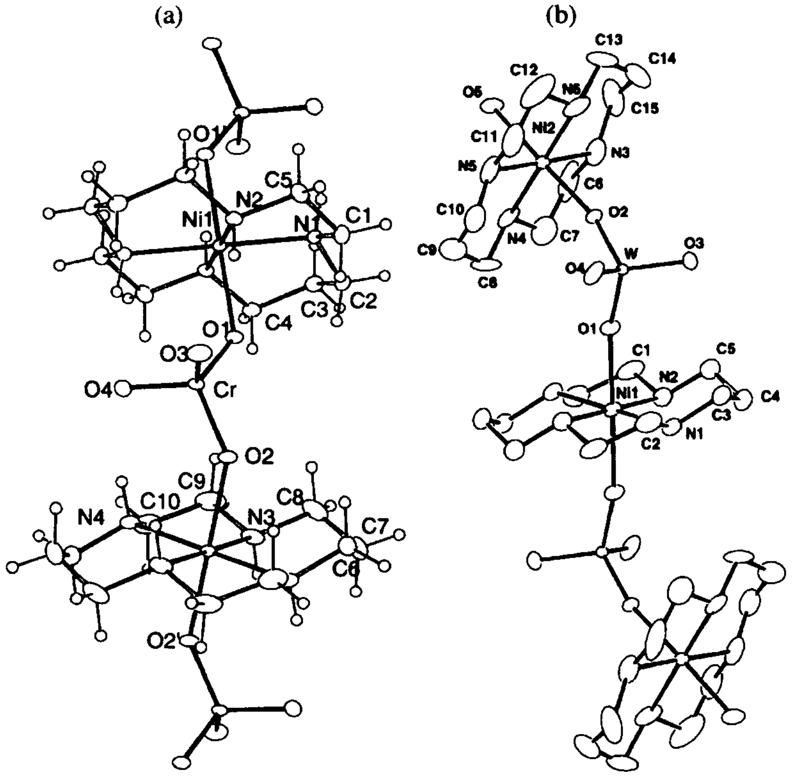


FIGURE 2. ORTEP diagrams of (a) *catena*-(μ-CrO_4)[Ni(cyclam)]·$2H_2O$ **3**, and (b) [{Ni(cyclam)}$_3$(μ-WO_4)$_2$(H_2O)$_2$](ClO_4)$_2$ **5**.

Magnetic Properties

Temperature dependent magnetic susceptibilities for the complexes have been measured down to 2.0 K with external field of 0.5 T and $\chi_m T$ values vs. temperature for **1** and **2** are plotted together in Figure 3, 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 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 ($H = -2JS_1 \cdot S_2$),[7] where the contribution of the intermolecular antiferromagnetic interaction (θ) was included in the calculations. The best fit parameters for **1** were $2J$ = +14.6(1) cm^{-1}, g = 2.12(1), and θ = -0.8(1) K. In contrast to **1**, the $\chi_m T$ 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 to the dimer model led to $2J$ = $-5.1(4)$ cm^{-1}, $g = 2.07(1)$, and $\theta = -1.2(1)$ 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 $g_{\perp} = 2.079$) at 77 K, which is characteristic of magnetically isolated copper(II) ions with the square planar coordination.

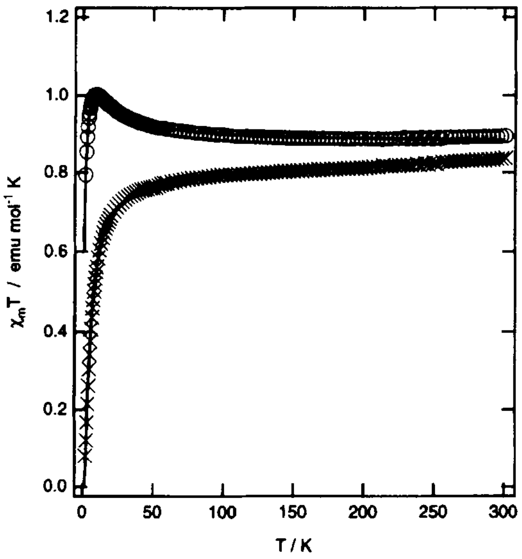


FIGURE 3. Plots of $\chi_m T$ *vs* T for (o) $[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]\cdot 4CH_3OH\text{-}4H_2O$ **1** and (x) $[\{Cu(acpa)\}_2(\mu\text{-}MoO_4)]\cdot 4H_2O$ **2**. Solid lines correspond to the best fit curves by using the parameters given in the text.

The magnetic susceptibility data for **3**, **4**, and **5** are shown in Figure 4 in the form of χ_{Ni} vs. T plots. $\chi_{Ni}T$ values for **3** increase as the temperature is lowered, which is indicative of a ferromagnetic interaction. In **3**, the Ni^{II} ($S = 1$) ions form the chain structure, therefore, the Fisher's model[8] for the classical-spin chain system was applied to the analysis of the magnetic data ($H_{chain} = -J\Sigma S_i \cdot S_{i+1}$). The least-squares fitting of the observed data above 9 K led to $J = +0.6(1)$ cm^{-1} $g = 2.13(1)$. In this fitting, the contribution of the zero field splitting of the Ni^{II} ion was ignored because of the octahedral coordination geometry of the Ni^{II} ions. Sudden decrease of $\chi_m T$ values below 9 K might be due to antiferromagnetic interchain interaction.

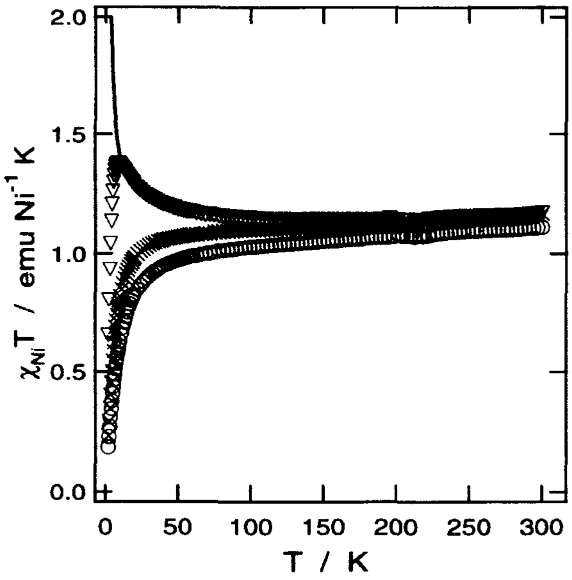


FIGURE 4. Plots of $\chi_{Ni}T$ vs T for (▽) *catena*-(μ-CrO_4)[Ni(cyclam)]·$2H_2O$ **3**, (O) [{Ni(cyclam)}$_3$(μ-MoO_4)$_2$(H_2O)$_2$](ClO_4)$_2$ **4**, and (x) [{Ni-(cyclam)}$_3$(μ-WO_4)$_2$(H_2O)$_2$](ClO_4)$_2$ **5**. Solid lines correspond to the best fit curves by using the parameters given in the text.

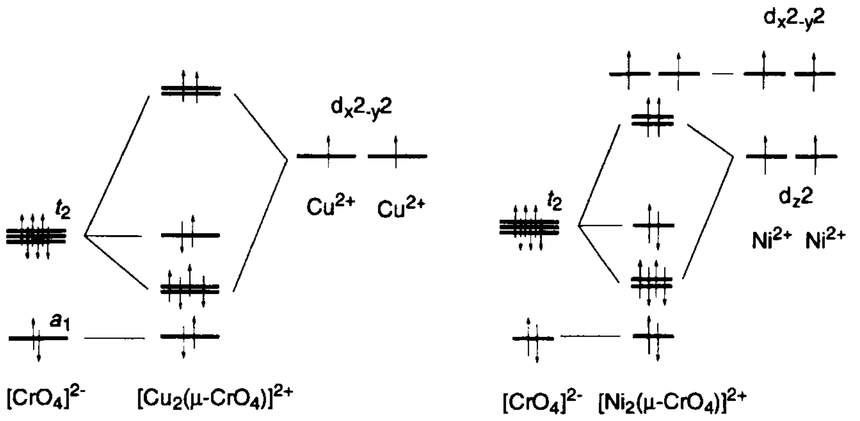
In contrast to **3**, the temperature dependencies of $\chi_{Ni}T$ values for **4** and **5** show the antiferromagnetic behavior, and magnetic data were analyzed by the trimer model ($H = -2J(S_1{\cdot}S_2+S_2{\cdot}S_3)$) with contribution of intertrimer interaction (θ). The g values, exchange coupling constants J for the Ni(II)-Ni(II), and θ values were obtained to be 2.13(1), -1.7 cm^{-1}, and -1.5(1) K for **4** and 2.10(1), -0.9 cm^{-1}, and -1.5(4) K for **5**.

DISCUSSION

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.

Now, we think about dinuclear Cu(II) and Ni(II) complexes bridged by metalate ions. If we assume that the ions $[MO_4]^{2-}$ (M = Cr, Mo, and W) have tetrahedral geometry, 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. When the $[CrO_4]^{2-}$ anion bridges Cu(II) or Ni(II) ions along the magnetic orbitals, that is, $d_{x^2-y^2}$ and d_{z^2} orbitals for Cu(II) and Ni(II) ions, respectively, 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 the magnetic orbitals of the Cu(II) and Ni(II) ions, and the remainder of the t_2 type orbitals remains nonbonding. The two unpaired electrons from the $d_{x^2-y^2}$ or d_{z^2} orbitals occupy the antibonding orbitals (Scheme I).

Scheme I



The complex **1** molecule has only mirror symmetry, hence the molecular geometry of the complex is C_s. Although the dinuclear Ni(II) unit taken from the one-dimensional system does not have any symmetry, the geometry of the Ni(II) dimer can be regarded as C_s

symmetry. It should be noted that there are no degenerate orbitals under the C_s symmetry. The magnetic susceptibility measurements of **1** and **3**, 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** and **3**, compounds **2**, **4**, and **5** bridged by $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ showed weak antiferromagnetic interactions. The lack of the substantial magnetic interaction in the complexes can be understood by orbital energy mismatch of the Mo and W atoms with O atoms, which can be estimated by uv-visible spectra of K_2CrO_4, K_2MoO_4 and K_2WO_4 in water. K_2CrO_4 shows strong absorption bands at 370 (ε = 3900 M^{-1} cm^{-1}) and 270 nm (ε = 3200 M^{-1} cm^{-1}) which are assigned to LMCT bands from O to Cr atom,[9] while the corresponding CT bands for K_2MoO_4 appear in the high energy region (226 nm with ε = 5000 M^{-1} cm^{-1} and 207 nm with ε = 9800 M^{-1} cm^{-1}) and that of K_2WO_4 appears at 200 nm (ε = 6100 M^{-1} cm^{-1}).[10] 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 is energetically inaccessible in $[MoO_4]^{2-}$ and $[WO_4]^{2-}$. In the complexes, the oxygen atoms of the metalate ions coordinate to the Cu(II) and Ni(II) ions, of which magnetic orbitals direct at the coordinated oxygen atoms, and the spins of the Cu(II) and Ni(II) ions are considered to be delocalized onto the coordinated oxygen atoms of the metalate ions. In the $[MoO_4]^{2-}$ and $[WO_4]^{2-}$-bridged complexes, however, the magnetic interaction between two delocalized spins on the oxygen atoms are disconnected by the Mo and W atoms due to the energy mismatching of the metalate d- and oxygen p-orbitals. Hence, the fairly weak antiferromagnetic interaction observed does not occur through $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ 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 Cu(II) dimer and one dimensional Ni(II) systems studied here 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.[11] 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 Fe(III) centers through the three chromate bridges.[12] The antiferromagnetic interaction in the Fe(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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