The First Tetranuclear Complex with a (μ-CrO_4-*O*,*O*′,*O*″) Bridge: Crystal Structure and Ferromagnetic Behavior of [{Cu(bpy)$_2$}$_3$(μ-CrO_4)](ClO_4)$_4$·H_2O

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A novel tetranuclear complex [{Cu(bpy)$_2$}$_3$(μ-CrO_4)](ClO_4)$_4$·H_2O (**1**) with a (μ-CrO_4-*O*,*O*′,*O*′′) bridge has been synthesized by the reaction of K_2CrO_4 with Cu(ClO_4)$_2$·6H_2O and bpy in CH_3CN/H_2O solution (bpy = 2,2′-bipyridine). A single crystal X-ray diffraction analysis showed that the chromate ion bridges three copper(II) ions showing a pesudo-C_{3v} symmetry. The coordination sphere of each copper(II) ion is best described as trigonal bipyramidal, implying that the magnetic orbital of copper(II) ion is d_{z^2}, which is also confirmed by the powder ESR spectra. Variable-temperature magnetic studies verify the validity of the chromate bridging unit to link the tricopper system with ferromagnetic coupling, with $2J = +1.8$ cm^{-1}.

The magnetochemistry of polynuclear metal complexes has attracted considerable interest from both physicists and chemists due to the peculiar behavior derived from the nature of these magnetic ions.[1−3] Ferromagnetic interactions can be achieved if the magnetic orbitals are orthogonal to each other.[4−6] The chromate ion has been known to act as a bridging ligand and tends to bridge metal centers to form oligo- and polymetallic systems with zero-, one-, two-dimensional structures.[7−14] Many chromate-bridged polynuclear metal complexes have been structurally and magnetically characterized. Some of them show ferromagnetic interaction due to the magnetic orbital orthogonality through the chromate bridge. For example, the one-dimensional metal(II) complexes *catena*-(μ-CrO_4-*O*,*O*′)[Ni^{II}-(cyclam)]·2H_2O (cyclam = 1,4,8,11-tetraazacyclotetradecane) and *catena*-(μ-CrO_4-*O*,*O*′)[M^{II}(L)]·5H_2O (M = Ni^{II}, Cu^{II}; L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0$^{1.18}$,0$^{7.12}$]docosane) revealed an octahedral geometry about each metal(II) ion and showed weak intrachain ferromagnetic interactions [$2J = +0.6(1)$, $+1.6(1)$ and $+0.10(1)$ cm^{-1}; $H = -2J\Sigma S_i{\cdot}S_{i+1}$] which is explained by means of an accidental degeneracy of the σ-type frontier orbitals.[8,10] In a dinuclear copper(II) complex [{Cu^{II}(acpa)}$_2$(μ-CrO_4)] (acpa = tridentate Schiff-base ligands), the coordination geometry about the copper(II) ions is square planar, and the ferromagnetic coupling has a $2J$ value of $+14.6$ cm^{-1} ($H = -2J\Sigma S_1{\cdot}S_2$).[7] Metal complexes with chromate bridge have been known to contain one, two, and three (μ-CrO_4-*O*,*O*′) ions.[7−14] However, to the best of our knowledge, no polynuclear metal complexes bridged by a chromate ion in a (μ-CrO_4-*O*,*O*′,*O*′′) mode have been reported. In this paper we report the crystal structure and magnetic properties of the first tetranuclear complex [{Cu(bpy)$_2$}$_3$(μ-CrO_4)](ClO_4)$_4$·H_2O (**1**) (bpy = 2,2′-bipyridine) with a (μ-CrO_4-*O*,*O*′,*O*′′) bridge.

The structure of **1** has been elucidated by X-ray crystallography. The molecular structure of **1** is presented in Figure 1. The coordination geometry about the chromium atom is a slightly distorted tetrahedron with O−Cr−O bond angles in the range 108.0(2)−111.6(2)°. The Cr−O bonds where O is also coordinated to Cu [1.648(4), 1.648(4), and 1.669(4) Å for Cu(1), Cu(2), and Cu(3), respectively] are slightly longer than the “uncoordinated” Cr−O bond [1.605(4) Å]. As can be seen from the figure, the chromate ion bridges the copper(II) ions with a pesudo-C_{3v} symmetry, with a Cu−Cr separation of 3.173−3.504 Å. The Cu−O bond lengths are 1.996(4), 1.961(4), and 1.970(3) Å, respectively. In each Cu(bpy)$_2^{2+}$ unit, the axial coordination sites of the copper(II) ion are occupied by two nitrogen atoms from bpy and the equatorial sites are occupied by two nitrogen atoms from bpy and an oxygen atom from the chromate ion. The bond angle of each axial N−Cu−N unit is almost 180° [177.5(2), 176.6(2), and 178.27(19)° for Cu(1), Cu(2), and Cu(3), respectively]. The axial Cu−N bond lengths are shorter than those of the equatorial Cu−N bonds. Thus, the coordination sphere of each copper(II) ion is best described as a trigonal bipyr-

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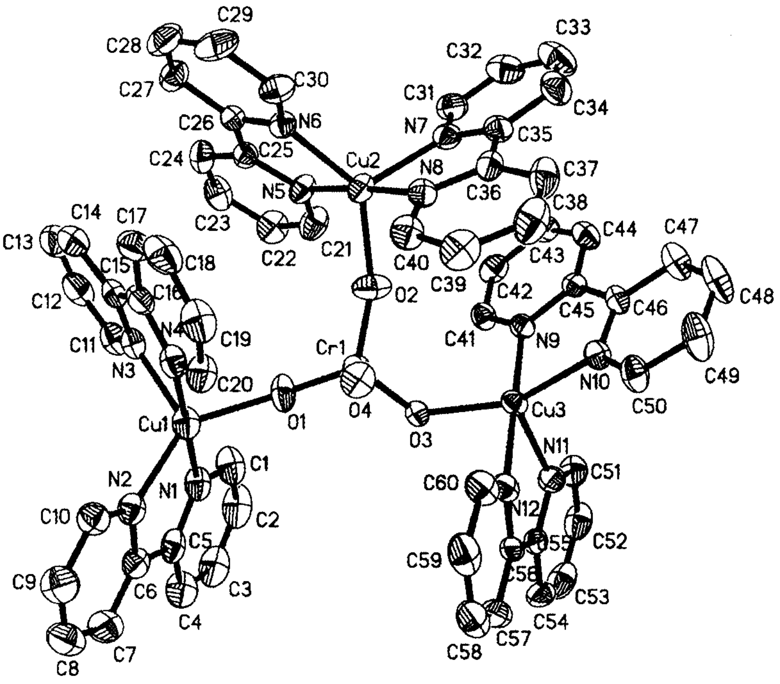

Figure 1. Molecular structure diagram of **1** (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity)

amid, which implies that the magnetic orbital of copper(II) ion is d_{z^2}.

The powder X-band ESR spectra of **1** was recorded at both room temperature and 77 K (Figure 2). The spectrum remains essentially the same down to 77 K, without any detectable alteration of the relative intensities of the peaks. The very weak ferromagnetic interaction between the copper(II) ions revealed by the magnetic measurements seems not to influence the powder ESR spectrum, where a quasi-isotropic signal centered at $g = 2.18$ is observed.

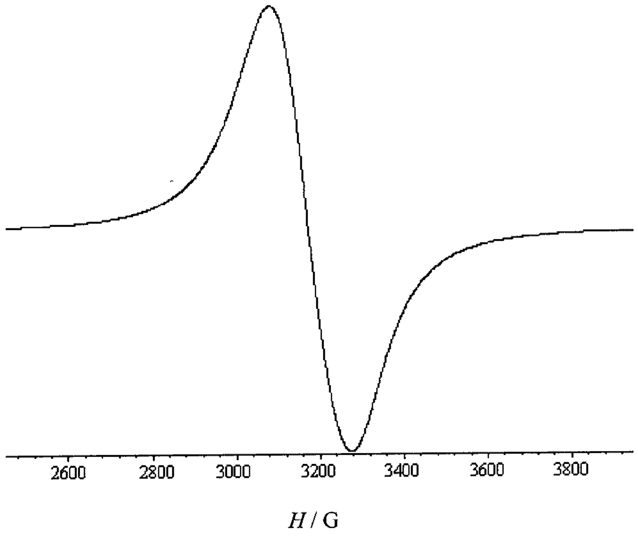

Figure 2. The powder X-band ESR spectrum of **1** at room temperature

A magnetic susceptibility measurement for **1** was carried out in the temperature range 5−300 K. The temperature dependence of the magnetic susceptibilities (χ_m) and the effective magnetic moments (μ_{eff}) versus T plot for **1** is shown in Figure 3. The tetranuclear complex has a room-temperature magnetic moment of 3.23 μ_B. The μ_{eff} value increases markedly below 20 K and reaches a maximum of 3.63 μ_B. This magnetic behavior suggests the operation of a ferromagnetic spin-exchange in the complex, which is probably due to the magnetic orbitals between copper(II) ions being orthogonal to each other through the bridging chromate ligand. The magnetic susceptibility data were fitted to the equation for a triangular unit of $S = 1/2$ spins. The parameters giving the best fit were $2J = +1.8\ \mathrm{cm}^{-1}$, $g = 2.15$, and $R = 1.4 \times 10^{-4}$ $\{R = [(\chi_m^{obs} - \chi_m^{calc})^2/(\chi_m^{obs})^2]\}$. These results confirmed that the spin coupling between copper(II) ions through the bridging chromate ligand is a ferromagnetic spin-exchange interaction.

Propagation of the ferromagnetic interaction in **1** can be understood from the orbital topology of the frontier orbitals (Figure 4). If we assume that the chromate ion has a tetrahedral geometry (the X-ray crystallographic analysis of **1** revealed a pesudotetrahedral symmetry), we would expect the d-orbitals of the chromium ion to be split into e- and t_2-type orbitals and the p-orbitals of the coordinated oxygen atoms to form a_1- and t_2-type orbitals.[7,8] 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 chromium ion, however, form triply degenerate bonding and antibonding orbitals with those of the oxygen p-orbitals and six electrons from the coordinated oxygen p-orbitals occupy the t_2-type bonding orbitals.

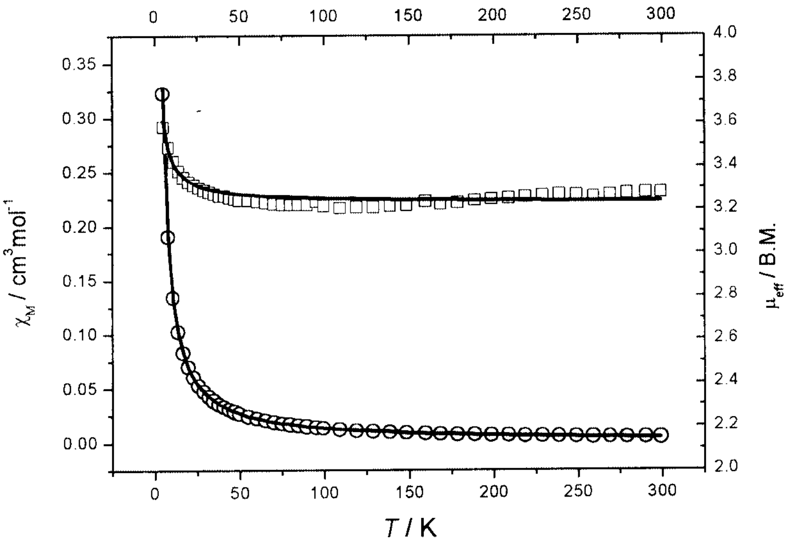

Figure 3. Plots of χ_m vs. *T* (O) and μ_{eff} vs. *T* (□) for **1**; the solid line represents the best fit of the experimental data using the parameters described in the text

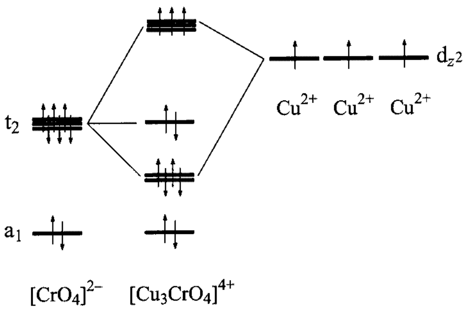

Figure 4. A proposed molecular orbital scheme for the $[Cu_3CrO_4]^{4+}$ chromophore

As revealed by previous measurements, the magnetic orbital of copper(II) ion is d_{z^2}. Thus, when the chromate anion bridges copper(II) ions, two of the t_2-type molecular orbitals of the chromate anion form two sets of σ-type bonding and antibonding orbitals with the d_{z^2} orbitals of the three copper(II) ions; the remainder of the t_2-type orbitals remains nonbonding. The d_{z^2} orbitals of the copper(II) ions and the oxygen p-orbitals interact to mix through the LMCT (O → Cu) interactions. Since the molecular geometry of the complex is pesudo-C_{3v}, orbitals do degenerate under C_{3v} symmetry. The three unpaired electrons from the d_{z^2} orbitals of copper(II) ions occupy three antibonding orbitals. The magnetic susceptibility measurement of **1** does show a ferromagnetic interaction between the copper(II) ions. Therefore, the three antibonding MOs with three spins must be energetically close enough to stabilize the high-spin state. It should be noted here that $[LFe^{III}(\mu\text{-}CrO_4)_3Fe^{III}L]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) shows an antiferromagnetic interaction ($2J = -15$ cm^{-1}) between the high-spin iron(III) centers through the three chromate bridges.[12] The antiferromagnetic interaction in the iron(III) complex might be understood by an extra π-orbital overlap between $[CrO_4]^{2-}$ and Fe^{III} ions leading to the nondegenerate frontier orbitals of the $[Fe_2^{III}(\mu\text{-}CrO_4)_3]$ chromophore.

In conclusion, the first tetranuclear complex $[\{Cu(bpy)_2\}_3(\mu\text{-}CrO_4)](ClO_4)_4\cdot H_2O$ bridged by a chromate ion in a (μ-CrO_4-*O*,*O*′,*O*″) mode is reported in this paper. This complex was structurally analyzed by X-ray diffraction crystallography. Variable-temperature magnetic studies verify the validity of the chromate bridging unit linking the tricopper system with ferromagnetic interactions. These results enhance the fruitful research field of the magnetochemistry of polynuclear metal complexes.

Experimental Section

General: Infrared spectra were recorded as KBr discs on a Shimadzu IR-408 infrared spectrometer in the 4000−600 cm^{-1} region. UV/Vis absorption spectra were recorded on a Shimadzu UV-2101 spectrophotometer. The X-band ESR spectra of polycrystalline powders were collected on a Bruker ER 200 D-SRC ESR spectrometer at both room temperature and 77 K. Magnetic susceptibility data were collected in the 5−300 K range using a Quantum Design MPMS-7 SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.[15]

Preparation of 1: A solution of K_2CrO_4 (97 mg, 0.5 mmol) in H_2O (5 mL) was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (186 mg, 0.5 mmol) and bpy (78 mg, 0.5 mmol) in CH_3CN (10 mL). The reaction mixture was then stirred for 30 min. Dark green single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature over several days. Yield: 70 mg (50%). $C_{60}H_{50}Cl_4CrCu_3N_{12}O_{21}$ (1659.54): calcd. C 43.39, H 2.89, N 10.16; found C 43.15, H 2.79, N 10.07. Important IR absorptions (KBr): $\tilde{\nu}$ = 3500 (br), 1610 (s), 1090 (br), 885 (s) cm^{-1}.

X-ray Crystallographic Analysis of 1:[16] A single crystal of **1** with approximate dimensions 0.20 × 0.25 × 0.30 mm was mounted on a glass fiber. A full data collection was performed with graphite monochromatized Mo-$K_α$ radiation ($λ = 0.71073$ Å) on a Bruker SMART 1000 diffractometer equipped with a CCD camera. Cell parameters were determined from a least-squares refinement. The intensities of the ±hkl reflections were measured up to $θ_{max} = 25.03°$ using a ω-2θ scan technique. The absorption correction was performed empirically.[17] The structure was solved by direct methods using SHELXS-97,[18] and refined by full-matrix least-squares on F^2 using SHELXL-97.[19] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were set in their calculated positions and treated as riding atoms with a common fixed isotropic thermal parameter. Further data of the X-ray structure analysis are given in Table 1.

Table 1. Crystallographic data for **1**

Empirical formula	$C_{60}H_{50}Cl_4CrCu_3N_{12}O_{21}$
Molecular weight	1659.54
T [K]	298(2)
Space group	$P\bar{1}$
a [Å]	12.0788(15)
b [Å]	13.3687(18)
c [Å]	22.489(3)
α [°]	83.337(2)
β [°]	75.063(2)
γ [°]	71.994(2)
V [Å]^3	3334.3(7)
Z	2
$ρ$ (calcd.) [g/cm^3]	1.653
F(000)	1682
μ [mm^{-1}]	1.348
$θ$ range [°]	0.94−25.03
Index ranges	$-11 \le h \le 14$, $-15 \le k \le 14$, $-19 \le l \le 26$
Reflections collected	13897
Independent reflections	11708 ($R_{int} = 0.0289$)
Observed reflections [$I > 2σ(I)$]	6750
Data/restraints/parameters	11708/0/928
Goodness-of-fit on F^2	0.991
$R1$[a] [$I > 2σ(I)$]; $wR2$[b][b]	0.0572; 0.1454
Largest diff. peak/hole [e/Å^3]	0.810, −0.549

[a] $R1 = Σ||F_o| - |F_c||/Σ|F_o|$. [b] $wR2 = [Σw(F_o{}^2 - F_c{}^2)^2/Σ(F_o{}^2)^2]^{1/2}$.

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[16] CCDC-155520 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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