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Ferromagnetic Dihydroxo-Bridged Cr(III)–Cu(II) and Cr(III)–Cu(II)–Cr(III) Complexes, $[Cr(tet\ b)(OH)_2Cu(bpy)(CH_3OH)](ClO_4)_3$ and $\{Cu[Cr(tet\ b)(OH)_2]_2\}(ClO_4)_4 \cdot H_2O$ (tet b = Racemic 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane and bpy = 2,2′-Bipyridine)

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A dihydroxo-bridged binuclear Cr(III)–Cu(II) complex, $[Cr(tet\ b)(OH)_2Cu(bpy)(CH_3OH)](ClO_4)_3$ (**1**) (and its methanol-free complex **1′**), and a trinuclear Cr(III)–Cu(II)–Cr(III) complex, $\{Cu[Cr(tet\ b)(OH)_2]_2\}(ClO_4)_4 \cdot H_2O$ (**2**) have been synthesized and characterized, where tet b = racemic 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and bpy = 2,2′-bipyridine. The cryomagnetic measurements (4.2–300 K) indicated the operation of a ferromagnetic interaction between the adjacent chromium(III) and copper(II) ions in both complexes. On the basis of spin Hamiltonians $\hat{H} = -2J\hat{S}_1\hat{S}_2$ for **1′** and $\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3)$ for **2** ($S_1 = S_3 = {}^3/_2$, $S_2 = {}^1/_2$), the spin-coupling constant J was evaluated at +25 cm^{-1} for **1′** and +40 cm^{-1} for **2**. Complex **1** ($C_{27}H_{50}N_6O_{15}Cl_3CrCu$) crystallized in monoclinic space group $P2_1/n$, with fw = 920.63, $a = 12.659$ (5) Å, $b = 24.008$ (9) Å, $c = 12.678$ (4) Å, $\beta = 96.13$ (3)°, $V = 3830.9$ Å^3, $Z = 4$, $R = 0.051$, and $R_w = 0.042$ for 3706 reflections with $I/\sigma(I) \geq 3$. The X-ray analysis showed a dihydroxo-bridged binuclear Cr(III)–Cu(II) structure with the Cr–Cu distance being 2.989 (2) Å, where the chromium and copper atoms assume a distorted-octahedral and a distorted-tetragonal-pyramidal geometry, respectively.

Introduction

Hetero-metal polynuclear complexes have been the subject of many recent studies with the hope of mimicking the active site of some metal enzymes containing dissimilar metal ions, such as cytochrome oxidase[1] and superoxide dismutase,[2] and elucidating the mechanism of spin coupling between paramagnetic metal ions in view of the electronic structures of the interacting metal ions.[3,4] Hetero-metal complexes exhibiting a ferromagnetic spin coupling are particularly interesting in view of elucidating fundamental factors, which give rise to such a ferromagnetic spin coupling,[3,4] and their potential use as a building unit in designing molecular-based ferromagnets.[5] However, examples of such heteronuclear complexes are still very limited. In most cases ferromagnetic interaction between metal ions arises from either the strict or the accidental orthogonality of the magnetic orbitals of the interacting metal ions.[3] The accidental orthogonality depends on some structural parameters in a quite subtle manner.[4] On the other hand, the strict orthogonality may be invoked by choosing appropriate metal ions.[3] A combination of metal ions to give rise to such a strict orthogonality of the magnetic orbitals may be chromium(III) and copper(II), because the unpaired electrons of octahedral chromium(III) reside in d_π orbitals whereas the unpaired electron of tetragonal copper(II) resides in a d_σ orbital. Only two examples of chromium(III)–copper(II) polynuclear complexes have been reported so far, though their crystal structures have not been determined.[6,7] One is a phenolato-bridged binuclear Cr(III)–Cu(II) complex by Kahn et al.[6] and another is an imidazolate-bridged trinuclear Cu(II)–Cr(III)–Cu(II) complex by Matsumoto et al.[7] In both cases the spin exchange between chromium(III) and copper(II) ions was found to be ferromagnetic.

In order to provide more examples of polynuclear Cr(III)–Cu(II) complexes with a new bridging system, in this study, a dihydroxo-bridged binuclear chromium(III)–copper(II) complex $[Cr(tet\ b)(OH)_2Cu(bpy)(CH_3OH)](ClO_4)_3$ (**1**) (and its methanol-free complex **1′**) and a trinuclear chromium(III)–copper(II)–chromium(III) complex $\{Cu[Cr(tet\ b)(OH)_2]_2\}(ClO_4)_4 \cdot H_2O$ (**2**) have been synthesized, where tet b = racemic 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and bpy = 2,2′-bipyridine. The chemical structures of **1** and **2** are given in Figure 1. Their magnetic properties were studied as functions of temperature down to liquid helium temperature, and complex **1** was subjected to single-crystal X-ray analysis.

Experimental Section

Reagents. All chemicals used in this work were reagent grade and used as commercially obtained.

Physical Measurements. Elemental analyses for C, H, and N were carried out at the Service Center of Elemental Analysis, Kyushu University. Metal (Cu and Cr) analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were measured on KBr disks with a JASCO IR-810 spectrophotometer. Electronic spectra were recorded by the diffuse-reflectance technique on a Shimadzu multipurpose spectrophotometer Model MPS-2000. Magnetic susceptibilities were measured by the use of a HOXAN HSM-D SQUID magnetometer in the temperature range 4.2–100 K and by the use of a Faraday balance in the temperature range 80–300 K. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$.[8] Diamagnetic corrections were made with Pascal's constants.[9] Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms. X-Band electron spin resonance spectra of powder samples were recorded at room temperature and liquid nitrogen temperature on a JEOL JES-FE3X ESR spectrometer.

Preparations. ***Caution!*** Perchlorate salts of metal complexes are potentially explosive. Only a small amount of materials should be prepared, and they should be handled with caution.

$[Cr(tet\ b)(OH)_2]ClO_4 \cdot 2H_2O$. This compound was prepared by the literature method.[10]

$[Cr(tet\ b)(OH)_2Cu(bpy)](ClO_4)_3$ (1′). Copper(II) perchlorate hexahydrate (93 mg, 0.25 mmol) and bpy (39 mg, 0.25 mmol) were dissolved in a CH_3OH–CH_3CN mixture (ca. 3:2 in volume, 6 cm^3). This solution was added to a methanol solution (6 cm^3) of $[Cr(tet\ b)(OH)_2]ClO_4 \cdot 2H_2O$ (126 mg, 0.25 mmol). The color of the solution changed immediately from blue to violet, and soon purple crystals were deposited. The crystals were collected by filter suction, washed with methanol, and desiccated in vacuo. Anal. Calcd for $C_{26}H_{46}N_6O_{14}Cl_3CrCu$: C, 35.14; H, 5.22; N, 9.46; Cr, 5.85; Cu, 7.15. Found: C, 35.03; H, 5.20; N, 9.49; Cr, 5.77; Cu, 7.28.

As the filtrate cooled in a refrigerator, single crystals of the mono-CH_3OH adduct (**1**) were obtained as purple plates and used for X-ray structure analysis. The same single crystals could be grown by keeping a diluted reaction solution in a refrigerator.

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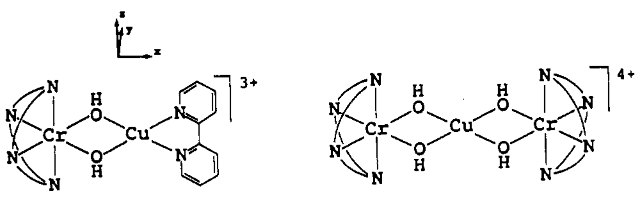

Figure 1. Schematic representations of the complexes: (a) $[Cr(tet\ b)(OH)_2Cu(bpy)(CH_3OH)]^{3+}$; (b) $\{Cu[Cr(tet\ b)(OH)_2]_2\}^{4+}$. The N_4 macrocycle denotes racemic 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet b).

Table I. Crystallographic Data for $[Cr(tet\ b)(OH)_2Cu(bpy)(CH_3OH)](ClO_4)_3$

formula $C_{27}H_{50}N_6O_{15}Cl_3CrCu$	fw = 920.6
a = 12.659 (5) Å	space group $P2_1/n$
b = 24.008 (9) Å	T = 20 °C
c = 12.678 (4) Å	λ = 0.71069 Å
β = 96.13 (3)°	ρ_{calcd} = 1.596 g cm^{-3}
V = 3830.9 Å^3	μ(Mo Kα) = 11.14 cm^{-1}
Z = 4	R = 0.051, R_w = 0.042

Table II. Positional and Isotropic Equivalent Thermal Parameters of Selected Atoms for $[Cr(tet\ b)(OH)_2Cu(bpy)(CH_3OH)](ClO_4)_3$

atom	x	y	z	B,[a] Å^2
Cr	0.36055 (8)	0.14869 (4)	0.27779 (8)	2.00 (3)
Cu	0.20234 (7)	0.05585 (4)	0.26439 (6)	2.69 (2)
OA	0.2306 (3)	0.1244 (2)	0.1924 (3)	2.6 (1)
OB	0.3406 (3)	0.0747 (2)	0.3371 (3)	2.5 (1)
N1	0.4751 (4)	0.1173 (2)	0.1813 (4)	2.5 (2)
N2	0.3639 (4)	0.2228 (2)	0.1913 (4)	2.9 (2)
N3	0.2696 (4)	0.1955 (2)	0.3793 (4)	2.6 (2)
N4	0.4926 (4)	0.1649 (2)	0.3875 (4)	2.4 (2)
N5	0.0605 (4)	0.0407 (2)	0.1886 (4)	3.1 (2)
N6	0.1531 (4)	0.0025 (2)	0.3698 (4)	2.8 (2)
OM	0.2745 (4)	−0.0240 (2)	0.1708 (4)	4.4 (2)
CM	0.2551 (6)	−0.0808 (3)	0.1999 (6)	4.7 (3)

[a] Values are given in the form of the equivalent displacement parameters defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos bc(\cos\alpha)\beta_{23}]$.

$\{Cu[Cr(tet\ b)(OH)_2]_2\}(ClO_4)_4\cdot H_2O$ (2). To a methanol solution (ca, 8 cm^3) of $[Cr(tet\ b)(OH)_2]ClO_4\cdot 2H_2o$ (168 mg, 0.33 mmol) was added a solution of copper(II) perchlorate hexahydrate (62 mg, 0.17 mmol) in a $CH_3OH–CH_3CN$ mixture (ca. 5:1 in volume, 6 cm^3). The resulting violet solution was left standing about 3 h to give red-purple crystals, which were collected by filter suction and dried in vacuo. Anal. Calcd for $C_{32}H_{78}N_8O_{21}Cl_4Cr_2Cu$: C, 31.49; H, 6.11; N, 9.18; Cr, 8.52; Cu, 5.21. Found: C, 31.32; H, 6.25; N, 9.12; Cr, 8.37; Cu, 5.17.

X-ray Structural Analysis of 1. Crystals of **1** were obtained as described earlier in this section, and X-ray data were collected on a Rigaku Denki AFC-5 four-circle automated diffractometer with graphite-monochromatized Mo Kα radiation at ambient temperature (20 ± 1 °C), as summarized in Table I. The cell parameters were determined by 25 reflections in the 2θ range $20° < 2\theta < 30°$. Standard reflections were monitored every 100 reflections and showed good stabilities. Intensity data were corrected for Lorentz and polarization effects, but no absorption correction was applied. A total of 3706 observed reflections with $I/\sigma(I) \geq 3$ was used for the structure determination.

The structure was solved by the standard heavy-atom method and refined by the block-diagonal least-squares method. Reliability factors were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, where the weights were taken as $w = 1/(\sigma(F))^2$. Atomic scattering factors were taken from ref 11. The hydrogen atoms were located by difference Fourier synthesis and included in the last cycle of least-squares calculation. The final difference Fourier synthesis was featureless. The computation was carried out on a FACOM VP-100 computer at the Computer Center of Kyushu University, by the use of the UNICS III program system.[12] Positional parameters of selected atoms are given in Table II.

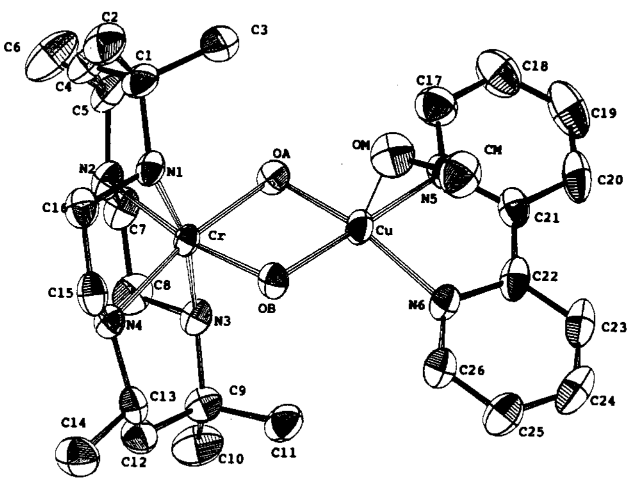

Figure 2. Molecular structure of $[Cr(tet\ b)(OH)_2Cu(bpy)(CH_3OH)]^{3+}$ with the atom-numbering scheme. Atoms are represented by their displacement ellipsoids at the 50% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Cr(tet\ b)(OH_2)Cu(bpy)(CH_3OH)](ClO_4)_3$[a]

	Bond Distances (Å)		
Cr–Cu	2.989 (2)	Cr–OA	1.959 (4)
Cr–OB	1.955 (4)	Cr–N1	2.132 (5)
Cr–N2	2.093 (5)	Cr–N3	2.135 (5)
Cr–N4	2.093 (5)	Cu–OA	1.933 (4)
Cu–OB	1.942 (4)	Cu–N5	1.978 (5)
Cu–N6	1.998 (5)	Cu–OM	2.479 (5)
	Bond Angles (deg)		
Cr–OA–Cu	100.4 (2)	Cr–OB–Cu	100.2 (2)
OA–Cr–OB	78.8 (2)	OA–Cr–N1	99.2 (2)
OA–Cr–N2	91.5 (2)	OA–Cr–N3	90.8 (2)
OA–Cr–N4	170.4 (2)	OB–Cr–N1	91.3 (2)
OB–Cr–N2	169.8 (2)	OB–Cr–N3	98.3 (2)
OB–Cr–N4	92.2 (2)	N1–Cr–N2	87.0 (2)
N1–Cr–N3	167.3 (2)	N1–Cr–N4	84.5 (2)
N2–Cr–N3	84.9 (2)	N2–Cr–N4	97.5 (2)
N3–Cr–N4	86.9 (2)	OA–Cu–OB	79.8 (2)
OA–Cu–N5	97.6 (2)	OA–Cu–N6	161.4 (2)
OB–Cu–N5	177.1 (2)	OB–Cu–N6	99.3 (2)
N5–Cu–N6	82.8 (2)	OA–Cu–OM	109.6 (2)
OB–Cu–OM	92.8 (2)	N5–Cu–OM	89.2 (2)
N6–Cu–OM	89.0 (2)		

[a] Number in parentheses are estimated standard deviations in the least significant digits.

Results and Discussion

Synthetic Route. Many bis(μ-hydroxo)dicopper(II) and bis(μ-hydroxo)dichromium(III) complexes have been prepared, and correlations have been established between structural parameters and spin coupling between two metal centers.[4] To the best of our knowledge, however, no dihydroxo-bridged chromium(III)–copper(II) heteronuclear complex has been reported so far.

In general, two synthetic strategies have been adopted for the preparation of hetero-metal polynuclear complexes. The first is to use designed polynucleating ligands, which offer dissimilar coordination sites suitable for dissimilar metal ions.[13-16] The

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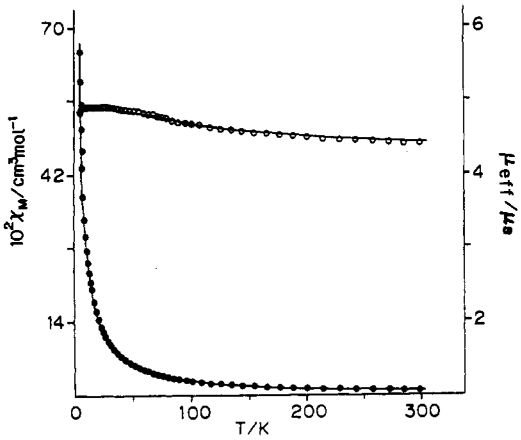

Figure 3. Temperature dependence of the magnetic susceptibility (●) and effective magnetic moment (○) per molecule for **1′**.

second is to use a complex as a "ligand" that contains potential donor groups capable of coordinating to another metal ion.[17-24] In this study we have adopted the latter strategy. As a "ligand complex" we have chosen [Cr(tet b)$(OH)_2$]$ClO_4 \cdot 2H_2O$ because this complex has a distorted cis octahedral structure with respect to the hydroxo groups[10-25] and is expected to function as a bidentate ligand to another metal ion through the hydroxo groups. In fact, the reaction of [Cr(tet b)$(OH)_2$]$ClO_4 \cdot 2H_2O$, copper(II) perchlorate hexahydrate, and bpy in the 1:1:1 mole ratio gave [Cr(tet b)$(OH)_2$Cu(bpy)]$(ClO_4)_3$ (**1′**) and its methanol adduct [Cr(tet b)$(OH)_2$Cu(bpy)(CH_3OH)]$(ClO_4)_3$ (**1**). Further, the reaction of [Cr(tet b)$(OH)_2$]$ClO_4 \cdot 2H_2O$ and copper(II) perchlorate hexahydrate in the 2:1 mole ratio gave a trinuclear complex {Cu[Cr(tet b)$(OH)_2]_2$}$(ClO_4)_4 \cdot H_2O$ (**2**).

X-ray Structure of 1. The crystal consists of a binuclear [Cr(tet b)$(OH)_2$Cu(bpy)(CH_3OH)]$^{3+}$ cation and perchlorate ions. A perspective view of the cation is given in Figure 2, together with the atom-numbering system. Relevant bond distances and angles with their estimated standard deviations are given in Table III.

The binuclear cation has a dihydroxo-bridged chromium(III)–copper(II) structure with a Cr- - -Cu distance of 2.989 (2) Å. The chromium atom is six-coordinated with the tetradentate tet b in the folded configuration and two hydroxo groups in cis position. Thus, the Cr(tet b)$(OH)_2$ entity of **1** is essentially similar to [Cr(tet b)$(OH)_2$]$ClO_4 \cdot 2H_2O$.[25] The two nitrogen atoms N2 and N4 of the tet b ligand and the two oxygen atoms, OA and OB, of the hydroxo groups delimit the equatorial plane of a distorted octahedron, and N1 and N3 of tet b occupy the apices. The equatorial four-coordinating atoms N2, N4, OA, and OB are nearly coplanar within the deviation 0.055 Å, and the chromium atom is located on the mean plane with a deviation of 0.006 Å. The apical bond distances Cr–N1 (2.133 (6) Å) and Cr–N3 (2.140 (6) Å) are similar to the corresponding distances (2.142 (2) Å) of mononuclear [Cr(tet b)$(OH)_2$]$ClO_4 \cdot 2H_2O$. The equatorial bond distances Cr–N2 (2.093 (5) Å) and Cr–N4 (2.093 (5) Å) are shorter than those (2.142 (2) Å) of the mononuclear species, whereas the equatorial distances Cr–OA (1.956 (4) Å) and Cr–OB (1.955 (4) Å) are longer than those (1.918 (2) Å) of the mononuclear species.

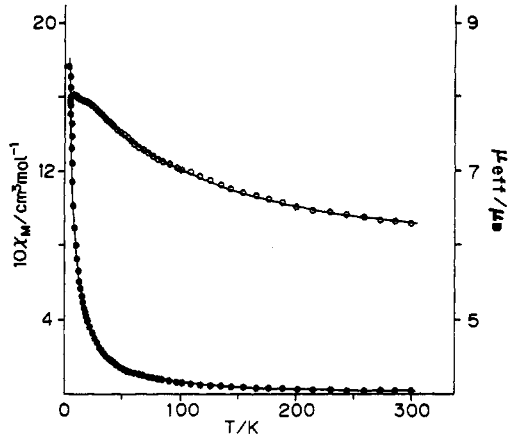

Figure 4. Temperature dependence of the magnetic susceptibility (●) and effective magnetic moment (○) per molecule for **2**.

The coordination geometry around the copper can be described as a square pyramid, where the basal coordination sites are occupied by the two hydroxo oxygens OA and OB and the two nitrogens N5 and N6 of bpy. At the apical site the oxygen atom OM of the methanol molecule is weakly coordinated with a Cu–OM distance of 2.479 (5) Å. In accord with the weak coordination, the methanol molecule is readily removed in the open atmosphere to give [Cr(tet b)$(OH)_2$Cu(bpy)]$(ClO_4)_4$ (**1′**). The basal donor atoms OA, OB, N5, and N6 deviate from the mean plane by ca. 0.15 Å, and the copper atom deviates by 0.14 Å toward OM. The dihedral angle between the plane depicted by Cu, OA, and OB and the plane depicted by Cu, N5, and N6 is 18.9°.

Magnetic Properties. Because complex **1** effloresced in the air to give the methanol-free complex **1′**, the cryomagnetic investigations were made for **1′**. The results are shown in Figure 3 in the form of plots of χ_M vs T and μ_{eff} vs T, where χ_M, μ_{eff}, and T denote magnetic susceptibility per molecule, effective magnetic moment per molecule, and temperature, respectively. The effective magnetic moment per molecule is 4.40 μ_B at room temperature, which is close to the spin-only value of 4.24 μ_B for the magnetically noninteracting Cr(III)–Cu(II) system ($S_1 = {}^3/_2$, $S_2 = {}^1/_2$). When the temperature is lowered, the magnetic moment increases gradually and reaches a plateau (μ_{eff} = 4.90 μ_B) at 34 K. Then the moment tends to decrease and reaches 4.85 μ_B at 4.5 K. The plateau value of 4.90 μ_B is equal to the spin-only value for S = 2, which may arise from a ferromagnetic spin coupling between the Cr(III) and Cu(II) ions. Thus, the observed magnetic behavior clearly demonstrates the operation of a intramolecular ferromagnetic spin-exchange interaction through the hydroxo bridges. A slight decrease in the magnetic moment below 5.5 K may be attributed to an intermolecular antiferromagnetic interaction or a zero-field splitting on Cr(III). The contribution of the intermolecular interaction and the zero-field splitting are evidently weaker than the intramolecular spin exchange. Therefore, the magnetic analysis of this complex has been made by neglecting the effects.

The magnetic susceptibility equation for the system, based on the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$, is given as follows:[26]

$$\chi_M = \frac{Ng^2\beta^2}{kT}\,\frac{10 + 2\exp(-4J/kT)}{5 + 3\exp(-4J/kT)} + N\alpha \qquad (1)$$

where each symbol has its usual meaning. As shown in Figure 3, good fits to the exoerimental data were attained with (1) by using magnetic parameters g = 2.00, J = +25 cm^{-1}, and $N\alpha$ =

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100×10^{-6} cm^3 mol^{-1}, where the discrepancy factor $[\sum(\mu_{\text{obsd}} - \mu_{\text{calcd}})^2/\sum\mu_{\text{obsd}}^2]^{1/2}$ was 0.005. The triplet–quintet energy gap ($4J$) is evaluated at 100 cm^{-1} in this case, which is about half of that of the phenolato-bridged Cr(III)–Cu(II) complex.[6]

The ESR spectrum of powdered sample **1** at room temperature presents at least 11 resonances at 200 G (g = 33.69), 589 G (g = 11.44), 1200 G (g = 5.62), 2038 G (g = 3.31), 2413 G (g = 2.79), 2832 G (g = 2.19), 3288 G (g = 2.05), 3500 G (g = 1.93), 4250 G (g = 1.59), 4800 G (g = 1.40), and 5275 G (g = 1.28). When the sample is cooled to liquid nitrogen temperature, the spectrum significantly changes and becomes less resolved. The most pronounced change is that the strong signal at g = 11.44 is weakened and becomes a shoulder around g = 10.8. The other resonances at about 78 K are at g = 34.97, 4.65, 2.75, 2.21, 2.05, 1.66, 1.41, and 1.19. The analysis of the spectrum was not made in this work.

The magnetic property of **2** is shown in Figure 4. The effective magnetic moment per molecule is 6.3 μ_B at room temperature, which is larger than the spin-only value of 5.74 μ_B for the magnetically noninteracting Cr(III)–Cu(II)–Cr(III) system ($S_1 = {}^3/_2$, $S_2 = {}^1/_2$, $S_3 = {}^3/_2$). As the temperature is lowered, the magnetic moment increases gradually, reaches a plateau (8.0 μ_B) at ca. 11 K, and then tends to decrease below 5 K to 7.88 μ_B at 4.4 K. The plateau value is close to the spin-only value of 7.94 μ_B for $S = {}^7/_2$, which may arise from a ferromagnetic spin coupling of the trinuclear system ($S_1 = {}^3/_2$, $S_2 = {}^1/_2$, $S_3 = {}^3/_2$). The magnetic behavior demonstrates that the magnetic interaction between the adjacent chromium(III) and copper(II) ions is ferromagnetic to afford the spin octet ($S_T = {}^7/_2$) ground state for the trinuclear complex. As in the case of **1′**, a slight decrease in the magnetic moment below 5 K may be attributed to an intermolecular antiferromagnetic interaction and/or a zero-field splitting on Cr(III). The second effect is very small and hence neglected in the following magnetic analysis.

On the basis of the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_2(\hat{S}_1 + \hat{S}_3)$ with $S_1 = S_3 = {}^3/_2$ and $S_2 = {}^1/_2$ and according to Kambe's procedure,[27] the low-lying spin states in zero field are obtained. The ground spin state is of the largest spin multiplicity ($S = {}^7/_2$). Upon going up in energy, the spin multiplicity first decreases from ${}^7/_2$ to ${}^1/_2$ and then increases from ${}^1/_2$ to ${}^5/_2$. Such an irregular spin order was pointed out by Kahn et al.[3,28] for trinuclear A–B–A complexes with a spin correlation $2S_A > (S_B + {}^1/_2)$. Even if the spin coupling is antiferromagnetic ($J < 0$), the ground spin state in such complexes is not of the smallest spin multiplicity but of $2S_A - S_B$. Here our emphasis is placed on the fact that complex **2** is the first example of irregular spin order structure with $J > 0$. By applying the Van Vleck equation,[29] the theoretical expression of magnetic susceptibility for the trinuclear Cr(III)–Cu(II)–Cr(III) system ($S_1 = {}^3/_2$, $S_2 = {}^1/_2$, $S_3 = {}^3/_2$) is given as follows:

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left(\frac{A}{B}\right) + N\alpha \qquad (2)$$

where $A = 84 + 35\exp(x) + 10\exp(2x) + \exp(3x) + \exp(5x) + 10\exp(6x) + 35\exp(7x)$, $B = 16 + 12\exp(x) + 8\exp(2x) + 4\exp(3x) + 4\exp(5x) + 8\exp(6x) + 12\exp(7x)$, and $X = -J/kT$.

The magnetic property of **2** could be well simulated with (2), as displayed by the traces in Figure 4. The fitting parameters are as follows: $g = 2.01$, $J = 40$ cm^{-1}, $N\alpha = 150 \times 10^{-6}$ cm^3 mol^{-1}, and the discrepancy factor 0.008.

The ESR spectrum of powdered sample **2** at room temperature presents at least seven resonances at 275 G (g = 24.53), 940 G (g = 7.18), 1425 G (g = 4.73), 1750 G (g = 3.86), 2387 G (g = 2.83), 3294 G (g = 2.05), and 4525 G (g = 1.49). When the sample is cooled down to about 78 K, the broad signal at g = 2.05 splits into three resonances: a peak at g = 2.36, a signal centered at g = 2.00, and a shoulder around g = 1.65. The other features show no significant changes. The analysis was not made in this paper.

The ferromagneticf spin-coupling observed for **1′** can be rationalized by considering the symmetry of the molecule after the manner of Kahn et al.[3] On the basis of the crystal structure analysis, the molecular symmetry of **1** (methanol adduct) is approximated by the C_s point group. If the methanol molecule is eliminated without any change in the binuclear structure, the molecular symmetry of **1′** may be regarded as C_{2v}. With the coordinate system defined as in Figure 1, the unpaired electron ofthe copper(II) ion resides on the d_{xy} orbital, which transforms as the b_1 irreducible representatioin of the C_{2v} point group. The three unpaired electrons of the chromium(III) ion occupy the $d_{x^2-y^2}$, d_{yz}, and d_{xz} orbitals, which transform as a_1, a_2, and b_2 irreducible representations of the C_{2v} point group, respectively. Hence, no orbital interaction is feasible between the magnetic orbitals of the two metal centers. The molecular symmetry of **2** is unknown, but we believe that it is most likely that the ferromagnetism is caused by essentially the same mechanism as that for **1**.

Concluding Remarks

The present study has shown that [Cr(tet b)(OH)$_2$]ClO$_4$·2H$_2$O acts as a ligand through its hydroxo groups in cis positions to afford dihydroxo-bridged Cr(III)–Cu(II) and Cr(III)–Cu(II)–Cr(III) complexes. Both complexes show a ferromagnetic spin exchange within a complex molecule, owing to the strict orthogonality of the magnetic orbitals of the metal ions.

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Supplementary Material Available: Figures of ESR spectra of powder samples for **1** and **2** at room temperature and at liquid nitrogen temperature and listings of detailed crystal data (Table S1), atomic positional parameters (Table S3), H atom coordinates (Table S4), and bond distances and angles (Table S5) (8 pages); a listing of observed and calculated structure factors (Table S6) (17 pages). Ordering information is given on any current masthead page.

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