

A Ferromagnetically Coupled CrCu₃ Tetramer and GdCu₄ Pentamer with a [15]N₄ Macrocyclic Ligand Incorporating an Oxamido Bridge

Lei Zhang,[†] Shi-Bin Wang,[†] Guang-Ming Yang,^{*†} Jin-kui Tang,[†] Dai-Zheng Liao,^{*†} Zong-Hui Jiang,[†] Shi-Ping Yan,[†] and Peng Cheng[‡]

Department of Chemistry, Nankai University, Tianjin 300071, P.R. China, and State Key Laboratory of Coordination Chemistry, Nanjin University, Nanjin 210093, P.R. China

Received July 19, 2002

The synthesis and structural and magnetic properties of heteropolynuclear complexes [(L³Cu)₃Cr](CH₃CN)₃(ClO₄)₃ (**2**) and [(L³Cu)₄Gd·H₂O](CH₃OH)(H₂O)(ClO₄)₃ (**3**) (H₂L³ ligand is 2,3-dioxo-5,6:14,15-dibenzo-1,4,8,12-tetraazacyclopentadeca-7,12-diene) and their precursor L³Cu (**1**) are presented. Complex **2** crystallizes in space group *P2₁/n* with cell parameters *a* = 20.828(6) Å, *b* = 18.321(5) Å, *c* = 7.578(5) Å, α = 90°, β = 91.990(8)°, γ = 90°, and *Z* = 4. The Cr^{III} center is coordinated by six oxygen atoms from three Cu^{II} precursors. The Cr–O bonds range over 1.948–1.982 Å. The coordination environments of all the terminal Cu^{II} ions change in comparison with their Cu^{II} precursor. The ferromagnetic coupling (*J* = 16.48(1) cm⁻¹) observed for **2** can be rationalized by symmetry considerations. For any pair of interacting magnetic orbitals, strict orthogonality is obeyed and the interaction is ferromagnetic. Complex **3** crystallizes in space group *P* $\bar{1}$ with cell parameters *a* = 14.805(4) Å, *b* = 16.882(5) Å, *c* = 17.877(5) Å, α = 75.403(5)°, β = 83.317(6)°, γ = 70.600(5)°, and *Z* = 2. The central Gd^{III} assumes an 8 + 1 coordination environment, namely eight oxygen atoms from four Cu^{II} precursors and one oxygen atom from H₂O. The fit of the experimental data gives *J* = 0.27(2) cm⁻¹, *g*_{Gd} = 1.98(1), and *g*_{Cu} = 2.05(1). This small and positive *J* value shows weak ferromagnetic interaction between metal ions.

Introduction

Molecular magnetism and macrocyclic complexes are active fields of research, encompassing chemistry, physics, biology, and material science.^{1–7} The magnetism of heteropolymetallic complexes containing multiatomic bridges has received considerable attention, and much work has been devoted to studying the magnetism of polynuclear macrocyclic complexes containing phenolato oxygens as bridges.^{8,9}

However, there has been little investigation of polynuclear complexes of macrocyclic ligands containing multiatomic bridges such as oxamido and oximato groups. Several years ago, Christodoulou et al. reported two such binuclear macrocyclic complexes¹⁰ [Ni(α-diketo-TAD-Me₄)]ZnCl₂ and [Ni(α-diketo-TAD-Me₄)]Cu(NO₃)₂ (α-diketo-TAD-Me₄ is 2,3-dioxo-5,6:13,14-dibenzo-7,12-dimethyl-9,10-(4',5'-dimethylbenzo)-1,4,8,11-tetraazacyclotetradeca-7,11-diene) by using the Ni^{II} precursor as a “complex ligand”, but the diamagnetic nature of the Ni^{II} ions in these complexes precluded studies of magnetic interactions between the metal ions. Recently, we have also prepared several binuclear complexes of formulas [(CuLⁱ)Ni(rac-cth)](ClO₄)₂ (rac-cth is 5,7,7,12-, 14,14, hexamethyl-1,4,8,11-tetraazacyclodecane)¹¹ and tetranuclear complex of formulas [(LⁱCu)₃M](ClO₄)₂ (M = Mn^{II}, Fe^{III})^{12–17} by using the paramagnetic Cu^{II} precursors whose chemical structures are shown in Figure 1. However, only

* To whom correspondence should be addressed. E-mail: coord@nankai.edu.cn. Fax: +86-022-23502779.

[†] Nankai University.

[‡] Nanjin University.

(1) Kahn, O. *Struct. Bonding* **1987**, *68*, 89.

(2) Kahn, O. *Adv. Inorg. Chem.* **1996**, *43*, 179.

(3) Melson, G. A., Ed. *Coordination Chemistry of Macrocyclic Compounds*; Plenum: New York, 1979.

(4) Colacio, E.; Ghazi, M.; Kivekas, R.; Moreno, J. M. *Inorg. Chem.* **2000**, *39*, 2882.

(5) Gao, E. Q.; Yang, G. M.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *J. Chem. Res.* **1999**, 278.

(6) Yang, G. M.; Shi, J.; Yan, S. P.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L. *Polyhedron* **1998**, *17*, 1587.

(7) Kahn, O.; Pei, Y.; Verdaguier, M.; Renard, J. P.; Sletten, J. J. *Am. Chem. Soc.* **1988**, *110*, 782.

(8) Vigato, P. A.; Tamburini, S.; Fenton, D. E. *Coord. Chem. Rev.* **1990**, *25*, 106.

(9) Mohanta, S.; Nanda, K. K.; Werner, R.; Haase, W.; Mukherjee, A. K.; Dutta, S. K.; Nag, K. *Inorg. Chem.* **1997**, *36*, 4656.

(10) Christodoulou, D.; Kanatzidis, M. G.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 191.

(11) Gao, E. Q.; Tang, J. K.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *Helv. Chim. Acta* **2001**, 908.

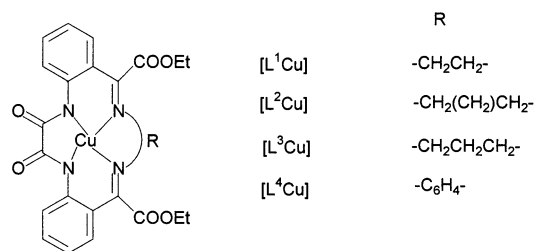


Figure 1. Chemical structures of Cu^{II} precursors.

few structures of these have been characterized by X-ray diffraction and cryomagnetic studies indicate all these complexes exhibiting antiferromagnetic coupling between Cu^{II} and M^{III} (M = Mn^{II}, Fe^{III}). From the viewpoint of molecular magnetism, the design of the high-spin molecules and ferromagnetic materials based on metal complexes has been one of the most important subjects in the field of inorganic chemistry. Several strategies have been proposed along this line. One of them consists of imposing a ferromagnetic interaction between nearest neighbor magnetic centers owing to the strict orthogonality of magnetic orbitals. Such a situation has been observed in several 3d–3d heterometal systems, such as Cu^{II}–VO^(IV), Cu^{II}–Cr^{III}, Ni^{II}–Cr^{III}, and low-spin Fe^{III}–Cu^{II} systems.^{18–21} However, such complexes are relatively rare, while a large number of complexes with antiferromagnetic coupling have been known. With this in mind, in continuation of our interest in polynuclear macrocyclic complexes and with the aim in designing a ferromagnetic interaction between two metal ions, we report here a new mononuclear Cu^{II} precursor L³Cu (**1**) (H₂L³ ligand is 2,3-dioxo-5,6:14,15-dibenzo-1,4,8,12-tetraazacyclo-pentadeca-7,12-diene) and two new heteropolynuclear complexes [(L³Cu)₃Cr](CH₃CN)₃(ClO₄)₃ (**2**) and [(L³Cu)₄Gd·H₂O](CH₃OH)(H₂O)(ClO₄)₃ (**3**) derived from the new mononuclear Cu^{II} precursor. We successively describe the synthesis, structure, and the magnetic properties of these two complexes. We will show that Cu₃Cr has a high-spin ground state arising from ferromagnetic interaction between Cr^{III} and Cu^{II} ions. To our knowledge, this constitutes the first example of such a heterotetranuclear Cu₃Cr assembling [15]-N₄ macrocyclic oxamide complex exhibiting ferromagnetic interaction.

- (12) Gao, E. Q.; Yang, G. M.; Tang, J. K.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P. *Polyhedron* **1999**, *18*, 3645.
 (13) Gao, E. Q.; Yang, G. M.; Wang, G. L. *Transition Met. Chem.* **1999**, *24*, 244.
 (14) Gao, E. Q.; Bu, W. M.; Yang, G. M.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *J. Chem. Soc., Dalton. Trans.* **2000**, 1431.
 (15) Tang, J. K.; Wang, Q. L.; Gao, E. Q.; Chen, J. T.; Liao, D. Z.; Jiang, Z. h.; Yan, S. P.; Cheng, P. *Helv. Chim. Acta* **2002**, *85*, 175.
 (16) Tang, J. K.; Li, Y. Z.; Wang, Q. L.; Gao, E. Q.; Liao, D. Z.; Jiang, Z. h.; Yan, S. P.; Cheng, P.; Wang, L. F.; Wang, Q. L. *Inorg. Chem.* **2002**, *41*, 2188.
 (17) Tang, J. K.; Wang, L. Y.; Zhang, L.; Gao, E. Q.; Liao, D. Z.; Jiang, Z. h.; Yan, S. P.; Cheng, P. *J. Chem. Soc., Dalton. Trans.* **2002**, 1607.
 (18) Kahn, O.; Galy, J.; Journaux, Y.; Jaud, J.; Morgenstern-badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 2165.
 (19) Journaux, Y.; Kahn, O.; Coudanne, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 624.
 (20) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1989**, *28*, 100.
 (21) Koch, C. A.; Reed, C. A.; Brewer, G. A.; RATH, N. P.; Scheidet, W. R.; Gupta, G.; Lang, G. J. *Am. Chem. Soc.* **1989**, *111*, 7645.

Experimental Section

General Procedures. All the starting chemicals were of AR grade and used as received. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Shimadzu IR-408 spectrometer as KBr pellets. Variable-temperature magnetic susceptibilities (4–300 K) were measured on a Quantum Design MPMS-7 SQUID magnetometer in a field of 5000 Oe. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

Caution! *Perchlorate salts are potentially explosive and should only be handled in small quantities.*

Synthesis of the LCu (1**) Precursors.** The L ligand (L is 2,2'-(oxalyldiimino)bis(benzaldehyde)) was prepared according to the literature.^{22,23} L³Cu (**1**) was prepared by refluxing and stirring L ligand (2.94 g, 0.01 mol), 1,3-propanediamine (1.6 mL, 0.02 mol), and CuAc·H₂O (2.00 g, 0.01 mol) for 2 h in 50 mL of MeOH with the presence of 4 drops of 2 M NaOH. After the mixture was cooled and filtered, the precipitate thus obtained was washed with water, methanol, and diethyl ether successively and dried under vacuum. The resulting deep green filtrate, kept at room temperature for several days, gave rise to green prismatic crystals suitable for X-ray analysis. Yield: 40%. Anal. Calcd: C, 57.64; H, 4.07; N, 14.15. Found: C, 57.92; H, 3.77; N, 14.44. IR (KBr disk, cm⁻¹): ν_{C=O} 1640, ν_{C=N} 1610, 1590.

Synthesis of [(L³Cu)₃Cr](CH₃CN)₃(ClO₄)₃ (2**).** L³Cu (**1**) (0.1422 g 0.36 mmol) and Cr(ClO₄)₃·6H₂O (0.05496 g 0.12 mmol) were added in 50 mL of acetonitrile under the conditions of stirring and slight heating. After cooling, the resulting clear solution was put into a 100 mL beaker which was sealed into another bigger vessel to undertake slowly gas-phase diffusion of diethyl ether. The dark green single crystals suitable for X-ray analysis were obtained in about 10 days. Yield: 26%. Anal. Calcd: C, 45.56; H, 3.46; N, 12.65. Found: C, 45.17; H, 3.47; N, 12.11. IR (KBr disk, cm⁻¹): ν_{C=O} 1636, ν_{C=N} 1600, 1558, ν_{Cl-O} 1086.

Synthesis of [(L³Cu)₄Gd·H₂O](CH₃OH)(H₂O)(ClO₄)₃ (3**).** L³Cu (**1**) (0.158 g, 0.4 mmol) and Gd(ClO₄)₃·6H₂O (0.04558 g, 0.1 mmol) were added into a 15 mL mixture of H₂O/CH₃OH (1:4 mole ratio) in a 25 mL stainless steel reactor with a Teflon liner. The reactor was heated at 180 °C for 72 h. After cooling, brown single crystals of complex **3** were obtained. Yield: 34%. Anal. Calcd: C, 43.79; H, 3.58; N, 10.48. Found: C, 43.53; H, 3.23; N, 10.21. IR (KBr disk, cm⁻¹): ν_{C=O} 1644, ν_{C=N} 1614, 1591, ν_{Cl-O} 1096.

X-ray Crystallography. Diffraction intensity data for single crystals of complexes **1–3** were collected at room temperature on a Bruker Smart 1000 CCD area detector equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by the full-matrix least-squares method on F² with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic data appear in Table 1. Selected bond lengths and angles are found in Tables 2–4.

Results

Description of the Structures. The structure of complex **1** consists of the neutral Cu^{II} complex of the [15]N₄

- (22) Smith, L. I.; Opie, J. W. *Organic Syntheses*; Wiley: New York, 1995; Collect. Vol. 3, p 56.
 (23) Armarego, W. L. F.; Willette, R. E. *J. Chem. Soc.* **1965**, 1258.

Table 1. Summary of Crystallographic Data

	complex 1	complex 2	complex 3
formula	C ₁₉ H ₁₆ CuN ₄ O ₂	C ₆₃ H ₅₇ Cl ₃ CrCu ₃ N ₁₅ O ₁₈	C ₇₈ H ₇₆ Cl ₃ Cu ₄ GdN ₁₆ O ₂₄
fw	395.90	1661.21	2139.31
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	9.810(5)	20.828(6)	14.805(4)
<i>b</i> , Å	9.688(5)	18.321(5)	16.882(5)
<i>c</i> , Å	16.528(9)	7.578(5)	17.877(5)
α , deg	90	75.403(5)	75.403(5)
β , deg	99.304	91.990(8)	83.317(6)
γ , deg	90	90	70.600(5)
<i>V</i> , Å ³	1550.1(14)	6704(3)	4075.9(19)
<i>Z</i>	4	4	2
ρ_{calc} , g/cm ³	1.696	1.646	1.743
μ (Mo K α), mm ⁻¹	1.433	1.300	2.016
<i>T</i> , K	298(2)	293(2)	293(2)
R1 ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0503	0.0539	0.0553
wR2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0890	0.1161	0.1110

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

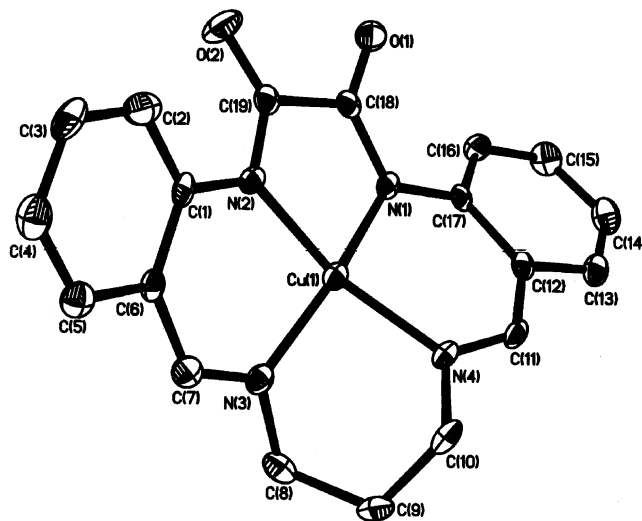
Table 2. Selected Bond Distances (Å) and Angles (deg) for 1

Cu(1)–N(1)	1.905(4)	N(1)–C(17)	1.391(6)
Cu(1)–N(2)	1.916(4)	O(1)–C(18)	1.216(5)
Cu(1)–N(3)	1.928(4)	O(2)–C(19)	1.217(5)
Cu(1)–N(4)	1.939(4)	C(18)–C(19)	1.529(7)
N(1)–C(18)	1.351(6)		
N(1)–Cu(1)–N(2)	86.68(17)	C(18)–N(1)–C(17)	121.8(4)
N(1)–Cu(1)–N(3)	164.86(16)	C(18)–N(1)–Cu(1)	112.5(3)
N(2)–Cu(1)–N(3)	94.85(18)	C(17)–N(1)–Cu(1)	125.4(3)
N(1)–Cu(1)–N(4)	94.78(17)	C(19)–N(2)–C(1)	123.2(4)
N(2)–Cu(1)–N(4)	155.32(16)	C(19)–N(2)–Cu(1)	112.7(3)
N(3)–Cu(1)–N(4)	90.09(18)	C(1)–N(2)–Cu(1)	124.0(3)

Table 3. Selected Bond Distances (Å) and Angles (deg) for 2

Cr(1)–O(5)	1.948(5)	Cu(2)–N(9)	1.955(6)
Cr(1)–O(6)	1.951(5)	Cu(2)–N(10)	1.957(6)
Cr(1)–O(1)	1.952(5)	Cu(3)–N(3)	1.943(7)
Cr(1)–O(4)	1.960(5)	Cu(3)–N(1)	1.946(6)
Cr(1)–O(3)	1.976(5)	Cu(3)–N(4)	1.969(7)
Cr(1)–O(2)	1.982(5)	Cu(3)–N(2)	1.990(6)
Cu(1)–N(6)	1.957(6)	O(1)–C(1)	1.274(8)
Cu(1)–N(8)	1.965(8)	O(2)–C(2)	1.265(8)
Cu(1)–N(5)	2.012(6)	O(3)–C(20)	1.268(8)
Cu(1)–N(7)	2.021(7)	O(4)–C(21)	1.280(8)
Cu(1)–N(13)	2.306(9)	O(5)–C(39)	1.283(8)
Cu(2)–N(12)	1.927(7)	O(6)–C(40)	1.271(8)
Cu(2)–N(11)	1.934(7)		
O(5)–Cr(1)–O(6)	82.2(2)	O(4)–Cr(1)–O(3)	82.2(2)
O(5)–Cr(1)–O(1)	90.9(2)	O(5)–Cr(1)–O(2)	172.4(2)
O(6)–Cr(1)–O(1)	93.05(19)	O(6)–Cr(1)–O(2)	94.6(2)
O(5)–Cr(1)–O(4)	94.40(19)	O(1)–Cr(1)–O(2)	82.41(19)
O(6)–Cr(1)–O(4)	90.5(2)	O(4)–Cr(1)–O(2)	92.51(19)
O(1)–Cr(1)–O(4)	174.0(2)	O(3)–Cr(1)–O(2)	93.7(2)
O(5)–Cr(1)–O(3)	90.4(2)	N(6)–Cu(1)–N(8)	173.4(3)
O(6)–Cr(1)–O(3)	169.1(2)	N(6)–Cu(1)–N(5)	83.3(3)
O(1)–Cr(1)–O(3)	95.0(2)	N(8)–Cu(1)–N(5)	90.3(3)
O(4)–Cr(1)–O(3)	82.2(2)	N(6)–Cu(1)–N(7)	89.1(3)

macrocyclic oxamido. A perspective view of complex 1 with labeling scheme is given in Figure 2. The macrocyclic ligand coordinates with the Cu^{II} ion via two deprotonated oxamido nitrogens and two imine nitrogens. The Cu^{II} ion is displaced from the N₄ least-squares plane by -0.0789 Å, while the deviations of the four nitrogen donors (N₁, N₂, N₃, N₄) from this plane are $-0.3789(1)$, $0.3788(1)$, $-0.3227(1)$, and $0.3228(1)$ Å, respectively, showing that the CuN₄ chromophore assumes a tetrahedral coordination sphere. Complex 2 crystallizes in space group *P*2₁/*c*. Figure 3 shows the

**Figure 2.** Perspective view of complex 1 with labeling scheme.**Table 4.** Selected Bond Distances (Å) and Angles (deg) for 3

Gd(1)–O(3)	2.415(6)	Cu(2)–N(5)	1.958(8)
Gd(1)–O(8)	2.425(6)	Cu(2)–N(7)	2.003(8)
Gd(1)–O(2)	2.428(6)	Cu(2)–N(6)	2.009(7)
Gd(1)–O(7)	2.445(6)	Cu(2)–N(8)	2.020(9)
Gd(1)–O(4)	2.455(6)	Cu(2)–O(22)	2.409(8)
Gd(1)–O(6)	2.469(6)	Cu(3)–N(12)	1.924(9)
Gd(1)–O(5)	2.476(7)	Cu(3)–N(10)	1.942(8)
Gd(1)–O(1)	2.492(6)	Cu(3)–N(11)	1.968(8)
Gd(1)–O(9)	2.512(7)	Cu(3)–N(9)	1.968(8)
Cu(1)–N(3)	1.978(9)	Cu(4)–N(16)	1.932(8)
Cu(1)–N(1)	1.978(8)	Cu(4)–N(14)	1.931(8)
Cu(1)–N(2)	1.981(8)	Cu(4)–N(13)	1.999(8)
Cu(1)–N(4)	2.022(9)	Cu(4)–N(15)	2.025(9)
O(3)–Gd(1)–O(8)	144.6(2)	O(3)–Gd(1)–O(5)	76.4(2)
O(3)–Gd(1)–O(2)	94.7(2)	O(8)–Gd(1)–O(5)	88.9(2)
O(8)–Gd(1)–O(2)	73.7(2)	O(2)–Gd(1)–O(5)	136.0(2)
O(3)–Gd(1)–O(7)	146.1(2)	O(7)–Gd(1)–O(5)	129.7(2)
O(8)–Gd(1)–O(7)	66.0(2)	O(4)–Gd(1)–O(5)	75.1(2)
O(2)–Gd(1)–O(7)	79.9(2)	O(6)–Gd(1)–O(5)	63.6(2)
O(3)–Gd(1)–O(4)	64.8(2)	O(3)–Gd(1)–O(1)	76.8(2)
O(8)–Gd(1)–O(4)	142.2(2)	O(3)–Gd(1)–O(9)	71.1(2)
O(2)–Gd(1)–O(4)	139.8(2)	O(8)–Gd(1)–O(9)	73.6(2)
O(7)–Gd(1)–O(4)	98.1(2)	O(2)–Gd(1)–O(9)	67.9(2)
O(3)–Gd(1)–O(6)	125.4(2)	O(7)–Gd(1)–O(9)	133.9(2)
O(8)–Gd(1)–O(6)	72.3(2)	O(4)–Gd(1)–O(9)	127.8(2)
O(2)–Gd(1)–O(6)	140.0(2)	O(6)–Gd(1)–O(9)	120.4(2)
O(7)–Gd(1)–O(6)	67.3(2)	O(5)–Gd(1)–O(9)	68.4(2)
O(4)–Gd(1)–O(6)	69.9(2)	O(1)–Gd(1)–O(9)	119.3(2)

coordination environments around Cr^{III} and Cu^{II} in the complex. The Cr^{III} center is coordinated by six oxygen atoms from three Cu^{II} precursors. The Cr–O bonds range over 1.948–1.982 Å. The coordination environments of all the terminal Cu^{II} ions change in comparison with the Cu^{II} precursor. Every Cu^{II} assumes a 4 + 1 coordination environment. Two of the three terminal Cu^{II} coordinate with an O atom from the perchlorate, and the other one coordinates with nitrogen of an acetonitrile from the solvent. However, the results of X-ray diffraction show that there are three acetonitrile molecules in the cell with one of them coordinating to one terminal copper ion and the other two being just free guests inside the cell without any coordination to metal ions. Complex 3 crystallizes in space group *P* $\bar{1}$. A perspective view is given in Figure 4. The central Gd^{III} assumes an 8 + 1 coordination environment, namely eight oxygen atoms from

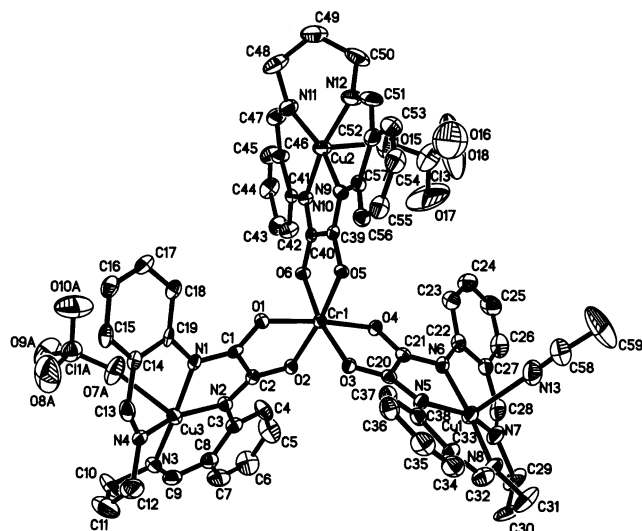


Figure 3. Perspective view of complex 2 with labeling scheme.

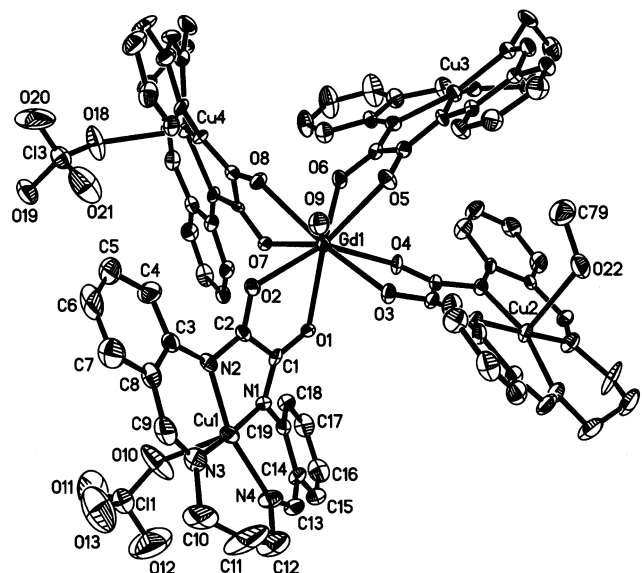
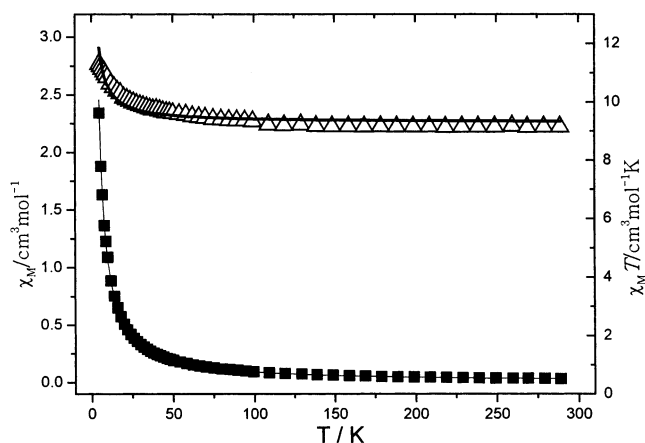


Figure 4. Perspective view of complex 3.

four Cu^{II} precursors and one oxygen atom from H₂O. The distances between Gd^{III} and Cu^{II} are 5.704(4) Å (Cu1), 5.839(4) Å (Cu2), 5.772(6) Å (Cu3), and 5.704(7) Å (Cu4), respectively. Cu1 and Cu4 coordinated with an O atom from the perchlorato, and Cu2 coordinated with an O atom from CH₃OH. Cu3 remains in the same coordination environment as the precursor. There are one H₂O, one perchlorato, and one CH₃OH molecule in the cell without coordination to metal ions.

Magnetic Behavior. The $\chi_M T$ versus T plot for complex 3 is shown in Figure 5. At room temperature, $\chi_M T$ is equal to 9.07 cm³·mol⁻¹·K. This value is lower than what is expected for one Gd^{III} and four Cu^{II} noninteracting magnetic centers (9.38 cm³·mol⁻¹·K). The $\chi_M T$ value remains essentially constant to 50 K and then increases slightly below 50 K and reaches its maximum value of 11.29 cm³·mol⁻¹·K at 4.82 K, showing the ferromagnetic interaction between Gd^{III} and Cu^{II} centers. The magnetic analysis was carried out by using the theoretical expression of the magnetic


 Figure 5. χ_M (o) and $\chi_M T$ (Δ) versus T plots of complex 3.

susceptibility deduced from the Heisenberg spin Hamiltonian

$$\hat{H} = -2J\hat{S}_{\text{Gd}}(\hat{S}_{\text{Cu1}} + \hat{S}_{\text{Cu2}} + \hat{S}_{\text{Cu3}} + \hat{S}_{\text{Cu4}})$$

and χ_M is given by

$$\chi_M = \frac{N\beta^2 [A]}{12KT[B]} \quad (1)$$

$$A = g_{11/2,2}^2 \times 858 + g_{9/2,2}^2 \times 495 \exp(11y) + g_{7/2,2}^2 \times 252 \exp(20y) + g_{5/2,2}^2 \times 105 \exp(27y) + g_{3/2,2}^2 \times 30 \exp(32y) + g_{9/2,1}^2 \times 1485 \exp(7y) + g_{7/2,1}^2 \times 756 \exp(16y) + g_{5/2,1}^2 \times 315 \exp(23y) + g_{7/2,0}^2 \times 504 \exp(14y)$$

$$B = 6 + 5 \exp(11y) + 4 \exp(20y) + 3 \exp(27y) + 2 \exp(32y) + 15 \exp(7y) + 12 \exp(16y) + 9 \exp(23y) + 8 \exp(14y)$$

$$y = -J/KT$$

where J is the exchange integral between Gd^{III} and Cu^{II} ions, $g_{s,s^*} = C_a g_{\text{Cu}} + C_b g_{\text{Gd}}$, $S^* = S_{\text{Cu1}} + S_{\text{Cu2}} + S_{\text{Cu3}} + S_{\text{Cu4}}$, $S = S^* + S_{\text{Gd}}$, g_{s,s^*} factors can be obtained by simple algebra,²⁴ and other symbols have their usual meanings. The fit of the experimental data gives $J = 0.27(2)$ cm⁻¹, $g_{\text{Cu}} = 2.04(1)$, $g_{\text{Gd}} = 1.98(1)$, and $R = 9.06 \times 10^{-4}$. R is defined as $R = \sum(\chi_M^{\text{obsd}} - \chi_M^{\text{caclcd}})^2 / \sum(\chi_M^{\text{obsd}})^2$. This small and positive J value shows weak ferromagnetic interaction between metal ions.^{25,26}

The molar magnetic susceptibility χ_M of complex 2 was investigated in the temperature scope of 4–300 K, and the results are shown in Figure 6 in the form of χ_M and $\chi_M T$ versus T plots. At 289 K, $\chi_M T$ is equal to 3.35 cm³·mol⁻¹·K that approximately corresponds to what is expected for one Cr^{III} and three Cu^{II} ions magnetically isolated. The $\chi_M T$ value, upon sample cooling, increases continuously and then reaches its peak of 5.83 cm³·mol⁻¹·K at 16 K. Below this temperature, $\chi_M T$ decreases sharply and ends with 5.23 cm³·mol⁻¹·K

(24) Bencini, A.; Gatteschi, D. *Electronic Paramagnetic Resonance of Exchange Coupled Systems*; Springer: Berlin, 1990.

(25) Benelli, C.; Caneschi, A.; Gatteschi, D.; Guillou, O.; Pardi, L. *Inorg Chem.* **1990**, *29*, 4153.

(26) Kdlmar, C.; Kaho, O. *Acc. Chem. Res.* **1993**, *26*, 259.

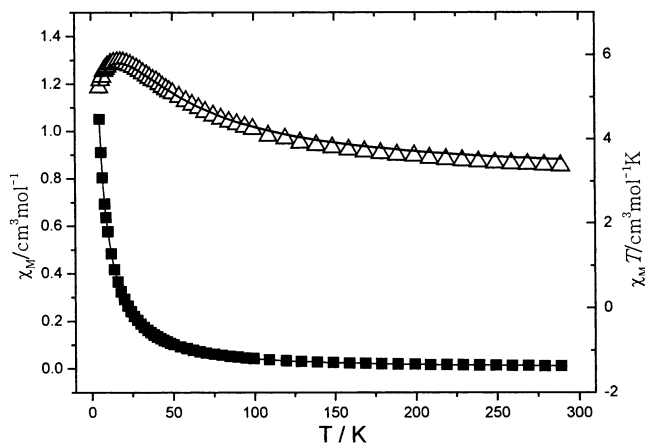


Figure 6. χ_M (\circ) and $\chi_M T$ (Δ) versus T plots of complex **2**.

at 4.98 K. This $\chi_M T$ versus T plot clearly shows that the $\text{Cr}^{\text{III}}-\text{Cu}^{\text{II}}$ interaction is ferromagnetic so that the ground state has the spin $S = 3$. The value of the maximum of $\chi_M T$ is close to what is expected for an $S = 3$ ground state in the temperature range where only this state is thermally populated. The expected value of $\chi_M T = 6.0 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ for spin $S = 3$ ground state is not reached which is indicative of intermolecular antiferromagnetic interactions and/or zero-field splitting effects in the ground state. To fit qualitatively the magnetic data, we first used the theoretical expression of the magnetic susceptibility χ_M from the spin Hamiltonian

$$\hat{H} = -2J\hat{S}_{\text{Cr}}[\hat{S}_{\text{Cu1}} + \hat{S}_{\text{Cu2}} + \hat{S}_{\text{Cu3}}]$$

And χ_M is given by

$$\chi_M = \frac{2N\beta^2[A]}{KT[B]} \quad (2)$$

$$A = g_{3,3/2}^2 \times 14 \exp(-6y) + g_{2,3/2}^2 \times 5 + g_{1,3/2}^2 \times \exp(4y) + g_{2,1/2}^2 \times 10 \exp(-3y) + g_{1,1/2}^2 \times 2 \exp(y)$$

$$B = 7 \exp(-6y) + 5 + 3 \exp(4y) + \exp(6y) + 10 \exp(-3y) + 6 \exp(y)$$

$$y = -J/KT$$

where g is Zeeman factor and the other symbols have their usual meaning. The fitting parameters were found to be $J = 18.11(3) \text{ cm}^{-1}$, $g_{\text{Cu}} = 2.00(2)$, and $g_{\text{Cr}} = 1.97(2)$. The discrepancy factor R defined as $R = \sum(\chi_M^{\text{obsd}} - \chi_M^{\text{cacld}})^2 /$

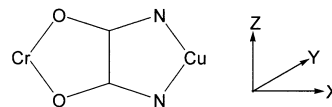


Figure 7. Symmetry of $\text{Cr}(\text{N}_2\text{O}_2)\text{Cu}$ bridging network.

$\sum(\chi_M^{\text{obsd}})^2$ was 6.3×10^{-3} , and for $T < 16 \text{ K}$ the data depart from the calculated value. In a second attempt, we neglected the zero-field splitting, which in any case is found to be very small as compared to J .^{1,20} and we assumed that weak intermolecular interactions could affect the experimental data. Thus, we used the molecular field exchange model which is shown as

$$\chi'_M = \frac{\chi_M}{1 - \left(\frac{2ZJ'}{Ng^2\beta^2}\right)\chi_M} \quad (3)$$

where the g factor is assumed to be $(g_{\text{Cu}} + g_{\text{Cr}})/2$, χ'_M is the corrected magnetic susceptibility, and ZJ' is the product of the molecular field exchange constant by the number of interacting nearest neighbors. The final parameters, after correction, are found as $J = 16.48(1) \text{ cm}^{-1}$, $g_{\text{Cu}} = 2.04(2)$, $g_{\text{Cr}} = 2.00(1)$, and $ZJ' = -0.007(1)$ with R value of 2.24×10^{-5} , i.e., 2 order of magnitude better than before.

The ferromagnetic coupling observed for complex **2** can be rationalized by the symmetry considerations.^{1,20} J in **2** refers to the $\text{Cu}^{\text{II}}-\text{Cr}^{\text{III}}$ pair. Therefore, it is justified to consider the symmetry of the $\text{Cr}(\text{N}_2\text{O}_2)\text{Cu}$ bridging network close to C_{2v} . In this C_{2v} symmetry, with the coordination system defined as in Figure 7, the unpaired electron of Cu^{II} ion resides on the d_{xy} orbital, which transforms as the b_1 irreducible representation. The three unpaired electrons of Cr^{III} 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, respectively. Hence, for any pair of interacting magnetic orbitals, strict orthogonality is obeyed and the interaction should be ferromagnetic.

Acknowledgment. This work is supported by the National Natural Science Foundation of China (Grant Nos. 59973008, 20071019, 50172021, and 90101028) and Natural Science Foundation of Tianjin (Grant No. 013603711).

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC020466D