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Structures and Magnetism of Two Novel Heptanuclear Lanthanide-Centered Trigonal Prismatic Clusters: $[LnCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4](ClO_4)_2\cdot 25H_2O$ (Ln = La, Tb; H_2L = Iminodiacetic Acid)

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The new heteronuclear iminodiacetic acid (H_2L) complexes $[LnCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4](ClO_4)_2\cdot 25H_2O$ with Ln = La (**1**) and Tb (**2**) have been prepared in aqueous solution and characterized by single-crystal X-ray diffraction to be isomorphous (crystallographic data for **1** and **2**: hexagonal, $P6_3/m$; $a = b = 12.6425(14)$ Å, $c = 24.541(5)$ Å, $Z = 2$ (**1**); $a = b = 12.5802(9)$ Å, $c = 24.285(4)$ Å, $Z = 2$ (**2**)). Ln^{3+} was found to be located in the center of the trigonal prismatic cage formed by six Cu^{2+} ions, with a tricapped trigonal prismatic coordination environment of nine O atoms. The magnetic properties of complexes **1** and **2** have been studied. The results indicate the presence of ferromagnetic couplings between Tb^{3+} and Cu^{2+} in compound **2**.

Introduction

Interest in the nature of magnetic interactions between lanthanides and transition metal ions has grown since 1985.[1] From isolated dimers up to three-dimensional networks, f−d metal complexes of various structural types have been prepared with different bridging ligands, such as Schiff bases,[1−4] pyridones,[5] oximates/oxmides,[6,7] cyano groups,[8,9] and carboxylic acids.[10−16] However, previous magnetic investigations of these complexes have mostly been focused on only the nature of Gd−

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Cu coupling, due to the fact that, for other Ln^{3+} ions, one has to consider the effects of both orbital contributions and crystal fields.[17,18] Thus, detailed analyses are difficult or even impossible. Up until now, reports on Ln−Cu complexes other than those of Gd have been rather scarce.[1c,4g,6e,g,7]

Many heteronuclear f−d metal complexes have been prepared and structurally characterized, though only one structural type of heptanuclear f−d clusters, $LnNi_6$ (Ln = Sm, La), centered by an icosahedral Ln^{3+}, was reported.[14] A number of rare earth metal complexes with iminodiacetic acid ligands have been synthesized,[19−22] but only a few of them are heteronuclear.[13] Furthermore, they all tend to form extended 3D networks. As a result, mixed, multinuclear lanthanide−copper complexes with H_2L ligands have not been obtained previously.

Herein we report the preparations and structural and magnetic characterizations of two novel mixed, heptanuclear lanthanide−copper complexes with iminodiacetic acid ligands, $[LaCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4](ClO_4)_2\cdot 25H_2O$ (**1**) and $[TbCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4](ClO_4)_2\cdot 25H_2O$ (**2**). Comparison of the variable-temperature magnetic susceptibility measurements for the two compounds indicates the existence of a ferromagnetic Tb−Cu interaction in compound **2**.

Experimental Section

Materials and Instrumentation. All starting materials were analytical reagents from the Beijing Chemical Reagent Co. Sodium iminodiacetate (Na_2L) was obtained by direct reaction of iminodiacetic acid with sodium hydroxide in aqueous solution. Analyses of C, H, and N were performed on a German Elementar Vario EL instrument. Metal contents were determined with an IRIS/AP plasma spectrometer. IR spectra were measured using KBr pellets with a Nicolet Magna-IR 750 spectrometer at 295 K. Thermal analyses were performed on a Du Pont 1090B thermal analyzer.

Synthesis of $[LaCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4](ClO_4)_2\cdot 25H_2O$ (1). Aqueous solutions of $Cu(ClO_4)_2$ (2.0 M, 0.5 mmol) and $La(ClO_4)_3$ (1.0 M, 0.5 mmol), 0.25 and 0.5 mL each, were mixed together. Under vigorous stirring, 1.0 mL of an aqueous solution of sodium iminodiacetate (0.5 M, 0.5 mmol) was then added to the mixture. The color of the solution turned immediately from sky to deep blue. The pH value of the solution was adjusted carefully to ca. 5.0 using aqueous ammonia. The reaction mixture was left to stand at room temperature for 2 days. Deep blue hexagonal prismatic crystals were collected thereafter. Previous to C, H, N analyses, the loosely bound crystalline waters were eliminated easily by keeping the products at 60 °C until constant weights were reached. Anal. Calcd for $LaCu_6C_{24}H_{67}N_6Cl_2O_{51}$ (after losing nine crystalline water molecules per complex molecule): C, 15.61; H, 3.66; N, 4.55. Found: C, 15.27; H, 3.45; N, 4.57. Calcd for $LaCu_6C_{24}H_{85}N_6Cl_2O_{60}$: La, 6.91; Cu, 19.0. Found: La, 6.89; Cu, 18.9.

Synthesis of $[TbCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4](ClO_4)_2\cdot 25H_2O$ (2). The Tb complex **2** was synthesized by the same procedure that for as **1**. Anal. Calcd for $TbCu_6C_{24}H_{67}N_6Cl_2O_{51}$ (after losing nine crystalline water molecules per complex molecule): C, 15.44; H, 3.62; N, 4.50. Found: C, 15.00; H, 3.21; N, 4.32. Calcd for $TbCu_6C_{24}H_{85}N_6Cl_2O_{60}$: Tb, 7.83; Cu, 18.8. Found: Tb, 8.13, Cu, 18.2.

X-ray Data Collection and Structure Determination. Crystals with the dimensions 0.38 × 0.32 × 0.24 mm (**1**) and 0.38 × 0.26 × 0.24 mm (**2**) were picked out from paraffin oil and sealed into thin-walled capillaries for structure determination. Intensity data were collected on a Siemens P4 diffractometer with Mo Kα radiation in the ω-scan mode. The unit-cell parameters of **1** and **2** were determined from a least-squares refinement of 46 (**1**) and 28 (**2**) reflections. Totals of 2043 and 2001 independent reflections were collected in the ranges $6.22° \le 2\theta \le 32.30°$ and $6.26° \le 2\theta \le 31.78°$ for **1** and **2**, respectively. Empirical absorption corrections were applied using the XPRED program.[23] The structures were solved and refined with direct methods and difference Fourier syntheses and then further refined with full-matrix least-squares calculations using the Siemens SHELXTL/PC system.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in the HL ligands of complexes **1** and **2** were assumed to be in a statistical distribution. Details of the data collections and refinements are listed in Table 1. Non-hydrogen atomic coordinates are given in Tables 2 and 3.

Table 1. Crystal Data for **1** and **2**

	1	**2**
chem formula	$LaCu_6C_{24}H_{85}Cl_2N_6O_{60}$	$TbCu_6C_{24}H_{85}Cl_2N_6O_{60}$
fw	2009.02	2029.04
cryst system	hexagonal	hexagonal
space group	$P6_3/m$	$P6_3/m$
T (K)	291	291
λ (Å)	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.964	2.025
μ (mm^{-1})	2.663	3.139
a (Å)	12.6425(14)	12.5802(9)
c (Å)	24.541(5)	24.285(4)
α (deg)	90	90
γ (deg)	120	120
V (Å^3)	3396.9(9)	3328.4(6)
Z	2	2
no. of indep reflns	2043	2001
R^a	0.0497	0.0495
R_w^b	0.1374	0.1374

[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)/\sum w(F_o)^2]^{1/2}$.

Table 2. Non-Hydrogen Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**

	x	y	z	U_{eq}^a
La	3333	6667	2500	18(1)
Cu	944(1)	4195(1)	1811(1)	31(1)
Cl	3333	6667	51(2)	65(1)
O1	1702(4)	5987(4)	1777(2)	28(1)
O2	1614(4)	7472(4)	1330(2)	35(1)
O3	−225(4)	2463(4)	1825(2)	44(1)
O4	−2035(7)	1134(6)	1504(4)	99(3)
O5	1775(5)	4360(5)	2500	23(1)
O6	3333	6667	607(6)	117(6)
O7	2140(9)	5823(11)	−126(5)	159(5)
O8	−24(10)	1282(7)	2500	66(3)
O9	2429(13)	2586(11)	2500	99(4)
O10	431(9)	8165(8)	590(4)	114(3)
O11	0	0	758(5)	101(5)
O12	0	0	1891(5)	106(5)
O13	891(11)	3398(10)	138(5)	139(4)
O14	−3845(10)	2213(10)	2500	28(2)
O15	−4805(11)	663(12)	2500	43(3)
N	120(5)	4209(5)	1136(2)	41(1)
C1	242(6)	5426(6)	1061(3)	36(2)
C2	1266(5)	6388(5)	1406(2)	26(1)
C3	−1099(7)	3140(7)	1149(4)	58(2)
C4	−1136(7)	2163(6)	1517(4)	53(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Magnetic Measurements. Magnetic measurements were performed on a Quantum Design MPMS-7 SQUID magnetometer and an Oxford MagLab2000 System in the temperature range 2−300 K and under an

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Table 3. Non-Hydrogen Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**

	x	y	z	U_{eq}[a]
Tb	3333	6667	2500	19(1)
Cu	966(1)	4221(1)	1817(1)	34(1)
Cl	3333	6667	46(2)	68(1)
O1	1761(4)	6032(4)	1791(2)	28(1)
O2	1657(4)	7510(4)	1335(2)	39(1)
O3	−222(5)	2482(4)	1833(2)	45(1)
O4	−2017(7)	1143(6)	1503(4)	104(3)
O5	1844(5)	4442(5)	2500	23(1)
O6	3333	6667	618(5)	106(5)
O7	2171(10)	5786(11)	−158(4)	156(5)
O8	6(11)	1304(7)	2500	67(3)
O9	2463(13)	2614(11)	2500	99(4)
O10	482(11)	8202(9)	555(5)	141(4)
O11	0	0	745(5)	100(5)
O12	0	0	1894(5)	108(5)
O13	861(12)	3337(12)	120(5)	167(5)
O14	−3811(11)	2254(12)	2500	32(3)
O15	−4791(12)	656(13)	2500	45(4)
N	132(6)	4244(6)	1134(3)	51(2)
C1	282(7)	5467(6)	1060(3)	40(2)
C2	1306(6)	6413(6)	1415(3)	30(2)
C3	−1079(8)	3161(8)	1135(4)	61(3)
C4	−1133(8)	2178(8)	1518(4)	56(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

applied external magnetic field of 1−10 kOe. Diamagnetic corrections were estimated on the basis of Pascal's constants.[24]

Results and Discussion

IR Spectroscopy. The IR resonances of [$-C(=O)-O-$], ν_{as}(COO) and ν_s(COO), in free (H_2L) and coordinated (HL) ligands were compared. After coordination to the metal centers, ν_{as}(COO) blue-shifted 42 cm^{-1}, from a value of 1583 in H_2L to 1625 cm^{-1} in HL of compound **1**. One of the symmetrical resonance frequencies, ν_s(COO), shifted 33 cm^{-1}, from 1397 up to 1430 cm^{-1}, and the other shifted 18 cm^{-1}, down to 1379 cm^{-1}, after coordination. This suggests there are two carboxyl group coordination modes for the metal ions.[25] The value of ν_s(C−N) in **1** shifted 92 cm^{-1} down to 1118 cm^{-1}, which indicates that the N atoms in the ligands are also coordinated to the metal ions. The presence of water molecules in **1** was proved by the strong and broad OH resonance, ν(OH), at 3426 cm^{-1}. The IR spectrum of **2** was found to be very similar to that of **1**.

Thermal Analyses. Crystalline compounds **1** and **2** were found to start losing part of their crystal lattice water molecules at relatively low temperatures (around 30 °C), as detected by thermal analyses. The rate reaches a maximum at 54 °C. A total of nine crystalline water molecules were lost for each molecule of compound **1** or **2** in the temperature range 30.0−60.0 °C. Loss of weight found: **1**, 7.98%; **2**, 8.03%. Loss of weight calculated for loss of nine water molecules: **1**, 8.07%; **2**, 7.99%. These values agree very well with the elemental analysis results.

Description of Structures. Compounds **1** and **2** are isomorphous, which was established by X-ray crystallography. An ORTEP drawing of **2** is shown in Figure 1. Selected bond lengths and angles are given in Table 4.

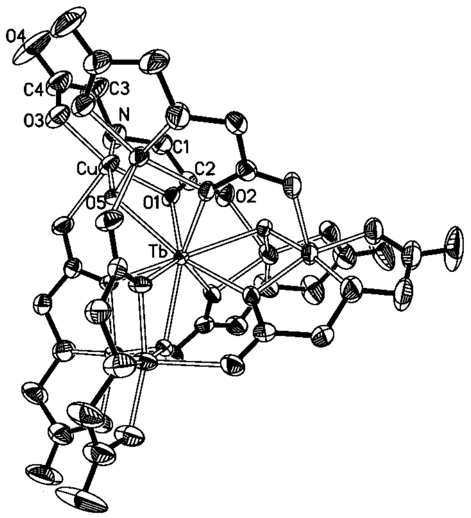

Figure 1. ORTEP drawing of complex **2**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **1** (Ln = La) and **2** (Ln = Tb)

	1	**2**
Ln−O1	2.523(4)	2.436(4)
Ln−O5	2.577(5)	2.470(6)
Cu−O1	1.972(4)	1.979(4)
Cu−O3	1.935(4)	1.938(5)
Cu−O5	1.947(3)	1.935(3)
Cu−N	1.961(5)	1.971(6)
Cu−O2E	2.354(4)	2.288(5)
O1−Ln−O1C	76.04(15)	75.59(16)
O1−Ln−O1B	89.33(19)	89.9(2)
O1−Ln−O1A	138.34(7)	138.56(8)
O1−Ln−O5	65.32(12)	66.23(13)
O1−Ln−O5C	73.15(13)	72.41(14)
O1−Ln−O5E	135.03(10)	134.85(11)
O5−Ln−O5C	120.000(1)	120.000(1)
O1−Cu−N	84.79(19)	85.6(2)
O1−Cu−O3	163.4(2)	164.0(2)
O1−Cu−O5	89.26(19)	86.4(2)
O1−Cu−O2E	94.60(17)	94.59(18)
O3−Cu−N	85.3(2)	85.3(2)
O3−Cu−O5	99.9(2)	101.9(2)
O3−Cu−O2E	99.0(2)	98.8(2)
O5−Cu−N	173.4(2)	171.8(3)
O5−Cu−O2E	90.97(18)	90.85(19)
N−Cu−O2E	92.3(2)	91.9(3)
Cu−O1−Ln	101.92(15)	102.44(17)
Cu−O5−Ln	100.81(17)	102.59(19)
Cu−O5−CuB	120.7(3)	118.1(3)

[a] Symmetry transformations used to generate equivalent atoms: (A) $-x + y, -x + 1, -z + {}^1/_2$; (B) $x, y, -z + {}^1/_2$; (C) $-x + y, -x + 1, z$; (D) $-y + 1, x - y + 1, -z + {}^1/_2$; (E) $-y + 1, x - y + 1, z$.

The coordination polyhedron with the nine-coordinated Tb^{3+} in the center can be described as a tricapped trigonal prism. The six carboxyl oxygen atoms (O1, O1A−O1E) from six different L's define one trigonal prism, and the three oxygen atoms from three μ_3-OH groups form the cap (Figure 2). The Tb−O(prism) bond lengths, 2.436(4) Å, are equal, as are the Tb−O(cap) bond lengths, 2.470(6) Å, which are slightly longer than the Tb−O(prism) bond lengths. The coordination environment thus defined around Tb^{3+} appears to be highly symmetrical. Two other mixed lanthanide−copper complexes with iminodiacetic acid ligands, $[Ln_2Cu_3(L)_6 \cdot 9H_2O]_n$ (Ln = Gd, Pr), have been reported.[13b,c] They are both large molecules composed of three-dimensional networks. The coordination polyhedrons around the lanthanide ions are distorted tricapped trigonal prisms. The observed geometries of nine-coordinated lanthanide

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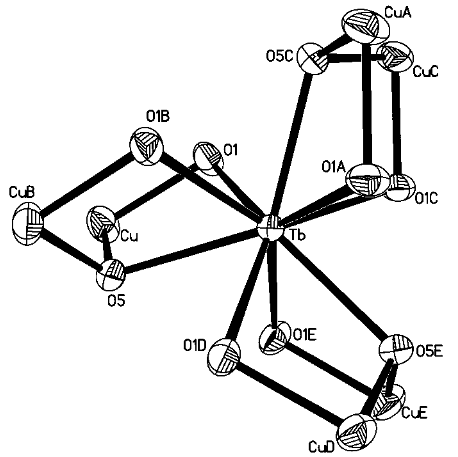

Figure 2. The trigonal prismatic cage formed by six Cu^{2+} ions and the bridges among Tb^{3+} and six Cu^{2+} ions (O5, O5C, and O5E are from the three μ_3-OH^- groups; O1 and O1A−O1E are from the carboxyl groups of six ligands).

ions are usually asymmetrical monocapped square antiprisms[10,26] or distorted tricapped trigonal prisms.[13,27] On the other hand, highly symmetrical coordination polyhedrons (C_{3h}), such as those for Tb^{3+} in complex **2**, have limited precedents among 4f−3d and 4f coordination complexes. The Cu^{2+} ions in **2** are all five-coordinated, exhibiting a distorted tetragonal pyramidal geometry. The bottom of the pyramid is defined by the two oxygen atoms (O1, O3) and one nitrogen atom from one L and by one oxygen atom from the μ_3-OH^- group. An oxygen atom (O2E) from another L occupies the apex position of the pyramid. Thus, L is a tridentate ligand chelating to one Cu^{2+} ion and is a monodentate ligand coordinating to the other. The ligand is chelated to Cu^{2+}, forming two five-membered rings. Because of the high stability of five-membered rings, the Cu−O (bottom) (Cu−O1 = 1.979 Å; Cu−O3 = 1.938 Å) and the Cu−N (1.971 Å) bond lengths are much shorter than the Cu−O (top) (Cu−O2E = 2.288 Å) bond length.

The cluster in **2** contains two parallel layers, each layer being composed of three Cu^{2+} ions and three ligands. Six Cu^{2+} ions form a trigonal prism with the Tb^{3+} ion located in the center. The six Tb···Cu distances, 3.453 Å, are equal, and they are comparable with the Sm···Ni separations, 3.70 Å, in another heptanuclear cluster complex, $SmNi_6$.[14a] The Cu···Cu separation between two different layers (3.32 Å) is much shorter than the Ni···Ni separation of 5.23 Å, while the Cu···Cu separation in the same layer (5.24 Å) is similar to the Ni···Ni separation (5.23 Å). Since the ion radius of Cu^{2+} is slightly larger than that of Ni^{2+}, the nonbonding distances between the metal ions in complex **2** are considerably short, compared to those in $SmNi_6$. The cause is probably associated with the magnetic properties of the complexes.

The Tb^{3+} ion lying between two layers is bridged to the six Cu^{2+} ions by three μ_3-OH^- groups and six carboxy μ_2-O atoms from six different ligands. The two layers are connected by the nine-coordinated Tb^{3+} and three μ_3-OH^- groups. Each μ_3-OH^- is coordinated to Tb^{3+} and to two Cu^{2+} ions from both layers, as shown in Figure 2.

The coordination modes of the two carboxyl groups in each ligand are different: one possesses a μ_3 bridge, in which O1 is coordinated to Tb^{3+} and Cu^{2+} and O2 is coordinated to another Cu^{2+} in the same layer, forming a Tb,Cu−μ_2-O−C−O−Cu mode; the other carboxyl group is monodentately coordinated to Cu^{2+}. This observation is consistent with the IR predictions.

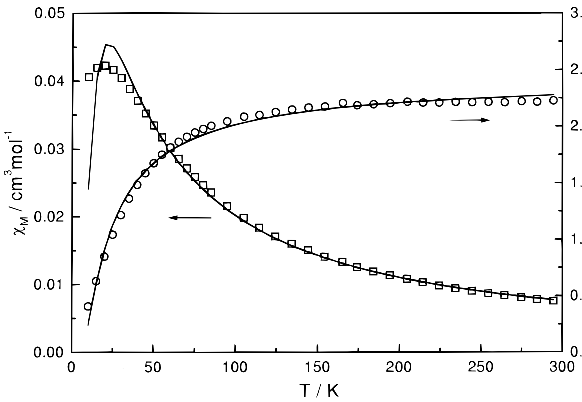

Figure 3. Plot of the magnetic susceptibility χ_M and the $\chi_M T$ product vs *T* for $[LaCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4](ClO_4)_2{\cdot}25H_2O$ (**1**). Solid lines show the best fit of the data (see text).

The closest intermolecular Tb···Tb and Cu···Cu distances are 12.58 and 8.35 Å, respectively. The O atoms of μ_3-OH^- groups, N, and all the carboxyl O atoms, except the bridging one, participate in hydrogen bondings. Among these atoms, O2, N, and O5 only participate in intramolecular H-bonding, the uncoordinated O4 only participates in intermolecular H-bonding, and O3 is involved in both intra- and intermolecular H-bondings. The rich intermolecular H-bondings involving O3, O4, and crystal lattice water molecules link the clusters into a 3D network.

The structural features of **1** are primarily the same as those of **2**, except that the volume of the crystal cell of **1** is slightly larger than that of **2**. This may be reflected in the lanthanide contraction.

Magnetic Properties. Temperature dependencies of magnetic susceptibilities χ_M and of χ_MT for **1** measured at 10 kOe field using the SQUID magnetometer are shown in Figure 3. The $\chi_M T$ value at room temperature (2.23 cm^3 mol^{-1} K) is very close to the expected value of 2.25 cm^3 mol^{-1} K for six noninteracting spin-only Cu^{2+} ions. As the temperature decreases, $\chi_M T$ first decreases slowly at higher temperatures (>100 K) and then drops very rapidly to a nonmagnetic ground state at low temperatures. χ_M reaches a maximum around 20 K. According to the structural data, compound **1** may be considered as “three interacting dimers”, $(Cu_2)_3$, with intra- and interdimer Cu···Cu separations of 3.32 and 5.24 Å, accordingly. The magnetic data were fit to a Bleaney−Bowers equation,[24] which was derived from the Hamiltonian $H = -J\mathbf{S}_1\mathbf{S}_2$, taking into account the mean field approach. The best-fit parameters are intradimer $J = -24(1)$ cm^{-1}, interdimer $zJ' = -13(2)$ cm^{-1}, $g = 2.07(1)$, and $R = \sum[\chi_M T_{cal} - \chi_M T_{obs}]^2/\sum[\chi_M T_{obs}]^2 = 6.4 \times 10^{-4}$. The results indicate that the interactions, either inter or intra, in the copper couples are all antiferromagnetic in character.

Temperature dependencies of $\chi_M T$ for compound **2** measured in the range 4−300 K at 10 kOe field using the SQUID magnetometer and the MagLab2000 system are overall superpositioned on each other, as shown in Figure 4. The $\chi_M T$ value at room temperature is 14.57 cm^3 mol^{-1} K, slightly larger than the calculated value (14.06 cm^3 mol^{-1} K) for one Tb^{3+} with free-ion ground state ($J = 6$, $g = {}^3/_2$)[28] and six spin-only Cu^{2+} ions. Upon cooling, $\chi_M T$ remains almost constant until ca. 100 K, where it begins to increase obviously noticeably, and reaches a maximum around 25−30 K. With further cooling, $\chi_M T$ decreases quickly. Due to the complexity of the system for **2**,

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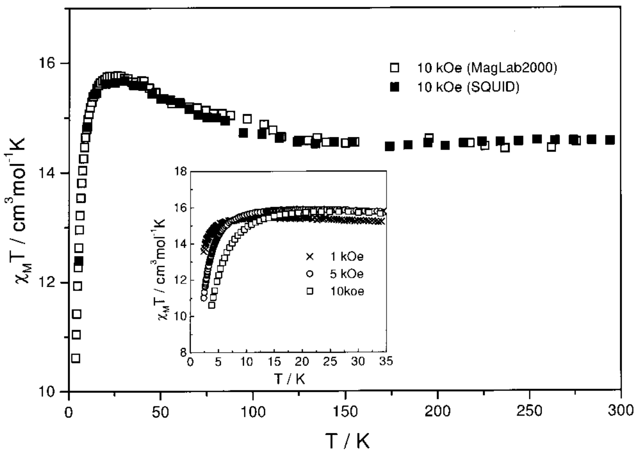

Figure 4. Plot of the $\chi_M T$ product vs T for $[TbCu_6(\mu_3\text{-}OH)_3(HL)_2(L)_4](ClO_4)_2 \cdot 25H_2O$ (**2**), measured at different external magnetic fields (see text).

its magnetic behavior will be affected by many factors, e.g., the Tb−Tb, Cu−Cu, and Tb−Cu interactions, ligand field effects of the Tb^{3+} ion, and field saturation effects. Because of the large separation between the Tb^{3+} ions (12.58 Å), the interactions between them are expected to be negligibly small. Since **2** is isomorphous with **1**, the geometry of the Cu^{2+} ions in **2** is very similar to that in **1**. The magnetic interactions between the Cu^{2+} ions in **2** might also be antiferromagnetic (AF) as in **1**. We noticed that the M···M exchange interactions might be sensitive to the M−O−M angles,[29] though it seems that the difference in the Cu−O−Cu angles (2.6°) between **2** and **1** is not large enough to change the AF nature of the Cu−Cu coupling in **2**. Meanwhile, the depopulation of the excited Tb^{3+} stark components will decrease the $\chi_M T$ value upon cooling.[30] On the other hand, low-temperature magnetic data (2−35 K) measured at different external fields from 1 to 10 kOe (shown in the insertion of Figure 4) suggest the presence of field saturation effects. Overall, all the factors mentioned above, except for the Tb−Cu interaction, could be contributing to the decrease in the $\chi_M T$ values upon cooling. Therefore, the increase of the $\chi_M T$ values upon cooling from 100 to 25−30 K provides a fair argument supporting the ferromagnetic nature of the coupling between Tb^{3+} and Cu^{2+}. The fast drop of $\chi_M T$ below 15 K may be due to increasing efficiency of the antiferromagnetic coupling between the copper couples, ligand field effects of Tb^{3+}, and field saturation effects, all of which void the ferromagnetic coupling between the Tb^{3+} and Cu^{2+} ions. Further investigations of the magnetic properties of heptanuclear complexes are in progress.

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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.

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