Inorg. Chem. **2005**, *44*, 3270–3274

Inorganic Chemistry
Article

Synthesis, Structures, and Magnetic Properties of Tri- and Dinuclear Copper(II)–Gadolinium(III) Complexes of Linear Oligooxime Ligands

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Received December 27, 2004

We have designed and synthesized a new Cu_2Gd heterotrinuclear complex, $[LCu_2Gd(OAc)_3]$ (**1**), where H_4L is a bis(salen)-type tetraoxime ligand useful in the synthesis of discrete $(3d)_2(4f)$ complexes. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, with unit cell parameters $a = 12.442(4)$ Å, $b = 13.397(3)$ Å, $c = 13.966(4)$ Å, $\alpha = 77.052(8)°$, $\beta = 88.656(10)°$, $\gamma = 77.761(8)°$, and $Z = 2$. In the crystal structure of **1**, Cu–Gd distances are 3.3–3.5 Å, whereas the two Cu atoms are separated by 6.08 Å. The corresponding dinuclear CuGd complexes, **2** and **3**, with mono(salen)-type chelate 3-MeOsalamo were also synthesized. Complex **2** crystallizes in the monoclinic system, space group $P2_1/c$, with unit cell parameters $a = 13.869(8)$ Å, $b = 13.688(7)$ Å, $c = 18.728(10)$ Å, $\beta = 92.861(8)°$, and $Z = 4$, and complex **3** crystallizes in the triclinic system, space group $P\bar{1}$, with unit cell parameters $a = 12.319(4)$ Å, $b = 13.989(4)$ Å, $c = 16.774(5)$ Å, $\alpha = 64.699(14)°$, $\beta = 66.672(13)°$, $\gamma = 76.891(17)°$, and $Z = 4$. Interaction between Cu^{II} and Gd^{III} in the dinuclear complexes **2** and **3** is ferromagnetic ($J = 4.5$ and 7.6 cm^{-1}, respectively, using spin Hamiltonian $H = -JS_{Cu}\cdot S_{Gd}$) as observed in the previously prepared $[LCuGdX_3]$ complexes, where L is a salen-type chelate. Magnetic data for the Cu_2Gd trinuclear complex can be reasonably interpreted with the use of a spin Hamiltonian $H = -J_{CuGd}S_{Cu1}\cdot S_{Gd} - J_{CuGd}S_{Cu2}\cdot S_{Gd} - J_{CuCu}S_{Cu1}\cdot S_{Cu2}$ with $J_{CuGd} = 5.0$ cm^{-1} and $J_{CuCu} = 0$ cm^{-1}. The $S = 9/2$ ground state resulted from the ferromagnetic interaction among the Cu^{II}–Gd^{III}–Cu^{II} triad was also supported by the saturation magnetization at 1.8 K.

Introduction

Multinuclear complexes containing both d- and f-block transition metals have been intensively investigated because of their interesting magnetic properties.[1] Recently, increasing interest has also been focused on their potential application to luminescence materials,[2] nonlinear optical materials,[3] near-infrared chiroptical sensors,[4] and single-source precursors for metal−organic chemical vapor deposition (MOCVD).[5] Among these 3d−4f complexes, particular attention has been paid to copper(II)/gadolinium(III) couples which display magnetic properties amenable to a rather simple analysis based on a spin-only Hamiltonian because the $^8S_{7/2}$ single-ion ground state of gadolinium(III) has no first-order orbital momentum to complicate the magnetic analysis. Ferromagnetic interaction between $Cu^{II}-Gd^{III}$ metal centers[6] has been observed in a number of dinuclear LCuGd systems, where L is a salen-type ligand.[7] However, the high coordination number favored by 4f-metal centers sometimes leads to unexpected formation of a trinuclear system $(LCu)_2Gd$.[8] Furthermore, various di-, tri-, or tetradentate ligands form interesting oligometallic Cu_n-

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(1) (a) Winpenny, R. E. P. *Chem. Soc. Rev.* **1998**, *27*, 447−452. (b) Kahn, O. *Acc. Chem. Res.* **2000**, *33*, 647−657. (c) Sakamoto, M.; Manseki, K.; Okawa, H. *Coord. Chem. Rev.* **2001**, *219−221*, 379−414. (d) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369−2387.

(2) (a) Edder, C.; Piguet, C.; Bünzli, J.-C. G.; Hopfgartner, G. *Chem.—Eur. J.* **2001**, *7*, 3014−3024. (b) Wong, W.-K.; Liang, H.; Wong, W.-Y.; Cai, Z.; Li, K.-F.; Cheah, K.-W. *New J. Chem.* **2002**, *26*, 275−278.

(3) Margeat, O.; Lacroix, P. G.; Costes, J.-P.; Donnadieu, B.; Lepetit, C.; Nakatani, K. *Inorg. Chem.* **2004**, *43*, 4743−4750.

(4) Subhan, M. A.; Suzuki, T.; Kaizaki, S. *J. Chem. Soc., Dalton Trans.* **2002**, 1416−1422.

(5) Gleizes, A.; Julve, M.; Kuzmina, N.; Alikhanyan, A.; Lloret, F.; Malkerova, I.; Sanz, J. L.; Senocq, F. *Eur. J. Inorg. Chem.* **1998**, 1169−1174.

(6) For the mechanism of ferromagnetic coupling in copper(II)−gadolinium(III) complexes, see the following: Paulovic, J.; Cimpoesu, F.; Ferbinteanu, M.; Hirao, K. *J. Am. Chem. Soc.* **2004**, *126*, 3321−3331.

(7) (a) Costes, J.-P.; Dahan, F.; Dupuis, A.; Laurent, J.-P. *Inorg. Chem.* **1996**, *35*, 2400−2402. (b) Costes, J.-P.; Dahan, F.; Dupuis, A.; Laurent, J.-P. *Inorg. Chem.* **1997**, *36*, 3429−3433. (c) Ramade, I.; Kahn, O.; Jeannin, Y.; Robert, F. *Inorg. Chem.* **1997**, *36*, 930−936. (d) Sasaki, M.; Horiuchi, H.; Kumagai, M.; Sakamoto, M.; Sakiyama, H.; Nishida, Y.; Sadaoka, Y.; Ohba, M.; Okawa, H. *Chem. Lett.* **1998**, 911−912. (e) Costes, J.-P.; Dahan, F.; Dupuis, A.; Laurent, J.-P. *New J. Chem.* **1998**, 1525−1529. (f) Costes, J.-P.; Dahan, F.; Dupuis, A. *Inorg. Chem.* **2000**, *39*, 165−168. (g) Sasaki, M.; Manseki, K.; Horiuchi, H.; Kumagai, M.; Sakamoto, M.; Sakiyama, H.; Nishida, Y.; Sakai, M.; Sadaoka, Y.; Ohba, M.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **2000**, 259−263. (h) Kido, T.; Nagasato, S.; Sunatsuki, Y.; Matsumoto, N. *Chem. Commun.* **2000**, 2113-2114. (i) Brewer, C.; Brewer, G.; Scheidt, W. R.; Shang, M.; Carpenter, E. E. *Inorg. Chim. Acta* **2001**, *313*, 65−70. (j) Kido, T.; Ikuta, Y.; Sunatsuki, Y.; Ogawa, Y.; Matsumoto, N. *Inorg. Chem.* **2003**, *42*, 398−408.

10.1021/ic0481677 CCC: $30.25

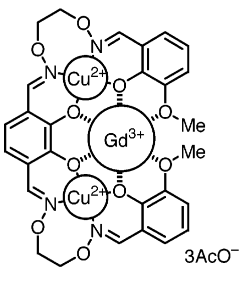
Table 1. Crystallographic Data for Cu/Gd Complexes **1**−**3**

param	1	2	3
formula	$[LCu_2Gd(OAc)_3]\cdot EtOH\cdot Et_2O$ $C_{40}H_{51}Cu_2GdN_4O_{18}$	$[(3\text{-}MeOsalamo)CuGd(OAc)_3]\cdot 2CHCl_3$ $C_{26}H_{29}Cl_6CuGdN_2O_{12}$	$[(3\text{-}MeOsalamo)CuGd(NO_3)_3]$ $C_{18}H_{18}CuGdN_5O_{15}$
cryst system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	12.442(4)	13.869(8)	12.319(4)
b/Å	13.397(3)	13.688(7)	13.989(4)
c/Å	13.966(4)	18.728(10)	16.774(5)
α/deg	77.052(8)		64.699(14)
β/deg	88.656(10)	92.861(8)	66.672(13)
γ/deg	77.761(8)		76.891(17)
V/Å^3	2216.6(10)	3551(3)	2394.0(12)
Z	2	4	4
D_{calc}/g cm^{-3}	1.738	1.861	2.123
R1^a ($I > 2\sigma(I)$)	0.0345	0.0817	0.0411
wR2^a (all data)	0.0914	0.2061	0.0976

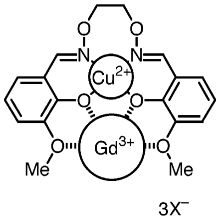
^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

Gd$_m$ complexes ranging from Cu$_2$Gd to Cu$_6$Gd$_{12}$ systems[9] by metal-assisted self-assembly, but their structures are sometimes difficult to predict on the basis of the structure of the ligands. Thus, a useful strategy for selective synthesis of Cu$_n$Gd$_m$ as a multi-metallosystem has been required.

We have recently developed a new linear tetraoxime ligand,[10] H$_4$L, consisting of two H$_2$salamo[11] (=1,2-bis((salicylideneamino)oxy)ethane) moieties. This ligand is used for the synthesis of Zn$_2$M heterotrinuclear complexes (M = Ca^{2+}, lanthanide(III)) by using the site-selective transmetalation of a Zn$_3$ homotrinuclear complex.[10] Synthesis of trinuclear complexes containing a discrete trinuclear Cu$_2$Gd core can be much simpler and more efficient via this method because the complex is formed from only one ligand. Here we report the synthesis, structure, and magnetic properties of a Cu$_2$Gd complex containing the trinucleating oxime ligand H$_4$L.



1 [LCu$_2$Gd(OAc)$_3$]



2 X = OAc
3 X = NO$_3$

Experimental Section

Synthesis of [LCu$_2$Gd(OAc)$_3$] (1). A solution of copper(II) acetate monohydrate (20.0 mg, 0.10 mmol) in ethanol (20 mL) and a solution of gadolinium(III) acetate tetrahydrate (20.3 mg, 0.050 mmol) in methanol/water (3:1, 20 mL) were added to a solution of H$_4$L[10] (29.2 mg, 0.050 mmol) in chloroform/ethanol (1:2, 15 mL). The solution was concentrated in vacuo, and vapor phase diffusion of ether into chloroform/methanol solution of the residue afforded dark brown crystals of **1** (34.0 mg, 79%). Anal. Calcd for $C_{34}H_{35}Cu_2GdN_4O_{16}\cdot 5H_2O$: C, 36.14; H, 4.01; N, 4.96. Found: C, 36.07; H, 4.07; N, 4.92.

Synthesis of [(3-MeOsalamo)CuGd(OAc)$_3$] (2). A solution of copper(II) acetate monohydrate (19.8 mg, 0.10 mmol) in ethanol (5 mL) and a solution of gadolinium(III) acetate tetrahydrate (40.4 mg, 0.10 mmol) in ethanol/water (5:1, 6 mL) were added to a solution of H$_2$(3-MeOsalamo)[11] (36.1 mg, 0.10 mmol) in ethanol (5 mL). The solution was concentrated in vacuo, and the residue was recrystallized from ethanol/ether to afford dark brown crystals of **2** (65.8 mg, 82%). Anal. Calcd for $C_{24}H_{27}CuGdN_2O_{12}\cdot 3H_2O$: C, 35.57; H, 4.10; N, 3.46. Found: C, 35.51; H, 3.93; N, 3.41.

Synthesis of [(3-MeOsalamo)CuGd(NO$_3$)$_3$] (3). A solution of copper(II) acetate monohydrate (20.1 mg, 0.10 mmol) in ethanol (5 mL) and a solution of gadolinium(III) nitrate pentahydrate (43.7 mg, 0.10 mmol) in ethanol (5 mL) were added to a solution of H$_2$(3-MeOsalamo) (36.1 mg, 0.10 mmol) in ethanol (5 mL). After the solution was allowed to stand at room temperature, precipitates were collected to afford dark green crystals of **3** (66.8 mg, 87%). Anal. Calcd for $C_{18}H_{18}CuGdN_5O_{15}$: C, 28.25; H, 2.37; N, 9.15. Found: C, 28.58; H, 2.45; N, 8.94.

X-ray Crystallographic Analysis of Cu/Gd Complexes. Intensity data were collected at 120 K on a Rigaku Mercury CCD diffractometer with Mo Kα radiation ($\lambda = 0.710\ 69$ Å). Reflection data were corrected for Lorentz and polarization factors and for absorption using the multiscan method. Crystallographic data are summarized in Table 1. The structure was solved by Patterson methods (DIRDIF-99)[12] and refined by full-matrix least squares on F^2 using SHELXL 97.[13] The non-hydrogen atoms were refined

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(8) (a) Bencini, A.; Benelli, C.; Caneschi, A.; Carlin, R. L.; Dei, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1985**, *107*, 8128−8136. (b) Bencini, A.; Benelli, C.; Caneschi, A.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1986**, *25*, 572−575.

(9) (a) Costes, J.-P.; Dahan, F.; Dupuis, A. *Inorg. Chem.* **2000**, *39*, 5994−6000. (b) Shiga, T.; Ohba, M.; Okawa, H. *Inorg. Chem.* **2004**, *43*, 4435−4446. (c) Chen, X.-M.; Wu, Y.-L.; Yang, Y.-Y.; Aubin, S. M. J.; Hendrickson, D. N. *Inorg. Chem.* **1998**, *37*, 6186−6191. (d) Benelli, C.; Caneschi, A.; Gatteschi, D.; Guillou, O.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1750−1755. (e) Benelli, C.; Blake, A. J.; Milne, P. E. Y.; Rawson, J. M.; Winpenny, R. E. P. *Chem.*−*Eur. J.* **1995**, *1*, 614−618. (f) Stemmler, A. J.; Kampf, J. W.; Kirk, M. L.; Atasi, B. H.; Pecoraro, V. L. *Inorg. Chem.* **1999**, *38*, 2807−2817. (g) Cutland, A. D.; Malkani, R. G.; Kampf, J. W.; Pecoraro, V. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2689−2691. (h) Chen, X.-M.; Aubin, S. M. J.; Wu, Y.-L.; Yang, Y.-S.; Mak, T. C. W.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9600−9601.

(10) (a) Akine, S.; Taniguchi, T.; Nabeshima, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 4670−4673. (b) Akine, S.; Taniguchi, T.; Saiki, T.; Nabeshima, T. *J. Am. Chem. Soc.* **2005**, *127*, 540−541.

(11) (a) Akine, S.; Taniguchi, T.; Nabeshima, T. *Chem. Lett.* **2001**, 682−683. (b) Akine, S.; Taniguchi, T.; Nabeshima, T. *Inorg. Chem.* **2004**, *43*, 6142−6144. (c) Akine, S.; Taniguchi, T.; Dong, W.; Masubuchi, S.; Nabeshima, T. *J. Org. Chem.* **2005**, *70*, 1704−1711.

(12) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1999.

(13) Sheldrick, G. M. *SHELXL 97, Program for crystal structure determination*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Selected Interatomic Distances (Å) of Cu/Gd Complexes **1**−**3**

Complex **1**			
Gd1−O1	2.349(2)	Cu1−O14	1.983(3)
Gd1−O2	2.765(3)	Cu1−N1	2.053(3)
Gd1−O5	2.386(3)	Cu1−N2	2.366(3)
Gd1−O6	2.368(3)	Cu2−O6	1.918(2)
Gd1−O9	2.460(2)	Cu2−O9	1.972(3)
Gd1−O10	2.525(3)	Cu2−O16	2.205(3)
Gd1−O11	2.385(3)	Cu2−N3	2.018(3)
Gd1−O13	2.412(2)	Cu2−N4	1.975(3)
Gd1−O15	2.344(2)	Gd1−Cu1	3.3092(9)
Cu1−O1	2.302(3)	Gd1−Cu2	3.4796(8)
Cu1−O5	1.932(2)	Cu1−Cu2	6.0798(14)
Cu1−O12	2.019(2)		
Complex **2**			
Gd1−O1	2.396(6)	Gd1−O12	2.394(6)
Gd1−O2	2.569(6)	Cu1−O1	1.929(6)
Gd1−O5	2.384(6)	Cu1−O5	1.995(6)
Gd1−O6	2.570(7)	Cu1−O8	2.139(7)
Gd1−O7	2.363(6)	Cu1−N1	1.975(8)
Gd1−O9	2.443(7)	Cu1−N2	2.009(8)
Gd1−O10	2.428(6)	Gd1−Cu1	3.433(2)
Gd1−O11	2.461(7)		
Complex **3**			
molecule A[a]		molecule B[a]	
Gd1−O1	2.361(3)	Gd2−O16	2.368(3)
Gd1−O2	2.484(3)	Gd2−O17	2.506(3)
Gd1−O5	2.397(3)	Gd2−O20	2.409(3)
Gd1−O6	2.484(3)	Gd2−O21	2.508(3)
Gd1−O7	2.514(3)	Gd2−O22	2.473(4)
Gd1−O8	2.469(4)	Gd2−O23	2.516(4)
Gd1−O10	2.512(4)	Gd2−O25	2.462(3)
Gd1−O11	2.567(4)	Gd2−O26	2.570(4)
Gd1−O13	2.502(4)	Gd2−O28	2.490(3)
Gd1−O14	2.490(3)	Gd2−O29	2.503(4)
Cu1−O1	1.926(3)	Cu2−O16	1.927(3)
Cu1−O5	1.929(3)	Cu2−O20	1.938(3)
Cu1−N1	1.996(4)	Cu2−N6	1.993(4)
Cu1−N2	1.947(4)	Cu2−N7	1.954(4)
Cu1−Gd1	3.4978(12)	Cu2−Gd2	3.4988(12)

[a] Crystallographically independent molecules.

anisotropically except for a minor component of carbon atoms in disordered dichloromethane. Hydrogen atoms were included at idealized positions refined by use of the riding models. Selected interatomic distances are summarized in Table 2.

Magnetic Measurements. Magnetic susceptibility data were collected on powdered samples of **1**−**3** using a Quantum Design model MPMS XL5 SQUID magnetometer. Data were collected at a magnetic field of 0.2 T between 300 and 1.8 K. Data were corrected for diamagnetism of the ligands estimated from Pascal's constants.[14] Magnetization was measured at 1.8 K under an applied field up to 5 T.

Results and Discussion

Synthesis and Structure of the Complexes. Trinuclear cluster **1** was synthesized by one-pot reaction of the free ligand H_4L[10] with 2 equiv of copper(II) acetate and 1 equiv of gadolinium(III) acetate in 79% yield. Dinuclear complexes **2** and **3** were obtained in high yield from each equimolar mixture of H_2(3-MeOsalamo),[11] copper(II) acetate, and gadolinium(III) salt. The crystal structures of the complexes **1**−**3** were determined by X-ray crystallography.

In the Cu_2Gd trinuclear complex **1**, the two copper atoms (Cu1 and Cu2) are located at the N_2O_2 salamo moieties (Figure 1). The four phenoxy oxygen atoms of the salamo moieties coordinate to Gd1 (Gd−O distances: 2.349−2.460 Å). In addition, weak coordination of the methoxy groups (Gd1−O2 2.765(3) Å, Gd1−O10 2.525(3) Å) was observed. The distance between Gd1−Cu1 (3.3092(9) Å), in which the two metals are doubly bridged by two μ_2-acetato ligands, is shorter than that of Gd1−Cu2 (3.4796(8) Å) possessing one μ_2-acetato bridge. The resulting geometries of Cu1 and Cu2 are octahedral and square pyramidal, respectively, and Gd1 is nonacoordinate. The two copper atoms Cu1 and Cu2 are separated by 6.0798(14) Å.

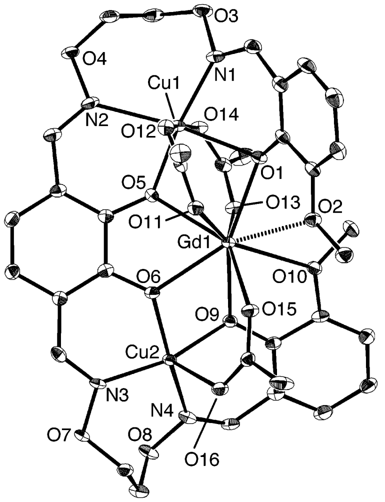

Figure 1. X-ray structure of $[LCu_2Gd(OAc)_3]$ (**1**) with ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

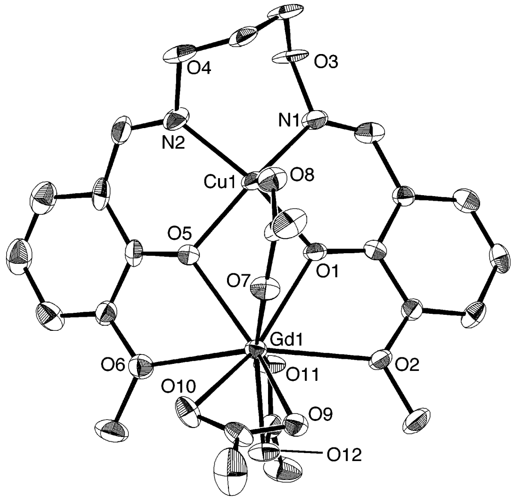

Figure 2. X-ray structure of $[(3\text{-MeOsalamo})CuGd(OAc)_3]$ (**2**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Complex **2** consists of a [(3-MeOsalamo)Cu] unit, a Gd atom, and three acetate ions (Figure 2). The copper atom Cu1 is located in an N_2O_2 site (N1, N2, O1, O5) of the salamo moiety. The phenoxo oxygens (O1, O5) of the chelate ligand and methoxy groups (O2, O6) coordinate to Gd1. One of the ligating acetate ions bridges the two metal atoms (Cu1−Gd1). The other two acetates coordinate to Gd1 in a bidentate fashion. Consequently, the geometry around Cu1 is square pyramidal and Gd1 is nonacoordinate. The distance between Cu1 and Gd1 is 3.433(2) Å, which is similar to

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(14) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5−70.

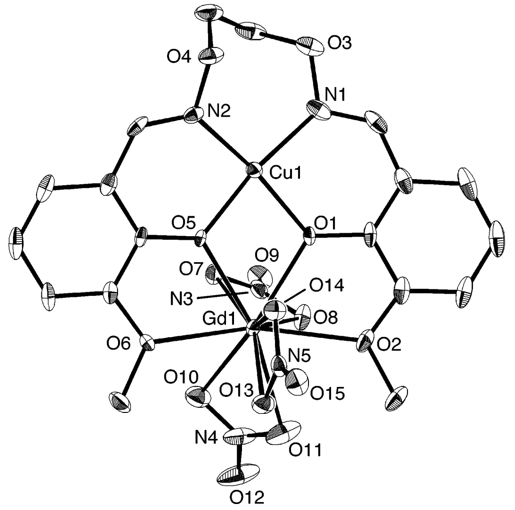

Figure 3. X-ray structure of [(3-MeOsalamo)CuGd($(NO_3)_3$)] (**3**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. One of the two crystallographically independent molecules is shown.

those for previously reported CuO_2Gd systems containing salen-type chelates.[7]

In the crystal of complex **3**, there are two crystallographically independent molecules of [(3-MeOsalamo)CuGd($(NO_3)_3$)], which have a similar conformation (Figure 3). The copper atom has a square planar geometry with an N_2O_2 chelate of the salamo ligand (N1, N2, O1, O5). The four oxygen atoms (O1, O2, O5, O6) of the [Cu(3-MeOsalamo)] unit act as a tetradentate O_4 ligand for Gd1, as seen in complex **2**. In addition, three nitrato ligands coordinate to Gd1 in a η^2-fashion. The distance between Cu1 and Gd1 is 3.4978(12) Å, which is slightly longer than that of complex **2**.

Magnetic Properties. Temperature dependence of magnetic susceptibility of the dinuclear complexes **2** and **3** is shown in Figure 4 in which χ_M is the molar magnetic susceptibility corrected for diamagnetism. The $\chi_M T$ of **2** and **3** at 300 K are 8.18 and 8.30 cm^3 K mol^{-1}, respectively, which roughly correspond to the value (8.25 cm^3 K mol^{-1}) expected for the two uncoupled metal ions ($S_{Cu} = 1/2$ and $S_{Gd} = 7/2$). At lower temperatures, $\chi_M T$ values of **2** and **3** increased and reached maximum of 9.6 and 10.3 cm^3 K mol^{-1} at 5.0 K, respectively. These values are comparable to the value (10.0 cm^3 K mol^{-1}) expected for the $S = 4$ spin state resulting from ferromagnetic coupling between Cu^{II} ($S = 1/2$) and Gd^{III} ($S = 7/2$) and assuming that $g_{Cu} = g_{Gd} = 2.0$. The abrupt decrease of $\chi_M T$ below 5 K may be attributable to antiferromagnetic interaction between the neighboring molecules.

Table 3. Magnetic Data for Cu−Gd Complexes **1**−**3**

	J (cm^{-1})	g	Θ (K)	10^5R^a
1	5.0(1)^b	2.027(2)	−0.057(8)	7.8
2	4.5(1)	1.978(1)	−0.235(6)	3.5
3^c	7.6(2)	1.991(1)		1.9

[a] $R = \Sigma(\chi_{obs}T - \chi_{calc}T)^2/\Sigma(\chi_{obs}T)^2$. [b] $J_{CuCu} = 0$. [c] Data at 10−300 K were used for calculations.

In the case of the trinuclear system **1**, similar temperature dependence of $\chi_M T$ was observed (Figure 4). The $\chi_M T$ is 8.99 cm^3 K mol^{-1} at 300 K, which corresponds to the value (8.63 cm^3 K mol^{-1}) expected for the three uncoupled metal ions (two Cu^{II}, one Gd^{III}). At lower temperatures, the $\chi_M T$ increased and reached a maximum of 12.9 cm^3 K mol^{-1} at 5.5 K. This clearly indicates that the copper(II)−gadolinium(III) interaction is ferromagnetic and that the ground state for the Cu_2Gd triad is $S = 9/2$, in which the three local spins aligned in a parallel fashion (expected $\chi_M T$ is 12.4 cm^3 K mol^{-1}).

The experimental data for complex **2** were analyzed on the basis of a spin-only expression derived from a spin Hamiltonian $H = -JS_{Cu}{\cdot}S_{Gd}$. Assuming that copper(II) and gadolinium(III) have the same g value, the experimental data fitted the expression

$$\chi_M = \frac{4Ng^2\beta^2}{k(T-\Theta)}\left[\frac{15 + 7\exp\left(-\frac{4J}{kT}\right)}{9 + 7\exp\left(-\frac{4J}{kT}\right)}\right] + N_\alpha$$

where β is the Bohr magneton, k is the Boltzmann constant, N_α is the temperature-independent paramagnetism, and Θ is the correction term for intermolecular magnetic interaction. Nonlinear least-squares fitting of the experimental data in the range of 1.8−300 K leads to $J = 4.5(1)$ cm^{-1}, $g = 1.978(1)$, and $\Theta = -0.235(6)$ K with the agreement factor $R = 3.5 \times 10^{-5}$; $R = \Sigma(\chi_{obs}T - \chi_{calc}T)^2/\Sigma(\chi_{obs}T)^2$ (Table 3). A negative Θ value can explain the considerable decrease of $\chi_M T$ observed in complex **2** at below 5 K, which suggests

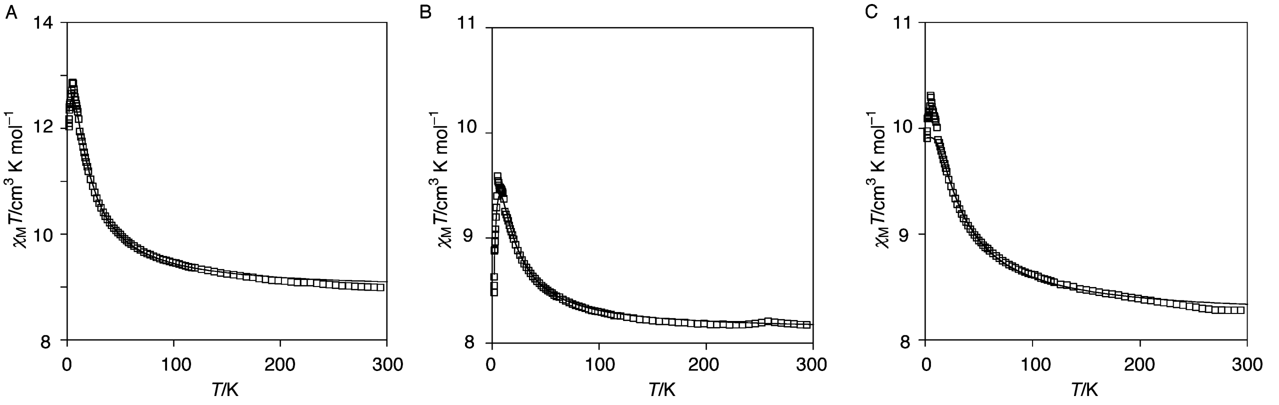

Figure 4. Experimental (open squares) and calculated (solid line) temperature dependence of the magnetic susceptibility of complexes **1** (A), **2** (B), and **3** (C) in the range of 1.8−300 K.

intermolecular antiferromagnetic interaction. In the case of complex **3**, analysis of the experimental data in the range of 10−300 K leads to $J = 7.6(2)$ cm^{-1} and $g = 1.991(1)$ with $R = 1.9 \times 10^{-5}$. However, deviation of the experimental $\chi_M T$ at 2−10 K from the calculated values cannot be explained, even if Θ was modulated in the calculation.

In a similar manner, the data for trinuclear system **1** were analyzed on the basis of a spin-only expression. In this analysis, the two copper(II) ions are assumed to be identical for the sake of simplicity. The coupling of the spin momentum of gadolinium and the two neighboring copper ions is described by the spin Hamiltonian $H = -J_{CuGd}S_{Cu1}\cdot S_{Gd} - J_{CuGd}S_{Cu2}\cdot S_{Gd} - J_{CuCu}S_{Cu1}\cdot S_{Cu2}$, where J_{CuGd} and J_{CuCu} are the Cu^{II}−Gd^{III} and Cu^{II}−Cu^{II} interaction parameters, respectively. The experimental data were analyzed using the expression

$$\chi_M = \frac{Ng^2\beta^2}{4k(T-\Theta)}\left\{\left[165 + 84\exp\left(-\frac{4.5J_{CuGd}}{kT}\right) + 84\exp\left(-\frac{3.5J_{CuGd}+J_{CuCu}}{kT}\right) + 35\exp\left(-\frac{8J_{CuGd}}{kT}\right)\right]\Big/\left[5 + 4\exp\left(-\frac{4.5J_{CuGd}}{kT}\right) + 4\exp\left(-\frac{3.5J_{CuGd}+J_{CuCu}}{kT}\right) + 3\exp\left(-\frac{8J_{CuGd}}{kT}\right)\right]\right\} + N_\alpha$$

In complex **1**, the interaction between Cu1 and Cu2 (J_{CuCu}) is assumed to be 0 because the two copper(II) ions are well separated (6.08 Å). A satisfactory theoretical curve fit to the experimental data was obtained for the following set of parameters: $J_{CuGd} = 5.0(1)$ cm^{-1}, $g = 2.027(2)$, and $\Theta = -0.057(8)$ K with $R = 7.8 \times 10^{-5}$.

Positive J values for Cu^{II}−Gd^{III} interaction for the dinuclear systems **2** and **3** indicate a ferromagnetic coupling, as observed in the previously prepared [LCuGdX$_3$] complexes, where L is a salen-type chelate.[7] The stabilization of the $S = 4$ state in GdO$_2$Cu systems has been attributed to the coupling between the Cu^{II}−Gd^{III} ground configuration and the Cu^{III}−Gd^{II} excited configuration caused by the electron transfer from the singly occupied 3d copper orbital to an empty 5d gadolinium orbital.[15] However, $J = 7.6$ cm^{-1} for **3** is significantly larger than that of **2** (4.5 cm^{-1}). It was reported that J_{CuGd} values strongly correlate with the dihedral angles between the two halves (OCuO and OGdO) of the CuO$_2$Gd core.[7f] Complex **3** has the dihedral angles of 9.29(11) and 13.59(10)° (for two independent molecules), which are considerably smaller than that of **2** (20.14(10)°). Thus, the difference may be attributed to the geometrical feature rather than the difference of the coordinating anions.

It is noteworthy that the observed J_{CuGd} value (5.0 cm^{-1}) of the trinuclear system **1** is very close to that of the dinuclear complex **2** (4.5 cm^{-1}). Consequently, this result suggests that there is ferromagnetic interaction at low temperatures among the Cu^{II}−Gd^{III}−Cu^{II} triad and resultant ground state $S = 9/2$, in which the three local spins are aligned in a parallel fashion.

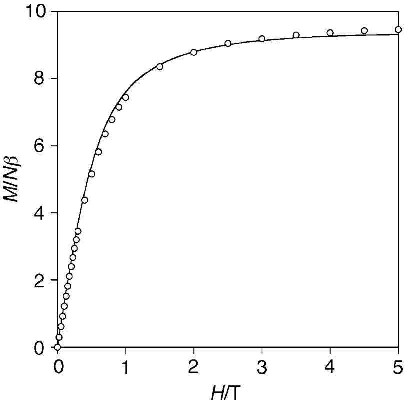

Figure 5. Field dependence of magnetization for complex **1** at 1.8 K. The solid line represents the Brillouin function for an $S_T = 2S_{Cu} + S_{Gd} = 9/2$ spin state with $g = 2.06$.

To confirm the nature of the ground state, we investigated the variation of the magnetization M versus the field H at 1.8 K. As expected, the $M = f(H)$ curve closely follows the Brillouin function for an $S = 9/2$ spin (Figure 5). Hence, only the ground state ($S = 9/2$) is significantly populated at this temperature.

Conclusion

We have synthesized a new discrete Cu$_2$Gd heterotrinuclear complex by the reaction of a bis(salen)-type tetradentate ligand H$_4$L with 2 equiv of Cu^{II} and 1 equiv of Gd^{III}. X-ray crystallographic analysis revealed that the two copper atoms are separated by 6.08 Å, whereas the distances between the copper and gadolinium atoms are 3.3−3.5 Å. The temperature dependence of the magnetic susceptibility clearly indicates ferromagnetic interaction among the Cu^{II}−Gd^{III}−Cu^{II} triad. The J_{CuGd} value was calculated to be 5.0 cm^{-1}, which is comparable to that of the corresponding dinuclear complex [(3-MeOsalamo)CuGdX$_3$] (**2**, X = OAc). Consequently, the $S = 9/2$ ground state of **1**, in which the three local spins are aligned in a parallel fashion, is significantly populated at low temperatures. We have already shown that the tetraoxime−heterotrinuclear complexes [L(3d)$_2$(4f)] have a helical conformation. Recently, magnetic materials bearing chirality have been attracting much interest because of their magnetochiral effects.[16] Helical arrangement of spins along the chelate sites of oligooximes is a promising strategy for such chiral magnetic materials.

Acknowledgment. We thank Prof. Hiroki Oshio and Dr. Takuya Shiga of the University of Tsukuba for measurement of the magnetic properties of **1**−**3** and their useful discussion. This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting Information Available: X-ray crystallographic data for **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0481677

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(15) Andruh, M.; Ramade, I.; Codjovi, E.; Guillou, O.; Kahn, O. Trombe, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 1822−1829.

(16) (a) Rikken, G. L. J. A.; Raupach, E. *Nature* **1997**, *390*, 493−494. (b) Rikken, G. L. J. A.; Raupach, E. *Nature* **2000**, *405*, 932−935. (c) Barron, L. D.; Buckingham, A. D. *Acc. Chem. Res.* **2001**, *34*, 781−789.