Inorg. Chem. **2006**, *45*, 7173–7181

Inorganic Chemistry

Article

Syntheses, Structures, and Properties of High-Nuclear 3d–4f Clusters with Amino Acid as Ligand: $\{Gd_6Cu_{24}\}$, $\{Tb_6Cu_{26}\}$, and $\{(Ln_6Cu_{24})_2Cu\}$ (Ln= Sm, Gd)

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Received April 11, 2006

Four novel high-nuclear 3d–4f heterometallic clusters were obtained through the self-assembly of Ln^{III}, Cu^{II}, and amino acid ligands (2-methylalalanine (mAla), glycine (Gly), and L-proline (Pro), respectively). The metal skeleton of cluster **1**, $[Gd_6Cu_{24}(\mu_3\text{-OH})_{30}(mAla)_{16}(ClO_4)(H_2O)_{22}]\cdot(ClO_4)_{17}\cdot(OH)_2\cdot(H_2O)_{20}$, may be described as a huge $\{Gd_6Cu_{12}\}$ octahedron connected with 12 additional Cu^{II} ions. The structure of cluster **2**, $Na_4[Tb_6Cu_{26}(\mu_3\text{-OH})_{30}(Gly)_{18}(ClO_4)(H_2O)_{22}]\cdot(ClO_4)_{25}\cdot(H_2O)_{42}$, may be described as a $\{Tb_6Cu_{24}\}$ main structure connected with two $[Cu(Gly)(H_2O)_2]^+$ groups. Compounds $\{[Ln_6Cu_{24}(\mu_3\text{-OH})_{30}(Pro)_{12}(Ac)_6(ClO_4)(H_2O)_{13}]_2Cu(Pro)_2\}\cdot(ClO_4)_{18}\cdot(OH)_{16}\cdot(H_2O)_{55}$ (Ln= Sm (**3**), Gd (**4**)) are 61-nuclear clusters, which represent the largest known 3d–4f clusters so far, the structure can be described as two $\{Ln_6Cu_{24}\}$ octahedral units connected by a trans-Cu(proline)$_2$ bridge. The electrical conductivity measurements reveal that they are temperature-sensitive semiconductors. The magnetic susceptibility measurements display that compound **4** is ferromagnetic.

Introduction

Despite extensive research on high-nuclear complexes that show fascinating structures and interesting properties,[1] only a little effort has been focused on the design and synthesis of high-nuclear 3d−4f clusters.[2] Until now, only several reports about 3d−4f clusters with seven or more metal ions have been published.[3−7] Most of the compounds have novel structural motifs and interesting magnetic properties.[3−7] Therefore, the design and synthesis of high-nuclear 3d−4f clusters are still significant.

Amino acids are one of the most important biological ligands. Research on the coordination of metal−amino acid complexes will help us better understand the complicated behavior of the active site of the metal enzyme. Up to now, many Ln−amino acid complexes[8] and 1:1 or 1:2 transition metal−amino acid complexes[9] with mononuclear or chain structural motifs have been synthesized. Recently, a series of polynuclear lanthanide clusters with the amino acid as a

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10.1021/ic060610l CCC: $33.50

Table 1. Crystallographic and Data Collection Parameters for **1**−**3**

	1	**2**	**3**
formula	$C_{64}H_{244}N_{16}O_{178}$-$Cl_{18}Cu_{24}Gd_6$	$C_{36}H_{230}N_{18}Na_4O_{234}$-$Cl_{26}Cu_{26}Tb_6$	$C_{154}H_{474}N_{26}O_{313}$-$Cl_{20}Cu_{49}Sm_{12}$
fw	7193.31	8279.60	13334.32
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2$
a (Å)	18.685(2)	18.4045(2)	30.119(1)
b (Å)	19.564(2)	18.9184(3)	27.761(1)
c (Å)	21.658(3)	19.8178(2)	29.293(1)
α (deg)	63.808(7)	75.60(0)	90
β (deg)	70.018(8)	88.52(0)	93.434(1)
γ (deg)	68.717(8)	80.29(0)	90
V (Å^3)	6461.8(14)	6586.74(14)	24449.5(15)
Z	1	1	2
d_{calcd} (g/cm^3)	1.849	2.087	1.811
$F(000)$	3550	4074	13194
no. of measured reflns	49 650	34 455	35 740
no. of independent reflns	29 068	23 108	26 845
R(int)	0.0268	0.0405	0.0528
GOF onF^2	1.033	1.133	1.163
R^a	0.0617	0.0816	0.0869
$R_w{}^b$	0.1847	0.2097	0.2169

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = \{\Sigma w[(F_o{}^2 - F_c{}^2)^2]/\Sigma w[(F_o{}^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, $P = (F_o{}^2 + 2F_c{}^2)/3]$. For **1**, $a = 0.1215$, $b = 52.7277$; **2**, $a = 0.1024$, $b = 165.0495$; **3**, $a = 0.0\ 895$, $b = 1616.854$.

ligand were reported (most of them display a Ln_4O_4−cubane structural motif).[10] It is also shown that amino acids are useful ligands for the construction of polynuclear copper clusters.[11]

Recently, our research interest has been focused on the syntheses of high-nuclear 3d−4f heterometallic clusters with an amino acid as the ligand.[3(b),7] In this paper, we report four high-nuclear 3d−4f heterometallic clusters: $[Gd_6Cu_{24}(\mu_3\text{-}OH)_{30}(mAla)_{16}(ClO_4)(H_2O)_{22}]\cdot(ClO_4)_{17}\cdot(OH)_2\cdot(H_2O)_{20}$ (**1**), $Na_4[Tb_6Cu_{26}(\mu_3\text{-}OH)_{30}(Gly)_{18}(ClO_4)(H_2O)_{22}]\cdot(ClO_4)_{25}\cdot(H_2O)_{42}$ (**2**), and $\{[Ln_6Cu_{24}(\mu_3\text{-}OH)_{30}(Pro)_{12}(Ac)_6(ClO_4)(H_2O)_{13}]_2Cu(Pro)_2\}\cdot(ClO_4)_{18}\cdot(OH)_{16}\cdot(H_2O)_{55}$ (Ln= Sm (**3**), Gd (**4**)). All of them have the same $\{Ln_6Cu_{24}\}$ unit. The crystal structures of **1**−**3** have been discussed. The electrical conductivity and magnetic susceptibility properties were studied.

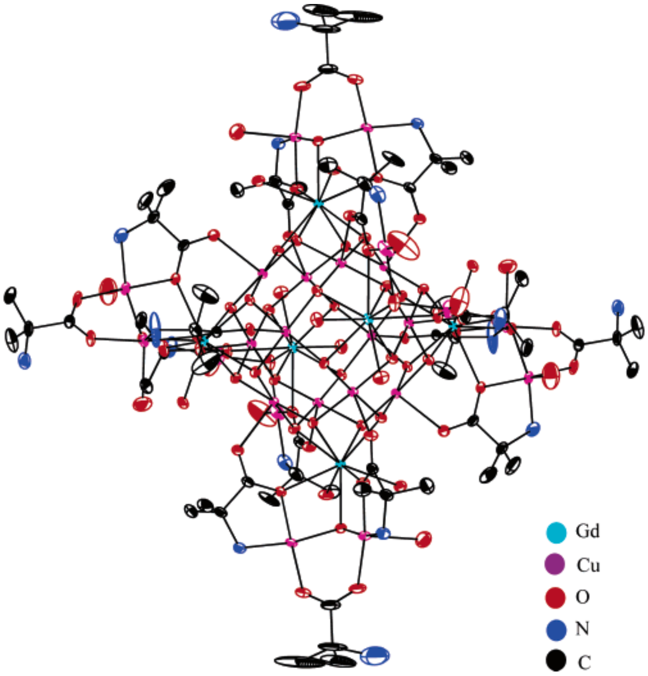

Figure 1. Structure of the cation of **1**.

Experimental Section

Caution: *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. The complexes described in this report have, so far, been found to be safe when used in small quantities.*

Materials and Instrumentation. $Ln(ClO_4)_3\cdot6H_2O$ complexes were synthesized by dissolving lanthanide oxide in an excess amount of perchloric acid. Other starting materials were of reagent grade and were used without further purification. Elemental analyses were carried out by the Elemental Analysis Lab of our Institute. Magnetic measurements were carried out with a Quantum Design PPMS model 6000 magnetometer.

Conductivity Measurements. The cylindrical pellets of the samples (0.1 cm in thickness and 0.4 cm in diameter) were coated with silver paint on either side. The conductivity measurements were carried out using a standard setup coupled with an Agilent 4284A LCR meter in the frequency range of 20 Hz to 1 MHz.

Syntheses of the Complexes. $[Gd_6Cu_{24}(\mu_3\text{-}OH)_{30}(mAla)_{16}(ClO_4)(H_2O)_{22}]\cdot(ClO_4)_{17}\cdot(OH)_2\cdot(H_2O)_{20}$ (1). To an aqueous solution (10 mL) of $Gd(ClO_4)_3\cdot6H_2O$ (1 mmol) were added $Cu(ClO_4)_2\cdot6H_2O$ and 2-methylalanine, and the proportion of the reactants was controlled to be 1:6:4 Gd^{3+}:Cu^{2+}:mAla. Then the pH value of the reaction mixture was carefully adjusted to about 6.6 by the slow addition of 0.1 M NaOH solution. After another 2 h of being stirred, the solution was filtrated and placed in a desiccator filled with phosphorus pentaoxide. Blue crystals were obtained about a month later. Yield: 0.25 g, 20.8%. Element anal. Calcd for $C_{64}H_{244}N_{16}O_{178}Cl_{18}Cu_{24}Gd_6$: C, 10.69; H, 3.42; N, 3.12; Cl, 8.87. Found: C, 10.93; H, 2.91; N, 3.25; Cl, 8.64.

$Na_4[Tb_6Cu_{26}(\mu_3\text{-}OH)_{30}(Gly)_{18}(ClO_4)(H_2O)_{22}]\cdot(ClO_4)_{25}\cdot(H_2O)_{42}$ (2). To an aqueous solution (10 mL) of $Tb(ClO_4)_3\cdot6H_2O$

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Table 2. Selected Bond Lengths (Å) for **1**[a]

Gd⋯Gd	6.941−6.976	Gd−O(OH)	2.409(4)−2.460(4)
Gd⋯Cu(inner)	3.448−3.509	Gd−O(OH_2)	2.429(5)−2.477(5)
Gd⋯Cu(outer)	3.529−3.586	Gd−O(carboxyl)	2.522(4)−2.573(4)
Cu(inner)⋯Cu(inner)	3.351−3.429	Cu(inner)−O(OH)	1.955(4)−1.988(4)
Cu(outer)⋯Cu(outer)	3.009−3.156	Cu(inner)−O(carboxyl)	2.302(4)−2.350(5)
Cu(7)−O(3)	1.948(4)	Cu(10)−O(5)	1.952(5)
Cu(7)−O(13)	1.937(5)	Cu(10)−O(44)	1.978(5)
Cu(7)−O(43)	1.966(4)	Cu(10)−O(58)	1.953(7)
Cu(7)−N(2)	1.968(7)	Cu(10)−N(3)	1.984(7)
Cu(7)−O(59)	2.331(8)	Cu(10)−O(73)#1	2.469(6)
Cu(8)−O(1)	1.956(4)	Cu(10)−O(71)#1	2.530(7)
Cu(8)−O(14)	1.955(4)	Cu(11)−O(7)	1.960(4)
Cu(8)−O(43)	1.967(4)	Cu(11)−O(15)	1.962(5)
Cu(8)−N(1)	1.949(7)	Cu(11)−O(45)	1.964(5)
Cu(8)−O(60)	2.299(7)	Cu(11)−N(4)	1.972(6)
Cu(9)−O(9)	1.960(4)	Cu(11)−O(72)	2.405(6)
Cu(9)−O(44)	1.973(5)	Cu(12)−O(11)	1.944(4)
Cu(9)−O(57)	1.950(6)	Cu(12)−O(16)	1.936(5)
Cu(9)−N(5)	1.973(7)	Cu(12)−O(45)	1.958(4)
Cu(9)−O(61)#1	2.502(10)	Cu(12)−N(6)	1.974(6)
Cu(9)−O(73)#1	2.498(6)	Cu(12)−O(201)	2.402(8)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $1 - y$, $1 - z$.

Table 3. Selected Bond Angles (deg) for **1**

Cu(outer)−O(carboxyl)−Gd	103.2(2)−104.0(2)	Cu(inner)−O(OH)−Gd	102.7(2)−105.8(2)
Cu(outer)−O(OH)−Gd	106.0(2)−107.5(2)	Cu(inner)−O(OH)−Cu(inner)	115.7(2)−120.8(2)
Cu(outer)−O(OH)−Cu(outer)	99.8(2)−106.0(2)		
O(31)−Gd(1)−O(34)	67.49(14)	O(43)−Cu(7)−N(2)	163.7(3)
O(34)−Gd(1)−O(40)	66.50(14)	N(1)−Cu(8)−O(1)	84.2(2)
O(40)−Gd(1)−O(42)	66.18(14)	N(1)−Cu(8)−O(14)	96.6(3)
O(42)−Gd(1)−O(31)	67.43(14)	O(14)−Cu(8)−O(1)	171.4(2)
O(1)−Gd(1)−O(3)	82.15(14)	N(1)−Cu(8)−O(43)	161.8(4)
O(3)−Gd(1)−O(52)	82.50(15)	O(57)−Cu(9)−N(5)	96.5(3)
O(52)−Gd(1)−O(51)	82.62(16)	O(9)−Cu(9)−N(5)	83.7(2)
O(1)−Gd(1)−O(51)	80.56(18)	O(57)−Cu(9)−O(9)	178.4(3)
O(43)−Gd(1)−O(1)	64.51(14)	N(5)−Cu(9)−O(44)	168.2(2)
O(43)−Gd(1)−O(3)	64.10(14)	O(5)−Cu(10)−O(44)	84.63(19)
O(43)−Gd(1)−O(51)	71.67(15)	O(58)−Cu(10)−O(44)	97.2(4)
O(43)−Gd(1)−O(52)	72.18(15)	O(5)−Cu(10)−O(58)	178.1(4)
O(1)−Gd(1)−O(31)	73.09(14)	O(44)−Cu(10)−N(3)	168.5(2)
O(1)−Gd(1)−O(34)	73.72(14)	O(7)−Cu(11)−O(45)	83.96(18)
O(31)−Cu(1)−O(32)	93.25(18)	O(15)−Cu(11)−O(45)	93.9(2)
O(31)−Cu(1)−O(34)	85.63(18)	O(7)−Cu(11)−O(15)	170.4(2)
O(31)−Cu(1)−O(35)	176.95(17)	O(45)−Cu(11)−N(4)	167.0(2)
O(32)−Cu(1)−O(34)	176.41(18)	O(16)−Cu(12)−O(45)	94.5(2)
O(3)−Cu(7)−N(2)	84.6(2)	O(11)−Cu(12)−O(45)	85.09(18)
O(13)−Cu(7)−N(2)	96.8(2)	O(16)−Cu(12)−O(11)	173.9(2)
O(13)−Cu(7)−O(3)	173.9(2)	O(45)−Cu(12)−N(6)	169.7(2)

(0.565 g, 1 mmol) was added glycine (0.075 g, 1 mmol). The pH value of the reaction mixture was carefully adjusted to about 6.6 by the slow addition of 0.1 M NaOH solution, and the solution was stirred at 50 °C for about 2 h. $Cu(ClO_4)_2{\cdot}6H_2O$ (0.73 g, 2 mmol) was then added, and the pH value of the reaction mixture was again adjusted to about 6.6. After another 2 h of being stirred, the solution was filtrated and placed in a desiccator filled with phosphorus pentaoxide. Blue crystals were obtained about a month later. Yield: 0.31 g, 22.7%. Element anal. Calcd for $C_{36}H_{230}Cl_{26}Cu_{26}N_{18}Na_4O_{234}Tb_6$: C 5.22; H, 2.80; N, 3.05; Na, 1.11; Cl, 11.13. Found: C, 5.43; H, 2.51; N, 3.25; Na, 1.36; Cl, 10.64.

{$[Ln_6Cu_{24}(\mu_3\text{-}OH)_{30}(Pro)_{12}(Ac)_6(ClO_4)(H_2O)_{13}]_2Cu(Pro)_2$}$\cdot$$(ClO_4)_{18}{\cdot}(OH)_{16}{\cdot}(H_2O)_{55}$ (Ln = Sm(3), Gd(4)). To an aqueous solution (10 mL) of $Ln(ClO_4)_3{\cdot}6H_2O$ (1 mmol) were added $Cu(ClO_4)_2{\cdot}6H_2O$, $NaAc{\cdot}3H_2O$, and L-Proline, and the proportion of the reactants was controlled to be 1:6:1:4 Ln^{3+}:Cu^{2+}:Pro:Ac^-. The pH value of the reaction mixture was then carefully adjusted to about 6.6 by the slow addition of 0.1 M NaOH solution. After 2 h of being stirred, the solution was filtrated and placed in a desiccator filled with phosphorus pentaoxide. Blue crystals were obtained about a month later. For **3**, yield = 0.26 g, 22.6%. Element anal. Calcd for $C_{154}H_{482}Cl_{20}Cu_{49}N_{26}O_{313}Sm_{12}$: C, 13.87; H, 3.64; N, 2.73; Cl, 5.32. Found: C, 13.59; H, 3.27; N, 2.92; Cl, 5.91. For **4**, elemental anal. Calcd for $C_{154}H_{482}Cl_{20}Cu_{49}N_{26}O_{313}Gd_{12}$: C, 13.79; H, 3.62; N, 2.71; Cl, 5.28. Found: C, 13.68; H, 3.31; N, 2.86; Cl, 5.74. Unit-cell parameters for Gd(**4**): a = 29.9771(5) Å, b = 27.6466(5) Å, c = 29.1622(3) Å, α = 90°, β = 93.470(1)°, γ = 90°.

X-ray Crystallography. Intensity data for **1** were collected at 130.15 K on a Rigaku Mercury CCD area detector, and data for **2**−**4** were collected at 293.15 K on a Siemens Smart/CCD area detector diffractometer with Mo Kα radiation (λ= 0.71073 Å). Data reduction and unit-cell refinement were performed with Smart-CCD software.[14] The structures were solved by direct methods using

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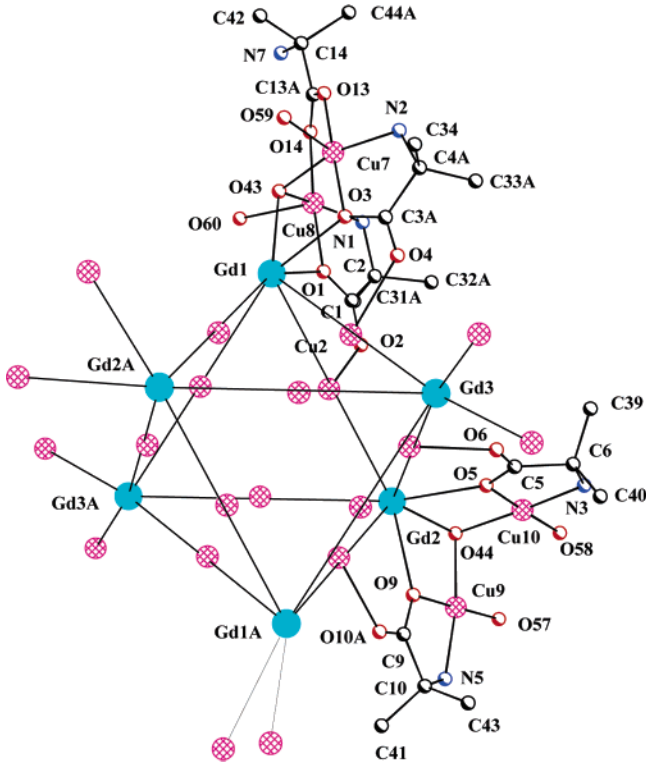

Figure 2. View of the structure of vertices of the octahedron of **1**.

SHELXS-97[15] and were refined by full-matrix least-squares methods using SHELXL-97.[16] The anisotropic displacement parameters were refined for all non-hydrogen atoms except some of the oxygen atoms from free water molecules and ClO_4^-. Final $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$, with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (where $P = (F_o^2 + 2F_c^2)/3$). The crystallographic data are summarized in Table 1.

Results and Discussion

Structure of the Clusters. The structure of the cation of **1** is shown in Figure 1. Selected bond distances and angles are shown in Tables 2 and 3, respectively. Complex **1** $\{Gd_6Cu_{24}\}$ is built from a huge Gd_6Cu_{12} octahedron with pseudocubic O_h symmetry (inner core) connect with twelve outer Cu^{2+}. Six Gd^{III} ions with an average distance of about 7 Å locate at the vertices of an octahedron and 12 inner Cu^{II} ions locate at the midpoints of the octahedral edges. The average Gd···Cu(inner) and Cu(inner)···Cu(inner) distances are about 3.5 and 3.4 Å, respectively. Each Gd^{III} ion also interconnects two outer Cu^{II} ions with the help of one outer μ_3-OH^- and two $[3.1_12_{23}1_3]$-coordinated 2-methylalanine ligands (as shown in Figure 2). The average Gd···Cu(outer) distance is about 3.5 Å, whereas that of two neighboring outer Cu^{2+} is about 3.0 Å. Thirty μ_3-OH^- groups, each linking one Gd^{III} and two Cu^{II} ions, are used to construct the metal framework. The angles of Cu(inner)−O−Cu(inner) and Gd−O−Cu(inner) are in the range of 116−120° and 103−106°, whereas the angles of Cu(outer)−O−Cu(outer) and Gd−O−Cu(outer) are in the range of 100−106 and 106−108°.

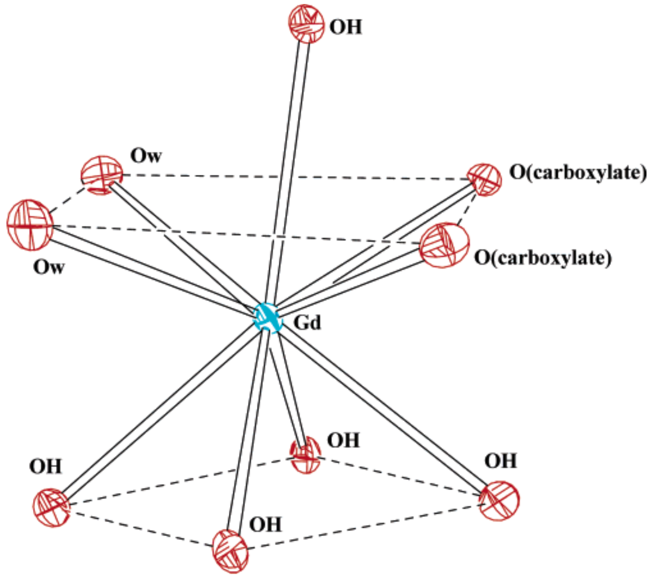

Figure 3. Coordination polyhedron of Gd^{3+} ion in **1**.

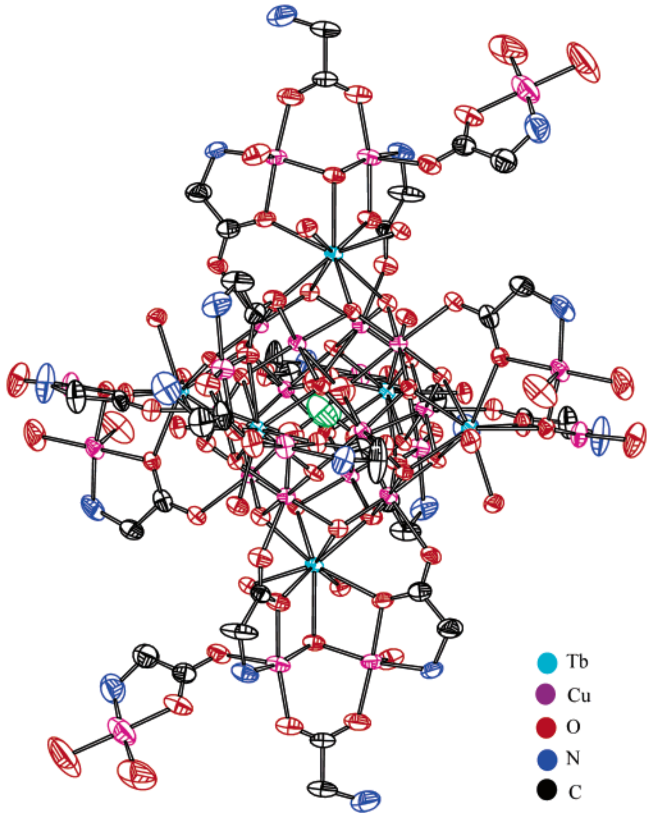

Figure 4. Structure of the cation of **2**.

The coordination polyhedron of the nine-coordinated Gd^{III} with an O_9 donor set may be best described as a monocapped square antiprism (four μ_3-OH^- groups coordinating to one Gd^{III} and two inner Cu^{II} constitute the lower plane. Two carboxylate oxygen atoms and two water molecules constitute the upper plane. One μ_3-OH^- coordinating to one Gd^{III} and two outer Cu^{II} acts as a "cap", as shown in Figure 3). The

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(14) *XSCANS*, version 2.1; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

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Table 4. Selected Bond Lengths (Å) for **2**

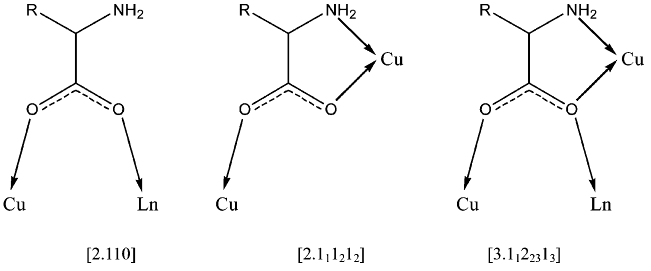
Tb···Tb	6.925−6.961	Tb−O(OH)	2.385(9)−2.464(8)
Tb···Cu(inner)	3.438−3.515	Tb−O(OH_2)	2.423(10)−2.476(9)
Tb···Cu(outer)	3.528−3.571	Tb−O(carboxyl)	2.497(9)−2.516(9)
Cu(inner)···Cu(inner)	3.334−3.411	Cu(inner)-O(OH)	1.955(8)−1.989(8)
Cu(outer)···Cu(outer)	3.048−3.139	Cu(inner)-O(carboxyl)	2.284(10)−2.325(10)
Cu(7)−O(1)	1.967(9)	Cu(10)−N(4)	1.956(16)
Cu(7)−O(13)	1.940(10)	Cu(10)−O(47)	2.391(13)
Cu(7)−O(33)	1.966(9)	Cu(11)−O(10)	1.953(10)
Cu(7)−N(1)	1.952(13)	Cu(11)−O(15)	1.930(11)
Cu(8)−O(3)	1.971(9)	Cu(11)−O(35)	1.951(10)
Cu(8)−O(14)	1.957(10)	Cu(11)−N(5)	1.962(13)
Cu(8)−O(33)	1.964(10)	Cu(12)−O(11)	1.982(10)
Cu(8)−N(2)	1.952(15)	Cu(12)−O(16)	2.002(11)
Cu(9)−O(5)	1.975(9)	Cu(12)−O(35)	1.958(9)
Cu(9)−O(34)	1.973(10)	Cu(12)−N(6)	1.982(13)
Cu(9)−O(50)	1.955(10)	Cu(12)−O(18)	2.265(12)
Cu(9)−N(3)	1.962(15)	Cu(13)−O(17)	1.949(13)
Cu(10)−O(7)	1.968(9)	Cu(13)−O(48)	1.979(19)
Cu(10)−O(34)	1.950(10)	Cu(13)−O(49)	1.94(2)
Cu(10)−O(51)	1.990(11)	Cu(13)−N(9)	1.98(2)

Table 5. Selected Bond Angles (deg) for **2**

Cu(outer)−O(carboxyl)−Gd	103.9(4)−104.7(4)	Cu(inner)−O(OH)−Gd	102.4(4)−106.5(4)
Cu(outer)−O(OH)−Gd	106.7(4)−108.6(4)	Cu(inner)−O(OH)−Cu(inner)	114.9(4)−120.2(5)
Cu(outer)−O(OH)−Cu(outer)	101.7(4)−106.0(5)	N(2)−Cu(8)−O(3)	85.0(5)
O(21)−Tb(1)−O(23)	68.1(3)	N(2)−Cu(8)−O(33)	168.6(5)
O(23)−Tb(1)−O(27)	67.1(3)	O(14)−Cu(8)−O(3)	170.4(5)
O(27)−Tb(1)−O(28)	65.8(3)	N(3)−Cu(9)−O(5)	84.8(5)
O(28)−Tb(1)−O(21)	65.9(3)	O(50)−Cu(9)−N(3)	99.0(6)
O(1)−Tb(1)−O(3)	87.0(3)	O(50)−Cu(9)−O(5)	174.6(5)
O(3)−Tb(1)−O(41)	81.5(3)	N(3)−Cu(9)−O(34)	168.0(5)
O(41)−Tb(1)−O(42)	76.6(3)	N(4)−Cu(10)−O(7)	85.0(5)
O(42)−Tb(1)−O(1)	83.3(3)	O(34)−Cu(10)−O(7)	83.8(4)
O(33)−Tb(1)−O(41)	72.1(3)	O(7)−Cu(10)−O(51)	174.0(6)
O(33)−Tb(1)−O(1)	64.1(3)	O(34)−Cu(10)−N(4)	168.6(5)
O(33)−Tb(1)−O(3)	64.2(3)	O(10)−Cu(11)−N(5)	85.5(5)
O(33)−Tb(1)−O(42)	73.6(3)	O(35)−Cu(11)−O(10)	84.2(4)
O(23)−Tb(1)−O(1)	73.1(3)	O(15)−Cu(11)−O(10)	172.0(5)
O(21)−Cu(1)−O(22)	96.8(4)	O(35)−Cu(11)−N(5)	169.6(5)
O(21)−Cu(1)−O(23)	85.2(4)	O(35)−Cu(12)−O(16)	94.1(5)
O(22)−Cu(1)−O(23)	176.3(4)	O(11)−Cu(12)−N(6)	84.8(5)
O(21)−Cu(1)−O(24)	176.2(4)	O(35)−Cu(12)−N(6)	166.4(5)
O(13)−Cu(7)−N(1)	96.0(5)	O(11)−Cu(12)−O(16)	169.8(5)
N(1)−Cu(7)−O(1)	85.6(4)	O(17)−Cu(13)−N(9)	85.7(6)
O(13)−Cu(7)−O(1)	174.6(5)	O(48)−Cu(13)−N(9)	91.4(10)
N(1)−Cu(7)−O(33)	168.5(5)	O(17)−Cu(13)−O(48)	173.7(8)
N(2)−Cu(8)−O(14)	97.0(5)	O(49)−Cu(13)−N(9)	173.7(8)

Gd−O bond distances are in the range of 2.41−2.57 Å. The inner Cu^{II} ion has a slightly distorted six-coordinated octahedral configuration with an O_6 donor set (The equatorial plane is determined by four μ_3-OH^- groups with Cu-O bond distances of about 1.96−1.99 Å, whereas the apical places are occupied by two oxygen atoms from one ClO_4^- and one carboxylate group, respectively, with Cu−O bond distances of about 2.3−2.4 Å). For the 12 outer Cu^{2+} ions, eight of them are five-coordinated in a NO_4 square-pyramidal geometry. Its square plane is determined by one nitrogen atom and one carboxylate oxygen atom from chelating 2-methylalanine, another carboxylate oxygen atom from bridging 2-methylalanine, and one μ_3-OH^-. The bond distances are in the range of 1.94−1.97 Å. The apical plane is occupied by an oxygen atom from a water molecule or a ClO_4^- anion. The bond distances are in the range of 2.30−2.41 Å. The other four outer Cu^{2+} ions adopt six-coordinated NO_5 in a slightly distorted octahedral configuration. Its square-plane is determined by one nitrogen atom and one carboxylate oxygen atom from chelating 2-methylalanine, one water molecule, and one μ_3-OH^- group. The apical plane is also occupied by an oxygen atom from a water molecule or a ClO_4^- anion. The bond distances are in the range of 2.46−2.53 Å.

Scheme 1. Three Coordination Modes of Glycinato Ligands Indicated by the Harris Notation[12]



There are two coordination modes for the 2-methylalanine ligands in this cluster (as shown in Scheme 1). (1) Four

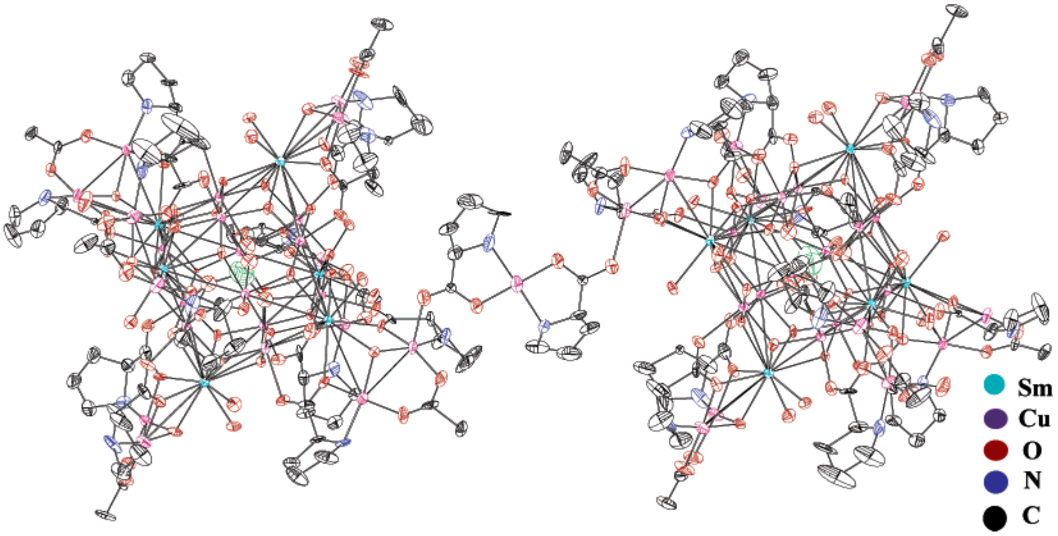


Figure 5. Structure of the cation of **3**·Sm.

Table 6. Selected Bond Lengths (Å) for **3**

Sm···Sm	6.980−7.027
Sm···Cu(inner)	3.465−3.543
Sm···Cu(outer)	3.562−3.604
Cu(inner)−Cu(inner)	3.317−3.420
Cu(outer)−Cu(outer)	2.988−3.079
Cu(13)−O(17)	1.96(2)
Cu(13)−O(54)	1.98(2)
Cu(13)−O(62)	1.94(2)
Cu(13)−N(9)	1.96(3)
Cu(14)−O(1)	1.96(2)
Cu(14)−O(54)	1.93(2)
Cu(14)−O(61)	1.95(2)
Cu(14)−N(1)	2.02(4)
Cu(15)−O(3)	1.96(2)
Cu(15)−O(55)	1.97(2)
Cu(15)−O(63)	1.93(2)
Cu(15)−N(2)	1.99(3)
Cu(15)−O(85)	2.39(3)
Cu(16)−O(11)	2.00(2)
Cu(16)−O(55)	1.98(2)
Cu(16)−O(64)	1.93(2)
Cu(16)−N(6)	1.99(3)
Cu(17)−O(5)	1.96(2)
Cu(17)−O(56)	1.98(3)
Cu(17)−O(65)	1.98(3)
Cu(17)−N(3)	1.99(3)
Cu(18)−O(13)	1.97(2)
Cu(18)−O(56)	1.97(2)
Cu(18)−O(66)	1.96(2)
Cu(18)−N(7)	1.99(3)
Cu(19)−O(23)	1.97(2)
Sm−O(OH)	2.40(2)−2.51(2)
Sm−O(OH_2)	2.43(2)−2.53(2)
Sm−O(carboxyl)	2.50(2)−2.60(2)
Cu(inner)−O(carboxyl)	2.31(2)−2.39(2)
Cu(inner)−O(OH)	1.92(2)−2.03(2)
Cu(19)−O(57)	1.95(2)
Cu(19)−O(67)	1.94(2)
Cu(19)−N(12)	2.02(3)
Cu(20)−O(7)	1.97(2)
Cu(20)−O(57)	1.96(2)
Cu(20)−O(68)	1.99(2)
Cu(20)−N(4)	2.03(3)
Cu(21)−O(15)	1.97(2)
Cu(21)−O(58)	1.96(2)
Cu(21)−O(69)	1.98(2)
Cu(21)−N(8)	2.00(3)
Cu(21)−O(25)	2.35(3)
Cu(22)−O(9)	1.96(2)
Cu(22)−O(58)	1.92(2)
Cu(22)−O(70)	1.96(2)
Cu(22)−N(5)	2.00(3)
Cu(23)−O(19)	1.98(2)
Cu(23)−O(59)	2.00(2)
Cu(23)−O(71)	1.94(2)
Cu(23)−N(10)	1.92(3)
Cu(24)−O(21)	1.98(2)
Cu(24)−O(59)	2.00(2)
Cu(24)−O(72)	1.99(2)
Cu(24)−N(11)	2.01(3)
Cu(25)−O(26)	1.89(2)
Cu(25)−N(13)	1.99(3)

[2.110]-coordinated 2-methylalanines, each coordinating to two neighboring outer Cu^{2+} ions; (2) 12 $[3.1_12_{23}1_3]$-coordinated 2-methylalanines, each chelating to one inner Cu^{II}, one outer Cu^{II}, and one Gd^{III} ion.

It should be noted that the ClO_4^- anion captured in the cage may play the role of a template. Each oxygen atom of the anion coordinates to three inner Cu^{II} ions that come from the same plane in the $\{Gd_6Cu_{12}\}$ octahedron.

The structure of the cation of **2** is shown in Figure 4. Selected bond distances and angles are shown in Tables 4 and 5, respectively. The structure of **2** may be described as a $\{Tb_6Cu_{24}\}$ main structure connected with two $[Cu(Gly)(H_2O)_2]^+$ groups. The $\{Tb_6Cu_{24}\}$ main structure is almost the same as that in **1** except for a slight difference in the 12 outer Cu^{2+} ions and the ligand. For the 12 outer Cu^{2+} ions, eight are four-coordinated in square-planar geometry. The other four adopt five-coordinated NO_4 square-pyramidal geometry. Two $[Cu(Gly)(H_2O)_2]^+$ groups are connected to the $\{Tb_6Cu_{24}\}$ main structure with the help of two $[2.1_11_21_2]$-coordinated glycinato ligands. The terminal Cu^{II} ion coordinates to two water molecules, one nitrogen atom, and one oxygen atom from a glycinato ligand. The spare carboxylate oxygen atom of the amino acid ligand occupies the fifth-coordinated site of an outer Cu^{II} ion (Cu12), and thus $[Cu(Gly)(H_2O)_2]^+$ groups and the $\{Tb_6Cu_{24}\}$ main body are connected.

Table 7. Selected Bond Angles (deg) for **3**[a]

Cu(outer)−O(carboxyl)−Sm	103.1(9)−105.2(10)	Cu(inner)−O(OH)−Sm	101.5(9)−106.9(8)
Cu(outer)−O(OH)−Sm	105.0(9)−109.6(10)	Cu(inner)−O(OH)−Cu(inner)	113.8(9)−120.4(9)
Cu(outer)−O(OH)−Cu(outer)	98.9(9)−105.0(8)		
O(30)−Sm(1)−O(39)	64.1(6)	O(56)−Cu(17)−N(3)	168.0(10)
O(39)−Sm(1)−O(45)	65.2(6)	O(5)−Cu(17)−N(3)	85.2(11)
O(45)−Sm(1)−O(42)	66.6(6)	O(65)−Cu(17)−N(3)	97.8(13)
O(42)−Sm(1)−O(30)	65.6(7)	O(66)−Cu(18)−O(13)	176.0(13)
O(1)−Sm(1)−O(17)	85.4(8)	N(7)−Cu(18)−O(56)	167.9(12)
O(17)−Sm(1)−O(74)	82.2(8)	O(66)−Cu(18)−N(7)	95.8(13)
O(74)−Sm(1)−O(73)	80.7(9)	O(13)−Cu(18)−N(7)	83.4(11)
O(73)−Sm(1)−O(1)	80.9(8)	O(23)−Cu(19)−O(67)	169.4(10)
O(54)−Sm(1)−O(1)	63.3(7)	O(57)−Cu(19)−N(12)	171.9(12)
O(54)−Sm(1)−O(17)	62.9(6)	O(23)−Cu(19)−N(12)	86.0(11)
O(54)−Sm(1)−O(73)	75.3(8)	O(67)−Cu(19)−N(12)	92.4(12)
O(54)−Sm(1)−O(74)	73.7(8)	O(7)−Cu(20)−O(68)	170.4(10)
O(30)−Sm(1)−O(1)	74.5(7)	O(57)−Cu(20)−N(4)	167.7(10)
O(42)−Sm(1)−O(1)	73.6(7)	O(7)−Cu(20)−N(4)	83.7(10)
O(31)−Cu(1)−O(30)	94.6(8)	O(68)−Cu(20)−N(4)	96.0(11)
O(42)−Cu(1)−O(30)	86.2(8)	O(69)−Cu(21)−O(15)	164.7(10)
O(42)−Cu(1)−O(31)	176.4(9)	O(58)−Cu(21)−N(8)	168.3(10)
O(30)−Cu(1)−O(43)	177.5(8)	O(69)−Cu(21)−N(8)	96.2(12)
O(62)−Cu(13)−N(9)	98.4(12)	O(15)−Cu(21)−N(8)	83.5(10)
N(9)−Cu(13)−O(17)	84.6(11)	O(70)−Cu(22)−O(9)	174.9(11)
N(9)−Cu(13)−O(54)	166.5(10)	O(58)−Cu(22)−N(5)	169.4(9)
O(62)−Cu(13)−O(17)	170.6(12)	O(70)−Cu(22)−N(5)	95.8(11)
O(61)−Cu(14)−O(1)	177.0(11)	O(9)−Cu(22)−N(5)	84.4(10)
O(54)−Cu(14)−N(1)	169.6(10)	O(71)−Cu(23)−O(19)	172.9(10)
O(61)−Cu(14)−N(1)	94.7(12)	N(10)−Cu(23)−O(59)	170.6(11)
O(1)−Cu(14)−N(1)	85.4(11)	O(71)−Cu(23)−N(10)	93.6(11)
O(63)−Cu(15)−O(3)	172.0(13)	N(10)−Cu(23)−O(19)	85.8(11)
O(55)−Cu(15)−N(2)	166.9(12)	O(21)−Cu(24)−O(72)	169.0(10)
O(3)−Cu(15)−N(2)	84.7(13)	O(59)−Cu(24)−N(11)	168.4(9)
O(63)−Cu(15)−N(2)	96.1(13)	O(21)−Cu(24)−N(11)	85.7(9)
O(64)−Cu(16)−O(11)	174.4(10)	O(72)−Cu(24)−N(11)	95.6(10)
O(55)−Cu(16)−N(6)	168.9(12)	O(26)−Cu(25)−O(26)#1	174.6(33)
O(64)−Cu(16)−N(6)	93.2(13)	N(13)−Cu(25)−N(13)#1	168.2(26)
O(11)−Cu(16)−N(6)	87.3(12)	O(26)−Cu(25)−N(13)	87.5(11)
O(5)−Cu(17)−O(65)	170.5(13)	O(26)#1−Cu(25)−N(13)	93.1(11)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1$, y, $-z + 1$.

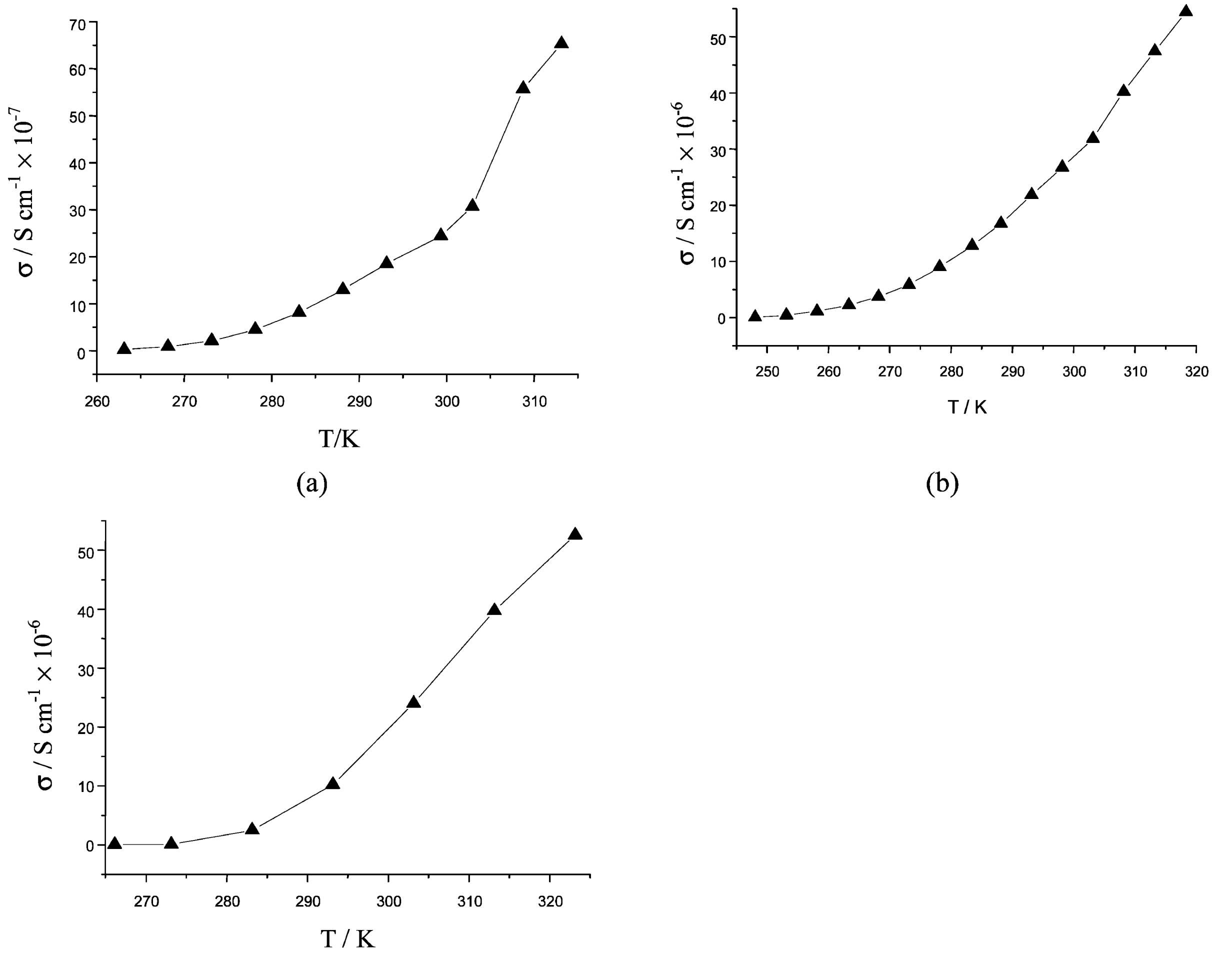
X-ray structure analyses showed that **3** (Sm) and **4** (Gd) are isomorphous, so only the structure of **3** (Sm) is reported here as an example**.** The structure of the cation of **3**·Sm is shown in Figure 5. Selected bond distances and angles are shown in Tables 6 and 7, respectively. The structure of **3**·Sm can be described as two {Sm_6Cu_{24}} octahedral units (almost the same as **1**) connected by a trans-Cu(pro)$_2$ bridge. For the 12 outer Cu^{II} ions, nine of them are four-coordinated in square-planar geometry. The other three adopt a five-coordinated NO_4 square-pyramidal geometry. Six bidentate acetate ligands, each coordinating to two neighboring outer Cu^{2+}, are also used to construct the cluster. In addition, Cu25 (bridge) coordinates to two $[2.1_11_21_2]$-coordinated proline ligands in trans form; the *trans*-Cu(pro)$_2$ bridge thus formed uses carboxylate oxygen atoms to coordinate to the fifth-coordinated site of Cu21 and the two {Sm_6Cu_{24}} units are connected.

The Ln_6Cu_{12} inner core in these structures is similar to the {Ln_6Cu_{12}} cluster with η_2-coordinated betaine as ligand.[5(b)] But as α-amino acids have more coordination modes than betaine, this leads to structures of the complexes that are much more beautiful and intriguing than the 0D 18-nuclear complex. In previous work,[7] we have shown when Ln^{3+} and Cu^{2+} ions react with amino acid ligands under different conditions, series of 0D, 1D, 2D, or 3D compounds based on a similar {Ln_6Cu_{24}} unit can be obtained. In this article, we found that if L-proline was used to replace glycine or L-alanine and react with Ln^{3+} and Cu^{2+} ions (in the presence of Ac^-), an unexpected 61-nuclear {$Ln_{12}Cu_{49}$} cluster, rather than 30-nuclear {Ln_6Cu_{24}} clusters, can be obtained.[7(c)] It can be viewed as a dimer of the {Ln_6Cu_{24}} unit (two {Ln_6Cu_{24}} octahedral units connected by a *trans*-Cu(proline)$_2$ bridge). The cluster also represents the largest known 3d−4f heteronuclear cluster so far. The large side chain of the L-prolinato ligand is proposed to play an important role in the great difference between them.

An impressive structural feature of the clusters is the large size. The sizes for **1**−**3** are 2.45 × 2.45 × 1.98, 2.69 × 2.47 × 1.98, and 4.33 × 2.38 × 2.38 nm^3, respectively, which are significantly larger than those of other high-nuclear 3d−4f heteronuclear clusters.[3−6]

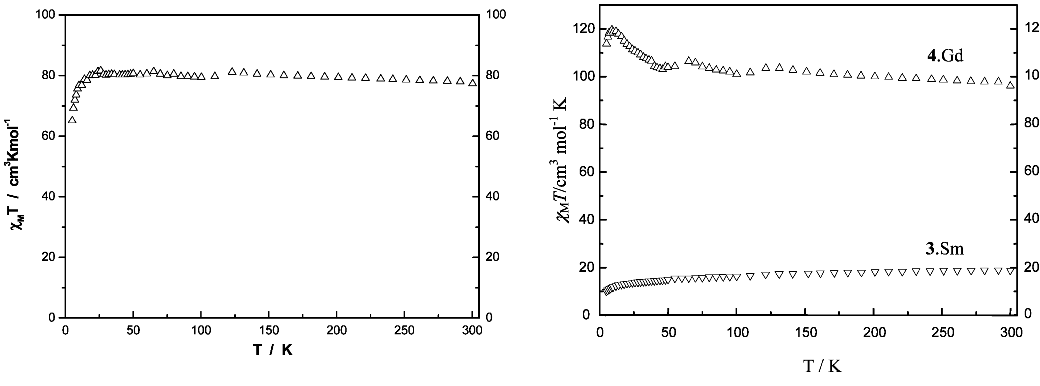
Electrical Conductivity and Magnetic Property. The electrical conductivities of **2**−**4** at different temperatures have been measured, as shown in Figure 6. It is very interesting that the high-nuclear 3d−4f heterometallic clusters with an amino acid are temperature-sensitive semiconductors.

The electrical conductivity of **2**, **3**·Sm, and **4**·Gd were determined as powder samples from ground crystals. The electrical conductivity of **2** at 263 K is 2.85×10^{-8} S cm^{-1} and increases to 6.53×10^{-6} S cm^{-1} at 313 K, which indicates that it is a temperature-sensitive semiconductor. **3**·



(a) (b) (c)

Figure 6. Temperature dependence of the electrical conductivity of (a) **2**, (b) **3**·Sm, and (c) **4**·Gd.



(a) $\{Tb_6Cu_{26}\}$ (b) $\{(Ln_6Cu_{24})_2Cu\}$

Figure 7. Temperature dependence of the magnetic susceptibility of **2**, **3**·Sm, and **4**·Gd. (5−300 K at 10 000 G).

Sm and **4**·Gd show similar conductivity behaviors and are also semiconductors. A large network of hydrogen bonds and the migration of some single-ion species, such as Na^+, OH^-, and H^+, are proposed to play an important role in the electrical conductivity of the discrete compound.[7(c),17]

The magnetic property of **1** can refer to the data in $[Gd_6Cu_{24}(\mu_3\text{-}OH)_{30}(Ala)_{12}(Ac)_6(ClO_4)(H2O)_{12}]\cdot(ClO_4)_{10}\cdot(OH)_7\cdot(H_2O)_{34}$.[7c] Temperature-dependent magnetic susceptibilities of complexes **2**−**4** were measured in the range of 5−300 K at 10 000 G and are shown in Figure 7. At 300 K, the $\chi_M T$ value per Tb_6Cu_{26} unit is 77.37 cm^3 mol^{-1} K, which is comparable to the expected value (80.62) for six Tb^{III} with the free-ion state and 26 spin-only Cu^{II} ions ($S = 1/2$, $g = 2$). With a decrease in temperature, the $\chi_M T$ value increases very slowly and reaches a maximum of 81.58 cm^3 mol^{-1} K around 26 K. This result shows the exchange interactions are very weak. A further decrease in $\chi_M T$ below 26 K might be due to spin−orbit coupling or field saturation effects.

Although ferromagnetic Tb···Cu interaction has been observed in several other polynuclear Tb−Cu clusters,[3d,13] we cannot tell the nature of the Tb···Cu interaction in **2** on the basis of the above experiments (we could not synthesize a crystalline isostructural [La_6Cu_{26}] compound).

A free-ion approximation for Sm(III) is not valid because of the presence of thermally populated excited states. The calculated $\chi_M T$ value at room temperature for **3**·Sm is about 18.96 $cm^3\ mol^{-1}$ K, close to the calculated value of 20.29 $cm^3\ mol^{-1}$ K (a $\chi_M T$ value of 0.32 $cm^3\ mol^{-1}$ K is used for Sm^{3+} ion[18]). For **4**·Gd, the $\chi_M T$ value at 300 K is 96.09 $cm^3\ mol^{-1}$ K, compared with the calculated value of 112.87 $cm^3\ mol^{-1}$ K. Upon cooling, the $\chi_M T$ value first increases slowly, reaches a maximum at ca. 9 K (119.6 $cm^3\ mol^{-1}$ K), and then decreases dramatically. This phenomenon corresponds to an overall ferromagnetic interaction, as confirmed by the Weiss constant (6.76 K). Because no isostructural La or Y sample is available for a comparison, we only know the Cu(inner)···Cu(inner) exchange interaction is antiferromagnetic according to the literature.[5(b)]

Conclusion

In summary, with L-proline, glycine, and 2-methylalanine as ligands, two isostructural 61-nuclear (the largest known 3d−4f heteronuclear clusters), one 32-nuclear cluster and one 30-nuclear 3d−4f cluster were synthesized through controlling the hydrolysis of metal ions. All of them are based on the {Ln_6Cu_{24}} octahedral unit. Previous[7] and current results show that the size of the side chain of the amino acid ligand plays an important role in affecting the final hydrolysis products of 3d and 4f metal ions. Similar results have also been observed in the hydrolysis of 4f ions.[10] Future work will focus on the research of amino acid ligands with side chains containing O- or N-donor atoms.

Acknowledgment. This research was supported by grants from the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), the Ministry of Science and Technology of China (001CB1089), the National Science Foundation (20333070, 90206040, 90406024) of China and Fujian Province (2005HZ01-1, 2004HZ01-1, 2004J041, Z0513022).

Supporting Information Available: Crystallographic information files (CIF) on the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060610L

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