Synthesis, Structures, and Magnetic Properties of Carboxylate-Bridged Tetranuclear Copper(II)−Lanthanoid(III) Complexes $[Cu_2Ln_2(betaine)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ and $[Cu_2Ln_2(betaine)_{12}(ClO_4)_2](ClO_4)_8$

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Synthesis, crystal structures, and magnetic properties of two types of carboxylate-bridged $Cu^{II}{}_2Ln^{III}{}_2$ complexes, formulated as $[Cu_2Ln_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ (**1**; $Ln^{III} = La^{III}$, Ce^{III}, or Gd^{III}; bet = betaine) and $[Cu_2Ln_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ (**2**; $Ln^{III} = Gd^{III}$ or Sm^{III}), have been described. **1**·La features a carboxylate-bridged, tetranuclear $[Cu_2La_2(bet)_{10}(H_2O)_8]^{10+}$ cation, crystallizing in the triclinic space group $P\bar{1}$, with $a = 12.778(4)$ Å, $b = 15.553(5)$ Å, $c = 16.041(5)$ Å, $\alpha = 110.18(2)°$, $\beta = 100.72(2)°$, $\gamma = 105.03(2)°$, and $Z = 1$; **1**·Ce is isomorphous with **1**·La, crystallizing in the triclinic space group $P\bar{1}$, with $a = 12.730(2)$ Å, $b = 15.489(2)$ Å, $c = 15.987(3)$ Å, $\alpha = 110.28(1)°$, $\beta = 100.70(1)°$, $\gamma = 105.00(2)°$, and $Z = 1$. In both **1**·La and **1**·Ce, a Cu^{II} atom is quadruply bridged to a Ln^{III} atom by the μ_2-carboxylate groups into a dinuclear subunit, and a pair of such dinuclear subunits is bridged by two carboxylate groups to form a tetranuclear cation. In the tetranuclear cation, each Cu^{II} atom is coordinated in a square pyramid by four carboxy oxygen atoms at the basal positions and by one aqua ligand at the apical position whereas each Ln^{III} atom is coordinated in a monocapped square antiprism by six carboxy oxygen atoms and three aqua ligands. **1**·Gd has been characterized to be an analogue of **1**·La. **2**·Gd consists of a different tetranuclear $[Cu_2Gd_2(bet)_{12}(ClO_4)_2]^{8+}$ cation, crystallizing in the orthorhombic space group *Pmcb* with $a = 12.323(3)$ Å, $b = 17.119(4)$ Å, $c = 26.381(7)$ Å, and $Z = 2$; **2**·Sm is isomorphous with **2**·Gd, crystallizing in the orthorhombic space group *Pmcb*, with $a = 12.496(2)$ Å, $b = 17.378(3)$ Å, $c = 26.767(5)$ Å, and $Z = 2$. In both **2**·Gd and **2**·Sm, a pair of dinuclear subunits analogous to those in **1**·La are linked by a quadruple carboxylate bridge between the pair of Ln^{III} atoms into a tetranuclear cation, where the apical ligand of the square pyramid about each Cu^{II} atom is a perchlorate and each Ln^{III} atom is coordinated in a square antiprism by eight carboxy oxygen atoms. The magnetic behavior of these complexes obeys the Curie−Weiss law, showing very weak antiferromagnetic interaction in the solid. Therefore, it may be concluded that shielding of the 4f electrons by the outer shell electrons very effectively precludes significant coupling interactions between the lanthanoid 4f electrons and copper 3d electrons in a carboxylate-bridged system.

Introduction

In the course of our investigation of metal−betaine complexes,[1,2] we synthesized an interesting monomeric Cu^{II} tetracarboxylate, namely, $[Cu(betaine)_4](NO_3)_2$ (betaine = trimethylammonioacetate, $Me_3N^+CH_2CO_2^-$; designated as bet hereafter),[3] in which the four zwitterionic carboxylate ligands act in the unsymmetric chelate mode in coordination to the Cu^{II} center. We have also found that the stable $[Cu(bet)_4]^{2+}$ core can be used as a "metallo ligand" to bind other hard metal ions such as Ca^{II} and Li^I to form heterometallic complexes,[2] thus providing a new synthetic route for heterometallic complexes in metal carboxylate chemistry. To our knowledge, heterometallic compounds consolidated by carboxylate groups have not been well documented,[4,5] although several examples have been reported, including some heterometallic $Zn^{II}−M^{II}$ (M = Mn, Co, Ni, etc.) and $Cu^{II}−M^{II}$ (M = Li, Mg, Ca, or Rb) complexes.[6,7]

More importantly, because lanthanoid(III) ions (designated as Ln^{III} hereafter) are very similar to hard Ca^{II} ions in coordination chemistry, the above-mentioned synthetic route may be utilized in preparation of heterometallic $Cu^{II}−Ln^{III}$ compounds, which have commonly been synthesized with

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heterodonor ligands with each of two types of ligating atoms (such as N and O) coordinated to Cu and Ln atom, respectively,[8−10] and are currently of interest for several reasons. For example, these kinds of compounds provide models for investigations of the nature of magnetic exchange interactions between transition and rare-earth metal ions in bridging systems;[8,9] they are also possible precursors for the production of high-temperature superconductors.[10]

We have recently reported a series of polynuclear $Cu^{II}-Ln^{III}$ complexes containing derivatives of bet, including the octadecanuclear $Cu^{II}_{12}Ln^{III}_{6}$ clusters.[11,12] In this paper, we report the synthesis, structures, and magnetic properties of two types of tetranuclear carboxylate-bridged $Cu^{II}_{2}-Ln^{III}_{2}$ complexes, formulated as $[Cu_2Ln_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ (**1**; $Ln^{III} = La^{III}$, Ce^{III}, or Gd^{III}) and $[Cu_2Ln_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ (**2**; $Ln^{III} = Gd^{III}$ or Sm^{III}).

Experimental Section

All of the reagents were commercially available and used as received. C, H, and N microanalyses were carried out with a Perkin-Elmer 240Q elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000−400 cm^{-1} on a Nicolet 5DX spectrometer. The variable-temperature magnetic-susceptibility data were measured with a Quantum Design MPMS5 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants.[13] **Safety Notes.** *Metal perchlorate containing organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.*

Preparation. **$[Cu_2La_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ (1·La).** A mixture of bet (4.0 mmol) and $Cu(NO_3)_2$ (1.0 mmol) was dissolved in distilled water (5 mL) and heated at 60 °C for 10 min; $La(NO_3)_3$ (1.0 mmol) was then added, after the solution was stirred for 10 min, an aqueous solution (2 mL) of $NaClO_4$ (5 mmol) was added. The resulting deep blue solution was allowed to stand in air at room temperature for about 1 week, yielding beautiful deep blue polyhedral crystals (ca. 80% yield). Anal. Calcd for $C_{50}H_{130}Cl_{10}Cu_2La_2N_{10}O_{70}$: C, 21.82; H, 4.76; N, 5.09. Found: C, 21.83; H, 4.74; N, 4.92. IR data (ν/cm^{-1}): 3437 s br, 3057 w, 3015 w, 2966 w, 2931 w, 1665 s, 1616 vs, 1482 m, 1433 s, 1405 s, 1342 m, 1236 w, 1145 vs, 1117 vs, 1082 vs, 990 w, 962 w, 927 m, 906 m, 730 w, 632 s, 547 w.

$[Cu_2Ce_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ (1·Ce). It was prepared as for **1**·La. Anal. Calcd for $C_{50}H_{130}Cl_{10}Cu_2Ce_2N_{10}O_{70}$: C, 21.81; H, 4.76; N, 5.09. Found: C, 22.04; H, 4.76; N, 4.95. IR data (ν/cm^{-1}): 3451 s br, 3050 w, 3015 w, 2966 w, 1693 s, 1623 vs, 1482 s, 1433 s, 1412 s, 1349 m, 1236 w, 1145 vs, 1117 vs, 1082 vs, 990 w, 962 w, 927 m, 906 m, 730 w, 625 s, 547 w.

$[Cu_2Gd_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ (1·Gd). It was prepared as for **1**·La. Anal. Calcd for $C_{50}H_{130}Cl_{10}Cu_2Gd_2N_{10}O_{70}$: C, 21.54; H, 4.70; N, 5.03. Found: C, 21.69; H, 4.56; N, 5.22. IR data (ν/cm^{-1}): 3451 s br, 3050 w, 3015 w, 2966 w, 1679 s, 1619 vs, 1482 m, 1431 s, 1409 s, 1345 m, 1235 w, 1146 vs, 1117 vs, 1080 vs, 990 w, 962 w, 927 m, 906 m, 730 w, 628 s, 549 w.

$[Cu_2Gd_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ (2·Gd). A mixture of bet (6.0 mmol) and $Cu(NO_3)_2$ (1.0 mmol) was dissolved in distilled water (3 mL) and heated at 60 °C for 10 min; $Gd(NO_3)_3$ (2.0 mmol) was then added, after the solution was stirred for 10 min, an aqueous solution (2 mL) of $NaClO_4$ (10 mmol) was added. The resulting deep blue solution was adjusted to pH $\approx$ 3.5, filtered, and allowed to stand in air at room temperature for about 1 week, yielding beautiful deep blue prismatic crystals (ca. 60% yield). Anal. Calcd for $C_{60}H_{132}Cl_{10}Cu_2Gd_2N_{12}O_{64}$: C, 25.36; H, 4.68; N, 5.92. Found: C, 25.24; H, 4.54; N, 5.85. IR data (ν/cm^{-1}): 3416 w, 3057 w, 3015 w, 2966 w, 1714 m 1651 vs, 1489 m, 1440 s, 1405 s, 1349 m, 1236 w, 1145 vs, 1117 vs, 1082 vs, 990 w, 962 w, 927 m, 906 m, 737 w, 625 s, 547 w, 470 w.

$[Cu_2Sm_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ (2·Sm). It was prepared as for **2**·Gd. Anal. Calcd for $C_{60}H_{132}Cl_{10}Cu_2Sm_2N_{12}O_{64}$: C, 25.48; H, 4.71; N, 5.94. Found: C, 25.40; H, 4.51; N, 6.08. IR data (ν/cm^{-1}): 3416 w, 3057 w, 3015 w, 2966 w, 1712 m, 1653 vs, 1490 m, 1440 s, 1405 s, 1350 m, 1236 w, 1147 vs, 1118 vs, 1085 vs, 990 w, 960 w, 925 m, 905 m, 737 w, 625 s, 546 w, 472 w.

X-ray Crystallography. A summary of selected crystallographic data for **1**·La, **1**·Ce, **2**·Gd, and **2**·Sm is given in Table 1. The data collections were carried out on a Siemens R3m diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at 294 K.

For each complex, determinations of the crystal class, orientation matrix, and cell dimensions were performed according to the established procedures. The intensity data were collected using the ω-scan mode. Two standard reflections were monitored after every 120 data measurements, showing only small random variations (<1.5%). Absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles.[14]

Most of the non-hydrogen atoms in each crystal structure were located with the direct methods, and subsequent Fourier syntheses were used to derive the remaining non-hydrogen atoms.[15] Although two space groups *P2cb* and *Pmcb* are possible for both crystals **2**·Gd and **2**·Sm, refinements of the structures confirmed the latter space group for the crystals. All of the non-hydrogen atoms were refined anisotropically; the 2-fold-disordered bet ligands (required by the crystallographic symmetry) bridging the pair of Ln^{III} atoms in **2**·Gd and **2**·Sm and the 2-fold-disordered oxygen atoms of the perchlorate anions in the four complexes were subjected to geometric restraints. Hydrogen atoms of water molecules were located from the difference maps; hydrogen atoms of the bet ligands were generated geometrically (C−H = 0.96 Å), assigned isotropic thermal parameters, and found to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the final stage of full-matrix least-squares

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Table 1. Crystallographic Data[a]

formula	$C_{50}H_{130}Cl_{10}Cu_2La_2N_{10}O_{70}$	$C_{50}H_{130}Cl_{10}Cu_2Ce_2N_{10}O_{70}$	$C_{60}H_{132}Cl_{10}Cu_2Gd_2N_{12}O_{64}$	$C_{60}H_{132}Cl_{10}Cu_2Sm_2N_{12}O_{64}$
fw	2751.04	2753.46	2841.86	2828.09
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*Pmcb* (No. 55)	*Pmcb* (No. 55)
a (Å)	12.778(4)	12.730(2)	12.323(3)	12.496(2)
b (Å)	15.553(5)	15.489(2)	17.119(4)	17.378(3)
c (Å)	16.041(5)	15.987(3)	26.381(7)	26.767(5)
α (deg)	110.18(2)	110.28(1)	90	90
β (deg)	100.72(2)	100.70(1)	90	90
γ (deg)	105.03(2)	105.00(1)	90	90
U ($Å^3$)	2753.2(15)	2721.0(8)	5565(2)	5813(2)
Z	1	1	2	2
ρ(calc) (g/cm^3)	1.659	1.680	1.696	1.616
T (K)	295	295	295	295
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα) (cm^{-1})	14.9	15.6	18.98	16.87
R_1 [$I > 2\sigma(I)$]	0.0439	0.0365	0.0721	0.0730
wR_2 (all data)	0.1101	0.0900	0.1933	0.1971

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + \{0.1[\max(0,F_o^2) + 2F_c^2]/3\}^2]^{-1}$.

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

	1·La	**1**·Ce		**1**·La	**1**·Ce
Ln(1)−O(51)	2.473(3)	2.443(3)	Ln(1)−O(12)	2.492(4)	2.467(3)
Ln(1)−O(32)	2.509(4)	2.483(3)	Ln(1)−O(52a)	2.536(3)	2.514(3)
Ln(1)−O(22)	2.554(4)	2.527(3)	Ln(1)−O(3w)	2.566(4)	2.533(3)
Ln(1)−O(2w)	2.597(4)	2.565(3)	Ln(1)−O(4w)	2.606(4)	2.579(3)
Ln(1)−O(42)	2.683(4)	2.672(3)	Cu(1)−O(21)	1.941(4)	1.929(3)
Cu(1)−O(41)	1.937(4)	1.934(3)	Cu(1)−O(31)	1.971(4)	1.967(3)
Cu(1)−O(11)	1.983(4)	1.977(3)	Cu(1)−O(1w)	2.245(4)	2.238(3)
O(52)−Ln(1a)	2.536(3)	2.514(3)			
O(51)−Ln(1)−O(12)	136.02(13)	136.01(11)	O(51)−Ln(1)−O(32)	71.66(12)	71.93(10)
O(12)−Ln(1)−O(32)	107.98(13)	108.69(11)	O(51)−Ln(1)−O(52a)	81.26(12)	80.97(10)
O(12)−Ln(1)−O(52a)	75.11(13)	74.84(10)	O(32)−Ln(1)−O(52a)	143.30(12)	143.61(10)
O(51)−Ln(1)−O(22)	69.32(13)	69.42(11)	O(12)−Ln(1)−O(22)	68.59(14)	68.70(11)
O(32)−Ln(1)−O(22)	74.19(13)	74.55(11)	O(52a)−Ln(1)−O(22)	73.31(12)	73.41(10)
O(51)−Ln(1)−O(3w)	92.09(14)	91.97(12)	O(12)−Ln(1)−O(3w)	130.92(15)	131.16(12)
O(32)−Ln(1)−O(3w)	73.49(14)	72.81(11)	O(52a)−Ln(1)−O(3w)	133.03(12)	133.13(10)
O(22)−Ln(1)−O(3w)	146.47(14)	146.16(12)	O(51)−Ln(1)−O(2w)	139.19(12)	138.70(10)
O(12)−Ln(1)−O(2w)	69.05(13)	69.05(11)	O(32)−Ln(1)−O(2w)	140.10(13)	139.92(11)
O(52a)−Ln(1)−O(2w)	76.07(12)	76.06(10)	O(22)−Ln(1)−O(2w)	132.54(13)	132.75(11)
O(3w)−Ln(1)−O(2w)	79.73(14)	79.85(12)	O(51)−Ln(1)−O(4w)	68.55(13)	68.52(11)
O(12)−Ln(1)−O(4w)	132.74(14)	132.30(12)	O(32)−Ln(1)−O(4w)	119.04(13)	118.74(11)
O(52a)−Ln(1)−O(4w)	70.39(12)	70.41(10)	O(22)−Ln(1)−O(4w)	127.34(13)	127.58(11)
O(3w)−Ln(1)−O(4w)	64.03(13)	64.01(11)	O(2w)−Ln(1)−O(4w)	72.01(13)	71.59(11)
O(51)−Ln(1)−O(42)	139.36(12)	139.81(10)	O(12)−Ln(1)−O(42)	67.43(13)	67.74(11)
O(32)−Ln(1)−O(42)	68.81(12)	68.99(10)	O(52a)−Ln(1)−O(42)	138.30(12)	138.26(10)
O(22)−Ln(1)−O(42)	107.69(12)	107.95(10)	O(3w)−Ln(1)−O(42)	68.12(13)	67.97(11)
O(2w)−Ln(1)−O(42)	74.03(12)	73.88(10)	O(4w)−Ln(1)−O(42)	124.82(12)	124.34(10)
O(41)−Cu(1)−O(21)	176.73(15)	176.60(13)	O(21)−Cu(1)−O(31)	89.06(18)	89.15(15)
O(41)−Cu(1)−O(31)	91.42(17)	91.23(14)	O(21)−Cu(1)−O(11)	88.75(18)	88.91(15)
O(41)−Cu(1)−O(11)	90.41(18)	90.32(15)	O(31)−Cu(1)−O(11)	173.23(15)	173.12(13)
O(21)−Cu(1)−O(1w)	88.30(17)	88.45(14)	O(41)−Cu(1)−O(1w)	94.94(17)	94.94(14)
O(31)−Cu(1)−O(1w)	88.76(17)	88.88(14)	O(11)−Cu(1)−O(1w)	97.57(17)	97.66(15)

[a] Symmetric code: (a) −*x*, −*y*, −*z*.

refinement based on F^2 using the SHELXL-97 program package.[16] Analytical expressions of the neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[17] Selected bond lengths and bond angles are listed in Tables 2 and 3. Additional crystallographic data are available as Supporting Information.

Results and Discussion

Crystal Structures. $[Cu_2La_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ (1·La). The crystal structure of **1**·La consists of a centrosymmetric tetranuclear $[Cu_2La_2(bet)_{10}(H_2O)_8]^{10+}$ cation, perchlorate anions, and lattice water molecules. An ORTEP view of the tetranuclear cation in **1**·La is shown in Figure 1. The Cu^{II} atom is coordinated by four carboxy oxygen atoms at the basal plane [Cu(1)−O = 1.937(4)−1.983(4) Å] and completed by an aqua ligand at the apical position [Cu(1)−O(1w) = 2.245(4) Å] to form a square-pyramidal geometry. The Cu^{II} atom is quadruply bridged to the La^{III} atom by the μ_2-carboxylate groups of bet ligands, giving rise a dinuclear subunit with the $Cu^{II}\cdots La^{III}$ distance of 3.803(1) Å. This dinuclear structure is similar to that found for the neutral pentanuclear $Cu^{II}_3Ln^{II}_2$ chloroacetate[5] and somewhat similar to those of the well-known $[Cu_2(\mu_2\text{-carboxylate})_4]$ complexes.[18] A pair of the centrosymmetrically

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(17) *International Tables for X-ray Crystallography*; Kluwer Academic Publisher: Dordrecht, Holland, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(18) Chen, X.-M.; Mak, T. C. W. *Struct. Chem.* **1993**, *4*, 247, Chen, X.-M.; Feng, X.-L.; Xu, Z.-T.; Zhang, X.-H.; Xue, F.; Mak, T. C. W. *Polyhedron* **1998**, in press and references therein.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**[a]

	2·Gd	**2**·Sm		**2**·Gd	**2**·Sm
Ln(1)−O(31)	2.315(5)	2.381(5)	Ln(1)−O(12)	2.368(5)	2.415(4)
Ln(1)−O(22)	2.376(4)	2.430(4)	Ln(1)−O(41)	2.417(7)	2.471(7)
O(32)−Ln(1a)	2.402(6)	2.468(5)	O(42)−Ln(1a)	2.363(6)	2.422(6)
Cu(1)−O(11)	1.919(4)	1.943(4)	Cu(1)−O(21)	1.919(4)	1.956(4)
Cu(1)−O(13)	2.342(5)	2.384(5)			
O(31)−Ln(1)−O(42a)	71.4(2)	70.9(2)	O(31)−Ln(1)−O(12b)	82.8(2)	82.6(2)
O(42a)−Ln(1)−O(12b)	71.7(2)	70.5(2)	O(31)−Ln(1)−O(12)	75.4(2)	75.4(2)
O(42a)−Ln(1)−O(12)	132.5(2)	131.4(2)	O(12b)−Ln(1)−O(12)	71.3(3)	71.3(3)
O(31)−Ln(1)−O(22b)	149.0(2)	148.9(2)	O(42a)−Ln(1)−O(22b)	83.1(2)	83.1(2)
O(12b)−Ln(1)−O(22b)	72.6(2)	72.6(2)	O(12)−Ln(1)−O(22b)	112.6(2)	112.5(1)
O(31)−Ln(1)−O(22)	136.9(2)	137.1(2)	O(42a)−Ln(1)−O(22)	150.9(2)	151.4(2)
O(12)−Ln(1)−O(22)	72.6(2)	72.6(2)	O(22b)−Ln(1)−O(22)	71.7(2)	71.5(2)
O(31)−Ln(1)−O(32a)	115.5(2)	116.0(2)	O(42a)−Ln(1)−O(32a)	70.8(2)	72.1(2)
O(12b)−Ln(1)−O(32a)	129.1(2)	128.8(2)	O(12)−Ln(1)−O(32a)	156.2(2)	156.2(2)
O(22b)−Ln(1)−O(32a)	69.8(2)	69.3(2)	O(22)−Ln(1)−O(32a)	86.6(2)	86.3(2)
O(31)−Ln(1)−O(41)	77.6(2)	77.0(2)	O(42a)−Ln(1)−O(41)	117.9(2)	119.0(2)
O(12b)−Ln(1)−O(41)	153.0(2)	152.1(2)	O(12)−Ln(1)−O(41)	85.9(2)	85.1(2)
O(22b)−Ln(1)−O(41)	131.4(2)	132.1(2)	O(22)−Ln(1)−O(41)	72.14(2)	72.5(2)
O(32a)−Ln(1)−O(41)	76.7(2)	77.9(2)	O(11)−Cu(1)−O(11b)	89.5(2)	89.4(2)
O(11)−Cu(1)−O(21b)	174.4(2)	174.6(2)	O(11)−Cu(1)−O(21)	90.7(2)	90.3(2)
O(21b)−Cu(1)−O(21)	88.6(3)	89.5(2)	O(11)−Cu(1)−O(13)	99.4(1)	99.02(1)
O(21)−Cu(1)−O(13)	86.0(1)	86.4(1)			

[a] Symmetric codes: (a) 1 − *x*, −*y*, −*z*; (b) 1 − *x*, *y*, *z*.

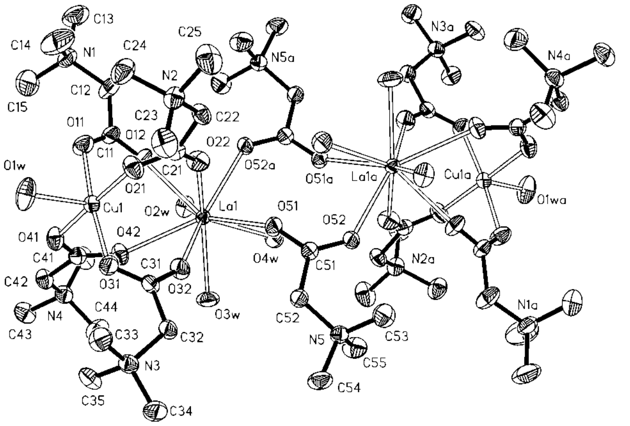

Figure 1. ORTEP drawing (at 35% probability level) of the tetranuclear cation in **1**·La. Symmetry code: (a) −*x*, −*y*, −*z*.

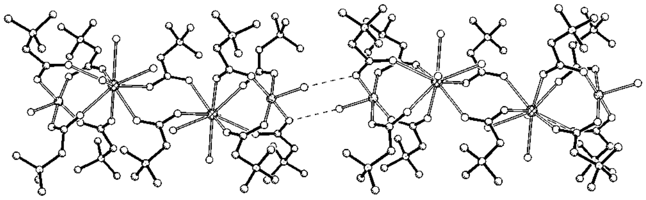

Figure 2. Intermolecular hydrogen bonding between the tetranuclear cations in **1**·La.

related La^{III} atoms in the adjacent dinuclear Cu^{II}La^{III} subunits are linked together by a pair of μ_2-carboxylate groups of bet ligands with an intramolecular La^{III}···La^{III} separation of 5.684(1) Å, resulting in the formation of a tetranuclear cation. Except for the six carboxy oxygen atoms [La−O = 2.473(4)−2.683(4) Å], the coordination sphere of each La^{III} ion is completed by three aqua ligands [La−O = 2.566(4)−2.606(4) Å] to form a nine coordination. The coordination polyhedron about the La^{III} ion can best be described as a distorted monocapped square antiprism; one square face consists of two carboxy oxygen atoms [O(51) and O(52a)] and two aqua oxygen atoms [O(2w) and O(3w)] whereas the other face is defined by four carboxy oxygen atoms [O(12), O(22), O(32), and O(42)] from the quadruple μ_2-carboxylate bridge between the pair of Cu^{II} and Gd^{III} atoms. The dihedral angle between the square faces is ca. 4.0°.

Hydrogen bonding plays an important role in consolidating the crystal structure. All of the water molecules participate in hydrogen bonding with carboxy oxygen atoms, other water molecules, or perchlorate oxygen atoms. It is noteworthy that, as illustrated in Figure 2, each pair of adjacent tetranuclear cations is linked through two hydrogen bonds between the apical aqua ligands of the Cu^{II} ions and the carboxy oxygen atoms bound to the Cu^{II} ions [O(1w)···O(41b) = 2.889(5) Å], resulting in a one-dimensional chain structure with an intermolecular Cu···Cu distance of 5.576(1) Å in the solid. It is also interesting that one of the aqua ligands coordinated to the La^{III} ion forms intramolecular hydrogen bonds with one carboxy oxygen atom of the bet ligand bridging the pair of La^{III} ions [O(4w)···O(51a) = 2.808(5) Å], which is similar to those found for the dinuclear complex [CuLa(pyb)$_5$(H$_2$O)$_5$](ClO$_4$)$_5$·2H$_2$O (pyb = pyridinioacetate)[12] and the monomeric complexes [Ln(bet)$_2$(NO$_3$)$_3$(H$_2$O)$_2$] (Ln = La or Sm),[19] although in the latter, carboxylate groups act in the monodentate coordination mode.

[Cu$_2$Ce$_2$(bet)$_{10}$(H$_2$O)$_8$](ClO$_4$)$_{10}$·2H$_2$O (1·Ce). The crystal structure of **1**·Ce is isomorphous to that of **1**·La; only very small metric differences have been observed for the two complexes. Because the radius of a Ce^{III} ion is slightly smaller than that of a La^{III} ion,[20] all of the metal−ligand bonds in **1**·Ce are slightly shorter than the corresponding bonds in **1**·La, as compared in Table 3; however, the bond angles in both **1**·La and **1**·Ce are almost the same.

[Cu$_2$Gd$_2$(bet)$_{10}$(H$_2$O)$_8$](ClO$_4$)$_{10}$·2H$_2$O (1·Gd). Although we have not characterized the crystal structure for **1**·Gd, the elemental analytical data and IR spectra confirmed that it has the same empirical formula as **1**·La and **1**·Ce. Hence, we can reasonably assume that **1**·Gd has the same tetranuclear structure as **1**·La.

[Cu$_2$Gd$_2$(bet)$_{12}$(ClO$_4$)$_2$](ClO$_4$)$_8$ (2·Gd). The crystal structure of **2**·Gd consists of a centrosymmetric tetranuclear [Cu$_2$Gd$_2$-

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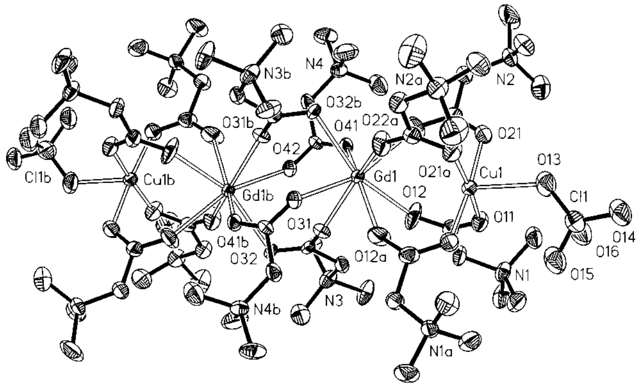

Figure 3. ORTEP drawing (at 35% probability level) of the tetranuclear cation in **2**·Gd. Symmetry codes: (a) 1 − *x*, −*y*, −*z*; (b) 1 − *x*, *y*, *z*.

$(bet)_{12}(ClO_4)_2]^{8+}$ cation (Figure 3) and perchlorate anions. In each tetranuclear cation, each pair of Cu^{II} and Gd^{III} atoms is bridged by four μ_2-carboxylate groups of the bet ligands to form a dinuclear subunit similar to those found for **1**·La and **1**·Ce, and the $Cu^{II}\cdots Gd^{III}$ separation in the subunit is 3.595(1) Å. The Cu^{II} atom is also coordinated in a square-pyramidal geometry with four carboxy oxygen atoms at the basal plane [Cu−O = 1.919(4) Å] and a perchlorate oxygen atom at the apical position [Cu(1)−O(13) = 2.342(5) Å]; in contrast, the apical position is occupied by an aqua ligand in **1**·La and **1**·Ce. The weaker ligation ability of the perchlorate anion at the apical position of the Cu^{II} atom, as compared to that of a water molecule, results in the significantly shorter basal Cu−O bond lengths; similar phenomenon has been observed for a number of $[Cu_2(\mu_2\text{-carboxylate})_4]$ complexes.[18] A pair of the dinuclear subunits are connected by a quadruple μ_2-carboxylate bridge into a tetranuclear structure, giving rise for a quadruple μ_2-carboxylate-bridged dinuclear Gd^{III}_2 core with the an intramolecular $Gd^{III}\cdots Gd^{III}$ separation of 4.542(1) Å. Similar quadruply μ_2-carboxylate-bridged dinuclear structures are well-known in homonuclear lanthanoid(III) carboxylates.[21,22] The quadruple μ_2-carboxylate bridge between the two Gd^{III} atoms not only brings the pair of Gd^{III} atoms much closer but also constructs a new tetranuclear cation different from those of the doubly μ_2-carboxylate-bridged tetranuclear cation in both **1**·La and **1**·Ce. Moreover, this result is consistent with the suggestion that in the $(\mu_2\text{-carboxylate})_n$-bridged systems the intramolecular metal−metal separation can be controlled by the number of carboxylate bridges.[1a] In **2**·Gd, each Gd^{III} atom is coordinated by eight carboxy oxygen atoms of the two quadruple μ_2-carboxylate bridges, resulting in a square antiprism with Gd−O bond distances from 2.315(5) to 2.417(7) Å, where one of the square faces consists of four carboxy oxygen atoms [O(12), O(22), O(32), and O(42)] from the quadruple μ_2-carboxylate bridge between the Cu^{II} and Gd^{III} atoms and the other square face is defined by four carboxy oxygen atoms [O(31), O(41), O(32b), and O(42b)] from the quadruple μ_2-carboxylate bridge between the pair of Gd^{III} atoms. The coordination geometry about the Gd^{III} atom is thus different from the distorted monocapped square-antiprism geometry in both **1**·La and **1**·Ce.

$[Cu_2Sm_2(bet)_{12}(ClO_4)_2](ClO_4)_8$ (2·Sm). The crystal structure of **2**·Sm is isomorphous to that of **2**·Gd, and because the radius of a Sm^{III} ion is slightly larger than that of a Gd^{III} ion,[20] all of the metal−ligand bonds in **2**·Sm are slightly longer (by 0.05 Å) than the corresponding bonds of **2**·Gd; however, the bond angles in both complexes **2**·Gd and **2**·Sm are very similar.

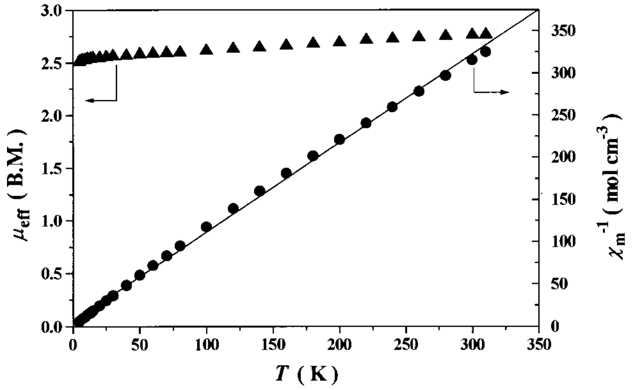

Figure 4. Plots of χ_m^{-1} (●) and molar magnetic moment (▲) vs temperature for **1**·La.

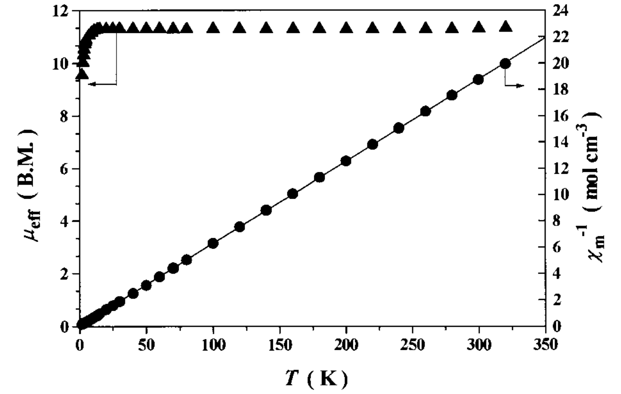

Figure 5. Plots of χ_m^{-1} (●) and molar magnetic moment (▲) vs temperature for **1**·Gd.

Magnetic Properties. The magnetic-susceptibility data were collected as polycrystalline samples in an external field of 10.0 kG. The magnetic data of **1**·La is represented in the form of χ_M^{-1} and effective magnetic moment (μ_{eff}) versus temperature (*T*) plots in Figure 4. The μ_{eff} of this complex at room temperature ($2.77\mu_B$) is only slightly smaller than the spin-only value ($2.83\mu_B$) of a dinuclear Cu^{II}_2 compound, and the magnetic moment decreases slightly with decreases in temperature. The observed susceptibility data were well-fitted to the Curie−Weiss law ($\chi_M = C/(T - \theta)$) with $C = 0.946$ K cm^3 mol^{-1} and $\theta = -5.29$ K, indicating very weak antiferromagnetic interaction. Because the La^{III} ion has no unpaired f electron and the intramolecular Cu···Cu distance [12.127(1) Å] is much longer than the intermolecular Cu···Cu distance, the weak magnetic interaction can reasonably be attributed to the intermolecular coupling between the Cu^{II} ions through the hydrogen bonding mentioned above (Figure 2). The magnetic data of **1**·Gd is depicted in Figure 5. The μ_{eff} of **1**·Gd at room temperature ($11.33\mu_B$) is also very slightly smaller than the spin-only value ($11.49\mu_B$), and it decreases slightly with decreases in temperature down to $11.23\mu_B$ at 11 K; afrer this, it decreases more significantly and reaches 9.55 at 2 K. The observed susceptibility data also obeys the Curie−Weiss law with $C = 16.00$ K cm^3 mol^{-1} and $\theta = -0.388$ K, thus showing very weak antiferromagnetic interaction. The magnetic behavior of **2**·Gd is virtually identical to that of **1**·Gd. The μ_{eff} of **2**·Gd at room temperature is $11.24\mu_B$, which decreases slightly with decreases in temperature down to $11.23\mu_B$ at 11 K; after this, it decreases more significantly and reaches 9.54 at 2 K. In contrast, very strong magnetic coupling is commonly observed for the $[Cu_2$-

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(μ_2-carboxylate)$_4$] complexes.[4,18] The magnetic behavior of the current carboxylate-bridged tetranuclear complexes and other results[5b,11a,22−24] demonstrate clearly that because of the effective shielding of the lanthanoid 4f electrons by the outer shell electrons, the coupling interaction between the lanthanoid 4f electrons and the copper 3d electrons should be very weak in a carboxylate-bridged system.

Conclusion

Two types of carboxylate-bridged tetranuclear $Cu^{II}_2Ln^{III}_2$ complexes have been synthesized with a minor change in the reaction condition using betaine and metal salts. Magnetic studies exhibit that shielding of the lanthanoid 4f electrons by the outer shell electrons very effectively precludes significant coupling interactions between the lanthanoid 4f electrons and the copper 3d electrons in a carboxylate-bridged system.

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Supporting Information Available: X-ray crystallographic data for **1**·La, **1**·Ce, **2**·Gd, and **2**·Sm (35 pages). Ordering information is given on any current masthead page.

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