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Two New Octadecanuclear Copper(II)–Lanthanide(III) Clusters Encapsulating μ_9-NO_3^- Anions. Synthesis, Structures, and Magnetic Properties of $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(C_5H_5NCH_2CO_2)_{12}(H_2O)_{18}(\mu_9\text{-}NO_3)](PF_6)_{10}(NO_3)_7 \cdot 12H_2O$ (Ln^{III} = Sm^{III} or Gd^{III})

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Two new octadecanuclear clusters $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(C_5H_5NCH_2CO_2)_{12}(H_2O)_{18}(\mu_9\text{-}NO_3)](PF_6)_{10}(NO_3)_7 \cdot 12H_2O$ [Ln^{III} = Sm^{III} (1) or Gd^{III} (2)] have been synthesized and characterized by X-ray diffraction. They are isomorphous and crystallize in the triclinic space group $P\bar{1}$ with $Z = 1$. The cell dimensions of 1 are $a = 17.366(1)$, $b = 17.790(1)$, and $c = 19.002(1)$ Å, $\alpha = 117.279(1)$, $\beta = 91.763(1)$, and $\gamma = 111.585(1)^\circ$. In the cluster, 6 Sm^{III} atoms are positioned at the vertices of an octahedron, while 12 Cu^{II} atoms are at the midpoints of the edges of the octahedron. The Cu^{II}–Sm^{III} metal framework is interconnected by the 24 similar μ_3-OH^- groups, each bridging one Sm^{III} and two Cu^{II} atoms. The octahedral cage encapsulates an unusual μ_9-NO_3^- anion with each oxygen atom coordinated to three Cu^{II} atoms. The 12 carboxylate ligands act as μ_2-carboxylate-O,O′ bridges, each linking a Sm^{III} and a Cu^{II} atom. The PF_6^- counteranion plays an important role in crystallization of the two complexes. © 2001 Academic Press

Key Words: **lanthanide; copper; cluster; heteronuclear complex; crystal structure.**

INTRODUCTION

A number of 3*d*, 4*f* heterometallic complexes have been studied for both magnetic and chemical interests (1–4). These compounds are important not only in coordination chemistry but also in understanding the nature of the magnetic exchange interactions between copper(II) and lanthanide(III) (designated as Ln^{III} hereafter) (3), which are potential magnetic materials (1–4). Inclusions of guest molecules into host structures have attracted great interest over the past two decades (5) and supramolecular chemistry of cationic or neutral guests has been widely studied (6). On the other hand, the supramolecular chemistry of small anions has received less attention (7), although recently a number of polynuclear metal complexes have been reported to serve as hosts for recognition of small molecules or ions (8–10).

During the past 10 years, we have taken advantage of the neutral carboxylate ligand betaine and its derivatives in charge compensation to assemble monomeric copper(II) tetracarboxylates, heterometallic Cu^{II}–Ca^{II} and Cu^{II}–Li^{I} complexes (11), and heterometallic $Cu^{II}Ln^{III}$ complexes including dinuclear Cu*Ln*, tetranuclear Cu_2Ln_2, pentanuclear Cu_3Ln_2, and several octadecanuclear $Cu_{12}Ln_6$ complexes (12–14). It is very interesting that a μ_{12}-ClO_4^- anion is encapsulated by the octadecanuclear cage, and the coordination mode of the perchlorate is so far unprecedented in other polynuclear complexes. This very interesting supramolecular phenomenon stimulated us to continue an investigation to understand how these high polynuclear complexes form and what role the ClO_4^- anion may play in the formation of the complexes. By introducing PF_6^- anions into the reaction system, we succeeded in isolation of some analogous $Cu_{12}Ln_6$ clusters, each of which encapsulates a μ_9-nitrate anion in the octadecanuclear cage. Herein we report the preparation and crystal structures of two new complexes, namely $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(C_5H_5NCH_2CO_2)_{12}(H_2O)_{18}(\mu_9\text{-}NO_3)](PF_6)_{10}(NO_3)_7 \cdot 12H_2O$ [*Ln* = Sm (**1**) or Gd (**2**)] ($C_5H_5NCH_2CO_2$, pyridinioacetate, designated as pyb). The magnetic susceptibility of **2** has also been measured. The results show that not the kind of the encapsulated anion but the counteranion plays an important role in the crystallization.

EXPERIMENTAL

Pyridinioacetate was synthesized by the literature method (15). KPF_6 was purchased from Fluka; the lanthan-

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ide(III) nitrates were converted from their oxides by nitric acid. The other reagents were commercially available and used as received. The C, H, and N microanalyses were carried out with an Elementar Vario EL analyzer. The copper and lanthanide analyses were carried out with an IRIS Advantage ICP-AES (TJA, USA). FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet 5DX spectrometer.

Caution. Metal perchlorate containing organic ligands is potentially explosive. Only a small amount of material should be prepared and handled with great care.

Preparation

$[Cu_{12}Sm_6(\mu_3\text{-}OH)_{24}(pyb)_{12}(H_2O)_{18}(\mu_9\text{-}NO_3)]$ $(PF_6)_{10}(NO_3)_7\cdot 12H_2O$ (**1**). A mixture of pyb (0.42 g, 3 mmol) and $Cu(NO_3)_2\cdot 6H_2O$ (0.12 g, 0.5 mmol) was dissolved in distilled water (6 cm^3) and heated at 50°C for 10 min. An aqueous solution (2 cm^3) of $Sm(NO_3)_3$ (1 mmol) was then added, followed by KPF_6 (0.184 g, 1 mmol) with stirring for 20 min. The pH value of the resulting deep blue solution was adjusted to ~5.4 by very slow addition of dilute aqueous KOH solution, and then the solution was filtered. The filtrate was allowed to evaporate slowly at room temperature. After about 5 days gray-blue polyhedral crystals began to appear, and the product was collected within 2 weeks (ca. 25% yield). Anal. Calcd for $C_{84}H_{168}Cu_{12}F_{60}N_{20}O_{102}P_{10}Sm_6$: C, 16.26; H, 2,73; N, 4.52; Cu, 12.29; Sm, 14.54%. Found: C, 16.38; H, 2.47; N, 4.55; Cu, 12.5; Sm, 15.0%. IR data ($\tilde{\nu}/cm^{-1}$): 3571m, 3402s (br), 3100w, 1637vs, 1489m, 1391s, 1314m, 1222w, 1194w, 1039w, 842vs, 779w, 709m, 624w, 600w, 554m.

$[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}(pyb)_{12}(H_2O)_{18}(NO_3)](PF_6)_{10}(NO_3)_7\cdot 12H_2O$ (**2**). This complex was synthesized by the same procedure as for **1** with $Gd(NO_3)_3$ instead of $Sm(NO_3)_3$. The yield was *ca.* 20%. Anal. Calcd for $C_{84}H_{168}Cu_{12}F_{60}Gd_6N_{20}O_{102}P_{10}$: C, 16.15; H, 2.71; N, 4.49; Cu, 12.21; Gd, 15.11%. Found: C, 16.64; H, 2.35 N, 4.30; Cu, 12.4; Gd, 15.6%. IR data ($\tilde{\nu}/cm^{-1}$): 3564m, 3374v (br), 3100w, 1637vs, 1489m, 1391s, 1307m, 1222w, 1194w, 1032w, 842vs, 779w, 709m, 674w, 610w, 554m.

X-Ray Crystallography

Diffraction intensities for **1** and **2** were collected at 168 K and 298 K on a Bruker Smart 1000 CCD diffractometer employing graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å), respectively, and absorption corrections were applied (16).

The structures were solved with direct methods and refined with the full-matrix least-squares technique using SHELXS-97 and SHELXL-97 programs, respectively (17, 18). Most of the nonhydrogen atoms were refined anisotropically. The disordered anions were subjected to geometric restraints. The organic hydrogen atoms were generated geometrically. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated (19). A summary of selected crystallographic data for **1** and **2** is given in Table 1. Final atomic coordinates and equivalent isotropic temperature factors for **1** and **2** are listed in Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2** are given in Table 3. The drawings were produced with SHELXTL (20).

TABLE 1
Crystallographic Data and Structure Refinement for 1 and 2

	1	**2**
Empirical formula	$C_{84}H_{168}Cu_{12}F_{60}N_{20}O_{102}P_{10}Sm_6$	$C_{84}H_{168}Cu_{12}F_{60}Gd_6N_{20}O_{102}P_{10}$
Formula weight	6204.66	6246.06
Temperature (K)	168(2)	298(2)
Unit cell dimensions		
a (Å)	17.366(1)	17.468(3)
b (Å)	17.790(1)	17.723(4)
c (Å)	19.002(1)	19.076(4)
α (°)	117.279(1)	117.86(3)
β (°)	91.763(1)	91.61(3)
γ (°)	111.585(1)	111.46(3)
Volume (Å^3)	4708.3(6)	4715(2)
Density (calc.) (Mg/m^3)	2.188	2.200
F (000)	3038	3050
Reflections collected	60773	33,947
Independent reflections	19,129	26,082
Data/restraints/parameters	19,129/196/1243	26,082/196/1295
Goodness-of-fit on F^2	1.044	0.967
$R_1/wR_2(I > 2\sigma)$	0.0430/0.1123	0.0535/0.1382
R_1/wR_2 (all data)	0.0562/0.1220	0.0950/0.1615

Note. Details in common: crystal system triclinic; space group $P\bar{1}$; $Z = 1$.

RESULTS AND DISCUSSION

Crystal Structures

X-ray crystallography has established that crystals of **1** and **2** are isomorphous; each consists of a discrete octadecanuclear $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(pyb)_{12}(H_2O)_{18}(\mu_9\text{-}NO_3)]^{17+}$ cation, nitrate anions, hexafluorophosphate anions, and lattice water molecules. A perspective view of the cation in **1** is illustrated in Fig. 1, the skeleton of which is very similar to those documented for the perchlorate ones (13). The cation possesses a $[Cu_{12}Sm_6(\mu_3\text{-}OH)_{24}]^{18+}$ core of pseudocubic O_h symmetry with 6 Sm^{III} atoms positioned at the vertices of a regular octahedron and 12 Cu^{II} atoms located at the midpoints of the 12 octahedral edges, as shown in Fig. 2. The polyhedron formed by the 12 Cu^{II} ions may be described as a cuboctahedron that is capped on the

TABLE 2
Atomic Coordinates and Equivalent Isotropic Temperature Factors for 1 and 2

Atoms	x	y	z	U_{eq}[a]
		1		
Sm(1)	2584(1)	4953(1)	6347(1)	16(1)
Sm(2)	5350(1)	7998(1)	5210(1)	16(1)
Sm(3)	2947(1)	3224(1)	2275(1)	16(1)
Cu(1)	3627(1)	3518(1)	5566(1)	16(1)
Cu(2)	4813(1)	5885(1)	6989(1)	16(1)
Cu(3)	3997(1)	6407(1)	5710(1)	16(1)
Cu(4)	6181(1)	7324(1)	6402(1)	17(1)
Cu(5)	4230(1)	5565(1)	3734(1)	15(1)
Cu(6)	2827(1)	4085(1)	4310(1)	16(1)
O(11)	3813(2)	4664(3)	6582(2)	17(1)
O(12)	2684(3)	3677(3)	5113(2)	19(1)
O(13)	4002(2)	6280(3)	6676(2)	18(1)
O(14)	2898(2)	5288(3)	5220(2)	18(1)
O(21)	6453(3)	7529(3)	5476(2)	18(1)
O(22)	5376(2)	6598(3)	4010(2)	17(1)
O(23)	5137(2)	7442(3)	6179(2)	20(1)
O(24)	4064(2)	6497(3)	4722(2)	18(1)
O(31)	4155(2)	2970(3)	2731(2)	19(1)
O(32)	4392(2)	4569(3)	2791(2)	17(1)
O(33)	2837(3)	2918(3)	3443(2)	19(1)
O(34)	3124(2)	4577(3)	3573(2)	17(1)
O(1w)	1193(3)	4167(3)	5348(3)	30(1)
O(2w)	2378(3)	6362(3)	6724(3)	28(1)
O(3w)	1390(3)	4988(3)	7093(3)	28(1)
O(4w)	6548(3)	8586(3)	4614(3)	26(1)
O(5w)	4390(3)	7720(3)	4028(3)	27(1)
O(6w)	5445(3)	9547(3)	5341(3)	34(1)
O(7w)	2387(3)	1497(3)	1723(3)	31(1)
O(8w)	3691(3)	2839(3)	1128(3)	30(1)
O(9w)	1914(3)	2328(3)	936(3)	31(1)
O(10w)	15(3)	3358(4)	6017(4)	41(1)
O(11w)	− 93(9)	1518(8)	5207(6)	133(5)
O(12w)	2576(5)	835(4)	169(4)	64(2)
O(13w)	1889(6)	2445(6)	− 426(5)	79(2)
O(14w)	3298(5)	4093(8)	210(5)	106(4)
N(1)	5000	5000	5000	40(1)
O(1)	4528(6)	4533(6)	4306(4)	40(1)
O(2)	4830(6)	4785(7)	5526(5)	40(1)
O(3)	5685(5)	5680(6)	5160(6)	40(1)
O(1A)	2652(3)	2610(3)	5982(3)	27(1)
O(2A)	2033(3)	3594(3)	6528(3)	25(1)
C(1A)	2168(4)	2898(4)	6393(4)	22(1)
C(2A)	1701(5)	2319(5)	6778(5)	39(2)
N(1A)	1289(3)	2787(3)	7382(3)	31(1)
C(3A)	416(3)	2523(3)	7202(3)	46(2)
C(4A)	49(2)	2997(4)	7787(4)	56(2)
C(5A)	555(4)	3735(4)	8552(3)	50(2)
C(6A)	1428(3)	3999(4)	8732(2)	57(2)
C(7A)	1795(2)	3525(4)	8147(3)	50(2)
O(1B)	4508(3)	6448(3)	8284(3)	26(1)
O(2B)	3076(3)	5711(3)	7816(3)	25(1)
C(1B)	3759(4)	6264(4)	8370(4)	22(1)
C(2B)	3601(4)	6666(5)	9227(4)	32(2)
N(1B)	4387(2)	7399(3)	9833(2)	29(1)
C(3B)	4897(3)	7173(2)	10206(3)	39(2)
C(4B)	5684(3)	7860(3)	10734(3)	40(2)
C(5B)	5962(2)	8772(3)	10888(3)	40(2)
C(6B)	5452(3)	8998(2)	10515(3)	45(2)
C(7B)	4664(3)	8311(3)	9988(3)	38(2)
O(1C)	3389(3)	7451(3)	6181(3)	26(1)
O(2C)	4333(3)	8493(3)	5912(3)	24(1)
C(1C)	3780(4)	8253(4)	6271(4)	21(1)
C(2C)	3560(5)	9009(5)	6909(5)	36(2)
N(1C)	4120(2)	9945(2)	7069(3)	26(1)
C(3C)	3835(2)	10380(3)	6742(3)	37(2)
C(4C)	4374(3)	11270(3)	6899(3)	45(2)
C(5C)	5198(3)	11725(2)	7383(3)	39(2)
C(6C)	5482(2)	11291(3)	7711(3)	38(2)
C(7C)	4943(3)	10401(3)	7554(3)	35(2)
O(1D)	6889(3)	8956(3)	7267(3)	30(1)
O(2D)	6292(3)	9326(3)	6479(3)	24(1)
C(1D)	6799(4)	9513(4)	7080(4)	24(1)
C(2D)	7339(5)	10570(5)	7663(5)	42(2)
N(1D)	8120(2)	10734(3)	8122(2)	29(1)
C(3D)	8820(3)	10751(4)	7783(3)	49(2)
C(4D)	9556(3)	10870(5)	8215(4)	70(3)
C(5D)	9593(3)	10972(4)	8988(4)	60(3)
C(6D)	8894(3)	10955(4)	9328(3)	49(2)
C(7D)	8157(3)	10836(3)	8895(2)	35(2)
O(1E)	3672(3)	5896(3)	2880(3)	23(1)
O(2E)	2831(3)	4380(3)	1951(3)	23(1)
C(1E)	3053(4)	5249(4)	2277(4)	21(1)
C(2E)	2567(4)	5597(5)	1901(5)	36(2)
N(1E)	1671(2)	4934(3)	1525(3)	31(1)
C(3E)	1033(3)	5096(3)	1908(3)	45(2)
C(4E)	189(3)	4431(5)	1560(4)	58(2)
C(5E)	− 16(2)	3603(4)	829(4)	59(3)
C(6E)	622(3)	3441(3)	446(3)	61(3)
C(7E)	1465(3)	4106(3)	794(3)	44(2)
O(1F)	1378(3)	3523(4)	3750(3)	33(1)
O(2F)	1541(3)	2961(4)	2463(3)	35(1)
C(1F)	1120(4)	3154(6)	3000(5)	36(2)
C(2F)	201(5)	2926(9)	2642(4)	67(3)
N(1F)	− 309(3)	2949(4)	3234(3)	42(2)
C(3F)	− 628(3)	2172(3)	3332(3)	52(2)
C(4F)	− 1093(4)	2172(4)	3914(4)	57(2)
C(5F)	− 1240(3)	2950(4)	4398(3)	54(2)
C(6F)	− 922(4)	3727(4)	4300(3)	54(2)
C(7F)	− 456(3)	3727(3)	3718(4)	61(3)
P(10)	4389(1)	4080(1)	8393(1)	29(1)
F(11)	3591(3)	3244(3)	8356(3)	51(1)
F(12)	4281(4)	4789(3)	9230(3)	67(2)
F(13)	3765(3)	4263(4)	7914(3)	52(1)
F(14)	4490(4)	3384(3)	7538(3)	60(1)
F(15)	5016(3)	3902(4)	8852(3)	62(2)
F(16)	5184(3)	4934(3)	8431(3)	49(1)
P(20)	8051(1)	3353(1)	9349(1)	32(1)
F(21)	7283(3)	2445(3)	9252(3)	52(1)
F(22)	8300(3)	3754(3)	10302(2)	42(1)
F(23)	7427(3)	3862(4)	9499(3)	55(1)
F(24)	7778(4)	2951(4)	8399(3)	66(2)
F(25)	8672(3)	2849(3)	9201(3)	51(1)
F(26)	8808(3)	4267(3)	9451(4)	66(2)
P(30)	2343(1)	8229(1)	8707(1)	37(1)
F(31)	1735(5)	7141(4)	8157(4)	116(3)

TABLE 2—*Continued*

TABLE 2—*Continued*

Atoms	*x*	*y*	*z*	U_{eq}[a]
F(32)	2354(7)	8131(7)	9480(4)	141(4)
F(33)	1530(3)	8431(5)	8837(4)	87(2)
F(34)	2292(5)	8242(6)	7887(4)	111(3)
F(35)	3143(4)	8001(5)	8556(4)	93(2)
F(36)	2925(5)	9291(4)	9241(6)	155(5)
P(40)	7547(5)	1634(6)	5877(5)	40(1)
F(41)	6963(7)	1329(9)	6420(8)	74(2)
F(42)	7601(7)	2656(6)	6365(7)	74(2)
F(43)	6695(6)	1310(8)	5267(7)	74(2)
F(44)	7449(7)	586(6)	5396(8)	74(2)
F(45)	8372(6)	1937(8)	6498(7)	74(2)
F(46)	8094(7)	1885(8)	5307(7)	74(2)
P(40′)	7606(5)	1644(6)	5905(5)	40(1)
F(41′)	6868(8)	1529(10)	6383(9)	83(2)
F(42′)	7037(8)	1810(9)	5378(7)	83(2)
F(43′)	7161(8)	557(7)	5237(8)	83(2)
F(44′)	8131(8)	1424(9)	6418(7)	83(2)
F(45′)	8059(8)	2717(6)	6563(7)	83(2)
F(46′)	8341(7)	1787(9)	5449(9)	83(2)
P(50)	1743(6)	516(7)	7456(6)	79(1)
F(51)	2193(9)	− 111(10)	7437(10)	83(2)
F(52)	1449(8)	509(9)	8252(7)	83(2)
F(53)	2615(6)	1401(7)	8015(8)	83(2)
F(54)	2011(8)	531(9)	6672(7)	83(2)
F(55)	862(6)	− 339(7)	6919(8)	83(2)
F(56)	1342(10)	1222(9)	7595(9)	83(2)
P(50′)	1791(6)	581(7)	7504(4)	79(1)
F(51′)	2222(13)	− 92(13)	7366(14)	147(4)
F(52′)	2275(10)	1161(11)	8452(8)	147(4)
F(53′)	2569(9)	1204(12)	7315(13)	147(4)
F(54′)	1293(10)	18(11)	6584(8)	147(4)
F(55′)	1005(9)	− 31(12)	7706(13)	147(4)
F(56′)	1414(13)	1318(12)	7721(13)	147(4)
N(10)	1678(3)	5560(4)	3813(4)	29(1)
O(011)	1844(3)	5016(4)	3197(3)	40(1)
O(012)	2214(3)	6057(4)	4478(3)	42(1)
O(013)	975(3)	5595(4)	3738(3)	42(1)
N(20)	4507(5)	984(5)	1663(4)	42(2)
O(021)	5073(4)	1449(4)	2306(3)	49(1)
O(022)	4180(4)	1376(4)	1419(3)	51(2)
O(023)	4226(6)	123(5)	1281(4)	85(3)
O(15w)	3671(4)	1050(13)	2133(17)	132(7)
N(30)	1295(7)	1225(8)	4057(7)	69(2)
O(031)	1192(9)	1948(8)	4459(9)	69(2)
O(032)	771(8)	506(9)	4018(9)	69(2)
O(033)	1882(8)	1263(9)	3706(8)	69(2)
O(15′)	1315(15)	1744(13)	3851(18)	132(7)
N(30′)	1355(9)	235(9)	4289(9)	84(2)
O(31′)	610(9)	− 292(12)	3869(10)	84(2)
O(32′)	1922(10)	710(11)	4066(10)	84(2)
O(33′)	1420(10)	235(12)	4949(9)	84(2)
N(1′)	0	0	0	150(6)
O(1′)	570(12)	776(10)	324(16)	150(6)
O(2′)	− 610(12)	− 70(2)	386(14)	150(6)
O(3′)	− 148(18)	− 790(11)	− 585(10)	150(6)
		2		
Gd(1)	2600(1)	4907(1)	6327(1)	25(1)
Gd(2)	5293(1)	7990(1)	5242(1)	24(1)
Gd(3)	2982(1)	3200(1)	2275(1)	25(1)

TABLE 2—*Continued*

Atoms	*x*	*y*	*z*	U_{eq}[a]
Cu(1)	3680(1)	3513(1)	5542(1)	26(1)
Cu(2)	4802(1)	5872(1)	6966(1)	25(1)
Cu(3)	3875(1)	6361(1)	5700(1)	25(1)
Cu(4)	6110(1)	7308(1)	6406(1)	25(1)
Cu(5)	4210(1)	5552(1)	3764(1)	25(1)
Cu(6)	2863(1)	4062(1)	4310(1)	25(1)
O(11)	3840(3)	4652(3)	6555(3)	26(1)
O(12)	2741(3)	3658(3)	5105(3)	27(1)
O(13)	3975(3)	6242(3)	6664(3)	26(1)
O(14)	2886(3)	5239(3)	5210(3)	26(1)
O(21)	6375(3)	7518(3)	5500(3)	26(1)
O(22)	5339(3)	6595(3)	4038(3)	26(1)
O(23)	5078(3)	7428(3)	6187(3)	27(1)
O(24)	4032(3)	6487(3)	4734(3)	25(1)
O(31)	4194(3)	2972(3)	2728(3)	26(1)
O(32)	4395(3)	4568(3)	2833(3)	27(1)
O(33)	2910(3)	2913(3)	3437(3)	25(1)
O(34)	3128(3)	4544(3)	3577(3)	25(1)
O(1w)	1228(3)	4065(4)	5317(3)	44(1)
O(2w)	2352(4)	6287(4)	6685(4)	42(1)
O(3w)	1432(4)	4935(4)	7064(4)	46(1)
O(4w)	6488(4)	8616(4)	4693(4)	42(1)
O(5w)	4390(4)	7719(4)	4054(3)	42(1)
O(6w)	5377(4)	9514(4)	5362(4)	48(2)
O(7w)	2475(4)	1496(4)	1713(3)	45(2)
O(8w)	3722(4)	2897(5)	1148(3)	49(2)
O(9w)	1977(4)	2324(4)	935(3)	46(2)
O(10w)	− 15(5)	3350(6)	6008(6)	76(2)
O(11w)	− 198(9)	1497(9)	5169(8)	136(4)
O(12w)	2427(10)	686(11)	106(9)	156(5)
O(13w)	2050(3)	2440(3)	− 450(3)	470(2)
O(14w)	3279(13)	3696(14)	100(12)	205(7)
N(1)	5000	5000	5000	70(2)
O(1)	4518(8)	4295(8)	4329(6)	70(2)
O(2)	4776(9)	5024(10)	5591(6)	70(2)
O(3)	5625(6)	5539(8)	4983(9)	70(2)
O(1A)	2718(4)	2574(4)	5950(4)	43(1)
O(2A)	2085(4)	3547(4)	6484(3)	38(1)
C(1A)	2234(5)	2865(6)	6353(5)	37(2)
C(2A)	1775(7)	2275(8)	6731(7)	61(3)
N(1A)	1338(6)	2742(6)	7330(5)	51(2)
C(3A)	495(10)	245(1)	7138(8)	87(4)
C(4A)	102(9)	291(1)	773(1)	96(5)
C(5A)	617(1)	366(1)	8475(9)	86(4)
C(6A)	143(1)	392(1)	8621(9)	99(5)
C(7A)	1777(8)	3449(10)	8045(9)	82(4)
O(1B)	4502(4)	6419(4)	8260(3)	41(1)
O(2B)	3092(3)	5681(4)	7784(3)	38(1)
C(1B)	3761(5)	6215(6)	8339(5)	34(2)
C(2B)	3616(6)	6651(8)	9195(5)	53(2)
N(1B)	4401(5)	7397(5)	9812(4)	44(2)
C(3B)	4857(7)	7195(8)	10202(6)	57(3)
C(4B)	5634(8)	7855(9)	10722(6)	64(3)
C(5B)	5940(7)	8740(9)	10843(6)	67(3)
C(6B)	5459(8)	8967(8)	10440(7)	67(3)
C(7B)	4674(7)	8251(8)	9929(7)	60(3)
O(1C)	3342(4)	7431(4)	6171(4)	42(1)
O(2C)	4292(3)	8480(4)	5911(3)	35(1)
C(1C)	3726(5)	8237(5)	6285(5)	33(2)

TABLE 2—*Continued*

Atoms	*x*	*y*	*z*	U_{eq}[a]
C(2C)	3534(6)	8997(6)	6921(6)	51(2)
N(1C)	4086(5)	9951(5)	7086(4)	40(2)
C(3C)	3807(8)	10367(8)	6795(7)	64(3)
C(4C)	4334(9)	11268(8)	6936(8)	77(4)
C(5C)	5123(8)	11697(8)	7369(7)	65(3)
C(6C)	5404(7)	11250(8)	7667(7)	66(3)
C(7C)	4886(7)	10378(7)	7527(6)	54(2)
O(1D)	6804(4)	8950(4)	7285(3)	38(1)
O(2D)	6227(3)	9327(4)	6507(3)	36(1)
C(1D)	6734(5)	9514(5)	7108(5)	33(2)
C(2D)	7286(6)	10565(6)	7679(6)	56(3)
N(1D)	8085(5)	10716(5)	8119(5)	44(2)
C(3D)	8697(8)	10682(8)	7746(7)	71(3)
C(4D)	9422(9)	1073(1)	8098(1)	95(5)
C(5D)	9503(8)	10851(9)	8847(9)	78(4)
C(6D)	8881(8)	10909(8)	9244(8)	71(3)
C(7D)	8145(7)	10834(7)	8856(6)	54(2)
O(1E)	3649(4)	5865(4)	2896(3)	41(1)
O(2E)	2838(4)	4337(4)	1976(3)	37(1)
C(1E)	3056(5)	5202(6)	2292(5)	34(2)
C(2E)	2587(6)	5535(7)	1890(6)	56(3)
N(1E)	1685(5)	4836(6)	1487(5)	57(2)
C(3E)	1083(9)	502(1)	183(1)	90(4)
C(4E)	25(1)	437(2)	148(2)	128(8)
C(5E)	51(1)	3557(17)	780(18)	14(1)
C(6E)	70(1)	338(1)	41(1)	129(8)
C(7E)	1497(9)	4035(9)	799(8)	85(4)
O(1F)	1404(4)	3397(5)	3701(4)	47(2)
O(2F)	1584(4)	2869(5)	2429(4)	48(2)
C(1F)	1159(6)	3008(7)	2953(6)	47(2)
C(2F)	235(6)	2664(12)	2575(7)	98(6)
N(1F)	− 268(5)	2794(8)	3167(5)	61(2)
C(3F)	− 595(8)	2124(12)	3332(9)	88(4)
C(4F)	− 161(9)	2157(14)	3885(10)	100(5)
C(5F)	− 1171(9)	2924(14)	4316(9)	91(5)
C(6F)	− 847(9)	3677(13)	4203(9)	94(5)
C(7F)	− 360(8)	3584(12)	3569(10)	97(5)
P(10)	4441(2)	4105(2)	8386(2)	55(1)
F(11)	3671(5)	3235(5)	8314(6)	118(3)
F(12)	4327(7)	4788(6)	9213(5)	151(4)
F(13)	3804(5)	4266(6)	7918(5)	107(3)
F(14)	4534(6)	3413(6)	7521(4)	124(3)
F(15)	5082(5)	3931(6)	8811(6)	123(3)
F(16)	5194(4)	4969(5)	8425(5)	107(3)
P(20)	8045(2)	3390(2)	9354(2)	58(1)
F(21)	7289(4)	2494(4)	9273(5)	95(2)
F(22)	8302(5)	3786(5)	10299(3)	84(2)
F(23)	7448(5)	3919(6)	9534(4)	105(3)
F(24)	7745(6)	2978(6)	8408(3)	125(4)
F(25)	8627(5)	2851(6)	9173(5)	105(3)
F(26)	8786(5)	4294(5)	9452(6)	129(4)
P(30)	2312(2)	8180(2)	8678(2)	61(1)
F(31)	1764(8)	7081(5)	8190(7)	202(7)
F(32)	2440(9)	8204(11)	9493(5)	221(8)
F(33)	1502(5)	8351(8)	8826(6)	155(5)

TABLE 2—*Continued*

Atoms	*x*	*y*	*z*	U_{eq}[a]
F(34)	2181(7)	8099(8)	7823(5)	152(4)
F(35)	3117(5)	7989(9)	8502(6)	164(5)
F(36)	2855(7)	9258(5)	9112(9)	234(9)
P(40)	7535(7)	1583(7)	5840(6)	65(1)
F(41)	6965(10)	1280(11)	6384(9)	117(3)
F(42)	7625(11)	2625(8)	6410(9)	117(3)
F(43)	6689(9)	1349(12)	5284(9)	117(3)
F(44)	7380(10)	528(8)	5260(9)	117(3)
F(45)	8345(8)	1804(12)	6408(9)	117(3)
F(46)	8042(10)	1884(11)	5278(9)	117(3)
P(40′)	7540(7)	1613(7)	5860(7)	65(1)
F(41′)	6868(13)	1677(15)	6415(13)	184(5)
F(42′)	7385(13)	2316(14)	5721(15)	184(5)
F(43′)	6767(11)	814(13)	5095(11)	184(5)
F(44′)	7629(14)	838(14)	5992(15)	184(5)
F(45′)	827(1)	2438(13)	6640(10)	184(5)
F(46′)	820(1)	1585(16)	5322(13)	184(5)
P(50)	1740(8)	62(1)	7590(9)	167(4)
F(51)	216(2)	− 6(2)	756(2)	184(4)
F(52)	144(1)	59(2)	836(1)	184(4)
F(53)	260(1)	149(1)	815(14)	184(4)
F(54)	201(2)	61(2)	680(1)	184(4)
F(55)	86(1)	− 26(1)	704(1)	184(4)
F(56)	133(2)	129(1)	766(1)	184(4)
P(50′)	1810(7)	78(1)	784(1)	167(4)
F(51′)	218(1)	4(1)	765(2)	173(5)
F(52′)	230(1)	132(1)	8761(1)	173(5)
F(53′)	2601(9)	138(1)	764(2)	173(5)
F(54′)	134(1)	22(1)	690(10)	173(5)
F(55′)	986(9)	15(1)	797(1)	173(5)
F(56′)	145(1)	152(1)	801(1)	173(5)
N(10)	1647(6)	5509(6)	3826(5)	54(2)
O(011)	1845(6)	5003(7)	3235(5)	87(3)
O(012)	2119(7)	5957(7)	4493(5)	102(4)
O(013)	966(5)	5562(7)	3710(5)	79(2)
N(20)	4595(7)	1006(7)	1647(5)	64(3)
O(021)	5107(6)	1429(7)	2290(4)	85(3)
O(022)	4287(7)	1411(7)	1435(5)	93(3)
O(023)	4343(9)	170(8)	1233(7)	140(5)
N(30)	1307(8)	12.1(1)	4040(9)	72(3)
O(031)	126(1)	196(1)	448(1)	72(3)
O(032)	75(1)	42(1)	388(1)	72(3)
O(033)	1925(9)	128(1)	374(1)	72(3)
O(15w)	160(4)	850(3)	1970(5)	440(4)
O(15′)	1270(5)	1830(4)	4160(6)	440(4)
N(30′)	145(2)	1190(2)	4160(2)	124(5)
O(31′)	78(2)	77(2)	430(2)	124(5)
O(32′)	205(2)	98(2)	403(2)	124(5)
O(33′)	111(2)	48(2)	422(2)	124(5)
N(1′)	0	0	0	163(8)
O(1′)	410(2)	865(7)	40(2)	163(8)
O(2′)	− 70(1)	− 250(3)	190(2)	163(8)
O(3′)	130(2)	− 620(2)	− 554(1)	163(8)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U tensor.

TABLE 3
Selected Bond Lengths (Å) and Bond Angles (°) for 1 and 2

Complexes	1	2
Ln(1)–O(11)	2.444(4)	2.436(5)
Ln(1)–O(12)	2.473(4)	2.450(5)
Ln(1)–O(14)	2.498(4)	2.473(5)
Ln(1)–O(13)	2.511(4)	2.480(5)
Ln(1)–O(2A)	2.442(4)	2.410(5)
Ln(1)–O(2B)	2.428(4)	2.405(5)
Ln(1)–O(1w)	2.490(4)	2.473(6)
Ln(1)–O(2w)	2.440(4)	2.423(5)
Ln(1)–O(3w)	2.552(4)	2.511(6)
Ln(2)–O(21)	2.474(4)	2.449(5)
Ln(2)–O(22)	2.509(4)	2.498(5)
Ln(2)–O(23)	2.438(4)	2.412(5)
Ln(2)–O(24)	2.488(4)	2.461(5)
Ln(2)–O(2D)	2.401(4)	2.382(5)
Ln(2)–O(2C)	2.424(4)	2.388(5)
Ln(2)–O(4w)	2.518(4)	2.491(6)
Ln(2)–O(5w)	2.494(4)	2.468(5)
Ln(2)–O(6w)	2.592(5)	2.551(6)
Ln(3)–O(31)	2.509(4)	2.499(5)
Ln(3)–O(32)	2.503(4)	2.483(5)
Ln(3)–O(33)	2.512(4)	2.493(5)
Ln(3)–O(34)	2.438(4)	2.429(5)
Ln(3)–O(2E)	2.472(4)	2.426(5)
Ln(3)–O(2F)	2.383(5)	2.354(6)
Ln(3)–O(7w)	2.503(4)	2.453(5)
Ln(3)–O(8w)	2.519(4)	2.484(6)
Ln(3)–O(9w)	2.476(4)	2.463(6)
Cu(1)–O(11)	1.965(4)	1.949(5)
Cu(1)–O(12)	1.996(4)	1.969(5)
Cu(1)–O(21)#1	1.954(4)	1.941(5)
Cu(1)–O(22)#1	2.004(4)	1.981(5)
Cu(1)–O(1A)	2.311(4)	2.332(6)
Cu(2)–O(11)	1.982(4)	1.948(5)
Cu(2)–O(13)	1.972(4)	1.962(5)
Cu(2)–O(31)#1	1.977(4)	1.953(5)
Cu(2)–O(32)#1	1.957(4)	1.943(5)
Cu(2)–O(1B)	2.357(4)	2.348(5)
Cu(3)–O(13)	1.949(4)	1.947(5)
Cu(3)–O(14)	1.967(4)	1.961(5)
Cu(3)–O(23)	1.952(4)	1.934(5)
Cu(3)–O(24)	1.960(4)	1.958(5)
Cu(3)–O(1C)	2.312(4)	2.372(6)
Cu(4)–O(21)	1.992(4)	1.965(5)
Cu(4)–O(23)	1.956(4)	1.947(5)
Cu(4)–O(31)#1	1.987(4)	1.970(5)
Cu(4)–O(33)#1	1.951(4)	1.935(5)
Cu(4)–O(1D)	2.350(4)	2.344(5)
Cu(5)–O(22)	1.993(4)	1.988(5)
Cu(5)–O(24)	1.973(4)	1.952(5)
Cu(5)–O(32)	1.979(4)	1.961(5)
Cu(5)–O(34)	1.964(4)	1.946(5)
Cu(5)–O(1E)	2.263(4)	2.277(5)
Cu(6)–O(12)	1.954(4)	1.945(5)
Cu(6)–O(14)	1.996(4)	1.972(5)
Cu(6)–O(33)	1.980(4)	1.972(5)
Cu(6)–O(34)	1.958(4)	1.939(5)
Cu(6)–O(1F)	2.339(4)	2.364(6)

TABLE 3—*Continued*

Complexes	1	2
O(2B)–Ln(1)–O(2A)	79.6(1)	80.5(2)
O(2B)–Ln(1)–O(2w)	82 (1)	82.8(2)
O(2A)–Ln(1)–O(2w)	138.8(1)	139.4(2)
O(2B)–Ln(1)–O(11)	73.7(1)	73.8(2)
O(2w)–Ln(1)–O(11)	134.1(1)	74.4(2)
O(2A)–Ln(1)–O(11)	74.1(1)	74.4(2)
O(2B)–Ln(1)–O(12)	137.6(2)	137.2(2)
O(2w)–Ln(1)–O(12)	137.9(1)	137.0(2)
O(2A)–Ln(1)–O(12)	75.1(1)	75.0(2)
O(11)–Ln(1)–O(12)	67.0(1)	66.2(2)
O(2B)–Ln(1)–O(1w)	136.6(1)	137.5(2)
O(2w)–Ln(1)–O(1w)	83.2(2)	84.4(2)
O(2A)–Ln(1)–O(1w)	85.4(2)	83.5(2)
O(11)–Ln(1)–O(1w)	139.8(1)	138.7(2)
O(12)–Ln(1)–O(1w)	74.6(1)	74.3(2)
O(2B)–Ln(1)–O(13)	76.4(1)	75.8(2)
O(2A)–Ln(1)–O(13)	137(1)	137.3(2)
O(2w)–Ln(1)–O(13)	71.1(1)	71.7(2)
O(11)–Ln(1)–O(13)	65.7(1)	65.2(2)
O(12)–Ln(1)–O(13)	100.5(1)	99.6(2)
O(1w)–Ln(1)–O(13)	135.1(1)	135.8(2)
O(14)–Ln(1)–O(13)	64.6(1)	65.0(2)
O(2B)–Ln(1)–O(14)	139.3(1)	139.0(0)
O(2w)–Ln(1)–O(14)	75.1(1)	74.3(2)
O(2A)–Ln(1)–O(14)	138.1(1)	137.5(2)
O(11)–Ln(1)–O(14)	99.1(1)	98.9(2)
O(12)–Ln(1)–O(14)	64.7(1)	64.4(2)
O(1w)–Ln(1)–O(14)	73.7(1)	73.5(2)
O(2B)–Ln(1)–O(3w)	66.6(1)	66.8(2)
O(2A)–Ln(1)–O(3w)	70.0(1)	70.9(2)
O(2w)–Ln(1)–O(3w)	68.8(1)	68.5(2)
O(11)–Ln(1)–O(3w)	130.0(1)	130.7(2)
O(12)–Ln(1)–O(3w)	131.4(1)	132.8(2)
O(1w)–Ln(1)–O(3w)	70.0(1)	70.8(2)
O(13)–Ln(1)–O(3w)	128.0(1)	127.5(2)
O(14)–Ln(1)–O(3w)	130.9(1)	130.3(2)
O(2D)–Ln(2)–O(2C)	79.6(1)	80.2(2)
O(2C)–Ln(2)–O(23)	73.4(1)	70.4(2)
O(2D)–Ln(2)–O(23)	75.7(1)	76.3(2)
O(2C)–Ln(2)–O(21)	136.5(1)	137.0(2)
O(2D)–Ln(2)–O(21)	76.1(1)	76.2(2)
O(23)–Ln(2)–O(21)	65.9(1)	65.8(2)
O(2C)–Ln(2)–O(24)	76.7(1)	77.0(2)
O(2D)–Ln(2)–O(24)	138.6(1)	139.6(2)
O(23)–Ln(2)–O(24)	65.3(1)	65.6(2)
O(21)–Ln(2)–O(24)	99.1(1)	98.9(2)
O(2C)–Ln(2)–O(5w)	81.6(1)	82.6(2)
O(2D)–Ln(2)–O(5w)	136.6(1)	136.3(2)
O(23)–Ln(2)–O(5w)	134.2(1)	135.6(2)
O(21)–Ln(2)–O(5w)	139.1(1)	137.8(2)
O(24)–Ln(2)–O(5w)	72.0(1)	72.7(2)
O(2C)–Ln(2)–O(4w)	138.7(1)	137.4(2)
O(2D)–Ln(2)–O(4w)	83.6(1)	81.8(2)
O(23)–Ln(2)–O(4w)	137.4(1)	137.1(2)
O(21)–Ln(2)–O(4w)	73.2(1)	73.5(2)
O(24)–Ln(2)–O(4w)	135.2(1)	136.1(2)
O(5w)–Ln(2)–O(4w)	85.5(1)	84.5(2)
O(22)–Ln(2)–O(4w)	72.4(1)	73.1(2)

TABLE 3—*Continued*

Complexes	1	2
O(2C)–Ln(2)–O(22)	139.6(1)	140.0(2)
O(2D)–Ln(2)–O(22)	138.7(1)	138.0(2)
O(23)–Ln(2)–O(22)	99.8(1)	99.9(2)
O(21)–Ln(2)–O(22)	65.0(1)	64.7(2)
O(24)–Ln(2)–O(22)	64.8(1)	65.0(2)
O(5w)–Ln(2)–O(22)	75.5(1)	74.7(2)
O(2C)–Ln(2)–O(6w)	67.3(1)	67.3(2)
O(2D)–Ln(2)–O(6w)	68.9(1)	69.5(2)
O(23)–Ln(2)–O(6w)	130.6(1)	131.6(2)
O(21)–Ln(2)–O(6w)	132.2(1)	132.7(2)
O(24)–Ln(2)–O(6w)	128.7(1)	128.3(2)
O(22)–Ln(2)–O(6w)	129.6(1)	128.5(2)
O(4w)–Ln(2)–O(6w)	71.5(1)	70.3(2)
O(5w)–Ln(2)–O(6w)	67.8(1)	66.8(2)
O(2F)–Ln(3)–O(34)	74.6(1)	75.7(2)
O(2F)–Ln(3)–O(2E)	84.0(2)	84.6(2)
O(34)–Ln(3)–O(2E)	73.6(1)	73.6(2)
O(2F)–Ln(3)–O(7w)	83.1(2)	82.2(2)
O(2E)–Ln(3)–O(7w)	142.0(1)	142.1(2)
O(34)–Ln(3)–O(7w)	135.6(1)	135.7(2)
O(9w)–Ln(3)–O(7w)	68.9(1)	70.3(2)
O(32)–Ln(3)–O(7w)	135.7(1)	135.1(2)
O(34)–Ln(3)–O(9w)	133.1(1)	132.4(2)
O(2E)–Ln(3)–O(9w)	73.0(1)	71.8(2)
O(2F)–Ln(3)–O(9w)	69.9(2)	69.5(2)
O(34)–Ln(3)–O(32)	66.1(1)	65.6(2)
O(2E)–Ln(3)–O(32)	72.13(1)	73.1(2)
O(2F)–Ln(3)–O(32)	138.3(1)	139.3(2)
O(9w)–Ln(3)–O(32)	130.2(1)	130.3(2)
O(2F)–Ln(3)–O(31)	136.6(1)	136.3(2)
O(34)–Ln(3)–O(31)	96.8(1)	135.4(2)
O(2E)–Ln(3)–O(31)	135.2(1)	96.9(2)
O(9w)–Ln(3)–O(31)	130.1(1)	73.6(2)
O(32)–Ln(3)–O(31)	64.3(1)	130.7(2)
O(7w)–Ln(3)–O(31)	73.9(1)	63.7(2)
O(2F)–Ln(3)–O(33)	73.2(1)	74.2(2)
O(34)–Ln(3)–O(33)	66.0(1)	137.0(2)
O(2E)–Ln(3)–O(33)	137.5(1)	65.2(2)
O(9w)–Ln(3)–O(33)	127.8(1)	72.0(2)
O(32)–Ln(3)–O(33)	101.8(1)	130.1(2)
O(7w)–Ln(3)–O(33)	71.0(1)	99.5(2)
O(31)–Ln(3)–O(33)	64.7(1)	64.022(2)
O(2F)–Ln(3)–O(8w)	139.1(1)	138.0(2)
O(2E)–Ln(3)–O(8w)	85.2(1)	83.3(2)
O(34)–Ln(3)–O(8w)	138.4(1)	137.2(2)
O(7w)–Ln(3)–O(8w)	81.6(2)	83.2(2)
O(9w)–Ln(3)–O(8w)	69.2(1)	68.6(2)
O(32)–Ln(3)–O(8w)	73.5(1)	73.5(2)
O(31)–Ln(3)–O(8w)	73.5(1)	74.9(2)
O(33)–Ln(3)–O(8w)	134.7(1)	136.4(2)
O(21)#1–Cu(1)–O(11)	173.3(2)	172.9(2)
O(21)#1–Cu(1)–O(12)	94.2(2)	94.7(2)
O(11)–Cu(1)–O(12)	86.5(2)	85.8(2)
O(21)#1–Cu(1)–O(22)#1	85.1(2)	85.0(2)
O(11)–Cu(1)–O(22)#1	93.8(2)	94.2(2)
O(12)–Cu(1)–O(22)#1	176.3(2)	177.3(2)
O(21)#1–Cu(1)–O(1A)	95.8(2)	96.3(2)
O(11)–Cu(1)–O(1A)	90.9(2)	90.8(2)
O(12)–Cu(1)–O(1A)	88.8(2)	88.8(2)

TABLE 3—*Continued*

Complexes	1	2
O(22)#1–Cu(1)–O(1A)	94.8(2)	93.9(2)
O(32)#1–Cu(2)–O(13)	175.6(2)	175.1(2)
O(32)#1–Cu(2)–O(31)#1	85.4(2)	84.9(2)
O(13)–Cu(2)–O(31)#1	95.5(2)	96.6(2)
O(32)#1–Cu(2)–O(11)	92.9(2)	92.9(2)
O(13)–Cu(2)–O(11)	85.7(2)	85.2(2)
O(31)#1–Cu(2)–O(11)	173.1(2)	173.8(2)
O(32)#1–Cu(2)–O(1B)	96.9(2)	97.1(2)
O(13)–Cu(2)–O(1B)	87.3(2)	87.4(2)
O(31)#1–Cu(2)–O(1B)	96.6(2)	95.8(2)
O(11)–Cu(2)–O(1B)	90.2(2)	90.2(2)
O(13)–Cu(3)–O(23)	92.6(2)	92.7(2)
O(13)–Cu(3)–O(24)	175.4(2)	177.2(2)
O(23)–Cu(3)–O(24)	85.7(2)	85.4(2)
O(13)–Cu(3)–O(14)	86.2(2)	85.9(2)
O(23)–Cu(3)–O(14)	174.9(2)	177.0(2)
O(24)–Cu(3)–O(14)	95.1(2)	95.9(2)
O(13)–Cu(3)–O(1C)	93.7(2)	93.9(2)
O(23)–Cu(3)–O(1C)	90.6(2)	89.0(2)
O(24)–Cu(3)–O(1C)	90.6(2)	88.0(2)
O(14)–Cu(3)–O(1C)	94.4(2)	93.8(2)
O(33)#1–Cu(4)–O(23)	174.7(2)	175.7(2)
O(33)#1–Cu(4)–O(31)#1	86.0(2)	85.3(2)
O(23)–Cu(4)–O(31)#1	93.4(2)	94.6(2)
O(33)#1–Cu(4)–O(21)	94.9(2)	94.9(2)
O(23)–Cu(4)–O(21)	85.2(2)	84.9(2)
O(31)#1–Cu(4)–O(21)	175.9(2)	177.0(2)
O(33)#1–Cu(4)–O(1D)	95.8(2)	95.1(2)
O(23)–Cu(4)–O(1D)	89.5(2)	89.3(2)
O(31)#1–Cu(4)–O(1D)	96.2(2)	95.3(2)
O(21)–Cu(4)–O(1D)	87.7(2)	87.7(2)
O(34)–Cu(5)–O(24)	91.4(2)	92.6(2)
O(34)–Cu(5)–O(32)	86.2(2)	85.8(2)
O(24)–Cu(5)–O(32)	175.1(2)	175.9(2)
O(34)–Cu(5)–O(22)	174.5(2)	175.7(2)
O(24)–Cu(5)–O(22)	85.0(2)	85.1(2)
O(32)–Cu(5)–O(22)	97.1(2)	96.2(2)
O(34)–Cu(5)–O(1E)	92.8(2)	92.5(2)
O(24)–Cu(5)–O(IE)	94.7(2)	94.4(2)
O(32)–Cu(5)–O(1E)	89.6(2)	89.4(2)
O(22)–Cu(5)–O(1E)	91.7(1)	91.4(2)
O(12)–Cu(6)–O(34)	172.8(2)	173.2(2)
O(12)–Cu(6)–O(33)	94.5(2)	95.2(2)
O(12)–Cu(6)–O(14)	84.6(2)	84.3(2)
O(34)–Cu(6)–O(33)	86.4(2)	85.5(2)
O(34)–Cu(6)–O(14)	94.0(2)	94.6(2)
O(33)–Cu(6)–O(14)	176.1(2)	176.7(2)
O(12)–Cu(6)–O(1F)	97.3(2)	97.3(2)
O(34)–Cu(6)–O(1F)	89.9(2)	89.5(2)
O(33)–Cu(6)–O(1F)	90.3(2)	88.5(2)
O(14)–Cu(6)–O(1F)	93.5(2)	94.8(2)
Cu(1)–O(11)–Cu(2)	123.8(2)	123.6(2)
Cu(1)–O(11)–Ln(1)	103.6(2)	103.9(2)
Cu(2)–O(11)–Ln(1)	104.6(2)	105.0(2)
Cu(6)–O(12)–Cu(1)	119.8(2)	119.8(2)
Cu(6)–O(12)–Ln(1)	106.2(2)	106.4(2)
Cu(1)–O(12)–Ln(1)	101.6(2)	102.8(2)
Cu(3)–O(13)–Cu(2)	120.6(2)	119.1(2)
Cu(3)–O(13)–Ln(1)	104.5(2)	104.8(2)

TABLE 3—*Continued*

Complexes	1	2
Cu(2)–O(13)–Ln(1)	102.5(2)	103.2(2)
Cu(3)–O(14)–Cu(6)	119.2(2)	116.9(2)
Cu(3)–O(14)–Ln(1)	104.4(2)	104.1(2)
Cu(6)–O(14)–Ln(1)	104.0(1)	104.5(2)
Cu(1)#1–O(21)–Cu(4)	119.8(2)	120.3(2)
Cu(1)#1–O(21)–Ln(2)	106.2(2)	106.6(2)
Cu(4)–O(21)–Ln(2)	102.4(2)	102.9(2)
Cu(5)–O(22)–Cu(1)#1	116.2(2)	115.7(2)
Cu(5)–O(22)–Ln(2)	104.2(2)	103.6(2)
Cu(1)#1–O(22)–Ln(2)	103.4(2)	103.5(2)
Cu(3)–O(23)–Cu(4)	124.4(2)	122.3(2)
Cu(3)–O(23)–Ln(2)	104.5(2)	105.1(2)
Cu(4)–O(23)–Ln(2)	104.8(2)	104.8(2)
Cu(3)–O(24)–Cu(5)	122.6(2)	119.7(2)
Cu(3)–O(24)–Ln(2)	102.5(2)	102.6(2)
Cu(5)–O(24)–Ln(2)	105.6(2)	106.1(2)
Cu(2)#1–O(31)–Cu(4)#1	119.7(2)	117.7(2)
Cu(2)#1–O(31)–Ln(3)	104.5(2)	105.1(2)
Cu(4)#1–O(31)–Ln(3)	104.0(2)	104.6(2)
Cu(2)#1–O(32)–Cu(5)	117.7(2)	119.0(2)
Cu(2)#1–O(32)–Ln(3)	105.4(2)	106.0(2)
Cu(5)–O(32)–Ln(3)	101.8(1)	102.3(2)
Cu(4)#1–O(33)–Cu(6)	117.5(2)	117.9(2)
Cu(4)#1–O(33)–Ln(3)	105.0(2)	105.9(2)
Cu(6)–O(33)–Ln(3)	101.4(2)	102.2(2)
Cu(6)–O(34)–Cu(5)	125.5(2)	123.9(2)
Cu(6)–O(34)–Ln(3)	104.7(2)	105.5(2)
Cu(5)–O(34)–Ln(3)	104.6(2)	104.7(2)

Symmetry code: #1, $1-x$, $1-y$, $1-z$.

6 square faces by the 6 Sm^{III} atoms. These Sm–Cu metal fragments are interconnected by 24 similar μ_3-OH^- bridges that are each linked to 1 Sm^{III} (Sm–O 2.438–2.512 Å) and 2 Cu^{II} (Cu–O 1.949–2.004 Å) atoms, such that each Sm(μ_3-OH)$_4$ fragment is square-pyramidal and each Cu(μ_3-OH)$_4$ fragment is square-planar, the coordination sphere of each Sm^{III} is completed by two oxygen atoms from two pyb μ_2-carboxylate groups (Sm–O 2.383–2.472 Å), and three aqua ligands (Sm–O 2.440–2.592 Å) to form a monocapped square-antipyrismatic nine-coordination geometry; except for four μ_3-OH groups coordinated at the basal plane, each Cu^{II} is ligated by a μ_2-carboxylate oxygen atom of pyb (Cu–O 2.263–2.357 Å) at the apical position to form a square-pyramidal geometry. In the cluster of **1**, each pair of the adjacent nonbonding Cu ⋯ Cu is linked by a single hydroxy bridge with the Cu ⋯ Cu distances in the range of 3.36–3.48 Å. Each Sm^{III} atom is linked to four adjacent Cu^{II} atoms by four μ_3-OH^- bridges with nonbonding Cu ⋯ Sm separations of 3.48–3.57 Å, and each pair of Sm^{III} atoms in each edge of the octahedron is separated at distances of 7.02–7.07 Å. The metal skeleton of **1** is very similar to that of the $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(pyb)_{12}(H_2O)_{18}(\mu_{12}\text{-}ClO_4)]^{17+}$ clusters (13), the octadecanuclear cage of which is

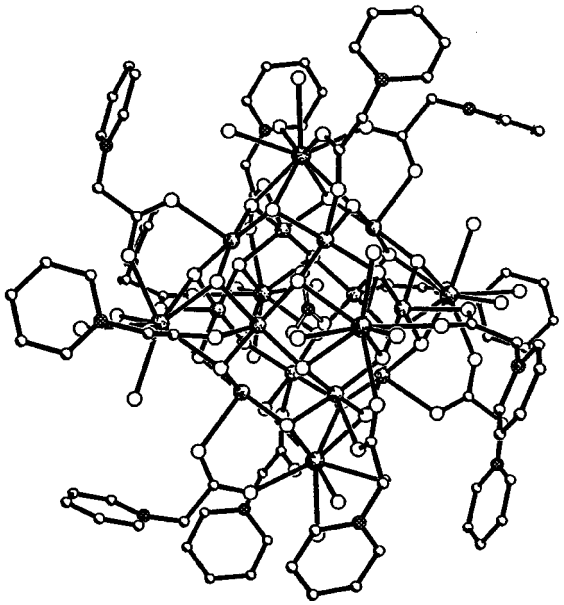

FIG. 1. Perspective view of the structure of $[Cu_{12}Sm_6(\mu_3\text{-}OH)_{24}(pyb)_{12}(H_2O)_{18}(NO_3)]^{17+}$ cation in **1**.

also constructed by 12 Cu^{II} atoms, 6 Ln^{III} atoms, 24 μ_3-OH^- groups, and 12 μ_2-carboxylate bridges in a high local pseudocubic O_h symmetry.

Of the six symmetry-independent lattice water molecules, one is disordered with respect to a nitrate ion. The other five

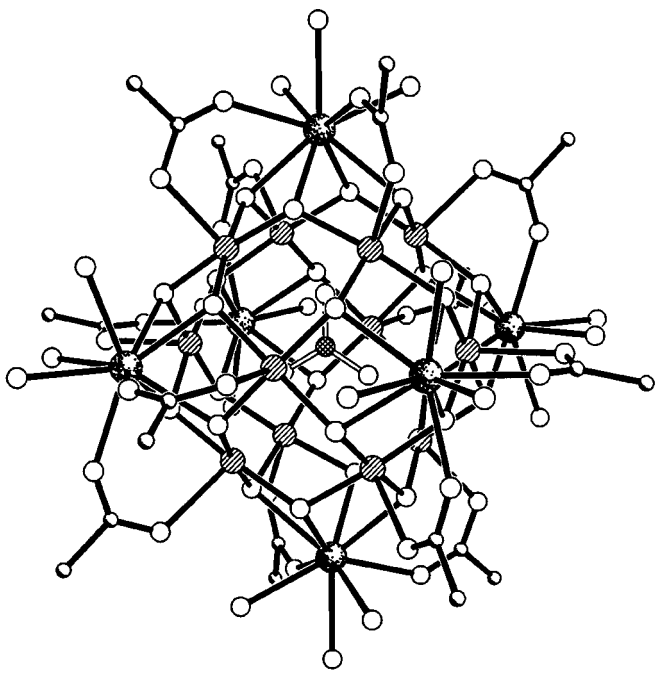

FIG. 2. Perspective view showing the structure of the octadecanuclear cation in **1**. For clarity, only the C–CO_2 fragments of pyb are shown. The Sm atoms are speckled, the Cu atoms are marked with lines, the N atoms are cross-hatched, and the O atoms are opened circles.

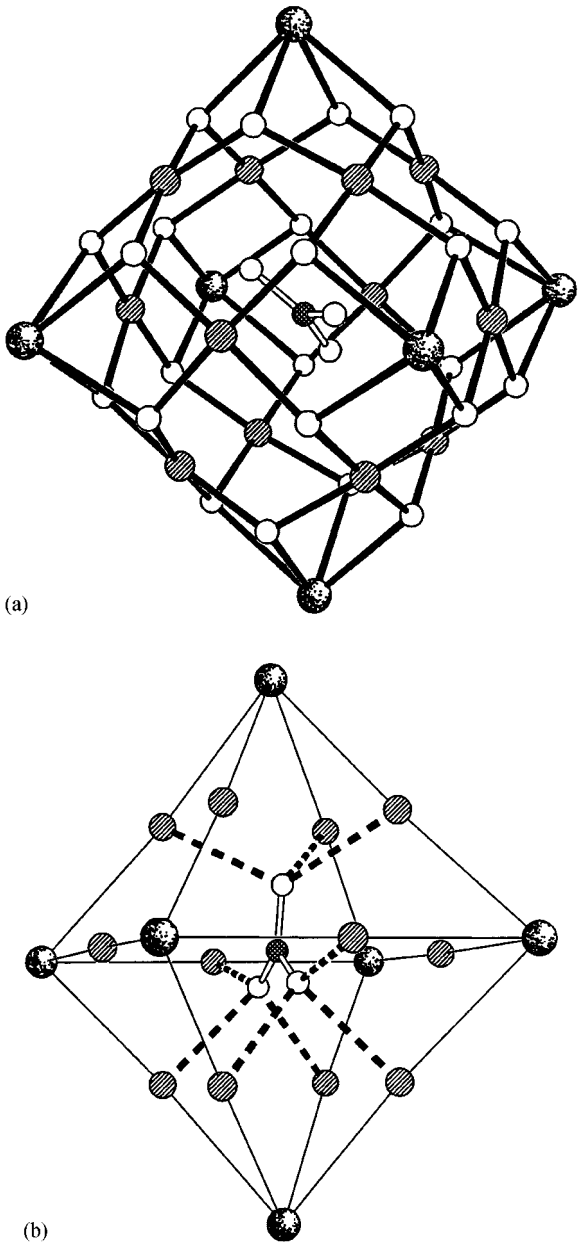

FIG. 3. Perspective views showing the structures of the octahedral cage of $[Cu_{12}Sm_6(\mu_3\text{-}OH)_{24}]^{18+}$ encapsulating a $\mu_9\text{-}NO_3^-$ anion (a) and the binding mode of the $\mu_9\text{-}NO_3^-$ anion (b) in **1**. The Sm atoms are speckled, the Cu atoms are marked with lines, and N atoms are cross-hatched, and the O atoms are opened circles.

are involved in hydrogen-bonding interactions with the aqua ligands, lattice water molecules, nitrate groups, and hexafluorophosphate groups. The number of such interactions varies from one to three; for example, the O10*w* atom is hydrogen-bonded to the O1*w*, O3*w*, and O11*w* atoms (av. $O \cdots O = 2.74$ Å) whereas the O13*w*, and 014*w* atoms are only linked to each other ($O \cdots O = 2.71$ Å). The hydrogen bonds furnish a three-dimensional network structure. There are no solvent-accessible voids in the crystal structure.

The most fascinating finding in the structure of **1** is an encapsulated $\mu_9\text{-}NO_3^-$ anion at the center of the octahedral $Cu^{II}_{12}Sm^{III}_6$ cage. As shown in Fig. 3, the nitrate anion exhibits a nine-coordination mode with each of the oxygen atoms weakly ligating three Cu^{II} atoms of the cage at the distances of 2.45–2.70 Å. This supramolecular phenomenon is similar to that in an icosanuclear $Cu_{12}La_8$ cluster reported by Winpenny *et al.*, which is the only known example of a cluster encapsulating a NO_3^- anion (8). An analogous phenomenon has also been observed in our previous octadecanuclear $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(pyb)_{12}(H_2O)_{18}(\mu_{12}\text{-}ClO_4)]^{17+}$ clusters, in which the octahedral $Cu^{II}_{12}Ln^{III}_6$ cage encapsulates a $\mu_{12}\text{-}ClO_4^-$ anion with Cu–O (perchlorate) distances of 2.32–2.47 Å (13).

Complex **2** is isomorphous to **1**. Due to the different radius of *Ln* ions and different temperatures of the data collection, there are minor differences between the cores of **1** and **2**. All the metal–ligand bonds in **2** are very close to the corresponding ones in **1**, and the difference falls usually within 0.04 Å, as shown in Table 3. Therefore, no structural plot of **2** is shown in this paper.

Magnetic Properties

Magnetic susceptibility data for **2** were collected with a polycrystalline sample in an external field of 10.0 kG, and are represented in the form of effective molar magnetic moment μ_{eff} versus T in Fig. 4. The observed susceptibility data were well fitted to the Curie–Weiss law ($\chi_M = C/(T-\theta)$, with $C = 0.00331\ K\,cm^3\,mol^{-1}$, $\theta = -1.46$ K), indicating very weak antiferromagnetic interaction in the cluster. The magnetic behavior of **2** is very similar to that of the analogous clusters $[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}(pyb)_{12}(H_2O)_{18}(ClO_4)](ClO_4)_{17}\cdot nH_2O$ (13a, 14). Since the magnetic

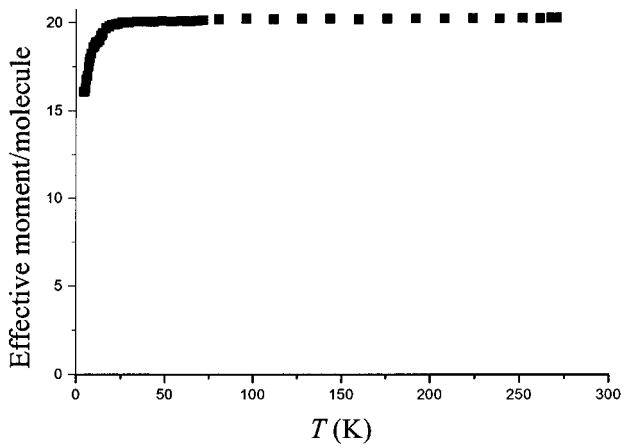

FIG. 4. A plot of the effective magnetic moment per mole versus temperature for **2**.

interactions within the octadecanuclear clusters are complicated, it is very difficult to derive the detailed coupling constants from such clusters, and the antiferromagnetic interaction between the $Cu^{II}\cdots Cu^{II}$ atoms are estimated at the magnitude of $-20\,cm^{-1}$, as shown in a yttrium(III) analogue (14). On the other hand, a weak ferromagnetic interaction between the $Cu^{II}\cdots Gd^{II}$ atoms has been found for a number of multinuclear Cu–Gd complexes (1, 2). Presumably, both a weak antiferromagnetic interaction between the $Cu^{II}\cdots Cu^{II}$ atoms and a weak ferromagnetic interaction between the $Cu^{II}\cdots Gd^{II}$ atoms coexist in **2.**

Synthesis

The PF_6^- anions play a very important role in the formation of the crystals. When the reaction solution contained only NO_3^- as the counteranion, no crystal of the octadecanuclear complexes appeared, even when the solution was nearly dry. When PF_6^- was added into the reaction solution, the gray-blue crystals of the octadecanuclear complexes began to deposit, which was what we observed when we introduced ClO_4^- in the analogous clusters (13, 14). On the other hand, due to the much weaker coordination ability and different geometry, a PF_6^- anion cannot be enclosed in the octahedral $Cu_{12}Ln_6$ cage. We have also used ClO_4^-, BF_4^-, or Cl^- as counterions in attempts to produce crystalline products. The addition of ClO_4^- and BF_4^- ions led to tiny gray-blue crystals, which are the analogous octadecanuclear clusters. The crystals containing PF_6^- counteranions were stable in air for about 2 months, while those containing ClO_4^- anions were stable for about a month, but the crystals of BF_4^- rapidly decomposed as they turned opaque after a few days. These observations suggest that the counteranions, rather than the enclosed anions, are critically important in the deposition of the octadecanuclear complexes, possibly due to a complicated equilibrium in the reaction solution, and that the large counterions are favored in the crystallization of the octadecanuclear complexes. Presumably, the encapsulation of the nitrate or perchlorate anion may be attributed to the shape and size recognition of these weak ligating anions in the formation process of the clusters. The observations above also suggest that the stability order of the counterions leading to crystallization of the clusters is $PF_6^- > ClO_4^- \gg NO_3^-$, which is similar to the order of crystallization, $PF_6^- > ClO_4^- > BF_4^- \gg NO_3^-$, reported for (tma)[Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$ (tma = tetrathethylammonium, pro = L-prolinate) (21).

CONCLUSION

This work presents two new octadecanuclear $Cu_{12}Ln_6$ complexes, which encapsulate an unusual nine-coordinate nitrate anion at the center of the cage. The counteranion is critically important for the formation of the clusters. The magnetic study further confirms our previous conclusion that the magnetic interaction within the cluster is very weak.

ACKNOWLEDGMENTS

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