A New Octadecanuclear Copper(II)-Lanthanide(III) Cluster Complex: Synthesis and Structural Characterization of $[Cu_{12}Nd_6(OH)_{24}(betaine)_{16}(NO_3)_3(H_2O)_{10}](NO_3)[PF_6]_{14}\cdot 5H_2O$

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Received August 4th, 2003.

Abstract. The new octadecanuclear Cu-Ln complex, $[Cu_{12}Nd_6(OH)_{24}(betaine)_{16}(NO_3)_3(H_2O)_{10}](NO_3)[PF_6]_{14}\cdot 5H_2O$, was synthesized, which crystallizes in triclinic $P\bar{1}$ space group, a = 18.649(6) Å, b = 20.363(7) Å, c = 19.865(7) Å, α = 116.61(2)°, β = 91.99(2)°, γ = 117.93(2)°, V = 5666(3) Å^3. Its crystal structure features a $[Cu_{12}Nd_6(OH)_{24}(betaine)_{16}(NO_3)_3(H_2O)_{10}]^{15+}$ core of pseudocubic O_h symmetry, with the six Nd ions positioned at the vertices of a regular octahedron and the twelve Cu ions located at the midpoints of the twelve octahedral edges. The Cu-Nd metal framework may be viewed as a cuboctahedron, which is interconnected by twenty-four μ_3-OH bridges that are each linked to one Nd ion and two Cu ions. In the centre of metal polyhedron, there is an encapsulated NO_3^- anion that exhibits a multi- coordinating mode.

Keywords: Cluster compounds; Copper; Lanthanides; Crystal structure; Betaine

Ein neuer achtzehnkerniger Kupfer(II)-Lanthanoid(III)-Cluster-Komplex: Synthese und strukturelle Charakterisierung von $[Cu_{12}Nd_6(OH)_{24}(betaine)_{16}(NO_3)_3(H_2O)_{10}](NO_3)[PF_6]_{14}\cdot 5H_2O$

Inhaltsübersicht. Der neue achtzehnkernige Cu-Ln-Komplex, $[Cu_{12}Nd_6(OH)_{24}(betaine)_{16}(NO_3)_3(H_2O)_{10}](NO_3)[PF_6]_{14}\cdot 5H_2O$, wurde synthetisiert und kristallographisch charakterisiert: Triklin, Raumgruppe $P\bar{1}$, a = 18.649(6) Å, b = 20.363(7) Å, c = 19.865(7) Å, α = 116.61(2)°, β = 91.99(2)°, γ = 117.93(2)°, V = 5666(3) Å^3. Die Kristallstruktur wird von einem Kern aus $[Cu_{12}Nd_6(OH)_{24}(betaine)_{16}(NO_3)_3(H_2O)_{10}]^{15+}$von pseudokubischer O_h-Symmetrie gebildet, mit den sechs Nd-Ionen an den Spitzen eines regulären Oktaeders und den zwölf Cu-Ionen in den Mitten der zwölf Oktaederkanten. Das Cu-Nd-Metallgerüst kann als ein Kuboktaeder angesehen werden, das durch 24 μ_3-OH-Brücken verbunden ist, jede von ihnen verbindet ein Nd-Ion und zwei Cu-Ionen. In der Mitte des Metallpolyeders ist ein NO_3^--Anion eingeschlossen.

Introduction

3d-4f heterometallic complexes have attracted considerable attention for both magnetic and chemical interests [1−3]. Inclusion of guest molecules into host structures had been interested over the past two decades [4], supramolecular chemistry of cationic or neutral guests has been widely studied [5]. On the other hand, that of small anions has received less attention [6], although recently a number of polynuclear metal complexes have been reported to serve as hosts for recognition of small molecules or ions [7−8].

During the past decade, we have taken the advantage of the neutral carboxylate ligands betaine and its derivatives in the charge compensation to assemble monomeric copper(II) tetracarboxylates, heterometallic Cu^{II}-Ca^{II} and Cu^{II}-Li^{I} complexes [9], as well as heterometallic $Cu^{II}Ln^{III}$ complexes including dinuclear CuLn, tetranuclear Cu_2Ln_2, pentanuclear Cu_3Ln_2, and several octadecanuclear $Cu_{12}Ln_6$ complexes [10−12]. In the pyridinioacetate ($C_5H_5N^+CH_2CO_2^-$, designated as pyb hereafter) system, 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. By introducing PF_6^- anions into the betaine ($Me_3N^+CH_2CO_2^-$, designated as bet) reaction system, we succeeded in isolation of an analogous $Cu_{12}Nd_6$ cluster, which encapsulates a nitrate anion in the octadecanuclear cage. Herein we report the preparation and crystal structures of the new complex$[Cu_{12}Nd_6(OH)_{24}(bet)_{16}(NO_3)_3(H_2O)_{10}](NO_3)[PF_6]_{14}\cdot 5H_2O$ (**1**) .

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Experimental Section

Betaine was purchased from Fluka, Nd^{III} nitrate was converted from its oxide by nitric acid. The other reagents were commercially available and used as received. The C, H and N microanalyses were

  DOI: 10.1002/zaac.200300267

Table 1 Crystallographic data of complex **1**

Complex	**1**
Formula	$C_{80}H_{230}Cu_{12}F_{84}N_{20}Nd_6O_{83}P_{14}$
Formula weight	6458.34
Measurement T /K	298(2)
Radiation wavelength /Å	0.71073
Crystal system	Triclinic
Space group	*P*-1 (No. 2)
a /Å	18.649(6)
b /Å	19.865(7)
c /Å	20.363(7)
α /°	91.99(2)
β /°	116.61(2)
γ /°	117.93(2)
Volume /A^3	5666(3)
Z	1
Density (ca.) /(Mg/m^{-3})	1.893
F(000)	3138
Crystal size /mm	0.55 x 0.45 x 0.25
Theta range for collection /°	2.01 to 26.00
Reflections collected/unique	22976/22255 [Rint=0.0291]
Max. and min. transmission	0.5525 and 0.3190
Data / restraints / parameters	22255 / 8523 / 1333
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.022
R indices [I > 2σ(I)]	R1 = 0.0608
R indices (all data)	wR2 = 0.1751

carried out with an Elementar Vario EL analyzer. FT-IR spectra were recorded from KBr pellets in range of 4000-400 cm^{-1} on a Nicolet 5DX spectrometer.

Synthesis

$[Cu_{12}Nd_6(OH)_{24}(bet)_{16}(NO_3)_3(H_2O)_{10}](NO_3)[PF_6]_{14}\cdot 5H_2O$ (**1**). A mixture of betaine (0.70 g, 6 mmol) and $Cu(NO_3)_2\cdot 6H_2O$ (0.30 g, 1 mmol) was dissolved in distilled water (10 cm^3) and heated at 50 °C for 5 min, an aqueous solution (2 cm^3) of $Nd(NO_3)_3$ (2 mmol) was then added and followed by KPF_6 (0.37 g, 2 mmol) with stirring for 10 min. The pH value of the resulting blue solution was adjusted to 6 by very slow addition of dilute aqueous KOH solution, and then filtered. The filtrate was allowed to evaporate slowly at room temperature, greenish-blue polyhedral crystals deposited after about 5 days, and the product was collected within one week (*ca.* 50 % yield). Anal. Calc for $C_{80}H_{230}Cu_{12}F_{84}N_{20}Nd_6O_{83}P_{14}$: C, 14.88; H, 3.59; N, 4.34 %. Found: C, 14.86; H, 3.68; N, 4.43 %.

IR data ($\tilde{\nu}$/cm^{-1}): 3571 m, 3469 s(br), 3071 w, 2913 w, 1630 vs, 1489 m, 1433 m, 1405 s, 1342 s, 1243 w, 1131 w, 962 w, 934 w, 842 vs, 561 m.

X-ray Crystallography

The data collection was carried out on a Siemens R3m diffractometer using graphitemonochromated Mo-Kα (λ = 0.71073 Å) radiation at 293(2) K. Determination 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 150 data measurements, showing only small random variations (<1.0 %). Absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles [13].

The structures were solved with direct methods and refined with full-matrix least-squares technique using SHELXS-97 and SHELXL-97 programs, respectively [14, 15]. Most of the non-hy-

Table 2 Selected bond lengths/Å and angles/° for complex **1**

Nd(1)-O(62)	2.427(6)	Cu(1)-O(1)	1.967(6)
Nd(1)-O(6)	2.451(5)	Cu(1)-O(3)	1.967(6)
Nd(1)-O(22)	2.458(6)	Cu(1)-O(4)	1.969(5)
Nd(1)-O(10)	2.479(6)	Cu(1)-O(2)	1.978(6)
Nd(1)-O(5)	2.499(5)	Cu(1)-O(11)	2.380(6)
Nd(1)-O(2W)	2.511(6)	Cu(2)-O(6)	1.937(5)
Nd(1)-O(16)	2.516(7)	Cu(2)-O(7)	1.948(6)
Nd(1)-O(9)#1	2.529(5)	Cu(2)-O(2)	1.975(6)
Nd(1)-O(15)	2.587(6)	Cu(2)-O(5)	2.007(6)
Nd(2)-O(81)	2.43(2)	Cu(2)-O(21)	2.328(6)
Nd(2)-O(42)	2.449(6)	Cu(3)-O(4)	1.956(6)
Nd(2)-O(12)	2.463(6)	Cu(3)-O(8)	1.966(6)
Nd(2)-O(1)	2.502(5)	Cu(3)-O(6)	1.968(5)
Nd(2)-O(4)	2.502(5)	Cu(3)-O(10)	1.975(5)
Nd(2)-O(1W)	2.522(7)	Cu(3)-O(61)	2.379(6)
Nd(2)-O(3W)	2.524(7)	Cu(4)-O(1)	1.967(5)
Nd(2)-O(13)	2.539(5)	Cu(4)-O(9)	1.976(5)
Nd(2)-O(8)	2.554(5)	Cu(4)-O(13)	1.993(6)
Nd(3)-O(52)	2.453(6)	Cu(4)-O(41)	2.286(6)
Nd(3)-O(32)	2.469(6)	Cu(5)-O(3)	1.971(5)
Nd(3)-O(71)	2.476(6)	Cu(5)-O(14)	1.974(6)
Nd(3)-O(14)	2.497(5)	Cu(5)-O(9)	1.990(6)
Nd(3)-O(5W)	2.511(7)	Cu(5)-O(31)	2.222(6)
Nd(3)-O(4W)	2.518(7)	Cu(6)-O(14)	1.939(6)
Nd(3)-O(3)	2.521(6)	Cu(6)-O(7)	1.979(6)
Nd(3)-O(7)	2.532(6)	Cu(6)-O(51)	2.301(6)
Nd(3)-O(2)	2.549(6)	Cu(4)-O(5)#1	1.954(5)
Nd(3)-Cu(5)	3.546(2)	Cu(5)-O(10)#1	1.973(5)
O(9)-Nd(1)#1	2.529(5)	Cu(6)-O(8)#1	1.982(5)
O(10)-Cu(5)#1	1.973(5)	Cu(6)-O(13)#1	1.938(5)
O(8)-Cu(6)#1	1.982(5)	O(5)-Cu(4)#1	1.954(5)
O(13)-Cu(6)#1	1.938(5)		
O(62)-Nd(1)-O(6)	77.17(19)	O(1)-Cu(1)-O(3)	93.5(2)
O(62)-Nd(1)-O(22)	83.9(2)	O(1)-Cu(1)-O(4)	86.2(2)
O(6)-Nd(1)-O(22)	74.03(19)	O(3)-Cu(1)-O(4)	175.3(2)
O(62)-Nd(1)-O(10)	75.95(19)	O(1)-Cu(1)-O(2)	175.2(2)
O(6)-Nd(1)-O(10)	66.08(18)	O(3)-Cu(1)-O(2)	84.6(2)
O(22)-Nd(1)-O(10)	138.24(19)	O(4)-Cu(1)-O(2)	95.3(2)
O(62)-Nd(1)-O(5)	142.1(2)	O(1)-Cu(1)-O(11)	86.4(2)
O(6)-Nd(1)-O(5)	66.88(18)	O(3)-Cu(1)-O(11)	93.1(2)
O(22)-Nd(1)-O(5)	75.47(19)	O(4)-Cu(1)-O(11)	91.6(2)
O(10)-Nd(1)-O(5)	98.93(18)	O(2)-Cu(1)-O(11)	98.2(2)
O(62)-Nd(1)-O(2W)	80.4(2)	O(6)-Cu(2)-O(7)	175.2(2)
O(6)-Nd(1)-O(2W)	137.3(2)	O(6)-Cu(2)-O(2)	93.4(2)
O(22)-Nd(1)-O(2W)	138.7(2)	O(7)-Cu(2)-O(2)	85.9(2)
O(10)-Nd(1)-O(2W)	73.5(2)	O(6)-Cu(2)-O(5)	87.5(2)
O(5)-Nd(1)-O(2W)	134.9(2)	O(7)-Cu(2)-O(5)	92.9(2)
O(62)-Nd(1)-O(16)	127.9(2)	O(2)-Cu(2)-O(5)	176.2(2)
O(6)-Nd(1)-O(16)	141.0(2)	O(6)-Cu(2)-O(21)	92.0(2)
O(22)-Nd(1)-O(16)	79.4(3)	O(7)-Cu(2)-O(21)	92.7(2)
O(10)-Nd(1)-O(16)	141.2(2)	O(2)-Cu(2)-O(21)	98.1(2)
O(5)-Nd(1)-O(16)	79.2(2)	O(5)-Cu(2)-O(21)	85.6(2)
O(2W)-Nd(1)-O(16)	80.7(3)	O(4)-Cu(3)-O(8)	85.5(2)
O(62)-Nd(1)-O(9)#1	137.9(2)	O(4)-Cu(3)-O(6)	93.2(2)
O(6)-Nd(1)-O(9)#1	100.69(18)	O(8)-Cu(3)-O(6)	175.3(2)
O(22)-Nd(1)-O(9)#1	136.72(19)	O(4)-Cu(3)-O(10)	174.8(2)
O(10)-Nd(1)-O(9)#1	65.45(17)	O(8)-Cu(3)-O(10)	94.9(2)
O(5)-Nd(1)-O(9)#1	63.60(18)	O(6)-Cu(3)-O(10)	85.9(2)
O(2W)-Nd(1)-O(9)#1	73.32(19)	O(4)-Cu(3)-O(61)	96.7(2)
O(16)-Nd(1)-O(9)#1	79.8(2)	O(8)-Cu(3)-O(61)	96.2(2)
O(62)-Nd(1)-O(15)	77.9(2)	O(6)-Cu(3)-O(61)	88.4(2)
O(6)-Nd(1)-O(15)	138.8(2)	O(10)-Cu(3)-O(61)	88.4(2)
O(22)-Nd(1)-O(15)	71.1(2)	O(5)#1-Cu(4)-O(1)	173.1(2)
O(10)-Nd(1)-O(15)	136.5(2)	O(5)#1-Cu(4)-O(9)	84.8(2)
O(5)-Nd(1)-O(15)	122.7(2)	O(1)-Cu(4)-O(9)	94.9(2)
O(2W)-Nd(1)-O(15)	68.3(2)	O(5)#1-Cu(4)-O(13)	93.9(2)
O(16)-Nd(1)-O(15)	50.0(2)	O(1)-Cu(4)-O(13)	85.6(2)
O(9)#1-Nd(1)-O(15)	119.69(19)	O(9)-Cu(4)-O(13)	173.8(2)
O(81)-Nd(2)-O(42)	68.8(5)	O(5)#1-Cu(4)-O(41)	95.8(2)
O(81)-Nd(2)-O(12)	72.4(8)	O(1)-Cu(4)-O(41)	91.0(2)
O(42)-Nd(2)-O(12)	81.7(2)	O(9)-Cu(4)-O(41)	100.0(2)
O(81)-Nd(2)-O(1)	131.8(7)	O(13)-Cu(4)-O(41)	86.2(2)
O(42)-Nd(2)-O(1)	74.3(2)	O(3)-Cu(5)-O(10)#1	175.4(2)
O(12)-Nd(2)-O(1)	72.58(18)	O(3)-Cu(5)-O(14)	85.9(2)
O(81)-Nd(2)-O(4)	133.6(7)	O(10)#1-Cu(5)-O(14)	91.6(2)
O(42)-Nd(2)-O(4)	137.6(2)	O(3)-Cu(5)-O(9)	96.0(2)
O(12)-Nd(2)-O(4)	75.65(19)	O(10)#1-Cu(5)-O(9)	86.2(2)
O(1)-Nd(2)-O(4)	64.99(17)	O(14)-Cu(5)-O(9)	175.5(2)
O(81)-Nd(2)-O(1W)	72.8(5)	O(3)-Cu(5)-O(31)	92.4(2)
O(42)-Nd(2)-O(1W)	141.7(2)	O(10)#1-Cu(5)-O(31)	91.4(2)
O(12)-Nd(2)-O(1W)	86.8(2)	O(14)-Cu(5)-O(31)	87.9(2)
O(1)-Nd(2)-O(1W)	136.1(2)	O(9)-Cu(5)-O(31)	96.1(2)
O(4)-Nd(2)-O(1W)	72.5(2)	O(13)#1-Cu(6)-O(14)	173.9(2)
O(81)-Nd(2)-O(3W)	69.6(8)	O(13)#1-Cu(6)-O(7)	95.0(2)
O(42)-Nd(2)-O(3W)	83.7(3)	O(14)-Cu(6)-O(7)	84.9(2)
O(12)-Nd(2)-O(3W)	142.0(2)	O(13)#1-Cu(6)-O(8)#1	84.8(2)

Table 2 *(Continued)*

O(1)-Nd(2)-O(3W)	135.6(2)	O(14)-Cu(6)-O(8)#1	95.0(2)
O(4)-Nd(2)-O(3W)	134.3(2)	O(7)-Cu(6)-O(8)#1	175.9(2)
O(1W)-Nd(2)-O(3W)	83.3(3)	O(13)#1-Cu(6)-O(51)	94.8(2)
O(81)-Nd(2)-O(13)	130.1(7)	O(14)-Cu(6)-O(51)	91.3(2)
O(42)-Nd(2)-O(13)	75.51(19)	O(7)-Cu(6)-O(51)	89.4(2)
O(12)-Nd(2)-O(13)	135.35(19)	O(8)#1-Cu(6)-O(51)	94.7(2)
O(1)-Nd(2)-O(13)	64.54(18)	Cu(1)-O(1)-Cu(4)	121.4(3)
O(4)-Nd(2)-O(13)	96.29(18)	Cu(1)-O(1)-Nd(2)	103.8(2)
O(1W)-Nd(2)-O(13)	133.3(2)	Cu(4)-O(1)-Nd(2)	105.1(2)
O(3W)-Nd(2)-O(13)	72.9(2)	Cu(2)-O(2)-Cu(1)	119.0(3)
O(81)-Nd(2)-O(8)	130.6(7)	Cu(2)-O(2)-Nd(3)	104.2(2)
O(42)-Nd(2)-O(8)	136.1(2)	Cu(1)-O(2)-Nd(3)	105.1(2)
O(12)-Nd(2)-O(8)	137.96(19)	Cu(1)-O(3)-Cu(5)	119.2(3)
O(1)-Nd(2)-O(8)	97.44(18)	Cu(1)-O(3)-Nd(3)	106.5(2)
O(4)-Nd(2)-O(8)	63.51(18)	Cu(5)-O(3)-Nd(3)	103.5(2)
O(1W)-Nd(2)-O(8)	72.3(2)	Cu(3)-O(4)-Cu(1)	119.7(3)
O(3W)-Nd(2)-O(8)	72.5(2)	Cu(3)-O(4)-Nd(2)	106.3(2)
O(13)-Nd(2)-O(8)	62.52(17)	Cu(1)-O(4)-Nd(2)	103.7(2)
O(52)-Nd(3)-O(32)	82.6(2)	Cu(4)#1-O(5)-Cu(2)	121.8(3)
O(52)-Nd(3)-O(71)	72.6(2)	Cu(4)#1-O(5)-Nd(1)	106.5(2)
O(32)-Nd(3)-O(71)	76.7(2)	Cu(2)-O(5)-Nd(1)	100.4(2)
O(52)-Nd(3)-O(14)	73.24(19)	Cu(2)-O(6)-Cu(3)	122.0(3)
O(32)-Nd(3)-O(14)	72.02(19)	Cu(2)-O(6)-Nd(1)	104.1(2)
O(71)-Nd(3)-O(14)	135.9(2)	Cu(3)-O(6)-Nd(1)	103.8(2)
O(52)-Nd(3)-O(5W)	143.1(2)	Cu(2)-O(7)-Cu(6)	120.8(3)
O(32)-Nd(3)-O(5W)	84.5(2)	Cu(2)-O(7)-Nd(3)	105.6(2)
O(71)-Nd(3)-O(5W)	70.8(2)	Cu(6)-O(7)-Nd(3)	103.6(2)
O(14)-Nd(3)-O(5W)	134.0(2)	Cu(3)-O(8)-Cu(6)#1	117.9(3)
O(52)-Nd(3)-O(4W)	83.0(2)	Cu(3)-O(8)-Nd(2)	104.1(2)
O(32)-Nd(3)-O(4W)	144.7(2)	Cu(6)#1-O(8)-Nd(2)	105.1(2)
O(71)-Nd(3)-O(4W)	68.2(2)	Cu(4)-O(9)-Cu(5)	117.3(3)
O(14)-Nd(3)-O(4W)	133.0(2)	Cu(4)-O(9)-Nd(1)#1	104.7(2)
O(5W)-Nd(3)-O(4W)	88.0(3)	Cu(5)-O(9)-Nd(1)#1	102.8(2)
O(52)-Nd(3)-O(3)	136.29(19)	Cu(5)#1-O(10)-Cu(3)	121.7(3)
O(32)-Nd(3)-O(3)	73.77(19)	Cu(5)#1-O(10)-Nd(1)	105.1(2)
O(71)-Nd(3)-O(3)	133.3(2)	Cu(3)-O(10)-Nd(1)	102.6(2)
O(14)-Nd(3)-O(3)	64.75(18)	Cu(6)#1-O(13)-Cu(4)	121.4(3)
O(5W)-Nd(3)-O(3)	71.0(2)	Cu(6)#1-O(13)-Nd(2)	107.1(2)
O(4W)-Nd(3)-O(3)	135.3(2)	Cu(4)-O(13)-Nd(2)	103.0(2)
O(52)-Nd(3)-O(7)	73.42(19)	Cu(6)-O(14)-Cu(5)	123.5(3)
O(32)-Nd(3)-O(7)	133.68(19)	Cu(6)-O(14)-Nd(3)	106.2(2)
O(71)-Nd(3)-O(7)	129.3(2)	Cu(5)-O(14)-Nd(3)	104.3(2)
O(14)-Nd(3)-O(7)	63.42(18)	O(71)-Nd(3)-O(2)	128.0(2)
O(5W)-Nd(3)-O(7)	136.5(2)	O(14)-Nd(3)-O(2)	95.96(18)
O(4W)-Nd(3)-O(7)	71.2(2)	O(5W)-Nd(3)-O(2)	74.2(2)
O(3)-Nd(3)-O(7)	97.13(18)	O(4W)-Nd(3)-O(2)	73.4(2)
O(52)-Nd(3)-O(2)	135.5(2)	O(3)-Nd(3)-O(2)	63.16(18)
O(32)-Nd(3)-O(2)	136.06(19)	O(7)-Nd(3)-O(2)	63.50(17)

Symmetry code: #1) −x, −y, −z+1

drogen 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 [16]. A summary of selected crystallographic data for **1** is given in Table 1. Selected bond lengths (Å) and bond angles (°) for **1** are given in Table 2. The graphic drawings were produced with SHELXTL [17].

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, deposition number: CCDC 211025. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Crystal structures

The crystal structure of **1** consists of a discrete octadecanuclear $[Cu_{12}Nd_6(OH)_{24}(bet)_{16}(NO_3)_3(H_2O)_{10}]^{15+}$ cation, nitrate anions, hexafluorophosphate anions and lattice water molecules. A perspective view of the cation in **1** is shown in Fig. 1, the skeleton of cation cluster is very similar to those documented for the pyrindinioacetate ones [11]. It possesses a $[Cu_{12}Nd_6(\mu_3\text{-}OH)_{24}]^{18+}$ core of pseudocubic O_h symmetry with six Nd^{III} atoms positioned at the vertices of a regular octahedron and twelve Cu^{II} atoms located at the midpoints of the twelve octahedral edges, as shown in Fig. 2. The polyhedron formed by the twelve Cu^{II} ions may be described as a cubic tetradecahedron containing eight trigonal and six square faces, that is capped on the six square faces by the six Nd^{III} atoms, so that a cuboctahedral metal skeleton is generated. This Cu-Nd metal framework is constructed by 24 μ_3-OH^- bridges that are each linked to one Nd^{III} (Nd−O 2.42-2.54 Å) and two Cu^{II} (Cu−O 1.94-2.02 Å) atoms, such that each $Nd(\mu_3\text{-}OH)_4$ fragment is square-pyramidal and each $Cu(\mu_3\text{-}OH)_4$ fragment is square-planar. In the surrounding of the cation core, there are sixteen bet, two nitrate and ten aqua ligands participated in coordination to the metal skeleton. Twelve of the sixteen bet bridge a Nd (Nd−O 2.42-2.52 Å) and a Cu (Cu−O 2.22-2.38 Å) atom by the μ_2-O,O′ carboxylate group, the other four bet each monodentately coordinates to a Nd atom (Nd−O 2.430, 2.476 Å), so that there are two types ofNd^{III} coordination environment: four Nd atoms at the equatorial plane of octahedron each is coordinated by four O atoms from μ_3-OH and two O atoms from two μ_2-O,O′ bet ligands, one O atom of a monodentate bet ligand and two aqua ligands (Nd−O 2.511-2.524 Å), to furnish a monocapped square-antipyrismatic nine-coordination geometry; except four μ_3-OH groups and two μ-carboxylate O atoms of bet, the other two Nd^{III} at apical position each is ligated by a bidentate nitrate anion (Nd−O 2.516, 2.587 Å) and an aqua ligand (Nd−O 2.511 Å), to form also a nine-coordination geometry. Besides four μ_3-OH groups coordinating at the basal plane, each Cu^{II} is ligated by a μ-carboxylate O atom at the apical position to form a square-

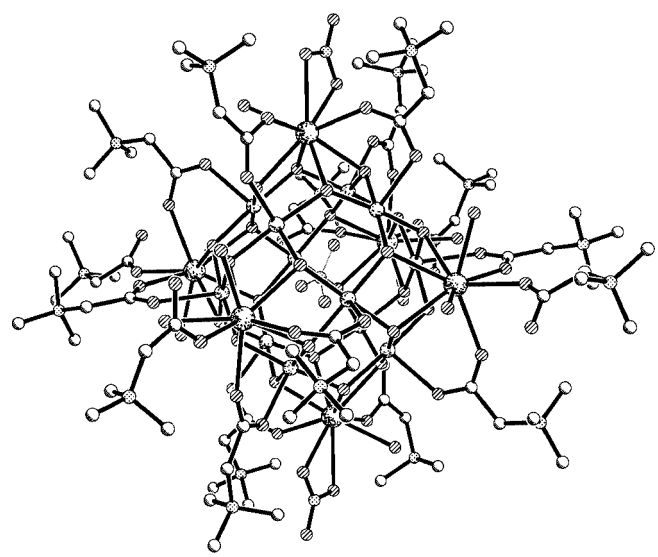

Fig. 1 Perspective view of $[Cu_{12}Nd_6(OH)_{24}(bet)_{16}(NO_3)_3(H_2O)_{10}]^{15+}$ cation in **1**.

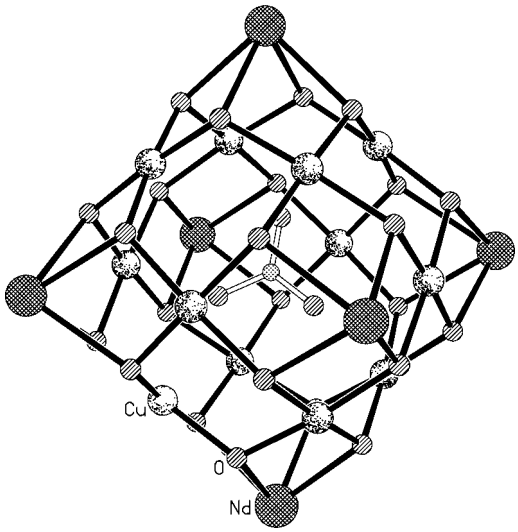

Fig. 2 Perspective view of the octadecanuclear skeleton consolidated by 24 μ_3-OH bridges in **1**.

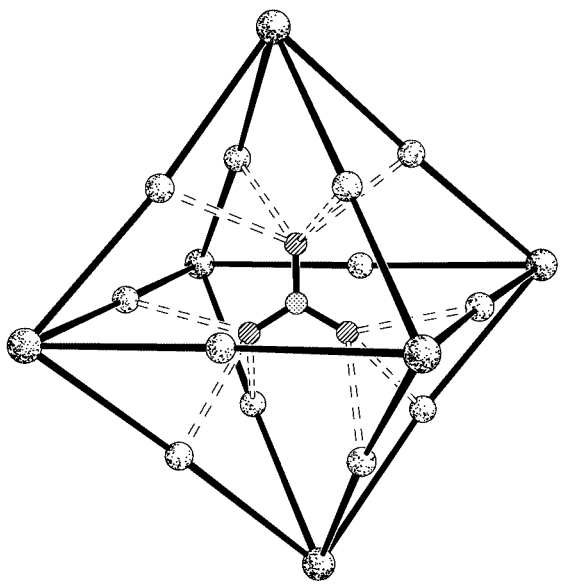

Fig. 3 Perspective view of the octahedral cage of $Cu_{12}Nd_6$ encapsulating a NO_3^- anion in **1**.

pyramidal geometry. In the cluster of **1**, each pair of the adjacent nonbonding Cu atoms are linked by a single hydroxy bridge with the Cu···Cu distances in the range of 3.38-3.46 Å. Each Nd^{III} atom is linked to four adjacent Cu^{II} atoms by four μ_3-OH^- bridges with nonbonding Cu···Nd separations of 3.48-3.62 Å, and each pair of Nd^{III} atoms in each edge of the octahedron are separated at distances of 7.06-7.17 Å.

It is noted that the cation of **1** encapsulates a nitrate anion at the center of the octahedral $Cu^{II}{}_{12}Nd^{III}{}_6$ cage. As shown in Fig. 3, the nitrate anion exhibits a multi-coordinating mode with each of its O atoms weakly ligating three or four Cu^{II} atoms of the cage at the distances of 2.45-2.98 Å. This supramolecular phenomenon is similar to that in an icosanuclear $Cu_{12}La_8$ cluster reported by *Winpenny* et al. [18], analogous phenomenon has also been observed in our previous octadecanuclear $[Cu_{12}Sm_6(\mu_3\text{-}OH)_{24}(pyb)_{12}(H_2O)_{18}(\mu_9\text{-}NO_3)]^{17+}$ cluster [11], which structure was characterized by low temperature (168 K) X-ray diffraction, and the encapsulated μ_9-NO_3^- was hardly disordered.

Of the 5 symmetry-independent lattice water molecules, three are disordered with respect to a nitrate anion, the weak or none coordinating nitrate anions are some disordered. The lattice water molecules are involved in hydrogen bonding interactions with the hydroxy groups, carboxylic groups, hexafluorophosphate groups or other water molecules, the distance between donor and accepter is 2.55−3.15 Å for O···O, or 2.81−3.11 Å for O···F. The hydrogen bonds also furnish a three-dimensional network.

Synthesis

Acidity of the reaction solution is critically important, a change in acidity of the reaction solution can cause a drastic change in the structures of the products. In our previous work, with the very similar reaction condition, but a slight low in pH value of the reaction solutions (pH ≈ 3.5), the tetranuclear complexes of$[Cu_2Ln_2(bet)_{10}(H_2O)_8](ClO_4)_{10}\cdot 2H_2O$ (Ln^{3+} = La^{3+}, Ce^{3+} or Gd^{3+}) and $[Cu_2Ln_2(bet)_{12}\text{-}(ClO_4)_2](ClO_4)_8$ (Ln^{3+} = Gd^{3+} or Sm^{3+}) are synthesized, all of they feature a centrosymmetric tetranuclear Cu_2Ln_2 cation [10], elevating the pH value to 6, the octadecanuclear cluster was assembled.The variation of the stoichiometry of the starting materials is less effected on crystal structure of products, in betaine reaction system, the starting materials in the ratio from 1: 1 to 1: 4 for Cu^{II} : Ln^{III} may lead to tetranuclear or octadecanuclear cluster, in the tetranuclear system the ratio of 1:1 for Cu^{II} : Ln^{III} produces higher yield, but in the octadecanuclear system the ratio of 1: 3 for Cu^{II} : Ln^{III} always gives a better yield.

Acknowledgements. This work was supported by the NSFC (29625102) and Ministry of Education of China and the University of Malaya (PJP 0758/2001A).

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