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FULL PAPER

Synthesis and structures of carboxylate-bridged polynuclear copper(II)–lanthanide(III) complexes $[CuLn(C_5H_5N^+CH_2CO_2^-)_5(H_2O)_5][ClO_4]_5\cdot2H_2O$ (Ln = La or Nd) and $[Cu_3Nd_2(C_5H_5N^+CH_2CO_2^-)_{10}(NO_3)_2(H_2O)_8][ClO_4]_{10}\cdot4H_2O$

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Received 25th January 1999, Accepted 23rd April 1999

Two types of carboxylate-bridged copper(II)–lanthanide(III) complexes, $[CuLn(C_5H_5N^+CH_2CO_2^-)_5(H_2O)_5][ClO_4]_5\cdot2H_2O$ **1** ($Ln^{III} = La^{III}$ **a** or Nd^{III} **b**) and $[Cu_3Nd_2(C_5H_5N^+CH_2CO_2^-)_{10}(NO_3)_2(H_2O)_8][ClO_4]_{10}\cdot4H_2O$ **2**, have been synthesized and characterized by X-ray structural analysis. Complexes **1a** and **1b** are isomorphous. In both, a Cu^{II} atom is quadruply bridged to a Ln^{III} atom by four μ-carboxylate groups at the basal positions, and co-ordinated by an aqua ligand at the apical position to form a square-pyramidal $CuO_4(OH_2)$ geometry, while the Ln^{III} atom is co-ordinated in a monocapped square antiprism by five carboxy oxygen atoms and four aqua ligands. In **2**, a pair of Cu^{II} atoms in two centrosymmetrically related tetrakis(μ-carboxylate)-bridged dinuclear $Cu^{II}Nd^{III}$ subunits is each linked to the central Cu^{II} atom by a single *syn-anti* μ-carboxylate bridge, resulting in a pentanuclear cation. The central Cu^{II} atom is co-ordinated by two carboxy oxygen atoms and two aqua ligands in a distorted square-planar fashion; the other two Cu^{II} atoms adopt the same square-pyramidal geometry, each being ligated by the four oxygen atoms from the quadruple carboxylate bridges at the basal plane and by one oxygen atom of the *syn-anti* μ-carboxylate group at the apical position. The Nd^{III} atom is co-ordinated in a distorted monocapped square antiprism by the four carboxy oxygen atoms, three aqua ligands and a chelate nitrate group.

We have recently found that the stable $[Cu(betaine)_4]^{2+}$ core found in the monomeric copper(II) tetracarboxylates (betaine = trimethylammonioacetate, $Me_3N^+CH_2CO_2^-$)[1] 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. Since lanthanide(III) ions (designated as Ln^{III} hereafter) are very similar to hard calcium ions in co-ordination chemistry, the above-mentioned interesting strategy can also be applied to the preparations of carboxylate-bridged heterometallic tetranuclear $Cu^{II}_2Ln^{III}_2$ compounds.[3] Heterometallic compounds consolidated by carboxylate groups have not been well documented;[4] only a few examples of heteronuclear Cu^{II}–Ln^{III} compounds have very recently been uncovered.[3,5,6] This may be attributed to the fact that Cu^{II} and Ln^{III} are very different in co-ordination ability. Therefore heteronuclear Cu^{II}–Ln^{III} compounds have commonly been synthesized with hetero-donor ligands comprising two types of ligating atoms (such as N and O) co-ordinated each to Cu and Ln atoms, respectively, which are currently of interest because of the magnetic interaction between transition and rare-earth metal ions in bridged systems, and their possible application in production of high temperature superconductors.[7–9]

We have recently reported a series of polynuclear Cu^{II}–Ln^{III} complexes containing chloroacetate, betaine and its derivatives, including tetranuclear $Cu^{II}_2Ln^{III}_2$,[3] pentanuclear $Cu^{II}_3Ln^{III}_2$,[5] octadecanuclear $Cu^{II}_{12}Ln^{III}_6$ clusters.[10,11] At high pH hydroxide participates in co-ordination, resulting in the formation of the octadecanuclear $Cu^{II}_{12}Ln^{III}_6$ clusters.[10,11] We expect that at low pH the $[Cu(carboxylate)_4]$ core can bind a Ln^{III} to form a stable dimeric $[CuLn(carboxylate)_4]$ compound, although the tetranuclear compounds have been isolated in the cases of betaine.[3] In this paper we document the synthesis and structures of the first tetrakis(μ-carboxylate)-bridged dinuclear $Cu^{II}Ln^{III}$ compounds of pyridinioacetate ($C_5H_5N^+CH_2CO_2^-$, designated as pyb hereafter) and a pentanuclear compound consisting of two $[CuLn(carboxylate)_4]$ cores, namely $[CuLn(pyb)_5(H_2O)_5][ClO_4]_5\cdot2H_2O$ **1** ($Ln^{III} = La^{III}$ **a** or Nd^{III} **b**) and $[Cu_3Nd_2(pyb)_{10}(NO_3)_2(H_2O)_8][ClO_4]_{10}\cdot4H_2O$ **2**.

Experimental

Pyridinioacetate was synthesized by the literature method.[12] Other reagents were commercially available and used as received. The 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 4000–400 cm⁻¹ on a Nicolet 5DX spectrometer.

CAUTION. Metal perchlorates containing organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with great care.

Preparation of compounds

$[CuLa(pyb)_5(H_2O)_5][ClO_4]_5\cdot2H_2O$ 1a. A mixture of pyb (3.0 mmol) and $Cu(NO_3)_2$ (0.5 mmol) was dissolved in distilled water (5 cm^3) and heated at 60 °C for 10 min, $La(NO_3)_3$ (1.0 mmol) was then added followed by an aqueous solution (2 cm^3) of $NaClO_4$ (5 mmol) upon stirring for 10 min. The resulting blue solution was adjusted to pH 2.5 and allowed to stand in air at room temperature for about 10, yielding blue prismatic crystals (*ca.* 20% yield) (Calc. for $C_{35}H_{49}Cl_5CuLaN_5O_{37}$: C, 27.81; H, 3.27; N, 4.63. Found: C, 28.04; H, 3.02; N, 4.83%). IR data for the carboxylate groups ($\tilde{\nu}$/cm⁻¹): 1688 (sh), 1637s and 1405vs.

Table 1 Crystallographic data for complexes **1a, 1b** and **2**

	1a	**1b**	**2**
Formula	$C_{35}H_{49}Cl_5CuLaN_5O_{37}$	$C_{35}H_{49}Cl_5CuN_5NdO_{37}$	$C_{70}H_{94}Cl_{10}Cu_3N_{12}Nd_2O_{78}$
M	1511.49	1516.82	3185.17
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a/Å	37.950(8)	37.51(2)	11.410(4)
b/Å	11.286(2)	11.172(2)	14.992(6)
c/Å	27.859(6)	27.557(14)	18.447(7)
α/°			73.380(10)
β/°	104.70(3)	104.810(10)	72.140(10)
γ/°			88.900(10)
U/Å^3	11542(4)	11166(9)	2869.8(19)
Z	8	8	1
μ/cm^{-1}	14.35	16.48	17.89
$R1/wR2$ ($I > 2\sigma$)	0.0539/0.1506	0.0657/0.1566	0.0497/0.1187
(all data)	0.0964/0.1773	0.1157/0.1850	0.0728/0.1317

[CuNd(pyb)$_5$(H$_2$O)$_5$][ClO$_4$]$_5$·2H$_2$O 1b. This was prepared as for complex **1a** (Calc. for $C_{35}H_{49}Cl_5CuN_5NdO_{37}$: C, 28.19; H, 3.10; N, 4.81. Found: C, 28.39; H, 3.06; N, 4.73%). IR data for the carboxylate groups ($\tilde{\nu}$/cm^{-1}): 1688 (sh), 1630vs and 1405vs.

[Cu$_3$Nd$_2$(pyb)$_{10}$(NO$_3$)$_2$(H$_2$O)$_8$][ClO$_4$]$_{10}$·4H$_2$O 2. This was prepared similarly to complex **1a**, but the blue solution was adjusted to pH 3.0, yielding deep blue polyhedral crystals after two weeks (Calc. for $C_{70}H_{94}Cl_{10}Cu_3N_{12}Nd_2O_{78}$: C, 26.40; H, 2.97; N, 5.28. Found: C, 26.25; H, 3.05; N, 5.31%). IR data for the carboxylate groups ($\tilde{\nu}$/cm^{-1}): 1686s, 1637s and 1405s.

X-Ray crystallography

A summary of selected crystallographic data for the three compounds is given in Table 1. The data collections were carried out on a Siemens R3m diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at 293(2) K. For each complex, 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 120 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]

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.[14] All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were held stationary and included in the final stage of full-matrix least-squares refinement based on F^2 using the SHELXL 97 program package.[15] Analytical expressions of the neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16] Selected bond lengths and bond angles are listed in Tables 2 and 3.

CCDC reference number 186/1436.

See http://www.rsc.org/suppdata/dt/1999/2005/ for crystallographic files in .cif format.

Results and discussion

Crystal structures

[CuLa(pyb)$_5$(H$_2$O)$_5$][ClO$_4$]$_5$·2H$_2$O 1a. The crystal structure of complex **1a** consists of discrete dinuclear [CuLa(pyb)$_5$(H$_2$O)$_5$]$^{5+}$ cation, perchlorate anions and lattice water molecules. An ORTEP[17] view of the dimeric cation is shown in Fig. 1. The Cu^{II} atom is co-ordinated by four carboxylate oxygen atoms at the basal plane [Cu(1)–O 1.929(4)–1.998(4) Å] (Table 2) and completed by an aqua ligand at the apical position [Cu(1)–O(5w) 2.232(4) Å] to form a square-pyramidal geometry. The La^{III} atom is quadruply bridged to the Cu^{II} atom by four μ-carboxylate bridges of pyb ligands [La(1)–O 2.525(4)–2.549(4) Å], giving rise to a dinuclear cation with the intramolecular Cu$^{II}\cdots$La^{III} distance of 3.764(2) Å. This dinuclear structure is similar to that found for the tetranuclear [Cu$^{II}_2$Ln$^{II}_2$(betaine)$_{10}$(H$_2$O)$_8$][ClO$_4$]$_{10}$·2H$_2$O (Ln = La, Ce or Gd),[3] and somewhat similar to those of the well known [Cu$_2$(μ-carboxylate)$_4$] complexes.[18] Except for the four μ-carboxylate oxygen atoms, the La^{III} atom is further co-ordinated by one monodentate carboxylate oxygen atom [La(1)–O(51) 2.487(4) Å] and four aqua ligands [La(1)–O = 2.556(5)–2.630(4) Å] to form nine-co-ordination. The co-ordination polyhedron about the La^{III} ion can be best described as a distorted monocapped square antiprism; one square face consists of one oxygen atom [O(51)] of the monodentate carboxylate group and three aqua oxygen atoms [O(1w), O(2w) and O(4w)], whereas the other face is defined by four carboxylate oxygen atoms [O(12), O(22), O(32) and O(42)] from the quadruple μ-carboxylate bridges between the pair of Cu^{II} and La^{III} atoms. The dihedral angle between the square faces is *ca.* 5°.

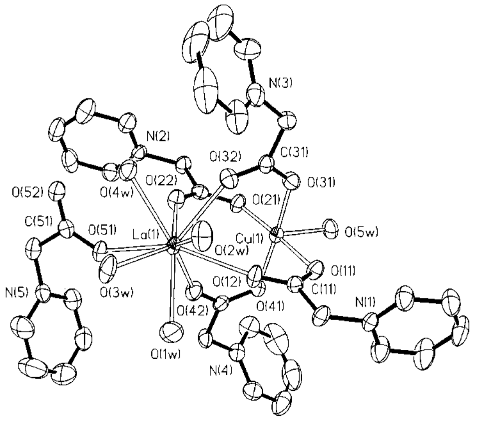

Fig. 1 An ORTEP view showing the dinuclear cation in complex **1a**.

[CuNd(pyb)$_5$(H$_2$O)$_5$][ClO$_4$]$_5$·2H$_2$O 1b. The crystal structure of complex **1b** is isomorphous to that of **1b**, only very small metric differences having been observed for the two complexes. Owing to the slightly smaller radius of Nd^{III} than that of La^{III},[19] all the metal–ligand bonds in **1b** are slightly shorter than the corresponding bonds in **1a**, as compared in Table 2, however the bond angles in both are almost the same. It is noteworthy that only one dinuclear Cu^{II}Ln^{III} compound has recently been reported so far,[20] in which a pair of Cu^{II} and La^{III} atoms are chelated by a polydentate Schiff base containing μ-phenoxy bridges. Therefore, **1a** and **1b** are novel dinuclear Cu^{II}Ln^{III} compounds with the pair of metal atoms bridged uniquely by carboxylate groups.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1a** and **1b**

	1a	**1b**		**1a**	**1b**
Ln(1)–O(51)	2.487(4)	2.418(5)	Ln(1)–O(42)	2.525(4)	2.454(5)
Ln(1)–O(12)	2.526(4)	2.459(5)	Ln(1)–O(32)	2.535(4)	2.469(5)
Ln(1)–O(22)	2.549(4)	2.478(5)	Ln(1)–O(1w)	2.556(5)	2.459(6)
Ln(1)–O(4w)	2.606(4)	2.506(5)	Ln(1)–O(3w)	2.608(4)	2.543(5)
Ln(1)–O(2w)	2.630(4)	2.542(6)	Cu(1)–O(21)	1.929(4)	1.920(5)
Cu(1)–O(31)	1.968(4)	1.939(5)	Cu(1)–O(11)	1.983(4)	1.962(5)
Cu(1)–O(41)	1.998(4)	1.965(5)	Cu(1)–O(5w)	2.232(4)	2.229(5)
O(51)–Ln(1)–O(42)	79.77(13)	78.47(17)	O(51)–Ln(1)–O(12)	149.78(14)	148.51(18)
O(42)–Ln(1)–O(12)	72.07(13)	72.36(17)	O(51)–Ln(1)–O(32)	130.16(13)	131.61(18)
O(42)–Ln(1)–O(32)	108.89(12)	110.10(16)	O(12)–Ln(1)–O(32)	71.15(13)	71.32(17)
O(51)–Ln(1)–O(22)	71.68(13)	71.38(17)	O(42)–Ln(1)–O(22)	68.62(13)	69.21(17)
O(12)–Ln(1)–O(22)	106.79(12)	107.89(16)	O(32)–Ln(1)–O(22)	67.15(13)	68.38(17)
O(51)–Ln(1)–O(1w)	90.97(16)	89.8(2)	O(42)–Ln(1)–O(1w)	68.92(15)	68.8(2)
O(12)–Ln(1)–O(1w)	69.04(15)	68.9(2)	O(32)–Ln(1)–O(1w)	138.57(15)	138.3(2)
O(22)–Ln(1)–O(1w)	136.26(16)	136.6(2)	O(51)–Ln(1)–O(4w)	73.37(13)	74.60(18)
O(42)–Ln(1)–O(4w)	140.17(13)	140.87(18)	O(12)–Ln(1)–O(4w)	136.41(13)	136.63(17)
O(32)–Ln(1)–O(4w)	70.04(12)	70.32(17)	O(22)–Ln(1)–O(4w)	75.23(12)	75.54(17)
O(1w)–Ln(1)–O(4w)	138.88(14)	137.76(18)	O(51)–Ln(1)–O(3w)	70.18(14)	69.91(19)
O(42)–Ln(1)–O(3w)	124.55(15)	124.5(2)	O(12)–Ln(1)–O(3w)	117.70(14)	118.10(18)
O(32)–Ln(1)–O(3w)	126.23(14)	125.15(19)	O(22)–Ln(1)–O(3w)	135.51(13)	134.01(17)
O(1w)–Ln(1)–O(3w)	66.27(15)	66.7(2)	O(4w)–Ln(1)–O(3w)	72.64(14)	71.06(19)
O(51)–Ln(1)–O(2w)	134.94(13)	134.97(18)	O(42)–Ln(1)–O(2w)	137.37(14)	137.63(18)
O(12)–Ln(1)–O(2w)	67.52(13)	67.73(18)	O(32)–Ln(1)–O(2w)	70.31(14)	69.89(18)
O(22)–Ln(1)–O(2w)	136.24(14)	136.84(19)	O(1w)–Ln(1)–O(2w)	84.23(18)	83.9(2)
O(4w)–Ln(1)–O(2w)	81.28(14)	80.65(19)	O(3w)–Ln(1)–O(2w)	66.92(14)	66.67(19)
O(21)–Cu(1)–O(31)	91.52(17)	91.4(2)	O(21)–Cu(1)–O(11)	176.98(15)	176.8(2)
O(31)–Cu(1)–O(11)	89.42(16)	89.6(2)	O(21)–Cu(1)–O(41)	89.19(16)	89.2(2)
O(31)–Cu(1)–O(41)	174.51(14)	173.83(19)	O(11)–Cu(1)–O(41)	89.60(16)	89.5(2)
O(21)–Cu(1)–O(5w)	93.84(15)	94.1(2)	O(31)–Cu(1)–O(5w)	95.09(15)	95.6(2)
O(11)–Cu(1)–O(5w)	88.94(15)	88.9(2)	O(41)–Cu(1)–O(5w)	90.29(14)	90.5(2)
C(11)–O(12)–Ln(1)	160.5(4)	160.5(5)	C(11)–O(11)–Cu(1)	111.7(3)	110.5(4)
C(21)–O(21)–Cu(1)	126.9(3)	126.4(5)	C(21)–O(22)–Ln(1)	141.1(3)	140.8(5)
C(31)–O(31)–Cu(1)	122.8(3)	122.7(5)	C(31)–O(32)–Ln(1)	146.3(3)	146.3(5)
C(41)–O(41)–Cu(1)	118.2(3)	118.3(4)	C(41)–O(42)–Ln(1)	150.8(4)	150.5(5)
C(51)–O(51)–Ln(1)	139.6(4)	139.5(5)			

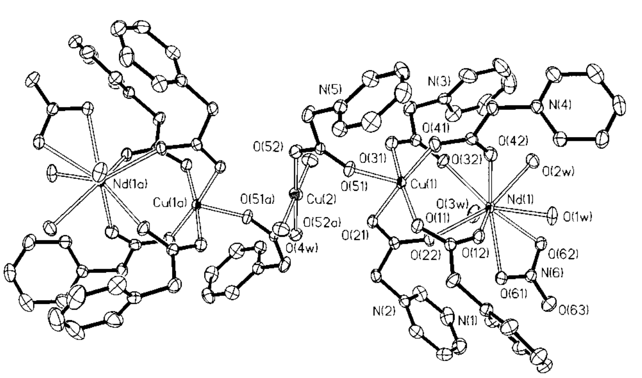

Fig. 2 An ORTEP view showing the pentanucler cation in complex **2**. Symmetry code: a −*x*, 1 − *y*, −*z*.

$[Cu_3Nd_2(pyb)_{10}(NO_3)_2(H_2O)_8][ClO_4]_{10}\cdot 4H_2O$ 2. The crystal structure of complex **2** consists of a centrosymmetrical pentanuclear $[Cu_3Nd_2(pyb)_{10}(NO_3)_2(H_2O)_8]^{10+}$ cation, perchlorate anions and lattice water molecules. As shown in Fig. 2, each Nd^{III} atom is quadruply bridged to a Cu^{II} atom by four *syn-syn* μ-carboxylate bridges of pyb ligands with an intramolecular $Cu^{II}\cdots Nd^{III}$ separation of 3.650(2) Å, resulting in a dinuclear $Cu^{II}Nd^{III}$ subunit, which is similar to those found in **1**. Besides the four carboxy oxygen atoms [Nd(1)–O 2.394(3)–2.440(3) Å] (Table 3), the co-ordination sphere of the Nd^{III} atom is completed by a bidentate nitrate group [Nd(1)–O 2.539(4) or 2.636(3) Å] and three aqua ligands [Nd(1)–O 2.449(3)–2.499(4) Å] to form a monocapped square-antiprism nine-co-ordination geometry. The Cu(1) atom in the subunit is ligated in a distorted square pyramid with the four oxygen atoms [Cu(1)–O 1.945(3)–1.981(3) Å] from the quadruple μ-carboxylate bridges at the basal plane and one oxygen atom from another carboxylate bridge at the apical position [Cu–O 2.154(3) Å]. A pair of Cu^{II} atoms in two centrosymmetrically related dinuclear $Cu^{II}Nd^{III}$ subunits are each linked to the central Cu(2) atom by a single *syn-anti* μ-carboxylate bridge, resulting in a centrosymmetrical pentanuclear cation. The Cu(2) atom, being located at the crystallographic inversion centre, is co-ordinated by two oxygen atoms of the carboxylate groups and two aqua oxygen atoms in a slightly distorted square-planar fashion with the O(4w)–Cu(2)–O(52) angle at 89.34(16)° and Cu(2)–O bonds at 1.912(3)–1.918(3) Å; the *trans*-related O(21) and O(21a) atoms are in close contact with the Cu(2) atom [Cu(2)···O(21) 2.828(3) Å], indicative of some weak interaction.[2] It is noteworthy that the central Cu(2) atom is linked to the Cu(1) atoms of both $Cu^{II}Nd^{III}$ subunits with the Cu(1)···Cu(2) distance of 3.837(2) Å, different from that of a pentanuclear $Cu^{II}_3Gd^{III}_2$ cluster bridged by chloroacetate groups.[5] In the chloroacetate compound the central Cu^{II} atom is linked to the Gd^{III} atoms in both of tetrakis(μ-carboxylate)-bridged $Cu^{II}Gd^{III}$ subunits by two *syn-anti* μ-carboxylate bridges, and the co-ordination sphere of this central Cu^{II} atom is completed by two monodentate carboxylate groups to form a distorted square-planar geometry.

Synthesis

Acidity of the reaction solution is critically important. Although it is difficult to explain, a subtle change in acidity of the reaction mixture can cause a drastic change in the structures of the products. Both complexes **1** and **2** are synthesized under similar conditions with a slight difference in pH values of the solutions; at low pH (pH < 3) the $[Cu(pyb)_4]^{2+}$ core can bind a Ln^{III} to form a dinuclear $[CuLn(pyb)_4]^{5+}$ core as found in **1**, which can be connected to construct larger clusters as found in **2**. At higher pH (≥3.5) hydroxide anions may participate in co-ordination to form

Table 3 Selected bond lengths (Å) and bond angles (°) for complex **2**

Nd(1)–O(22)	2.394(3)	Cu(1)–O(41)	1.945(3)
Nd(1)–O(32)	2.402(3)	Cu(1)–O(11)	1.954(4)
Nd(1)–O(42)	2.411(3)	Cu(1)–O(31)	1.969(4)
Nd(1)–O(12)	2.440(3)	Cu(1)–O(21)	1.981(3)
Nd(1)–O(1w)	2.449(3)	Cu(1)–O(51)	2.154(3)
Nd(1)–O(2w)	2.470(4)	Cu(2)–O(4w)	1.913(4)
Nd(1)–O(3w)	2.499(4)	Cu(2)–O(52)	1.918(3)
Nd(1)–O(61)	2.539(4)	Nd(1)–O(62)	2.636(3)
O(22)–Nd(1)–O(32)	73.74(13)	O(41)–Cu(1)–O(11)	90.96(16)
O(22)–Nd(1)–O(42)	110.40(11)	O(41)–Cu(1)–O(31)	89.00(17)
O(32)–Nd(1)–O(42)	70.60(13)	O(11)–Cu(1)–O(31)	172.67(13)
O(22)–Nd(1)–O(12)	70.31(12)	O(41)–Cu(1)–O(21)	174.65(13)
O(32)–Nd(1)–O(12)	113.67(11)	O(11)–Cu(1)–O(21)	88.65(15)
O(42)–Nd(1)–O(12)	72.57(12)	O(31)–Cu(1)–O(21)	90.71(15)
O(22)–Nd(1)–O(1w)	134.09(13)	O(41)–Cu(1)–O(51)	92.52(13)
O(32)–Nd(1)–O(1w)	142.90(13)	O(11)–Cu(1)–O(51)	90.79(13)
O(42)–Nd(1)–O(1w)	75.60(13)	O(31)–Cu(1)–O(51)	96.53(14)
O(12)–Nd(1)–O(1w)	68.63(11)	O(21)–Cu(1)–O(51)	92.82(12)
O(22)–Nd(1)–O(2w)	149.21(13)	O(4w)–Cu(2)–O(52)	89.34(16)
O(32)–Nd(1)–O(2w)	81.67(12)	O(22)–Nd(1)–O(62)	112.35(11)
O(42)–Nd(1)–O(2w)	77.41(12)	O(32)–Nd(1)–O(62)	131.83(12)
O(12)–Nd(1)–O(2w)	138.31(12)	O(42)–Nd(1)–O(62)	136.01(11)
O(1w)–Nd(1)–O(2w)	76.41(13)	O(12)–Nd(1)–O(62)	113.03(11)
O(22)–Nd(1)–O(3w)	76.31(13)	O(1w)–Nd(1)–O(62)	67.61(12)
O(32)–Nd(1)–O(3w)	69.93(12)	O(2w)–Nd(1)–O(62)	71.34(12)
O(42)–Nd(1)–O(3w)	135.84(14)	O(3w)–Nd(1)–O(62)	65.97(12)
O(12)–Nd(1)–O(3w)	143.09(13)	O(61)–Nd(1)–O(62)	48.72(11)
O(1w)–Nd(1)–O(3w)	132.02(11)	O(12)–Nd(1)–O(61)	75.47(11)
O(2w)–Nd(1)–O(3w)	78.06(13)	O(1w)–Nd(1)–O(61)	79.34(13)
O(22)–Nd(1)–O(61)	71.27(11)	O(2w)–Nd(1)–O(61)	120.04(11)
O(32)–Nd(1)–O(61)	137.75(12)	C(11)–O(11)–Cu(1)	124.9(3)
O(3w)–Nd(1)–O(61)	79.35(13)	C(21)–O(21)–Cu(1)	113.1(3)
O(42)–Nd(1)–O(61)	144.79(13)	C(21)–O(21)–Cu(2)	139.9(3)
N(6)–O(61)–Nd(1)	99.0(3)	Cu(1)–O(21)–Cu(2)	104.50(12)
N(6)–O(62)–Nd(1)	94.1(2)	C(31)–O(31)–Cu(1)	117.7(3)
C(11)–O(12)–Nd(1)	140.2(3)	C(41)–O(41)–Cu(1)	124.5(3)
C(21)–O(22)–Nd(1)	157.0(3)	C(51)–O(51)–Cu(1)	133.9(3)
C(31)–O(32)–Nd(1)	150.9(3)	C(51)–O(52)–Cu(2)	123.8(3)
C(41)–O(42)–Nd(1)	142.8(3)		

larger clusters, and the formation of octadecanuclear clusters[10] may be promoted.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (29625102) and Science Foundation of Guangdong. We are also indebted to the Chemistry Department of the Chinese University of Hong Kong for donation of the diffractometer.

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Paper 9/00647H