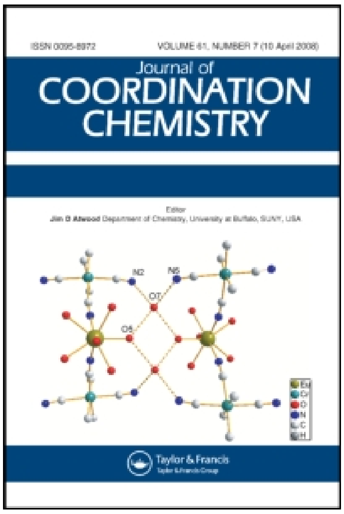

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

New 1D and 2D metal oxygen connectivities in Cu(II) succinato and glutarato coordination polymers: $[Cu_3(H_2O)_2(OH)_2(C_4H_4O_4)_2] \cdot 4H_2O$, $[Cu_4(H_2O)_2(OH)_4(C_4H_4O_4)_2] \cdot 5H_2O$ and $[Cu_5(OH)_6(C_5H_6O_4)_2] \cdot 4H_2O$

Yue-Qing Zheng[a]; Jian-Li Lin[a]
[a] State Key Laboratory Base of Novel Functional Materials and Preparation Science, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo, P. R. China

To cite this Article Zheng, Yue-Qing and Lin, Jian-Li(2008) 'New 1D and 2D metal oxygen connectivities in Cu(II) succinato and glutarato coordination polymers: $[Cu_3(H_2O)_2(OH)_2(C_4H_4O_4)_2] \cdot 4H_2O$, $[Cu_4(H_2O)_2(OH)_4(C_4H_4O_4)_2] \cdot 5H_2O$ and $[Cu_5(OH)_6(C_5H_6O_4)_2] \cdot 4H_2O$', Journal of Coordination Chemistry, 61: 21, 3420 — 3437
To link to this Article: DOI: 10.1080/00958970802061156
URL: http://dx.doi.org/10.1080/00958970802061156

Journal of Coordination Chemistry
Vol. 61, No. 21, 10 November 2008, 3420–3437

New 1D and 2D metal oxygen connectivities in Cu(II) succinato and glutarato coordination polymers: $[Cu_3(H_2O)_2(OH)_2(C_4H_4O_4)_2]\cdot 4H_2O$, $[Cu_4(H_2O)_2(OH)_4(C_4H_4O_4)_2]\cdot 5H_2O$ and $[Cu_5(OH)_6(C_5H_6O_4)_2]\cdot 4H_2O$

YUE-QING ZHENG* and JIAN-LI LIN

State Key Laboratory Base of Novel Functional Materials and Preparation Science,
Faculty of Materials Science and Chemical Engineering, Ningbo University,
Ningbo, 315211, P. R. China

(*Received 28 September 2007; in final form 19 November 2007*)

Two Cu(II) hydroxo succinates $[Cu_3(H_2O)_2(OH)_2(C_4H_4O_4)_2]\cdot 4H_2O$ (**1**) and $[Cu_4(H_2O)_2(OH)_4(C_4H_4O_4)_2]\cdot 5H_2O$ (**2**) and one Cu(II) hydroxo glutarate $[Cu_5(OH)_6(C_5H_6O_4)_2]\cdot 4H_2O$ (**3**) have been prepared and structurally characterized by single crystal X-ray diffraction methods. They feature 1D and 2D copper oxygen connectivity of elongated $\{CuO_6\}$ octahedra in "4+1+1" and "4+2" coordination geometries. Within **1**, linear trimers of three edge-sharing $\{CuO_6\}$ octahedra are connected into copper oxygen chains, which are bridged by the anti conformational succinate anions to generate 2D layers with mono terminally coordinating gauche succinate anions on both sides. The layers are assembled into a 3D framework by interlayer hydrogen bonds with lattice H_2O molecules distributed in channels. Different from **1**, the principal building units in **2** are linear tetramers of four edge-sharing $\{CuO_6\}$ octahedra. The tetramers are condensed into copper oxygen chains and the succinate anions interlink them into a 3D framework with triangular channels filled by lattice H_2O molecules. The $\{CuO_6\}$ octahedra in **3** are edge-shared to form unprecedented 2D inorganic layers with mono terminally coordinating glutarate anions on both sides. Interlayer hydrogen bonding interactions are responsible for supramolecular assembly of the layers into a 3D framework with lattice H_2O molecules in the channels. The inorganic layers in **3** can be described as hexagonal close packing of oxygen atoms with the Cu atoms in the octahedral cavities. The title compounds were further characterized by elemental analyses, IR spectra and thermal analyses.

Keywords: Copper; Copper oxygen connectivity; Coordination polymers; Dicarboxylates; X-ray structures

1. Introduction

Coordination polymers built up of transition metals and organic ligands [1] offer significant scientific and technological opportunities by combining attractive features of both inorganic and organic moieties within a single material. By judicious choice of

---

*Corresponding author. Email: zhengcm@nbu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802061156

ligand and metal coordination geometries, control over the topology and geometry of the infinite networks can be achieved. Additionally, more subtle conditions such as choice of solvent or counter ion can also be used to modify structures. Such control could allow deliberate design of materials with a range of useful properties including electronic properties, magnetic properties, microporosity, non-linear optical effects, luminescent properties, molecular-based magnetism and hydrogen storage [1, 2].

Coordination polymers based on self-assembly of polycarboxylate anions and metal ions have aroused enormous attention [3]. Our research has focused on construction of coordination polymers by exploiting saturated aliphatic α,ω-dicarboxylate ligands, which have conformational versatility. Self-assembly of metal cations and α,ω-dicarboxylate anions under mild conditions affords a variety of supramolecular motifs featuring discrete metal-oxygen polyhedra interconnected by organic spacers to form 1D polymeric chains [4], 2D layers [5] and 3D frameworks [6], and under hydrothermal conditions tends to give polymeric coordination compounds with metal oxygen connectivity of metal oxygen polyhedra. For example, oligomeric metal oxygen connectivity has been observed in hydrothermally synthesized $Co(H_2O)_2(C_4H_4O_4)$ [7], which can be visualized as substitution of the linear trimer of three edge-sharing $\{CoO_6\}$ octahedra for the discrete $\{CoO_6\}$ octahedra in polymeric chains in $Co(H_2O)_4(C_4H_4O_4)$ [4d, 8], which could be easily obtained under mild ambient conditions [4d]. The 1D zigzag metal oxygen connectivity of corner-sharing Mn oxygen bi-octahedra are present in a family of Mn dicarboxylates $Mn_2(H_2O)(O_2C(CH_2)_nCO_2)$ with $n = 3–12$ [9], and 2D metal oxygen connectivity was found in a series of hydrothermally prepared cobalt hydroxo succinate polymers $Co_4(OH)_2(H_2O)_2(C_4H_4O_4)_3 \cdot 2H_2O$, $Co_5(OH)_2(C_4H_4O_4)_4$ and $Co_6(OH)_2(C_4H_4O_4)_5 \cdot H_2O$ with the layers pillared by dicarboxylate anions [10]. Furthermore, a 3D metal oxygen connectivity of $\{NiO_6\}$ octahedra was reported for an open Ni(II) succinate $[Ni_7(C_4H_4O_4)_6(OH)_2(H_2O)_2] \cdot 2H_2O$, which was obtained by using bi-phasic solvothermal reaction [11].

Our previous investigation indicated that hydrothermal conditions are not a prerequisite to formation of 1D, 2D and 3D metal-oxygen-metal connectivity in transition metal dicarboxylates [7]. For example, a cobalt hydroxo succinate $Co_3(OH)_2(C_4H_4O_4)_2 \cdot 10H_2O$ possesses 1D metal oxygen chains generated from edged-sharing $\{Co_2O_{10}\}$ bioctahedra corner-bridged by $\{CoO_6\}$ octahedra and a 3D open framework is built by connection of succinato ligands [12]. However, self-assembly of Co^{2+} cations with glutarate anions under ambient conditions yielded a 3D coordination polymer with discrete metal oxygen tetrahedra interlinked by dicarboxylato ligands [13]. Intensive investigation on the cobalt succinate system has been performed. However, the copper dicarboxylate system is far less investigated. Ambient aqueous self-assembly of Cu^{2+} ions and succinate ions gave $Cu(C_4H_4O_4) \cdot 2H_2O$ and $Cu(C_4H_4O_4) \cdot H_2O$ [14]. In the former, paddle-wheel dimeric Cu_2 units are doubly bridged by *bis*-bidentate gauche succinate anions to generate 1D chains [14a], while the Cu atoms in the latter are interlinked by dicarboxylate anions into 2D layers [14b]. In addition, self-assembly of Cu^{2+} ions and adipate ions under mild conditions produced a linear polymeric compound $Cu(H_2O)(C_6H_6O_4)$ [15]. Biphasic solvothermal reaction of copper acetate dissolved in water with adipic acid dissolved in cyclohexanol led to an open-framework copper adipate $Cu_3(C_6H_8O_4)_3(H_2O)_2(C_6H_{11}OH)$ [16]. To the best of our knowledge, no copper hydroxo dicarboxylate has been reported. Here we report two Cu(II) hydroxo succinato coordination polymers $[Cu_3(H_2O)_2(OH)_2(C_4H_4O_4)_2] \cdot 4H_2O$ (**1**) and $[Cu_4(H_2O)_2(OH)_4(C_4H_4O_4)_2] \cdot 5H_2O$ (**2**) along with one polymeric hydroxo glutarato compound $[Cu_5(OH)_6(C_5H_6O_4)_2]\cdot 4H_2O$ (**3**). All are obtained from self-assembly of Cu^{2+} ions and corresponding dicarboxylate ions in aqueous solution under ambient conditions and feature 1D and 2D metal oxygen connectivities based on $\{CuO_6\}$ octahedra. In particular, the 2D metal oxygen connectivity in **3** can be viewed as hexagonal close packing of oxygen atoms with Cu atoms in octahedral cavities.

2. Results and discussion

2.1. *Syntheses*

Dropwise addition of $Cu(NO_3)_2$ to an aqueous solution of succinic acid and Na_2CO_3 resulted in pale blue $Cu(H_2O)(C_4H_4O_4)\cdot 2H_2O$ [14a] precipitate, and filtration gave a nearly colorless filtrate, in which blue needle-like crystals of **2** were grown in extremely low yield. In order to raise the synthetic yield of **2**, the above synthetic procedure was modified by dropping ammonia to an aqueous suspension of fresh Cu(II) succinate precipitate obtained from reaction of sodium succinate with $CuCl_2\cdot 2H_2O$, resulting in a blue ammoniac solution (pH = 11.2). Obviously, dissolution of insoluble Cu(II) succinate is due to complexation of Cu(II) with ammonia. On standing at room temperature, pale blue oil formed readily on the surface of the ammoniac solution and pH value decreased from 11.2 to 7.2. With time, the solution turned gradually sky blue, indicating evaporation of ammonia. Finally, a small amount of crystals of **1** were grown rather than **2**. Apparently, continuous removal of the oily slick is responsible for the low yield of **1**. The ammonia assisted reaction of fresh $Cu(OH)_2\cdot yH_2O$ precipitate with glutaric acid produced a very small amount of **3** as a minor product besides unidentifiable amorphous deposit. Formation of **1** and **3** underwent initial complexation of Cu(II) with ammonia, dissociation of the Cu(II) ammonia complex due to liberation of ammonia from aqueous solution, followed by self-assembly of the released Cu(II) ions with hydroxide and dicarboxylate anions. In order to develop efficient synthetic methods, we turned to hydro/solvo-thermal techniques, which are often employed to synthesize transition metal dicarboxylato coordination polymers [7–10, 16–18]. Unfortunately, all efforts failed to isolate desirable products. Within the hydrothermal reaction vessels heated at temperature over 120–180°C, small amounts of tiny red crystalline products have been found instead and characterizations on them are now under way.

2.2. *Thermal analyses*

Thermogravimetric analyses suggest that dehydration of **1** starts at 55°C and terminates at 225°C, at which temperature the observed weight loss of 18.3% corresponds well to the calculated value of 19.1% for six H_2O molecules per formula unit. Over 225–375°C, the sample loses additional weight of 39.8% close to the calculated value of 38.6% expected for liberation of one H_2O and two succinic anhydride ($C_4H_4O_3$) molecules. When heated, **2** loses weight gradually and the weight loss at 263°C reaches 24.3% close to the calculated value of 23.8% for nine H_2O molecules per formula unit. The weight loss of 29.3% over 263–375°C corresponds well to sublimation of two succinic anhydride ($C_4H_4O_3$) molecules (calculated value: 29.4%). The combined TG/DTA measurements performed on a hand-picked crystalline sample indicated that **3** undergoes three endothermic decompositions when heated up to 600°C (peaks on a DTA curve: 122, 322 and 403°C). The observed weight loss of 12.1% over 85–175°C is in good agreement with the calculated value of 12.9% for liberation of four H_2O molecules per formula unit. The weight losses over 295–380°C and 380–410°C are 28.0% and 25.9%, respectively. The residue was identified as copper metal. However, the residual weight of 34.2% corresponds only to three moles of copper metal (Calculated value 34.1%), significantly less than the expected value of 45.5% for four moles of copper metal, which is at present very difficult to interpret.

2.3. *Structure of* $[Cu_3(H_2O)_2(OH)_2(C_4H_4O_4)_2]\cdot 4H_2O$ *(1)*

The asymmetric unit consists of three Cu atoms (Cu(1), Cu(2) and Cu(3)), two μ_3 hydroxides (O(1) and O(2)), two aqua ligands (O(3) and O(4)), two succinate anions (L(1): O(5) to O(8), C(1) to C(4); L(2): (O(9) to O(12), C(5) to C(8)), and four lattice H_2O molecules (O(13), O(14), O(15) and O(16)). As depicted in figure 1, all Cu atoms

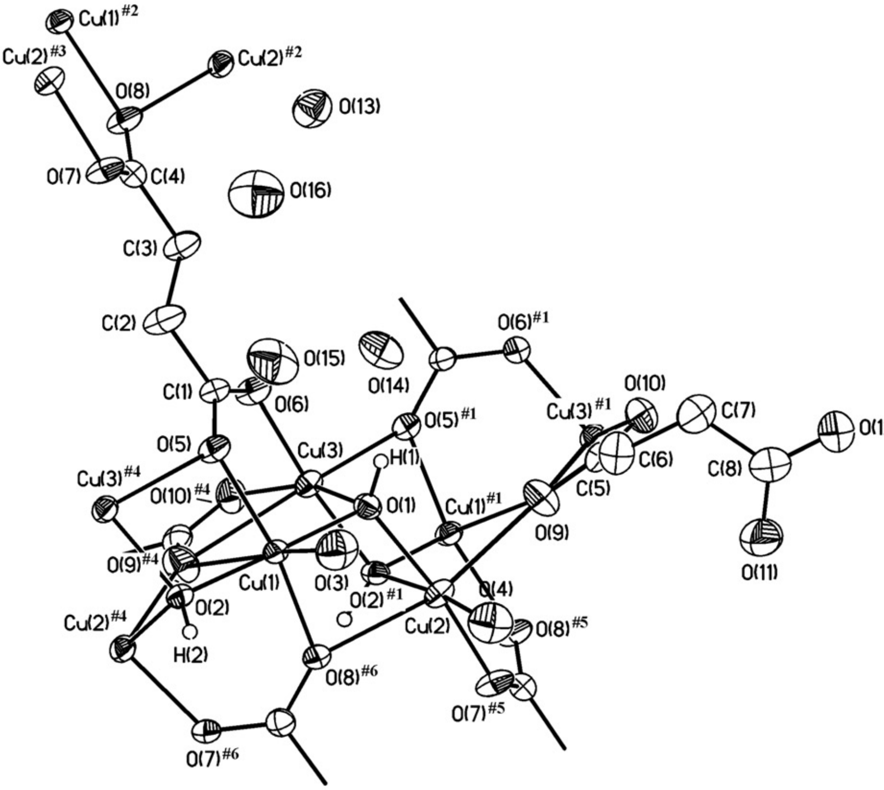

Figure 1. ORTEP view of coordination environments of Cu atoms along with the coordination modes of both bridging and mono terminally coordinating succinate anions and the atomic labelling for 1. The displacement ellipsoids are drawn at 60% probability (Symmetry transformations used to generate equivalent atoms: #1 = x, $-y+1/2$, z–1/2; #2 = $x+1$, $-y+1/2$, $z+1/2$; #3 = $x+1$, y, $z+1$; #4 = x, $-y+1/2$, $z+1/2$; #5 = $x-1$, y, $z-1$; #6 = $x-1$, $-y+1/2$, $z-1/2$).

are in distorted octahedral environments, Cu(1) and Cu(2) coordinated by one aqua oxygen, two hydroxides and three carboxylate oxygens of succinate anions, but Cu(3) by two hydroxides and four carboxylate oxygens of three dicarboxylate anions. The two hydroxides bonded to Cu(1) atom are *trans*, while they occupy *cis* positions around Cu(2) and Cu(3). The Cu–O bond distances (table 2) indicate that Cu(1) exhibits "$4+1+1$" coordination, and the Cu(2) and Cu(3) atoms are a tetragonally elongated "$4+2$" due to the Jahn–Teller effect.

The building blocks are linear edge-shared tri-octahedra, each of which is generated from a Cu(1)O_6 octahedron sharing two opposite edges with the Cu(3)O_6 and Cu(2)O_6 neighbors. As shown in figure 2(a), the resulting trimers are corner-shared to one another to form single chains, which are pairwise condensed into polyhedral copper oxygen chains extending in the [001] direction. The chains display a shortest intrachain Cu $\cdots$ Cu distance of 2.897 Å between two Cu atoms bridged by two hydroxides, comparable with those observed for hydroxo-bridged dicopper complexes such as $[Cu_2(H_2O)_2(phen)_2(OH)_2][Cu_2(phen)_2(OH)_2(CO_3)_2] \cdot 10H_2O$ [19].

The crystallographically distinct succinate anions L(1) and L(2) exhibit different coordination modes, the anti conformational L(1) anion acting as a *bis*-tridentate ligand with the two *trans* carboxylate oxygen atoms (O(5) and O(8)) each monoatomically bridging two Cu atoms and the remaining two *trans* oxygen atoms (O(6) and O(7)) each bonded to one Cu, and the gauche L(2) anion (torsion angle: $-75.4(7)^\circ$ for C(5)–C(6)–C(7)–C(8)) offering one terminal carboxylate group to chelate one Cu atom with one chelating atom additionally bridging two Cu atoms. As a result, polyhedral copper oxygen chains are interlinked by anti conformational L(1) succinate anions into 2D layers parallel to (010) with the gauche conformation L(2) succinate anions pendant on both sides (figure 2b). The spaces between the neighboring anti conformational L(1) bridges within the layer are very small due to the methylene hydrogen atoms. Along the crystallographic *b* axis, the 2D layers are stacked, and interlayer hydrogen bonds from aqua ligands to oxygen atoms of the uncoordinating carboxylate groups of the gauche succinate anion with $d(O(3) \cdots O(11)^{\#7}) = 2.769$ Å and $d(O(4) \cdots O(11)^{\#7}) = 3.185$ Å ($\#7 = -x, -y, -z$) are responsible for stabilization of a 3D framework (figure 2c) with 1D tunnels parallel to both [100] and [001] (figure 2c). The lattice H_2O molecules are located at the crossing positions of the tunnels.

2.4. *Structure of* $[Cu_4(H_2O)_2(OH)_4(C_4H_4O_4)_2] \cdot 5H_2O$ *(2)*

As shown in figure 3(a), the asymmetric unit contains four Cu atoms (Cu(1) to Cu(4)), four halves of succinate anions (L(1): O(1), O(2), C(1) C(2); L(2): O(3), O(4), C(3) C(4); L(3): O(5), O(6), C(5) C(6); L(4): O(7), O(8), C(7) C(8)), four hydroxo groups (O(9) to O(12)), two aqua ligands (O(13) and O(14)) and five lattice water molecules (O(15) to O(19)). The structural refinement indicated that the sites for the lattice water molecules are partially populated. Similar to **1**, all Cu atoms are in octahedral coordination spheres. The Cu(1) and Cu(2) atoms are coordinated by one succinate anion, four hydroxides and one aqua ligand, exhibiting "$4+2$" coordination geometries with the aqua and one hydroxide at axial positions. The Cu(3) and Cu(4) atoms, each of which is coordinated by three hydroxides and three succinate oxygen atoms, display "$4+1+1$" coordination spheres (table 3).

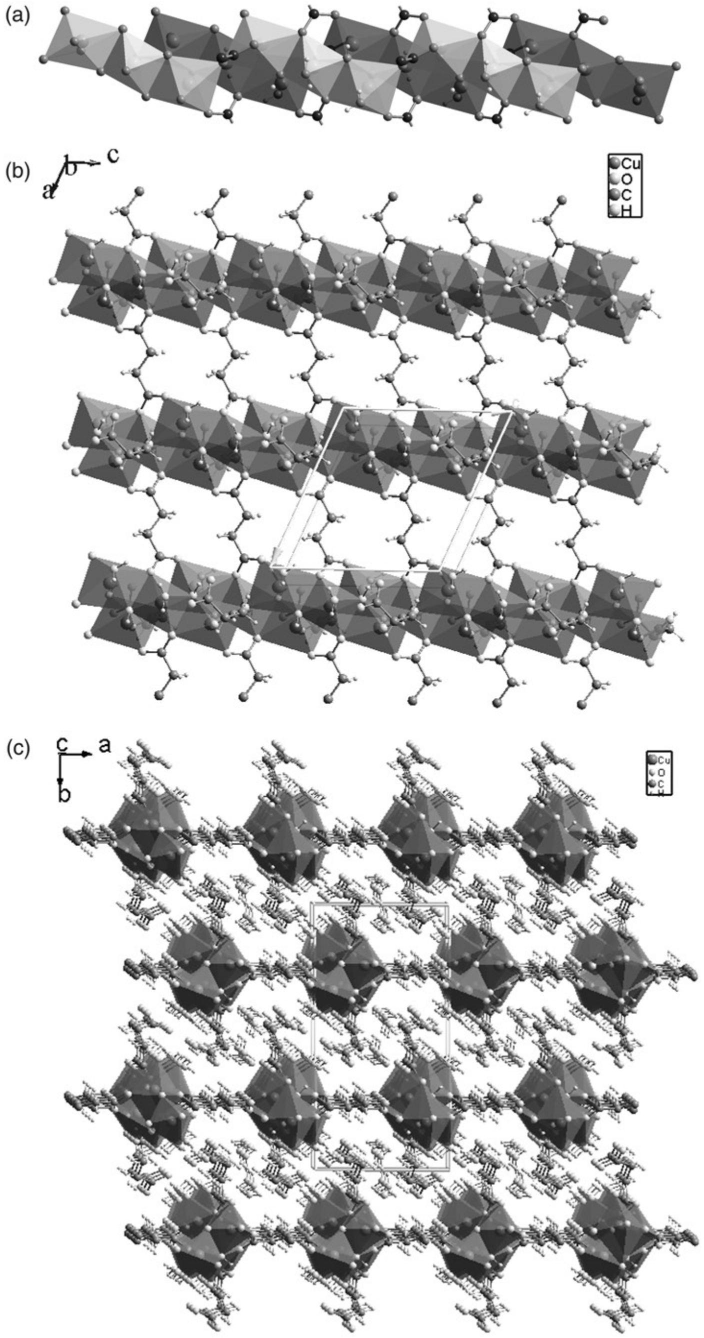

Figure 2. (a) 1D copper oxygen bi-chains built up from linear trimers of edge-sharing CuO6 octahedra for **1**. (b) 1D copper oxygen bi-chains are bridged by the anti formational succinate anions into 2D layer with mono terminally coordinating gauche succinate anions on both sides for **1**. (c) Assembly of 2D layers for **1**.

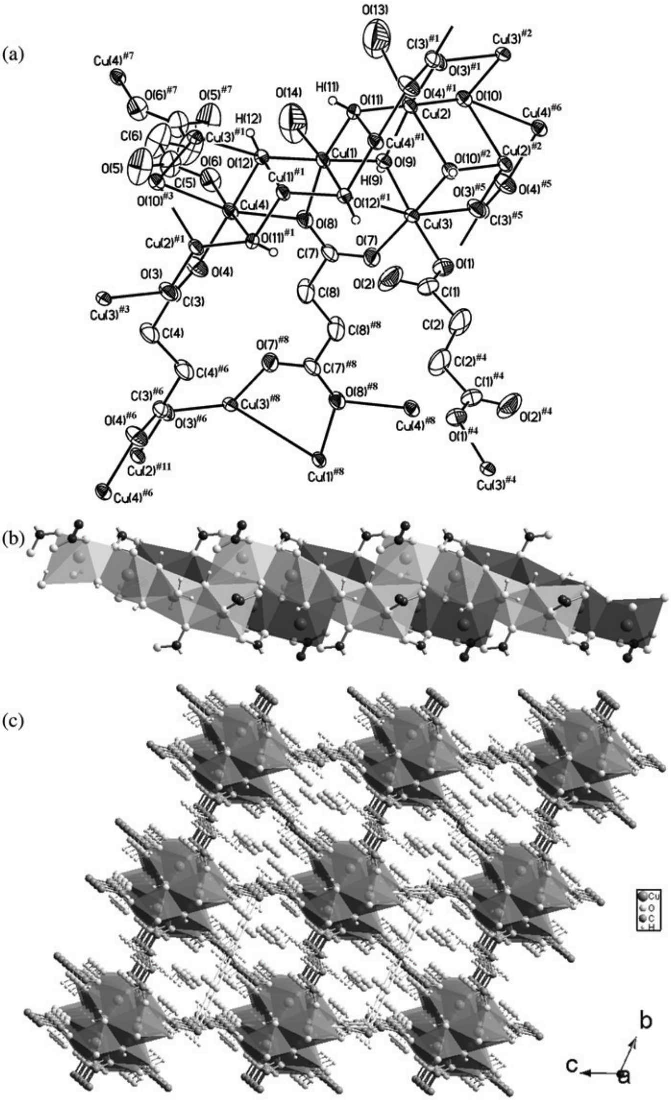

Figure 3. (a) ORTEP view of coordination environments of Cu atoms along with the bridging of succinate ligands and the atomic labelling for **2**. The displacement ellipsoids are drawn at 60% probability (Symmetry transformations used to generate equivalent atoms: $\#1 = -x+1, -y, -z+1$; $\#2 = -x, -y, -z+1$; $\#3 = x+1, y, z$; $\#4 = -x+1, -y+1, -z+2$; $\#5 = x-1, y, z$; $\#6 = -x+2, -y+1, -z+1$; $\#7 = -x+1, -y, -z$; $\#8 = -x+1, -y+1, -z+1$; $\#9 = x, y, z-1$; $\#10 = x, y, z+1$; $\#11 = x+1, y+1, z+1$). (b) 1D copper oxygen bi-chains built up from linear tetramers of edge-sharing CuO6 octahedra. (c) Crystal structure of **2**.

Four adjacent CuO_6 octahedra are edge-shared to afford linear tetra-octahedra in a sequence Cu(4)–Cu(1)–Cu(2)–Cu(3) with each tetramer sharing two distal edges with neighbors to form zigzag single-chains extending along [100]; two single-chains are fused to give the polyhedral copper oxygen connectivity chains (figure 3b). The closest intrachain $Cu \cdots Cu$ separation of 2.987 Å due to two bridging hydroxides is slightly longer than that of 2.897 Å in **1**.

The four crystallographically distinct succinate anions possess inversion centers at the midpoint of C–C bonds and assume anti conformations bridging two and six Cu atoms, respectively. The L(1) and L(3) succinate anions are *bis*-unidentate bridging ligands and L(2) and L(4) *bis*-tridentate ligands with two *trans* carboxylate oxygen atoms bonded to one Cu atom and the others monoatomically bridging two Cu atoms. Due to coordination, each terminal carboxylate plane is twisted from the plane defined by the skeleton carbon atoms, the dihedral angles being 39.2(8)°, 75.7(5)°, 14.6(1)° and 24.6(7)° for L(1), L(2), L(3) and L(4), respectively.

The copper oxygen chains in **2** are interconnected by succinate ligands to form a 3D open framework with triangular channels propagating along [100] (figure 3c). The lattice H_2O molecules are located in channels and hydrogen bonded to the framework.

2.5. *Structure of* $[Cu_5(OH)_6(C_5H_6O_4)_2]\cdot 4H_2O$ *(3)*

As illustrated in figure 4(a), the asymmetric unit contains one glutarate $(C_5H_6O_4)^{2-}$ anion, six hydroxides, one aqua ligand (O(11)), three lattice H_2O molecules and five Cu atoms, of which Cu(1), Cu(2) and Cu(3) are located at three general positions and Cu(4) and Cu(5) at the specific 1*c* and 1*d* sites, respectively. The disordered lattice H_2O molecules are modeled over two equally populated positions (O(14a) and O(14b)) related by a 0.55(5)Å shift. Similar to **1** and **2**, all Cu atoms are strongly distorted octahedra, Cu(1) with a "$4+1+1$" coordination geometry and the remaining Cu atoms (Cu(2) to Cu(5)) with "$4+2$" coordination environments (table 4). For the "$4+2$" coordination geometries, all equatorial oxygen atoms come from hydroxides, while the axial ligands are two hydroxides for Cu(2), one glutarate anion and one aqua ligand for Cu(3), two aqua ligands for Cu(4) and two carboxylate groups of different glutarate anions for Cu(5). Each CuO_6 polyhedron is edge-shared with six neighbors, resulting in corrugated Cu oxygen layers parallel to (001) (figure 4b). The formed layers can be viewed as hexagonal close packing of oxygen atoms with the Cu atoms situated in octahedral cavities. To the best of our knowledge, **3** represents a first example of metal dicarboxylates with metal oxygen inorganic layers built up of CuO_6 octahedra. The closest $Cu\cdots Cu$ distance due to two bridging hydroxides is 2.983 Å, very close to 2.987 Å observed in **2**.

The glutarate $(C_5H_6O_4)^{2-}$ anions have normal bond distances and angles (table 4) and adopt an anti-anti conformation with one carboxylate oxygen (O(1)) bridging three Cu atoms. Around the terminal C(1)–C(2) bond, the coordinating carboxylate group is significantly twisted away from the skeleton carbon plane (dihedral angle: 23.7(6)°), while the other end is nearly coplanar with the carbon skeleton (dihedral angle: 2.9(5)°). The bonded glutarate groups are almost perpendicular to the Cu oxygen layer on both sides. Along the crystallographic [001] direction, the layers are stacked so that each glutarate of one layer protrudes into the void between two adjacent glutarate groups of the neighboring layers and all dicarboxylate anions orientate nearly parallel in the [010] direction (figure 4c). The interlayer hydrogen bonds from hydroxides or aqua ligands to uncoordinated carboxylate groups assemble the layers into a 3D framework with 1D channels along [010] occluded by the lattice water molecules.

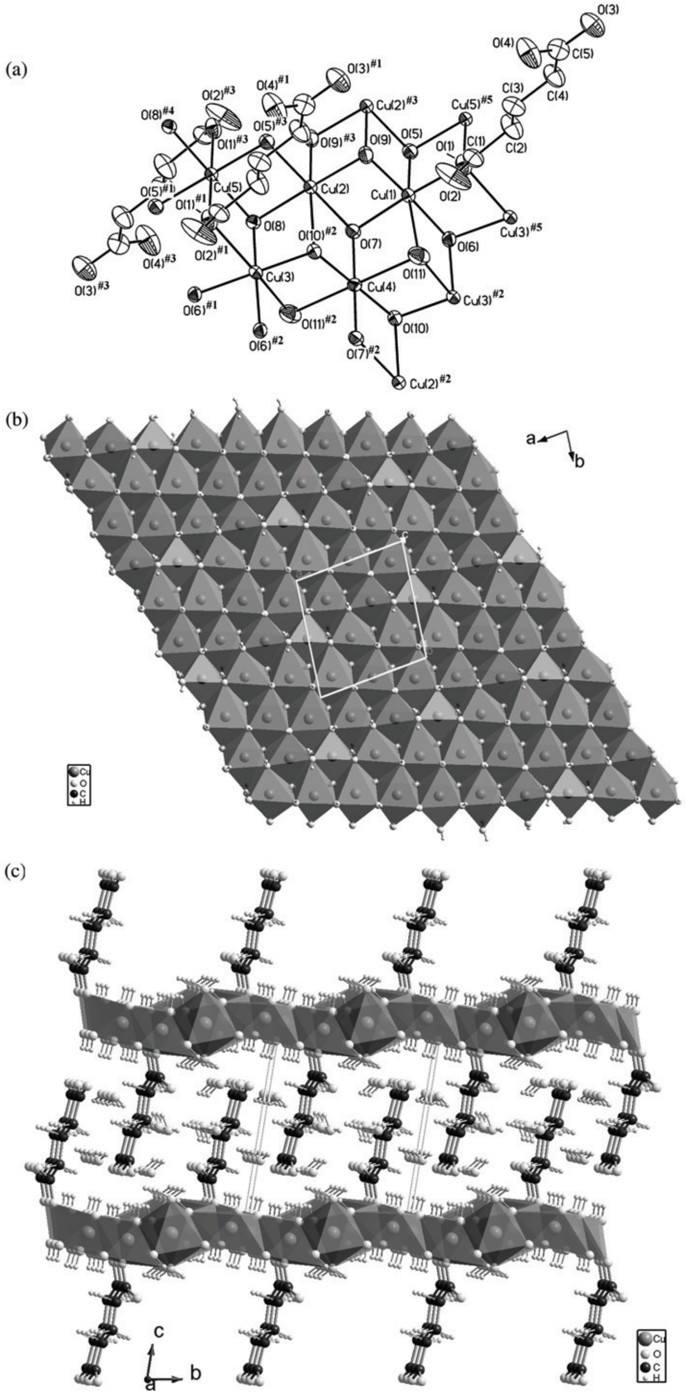

Figure 4. (a) ORTEP view of coordination environments of Cu atoms along with the coordination of glutarate anions and the atomic labelling for **3**. The displacement ellipsoids are drawn at 60% probability (Symmetry transformations used to generate equivalent atoms: #1 = $x-1$, y, z; #2 = $-x$, $-y+1$, $-z$; #3 = $-x$, $-y+2$, $-z$; #4 = $-x-1$, $-y+2$, $-z$; #5 = $x+1$, y, z; #5 = $-x-1$, $-y+1$, $-z$). (b) 2D copper oxygen layer formed by edge-sharing CuO_6 octahedra. (c) Crystal structure of **3**.

2.6. *Coordination modes of the anionic ligands*

The three coordination polymers contain two anionic ligands, i.e. hydroxide and dicarboxylate anions (succinate in **1** and **2**, glutarate in **3**). The hydroxides are bonded to three Cu atoms to complete tetrahedral coordination of the oxygens [20]. The dicarboxylate anions with normal bond distances and angles [21] are bridging and mono terminally coordinating ligands. The anti conformational bridging succinate anions in **1** and **2** are bonded to six and two Cu atoms, respectively, and the mono terminally coordinating gauche succinate anions are bonded to three Cu atoms. The mono terminally coordinating glutarate anions in **3** mono atomically bridge three Cu atoms.

Dicarboxylate anions exhibit rich coordination chemistry due to the ligating capability of each oxygen atom in combination with a variety of structural conformations of the flexible alkyl chains, as well as the orientation of the terminal carboxylate with respect to the carbon skeleton. Rarely do dicarboxylate anions employ only one carboxylate group to coordinate metal atoms. Survey of reported dicarboxylate compounds indicates that the number of metal atoms coordinated to succinate and glutarate anions ranges from one to six.

When coordinated to two metal atoms, succinates have four different coordination modes. In the first case, the succinate anion *bis*-monodentately bridges two metal atoms [8, 22] in a fashion similar to L(1) and L(3) in **2**. In the second case, succinato ligands *bis*-chelate two metal atoms [19, 21b]. In the third case, two terminal carboxylate groups behave differently, for example, the anti conformational succinate anions in $[Cu_2(phen)_2(OH)Cl(C_4H_4O_4)] \cdot 8H_2O$ offering only one terminal group to bridge two Cu atoms in syn–syn fashion [23], and finally, the gauche dicarboxylate anions in $Co(phen)(H_2O)(C_4H_4O_4)$ affording one end mono atomically to bond one Co atom and the other to chelate one metal atom [24].

When coordinating three metal atoms, the gauche succinates exhibit three different coordination modes observed in $Cu(C_4H_4O_4) \cdot H_2O$ [14b], $Co(H_2O)_2(C_4H_4O_4)$ [7], $Cd(H_2O)_2(C_4H_4O_4)$ [5b, 17] and $Cd(H_2O)_2(C_4H_4O_4) \cdot 0.5H_2O$ [25]. In $Cu(C_4H_4O_4) \cdot H_2O$ [14b], a gauche succinate chelates one Cu atom through two distal carboxylate oxygens to form a seven-membered ring with each non-chelating oxygen additionally bonded to the second Cu. The gauche dicarboxylate anion in $Co(H_2O)_2(C_4H_4O_4)$ forms a similar seven-membered ring by chelating one Co atom via two distal carboxylate oxygen atoms, each of which is additionally coordinated to a second metal [7]. Within two Cd succinates, $Cd(H_2O)_2(C_4H_4O_4)$ [5b, 17] and $Cd(H_2O)_2(C_4H_4O_4) \cdot 0.5H_2O$ [25], the gauche succinate anions *bis*-chelate two Cd atoms and the third Cd is bonded to one oxygen. The gauche succinate anion in **1** with one terminal carboxylate chelating one Cu atom and one chelating oxygen atom additionally bridging two Cu atoms represents a new coordination mode.

When coordinating to six metal atoms, the anti conformational succinate anions in **1** and **2** *bis*-bidentately bridge four Cu atoms with two *trans* oxygens bonded to an additional Cu. Such coordination of the anti conformational succinate is different from those found in two isostructural succinato coordination polymers $M_5(OH)_2(C_4H_4O_4)_4$ with M = Co(II), Mn(II) [10a, 26], where one carboxylate group bridges two metal atoms in syn–syn fashion and the oxygens of the other end are each bonded to two metal atoms.

Hitherto, a Mn glutarato complex $[Mn(phen)]_2(C_5H_6O_4)_2$ has represented a unique example with the glutarate anions coordinating three metal atoms, of which one is chelated by a terminal carboxylate and the remaining two manganese centers are bridged by the other carboxylate [27]. In this sense, the glutarato coordination polymer **3** is a first dicarboxylate compound with the dicarboxylate anions mono atomically bridging three metal atoms.

2.7. *Conclusion*

Three new copper(II) coordination polymers $[Cu_3(H_2O)_2(OH)_2(C_4H_4O_4)_2]\cdot 4H_2O$ (**1**), $[Cu_4(H_2O)_2(OH)_4(C_4H_4O_4)_2]\cdot 5H_2O$ (**2**) and $[Cu_5(OH)_6(C_5H_6O_4)_2]\cdot 4H_2O$ (**3**) are obtained from self-assembly of Cu^{2+} and succinate or glutarate in aqueous solution under ambient conditions. The Cu atoms show "4 + 1 + 1" and "4 + 2" coordination geometries. The remarkable building units are polyhedral copper oxygen connectivity chains generated from condensation of the edge-shared tri- and tetra-octahedra in **1** and **2**, respectively, as well as the 2D polyhedral copper oxygen connectivity layers resulting from edge-shared CuO_6 octahedra in **3**. The polyhedral copper oxygen connectivities are bridged by succinate anions into 2D layers and 3D frameworks. The 2D copper oxygen layers within **3** can be described as hexagonal close packing of oxygens with copper in octahedral cavities. To the best of our knowledge, **3** represents a first example of a coordination polymer with 2D polyhedral copper oxygen connectivity layers formed by edge-sharing metal oxygen octahedra. The title compounds show varied coordination modes of succinate and glutarate anions. Although many attempts have been dedicated to raise the yields, all efforts failed. Obviously, efficient synthetic methods are essential for the systematic magnetic characterizations, which is now in progress.

3. Experimental

All chemicals of p.a. grade were commercially available and used without further purification. The C and H microanalyses were performed with a PE 2400 CHNO/S elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. The combined measurements on thermogravimetric and differential thermal analyses (TG/DTA) were carried out between 25–600°C on powdered samples in nitrogen stream using Seiko Exstar6000 TG/DTA6300 equipment with a heating rate of 10°C min^{-1}.

3.1. *Preparation of $[Cu_3(H_2O)_2(OH)_2(C_4H_4O_4)_2]\cdot 4H_2O$ (1)*

An aqueous solution of sodium succinate (0.281 g, 1.04 mmol) in 5.0 ml H_2O was dropwise added to an aqueous solution of $CuCl_2\cdot 2H_2O$ (0.089 g, 0.52 mmol) in 3.0 ml H_2O to give fine blue precipitate, which was separated by centrifuging and washed with water until no Cl^- anions were detectable in supernatant. The collected blue precipitate was mixed with 4.0 ml H_2O and dissolved by dropwise addition of 0.6 ml concentrated ammonia to give dark blue solution (pH = 11.2), which was then left to stand at room temperature. On standing, pale blue oily slick agglutinated on the surface. Every time the oily slick formed, the mixture was filtered. Finally, only a small amount of blue slender crystals were grown in solution (pH = 7.2). The yield is less than 5.0% based on the initial $CuCl_2 \cdot 2H_2O$. Anal. Calcd for $C_8H_{22}Cu_3O_{16}$ (%): C, 17.01; H, 3.93. Found: C, 17.12; 4.05. IR (cm^{-1}): 3344s (broad), 3182s (broad), 1624 (shoulder), 1566vs, 1529vs, 1416vs (sharp), 1296m (sharp), 1267w, 1236m (sharp), 1180w (doublet), 1065vw, 980vw, 961vw, 895w, 870w, 800w, 687m, 486m.

3.2. *Preparation of [$Cu_4(H_2O)_2(OH)_4(C_4H_4O_4)_2$] • $5H_2O$ (2)*

A mixture consisting of 0.50 g (4.23 mmol) succinic acid and 0.45 g (4.23 mmol) Na_2CO_3 was added to 50 mL water and vigorously stirred until no further CO_2 bubbles were released. Then 2.0 mL (1 M) $Cu(NO_3)_2$ was added dropwise to the mixture to yield pale blue precipitate, which was filtered off. The nearly colorless filtrate (pH = 6.1) was allowed to stand at room temperature. Blue needle-like crystals grew by slow evaporation for several weeks. The yield is less than 5.0% based on the initial $Cu(NO_3)_2$. Anal. Calcd for $C_8H_{26}Cu_4O_{19}$ (%): C, 14.12; H, 3.85. Found: C, 14.39; H, 3.78. IR (cm^{-1}): 3388s (broad), 1655s, 1558vs (sharp), 1530vs (sharp), 1508s, 1474w, 1456m, 1396vs, 1340w, 1234w, 1165w, 808vw, 687m, 457s.

3.3. *Preparation of [$Cu_5(OH)_6(C_5H_6O_4)_2$] • $4H_2O$ (3)*

Dropwise addition of 7.0 ml (1 M) NaOH to an aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.51 g, 3.00 mmol) in 5.0 ml H_2O produced blue precipitate, which was separated out and washed with H_2O until no Cl^- anions were detectable in the supernatant. The fresh $Cu(OH)_2 \cdot yH_2O$ precipitate was then added to a stirred aqueous solution of glutaric acid (0.40 g, 3.00 mmol) in 50 ml H_2O to form a blue suspension, to which 1.0 ml concentrated ammonia was added. The mixture was then filtered and the blue filtrate (pH = 8.80) was maintained at 50°C and a small amount of blue plate-like crystals of **3** formed in the deposited slurry, which was unfortunately unidentifiable with powder X-ray diffraction methods. Anal. Calcd for $C_8H_{26}Cu_4O_{19}$ (%): C, 10.76; H, 3.61. Found: C, 10.69; H, 3.67. IR (cm^{-1}): 3412s (broad), 1628vs (sharp), 1597vs (sharp), 1458s, 1414vs (sharp), 1319w, 1204w, 1069w, 962w, 899vw, 820w, 800w, 764w, 689m.

3.4. *Crystal structure determination*

The reflection intensities of **1**, **2** and **3** were collected at 293 K on a Bruker P4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the θ–2θ scan technique. SHELXS-97 [28] and SHELXL-97 [29] were used for structure determination and refinements. The structures were solved by using direct methods and

Table 1. Crystal data and structure refinement parameters for **1**, **2** and **3**.

Compounds	**1**	**2**	**3**
Empirical formula	$C_8H_{22}Cu_3O_{16}$	$C_8H_{26}Cu_4O_{19}$	$C_5H_{20}Cu_5O_{14}$
Formula mass	564.89	680.47	558.39
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a(Å)	10.263(2)	9.732(2)	8.112(2)
b(Å)	18.750(2)	10.596(2)	8.651(2)
c(Å)	9.883(2)	12.592(2)	11.318(2)
α(°)		111.37(1)	80.07(3)
β(°)	113.24(1)	106.05(1)	84.18(3)
γ(°)		96.36(1)	80.23(3)
Volume (Å^3)	1747.5(5)	1129.2(4)	768.9(3)
Z	4	2	2
D_{Calcd} (g cm^{-3})	2.147	2.001	2.412
$F(000)$	1140	684	556
μ (mm^{-1})	3.621	3.716	5.405
θ range (°)	2.16–27.49	1.85–27.50	2.00–27.50
Total no. of data collected	4023	5023	3521
No. of obsd. data ($I \geq 2\sigma(I)$)	2675	4237	2908
R_1, wR_2 [$I \geq 2\sigma$ (I)]^a	0.0469, 0.1131	0.0414, 0.1207	0.0496, 0.1238
R_1, wR_2 (all data)^a	0.0795, 0.1370	0.0504, 0.1278	0.0594, 0.1327
Goodness-of-fit on F^2	1.052	1.068	1.053
No. of variables	247	285	217
Largest diff. peak and hole (e Å^{-3})	0.920 and −1.318	0.914 and −0.563	1.485 and −1.704

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma(F_o^2) + (aP)^2 + bP]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. For **1**: $a = 0.0682$, $b = 0.5688$. For **2**: $a = 0.0602$, $b = 3.7734$. For **3**: $a = 0.0922$, $b = 0.2282$.

followed by successive Fourier and difference Fourier syntheses. All hydrogens of dicarboxylate anions were geometrically generated. The hydroxide and aqua hydrogen atoms were located from successive difference Fourier syntheses, whereas the hydrogen atoms of four partially populated water molecules in **2** and those of a disordered water in **3** are not located. All non-hydrogen atoms except the partially populated water oxygen atoms in **2** were refined with anisotropic displacement parameters by full-matrix least-squares and hydrogen atoms and the partially populated water oxygen atoms with isotropic displacement parameters. Detailed information about the crystal data and structure determination is summarized in table 1. Selected interatomic distances and bond angles are given in tables 2–4.

Supplementary data

Supplementary data for the three structures are available form the Cambridge CB2 1EZ, UK (Fax: +44-1223-336033. Email: deposit@ccdc.cam.ac.uk), on request quoting the deposition numbers CCDC 243791, CCDC 243792 and CCDC 243793, respectively.

Table 2. Selected interatomic distances (Å) and bond angles (°) for **1**.[a]

Cu(1)–O(1)	1.943(3)	Cu(2)–O(4)	1.960(5)	Cu(3)–O(9)#4	2.526(4)	C(4)–O(8)	1.268(6)
Cu(1)–O(2)	1.918(4)	Cu(2)–O(7)#5	1.960(3)	Cu(3)–O(10)#4	1.974(4)	C(5)–O(9)	1.235(7)
Cu(1)–O(3)	2.239(4)	Cu(2)–O(8)#6	2.512(4)	C(1)–O(5)	1.275(6)	C(5)–O(10)	1.266(6)
Cu(1)–O(5)	1.999(3)	Cu(2)–O(9)	2.401(4)	C(1)–O(6)	1.255(6)	C(5)–C(6)	1.524(8)
Cu(1)–O(8)#6	1.974(3)	Cu(3)–O(1)	1.977(4)	C(1)–C(2)	1.493(7)	C(6)–C(7)	1.527(8)
Cu(1)–O(9)#4	2.890(4)	Cu(3)–O(2)#1	1.958(3)	C(2)–C(3)	1.499(7)	C(6)–C(8)	1.512(8)
Cu(2)–O(1)	1.999(3)	Cu(3)–O(5)#1	2.373(4)	C(3)–C(4)	1.505(7)	C(8)–O(11)	1.244(7)
Cu(2)–O(2)#1	1.968(4)	Cu(3)–O(6)	1.937(4)	C(4)–O(7)	1.249(6)	C(8)–O(12)	1.238(8)

O(1)–Cu(1)–O(2)	174.4(2)	O(1)–Cu(2)–O(7)#5	170.4(2)	O(1)–Cu(3)–O(9)#4	104.4(1)
O(1)–Cu(1)–O(3)	93.8(2)	O(1)–Cu(2)–O(8)#6	71.6(1)	O(1)–Cu(3)–O(10)#4	160.0(1)
O(1)–Cu(1)–O(5)	94.4(1)	O(1)–Cu(2)–O(9)	91.1(1)	O(2)#1–Cu(3)–O(5)#1	74.0(1)
O(1)–Cu(1)–O(8)#6	85.9(2)	O(2)#1–Cu(2)–O(4)	172.3(2)	O(2)#1–Cu(3)–O(6)	173.6(2)
O(1)–Cu(1)–O(9)#4	93.3(1)	O(2)#1–Cu(2)–O(7)#5	91.3(2)	O(2)#1–Cu(3)–O(9)#4	95.6(1)
O(2)–Cu(1)–O(3)	91.9(2)	O(2)#1–Cu(2)–O(8)#6	88.2(1)	O(2)#1–Cu(3)–O(10)#4	93.4(2)
O(2)–Cu(1)–O(5)	84.3(1)	O(2)#1–Cu(2)–O(9)	94.1(1)	O(5)#1–Cu(3)–O(6)	103.5(1)
O(2)–Cu(1)–O(8)#6	93.6(2)	O(4)–Cu(2)–O(7)#5	89.3(2)	O(5)#1–Cu(3)–O(9)#4	147.1(1)
O(2)–Cu(1)–O(9)#4	81.1(3)	O(4)–Cu(2)–O(8)#6	84.2(2)	O(5)#1–Cu(3)–O(10)#4	92.1(1)
O(3)–Cu(1)–O(5)	102.2(2)	O(4)–Cu(2)–O(9)	93.6(2)	O(6)–Cu(3)–O(9)#4	89.7(2)
O(3)–Cu(1)–O(8)#6	96.9(2)	O(7)#5–Cu(2)–O(8)#6	104.0(1)	O(6)–Cu(3)–O(10)#4	92.6(2)
O(3)–Cu(1)–O(9)#4	172.9(1)	O(7)#5–Cu(2)–O(9)	93.9(2)	O(9)#4–Cu(3)–O(10)#4	56.8(1)
O(5)–Cu(1)–O(8)#6	160.8(2)	O(8)#6–Cu(2)–O(9)	161.9(1)	O(5)–C(1)–O(6)	124.2(5)
O(5)–Cu(1)–O(9)#4	78.1(1)	O(1)–Cu(3)–O(2)#1	80.9(1)	O(7)–C(4)–O(8)	125.3(5)
O(8)#6–Cu(1)–O(9)#4	82.7(1)	O(1)–Cu(3)–O(5)#1	104.6(1)	O(9)–C(5)–O(10)	122.7(5)
O(1)–Cu(2)–O(2)#1	80.1(1)	O(1)–Cu(3)–O(6)	94.2(2)	O(11)–C(8)–O(12)	123.8(6)
O(1)–Cu(2)–O(4)	98.6(2)				

[a] Symmetry transformations used to generate equivalent atoms: #1 = x, $-y+1/2$, $z-1/2$; #2 = $x+1$, $-y+1/2$, $z+1/2$; #3 = $x+1$, y, $z+1$; #4 = x, $-y+1/2$, $z+1/2$; #5 = $x-1$, y, $z-1$; #6 = $x-1$, $-y+1/2$, $z-1/2$.

Table 3. Selected interatomic distances (Å) and bond angles (°) for **2**.[a]

Cu(1)–O(8)	1.986(3)	Cu(3)–O(7)	1.942(3)	C(2)–C(2)#4	1.407(9)
Cu(1)–O(9)	1.954(3)	Cu(3)–O(9)	1.978(3)	C(3)–O(3)	1.255(6)
Cu(1)–O(11)	2.004(3)	Cu(3)–O(10)#2	1.938(3)	C(3)–O(4)	1.260(5)
Cu(1)–O(12)	1.941(3)	Cu(3)–O(12)#1	2.887(3)	C(3)–C(4)	1.520(6)
Cu(1)–O(12)#1	2.409(3)	Cu(4)–O(4)	1.960(3)	C(4)–C(4)#6	1.517(9)
Cu(1)–O(14)	2.448(5)	Cu(4)–O(6)	1.954(3)	C(5)–O(5)	1.240(7)
Cu(2)–O(3)#1	2.003(3)	Cu(4)–O(8)	2.366(3)	C(5)–O(6)	1.262(6)
Cu(2)–O(9)	1.990(3)	Cu(4)–O(10)#3	2.946(3)	C(5)–C(6)	1.515(7)
Cu(2)–O(10)	1.934(3)	Cu(4)–O(11)#1	1.979(3)	C(6)–C(6)#7	1.480(9)
Cu(2)–O(10)#2	2.404(3)	Cu(4)–O(12)	1.945(3)	C(7)–O(7)	1.254(6)
Cu(2)–O(11)	1.946(3)	C(1)–O(1)	1.267(7)	C(7)–O(8)	1.263(6)
Cu(2)–O(13)	2.430(6)	C(1)–O(2)	1.247(7)	C(7)–C(8)	1.506(6)
Cu(3)–O(1)	1.951(3)	C(1)–C(2)	1.518(7)	C(8)–C(8)#8	1.478(9)
Cu(3)–O(3)#5	2.413(3)				
O(8)–Cu(1)–O(9)	92.9(1)	O(9)–Cu(2)–O(11)	81.1(1)	O(9)–Cu(3)–O(12)#1	82.5(1)
O(8)–Cu(1)–O(11)	164.2(1)	O(9)–Cu(2)–O(13)	107.2(2)	O(10)#2–Cu(3)–O(12)#1	85.6(1)
O(8)–Cu(1)–O(12)	87.8(1)	O(10)–Cu(2)–O(10)#2	84.0(1)	O(4)–Cu(4)–O(6)	90.1(2)
O(8)–Cu(1)–O(12)#1	93.8(1)	O(10)–Cu(2)–O(11)	177.4(1)	O(4)–Cu(4)–O(8)	105.2(1)
O(8)–Cu(1)–O(14)	86.1(2)	O(10)–Cu(2)–O(13)	89.2(2)	O(4)–Cu(4)–O(10)#3	92.8(1)
O(9)–Cu(1)–O(11)	80.5(1)	O(10)#2–Cu(2)–O(11)	98.0(1)	O(4)–Cu(4)–O(11)#1	92.4(1)
O(9)–Cu(1)–O(12)	177.4(1)	O(10)#2–Cu(2)–O(13)	173.2(2)	O(4)–Cu(4)–O(12)	175.9(1)
O(9)–Cu(1)–O(12)#1	96.9(1)	O(11)–Cu(2)–O(13)	88.8(2)	O(6)–Cu(4)–O(8)	89.6(1)
O(9)–Cu(1)–O(14)	89.1(2)	O(1)–Cu(3)–O(3)#5	88.4(1)	O(6)–Cu(4)–O(10)#3	99.1(1)
O(11)–Cu(1)–O(12)	99.4(1)	O(1)–Cu(3)–O(7)	91.0(2)	O(6)–Cu(4)–O(11)#1	177.5(1)
O(11)–Cu(1)–O(12)#1	73.0(1)	O(1)–Cu(3)–O(9)	176.4(1)	O(6)–Cu(4)–O(12)	92.9(1)
O(11)–Cu(1)–O(14)	108.0(2)	O(1)–Cu(3)–O(10)#2	92.2(1)	O(8)–Cu(4)–O(10)#3	160.0(1)
O(12)–Cu(1)–O(12)#1	85.5(1)	O(1)–Cu(3)–O(12)#1	99.3(1)	O(8)–Cu(4)–O(11)#1	89.2(1)
O(12)–Cu(1)–O(14)	88.5(2)	O(3)#5–Cu(3)–O(7)	102.5(1)	O(8)–Cu(4)–O(12)	77.7(1)
O(12)#1–Cu(1)–O(14)	174.0(2)	O(3)#5–Cu(3)–O(9)	89.0(1)	O(10)#3–Cu(4)–O(11)#1	81.4(1)
O(3)#1–Cu(2)–O(9)	164.6(1)	O(3)#5–Cu(3)–O(10)#2	77.8(1)	O(10)#3–Cu(4)–O(12)	83.9(1)
O(3)#1–Cu(2)–O(10)	88.8(1)	O(3)#5–Cu(3)–O(12)#1	161.9(1)	O(11)#1–Cu(4)–O(12)	84.7(1)
O(3)#1–Cu(2)–O(10)#2	93.9(1)	O(7)–Cu(3)–O(9)	92.0(1)	O(1)–C(1)–O(2)	125.7(5)
O(3)#1–Cu(2)–O(11)	92.7(1)	O(7)–Cu(3)–O(10)#2	176.9(1)	O(3)–C(3)–O(4)	125.9(4)
O(3)#1–Cu(2)–O(13)	86.7(2)	O(7)–Cu(3)–O(12)#1	93.8(1)	O(5)–C(5)–O(6)	124.7(5)
O(9)–Cu(2)–O(10)	98.0(1)	O(9)–Cu(3)–O(10)#2	84.8(1)	O(7)–C(7)–O(8)	125.9(4)
O(9)–Cu(2)–O(10)#2	73.2(1)				

[a] Symmetry transformations used to generate equivalent atoms: #1 = $-x+1$, $-y$, $-z+1$; #2 = $-x$, $-y$, $-z+1$; #3 = $x+1$, y, z; # = $-x+1$, $-y+1$, $-z+2$; #5 = $x-1$, y, z; #6 = $-x+2$, $-y+1$, $-z+1$; #7 = $-x+1$, $-y$, $-z$; #8 = $-x+1$, $-y+1$, $-z+1$; #9 = x, y, $z-1$; #10 = x, y, $z+1$; #11 = $x+1$, $y+1$, $z+1$.

Table 4. Selected interatomic distances (Å) and bond angles (°) for **3**.[a]

Cu(1)–O(1)	2.000(3)	Cu(3)–O(6)#1	1.956(3)	Cu(5)–O(5)#1	1.945(3)
Cu(1)–O(5)	2.255(3)	Cu(3)–O(6)#2	2.019(3)	Cu(5)–O(5)#3	1.945(3)
Cu(1)–O(6)	2.000(3)	Cu(3)–O(8)	2.015(3)	Cu(5)–O(8)	1.963(3)
Cu(1)–O(7)	1.993(3)	Cu(3)–O(10)#2	1.901(3)	Cu(5)–O(8)#4	1.963(3)
Cu(1)–O(9)	1.923(3)	Cu(3)–O(11)#2	2.563(3)	C(1)–O(1)	1.277(5)
Cu(1)–O(11)	2.802(3)	Cu(4)–O(7)	1.984(3)	C(1)–O(2)	1.239(6)
Cu(2)–O(5)#3	1.962(3)	Cu(4)–O(7)#2	1.984(3)	C(1)–C(2)	1.506(6)
Cu(2)–O(7)	2.004(3)	Cu(4)–O(10)	1.946(3)	C(2)–C(3)	1.511(6)
Cu(2)–O(8)	2.007(3)	Cu(4)–O(10)#2	1.946(3)	C(3)–C(4)	1.522(6)
Cu(2)–O(9)	1.938(3)	Cu(4)–O(11)	2.458(3)	C(4)–C(5)	1.514(6)
Cu(2)–O(9)#3	2.503(3)	Cu(4)–O(11)#2	2.458(3)	C(5)–O(3)	1.262(6)
Cu(2)–O(10)#2	2.460(3)	Cu(5)–O(1)#1	2.579(3)	C(5)–O(4)	1.254(6)
Cu(3)–O(1)#1	2.482(3)	Cu(5)–O(1)#3	2.579(3)		
O(1)–Cu(1)–O(5)	89.2(1)	O(8)–Cu(2)–O(10)#2	73.0(1)	O(7)#2–Cu(4)–O(11)	92.3(1)
O(1)–Cu(1)–O(6)	86.8(1)	O(9)–Cu(2)–O(9)#3	80.3(1)	O(7)#2–Cu(4)–O(11)#2	92.3(1)
O(1)–Cu(1)–O(7)	169.0(1)	O(9)–Cu(2)–O(10)#2	104.4(1)	O(10)–Cu(4)–O(10)#2	180.0
O(1)–Cu(1)–O(9)	97.3(1)	O(9)#3–Cu(2)–O(10)#2	81.4(1)	O(10)–Cu(4)–O(11)	89.9(1)
O(1)–Cu(1)–O(11)	86.9(1)	O(1)#1–Cu(3)–O(6)#1	75.5(1)	O(10)–Cu(4)–O(11)#2	90.1(1)
O(5)–Cu(1)–O(6)	89.7(1)	O(1)#1–Cu(3)–O(6)#2	107.0(1)	O(10)#2–Cu(4)–O(11)	90.1(1)
O(5)–Cu(1)–O(7)	101.7(1)	O(1)#1–Cu(3)–O(8)	82.7(1)	O(10)#2–Cu(4)–O(11)#2	89.9(1)
O(5)–Cu(1)–O(9)	89.1(1)	O(1)#1–Cu(3)–O(10)#2	100.9(1)	O(11)–Cu(4)–O(11)#2	180.0
O(5)–Cu(1)–O(11)	71.3(1)	O(1)#1–Cu(3)–O(11)#2	161.6(1)	O(1)#1–Cu(5)–O(1)#3	180.0
O(6)–Cu(1)–O(7)	94.8(1)	O(6)#1–Cu(3)–O(6)#2	80.3(1)	O(1)#1–Cu(5)–O(5)#1	81.6(1)
O(6)–Cu(1)–O(9)	175.8(1)	O(6)#1–Cu(3)–O(8)	98.1(1)	O(1)#1–Cu(5)–O(5)#3	98.5(1)
O(6)–Cu(1)–O(11)	81.9(1)	O(6)#1–Cu(3)–O(10)#2	173.8(1)	O(1)#1–Cu(5)–O(8)	81.2(1)
O(7)–Cu(1)–O(9)	81.5(1)	O(6)#1–Cu(3)–O(11)#2	97.1(1)	O(1)#1–Cu(5)–O(8)#4	98.8(1)
O(7)–Cu(1)–O(11)	82.5(1)	O(6)#2–Cu(3)–O(8)	169.2(1)	O(1)#3–Cu(5)–O(5)#1	98.5(1)
O(9)–Cu(1)–O(11)	99.5(1)	O(6)#2–Cu(3)–O(10)#2	96.2(1)	O(1)#3–Cu(5)–O(5)#3	81.6(1)
O(5)#3–Cu(2)–O(7)	173.7(1)	O(6)#2–Cu(3)–O(11)#2	88.0(1)	O(1)#3–Cu(5)–O(8)	98.8(1)
O(5)#3–Cu(2)–O(8)	79.9(1)	O(8)–Cu(3)–O(10)#2	86.4(1)	O(1)#3–Cu(5)–O(8)#4	81.2(1)
O(5)#3–Cu(2)–O(9)	100.6(1)	O(8)–Cu(3)–O(11)#2	81.6(1)	O(5)#1–Cu(5)–O(5)#3	180.0
O(5)#3–Cu(2)–O(9)#3	81.4(1)	O(10)#2–Cu(3)–O(11)#2	87.8(1)	O(5)#1–Cu(5)–O(8)	98.5(1)
O(5)#3–Cu(2)–O(10)#2	112.3(1)	O(7)–Cu(4)–O(7)#2	180.0	O(5)#1–Cu(5)–O(8)#4	81.5(1)
O(7)–Cu(2)–O(8)	99.0(1)	O(7)–Cu(4)–O(10)	93.9(1)	O(5)#3–Cu(5)–O(8)	81.5(1)
O(7)–Cu(2)–O(9)	80.8(1)	O(7)–Cu(4)–O(10)#2	86.1(1)	O(5)#3–Cu(5)–O(8)#4	98.5(1)
O(7)–Cu(2)–O(9)#3	92.8(1)	O(7)–Cu(4)–O(11)	92.3(1)	O(8)–Cu(5)–O(8)#4	180.0
O(7)–Cu(2)–O(10)#2	73.1(1)	O(7)–Cu(4)–O(11)#2	87.7(1)	O(1)–C(1)–O(2)	123.2(4)
O(8)–Cu(2)–O(9)	177.3(1)	O(7)#2–Cu(4)–O(10)	86.1(1)	O(3)–C(5)–O(4)	123.3(4)
O(8)–Cu(2)–O(9)#3	102.5(1)	O(7)#2–Cu(4)–O(10)#2	93.9(1)		

[a] Symmetry transformations used to generate equivalent atoms: #1 = $x-1$, y, z; #2 = $-x$, $-y+1$, $-z$; #3 = $-x$, $-y+2$, $-z$; #4 = $-x-1$, $-y+2$, $-z$; #5 = $x+1$, y, z; #5 = $-x-1$, $-y+1$, $-z$.

Acknowledgements

The project was supported by the Expert Project of Key Basic Research of the Ministry of Science and Technology of China (Grant 2003CCA00800), Zhejiang Provincial Natural Science Foundation (Grant Z203067), and Ningbo Municipal Natural Science Foundation (Grant 2006A610061).

References

[1] (a) D. Maspoch, D. Ruiz-Molina, J. Veciana. *Chem. Soc. Rev.*, **35**, 770 (2007); (b) R. Horikoshi, T. Mochida. *Coord. Chem. Rev.*, **250**, 2595 (2006); (c) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange. *Acc. Chem. Res.*, **38**, 217 (2005); (d) S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004); (e) S.L. James. *Chem. Soc. Rev.*, **32**, 276 (2003); (f) O.R. Evans, W. Lin. *Acc. Chem. Res.*, **35**, 511 (2002); (g) B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001); (h) G.F. Swiegers, T.J. Malefeste. *Chem. Rev.*, **100**, 3483 (2000); (i) C. Kaes, A. Katz, M.W. Hosseini. *Chem. Rev.*, **100**, 3553 (2000); (j) L. Carlucci, G. Ciani, M. Moret, D.M. Proserpio, S. Rizzato. *Angew. Chem. Int. Ed.*, **39**, 1506 (2000); (k) M.J. Zaworotko. *Angew. Chem. Int. Ed.*, **39**, 3052 (2000); (l) S.R. Batten, R. Robson. *Angew. Chem. Int. Ed.*, **37**, 1460 (1998); (m) P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 2638 (1999).

[2] (a) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E.B. Lobkovsky. *Adv. Mater.*, **19**, 1693 (2007); (b) N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O.M. Yaghi. *J. Am. Chem. Soc.*, **127**, 1504 (2005); (c) N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi. *Science*, **300**, 1127 (2003).

[3] (a) H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi. *Nature*, **18**, 276 (1999); (b) S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. William. *Science*, **283**, 1148 (1999).

[4] (a) M.P. Gupta, B.P. Devi. *Curr. Sci.*, **47**, 336 (1978); (b) P. Sharrock, T. Theophanides. *Can. J. Chem.*, **53**, 98 (1975); (c) Y.-Q. Zheng, J.-L. Lin. *Z. Kristallogr. New Cryst. Struct.*, **215**, 157 (2000); (d) Y.-Q. Zheng, J.-L. Lin. *Z. Kristallogr. New Cryst. Struct.*, **215**, 159 (2000); (e) E. Suresh, M.M. Bhadbhade, K. Venkatasubramanian. *Polyhedron*, **18**, 657 (1999); (f) Y.-Q. Zheng, A.-Y. Pan, J.-L. Lin. *Z. Kristallogr. New Cryst. Struct.*, **215**, 263 (2000); (g) Y.-Q. Zheng, J.-L. Lin, J. Sun, H.-L. Zhang. *Z. Kristallogr. New Cryst. Struct.*, **215**, 163 (2000); (h) Y.-Q. Zheng, S.-Q. Zhou, J.-L. Lin. *Z. Kristallogr. New Cryst. Struct.*, **216**, 265 (2001); (i) Y.-Q. Zheng, J.-L. Lin, W.-J. Chen. *Z. Kristallogr. New Cryst. Struct.*, **216**, 269 (2001); (j) Y.-Q. Zheng, J.-L. Lin. *Z. Kristallogr. New Cryst. Struct.*, **215**, 165 (2000).

[5] (a) Y.-Q. Zheng, J.-L. Lin, A.-Y. Pan. *Z. Anorg. Allg. Chem.*, **626**, 1718 (2000); (b) M. Fleck, E. Tillmanns, L. Bohaty. *Z. Kristallogr. New Cryst. Struct.*, **215**, 619 (2000); (c) R.K. Rastsvetaeva, D. Yu. Pushcharovsky, N.G. Furmanova. *Z. Kristallogr.*, **211**, 808 (1996); (d) Y.-Q. Zheng, J.-L. Lin, J. Sun, A.-Y. Pan. *Z. Kristallogr. New Cryst. Struct.*, **215**, 161 (2000).

[6] (a) Y.-Q. Zheng, K. Peters, H.G. von Schnering. *Chem. Res. in Chin. Univ.*, **17**, 20 (2001); (b) Y.-Q. Zheng, J.-L. Lin, H.-L. Zhang. *Z. Kristallogr. New Cryst. Struct.*, **215**, 535 (2000); (c) Y.-Q. Zheng, A.-Y. Pan, J.-L. Lin. *Z. Kristallogr. New Cryst. Struct.*, **216**, 267 (2001); (d) A. Michaelides, V. Kiritsis, S. Skoulika, A. Aubry. *Angew. Chem. Int. Ed.*, **32**, 1495 (1993).

[7] P.M. Forster, A.R. Burbank, C. Livage, G. Férey, A.K. Cheetham. *Chem. Commun.*, 368 (2004).

[8] C. Livage, C. Egger, G. Férey. *Chem. Mater.*, **13**, 410 (2001).

[9] (a) Y.-Q. Zheng, Z.-P. Kong. *J. Solid State Chem.*, **166**, 279 (2002); (b) Y.J. Kim, E.W. Lee, D.-Y. Jung. *Chem. Mater.*, **13**, 2684 (2001); (c) Y.J. Kim, D.-Y. Jung. *Inorg. Chem.*, **39**, 1470 (2000); (d) Y.J. Kim, D.-Y. Jung. *Bull. Korean Chem. Soc.*, **21**, 656 (2000).

[10] (a) C. Livage, C. Egger, G. Férey. *Chem. Mater.*, **11**, 1546 (1999); (b) C. Livage, C. Egger, G. Férey. *J. Mater. Chem.*, **8**, 2743 (1998); (c) L.-S. Long, X.-M. Chen, M.-L. Tong, Z.-G. Sun, Y.-P. Ren, R.-B. Huang, L.-S. Zheng. *J. Chem. Soc., Dalton Trans.*, 2888 (2001).

[11] P.M. Forster, A.K. Cheetham. *Angew. Chem. Int. Ed.*, **41**, 457 (2002).

[12] Y.-Q. Zheng, J.-L Lin, Z. Kristallogr. *New Cryst. Struct.*, **216**, 139 (2001).

[13] (a) E.W. Lee, Y.J. Kim, D.-Y. Jung. *Inorg. Chem.*, **41**, 501 (2002); (b) C. Livage, C. Egger, G. Férey. *C. R. Acad. Sci. Ser. Iic: Chim.*, **4**, 221 (2001).

[14] (a) B.H. O'Connor, E.N. Maslen. *Acta Cryst.*, **20**, 824 (1966); (b) R.K. Rastsvetaeva, D. Yu. Pushcharovsky, N.G. Furmanova. *Z. Kristallogr.*, **211**, 808 (1996).

[15] E.G. Bakalbassis, M. Korabik, A. Michailides, J. Mrozinski, C. Raptopoulou, S. Skoulika, A. Terzis, D. Tsaousis. *J. Chem. Soc., Dalton Trans.*, 850 (2001).

[16] P.M. Forster, P.M. Thomas, A.K. Cheetham. *Chem. Mater.*, **14**, 17 (2002).
[17] R. Vaidhyanathan, S. Natarajan, C.N.R. Rao. *Inorg. Chem.*, **41**, 5226 (2002).
[18] N. Guillou, C. Livage, W. van Beek, M. Noguès, G. Férey. *Angew. Chem. Int. Ed.*, **42**, 644 (2003).
[19] Y.-Q. Zheng, J.-L. Lin, J. Sun. *Z. Anorg. Allg. Chem.*, **627**, 1647, (2001) and references therein.
[20] M. Kurmoo, H. Kumagai, M.A. Green, B.W. Lovett, S.J. Blundell, A. Ardavan, J. Singleton. *J. Solid State Chem.*, **159**, 343 (2001).
[21] (a) M.R.S.J. Foreman, M.J. Plater, J.M.S. Skakle. *J. Chem. Soc., Dalton Trans.*, 1897 (2001); (b) R. Vaidhyanathan, S. Natarajan, C.N.R. Rao. *Cryst. Growth Des.*, **3**, 47 (2003); (c) E. Whelan, M. Devereux, M. McCann, V. McKeec. *Chem. Commun.*, 427 (1997); (d) F. Serpaggi, G. Férey. *Microporous Mesoporous Mater.*, **32**, 311 (1999).
[22] T.A. Bowden, H.L. Milton, A.M.Z. Slawin, P. Lightfoot. *J. Chem. Soc., Dalton Trans.*, 936 (2003).
[23] J.-L. Lin, J. Sun, Y.-Q. Zheng. *J. Ningbo Univ.*, **14**, 5 (2001).
[24] Y.-Q. Zheng, Z.-P. Kong, Z. Kristallogr. *New Cryst. Struct.*, **218**, 223 (2003).
[25] E.A.H. Griffith, N.G. Charles, E.L. Amma. *Acta Cryst.*, **B38**, 262 (2001).
[26] Y.-Q. Zheng, J. Sun. *J. Solid State Chem.*, **172**, 288 (2003).
[27] Y.-Q. Zheng, W.-H. Liu, J.-L. Lin. *Z. Anorg. Allg. Chem.*, **628**, 824 (2002).
[28] G.M. Sheldrick. *SHELXS-97*, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen (1997).
[29] G.M. Sheldrick. *SHELXL-97*, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen (1997).