



Homochiral frameworks derived from magnesium, zinc and copper salts of L-tartaric acid

Jeffrey A. Rood¹, Bruce C. Noll, Kenneth W. Henderson*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556-5670, USA

ARTICLE INFO

Article history:

Received 11 June 2009

Received in revised form

21 October 2009

Accepted 1 November 2009

Available online 8 December 2009

Keywords:

Metal-organic frameworks

Homochiral

Divalent metals

X-ray crystallography

ABSTRACT

Five metal-organic frameworks derived from L-tartrate ($L\text{-tart} = \text{C}_4\text{H}_4\text{O}_6$) and the divalent metal ions magnesium, zinc or copper have been prepared and structurally characterized. The frameworks were prepared from the reaction of potassium L-tartrate [$\text{KC}_4\text{H}_5\text{O}_6$] with the appropriate metal salt in water solutions. The magnesium compound [$\text{Mg}(L\text{-tart})(\text{H}_2\text{O}) \cdot 1.5\text{H}_2\text{O}$], **1**, crystallizes as a two-dimensional 6^3 sheet structure. The addition of the divergent linker molecules 4,4'-bipyridine (bipy) or *trans*-1,2-bispyridylethylene (bpe) to systems involving Zn^{2+} and Cu^{2+} results in the formation of the homochiral three-dimensional structures [$\text{Zn}_2(L\text{-tart})(\text{bipy})(\text{H}_2\text{O}) \cdot 5.25\text{H}_2\text{O}$], **2**, [$\text{Cu}(L\text{-tart})(\text{bipy}) \cdot 2.33\text{H}_2\text{O}$], **3**, and [$\text{Cu}(L\text{-tart})(\text{bpe}) \cdot 8\text{H}_2\text{O}$], **5**. Removal of solvent water molecules from **3** resulted in [$\text{Cu}(L\text{-tart})(\text{bipy}) \cdot 0.2\text{H}_2\text{O}$], **4**. Similar experiments on **2** and **5** resulted in breakdown of the frameworks, illustrating the dependence of the stability of these structures on the guest water molecules. This study reports the structures of two new topological types of binodal nets.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Metal-organic frameworks (MOFs) have received considerable interest in recent times due to their potential applications [1] in areas such as catalysis [2], optics [3], electronics [4], small molecule storage [5], and separation science [6]. An attractive strategy for the synthesis of these networks has been through the reaction of transition metal salts with ditopic carboxylate ligands [7]. Our group [8] and others [9] have expanded these studies to include the synthesis of porous magnesium carboxylate frameworks. These materials have proven to be more thermally robust than their transition metal analogues, can be used in the molecular exchange of small molecules, and may be used in the sorption of various gases including dihydrogen. We have sought to extend our work in this area towards the formation of homochiral frameworks for use in enantioselective separations and heterogeneous asymmetric syntheses [10–19]. Recently, we have shown that camphorate is a reliable and robust chiral linker molecule for the preparation of MOF materials [20]. In a similar vein we wished to study the use of the dicarboxylate ligand L-tartrate ($L\text{-tart} = \text{C}_4\text{H}_4\text{O}_6$) in framework synthesis. A recent study by Cheetham on magnesium tartrates has shown that an unexpectedly diverse series of complex structures can be

obtained by varying the reaction conditions for crystallization [21]. We were drawn to the idea of incorporating tartrate into MOFs not only for its inherent chirality, but also because of the possibility of performing post-synthetic modifications [22] to the materials. Specifically, the hydroxyl substituents of the ligand are attractive units to chemically alter following assembly of a porous MOF. Herein, we report on the syntheses, solid-state structures and physical properties of five materials composed of the divalent metals magnesium, zinc and copper and L-tartrate.

2. Experimental details

2.1. General procedures

All reagents, magnesium acetate tetrahydrate [$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$] (98%, Aldrich), zinc acetate [$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$] (99%, Alfa Aesar), copper (II) nitrate trihydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$] (p.a., Acros), potassium L-tartrate [$\text{KC}_4\text{H}_5\text{O}_6$] (99%, Acros), 4,4'-bipyridine (bipy) (98%, TCI America), and *trans*-1,2-bispyridylethylene (bpe) (98%, Acros) were purchased and used without further purification. Elemental analyses were performed at Midwest Microlab, Indianapolis, IN. Thermogravimetric analyses were performed on a TA instruments Hi-Res Modulated TGA 2950 thermogravimetric analyzer at the rate of $10^\circ\text{C}/\text{min}$ under N_2 . FT-IR spectra were obtained as KBr pellets on a Nicolet Nexus 870 FT-IR spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$.

* Corresponding author. Fax: +1 574 631 6652.

E-mail address: khenders@nd.edu (K.W. Henderson).

¹ Current address: Department of Chemistry and Biochemistry, 1 Alpha Drive, Elizabethtown, PA 17022.

2.2. Synthesis of $[Mg(l\text{-tart})(H_2O) \supset 1.5H_2O]$, **1**

$Mg(C_2H_3O_2)_2 \cdot 4H_2O$ (0.66 mmol, 0.141 g) and $l\text{-KC}_4\text{H}_5\text{O}_6$ (0.66 mmol, 0.124 g) were added to 3 mL of deionized water in a 20 mL scintillation vial. The vial was tightly capped and placed in a 60 °C silicon oil bath. Within 5 min a solution had formed. After sitting for 16 h, a large batch of colorless crystals deposited in the vial. Yield: 0.11 g, 78%. Elemental analysis found (wt %): C, 21.93; H, 4.02. Calculated (wt%) C, 22.13; H, 3.92. IR bands (cm^{-1}) for **1** (KBr pellet): 3460 s, 1656 s, 1447 s, 1383 s, 1310 s, 1291 s, 1238 m, 1122 s, 1088 s, 1050 m, 1007 w, 938 w, 843 w, 725 m, 632 m, 519 m, 446.5 m, 410 m.

2.3. Synthesis of $[Zn_2(l\text{-tart})_2(bipy)(H_2O) \supset 5.25H_2O]$, **2**

$Zn(C_2H_3O_2)_2$ (0.66 mmol, 0.121 g), $l\text{-KC}_4\text{H}_5\text{O}_6$ (0.66 mmol, 0.124 g), and 4,4'-bipyridine (0.66 mmol, 0.1 g) were added to 8 mL of deionized water in a 20 mL scintillation vial. The mixture was stirred until a solution formed. The vial was tightly capped and placed in a silicon oil bath at 60 °C. After 18 h, small, colorless plates had formed. Yield: 0.47 g, 72%. Elemental analysis found (wt%): C, 30.96; H, 3.09; N, 4.14. Calculated (wt %) C, 31.43; H, 2.98; N, 4.07. IR bands (cm^{-1}) for **2** (KBr pellet): 3387 s, 1604 s, 1490 w, 1415 s, 1219 w, 1109 m, 1068 w, 1009 w, 928 w, 895 w, 816 m, 729 m, 634 m, 525 w, 420 w.

2.4. Synthesis of $[Cu(l\text{-tart})(bipy) \supset 2.33H_2O]$, **3**

$Cu(NO_3)_2 \cdot 3H_2O$ (0.66 mmol, 0.160 g), $l\text{-KC}_4\text{H}_5\text{O}_6$ (0.66 mmol, 0.124 g) and 4,4'-bipyridine (0.66 mmol, 0.1 g) were added to 8 mL of deionized water in a 20 mL scintillation vial. The mixture was stirred until a solution formed. The vial was tightly capped and placed in a silicon oil bath at 60 °C. After 36 h, the vial was removed and a mixture of blue powder and small, blue, block-like crystals had formed. Phase purity was confirmed by PXRD studies. Yield: 0.21 g, 78%. Elemental analysis found (wt %): C, 41.62; H, 2.89; N, 6.97. Calculated (wt%) C, 41.00; H, 3.03; N, 6.83. IR bands (cm^{-1}) for **3** (KBr pellet): 3355 m, 2293 m, 2889 w, 2360 w, 2339 w, 1613 s, 1572 s, 1538 m, 1490 m, 1456 s, 1415 s, 1328 s, 1241 w, 1218 m, 1115 s, 1069 s, 1013 w, 992 w, 936 w, 921 w, 877 w, 845 w, 824 w, 810 w, 726 m, 673 m, 646 s, 550 m, 470 m 421 w, 408 w.

2.5. Synthesis of $[Cu(l\text{-tart})(bipy) \supset 0.2H_2O]$, **4**

A crystalline sample of **3** was evacuated using a two-stage rotary pump and heated to 110 °C for 36 h. The crystals were subsequently used for single-crystal and powder XRD studies. Powder XRD studies are consistent with retention of the framework upon evacuation. IR bands (cm^{-1}) for **4** (KBr pellet): 3352 w, 2294 m, 2889 w, 2358 w, 2336 w, 1613 s, 1573 s, 1537 m, 1490 m, 1456 s, 1413 s, 1328 s, 1241 w, 1218 m, 1115 s, 1069 s, 1013 w, 992 w, 936 w, 921 w, 875 w, 810 w, 726 m, 673 m, 646 s, 550 m, 470 m 421 w, 409 w.

2.6. Synthesis of $[Cu(l\text{-tart})(bpe) \supset 8H_2O]$, **5**

$Cu(NO_3)_2 \cdot 3H_2O$ (0.49 mmol, 0.118 g), $l\text{-KC}_4\text{H}_5\text{O}_6$ (0.66 mmol, 0.124 g) and *trans*-1,2-bispyridylethylene (0.66 mmol, 0.120 g) were added to 8 mL of deionized water in a 20 mL scintillation vial. This stoichiometric ratio of reagents was necessary for obtaining suitable crystals. The vial was tightly capped and placed in a silicon oil bath at 60 °C. After 36 h, the vial was removed and a mixture of light blue powder and small, blue, block-like crystals had formed. An individual yield could not be

calculated due co-precipitation of unreacted starting materials. For this reason elemental analyses were not carried out on the sample. The presence of contaminants was confirmed from the appearance of additional signals in the PXRD pattern of **5**.

2.7. Polarimetry experiments

For each of the frameworks discussed in this work, the retention of homochirality by the tartrate ligands was confirmed crystallographically by refinement of the Flack parameter and through polarimetry experiments. In each case, a crystalline sample of the materials was dissolved in 1 M NaOH solution and the rotation was compared to a standard solution of potassium *l*-tartrate in 1 M NaOH. In each case, this studied verified that the bulk sample maintained its chirality.

2.8. X-ray crystallography

Powder XRD patterns were obtained on a Bruker Smart Apex diffractometer with Cu $K\alpha$ radiation. The sample was mounted in a capillary. Data were collected by the 2D Apex detector fixed at 100 mm, $20^\circ 2\theta$, $0^\circ \omega$, $0^\circ \phi$ for 10 min.

Single-crystals were examined under Infineum V8512 oil. The datum crystal was affixed to either a thin glass fiber atop a tapered copper mounting pin or Mitegen mounting loop and transferred to the 100K nitrogen stream of a Bruker APEX II diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Cell parameters were determined using reflections harvested from three sets of $12 \times 0.5^\circ \phi$ scans. The orientation matrix derived from this was transferred to COSMO [23] to determine the optimum data collection strategy requiring a minimum of 4-fold redundancy. Cell parameters were refined using reflections harvested from the data collection with $I \geq 10\sigma(I)$. All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS [24].

The structures were solved from partial datasets using the Autostructure option in APEX 2 [25]. This option employs an iterative application of the direct methods, Patterson synthesis, and dual-space routines of SHELXTL [26]. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to $1.2 \times$ or $1.5 \times$ the equivalent isotropic U of the parent atom (Table 1).

3. Results and discussion

The reaction of *l*-potassium hydrogen tartrate ($l\text{-KC}_4\text{H}_5\text{O}_6$) with magnesium acetate in water at 60 °C resulted in the deposition of high quality crystals of $[Mg(l\text{-tart})(H_2O) \supset 1.5H_2O]$, **1**, over a period of 16 h. The chirality of the tartrate ligand was preserved under these conditions, as confirmed by refinement of the Flack parameter and polarimetry experiments. The asymmetric unit of **1** consists of two independent magnesium atoms. Each magnesium lies in a distorted octahedral coordination environment (Fig. 1). Two independent tartrate anions chelate to the metal centers through a carboxylate oxygen atom (Mg1–O11/Mg1–O6 and Mg2–O1/Mg2–O7) and a hydroxyl oxygen atom (Mg1–O4/Mg1–O10 and Mg2–O3/Mg1–O8). The fifth coordination site is occupied by a aquo ligand (Mg1–O1W and Mg2–O2W). The final site on the metal is filled by a carboxylate oxygen atom from a neighboring dimer (Mg1–O2* and Mg2–O5*). The structure of **1** is the enantiomer of the recently reported $[Mg(D\text{-tart})(H_2O) \supset 1.5H_2O]$ by Cheetham and co-workers [21].

Table 1
Crystallographic data for compounds **1–5**.

	1	2	3	4	5
Formula	C ₈ H ₁₇ Mg ₂ O ₁₇	C ₁₈ H _{20.5} Zn ₂ N ₂ O _{18.25}	C ₁₄ H _{16.66} CuN ₂ O _{8.33}	C ₁₄ H _{12.4} CuN ₂ O _{6.2}	C ₃₀ H ₄₄ Cu ₂ N ₄ O ₂₀
fw	433.84	687.28	409.78	371.15	907.77
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P222 ₁	P4 ₁ 2 ₁ 2	P4 ₁ 2 ₁ 2	P2 ₁ 2 ₁ 2 ₁
a, Å	7.862(2)	8.8029(2)	8.572(1)	8.5385(1)	8.575(2)
b, Å	11.061(2)	12.7585(2)	8.572(1)	8.5385(1)	8.575(2)
c, Å	18.080(4)	23.4976(5)	43.284(7)	43.502(1)	52.52(1)
α, deg.	90	90	90	90	90
β, deg.	90	90	90	90	90
γ, deg.	90	90	90	90	90
V, Å ³	1572.3(5)	2639.06(9)	3180.5(7)	3171.56(11)	3861.8(13)
Z	4	4	8	8	4
D, Mg/m ³	1.833	2.530	1.440	1.616	1.561
μ, (Mo Kα), mm ⁻¹	0.251	1.984	1.389	1.412	1.187
Fack parameter	0.04(16)	0.002(14)	0.00(2)	0.06(3)	0.09(3)
Cryst size, mm	0.22 × 0.21 × 0.14	0.10 × 0.12 × 0.19	0.14 × 0.15 × 0.15	0.15 × 0.16 × 0.16	0.19 × 0.20 × 0.32
T _{max} and T _{min}	0.97 and 0.98	0.77 and 0.86	0.79 and 0.86	0.74 and 0.80	0.73 and 0.80
θ _{min} , θ _{max} , deg.	2.16 to 31.56	1.73 to 27.10	1.88 to 26.04	1.87 to 27.14	0.78 to 25.00
Reflections	28,130	30,520	37,924	25,253	60,362
Ind reflections	5225	5809	3142	3508	6807
R(int)	0.0354	0.0428	0.0859	0.0484	0.0768
R1 ^a , wR2 ^b [I > 2σ(I)]	0.0329, 0.0727	0.0382, 0.0983	0.0448, 0.0553	0.0588, 0.1318	0.0799, 0.2107
R1 ^a , wR2 ^b (all data)	0.0399, 0.0770	0.0478, 0.1033	0.0665, 0.0670	0.0612, 0.1328	0.0806, 0.2118
GOOF, F ²	1.044	1.002	1.057	1.307	1.063
Largest peak/hole, e. Å ⁻³	0.520 and -0.240	0.899 and -0.552	0.510 and -0.500	0.603 and -0.726	1.373 and -0.960

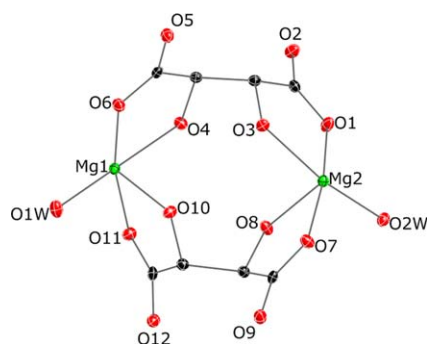


Fig. 1. The repeating dimeric unit found in **1**. Hydrogen atoms and solvent water molecules are omitted for clarity.

Structures incorporating the dimeric unit shown in Fig. 1 are well documented for tartrate salts of various divalent metals [27].

The extended structure of **1** may be described as a two-dimensional 6³-hcb net, where each magnesium center acts as a trigonal node (Fig. 2) [28]. The 6³-hcb nets pack as interdigitated corrugated layers in the solid state, with the solvent water molecules captured within the channels created by the hexagonal rings. The enclathrated water molecules are involved in hydrogen bonding to both the metal-coordinated water and the tartrate hydroxyl groups.

We were attracted by the possibility of replacing the coordinated water molecules in **1** by a neutral divergent linker. If successful this could lead to the formation of isorecticular 3D frameworks incorporating the 6³-hcb net structure. Attempts to use 4,4'-bipyridine in association with this magnesium system failed, likely due to the poor compatibility of these components [29]. We then focused on preparing the zinc analogue of **1** with 4,4'-bipyridine as a linker. The reaction of (+)-potassium hydrogen tartrate with zinc acetate at 60 °C in the presence of one equivalent of 4,4'-bipyridine resulted in the deposition of high quality crystals of [Zn₂(L-tart)₂(bipy)(H₂O)]·5.25H₂O, **2**.

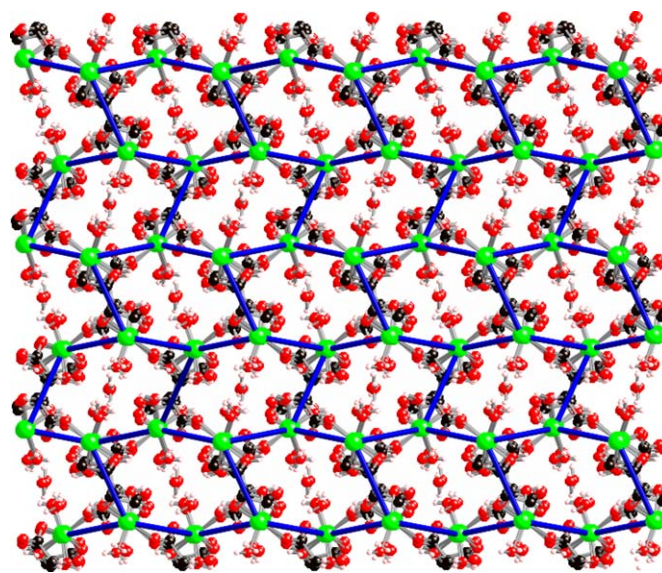


Fig. 2. The overall 6³-hcb net found in **1**, illustrated by blue rods connecting the magnesium centers. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

A single crystal X-ray diffraction study of **2** revealed a rather surprising structure. The building blocks are metal dimers similar to those found in **1**, and these connect to create a 6³-hcb net as desired. However, two different types of zinc dimers are present, one solvated by water akin to **1**, and a second solvated by 4,4'-bipyridine (Fig. 3). The 4,4'-bipyridine molecules act as bridges (or pillars) between independent hcb layers by binding to a zinc center of one layer and forming a hydrogen bond to the hydroxyl moiety of a tartrate on a neighboring hcb layer. The overall framework structure of **2** is shown in Fig. 4, with the hydrogen bond between N2 and O9 (the hydroxyl proton bound to O9) highlighted. These hydrogen bonds are relatively strong, as judged

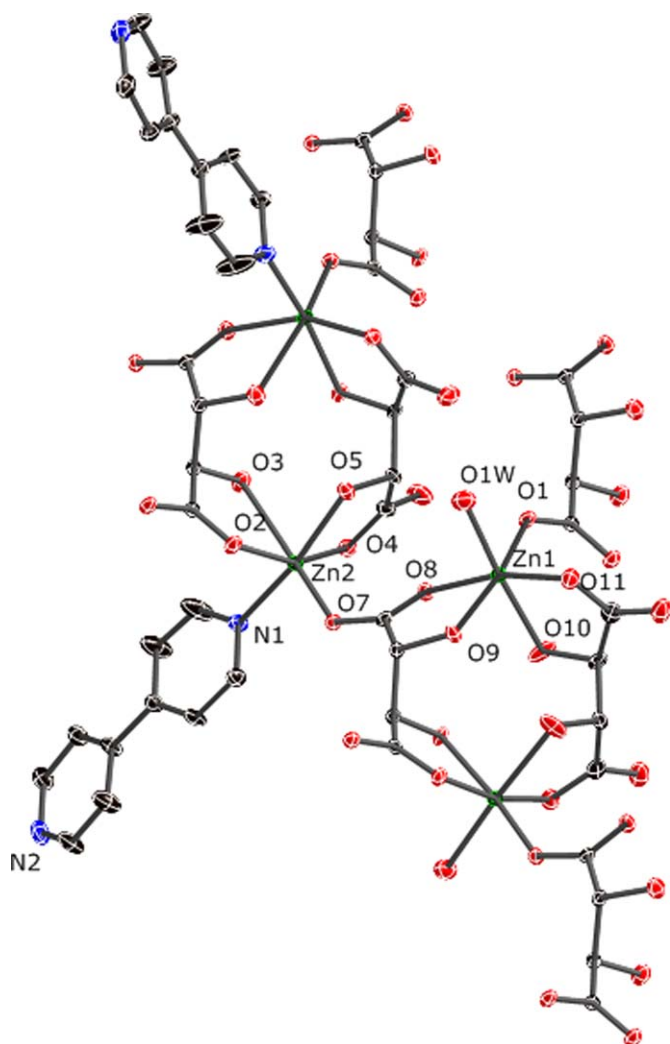


Fig. 3. Coordination environments of the two zinc centers found in **2**. Hydrogen atoms and solvent water molecules are omitted for clarity.

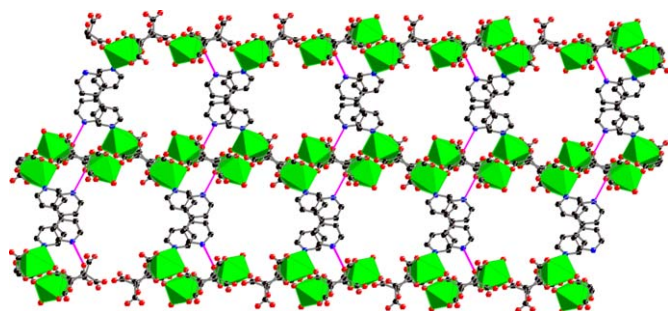


Fig. 4. The extended structure of **2** with the N2–H09 hydrogen bond represented as a pink bar. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by the N2–H09 and the N2–O9 distances of 1.78(7) and 2.596(5) Å, respectively, and with a N2–H09–O9 angle of 157.16(5)° [30]. The average Zn–O distance in **2** is 2.105(3) Å [range 2.001(3) to 2.376(3)], with the shorter distances being the Zn–carboxylate interactions and the longer distances being the Zn to dative hydroxyl interactions. The Zn2–N1 distance is 2.092(4) Å.

Analysis of **2** with the TOPOS software reveals that the structure can be described as a binodal net, were the two distinct

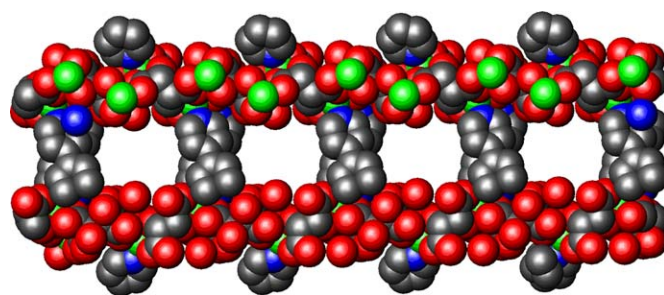


Fig. 5. Space filling model of **2** showing the potential void space.

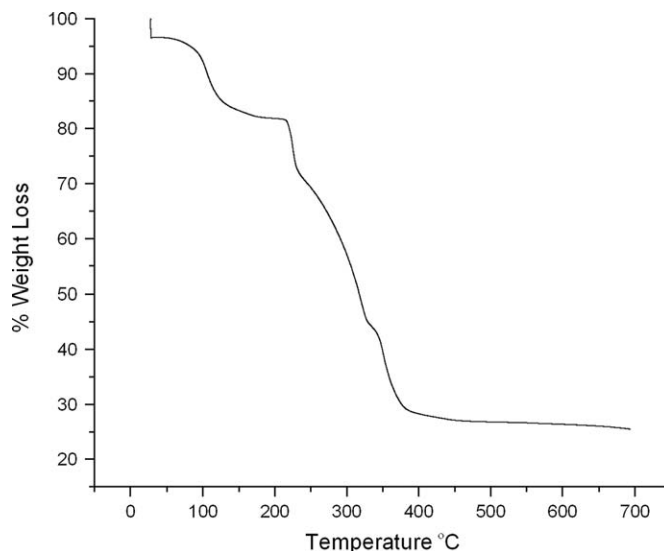


Fig. 6. Thermogravimetric analysis of **2** (10 °C/min under N₂).

environments around the zinc centers act as four-connected nodes to give a self-catenated binodal (4,4) net with the Schläfli symbol being (6⁵.8)(6⁶) [31]. The structure of **2** is an open and potentially porous net. Free water molecules reside within the hexagonal channels of the network running down the crystallographic *a*-axis. These water molecules form hydrogen bonds among themselves as well as to the framework. Removal of the enclathrated water molecules would result in a potential void space of 852.4 Å³ or 31%, as calculated by PLATON (Fig. 5) [32].

TGA was performed on a sample of **2** to monitor water loss and investigate if the material was robust. The TGA results shown in Fig. 6 suggest that a solvent-free material may be obtained between 175 and 200 °C, prior to decomposition of the framework. However, attempts at removing the free water by heating under vacuum at 120 °C or by heating at ambient pressure at 160 °C caused the framework to fracture. The numerous hydrogen bonding interactions that exist between the solvent water molecules and the framework may play a critical role in the overall framework stability. Furthermore, the hydrogen bonding utilized for the pillars of the structure may not be stable under these conditions. Attempts to exchange the guest water molecules by soaking in other solvents such as MeOH or CHCl₃, followed by heating under vacuum, were not successful.

We wished to further extend this class of materials by investigating the use of other metal centers. Copper complexes have also been shown to adopt similar dimeric motifs to that of **1** and **2**.²⁷ The reaction of Cu(NO₃)₂ · 3H₂O with 1(+)-potassium hydrogen tartrate and 4/4'-bipyridine in water resulted in batch of blue, block-like, crystals of [Cu(1-tart)(bipy)]₂ · 2.33H₂O, **3**. Single crystal X-ray diffraction studies of **3** revealed that the Cu centers

were indeed linked by 4,4'-bipyridine, however the dimeric motif seen in **1** and **2** is no longer present. As shown in Fig. 7, the pseudo square-based pyramidal copper centers bind to carboxylate oxygen atoms of three distinct tartrates and two 4,4'-bipyridine molecules. The extended 3D structure is composed of copper-linked tartrate sheets with 4,4'-bipyridine pillars (Fig. 8). The copper centers are a 5-connect nodes. Unlike the dimers seen in compounds **1** and **2**, the hydroxyl groups of the tartrate ligand do not connect to the copper centers, but they are involved in hydrogen bonding to the solvent water molecules. The tartrate molecules coordinate in an unsymmetrical fashion and act as a

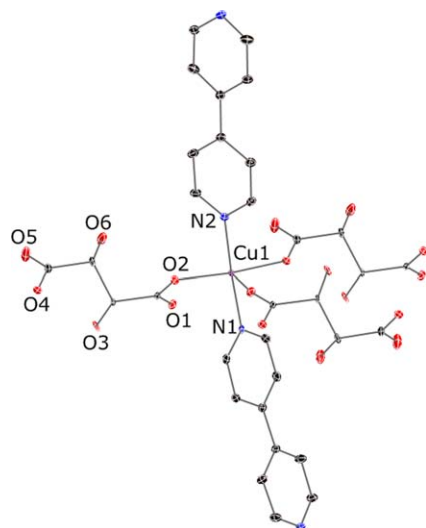


Fig. 7. Coordination environment of the Cu1 center in **3**. Hydrogen atoms are omitted for clarity.

3-connect node in two dimensions, with one carboxylate binding to a single copper center while the second carboxylate binds to two separate metals. In **3**, the average Cu–O distance is 2.050(3) Å [range 1.938(3)–2.259(3) Å] and the Cu–N distances are 1.977(3) and 1.995(3) Å. The overall extended structure results in a bimodal (3,5)-connected net. This topology has recently been reported as a theoretical net derived by the procedure of Blatov [33]. Using the methodology from this report, the (3,5) binodal net is called **fsc-3,5-P₄2₁2**, with a Schläfli symbol of (6³)(6⁹.8).

Association of the 2D sheets by 4,4'-bipyridine creates small channels that run along the crystallographic *b*-axis. Within these channels reside solvent water molecules that hydrogen bond between themselves and also to the free hydroxyl groups of the tartrate ligands. The potential void space upon removal of the water molecules was calculated by PLATON to be ~18%. Thermogravimetric analysis showed an initial weight loss of 8.5% through ~175 °C, corresponding to loss of the solvent water molecules (10.2% theoretical) followed by framework decomposition at 250 °C (Fig. 9).

A crystalline sample of **3** was heated at 110 °C overnight in an attempt to obtain the solvent-free framework. A subsequent single crystal X-ray diffraction study was carried out and it was found that nearly all of the water in the pores of **3** could be removed to give [Cu(*l*-tart)(bipy)·0.2H₂O], **4** (one residual peak of 1.5 electrons was modeled as a partially occupied water molecule). As shown in Fig. 10, powder X-ray diffraction studies showed that the bulk material remained crystalline upon evacuation of the pores.

Removal of the solvent water molecules has very little effect of the framework itself, with the average Cu–O distance in **4** being 2.013(5) Å [range 1.938(4)–2.271(4)] and the Cu–N distances being slightly longer at 2.005(5) and 2.021(5) Å. Due to the chiral nature of the framework, uptake studies on small, racemic chiral alcohols were carried out on **4**. Because of the small size of the channels, no uptake was seen for 2-butanol or 1,3-butanediol. This was confirmed both by crystallography and ¹H NMR after framework digestion.

In an attempt to increase the pore size for better uptake properties, reaction of Cu(NO₃)₂·3H₂O with *l*(+)-potassium hydrogen tartrate and the longer divergent linker, trans-1,2-bispyridylethylene were carried out in water at 60 °C. Reaction conditions involving an excess of tartrate and linker were necessary to obtain a crystalline sample for XRD studies.

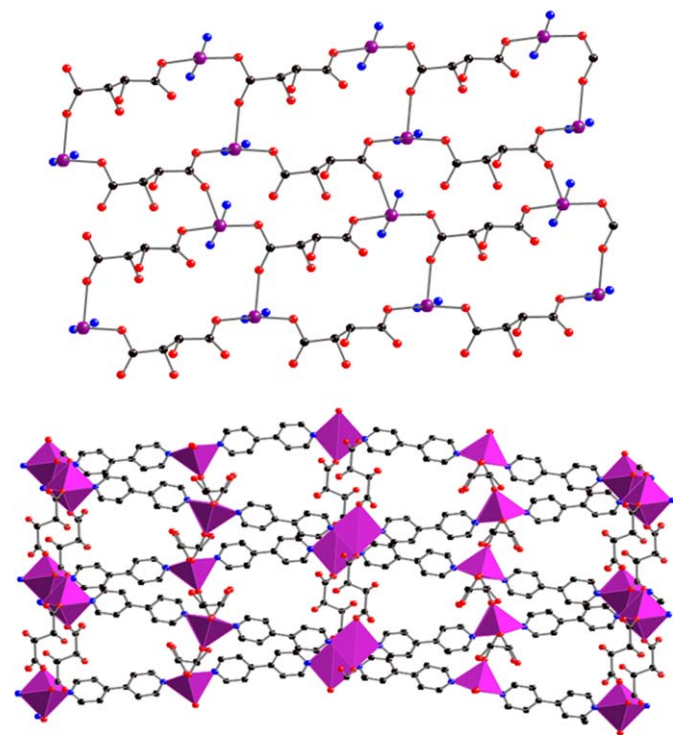


Fig. 8. The 6³-net formed in two dimensions through the tartrate ligands (top). The orthogonal 2D sheets linked into a 3D framework through 4,4'-bipyridine pillars (bottom). Hydrogen atoms and water solvent molecules are omitted for clarity.

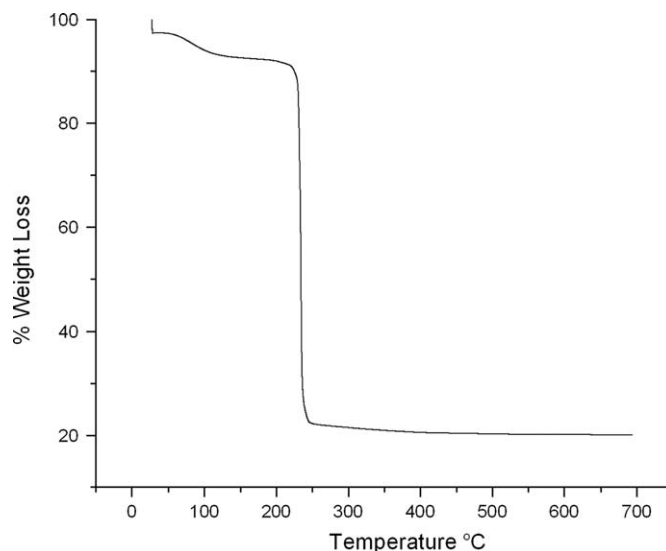


Fig. 9. Thermogravimetric analysis of **3** (10 °C/min under N₂).

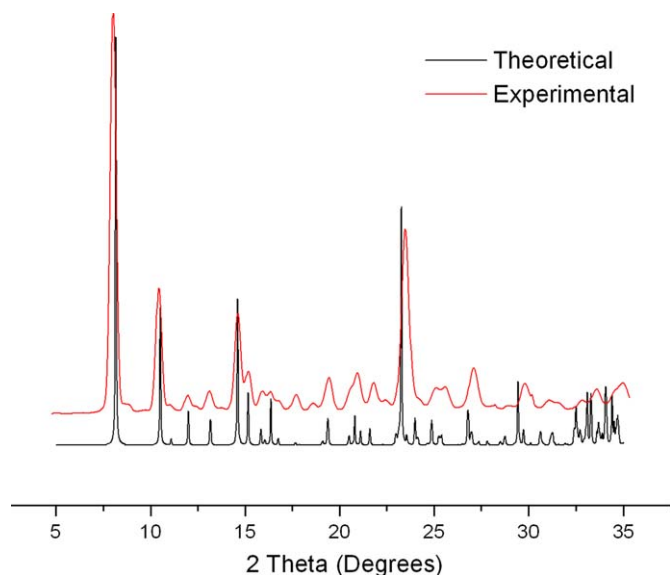


Fig. 10. PXRD diffraction pattern of the bulk material **4** (red) compared to the theoretical pattern (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

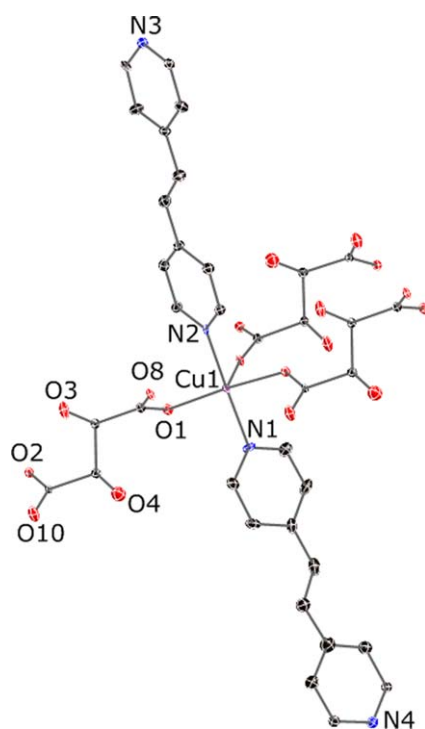


Fig. 11. Coordination environment around Cu1 in **5**. Hydrogen atoms are omitted for clarity.

A mixture of light blue powder and dark blue crystals were obtained from the reaction. Single crystal X-ray diffraction studies showed that the crystals were indeed the isorecticular framework $[\text{Cu}(\text{l-C}_4\text{H}_5\text{O}_6)(\text{C}_{12}\text{H}_{10}\text{N}_2 \cdot 8\text{H}_2\text{O})]$, **5**, a (3,5) binodal net incorporating the longer trans-1,2-bispyridylethylene linker. Fig. 11 shows the environment around a single Cu center.

Within **5**, the average Cu–O bond distance is 2.067(7) Å [range 1.963(6) to 2.324(8) Å]. The average Cu–N distance is 2.003(8) Å [range 1.996(8) to 2.015(8) Å]. As shown in Fig. 12, the longer trans-1,2-bispyridylethylene linker does serve to create slightly larger channels than were seen in **3**. Within the channels are eight

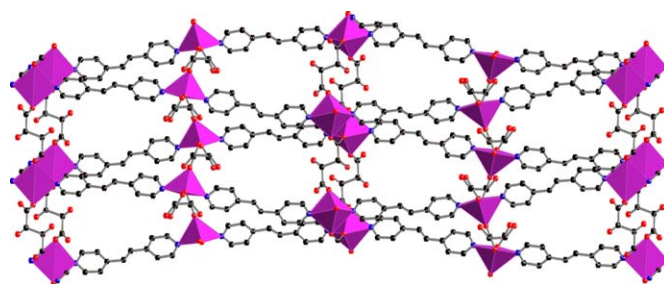


Fig. 12. The orthogonal 2D sheets linked into a 3D framework through trans-1,2-bispyridylethylene pillars. Hydrogen atoms and water solvent molecules are omitted for clarity.

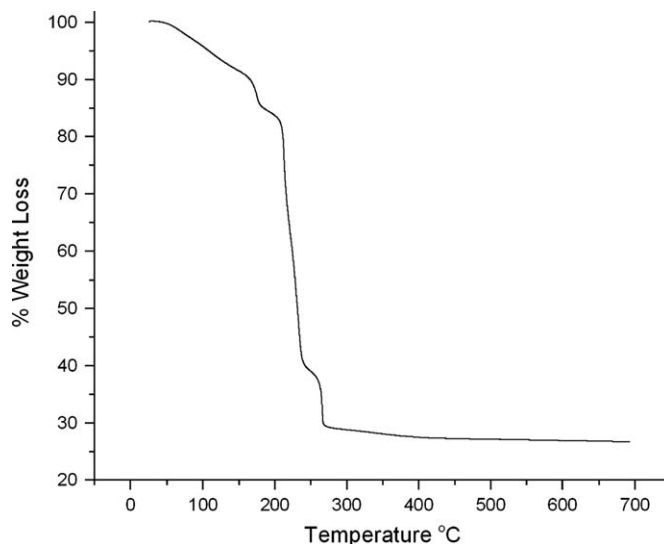


Fig. 13. Thermogravimetric analysis of **5** (10 °C/min under N_2).

highly disordered water molecules per formula unit that were modeled with the SQUEEZE routine in PLATON. Through this, the potential void space within the framework was calculated to be ~20%.

Thermogravimetric analysis of **5** showed a weight loss step of 18.5% followed immediately by decomposition at 215 °C (Fig. 13). Presumably the loss of 18.5% includes some decomposition, as loss of the eight water molecules per formula unit accounts for 15.8% weight loss. Attempts to obtain the solvent-free form of **5** by heating under vacuum overnight at 100 °C resulted in the loss of crystallinity of the material. PXRD diffraction studies revealed that the structure of the framework was not retained under these conditions. Unlike **3**, the role of the water molecules within the pores of **5** must be more crucial for overall structure stability, likely though hydrogen bonds between the solvent molecules and to the framework itself.

4. Conclusions

Our studies show that under the given conditions, $\iota(+)$ -tartrate is a robust ligand for the formation of homochiral metal-organic frameworks. These investigations also suggest that the more potentially open and porous structures obtained from synthesis in water rely upon the heavily upon the hydrogen bonding of the guest H_2O molecules for overall framework stability. Nonetheless, the stability of the tartrate anions against epimerization warrants further investigations into their use in MOFs.

Current studies are underway examining different solvent systems for the syntheses of permanently porous, homochiral, MOFs incorporating tartrate.

Acknowledgments

We gratefully acknowledge the Petroleum Research Fund (41716-AC3) and the National Science Foundation (Grant CHE-0443233) for support. Also, thanks to Professor Paul McGinn and Changsheng Su (University of Notre Dame) for help with the TGA studies.

References

- [1] [a] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, *J. Mater. Chem.* 16 (2006) 626;
[b] N.R. Champness, *Dalton Trans.* 16 (2006) 626;
[c] N.R. Champness, M. Schröder, *Curr. Opin. Solid State Mater.* 3 (1998) 419;
[d] C. Janiak, *Dalton Trans.* (2003) 2781;
[e] G.S. Papaefstathiou, L.R. MacGillivray, *Coord. Chem. Rev.* 246 (2003) 169;
[f] D. Braga, *Chem. Commun.* (2003) 2751;
[g] S.L. James, *Chem. Soc. Rev.* 32 (2003) 276;
[h] S.R. Batten, *Curr. Opin. Solid State Mater.* 5 (2001) 107;
[i] M.J. Zaworotko, *Chem. Commun.* (2001) 1;
[j] D. Braga, *J. Chem. Soc. Dalton Trans.* (2000) 3705;
[k] M.J. Zaworotko, *Angew. Chem. Int. Ed.* 39 (2000) 3052.
- [2] [a] C. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* 127 (2005) 8940;
[b] J. Perles, M. Iglesias, M. Martin-Luengo, M.A. Monge, C. Ruiz-Valero, N. Snejko, *Chem. Mater.* 17 (2005) 5837;
[c] T. Uemara, K. Kitagawa, S. Horike, T. Kawamura, S. Kitagawa, *Chem. Commun.* (2005) 5968;
[d] K. Schlichte, T. Kratzke, S. Kaskel, *Microporous Mesoporous Mater.* 73 (2004) 81;
[e] J.S. Seo, D.W. Whang, H. Lee, S.I. Jun, J. Oh, Y. Jeon, K. Kim, *Nature* 404 (2000) 982;
[f] M. Fujita, Y.J. Kwon, S. Washizu, K.J. Ogura, *J. Am. Chem. Soc.* 116 (1994) 1151.
- [3] [a] L. Zhang, J. Yu, J. Xu, J. Lu, H. Bie, X. Zhang, *Inorg. Chem. Commun.* 8 (2005) 638;
[b] B. Zhao, X.Y. Chen, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, *J. Am. Chem. Soc.* 126 (2004) 15394.
- [4] [a] L. Wang, M. Yang, Z. Shi, Y. Chen, J. Feng, *J. Solid State Chem.* 178 (2005) 3359;
[b] P.D.C. Dietzel, Y. Morita, R. Blom, H. Fjellvaag, *Angew. Chem. Int. Ed.* 44 (2005) 6354;
[c] R.D. Poulsen, A. Bentien, M. Chevalier, B.B. Iversen, *J. Am. Chem. Soc.* 127 (2005) 9156;
[d] H. Cui, K. Takahashi, Y. Okano, H. Kobayashi, Z. Wang, A. Kobayashi, *Angew. Chem. Int. Ed.* 44 (2005) 6508.
- [5] [a] Y.J. Lee, J. Li, J. Jagiello, *J. Solid State Chem.* 178 (2005) 2527;
[b] Q.M. Wang, D.M. Shen, M. Bulow, M.L. Lau, S.G. Deng, F.R. Fitch, N.O. Lemcoff, J. Semanscin, *Microporous Mesoporous Mater.* 55 (2002) 217;
[c] A.J. Fletcher, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, *J. Am. Chem. Soc.* 123 (2001) 10001.
- [6] [a] B. Chen, C. Liang, J. Yang, D.S. Contreras, Y.L. Clancy, E.B. Lobkovsky, O.M. Yaghi, S. Dai, *Angew. Chem. Int. Ed.* 45 (2006) 1390;
[b] H.J. Choi, M.P. Suh, *J. Am. Chem. Soc.* 126 (2004) 15844;
[c] O. Ohmori, M. Kawano, M. Fujita, *J. Am. Chem. Soc.* 126 (2004) 16292;
[d] D.N. Dybtsev, H. Chun, K. Kim, *Angew. Chem. Int. Ed.* 43 (2004) 5033;
[e] J.Y. Lu, A.M. Babb, *Chem. Commun.* (2002) 1340.
- [7] [a] J.L.C. Roswell, O.M. Yaghi, *Angew. Chem. Int. Ed.* 44 (2005) 4670;
[b] N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keefe, O.M. Yaghi, *J. Am. Chem. Soc.* 127 (2005) 1504;
[c] O.M. Yaghi, M. O'Keefe, N. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, *Nature* 423 (2003) 705;
[d] M. Eddaoudi, D. Moler, H. Li, T.M. Reinke, M. O'Keefe, O.M. Yaghi, *Acc. Chem. Res.* 34 (2001) 319;
[e] J. Kim, B. Chen, T.M. Reinke, H. Li, M. Eddaoudi, D.B. Moler, M. O'Keefe, O.M. Yaghi, *J. Am. Chem. Soc.* 123 (2001) 8239;
[f] M. O'Keefe, M. Eddaoudi, H. Li, T.M. Reinke, O.M. Yaghi, *J. Solid State Chem.* 152 (2000) 3;
[g] T.M. Reinke, M. Eddaoudi, M. O'Keefe, O.M. Yaghi, *Angew. Chem. Int. Ed.* 38 (1999) 2590;
- [h] M. Eddaoudi, H. Li, T.M. Reinke, M. Fehr, D. Kelley, T.L. Groy, O.M. Yaghi, *Top. Catal.* 9 (1999) 105.
- [8] [a] J.A. Rood, B.C. Noll, K.W. Henderson, *Inorg. Chem.* 45 (2006) 5521;
[b] J.A. Rood, B.C. Noll, K.W. Henderson, *Main Group Chem.* 5 (2006) 21.
- [9] [a] M. Dincă, J.R. Long, *J. Am. Chem. Soc.* 127 (2005) 9376;
[b] I. Senkovska, S. Kaskel, *Eur. J. Inorg. Chem.* (2006) 4564;
[c] D.-R. Xiao, E.-B. Wang, H.-Y. An, Y.-G. Li, Z.M. Su, C.-Y. Sun, *Chem. Eur. J.* 12 (2006) 6528;
[d] R.P. Davies, R.J. Less, P.D. Lickless, A.J.P. White, *Dalton Trans.* (2007) 2528.
- [10] B.F. Abrahams, M. Moylan, S.D. Orchard, R. Robson, *Angew. Chem. Int. Ed.* 42 (2003) 1848.
- [11] [a] R. Vaidhyanathan, D. Bradshaw, J.-N. Rebilly, J.P. Barrio, J.A. Gould, N.G. Berry, M.J. Rosseinsky, *Angew. Chem. Int. Ed.* 45 (2006) 6495;
[b] E.V. Anokhina, Y.B. Go, Y. Lee, T. Vogt, A.J. Jacobson, *J. Am. Chem. Soc.* 128 (2006) 9957.
- [12] S. Thushari, J.A.K. Cha, H.-Y. Sung, S.-Y. Chui, A.L.-F. Leung, Y.-F. Yen, I.D. Williams, *Chem. Commun.* (2005) 5515.
- [13] A.S.-F. Au-Yeung, H.-Y. Sung, J.A.K. Cha, A.W.-H. Siu, S.-Y. Chui, I.D. Williams, *Inorg. Chem. Commun.* 9 (2006) 507.
- [14] J.-Q. Liu, Y.-Y. Wang, P. Liu, W.-P. Wu, X.-R. Zeng, F. Zhong, Q.-Z. Shi, *Inorg. Chem. Commun.* 10 (2007) 343.
- [15] A. Beghidja, G. Rogez, P. Rabu, R. Welter, M. Drillon, *J. Mater. Chem.* 16 (2006) 2715.
- [16] Y.-S. Song, B. Yan, Z.-X. Chen, *J. Solid State Chem.* 179 (2006) 4037.
- [17] [a] Z.-F. Chen, J. Zhang, R.-G. Xiong, X.-Z. You, *Inorg. Chem. Commun.* 3 (2000) 493;
[b] R.-G. Xiong, J.-L. Zuo, X.-Z. You, H.-K. Fun, S.S.S. Raj, *New J. Chem.* 23 (1999) 1051;
[c] D.N. Dybtsev, A. Nuzhdin, V. Fedin, K. Kim, *Angew. Chem. Int. Ed.* 45 (2006) 916.
- [18] [a] C.-D. Wu, W. Lin, *Dalton Trans.* (2006) 4563;
[b] C.-D. Wu, W. Lin, *Chem. Commun.* (2005) 3673.
- [19] G. Li, W. Yu, Y. Cui, *J. Am. Chem. Soc.* 130 (2008) 4582.
- [20] J.A. Rood, W.C. Boggess, B.C. Noll, K.W. Henderson, *J. Am. Chem. Soc.* 129 (2007) 13675.
- [21] K.C. Kam, K.L.M. Young, A.K. Cheetham, *Cryst. Growth Des.* 7 (2007) 1522.
- [22] [a] Z.Q. Wang, S.M. Cohen, *J. Am. Chem. Soc.* 129 (2007) 12368;
[b] Z.Q. Wang, S.M. Cohen, *Angew. Chem. Int. Ed. Advance Article* DOI:10.1002/anie.200800686.
- [23] Bruker-Nonius AXS (2005). APEX2 and COSMO. Bruker-Nonius AXS, Madison, Wisconsin, USA.
- [24] G.M. Sheldrick, (2004). SADABS. Bruker-Nonius AXS, Madison, Wisconsin, USA.
- [25] Bruker-Nonius AXS (2005). APEX2 and COSMO. Bruker-Nonius AXS, Madison, Wisconsin, USA.
- [26] G.M. Sheldrick, *Acta Cryst. A* 64 (2008) 112.
- [27] [a] L.K. Templeton, D.H. Templeton, D. Zhang, A. Zalkin, *Acta Cryst. C* 41 (1985) 363;
[b] S. Adama, G. Mohamed, S.A. Salam, B. Aliou Hamady, D. Ahmed, *Acta Cryst. E* 63 (2007) m574;
[c] H. Soyulu, Hacettepe Bull. Nat. Sci. Eng. 11 (1982) 61;
[d] C.K. Prout, J.R. Carruthers, F.J.C. Rossotti, *J. Chem. Soc. A* (1971) 3336;
[e] F. Jian, P. Zhao, Q. Wang, *J. Coord. Chem.* 58 (2005) 1133;
[f] L.J. Bostelaar, R.A.G. de Graaff, F.B. Hulsberger, J. Reedijk, W.M.H. Sachtler, *Inorg. Chem.* 23 (1984) 2294;
[g] S. Scherb, C. Nather, W. Bensch, *Acta Cryst. C* 41 (2002) m135;
[h] F. Jian, Q. Yu, H. Xiao, P. Sun, *Anal. Sci.: X-ray Struct. Anal. Online* 21 (2005) x95;
[i] R. Wicharz, R. Warchow, M. Jaeckel, Z. Kristallogr. New Cryst. Struct. 212 (1977) 81;
[j] X.-F. Zheng, X.-Q. Shen, X.-S. Wan, H.-Y. Zhang, H. Wang, R. Yang, C.-Y. Niu, *J. Coord. Chem.* 60 (2007) 1317;
[k] C. Gonzalez-Silgo, J. Gonzalez-Platas, C. Ruiz-Perez, T. Lopez, M.E. Torres, *Acta Cryst. C* 55 (1999) 710.
- [28] [a] O.D. Friedrichs, M. O'Keefe, O.M. Yaghi, *Acta Cryst. A* 59 (2003) 22;
[b] M. O'Keefe, M.A. Peskov, S.J. Ramsden, O.M. Yaghi, *Acc. Chem. Res.* 41 (2008) 1782.
- [29] [a] B.W. Skelton, A.F. Waters, C.R. Whitaker, A.H. White, *Acta Cryst. C* 59 (2003) m435;
[b] D.-R. Xiao, E.-B. Wang, H.-Y. An, Y.-G. Li, Z.-M. Su, C.-Y. Sun, *Chem. Eur. J.* 12 (2006) 6526.
- [30] G.A. Jeffery, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, NY, 1997.
- [31] <http://www.topos.ssu.samara.ru>
- [32] A. L. Spek, PLATON, A multipurpose crystallographic tool, Utrecht University, Utrecht, The Netherlands (2001).
- [33] V.A. Blatov, D.M. Prosperio, *Acta Cryst. A* 65 (2009) 202.