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Structure and host–guest properties of the nanoporous diaquatetrakis(*p*-nitrobenzoato)dicopper(II) framework

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$[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2]\cdot Me_2CO$ has been prepared and characterized by single crystal X-ray diffraction. The Cu–Cu distance is 2.608(1) Å with the four *p*-nitrobenzoate ligands coordinated in bidentately bridging fashion, such that the copper atoms have a square pyramidal coordination. It possesses a framework structure with continuous channels parallel to the *c* axis with an opening size of ≈5.6 × 7.9 Å, giving a solvent accessible volume of 22% of the crystal volume. The framework remains intact and crystalline after removal of the included acetone molecule, as determined by X-ray powder diffraction. It is shown, by thermogravimetric measurements, that also benzene and water guest molecules can reversibly be incorporated and released. For comparison, $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(EtOH)_2]$ was prepared and characterized by single crystal X-ray diffraction. Here, the channels are occupied by the axial ethanol ligands.

Introduction

Nanoporous, polymeric co-ordination network structures are of considerable current interest in the field of new zeolite-type materials with potential applications such as molecular selection, ion exchange or catalysis. A common approach for the construction of such materials is the use of metal centres coordinated to multifunctional, neutral and rigid spacer ligands, such as the typical 4,4′-bipyridine. By controlling the metal coordination geometry and stereochemistry of the organic spacer ligand, the topology of the resultant polymeric network can be directed. The resulting structures can then further be elaborated by a systematic variation of the ligand characteristics or by the choice of counter ion. In this way a wide variety of network topologies has been designed.[1] Another approach is the use of sol–gel techniques employing metal alkoxide precursors and dihydroxy-functionalized aromatics to obtain covalent metal–aryl oxide network materials.[2] A frequently encountered phenomena in the design of materials with empty voids for guest molecule insertion is an entanglement, or interpenetration, of multiple networks, often resulting in fascinating structures, but always drastically diminishing the potential volume for guest molecule inclusion. Another problem is a framework breakdown upon removal of the included guest molecule, since phase transitions to denser structures frequently occur. Only relatively few examples of metal–organic materials possessing large cavities with non-destructive removal of the absorbates, allowing reversible guest exchange with intact, crystalline host frameworks, have been presented.[3]

Structural studies of transition metal complexes with functionalized benzoate ligands suggest that such complexes can be used to form neutral, zeolite-like three-dimensional frameworks. It has, for example, been shown, by powder X-ray diffraction and thermogravimetric analysis, that *para*-substituted Zn^{2+}, Cu^{2+} and Ag^+ benzoates consist of polymeric structures with channels, where guest molecules can selectively and reversibly be incorporated.[4] With the 4-pyridinecarboxylate ion using Cd^{2+} as metal centre, structures are observed with interpenetrated diamondoid networks.[5] Within these neutral frameworks there exist open cavities, which can be occupied by exchangeable and removable guest molecules. The crystal structures are stable upon removal of the guest molecules, which suggest their use as molecular sieves resembling zeolites. Another highly porous, stable metal coordination polymer is formed by the Cu^{2+} cation with benzene-1,3,5-tricarboxylic acid, containing an intersecting three-dimensional system of channels with an opening size of 9 × 9 Å.[6]

In this paper a strategy different from those using multifunctional ligands to connect the metal centres is described, namely to use molecular building blocks with rigid structures such that packing into dense forms is inconceivable. Tetra(arenecarboxylato)dicopper(II), $Cu_2(RC_6H_4CO_2)_4L_2$, where L represents axial ligands and R substituents on the aromatic ring, are promising candidates in this respect. A number of structural studies on these systems are published.[7] The Cu–Cu distances are found in the 2.59–2.70 Å range with the four bidentately bridging benzoate ligands coordinated in a “paddle-steamer” geometry. Several of these structures contain solvate molecules, and therefore potential solvent accessible voids, but in none of these studies attention has been given to guest molecule insertion and removal processes. In this paper we report the characterization, by single crystal X-ray diffraction, of $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2]\cdot Me_2CO$ **1** which possesses a framework structure with continuous channels with an opening size of ≈5.6 × 7.9 Å. It is shown, by X-ray powder diffraction, that the framework remains intact and crystalline after removal of the included acetone molecule. It is also shown, by thermogravimetric measurements, that also benzene and water guest molecules can reversibly be incorporated and released. For comparison, $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(EtOH)_2]$ **2** was prepared and characterized by single crystal X-ray diffraction.

Results and discussion

Crystal structures

The molecular structure of **1** is shown in Fig. 1. Four *p*-nitrobenzoate groups and two water molecules surround

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Table 1 Selected bond lengths (Å) and angles (°) for compounds **1** and **2**. For comparison average, minimum and maximum values observed for 42 tetra(arenecarboxylato)dicopper compounds in the Cambridge Structural Database are given

	Compound		CSD database		
	1	**2**	Average	Min.	Max.
Cu–Cu	2.6080(11)	2.6055(12)	2.64(3)	2.597	2.702
Cu–O_B (av)[a]	1.965(5)	1.960(2)	1.97(2)	1.897	2.017
Cu–O_L[b]	2.141(4)	2.151(3)	2.16(3)	2.097	2.238
O_B–Cu–O_L (av)[a]	95.5(1.0)	95.6(1.9)	96(3)	87.3	105
Cu–Cu–O_L	177.2(1)	177.3(1)	174(4)	164.3	179.4
α[c]	4.0(3), 5.8(3)	2.4(3), 4.2(3)	5(4)	0.18	17.98
β[d]	9.2(5), 4.1(7)	5.8(4), 1.0(4)	18(20)	0	88.963

O_B = Carboxylic oxygen atom, O_L = axial ligand oxygen atoms (H_2O for **1**, EtOH for **2**). [a] Average of four independent values. [b] CSD data for 22 compounds with oxygen donating axial ligands. [c] The bending angle of the OCO moiety of the benzoate ligand relative to the Cu_2O_4 plane as depicted in Fig. 1. [d] The rotation angle of the phenyl ring to the OCO plane of the carboxylic group (Fig. 1).

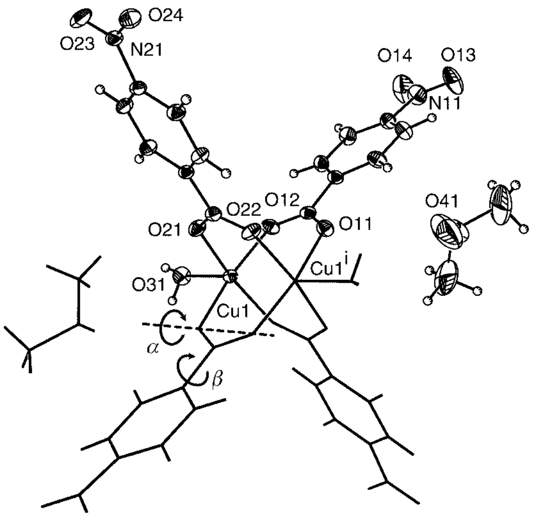

Fig. 1 Molecular structure of $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2]\cdot Me_2CO$ **1** with the asymmetric unit shown with displacement ellipsoids at the 30% probability level.

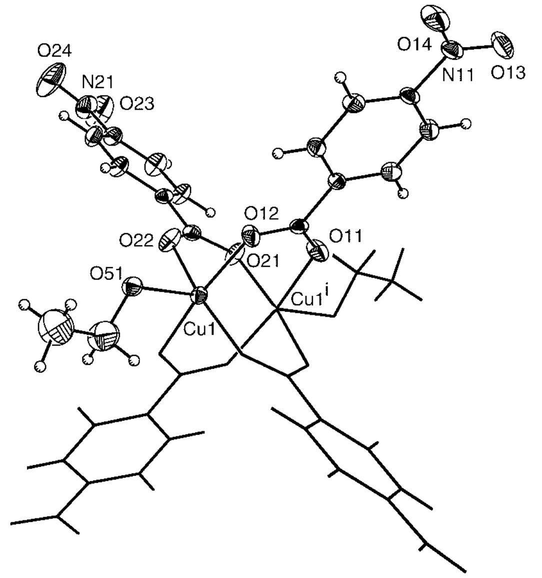

Fig. 2 Molecular structure of $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(EtOH)_2]$ **2**. Details as in Fig. 1.

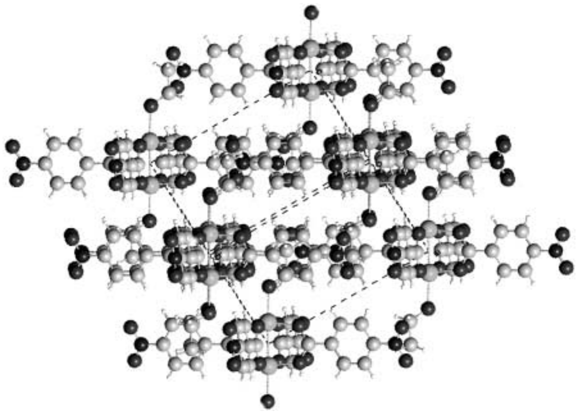

Fig. 3 View of the extended lattice formed by compound **2** down the 111 plane.

the two Cu^{2+} atoms. The Cu–Cu distance is 2.608(1) Å. Each copper atom is joined to four oxygen atoms from the benzoate ligands, which form a square plane. The Cu atom lies 0.189 Å from this plane in the axial direction towards the water molecule. The coordination about the copper atom is therefore square pyramidal, neglecting the Cu–Cu interaction. The bond lengths and angles observed show no significant deviations from those previously reported. Selected bond lengths and angles for compounds **1** and **2** are given in Table 1 together with average, minimum and maximum values for 42 tetra(arenecarboxylato)dicopper(II) compounds, where atomic coordinates were available in the Cambridge Structural Database (CSD).[8] The angle between the two Cu_2O_4 planes, which have an average atomic deviation from the plane of 0.01 Å, is 90.1°. The phenyl groups are both somewhat bent (angle α in Fig. 1) relative to the Cu_2O_4 planes and rotated (β) relative to the COO moiety (Table 1). The acetone molecule is clearly defined with relatively large thermal displacement amplitudes as expected for this loosely constraining environment. Compound **2** has a similar molecular structure with a unit cell volume of 900.1(2) Å^3, as compared with 931.3(2) Å^3 for **1**. The ethanol axial ligands are well defined and with no sign of rotational disorder (Fig. 2). The crystal structure of the closely related $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2]\cdot 2H_2O$ is basically in good agreement even though detailed comparison is prohibited by the limited accuracy of this structure determination ($R = 0.098$).[9] The unit cell volume here is 936.0 Å^3.

The crystals of **1** and **2** are assembled by discrete $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(L)_2]$ units where L = H_2O for **1** and EtOH for **2**. Paradoxically, for these porous substances, it appears that close packing is the dominating force for the crystal organization but also aromatic π–π interactions have an appreciable importance. The shortest distance between the aromatic planes is 3.59 Å, which can be compared with *e.g.* interplanar distances between 3.29 and 3.72 Å observed for crystalline polycyclic aromatic hydrocarbons.[10] The molecular units of both **1** and **2** are stacked to form layers parallel to the 111 plane as depicted in Fig. 3. Perpendicular to the layers, channels are observed which, for compound **1**, are occupied by acetone molecules

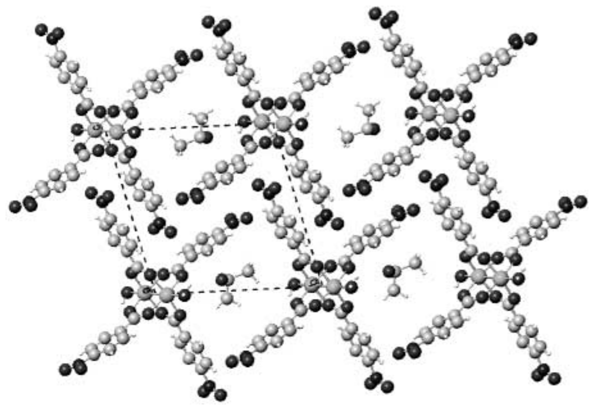

Fig. 4 View of the extended lattice formed by compound **1** down the *c* axis showing channels occupied by acetone molecules.

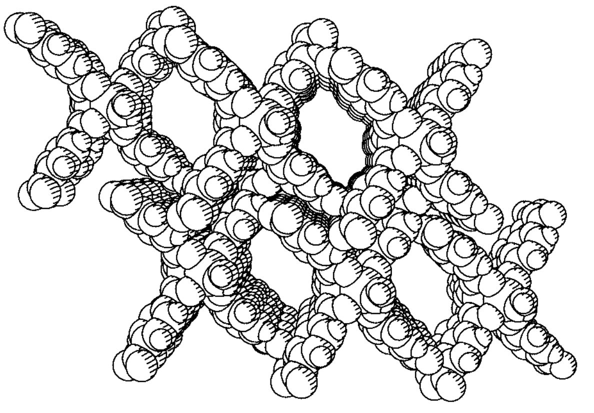

Fig. 5 A space filling view of compound **1** parallel to the *c* axis, showing continuous channels with an opening size of ≈5.6 × 7.9 Å where acetone, benzene and water guest molecules can reversibly be incorporated and released.

(Fig. 4). The channels are disposed to form continuous channels parallel to the *c* axis. With a van der Waals radius of 1.69 Å for the carbon atom, the void size is ≈5.6 × 7.9 Å in the layer plane (Fig. 5). The potential solvent accessible volume, as calculated with the Platon software,[11] is 207 Å^3, thus 22% of the total unit cell volume, to be compared with the expected volume for *e.g.* a water molecule of 40 Å^3. The successive layers are parallel displaced by 3.9 Å, giving the possibility of the axial ligands of one layer being interpenetrated into the voids of the neighbouring layer. This is observed for compound **2** with ethanol as axial ligands, resulting in the solvent accessible volume being decreased to 39 Å^3 since the major part of the voids is occupied by the C_2H_5 groups from ethanol molecules from adjacent layers (Fig. 6). Fig. 4 also clearly shows the decisive importance of the nitro groups to expand the void volume.

Removal and insertion of guest molecules

Thermogravimetric analysis (TGA) of **1** under an atmosphere of ambient air reveals two distinct weight losses. In the first step the included acetone molecules are removed at an onset temperature of 115 °C. The weight loss corresponds to 1.15(5) acetone molecules per formula unit. The second step, at 309 °C, results in complete collapse of the structure. With benzene and water guest molecules, the first weight loss is observed at 99.5 and 123 °C, respectively, with weight losses corresponding to 0.73(5) benzene and 2.02(5) water molecules. The second step is also in these cases observed at 309 °C. With $[Cd(L)_2(EtOH)_2]\cdot EtOH$ (L = isonicotinate), consisting of a twofold interpenetrated diamondoid structure with channels with an opening size of 4.5 × 3.4 Å, the TGA curve showed two discrete weight losses at onset temperatures of 100 and 160 °C, corresponding to removal of the included and coordinated ethanol molecules. Also here, a reversible guest removal insertion and removal process with an intact, crystalline host was demonstrated.[5]

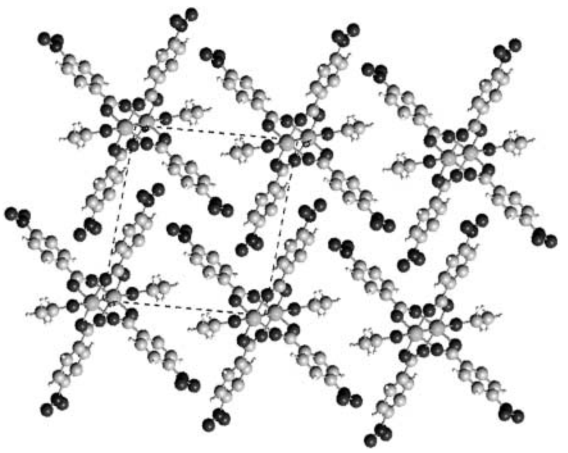

Fig. 6 View of the extended lattice formed by compound **2** down the *c* axis showing where the channels observed for **1** in this case are occupied by the axial ethanol ligands.

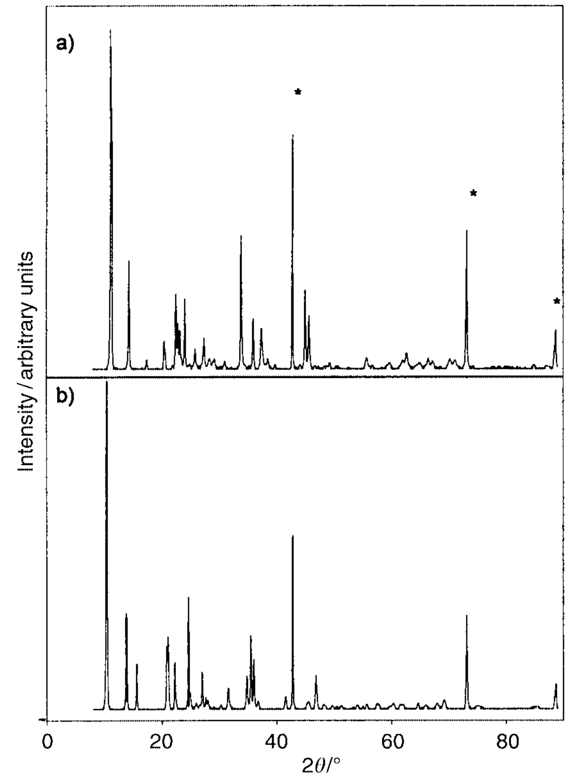

Fig. 7 XPD for $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2]\cdot 2H_2O$ before (a) and after (b) removal of the included water molecules. Reflections from the silicon internal standard are marked with *.

The X-ray powder diffractogram of $[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2]\cdot 2H_2O$ is shown in Fig. 7(a). The sample was then heated at 150 °C for 1 h, and the diffractogram remeasured under vacuum, Fig. 7(b). It is seen that crystallinity is retained and, by comparison of the intensity relative to the silicon internal standard, no appreciable amounts of amorphous material have been formed. The diffractogram in (a) agrees well with synthetic powder profiles calculated with atomic positions from single crystal diffraction. Rietveld profile refinement also gives results in good agreement. Evacuation of the sample results in a number of peak position changes and appearances of new bands. For example, the peaks originating from the 001 and 010 planes, observed at $2\theta = 11.16$ and 11.22° in (a),

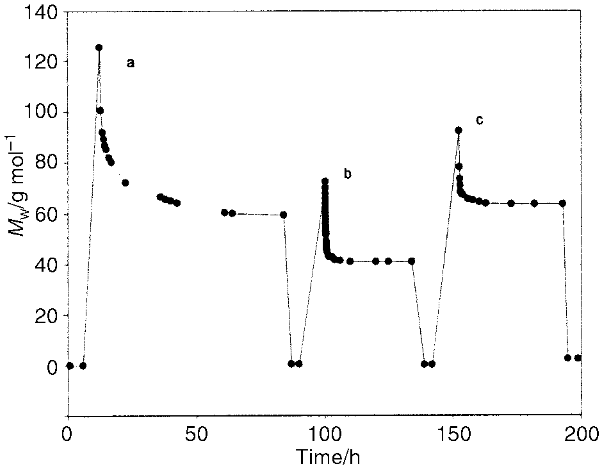

Fig. 8 The weight change of **1** on heating at 150 °C to remove guest molecules and exposure to vapour of acetone (a), water (b) and benzene (c) guest molecules. The diagram shows the mass of the included guest molecules per mol [$Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2$] as a function of time, showing four desorption and three absorption processes.

are changed to 10.46 and 10.50° in the evacuated sample. Furthermore, the powder diffraction pattern agrees well, up to $2\theta = 35°$, with that of the simulated XPD of compound **1** without guests. We thus conclude that the basic framework thus remains intact and crystalline during the desorption process and that it can undergo small rearrangements in response to packing factors.

The removal and insertion of guest molecules was further examined by heating **1** to 150 °C to remove the acetone guest molecules, and subsequent exposure to acetone vapour. This procedure was repeated using benzene and water vapour. The result is shown in Fig. 8, where the molecular weight of the guest molecules is plotted as a function of time. After heating the minimum weight is obtained corresponding to the empty framework. After exposure to acetone vapour there is a weight gain which gradually decreases until a constant value corresponding to 0.98 acetone molecules per formula unit is observed. This decrease is slow for acetone, taking 48 h for a weight change less than 0.1%. This indicates that the channels have a possibility for a variable stoichiometry for the acetone molecules. With benzene and water guest molecules, constant weight was obtained corresponding to 0.79 benzene and 2.27 water molecules. The desorption processes to constant weight are in these cases considerably more rapid, taking *ca.* 30 min. These results conclusively show the reversibility of the guest molecule insertion and removal processes. More detailed quantitative aspects, such as selectivity in mixtures, demand further studies, which are in progress at this laboratory.

Comparison with related structures

The basic structural features of tetra(arenecarboxylato)-dicopper compounds are well known and average geometrical parameters from 42 structures found in the CSD database of the $Cu_2(RCO_2)_4L_2$ core are given in Table 1. The most variable parameter is the rotation angle of the phenyl ring to the OCO plane of the carboxylic group (angle β in Fig. 1) with values between 0 and 88.96°, an angle which appears to be highly dependent of the steric repulsion's from the axial ligands L. Several of these structures contain solvate molecules and, therefore, potential solvent accessible voids. Further to examine these frameworks, atomic coordinates were taken from the Cambridge Structural Database[8] and, when necessary, hydrogen atoms generated in idealized positions with the SHELXTL program package.[12] The solvate molecules were removed from the atom list and the crystal packing efficiency and solvent accessible void volumes then calculated, as obtained by using gridpoints at least 1.2 Å from the nearest van der Waals surface with the Platon software.[11]

Tetrakis(benzoato)bis(methanol)copper(II), determined as the methanol solvate (CSD entry code: dayjiv), exhibits relatively narrow channels with a diameter of *ca.* 3.1 Å, resulting in a packing efficiency of 52.7% and solvent accessible volume of 22.3% of the total unit cell volume.[13] The crystal organisation suggests that crystallinity might be retained upon solvate removal since the solvate molecules do not act as the only spacer between structural elements. Bis(dimethylsulfoxide)-tetrakis(*p*-hydroxybenzoato)dicopper(II) (dayjoc) presents a highly porous structure with the solvent accessible volume equal to 39.5% of the total unit cell volume.[13] The axial dmso ligands have a decisive importance for the framework structure implying that entirely different framework organizations will result with other axial ligands, contrasting compound **2** in this study where the ethanol axial ligands have no direct structural role but instead fill a space which otherwise is filled with solvate molecules (compound **1**). Another example of a highly porous framework is tetrakis(*m*-chlorobenzoato)bis(pyridine)-dicopper(II) (vubsiu) with a packing efficiency of 49.1% and a solvent accessible volume of 34.9%.[14] The related bis(2-amino-pyridine)tetrakis(benzoato)dicopper(II) (zezhob) has a comparable packing efficiency (45.2%) and solvent accessible volume (39.9%) suggesting that relatively large and rigid axial ligands play an important role in stretching the framework structure.[15] Bis(μ-1,4-dioxane)tetrakis(pentafluorobenzoato)dicopper(II) 1,4-dioxane (1/2) (vuscuh) consists of sheets of $Cu_2(RCO_2)_4$ units joined by bridging dioxane ligands; the intersheet volume contains three dioxane molecules per formula unit, one bridging axial and two solvate molecules.[16] In this case it appears unlikely that the crystal will retain its basic framework structure upon solvate removal due to the floppiness of the bridging dioxane molecule. On the other hand, rigid bifunctional axial ligands like pyrazine or, possibly, 4,4′-bipyridine might give structures with both high porosity and robustness to withstand guest molecule removal.

The diaquatetrakis(*p*-nitrobenzoato)dicopper(II) framework structure presented in this paper is thus not unique among tetra(arenecarboxylato)dicopper compounds in having a nanoporous structure. A large number of combinations of substituents on the aryl ring and the nature of the axial ligand can be used to optimize the solvent accessible volume, void dimensions or anisotropic properties. Several examples described above have structures suggesting that the basic framework might be retained after solvent removal, since the solvate molecules do not act as the only spacer between structural elements. This is however a property still to be investigated. The present data suggest that it might be conceivable to design frameworks with crystal packing efficiencies of 35–40% and solvent accessible volumes of 45–50% of the total unit cell volumes. An interesting point is whether nature's *horror vacui* will accept such porous frameworks or if the solvent removal will result in a crystal rearrangement with higher packing efficiency.

Another family of compounds with related properties is divalent transition metal complexes M(II)(pyridine)$_4$X$_2$, where X is a monovalent anion. These compounds contain channels within the molecular framework where guest molecules can be included.[17] With a copper(II) acetylacetonate derivative, a 3-D polymer with isolated straight channels with an opening size of ≈6 Å was observed, with the ability to absorb volatile organic guests reversibly.[18] Sorption isotherms were determined for several organic guest molecules, suggesting a physical mode of sorption on the inner hydrophobic surface of the host pores.[19]

Conclusion

Diaquatetrakis(*p*-nitrobenzoato)dicopper(II) possesses a framework structure with continuous channels with an opening size of ≈5.6 × 7.9 Å where acetone, benzene and water guest

Table 2 Crystallographic data for compounds **1** and **2**

	1	**2**
Formula	$[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2]\cdot Me_2CO$	$[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(EtOH)_2]$
M/g mol^{-1}	885.64	881.65
T/K	295	295
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	6.7335(9)	6.6724(8)
b/Å	11.9248(15)	11.1582(14)
c/Å	12.4536(16)	12.5549(16)
α/°	101.657(2)	93.982(2)
β/°	104.520(2)	103.863(2)
γ/°	97.283(2)	94.956(2)
U/Å^3	931.3(2)	900.18(19)
Z	1	1
μ(Mo-Kα)/cm^{-1}	1.227	1.267
Reflections measured	5556	5247
Unique reflections (R_{int})	3957 (0.0321)	3762 (0.0582)
Observed reflections, $I > 2\sigma(I)$	2523	2226
$R1$ (observed reflections)	0.0574	0.0656
$wR2$ (all reflections)	0.1315	0.1543

molecules can be reversibly incorporated and released. The framework remains intact and crystalline during these processes. An advantage with the tetra(arenecarboxylato)dicopper family of compounds is the convenient number of variable parameters to fine-tune the host capabilities. The nature of the aryl ring substituents and axial ligand can be used to optimize the solvent accessible volume, void dimensions or anisotropic properties. Unlike zeolites, these materials not only exhibit hydrophilic properties but also the ability to absorb organic molecules which, together with the possibility of additional substituents on the benzoate molecule to introduce *e.g.* hydrogen bond capabilities, may enable specific sorptions of a broad range of molecules. Work is currently in progress at this laboratory with a systematic investigation of these parameters.

Experimental

Materials and methods

Chemicals were purchased from Aldrich Chemicals and used with no further purification. Analyses for C, H and N were performed on a Carbo Erba 1108 I analyser by Mikrokemi AB, Uppsala, Sweden. Thermogravimetric measurements were performed with a Setraram TG-DTA 92 thermoanalyser with an atmosphere of ordinary air using Al_2O_3 crucibles. The heating rate was 5 °C min^{-1}. IR spectra were recorded on a Perkin-Elmer 1720 × FT-IR spectrometer in the 4000–400 cm^{-1} region with 2 cm^{-1} resolution using KBr pellets.

Preparation

$[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(H_2O)_2]\cdot Me_2CO$ 1. To 250 ml water–Me_2CO (50 : 50) containing $KC_7H_5NO_4$ (10 mmol, 1.6712 g) was added $Cu(NO_3)_2\cdot 3H_2O$ (5 mmol, 2.416 g) which yielded a blue precipitate. After boiling for 2 h while stirring the solution was filtered while hot. Slow cooling of the mother liquid yielded blue crystals of X-ray quality. The two solids formed were identical as shown by superimposable IR spectra. Total yield >90% (Found: C, 42.0; H, 3.0; N, 6.3. $C_{32}H_{36}Cu_2N_4O_{20}$ requires C, 41.6; H, 2.8; N, 6.3%). IR ($\tilde{\nu}_{max}$/cm^{-1}): 555(m), 725(m), 797(m), 833(m), 865(vw), 879(w), 1012(vw), 1107(w), 1143(vw), 1170(vw), 1231(vw), 1321(w), 1350(s), 1412(s), 1491(vw), 1528(m), 1598(m), 1629(m), 1705(w), 2853(vw), 3056(vw), 3090(vw), 3111(vw) and 3425(m,br).

$[Cu_2(p\text{-}O_2NC_6H_4CO_2)_4(EtOH)_2]$ 2. To 250 ml abs. EtOH containing $KC_7H_5NO_4$ (10 mmol, 1.6712 g) was added $Cu(NO_3)_2\cdot 3H_2O$ (5 mmol, 2.416 g) which yielded a blue precipitate. After boiling for 2 h, the solution was filtered while hot. Slow cooling of the mother liquid yielded blue crystals of X-ray quality. The two solids formed were identical as shown by superimposable IR spectra. Total yield >90% (Found: C, 43.4; H, 3.1; N, 6.3. $C_{28}H_{32}Cu_2N_4O_{18}$ requires C, 43.5; H, 3.2; N, 6.3%). IR ($\tilde{\nu}_{max}$/cm^{-1}): 458(vw), 555(m), 725(m), 797(m), 833(m), 878(w), 1013(w), 1046(w), 1080(w), 1107(w), 1114(vw), 1171(vw), 1351(s), 1413(s), 1490(w), 1527(m), 1598(m), 1628(m), 17643(m), 2853(w), 2900(w), 2923(w), 2974(w), 3057(w), 3091(w), 3116(w), 3421(s).

Removal and reintroduction of guest molecules

A sample of **1** (0.74225 g) was heated to 140 °C during 30 min. The weight loss was 0.04770 g, equivalent to 0.98 acetone molecules per formula unit. When this evacuated sample was exposed to acetone vapour in a desiccator during 12 h at room temperature it experienced a weight gain of 0.05319 g, when constant weight was obtained after 24 h, equivalent to 1.09 acetone molecules. Repeated procedures with benzene and water resulted in weight gains of 0.05324 and 0.03441 g, corresponding to 0.79 benzene and 2.27 water molecules per formula unit.

Single crystal X-ray crystallography

Single crystal diffraction data were collected at 298 K using Mo-Kα radiation on a Bruker SMART platform equipped with a CCD area detector and a graphite monochromator. Cell parameters were refined using 2523 reflections for **1** and 2226 for **2**. A hemisphere of data (1291 frames) was collected for each structure using the ω-scan method (0.3° frame width) with 40 s exposure time. The first 50 frames were re-measured at the end of the data collection to monitor instrument and crystal stability. Intensity decay was negligible for both **1** and **2**. Data reduction and empirical absorption correction were performed using the Bruker program packages SAINT and SADABS, respectively.[12] The structures were solved by the direct methods in SHELXTL and refined using full-matrix least squares on F^2. Non-H atoms were treated anisotropically. Hydrogen atoms were generated in ideal positions riding on their respective carbon atom. Crystal and experimental data are summarized in Table 2.

CCDC reference numbers 157260 and 157261.

See http://www.rsc.org/suppdata/dt/b1/b100734n/ for crystallographic data in CIF or other electronic format.

Powder X-ray diffraction

The intensity data were obtained from measurements made with an automatic microdensitometer on powder films exposed on a Guiner–Hägg focusing camera with Cr-Kα_1 radiation ($\lambda = 2.28975$ Å) with silicon as internal calibration standard. The exposures were made under vacuum at 298 K. Profile refinements were done with the FullProf Rietveld software with the WinPlotr interface.[20]

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