

Two pseudo-polymorphic copper–benzene-1,2,4,5-tetracarboxylate complexes

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Received 24 March 2007

Accepted 20 April 2007

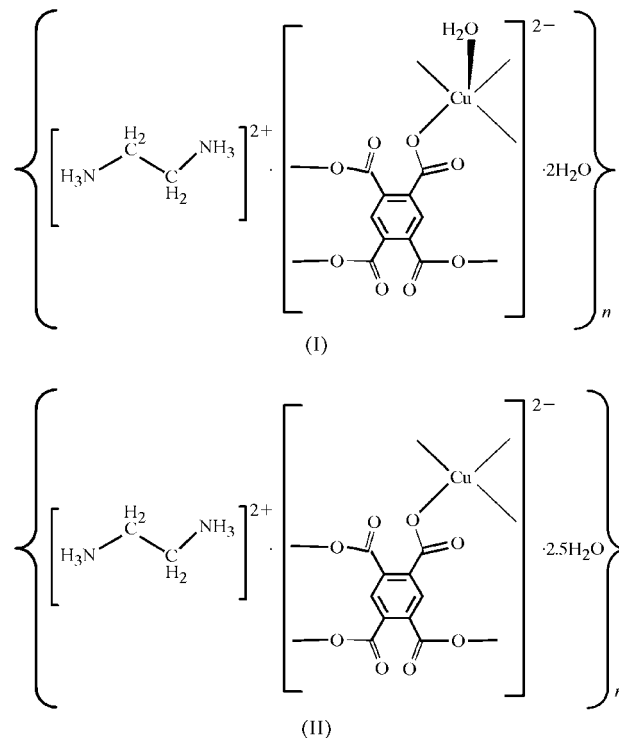
Online 31 May 2007

Two pseudo-polymorphic polymers, poly[ethylenediammonium [[aquacopper(II)]- μ_4 -benzene-1,2,4,5-tetracarboxylato] dihydrate], $\{(C_2H_{10}N_2)[Cu(C_{10}H_2O_8)(H_2O)] \cdot 2H_2O\}_n$, (I), and poly[ethylenediammonium [copper(II)- μ_4 -benzene-1,2,4,5-tetracarboxylato] 2.5-hydrate], $\{(C_2H_{10}N_2)[Cu(C_{10}H_2O_8)] \cdot 2.5H_2O\}_n$, (II), contain two-dimensional anionic layers, ethylenediammonium (H_2en) cations acting as counter-ions and free water molecules. Although the topological structures of the two anionic layers are homologous, the coordination environments of the Cu^{II} centres are different. In (I), the Cu^{II} centre, sitting on a general position, has a square-pyramidal environment. The two independent benzene-1,2,4,5-tetracarboxylate (btc) anions rest on centres of inversion. The Cu^{II} cation in (II) is located on a twofold axis in a square-planar coordination. The H_2en cation is on an inversion centre and the btc ligand is split by a mirror plane. Extensive hydrogen-bonding interactions between the complexes, H_2en cations and water molecules lead to the formation of three-dimensional supramolecular structures.

Comment

Research on metal–organic coordination polymers (MOCPs) has received continuous interest due to their novel topologies and potential application as functional materials (Yaghi *et al.*, 1998). A key strategy in the design of MOCPs is to select suitable bi- or multidentate bridging ligands. Recently, MOCPs using polycarboxylic acids as bridging ligands have become the most fruitful family in this field (Eddaoudi *et al.*, 2001; Shi *et al.*, 2001). A prime example of such a ligand is benzene-1,2,4,5-tetracarboxylic acid (H_4btc), which has a very versatile coordination behaviour to generate many unexpected and interesting MOCPs (Barthelet *et al.*, 2003; Kumagai *et al.*, 2002). However, polycarboxylic acid-based MOCPs with protonated organic amines as counter-ions remain rare (Cheng *et al.*, 2002), which might be due to the propensity of amines to coordinate metal cations (Ganesan &

Natarajan, 2004). We report here the synthesis and structure of two pseudo-polymorphic coordination polymers, (I) and (II). Both complexes exhibit two-dimensional structures and contain protonated ethylenediamine molecules (H_2en) as counter-ions.



The asymmetric part of the anionic layer of (I) contains one Cu^{II} cation, one water molecule and two btc ligands on inversion centres. The Cu^{II} cation has a square-pyramidal environment, completed by one aqua O atom in the axial position and four carboxyl O atoms from four btc ligands in the basal plane of the square pyramid (Fig. 1). As expected, the $Cu-O_{aqua}$ bond length is noticeably longer than the $Cu-O_{carboxyl}$ bonds. Both of the btc ligands adopt a $\mu_4-\eta^1:\eta^1:\eta^1:\eta^1$ bridging mode connecting four Cu^{II} cations, resulting in a two-dimensional $[Cu(btc)(H_2O)]_n^{2-}$ anionic layer with a (4,4)

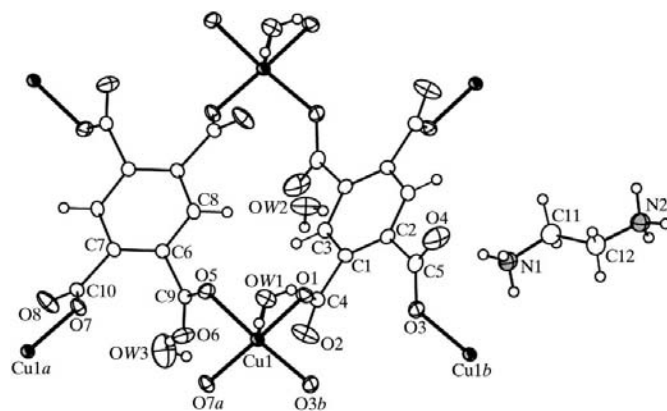


Figure 1

The structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. [Symmetry codes: (a) $2-x, -y, 2-z$; (b) $2-x, 1-y, 1-z$.]

topological network running parallel to the (011) plane (Fig. 2).

A notable feature of complex (I) is that the two btc ligands form distinctly different arrays. The aromatic groups of two btc ligands are tilted by different amounts with respect to the $[\text{CuO}_4(\text{H}_2\text{O})]_n^{2n-}$ anionic layer: $25.48(8)^\circ$ for the C7/C6/C8/C7ⁱ/C6ⁱ/C8ⁱ plane and $42.37(7)^\circ$ for the C2/C1/C3/C2ⁱⁱ/C1ⁱⁱ/C3ⁱⁱ plane [symmetry codes: (i) $1 - x, -y, 2 - z$; (ii) $1 - x, 1 - y, 1 - z$].

Within the anionic layer, the water molecules coordinated to the Cu^{II} cations are alternately directed up and down (Fig. 2). These anionic layers are separated by the H_2en cations and two free water molecules. Extensive $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions, with $\text{N}\cdots\text{O}$ or $\text{O}\cdots\text{O}$ distances within the 3 Å range, connect the two-dimensional networks, H_2en cations and free water molecules, resulting in a three-dimensional supramolecular structure.

In (II), the asymmetric unit contains one Cu^{II} atom sitting on a twofold axis, one H_2en cation on an inversion centre, one btc ligand straddling a mirror plane and free water molecules

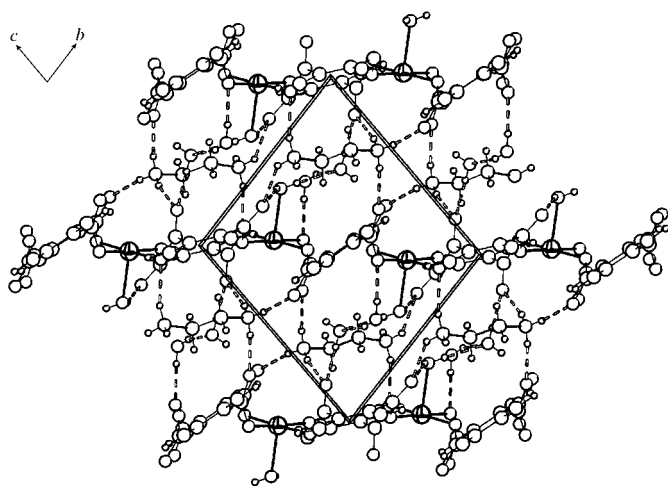


Figure 2
A packing diagram for (I), viewed down the *a* axis. Anionic layers run parallel to the (011) plane. Hydrogen bonds are shown as open dashed lines.

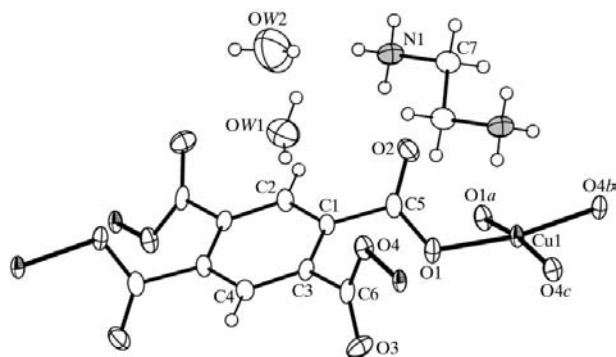


Figure 3
The structure of (II), showing the atom-labelling scheme and 50% probability displacement ellipsoids. [Symmetry codes: (a) $1 - x, y, -z$; (b) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (c) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.]

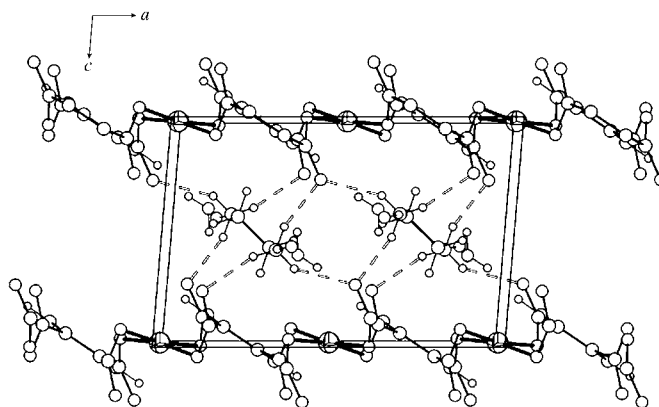


Figure 4
A packing diagram for (II), viewed along the *b* axis. Anionic layers run parallel to the *ab* plane. Hydrogen bonds are shown as open dashed lines.

in general positions. The water molecule of crystallization (OW2) is disordered across a mirror plane and the occupancy was fixed at 0.5. The Cu^{II} centre has a square-planar coordination with four carboxyl O atoms from four btc ligands (Fig. 3). The coordination mode of the btc ligand and the topological structure of the anionic layer are essentially the same as in (I), producing the $[\text{Cu}(\text{btc})]_n^{2n-}$ anionic layer parallel to the *ab* plane. The aromatic groups of the btc ligands are tilted with respect to the $[\text{CuO}_4]_n^{2n-}$ anionic layer by $34.32(7)^\circ$ for the C1/C3/C4/C3ⁱ/C1ⁱ/C2 plane [symmetry code: (i) $x, 1 - y, z$] (Fig. 4). As in (I), there are also many hydrogen-bonding interactions with $\text{N}\cdots\text{O}$ or $\text{O}\cdots\text{O}$ distances within the 3 Å range, which lead to a three-dimensional supramolecular structure for (II).

Comparison of complexes (I) and (II) with a zinc pyromellitate previously reported by Ganesan *et al.* (2004) shows that, in both cases, there are anionic layers with the same topological network and a similar connection mode between the metal centres and the btc ligands. However, the tetrahedral coordination environment of the Zn centre is significantly different from the Cu coordination in (I) and (II), resulting in a corrugated anionic layer in $[\text{Zn}(\text{btc})]_n^{2n-}$.

Experimental

For the preparation of (I), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (85 mg, 0.5 mmol), benzene-1,2,4,5-tetracarboxylic anhydride (109 mg, 0.5 mmol) and a 2 M ethylenediamine solution (0.25 ml) were dissolved in water (18 ml). The mixture was stirred and then a small quantity of a 2 M HCl solution was added to adjust the pH to 3.0. The resulting solution was filtered and left to stand at room temperature. After approximately one week, blue block-shaped crystals of (I) suitable for X-ray crystallographic study were obtained.

For the preparation of (II), a 2 M ethylenediamine solution (0.25 ml), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (170 mg, 1 mmol) and benzene-1,2,4,5-tetracarboxylic anhydride (164 mg, 0.75 mmol) were dissolved in water (15 ml). The mixture was heated to 333 K for 20 min and a small quantity of a 2 M NaOH solution was added to adjust the pH to 4.0. The resulting solution was left to stand at room temperature for about 3 d, after which blue needle-shaped crystals of (II) were collected for X-ray analysis.

Compound (I)

Crystal data

(C₂H₁₀N₂)[Cu(C₁₀H₂O₈)(H₂O)]·2H₂O
M_r = 429.83
 Triclinic, *P* $\bar{1}$
a = 9.2104 (18) Å
b = 9.4058 (19) Å
c = 10.225 (2) Å
 α = 75.00 (3)°
 β = 75.50 (3)°
 γ = 75.15 (3)°
V = 810.8 (3) Å³
Z = 2
 Mo *K* α radiation
 μ = 1.41 mm⁻¹
T = 293 (2) K
 0.30 × 0.28 × 0.28 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 3715 measured reflections
 3715 independent reflections
 3467 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.033

Refinement

R[*F*² > 2 σ (*F*²)] = 0.026
wR(*F*²) = 0.072
S = 1.05
 3715 reflections
 308 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max}$ = 0.57 e Å⁻³
 $\Delta\rho_{\min}$ = -0.40 e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

Cu1—O3 ⁱ	1.9372 (15)	Cu1—O5	1.9940 (14)
Cu1—O1	1.9522 (14)	Cu1—OW1	2.2644
Cu1—O7 ⁱⁱ	1.9693 (14)		
O3 ⁱ —Cu1—O1	89.85 (6)	O3 ⁱ —Cu1—OW1	91.81 (6)
O3 ⁱ —Cu1—O7 ⁱⁱ	92.83 (6)	O1—Cu1—OW1	90.55 (5)
O1—Cu1—O7 ⁱⁱ	175.78 (5)	O7 ⁱⁱ —Cu1—OW1	92.61 (5)
O1—Cu1—O5	85.27 (6)	O5—Cu1—OW1	90.64 (5)
O7 ⁱⁱ —Cu1—O5	91.91 (6)		

Symmetry codes: (i) -*x* + 2, -*y* + 1, -*z* + 1; (ii) -*x* + 2, -*y*, -*z* + 2.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H3···O5 ⁱⁱⁱ	0.86 (3)	2.04 (3)	2.843 (2)	156 (3)
N1—H4···O4	0.84 (3)	1.87 (3)	2.701 (2)	169 (3)
N1—H7···O6 ⁱ	0.84 (3)	1.97 (3)	2.794 (2)	167 (3)
N1—H8···O2 ^{iv}	0.86 (3)	1.99 (3)	2.839 (2)	173 (3)
N2—H9···OW2 ^v	0.96 (3)	1.75 (3)	2.716 (2)	175 (3)
OW1—HW1A···O8 ⁱⁱ	0.82	1.94	2.7059 (17)	155.1
N2—H13···O8 ^{vi}	0.85 (3)	2.12 (3)	2.820 (2)	140 (2)
OW2—HW2A···O1	0.82	1.98	2.7749 (18)	162
OW1—HW1B···OW3 ^{iv}	0.82	1.98	2.791	172.6
OW3—HW3A···O6	0.82	1.94	2.7334 (16)	164
OW2—HW2B···OW3 ^{iv}	0.82	2.04	2.794	152

Symmetry codes: (i) -*x* + 2, -*y* + 1, -*z* + 1; (ii) -*x* + 2, -*y*, -*z* + 2; (iii) *x*, *y* + 1, *z* - 1; (iv) *x*, *y* + 1, *z*; (v) -*x* + 1, -*y* + 2, -*z* + 1; (vi) *x*, *y* + 2, *z* - 1.

Compound (II)

Crystal data

(C₂H₁₀N₂)[Cu(C₁₀H₂O₈)]·2.5H₂O
M_r = 420.83
 Monoclinic, *C*2/*m*
a = 11.432 (2) Å
b = 18.484 (4) Å
c = 7.4981 (15) Å
 β = 94.80 (3)°
V = 1578.8 (5) Å³
Z = 4
 Mo *K* α radiation
 μ = 1.45 mm⁻¹
T = 293 (2) K
 0.36 × 0.28 × 0.28 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 1871 measured reflections
 1871 independent reflections
 1406 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.044

Refinement

R[*F*² > 2 σ (*F*²)] = 0.033
wR(*F*²) = 0.079
S = 0.98
 1870 reflections
 130 parameters
 4 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max}$ = 0.44 e Å⁻³
 $\Delta\rho_{\min}$ = -0.41 e Å⁻³

Table 3

Selected geometric parameters (Å, °) for (II).

Cu1—O4 ⁱ	1.949 (2)	Cu1—O1	1.952 (2)
O4 ⁱ —Cu1—O4 ⁱⁱ	88.96 (13)	O1 ⁱⁱⁱ —Cu1—O1	88.77 (13)
O4 ⁱ —Cu1—O1	92.05 (9)		

Symmetry codes: (i) -*x* + $\frac{1}{2}$, -*y* + $\frac{1}{2}$, -*z*; (ii) *x* + $\frac{1}{2}$, -*y* + $\frac{1}{2}$, *z*; (iii) -*x* + 1, *y*, -*z*.

Table 4

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1A···O2 ^{iv}	0.89	2.14	2.938 (3)	149
N1—H1B···O3 ^v	0.89	2.09	2.837 (3)	142
N1—H1C···O2	0.89	2.00	2.831 (3)	155

Symmetry codes: (iv) -*x* + 1, *y*, -*z* + 1; (v) *x*, *y*, *z* + 1.

In (I), all H atoms bonded to C and N atoms were located in difference Fourier maps and refined isotropically. For both compounds, H atoms bonded to water O atoms were located in difference maps and treated as riding atoms, with a DFIX restraint of O—H = 0.82 Å and with *U*_{iso}(H) = 1.2*U*_{eq}(O). H atoms bonded to C atoms were refined in idealized positions using the riding-model approximation, with C—H = 0.93 and 0.97 Å, and *U*_{iso}(H) = 1.2*U*_{eq}(C). H atoms bonded to N atoms were refined as riding, with N—H = 0.89 Å and *U*_{iso}(H) = 1.5*U*_{eq}(N). The occupancy factor of water atom OW2 was initially calculated by linking it to a free variable; it was then fixed at 0.5 according to the value found after ten least-squares cycles.

For both compounds, data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL97-2* (Sheldrick, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3073). Services for accessing these data are described at the back of the journal.

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