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Key indicators

Single-crystal X-ray study
T = 93 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.034
wR factor = 0.077
Data-to-parameter ratio = 12.5

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

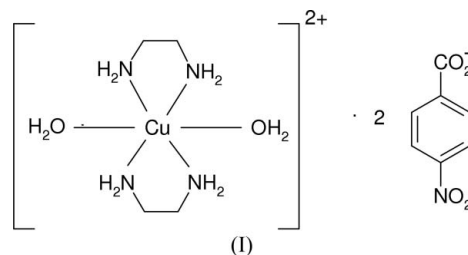
Diaquabis(ethylenediamine)copper(II) bis(4-nitrobenzoate)

In the title compound, $[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_7\text{H}_4\text{NO}_4)_2$, the component complex cations and organic anions interact by way of $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, leading to a layered structure. The Cu atom has site symmetry $\bar{1}$.

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Comment

The title compound, (I), was prepared as part of our ongoing studies of second-sphere hydrogen-bonding interactions in compounds containing cationic metal complexes and organic counter-anions (Sharma, Bala *et al.*, 2006; Sharma, Sharma *et al.*, 2006).



The geometrical parameters for the component species in (I) fall within their expected ranges (Allen *et al.*, 1987). The well known $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2(\text{H}_2\text{O})_2]^{2+}$ complex cation in (I) is built up from a central copper(II) ion (site symmetry $\bar{1}$) chelated by two ethylenediamine molecules to form an approximate CuN_4 square. The Jahn–Teller distorted copper coordination is completed by two *trans* water molecules (Table 1). The Cu–N and Cu–O bond lengths in (I) are very similar to the equivalent values observed for the same complex cation in its bis(naphthalene-2-sulfonate) (Sharma *et al.*, 2005) and bis(4-fluorobenzoate) (Liu *et al.*, 2004) salts.

The 4-nitrobenzoate anion in (I) is almost planar, the dihedral angles between the mean plane of the C3–C8 benzene ring and the planes of its attached C9/O2/O3 carboxylate and N3/O4/O5 nitro groups being 2.14 (17) and 1.9 (2)°, respectively. The carboxylate C–O bond lengths are almost equal, suggesting charge delocalization.

As well as electrostatic forces, the component species in (I) interact by way of $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2). Firstly, adjacent complex cations are linked into chains propagating along [100] by way of translation-related pairs of $\text{N1}-\text{H1}\cdots\text{O1}^i$ bonds (see Table 2 for symmetry code). A bridging carboxylate atom O3 also helps to consolidate the chains (Fig. 2). Then, adjacent cations and anions form a distinctive bridged chain propagating along [010] (Fig. 3), where each carboxylate group in the chain accepts no fewer than four hydrogen bonds from its two adjoining cations.

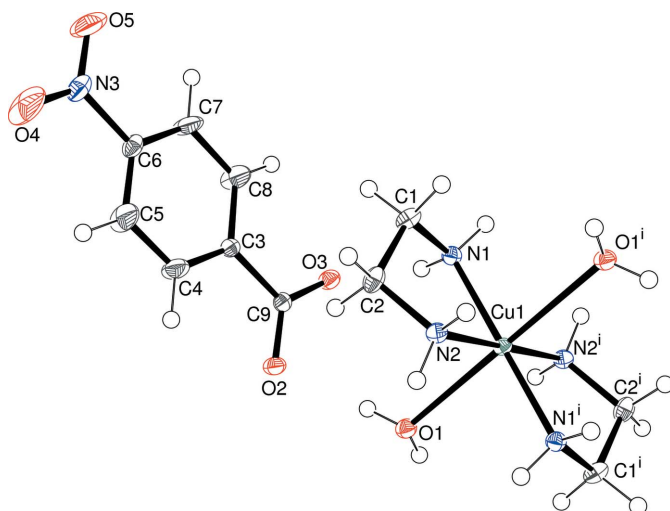


Figure 1
View of the molecular structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

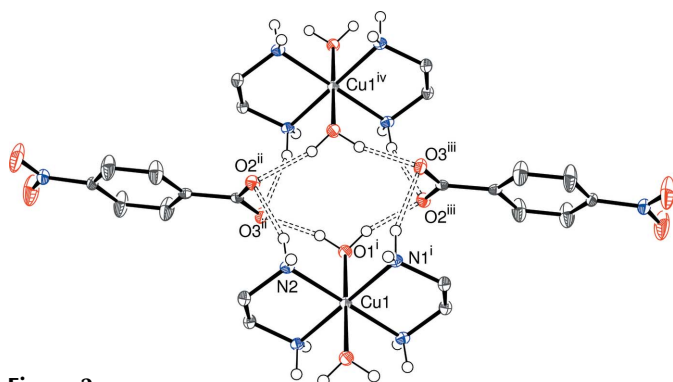


Figure 2
Detail of (I), showing part of a [100] chain arising from hydrogen-bonding interactions (dashed lines). C-bound H atoms have been omitted. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $1 + x, y, z$; (iv) $1 + x, 1 + y, z$.]

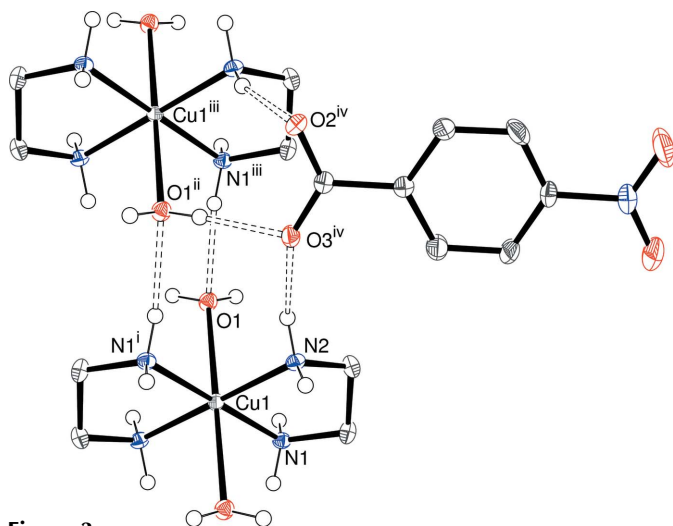


Figure 3
Detail of (I), showing part of a [010] chain arising from hydrogen-bonding interactions (dashed lines). C-bound H atoms have been omitted. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $x, 1 + y, z$.]

Combining these hydrogen-bonding motifs results in (001) sheets of tightly bound cations and anions. It is notable that the nitro O atoms do not serve as acceptors for any of the hydrogen bonds.

Experimental

Compound (I) was prepared by taking a suspension of $[\text{Cu}(\text{H}_2\text{O})_6](\text{C}_7\text{H}_4\text{NO}_4)_2$ [obtained by reacting basic copper(II) carbonate with *p*-nitrobenzoic acid in water] and adding a methanol solution of ethylenediamine dropwise until a slight excess of a 1:2 Cu-en stoichiometry was achieved, resulting in a deep-blue solution, which was allowed to evaporate at room temperature to obtain purple crystals of (I) after a few days. Crystals were filtered off and dried in air.

Crystal data

$[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_7\text{H}_4\text{NO}_4)_2$	$V = 583.69 (15) \text{ \AA}^3$
$M_r = 552.00$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.570 \text{ Mg m}^{-3}$
$a = 6.0019 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.1230 (4) \text{ \AA}$	$\mu = 1.00 \text{ mm}^{-1}$
$c = 15.370 (2) \text{ \AA}$	$T = 93 (2) \text{ K}$
$\alpha = 95.48 (2)^\circ$	Cube, purple
$\beta = 98.43 (2)^\circ$	$0.10 \times 0.10 \times 0.10 \text{ mm}$
$\gamma = 114.26 (2)^\circ$	

Data collection

Rigaku Mercury CCD diffractometer	3754 measured reflections
φ and ω scans	2055 independent reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	1930 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.856, T_{\max} = 1.000$ (expected range = 0.774–0.905)	$R_{\text{int}} = 0.015$
	$\theta_{\max} = 25.3^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.5044P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.077$	$(\Delta/\sigma)_{\max} = 0.002$
$S = 1.08$	$\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$
2005 reflections	$\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$
160 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (\AA).

Cu1—N1	2.0146 (18)	C9—O2	1.256 (3)
Cu1—N2	2.0272 (19)	C9—O3	1.261 (3)
Cu1—O1	2.5369 (17)		

Table 2
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots O1 ⁱ	0.92	2.11	3.018 (2)	170
N1—H2 \cdots O3	0.92	2.20	3.081 (2)	161
N2—H3 \cdots O3 ⁱⁱ	0.92	2.24	3.037 (3)	145
N2—H4 \cdots O2 ⁱⁱⁱ	0.92	2.07	2.960 (2)	162
O1—H5 \cdots O3 ^{iv}	0.89	1.88	2.754 (2)	166
O1—H6 \cdots O2	0.86	1.93	2.767 (2)	164

Symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y + 1, z$; (iii) $x, y + 1, z$; (iv) $-x + 1, -y, -z + 1$.

The O-bound H atoms were located in a difference map and refined as riding in their as-found relative positions with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The C- and N-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å, N–H = 0.92 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: *CrystalClear* (Rigaku, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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