Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

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

**William T. A. Harrison,[a]* Alexandra M. Z. Slawin,[b] Raj Pal Sharma,[c]* Bhavna Sharma[c] and Shekar Bhama[c]**

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, [b]Department of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, and [c]Panjab University, Department of Chemistry, Chandigarh 160 014, India

Correspondence e-mail:
w.harrison@abdn.ac.uk,
rpsharma@yahoo.co.in

Received 27 October 2006
Accepted 6 December 2006

In the title compound, $[Cu(C_2H_8N_2)_2(H_2O)_2](C_7H_4NO_4)_2$, the component complex cations and organic anions interact by way of N—H···O and O—H···O hydrogen bonds, leading to a layered structure. The Cu atom has site symmetry $\bar{1}$.

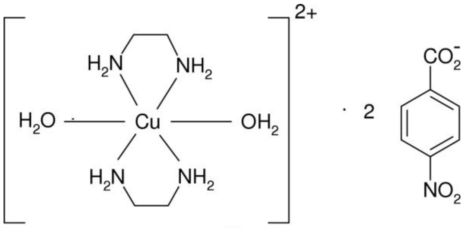
**Key indicators**

Single-crystal X-ray study
$T$ = 93 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ 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.

## 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).



(I)

The geometrical parameters for the component species in (I) fall within their expected ranges (Allen *et al.*, 1987). The well known $[Cu(C_2N_2H_8)_2(H_2O)_2]^{2+}$ 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 O—H···O and N—H···O hydrogen bonds (Table 2). Firstly, adjacent complex cations are linked into chains propagating along [100] by way of translation-related pairs of N1—H1···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.

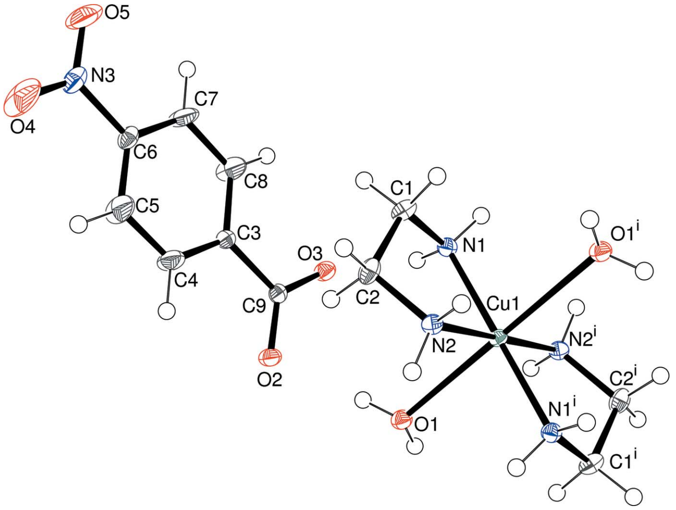


**Figure 1**
View of the molecular structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

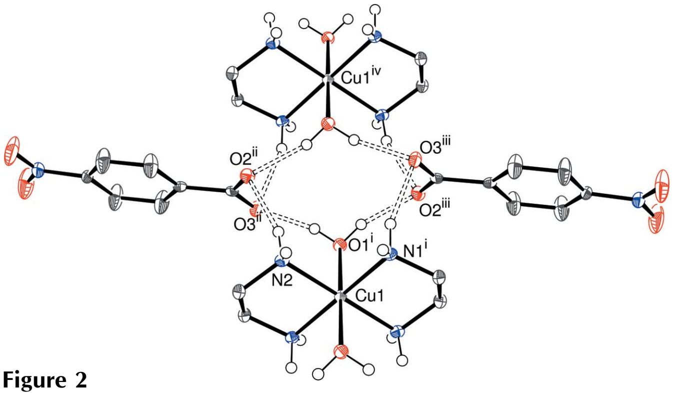


**Figure 2**
Detail of (I), showing part of a [100] chain arising from hydrogen-bonding interactions (dashed lines). C-bound H atoms have been omitted. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $1 + x, y, z$; (iv) $1 + x, 1 + y, z$.]

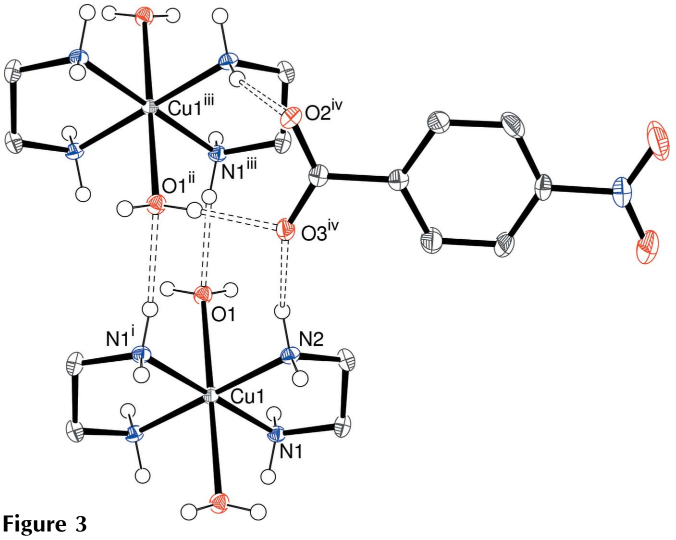


**Figure 3**
Detail of (I), showing part of a [010] chain arising from hydrogen-bonding interactions (dashed lines). C-bound H atoms have been omitted. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $x, 1 + y, z$.]

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 $[Cu(H_2O)_6](C_7H_4NO_4)_2$ [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*

$[Cu(C_2H_8N_2)_2(H_2O)_2](C_7H_4NO_4)_2$
$M_r = 552.00$
Triclinic, $P\bar{1}$
$a = 6.0019$ (5) Å
$b = 7.1230$ (4) Å
$c = 15.370$ (2) Å
$\alpha = 95.48$ (2)°
$\beta = 98.43$ (2)°
$\gamma = 114.26$ (2)°
$V = 583.69$ (15) Å$^3$
$Z = 1$
$D_x = 1.570$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 1.00$ mm$^{-1}$
$T = 93$ (2) K
Cube, purple
0.10 × 0.10 × 0.10 mm

### *Data collection*

Rigaku Mercury CCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.856$, $T_{max} = 1.000$ (expected range = 0.774–0.905)
3754 measured reflections
2005 independent reflections
1930 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 25.3°$

### *Refinement*

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

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| 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 (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O1$^{i}$ | 0.92 | 2.11 | 3.018 (2) | 170 |
| N1—H2···O3 | 0.92 | 2.20 | 3.081 (2) | 161 |
| N2—H3···O3$^{ii}$ | 0.92 | 2.24 | 3.037 (3) | 145 |
| N2—H4···O2$^{iii}$ | 0.92 | 2.07 | 2.960 (2) | 162 |
| O1—H5···O3$^{iv}$ | 0.89 | 1.88 | 2.754 (2) | 166 |
| O1—H6···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) $-x + 1, -y, -z + 1$.

*Acta Cryst.* (2007). E**63**, m178–m180 Harrison *et al.* • $[Cu(C_2H_8N_2)_2(H_2O)_2](C_7H_4NO_4)_2$ **m179**

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

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*.

The authors gratefully acknowledge the financial support of UGC vide grant No. F.12-38/2003(SR).

## References

Allen, F. H., Kennard, O., Watson, D., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Liu, Z.-D., Tan, M.-Y. & Zhu, H.-L. (2004). *Acta Cryst.* E**60**, m1081–m1083.

Rigaku (2004). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.

Sharma, R. P., Bala, R., Sharma, R., Perez, J. & Miguel, D. (2006). *J. Mol. Struct.* **797**, 49–55.

Sharma, R. P., Sharma, R., Bala, R., Burrows, A. D., Mahon, M. F. & Cassar, K. (2006). *J. Mol. Struct.* **794**, 173–180.

Sharma, R. P., Sharma, R., Bala, R., Rychlewska, U. & Warzajtis, B. (2005). *J. Mol. Struct.* **738**, 291–298.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

**m180** Harrison *et al.* • $[Cu(C_2H_8N_2)_2(H_2O)_2](C_7H_4NO_4)_2$ *Acta Cryst.* (2007). E**63**, m178–m180