Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tetrakis(benzylammonium) tetranitratocuprate(II) dinitrate

Melanie Rademeyer

School of Chemistry, University of KwaZulu-Natal, Howard College Campus, Durban 4041, South Africa

Correspondence e-mail:
rademeyerm@ukzn.ac.za

Received 14 December 2005
Accepted 3 January 2006

The crystal structure of the title compound, $(C_6H_5CH_2NH_3)_4[Cu(NO_3)_4](NO_3)_2$, consists of alternating organic and inorganic layers. The aromatic groups constitute the organic layer, while the nitrate ions, ammonium groups and $[Cu(NO_3)_4]^{2-}$ anions form the inorganic layer; the complex anions lie on twofold rotation axes. Strong classical N—H···O hydrogen bonds in the inorganic layer result in a complex two-dimensional hydrogen-bonding network.

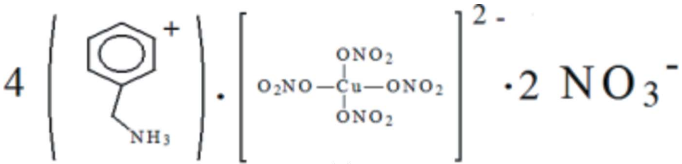
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.127
Data-to-parameter ratio = 23.0

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

Comment

The title compound, (I), is a double salt of benzylammonium nitrate and $Cu(NO_3)_2$, and its structure was determined as part of an ongoing study of organic–inorganic hybrid materials. No structure containing a Cu atom coordinated by four nitrate ligands could be located in the Cambridge Structural Database (November 2004, Version 5.26, August 2005 update; Allen, 2002). A structure containing a chlorotrinitratocopper(II) ion has been reported (Indira *et al.*, 1993).



(I)

The asymmetric unit of (I) contains two benzylammonium cations, one independent nitrate anion and half of a $[Cu(NO_3)_4]^{2-}$ anion, with the Cu atom located on a twofold rotation axis. The molecular geometry and labelling employed are illustrated in Fig. 1.

The $[Cu(NO_3)_4]^{2-}$ ion deviates slightly from a square-planar geometry, with the four coordinating O atoms deviating by ±0.173 Å from their mean plane. Cu—O bond lengths are 1.972 (2) and 1.984 (2) Å and *cis* O—Cu—O angles are 88.77 (8) and 92.07 (8)°.

As illustrated in Fig. 2, a crystal structure comprising organic and inorganic layers is formed. The organic layer contains the benzyl groups, and the inorganic layer is composed of isolated nitrate anions, ammonium groups and $[Cu(NO_3)_4]^{2-}$ anions.

In the organic layer, the aromatic groups pack to form three aromatic sub-layers. The benzyl groups forming the central sub-layer are interdigitated, but the outer benzyl groups are non-interdigitated. No π–π stacking interactions are observed, with the centroid-to-centroid distance being 4.803 (8) Å.

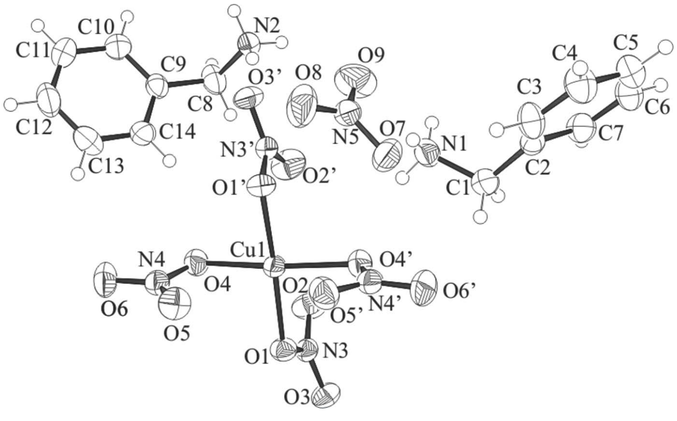


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and with displacement ellipsoids at the 50% probability level. Primed atoms are at the symmetry position ($-x, y, \frac{1}{2} - z$).

The ammonium groups, isolated nitrate anions and $[Cu(NO_3)_4]^{2-}$ anions all interact *via* hydrogen bonding, with the ammonium groups acting as hydrogen-bond donors and the O atoms accepting hydrogen bonds. A complex two-dimensional hydrogen-bonding sheet is formed parallel to the *bc* plane. Hydrogen-bonding interaction parameters are listed in Table 1, and the interactions are illustrated in Fig. 2. The two crystallographically non-equivalent benzylammonium cations do not display the same hydrogen-bonding interactions. The cation containing atom N1 interacts with two different $[Cu(NO_3)_4]^{2-}$ anions *via* atom H1*A*, with an isolated nitrate ion through atom H1*B*, and with an isolated nitrate ion through atom H1*C*. The second cation, which contains atom N2, interacts with an $[Cu(NO_3)_4]^{2-}$ anion and with an isolated nitrate ion through atom N2*A*, with a different $[Cu(NO_3)_4]^{2-}$ anion through atom H2*B*, and with two isolated nitrate anions and one $[Cu(NO_3)_4]^{2-}$ anion through atom H2*C*.

Experimental

Benzylammonium nitrate was prepared by the dropwise addition of concentrated nitric acid (70%, Aldrich) to a solution of benzylamine (99%, Saarchem; 20 ml) in chloroform (50 ml). The resulting precipitate was filtered. Tetrakis(benzylammonium) tetranitratocuprate(II) dinitrate was crystallized by dissolving stoichiometric amounts of benzylammonium nitrate and $Cu(NO_3)_2{\cdot}2.5H_2O$ (98%, Aldrich) (molar ratio 2:1) in water. Blue crystals of (I) formed on evaporation at room temperature.

Crystal data

$(C_7H_{10}N)_4[Cu(NO_4)_3](NO_3)_2$
$M_r = 868.24$
Monoclinic, $C2/c$
$a = 30.79$ (3) Å
$b = 5.749$ (9) Å
$c = 21.293$ (14) Å
$\beta = 97.93$ (7)°
$V = 3733$ (7) Å^3
$Z = 4$
$D_x = 1.545$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 476 reflections
$\theta = 2$–31°
$\mu = 0.68$ mm^{-1}
$T = 295$ (2) K
Block, blue
0.50 × 0.50 × 0.50 mm

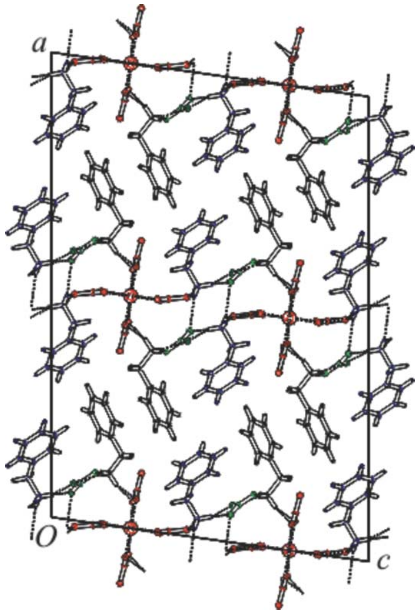


Figure 2
A packing diagram for (I), viewed along the *b* axis. Hydrogen-bonding interactions are shown as dashed lines.

Data collection

Oxford Excalibur2 diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.714$, $T_{max} = 0.714$
17698 measured reflections
5929 independent reflections
4603 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 32.0$°
$h = -44 \rightarrow 45$
$k = -8 \rightarrow 5$
$l = -30 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.127$
$S = 1.08$
5929 reflections
258 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.071P)^2 + 0.4182P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1*A*$\cdots$O4^{i}	0.89	2.37	2.997 (3)	127
N1—H1*A*$\cdots$O5^{ii}	0.89	2.48	3.156 (3)	133
N1—H1*B*$\cdots$O7^{iii}	0.89	1.96	2.803 (4)	158
N1—H1*B*$\cdots$N5^{iii}	0.89	2.66	3.509 (4)	159
N1—H1*C*$\cdots$O9	0.89	2.13	2.953 (4)	153
N1—H1*C*$\cdots$O7	0.89	2.42	3.228 (5)	151
N1—H1*C*$\cdots$N5	0.89	2.65	3.530 (4)	169
N2—H2*A*$\cdots$O3^{ii}	0.89	2.37	3.096 (5)	139
N2—H2*A*$\cdots$O8^{iii}	0.89	2.50	3.036 (4)	120
N2—H2*A*$\cdots$O1^{ii}	0.89	2.54	3.154 (3)	127
N2—H2*B*$\cdots$O3^{i}	0.89	2.12	3.006 (4)	172
N2—H2*C*$\cdots$O9^{iv}	0.89	2.17	2.891 (3)	138
N2—H2*C*$\cdots$O8^{v}	0.89	2.55	3.072 (3)	118
N2—H2*C*$\cdots$O3^{vi}	0.89	2.65	3.136 (3)	116

Symmetry codes: (i) $-x, y, -z + \frac{3}{2}$; (ii) $-x, y - 1, -z + \frac{3}{2}$; (iii) $x, y - 1, z$; (iv) $-x, -y, -z + 1$; (v) $-x, -y + 1, -z + 1$; (vi) $x, -y, z - \frac{1}{2}$.

All H atoms were placed in calculated positions, with aromatic C—H distances of 0.93 Å, methylene C—H distances of 0.79 Å and N—H distances of 0.89 Å, and were refined using a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$ of the parent atom (1.5$U_{\rm eq}$ for methyl groups).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON* and *WinGX* (Farrugia, 1999).

The author acknowledges funding received for this work from the University of KwaZulu-Natal Research Office, and the National Research Foundation (Thuthuka, WiR, GUN:2054350).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

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

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Indira, A., Babu, A. M., Bellad, S. B., Sridhar, M. A. & Shashidhara Prasad, J. (1993). *Curr. Sci.* **64**, 247–252.

Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.170. Oxford Diffraction Ltd., Abingdon, Oxford, England.

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

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.