

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Editors: **W. Clegg** and **D. G. Watson**

Bis{ μ -2-[bis(2-hydroxyethyl)amino]ethanolato}bis(4-methylbenzoato)dicopper(II) dihydrate

Alexander M. Kirillov, Matti Haukka, Maximilian N. Kopylovich and Armando J. L. Pombeiro

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.

Alexander M. Kirillov,^a Matti Haukka,^{b*} Maximilian N. Kopylovich^a and Armando J. L. Pombeiro^a

^aCentro de Química Estrutural, Complexo Interdisciplinar, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, and ^bDepartment of Chemistry, University of Joensuu, P.O. Box 111, 80101 Joensuu, Finland

Correspondence e-mail: matti.haukka@joensuu.fi

Key indicators

Single-crystal X-ray study
 T = 120 K
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 R factor = 0.040
 wR factor = 0.086
 Data-to-parameter ratio = 16.9

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

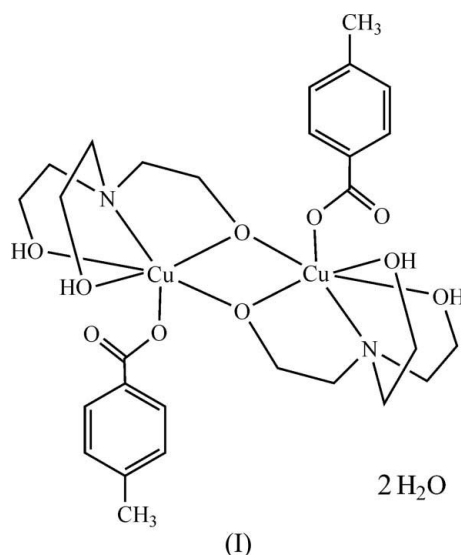
Bis{ μ -2-[bis(2-hydroxyethyl)amino]ethanolato}-bis(4-methylbenzoato)dicopper(II) dihydrate

The title compound, $[\text{Cu}_2(\text{C}_8\text{H}_7\text{O}_2)_2(\text{C}_6\text{H}_{14}\text{NO}_3)_2]\cdot 2\text{H}_2\text{O}$, contains a centrosymmetric binuclear $[\text{Cu}_2(\text{H}_2\text{tea})_2]^{2+}$ fragment (H_3tea is triethanolamine), with two bound 4-methylbenzoate anions. All O atoms of H_2tea , one O atom of 4-methylbenzoate and two solvent water molecules are involved in O—H \cdots O hydrogen bonding, providing additional stabilization of the binuclear molecular units and also linking them into one-dimensional hydrogen-bonded chains.

Received 26 December 2006
 Accepted 13 January 2007

Comment

The title compound, (I), has been previously obtained (Kirillov *et al.*, 2006) and applied as a catalyst or catalyst precursor for the mild peroxidative oxidation of cyclohexane within our ongoing research on the synthesis and catalytic properties of various Cu (Kirillov, Kopylovich, Kirillova, Haukka *et al.*, 2005; Karabach *et al.*, 2006), Re (Kirillov, Haukka *et al.*, 2005) and Ni (Haukka *et al.*, 2005) complexes derived from triethanolamine (H_3tea). Compound (I) has been characterized previously by FT-IR, FAB⁺-MS and elemental analysis. We report here its X-ray crystal structure.



The crystal structure of (I) (Fig. 1) consists of binuclear $[\text{Cu}_2(\text{H}_2\text{tea})_2]^{2+}$ units linked to two monodentate 4-methylbenzoate anions. Each Cu^{II} centre has a distorted tetragonal-bipyramidal geometry and each H_2tea acts as a tetradentate ligand with one bridging alkoxo-group generating a centrosymmetric planar $\text{Cu}_2(\mu\text{-O})_2$ core, in which the Cu \cdots Cu separation is 2.9070 (7) Å. Most of the bonding parameters of (I) (Table 1) are comparable to those of related copper

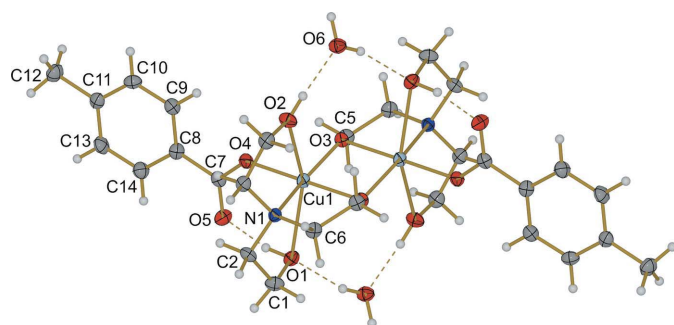


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level for non-H atoms. Unlabelled atoms are related to labelled atoms by the symmetry operator $(1 - x, -y, 2 - z)$. Dashed lines denote hydrogen bonds.

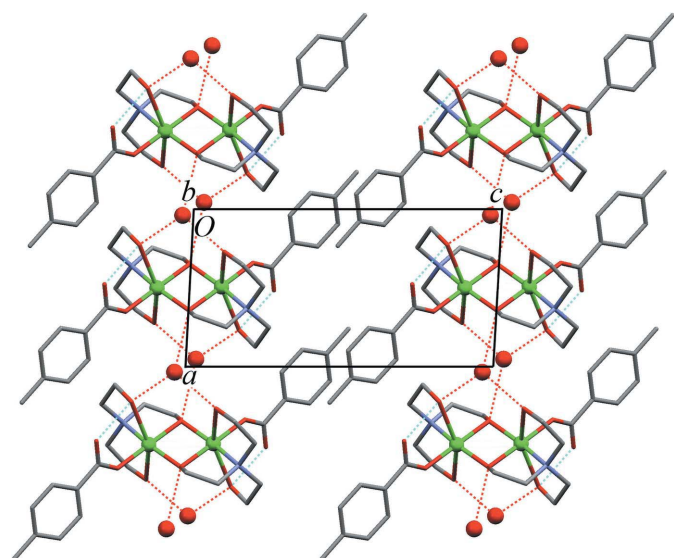


Figure 2
View of (I) along the b axis, showing the $O-H \cdots O$ hydrogen-bonding network (dashed lines). H atoms are omitted. O atoms of the solvent water molecules are shown as red spheres.

triethanolamine dimeric or polymeric complexes in which the $[Cu_2(H_2tea)_2]^{2+}$ unit is linked to benzoate and terephthalate (Kirillov, Kopylovich, Kirillova, Haukka *et al.*, 2005), 3-chlorobenzoate (Kirillov *et al.*, 2006), saccharinate (Topcu *et al.*, 2002) or *trans*-1,2-bis(4-pyridyl)ethylene (Tudor *et al.*, 2003).

In (I), the binding of the 4-methylbenzoate anion is additionally stabilized by intramolecular $O1-H10 \cdots O5$ hydrogen bonds (Fig. 1, Table 2) between an OH group of H_2tea and the free carboxylate oxygen, forming an almost planar six-membered $O1/H10/O5/C7/O4/Cu1$ ring. Each solvent water molecule acts as both a hydrogen-bond acceptor and donor (Table 2), bridging between triethanolamine OH groups, providing further reinforcement of the binuclear units (Fig. 1). The water molecules also interact with the $\mu-O$ atoms of H_2tea in neighbouring molecular units, forming one-dimensional hydrogen-bonded polymers running along the a axis (Fig. 2).

Experimental

The title compound was obtained according to the previously described procedure (Kirillov *et al.*, 2006). Pale-blue crystals were formed in a few days upon evaporation of the aqueous reaction mixture in air at ambient temperature.

Crystal data

$[Cu_2(C_8H_7O_2)_2(C_6H_{14}NO_3)_2] \cdot 2H_2O$	$V = 782.69 (9) \text{ \AA}^3$
$M_r = 729.75$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.548 \text{ Mg m}^{-3}$
$a = 7.5137 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.9384 (5) \text{ \AA}$	$\mu = 1.42 \text{ mm}^{-1}$
$c = 14.3761 (10) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\alpha = 75.422 (3)^\circ$	Plate, pale blue
$\beta = 87.976 (4)^\circ$	$0.17 \times 0.15 \times 0.04 \text{ mm}$
$\gamma = 70.805 (4)^\circ$	

Data collection

Nonius KappaCCD diffractometer	12377 measured reflections
φ and ω scans	3429 independent reflections
Absorption correction: numerical (XPRED; Bruker, 2005)	2743 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.794, T_{\max} = 0.944$	$R_{\text{int}} = 0.055$
	$\theta_{\text{max}} = 27.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.6222P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
3429 reflections	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
203 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Cu1—O1	2.5249 (18)	Cu1—O3 ⁱ	1.9497 (17)
Cu1—O2	2.4535 (18)	Cu1—O4	1.9491 (18)
Cu1—O3	1.9443 (17)	Cu1—N1	2.051 (2)
O3—Cu1—O4	95.09 (7)	N1—Cu1—O2	76.44 (7)
O3—Cu1—O3 ⁱ	83.42 (7)	O3—Cu1—O1	114.12 (6)
O3—Cu1—N1	161.95 (8)	O4—Cu1—O1	88.55 (7)
O4—Cu1—N1	96.98 (8)	N1—Cu1—O1	79.62 (7)
O3—Cu1—O2	91.36 (7)	O2—Cu1—O1	154.18 (6)
O4—Cu1—O2	84.90 (7)	Cu1—O3—Cu1 ⁱ	96.58 (7)

Symmetry code: (i) $-x + 1, -y, -z + 2$.

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1O \cdots O5	0.91	1.70	2.594 (3)	168
O2—H2O \cdots O6 ⁱ	0.87	1.82	2.680 (3)	174
O6—H6O \cdots O1	0.82	2.02	2.824 (3)	165
O6—H6P \cdots O3 ⁱⁱ	0.90	2.07	2.891 (2)	151

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

H atoms bound to C atoms were positioned geometrically and constrained to ride on their parent atoms, with $C-H = 0.95-0.99 \text{ \AA}$ and $U_{\text{iso}} = 1.2U_{\text{eq}}(C)$, or $1.5U_{\text{eq}}(C)$ for the methyl group. H atoms bound to O atoms were located in difference Fourier maps, then constrained to ride on their parent atoms in their as-found positions (distances given in Table 2), with $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$.

metal-organic papers

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, its POCI 2010 programme (FEDER funded), by a Human Resources and Mobility Marie-Curie Research Training Network (AQUA-CHEM project, CMTN-CT-2003-503864), and by the Academy of Finland. AMK and MNK are grateful to the FCT and the POCI programme for fellowships (BPD/28729/2006 and BPD/14465/2003).

References

- Brandenburg, K. (2006). *DIAMOND*. Release 3.1d. Crystal Impact GbR, Bonn, Germany.
- Bruker (2005). *XPREP* in *SHELXTL*. Version 6.14-1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Burla, M. C., Caliendo, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Haukka, M., Kirillov, A. M., Kopylovich, M. N. & Pombeiro, A. J. L. (2005). *Acta Cryst.* **E61**, m2746–m2748.
- Karabach, Y. Y., Kirillov, A. M., da Silva, M. F. C. G., Kopylovich, M. N. & Pombeiro, A. J. L. (2006). *Cryst. Growth Des.* **6**, 2200–2203.
- Kirillov, A. M., Haukka, M., da Silva, M. F. C. G. & Pombeiro, A. J. L. (2005). *Eur. J. Inorg. Chem.* pp. 2071–2080.
- Kirillov, A. M., Kopylovich, M. N., Kirillova, M. V., Haukka, M., da Silva, M. F. C. G. & Pombeiro, A. J. L. (2005). *Angew. Chem. Int. Ed.* **44**, 4345–4349.
- Kirillov, A. M., Kopylovich, M. N., Kirillova, M. V., Karabach, E. Y., Haukka, M., da Silva, M. F. C. G. & Pombeiro, A. J. L. (2006). *Adv. Synth. Catal.* **348**, 159–174.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Gottingen, Germany.
- Topcu, Y., Andac, O., Yilmaz, V. T. & Harrison, W. T. A. (2002). *J. Coord. Chem.* **55**, 805–815.
- Tudor, V., Marin, G., Kravtsov, V., Simonov, Y. A., Lipkowski, J., Brezeanu, M. & Andruh, M. (2003). *Inorg. Chim. Acta*, **353**, 35–42.