Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Triaqua{μ-2-[*N*,*N*-bis(carboxylatomethyl)aminomethyl]-6-[*N*-(carboxylatomethyl)-*N*-(carboxymethyl)aminomethyl]-4-nitrophenolato}dicopper(II) trihydrate

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Received 27 July 2004
Accepted 6 August 2004
Online 13 August 2004

Key indicators

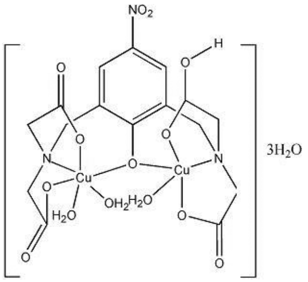
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
R factor = 0.066
wR factor = 0.162
Data-to-parameter ratio = 12.3

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

The structure of the title compound, $[Cu_2(C_{16}H_{15}N_3O_{11})(H_2O)_3]\cdot 3H_2O$, shows two distinct distorted octahedral Cu^{II} centres, with each Cu^{II} ion bound to carboxylate O atoms, amine N atoms, a phenolate O atom and water O atoms.

Comment

The synthesis and characterization of dinuclear Cu^{II} complexes have received a great deal of attention, owing to their importance in haemocyanin, tyrosinase, laccase and ascorbate oxidase (Kitajima & Moro-oka, 1994; Solomon *et al.*, 1994; Sorrell, 1989; Karlin, 1993). The *R*-HXTA ligands [where *R* is Cl or CH_3 and HXTA is *N*,*N*′-(2-hydroxy-5-*R*-1,3-xylene)bis(*N*-carboxymethylglycine)] have been used extensively to incorporate various dinuclear cores, such as Cu, Fe, Ni and Ce (Holz *et al.*, 1994; Murch *et al.*, 1987; Meng, Huang & Gao, 2004; Meng, Gao & Zhu, 2004; Branum *et al.*, 2001). In this paper, we report the title novel triaquadicopper complex of NO_2-HXTA, (I).



(I)

A displacement ellipsoid drawing of (I) is shown in Fig. 1. Each Cu^{II} ion exhibits a distorted octahedral geometry, the two environments being different. The coordination sphere of Cu1 is composed of atoms O1, O2, O6 and N2 forming a plane, with carboxylate distances Cu1—O4 = 2.286 (5) and Cu—O3^{v} = 3.018 (5) Å [symmetry code: (v) $1 - x, -y, -z$]; the long Cu—O3^{v} distance is to a ligand in a neighbouring complex. The coordination sphere of Cu2 has atoms O7, O9, O13 and N3 in a plane, with Cu2—O1 = 2.301 (4) and Cu2—O14 = 2.674 (5) Å. Hydrogen bonds are formed between the uncoordinated water molecules and the carboxylate carbonyl O atoms, as well as the coordinated water molecules.

The structural aspects of (I) are similar to those of the analogous complex $[Cu_2(CH_3\text{-HXTA})H(H_2O)_2]\cdot 4H_2O$ (Holz *et al.*, 1994; Meng, Huang & Gao, 2004). However, the Cu—O$_{phenolate}$ distances in (I) [1.922 (4) and 2.301 (4) Å] are longer than those found in $[Cu_2(CH_3\text{-HXTA})H(H_2O)_2]\cdot 4H_2O$ [1.897 (3) and 2.246 (4) Å (Holz *et al.*, 1994), and 1.906 (2) and 2.229 (2) Å (Meng, Huang & Gao, 2004)].

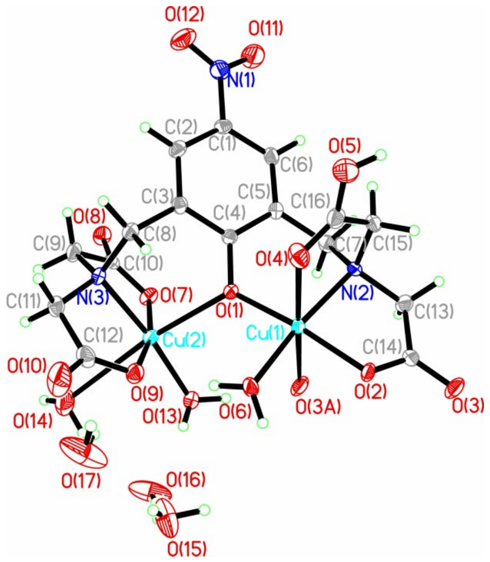


Figure 1
The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (A) $1 - x, -y, -z$.]

Interestingly, we also note that one H atom is attached to a carboxylate carbonyl O atom in (I), as was observed in $[Cu_2(CH_3\text{-HXTA})H(H_2O)_2]\cdot 4H_2O$ (Meng, Huang & Gao, 2004).

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China. The NO_2-HXTA ligand was synthesized by a modification of published procedures (Murch *et al.*, 1987; Branum *et al.*, 2001). To an aqueous solution (100 ml) containing iminodiacetic acid (0.125 mol) and *p*-nitrophenol (0.063 mol) was added NaOH (0.25 mol) in water (40 ml), and the mixture was cooled in an ice–water bath. Upon dissolution, 37% formaldehyde (15 ml) was added dropwise at 273 K. The solution was stirred for 30 min, heated at 343 K for 4 h, and then concentrated to dryness. Recrystallization of the solid from methanol yielded the product $Na_4(NO_2\text{-HXTA})$. $Cu(ClO_4)_2\cdot 6H_2O$ (0.5422 g, 0.002 mol) and $Na_4(NO_2\text{-HXTA})$ (0.4293 g, 0.001 mol) were dissolved in water (10 ml). After stirring for 10 min, the solution was left in the refrigerator for 10 d. Dark-green crystals of (I) were obtained by slow evaporation of the aqueous solvent.

Crystal data

$[Cu_2(C_{16}H_{15}N_3O_{11})(H_2O)_3]\cdot 3H_2O$
$M_r = 660.49$
Monoclinic, $P2_1/n$
$a = 15.137\ (4)$ Å
$b = 10.787\ (3)$ Å
$c = 15.240\ (4)$ Å
$\beta = 104.936\ (3)^\circ$
$V = 2404.3\ (10)$ Å^3
$Z = 4$
$D_x = 1.825$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2284 reflections
$\theta = 2.3$–23.2°
$\mu = 1.86$ mm^{-1}
$T = 298\ (2)$ K
Block, green
$0.20 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{\min} = 0.708$, $T_{\max} = 0.836$
9744 measured reflections
4233 independent reflections
3335 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$
$\theta_{\max} = 25.0^\circ$
$h = -18 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.162$
$S = 1.00$
4233 reflections
343 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0884P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.922 (4)	Cu2—O9	1.960 (4)
Cu1—O2	1.939 (4)	Cu2—O7	1.960 (4)
Cu1—O6	1.954 (4)	Cu2—N3	2.004 (5)
Cu1—N2	2.040 (4)	Cu2—O1	2.301 (4)
Cu1—O4	2.286 (5)	Cu2—O14	2.674 (5)
Cu2—O13	1.954 (4)		
O1—Cu1—O2	166.71 (19)	O13—Cu2—N3	172.90 (19)
O1—Cu1—O6	91.49 (17)	O9—Cu2—N3	83.36 (19)
O2—Cu1—O6	89.11 (17)	O7—Cu2—N3	84.70 (19)
O1—Cu1—N2	96.11 (18)	O13—Cu2—O1	94.44 (16)
O2—Cu1—N2	83.87 (17)	O9—Cu2—O1	92.35 (17)
O6—Cu1—N2	172.24 (19)	O7—Cu2—O1	93.84 (16)
O1—Cu1—O4	90.16 (18)	N3—Cu2—O1	92.61 (17)
O2—Cu1—O4	102.90 (19)	O13—Cu2—O14	80.93 (17)
O6—Cu1—O4	98.2 (2)	O9—Cu2—O14	81.13 (18)
N2—Cu1—O4	80.21 (18)	O7—Cu2—O14	93.65 (18)
O13—Cu2—O9	95.53 (19)	N3—Cu2—O14	91.97 (18)
O13—Cu2—O7	95.62 (19)	O1—Cu2—O14	171.55 (16)
O9—Cu2—O7	166.78 (17)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O17—H75$\cdots$O4$^{\rm i}$	0.87	2.07	2.793 (8)	141
O16—H73$\cdots$O15	0.85	2.00	2.851 (10)	173
O17—H76$\cdots$O10	0.84	1.84	2.531 (9)	138
O16—H74$\cdots$O8$^{\rm ii}$	0.85	1.95	2.741 (7)	155
O15—H72$\cdots$O8$^{\rm iii}$	0.85	2.00	2.841 (7)	169
O14—H66$\cdots$O16	0.85	2.43	3.154 (10)	144
O15—H71$\cdots$O17	0.85	2.26	3.005 (12)	147
O14—H65$\cdots$O3$^{\rm iv}$	0.85	2.05	2.888 (7)	169
O13—H64$\cdots$O16	0.85	1.82	2.631 (7)	159
O13—H63$\cdots$O3$^{\rm v}$	0.85	1.84	2.689 (6)	174
O6—H62$\cdots$O8$^{\rm iii}$	0.85	1.90	2.728 (6)	167
O6—H61$\cdots$O9	0.85	1.86	2.708 (6)	172
O5—H5$\cdots$O17$^{\rm vi}$	0.86	1.69	2.541 (9)	170

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

H atoms attached to C atoms were placed in geometrically idealized positions, with Csp^3—H = 0.97 and Csp^2—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. H atoms attached to O atoms were located in difference Fourier maps and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*/*PC*.

The authors are grateful to the Natural Science Foundation of Shanxi Province for financial support (project No. 20041012).

m1252 Jiang *et al.* • $[Cu_2(C_{16}H_{15}N_3O_{11})(H_2O)_3]\cdot 3H_2O$ *Acta Cryst.* (2004). E**60**, m1251–m1253

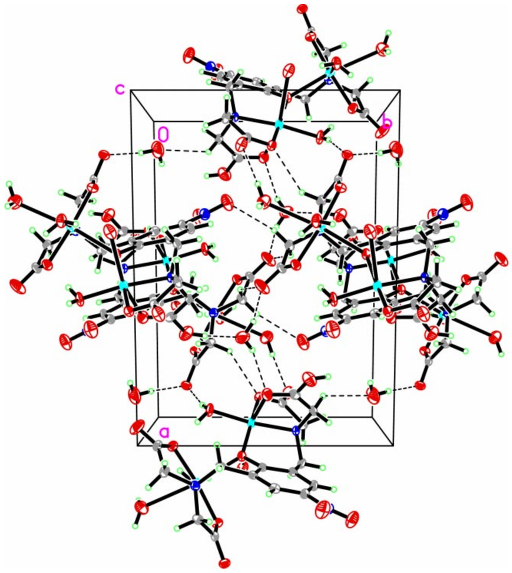


Figure 2
A packing diagram for the structure of (I), viewed along the *c* axis. The dashed lines represent hydrogen bonds.

References

Branum, M. E., Tipton, A. K., Zhu S. & Que, L. (2001). *J. Am. Chem. Soc.* **123**, 1898–1904.

Bruker (2000). *SMART* (Version 5.0) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Holz, R. C., Brink, J. M., Gobena, F. T. & O'Connor, C. J. (1994). *Inorg. Chem.* **33**, 6086–6092.

Karlin, K. D. (1993). *Science*, **262**, 1499.

Kitajima, N. & Moro-oka, Y. (1994). *Chem. Rev.* **94**, 737–757.

Meng, B., Huang, S. & Gao, F. (2004). *Acta Cryst.* E**60**, m797–m799.

Meng, B.-H., Gao, F. & Zhu, M.-L. (2004). *Acta Cryst.* C**60**, m308–m310.

Murch, B. P., Bradley, F. C., Boyle, P. D., Papaefthymiou, V. & Que, L. Jr (1987). *J. Am. Chem. Soc.* **109**, 7993–8003.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (1999). *SHELXTL/PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2000). *SADABS*. University of Göttingen, Germany.

Solomon, E. I., Tuczek, F., Root, D. E. & Brown, C. A. (1994). *Chem. Rev.* **94**, 827–856.

Sorrell, T. N. (1989). *Tetrahedron*, **45**, 3–68.

Acta Cryst. (2004). E**60**, m1251–m1253 Jiang *et al.* • $[Cu_2(C_{16}H_{15}N_3O_{11})(H_2O)_3]\cdot 3H_2O$ **m1253**