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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
 R factor = 0.053
 wR factor = 0.086
Data-to-parameter ratio = 11.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Aqua[*N*-(2-hydroxy-5-nitrobenzyl)imino-
diacetato- $\kappa^4\text{O},\text{N},\text{O}',\text{O}''$]copper(II)The structure of the title compound, $[\text{Cu}(\text{NO}_2\text{-XDAH})(\text{H}_2\text{O})]$ [where $\text{NO}_2\text{-XDAH}_3$ is *N*-(2-hydroxy-5-nitrobenzyl)iminodiacetic acid, $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_7$], shows that the mononuclear complex unit contains a CuNO_4 distorted square pyramid. The H atom attached to the phenolic O atom is retained, while the two carboxylate groups are deprotonated in the complex.

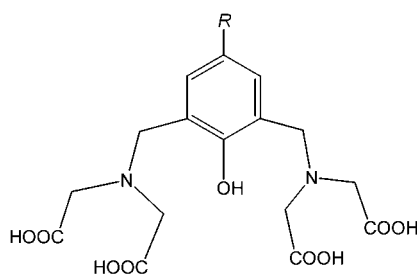
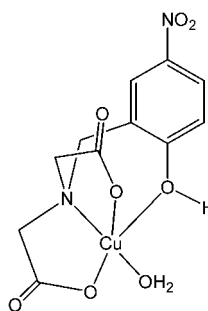
Received 29 June 2004

Accepted 6 July 2004

Online 17 July 2004

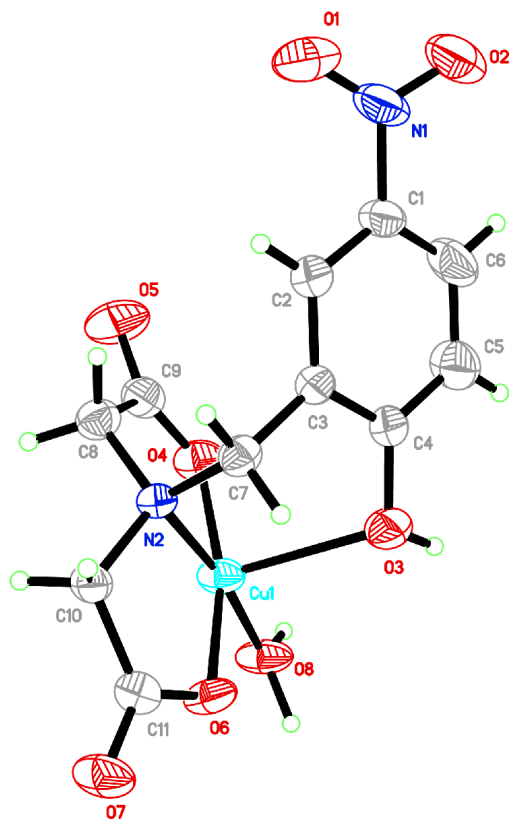
Comment

$\text{CH}_3\text{-XTAH}_5$ [2,6-bis[[bis(carboxymethyl)amino]methyl]-4-chlorophenol, (I)] and Cl-XTAH_5 [the corresponding 5-chloro compound, (II)] are versatile acidic dinucleating ligands, in which the position *para* to the aromatic hydroxy group is blocked and they are suitable for incorporating various dinuclear cores; they were first reported by Murch *et al.* (1987). We have previously reported two dinuclear complexes, *viz.* $[\text{Cu}_2(\text{CH}_3\text{XTAH})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ (Meng, Huang & Gao, 2004) and $[\text{Na}(\text{H}_2\text{O})_3][\text{Ni}_2(\text{Cl-XTA})(\text{H}_2\text{O})_4]\cdot 5\text{H}_2\text{O}$ (Meng, Gao & Zhu, 2004). In the present work, a new ligand $\text{NO}_2\text{-XDAH}_3$ [*N*-(2-hydroxy-5-nitrobenzyl)iminodiacetic acid] has been synthesized by the same method. It has only two methoxycarbonyl chelating arms, giving potentially three O and one N coordination sites. We report here the crystal structure of the mononuclear complex, (III), of $\text{NO}_2\text{-XDAH}^{2-}$ and Cu^{II} .

(I) $R = \text{CH}_3$ (II) $R = \text{Cl}$ 

(III)

Selected molecular geometry parameters of (III) are listed
in Table 1 and the molecular structure is shown in Fig. 1. In this

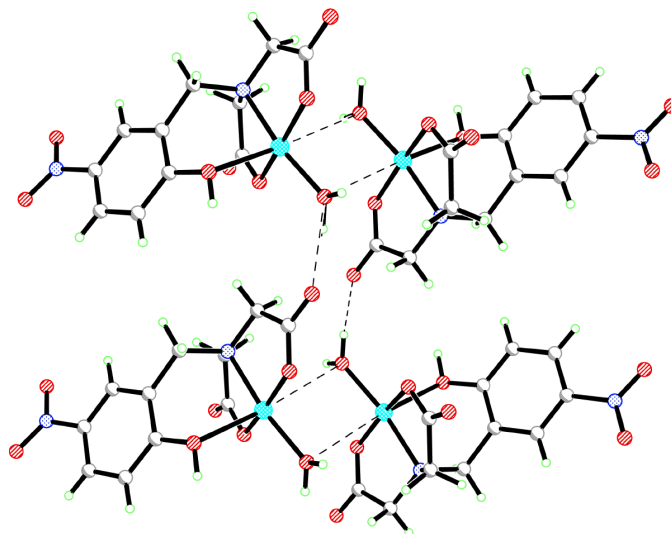

Figure 1

A view of the molecular structure of (III), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

mononuclear complex, the Cu^{2+} ion is located in a distorted square-pyramidal environment consisting of two carboxylate O atoms, a tertiary N atom, one water molecule and the phenolic O atom. The phenolic O atom is apical and the other atoms constitute the base of the pyramid. This structure has some similarities to that of the complex $[\text{Cu}_2(\text{CH}_3\text{XTAH})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ (Meng, Huang & Gao, 2004), but the latter has two Cu atoms. The Cu–O3 bond length for (III) is 2.404 (4) Å, significantly longer than that observed for the previous structure, 2.2288 (17) Å. However, the Cu–O(carboxylate) bond lengths of (III) are 1.923 (3) and 1.927 (3) Å, shorter than those of the previous structure, 1.9624 (18) and 1.9866 (18) Å. These differences result from the introduction of a stronger electron-withdrawing *para* substituent.

In the structure of $[\text{Cu}_2(\text{CH}_3\text{XTAH})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$, one H atom attached to a carboxyl atom is retained for charge balance, while in (III), the H atom of the phenol group is retained. The title complex is anhydrous. The Cu^{2+} ion is weakly coordinated at the second apical position by an O atom from the coordinated water molecule of a neighbouring complex.

The hydrogen-bonding geometry in (I) is listed in Table 2 and illustrated in Fig. 2. A number of intermolecular hydrogen bonds stabilize the crystal structure. They are mainly formed between the water molecules and carboxylate O atoms. Two


Figure 2

Hydrogen bonding and weak additional coordination (dashed lines) in the cyclic tetramers.

hydrogen bonds combine with the weak axial aqua coordination in four neighbouring molecules to form a cyclic tetrameric unit.

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China, and were used without further purification. The ligand $\text{NO}_2\text{-XDAH}_3$ was synthesized by a modification of published procedures (Murch *et al.*, 1987; Branum *et al.*, 2001). To an aqueous solution (80 ml) containing iminodiacetic acid (8.35 g, 0.0625 mol) and *p*-nitrophenol (8.688 g, 0.0625 mol) cooled in an ice–water bath was added NaOH (5.25 g, 0.125 mol) in water (20 ml). Formaldehyde (7.5 ml, 37%) was then added dropwise at 273 K. The solution was stirred for 30 min, heated at 343 K for 4 h and then evaporated to dryness. Recrystallization of the solid from methanol yielded yellow crystals of $\text{Na}_2(\text{NO}_2\text{-XDAH})$ (yield 90%). $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.171 g, 1 mmol) and $\text{Na}_2(\text{NO}_2\text{-XDAH})$ (0.328 g, 1 mmol) were dissolved separately in water (2×5 ml), mixed and stirred at 323 K for 3 h. The resulting blue–green solution was filtered and the filtrate left to stand at room temperature. Sea-blue crystals of the title compound appeared after 10 d by slow evaporation.

Crystal data

$[\text{Cu}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_7)(\text{H}_2\text{O})]$
 $M_r = 363.77$
 Monoclinic, $P2_1/c$
 $a = 15.341$ (11) Å
 $b = 7.400$ (5) Å
 $c = 12.149$ (9) Å
 $\beta = 98.902$ (11)°
 $V = 1362.6$ (17) Å³
 $Z = 4$

$D_x = 1.773$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 741 reflections
 $\theta = 3.1\text{--}21.1^\circ$
 $\mu = 1.65$ mm⁻¹
 $T = 293$ (2) K
 Plate, blue
 0.20 × 0.20 × 0.02 mm

Data collection

Bruker SMART 1K CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\text{min}} = 0.734$, $T_{\text{max}} = 0.968$
 5397 measured reflections

2399 independent reflections
 1536 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -17 \rightarrow 18$
 $k = -8 \rightarrow 7$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.086$
 $S = 0.87$
 2399 reflections
 203 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0191P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

Cu1—O6	1.923 (3)	Cu1—N2	2.013 (4)
Cu1—O4	1.927 (3)	Cu1—O3	2.404 (4)
Cu1—O8	1.942 (3)		
O6—Cu1—O4	166.55 (15)	O8—Cu1—N2	171.63 (15)
O6—Cu1—O8	88.83 (14)	O6—Cu1—O3	96.43 (14)
O4—Cu1—O8	98.24 (15)	O4—Cu1—O3	94.42 (14)
O6—Cu1—N2	84.92 (15)	O8—Cu1—O3	94.40 (15)
O4—Cu1—N2	86.82 (15)	N2—Cu1—O3	91.83 (15)

Table 2
 Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3 \cdots O5 ⁱ	0.93 (5)	1.68 (5)	2.590 (5)	168 (5)
O8—H8D \cdots O7 ⁱⁱ	1.01	1.90	2.887 (5)	166
O8—H8C \cdots O7 ⁱⁱⁱ	0.92	1.79	2.648 (5)	154

Symmetry codes: (i) $x, \frac{5}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, 1 + y, z$.

H atoms attached to C atoms were placed in geometrically idealized positions, with $Csp^3-H = 0.97 \text{ \AA}$ and $Csp^2-H = 0.93 \text{ \AA}$, and

constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms attached to O8 (water) were located in a difference Fourier map and constrained to ride on their parent atom, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The phenol H atom was located in a difference map and refined freely.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

This work is financially supported by the Provincial Natural Science Foundation of Shanxi and the Overseas Returned Scholar Foundation of Shanxi Province (for FG).

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