

Sema Öztürk,<sup>a</sup> Mehmet Akkurt,<sup>a\*</sup> Nebahat Demirhan,<sup>b</sup> Bahattin Kahveci,<sup>c</sup> Hoong-Kun Fun<sup>d</sup> and Nüket Öcal<sup>b</sup>

<sup>a</sup>Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey, <sup>b</sup>Chemistry Department, Faculty of Arts and Sciences, Yıldız Technical University, 34210 Esenler - İstanbul, Turkey, <sup>c</sup>Chemistry Department, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey, and <sup>d</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Correspondence e-mail: akkurt@erciyes.edu.tr

#### Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{N}-\text{N}) = 0.007\text{ \AA}$

$R$  factor = 0.051

$wR$  factor = 0.110

Data-to-parameter ratio = 16.2

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

## Tetra- $\mu$ -nitroamino-bis[aquacopper(II)]

The title molecule,  $[\text{Cu}_2(\text{H}_2\text{N}_2\text{O}_2)_4(\text{H}_2\text{O})_2]$ , possesses a center of symmetry and contains two almost planar eight-membered central rings which are nearly normal to each other. Molecules are linked by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds to form a three-dimensional network.

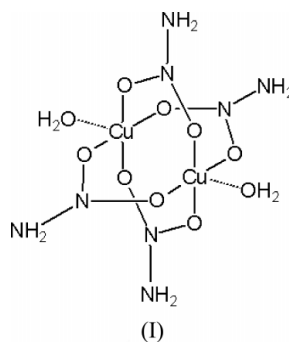
Received 11 June 2003

Accepted 12 June 2003

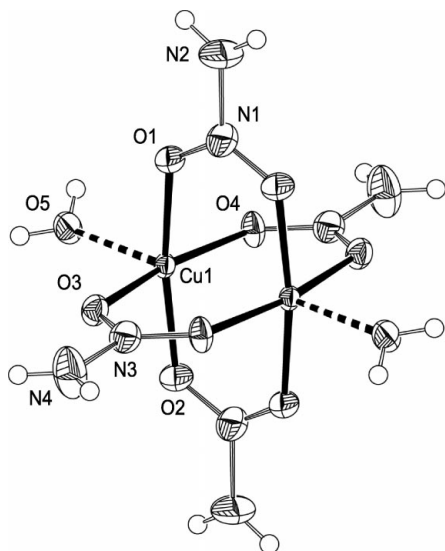
Online 10 July 2003

#### Comment

The primary aim of our work was to synthesize crystalline  $\text{Cu}^{\text{II}}$  complexes of 3-benzyl-4-(4-chlorophenylmethylideneamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (*L*). *L* can be obtained from the reaction of 3-benzyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-ones with 4-chlorobenzaldehyde, according to a literature procedure (Kahveci & İkizler, 2000). The title dinuclear pentacoordinated nitroamine- $\text{Cu}^{\text{II}}$  complex, (I), was obtained in glacial acetic acid solution upon decomposition of *L*. Nitroamine complexes of  $\text{Co}^{\text{II}}$  have also been synthesized by methods described in the literature (Stepanyan *et al.*, 2000). Nitroamine itself is the simplest model for a nitroamine energetic compound that can be used as an explosive, but research already performed has focused only on the monomer (Ju & Xiao, 2002; Hughes & Wimbledon, 1982). The title compound, (I), was identified by FT-IR spectroscopy and the X-ray structure determination undertaken.



The title molecule (which is shown in Fig. 1) contains two eight-membered rings, four  $\text{NH}_2$  groups bonded to the N atoms of these rings [average  $\text{N}-\text{N} = 1.491(7)\text{ \AA}$ ; Table 1] and two water molecules attached Cu atoms [ $\text{Cu}-\text{O} = 2.159(4)\text{ \AA}$ ]. The bridging ligand is anionic, for charge balance. The two eight-membered rings in (I) are almost planar, with torsion angles of  $-3.0(6)$  and  $3.2(6)^\circ$  for  $\text{Cu1}-\text{O1}-\text{N1}-\text{O2}^{\text{i}}$  and  $\text{Cu1}-\text{O3}-\text{N3}-\text{O4}^{\text{i}}$ , respectively [symmetry code: (i)  $-x, 1-y, 1-z$ ]. These rings are nearly normal to one another, with an  $\text{N1}-\text{O1}-\text{Cu1}-\text{O3}$  torsion angle of  $88.4(4)^\circ$ . In (I), the  $\text{Cu1}\cdots\text{Cu1}^{\text{i}}$  separation is


**Figure 1**

An ORTEP-3 (Farrugia, 1997) plot of the title compound, with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. The unlabeled part of the molecule is related by the symmetry operation  $(-x, 1 - y, 1 - z)$ .

2.6156 (9) Å. Centrosymmetric molecules are linked by  $O_{\text{water}}-\text{H}\cdots O_{\text{nitroamine}}$  hydrogen bonds to form a three-dimensional network (see Table 2 and Fig. 2). The  $\text{NH}_2$  groups are not involved in hydrogen bonding.

## Experimental

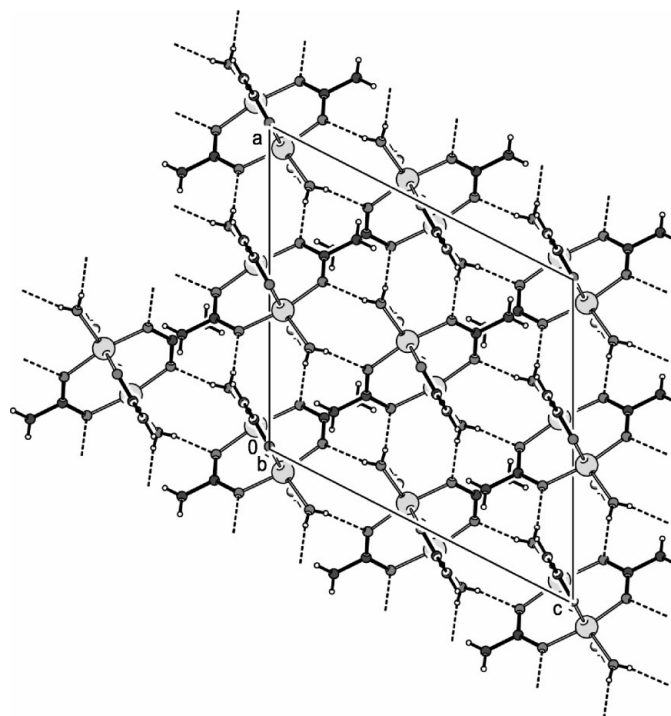
3-Benzyl-4-(4-chloromethylidenamino)-4,5-dihydro-1H,1,2,4-triazol-5-one (0.623 g, 2 mmol) was dissolved in absolute ethanol (50 ml) and  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  (0.344 g, 2 mmol) in 50 ml of absolute ethanol was added. After addition of 0.05 N NaOH solution in ethanol to raise the pH to 8.0–8.5, the mixture was stirred at 338 K for 30 min on a water bath. A green–blue complex precipitated very rapidly. The solid was filtered, washed with absolute ethanol and dried with diethyl ether. IR (KBr): 3387, 3055, 1651, 1574, 1472, 1421, 1293, 1114, 834, 731  $\text{cm}^{-1}$ . The  $\text{Cu}^{\text{II}}$  complex was soluble in hot glacial acetic acid and a green solution was obtained. A shiny green–blue crystalline complex was isolated after standing for two weeks at room temperature. The crystals were filtered and washed with ether. IR (KBr): 3489, 3387, 3285, 1625, 1472, 706, 731  $\text{cm}^{-1}$ .

### Crystal data

$[\text{Cu}_2(\text{H}_2\text{N}_2\text{O}_2)_4(\text{H}_2\text{O})_2]$	$D_x = 1.952 \text{ Mg m}^{-3}$
$M_r = 409.26$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2792 reflections
$a = 13.1677 (18) \text{ \AA}$	$\theta = 2.9\text{--}28.3^\circ$
$b = 8.5716 (12) \text{ \AA}$	$\mu = 3.12 \text{ mm}^{-1}$
$c = 13.8499 (19) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 117.024 (2)^\circ$	Slab, green–blue
$V = 1392.5 (3) \text{ \AA}^3$	$0.36 \times 0.28 \times 0.22 \text{ mm}$
$Z = 4$	

### Data collection

Siemens SMART CCD area-detector diffractometer	1624 independent reflections
$\omega$ scans	1391 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.030$
$T_{\text{min}} = 0.400$ , $T_{\text{max}} = 0.547$	$\theta_{\text{max}} = 28.3^\circ$
3874 measured reflections	$h = -17 \rightarrow 17$
	$k = -11 \rightarrow 11$
	$l = -14 \rightarrow 18$


**Figure 2**

A view of the crystal packing in the unit cell, with hydrogen bonds shown as dashed lines.

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.110$   
 $S = 1.29$   
 1624 reflections  
 100 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 5.3609P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.55 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.63 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0022 (5)

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O1	1.954 (4)	O2—N1 <sup>i</sup>	1.271 (6)
Cu1—O2	1.946 (4)	O3—N3	1.258 (5)
Cu1—O3	1.983 (3)	O4—N3 <sup>i</sup>	1.265 (5)
Cu1—O4	1.995 (3)	N1—N2	1.505 (7)
Cu1—O5	2.159 (4)	N3—N4	1.477 (6)
O1—N1	1.243 (6)		
O1—Cu1—O2	168.72 (17)	Cu1—O1—N1	125.0 (4)
O1—Cu1—O3	90.88 (15)	Cu1—O2—N1 <sup>i</sup>	120.8 (3)
O1—Cu1—O4	89.43 (15)	Cu1—O3—N3	121.8 (3)
O1—Cu1—O5	93.68 (17)	Cu1—O4—N3 <sup>i</sup>	125.5 (2)
O2—Cu1—O3	87.48 (15)	O2 <sup>i</sup> —N1—N2	116.0 (4)
O2—Cu1—O4	89.99 (15)	O1—N1—O2 <sup>i</sup>	125.4 (5)
O2—Cu1—O5	97.60 (16)	O1—N1—N2	118.6 (4)
O3—Cu1—O4	168.61 (12)	O3—N3—O4 <sup>i</sup>	123.8 (4)
O3—Cu1—O5	98.02 (14)	O4 <sup>i</sup> —N3—N4	117.4 (4)
O4—Cu1—O5	93.33 (14)	O3—N3—N4	118.8 (4)
O3—Cu1—O1—N1	88.4 (4)	Cu1—O1—N1—O2 <sup>i</sup>	−3.0 (6)
O5—Cu1—O1—N1	−173.5 (4)	Cu1—O2—N1 <sup>i</sup> —N2 <sup>i</sup>	177.9 (3)
O5—Cu1—O2—N1 <sup>i</sup>	175.8 (3)	Cu1—O3—N3—N4	−177.4 (3)
O5—Cu1—O3—N3	−176.4 (3)	Cu1—O3—N3—O4 <sup>i</sup>	3.2 (6)
O5—Cu1—O4—N3 <sup>i</sup>	172.0 (4)	Cu1—O4—N3 <sup>i</sup> —N4 <sup>i</sup>	−174.8 (3)
Cu1—O1—N1—N2	176.5 (3)		

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

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H50 $\cdots$ O3 <sup>ii</sup>	0.80 (7)	2.13 (7)	2.928 (5)	174 (6)
O5—H51 $\cdots$ O4 <sup>iii</sup>	0.72 (5)	2.12 (5)	2.828 (5)	167 (6)

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

All H atoms bonded to N atoms were placed in calculated positions, with N—H distances of 0.86 Å, and included in the refinement in the riding-model approximation, with  $U_{\text{iso}}$  values equal to  $1.2U_{\text{eq}}$  of the carrier atom. The H atoms of the water molecules were found in a difference Fourier map and refined independently, with isotropic displacement parameters.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; 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); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *WinGX* publication routines (Farrugia, 1999).

## References

- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Hughes, M. N. & Wimbledon, P. E. (1982). *Inorg. Chim. Acta*, **65**, 129–130.  
 Ju, X. H. & Xiao, H. M. (2002). *Chin. J. Chem.* **20**, 227–234.  
 Kahveci, B. & İkizler, A. A. (2000). *Turk. J. Chem.* **24**, 343–351.  
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.  
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Siemens (1996). *SMART* and *SAINT*. Versions 4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Stepanyan, T. G., Akopyan, M. E. & Kurtkryan, T. S. (2000). *Russ. J. Coord. Chem.* **26**, 425–428.