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Comment on $\mu_{1,3}$-azido-diazido-tetrakis(1,10-phenanthroline)-dicopper(II) azide tetrahydrate

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The supramolecular structure of the title dimeric azido complex of copper(II), $[Cu_2(\mu_{1,3}\text{-}N_3)(N_3)_2(phen)_4](N_3)\cdot 4H_2O$ (phen is 1,10-phenanthroline, $C_{12}H_8N_2$) [Cheng, Hu, Wang & Ye (2002). *Acta Cryst.* C**58**, m12–m13], which was originally described in terms of hydrogen-bonded chains, has been re-interpreted as two-dimensional hydrogen-bonded sheets built from $R_6^4(12)$ and $R_{10}^{10}(28)$ rings, taking into account the complete hydogen-bonding pattern.

Comment

In a recent paper, Cheng *et al.* (2002) reported a dimeric azido complex of copper(II), *viz.* $[Cu_2(\mu_{1,3}\text{-}N_3)(N_3)_2(phen)_4](N_3)\cdot 4H_2O$. Although the correct formula was given, the molecular unit was described as being comprised of a dimeric cation, two azide anions and four water molecules. However, re-examination of the structure using the deposited coordinates shows that the molecular unit possesses a dimeric cation along with only one azide anion and four water molecules. This is evident from the fact that both the central N2 and N11 atoms of the two azide ions lie on the special positions at $(0,0,\frac{1}{2})$ and (0,0,0), respectively.

The authors also showed that there were hydrogen-bonding and aromatic π–π interactions producing, respectively, a one-dimensional chain and a two-dimensional supramolecular array. However, re-examination using *PLATON* (Spek, 2001) clearly reveals further relatively strong hydrogen bonds that were overlooked in the original report, namely the O1*W*—H1*WA*···O2*W*$^{\rm i}$ and O2*W*—H2*WA*···N10$^{\rm i}$ hydrogen bonds [symmetry code: (i) $1-x$, $-y$, $-z$]. These intermolecular hydrogen bonds are involved in the formation of a two-dimensional sheet consisting of $R_6^4(12)$ and $R_{10}^{10}(28)$ rings (Fig. 1) (Etter, 1990; Bernstein *et al.*, 1995). The $R_6^4(12)$ rings adopt a chair conformation and if the weak O1*W*—H1*WA*···O2*W*$^{\rm i}$ component of the nearly planar three-centre hydrogen-bonding system is also considered, then this ring is itself divided into three smaller rings (Fig. 1), one of the $R_4^4(8)$ type and two of the $R_2^2(4)$ type.

Thus, the structure is now correctly described with a complete hydrogen-bonding pattern which dominates the overall structure and plays an important role in the crystal packing (Jeffrey, 1997).

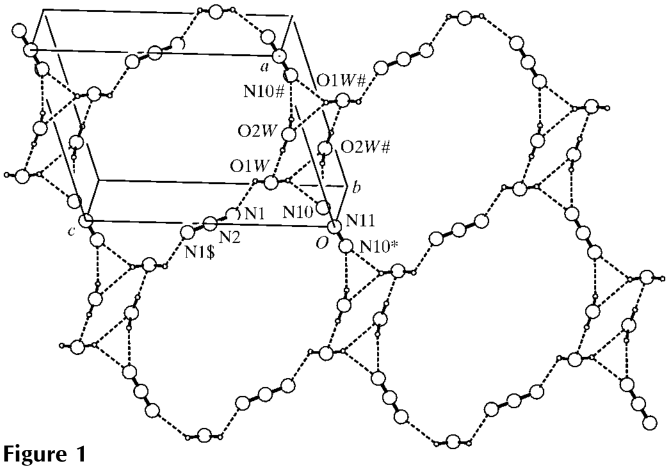

Figure 1
Part of the crystal structure depicting a two-dimensional sheet built from large and small hydrogen-bonded rings. Atoms labelled with an asterisk (*), hash (#) and dollar sign ($) are at the symmetry positions ($-x$, $-y$, $-z$), ($1-x$, $-y$, $-z$) and ($-x$, $-y$, $1-z$), respectively.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···N10	0.94	2.25	2.792 (7)	116
O1*W*—H1*WA*···O2*W*$^{\rm i}$	0.94	2.53	3.369 (6)	149
O1*W*—H1*WB*···N1	0.94	2.24	2.908 (6)	128
O2*W*—H2*WA*···N10$^{\rm i}$	0.94	2.33	3.245 (8)	163
O2*W*—H2*WB*···O1*W*	0.94	1.92	2.857 (6)	178

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

The author wishes to thank the referees for their helpful suggestions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1188). Services for accessing these data are described at the back of the journal.

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$\mu_{1,3}$-Azido-diazidotetrakis(1,10-phenanthroline)dicopper(II) azide tetrahydrate

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In the title compound, $[Cu_2(\mu\text{-}_{1,3}\text{-}N_3)(N_3)_2(phen)_4](N_3)\cdot 4H_2O$ (phen is 1,10-phenanthroline, $C_{12}H_8N_2$), each of the two Cu atoms is surrounded by two N atoms of two azide anions and by four N atoms of two 1,10-phenanthroline ligands [Cu—N distances are 1.964 (3), 2.009 (3), 2.018 (3), 2.054 (3), 2.306 (3) and 2.759 (4) Å], forming an elongated CuN_6 octahedron. An ideally linear $\mu_{1,3}$-azide anion bridges two Cu atoms to form a dimeric structure with the central N atom located on a centre of inversion. Moreover, the adjacent dimeric units are connected by hydrogen-bond interactions to produce one-dimensional chains. A two-dimensional supramolecular array is formed by π–π interactions between the aromatic rings of 1,10-phenanthroline ligands of adjacent dimeric units.

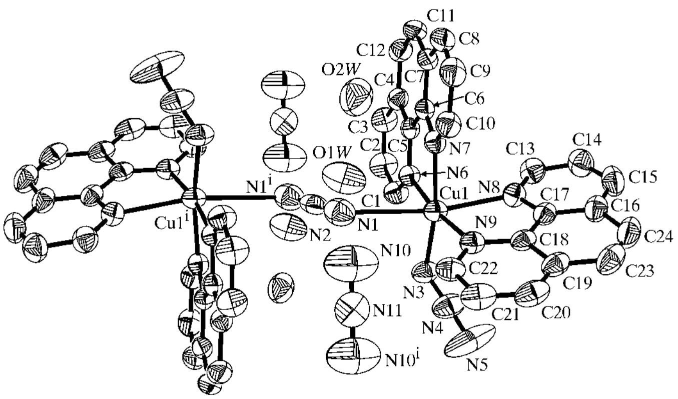
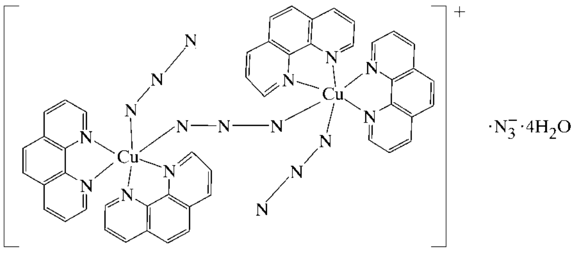


Figure 1
A view (Sheldrick, 1998) of the coordination environment in the title compound shown with 50% probability displacement ellipsoids. [Symmetry code: (i) $-x, -y, 1-z$.]

Comment

Studies on the synthesis and properties of bi- and polynuclear complexes bridged by the pseudohalide azide anion (N_3^-) have attracted much attention in recent years (Ribas *et al.*, 1999; Goher *et al.*, 1998; Zhang *et al.*, 2001) owing to their intriguing structural diversity, potential functions as models for metalloenzymes, and ferromagnetic or antiferromagnetic interactions (Baffert *et al.*, 2001; Aebersold *et al.*, 1998; Zhang *et al.*, 2000). The azide anion can bind to metal ions in a number of modes, *e.g.* as a terminal ligand *via* one nitrogen donor, as a bridge in the $\mu_{1,1}$ manner *via* one nitrogen donor, and in a $\mu_{1,3}$ manner *via* both of the peripheral donor N atoms (Sheppard *et al.*, 1996). Despite the fact that a substantial array of copper(II)–azido complexes have been synthesized (Goher & Mautner, 1999), to our knowledge, dimeric single-bridged compounds with 1,10-phenanthroline that have not been reported so far. We report here the preparation and crystal structure of a dimeric azido complex of copper(II), namely $[Cu_2(\mu_{1,3}\text{-}N_3)(N_3)_2(phen)_4](N_3)\cdot 4H_2O$, (I).



(I)

The molecular unit of the title compound comprises a dimeric $[Cu_2(phen)_4(\mu_{1,3}\text{-azido})(N_3)_2]^+$ cation, two azide anions and four water molecules. As shown in Fig. 1, the Cu atom is surrounded by two N atoms of two azide anions and by four N atoms of two 1,10-phenanthroline ligands, forming an elongated CuN_6 octahedron. The apical Cu1—N1 and Cu1—N8 bond lengths are much longer than the equatorial Cu—N bond lengths, due to the Jahn–Teller effects of Cu^{II}. An ideally linear $\mu_{1,3}$-azide anion bridges two Cu atoms to form a dimeric

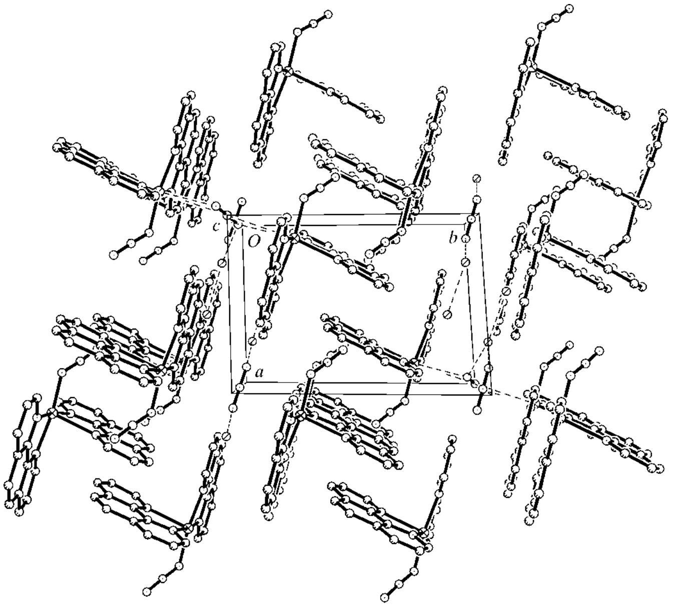


Figure 2
The crystal structure of the title compound.

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entity, with the central N atom located on a centre of inversion; the Cu$\cdots$Cu distance is 6.783 (4) Å.

It should be noted that hydrogen-bonding interactions and π–π interactions play an important role in the solid-state structure of (I), as shown in Fig. 2. Adjacent dimeric units are connected by hydrogen-bond interactions [O1*W*$\cdots$O2*W*, O1*W*$\cdots$N10, O1*W*$\cdots$N1 and C9$\cdots$N10($1-x, -y, -z$)], producing chains. It is interesting that there are interchain π–π interactions between the 1,10-phenanthroline rings of adjacent chains (face-to-face separation of *ca* 3.47 Å), which is different from other related compounds (Diaz *et al.*, 2001), resulting in an interesting two-dimensional structure.

Experimental

A mixture of copper(II) nitrate hexahydrate (1.0 mmol), 1,10-phenanthroline (2 mmol) and sodium azide (2 mmol) in 60 ml of a water and ethanol mixture (2:1 *v*:*v*) was stirred for 30 min at room temperature. After 4 d, dark-green crystals of the title compound were obtained in 85% yield.

Crystal data

$[Cu_2(N_3)_3(C_{12}H_8N_2)_4](N_3)\cdot 4H_2O$
$M_r = 1088.08$
Triclinic, $P\overline{1}$
$a = 8.676$ (5) Å
$b = 11.843$ (8) Å
$c = 12.279$ (8) Å
$\alpha = 80.81$ (1)°
$\beta = 71.74$ (1)°
$\gamma = 84.60$ (1)°
$V = 1181.4$ (13) Å^3

$Z = 1$
$D_x = 1.529$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 74 reflections
$\theta = 1.5$–24.3°
$\mu = 0.97$ mm^{-1}
$T = 293$ (2) K
Block, dark green
0.20 × 0.15 × 0.12 mm

Data collection

Bruker CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick 1996)
$T_{\min} = 0.858$, $T_{\max} = 0.890$
6191 measured reflections
4133 independent reflections

3239 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\max} = 25°$
$h = -9 \rightarrow 10$
$k = -14 \rightarrow 13$
$l = -14 \rightarrow 12$
50 standard frames at start and end of data collection

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.121$
$S = 1.03$
4133 reflections
337 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.7136P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}

All H atoms were constrained and all constrained C—H distances were 0.94 Å.

Data collection: *SMART*1000 (Bruker, 1998); cell refinement: *SMART*1000; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.964 (3)	Cu1—N7	2.054 (3)
Cu1—N6	2.009 (3)	Cu1—N8	2.306 (3)
Cu1—N9	2.018 (3)	Cu1—N1	2.759 (4)

N3—Cu1—N6	92.21 (12)	N7—Cu1—N8	85.46 (11)
N3—Cu1—N9	92.55 (12)	N3—Cu1—N1	89.61 (13)
N6—Cu1—N9	171.83 (11)	N6—Cu1—N1	84.32 (12)
N3—Cu1—N7	170.71 (12)	N9—Cu1—N1	102.36 (12)
N6—Cu1—N7	81.49 (11)	N7—Cu1—N1	83.02 (11)
N9—Cu1—N7	94.53 (11)	N8—Cu1—N1	168.45 (11)
N3—Cu1—N8	101.94 (13)	N2—N1—Cu1	112.5 (2)
N6—Cu1—N8	94.74 (11)	N4—N3—Cu1	123.4 (3)
N9—Cu1—N8	77.76 (11)		

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1*W*—H1*WA*$\cdots$N10	0.94	2.25	2.792 (6)	116
O1*W*—H1*WB*$\cdots$N1	0.94	2.24	2.908 (5)	128
O2*W*—H2*WB*$\cdots$O1*W*	0.94	1.92	2.857 (5)	178
C9—H9*A*$\cdots$N10$^{\rm i}$	0.94	2.50	3.411 (7)	163

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1175). Services for accessing these data are described at the back of the journal.

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