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Acta Cryst. (2006). E**62**, m1958–m1960 Gernon *et al.* · $[Cu_2Cl_2(C_4H_{13}N_3)_2(H_2O)]Cl_2$

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Aquadi-μ-chloro-bis(diethylenetriamine)dicopper(II) dichloride: a redetermination at 180 K

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The structure of the title compound, $[Cu_2Cl_2(C_4H_{13}N_3)_2(H_2O)]Cl_2$, at 180 K is described in space group $P2_1/n$ with a unit-cell volume twice that reported previously for the structure at 293 K [Willett (2001). *Acta Cryst.* E**57**, m605–m606]. In the smaller unit cell, in space group $P2_1/m$, the complex has imposed mirror symmetry and unusually elongated displacement ellipsoids. At 180 K, refinement in the larger unit cell with no imposed symmetry resolves this issue. With room-temperature data collected from the same crystal, however, refinement using the larger unit cell gives no significant improvement, and the previously reported structure is considered to be most appropriate.

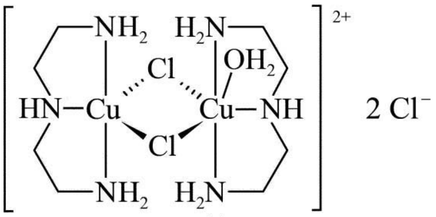
Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.002 Å
R factor = 0.020
wR factor = 0.054
Data-to-parameter ratio = 20.4

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

Comment

The crystal structure of the title compound, (I), at 293 K has been reported previously (Willett, 2001). The structure was described in space group $P2_1/m$, with unit-cell parameters a = 6.7155 (8), b = 14.6106 (11) and c = 10.3011 (8) Å, and β = 95.333 (10)°. In this description, the dinuclear cation exhibits crystallographic mirror symmetry, with the mirror plane passing through all four atoms of the central Cu_2Cl_2 unit, the central N atom of each diethylenetriamine ligand and the water molecule bound to one of the Cu^{II} ions. Crystals of the title compound were obtained inadvertently as a by-product of an intended synthesis, and examined at 180 K. At the lower temperature, the structure is best described in space group $P2_1/n$ with a unit-cell volume twice that of Willett's description. The $P2_1/n$ and $P2_1/m$ descriptions are clearly related: transformation of Willett's unit cell by the matrix [1 0 1 / 0 −1 0 / 1 0 −1] yields the unit cell a = 11.762, b = 14.611 and c = 12.809 Å, and β = 113.89°. In the larger unit cell, the complex exhibits no crystallographic symmetry (Fig. 1).



(I)

In the structure reported by Willett, the diethylenetriamine ligand bound to the five-coordinate Cu^{II} ion displays significantly elongated displacement ellipsoids, while the ligand bound to the six-coordinate Cu^{II} ion appears more usual. Willett noted that this may be 'indicative of unresolved disorder'. The observation can be accounted for by consid-

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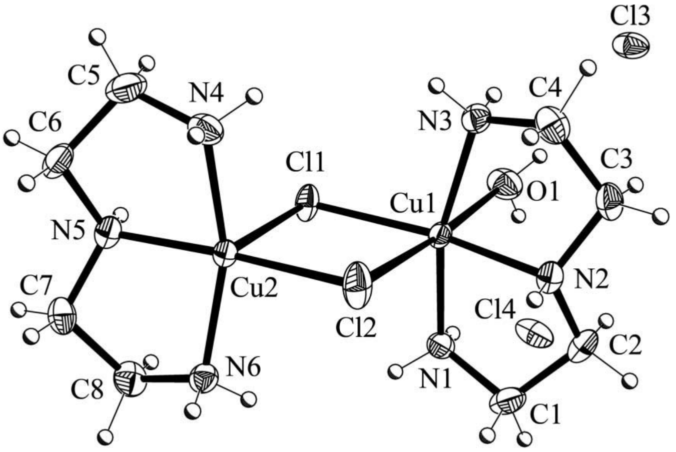

Figure 1
The asymmetric unit of (I) in the larger unit cell (space group $P2_1/n$) at 180 K, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

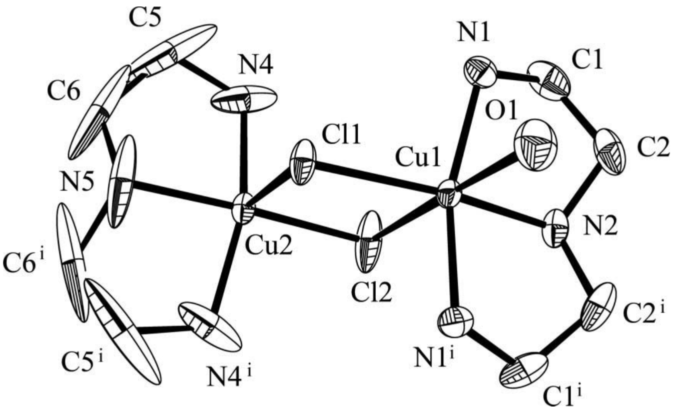

Figure 2
The cationic complex in (I) refined in the smaller unit cell (space group $P2_1/m$) at 180 K, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted. The grossly distorted displacement parameters are a result of site averaging imposed by false mirror symmetry. [Symmetry code (i): $x, \frac{1}{2} - y, z$].

ering the $P2_1/n$ structure. The coordination environment of each Cu^{II} ion exhibits a local mirror plane: for Cu1, this plane passes through atoms Cu1, N2, O1 and Cl1, while for Cu2, the plane passes through atoms Cu2, Cl2, Cl1 and N5. These two planes are not coincident, forming a dihedral angle of 6.4 (1)°. If the $P2_1/n$ structure is transformed into the smaller unit cell (transformation matrix $[\frac{1}{2}\,0\,\frac{1}{2}\,/\,0\,-1\,0\,/\,\frac{1}{2}\,0\,-\frac{1}{2}]$) and described in space group $P2_1/m$, the mirror plane through atoms Cu1, N2, O1 and Cl1 becomes crystallographic, but the local mirror plane through atoms Cu2, Cl2, Cl1 and N5 does not coincide with this plane. As a result, application of the crystallographic mirror symmetry produces two closely spaced atomic positions for each of the atoms of the diethylenetriamine ligand bound to Cu2. In the $P2_1/m$ description, each such pair is averaged into a single atomic position with an elongated displacement ellipsoid. For the 180 K data, refined using the smaller unit cell, this elongation is dramatic and clearly unacceptable (Fig. 2).

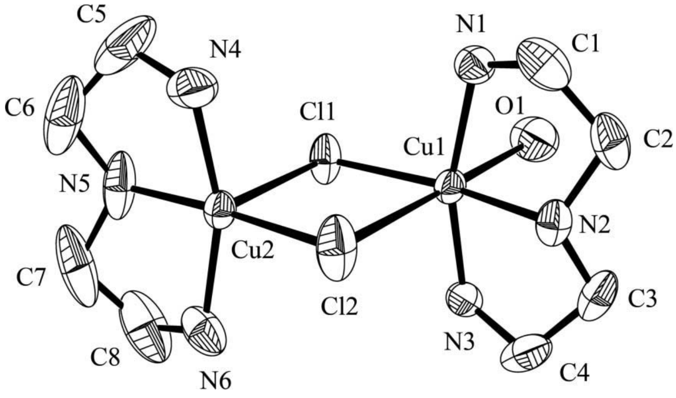

Figure 3
The cationic complex in (I) refined in the larger unit cell (space group $P2_1/n$) at 293 K, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted.

In order to assess whether Willett's structure represents a fair description at 293 K, data were re-collected from the same crystal at room temperature. When described by the larger unit cell, reflections (hkl) with $h+l$ odd become systematically weak, indicating pseudo-B-centring. If this centring were genuine, the unit cell should be transformed to the smaller description in $P2_1/m$. Of 39 277 such reflections measured, 3653 were observed at the $3\sigma(I)$ level, although the mean $I/\sigma(I)$ for all these reflections is only 1.1. Refinement in the larger unit cell produces a structure in which the local mirror planes through each Cu^{II} ion are much closer to coincidence [dihedral angle 1.5 (1)°], and the bond lengths of the complex related by the pseudo-mirror plane do not differ significantly. In addition, the displacement ellipsoids of the diethylenetriamine ligand bound to Cu2 become elongated (Fig. 3). Although the elongation is less dramatic than that reported by Willett, the shapes of the displacement ellipsoids are closely comparable for the same data set refined using either description of the structure. Under these circumstances, no significant improvement is achieved by refinement in the larger unit cell, and Willett's structure should therefore be considered more appropriate at 293 K.

Experimental

Crystals of (I) were obtained as a decomposition product from the reaction of a bis[(methylamide)ethyl]amino-substituted *tert*-butylcalix[4]arene with copper(II) chloride in a 1:1 ratio in refluxing methanol. The compound can be prepared directly by the procedure reported previously (Willett, 2001).

Crystal data

$[Cu_2Cl_2(C_4H_{13}N_3)_2(H_2O)]Cl_2$
$M_r = 493.24$
Monoclinic, $P2_1/n$
$a = 11.6882$ (5) Å
$b = 14.5158$ (6) Å
$c = 12.7477$ (6) Å
$\beta = 114.124$ (1)°
$V = 1973.93$ (15) Å^3

$Z = 4$
$D_x = 1.660$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.70$ mm^{-1}
$T = 180$ (2) K
Block, blue
0.30 × 0.20 × 0.15 mm

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Data collection

Bruker Nonius X8 APEXII CCD area-detector diffractometer
Thin–slice ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\rm min} = 0.483$, $T_{\rm max} = 0.691$
46464 measured reflections
4892 independent reflections
4308 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.054$
$S = 1.10$
4892 reflections
240 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.4572P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.82$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—Cl1	2.2813 (3)	Cu2—Cl1	2.6495 (4)
Cu1—Cl2	3.0330 (4)	Cu2—Cl2	2.2792 (4)
Cu1—N1	2.0009 (11)	Cu2—N4	1.9938 (11)
Cu1—N2	2.0037 (11)	Cu2—N5	2.0139 (11)
Cu1—N3	2.0001 (11)	Cu2—N6	2.0000 (11)
Cu1—O1	2.5740 (12)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$Cl3	0.76 (2)	2.42 (2)	3.1451 (12)	163 (2)
O1—H2$\cdots$Cl4	0.75 (2)	2.39 (2)	3.1229 (11)	163 (2)
N1—H11$\cdots$Cl4	0.86 (1)	2.53 (1)	3.3252 (12)	155 (1)
N1—H12$\cdots$Cl4$^{\rm i}$	0.86 (1)	2.49 (1)	3.3045 (11)	159 (2)
N2—H21$\cdots$Cl1$^{\rm ii}$	0.84 (1)	2.54 (1)	3.2448 (12)	143 (2)
N3—H31$\cdots$Cl3	0.86 (1)	2.79 (1)	3.5294 (12)	145 (1)
N3—H32$\cdots$Cl3$^{\rm iii}$	0.85 (1)	2.45 (1)	3.2666 (11)	162 (2)
N4—H42$\cdots$Cl3$^{\rm iii}$	0.86 (1)	2.55 (1)	3.3721 (12)	160 (2)
N4—H41$\cdots$Cl4$^{\rm iv}$	0.85 (1)	2.48 (1)	3.2901 (12)	160 (1)
N5—H51$\cdots$Cl2$^{\rm v}$	0.84 (1)	2.49 (1)	3.2882 (11)	160 (2)
N6—H61$\cdots$Cl3$^{\rm iv}$	0.85 (1)	2.48 (1)	3.2707 (12)	156 (1)
N6—H62$\cdots$Cl4$^{\rm i}$	0.86 (1)	2.55 (1)	3.3063 (11)	147 (1)

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

H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C—H = 0.99 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). H atoms bound to N and O atoms were located in difference Fourier maps and refined with isotropic displacement parameters. The two O—H distances were restrained to a common value and the H$\cdots$H distance was restrained to 1.58 times that value. All N—H distances were restrained to a common value and the H$\cdots$H distance (where appropriate) was restrained to 1.63 times that value. The refined parameters were 0.75 (2) and 0.85 (1) Å for O—H and N—H, respectively.

Data collection: *APEX2* (Bruker Nonius, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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