Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Di-μ-hydroxo-bis({bis[2-(2-pyridyl)-ethyl]amine-κ^3N}copper(II)) dichloride hexahydrate

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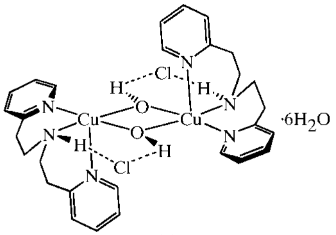
Received 31 October 2003
Accepted 11 November 2003
Online 6 December 2003

The title compound, $[Cu_2(OH)_2(C_{14}H_{17}N_3)_2]Cl_2{\cdot}6H_2O$, is a crystallographically centrosymmetric dimer of square-pyramidal Cu^{II} centres, with a basal–basal $[Cu_2(\mu\text{-}OH)_2]^{2+}$ bridging motif and apical pyridyl donors. The Cl^- anion is hydrogen bonded to one O—H and one N—H group, and to three different water molecules. Because of disorder, the network of intramolecular hydrogen bonding in the hydrated lattice is only partly resolved.

Comment

We have recently reported an investigation of the coordination chemistry of bis[2-(2-pyridyl)ethyl]hydroxylamine and its conversion to bis[2-(2-pyridyl)ethyl]amine (bpea; Leaver *et al.*, 2003). During the course of this work, we also crystallized the title compound, (I). Three other crystal structures are available of salts of related $[Cu_2(\mu\text{-}OH)_2(L)_2]^{2+}$ complexes, where *L* is an *N*-alkylated bpea derivative (Karlin *et al.*, 1984, 1990; Obias *et al.*, 1998). One of these, however, has an unusual basal–apical pattern of $[Cu_2(\mu\text{-}OH)_2]$ bridging (Karlin *et al.*, 1984), which is not structurally comparable with that in (I).



(I)

The asymmetric unit of (I) contains half a formula unit, with the crystallographic inversion centre $(1 - x, 1 - y, -z)$ lying at the centre of the $[Cu_2(\mu\text{-}OH)_2]^{2+}$ moiety. The five-coordinate Cu centre shows only small deviations from an ideal square-pyramidal geometry, with two basal OH^- ligands and a bpea pyridyl donor at the apical site. The τ value calculated from the bond angles at Cu1 is 0.039 (2), which is very close to the ideal value of 0 for a square pyramid (Addison *et al.*, 1984). The $[Cu_2(\mu\text{-}OH)_2]^{2+}$ unit forms a near-perfect diamond shape, with the two unique distances Cu1—O2 and Cu1—O2^{i} being identical within 3 s.u. [symmetry code: (i) $1 - x, 1 - y, -z$]. The Cu1—O2—Cu1^{i} angle and Cu1$\cdots$Cu1^{i} distance are similar to those shown by the other two known $[Cu_2(\mu\text{-}OH)_2(L^R)_2]^{2+}$ complexes with basal–basal $[Cu_2(\mu\text{-}OH)_2]$ bridging, which lie in the ranges 98.4 (3)–100.9 (1)° and 3.012 (1)–3.119 (1) Å, respectively (Karlin *et al.*, 1990; Obias *et al.*, 1998). The Cl^- anion Cl20 is hydrogen bonded to the bpea N—H function and to the hydroxide O—H group. Atom Cl20 also accepts hydrogen bonds from three different water molecules (Table 2), yielding a distorted square-pyramidal coordination geometry at this atom [the τ value calculated from the H$\cdots$Cl20$\cdots$H angles is 0.26 (2)].

There are three unique water molecules in the lattice of (I). One of these, O22, is crystallographically ordered and forms hydrogen bonds to two different Cl^- anions. Another, water molecule O21, also has an ordered O atom. However, only one H atom attached to water molecule O21 could be located in the difference map and this also hydrogen bonds to atom Cl20. The second H atom is probably involved in a hydrogen bond to water molecule O21^{iii} [Table 3; symmetry code: (iii) $x, 1 - y, 1 - z$]. In that case, the putative atom H21*B* must be disordered over at least two sites, being 50% occupied at a position lying near the O21$\cdots$O21^{iii} vector. This would explain our inability to locate this H atom. Finally, the third water molecule is disordered over three orientations, labelled O23*A*–O23*C*. Although the positions of the H atoms bonded to these

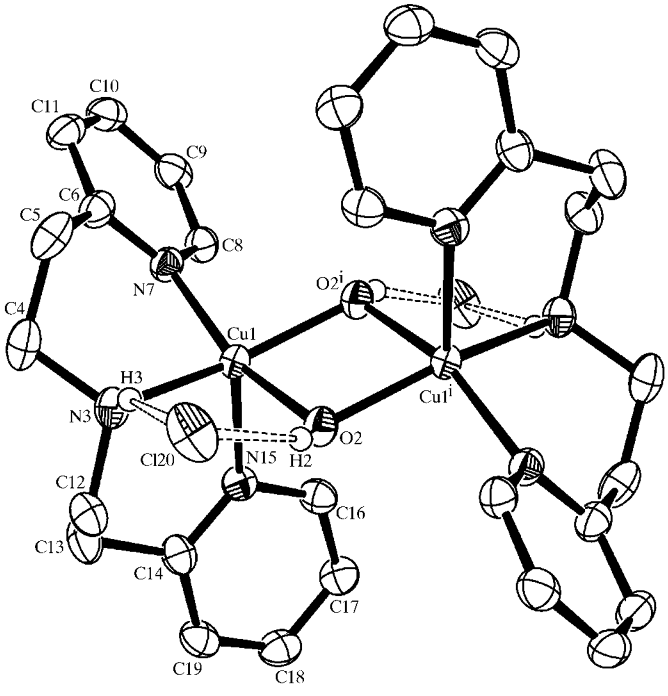


Figure 1
The molecular structure of the $[Cu_2(\mu\text{-}OH)_2(bpea)_2]Cl_2$ moiety in (I), drawn with 50% probability displacement ellipsoids, showing the atom-numbering scheme employed. All C-bound H atoms have been omitted for clarity. [Symmetry code: (i) $1 - x, 1 - y, -z$.]

DOI: 10.1107/S0108270103026064

partial O atoms could not be located, atoms O23*A*–O23*C* have several potential hydrogen-bonding partners lying 2.65–3.10 Å away (Table 3). There are also some short intermolecular distances, *viz.* O23*A*···O23*A*^{iv} [2.592 (12) Å], O23*A*···O23*C*^{iv} [2.511 (12) Å] and O23*C*···O23*C*^{iv} [2.60 (2) Å], which are substantially closer than the sum of the van der Waals radii of two O atoms (2.8 Å; Pauling, 1960) [symmetry code: (iv) $2 - x, -y, 1 - z$]. This implies that when the O23*A* or O23*C* sites are occupied, only site O23*B*^{iv} can be occupied in the neighbouring disordered region, but, when site O23*B* is occupied, any one of O23*A*^{iv}, O23*B*^{iv} or O23*C*^{iv} can be present. However, the fractional occupancies for O21*A*:O21*B*:O21*C* predicted by this simple model (0.20:0.60:0.20) do not match those observed (0.40:0.35:0.25). Thus, there must be additional geometric or steric factors controlling the disorder of this water molecule, which cannot be elucidated in the absence of the partial H-atom positions attached to O21 and O23*A*–O23*C*. There are no other noteworthy intermolecular interactions in the crystal lattice.

Experimental

Addition of bpea·0.5H_2O (0.23 g, 1.0 mmol) (Leaver *et al.*, 2003) to a solution of $CuCl_2\cdot 2H_2O$ (0.18 g, 1.0 mmol) in MeOH (30 ml) afforded a deep-blue solution. Slow evaporation of this solution gave dark-blue plates of (I) that were filtered off, washed with water and dried *in vacuo* (yield 0.25g, 73%). The dried material contains a reduced water content compared with the freshly prepared single crystals, analysis showing it to be the monohydrate of the complex. Analysis found: C 47.6, H 5.6, N 11.2%; calculated for $C_{28}H_{36}Cl_2Cu_2N_6O_2\cdot H_2O$: C 47.7, H 5.4, N 11.9%.

Crystal data

$[Cu_2(OH)_2(C_{14}H_{17}N_3)_2]Cl_2\cdot 6H_2O$
M_r = 794.70
Triclinic, $P\bar{1}$
a = 9.2875 (2) Å
b = 9.9802 (2) Å
c = 10.9261 (2) Å
α = 63.4321 (8)°
β = 82.2565 (7)°
γ = 77.9460 (8)°
V = 884.85 (3) Å^3

Z = 1
D_x = 1.491 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 493 reflections
θ = 2.9–27.5°
μ = 1.41 mm^{-1}
T = 150 (2) K
Plate, dark blue
0.36 × 0.21 × 0.07 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.631, T_{max} = 0.908
17 493 measured reflections

4033 independent reflections
3781 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 27.5°
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.088
S = 1.06
4033 reflections
228 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.5339P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.9528 (13)	Cu1—N7	2.0175 (16)
Cu1—O2^i	1.9527 (14)	Cu1—N15	2.2646 (16)
Cu1—N3	2.0298 (16)	Cu1—Cu1^i	3.0194 (4)
O2^i—Cu1—O2	78.73 (6)	O2^i—Cu1—N15	101.78 (6)
O2^i—Cu1—N7	91.06 (6)	O2—Cu1—N15	93.65 (6)
O2—Cu1—N7	162.93 (6)	N7—Cu1—N15	101.88 (6)
O2^i—Cu1—N3	160.57 (7)	N3—Cu1—N15	95.24 (6)
O2—Cu1—N3	91.00 (6)	Cu1^i—O2—Cu1	101.27 (6)
N7—Cu1—N3	94.57 (7)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···Cl20	0.75 (2)	2.51 (2)	3.2379 (15)	162 (3)
N3—H3···Cl20	0.77 (3)	2.57 (3)	3.3132 (18)	162 (3)
O21—H21*A*···Cl20	0.73 (2)	2.48 (2)	3.190 (2)	166 (3)
O22—H22*A*···Cl20^{ii}	0.80 (2)	2.45 (2)	3.241 (2)	175 (3)
O22—H22*B*···Cl20	0.81 (2)	2.40 (2)	3.206 (2)	176 (3)

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

Table 3
Intermolecular O···O distances (Å) in the range 2.65–3.10 Å in the structure of (I) that could correspond to O—H···O hydrogen bonds involving unlocated H atoms.

O21···O21^{iii}	2.831 (4)	O23*B*···O22	2.706 (9)
O23*A*···O21^v	2.869 (6)	O23*C*···O22	2.766 (11)
O23*B*···O21^v	2.663 (9)	O23*A*···O23*B*^{iv}	2.862 (10)
O23*C*···O21^v	2.881 (11)	O23*B*···O23*C*^{iv}	2.928 (15)
O23*A*···O22	2.803 (6)		

Symmetry codes: (iii) $x, 1 - y, 1 - z$; (iv) $2 - x, -y, 1 - z$; (v) $1 + x, y, z$.

The asymmetric unit of (I) contains half a dimeric complex dication lying across a crystallographic inversion centre, one Cl^- anion, two wholly occupied water molecules (O21 and O22), and a disordered region comprising three O atoms (O23*A*–O23*C*) with refined occupancies of 0.40 (O23*A*), 0.35 (O23*B*) and 0.25 (O23*C*). All non-H atoms, except for the three disordered O atoms, were refined anisotropically. All C-bound H atoms were placed in calculated positions and refined using a riding model. The fixed C—H distances were C—H(aryl) = 0.95 Å and C—H(alkyl) = 0.99 Å, with all U_{iso}(H) = 1.2U_{eq}(C). The H atoms bound to atoms O2, N3 and O22, and one of the H atoms bound to O21 (see *Comment*) were located in a difference map and allowed to refine freely with a common displacement parameter, and (for atoms H2, H21*A*, H22*A* and H22*B*) subject to a restrained O—H distance of 0.77 (2) Å; no N3—H3 restraint was applied. H atoms associated with the disordered atoms O23*A*–O23*C* were not located.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

The authors acknowledge the Royal Society of London for University Research Fellowships to MAH, the EPSRC and the University of Leeds.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1551). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Karlin, K. D., Gan, Q.-F., Farooq, A., Liu, S. & Zubieta, J. (1990). *Inorg. Chem.* **29**, 2549–2551.

Karlin, K. D., Gultneh, Y., Hayes, J. C. & Zubieta, J. (1984). *Inorg. Chem.* **23**, 519–521.

Leaver, S. A., Palaniandavar, M., Kilner, C. A. & Halcrow, M. A. (2003). *J. Chem. Soc. Dalton Trans.* pp. 4224–4225.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Obias, H. V., Lin, Y., Murthy, N. N., Pidcock, E., Solomon, E. I., Ralle, M., Blackburn, N. J., Neuhold, Y.-M., Zuberbühler, A. D. & Karlin, K. D. (1998). *J. Am. Chem. Soc.* **120**, 12960–12961.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed, pp. 257–264. Ithaca: Cornell University Press.

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