N3—H2N3···N1	0.88 (3)	2.29 (3)	2.656 (3)	105 (2)
N3—H1N3···S2^{i}	0.88 (3)	2.64 (3)	3.512 (2)	175 (2)
N5—H1N5···S1^{i}	0.82 (3)	2.86 (3)	3.656 (2)	163 (2)
N3—H3N3···N1^{ii}	0.88 (3)	2.43 (2)	3.128 (2)	137 (2)
N6—H2N6···O1*W*^{iii}	0.81 (3)	2.35 (3)	2.962 (3)	133 (3)

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

All H atoms were refined isotropically; the C—H distances are in the range 0.84 (5)–1.00 (3) Å.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1259). Services for accessing these data are described at the back of the journal.

References

Fun, H.-K., Sivakumar, K., Yip, B.-C., Tian, Y.-P., Duan, C.-Y., Lu, Z.-L. & You, X.-Z. (1995). *Acta Cryst.* C51, 2080–2083.

Garg, B. S. & Kapur, L. (1990). *Inorg. Chim. Acta*, **173**, 223–227.

Haaland, A. & Sikson, J. E. (1968). *Chem. Commun.* pp. 88–89.

Houlton, A., Dilworth, J. R., Roberts, R. G. M. & Silver, J. (1990). *Polyhedron*, **9**, 2751–2757.

Houlton, A., Jasim, N., Roberts, R. G. M., Silver, J., Cunningham, D., McArdle, P. & Higgins, T. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2235–2242.

Ismail, K. Z. (1997). *Transition Met. Chem.* **22**, 565–569.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Neuse, E. W., Meirim, M. G. & Blom, N. F. (1988). *Organometallics*, **7**, 2562–2566.

Osborne, A. G., da Siva, M. W., Hursthouse, M. B., Malik, K. M. A., Opromolla, G. & Zanello, P. (1996). *J. Organomet. Chem.* **516**, 167–176.

Palenik, J. (1970). *Inorg. Chem.* **9**, 2424–2430.

Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL. Structure Determination Programs.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Tian, Y. P., Duan, C. Y., Lu, Z. L., You, X. Z., Luo, B. S. & Chen, L. R. (1996). *Chin. J. Struct. Chem.* **15**, 307–310.

Tian, Y. P., Duan, C. Y., You, X. Z., Mak, T. C. W., Luo, Q. & Zhou, J. Y. (1998). *Transition Met. Chem.* **23**, 17–23.

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Di-μ-azido-bis{[2-(2-aminoethyl)pyridine-*N*,*N*′]aquacopper(II)} diperchlorate

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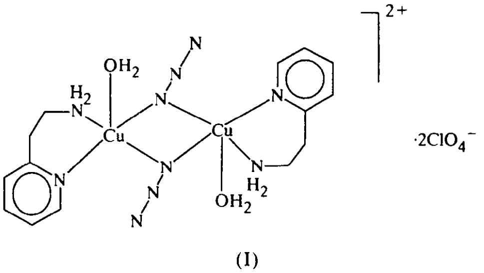
Abstract

In the title compound, $[Cu_2(N_3)_2(C_7H_{10}N_2)_2(H_2O)_2](ClO_4)_2$, the Cu atom is in a distorted square-pyramidal environment with the basal positions occupied by four N atoms, two from a bidentate 2-(2-aminoethyl)pyridine ligand and another two from a centrosymmetrically related azide bridge. The water molecule occupies the axial position. In the crystal, the molecules are in a stacked arrangement and form layers connected by hydrogen bonds involving water molecules and perchlorate ions.

Comment

Copper(II) complexes bridged by azide ligands are of interest because of their bonding mode and magnetic interactions, and also because they exhibit a rich variety of stereochemistries (Kahn, 1993; Hathaway, 1981, 1982). In this paper, we report the synthesis and structure of di-μ-azido-bis{[2-(2-aminoethyl)pyridine-*N*,*N*′]aquacopper(II)} diperchlorate, (I).



(I)

The asymmetric unit consists of one half of the $[Cu(C_7H_{10}N_2)(H_2O)(N_3)]_2^{2+}$ cation and a perchlorate anion. The other half of the cation is generated by a crystallographic inversion centre. The coordination around the Cu atom is a distorted square pyramid, with

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the basal plane occupied by N atoms. Two of the N atoms, N1 and N2, are from a bidentate 2-(2-aminoethyl)pyridine ligand, while the other two, N3 and N3*A*, are from a centrosymmetrically related azide bridge. The Cu—N bond lengths agree with reported values (Orpen *et al.*, 1989). The Cu atom deviates from the basal plane by 0.0886 (3) Å. The axial position is occupied by the water molecule, with a Cu—O1*W* distance of 2.442 (2) Å. This distance is comparable with another reported value (Shanmuga Sundara Raj *et al.*, 1999).

The Cu···Cu distance [3.1120 (4) Å] is comparable to that found in a previous report (Söderquist, 1968). The Cu—N—Cu angle [101.42 (8)°] is in the range observed in the bis(end-on μ-azido)complexes (Escuer *et al.*, 1997). The end-on azido bridge is almost linear, with an N3—N4—N5 bond angle of 178.6 (3)°. The other Cu···N short contacts observed in the structure are Cu1···N4 2.837 (2) Å and Cu1···N4($-x$, $1-y$, $-z$) 2.855 (2) Å. The N3—N4 and N4—N5 bond lengths are 1.237 (3) and 1.149 (3) Å, respectively, with the longer distance involving the N atom linked to the Cu atom.

The water molecule forms two hydrogen bonds, one (O—H···O) intramolecular and one (O—H···O) intermolecular, while the N2 atom forms an N—H···O hydrogen bond (Table 2). The molecules are stacked together with a distance of 3.695 Å between the centroids of the pyridine rings. The stacking arrangement forms layers which are connected by O—H···O and N—H···O hydrogen bonds involving water molecules and perchlorate anions.

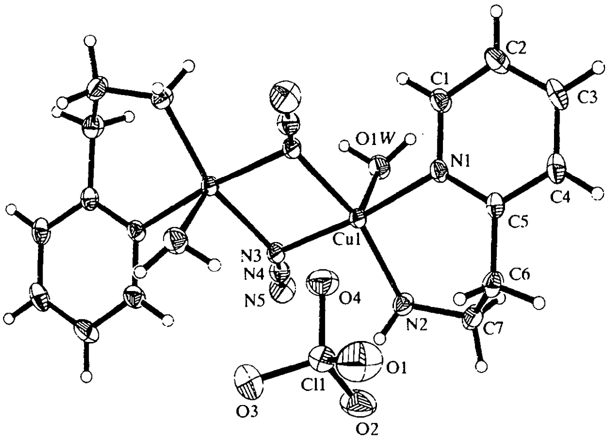

Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

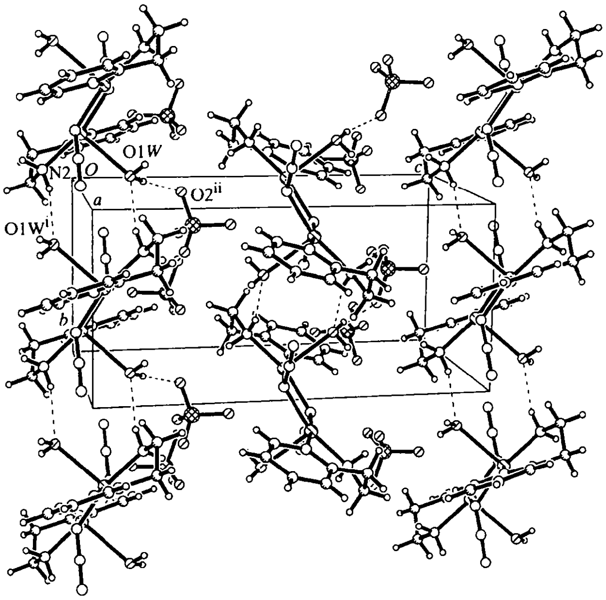

Fig. 2. A part of the layers formed by the stacking arrangement.

Experimental

$Cu(ClO_4)_2 \cdot 6H_2O$ (370 mg, 1 mmol) in water (30 ml) was added to 2-(2-aminoethyl)pyridine (112.2 mg, 1 mmol) while stirring at room temperature. Upon slow addition of NaN_3 (65 mg, 1 mmol) dissolved in a minimum quantity of water, a dark-blue mixture was formed and then stirred for about 30 min. Well formed dark-blue crystals of the title compound were obtained by allowing the filtrate of the final mixture to stand for several weeks.

Crystal data

$[Cu_2(N_3)_2(C_7H_{10}N_2)_2(H_2O)_2](ClO_4)_2$
$M_r = 690.41$
Monoclinic
$P2_1/c$
$a = 10.7817$ (3) Å
$b = 7.4435$ (2) Å
$c = 15.9041$ (4) Å
$\beta = 95.405$ (1)°
$V = 1270.69$ (6) Å^3
$Z = 2$
$D_x = 1.804$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6450 reflections
$\theta = 3.02$–33.17°
$\mu = 1.954$ mm^{-1}
$T = 293$ (2) K
Slab
0.48 × 0.28 × 0.15 mm
Dark blue

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.454$, $T_{max} = 0.758$
7931 measured reflections
2909 independent reflections

2537 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.082$
$S = 1.10$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: none

2909 reflections
180 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.8385P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N2	1.9880 (19)	Cu1—N3	2.0258 (17)
Cu1—N3^i	1.9951 (19)	Cu1—O1*W*	2.442 (2)
Cu1—N1	2.0130 (17)		
N2—Cu1—N3^i	163.07 (8)	N2—Cu1—N3	90.76 (8)
N2—Cu1—N1	95.52 (8)	N3^i—Cu1—N3	78.58 (8)
N3^i—Cu1—N1	95.72 (7)	N1—Cu1—N3	173.44 (7)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O4^i	0.90 (3)	2.13 (3)	2.980 (3)	158 (3)
N2—H2*C*···O1*W*^{ii}	0.90	2.25	3.132 (3)	164
O1*W*—H2*W*···O2^{iii}	0.90 (3)	2.05 (3)	2.930 (3)	167 (3)

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

After checking their presence in the difference map, the H atoms were fixed geometrically and allowed to ride on the atoms to which they were attached, except for the H atoms of the water molecules, which were located from a difference Fourier map and refined isotropically.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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References

Escuer, A., Vicente, R., Mautner, F. A. & Goher, M. A. S. (1997). *Inorg. Chem.* **36**, 1233–1236.
Hathaway, B. J. (1981). *Coord. Chem. Rev.* **35**, 211–252.
Hathaway, B. J. (1982). *Coord. Chem. Rev.* **41**, 423–487.
Kahn, O. (1993). In *Molecular Magnetism*. New York: VCH Publishers Inc.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.
Shanmuga Sundara Raj, S., Velmurugan, D., Gunasekaran, K., Fun, H. K., Manonmani, J. & Kandaswamy, M. (1999). *Acta Cryst.* C**55**, 1222–1224.
Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL. Structure Determination Software Programs.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Söderquist, R. (1968). *Acta Cryst.* B**24**, 450–455.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Acta Cryst. (1999). C**55**, 1766–1769

(1*R*,2*R*)-(−)-[Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]chloromanganese(III), an (*R*,*R*)-Jacobsen catalyst

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Abstract

In the title compound, (−)-chloro{(1*R*,2*R*)-4,4′,6,6′-tetra-*tert*-butyl-2,2′-[cyclohexane-1,2-diylbis(nitrilomethylidyne)]diphenolato}manganese(III), $[MnCl(C_{36}H_{52}N_2O_2)]$, the Mn atom is pentacoordinated in a distorted square-pyramidal environment. Two independent molecules have similar bent structures, with dihedral angles between the two planar salicylideneimine moieties of 20.5 (1) and 27.7 (1)°.

Comment

Optically pure amino alcohols are pharmaceutically important and can be produced efficiently from the corresponding chiral epoxides by acid- or base-catalysed epoxide ring-opening reactions. Cationic metal complexes of the salen ligand *N*,*N*′-ethylenebis(salicylideneaminate) are effective catalysts for the epoxidation of various olefins, and their catalytic activities can be modulated by substituents on the ligands (Srinivasan *et al.*, 1986). In particular, Jacobsen's catalyst, (I), a manganese(III) complex of a chiral salen ligand, catalyses highly enantioselective epoxidation of unfunctionalized olefins (Chang *et al.*, 1994). The crystal structures of several salen–metal complexes have been reported (Pahor *et al.*, 1976; Srinivasan *et al.*, 1986; Oki & Hodgson, 1990), but reports of chiral salen ligands and their metal complexes are rare. Pospisil *et al.* (1996) reported the crystal structures of (I) and its analogue containing triisopropylsiloxyl groups instead of *tert*-butyl groups at