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A redetermination of *cis*-aquabis(glycinato-$\kappa^2 N,O$)copper(II)

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.006 Å
R factor = 0.046
wR factor = 0.097
Data-to-parameter ratio = 17.2

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

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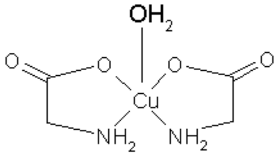
The crystal structure of the title compound, $[Cu(C_2H_4NO_2)_2(H_2O)]$, reported by Freeman *et al.* [(1964). *Acta Cryst.* **17**, 1463–1470], has been reinvestigated and its absolute configuration established by anomalous dispersion effects. The origin of chirality in the crystalline state of this compound is the formation of right-handed helices from a Cu^{II} coordination network self-resolved into a pure enantiomeric phase.

Comment

Solids that crystallize in non-centrosymmetric space groups have attracted considerable attention due to potential applications in electrooptical devices, chiral separations and solid phase syntheses of chiral compounds. In this context, formation of chiral solids from achiral molecules is even more fascinating. Copper plays an important role in biological processes and appears in the active site of many important proteins (Tsai *et al.*, 1995). Bis(amino acid) complexes have been studied in order to increase the understanding of more complicated metal-protein systems. These systems use the copper site to transport electrons between different protein complexes. In these active sites, the copper ions are coordinated by N, O or S atoms.

Investigations on the bis(glycinato)copper(II) system (Delf *et al.*, 1979; Moussa *et al.*, 1998, 2002) have shown that four crystalline phases can be obtained: *cis*- and *trans*-aquabis(glycinato)copper(II) and the corresponding anhydrous forms. The crystal structure of *cis*-aquabis(glycinato)copper(II), (I), was first determined using Weissenberg film data (Freeman *et al.*, 1964). Recently, Moussa *et al.* (2002) reported the crystal structures of the above crystalline phases using data from neutron and synchrotron powder diffraction techniques.



(I)

The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The four glycinate ligand atoms chelating the copper ion (N1, O1, N2 and O3) are almost coplanar. The r.m.s. deviation from their least-squares plane is 0.035 Å. In addition, coordination of the copper center by a water molecule (O5) affords a square-pyramidal geometry for the copper complex. In the solid state, a carbonyl O atom (O4^i) [symmetry code: (i) $\frac{1}{2}+x$, $\frac{1}{2}-y, 1-z$] bonds to the Cu^{II} ion at a distance of 2.655 (3) Å, generating a highly distorted octahedral geometry. The O5—

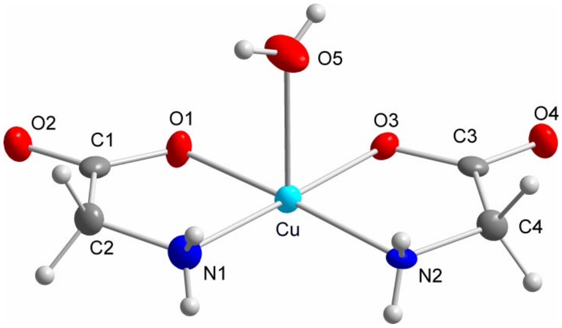


Figure 1
Perspective view of the molecular structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

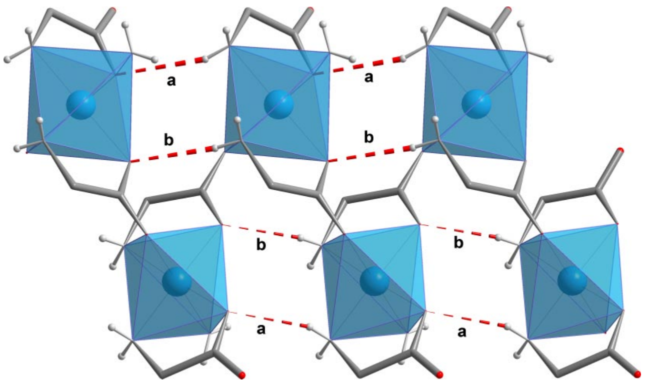


Figure 2
A chain arrangement of molecules, parallel to the *a* axis, mediated *via* the carbonyl oxygen coordinating to the copper(II) and by hydrogen bonds (see Table 2). Hydrogen bonds are shown as dashed lines. C-bound H atoms are not shown for clarity.

Cu—O4^i angle [171.04 (13)°] can be attributed to geometrical strain from the linkage of copper(II) centers *via* glycinate moieties. This results in a chain polymeric arrangement of copper centers parallel to the *a* axis, as represented in Fig. 2. The intermolecular N—H···O hydrogen bonds (Table 2) augment the stability of these chains. Each polymeric chain comprises a right-handed helical backbone, inducing chirality to the network of achiral copper complex units (see Fig. 3). These helices are held together *via* N—H···O and O—H···O hydrogen bonds, as shown in Fig. 4, forming a three-dimensional network. Thus, crystallization of (I) results in the self-resolution of such a pure homochiral network.

Experimental

Hot ethanol (3 ml) was added to an aqueous solution (3 ml) of copper(II) acetate monohydrate (0.2 g). Glycine (0.15 g) dissolved in water (2.5 ml) was then added to the solution. This mixture was gently heated to 343 K for 15 min and then chilled in an ice-bath, affording a precipitate of needle-like crystals of *cis*-[Cu(NH$_2$CH$_2$-COO)$_2$H$_2$O]. The product was characterized by IR spectroscopy. A UV–vis spectrum of the product dissolved in water shows a broad absorption band with a maximum at 627 nm. Our attempts to obtain solid-state CD (circular dichroism) spectra of (I) were unsuccessful, probably due to a weak signal of the copper(II) chromophore. Fine light-blue needle-shaped crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an aqueous solution.

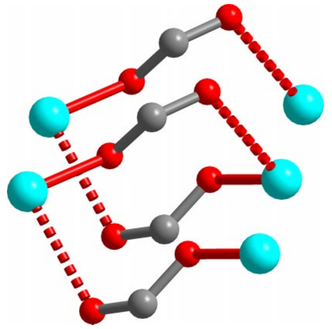


Figure 3
Representation of a right-handed helix inducing chirality in the solid state of (I). The dashed line is the longer Cu—O bond.

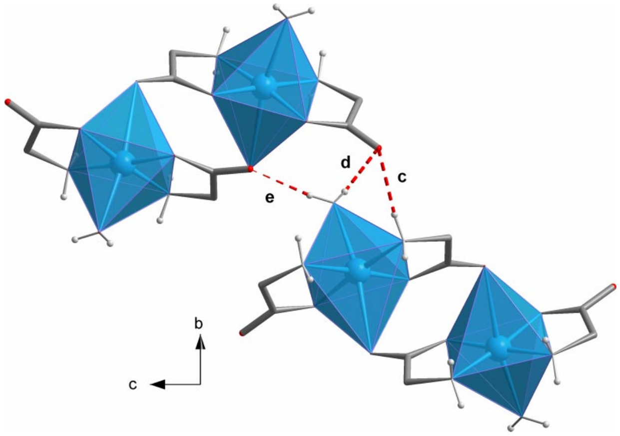


Figure 4
Polymeric chains linked together by O—H···O and N—H···O hydrogen bonds (dashed lines). C-bound H atoms are not shown for clarity.

Crystal data

[Cu(C$_2$H$_4$NO$_2$)$_2$(H$_2$O)]
M_r = 229.68
Orthorhombic, $P2_12_12_1$
a = 5.1920 (3) Å
b = 10.6850 (6) Å
c = 13.5535 (8) Å
V = 751.90 (8) Å^3
Z = 4
D_x = 2.029 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3850 reflections
θ = 2.4–30.5°
μ = 2.89 mm^{-1}
T = 173 (2) K
Needle, light blue
0.24 × 0.03 × 0.02 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min}$ = 0.544, $T_{\max}$ = 0.944
10 748 measured reflections
2301 independent reflections
1775 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.083
$\theta_{\max}$ = 30.5°
$h = -7 \rightarrow 7$
$k = -15 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.097
S = 1.01
2301 reflections
134 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.53 e Å^{-3}
$\Delta\rho_{\min}$ = −0.66 e Å^{-3}
Absolute structure: Flack (1983), 944 Friedel pairs
Flack parameter = 0.02 (3)

m1950 Barbara M. Casari *et al.* • [Cu(C$_2$H$_4$NO$_2$)$_2$(H$_2$O)] *Acta Cryst.* (2004). E**60**, m1949–m1951

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.955 (3)	Cu—N1	2.006 (4)
Cu—O3	1.956 (3)	Cu—O5	2.373 (4)
Cu—N2	1.996 (4)	Cu—O4^{i}	2.655 (3)
O1—Cu—O3	93.32 (12)	N2—Cu—N1	97.17 (16)
O3—Cu—N2	84.91 (13)	O5—Cu—O4^{i}	171.04 (13)
O1—Cu—N1	84.54 (15)		
O5—Cu—N1—C2	83.8 (4)	O5—Cu—O1—C1	−88.6 (3)
O4^{i}—Cu—N1—C2	−88.2 (3)	O4^{i}—Cu—O1—C1	88.0 (3)
O5—Cu—N2—C4	−86.4 (3)	O5—Cu—O3—C3	94.4 (3)
O4^{i}—Cu—N2—C4	96.7 (3)	O4^{i}—Cu—O3—C3	−93.8 (3)

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···O1^{ii}	0.76 (6)	2.37 (6)	3.093 (5)	159 (6)
N2—H1N2···O3^{ii}	0.79 (5)	2.24 (5)	2.992 (5)	159 (5)
N2—H2N2···O2^{iii}	0.84 (6)	2.12 (6)	2.950 (5)	170 (5)
O5—H1O5···O2^{iv}	0.69 (6)	2.13 (6)	2.808 (5)	171 (7)
O5—H2O5···O4^{v}	0.76 (6)	2.01 (6)	2.759 (5)	170 (6)

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

The amino and water H atoms were located in difference Fourier maps and refined freely with isotropic displacement parameters. For the C-bound H atoms, a riding model was used [C—H = 0.99 Å and $U_{\rm iso}$ = 1.2$U_{\rm eq}$(C)].

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXTL*.

References

Brandenburg, K. (2001). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.

Bruker (2001). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Delf, B. W., Gillard, R. D. & O'Brien, P. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1301–1305.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Freeman, H. C., Snow, M. R., Nitta, I. & Tomita, K. (1964). *Acta Cryst.* **17**, 1463–1470.

Moussa, S. M., Fenton, R. R., Hunter, B. A. & Kennedy, B. J. (2002). *Aust. J. Chem.* **55**, 331–341.

Moussa, S. M., Fenton, R. R. & Kennedy, B. J. (1998). *Mater. Sci. Forum*, 278–281, 912–917.

Sheldrick, G. M. (2002). *SADABS*. Version 2.03. University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT*, Siemens Analytical X-ray Instruments Inc., Wisconsin, Madison, USA.

Tsai, L.-C., Sjölin, L., Langer, V., Pascher, T. & Nar, H. (1995). *Acta Cryst.* D**51**, 168–176.

Acta Cryst. (2004). E**60**, m1949–m1951 Barbara M. Casari *et al.* • [Cu($C_2H_4NO_2$)$_2$(H_2O)] **m1951**