

Acta Crystallographica Section C

**Crystal Structure
Communications**

ISSN 0108-2701

Aquabis(crotonato)bis(pyridine)copper(II)

Ricardo Baggio *et al.*

Electronic paper

This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

© 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

Aquabis(crotonato)bis(pyridine)- copper(II)

Ricardo Baggio,^{a*} Bruce Foxman,^b Maria Teresa Garland,^c
Mireille Perec^d and Wen Shang^b

^aDepartamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, ^bDepartment of Chemistry, MS 015, Brandeis University, Waltham, MA 02454-9110, USA, ^cDepartamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago de Chile, Chile, and ^dDepartamento de Química Inorgánica, Analítica y Química Física, INQUIMAE, Facultad de Ciencias Exactas y Naturales, UNBA, Buenos Aires, Argentina
Correspondence e-mail: baggio@cnea.gov.ar

Received 11 September 2000

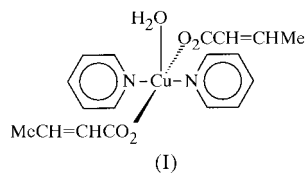
Accepted 4 October 2000

Data validation number: IUC0000281

The title compound, $[\text{Cu}(\text{O}_2\text{CCH}=\text{CHCH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})]$, crystallizes as a monomer, with the copper ion in a pentacoordinated square-pyramidal environment, bisected by a twofold axis passing through the metal atom and the apex. The molecules organise in chains connected by hydrogen bonds running along the unique *b* axis.

Comment

The structure of the title compound, (I), is formed by mononuclear $[\text{Cu}(\text{O}_2\text{CCH}=\text{CHCH}_3)_2(\text{py})_2(\text{H}_2\text{O})]$ units ($\text{O}_2\text{CCH}=\text{CHCH}_3$ is *trans*-2-butenate and py is pyridine), in which the metal ion as well as the water molecule lie on a twofold symmetry axis, so that only one *trans*-2-butenate and one pyridine ligand are independent. The copper coordination geometry is that of a square pyramid, with the N atoms from the py ligands [$\text{Cu}-\text{N}1$ 2.034 (2) Å] and the bonded carboxylate O atoms from the *trans*-2-butenate [$\text{Cu}-\text{O}8$ 1.938 (2) Å] defining the quasi-planar square base (maximum deviation from the mean plane for N1, 0.12 Å), and the copper ion slightly shifted by 0.08 (1) Å towards the apex. The apical



site is occupied by the water molecule [$\text{Cu}-\text{O}1\text{W}$ 2.211 (3) Å], a bond which coincides with the twofold symmetry axis and is thus exactly perpendicular to the basal plane. The arrangement of the CuN_2O_3 core is nearly identical to that reported for the related imidazole (Im) complex

$[\text{Cu}(\text{O}_2\text{CCH}=\text{CHCH}_3)_2(\text{Im})_2(\text{H}_2\text{O})]$ (Escriva *et al.*, 1996).

The *trans*-2-butenate ligand is built up by two strictly planar sub-groups defined by O7/O8/C9/C10 and C9/C10/C11/C12, with deviations from the mean planes of less than 0.01 Å. These two planes are rotated around the C9—C10 bond by *ca* 15°.

The C—O bond of the outer carboxylate (C9—O7) is only slightly shorter than the C—O bond (C9—O8) to the copper ion, 1.231 (4) versus 1.274 (3) Å, suggesting the engagement of O7 in hydrogen bonding as described below. The pyridine group hardly deviates from planarity (maximum deviation 0.013 Å for C6) and binds to the cation adopting a slanted position with respect to the basal plane [120.7 (1)°]. This appears to be due to the steric hindrance between adjacent pyridine units along the short unique *b* axis and determines that the nearest H atoms of neighbouring py rings are found at a non-interacting distance of ~3.20 Å. The rotation of the py groups determines the 15° rotation of the carboxylate end of the *trans*-2-butenate mentioned above. Steric reasons also, now involving the pairs H2A—O7 and H6A—O8 (H atoms from py and O atoms from *trans*-2-butenate), stabilize the H...O distances at ~2.9 Å, which is beyond the distance of van der Waals interactions.

The monomers pack into rows parallel to $\langle 010 \rangle$. The interaction among neighbouring units is achieved through a couple of strong hydrogen bonds duplicated by symmetry [$\text{O}1\text{W}-\text{H}1\text{W}\cdots\text{O}7^i$: $\text{O}1\text{W}-\text{H}1\text{W}$ 0.78 (3) Å, $\text{H}1\text{W}\cdots\text{O}7^i$ 1.95 (3) Å, $\text{O}1\text{W}-\text{H}1\text{W}\cdots\text{O}7^i$ 170 (3)°; symmetry code: (i) $x, y-1, z$]. These one-dimensional structures parallel to $\langle 010 \rangle$ stack in such a way that the protruding organic ligands in a chain fit into the voids left by adjacent equivalent groups in the neighbouring chains. The result is that the C10=C11 double bonds in the *trans*-2-butenate end up facing each other, parallel and separated by distances of *ca* 3.90 Å. The pyridinic cycles face the terminal methyl H atoms at distances in the range 3.70–3.90 Å. These facts suggest the possibility of secondary interactions between chains, which may contribute to the crystal structure stabilization.

Experimental

To a 1:1 pyridine–ethanol solution (25 ml) at room temperature was added copper crotonate prepared from crotonic acid (1.0 g, 11 mmol) and freshly prepared $\text{Cu}(\text{OH})_2$ (0.5 g, 5 mmol). A deep-blue solution was formed under continuous stirring; after two weeks, crystals of the pyridine adduct were removed by filtration, washed with cold water and dried in air (yield: 1.6 g, 80%). Analysis calculated (found) for $\text{C}_{18}\text{H}_{22}\text{CuN}_2\text{O}_5$: C 52.75 (52.60), H 5.40 (5.30), N 6.80 (6.95), Cu 15.50%. IR (KBr disc, cm^{-1}): 3235 (*m*), 3077 (*m*), 3014 (*m*), 1661 (*vs*), 1605 (*s*), 1578 (*sv*), 1567 (*vs*), 1488 (*m*), 1449 (*vs*), 1390 (*vs*), 1371 (*s*), 1217 (*m*), 1071 (*m*), 979 (*s*), 856 (*m*), 760 (*m*), 733 (*m*), 696 (*s*), 640 (*m*), 268 (*m*). The reactants (Aldrich Chemical Co.) were used without further purification. The elemental analyses (CHN) were performed on a Carlo Erba EA 1108 instrument; the IR spectra were recorded with a Nicolet 510P FT-IR spectrophotometer.

Crystal data

[Cu(C₄H₅O₂)₂(C₅H₅N)₂(H₂O)]
M_r = 409.92
 Monoclinic, *C*2/*c*
a = 15.922 (2) Å
b = 5.7331 (8) Å
c = 21.341 (3) Å
 β = 91.097 (11)°
V = 1947.6 (5) Å³
Z = 4

D_x = 1.398 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 7.5–12.5°
 μ = 1.15 mm⁻¹
T = 293 (2) K
 Plate, blue
 0.36 × 0.16 × 0.08 mm

Data collection

Siemens *R3m* diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (*XEMP* in *SHELXTL/PC*; Sheldrick, 1994)
T_{min} = 0.50, *T_{max}* = 0.73
 1866 measured reflections
 1699 independent reflections
 1476 reflections with *I* > 2σ(*I*)

R_{int} = 0.026
 θ_{max} = 25°
h = 0 → 18
k = 0 → 6
l = -25 → 25
 2 standard reflections every 98 reflections
 intensity decay: <2%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.031
wR (*F*²) = 0.082
S = 1.068
 1699 reflections
 123 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 2P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu—O8	1.9381 (17)	Cu—O1W	2.211 (3)
Cu—N1	2.034 (2)		
O8 ⁱ —Cu—O8	178.13 (12)	N1—Cu—N1 ⁱ	169.26 (12)
O8 ⁱ —Cu—N1	90.77 (8)	O8—Cu—O1W	89.07 (6)
O8—Cu—N1	89.41 (8)	N1—Cu—O1W	95.37 (6)

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

H atoms attached to carbon were included in idealized positions and refined using a riding scheme, both for coordinates and for displacement parameters. Those pertaining to the aqua molecule were found in the difference Fourier map and were refined with restraints on the O—H and H···H distances.

Data collection: *P3/P4-PC* (Siemens, 1991); cell refinement: *P3/P4-PC*; data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *CIFTAB* in *SHELXTL/PC* and *PARST* (Nardelli, 1983).

This work was supported by the Universidad de Buenos Aires and by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina). The work at Brandeis University was supported in part by the National Science Foundation, through grant DMR-9629994. MP is a member of CONICET. We thank Miss A. Petragalli for the TGA measurements. The provision of a free-of-charge license to the CSD system by the Spanish Research Council (CSIC) is gratefully acknowledged.

References

- Escriba, E., Sanau, M., Folgado, J.-V., Garcia-Lozano, J. & Aarif, A. M. (1996). *Polyhedron*, **15**, 3271–3276.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
 Siemens (1991). *P3/P4-PC*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.