# Structure of Tetrakis(μ-methacrylato-*O,O'*)-bis[(4-vinylpyridine)copper(II)]

By A. Deeg, D. Mootz and H. Wunderlich

*Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf,*
*Universitätsstrasse 1, D-4000 Düsseldorf, Federal Republic of Germany*

**Abstract.** [$Cu_2(C_4H_5O_2)_4(C_7H_7N)_2$], $M_r = 677.7$, monoclinic, $P2_1/c$, $a = 10.473$ (4), $b = 14.234$ (5), $c = 11.864$ (4) Å, $\beta = 112.93$ (3)°, $V = 1628.8$ Å$^3$, $Z = 2$, $D_m = 1.385$, $D_x = 1.382$ Mg m$^{-3}$, Mo $K\bar{\alpha}$, $\lambda = 0.71073$ Å, $\mu = 1.36$ mm$^{-1}$, $F(000) = 700$, room temperature, $R = 0.043$ for 2028 unique observed reflections and 227 refined parameters. The complex has point symmetry $\bar{1}$, the two Cu atoms are bridged by four methacrylato ligands, and the distorted octahedral coordination of each Cu atom is completed by a vinylpyridine ligand and the other Cu atom at a distance of 2.655 (1) Å. The methacrylato ligands show a twofold positional disorder with the methyl and methylene groups superimposed on each other.

**Experimental.** Monoclinic green to turquoise prismatic crystals of the title compound have been prepared by Kuchen & Schram (1988). Photographs revealed the symmetry of the monoclinic Laue group $2/m$ and systematic absences unique for the space group $P2_1/c$. $D_m$ ($= 1.385$ Mg m$^{-3}$) was measured by flotation, resulting in two formula units per cell [fully reduced mesh, cell choice 1, *International Tables for Crystallography* (1983)]. A crystal approximately $0.3 \times 0.3 \times 0.5$ mm was used for the determination of the cell constants (16 reflections, $30 < 2\theta < 31°$, Mo $K\alpha$, crystal monochromator, Siemens AED2 diffractometer) and for the data collection (variable $\omega{:}\theta$ scan, 40 steps of $0.025°$ plus separation of $\alpha_1/\alpha_2$, time per step $0.5$–$3$ s). The intensities of all 3894 symmetry-independent reflections up to $(\sin\theta)/\lambda = 0.65$ Å$^{-1}$ were measured. The final set of data contained 3176 reflections with $I > 0$ of which 2028 were treated as observed [$I > 1.96\sigma(I)$]. Three standard reflections showed a continuous decay of the crystal and were used for a correction of the intensities by factors between $1.0$ and $1.085$. The indices $h$, $k$, $l$ ranged from 0 to 13, 0 to 18 and $-14$ to 14, respectively.

Initial coordinates of the Cu atom were obtained from the Patterson function. The asymmetric unit (one half of the formula unit) was completed in the usual way. Straightforward refinement yielded unsatisfactory accuracy paralleled by displacement parameters of the terminal C atoms of the methacry-

lato ligands of up to $U_{ii} = 0.32$ Å$^2$ and by identical lengths of $1.42$ Å for both the single and double C—C bonds involved. These inconsistencies together with the low percentage of observed reflections pointed strongly to a twofold disorder with the methyl and methylene groups superimposed on each other. Thus, the final refinement was carried out with split atom positions (site-occupancy factors of $0.5$) and geometrical constraints for these C atoms. All H atoms were constructed and treated as fixed-atom contributions. The refinement on $F$ (227 parameters) converged at $S = 1.87$ with all $\Delta/\sigma < 0.05$. Weights were derived from $1/w = \sigma_F^2 + cF_o^2$ with $c$ adjusted to $0.00012$; $R = 0.043$ ($0.083$) and $wR = 0.041$ ($0.045$) for the observed (all) data. Residual electron densities ranged from $-0.30$ to $0.26$ e Å$^{-3}$. Atomic scattering factors were used as implemented in the program system *SHELXTL* (Sheldrick, 1983). The

Table 1. *Atomic positions and equivalent isotropic displacement parameters* ($Å^2 \times 10^2$) *of the non-*H *atoms with e.s.d.'s in parentheses*

Three-digit numbering is given for the split atoms (occupancy factors of 0.5). $U_{eq} = 1/3(U_{11}a^{*2}a^2 + 2U_{12}a^*b^*ab\cos\gamma + ...)$.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cu | 0.09017 (4) | 0.02866 (3) | 0.45372 (3) | 6.76 (2) |
| O1 | −0.0651 (2) | −0.0030 (2) | 0.3002 (2) | 8.4 (1) |
| O2 | 0.2182 (2) | 0.0498 (2) | 0.6247 (2) | 8.5 (1) |
| O3 | 0.1506 (2) | −0.1024 (2) | 0.4714 (2) | 8.8 (1) |
| O4 | 0.0033 (2) | 0.1513 (2) | 0.4545 (2) | 8.7 (1) |
| N | 0.2182 (2) | 0.0815 (2) | 0.3612 (2) | 6.9 (1) |
| C1 | 0.3432 (3) | 0.0475 (3) | 0.3802 (3) | 9.1 (2) |
| C2 | 0.4287 (3) | 0.0849 (3) | 0.3294 (3) | 9.0 (2) |
| C3 | 0.3874 (3) | 0.1604 (2) | 0.2520 (3) | 7.1 (1) |
| C4 | 0.2558 (4) | 0.1937 (3) | 0.2275 (3) | 8.3 (2) |
| C5 | 0.1771 (3) | 0.1538 (3) | 0.2839 (3) | 8.2 (2) |
| C6 | 0.4819 (4) | 0.2004 (3) | 0.1987 (4) | 9.6 (2) |
| C7 | 0.4529 (5) | 0.2658 (3) | 0.1209 (4) | 13.7 (3) |
| C8 | −0.1810 (3) | −0.0348 (2) | 0.2888 (3) | 6.8 (1) |
| C9 | −0.2792 (3) | −0.0558 (2) | 0.1622 (3) | 7.3 (2) |
| C101 | −0.2333 (18) | −0.0419 (15) | 0.0579 (12) | 8.8 (6) |
| C102 | −0.2255 (16) | −0.0704 (15) | 0.0797 (12) | 10.4 (7) |
| C111 | −0.4127 (6) | −0.0600 (11) | 0.1408 (14) | 7.4 (5) |
| C112 | −0.4222 (7) | −0.0917 (10) | 0.1399 (18) | 7.5 (5) |
| C12 | −0.0957 (3) | 0.1647 (3) | 0.4878 (3) | 7.6 (1) |
| C13 | −0.1504 (4) | 0.2619 (3) | 0.4791 (4) | 9.8 (2) |
| C141 | −0.2519 (15) | 0.2741 (12) | 0.5177 (18) | 13.7 (9) |
| C142 | −0.2178 (18) | 0.2921 (13) | 0.5646 (17) | 12.7 (8) |
| C151 | −0.1368 (16) | 0.3292 (12) | 0.3864 (14) | 13.1 (7) |
| C152 | −0.0953 (16) | 0.3262 (8) | 0.4314 (14) | 11.5 (8) |
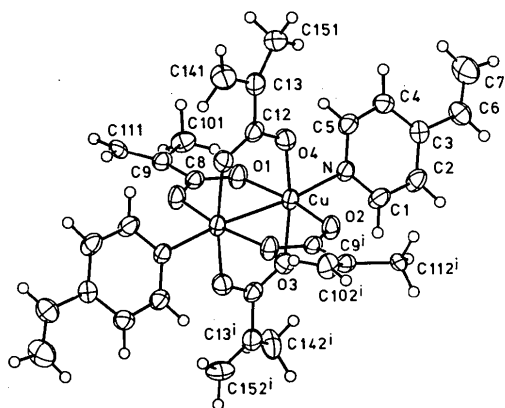
Fig. 1. Crystal structure of the title complex with displacement ellipsoids of 25% probability in arbitrary crystallographic orientation. The point symmetry of the complex is $\bar{1}$. The terminal C atoms of the methacrylato groups are twofold disordered. As a deviation from the point symmetry $\bar{1}$ of the complex each of the split positions of these atoms is displayed only once on one side of the molecule. Symmetry code: (i) $-x$, $-y$, $1-z$.

final parameters of the non-H atoms are given in Table 1.*

Fig. 1 shows one molecule of the complex, main bond lengths are given in Table 2. The five-membered rings formed by each carboxyl group and the two Cu atoms are planar within 0·02 Å and approximately coplanar with the terminal 2-propenyl groups. Including the Cu—Cu distance of 2·655 (1) Å the coordination of the Cu atom is distorted octahedral with deviations from idealized angles up to 13°. The center of symmetry of the complex is located halfway between the two Cu

---

* Lists of anisotropic displacement parameters, calculated H-atom positions, bond angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52945 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths (Å) of the complex*

The e.s.d.'s are 0·001–0·003 Å for distances including the Cu atom, 0·004–0·006 Å for other distances except 0·01–0·02 Å for split-atom participation.

| | | | | | |
|---|---|---|---|---|---|
| Cu—Cu$^i$ | 2·655 | C9—C111 | 1·320 | N—C1 | 1·328 |
| Cu—O1 | 1·963 | C9—C112 | 1·504 | C1—C2 | 1·367 |
| Cu—O2 | 1·971 | O2—C8$^i$ | 1·249 | C2—C3 | 1·370 |
| Cu—O3 | 1·955 | O3—C12$^i$ | 1·252 | C3—C4 | 1·377 |
| Cu—O4 | 1·971 | O4—C12 | 1·259 | C4—C5 | 1·370 |
| Cu—N | 2·170 | C12—C13 | 1·486 | N—C5 | 1·334 |
| O1—C8 | 1·252 | C13—C141 | 1·322 | C3—C6 | 1·479 |
| C8—C9 | 1·483 | C13—C142 | 1·507 | C6—C7 | 1·262 |
| C9—C101 | 1·505 | C13—C151 | 1·507 | | |
| C9—C102 | 1·321 | C13—C152 | 1·321 | | |

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

atoms which are bridged by four methacrylato ligands.

**Related literature.** This skeleton has been characterized already in previous, less accurate X-ray studies of Cu₂(CH₃COO)₄.2H₂O (van Niekerk & Schoening, 1953) and of two modifications of Cu₂(CH₃COO)₄.2C₅H₅N (Barclay & Kennard, 1961; Hanic, Stempelova & Hanicova, 1964). A comparable study of Cu₂(CH₃COO)₄.2H₂O by neutron diffraction has been reported by Brown & Chidambaram (1973).

**References**

BARCLAY, G. A. & KENNARD, C. H. L. (1961). *J. Chem. Soc.* pp. 5244–5251.
BROWN, G. M. & CHIDAMBARAM, R. (1973). *Acta Cryst.* B29, 2393–2402.
HANIC, F., STEMPELOVA, D. & HANICOVA, K. (1964). *Acta Cryst.* 17, 633–639.
*International Tables for Crystallography* (1983). Vol. A, pp. 35–37. Dordrecht: Kluwer Academic Publishers.
KUCHEN, W. & SCHRAM, J. (1988). *Angew. Chem.* 100, 1757–1758; *Angew. Chem. Int. Ed. Engl.* 27, 1695–1697.
NIEKERK, J. N. VAN & SCHOENING, F. R. L. (1953). *Acta Cryst.* 6, 227–232.
SHELDRICK, G. M. (1983). *SHELXTL Users Manual.* Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

---

# Triaquabis[dihydrogen-1,2,3-benzenetricarboxylato(1 − )]copper(II) Trihydrate

BY R. PECH AND J. PICKARDT*

*Technische Universität Berlin, Straße des 17 Juni 135, 1000 Berlin 12, Federal Republic of Germany*

**Abstract.** $M_r = 589·94$, monoclinic, $C2/c$ (disordered), $a = 28·600$ (5), $b = 6·728$ (2), $c = 11·747$ (2) Å, $\beta = 95·14$ (2)°, $V = 2251·5$ Å³, $Z = 4$, $D_m = 1·85$, $D_x = 1·74$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 9·95$ cm⁻¹, $F(000) = 1212$, $T = 293$ K, $R = 0·065$, for 2335 reflexions with $|F_o| > 4\sigma(|F_o|)$. The coordination

* To whom correspondence should be addressed.

    