

Bis(3-allylacetylacetonato)copper(II),* C₁₆H₂₂CuO₄

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Abstract. $M_r = 341.9$, monoclinic, $P2_1/n$, $a = 13.544$ (5), $b = 4.677$ (3), $c = 13.861$ (7) Å, $\beta = 110.79$ (3)°, $V = 820.8$ Å³, $Z = 2$, $d_x = 1.38$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71067$ Å, $\mu = 14.0$ cm⁻¹, $T = 290$ K. Final $R = 0.056$ for 1476 contributing reflections. Cu at (0,0,0) is centrosymmetrically bonded to four O atoms, the CuO₄ plane making an angle of 46.7 (1)° with the ac plane along a line 34.5 (1)° away from a toward c . The shortest Cu–Cu distance is 4.677 (3) Å and the closest intermolecular Cu contact is 3.185 (4) Å, with C(3).

Introduction. Horng Chin Yeh (1981) prepared bis(3-allylacetylacetonato)copper(II) as one of a number of model compounds to be polymerized or copolymerized to obtain transition-metal-complex cross-linked elastomers. He and Professor B. E. Eichinger also asked whether the crystal structure is such as to facilitate polymerization by way of the allyl groups either within the crystal or at the crystal surface.

Experimental. Fragile, platy, green–gray needles with a touch of metallic luster were obtained by dissolving small amounts of the powder in a mixture of petroleum ether and methanol and letting the solvent evaporate slowly, crystal $1.45 \times 0.15 \times 0.05$ mm mounted along the needle axis (**b**) used for the photographic work as well as the subsequent diffractometry; precession and Weissenberg photographs, systematic absences $0k0$ for k odd and $h0l$ for $h + l$ odd; Picker FACS-1 diffractometer, unit cell: 15 reflections, $2\theta > 23^\circ$, centered at $\pm 2\theta$, least-squares refinement; intensity measurements with Nb(0.076 mm)-filtered Mo $K\alpha$ radiation by θ – 2θ scans at 2° min^{-1} in 2θ with 20s background counts fore and aft, base width 2° plus $\alpha_1 - \alpha_2$ dispersion, 1556 reflections in quadrant $\pm h, k, l$, $3 < 2\theta < 60^\circ$, about 800 reflections in range $45 < 2\theta < 60^\circ$ passed by on the grounds that an initial 2s peak count was less than 40, for every 250 reflections five standards monitored and orientation checked, standards did not decline appreciably in intensity and indicated $p = 1\%$ (instability constant), included in estimating the standard deviations of the integrated intensities by $\sigma_I^2 = S + t^2B + p^2I^2$, $I = S - tB$, no reflections strong

enough to require coincidence-loss correction; programs of the XRAY system (Stewart, Machin, Ammon, Dickinson, Heck & Flack, 1976) used for data reduction and all subsequent calculations; all C and O atoms located on a series of Fourier maps phased initially on the Cu atom at (0,0,0); after several cycles of full-matrix least squares ($R < 10\%$) a difference map showed all the H atoms (one H of each CH₃ is *cis* to an O) except H(7), H(81), and H(82), which were then placed at bond lengths C–H = 1.0 Å and appropriate bond angles and refined in position and U (never simultaneously) with the rest of the structure; final cycle of anisotropic least-squares, on F with the usual form factors [Stewart, Davidson & Simpson (1965) for H, *International Tables for X-ray Crystallography* (1974) otherwise], $F(000) = 358$, $1/\sigma_{F_o}^2$ weights, inclusion rule $|F_c|$ or $F_o > 1.1\sigma(F_o)$ {1476 contributing F_o 's, 80 of the 100 'less-thans' excluded, $(\Delta/\sigma)_{av} = 0.05$, $(\Delta/\sigma)_{max} = 0.88$ for $U[\text{H}(81)]$ }, $wR = 0.050$, $S = 1.3$; no corrections made for anomalous dispersion, extinction, absorption (estimated range of A about 0.80 to 0.93, almost entirely due to the 1:3 cross section of the specimen), or variation with θ and χ of length of illumination of specimen in X-ray beam, defined by a 0.5 mm collimator, from 1.00 min at $\chi = 0^\circ$, all 2θ , or $\chi = 90$, $2\theta = 0^\circ$, to 1.10 min at $\chi = 90$, $2\theta = 50^\circ$, H positions held fixed (averages: C–H = 0.96 Å, sp^3 H–C–H = 107°; scatter e.s.d.'s for single values 0.06 Å and 6° *vs* average e.s.d.'s of 0.04 Å and 4° from the next-to-last least-squares cycle); extrema of subsequent difference map all less than 0.45 e Å⁻³.

It did not seem worthwhile to make the absorption and illumination corrections. They would no doubt change the U_{ij} 's considerably, but would have almost no effect on the atom positions or the statistics of fit.

Discussion. The atomic parameters are given in Table 1† and Fig. 1 shows a perspective view of the molecule.

As in the six earlier copper 'acac' structures (see summary, Table 6, Robertson & Truter, 1967; Blackstone, van Thuijl & Romers, 1966) and in

† Lists of F_o , F_c and $\sigma(F_o)$ and of the Gaussian amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38177 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* IUPAC name: Bis(3-allyl-2,4-pentanedionato)copper(II).

Cr(acac)₂ (Cotton, Rice & Rice, 1977), the coordination is square planar (Tables 2 and 3), with Cu—O = 1.905 (3) and 1.904 (3) Å *vs* 1.914 (2) Å, O(1)—Cu—O(2) = 91.8 (1)° *vs* 92.9 (1)°, and 'bite' distance O(1)···O(2) = 2.734 (4) Å *vs* 2.772 (4) Å, the comparisons being with the averages of the other structures. In all these structures except Cu(3-phenylacac)₂, which differs markedly in its packing from the others, there are also notably short contacts (Table 3; the nominal Cu···C van der Waals distance is about 3.7 Å) in rather precisely the remaining orthogonal directions, the molecules stacking tightly but steeply tilted into columns along the shortest crystal axis, neither the tilt nor the axial length changing much with the substitutions except in Cu(dibenzoylmethanato)₂, where the short contact is displaced from C(3) to the α-C atom of a phenyl group. The columns pack together more loosely and with or without alternations in orientation to accommodate the substituents. Whether the short Cu···C contacts represent substantial bonding has been both suggested and doubted (see Robertson & Truter, 1967), but they do occur in most of the structures, and in the present structure both the angles Cu···C(3)—C(2) = 91.7 (3), Cu···C(3)—C(4) = 90.8 (3), and Cu···C(3)—C(6) = 91.2 (3)° and the sequence of stacking contacts {Cu···C(3) = 3.18; O(1)···C(4) = 3.23, O(2)···C(2) = 3.23, O(1)···O(2) = 3.29, C(2)···C(4) = 3.63; Cu···C(3) = 3.18; C(6)···[Cu = 3.56, O(1) = 3.53, O(2) = 3.56, C(2) = 3.70, C(4) = 3.72, and C(3) = 3.80 Å]} strongly suggest that C(3) is attracted toward Cu while the other stacking contacts are repulsive, causing the molecular plates to bend away from the mean planes in the somewhat complex pattern shown in Table 4. The pattern illustrated by Cotton *et al.* (1977) for Cr(acac)₂ is similar, and the metallic cast of the present crystals is also suggestive. Further study seems to be indicated.

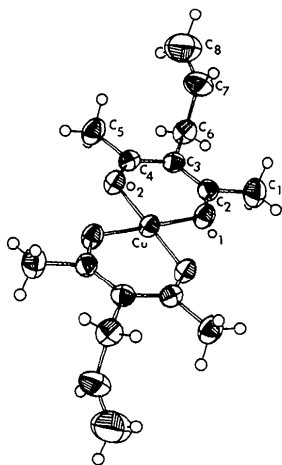


Fig. 1. ORTEP drawing of the molecule (Johnson, 1965).

Table 1. Atomic coordinates and isotropic thermal parameters

$U_{eq} = \frac{1}{3} \text{trace } U$, where U is the diagonalized U_{ij} matrix.

	x	y	z	U_{eq}/U_{iso} (Å ² × 10 ²)*
Cu	0.0000	0.0000	0.0000	3.7
O(1)	0.0781 (2)	0.2045 (5)	0.1222 (2)	4.2
O(2)	-0.1253 (2)	0.2083 (5)	-0.0147 (2)	4.3
C(1)	0.1283 (3)	0.5254 (10)	0.2606 (3)	5.6
C(2)	0.0454 (3)	0.4046 (8)	0.1655 (3)	3.9
C(3)	-0.0582 (3)	0.5155 (8)	0.1319 (3)	3.8
C(4)	-0.1367 (3)	0.4076 (8)	0.0428 (3)	3.9
C(5)	-0.2473 (3)	0.5365 (10)	0.0046 (4)	5.9
C(6)	-0.0864 (3)	0.7380 (9)	0.1976 (3)	5.0
C(7)	-0.1162 (4)	0.6085 (14)	0.2829 (4)	7.6
C(8)	-0.0801 (6)	0.6595 (21)	0.3769 (5)	12.4
H(11)	0.109 (3)	0.515 (9)	0.321 (3)	7.3
H(12)	0.193 (3)	0.428 (8)	0.279 (3)	6.4
H(13)	0.141 (3)	0.712 (9)	0.251 (3)	6.5
H(51)	-0.276 (3)	0.542 (8)	0.058 (3)	8.3
H(52)	-0.241 (4)	0.729 (10)	-0.010 (4)	8.1
H(53)	-0.294 (3)	0.414 (10)	-0.051 (4)	8.2
H(61)	-0.137 (3)	0.856 (9)	0.157 (3)	7.1
H(62)	-0.032 (3)	0.865 (9)	0.225 (3)	5.5
H(7)	-0.147 (3)	0.423 (9)	0.285 (4)	6.9
H(81)	-0.029 (3)	0.826 (9)	0.394 (3)	18.0
H(82)	-0.107 (3)	0.528 (8)	0.431 (3)	17.2

* E.s.d.'s are of the order of 5% for non-H atoms and 20% for H atoms.

Table 2. Bond lengths (Å) and angles (°)

Cu—O(1)	1.905 (3)	C(3)—C(4)	1.407 (5)
Cu—O(2)	1.904 (3)	C(4)—C(5)	1.524 (6)
O(1)—C(2)	1.273 (5)	C(3)—C(6)	1.518 (6)
O(2)—C(4)	1.271 (5)	C(6)—C(7)	1.506 (8)
C(1)—C(2)	1.505 (5)	C(7)—C(8)	1.241 (9)
C(2)—C(3)	1.411 (5)		
O(1)—Cu—O(2)	91.76 (12)	C(2)—C(3)—C(6)	119.1 (3)
Cu—O(1)—C(2)	127.8 (2)	C(4)—C(3)—C(6)	120.0 (3)
Cu—O(2)—C(4)	127.6 (2)	O(2)—C(4)—C(3)	126.3 (3)
O(1)—C(2)—C(1)	114.4 (3)	O(2)—C(4)—C(5)	113.3 (3)
O(1)—C(2)—C(3)	125.8 (3)	C(3)—C(4)—C(5)	120.4 (4)
C(1)—C(2)—C(3)	119.7 (4)	C(3)—C(6)—C(7)	112.9 (4)
C(2)—C(3)—C(4)	120.8 (4)	C(6)—C(7)—C(8)	129.2 (6)

Table 3. Stacking comparisons

Compound	Stacking axis	Tilt of CuO ₄ *	Shortest Cu···C	Reference
Cu(benzoylacetonato) ₂	<i>a</i> = 4.475 (5) Å	44.3°†	3.02 Å‡	(1)
Cu(ethyl acetoacetato) ₂	<i>b</i> = 4.527 (2)	45.0	3.12	(2)
Cu(3-allylacac) ₂	<i>b</i> = 4.677 (3)	46.7	3.19	(3)
Cu(acac) ₂	<i>b</i> = 4.71 (1)	45.1	3.01	(4a)
Cu(acac) ₂	<i>b</i> = 4.71	44.9	3.09	(4b)
Cu(3-methylacac) ₂	<i>b</i> = 4.81 (1)	47.3	3.216	(5)
Cu(dibenzoylmethanato) ₂	<i>b</i> = 6.07	59.2	3.14	(6)
Cu(3-phenylacac) ₂	—	—	3.65	(7)
Cr(acac) ₂	<i>b</i> = 4.748 (1)	46.1	3.048	(8)

References: (1) Ping-Kay Hon, Pfluger & Belford (1966); (2) Barclay & Cooper (1965); (3) this work; (4a) Starikova & Shugam (1969); (4b) Dahl, cited by Piper & Belford (1962) [reference 5 gives Cu···C(3) = 3.075 Å, citing Dahl]; (5) Robertson & Truter (1967); (6) Blackstone *et al.* (1966); (7) Carmichael, Steinrauf & Belford (1965); (8) Cotton *et al.* (1977).

* Tilt is the angle between the normal to the CuO₄ plane and the stacking axis.

† E.s.d.'s about 0.1°.

‡ E.s.d.'s about 0.005 Å.

Table 4. Distances (Å) from least-squares planes

	A	B	C	A	B	C	
Cu	-0.041	0.000	-0.000	C(4)	0.021	0.025	-0.019
O(1)	-0.015	0.007	0.000	C(5)	-0.030	-0.038	-0.101
O(2)	0.006	0.028	0.000	C(6)	0.156	0.126	0.063
C(1)	-0.009	-0.017	-0.042	C(7)	1.578	1.541	1.473
C(2)	0.001	0.004	-0.020	C(8)	2.113	2.066	1.993
C(3)	0.026	0.019	-0.024				

Planes defined by Cu, C(1)–C(5), O(1) and O(2) (A), by the atoms for plane A plus their centric mates (B), and by Cu, O(1) and O(2) (C). Dihedral angles: 0.84 (A and B), 0.87 (B and C), 1.66 (A and C), 48.3 (A and ac), 46.7 (B and ac), and 47.5° (C and ac). Angles from **a** towards **c** of the lines of intersection of A, B, and C with ac: 34.19, 34.62, and 34.58°. E.s.d.'s of atom positions about 0.005 Å; of points on the plane not available, but considerably different for the different planes and for different points on a given plane, the greatest possibly being no more than 0.01 Å.

The allyl torsion angles are C(8)–C(7)–C(6)–C(3) = 126.7 (8) (vinyl *cis* to methylene H as expected; see *e.g.* Pauling, 1960), C(7)–C(6)–C(5)–C(4) = 91.9 (5), and C(7)–C(6)–C(3)–C(2) = -83.8 (5)°, the C–C bond of the allyl group twisting down about 90° from the ligand plane. At 1.241 (8) Å, C(7)=C(8) is excessively short, mainly, we feel, by foreshortening, $U[C(8)]$ being very large, and much larger than $U[C(7)]$. There are only two short C(8) contacts with non-H atoms, at 3.65 (1) Å with a C(8) and at 3.74 (1) Å with a C(5), and none along **b**, on which $U[C(8)]$ has its largest component. It is not obvious whether the C(8) contacts, along with C(7)–C(7) at

4.13 (1) Å, are short enough or so disposed as to support the original suggestion that a solid-state polymerization might be possible.

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Structure of catena- μ -Aqua-bis(benzimidazole)diformatocopper(II), [Cu(C₇H₆N₂)₂(CHO₂)₂(H₂O)]

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Abstract. $M_r = 407.9$, monoclinic, $C2/c$, $a = 12.94$ (4), $b = 12.70$ (4), $c = 10.40$ (2) Å, $\beta = 96.0$ (3)°, $V = 1699.8$ Å³, $Z = 4$, $D_x = 1.590$, $D_m = 1.62$ (2) Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å. The structure determination was based upon 844 independent reflections. Full-matrix least-squares refinement yielded a conventional R factor of 0.065. A specific one-dimensional polymeric structure has been established. The formate ions and benzimidazole molecules are monodentate ligands, forming two Cu–O bonds of 1.997 (5) Å and two Cu–N bonds of 2.017 (6) Å. The square coordination is expanded to elongated octahedral coordination by the

bridging H₂O molecules with Cu–O(H₂O) distances of 2.625 (2) Å and an angle Cu–O(H₂O)–Cuⁱ of 164.2 (5)°.

Introduction. The interaction of imidazole and benzimidazole or their derivatives with transition-metal ions is believed to be important in determining the activity of many biologically important molecules (Sundberg & Martin, 1974). In proteins, the imidazole groups of histidine residues are known to be metal-binding sites (Freeman, 1967). The behaviour of imidazole groups as ligands has hitherto been charac-