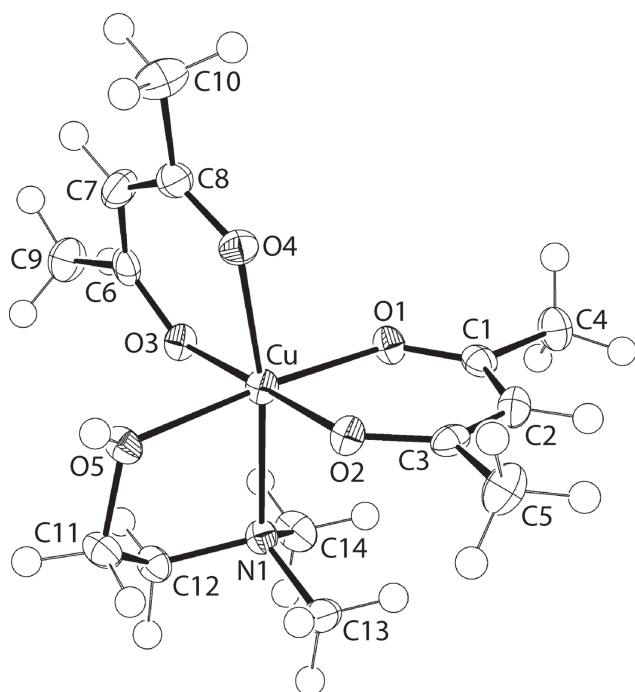


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# Crystal structure of bis(acetylacetonato- $\kappa^2O,O'$ )-(ethanolamine- $\kappa^2N,O$ )copper(II), $C_{14}H_{25}CuNO_5$



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## Abstract

$C_{14}H_{25}CuNO_5$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 7.7319(3)$  Å,  $b = 9.9198(5)$  Å,  $c = 11.6827(5)$  Å,  $\alpha = 81.866(4)^\circ$ ,  $\beta = 75.576(4)^\circ$ ,  $\gamma = 74.562(4)^\circ$ ,  $V = 833.78(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{gt}(F) = 0.0287$ ,  $wR_{ref}(F^2) = 0.0807$ ,  $T = 100(2)$  K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

Crystal:	Blue prism
Size:	0.20 × 0.15 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
$\mu$ :	1.33 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{max}$ , completeness:	25.2°, >99%
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	6693, 2993, 0.020
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2\sigma(I_{obs})$ , 2850
$N(param)_{refined}$ :	199
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

## Source of material

All chemicals and solvents were used as purchased without further purification. The melting point of the complex was measured on a Mel-Temp II digital melting point apparatus and was uncorrected. The IR spectrum was measured on a Bruker Vertex 70v FTIR spectrophotometer from 4000 to 400 cm<sup>-1</sup>.

Bis(acetylacetonato)copper(II) was synthesized according to the literature method [5]. Bis(acetylacetonato)copper(II) (0.26 g, 1 mmol) and *N,N*-dimethylaminoethanol (Sigma-Aldrich, 0.18 g, 2 mmol) were dissolved in ethanol (25 mL) and refluxed for 3 h. The filtrate was evaporated until a light-blue precipitate was obtained. The precipitate was washed with *n*-hexane and recrystallised from its methanol solution. Light-blue crystals were obtained upon slow evaporation of the filtrate. Yield: 0.28 g (34%). M.pt: >573 K. IR (cm<sup>-1</sup>) 1576 (s)  $\nu$ (C–N), 1521 (m)  $\nu$ (C–O), 1066 (s)  $\nu$ (C–O), 1017 (m)  $\nu$ (C–O).

## Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with  $U_{iso}(H) = 1.2–1.5U_{eq}(C)$ . The O-bound H-atom was located from difference Fourier maps and then refined with O–H =  $0.84 \pm 0.01$  Å, and with  $U_{iso}(H) = 1.5U_{eq}(O)$ .

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	$U_{iso}^*/U_{eq}$
Cu	0.56895(3)	0.51741(3)	0.76281(2)	0.01278(11)
O1	0.7586(2)	0.44364(16)	0.61990(12)	0.0138(3)
O2	0.6933(2)	0.35962(16)	0.86834(12)	0.0128(3)
O3	0.4413(2)	0.67769(16)	0.66269(13)	0.0138(3)
O4	0.7137(2)	0.64086(16)	0.80112(13)	0.0147(3)
O5	0.3553(2)	0.58506(17)	0.90843(13)	0.0143(3)
H5O	0.362(4)	0.604(3)	0.9729(13)	0.021*
N1	0.3764(2)	0.40014(19)	0.74762(15)	0.0125(4)
C1	0.8800(3)	0.3304(2)	0.61609(19)	0.0139(4)
C2	0.9146(3)	0.2362(2)	0.71505(19)	0.0157(5)
H2	1.006858	0.151833	0.699858	0.019*
C3	0.8259(3)	0.2559(2)	0.83238(19)	0.0134(4)
C4	0.9971(3)	0.2949(3)	0.49525(19)	0.0187(5)
H4A	0.917539	0.298797	0.440763	0.028*
H4B	1.076697	0.200235	0.500969	0.028*
H4C	1.073127	0.362632	0.465428	0.028*
C5	0.8881(3)	0.1479(2)	0.9273(2)	0.0198(5)
H5A	0.943719	0.189436	0.975965	0.030*
H5B	0.979090	0.067826	0.890309	0.030*
H5C	0.782131	0.116078	0.977387	0.030*
C6	0.4456(3)	0.8044(2)	0.66060(18)	0.0148(4)
C7	0.5564(3)	0.8541(2)	0.7141(2)	0.0187(5)
H7	0.544212	0.952659	0.706524	0.022*
C8	0.6836(3)	0.7722(2)	0.77759(19)	0.0155(5)
C9	0.3184(3)	0.9088(2)	0.5933(2)	0.0223(5)
H9A	0.347115	0.884856	0.510966	0.033*
H9B	0.334657	1.003191	0.594665	0.033*
H9C	0.190644	0.906364	0.630368	0.033*
C10	0.7988(4)	0.8448(3)	0.8233(2)	0.0244(5)
H10A	0.763133	0.840837	0.910104	0.037*
H10B	0.778927	0.942971	0.790957	0.037*
H10C	0.929183	0.797575	0.798602	0.037*
C11	0.2038(3)	0.5221(2)	0.92577(19)	0.0160(5)
H11A	0.087672	0.588187	0.960320	0.019*
H11B	0.220929	0.436283	0.980597	0.019*
C12	0.1966(3)	0.4859(2)	0.80598(19)	0.0148(4)
H12A	0.100775	0.433255	0.815897	0.018*
H12B	0.163003	0.573248	0.755372	0.018*
C13	0.4072(3)	0.2570(2)	0.8052(2)	0.0187(5)
H13A	0.307256	0.215299	0.801758	0.028*
H13B	0.410027	0.259934	0.888204	0.028*
H13C	0.524775	0.200327	0.764110	0.028*
C14	0.3749(3)	0.3929(3)	0.62278(19)	0.0187(5)
H14A	0.492150	0.333995	0.583543	0.028*
H14B	0.357440	0.487526	0.582496	0.028*
H14C	0.273952	0.352278	0.619282	0.028*

### Comment

Bis(acetylacetonato)copper(II), Cu(acac)<sub>2</sub>, and derivatives have been long known to form stable 5- and 6-coordinate complexes when also complexed with monodentate nitrogen donor ligands [6]. In the case of bidentate ligands, there are at least two possible reaction outcomes, namely i) the formation

of a six-coordinate copper complex by the addition of the bidentate ligand or ii) the replacement of the acetylacetonato ligand(s) resulting in the formation of a new copper complex [6, 7]. The reactions of Cu(acac)<sub>2</sub>, and derivatives, with bidentate *N,N* ligands have been the most frequently investigated, with very few examples of analogous reactions with potentially *N,O* bidentate ligands found in the literature. A relevant example of the latter is the bis(hexafluoroacetylacetonato)copper(II) complex with *N,O*-chelating ethanolamine, which was prepared to evaluate its suitability as a synthetic precursor for copper thin films in the absence of an external reductant [8]. Herein, we report the synthesis and X-ray structure determination of the parent Cu(acac)<sub>2</sub> complex with ethanolamine, (I).

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The copper(II) atom is bis-chelated by two acac anions and a *N,O*-chelating ethanolamine molecule. The Cu—O(acac) bond lengths formed by the O1-acac ligand are not equivalent, indicating an asymmetric mode of coordination, i.e. Cu—O1, O2 = 2.0070(15) and 2.0340(15) Å. These differences are also reflected in the associated C—O bond lengths with the shorter C1—O1 bond [1.256(3) Å] involving the more tightly bound O1 atom and the longer C3—O2 bond [1.278(3) Å] involving the less tightly bound O3 atom. This disparity in the Cu—O1, O2 bond lengths can be traced, in part, to the weak *trans* influence exerted by the weakly bound hydroxy-O5 donor atom of the neutral ethanolamine ligand; the O2 atom also participates in a hydrogen bonding interaction in the crystal (see below). For the O3-acac ligand the Cu—O3, O4 bond lengths are 2.0207(15) and 2.0216(15) Å, respectively, indicating a symmetric mode of coordination. For the ethanolamine ligand, the hydroxy-O5 atom forms the longest Cu—O distance in (I), i.e. 2.0992(15) Å; the Cu—N bond length is 2.1710(18) Å. The N<sub>2</sub>O<sub>4</sub> donor set defines a distorted octahedral geometry with the three O1—Cu—O5, O2—Cu—O3 and O4—Cu—N1 *trans* angles being 174.91(6), 178.13(6) and 169.98(6)°, respectively. The mode of coordination of the acac ligands leads to the formation of six-membered chelate rings, neither of which is strictly planar. The best description of the configuration in each case in an envelope with the Cu atom being the flap atom, i.e. for the O1-chelate ring, the Cu atom lies 0.170(2) Å out of the plane through the remaining five atoms (O1, O2, C1—C3) which has a r.m.s. deviation = 0.0087 Å; the equivalent values for the O3-chelate are 0.238(2) and 0.0094 Å, respectively. The five-membered chelate ring defined by the chelating ethanolamine ligand, comprising the Cu, O5, N1, C11 and C12 atoms, has the most pronounced envelope configuration in (I) with the C12 atom lying 0.642(3) Å out of the plane through the remaining four atoms (r.m.s. deviation = 0.0102 Å).

The most prominent feature of the supramolecular association in the crystal is the formation of centrosymmetric dimeric aggregates sustained by hydroxy-O—H...O(acac) hydrogen bonding [ $O5-H5O \cdots O2^i$ :  $H5O \cdots O2^i = 1.862(16)$  Å,  $O5 \cdots O2^i = 2.655(2)$  Å with angle at  $H5O = 163(3)^\circ$  for symmetry operation (i)  $1 - x, 1 - y, 2 - z$ ]. These interactions involve the less tightly coordinating O2 atom (see above) and give rise to a non-planar eight-membered  $\{\cdots OHCuO\}_2$  synthon. The dimeric aggregates are connected into a supramolecular chain approximately parallel to  $[\bar{1} 0 3]$  by methyl-C—H...O(acac) interactions [ $C4-H4c \cdots O1^{ii}$ :  $H4c \cdots O1^{ii} = 2.55$  Å,  $C4 \cdots O1^{ii} = 3.530(3)$  Å with angle at  $H4c = 174^\circ$  for (ii)  $2 - x, 1 - y, 1 - z$ ]. The chains assemble in the crystal without directional interactions between them.

A further analysis of the supramolecular association was performed by calculating the Hirshfeld surfaces and two-dimensional fingerprint plots, i.e. both full and delineated plots, using established protocols [9] and Crystal Explorer [10]. The consideration of the supramolecular association described in detail above leads to supramolecular chains, surface contacts of the type  $O \cdots H/H \cdots O$  [14.3%] make a significant contribution. The most dominant surface contacts are  $H \cdots H$  contacts, contributing in total 78.8% of all contacts in the crystal of (I) with the only other contribution to the surface contacts being from  $C \cdots H/H \cdots C$  contacts [6.9%].

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