One-dimensional self-assembly of bis(3-benzylpentane-2,4-dionato)copper(II) in the solid state, mediated by weak C—H···O hydrogen bonding

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In the title complex, $[\mathrm{Cu}(C_{12}H_{13}O_2)_2]$, the copper(II) ion lies on a crystallographic centre of symmetry and exhibits a square-planar coordination environment formed by four O atoms of two chelate β-diketonate ligands. The nearest neighbours of the copper(II) ion in the apical direction are two α-C atoms of β-diketonate ligands, 3.263 (2) Å away from the metal ion. Molecules in the crystal are stacked face-to-face and held together by weak C—H···O hydrogen bonding and π–π stacking interactions.

Comment

Copper(II) β-diketonate molecules are often planar and coordinatively unsaturated. As a means of achieving coordinative saturation the molecules readily self-assemble by way of weak intermolecular forces. Oligomers and polymers that form in such a way exhibit physical and chemical properties that render the compounds interesting in the context of materials science (Soldatov *et al.*, 2003).

(I)
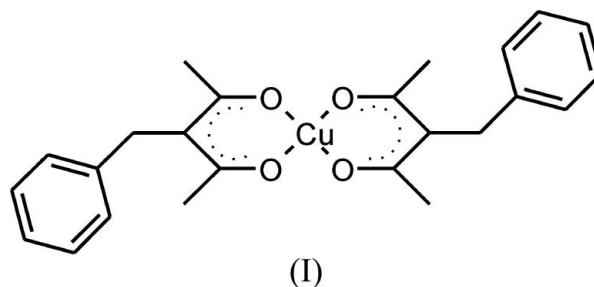
As a part of a study on the effects of weak interactions on the self-assembly properties of copper(II) β-diketonates, a series of β-diketonate ligands carrying sterically demanding groups in the α-position was prepared, including 3-benzylpentane-2,4-dione, α(Bzl)Hacac (Judaš & Kaitner, 2005).

In this paper we report the crystal structure of bis(3-benzylpentane-2,4-dionato)copper(II), $\mathrm{Cu}[\alpha(\mathrm{Bzl})\mathrm{acac}]_2$, (I).

In the $\mathrm{Cu}[\alpha(\mathrm{Bzl})\mathrm{acac}]_2$ complex molecule, which possesses a crystallographically imposed centre of symmetry (Fig. 1), four O atoms of two β-diketonato ligands surround the copper(II) ion to form a coordination environment that is square-planar by symmetry. The six-membered chelate rings are folded at an angle of 2.5 (3)° about the O1···O2 vector. The phenyl ring of the benzyl substituent is almost perpendicular to the chelate mean plane [dihedral angle 81.00 (7)°]. The significant distortion of the tetrahedral configuration of atom C6, reflected in the value of the C3—C6—C7 angle of 114.06 (15)°, is most probably caused by the effects of molecular packing rather than intramolecular steric hindrance.
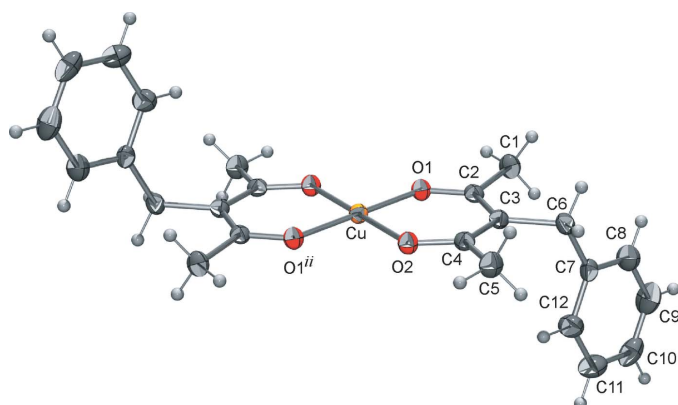
Figure 1
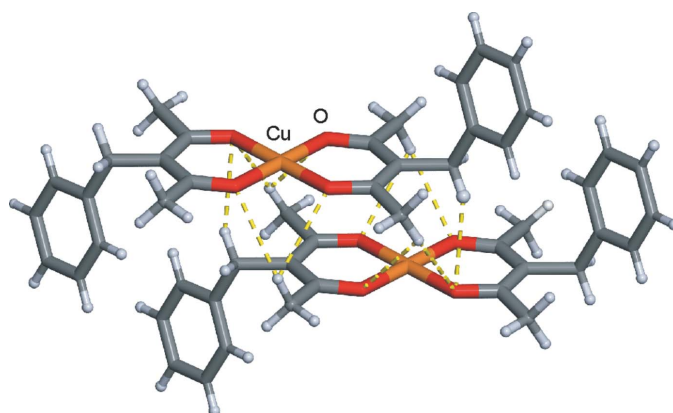A view of (I), showing 30% probability displacement ellipsoids. [Symmetry code: (ii) $-x, -y, -z$.]

Figure 2
A crystal packing diagram of (I), showing cooperative C—H···O hydrogen bonding (dashed lines) between the molecules.

Molecules are linked together in the crystal structure by several weak cooperative C—H···O hydrogen bonds (Table 1). Specifically, the C1···O1[i] and C5···O2[i] hydrogen bonds [symmetry code: (i) $1 + x, y, z$] are responsible for the bending of the carbon backbone of the molecule (Fig. 2), so as to tilt the atoms C1 and C5 out of the plane defined by atoms C2, C3, C4, O1, O2 and Cu by 0.142 (4) and 0.165 (4) Å, respectively.

The molecules in the crystal structure exhibit significant π–π stacking interactions involving chelate rings. In summary, self-assembly of copper complex molecules through C–H···O hydrogen bond and π–π stacking forces link the molecules into one-dimensional ribbons running parallel to the *a* axis (Fig. 3).

Comparison of the structures of the title compound and its analogue bis(pentane-2,4-dionato)copper(II) (Starikova & Shugam, 1969; Lebrun *et al.*, 1986) suggests that the introduction of a bulky benzyl substituent at the α-position of the ligand affects the crystal structure more than the molecular structure of the bis(chelato)copper(II) complex.

Experimental

The ligand 3-benzylpentane-2,4-dione was prepared from sodium acetylacetonate and benzyl bromide by a previously described method (Morgan & Taylor, 1925) as a yellow oil. The title compound was prepared by the reaction of freshly prepared 3-benzylpentane-2,4-dione with copper(II) acetate in ethanol using triethylamine as a catalyst. Specifically, copper(II) acetate monohydrate (0.25 g, 1.3 mmol) was dissolved in hot ethanol (35 ml) containing a few drops of triethylamine. The ligand solution was prepared separately by dissolving 3-benzylpentane-2,4-dione (0.50 g, 2.6 mmol) in ethanol (10 ml). The hot solution of the ligand was added dropwise to the stirred hot solution of copper(II) acetate and catalyst until a precipitate of metallic grey colour separated. The solid was filtered off by suction and washed with one portion of cold ethanol, one portion of distilled water and one further portion of cold ethanol. The product was dried and recrystallized from benzene (yield 71%). Single crystals of the title compound were prepared by a diffusion method. A warm ethanol solution (328 K) of the complex was overlayed with *n*-hexane (5 ml) to yield long and fragile needles of Cu[α(Bzl)acac]$_2$. Thermal analyses (thermo-gravimetric and differential scanning calorimetry) of purified Cu[α(Bzl)acac]$_2$ were performed using
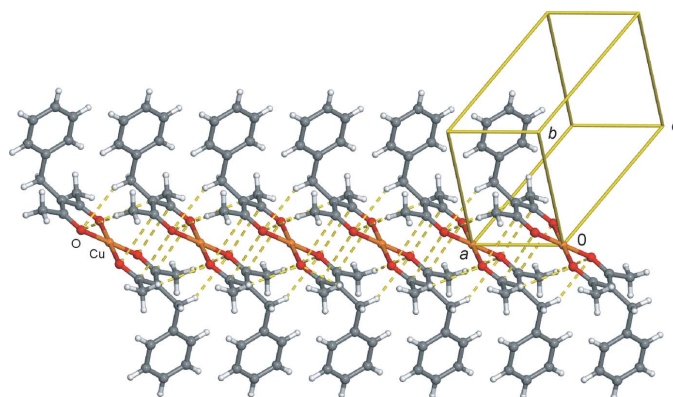

Figure 3
Self-assembly of molecules of (I) through C—H···O hydrogen-bond and π–π-stacking forces (dashed lines) into one-dimensional ribbons parallel to the *a* axis.

Mettler thermal analysis modules. The complex compound begins to melt with decomposition at 449 K in an oxygen atmosphere. In a nitrogen atmosphere the complex melts at 482 K, $\Delta H_{fus} = 47.3$ kJ mol^{-1}.

Crystal data

[Cu(C$_{12}$H$_{13}$O$_2$)$_2$]	$D_m = 1.38$ Mg m^{-3}
$M_r = 441.99$	D_m measured by flotation in
Triclinic, $P\bar{1}$	Thoulet solution
$a = 4.9124$ (13) Å	Mo $K\alpha$ radiation
$b = 9.9691$ (2) Å	Cell parameters from 40
$c = 11.887$ (3) Å	reflections
$\alpha = 110.970$ (14)°	$\theta = 11$–17°
$\beta = 99.044$ (12)°	$\mu = 1.07$ mm^{-1}
$\gamma = 98.254$ (12)°	$T = 293$ (2) K
$V = 524.1$ (2) Å^3	Needle, black
$Z = 1$	$0.80 \times 0.17 \times 0.13$ mm
$D_x = 1.400$ Mg m^{-3}	

Data collection

Philips PW1100 diffractometer	2132 reflections with $I > 2\sigma(I)$
ω scan	$R_{int} = 0.026$
Absorption correction: ψ scan	$\theta_{max} = 27.0°$
(North *et al.*, 1968)	$h = -6 \rightarrow 6$
$T_{min} = 0.770$, $T_{max} = 0.867$	$k = -12 \rightarrow 12$
4582 measured reflections	$l = -15 \rightarrow 15$
2291 independent reflections	

4 standard reflections
frequency: 60 min
intensity decay: 2.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 0.086P]$
$wR(F^2) = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
2291 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
135 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
H-atom parameters constrained	

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$B\cdots$O1^i	0.96	2.79	3.684 (3)	156
C5—H5$C\cdots$O2^i	0.96	2.88	3.734 (3)	149
C6—H6$B\cdots$O1^i	0.97	2.78	3.604 (2)	143

Symmetry code: (i) $x + 1, y, z$.

H atoms were positioned geometrically, with C—H distances of 0.93 Å for phenyl, 0.97 Å for methylene and 0.96 Å for methyl groups. The H atoms were included in the refinement using the riding-model approximation. U_{iso}(H) were defined as 1.2U_{eq} of the parent C atoms for phenyl and methylene groups and 1.5U_{eq} of the parent C atoms for the methyl groups.

Data collection: *STADI4* (Stoe & Cie, 1995); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *MERCURY* (Bruno *et al.*, 2002), *RasTop* (Valadon, 2004) and *POVRay* (Persistence of Vision Pty, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Judaš, N. & Kaitner, B. (2005). *Acta Cryst.* E**61**, o4008–o4010.
Lebrun, P. C., Lyon, W. D. & Kuska, H. A. (1986). *J. Crystallogr. Spectrosc. Res.* **16**, 889–891.
Morgan, G. T. & Taylor, C. J. A. (1925). *J. Chem. Soc.* **797**, 127–135.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Persistence of Vision Pty (2004). *Persistence of Vision Raytracer* (*POV-Ray*). Version 3.6. http://www.povray.org/download/.
Sheldrick, G. M. (1997) *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Soldatov, D. V., Tinnemans, P., Enright, G. D., Ratcliff, C. I., Diamente, P. R. & Ripmeester, J. A. (2003). *Chem. Mater.* **15**, 3826–3840.
Starikova, Z. A. & Shugam, E. A. (1969). *Zh. Strukt. Khim. (Russ. J. Struct. Chem.)*, **10**, 290–293.
Stoe & Cie (1995). *STADI4* (Version 1.05b) and *X-RED* (Version 1.05). Stoe & Cie, Darmstadt, Germany.
Valadon, P. (2004). *RasTop*. Version 2.0.3. Philippe Valadon, PO Box 928064, La Jolla, CA 92192-8064, USA. http://www.geneinfinity.org/rastop/.