A new polymorph of tetra-μ-benzoato-$\kappa^8O:O'$-bis[(dimethyl sulfoxide-κO)copper(II)]

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.134
Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

This paper reports a new polymorph of the title compound, [Cu$_2$(C$_7$H$_5$O$_2$)$_4$(C$_2$H$_6$OS)$_2$], a paddlewheel dimer of a tetra-benzoate-bridged dinuclear copper(II) core, with two apically positioned is dordered dimethyl sulfoxide ligands. The Cu—Cu distance is 2.6490 (6)Å.

Comment

Copper(II) carboxylates are based on a robust dinuclear paddlewheel unit to which additional ligands are attached by coordinating in the apical positions. Their simple syntheses have made copper(II) carboxylates interesting for materials science, especially for constructing porous metal–organic frameworks (Papaefstathiou & MacGillivray, 2002, 2003). The previously reported structure of the title compound, (I) (Melník & Dunaj-Jurčo, 1984), with the unit cell a = 19.030 (8) Å, b = 15.494 (9)Å, c = 23.828 (11) Å and β = 103.73 (4)°, space group $C2/c$, is a polymorph of the structure reported here.
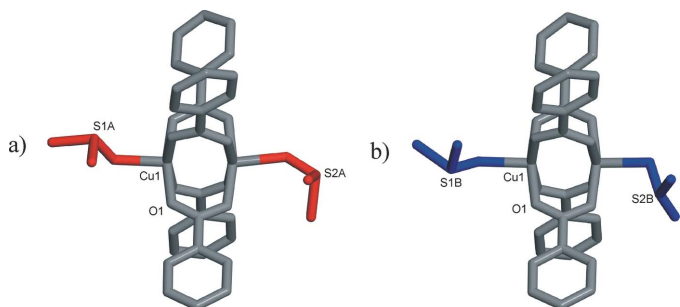

(II)
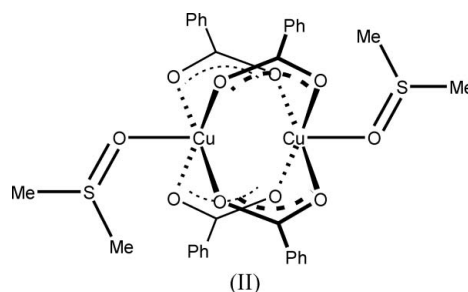
The previously published structure is assigned as polymorph I and the structure reported here as polymorph II. Both polymorphs reveal discrete paddlewheel complexes (Fig. 1). Their geometries are compared in Table 1. However, differences are observed in the apically positioned dimethylsulfoxide (dmso) ligands. The dmso ligands in polymorph II are disordered over two positions with relative occupancies 0.90 and 0.10 (Fig. 2), which affects the packing.

The crystal packing reveals cavities (*ca* 25 Å^3) occurring between six phenyl groups of six molecules. The presence of such cavities explains the different packing densities of polymorphs I and II (1.49 and 1.476 Mg m^{-3}, respectively). In the crystal packing of polymorph II, there are channels running parallel to the crystallographic a direction, into which DMSO ligands are oriented (Fig. 3).

The most significant contacts between neighbouring molecules in the crystal structure of polymorph II include C—H···O and C—H···π interactions (Nishio, 2004), most of which involve the methyl groups of the DMSO ligands (Table 2 and Fig. 4).
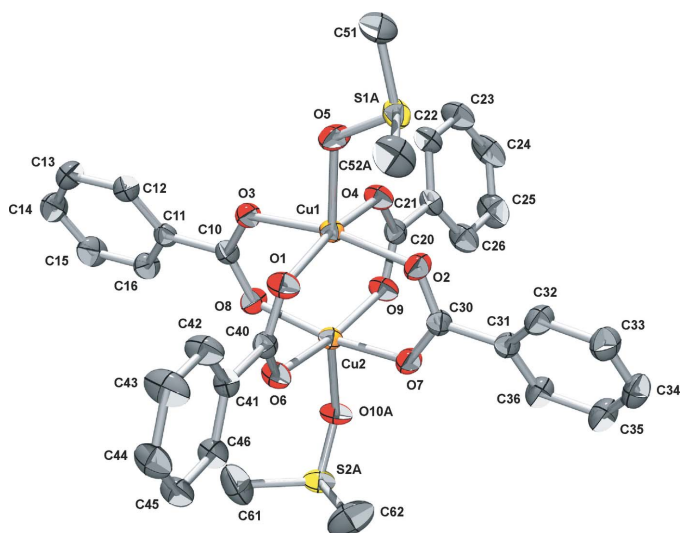
Figure 1
The asymmetric unit of polymorph II; the labelling scheme has been adopted from polymorph I. Displacement ellipsoids are drawn at the 30% probability level. For clarity, H atoms and atoms from the minor component of the disorder have been omitted.

Figure 3
Mixed ball-and-stick and wireframe representations of a channel in the polymorph II structure, viewed along (*a*) the crystallographic *a* axis and (*b*) the crystallographic *b* axis. The DMSO molecules are shown in blue.

Figure 2
Wireframe models of the complex molecule, showing disordered DMSO molecules with (*a*) 90% and (*b*) 10% occupancy. The atoms of the paddlewheel core are coloured gray, while the atoms of the DMSO ligands are shown in red and blue.

Figure 4
A crystal packing diagram showing the C—H···π interactions (dashed lines) between four paddlewheel units.
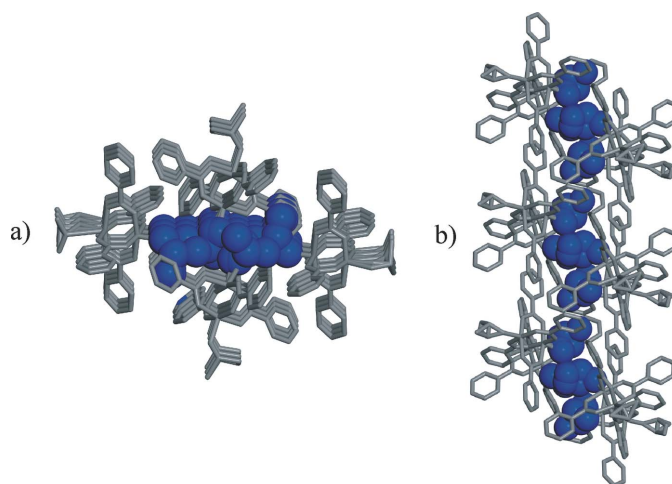
Experimental

The new polymorph of the title compound was obtained as a by-product during the synthesis of a copper(II) complex with 3-benzoylpentane-2,4-dione. Recrystallisation of the resulting reaction product from hot dimethyl sulfoxide yielded polymorph II in the form of dark-green prisms.
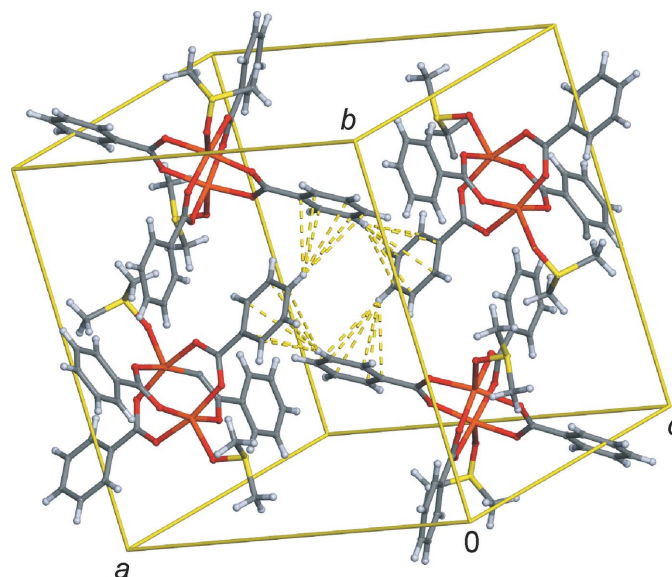
Crystal data

$[Cu_2(C_7H_5O_2)_4(C_2H_6OS)_2]$	$D_x = 1.476$ Mg m^{-3}
$M_r = 767.78$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 35
$a = 12.0320$ (7) Å	reflections
$b = 17.0770$ (8) Å	$\theta = 11$–17°
$c = 17.2590$ (11) Å	$\mu = 1.41$ mm^{-1}
$\beta = 103.040$ (5)°	$T = 291$ (1) K
$V = 3454.8$ (3) Å^3	Prism, green
$Z = 4$	$0.53 \times 0.47 \times 0.41$ mm

Data collection

Philips PW1100 diffractometer	$R_{int} = 0.020$
ω scans	$\theta_{max} = 27.0°$
Absorption correction: ψ scan	$h = -15 \rightarrow 14$
(North *et al.*, 1968)	$k = 0 \rightarrow 21$
$T_{min} = 0.396$, $T_{max} = 0.552$	$l = 0 \rightarrow 22$
7794 measured reflections	4 standard reflections
7550 independent reflections	frequency: 120 min
4830 reflections with $I > 2\sigma(I)$	intensity decay: 3.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0785P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 0.1835P]$
$wR(F^2) = 0.134$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.002$
7550 reflections	$\Delta\rho_{max} = 0.4$ e Å^{-3}
450 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}
H-atom parameters constrained	

Table 1
Comparative geometric parameters (Å) for polymorphs II and I.

Distance	Polymorph II	Polymorph I
Cu1—Cu2	2.6490 (6)	2.627 (2)
Cu1—O1	1.963 (3)	1.96 (1)
Cu1—O2	1.988 (3)	1.93 (1)
Cu1—O3	1.975 (3)	1.97 (1)
Cu1—O4	1.966 (3)	1.99 (1)
Cu1—O5	2.135 (2)	2.16 (1)
Cu2—O6	1.979 (3)	1.95 (1)
Cu2—O7	1.946 (3)	1.95 (1)
Cu2—O8	1.973 (3)	2.00 (1)
Cu2—O9	1.950 (3)	1.95 (1)
Cu2—O10*A*	2.169 (4)	2.17 (1)
Cu2—O10*B*	2.17 (2)	

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C51—H51*B*$\cdots$O9[i]	0.96	2.60	3.471 (6)	151
C52*A*—H52*C*$\cdots$C21[i]	0.96	2.74	3.687 (8)	171
C62—H62*D*$\cdots$C22[ii]	0.96	2.70	3.505 (8)	142
C35—H35$\cdots$C12[ii]	0.93	2.87	3.627 (6)	140
C62—H62*B*$\cdots$C14[iii]	0.96	2.88	3.726 (8)	148
C61—H61*C*$\cdots$C46[iii]	0.96	2.85	3.791 (8)	165

Symmetry codes:(i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $2 - x, 1 - y, -z$.

Both molecules of dimethyl sulfoxide in the asymmetric unit were found to be disordered over two sites, with relative population parameters 0.90 and 0.10. For the dimethyl sulfoxide molecule that contains disordered atoms S1*A* and S1*B* (population parameters 0.90 for S1*A* and 0.10 for S1*B*), atom C51 was refined as common to both disordered sites. In the dimethyl sulfoxide molecule comprising disordered atoms S2*A* and S2*B* (population parameters 0.90 for S2*A* and 0.10 for S2*B*), both C atoms (C61 and C62) were found to be common to both disordered forms of the molecule. The positions of

all H atoms were calculated, with C—H distances of 0.95 for phenyl and 0.96 Å for methyl groups. The H atoms were included in the refinement using the riding-model approximation, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}$ or $1.5U_{\mathrm{eq}}$ of the parent C atom for phenyl and methyl groups, respectively. The relative population parameters for the disordered ligands were estimated during the refinement and then blocked.

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