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Two new polymorphs of *trans*-bis(hinokitiolato)copper(II)

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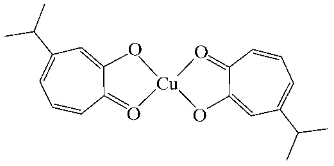
The title complex [systematic name: *trans*-bis(3-isopropyl-7-oxocyclohepta-1,3,5-trienolato)copper(II)], $[Cu(C_{10}H_{11}O_2)_2]$, is a substance possessing antimicrobial activity. The compound crystallizes in a number of polymorphic forms, the structures for two of which are reported here. Stacks of square-planar molecules exhibiting weak intermolecular copper–olefin π interactions (not observed in earlier reports on this substance) are described. The molecules have crystallographically imposed inversion symmetry, with stacking and copper–olefin π distances ranging from 3.226 (2) to 3.336 (1) Å.

Comment

Metal complexes of tropolone derivatives have engaged the interest of researchers in such diverse areas as materials science and medicinal chemistry. Some of that interest has been focused on hinokitiol (β-thujaplicin), a tropolone and natural product first isolated from *Chamaecyparis taiwanensis* (Nozoe, 1936). Hinokitiol and its metal complexes have since been shown to exhibit a wide variety of biological activities, *e.g.* antibacterial, antifungal and antiviral activities, among others (Miyamoto *et al.*, 1998; Arima *et al.*, 2003; Morita *et al.*, 2003). Hinokitiol complexes of Cu, Zn and Sn have also been reported to be effective in oral care formulations (Creeth *et al.*, 2000), and the structures of a copper hinokitiol monomer and a modification containing both monomers and dimers have been published as part of those studies (Barret *et al.*, 2002). We have observed, however, that the title monomer, *i.e.* *trans*-bis(hinokitiolato)copper(II), (I), actually exists in a number of additional polymorphic forms: a triclinic form, (I*a*), and a new monoclinic form, (I*b*), have been obtained from ethanol–water solutions and are reported here. The previously published monoclinic form, (I*c*), was obtained from ethanol. Views of the molecules of forms (I*a*) and (I*b*) are given in Fig. 1, and selected distances and angles are summarized in Table 1.

Form (I*a*) crystallizes in the triclinic space group $P\overline{1}$, while forms (I*b*) and (I*c*) crystallize in the monoclinic space group $P2_1/c$. In all three forms, the Cu atoms reside on centers of crystallographic inversion symmetry and have square-planar coordination geometries. The Cu—O bonds in (I*a*) are statistically non-equivalent, while those in (I*b*) are equivalent. The Cu—O bonds in (I*c*) are also equal in length, albeit significantly shorter than those observed in (I*b*). Comparable equivalent and non-equivalent Cu—O bonds have been observed in related copper–tropolonate complexes (Hasegawa *et al.*, 1997; Chipperfield *et al.*, 1998) and in copper complexes involving α- or β-hydroxy ketone ligands (Lim *et al.*, 1994; Odoko *et al.*, 2002). The O—Cu—O bite angles for the chelating hinokitiolate ligands in all three polymorphs are also statistically equivalent.



(I)

trans-Bis(hinokitiolato)copper(II) is essentially a planar molecule. The r.m.s. deviation of atoms from the least-squares plane through the molecule (excluding the isopropyl atoms) is 0.017 (2) Å for (I*a*) and 0.071 (2) Å for (I*b*). The less planar

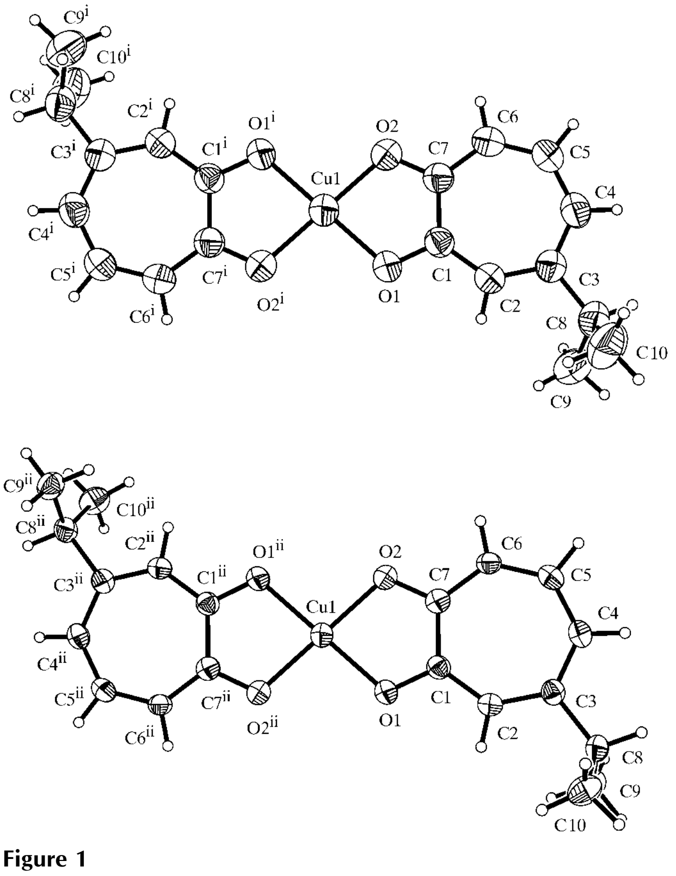


Figure 1
Polymorphs (I*a*) at 298 K (top) and (I*b*) at 200 K (bottom). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, 1-y, 2-z$; (ii) $1-x, -y, -z$.]

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nature of (I*b*) is visible in Fig. 2 as a slight folding of the molecule along the O1$\cdots$O2 and O1$^{ii}\cdots$O2^{ii} vectors [the interplanar angle between the CuO$_4$ coordination plane and each tropolone ligand plane is 172.9 (1)°; symmetry code: (ii) $1 - x, -y, -z$]. In contrast, the molecules of (I*a*) and (I*c*) are essentially planar, with corresponding interplanar angles of 178.3 (1) and 178.9 (2)°, respectively. These conformational differences in the *trans*-bis(hinokitiolato)copper(II) molecules are attributed to packing forces.

The packings of the *trans*-bis(hinokitiolato)copper(II) molecules in (I*a*) and (I*b*) share a number of similarities (Fig. 2) but differ completely from the packing observed in previously published form (I*c*). Most notably, the molecules in (I*a*) and (I*b*) pack into extended columns or stacks, while those in (I*c*) do not. Consequently, the Cu atoms in (I*a*) and (I*b*) are pseudo-six-coordinate, with weak apical interactions, while the Cu atoms in (I*c*) are formally four-coordinate. Interestingly, the apical interactions in (I*a*) and (I*b*) also differ. The apical interactions in (I*a*) are best described as involving π-electron densities distributed over the C1—C7—C6—C5—C4 portion of neighboring hinokitiolate ligands, while the apical interactions in (I*b*) involve only the C4—C5 edge of neighboring molecules. The Cu atom is 3.336 (1) Å from the centroid defined by atoms C1, C4, C5, C6 and C7 in (I*a*), and 3.226 (2) Å from the centroid of the C4—C5 bond in (I*b*). These distances are comparable to values (3.25–3.55 Å) observed for longer-range non-covalent Cu$^{II}\cdots$arene contacts (Mascal *et al.*, 2000).

Thus, the packing and stacking of molecules in (I*a*) and (I*b*) are consistent with the presence of weak apical η^5 and η^2 Cu–olefin–π interactions, respectively. The distance between the least-squares planes through adjacent molecules, or stacking distance, is 3.336 (1) Å in (I*a*) and 3.235 (2) Å in (I*b*), and the Cu$\cdots$Cu distances between neighboring molecules within the stacks are 5.1549 (3) Å in (I*a*) and 6.7470 (1) Å in (I*b*), *i.e.* a unit translation in the crystallographic *a* and *b* directions, respectively. Furthermore, as shown in Fig. 2, the molecules do not stack directly on top of one another but instead slide over each other by 3.930 (1) and 5.921 (2) Å in (I*a*) and (I*b*), respectively.

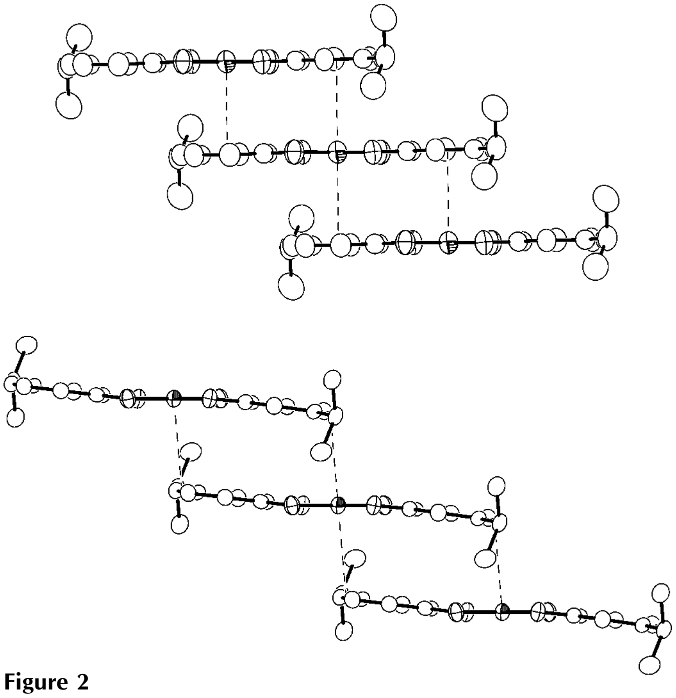

Figure 2
Stacking and π interactions in polymorphs (I*a*) (top) and (I*b*) (bottom).

The triclinic form also differs from (I*b*) in that there are weak interstack C—H$\cdots$O hydrogen-bonding interactions present in (I*a*). The C6—H6, H6$\cdots$O2^{iii} and C6$\cdots$O2^{iii} distances are 0.93, 2.51 and 3.348 (4) Å, respectively, and the C6—H6$\cdots$O2^{iii} angle is 150° [symmetry code: (iii) $1 - x, -y, 2 - z$]. Whether these hydrogen-bonding interactions contribute to the non-equivalence of the Cu—O bonds in (I*a*) is not known at this time.

Experimental

The title compound was isolated from the reaction of copper gluconate and hinokitiol (Aldrich Chemical Company) in a 1:2 molar ratio. An aqueous solution of copper gluconate was added to a solution of hinokitiol in ethanol and the mixture was stirred for 1 h. The resulting green precipitate was collected and recrystallized from aqueous ethanol. An assortment of crystal morphologies was immediately evident in the recrystallized product. Both (I*a*) and (I*b*) crystallize as green–yellow needles, but the two forms have noticeably different physical properties that aid in their identification. Crystals of (I*a*) are soft and often distort or split into layers when attempts are made to cut them. Crystals of (I*b*) are dichroic, *i.e.* green–yellow when viewed perpendicular to the 001 face and olive green when viewed perpendicular to the 100 face. The previously published polymorph, (I*c*), crystallizes as olive-green multifaceted prisms.

Polymorph (I*a*)

Crystal data

[Cu(C$_{10}$H$_{11}$O$_2$)$_2$]
$M_r = 389.92$
Triclinic, $P\overline{1}$
$a = 5.1549$ (3) Å
$b = 6.9872$ (4) Å
$c = 13.9097$ (8) Å
$\alpha = 77.747$ (3)°
$\beta = 84.255$ (3)°
$\gamma = 70.508$ (3)°
$V = 461.30$ (5) Å^3
$Z = 1$
$D_x = 1.404$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6146 reflections
$\theta = 1.5$–27.5°
$\mu = 1.20$ mm^{-1}
$T = 298$ (2) K
Needle, green–yellow
0.29 × 0.08 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: Gaussian (*SHELXTL*; Sheldrick, 1996)
$T_{\rm min} = 0.786$, $T_{\rm max} = 0.955$
6146 measured reflections
2096 independent reflections
1541 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\rm max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 9$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.107$
$S = 1.08$
2095 reflections
118 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.197P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.51$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.032 (7)

Polymorph (I*b*)

Crystal data

$[Cu(C_{10}H_{11}O_2)_2]$
$M_r = 389.92$
Monoclinic, $P2_1/c$
$a = 8.7410\ (2)$ Å
$b = 6.7470\ (1)$ Å
$c = 15.3448\ (4)$ Å
$\beta = 100.800\ (1)^\circ$
$V = 888.94\ (3)$ Å^3
$Z = 2$
$D_x = 1.457$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 670 reflections
$\theta = 2.4$–27.5°
$\mu = 1.25$ mm^{-1}
$T = 200\ (2)$ K
Needle, green–yellow
0.22 × 0.12 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: Gaussian (*SHELXTL*; Sheldrick, 1996)
$T_{min} = 0.794$, $T_{max} = 0.948$
23 670 measured reflections
2040 independent reflections
1591 reflections with $I > 2\sigma(I)$
$R_{int} = 0.076$
$\theta_{max} = 27.5^\circ$
$h = -11 \rightarrow 11$
$k = -8 \rightarrow 7$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.112$
$S = 1.12$
2040 reflections
117 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 1.192P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

	(I*a*)†	(I*b*)†	(I*c*)‡
Cu1—O1	1.915 (2)	1.918 (2)	1.900 (2)
Cu1—O2	1.901 (2)	1.913 (2)	1.904 (2)
O1—C1	1.295 (3)	1.292 (3)	1.296 (5)
O2—C7	1.289 (4)	1.293 (3)	1.293 (5)
O1—Cu1—O2	83.70 (9)	83.90 (8)	83.84 (13)
Cu1—O1—C1	113.0 (2)	112.9 (2)	113.5 (3)
Cu1—O2—C7	113.5 (2)	112.7 (2)	113.5 (3)

† This work. ‡ Barret *et al.* (2002).

All H atoms were allowed to ride on their respective C atoms, with C—H distances constrained to the *SHELXTL* (Sheldrick, 1996) default values for the specified functional groups and temperatures. The *SHELXTL* internal defaults for the tropolone, isopropyl methine and methyl H atoms are 0.93, 0.98 and 0.96 Å, respectively, for polymorph (I*a*) at 298 K, and 0.95, 1.00 and 0.98 Å for (I*b*) at 200 K. The U_{iso}(H) values were set at $1.2U_{eq}$(C) for the tropolone and isopropyl methine H atoms, and $1.5U_{eq}$(C) for the methyl H atoms.

For both forms, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SHELXTL* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990) for (I*a*) and *SHELXTL* for (I*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1457). Services for accessing these data are described at the back of the journal.

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