Bis(hinokitiolato)copper(II): modification (III)

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Bis(hinokitiolato)copper(II), Cu(hino)$_2$, exhibits both antibacterial and antiviral properties, and has been previously shown to exist in two modifications. A third modification has now been confirmed, namely tetrakis(μ_2-3-isopropyl-7-oxocyclohepta-1,3,5-trien-1-olato)bis(3-isopropyl-7-oxocyclohepta-1,3,5-trien-1-olato)tricopper(II)–bis(μ_2-3-isopropyl-7-oxocyclohepta-1,3,5-trien-1-olato)bis[(3-isopropyl-7-oxocyclohepta-1,3,5-trien-1-olato)copper(II)] (1/1), [Cu(C$_{10}$H$_{11}$O$_2$)$_2$]$_3$·[Cu(C$_{10}$H$_{11}$O$_2$)$_2$]$_2$, where 3-isopropyl-7-oxocyclohepta-1,3,5-trien-1-olate is the systematic name for the hinokitiolate anion. This new modification is composed of discrete [cis-Cu(hino)$_2$]$_2$[trans-Cu(hino)$_2$] trimers and [cis-Cu(hino)$_2$]$_2$ dimers. The Cu atoms are bridged by μ_2-O atoms from the hinokitiolate ligands to give distorted square-pyramidal and distorted octahedral Cu^{II} coordination environments. Hence, the Cu^{II} environments are CuO$_5$/CuO$_6$/CuO$_5$ for the trimer and CuO$_5$/CuO$_5$ for the dimer. Each trimer and dimer has crystallographically imposed inversion symmetry. The trimer has never been observed before, the dimer has been seen only once before, and the combination of the two together in the same lattice is unprecedented. The CuO$_5$ cores exhibit four strong basal Cu—O bonds [1.915 (2)–1.931 (2) Å] and one weak apical Cu—O bond [2.652 (2)–2.658 (2) Å]. The CuO$_6$ core exhibits four strong equatorial Cu—O bonds [1.922 (2)–1.929 (2) Å] and two very weak axial Cu—O bonds [2.911 (3) Å]. The bite angles for the chelating hinokitiolate ligands range from 83.13 (11) to 83.90 (10)°.

Comment

Hinokitiol (β-thujaplicin) and metal complexes of the hinokitiolate anion have been known for 74 years (Nozoe, 1936). The former is a natural product and of interest for its broad range of biological activities, e.g. antitumor, antibacterial, antifungal and insecticidal properties (Inamori et al., 1993, 2000; Arima et al., 2003; Morita et al., 2003), while the latter metal complexes exhibit antiviral and antimicrobial properties (Miyamoto et al., 1998; Nomiya et al., 2009). Among these compounds, the Cu complex reported by Nozoe in 1936 is arguably the most structurally intriguing. In 2002, initial

insights into the 'unusual structural chemistry of Cu^{II} hinokitiol' [also referred to as bis(hinokitiolato)copper(II) or Cu(hino)$_2$] were provided by Molloy and co-workers, who found that Cu(hino)$_2$ could be crystallized in two modifications (Barret et al., 2002). Modification (I) turned out to be monomeric trans-Cu(hino)$_2$, while modification (II) is composed of monomers and dimers, i.e. [cis-Cu(hino)$_2$]$_2$·[trans-Cu(hino)$_2$]$_2$·trans-Cu(hino)$_2$. Subsequent studies have further revealed that (I) is polymorphic (Barret et al., 2002; Nomiya et al., 2004; Arvanitis et al., 2004; Ho et al., 2009). A third modification, (III), has now been discovered and is reported here. This new modification is composed of dimers and trimers, i.e. [cis-Cu(hino)$_2$]$_2$[trans-Cu(hino)$_2$]·[cis-Cu(hino)$_2$]$_2$. Views of the trimer and dimer are given in Figs. 1 and 2, respectively, and selected bond distances and bond valences are summarized in Table 1.


(I) = trans-Cu(hino)$_2$ cis-Cu(hino)$_2$

(II) = [cis-Cu(hino)$_2$]$_2$ · [trans-Cu(hino)$_2$]$_2$ · trans-Cu(hino)$_2$

(III) = [cis-Cu(hino)$_2$]$_2$[trans-Cu(hino)$_2$] · [cis-Cu(hino)$_2$]$_2$
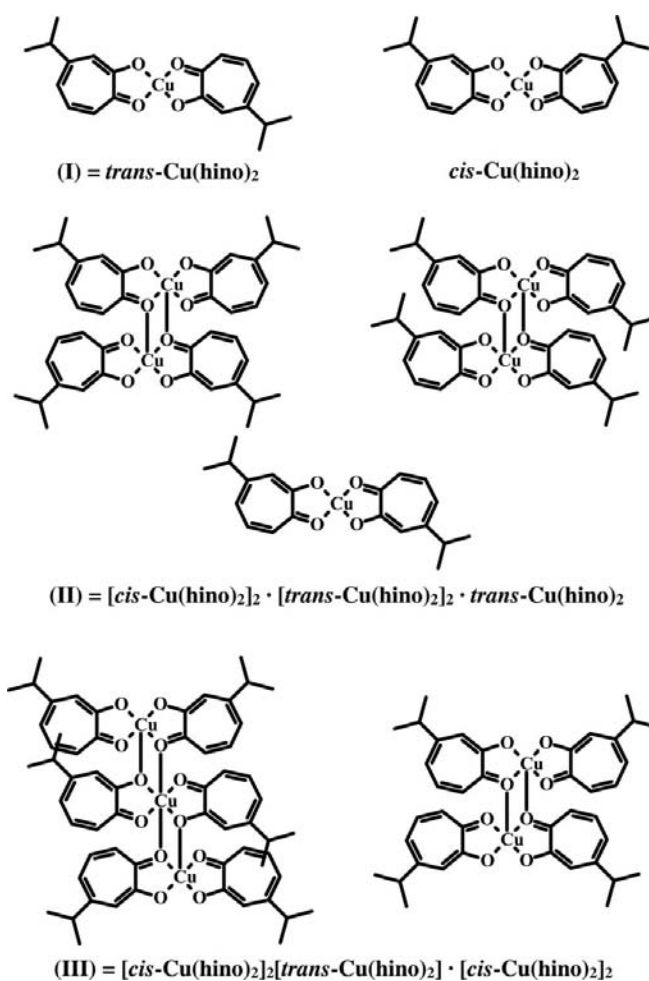
Trimeric Cu^{II} hinokitiol has never been observed before and therefore constitutes the most notable feature of this study. As shown in Fig. 1, the trimer consists of a single planar trans-Cu(hino)$_2$ moiety sandwiched between two visibly twisted cis-Cu(hino)$_2$ moieties. Atom Cu1 is situated at Wyckoff position 1h [space group $P\bar{1}$ (No. 2)], requiring that the trimer possess crystallographic inversion symmetry. Atoms Cu1, O1, O2, O1^i and O2^i are also required by symmetry to be exactly coplanar [symmetry code: (i) $-x + 1, -y + 1, -z + 1$].

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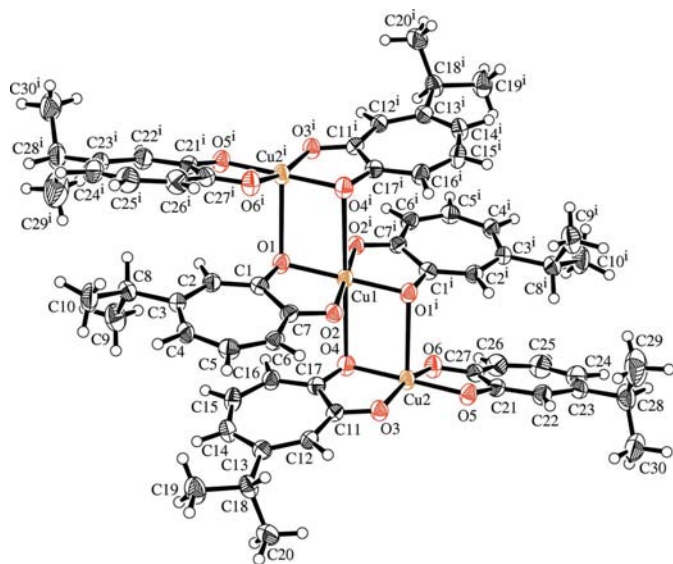
Figure 1
The *cis,trans,cis* trimer in modification (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

Figure 2
The *cis,cis* dimer in modification (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (ii) $-x$, $-y$, $-z + 2$.]

In contrast, atoms Cu2/O3–O6 in the nonplanar *cis* moieties exhibit displacements of -0.109 (1), 0.168 (1), -0.111 (1), -0.114 (1) and 0.166 (1) Å, respectively, from the least-squares plane defined by those atoms. The end-to-end distances for the Cu(hino)$_2$ moieties (excluding the isopropyl groups) are 11.358 (7) and 11.274 (6) Å for C4···C4^{i} and C14···C24, respectively. The shortening of the C14···C24 distance is consistent with the *cis* moieties being slightly bowed in addition to being twisted. Four of the six hinokitiolate ligands participate in asymmetric μ_2-O bridges to yield the final trimeric structure, with atom Cu1 having a distorted octahedral CuO$_6$ coordination geometry and atom Cu2 having a distorted CuO$_5$ square-pyramidal coordination environment. The twisting and bowing of the *cis* moieties help to facilitate the bridge bonding, and to alleviate steric repulsions between the C21–C27 and C21^{i}–C27^{i} cycloheptatriene rings and atoms H8 and H8^{i} of the central *trans* moiety, respectively.

The dimeric Cu^{II} hinokitiol component in (III), while less novel than the *cis,trans,cis* trimer, is nevertheless also unusual, having been observed only once before, *i.e.* in modification (II). The *cis,cis* dimers in (II) and (III) are quite synonymous, but the Cu atoms in both dimers are probably better described as five-coordinate with square-pyramidal environments, rather than 'four-coordinate and in a square-planar environment' (Barret *et al.*, 2002). In both (II) and (III), the *cis,cis* dimers possess crystallographically imposed inversion symmetry. For (III), the dimer is centered on Wyckoff position 1*a*, *i.e.* the mid-point between atoms Cu3 and Cu3^{ii} in Fig. 2 [symmetry code: (ii) $-x$, $-y$, $-z + 2$]. Atom Cu3 is 0.105 (1) Å above the least-squares plane defined by atoms O7–O10 and displaced towards atom O9^{ii}. The C34···C44 end-to-end distance is 11.166 (6) Å, indicating that the *cis* moieties in the dimer are even more bowed than those in the trimer. In contrast, atom
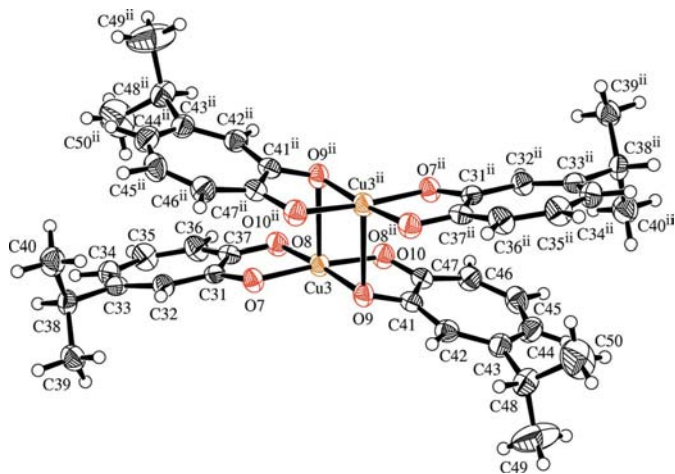
Cu1 in (II) is coplanar with atoms O1–O4. The displacements from the least-squares plane defined by these five atoms are -0.103 (1), -0.088 (2), 0.145 (2), 0.141 (2) and -0.095 (2) Å, respectively. The *cis* moieties in (II) are, however, also bowed, with the C5···C15 end-to-end distance being 11.176 (5) Å. These observations are more consistent with CuO$_5$ cores and covalent bonding, rather than CuO$_4$ cores and a fifth axial intermolecular interaction.

A bond-valence analysis (Brown, 2002, 2009) of the CuO$_x$ bonding in the *cis,trans,cis* trimer and *cis,cis* dimer is given in Table 1. The CuO$_6$ values in (III) are compared with those for bis(tropolonato)copper(II), Cu(trop)$_2$, which is most often viewed as a square-planar CuO$_4$ monomer (Robertson, 1951; Macintyre *et al.*, 1966; Berg *et al.*, 1978). The latter view has, however, been challenged by a subsequent claim that Cu(trop)$_2$ 'exists as a sandwich-type dimer' (Hasegawa *et al.*, 1997); a claim reiterated in a recent review article (Vigato *et al.*, 2009). Suffice to say that it is crystallographically impossible for discrete dimers to exist in that 1997 determination. Cu(trop)$_2$ is either a solid-state monomer or, as entertained below, possibly a solid-state polymer with CuO$_6$ bonding. Finally, the CuO$_5$ values for (III) are compared with those for (II). For completeness, the *trans,trans* dimer values for (II) are also provided.

The CuO$_6$ equatorial bonds in the *trans* moiety of the trimer are in the range 1.922 (2)–1.929 (2) Å and are noticably longer than the range of 1.900 (2)–1.918 (2) Å observed in the *trans*-Cu(hino)$_2$ monomer, (I). This lengthening of the Cu—O bonds is consistent with oligomerization; the Cu—O bonds in the *trans,trans* dimer in (II) also experience a similar lengthening [1.915 (2)–1.939 (2) Å]. The CuO$_6$ axial bonds in (III) are long at 2.911 (3) Å, while those in Cu(trop)$_2$ are even longer at 3.144 (2) Å. The comparable literature values for CuO$_6$ equatorial and axial bonds are 1.908 (2)–1.948 (6) and 2.797 (2)–2.948 (2) Å, respectively (Table 2). The CuO$_6$ average bond valence, bond-valence sum, s/s' and distortion index ΔR are 0.355, 2.128, 0.101–1.462 and 0.191, respectively,

for (III), and 0.358, 2.150, 0.053–1.475 and 0.266, respectively, for Cu(trop)$_2$, while the literature s/s' and ΔR values are 0.07–1.50 and 0.048–0.146, respectively, for Jahn–Teller-distorted CuO$_6$ octahedra (Brown, 2006). All of the numerical values for (III) are in excellent agreement with the presence of a Jahn–Teller-elongated CuO$_6$ octahedron. Cu(trop)$_2$, on the other hand, is at or beyond the limits of such a description. While axial bonds beyond 3 Å do potentially exist (see Table 2), Cu(trop)$_2$ is probably better described as a square-planar CuO$_4$ monomer.

The CuO$_5$ basal bonds in the *cis* moieties in both the trimer and dimer in (III) are in the range 1.915 (3)–1.931 (3) Å and are comparable with the range of 1.919 (2)–1.933 (2) Å observed in the *cis,cis* dimer in (II). The CuO$_5$ apical bonds in (III) are 2.658 (3) and 2.652 (3) Å for the trimer and dimer, respectively, but only 2.476 (2) Å in the *cis,cis* dimer in (II). The comparable literature values for CuO$_5$ basal and apical bonds are 1.898 (3)–1.962 (3) and 2.392 (3)–2.878 (3) Å, respectively (Table 2). The CuO$_5$ average bond valence, bond-valence sum, s/s' and distortion index ΔR are 0.429, 2.157, 0.167–1.226 and 0.077, respectively, for (III), and 0.431, 2.154, 0.267–1.205 and 0.048, respectively, for (II). All of these values are in excellent agreement with the *cis* moieties in (III) having distorted CuO$_5$ square-pyramidal coordination geometries.

The trimers form hydrogen-bonded ribbons in the solid state *via* the two interactions C5—H5···O5^{iii} [C5—H5 = 0.95 Å, H5···O5^{iii} = 2.40 Å, C5···O5^{iii} = 3.328 (4) Å and C5—H5···O5^{iii} = 165°; symmetry code: (iii) $-x$, $-y + 1$, $-z + 1$] and C6—H6···O3^{iii} [C6—H6 = 0.95 Å, H6···O3^{iii} = 2.43 Å, C6···O3^{iii} = 3.302 (4) Å and C6—H6···O3^{iii} = 153°]. Chains of dimers are present, but there are no dimer–dimer hydrogen-bonding, π–π stacking or Cu···π interactions involved. The closest dimer–dimer contact is Cu3···C34^{iv} = 3.399 (4) Å [symmetry code: (iv) $-x + 1$, $-y$, $-z + 2$]. Finally, the ribbons of trimers and chains of dimers are linked *via* the two inter-actions C24—H24···O8^{v} [C24—H24 = 0.95 Å, H24···O8^{v} = 2.52 Å, C24···O8^{v} = 3.446 (5) Å and C24—H24···O8^{v} = 164°; symmetry code: (v) x, $y + 1$, z] and C45—H45···O3 [C45—H45 = 0.95 Å, H45···O3 = 2.58 Å, C45···O3 = 3.397 (5) Å, and C45—H45···O3 = 145°].

In summary, structural details have been presented for a third modification of the bioactive substance Cu^{II} hinokitiol. This new modification, (III), is [*cis*-Cu(hino)$_2$]$_2$[*trans*-Cu(hino)$_2$]·[*cis*-Cu(hino)$_2$]$_2$, containing a previously undocumented *cis,trans,cis* trimer. The results from a bond-valence analysis are consistent with the central Cu^{II} atom having a Jahn–Teller-distorted octahedral environment. The 'unusual structural chemistry of Cu^{II} hinokitiol' now encompasses six crystalline forms, *i.e.* modification (I) with four forms, (II) with one form and (III) with one form. The *trans*:*cis* ratios are 1:0, 3:2 and 1:4 for modifications (I)–(III), respectively, making (III) the most *cis*-enriched modification so far uncovered.

Experimental

Modification (III) was isolated from a mixture of assorted crystals of Cu(hino)$_2$, prepared as described by Arvanitis *et al.* (2004).

All H atoms were allowed to ride on their respective C atoms, with C—H = 0.95, 1.00 and 0.98 Å for the cycloheptatriene, methine and methyl H atoms, respectively, and with U_{iso}(H) = $1.2U_{eq}$(C) for the cycloheptatriene and methine H atoms or $1.5U_{eq}$(C) for the methyl H atoms. Bond-valence parameters for Cu and O were taken from

Table 1
Selected bond distances (Å) and bond valences (s).

The average bond valence s' is defined as $(\Sigma s)/N$, where N corresponds to the coordination number (*e.g.* 5 or 6) for the Cu atom in question.

CuO$_x$	Bond	Length	s	s/s'
CuO$_6$	Cu1—O1	1.929 (2)	0.509	1.434
In (III), trimer^a	Cu1—O2	1.922 (2)	0.519	1.462
	Cu1—O4	2.911 (3)	0.036	0.101
CuO$_5$	Cu2—O3	1.918 (2)	0.524	1.221
In (III), trimer^a	Cu2—O4	1.921 (3)	0.520	1.212
	Cu2—O5	1.917 (3)	0.526	1.226
	Cu2—O6	1.931 (2)	0.506	1.179
	Cu2—O1^i	2.658 (3)	0.071	0.166
CuO$_5$	Cu3—O7	1.915 (2)	0.528	1.225
In (III), dimer^a	Cu3—O8	1.915 (3)	0.528	1.225
	Cu3—O9	1.931 (3)	0.506	1.174
	Cu3—O10	1.921 (3)	0.520	1.206
	Cu3—O9^{ii}	2.652 (3)	0.072	0.167
CuO$_6$	Cu1—O1	1.915 (2)	0.528	1.475
In Cu(trop)$_2$^{b}	Cu1—O2	1.915 (3)	0.528	1.475
	Cu1—O1^{iv}	3.144 (2)	0.019	0.053
CuO$_5$	Cu1—O1	1.919 (2)	0.523	1.205
In (II), dimer^c	Cu1—O2	1.920 (2)	0.521	1.200
	Cu1—O3	1.932 (2)	0.505	1.164
	Cu1—O4	1.933 (2)	0.503	1.159
	Cu1—O4^{vi}	2.476 (2)	0.116	0.267
CuO$_5$	Cu2—O5	1.915 (2)	0.528	1.219
In (II), dimer^d	Cu2—O6	1.921 (2)	0.520	1.201
	Cu2—O7	1.939 (2)	0.495	1.143
	Cu2—O8	1.922 (2)	0.519	1.199
	Cu2—O8^{vii}	2.512 (2)	0.105	0.242

References: (*a*) this work; (*b*) Hasegawa *et al.* (1997) (trop is the tropolonate anion); (*c*) Barret *et al.* (2002) (*cis,cis* dimer); (*d*) Barret *et al.* (2002) (*trans,trans* dimer). Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $-x$, $-y$, $-z + 2$; (iv) x, y, $z - 1$; (vi) $-x + 1$, $-y$, $-z$; (vii) $-x + 1$, $-y$, $-z + 1$.

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Table 2
Cu—O bond lengths (Å) in selected α- and β-diketonate and dicarboxylate complexes.

Complex	CuO_x	Cu—O(basal/equatorial)	Cu—O(apical/axial)
$[Cu_2(L1)_2]^{2+}$	5	1.910 (3)–1.962 (3)	2.878 (3)
$[Cu_2(L2)_2]^{2+}$	6	1.921 (4)–1.944 (3)	3.001 (4)†
$Cu_2(L3)_4$	5	1.898 (3)–1.933 (3)	2.545 (3)‡
$Cu_2(L4)_4$	5	1.918 (4)–1.955 (4)	2.416 (4)
$Cu_4(L4)_4(OEt)_4$	5	1.934 (5)–1.952 (4)	2.561 (4)
$Cu_4(L5)_4(OMe)_4$	5	1.898 (6)–1.923 (5)	2.925 (6)†
$[Cu_4(L6)_8(H_2O)_2]^{8-}$	6	1.908 (2)–1.940 (2)	2.797 (2)–2.948 (2)
$[Cu_n(L6)_{2n}]^{2n-}$	5	1.912 (9)–1.942 (8)	2.798 (3)
$Cu_6(L7)_6(OMe)_6$	5	1.918 (6)–1.952 (5)	2.843 (7)
	6	1.923 (6)–1.948 (6)	3.019 (7)†
$Cu_6(L8)_6(OMe)_6$	5	1.915 (2)–1.932 (2)	2.392 (2)–2.418 (2)
	6	1.923 (2)–1.927 (2)	3.020 (2)†

† Potential apical or axial bonds. ‡ The published value of 2.242 (3) Å is a literature error. Notes: L1 = 1-(2-{4,10-dimethyl-7-[2-(3-oxido-2-oxo-1-pyridyl)acetyl]-1,7,10-triaza-4-azoniacyclododec-1-yl]-2-oxoethyl)-2-oxopyridin-3-olate (Ambrosi *et al.*, 2005); L2 = 1-[2-(methyl{2-[methyl(2-{methyl[2-(3-oxido-2-oxo-1-pyridyl)acetyl]amino}ethyl)-ammonio]ethyl}amino)-2-oxoethyl]-2-oxopyridin-3-olate (Ambrosi *et al.*, 2005); L3 = *o*-vanillinate (Lin *et al.*, 2006); L4 = 3,5-di-*tert*-butyl-*o*-semiquinate (Thompson & Calabrese, 1986; Bencini *et al.*, 2003); L5 = 2,2,6,6-tetramethyl-3,5-heptanedionate (Watson & Holley, 1984); L6 = oxalate (Kadir *et al.*, 2006; Li *et al.*, 2008); L7 = 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionate (Olejnik *et al.*, 1986); L8 = 3-cyanoacetyl-acetonate (Burrows *et al.*, 2007).

bvparm2009.cif and the calculations made with the bond-valence calculator *Valence 2.0* distributed by Brown (http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3* (Version 2.02; Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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