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trans-Bis(2,2-diphenylethylamine-κ*N*)bis(5,5-diphenylhydantoinato-κN^3)copper(II) and its chloroform disolvate

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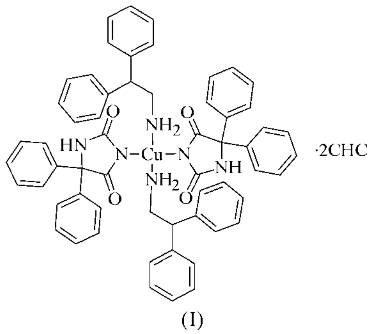
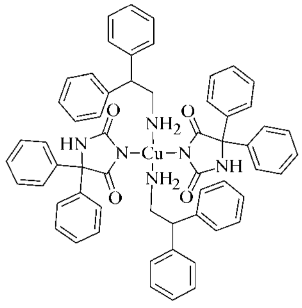
The crystal structures of the title compounds, $[Cu(C_{15}H_{11}N_2O_2)_2(C_{14}H_{15}N)_2]$ and $[Cu(C_{15}H_{11}N_2O_2)_2(C_{14}H_{15}N)_2]\cdot 2CHCl_3$, respectively, have been determined. The red disolvate complex affords a square-planar CuN_4 coordination environment in which the Cu^{II} atom lies on a centre of symmetry. The blue solvent-free complex affords a distorted square-pyramidal CuN_4O coordination environment and adjacent molecules form centrosymmetric dimers. A comparison of the different crystal structures focuses on the role of the solvent molecules in supramolecular assemblies of the copper(II) complexes.

Comment

In recent years, studies of supramolecular self-assembling metal–organic frameworks of metal complexes have been extensively carried out with the aim of rational construction of desired crystal structures and fine-tuning of their functions (Eddaoudi *et al.*, 2001; Evans *et al.*, 2002; Yaghi *et al.*, 1998). In particular, host–guest inclusion of small molecules and hydrogen-bonded flexible self-assemblies enable the realization of appropriate crystal packing containing guest molecules (Holman *et al.*, 2001), which depends on the novelty of the secondary building units. In this respect, for example, vapochromic switching of optoelectronic properties may be one of the most promising strategies for the preparation of functional materials (Kato *et al.*, 2002; Fernandez *et al.*, 2003). It is well known that copper(II) complexes exhibit a remarkable variety in their coordination geometries and corresponding optoelectronic properties. Some copper(II) complexes incorporating monodentate 5,5-diphenylhydantoinate ligands have been studied previously. In the solid state, most of these complexes afford a four-coordinated square-planar CuN_4 coordination geometry (Akitsu, Komorita & Urushiyama, 2001) with the aid of crystal-packing forces. Appropriate steric factors of the ligands can lead to a tetrahedrally distorted square-planar CuN_4 coordination geometry (Akitsu *et al.*, 2003) or a five-coordinated square-pyramidal CuN_4O coordination geometry (Akitsu *et al.*, 1997). To date, structural regulation by other means, such as solvent in the crystal (Tynan *et al.*, 2004), has not been observed for analogous complexes. We report here a structural comparison of *trans*-bis(2,2-diphenylethylamine)bis(5,5-diphenylhydantoinato)copper(II) chloroform disolvate, (I), and dimeric *trans*-bis(2,2-diphenylethylamine)bis(5,5-diphenylhydantoinato)-copper(II), (II).



(I)



(II)

Complex (I), the chloroform disolvate, affords a square-planar CuN_4 coordination geometry, in which the Cu atom lies on an inversion centre (Fig. 1). Both the neutral 2,2-

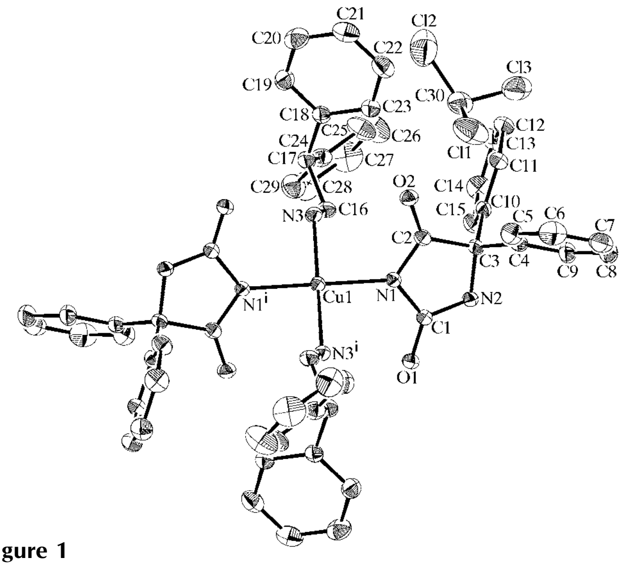


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Only one chloroform solvent molecule is shown. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

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diphenylethylamine ligands and the anionic deprotonated 5,5-diphenylhydantoinate ligands act as monodentate ligands with N-atom donors, and they are coordinated on *trans* sites with respect to the Cu atom. The Cu—N bond distances (Table 1) are within the range found in related complexes, some of which are planar and some of which exhibit some tetrahedral distortion, *viz*. the Cu—N(imide) distances range from 1.975 (5) to 2.05 (1) Å, whereas the Cu—N(amine) distances range from 1.97 (1) to 2.030 (4) Å (Akitsu, Komorita & Kushi, 2001; Akitsu *et al.*, 2003; Akitsu & Einaga, 2004). The *cis*-N1—Cu1—N3 angles are close to being right angles. The dihedral angle between the Cu1/N1/N3/N1^{i}/N3^{i} mean plane of the coordination sphere and the N1/C1/N2/C2/C3 plane of the ligands is 139.4 (1)°, and those between the five-membered C3/C2/N1/C1/N2 ring of the 5,5-diphenylhydantoinate ligand and the connecting phenyl groups, *i.e.* C4–C9 and C10–C15, are 57.7 (1) and 123.0 (1)°, respectively [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

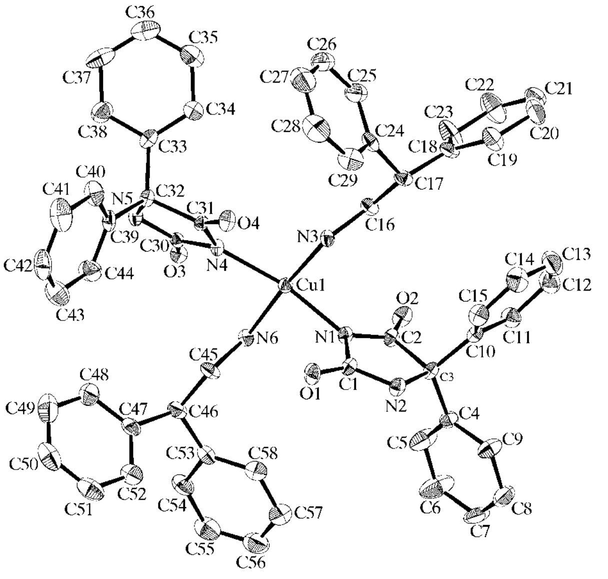

Figure 2
The molecular structure of (II) as a monomer, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

The solvent-free complex, (II), affords a slightly distorted pyramidal CuN$_4$ coordination geometry (Fig. 2) and adjacent molecules form centrosymmetric dimers, with a Cu1—O3^{iii} distance of 2.397 (4) Å [symmetry code: (iii) $2 - x, 1 - y, 1 - z$] (Fig. 3). The Cu—N bond distances are also within the range found in related complexes (Table 3). The dihedral angle between the N1/Cu1/N3 and N4/Cu1/N6 planes is 16.69 (1)°. The Cu atom deviates slightly from the N1/N3/N4/N6 plane, by 0.178 (2) Å. The dihedral angle between the Cu1/N1/N3/N4/N6 and N1/C1/N2/C2/C3 planes is 94.7 (2)°, while that between the Cu1/N1/N3/N4/N6 and N4/C30/N5/C31/C32 planes is 35.2 (2)°. Although the planarity of the coordination environment is broken, the *sp*^{2} character of the N-donor atoms of the 5,5-diphenylhydantoinate ligands is still maintained; the C1—N1—C3 and C30—N4—C31 bond angles are 108.0 (5) and 106.2 (5)°, respectively.

To the best of our knowledge, this is the first case of related complexes which exhibit different coordination geometries in the presence or absence of solvent molecules in the crystal. In the crystal structure of (I), four intramolecular hydrogen bonds are formed around the coordination sphere, *i.e.* N3—H13···O2 and N3—H12···O1^{i} (Table 2). Furthermore, adjacent molecules are linked by double complementary intermolecular N2—H1···O1^{ii} hydrogen bonds along the crystallographic *b* axis [N···O = 2.900 (3) Å; symmetry code: (ii) $1 - x, 1 - y, -z$]. The chloroform solvent molecules also play an important role in stabilizing the crystal packing of (I) *via* a C30—H27···O2 hydrogen bond [C···O = 3.507 (5) Å]. On the other hand, the crystal-packing mode of (II) is quite different (Fig. 4). Only two intramolecular hydrogen bonds, namely N3—H12···O4 and N6—H39···O3, are formed on one side of the coordination sphere (Table 4). Moreover,

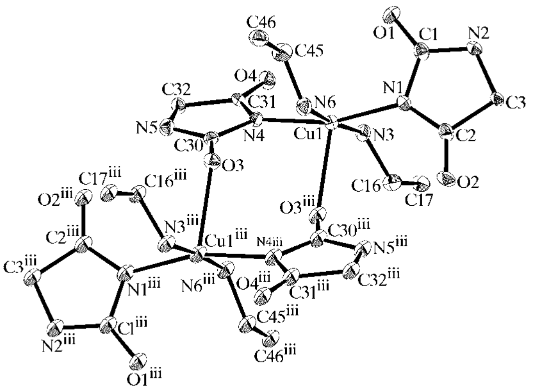

Figure 3
The dimeric structure of (II). Displacement ellipsoids are drawn at the 30% probability level. H atoms and phenyl groups have been omitted for clarity. [Symmetry code: (iii) $2 - x, 1 - y, 1 - z$.]

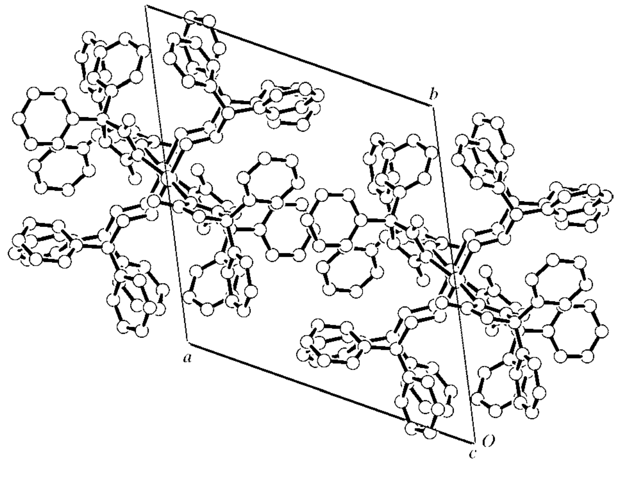

Figure 4
A molecular packing diagram of (II), viewed down the crystallographic *c* axis.

intermolecular hydrogen bonds, *i.e.* N5—H27$\cdots$O2^{iii} and N2—H1$\cdots$O4^{iv}, link adjacent molecules to form hydrogen-bonded networks [symmetry codes: (iii) $2 - x, 1 - y, 1 - z$; (iv) $2 - x, 1 - y, -z$].

Experimental

Treatment of equimolar quantities of copper(II) acetate (0.454 g, 2.50 mmol), 5,5-diphenylhydantoin (1.26 g, 5.00 mmol) and 2,2-diphenylethylamine (0.99 g, 5.00 mmol) in ethanol (100 ml) at 323 K for 2 h gave rise to crude precipitates. Red–violet plate-like crystals of (I) were obtained from a solution in chloroform–methanol (4:1 *v*/*v*) kept at 298 K over a period of several days. IR (KBr): 1644 cm^{-1} (amide I band); m.p. 629 K (decomposition). Recrystallization of the crude precipitates from a solution in chloroform–methanol (4:1 *v*/*v*) at 283 K overnight yielded only a small amount of blue–violet plate-like crystals of solvent-free complex (II). IR (KBr): 1645 cm^{-1} (amide I band); m.p. 605 K (decomposition).

Compound (I)

Crystal data

$[Cu(C_{15}H_{11}N_2O_2)_2(C_{14}H_{15}N)_2]\cdot 2CHCl_3$
$M_r = 1199.34$
Orthorhombic, *Pbca*
$a = 19.37$ (1) Å
$b = 29.796$ (7) Å
$c = 9.910$ (3) Å
$V = 5720$ (4) Å^3
$Z = 4$

$D_x = 1.393$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.3$–$12.6°$
$\mu = 0.72$ mm^{-1}
$T = 298$ (1) K
Plate, red–violet
$0.41 \times 0.16 \times 0.10$ mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.872$, $T_{max} = 0.931$
8516 measured reflections
6565 independent reflections
3338 reflections with $I > 2\sigma(I)$

$R_{int} = 0.021$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 25$
$k = 0 \rightarrow 38$
$l = -12 \rightarrow 5$
3 standard reflections every 150 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.163$
$S = 0.99$
3338 reflections
302 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N1	2.009 (3)	Cu1—N3	2.005 (3)
N1—Cu1—N3	89.2 (1)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N2—H1$\cdots$O1^i	0.95	2.02	2.900 (3)	153
N3—H12$\cdots$O1^{ii}	0.95	2.06	2.837 (3)	137
N3—H13$\cdots$O2	0.95	2.13	2.922 (3)	140
C30—H27$\cdots$O2	0.95	2.57	3.507 (5)	170

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.

Compound (II)

Crystal data

$[Cu(C_{15}H_{11}N_2O_2)_2(C_{14}H_{15}N)_2]$
$M_r = 960.63$
Triclinic, $P\overline{1}$
$a = 14.313$ (4) Å
$b = 15.888$ (5) Å
$c = 11.863$ (4) Å
$\alpha = 90.13$ (3)°
$\beta = 95.00$ (3)°
$\gamma = 63.58$ (2)°
$V = 2404.7$ (14) Å^3

$Z = 2$
$D_x = 1.327$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0$–$12.4°$
$\mu = 0.51$ mm^{-1}
$T = 298$ (1) K
Plate, blue–violet
$0.50 \times 0.40 \times 0.20$ mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.783$, $T_{max} = 0.903$
12 233 measured reflections
12 233 independent reflections
11 075 reflections with $I > 0\sigma(I)$

$R_{int} = 0.087$
$\theta_{max} = 27.5°$
$h = -18 \rightarrow 18$
$k = -20 \rightarrow 20$
$l = -6 \rightarrow 15$
3 standard reflections every 150 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.161$
$S = 0.85$
11075 reflections
527 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -1.31$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1—O3^i	2.397 (4)	Cu1—N4	2.026 (4)
Cu1—N1	1.990 (4)	Cu1—N6	2.032 (4)
Cu1—N3	2.030 (3)		
O3^i—Cu1—N1	109.8 (1)	N1—Cu1—N4	163.5 (2)
O3^i—Cu1—N3	92.2 (1)	N1—Cu1—N6	89.1 (2)
O3^i—Cu1—N4	86.7 (1)	N3—Cu1—N4	93.7 (2)
O3^i—Cu1—N6	91.9 (1)	N3—Cu1—N6	175.0 (2)
N1—Cu1—N3	86.9 (2)	N4—Cu1—N6	89.2 (2)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N2—H1$\cdots$O4^{ii}	0.95	2.00	2.915 (6)	160
N3—H12$\cdots$O4	0.95	2.17	2.915 (6)	135
N5—H27$\cdots$O2^i	0.95	2.09	2.857 (5)	136
N6—H39$\cdots$O3	0.95	2.07	2.817 (5)	134

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z$.

All H atoms were placed in calculated positions, with C—H = N—H = 0.95 Å, and included in the final cycles of refinement using a riding model, with $U_{iso}(H) = 1.2U_{eq}$(parent atom). The C atoms of the phenyl groups, *viz.* C4–C9, C10–C15, C18–C23 and C24–C29 for (I), and C4–C9, C10–C15, C18–C23, C24–C29, C33–C38, C39–C44, C47–C52 and C53–C58 for (II), were treated as rigid groups of anisotropic atoms. The intensity of the data was relatively weak, similar to some analogous mononuclear copper complexes with large organic ligands. The largest hole in the difference map of (II) is near atom Cu1, at (0.9919, 0.4909, 0.2953).

For both compounds, data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); programs used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1482). Services for accessing these data are described at the back of the journal.

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