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The first square-planar copper(II) 1:2 complex with differently coordinated 2-hydroxybenzaldehyde 4-allylthiosemicarbazone ligands

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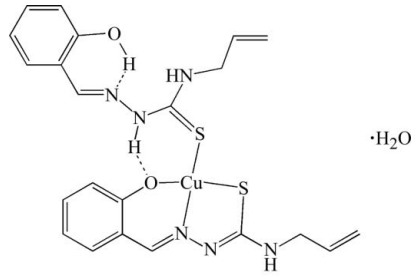
The title compound, [(*Z*)-4-allyl-2-(2-hydroxybenzylidene)-thiosemicarbazide-κS][(*E*)-4-allyl-1-(2-oxidobenzylidene)-thiosemicarbazidato-$\kappa^3 O,N^1,S$]copper(II) monohydrate, [Cu($C_{11}H_{11}N_3OS$)($C_{11}H_{13}N_3OS$)]·H_2O, crystallized as a rotational twin in the monoclinic crystal system (space group *Cc*) with two formula unit ($Z' = 2$) in the asymmetric unit, one of which contains an allyl substituent disordered over two positions. The Cu^{II} atom exhibits a distorted square-planar geometry involving two differently coordinated thiosemicarbazone ligands. One ligand is bonded to the Cu^{II} atom in a tridentate manner *via* the phenolate O, azomethine N and thioamide S atoms, while the other coordinates in a monodentate manner *via* the S atom only. The complex is stabilized by an intramolecular hydrogen bond, which creates a six-membered pseudo-chelate metalla-ring. The structure analysis indicates the presence of the *E* isomer for the tridentate ligand and the *Z* isomer for the monodentate ligand. The crystal structure contains a three-dimensional network built from intermolecular O—H···O, N—H···O, O—H···N and N—H···S hydrogen bonds.

Comment

Thiosemicarbazones and their metal complexes attract constant scientific interest due to their antimicrobial, antifungal and antitumour activities (Garoufilis *et al.*, 2009; Stanojkovic *et al.*, 2010). Some thiosemicarbazones are also used as reagents for the determination of Co^{II}, Ni^{II}, Cu^{II} and Pd^{II} by solid-phase microextraction in high-performance liquid chromatography (Kaur *et al.*, 2007).

The potentially tridentate salicylaldehyde thiosemicarbazone derivatives can give mono-, bi- or polynuclear complexes with transition metals, in each of which the multiple ligands usually all coordinate to the metal centre in the same manner (Soriano-García *et al.*, 1985; Labisbal *et al.*, 2003). However, the Cambridge Structural Database (Version 5.31 of November 2009; Allen, 2002) records two structures of 1:2 square-planar Pd^{II} and Pt^{II} complexes, each containing two differently coordinated thiosemicarbazone ligands (Papathanasis *et al.*, 2004). The present paper reports the structure of the title square-planar copper(II) complex, (I), containing two salicylaldehyde 4-allylthiosemicarbazone ligands which exhibit different coordination behaviours.



(I)

Compound (I) crystallizes in the noncentrosymmetric space group *Cc* as an inversion twin, with two molecules of the metal complex and two solvent water molecules in the asymmetric unit. The geometric parameters of the two independent complexes are very similar (Fig. 1 and Table 1); the only difference between them is the presence of a disordered allyl fragment (atoms C9 and C10) in one of them. The Cu^{II} centres exhibit a distorted square-planar coordination geometry, with mean deviations from the Cu1/O1/N2/S1/S2 and Cu2/O3/N8/S3/S4 planes of 0.164 and 0.150 Å, respectively.

The main interest in the structure lies in the different coordination modes of the two ligands around each Cu^{II} ion: one ligand is bonded in a tridentate manner *via* phenolate O, azomethine N and thioamide S atoms, while the other is coordinated in a monodentate fashion *via* the thioamide S

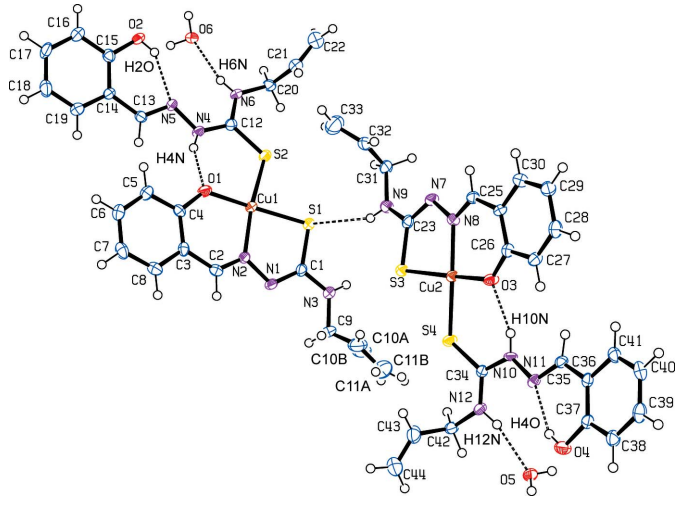


Figure 1
The asymmetric unit of the title compound, showing the atom-numbering scheme and the disordered allyl fragment. Displacement ellipsoids are shown at the 50% probability level. Dashed lines indicate hydrogen bonds.

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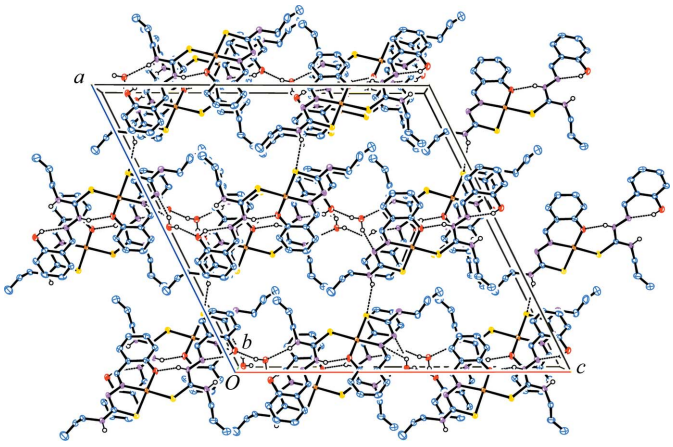

Figure 2
The crystal packing of the title compound, viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

atom only (Fig. 1). The resulting six-membered Cu1/N2/C2/C3/C4/O1 (*A*) and Cu2/N8/C24/C25/C26/O3 (*B*) rings and five-membered Cu1/S1/C1/N1/N2 (*C*) and Cu2/S3/C23/N7/N8 (*D*) rings are nearly planar, with mean deviations from the planes of 0.011, 0.054, 0.019 and 0.066 Å, respectively. The dihedral angles between planes *A*/*C* and *B*/*D* are 9.78 (14) and 9.87 (14)°, respectively, which confirms the slight tetrahedral distortion of the coordination geometry at the Cu^{II} ion. The values of the Cu—O and Cu—N bond lengths (Table 1) are in good agreement with those in related structures (Bon *et al.*, 2010). The Cu1—S1 and Cu2—S3 bonds are shorter than Cu1—S2 and Cu2—S4 (Table 1), which can be explained by the strong influence of the chelate effect in the former case.

The C—S bond lengths (Table 1) do not permit a clear assignment of the dominant tautomeric form of the coordinated ligands, although the C—S bond lengths in the tridentate ligands are closer to the value expected for the thiolic tautomeric form, while the monodentate ligands have slightly shorter C—S bonds (Table 1). The values of adjacent angles around the Cu^{II} ions are in the range 84.48 (4)–98.83 (9)° (Table 1), which confirms the distorted square-planar geometry. The valence angles O1—Cu1—S2 and O3—Cu2—S4 deviate significantly from ideal square-planar values (Table 1), which can be explained in terms of the six-membered pseudo-chelate metalla-rings Cu1/S2/C12/N4/H4N/O1 and Cu2/S4/C34/N10/H10N/O3, formed *via* intramolecular hydrogen bonds (Fig. 1 and Table 2). The torsion angles N2—N1—C1—N3, N5—N4—C12—N6, N8—N7—C23—N9 and N11—N10—C34—N12 (Table 1) confirm the presence of the *E* isomer in the tridentate ligands and the *Z* isomer in the monodentate ligands. The intramolecular O2—H2O···N5 and O4—H4O···N11 hydrogen bonds (Table 2) are characteristic for structures containing noncoordinated azomethine fragments (Rubčić *et al.*, 2008). The crystal structure of (I) contains an extended three-dimensional network of intermolecular O—H···O, N—H···O, O—H···N and N—H···S hydrogen bonds (Fig. 2 and Table 2).

Experimental

An aqueous solution of copper(II) acetate (20 ml, 5 m*M*) was stirred for 2 h with an ethanolic solution of salicylaldehyde 4-allylthiosemicarbazone (20 ml, 10 m*M*). The resulting solution was then set aside for 3 d in the dark, after which time violet needle-like crystals of (I) suitable for single-crystal X-ray diffraction were obtained.

Crystal data

$[Cu(C_{11}H_{11}N_3OS)(C_{11}H_{13}N_3OS)]\cdot H_2O$
M_r = 550.15
Monoclinic, *Cc*
a = 25.763 (3) Å
b = 8.5526 (9) Å
c = 24.496 (3) Å
β = 116.458 (3)°
V = 4832.1 (10) Å^3
Z = 8
Mo *K*α radiation
μ = 1.11 mm^{-1}
T = 173 K
0.50 × 0.05 × 0.05 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.606, T_{max} = 0.946
25072 measured reflections
8043 independent reflections
6716 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.074
S = 1.03
8043 reflections
656 parameters
16 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Absolute structure: Flack (1983), with 3047 Friedel pairs
Flack parameter: 0.464 (13)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.906 (3)	Cu2—O3	1.908 (3)
Cu1—N2	1.949 (4)	Cu2—N8	1.964 (4)
Cu1—S1	2.2519 (13)	Cu2—S3	2.2401 (13)
Cu1—S2	2.3347 (12)	Cu2—S4	2.3320 (12)
S1—C1	1.733 (5)	S3—C23	1.747 (4)
S2—C12	1.721 (4)	S4—C34	1.714 (4)
O1—Cu1—N2	93.03 (13)	O3—Cu2—N8	93.19 (13)
N2—Cu1—S1	85.32 (11)	N8—Cu2—S3	85.19 (11)
O1—Cu1—S2	98.68 (9)	O3—Cu2—S4	98.83 (9)
S1—Cu1—S2	85.02 (5)	S3—Cu2—S4	84.48 (4)
N2—N1—C1—N3	177.3 (4)	N8—N7—C23—N9	−178.9 (4)
N5—N4—C12—N6	−10.0 (7)	N11—N10—C34—N12	−13.1 (6)

The structure refinement indicated disorder of one allyl group, atoms C10 and C11, over two sets of positions with occupancies initially refined to 0.669 (8) and 0.331 (8) and subsequently fixed at 0.67 and 0.33 for the major and minor conformations, respectively. The anisotropic displacement parameters of the two positions for each of atoms C10 and C11 were constrained to be equal, while the C9—C10*A*/C9—C10*B* and C10*A*—C11*A*/C10*B*—C11*B* bond lengths were restrained to 1.52 (2) and 1.33 (2) Å, respectively. The positions of the H atoms bonded to N or O atoms were found from a Fourier difference map and refined, with U_{iso}(H) = 1.2U_{eq}(N) or 1.5U_{eq}(O), using distance restraints of 0.82 (4) Å for O4—H4O, O5—H51O,

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···N5	0.75 (5)	2.05 (5)	2.718 (5)	148 (6)
N4—H4N···O1	0.83 (3)	1.94 (3)	2.715 (5)	155 (4)
N6—H6N···O6	0.79 (3)	2.14 (4)	2.876 (5)	154 (5)
O4—H4O···N11	0.79 (3)	2.00 (4)	2.714 (5)	151 (6)
N9—H9N···S1	0.81 (3)	2.71 (3)	3.460 (4)	154 (4)
N10—H10N···O3	0.82 (3)	1.96 (3)	2.753 (5)	160 (4)
N12—H12N···O5	0.84 (5)	2.06 (5)	2.864 (5)	159 (5)
O5—H51O···O2^{i}	0.75 (3)	2.13 (4)	2.833 (4)	157 (5)
O5—H52O···N1^{ii}	0.78 (4)	2.19 (5)	2.912 (6)	155 (5)
O6—H61O···N7^{iii}	0.89 (3)	2.07 (3)	2.890 (5)	153 (4)
O6—H62O···O4^{iv}	0.87 (3)	1.97 (3)	2.827 (4)	165 (4)

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

O6—H61O and O6—H62O, and 0.87 (4) Å for N3—H3N, N4—H4N, N6—H6N, N9—H9N and N10—H10N. All other H atoms were treated as riding, with C—H = 0.95 or 0.99 Å, and with U_{iso}(H) = 1.2U_{eq}(C). The structure was handled as an inversion twin, with a major twin fraction of 0.535 (13).

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3359). Services for accessing these data are described at the back of the journal.

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