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Crystal structure and Hirshfeld surface analysis of mono/bis(aqua-κO)[N-(2-oxidobenzylidene)-valinato-$\kappa^3 O,N,O'$]copper(II): dimeric Schiff base copper(II) complexes having different numbers of coordinated water molecules

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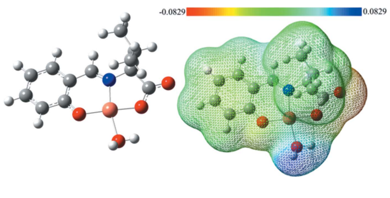
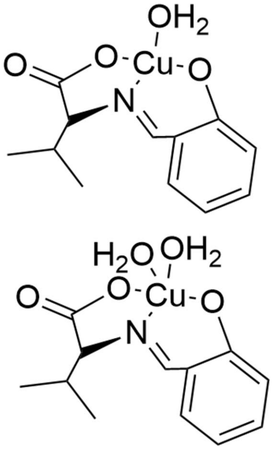
The molecular structure of the title compound, $[Cu(C_{12}H_{13}N_2O_3)(H_2O)_2]\cdot[Cu(C_{12}H_{13}N_2O_3)(H_2O)]$, consists of two different molecules in the asymmetric unit. Both of the structures consist of a tridentate ligand synthesized from L-valine and salicylaldehyde, and one water molecule or two water molecules coordinating to Cu^{II}. They have a square-planar (molecule 1) or a square-pyramidal (molecule 2) coordination geometry. In the crystal, the molecules form intra- and intermolecular $O-H\cdots O$ hydrogen bonds involving the coordinated water molecules and other sites. A Hirshfeld surface analysis indicated that the most important contributions to the packing are from $H\cdots H$ [52.9% (molecule 1) and 51.1% (molecule 2)] and $H\cdots O$/ $O\cdots H$ [21.2% (molecule 1) and 25.8% (molecule 2)] contacts. In addition, an electrostatic potential map was also obtained from DFT calculations to support the discussion of the intermolecular interactions.



1. Chemical context

Amino acid Schiff bases, which can easily be synthesized by mixing primary amines and carbonyl components, are organic ligands having an azomethine (C═N) group. They play an important and diverse role in coordination chemistry (Qiu *et al.*, 2008; Li *et al.*, 2010; Xue *et al.*, 2009; Katsuumi *et al.*, 2020). We recently published a review (Akitsu *et al.*, 2022) of the synthesis of amino acid Schiff base–metal complexes. According to the literature, in general, Schiff bases and their metal complexes are multipurpose compounds and are extensively utilized in many research and industrial applications. These compounds can be utilized alone or for the preparation of various hybrid materials, such as, for example, supramolecular elastomers with imine-functionalized polysiloxanes (Hu *et al.*, 2010), conducting metallopolymers for electrochemical sensing (González *et al.*, 2021), while recently reported co-crystals of a Schiff base with lead iodide perovskite show photo-triggered ferroelectricity (Deng *et al.*, 2022). Furthermore, Schiff base complexes are considered to be an important class of organic compounds with a wide range of biological properties, including free radical scavenging, antibacterial, antitumor activities (Mo *et al.*, 2022). In our laboratory, novel mono-chlorinated Schiff base Cu^{II} complexes have been synthesized and their antibacterial activities tested against Gram-positive and Gram-negative bacteria; the most active were then tested for their antioxidant activities, and as *E. coli*, in particular, was found to be sensitive to these compounds, their interaction with this bacterium was investigated (Otani *et al.*, 2022). Microwave irradiation is suitable for the synthesis of amino acid Schiff bases Cu$^{\rm II}$ complexes in order to shorten the synthesis time and to obtain high purity. In the present study, the title compound was therefore synthesized by using microwave irradiation (Otani *et al.*, 2022). Differences in chemical properties as a result of differences in structure are remarkable and it is important to report different crystal structures to discuss these features. In this study, we report the structure of the title Schiff base Cu$^{\rm II}$ complex (Fig. 1) derived from L-valine and salicylaldehyde, which has a similar structure to that of one we reported previously (Katsuumi *et al.*, 2020).



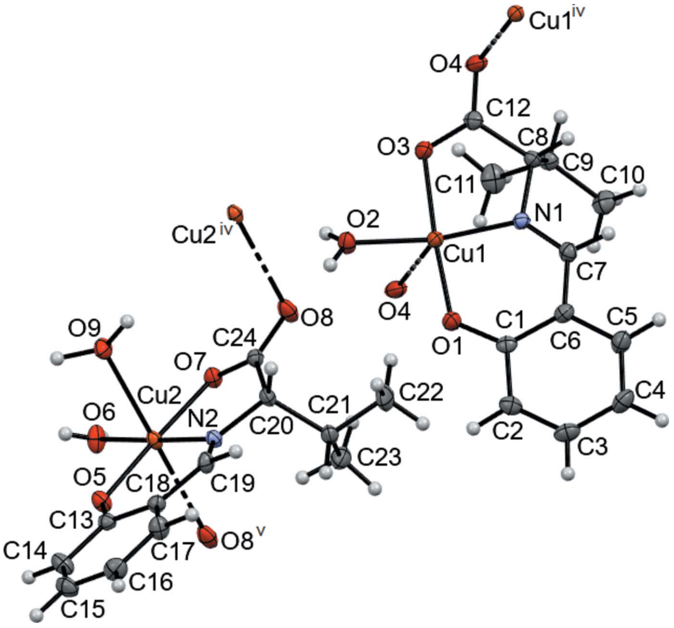


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (iv) $x - 1, y, z$; (v) $x + 1, y, z$.]

2. Structural commentary

The asymmetric unit of the title compound consists of two different molecules, molecule 1 (containing atom Cu1) and molecule 2 (including Cu2). In molecule 1, Cu1 has square-planar geometry, being coordinated by a tridentate ligand synthesized from L-valine and salicylaldehyde in the equatorial plane and by one water molecule. The C7=N1 double-bond distance is 1.284 (3) Å, which is close to the typical C=N double bond length for imines (Katsuumi, *et al.*, 2020). The Cu1—O1, Cu1—O2 and Cu1—O3 bond lengths are 1.8995 (15), 1.9339 (16), and 1.9629 (15) Å, respectively, close to a typical Cu—O coordination bond length (Katsuumi *et al.*, 2020). The Cu1—N1 bond length of 1.9205 (16) Å corresponds to typical Cu—N bond length (Katsuumi *et al.*, 2020). The lengths of these four coordination bonds in molecule 1 are almost the same. Finally, the bond the other interacting O atom, Cu1$\cdots$O4($1 + x, y, z$), is 2.6586 (17) Å.

In contrast, in molecule 2 the Cu2 atom exhibits a square-pyramidal geometry, being coordinated by the same tridentate ligand in the equatorial plane and by two water molecules in the equatorial and axial positions. The C19=N2 double-bond distance is 1.278 (3) Å, which is again close to the typical C=N double-bond length for imines (Katsuumi *et al.*, 2020). The Cu2—O5, Cu2—O6, and Cu2—O7 bond lengths are 1.9432 (14), 1.9411 (15), and 1.9956 (14) Å, respectively, which are close to a typical Cu—O bond length (Katsuumi *et al.*, 2020). The Cu2—N2 bond length of 1.9243 (17) Å corresponds to a typical Cu—N bond length (Katsuumi *et al.*, 2020). Again, these four coordination bonds are almost the same length. The bond lengths involving the other interacting O atoms are Cu2$\cdots$O8($1 + x, y, z$) = 2.7937 (16) Å and Cu2—O9 = 2.3663 (16) Å; the latter is longer than Cu2—O6 because of the pseudo-Jahn–Teller effect. The Cu2—O6 bond is slightly longer than Cu1—O2 as a result of the crowding that occurs as the number of coordinating water molecules increases.

3. Supramolecular features

Six intermolecular O—H$\cdots$O hydrogen bonds (Table 1 and Fig. 2) are observed in the unit cell; (O2—H2*B*$\cdots$O8, O2—H2*A*$\cdots$O9$^{\rm i}$, O6—H6$\cdots$O3$^{\rm ii}$, O6—H10$\cdots$O7$^{\rm iii}$, O9—H11$\cdots$O5$^{\rm iv}$, and O9—H12$\cdots$O4$^{\rm ii}$; symmetry codes as in Table 1). The angle O4($1 + x, y, z$)—Cu1—N1 [102.50 (6)°] is tilted by much more than 90° as a result of the O9—H12$\cdots$O4$^{\rm ii}$ hydrogen bond. Similarly, the angle O8($1 + x, y, z$)—Cu2—N2 [98.58 (6)°] is tilted by more than 90° because of the effect of the O2—H2*B*$\cdots$O8 hydrogen bond. In the crystal, the molecules form an infinite chain as a result of the interaction of these six hydrogen bonds and the Cu$^{\rm II}$ atom with the carbonyl groups of the ligands (Figs. 2 and 3). These six hydrogen bonds also form strong interactions between molecules 1 and 2 unit. The equatorial planes of ligands in the same type of molecule are parallel to each other, while those of molecules 1 and molecule 2 intersect at an angle of 52.29 (2)°.

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$A\cdots$O9$^{\rm i}$	0.83	1.87	2.688 (2)	167
O2—H2$B\cdots$O8	0.72 (3)	1.93 (3)	2.645 (2)	169 (4)
O6—H6$\cdots$O3$^{\rm ii}$	0.72	2.07	2.784 (2)	171
O6—H10$\cdots$O7$^{\rm iii}$	0.77 (3)	2.01 (3)	2.764 (2)	169 (3)
O9—H11$\cdots$O5$^{\rm iv}$	0.94 (2)	1.80 (2)	2.738 (2)	172 (3)
O9—H12$\cdots$O4$^{\rm ii}$	1.01 (2)	1.74 (2)	2.703 (2)	157 (3)

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

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009; McKinnon *et al.*, 2007) was performed to better understand the intermolecular interactions and contacts. The intermolecular O—H$\cdots$O hydrogen bonds are indicated by bright-red spots appearing near atoms O4, O5, O8, O9 and water H atoms on the Hirshfeld surfaces mapped over $d_{\rm norm}$ and by two sharp spikes of almost the same length in the region $1.6 < (d_{\rm e} + d_{\rm i}) < 2.0$ Å in the 2D fingerprint plots (Fig. 4). In molecule 1, the contributions to the packing from H$\cdots$H, C$\cdots$C, C$\cdots$H/H$\cdots$C and H$\cdots$O/O$\cdots$H contacts are 52.9, 0.3, 18.6 and 21.2%, respectively, and in molecule 2, the contributions of the H$\cdots$H, C$\cdots$C, C$\cdots$H/H$\cdots$C and H$\cdots$O/O$\cdots$H contacts are 51.1, 0.6, 17.3 and 25.8%, respectively (Fig. 4). A common feature of the two structures is the high values for the contributions of H$\cdots$H/H$\cdots$H and C$\cdots$H/H$\cdots$C contacts, with H$\cdots$H/H$\cdots$H representing the influence of van der Waals forces and C$\cdots$H/H$\cdots$C representing the influence of C—H$\cdots\pi$ interactions as a result of the presence of aromatic rings in the structures. The reason for the low C$\cdots$C/C$\cdots$C ratio is thought to be that the aromatic rings do not overlap, as indicated by the packing structure, and thereby the contribution of π–π stacking is low. Compared to molecule 1, molecule 2 has a larger number of water molecules and a higher H$\cdots$O/O$\cdots$H value, which seems to have resulted in a larger contribution from hydrogen bonding and corresponding decreases in the C$\cdots$H/H$\cdots$C and H$\cdots$H/H$\cdots$H values.

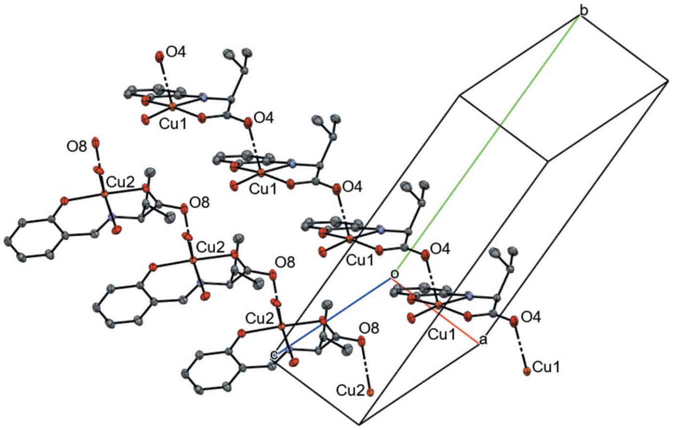


Figure 3
The chains resulting from the coordination bonding of the carbonyl groups to the copper(II) atoms. Hydrogen atoms are omitted for clarity.

4. DFT calculations

Quantum chemical calculations were carried out to compare the structure in the gas phase with that of in the crystal. The optimized structure of the title compound in the gas phase was calculated by density functional theory (DFT) and the calculation was performed using the *Gaussian 09W* software package (Revision D.02; Frisch *et al.*, 2009). The Lanl2DZ basis set was applied to the central metal atom (Cu), the 6-31G(d) basis set to the other atoms (C, O, N, H), and the effective core potential (ECP) to the central metal. Calculations were performed for square-pyramidal and square-planar geometries. The initial structure was obtained from X-ray refinement data. However, in the optimizing calculations for the square-pyramidal geometry, the molecule was unable to maintain the square-pyramidal structure, and the axial water molecules moved outside the first coordination sphere of the central metal atom. This indicates that the square-pyramidal structure of this molecule is not stable in the gas phase. The axial water molecules are stabilized by hydrogen bonds with

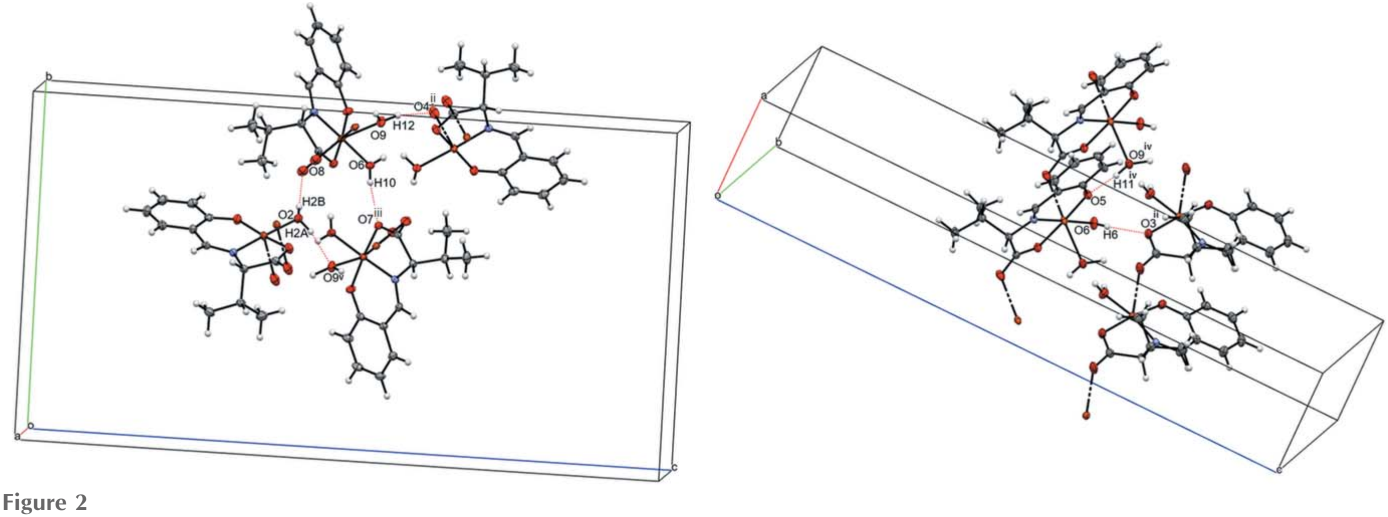


Figure 2
A view of the intra- and intermolecular O—H$\cdots$O hydrogen bonds, shown as dashed lines. [Symmetry codes: (ii) $x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (iv) $x - 1, y, z$; (v) $x + 1, y, z$.]

Table 2
Comparison of selected (X-ray and DFT) bond lengths and angles (Å, °).

Square-planar molecule 1		Square-pyramidal molecule 2		
Bonds/Angles	X-ray	Bonds/Angles	X-ray	B3LYP/6–31G(*d*) (C, N, O, H); Lanl2DZ (Cu)
Cu1—O1	1.8955 (15)	Cu2—O5	1.9432 (14)	1.881
Cu1—O2	1.9339 (16)	Cu2—O6	1.9411 (15)	2.079
Cu1—O3	1.9629 (15)	Cu2—O7	1.9956 (14)	1.913
Cu1—N1	1.9205 (16)	Cu2—N2	1.9243 (17)	1.944
O2···O3	2.707 (2)	O6···O7	2.903 (2)	2.611
N1—Cu1—O2	170.16 (7)	N2—Cu2—O6	177.73 (7)	167.07

neighboring molecules and the square-pyramidal structure is considered to be preserved.

The bond lengths and bond angles of the square-planar sites are generally consistent between the crystal structure and the optimized structure (Table 2). In the DFT-optimized structure, the hydrogen atoms of the water molecule are oriented towards the carboxyl group and appear to be involved in an intermolecular hydrogen bond. The orientation of the water molecules in the crystal is largely influenced by the hydrogen-bonding network. It can be seen that the carboxy group of the ligand is charged electron rich, while the hydrogen atom of water shows an electron deficiency. Therefore, the carboxy

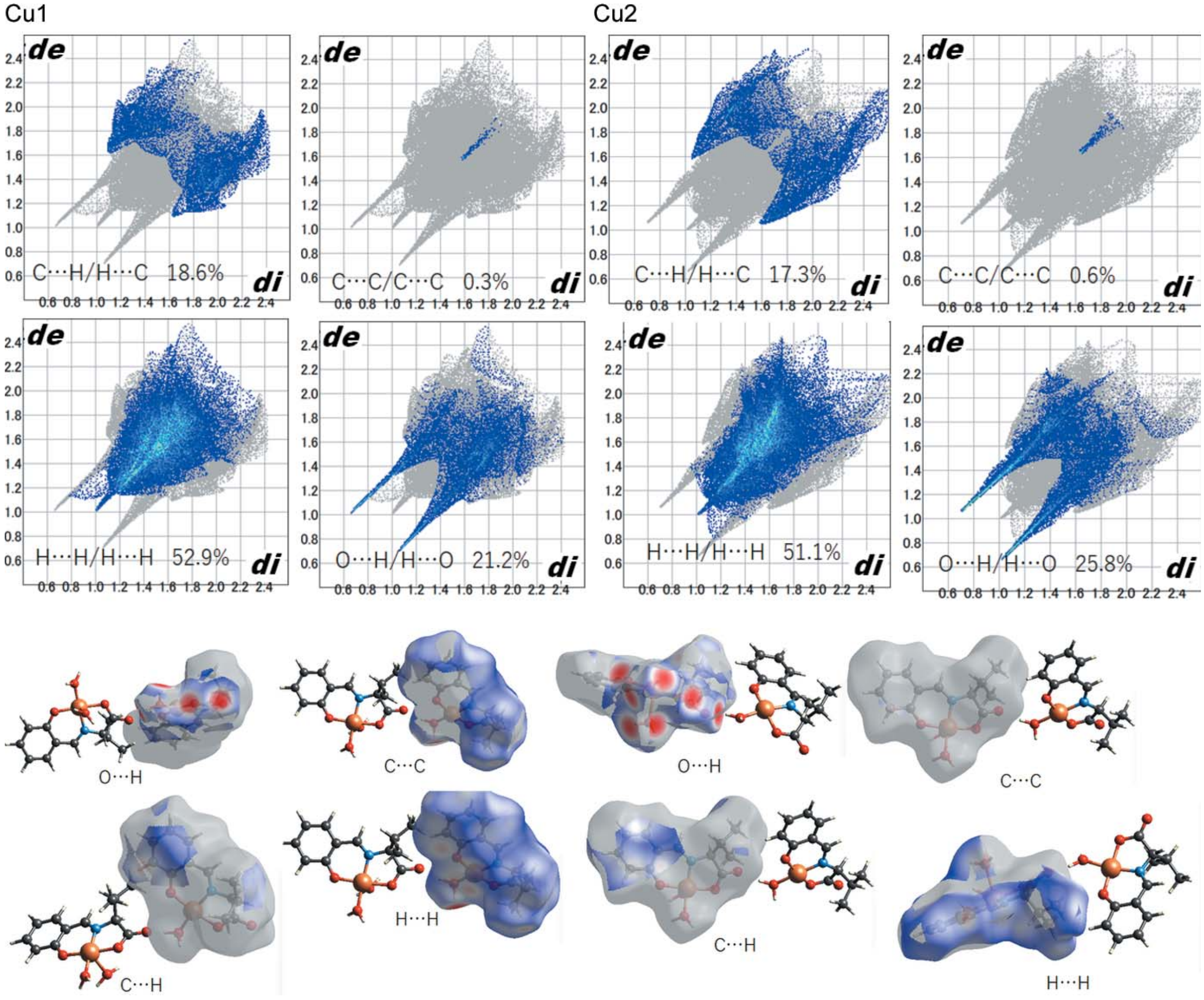


Figure 4
Hirshfeld surfaces mapped over d_{norm} and two-dimensional fingerprint plots.

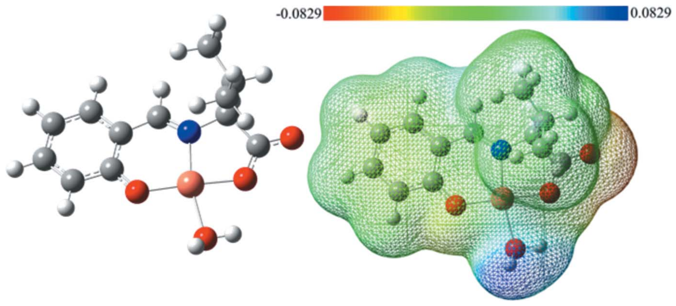


Figure 5
Optimized structure and electrostatic potential map for the title compound.

group is considered to be an electron donor and the water hydrogen atoms are electron acceptor, which is also consistent with the crystal structure (Fig. 5).

5. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.43, update of March 2022; Groom *et al.*, 2016) for similar structures returned three relevant entries: (aqua-*O*)(methanol-*O*)[*N*-salieylidene-L-threoninato]copper(II) (YUYFUW; Katsuumi *et al.*, 2020), (aqua-*O*)[*N*-salieylidene-L-threoninato]copper(II) (SLCDCU; Korhonen & Hämäläinen, 1981), and (aqua-*O*)[*N*-salieylidene-L-valinato]copper(II) (SAVACU; Korhonen & Hamalainen, 1979). In the crystal of YUYFUW, a chain along the *a*-axis direction is formed by one hydrogen bond while the other two hydrogen bonds form a hydrogen-bonded ring. The molecules are packed in a double-column along the *a*-axis direction *via* these three hydrogen bonds. In the crystal of SLCDCU, two molecules form square planes by two intermolecular hydrogen bonds. The crystal of SAVACU has a very similar structure to that of the title complex. In SAVACU, there are two molecules in the unit cell. They have a coordination water per molecule in the unit cell, while the title compound has one or two coordination waters per molecule in the unit cell.

6. Synthesis and crystallization

L-valine (117.7 mg, 1.01 mmol) was reacted with salicylaldehyde (121.5 mg, 0.996 mmol) in methanol (20 mL), which was treated with microwave irradiation at 358 K for 5 min to yield a yellow ligand solution. Copper(II) acetate monohydrate (200.9 mg, 1.01 mmol) was added to the ligand solution and treated with microwave irradiation at 358 K for 5 min to yield a green solution. For recrystallization, the green solution was placed in the air at 300 K for several days, and the title complex was obtained (135.4 mg, 0.437 mmol, yield 43.9%) as green needle-shaped single crystals suitable for single-crystal X-ray diffraction experiments. Elementary analysis: found: C, 47.78; H, 5.12; N, 4.61%. Calculated: $C_{24}H_{32}Cu_2N_2O_9$, C, 46.52; H, 5.21; N, 4.52%. IR (KBr): 1026 cm^{-1} (*m*), 1076 cm^{-1} (*w*), 1134 cm^{-1} (*w*), 1152 cm^{-1} (*m*), 1197 cm^{-1} (*m*), 1286 cm^{-1} (*w*), 1317 cm^{-1} (*m*), 1370 cm^{-1} (*m*), 1450 cm^{-1} (*s*, C═C double bond), 1455 cm^{-1} (*m*), 1535 cm^{-1} (*m*), 1600 cm^{-1} (*s*, C═O double bond), 1639 cm^{-1} (*s*, C═N double bond), 2960 cm^{-1} (*w*), 3300 cm^{-1} (*br*, O—H). UV–vis: 269 nm (ε = 25000 L mol^{-1} cm^{-1}, n–π^*); 367 nm (ε = 9330 L mol^{-1} cm^{-1}, π–π^*); 664 nm (ε =163 L mol^{-1} cm^{-1}, *d*–*d*).

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_{12}H_{13}N_2O_3)(H_2O)_2]\cdot[Cu(C_{12}H_{13}N_2O_3)(H_2O)]$
M_r	619.59
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	173
a, b, c (Å)	5.2966 (3), 15.8698 (10), 29.5216 (16)
V (Å^3)	2481.5 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.77
Crystal size (mm)	0.30 × 0.30 × 0.20
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.46, 0.72
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31718, 6889, 6586
R_{int}	0.036
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.732
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.053, 1.04
No. of reflections	6889
No. of parameters	358
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.31
Absolute structure	Flack x determined using 2499 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.011 (4)

Computer programs: *SAINT* (Bruker, 2019), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), and *ShelXle* (Hübschle *et al.*, 2011).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All C-bound H atoms were placed in geometrically calculated positions (C—H = 0.93–0.98 Å) and were constrained using a riding model with U_{iso}(H) = 1.2U_{eq}(C) for R2CH and R3CH H atoms and 1.5U_{eq}(C) for the methyl H atoms. The O-bound H atoms were located based on a difference-Fourier map and refined isotropically (H2*B*, H10, H11, and H12) or using riding model (H2*A* and H6) with O—H = 0.82 Å. Water H atoms were freely refined.

Funding information

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supporting information

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Crystal structure and Hirshfeld surface analysis of mono/bis(aqua-κO)[N-(2-oxidobenzylidene)valinato-$\kappa^3 O,N,O'$]copper(II): dimeric Schiff base copper(II) complexes having different numbers of coordinated water molecules

Yukihito Akiyama, Soma Suzuki, Shintaro Suda, Yuji Takiguchi, Daisuke Nakane and Takashiro Akitsu

Computing details

Cell refinement: *SAINT* V8.40B (Bruker, 2019); data reduction: *SAINT* V8.40B (Bruker, 2019); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ShelXle* (Hübschle *et al.*, 2011).

Bis(aqua-κO)[N-(2-oxidobenzylidene)valinato-$\kappa^3 O,N,O'$]copper(II)–(aqua-κO)[N-(2-oxidobenzylidene)valinato-$\kappa^3 O,N,O'$]copper(II)

Crystal data

$[Cu(C_{12}H_{13}N_2O_3)(H_2O)_2]\cdot[Cu(C_{12}H_{13}N_2O_3)(H_2O)]$
$M_r = 619.59$
Orthorhombic, $P2_12_12_1$
$a = 5.2966$ (3) Å
$b = 15.8698$ (10) Å
$c = 29.5216$ (16) Å
$V = 2481.5$ (2) Å^3
$Z = 4$
$F(000) = 1280$
$D_x = 1.658$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9895 reflections
$\theta = 2.4–31.1°$
$\mu = 1.77$ mm^{-1}
$T = 173$ K
Prism, green
0.30 × 0.30 × 0.20 mm

Data collection

Bruker D8 QUEST diffractometer
Detector resolution: 7.3910 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.46$, $T_{max} = 0.72$
31718 measured reflections
6889 independent reflections
6586 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 31.4°$, $\theta_{min} = 2.4°$
$h = -7 \rightarrow 7$
$k = -22 \rightarrow 22$
$l = -40 \rightarrow 40$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.053$
$S = 1.04$
6889 reflections
358 parameters
6 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.2409P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$

$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Absolute structure: Flack x determined using 2499 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.011 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Cu1	0.11262 (5)	0.88425 (2)	0.63867 (2)	0.01477 (6)
O1	0.3595 (3)	0.83347 (9)	0.67629 (5)	0.0192 (3)
N1	−0.0502 (3)	0.94302 (10)	0.68746 (6)	0.0143 (3)
C1	0.3607 (4)	0.83347 (12)	0.72030 (7)	0.0161 (4)
O2	0.2196 (3)	0.82454 (11)	0.58489 (5)	0.0196 (3)
H2A	0.244 (5)	0.8586 (12)	0.5641 (8)	0.029*
H2B	0.302 (7)	0.788 (2)	0.5828 (10)	0.037 (9)*
Cu2	1.10130 (5)	0.59080 (2)	0.52618 (2)	0.01400 (6)
N2	0.9488 (3)	0.52729 (10)	0.57450 (6)	0.0142 (3)
C2	0.5531 (4)	0.78889 (14)	0.74338 (8)	0.0207 (4)
H2	0.678688	0.760457	0.726235	0.025*
O3	−0.1792 (3)	0.92508 (10)	0.60406 (5)	0.0200 (3)
C3	0.5636 (4)	0.78553 (14)	0.78973 (8)	0.0238 (5)
H3	0.696009	0.754944	0.803896	0.029*
C4	0.3851 (5)	0.82577 (14)	0.81637 (7)	0.0256 (5)
H4	0.393972	0.823083	0.848482	0.031*
O4	−0.5423 (3)	0.99473 (11)	0.61129 (5)	0.0260 (4)
O5	1.3524 (3)	0.50427 (9)	0.51440 (5)	0.0180 (3)
C5	0.1956 (5)	0.86955 (14)	0.79529 (7)	0.0229 (5)
H5	0.070134	0.896356	0.813204	0.027*
C6	0.1819 (4)	0.87587 (13)	0.74778 (7)	0.0173 (4)
O6	1.2451 (3)	0.65830 (10)	0.47779 (5)	0.0213 (3)
H6	1.255 (6)	0.6333 (13)	0.4577 (9)	0.032*
H10	1.268 (5)	0.7058 (17)	0.4757 (9)	0.021 (7)*
C7	−0.0186 (4)	0.92620 (12)	0.72964 (7)	0.0169 (4)
H7	−0.137447	0.948897	0.750431	0.02*
O7	0.8331 (3)	0.67403 (9)	0.54208 (5)	0.0169 (3)
O8	0.4592 (3)	0.67902 (10)	0.57700 (5)	0.0233 (4)
C8	−0.2649 (4)	0.99514 (13)	0.67389 (7)	0.0147 (4)
H8	−0.40969	0.983539	0.694712	0.018*
C9	−0.2066 (4)	1.09107 (13)	0.67467 (7)	0.0175 (4)
H9	−0.369691	1.120986	0.668994	0.021*
O9	0.7962 (3)	0.54667 (10)	0.47266 (5)	0.0199 (3)
H11	0.639 (4)	0.5298 (17)	0.4845 (9)	0.036 (8)*
C10	−0.1127 (5)	1.11970 (13)	0.72084 (7)	0.0257 (5)

H10A	0.052137	1.094098	0.726988	0.039*
H10B	−0.233321	1.102247	0.744205	0.039*
H10C	−0.09647	1.181214	0.721102	0.039*
C11	−0.0264 (5)	1.11791 (15)	0.63772 (8)	0.0302 (5)
H11A	−0.095199	1.101598	0.608178	0.045*
H11B	0.137196	1.090352	0.642289	0.045*
H11C	−0.004356	1.179195	0.638722	0.045*
C12	−0.3387 (4)	0.96951 (13)	0.62616 (7)	0.0177 (4)
H12	0.888 (6)	0.5219 (18)	0.4458 (9)	0.083 (13)*
C13	1.3597 (4)	0.42803 (12)	0.53182 (7)	0.0152 (4)
C14	1.5490 (4)	0.37100 (13)	0.51776 (8)	0.0218 (5)
H14	1.667897	0.388197	0.495506	0.026*
C15	1.5648 (4)	0.29095 (14)	0.53564 (8)	0.0225 (5)
H15	1.694644	0.254278	0.525437	0.027*
C16	1.3961 (5)	0.26255 (13)	0.56815 (7)	0.0234 (4)
H16	1.40961	0.207391	0.580411	0.028*
C17	1.2097 (5)	0.31627 (13)	0.58204 (7)	0.0213 (5)
H17	1.090484	0.29721	0.603799	0.026*
C18	1.1888 (4)	0.39903 (12)	0.56511 (7)	0.0154 (4)
C19	0.9900 (4)	0.44974 (13)	0.58356 (7)	0.0169 (4)
H19	0.878687	0.423325	0.604428	0.02*
C20	0.7350 (4)	0.56826 (13)	0.59688 (7)	0.0150 (4)
H20	0.587525	0.528907	0.596481	0.018*
C21	0.7975 (4)	0.59083 (14)	0.64687 (7)	0.0186 (4)
H21	0.913474	0.546104	0.658543	0.022*
C22	0.5643 (5)	0.58942 (17)	0.67622 (8)	0.0289 (5)
H22A	0.446763	0.633181	0.666033	0.043*
H22B	0.611852	0.600033	0.707791	0.043*
H22C	0.482905	0.534139	0.6739	0.043*
C23	0.9366 (5)	0.67446 (15)	0.65091 (8)	0.0248 (5)
H23A	1.075345	0.676035	0.62896	0.037*
H23B	1.004679	0.680335	0.681614	0.037*
H23C	0.819359	0.720835	0.644748	0.037*
C24	0.6677 (4)	0.64671 (13)	0.56966 (7)	0.0150 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01555 (12)	0.01609 (11)	0.01265 (11)	0.00322 (11)	−0.00113 (10)	−0.00101 (8)
O1	0.0201 (8)	0.0222 (7)	0.0153 (7)	0.0047 (7)	−0.0001 (6)	0.0007 (5)
N1	0.0144 (8)	0.0138 (8)	0.0149 (8)	0.0019 (7)	−0.0025 (6)	−0.0010 (6)
C1	0.0151 (10)	0.0138 (9)	0.0194 (9)	−0.0022 (8)	−0.0024 (8)	0.0005 (7)
O2	0.0259 (8)	0.0170 (7)	0.0160 (7)	0.0069 (7)	0.0024 (6)	0.0013 (6)
Cu2	0.01489 (11)	0.01297 (11)	0.01415 (11)	0.00229 (10)	0.00415 (10)	0.00287 (8)
N2	0.0142 (8)	0.0140 (8)	0.0145 (8)	0.0030 (7)	0.0020 (6)	0.0010 (6)
C2	0.0178 (11)	0.0195 (10)	0.0247 (11)	0.0016 (9)	−0.0010 (8)	0.0022 (8)
O3	0.0200 (7)	0.0238 (8)	0.0161 (7)	0.0059 (6)	−0.0036 (6)	−0.0054 (6)
C3	0.0235 (12)	0.0221 (10)	0.0257 (11)	0.0013 (10)	−0.0078 (9)	0.0050 (8)

C4	0.0328 (12)	0.0271 (11)	0.0168 (10)	0.0003 (12)	−0.0061 (10)	0.0025 (8)
O4	0.0216 (8)	0.0318 (9)	0.0246 (8)	0.0093 (7)	−0.0096 (6)	−0.0086 (7)
O5	0.0176 (8)	0.0147 (6)	0.0217 (7)	0.0011 (6)	0.0051 (6)	0.0040 (5)
C5	0.0298 (12)	0.0217 (11)	0.0172 (10)	0.0037 (10)	−0.0014 (9)	−0.0010 (8)
C6	0.0200 (10)	0.0164 (9)	0.0155 (9)	−0.0004 (9)	−0.0034 (8)	0.0000 (8)
O6	0.0331 (9)	0.0128 (7)	0.0181 (8)	−0.0045 (7)	0.0085 (7)	0.0004 (6)
C7	0.0194 (10)	0.0138 (9)	0.0174 (10)	0.0015 (8)	0.0005 (8)	−0.0022 (7)
O7	0.0207 (8)	0.0144 (6)	0.0157 (7)	0.0036 (6)	0.0034 (6)	0.0031 (5)
O8	0.0227 (8)	0.0216 (8)	0.0256 (8)	0.0093 (7)	0.0066 (6)	0.0032 (6)
C8	0.0139 (9)	0.0151 (9)	0.0152 (9)	0.0027 (8)	−0.0008 (7)	−0.0013 (7)
C9	0.0186 (9)	0.0136 (9)	0.0203 (10)	0.0018 (9)	−0.0011 (8)	−0.0001 (8)
O9	0.0178 (7)	0.0258 (8)	0.0163 (7)	−0.0040 (6)	0.0039 (6)	0.0011 (6)
C10	0.0297 (12)	0.0191 (10)	0.0282 (11)	−0.0009 (11)	−0.0040 (11)	−0.0054 (8)
C11	0.0385 (14)	0.0216 (11)	0.0305 (12)	−0.0026 (10)	0.0070 (11)	0.0028 (10)
C12	0.0177 (11)	0.0158 (9)	0.0197 (10)	0.0006 (8)	−0.0019 (8)	−0.0028 (7)
C13	0.0143 (9)	0.0146 (8)	0.0167 (9)	0.0005 (8)	−0.0019 (8)	−0.0019 (7)
C14	0.0182 (11)	0.0182 (10)	0.0289 (11)	0.0015 (8)	0.0049 (8)	−0.0014 (8)
C15	0.0194 (11)	0.0184 (10)	0.0298 (12)	0.0056 (9)	0.0001 (9)	−0.0041 (8)
C16	0.0309 (11)	0.0143 (9)	0.0249 (10)	0.0044 (11)	−0.0035 (11)	0.0004 (8)
C17	0.0270 (11)	0.0167 (10)	0.0203 (11)	0.0026 (9)	0.0041 (9)	0.0031 (8)
C18	0.0178 (9)	0.0139 (9)	0.0146 (9)	0.0020 (8)	−0.0001 (7)	0.0008 (7)
C19	0.0201 (10)	0.0168 (10)	0.0139 (9)	−0.0003 (8)	0.0038 (8)	0.0030 (7)
C20	0.0144 (9)	0.0157 (9)	0.0150 (9)	0.0024 (8)	0.0040 (7)	0.0007 (7)
C21	0.0197 (10)	0.0212 (10)	0.0149 (9)	0.0053 (9)	0.0025 (8)	0.0010 (8)
C22	0.0291 (13)	0.0383 (13)	0.0192 (10)	−0.0018 (12)	0.0094 (9)	−0.0006 (9)
C23	0.0247 (12)	0.0300 (11)	0.0198 (10)	−0.0033 (10)	−0.0002 (9)	−0.0029 (9)
C24	0.0161 (10)	0.0151 (9)	0.0137 (9)	0.0018 (8)	−0.0006 (7)	−0.0018 (7)

Geometric parameters (Å, º)

Cu1—O1	1.8955 (15)	O5—C13	1.315 (2)
Cu1—N1	1.9205 (16)	C5—C6	1.408 (3)
Cu1—O2	1.9339 (16)	C6—C7	1.433 (3)
Cu1—O3	1.9629 (15)	O7—C24	1.272 (2)
O1—C1	1.299 (2)	O8—C24	1.237 (3)
N1—C7	1.284 (3)	C8—C12	1.518 (3)
N1—C8	1.462 (3)	C8—C9	1.554 (3)
C1—C2	1.415 (3)	C9—C11	1.511 (3)
C1—C6	1.417 (3)	C9—C10	1.520 (3)
Cu2—N2	1.9243 (17)	C13—C18	1.413 (3)
Cu2—O6	1.9411 (15)	C13—C14	1.413 (3)
Cu2—O5	1.9432 (14)	C14—C15	1.378 (3)
Cu2—O7	1.9956 (14)	C15—C16	1.387 (3)
Cu2—O9	2.3663 (16)	C16—C17	1.367 (3)
N2—C19	1.278 (3)	C17—C18	1.410 (3)
N2—C20	1.464 (3)	C18—C19	1.433 (3)
C2—C3	1.370 (3)	C20—C24	1.524 (3)
O3—C12	1.279 (3)	C20—C21	1.554 (3)

C3—C4	1.386 (3)	C21—C22	1.509 (3)
C4—C5	1.370 (3)	C21—C23	1.523 (3)
O4—C12	1.231 (3)		

O1—Cu1—N1	94.40 (7)	C5—C6—C7	116.7 (2)
O1—Cu1—O2	94.04 (7)	C1—C6—C7	123.11 (18)
N1—Cu1—O2	170.16 (7)	N1—C7—C6	125.1 (2)
O1—Cu1—O3	171.32 (7)	C24—O7—Cu2	114.52 (12)
N1—Cu1—O3	82.90 (7)	N1—C8—C12	107.65 (16)
O2—Cu1—O3	88.01 (7)	N1—C8—C9	113.31 (17)
C1—O1—Cu1	126.10 (14)	C12—C8—C9	109.13 (17)
C7—N1—C8	118.99 (17)	C11—C9—C10	110.89 (19)
C7—N1—Cu1	124.59 (15)	C11—C9—C8	113.03 (18)
C8—N1—Cu1	114.74 (12)	C10—C9—C8	111.79 (17)
O1—C1—C2	119.00 (19)	O4—C12—O3	125.1 (2)
O1—C1—C6	124.71 (19)	O4—C12—C8	118.02 (18)
C2—C1—C6	116.29 (19)	O3—C12—C8	116.81 (18)
N2—Cu2—O6	177.73 (7)	O5—C13—C18	123.56 (18)
N2—Cu2—O5	92.86 (6)	O5—C13—C14	119.67 (19)
O6—Cu2—O5	89.41 (7)	C18—C13—C14	116.76 (18)
N2—Cu2—O7	82.74 (6)	C15—C14—C13	121.4 (2)
O6—Cu2—O7	95.00 (7)	C14—C15—C16	121.7 (2)
O5—Cu2—O7	175.60 (6)	C17—C16—C15	118.1 (2)
N2—Cu2—O9	93.05 (7)	C16—C17—C18	122.1 (2)
O6—Cu2—O9	86.56 (7)	C17—C18—C13	119.99 (19)
O5—Cu2—O9	97.98 (6)	C17—C18—C19	116.49 (19)
O7—Cu2—O9	82.34 (6)	C13—C18—C19	123.52 (18)
C19—N2—C20	117.73 (17)	N2—C19—C18	125.9 (2)
C19—N2—Cu2	126.01 (15)	N2—C20—C24	107.80 (16)
C20—N2—Cu2	115.27 (12)	N2—C20—C21	111.48 (17)
C3—C2—C1	122.0 (2)	C24—C20—C21	111.23 (17)
C12—O3—Cu1	115.88 (13)	C22—C21—C23	111.35 (19)
C2—C3—C4	121.4 (2)	C22—C21—C20	111.56 (18)
C5—C4—C3	118.4 (2)	C23—C21—C20	112.23 (17)
C13—O5—Cu2	126.88 (13)	O8—C24—O7	125.85 (19)
C4—C5—C6	121.8 (2)	O8—C24—C20	117.06 (18)
C5—C6—C1	120.1 (2)	O7—C24—C20	117.07 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O9^{i}	0.83	1.87	2.688 (2)	167
O2—H2*B*···O8	0.72 (3)	1.93 (3)	2.645 (2)	169 (4)
O6—H6···O3^{ii}	0.72	2.07	2.784 (2)	171
O6—H10···O7^{iii}	0.77 (3)	2.01 (3)	2.764 (2)	169 (3)

O9—H11···O5^{iv}	0.94 (2)	1.80 (2)	2.738 (2)	172 (3)
O9—H12···O4^{ii}	1.01 (2)	1.74 (2)	2.703 (2)	157 (3)

Symmetry codes: (i) *x*−1/2, −*y*+3/2, −*z*+1; (ii) *x*+3/2, −*y*+3/2, −*z*+1; (iii) *x*+1/2, −*y*+3/2, −*z*+1; (iv) *x*−1, *y*, *z*.