

КРАТКИЕ СООБЩЕНИЯ

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STRUCTURAL CHARACTERIZATION OF TWO COPPER(II) COMPLEXES WITH OXIME-TYPE LIGANDS

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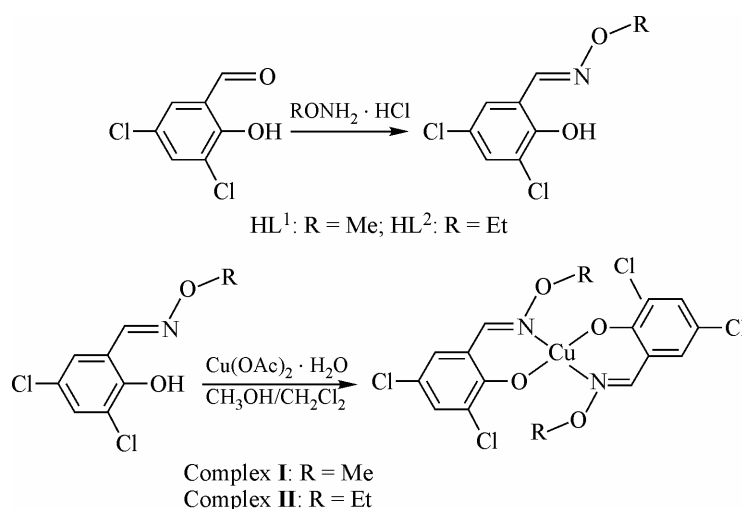
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Two new linear Cu^{II} complexes [Cu(L¹)₂] (**I**) (HL¹ = (*E*)-3,5-dichloro-2-hydroxy benzaldehyde *O*-methyl oxime) and [Cu(L²)₂] (**II**) (HL² = (*E*)-3,5-dichloro-2-hydroxy benzaldehyde *O*-ethyl oxime) are synthesized and characterized by elemental analysis, IR, UV–Vis, and X-ray diffraction methods. X-ray crystallographic analyses indicate that complexes **I** and **II** have a similar structure consisting of one Cu^{II} ion and two L[−] units. In the complexes, the Cu^{II} ion lying on an inversion centre is four-coordinated in a *trans*-CuN₂O₂ square planar geometry by two phenolate O and two oxime N atoms from two symmetry-related N,O-bidentate oxime-type ligands. However, the crystal structure of the two complexes is different: complex **I** forms an infinite three-dimensional supramolecular network structure through intermolecular hydrogen bonding and π⋯π interaction, while complex **II** forms an infinite one-dimensional supramolecular structure through intermolecular hydrogen bonds.

Keywords: synthesis, characterization, crystal structure, oxime-type ligand, copper(II) complex.

Oximes are a traditional class of chelating ligands widely used in coordination and analytical chemistry and extraction metallurgy [1, 2]. Due to the marked ability to form bridges with metal ions, oxime ligands may be used to obtain polynuclear compounds with molecular magnetism and supramolecular structure [3, 4]. Also, oxime-containing ligands are strong donors, and therefore, they

Scheme 1. Synthetic routes of HL¹, HL² and their Cu^{II} complexes

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were found to efficiently stabilize high oxidation states of metal ions such as Cu^{II} and Ni^{II} [5, 6]. The presence of additional donor groups together with the oxime group in the ligand molecule may result in a significant increase in chelating efficiency and ability to form polynuclear complexes. Herein, two new Cu^{II} complexes with the oxime ligand, $[\text{Cu}(\text{L}^1)_2]$ (**I**) ($\text{HL}^1 = (E)$ -3,5-dichloro-2-hydroxy benzaldehyde *O*-methyl oxime) and $[\text{Cu}(\text{L}^2)_2]$ (**II**) ($\text{HL}^2 = (E)$ -3,5-dichloro-2-hydroxy benzaldehyde *O*-ethyl oxime) have been synthesized and characterized by elemental analyses, IR and UV—Vis. spectroscopy. X-ray crystallographic analyses reveal that the structures of complexes **I** and **II** are very similar. They are both mononuclear structures and all the Cu^{II} ions are four-coordinated. However, the bond angles and distances vary because of different substituents in the ligand.

Experimental. Reagents and physical measurements. Methoxyamine and ethoxyamine from Alfa Aesar were used without further purification. 3,5-dichlorosalicylaldehyde, other reagents, and the solvent were analytical grade from Tianjin Chemical Reagent Factory. C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. IR spectra were recorded on a VERTEX70 FT—IR spectrophotometer with samples prepared as KBr (500—4000 cm^{-1}) and CsI (100—500 cm^{-1}) pellets. The X-ray single crystal structure determination was carried out on a Bruker Smart APEX CCD diffractometer. The UV—Vis spectrum was taken on a Shimadzu UV-240 spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A type conductivity bridge using a $1.0 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ solution in DMF at room temperature.

Preparation of HL^1 , HL^2 . HL^1 ((*E*)-3,5-dichloro-2-hydroxybenzaldehyde *O*-methyl oxime) and HL^2 ((*E*)-3,5-dichloro-2-hydroxybenzaldehyde *O*-ethyl oxime) were synthesized according to the analogous method [7, 8].

Preparation of $[\text{Cu}(\text{L}^1)_2]$ (I**).** A solution of copper(II) acetate monohydrate (1.3 mg, 0.007 mmol) in methanol (4 ml) was added dropwise to a solution of HL^1 (1.2 mg, 0.005 mmol) in dichloromethane (5 ml) at room temperature. The color of the mixing solution turned pale yellow immediately, and it was allowed to stand at room temperature for one week. Then the solvent partially evaporated and yellow prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Anal. Calc. for $\text{C}_{16}\text{H}_{12}\text{Cl}_4\text{CuN}_2\text{O}_4$ (%): C, 38.31; H, 2.41; N, 5.58; Cu, 12.67. Found: C, 38.25; H, 2.46; N, 5.39; Cu, 12.69.

Preparation of $[\text{Cu}(\text{L}^2)_2]$ (II**).** A solution of copper(II) acetate monohydrate (2.3 mg, 0.01 mmol) in methanol (3 ml) was added dropwise to a solution of HL^2 (5.4 mg, 0.02 mmol) in dichloromethane (5 ml) at room temperature. The color of the mixing solution turned pale yellow immediately, and allowed to stand at room temperature for two weeks. Then the solvent partially evaporated and yellow prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Anal. Calc. for $\text{C}_{18}\text{H}_{16}\text{Cl}_4\text{CuN}_2\text{O}_4$ (%): C, 40.82; H, 3.04; N, 5.29; Cu, 12.00. Found: C, 40.71; H, 3.09; N, 4.98; Cu, 12.13.

Crystal structure determination. The single crystals of complexes **I** and **II** with approximate dimensions of $0.38 \times 0.11 \times 0.06 \text{ mm}$ and $0.28 \times 0.19 \times 0.10 \text{ mm}$ were placed on a Bruker Smart 1000 CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radiation ($\lambda = 0.071073 \text{ nm}$) at 298(2) K. The LP factor and semi-empirical absorption corrections were applied to the intensity data. The structures were solved using the SHELXS-97 program, and refined by the full-matrix least squares fitting on F^2 using SHELXS-97. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. Details of the data collection and refinements of complexes **I** and **II** are given in Table 1. The full crystallographic data were deposited in the form of CIF files at the Cambridge Structural Database (CCDC Nos. 757705 and 757700 for **I** and **II**, respectively) and are available freely upon request citing the deposition number from the web site: www.ccdc.cam.ac.uk/data_request/cif.

Analysis of FT—IR spectra. The FT—IR spectra of HL^1 , HL^2 , and their corresponding Cu^{II} complexes exhibit various bands in the 400—4000 cm^{-1} region. The most important FT—IR bands for HL^1 , HL^2 , and complexes **I** and **II** are given in Table 4. Free HL^1 and HL^2 ligands exhibit characteristic C=N stretching bands at 1608 cm^{-1} and 1607 cm^{-1} , while C=N of complexes **I** and **II** were observed in the 1602 cm^{-1} and 1601 cm^{-1} respectively. The C=N stretching frequencies are all shifted to

Table 1

Crystal data and structure refinement for complexes I and II

Parameter	I	II
Empirical formula	C ₁₆ H ₁₂ Cl ₄ CuN ₂ O ₄	C ₁₈ H ₁₆ Cl ₄ CuN ₂ O ₄
Formula weight	501.62	529.67
Temperature, K	298(2)	298(2)
Wavelength Å	0.71073	0.71073
Crystal system, space group	Monoclinic, <i>P</i> 2(1)/ <i>c</i>	Triclinic, <i>P</i> -1
Unit cell dimensions		
<i>a</i> , <i>b</i> , <i>c</i> , Å	3.9066(5), 13.544(1), 17.108(2)	7.923(1), 8.005(1), 8.857(1)
α, β, γ, deg.	90, 94.298(1), 90	106.315(2), 100.735(1), 100.194(1)
Volume, Å ³	902.7(2)	513.8(1)
Z, Calculated density, mg/m ³	2, 1.846	1, 1.712
Absorption coefficient, mm ⁻¹	1.829	1.611
<i>F</i> (000)	502	267
Crystal size, mm ³	0.38×0.11×0.06	0.28×0.19×0.10
θ range for data collection, deg.	1.92—25.02	2.47—25.02
Limiting indices	-4 ≤ <i>h</i> ≤ 4, -16 ≤ <i>k</i> ≤ 15, -16 ≤ <i>l</i> ≤ 20	-9 ≤ <i>h</i> ≤ 9, -7 ≤ <i>k</i> ≤ 9, -10 ≤ <i>l</i> ≤ 9
Reflections collected / unique	4657 / 1594 [<i>R</i> _{int} = 0.0393]	2683 / 1790 [<i>R</i> _{int} = 0.0310]
Completeness to θ, deg.	99.7 % (θ = 25.02)	98.2 % (θ = 25.02)
Absorption correction	Semi-empirical fom equivalents	Semi-empirical from equivalents
Max. / min. transmission	0.8982 / 0.5433	0.8555 / 0.6611
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1594 / 0 / 125	1790 / 0 / 134
GOOF <i>F</i> ²	1.027	1.061
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0310, <i>wR</i> ₂ = 0.0744	<i>R</i> ₁ = 0.0499, <i>wR</i> ₂ = 0.1411
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0434, <i>wR</i> ₂ = 0.0786	<i>R</i> ₁ = 0.0564, <i>wR</i> ₂ = 0.1482
Largest diff. peak / hole, e/Å ⁻³)	0.328 / -0.324	0.565 / -0.881

lower frequencies by *ca.* 6 cm⁻¹ upon complexation, indicating a decrease in the C=N bond order due to the coordinated bond of the Cu^{II} atom with the oxime nitrogen lone pair [9]. In the 1448–1571 cm⁻¹ region, the observed bands were attributed to aromatic C=C vibrations. Upon coordination, these bands shift to lower frequencies for the Cu^{II} complexes [10]. The Ar—O stretching frequency appears as a strong band within 1263–1213 cm⁻¹, as reported for similar ligands [11]. This band occurs at 1264 cm⁻¹ for the ligand HL¹, and at 1214 cm⁻¹ for complex I, the band occurs at 1273 cm⁻¹ for the ligand HL², and at 1215 cm⁻¹ for complex II. The Ar—O stretching frequency is shifted to a lower frequency, indicating that the Cu—O bond formed between the Cu^{II} ion and oxygen of the phenolic group [9, 10]. The far-infrared spectra of complexes I and II was also obtained in the 500–100 cm⁻¹ region in order to identify frequencies belonging to Cu—O and Cu—N bonds. The FT—IR spectrum of complex I showed the ν(Cu—N) and ν(Cu—O) vibrational absorption frequencies at 505 cm⁻¹ and 421 cm⁻¹ (or 496 cm⁻¹ and 420 cm⁻¹ for complex II) respectively. These assignments are consistent with the literature frequency values [12].

Analysis of UV—Vis spectra. The absorption spectra of HL¹, HL² ligands and their corresponding Cu^{II} complexes in a diluted DMF solution show that the spectra are similar to each other. The UV—Vis spectra of the free HL¹ ligand and complex I exhibit absorption peaks at *ca.* 311 nm and 313 nm respectively. Compared with HL¹ and its complex, HL² and complex II both have similar UV—Vis spectra and the absorption peaks occur at *ca.* 313 nm and 314 nm respectively. These absorption peaks show a hypsochromic shift (*ca.* 1–2 nm) further demonstrating the coordination beha-

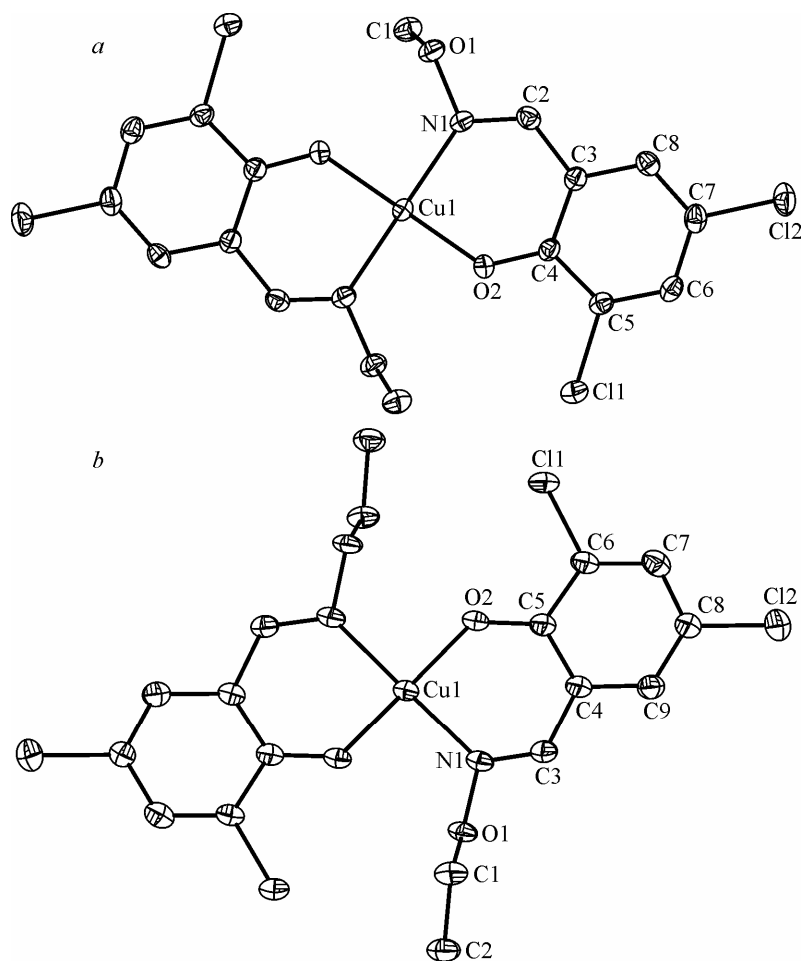


Fig. 1. Molecular structure of **I** (a) and **II** (b) with atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level

avior of Cu^{II} ions and the ligands. Compared with the ligands HL^1 and HL^2 , an important feature of the absorption spectrum of the complex **I** and **II** is shown that a new absorption peak assigned to $\pi-\pi^*$ transition is observed at *ca.* 371 nm and *ca.* 370 nm respectively [13, 14], which is absent in the spectra of HL^1 and HL^2 .

Results and discussion. Crystal structure description. The single crystal structures of complexes **I** and **II** were confirmed by X-ray crystallography (Fig. 1). The selected bond lengths and angles of complexes **I** and **II** are in Tables 2 and 3. The X-ray structural studies reveal that complex **I** is in the monoclinic system, $P2(1)/c$ space group, and complex **II** is in the triclinic system, $P-1$ space group. The structures of the two complexes are found to be identical, except that the oxime portion of the two differs by only a $-\text{CH}_2-$ group. Both compounds can be described as centrosymmetric mononuclear Cu^{II} complexes; the Cu^{II} ion lying on the inversion centre is four-coordinated in a *trans*- CuN_2O_2 square planar geometry with two phenolate O and two oxime N atoms from two N,O-bidentate oxime-type ligands (HL^1 and HL^2). In both the cases, two oxime nitrogen and two phenolicoxygen atoms form the square base with the $\text{Cu}-\text{N}$ bonds being slightly longer than the corresponding $\text{Cu}-\text{O}$ bonds. The elongation of the coordinated bonds, $\text{Cu}-\text{O}$ and $\text{Cu}-\text{N}$, indicates a weaker interaction of the HL^- unit with the Cu^{II} center, probably due to the weakening of the coordination abilities of coordinating nitrogen atoms by the larger electronegativity of oxygen atoms of the oxime group. This significant elongation has been observed in the Cu^{II} complex with the Salen ligand [15]. However, due to the presence of an extra $-\text{CH}_2-$ group in the bidentate ligand, the bond lengths and angles vary. The coordination $\text{Cu}-\text{N}$ bond (2.006 Å) of complex **I** is longer than $\text{Cu}-\text{N}$ (1.989 Å) of complex **II**, but $\text{Cu}-\text{O}$ (1.904 Å) of complex **I** is shorter than $\text{Cu}-\text{O}$ (1.886 Å) of complex **II**. The $\text{N1}-\text{Cu1}-\text{O2}$ angle (89.80°) in complex **I** is similar to the $\text{N1}-\text{Cu1}-\text{O2}$ angle (89.78°) in complex **II**.

Table 2

Selected bond lengths (Å) and bond angles (deg.) for complex I

Bond lengths					
Cu(1)—O(2)#1	1.904(2)	N(1)—C(2)	1.275(3)	C(3)—C(4)	1.422(4)
Cu(1)—O(2)	1.904(2)	N(1)—O(1)	1.419(3)	C(4)—C(5)	1.420(4)
Cu(1)—N(1)	1.989(2)	O(1)—C(1)	1.425(3)	C(5)—C(6)	1.368(4)
Cu(1)—N(1)#1	1.989(2)	O(2)—C(4)	1.286(3)	C(6)—C(7)	1.388(4)
Cl(1)—C(5)	1.734(3)	C(2)—C(3)	1.431(4)	C(7)—C(8)	1.365(4)
Cl(2)—C(7)	1.733(3)	C(3)—C(8)	1.398(4)		
Bond angles					
O(2)#1—Cu(1)—O(2)	180.000(2)	N(1)—O(1)—C(1)	109.4(2)	C(6)—C(5)—C(4)	123.6(2)
O(2)#1—Cu(1)—N(1)	90.22(8)	C(4)—O(2)—Cu(1)	130.5(2)	C(6)—C(5)—Cl(1)	118.6(2)
O(2)—Cu(1)—N(1)	89.78(8)	N(1)—C(2)—C(3)	125.9(2)	C(4)—C(5)—Cl(1)	117.8(2)
O(2)#1—Cu(1)—N(1)#1	89.78(8)	C(8)—C(3)—C(4)	121.3(3)	C(5)—C(6)—C(7)	119.6(3)
O(2)—Cu(1)—N(1)#1	90.22(8)	C(8)—C(3)—C(2)	117.4(2)	C(8)—C(7)—C(6)	119.8(3)
N(1)—Cu(1)—N(1)#1	180.000(2)	C(4)—C(3)—C(2)	121.2(2)	C(8)—C(7)—Cl(2)	120.8(2)
C(2)—N(1)—O(1)	110.7(2)	O(2)—C(4)—C(3)	124.5(2)	C(6)—C(7)—Cl(2)	119.4(2)
C(2)—N(1)—Cu(1)	127.3(2)	O(2)—C(4)—C(5)	120.9(2)	C(7)—C(8)—C(3)	121.0(3)
O(1)—N(1)—Cu(1)	121.7(2)	C(3)—C(4)—C(5)	114.6(2)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+3$.

Table 3

Selected bond lengths (Å) and bond angles (deg.) for complex II

Bond lengths					
Cu(1)—O(2)	1.886(2)	N(1)—C(3)	1.283(5)	C(4)—C(5)	1.414(5)
Cu(1)—O(2)#1	1.886(2)	N(1)—O(1)	1.432(4)	C(4)—C(9)	1.417(5)
Cu(1)—N(1)#1	2.006(3)	O(1)—C(1)	1.442(4)	C(5)—C(6)	1.425(5)
Cu(1)—N(1)	2.006(3)	O(2)—C(5)	1.306(4)	C(6)—C(7)	1.373(5)
Cl(1)—C(6)	1.738(4)	C(1)—C(2)	1.505(6)	C(7)—C(8)	1.383(6)
Cl(2)—C(8)	1.755(4)	C(3)—C(4)	1.455(5)	C(8)—C(9)	1.374(6)
Bond angles					
O(2)—Cu(1)—O(2)#1	180.000(1)	N(1)—O(1)—C(1)	110.0(3)	C(4)—C(5)—C(6)	115.5(3)
O(2)—Cu(1)—N(1)#1	90.2(1)	C(5)—O(2)—Cu(1)	131.2(2)	C(7)—C(6)—C(5)	122.7(4)
O(2)#1—Cu(1)—N(1)#1	89.8(1)	O(1)—C(1)—C(2)	107.5(3)	C(7)—C(6)—Cl(1)	119.3(3)
O(2)—Cu(1)—N(1)	89.8(1)	N(1)—C(3)—C(4)	124.2(3)	C(5)—C(6)—Cl(1)	118.0(3)
O(2)#1—Cu(1)—N(1)	90.2(1)	C(5)—C(4)—C(9)	121.7(3)	C(6)—C(7)—C(8)	119.8(4)
N(1)#1—Cu(1)—N(1)	180.0(2)	C(5)—C(4)—C(3)	121.9(3)	C(9)—C(8)—C(7)	121.0(4)
C(3)—N(1)—O(1)	109.8(3)	C(9)—C(4)—C(3)	116.4(3)	C(9)—C(8)—Cl(2)	120.1(3)
C(3)—N(1)—Cu(1)	127.8(3)	O(2)—C(5)—C(4)	124.5(3)	C(7)—C(8)—Cl(2)	118.9(3)
O(1)—N(1)—Cu(1)	121.7(2)	O(2)—C(5)—C(6)	120.0(3)	C(8)—C(9)—C(4)	119.3(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$.

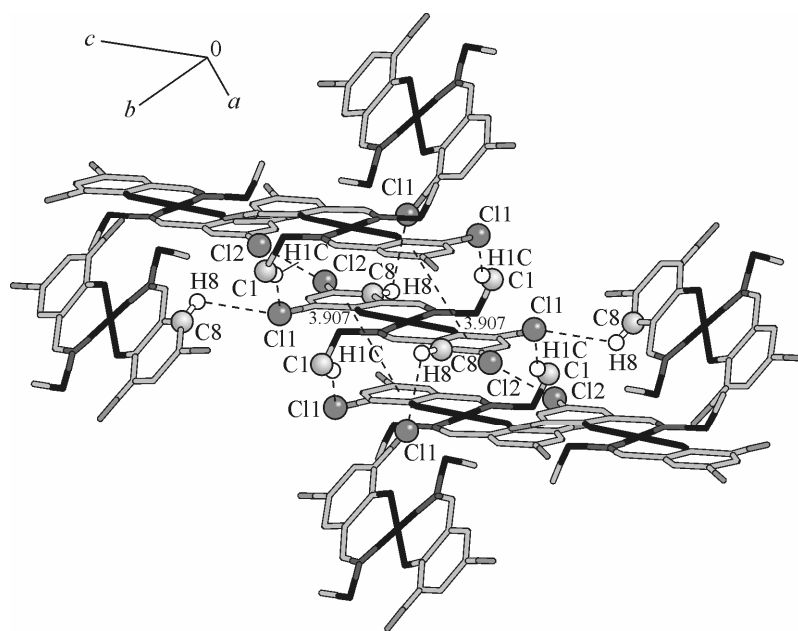


Fig. 2. Part of the 3-D supramolecular structure of complex I, which shows the formation of C8—H8...C11, C1—H1C...C11 hydrogen bonds, the Cl2...Cl2 short interaction and the π...π stacking interaction

Table 4

Most important IR bands for the ligands and their complexes (cm⁻¹)

	$\nu(\text{C}=\text{N})$	$\nu(\text{Ar}-\text{O})$	$\nu(\text{Cu}-\text{N})$	$\nu(\text{Cu}-\text{O})$	$\nu(\text{C}=\text{C})$ benzene ring skeleton		
HL ¹	1608	1264			1574	1559	1547
Complex I	1602	1214	505	421	1526	1503	1448
HL ²	1607	1273			1564	1550	1509
Complex II	1601	1215	496	420	1549	1523	1451

Table 5

Hydrogen bonding (Å, deg.) complexes I and II

	D—H...A	$d(\text{D}-\text{H})$	$d(\text{H}\cdots\text{A})$	$\angle\text{DHA}$	$d(\text{D}\cdots\text{A})$	Symmetric code
Complex I	C1—H1C...C11	0.960	2.85	155.0	3.741(3)	$-x, 1-y, 3-z$
	C8—H8...C11	0.930	2.95	118.2	3.487(3)	$-x, -1/2+y, 7/2-z$
Complex II	C3—H3...O1	0.930	2.59	121.0	3.174(5)	$1-x, -y, 1-z$

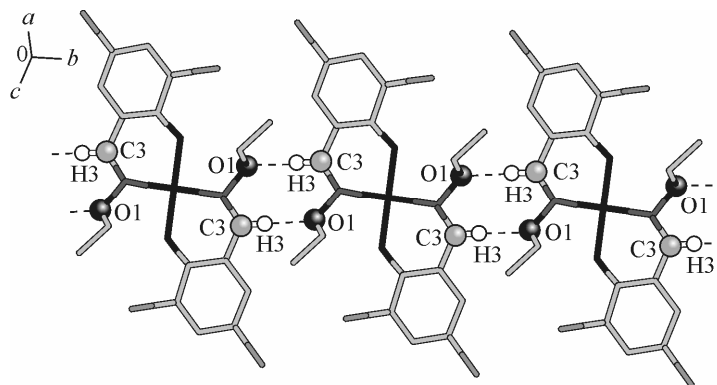


Fig. 3. Part of the 1-D supramolecular structure of complex II, which shows the formation of the C3—H3...O1 hydrogen bond

As shown in Fig. 2 and Table 5, in complex **I**, the intermolecular C—H \cdots Cl hydrogen bond and a short Cl \cdots Cl contact (with a distance of 3.474(2) Å) exist along with a weaker π — π stacking interaction (centroids of the benzene ring C3—C8) with a distance between the centroids of 3.907(1) Å, thus forming an infinite three-dimensional supramolecular structure. In Fig. 3 and Table 5, the crystal structure of complex **II** is shown to be further stabilized by pair of intermolecular C3—H3 \cdots O1 hydrogen bonds with a graph-motif R₂²(8), which link the neighbouring molecules into extended chains along the *b*-axis, thus forming an infinite one-dimensional supramolecular structure.

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