Complex of Cu^{II} with a chiral Schiff base (H_2L) derived from the natural monoterpene (+)-α-pinene. Synthesis and the properties of the complex and its solvate with acetonitrile. Crystal structure of $[Cu(HL)Cl] \cdot H_2O$

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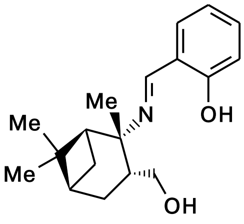
A reaction of $CuCl_2$ with a chiral Schiff base (H_2L) derived from (+)-α-pinene leads to paramagnetic complex Cu(HL)Cl (**1**) (μ_{eff} = 2.03 μ_B) and solvate $Cu(HL)Cl \cdot MeCN$ (**2**) (μ_{eff} = 1.87 μ_B). Monocrystals of hydrate $[Cu(HL)Cl] \cdot H_2O$ (**3**) were grown for the X-ray diffraction study, which showed that the crystal structure of **3** consists of the molecules of a mononuclear complex [Cu(HL)Cl] containing tridentate chelating ligand HL^-, and water molecules. Coordination polyhedron $ClNO_2$ is a distorted tetrahedron. Intermolecular contacts in the structure **3** lead to the formation of supramolecular chains, parallel to the axis *a*. Compounds **1** and **2** were studied by ESR and IR spectroscopy.

Key words: synthesis, copper(II) complexes, chiral Schiff bases, (+)-α-pinene, X-ray diffraction analysis.

In the last years, a number of works on the synthesis and study of metal coordination compounds with various classes of substances derived from chiral natural compounds rapidly grows. Derivatives of optically active natural terpenes obtained from renewable wood chemical material are of special interest as the ligands.[1—4] Coordination compounds with ligands of this type are of interest as objects for the study of stereochemistry, optical activity, and magnetochemistry of complexes, as well as promising catalysts for enantioselective synthesis. Complexes containing derivatives of chiral natural terpenoids can posses biological activity.

The major part of the works published so far describes metal complexes with chiral ligands having donor N atoms. Among them[5] are copper(II) complexes with optically active imino alcohol derived from (+)-3-carene, which contains donor N and O atoms. It seems interesting to synthesize coordination compounds with other chiral ligands having these donor atoms. In this regard, chiral Schiff bases containing OH groups are very prospective, since metal complexes with achiral Schiff bases are well known.[6] A number of new chiral Schiff bases are described,[7] which were obtained by the reaction of amino alcohols derived from (+)- and (−)-α-pinenes with salicylaldehyde and its derivatives. Vanadium complexes with these reagents, which were not isolated in the solid state, exhibit catalytic activity in the asymmetric oxidation of sulfides,[7] important for obtaining optically active omeprazole.[8] The best enantioselectivity in the synthesis of optically active omeprazole was reached when the complex of vanadyl acetylacetonate with the ligand 2-{[(1*S*,2*S*,3*R*,5*S*)-3-hydroxymethyl-2,6,6-trimethylbicyclo[3.1.1]hept-2-ylimino]methyl}phenol (H_2L), derived from the natural monoterpene (+)-α-pinene,[8] was used as the catalyst.



H_2L

The reaction of ligands of this type with ions of other 3d-transition metal has not been studied.

This work is devoted to the synthesis and study of structure and properties of the copper(II) complex with a Schiff

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base H_2L. The features of topology of the donor fragments in H_2L appear to imply the presence of a tridentate ligand function.

Results and Discussion

The reaction of $CuCl_2$ with H_2L in the Pr^{i}OH—MeCN solvent mixture at the molar ratio Cu : H_2L = 1 : 1 ([Cu] ~0.02 mol L^{-1}) leads to the complex **1** of the form Cu(HL)Cl. The low yield of the complex **1** apparently is due to its considerable solubility in this solvent mixture. In order to increase the yield, we carried out the synthesis in MeCN, which resulted in a stable solvate **2** containing one molecule of MeCN. Monocrystals of unstable hydrate **3** were grown by a long-time crystallization from solution of complex **1** in the Pr^{i}OH—MeCN solvent mixture. Apparently, formation of the hydrate occurs due to the presence of water in Pr^{i}OH, which was not preliminary dried.

The crystal structure of hydrate **3** is made of the molecules of the homonuclear complex [Cu(HL)Cl], whose all the atoms are in general positions, and water molecules (Fig. 1).

The coordination sphere of the central Cu^{2+} ion includes the N atom of the tridentate chelating ligand, HL$^-$ anion (the Cu—N distance is 1.978(3) Å), the O atoms of the deprotonated phenol fragment (the Cu—O distance is 1.891(2) Å), and OH groups of the terpene fragment (the Cu—O distance is 1.972(2) Å), as well as the Cl atom (the Cu—Cl distance is 2.2640(9) Å). The coordination interaction of Cu^{2+} ion with HL$^-$ leads to the closure of two six-membered chelate ring CuNC$_3$O. The coordination polyhedron ClNO$_2$ has the shape of a distorted tetrahedron with the edge lengths N(1)—O(1), N(1)—O(2), Cl(1)—O(1), and Cl(1)—O(2) being 2.803(4), 2.857(4), 3.023(3), and 3.035(2) Å, respectively.

The chelate ring Cu(1)N(1)C(12)C(13)C(14)O(2) adopts the envelope conformation: the Cu(1) atom are displaced 0.459(4) Å from the mean-statistic plane of the rest five atoms. The second chelate ring Cu(1)N(1)C(2)C(3)C(11)O(1) has the boat conformation: displacements of the C(11) and N(1) atoms from the mean-statistic plane of the four atoms are 0.736(4) and 0.661(4) Å, respectively.

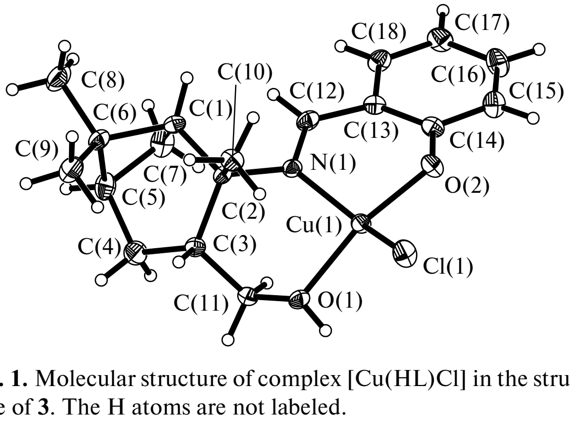

Fig. 1. Molecular structure of complex [Cu(HL)Cl] in the structure of **3**. The H atoms are not labeled.

Upon packing of the complex molecules (Fig. 2), a strong H-bond is formed between the O atoms and OH groups of the neighboring molecules (the O(1)...O(2) distance is 2.559(8) Å). In addition to the H-bond between the neighboring molecules, there emerges a Cu...Cl contact, whose distance (3.055(1) Å) is less than the sum of the Van der Waals radii for Cu and Cl (3.70 Å).[9] Due to these contacts, the complex molecules are combined into supramolecular zigzag chains, placed along the *a* axis (see Fig. 2). As it is shown in Fig. 3, the water molecules occupy the cavities formed between the complex chains and bind the chains together in the direction of the *b* axis due to the van der Waals interactions.

Compound **1** and **2** are paramagnetic, the values μ_{eff} are 2.03 and 1.87 μ_B, respectively, that corresponds to the d^9 electron configuration.

The IR spectrum of complex **1** exhibits no absorption in the region 3600—3300 cm^{-1} and in the region of the librational vibrations (600 cm^{-1}), that indicates the absence of water molecules in its composition. The spectrum of compound **2** contains an intensive band at 2250 cm^{-1}, which is related to the stretching vibration of the C≡N bond of acetonitrile, that confirms formation of the solvate. The overlapped bands ν(C=N) and ν(C=C) at 1621 and 1597 cm^{-1} for compounds **1** and **2** are displaced with respect to the positions of these bands in the spectrum of H_2L (1628 and 1584 cm^{-1}), that is an evidence of coordination of the N atom in the C=N fragment to Cu^{2+} ion.

The ESR spectrum of the solid phase of compounds **1** and **2** at room temperature exhibits a single line with an average *g*-factor of ~2.1 and a width of 1200 G. Such a broadening is due to the presence of the exchange interactions in the crystal lattice between the neighboring molecules of the complex [Cu(HL)Cl], apparently, due to the existence of additional Cu...Cl contact. Consequently, according to the ESR data two Cu atoms are bridged by the Cl atom, that agrees with the X-ray results for hydrate **3**.

Upon dissolution of compounds **1** and **2** in CH_2Cl_2, the intermolecular interactions do not completely disappear. In the frozen solution, a single line with a *g*-factor of 2.12 and a line width of 160 G is observed, which is related to the associated molecules of complex [Cu(HL)Cl]. Upon dissolution in EtOH, the intermolecular contacts are destroyed, and a frozen solution exhibits spectra of the isolated Cu^{II} polyhedrons in the molecules produced by the reaction between the complex with the solvent.

Based on the IR and ESR spectroscopic data, it can be suggested that the structure of the complex molecules in compounds **1** and **2** is the same as in hydrate **3**. In the structures **1** and **2**, the chains from the [Cu(HL)Cl] molecules are apparently formed as well.

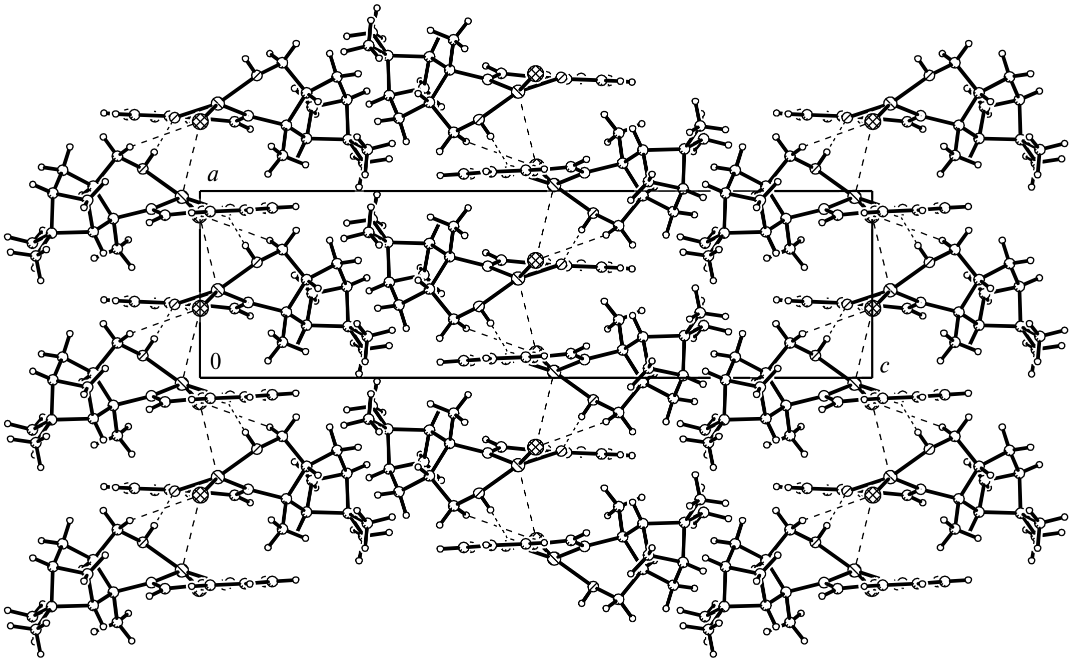

Fig. 2. Projection of the crystal structure of **3** on the plane (010). The short contacts (the dashed lines) combine neighboring molecules into supramolecular chains parallel to the *a* axis.

Comparison of the [α] values for H_2L and solvate **2** shows that on coordination of dextrorotatory H_2L to Cu^{2+} ion, the dextrorotatory complex is formed with a significant increase in the value of specific rotation.

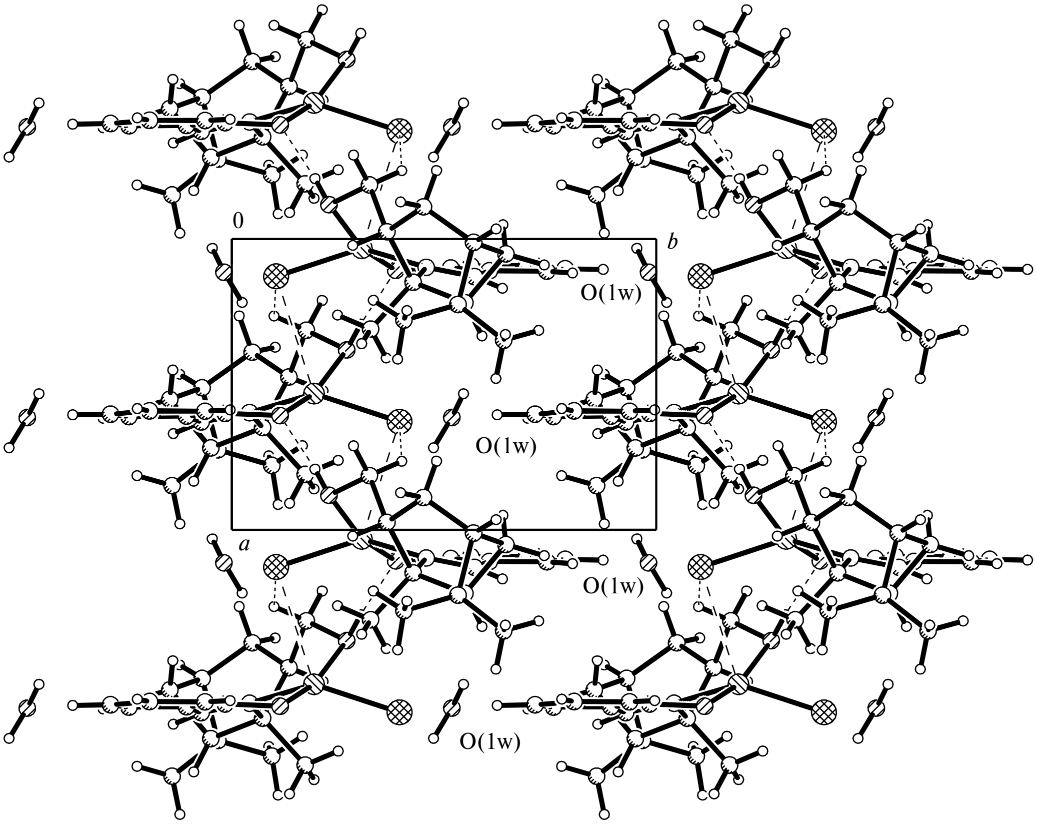

Fig. 3. Packing of the molecules in the structure of hydrate **3** in the layer for $z \approx 0.5$ (projection along the direction [001]).

The studies performed resulted in the synthesis of Cu^{II} complexes with H_2L, a representative of a new class of ligands, *viz.*, chiral Schiff bases based on the available (+)-α-pinene. This allows one to expect that complexes of H_2L with other metals and complexes based on the related Schiff bases can be obtained.

Experimental

The following reagents were used in the work: $CuCl_2 \cdot 2H_2O$ (pure grade), Pr^iOH (chemically pure grade), MeCN (pure for analysis grade). Ligand H_2L was obtained according to the procedure described earlier,[7] $[\alpha]_{580}{}^{23}$ +2.8 (*c* 2.8, $CHCl_3$). Microanalyses were performed on a Hewlett Packard 185 and Carlo Erba 1106 analyzers. Magnetic susceptibility of polycrystals of compounds **1** and **2** was measured by the Faraday method at ~20 °C. ESR spectra were recorded on a Varian E-109 radiospectrometer equipped with an analog-digital device for the transformation of a signal and original software for accumulation and initial processing of spectra. The studies were performed in the X-range at ~20 °C and in frozen solutions (10^{-2}—10^{-3} mol L^{-1}) at the temperature of liquid nitrogen. For the calibration of the operating frequency of the instrument, spectra of compounds studied were recorded together with a standard sample. A magnesium oxide powder with impurities of Mn^{2+} ions in the ratio 1 : 5000 ($g = 2.003$, $a = 86.8$ G) was used as the standard. Parameters of the ESR spectra given were obtained from the analysis of the spectra and refined by simulation of theoretical spectra using the Simfonia program (Bruker). IR spectra were recorded on a Scimitar FTS 2000 IR Fourier-spectrometer in the region 4000—400 cm^{-1}. Samples were prepared in KBr pellets and in Nujol. A specific rotation value $[\alpha]_{580}$ was determined on a Polamat A spectrometer, concentration of solution is given in *c*/g (100 mL)$^{-1}$.

Chloro(2-{[(1*S*,2*S*,3*R*,5*S*)-3-hydroxymethyl-2,6,6-trimethylbicyclo[3.1.1]hept-2-ylimino]methyl}phenolato)copper(II) Cu(HL)Cl (1). A solution of H_2L (0.058 g, 0.2 mmol) in Pr^iOH—MeCN (1 : 1, v/v, 6 mL) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.034 g, 0.2 mmol) in the same mixture (3 mL). The dark green solution was kept for 1—2 h at ~8—10 °C, resulting in precipitation of light green needle-like crystals. The solvent was evaporated to the minimum volume (~2 mL). The precipitate was filtered off under reduced pressure, washed with cold Pr^iOH, and dried in vacuum desiccator. The yield was 0.018 g (22%). Found (%): C, 54.2; H, 6.4; Cl, 10.1; N, 3.7. $C_{18}H_{24}ClCuNO_2$. Calculated (%): C, 56.1; H, 6.3; Cl, 9.2; N, 3.6. IR, ν/cm^{-1}: 596, 723, 761, 881, 933, 1018, 1082, 1145, 1220, 1294, 1440, 1469; 1551, 1597, 1621 (C=N), (C=C); 2854, 2926, 3636 (O—H).

Chloro(2-{[(1*S*,2*S*,3*R*,5*S*)-3-hydroxymethyl-2,6,6-trimethylbicyclo[3.1.1]hept-2-ylimino]methyl}phenolato)copper(II) hydrate [Cu(HL)Cl] · H_2O (3). Monocrystals of hydrate **3** were grown by a slow evaporation of a solution of complex **1** in Pr^iOH—MeCN (1 : 1, v/v). Monocrystals were taken from the solution and immediately placed into Nujol, since upon drying they undergo decrepitation and became unsuitable for X-ray diffraction.

Chloro(2-{[(1*S*,2*S*,3*R*,5*S*)-3-hydroxymethyl-2,6,6-trimethylbicyclo[3.1.1]hept-2-ylimino]methyl}phenolato)copper(II) acetonitrile Cu(HL)Cl · MeCN (2). A solution of H_2L (0.029 g, 0.1 mmol) in MeCN (2 mL) was added to a solution of $CuCl_2 \cdot H_2O$ (0.017 g, 0.1 mmol) in MeCN (2.5 mL). The brown solution obtained was kept at ~20 °C until the solvent was evaporated to the minimum volume (~2 mL). The light green needle-like crystals formed were filtered off using reduced pressure, washed with cold MeCN, and dried in vacuum desiccator. The yield was 0.020 g (47%), $[\alpha]_{580}{}^{26}$ +433 (*c* 0.14, EtOH). Found (%): C, 54.9; H, 6.5; Cl, 10.2; N, 6.7. $C_{20}H_{27}ClCuN_2O_2$. Calculated (%): C, 56.3; H, 6.4; Cl, 8.3; N, 6.6. IR, ν/cm^{-1}: 596, 619, 761, 879, 933, 1034, 1124, 1171, 1295, 1388, 1443, 1469; 1551, 1597, 1621 (C=N), (C=C); 1937, 2250 (C≡N); 2583, 2930, 3430, 3638 (O—H).

X-ray diffraction analysis of hydrate 3. A green needle-like crystal of **3** was manually selected. Parameters of the unit cell and intensities of reflections were measured at low temperature (150 K) on a Bruker X8 Apex CCD autodiffractometer equipped with a two-coordinate detector using standard procedure (Mo-Kα irradiation, λ = 0.71073 Å, a graphite monochromator). Crystallographic characteristics, details of the X-ray diffraction experiment and refinement of the structure of compound **3** are given in Table 1.

The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 in the anisotropic approximation for nonhydrogen atoms using the SHELXL-97 program package.[10] Positions of the H atoms of the water mole-

Table 1. Crystallographic characteristics, details of experiment and refinement of the structure of hydrate **3**

Parameter	Value
Molecular formula	$C_{18}H_{26}NClCuO_3$
Molecular weight	403.39
Crystal system	Ortorhombic
Space group	$P2_12_12_1$
a/Å	7.0226(3)
b/Å	10.2069(4)
c/Å	25.2806(9)
V/Å^3	1812.09(12)
Z	4
d_{calc}/g cm^{-3}	1.479
μ/mm^{-1}	1.368
Crystal size/mm^3	0.24×0.12×0.08
Region of scanning, θ/deg	2.15—25.50
Number of measured reflections	9673
Number of independent reflections	3357
R_{int}	0.02391
Number of reflections with $I > 2\sigma(I)$	3215
Method of refinement	Full-matrix LSM on F^2
Number of refining parameters	253
GOOF on F^2	1.052
R-Factors ($I > 2\sigma(I)$)	
R_1	0.0330
wR_2	0.0840
R-Factors (on all I_{hkl})	
R_1	0.0348
wR_2	0.0846
Absolute structural parameter	0.035(15)
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	1.072/—0.608

Table 2. Principal interatomic distances (*d*) and bond angles (ω) in the structure of hydrate **3**

Parameter	Value
Bond distance	*d*/Å
Cu(1)—O(2)	1.891(2)
Cu(1)—O(1)	1.972(2)
Cu(1)—N(1)	1.978(3)
Cu(1)—Cl(1)	2.264(1)
O(1)—C(11)	1.441(4)
O(1)—H(10)	0.833(10)
O(2)—C(14)	1.336(4)
N(1)—C(12)	1.288(4)
N(1)—C(2)	1.512(4)
C(1)—C(2)	1.539(4)
C(1)—C(7)	1.552(5)
C(1)—C(6)	1.572(4)
C(2)—C(10)	1.532(4)
C(2)—C(3)	1.570(4)
C(3)—C(11)	1.512(5)
C(3)—C(4)	1.566(4)
C(4)—C(5)	1.525(5)
C(5)—C(7)	1.541(5)
C(5)—C(6)	1.548(5)
C(6)—C(8)	1.519(5)
C(6)—C(9)	1.533(5)
C(12)—C(13)	1.453(4)
Bond distance	*d*/Å
C(13)—C(14)	1.404(4)
C(13)—C(18)	1.412(4)
C(14)—C(15)	1.404(4)
C(15)—C(16)	1.361(5)
C(16)—C(17)	1.395(5)
C(17)—C(18)	1.376(4)
O(1w)—H(1wa)	1.016(10)
O(1w)—H(1wb)	1.018(10)
Angle	ω/deg
O(2)—Cu(1)—O(1)	163.9(1)
O(2)—Cu(1)—N(1)	95.2(1)
O(1)—Cu(1)—N(1)	90.4(1)
O(2)—Cu(1)—Cl(1)	93.41(7)
O(1)—Cu(1)—Cl(1)	90.80(7)
N(1)—Cu(1)—Cl(1)	144.06(9)
C(11)—O(1)—Cu(1)	113.6(2)
C(14)—O(2)—Cu(1)	122.8(2)
C(12)—N(1)—Cu(1)	121.4(2)
C(2)—N(1)—Cu(1)	116.0(2)
C(2)—C(1)—C(7)	109.7(3)
C(2)—C(1)—C(6)	114.4(3)
Angle	ω/deg
C(7)—C(1)—C(6)	87.4(2)
N(1)—C(2)—C(3)	111.0(3)
C(1)—C(2)—C(3)	109.7(2)
C(11)—C(3)—C(2)	113.6(2)
C(4)—C(3)—C(2)	115.2(3)
C(5)—C(4)—C(3)	113.9(3)
C(4)—C(5)—C(7)	107.2(3)
C(4)—C(5)—C(6)	111.1(3)
C(7)—C(5)—C(6)	88.6(3)
C(8)—C(6)—C(9)	106.8(3)
C(5)—C(6)—C(1)	85.2(3)
C(5)—C(7)—C(1)	86.1(2)
O(1)—C(11)—C(3)	109.8(3)
N(1)—C(12)—C(13)	125.7(3)
C(14)—C(13)—C(18)	119.4(3)
O(2)—C(14)—C(13)	122.9(3)
C(15)—C(14)—C(13)	118.3(3)
C(16)—C(15)—C(14)	121.4(3)
C(15)—C(16)—C(17)	120.9(3)
C(18)—C(17)—C(16)	119.1(3)
C(17)—C(18)—C(13)	120.9(3)

cule and on the O(1) atom were found from the differential synthesis of electron density and refined isotropically. The rest of the H atoms are calculated geometrically and included in the refinement in the isotropic approximation together with nonhydrogen atoms. The values of principal interatomic distances and bond angles are given in Table 2.

Full Tables of the atomic coordinates, bond distances, and bond angles were deposited with the Cambridge Structural Database (CCDC-711687) and can be obtained from the authors.

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