Helical 1D Coordination Polymers − Structure and Magnetic Properties of *catena*-Poly[chloro(μ-({2-[(hydroxyimino)methyl]phenoxy}acetato-*N*,*O*,*O*,O′)copper(II)]

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A new compound $[CuHLCl]_n$, where H_2L is the product of the condensation reaction between 2-formylphenoxyacetic acid and hydroxylamine, has been synthesized and its crystal structure determined. The copper(II) atom is in an O_3NCl coordination environment and the helical chains of the complex are formed by square-pyramidal copper(II) ions bridged by *anti-anti* carboxylate ligands in basal-apical positions. The chloride ion acts as monodentate ligand and is involved in intramolecular hydrogen bonding to the oxime group. The results of magnetic susceptibility and EPR measurements performed on the polycrystalline sample over a wide temperature range are presented. The magnetic susceptibility data have been fitted by use of the linear chain model and $J = -2.5\ cm^{-1}$ as the value of antiferromagnetic interaction. The value of the exchange exceeds the Zeeman energy difference for two adjacent magnetically nonequivalent copper centers, and signals of these centers are averaged out. The temperature dependence of the EPR spectra shows increases in the linewidth and the shifts of the signals as the temperature decreases, indicating a short-range-order effect in the chain. Shifts of the EPR signals in the Q-band were discovered for the orientations perpendicular to the chain direction as the temperature decreased below 10 K. The nature of this shift is discussed.

Introduction

The quasi-one-dimensional magnetic systems of transition metal ions (metallopolymers) are of particular interest for physicists and chemists because of their special properties resulting from the nature of the magnetic ions. On the other hand, one-dimensional polymeric helical motifs are also attracting increased attention in supramolecular chemistry,[1−4] which certainly originates from the observed importance of these motifs in biological systems and enantioselective catalysis.[5−7]

This paper reports the synthesis, crystal structure, and magnetic properties of an anhydrous copper(II) complex existing in crystals in the form of a helical polymeric chain of formula $[Cu(HL)Cl]_n$, where H_2L is the product of the condensation reaction between 2-formylphenoxyacetic acid and hydroxylamine. There is currently renewed interest in copper(II) complexes with carboxylic ligands[8−13] because carboxylic groups can exhibit several different coordination modes to the central atom, giving rise to compounds with ferromagnetic or antiferromagnetic properties[14,15] depending on the copper magnetic orbitals involved in bonding and the coordination mode of the carboxylic group. Studies of structure and magnetic exchange interactions in this type of compounds are aimed at understanding of the structural and chemical features determined by the magnitude and sign of the exchange interaction.

Results and Discussion

Synthesis

The template synthesis of the copper(II) coordination compound was carried out according to Scheme 1.

Copper(II) chloride and acetate were used for the reaction, but the yield was less when the acetate was used instead of the chloride. The compound [Cu(HL)Cl] was also formed when copper(II) chloride reacted directly with the oxime.

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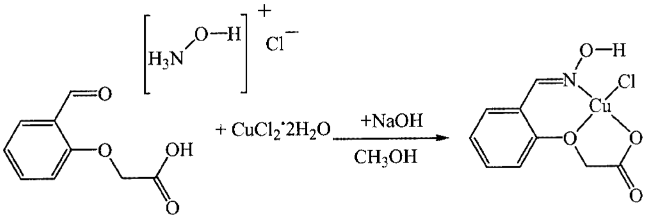


Scheme 1

IR Spectra

The IR spectrum of $[Cu(HL)Cl]_n$ does not contain absorption bands attributable to the vibration of the aldehyde group of 2-formylphenoxyacetic acid [ν(CH=O): $\tilde{\nu}$ = 1754, 1712 cm^{-1}], but it does show the vibration bands of the coordinated imino group [ν(C=N): $\tilde{\nu}$ = 1604 cm^{-1}], indicating that the template reaction is accompanied by condensation between 2-formylphenoxyacetic acid and hydroxylamine.[16] In addition, the IR spectrum of the complex shows the characteristic absorption bands of the carboxyl group of the formylphenoxyacetic fragment [$\nu_{as}(COO^-)$: $\tilde{\nu}$ = 1570 cm^{-1}; $\nu_s(COO^-)$: $\tilde{\nu}$ = 1414cm^{-1}], which were assigned according to ref.[17] The 156 cm^{-1} difference in the wavenumbers of the absorption bands $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ suggests the bidentate bridge mode of coordination. The shift of the ν_s(C−O−C) absorption band (1164 cm^{-1}) of the ether group by 52 cm^{-1} in the lower wavenumber range and of the ν_{as}(C−O−C) band (1244 cm^{-1}) by 4 cm^{-1} in the higher wavenumber range (relative to their counterparts in 2-formylphenoxyacetic acid) confirm the participation of the ether oxygen atom in coordination. The presence of the absorption band of the stretching frequency ν(OH) at $\tilde{\nu}$ = 3100−3300 cm^{-1} testifies to the presence of the protonated aldoxime group.

Structure

The crystal of the complex $[Cu(HL)Cl]_n$ consists of infinite helical chains directed along the *b* axis. Two antiparallel enantiomorphic helices in the crystal are shown in Figure 1, together with the atom-labeling scheme. The monomeric units of the $[Cu(HL)Cl]_n$ chain are sequentially bridged by *anti-anti* carboxylate groups. The monodeprotonated HL^- anion acts as a tridentate ligand towards one copper(II) ion and as a monodentate ligand towards another copper(II) center. The copper(II) ions each exist in distorted square-pyramidal coordination with the O_3NCl atom-donor set. The basal coordination sites are occupied by three donor atoms of the ligand [Cu−O(1) 2.089(3), Cu−O(2) 1.908(3) and Cu−N(1) 1.966(3) Å] and the chlorine atom [Cu−Cl 2.245(1) Å], whereas the carboxylate O(3) atom of the ligand from the adjacent monomeric unit along the chain resides in the apical position [Cu−O(3)′ 2.189(3) Å]. Thus, each *anti-anti* carboxylate group is located in the basal-apical positions of the coordination polyhedra and bridges two copper(II) ions. The Cu atom is displaced by 0.208 Å from the OONCl plane toward the axially coordinated O(3)′ atom. The distance between the nearest Cu atoms along the chain, 5.845 Å, is longer than those observed in similar helical chains but with the *syn-anti* carboxylate coordination mode.[12] The H-atom of the oxime group is involved in intramolecular hydrogen bonding [O(4)···Cl 3.058 Å, H···Cl 2.34 Å, OHCl 150°], closing a five-membered ring. No intermolecular hydrogen bonds are formed in this crystal; however, there is some overlap of the aromatic rings belonging to adjacent helical chains, with the distances between the ring atoms being in the 3.22−3.62 Å range, suggesting that π-π interactions may be of some importance in stabilizing this crystal structure (Figure 1). In the lattice, right- and left-handed helices alternate, resulting in an optically inactive racemic crystal, spontaneous resolution of two isomers being rare.[11,12]

Magnetic Susceptibility

The temperature dependence of the magnetic susceptibility and χT is presented in Figure 2. The value of χT (see a in Figure 2) decreases as the temperature decreases, indicating antiferromagnetic behavior. The Hamiltonian appropriate for a Heisenberg linear chain of S = 1/2 spins is given by Equation (1).

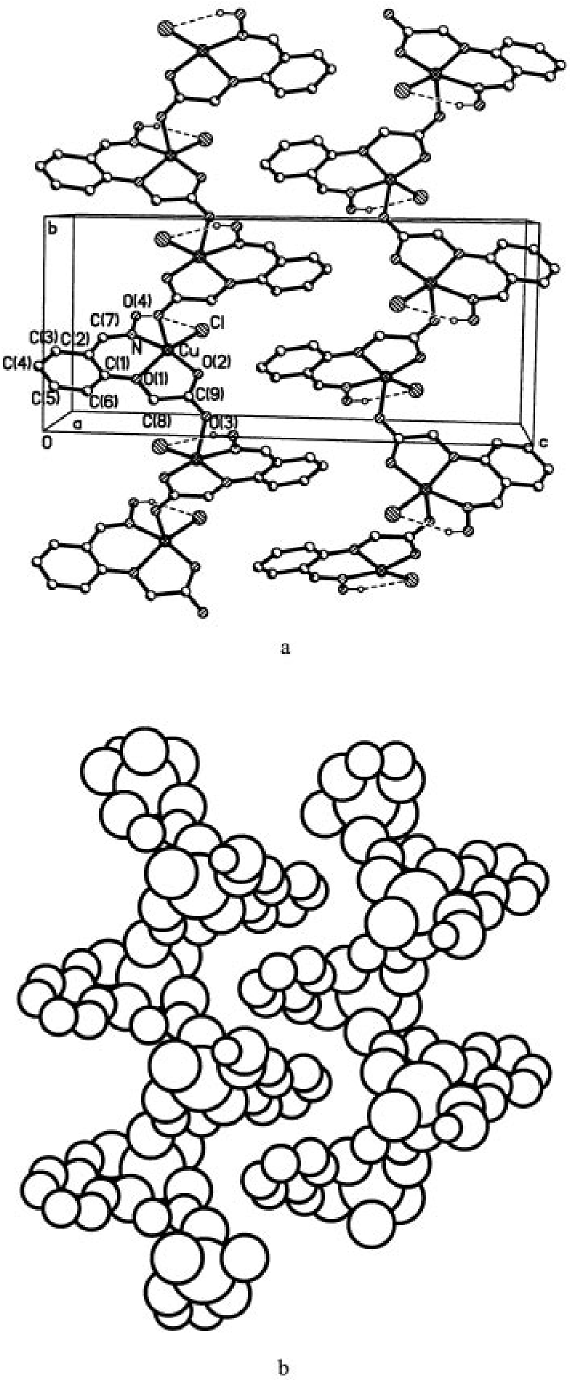
$$H = J\Sigma S_i{\cdot}S_{i+1} \tag{1}$$

The experimental data for the variation of susceptibility with temperature can be satisfactorily fitted into the analytic expression introduced to represent the Bonner−Fisher model[18] for a uniformly spaced Heisenberg chain of spins with S = 1/2 [Equation (2)].[19]

$$\chi = \left(\frac{Ng^2\beta^2}{kT}\right)\left\{\frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3}\right\} \quad x = \left|\frac{J}{kT}\right| \text{with.} \tag{2}$$

The solid line in Figure 2 (part b) is the curve calculated according to Equation (2) with J = 2.5 cm^{-1}, g = 2.15. It shows good agreement between experimental data and calculated $\chi(T)$. Although the decrease in $\chi(T)$ in the temperature range studied is not observed experimentally, the measured values of $\chi(T)$ in the low-temperature range (inset in part b of Figure 2) would allow the presence of the maximum in this range. We considered the one-dimensional model, neglecting the interaction between the chains, as the distances between the paramagnetic copper centers in adjacent chains (R = 9.50 Å) exceed the intrachain copper distance (R = 5.85 Å) and there are no channels for indirect exchange between neighboring chains. Hence the antiferromagnetic interaction is produced only inside the chains.

It should be noted that the given data are in good agreement with a model chain of equally spaced copper(II) ions. In fact, the bridging fragments between the copper complexes in the chains coincide completely, although the chain is built up of magnetically nonequivalent copper centers: square-pyramidal copper(II) polyhedra $CuClNO_3$ are rotated with respect to each other along the direction of the chain. This chain structure results in a small value for the



a

b

Figure 1. Crystal structure of $[Cu(HL)Cl]_n$: ball-and-stick model showing atom labelling (a); space-filling diagram of two adjacent enantiomorphic helices (b)

antiferromagnetic interaction between the copper centers in the chains.

The value of the isotropic exchange interaction is determined by the overlap integral between ground-state orbitals, which for an indirect exchange is produced through intermediate orbitals of bridging ligands (the ground state of a square-pyramidal copper complex is the $d_{x^2-y^2}$ orbital). A weak antiferromagnetic coupling is justified by the small overlap of the magnetic orbitals according to the Goodenough−Kanamori rule.[20−22]

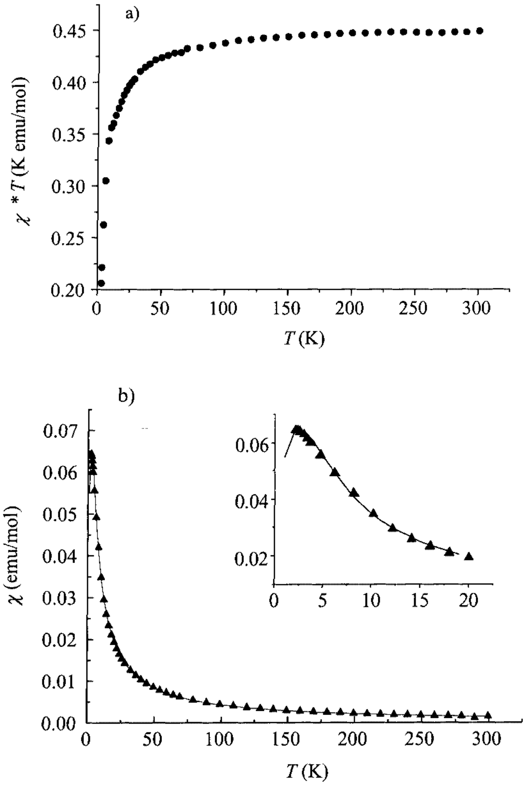


Figure 2. Temperature dependence of the experimental values of χT (a) and measured (black triangles) and calculated (solid line) of the values $\chi(T)$ (b); the inset presents the low-temperature range of $\chi(T)$ on a larger scale

EPR Investigation

EPR spectra of the polycrystalline sample are shown in Figures 3 and 4. The spectrum is typical for the state $S = 1/2$ with the rhombic symmetry of the $\{g\}$ tensor. The temperature dependence of the spectra at the *Q*-band indicates the change of the values of the {g} tensor: $g_1 = 2.239 \pm 0.002$, $g_2 = 2.159 \pm 0.002$, $g_3 = 2.060 \pm 0.002$ at $T = 293$ K; $g_1 = 2.236 \pm 0.002$, $g_2 = 2.129 \pm 0.002$, $g_3 = 2.044 \pm 0.002$ at $T = 4.2$K.

The *X*-band anisotropy of the spectra is not resolved completely, but computer analysis of the spectra has allowed the temperature dependence of the *g* factor anisotropy and linewidths to be estimated. The temperature dependence of the linewidth for the high-field signal (Figure 5) shows that the appreciable changes are already detectable at $T = 10$ K and that the effect increases as the temperature decreases.

As we have already noted, the principal axes of *g* tensors of the neighboring copper ions are rotated with respect to each other. As the exchange interaction exceeds the difference of Zeeman energies for two magnetically inequivalent molecules, collapse of the lines occurs and for this spectrum the temperature dependence of the *g* tensor is detectable due to the merging effect. In principle, the temperature de-

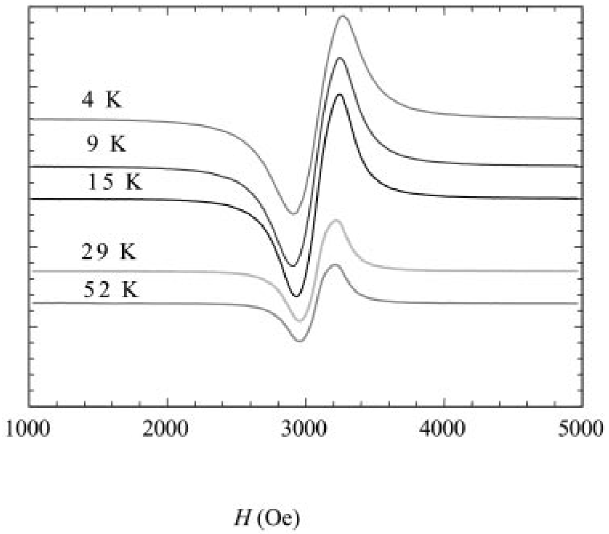


Figure 3. Temperature dependence of the EPR spectra of the polycrystalline sample of $[Cu(HL)Cl]_n$ at the *X*-band

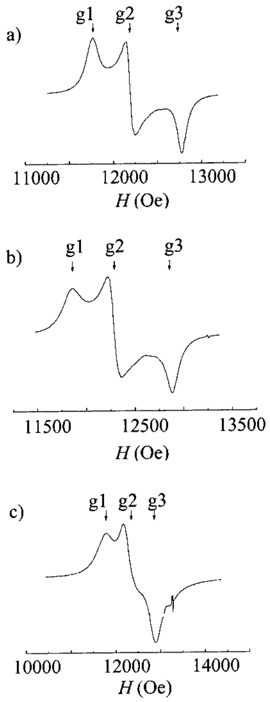


Figure 4. The EPR spectra at the *Q*-band at 298 K (a), 77 K (b), 4.2 K (c)

pendence of the positions of the signals may be due to small structural changes and to short-range order effects in the chain. Consider the correlation between observed g_1, g_2, g_3 components and molecular $\{g\}$ tensors. On the assumption of the axial symmetry of the molecular g tensor ($g_{\|}$, $g_{\perp}$) the resulting components of the g tensor are given by Equation (3).[23]

$$\begin{aligned} g_3 &= g_{\perp} \\ g_1 &= (g_{\|}^2 \cos^2\gamma + g_{\perp}^2 \sin^2\gamma)^{1/2} \qquad (3) \\ g_2 &= (g_{\|}^2 \sin^2\gamma + g_{\perp}^2 \cos^2\gamma)^{1/2} \end{aligned}$$

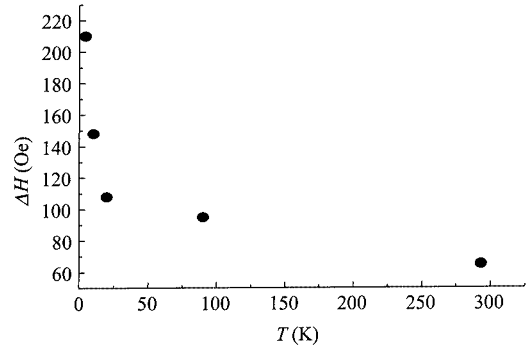


Figure 5. The temperature dependence of the linewidth of the high-field signal at the *X*-band

The 2γ term is the angle between the g_z directions of two neighboring complexes. It might be expected that this angle should be equal to the angle between the directions of the apical Cu−O bonds of two consecutive copper positions. According to Equation (3), for $\gamma \approx 36°$ and typical values of $g_{\|}$ and $g_{\perp}$ for the square-pyramidal copper complexes it would be expected that the change in the g_2 value due to possible small structural changes with temperature should not exceed the change of the g_1 value. However, the g_1 value is practically independent of the temperature and the supposition about the temperature dependence of the g value due to the availability of the short-range order effect is preferable. Analysis of the expressions of Equation (3) indicates that the g_1 component corresponds to the orientation of the magnetic field along the chain and the $g_{2,3}$ components are perpendicular to the chain direction.

The temperature dependence of the EPR spectra unequivocally shows that the linewidth for all orientations increases as the temperature decreases, and that the g factors shift for orientations perpendicular to the direction of the chain. No shift of the signal relative to the direction of the magnetic field along the direction of the chain is observed. The effects of the increase in the linewidth and the shifts of the signals for quasi-one-dimensional systems as the temperature approaches the value of the exchange interaction inside a chain have previously been explained in terms of the availability of the short-range order and the presence of the preferable direction for antiferromagnetic or ferromagnetic ordering due to the anisotropy of the interaction.[24−26] Changes of different signs were observed for the g factor, depending on the direction of a magnetic field: parallel or perpendicular to the direction of the chain. These experimental data are satisfactorily described by the assumption that the anisotropy of the interaction has a dipole-dipole character.

The $[Cu(HL)Cl]_n$ crystal provides an example of a new type of behavior of magnetic properties close to the temperature $T \approx J$. The change in behavior is probably connected with the change of the nature of the anisotropy of the interaction. For $[Cu(HL)Cl]_n$, the distance between the copper centers in a chain (R = 5.85 Å), allows us to assume that the main role is played by the anisotropy of the exchange interaction, including the antisymmetric interaction. For the orientations of the magnetic field in the plane perpendicular to the direction of the chain, as the temperature decreases in the range $T \approx J$, the EPR signals shift to higher fields.

In principle, interaction between copper ions of adjacent chains in the plane perpendicular to the direction of the chains could give a similar effect. Because of the absence of the channels for such indirect exchange between copper ions of neighboring chains, however, this supposition is improbable. Measurements on single crystals would be necessary for more detailed investigation, because the spectrum of the polycrystalline sample contains only the signals corresponding to appropriate orientations of the magnetic field along the principal axes of the g tensor.

Experimental Section

Synthesis of $[Cu(HL)Cl]_n$: 2-Formylphenoxyacetic acid (0.9 g, 0.005 mol) was added to $CuCl_2 \cdot 2H_2O$ (0.85 g, 0.005 mol) in methanol (20 mL). A mixture of hydroxylamine−hydrochloride (0.35 g, 0.005mol) and NaOH (0.4 g, 0.01 mol) in methanol (25 mL) was then added, with stirring, to the resulting solution. The obtained solution was heated in a water bath at 50 °C for 30 min. The dark blue crystals, precipitating after cooling, were filtered, washed with cold methanol, and dried in air. Yield: 1.025 g, 70%. $C_9H_8ClCuNO_4$ (293): calcd. C 36.86, H 2.73, Cl 12.12, Cu 21.67, N 4.78; found C 36.93, H 2.76, Cl 12.09, Cu 21.78, N 4.80.

IR Spectra: These were recorded as oil suspensions with a Specorde M-80 spectrometer in the 4000−400 cm^{-1} range.

X-ray Crystal Structure Analysis: The crystal used for measurements was a prism of approximate dimensions 0.4 × 0.4 × 0.2 mm. The crystal was a non-mesohedral twin with the twin matrix [1 0 0 0 −1 0 −0.5 0 −1]. The data were collected with a Kuma Diffraction KM4 diffractometer by use of graphite-monochromatized Cu-K_α radiation. Lattice parameters were obtained from the least-squares refinement of 27 reflections with $16° \leq 2\theta \leq 70°$. The intensities were measured by the $\omega/2\theta$ scan technique up to $2\theta_{max} = 129.6°$. The intensities of three reflections were checked every 100 measurements to monitor instrument and crystal stability. Their intensity variation was within 3%. The structure was solved by direct methods with SHELXS-86[27] and refined by full-matrix, least squares on F^2 with SHELXL-93.[28] Instruction HKLF5 from SHELXL-93 was used for the refinement, because half of all the reflections belonged to both twin domains while the second half belonged to one domain. The non-hydrogen atoms were refined by the least-squares method in the anisotropic approximation. The positions of H atoms bonded to C atoms were calculated by assuming C−H distances of 0.96 Å. Positional parameters of the oxime H atom were obtained from difference Fourier syntheses and verified by the hydrogen bond geometric parameters. Isotropic displacement parameters of H atoms were fixed at $1.2 \times U_{eq}$ for the relevant C and O atoms. The main crystallographic parameters and structure refinement details are summarized in Table 1, bond lengths and angles in Table 2. CCDC-182198 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

EPR and Magnetic Measurements: The measurements were carried out on the polycrystalline sample of $[Cu(HL)Cl]_n$. The static magnetic susceptibility was measured over the 2−300 K temperature range. The data were corrected for a diamagnetic contribution by use of Pascal constants.[29] The magnetization vs. B was recorded

Table 1. Crystal data for $[Cu(HL)Cl]_n$

Empirical formula	$C_9H_8ClCuNO_4$
M	293.15
Temperature [K]	293(2)
Wavelength [Å]	1.54178
Space group	$P2_1/c$
a [Å]	6.5090(10)
b [Å]	8.311(2)
c [Å]	18.923(4)
β [°]	94.98(3)
V [Å^3]	1019.8(4)
Z	4
$\rho_{calcd.}$ [Mg/m^3]	1.909
μ_{Mo} [mm^{-1}]	5.457
F(000)	588
Crystal size [mm]	0.4 × 0.4 × 0.2
θ range [°]	4.69−64.82
Index ranges	$-7 \leq h \leq 7$, $-9 \leq k \leq 9$, $-22 \leq l \leq 22$
Number of reflections:	
measured	2772
unique	1811 [$R_{(int)} = 0.048$]
Number of refined parameters	147
GOOF for F^2	1.130
R factor [$I > 2\sigma(I)$]	$R_1 = 0.0648$, $wR_2 = 0.1608$
R factor (all data)	$R_1 = 0.0670$, $wR_2 = 0.1621$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^3]	1.413, −1.213

Table 2. Selected bond lengths [Å] and angles [°]; symmetry transformations: (′): $-x, y + 1/2, -z + 1/2$; (′′): $-x, y - 1/2, -z + 1/2$

Cu−O(2)	1.908(3)	N−C(7)	1.293(6)
Cu−N	1.966(3)	C(1)−C(6)	1.372(6)
Cu−O(1)	2.089(3)	C(1)−C(2)	1.417(6)
Cu−O(3)′	2.189(3)	C(2)−C(3)	1.406(6)
Cu−Cl	2.245(1)	C(2)−C(7)	1.424(6)
O(1)−C(1)	1.374(5)	C(3)−C(4)	1.381(7)
O(1)−C(8)	1.452(5)	C(4)−C(5)	1.364(7)
O(2)−C(9)	1.274(5)	C(5)−C(6)	1.391(6)
O(3)−C(9)	1.223(5)	C(8)−C(9)	1.505(5)
O(4)−N	1.391(5)		
O(2)−Cu−N	167.0(1)	O(4)−N−Cu	120.9(3)
O(2)−Cu−O(1)	81.9(1)	C(6)−C(1)−O(1)	123.0(4)
N−Cu−O(1)	87.5(1)	C(6)−C(1)−C(2)	120.2(4)
O(2)−Cu−O(3)′	96.9(1)	O(1)−C(1)−C(2)	116.8(4)
N−Cu−O(3)	89.6(1)	C(3)−C(2)−C(1)	117.2(4)
O(1)−Cu−O(3)′	85.0(1)	C(3)−C(2)−C(7)	115.8(4)
O(2)−Cu−Cl	93.6(1)	C(1)−C(2)−C(7)	127.0(4)
N−Cu−Cl	94.9(1)	C(4)−C(3)−C(2)	121.8(4)
O(1)−Cu−Cl	165.42(9)	C(5)−C(4)−C(3)	119.7(4)
O(3)′−Cu−Cl	109.36(9)	C(4)−C(5)−C(6)	120.3(4)
C(1)−O(1)−C(8)	117.1(3)	C(1)−C(6)−C(5)	120.8(4)
C(1)−O(1)−Cu	128.8(2)	N−C(7)−C(2)	127.2(4)
C(8)−O(1)−Cu	110.6(2)	O(1)−C(8)−C(9)	109.3(3)
C(9)−O(2)−Cu	118.3(2)	O(3)−C(9)−O(2)	123.9(3)
C(9)−O(3)−Cu′′	131.5(3)	O(3)−C(9)−C(8)	117.5(4)
C(7)−N−O(4)	111.1(3)	O(2)−C(9)−C(8)	118.6(3)
C(7)−N−Cu	127.8(3)		

at 2.5 and 4.5 K. EPR spectra were recorded at the *X*-band in the temperature range from room temperature to 4 K and at the *Q*-band at $T = 298, 77, 4.2$ K.

Acknowledgments

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