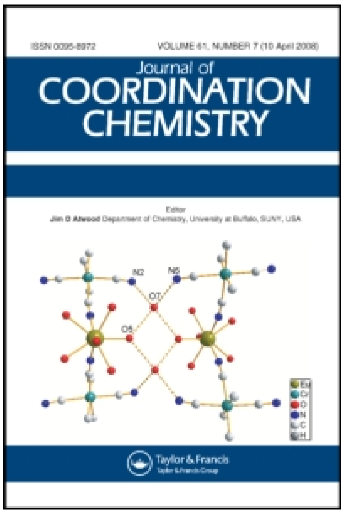

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CRYSTAL STRUCTURE, SPECTRAL AND MAGNETIC BEHAVIOR OF COPPER(II)(5-CHLOROSALICYLATO)$_2$ (AQUA)$_2$

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The synthesis and characterization of $Cu(5\text{-}Clsal)_2(H_2O)_2$ (5-Clsal = 5-chlorosalicylate) are reported. Characterization of the compound was based on elemental analysis, electronic and EPR spectra, and magnetic susceptibility measurement over a temperature range 93–239 K.

An X-ray analysis of $Cu(5\text{-}Clsal)_2(H_2O)_2$ was carried out, showing a polymeric chain of copper(II) atoms bridged by pairs of water molecules with Cu–O(bridge) bond lengths of 1.970(2) and 2.718(2) Å. The coordination sphere about each copper(II) atom is completed (on the X-axis) by a *trans*-pair of unidentate 5-chlorosalicylate anions. The bridging oxygen atoms arrange a planar Cu_2O_2 rhombus. The relationship between degree of distortion and g-values from EPR spectra is also discussed.

Keywords: Copper(II) 5-chlorosalicylate; X-ray crystal structure; Polymer structure

INTRODUCTION

The ability of salicylic acid to act as an oxygen donor and to form complexes with different ions is well known. Chlorosalicylic acid has not been studied so extensively as unsubstituted salicylic acid. Copper(II) compounds with 5-chlorosalicylic, 5-bromosalicylic, 3,5-dibromosalicylic and 5-iodosalicylic acid were studied by spectral and magnetic methods [1,2]. We have also

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studied the spectroscopic and magnetic properties of copper(II) compounds with 4-chlorosalicylic and 3,5-diiodosalicylic acid [3].

To our knowledge, there is no example of copper(II) halogenosalicylates studied by X-ray analysis; therefore we prepared $Cu(5\text{-}Clsal)_2(H_2O)_2$ (5-Clsal = 5-chlorosalicylate) and studied by spectral and magnetic methods as well as by X-ray analysis.

EXPERIMENTAL

Preparative

A solution of 5-chlorosalicylic acid was prepared, the pH adjusted to 4.5–5 and on aqueous solution of copper sulfate in the molar ratio 1:2 was added. The turquoise-blue product that precipitated instantly was isolated, washed with water and dried at room temperature. Crude product was recrystallized from methanol-water solution. Turquoise-blue crystals were obtained. Anal. calc. for $Cu(5\text{-}Clsal)_2(H_2O)_2$(%): C, 37.96; H, 2.73; Cu, 14.36. Found: C, 38.0; H, 2.75; Cu, 14.35.

Spectral Studies

The Electronic spectrum (in Nujol) in the region 10–28 kK was measured with a Perkin-Elmer 450 spectrophotometer. An EPR spectrum was run on a Varian model E-4 spectrometer at 295 and at 77 K.

Magnetic Studies

A magnetic susceptibility measurement for the compound was obtained over the temperature range 93–293 K. The calibrant employed was $HgCo(SCN)_4$ [4] for which the magnetic susceptibility was taken as $16.44 \times 10^{-6}\,cm^3\,g^{-1}$. A diamagnetic correction was calculated from Pascal's constant [5] and found to be $222.5 \times 10^{-6}\,cm^3\,mol^{-1}$. The effective magnetic moment was calculated using the expression $\mu_{eff} = 2.83(\chi_M^{corr} \times T)^{1/2}$.

X-ray Measurements

Data collection and cell refinement were carried out using KUMA KM4 diffractometer software [6]. Intensity data were corrected for Lorenz and polarization factors. The structure was solved by the heavy atom method with SHELXS86 [7], and subsequent Fourier synthesis using SHELXL93

[8], anisotropic thermal parameters were refined for all non-hydrogen atoms. Geometrical analysis was performed using SHELXL93 [8]. The structure was drawn using ORTEP [9]. The final parameters after refinement are summarized in Table I. Independent atomic coordinates and equivalent isotropic thermal parameters are given in Table II. Selected inter-atomic

TABLE I Crystal data and structure refinement for $[Cu(5\text{-}Clsal)_2(H_2O)_2]$

Identification code	kom981
Empirical formula	$C_7H_6ClCu_{0.5}O_4$
Formula weight	221.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P − 1
Unit cell dimensions	$a = 3.703(2)$ Å $\alpha = 77.29(3)^\circ$
	$b = 7.3740(2)$ Å $\beta = 88.21(3)^\circ$
	$c = 14.634(3)$ Å $\gamma = 84.59(3)^\circ$
Volume	388.04(20) $Å^2$
Z	2
Density (calculated)	1.894 Mg/m^3
Absorption coefficient	1.795 mm^{-1}
$F(000)$	223
Crystal size	0.1 × 0.15 × 0.25 mm
θ range for data collection	5.6 to 50.1°
Index ranges	$-4 \leq h \leq 4$, $-8 \leq k \leq 8$, $0 \leq l \leq 17$
Reflection collected/unique	1382/115
Independent reflection	2563 ($R_{int} = 0.0150$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1252/0/115
Goodness-of-fit on F^2	1.074
Final R indices $[I > 2\sigma(I)]$	$R = 0.0256$, $wR2 = 0.0707$
R indices (all data)	$R = 0.0291$, $wR2 = 0.0729$
Largest diff. peak and hole	0.395 and −0.408 $eÅ^{-3}$

TABLE II Atomic coordinates and equivalent isotropic displacement parameters for $Cu(5\text{-}Clsal)_2(H_2O)_2$ U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	$U(eq)$
Cu	0.5000	0.5000	0.5000	0.02543(14)
Cl	0.82137(18)	0.27985(8)	−0.00721(4)	0.03970(18)
O(1)	0.5192(5)	0.33659(19)	0.41336(10)	0.0309(4)
O(2)	0.8013(5)	0.5340(2)	0.30355(11)	0.0345(4)
O(3)	0.8947(5)	0.33413(19)	0.56981(10)	0.0290(3)
O(4)	0.3729(5)	0.0199(2)	0.38424(11)	0.0356(4)
C(1)	0.6138(6)	0.2623(3)	0.26458(14)	0.0229(4)
C(2)	0.4845(6)	0.0856(3)	0.29440(15)	0.0252(4)
C(3)	0.4720(7)	−0.0297(3)	0.23106(15)	0.0303(5)
C(4)	0.5751(6)	0.0300(3)	0.13929(15)	0.0308(5)
C(5)	0.6949(6)	0.2058(3)	0.10969(15)	0.0272(4)
C(6)	0.7155(6)	0.3217(3)	0.17107(15)	0.0250(4)
C(7)	0.6505(6)	0.3893(3)	0.32989(14)	0.0240(4)

TABLE III Selected bond lengths [Å] and angles [°] for $Cu(5\text{-}Clsal)_2(H_2O)_2$

Cu-O(1)	1.927(1)	Cu-O(3)[a]	2.718(2)
Cu-O(3)	1.970(2)	Cl-C(5)	1.741(2)
O(1)-C(7)	1.292(3)	C(1)-C(7)	1.495(3)
O(2)-C(7)	1.232(3)	C(2)-C(3)	1.393(3)
O(4)-C(2)	1.363(3)	C(3)-C(4)	1.372(3)
C(1)-C(6)	1.393(3)	C(4)-C(5)	1.384(3)
C(1)-C(2)	1.404(3)	C(5)-C(6)	1.377(3)
O(1)-Cu-O(1)[b]	180.0	O(1)-Cu-O(3)	88.14(7)
O(1)-Cu-O(3)[b]	91.86(7)	O(3)[b]-Cu-O(3)	180.0
C(7)-O(1)-Cu	120.3(1)	C(3)-C(4)-C(5)	119.6(2)
C(6)-C(1)-C(2)	119.2(2)	C(6)-C(5)-C(4)	121.1(2)
C(6)-C(1)-C(7)	118.4(2)	C(6)-C(5)-Cl	120.0(2)
C(2)-C(1)-C(7)	122.4(2)	C(4)-C(5)-Cl	119.0(2)
O(4)-C(2)-C(3)	117.9(2)	C(5)-C(6)-C(1)	119.9(2)
O(4)-C(2)-C(1)	122.5(2)	O(2)-C(7)-O(1)	123.5(2)
C(3)-C(2)-C(1)	119.6(2)	O(2)-C(7)-C(1)	120.3(2)
C(4)-C(3)-C(2)	120.6(2)	O(1)-C(7)-C(1)	116.1(2)

Symmetry transformations used to generate equivalent atoms:
[a] $-x+1,\ -y+1,\ -z+1$;
[b] $-x+2,\ -y+1,\ -z+1$.

distances and bond angles are given in Table III. Supplementary material including hydrogen atomic coordinates (× 10^4) and anisotropic displacement parameters for non-hydrogen atoms (Å × 10^3) have been deposited at the Cambridge Crystallographic Data Center. Observed and calculated structure factors are available on request from the authors.

RESULTS AND DISCUSSION

The electronic spectrum of $Cu(5\text{-}Clsal)_2(H_2O)_2$ shows a wide and symmetrical band at about 15.2 kK and a shoulder at about 24.8 kK. The band at about 15.2 kK is due to *d–d* transitions and a shoulder may be assigned as a change-transfer (O→Cu).

EPR spectrum of the compound at 295 and 77 K displays two *g* values, $g_{\|} = 2.34$ and $g_{\perp} = 2.055$ and $g_{\|} = 2.36$ and $g_{\perp} = 2.06$, respectively. This points to the presence of a structure with a value of the effective spin $S = 1/2$ and basic state $d_{x^2-y^2}$.

Magnetic susceptibility on a polycrystalline sample of the compound between 93 and 293 K shows a dependence on the temperature (Tab. IV). Magnetic susceptibility data obey the Curie-Weiss law

$$\chi_M^{\text{corr}} = C/(T - \theta)$$
$$\text{where } C = Ng^2\beta^2 S(S+1)/3\text{k}$$

TABLE IV Magnetic data for $Cu(5\text{-}Clsal)_2(H_2O)_2$

$T(K)$	$\chi_M^{corr} \times 10^6$	μ_{eff}, *B.M.*
93	4246	1.78
113	3578	1.80
133	3042	1.80
153	2726	1.83
173	2345	1.80
193	2147	1.82
213	1950	1.82
233	1802	1.83
253	1638	1.82
273	1520	1.82
293	1432	1.83

with $S = 1/2$ and the other symbols have their usual meaning. The Curie constant (C) is 0.429 and Weiss constant (θ) of $-10(2)$ K indicates that there is a weak antiferromagnetic exchange interaction between the copper(II) atoms in a polymeric chain.

The molecular structure of $Cu(5\text{-}Clsal)_2(H_2O)_2$ is shown in Figure 1. An X-ray analysis of the complex shows the polymeric chain of copper(II) atoms are bridged by pairs of water molecules with Cu−O(bridge) bond distances of 1.970(2) and 2.718(2) Å. The coordination sphere about each copper(II) atom is completed by a *trans*-pair of unidentate 5-chlorosalicylate anions with a Cu−O bond distance of 1.927(1) Å. The bridging oxygen atoms arrange a planar central Cu_2O_2 rhombus with $\mu O-Cu-\mu O$ and Cu−O−Cu bond angles of 103.18(6)° and 76.82(6)°, respectively. The $Cu-\mu OH_2$ bond distances found in the complex lie in the range found in

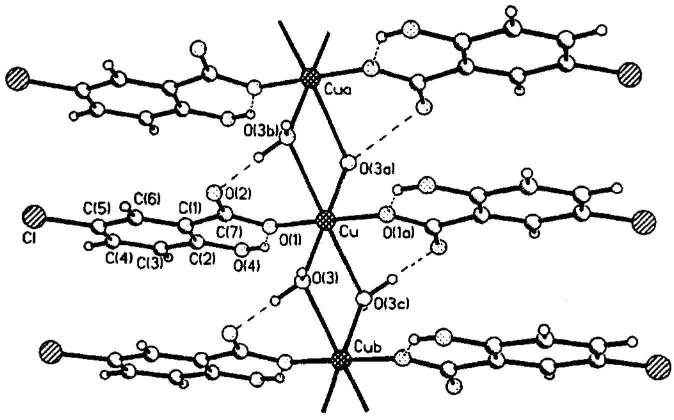

FIGURE 1 The molecular structure of $Cu(5\text{-}Clsal)_2(H_2O)_2$.

the series of hexacoordinate polymeric copper(II) compounds, with the range 1.91 – 1.99 Å (Cu – μO(equatorial)) and 2.37 – 2.99 Å (Cu – μO(apical)) [10]. The Cu···O(2) and Cu···O(4) distances (Fig. 1) of 3.018(2) and 3.826(2) Å are somewhat longer than the longest found in the series of hexacoordinated polymeric copper(II) compounds of 2.99 Å [10]. Both exclude a real metal-ligand bond.

The Cu – Cu distance of 3.702(2) Å is in the range found in the series of hexacoordinate polymeric copper(II) compounds (2.977(2) – 11.0229(2) Å) [10] without a direct metal – metal bond.

From the data (Tab. III) one can see that the six oxygen atoms about each copper(II) atom form an elongated tetragonal bipyramidal geometry with the tetragonality (T) of 0.717, calculated according by Procter *et al.* [11]. In the series of copper(II) compounds, with the chromophore CuO_6 [12] the parameter of tetragonality (T) ranges from 0.53 to 1.0 because of the Jahn – Teller effect.

The g-factors of Cu(II) coordination compounds reflect the symmetry of the donor atoms, the character of the bonds to the central atom-donor, electron delocalization, *etc.*, thus it is logical to expect that for Cu(II) complexes of tetragonal symmetry the g-factors will be influenced by the degree of the tetragonal distortion. Based on the MO-model, Smith [13] developed detailed expression for the values of $g_{\parallel}$ and $g_{\perp}$ for tetragonal Cu(II)-systems. He investigated the correlation between the g-values and the tetragonality and found that owing to greater equatorial metal-ligand distances in lowering the tetragonal distortion the $g_{\parallel}$ values for a series of complexes $Cu(NH_3)_4X_2$ and their tetragonalities. In the group of complexes with the CuO_6 chromophore a dependence between the g_{av} values and the parameter of tetragonality T also was found [14]; when the parameter T increases the g_{av} value also increases. The compound under study with $g_{av} = 2.15$ and T parameter of 0.717 follows this trend [14].

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