

One-Dimensional Network Constructed by Salicylate and Phenanthroline Ligands with Copper(II)

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A novel complex, $[\text{Cu}_2(\text{phen})(\text{sal})(\text{Hsal})_2]_n$ (**1**), was synthesized and structurally characterized. The basic dimeric units are held by sal ligands and extended into 1-D network. The carboxylate groups of salicylates coordinate to the central ion in three different coordination modes: chelating, bridging and bridging-chelating. In the case of bridging-chelating of the carboxylate group of the salicylate, all three oxygen atoms of salicylate are bidentately coordinated to copper ion, namely, μ_4 - η^3 binding mode.

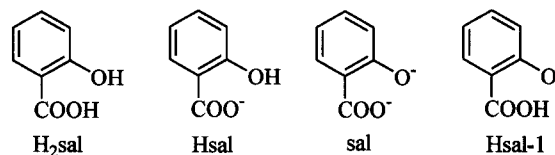
Keywords crystal structure, 1,10-phenanthroline, network, coordination polymer, salicylic acid

Introduction

Salicylic acid (H_2sal) is an interesting versatile ligand and its complexes are of continuous interest from both structural and biological viewpoints.¹⁻² H_2sal has two functional groups, the carboxylate and phenoxide, which have been widely employed in the synthesis of mononuclear or multinuclear coordination compounds.³⁻⁶ Few examples were reported for the mode of Hsal .⁷⁻⁹ Many complexes of salicylates have been reported, but the synthetic example of coordination polymer is rare,¹⁰⁻¹² and the ligand mostly shows monodentate or bidentate carboxylate coordination through the carboxylic and phenolic oxygen atoms (Scheme 1). One binding model occurred in the complex of $[\text{Mn}_9\text{O}_4(\text{O}_2\text{CPh})_8(\text{sal})(\text{Hsal})_2(\text{py})_4]$, is extremely rare in which each sal is μ_3 - η^3 binding mode.¹³ Although several compounds bearing salicylate and 1,10-phenanthroline (phen) ligands have been reported,¹⁴⁻¹⁵

these compounds were crystallized in form of mononuclear or multinuclear compounds and showed common coordination modes of salicylate ligand. Herein, we report the synthesis and structural characterization of the novel one-dimensional complex, $[\text{Cu}_2(\text{phen})(\text{sal})(\text{Hsal})_2]_n$ (**1**), in which the sal is μ_4 - η^3 binding mode.

Scheme 1 Forms of salicylic acid and salicylates



Experimental

Materials and general methods

All the reagents for synthesis were of analytical grade and used without further purification. The IR spectrum (KBr pellet) was recorded on a FT-IR 170SX (Nicolet) spectrometer. The magnetic susceptibility data of compound **1** were collected on a Quantum Design MPMS, SQUIT at temperatures from 2 to 300 K at a field of 10000 G.

Synthesis of the complex **1**

Compound **1** was synthesized using three-layered so-

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lution technique in a tube with 0.8 cm diameter. The upper layer was 1 mL of methanol solution containing $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.05 mol/L) and H_2sal (0.2 mol/L). The middle layer was 1 mL of mixed solvents MeOH/water with the volume ratio of 1:1. The bottom layer was 1 mL of *N,N'*-dimethylformamide (DMF) and water (1:1) solution containing 0.05 mol/L of 4,4'-bipyridyl (4,4'-bipy) and 0.05 mol/L of phen $\cdot \text{H}_2\text{O}$. Green crystals were obtained after three days. IR (KBr) ν : 1619 (m), 1606 (s), 1582 (m), 1554 (s), 1521 (m), 1500 (s), 1483 (m), 1449 (vs), 1430 (m), 1409 (m), 1394 (s), 1371 (w), 1332 (m), 1244 (s), 866 (w), 645 (m), 765 (m), 757 (s), 721 (m), 704 (w), 673 (m), 439 (w) cm^{-1} . Anal. calcd for $[\text{Cu}_2(\text{phen})(\text{Hsal})_2(\text{sal})]_n$: C 55.23, N 3.90, H 3.09; found C 55.24, N 3.93, H 3.10. The crystals of **1** are very stable in the air. If 4,4'-bipy was absent in the synthetic system, compound **1** could not be obtained. In our synthetic procedure two products, **1** and **2**, were precipitated, and compound **2** was $\{[\text{Cu}(4,4'\text{-bipy})(\text{Hsal})_2] \cdot$

$2\text{H}_2\text{O}\}_n$, deep blue. When crystals were kept in the solution after they were precipitated, **1** will gradually disappear. However, It is easy to distinguish and separate **1** and **2** from their colors.

X-Ray crystallography

A green plate crystal was mounted on a glass fiber. The data were collected at room temperature and low temperature on a Rigaku Mercury Charge-Coupled Detector diffractometer with graphite monochromated Mo $\text{K}\alpha$ ($\lambda = 0.071069$ nm). The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections [$I > 3.0\sigma(I)$]. All computations are carried on a OS2 Workstation using teXsan software. Crystal data for the complex **1** at low and room temperatures are recorded in Table 1.

Table 1 Data collection for complex 1

	103 K	Room temperature (296 K)
Temperature	103 K	Room temperature (296 K)
Formula	$\text{C}_{33}\text{H}_{22}\text{Cu}_2\text{N}_2\text{O}_9$	$\text{C}_{33}\text{H}_{22}\text{Cu}_2\text{N}_2\text{O}_9$
M_r	717.64	717.64
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (nm)	1.30756(6)	1.32402(6)
b (nm)	1.03423(4)	1.03757(3)
c (nm)	2.1152(1)	2.13011(8)
β ($^\circ$)	97.9173(8)	97.6789(5)
Crystal size (mm)	$0.8 \times 0.5 \times 0.2$	$0.8 \times 0.5 \times 0.2$
V (nm^3)	2.8332(2)	2.9000(2)
Z	4	4
D_c ($\text{Mg} \cdot \text{m}^{-3}$)	1.682	1.644
μ (Mo $\text{K}\alpha$) (cm^{-1})	15.65	15.29
$F(000)$	1456	1456
Reflections measured	13356	14311
$2\theta_{\text{max}}$ ($^\circ$)	55.5	55.5
Independent reflections [$I > 3\sigma(I)$]	3288	3238
R	0.028	0.037
R_w	0.046	0.059
Goodness-of-fit on F^2	2.64	2.96
Parameters	487	424

Results and discussion

The atomic coordinate and thermal parameters are listed in Table 2. The selected bond lengths and angles for the low temperature measurement are given in Table 3, while the bond lengths related to Cu—O and Cu—N measured at room temperature are listed in Table 4. The binding modes of salicylates are clearly demonstrated by single-crystal X-ray diffraction analysis as shown in Fig. 1.

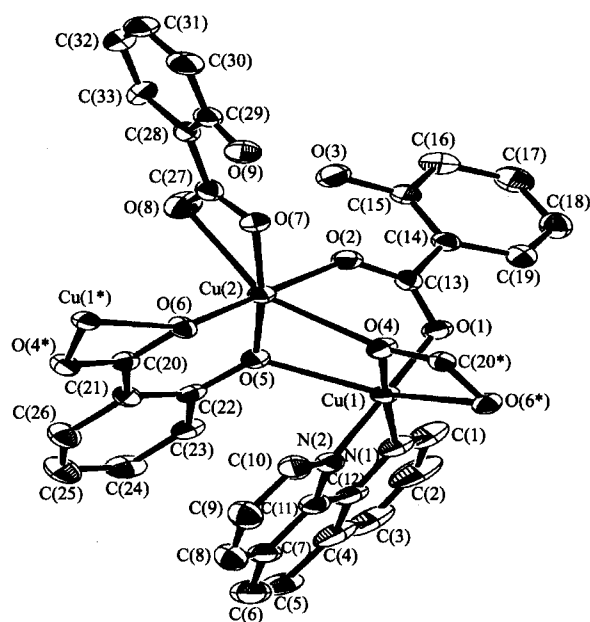


Fig. 1 ORTEP viewing of complex 1 at low temperature.

The atom O(9) is in disorder even the data collected at low temperature. The basic motif of the molecular structure is an asymmetric dimer, in which each copper atom possesses a distorted octahedral geometry. One of the octahedral geometry is completed by N(1), N(2), O(1), O(4), O(5) and O(6*) atoms with O(1) and N(2) atoms in axial positions. Another distorted octahedral ge-

ometry consists of O(5), O(4), O(7), O(8), O(2) and O(6) atoms with O(2) and O(6) atoms are in axial positions. The dihedral angle of two basal planes is 23.175°. There are two kinds of separations between copper atoms, the distance of Cu(1)—Cu(2) is 0.31067(5) nm and that of Cu(1*)—Cu(2) is 0.43843(5) nm. The basic dimeric units are held together by sal ligands and extended into 1-D network, which is depicted in Fig. 2. The 1-D coordination framework of $[\text{Cu}^{\text{II}}\text{-sal}]_n$ is created without Hsal linking and phen coordination, although the phen and Hsal could be necessary in the formation of compound 1.

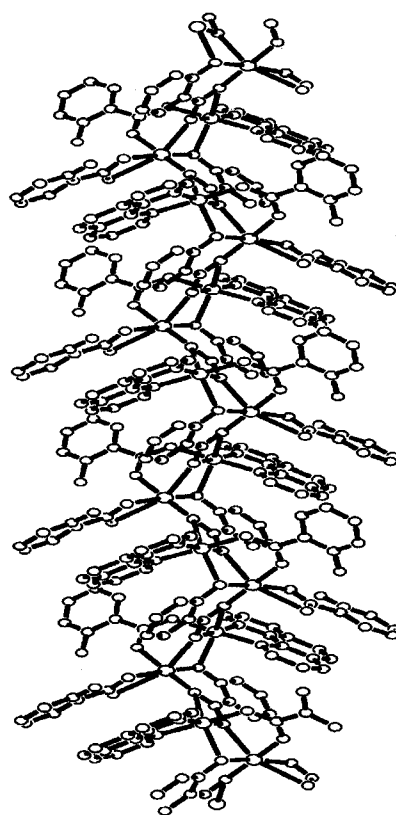


Fig. 2 One-dimensional network of complex 1 at low temperature.

Table 2 Non-hydrogen atomic coordinates and thermal parameters for complex 1 at low temperature

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^a
Cu(1)	-0.01922(2)	0.23248(3)	0.33992(2)	1.272(10)
Cu(2)	0.12926(2)	0.01405(3)	0.30897(2)	1.40(1)
O(1)	0.1103(1)	0.3043(2)	0.38236(9)	1.64(4)
O(2)	0.2159(1)	0.1418(2)	0.36064(9)	1.62(4)
O(3)	0.3841(2)	0.1019(2)	0.4395(1)	1.90(5)

Continued

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}^a</i>
O(4)	0.0408(1)	0.2115(2)	0.26054(9)	1.46(4)
O(5)	0.0327(1)	0.0219(2)	0.36824(9)	1.36(4)
O(6)	0.0454(1)	-0.1077(2)	0.25596(9)	1.44(4)
O(7)	0.2412(1)	-0.0167(2)	0.25766(10)	1.69(5)
O(8)	0.2883(2)	-0.1302(2)	0.3453(1)	2.68(5)
O(9) ^b	0.3363(3)	-0.0617(4)	0.1624(2)	1.87(9)
O(9') ^b	0.4437(4)	-0.2652(5)	0.3493(2)	1.5(1)
N(1)	-0.0900(2)	0.2636(2)	0.4163(1)	1.74(6)
N(2)	-0.1565(2)	0.1594(2)	0.3046(1)	1.51(5)
C(1)	-0.0522(3)	0.3100(3)	0.4727(2)	2.24(7)
C(2)	-0.1028(3)	0.2990(4)	0.5262(2)	3.00(8)
C(3)	-0.1953(3)	0.2350(3)	0.5213(2)	3.06(9)
C(4)	-0.2385(2)	0.1849(3)	0.4619(2)	2.39(7)
C(5)	-0.3339(3)	0.1117(3)	0.4506(2)	3.10(9)
C(6)	-0.3679(3)	0.0626(3)	0.3935(2)	2.97(9)
C(7)	-0.3118(2)	0.0760(3)	0.3405(2)	2.24(7)
C(8)	-0.3405(3)	0.0227(3)	0.2800(2)	2.50(8)
C(9)	-0.2778(2)	0.0362(3)	0.2341(2)	2.39(8)
C(10)	-0.1859(2)	0.1044(3)	0.2485(2)	1.78(7)
C(11)	-0.2190(2)	0.1458(3)	0.3501(1)	1.72(6)
C(12)	-0.1829(2)	0.2016(3)	0.4112(1)	1.87(7)
C(13)	0.1964(2)	0.2454(3)	0.3891(1)	1.50(6)
C(14)	0.2816(2)	0.2988(3)	0.4359(1)	1.37(6)
C(15)	0.3666(2)	0.2232(3)	0.4600(1)	1.45(6)
C(16)	0.4374(2)	0.2716(3)	0.5092(1)	1.90(7)
C(17)	0.4260(2)	0.3939(3)	0.5328(2)	1.89(7)
C(18)	0.3444(2)	0.4711(3)	0.5079(1)	1.85(7)
C(19)	0.2726(2)	0.4231(3)	0.4605(1)	1.75(7)
C(20)	-0.0163(2)	-0.1893(3)	0.2747(1)	1.23(6)
C(21)	-0.0600(2)	-0.1751(3)	0.3340(1)	1.29(6)
C(22)	-0.0348(2)	-0.0713(3)	0.3767(1)	1.41(6)
C(23)	-0.0831(2)	-0.0653(3)	0.4318(1)	1.52(6)
C(24)	-0.1550(2)	-0.1553(3)	0.4437(1)	1.95(7)
C(25)	-0.1815(3)	-0.2578(3)	0.4019(2)	2.28(7)
C(26)	-0.1344(2)	-0.2673(3)	0.3484(1)	1.87(7)
C(27)	0.3020(2)	-0.0957(3)	0.2911(2)	2.01(7)
C(28)	0.3915(2)	-0.1476(3)	0.2613(1)	1.78(6)
C(29)	0.4638(3)	-0.2280(3)	0.2976(2)	2.43(8)
C(30)	0.5454(3)	-0.2784(3)	0.2708(2)	2.78(8)
C(31)	0.5556(3)	-0.2524(3)	0.2081(2)	2.75(8)
C(32)	0.4857(2)	-0.1754(3)	0.1723(2)	2.51(8)
C(33)	0.4030(2)	-0.1226(3)	0.1978(1)	1.72(7)

$${}^a B_{\text{eq}} = \frac{8}{3} \pi^2 [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*) + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha].$$

^b OCC of O(9) and O(9') are 0.6 and 0.4, respectively.

Table 3 Selected bond lengths (nm) and angles ($^{\circ}$) for complex **1** at low temperature^a

Cu(1)—O(1)	0.1951(2)	Cu(1)—O(4)	0.1961(2)
Cu(1)—O(5)	0.2334(2)	Cu(1)—O(6 [*])	0.2602(2)
Cu(1)—N(1)	0.1995(3)	Cu(1)—N(2)	0.1995(2)
Cu(2)—O(2)	0.1971(2)	Cu(2)—O(4)	0.2496(2)
Cu(2)—O(5)	0.1900(2)	Cu(2)—O(6)	0.1925(2)
Cu(2)—O(7)	0.1965(2)	Cu(2)—O(8)	0.2588(2)
O(1)-Cu(1)-O(4)	90.68(8)	O(1)-Cu(1)-O(5)	91.95(7)
O(1)-Cu(1)-O(6 [*])	97.43(7)	O(1)-Cu(1)-N(1)	92.07(9)
O(1)-Cu(1)-N(2)	174.53(9)	O(4)-Cu(1)-O(5)	88.85(7)
O(4)-Cu(1)-O(6 [*])	55.11(7)	O(4)-Cu(1)-N(1)	174.88(9)
O(4)-Cu(1)-N(2)	94.75(9)	O(5)-Cu(1)-O(6 [*])	142.64(6)
O(5)-Cu(1)-N(1)	95.37(8)	O(5)-Cu(1)-N(2)	87.55(8)
O(6 [*])-Cu(1)-N(1)	120.18(8)	O(6 [*])-Cu(1)-N(2)	86.21(8)
N(1)-Cu(1)-N(2)	82.56(10)	O(2)-Cu(2)-O(4)	82.99(7)
O(2)-Cu(2)-O(5)	89.38(8)	O(2)-Cu(2)-O(6)	178.10(8)
O(2)-Cu(2)-O(7)	89.97(8)	O(2)-Cu(2)-O(8)	81.07(7)
O(4)-Cu(2)-O(5)	85.59(7)	O(4)-Cu(2)-O(6)	95.82(7)
O(4)-Cu(2)-O(7)	104.13(7)	O(4)-Cu(2)-O(8)	154.34(7)
O(5)-Cu(2)-O(6)	92.01(8)	O(5)-Cu(2)-O(7)	170.11(8)
O(5)-Cu(2)-O(8)	114.11(8)	O(6)-Cu(2)-O(7)	88.88(8)
O(6)-Cu(2)-O(8)	99.53(7)	O(7)-Cu(2)-O(8)	56.06(8)
Cu(1)-O(4)-Cu(2)	87.51(7)	Cu(1)-O(5)-Cu(2)	93.83(8)
O(1)-C(13)-O(2)	125.7(2)	Cu(1)-O(1)-C(13)	124.6(2)
Cu(2)-O(2)-C(13)	133.6(2)		

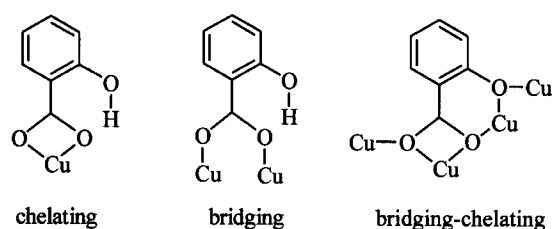
^a Symmetry code: * - x , $y + 1/2$, $-z + 1/2$

Table 4 Selected bond lengths (nm) of complex **1** at room temperature

Cu(1)—O(1)	0.1951(3)	Cu(2)—O(2)	0.1973(3)
Cu(1)—O(4)	0.1962(3)	Cu(2)—O(4)	0.2544(3)
Cu(1)—O(5)	0.2353(2)	Cu(2)—O(5)	0.1895(3)
Cu(1)—O(6 [*])	0.2624(2)	Cu(2)—O(6)	0.1925(2)
Cu(1)—N(1)	0.1994(4)	Cu(2)—O(7)	0.1961(3)
Cu(1)—N(2)	0.2004(3)	Cu(2)—O(8)	0.2575(3)

Two kinds of salicylates, sal and Hsal, are in compound **1**. The phenyl ring of sal ligand is nearly perpendicular to two-salicylate (Hsal) phenyl rings, the dihedral angles between phenyl rings of the sal and two-salicylate ligands are 82.8° and 87.3° , respectively. Furthermore, there is a strong intra-molecular interaction between sal and phen ligands, the dihedral and distance of two planes are 4.557° and about 0.33 nm, respectively. Interestingly, the carboxylate groups coordinate to central ion in three different modes: chelating, bridging and bridging-

chelating (Scheme 2). Although in $Y_2(\text{Hsal})_6(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ the carboxylate groups are also associated with three different modes, none of phenolic oxygen atoms is coordinated.¹¹ In the $\mu_4\text{-}\eta^3$ binding mode of sal, all three oxygen atoms from the carboxylate and phenolate are bidentately coordinated to copper ion. To our knowledge, $\mu_4\text{-}\eta^3$ coordination mode for salicylate is first reported. The magnetic curve is depicted in Fig. 3. The magnetic behavior suggests a weak antiferromagnetic interaction between copper atoms.

Scheme 2 Coordination modes of three salicylates in complex **1**

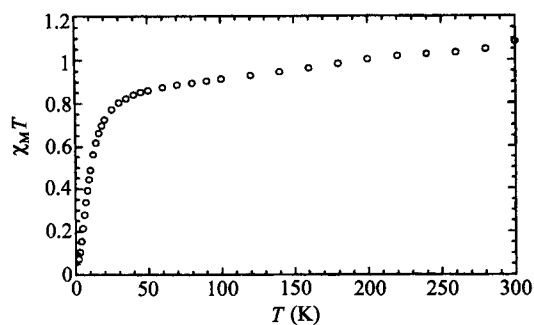


Fig. 3 Plot of $\chi_M T$ vs. T for magnetic susceptibility of complex 1.

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