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Syntheses and crystal structures of three one-dimensional copper(II) complexes constructed by salicylate and 4,4'-bipyridine: ladder, zig-zag, and linear polymeric assembly

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Abstract

Syntheses and crystal structures of three new compounds $\{trans-[Cu(Hsal)_2(4,4'-bipy)](DMF)\}_n$ (1), $\{cis-[Cu(Hsal)_2(4,4'-bipy)]_n$ (2), and $[Cu_2(Hsal)_4(4,4'-bipy)]_n$ (3) are reported. These three compounds have *trans-*, *cis-*, and dimer geometries bearing a common motif $[Cu(Hsal)_2(4,4-bipy)_n]$ leading to ladder, zig-zag, and linear one-dimensional (1-D) networks, respectively. The Cu···Cu distances separated by 4,4'-bipy are different in these three compounds, which leads to an extension structure in compound 3 and a compact structure in compound 2. Conformations of 4,4'-bipy ligands in these three compounds are also different. In compound 1 there is stacking of the bidentate salicylate and the bridging salicylate from another molecule. There is also stacking of salicylate and 4,4'-bipy from another molecule in compound 2.

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1. Introduction

Recently much attention has been paid in the field of crystal engineering using bridging heterocyclic amine bidentate ligands with transition metals to form coordination polymers [1]. The 4,4'-bipyridine (4,4'-bipy) ligand and its analogues have been used in much of this work. The coordination polymers bearing 4,4'-bipy ligands have been shown to form a wide range of interesting network topologies, for example, chains, ladders, grids, and adamantoid networks [2], and 4,4'bipyridine is very popular for the construction of porous organic–inorganic hybrid solids with potential applications as catalytic, gas adsorption, or molecular sieve materials [3]. One-dimensional (1-D) chain compounds have been the focus of very active research because of their special and excellent physicochemical properties

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[4]. Although transition metal complexes with 4,4'bipyridine have shown many interesting networks 3d[5], few trans- and cis- coordination motifs of 4,4'bipy in the same formulated compounds were reported. Examples of linear chain compounds of copper are still limited despite a vast number of dimeric copper carboxylates and their adducts [6]. Complexes of salicylic acid (H₂sal) are of interest from structural and biological viewpoints [7]. The combination of 4,4'bipy and H₂sal is expected to construct various polymeric compounds. Since it is useful to understand the construction strategy of novel geometric polymers, elucidation of the structure-directing effects of various solvents will enable a better understanding possibilities of crystal engineering for the synthesis of complexes using different solvent systems. Herein, we report examples of trans-, cis-, and dimer geometries bearing a common motif $[Cu(Hsal)_2(4,4'-bipy)_n]$ (*n* = 1 for **1** and 2, n = 0.5 for 3) in three 1-D compounds, {trans- $[Cu(Hsal)_2(4,4'-bipy)](DMF)\}_n$ (1), {*cis*-[Cu(Hsal)_2- $(4,4'-bipy)](2H_2O)_n$ (2), and $[Cu_2(Hsal)_4(4,4'-bipy)]_n$ (3).

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2. Experimental

2.1. Preparation of the complexes

2.1.1. $\{trans - [Cu(Hsal)_2(4, 4'-bipy)](DMF)\}_n$ (1)

Crystals were grown by layer-method using two- or three-layer solutions in a slender tube with a 0.8 cm diameter. The upper layer solution was 1.5 ml methanol containing 0.05 mol 1⁻¹ Cu₂(CH₃COO)₄·2H₂O and 0.20 mol 1⁻¹ salicylic acid (H₂sal), the bottom layer solution was 1.5 ml 0.05 mol 1⁻¹ 4,4'-bipyridine in DMF and water mixed solvents (ratio of DMF–H₂O was 1:1). After standing for several days, sky blue crystals grew. They were collected by suction filtration. *Anal.* Calc. for C₂₇H₂₅N₃O₇Cu: C, 57.19; H, 4.44; N, 7.41. Found: C, 57.13; H, 4.40; N, 7.28%. IR (KBr pellet, cm⁻¹): 1681(s), 1610(s), 1589(s), 1559(s), 1485(s), 1450(s), 1415(s), 1393(vs), 1253(m), 864(w), 822(m), 754(m), 703(w), 670(w), 645(w).

2.1.2. $\{cis - [Cu(Hsal)_2(4, 4'-bipy)](2H_2O)\}_n$ (2)

Crystals were grown using a similar layer-method as reported for 1. The upper layer solution was 1.5 ml methanol containing 0.05 mol 1^{-1} Cu₂(CH₃COO)₄· 2H₂O and 0.20 mol 1^{-1} salicylic acid, the bottom layer solution was 2.5 ml 0.025 mol 1^{-1} 4,4'-bipyridine in water and the middle layer was 1.0 ml water-methanol (1:1) mixed solvent system. After standing for several days, dark blue crystals grew. They were filtered by suction filtration, washed with small amount of water, and then dried in air. *Anal.* Calc. for C₂₄H₂₂N₂O₈Cu: C, 54.39; H, 4.18; N, 5.29. Found: C, 54.50; H, 4.12; N, 5.42%. IR (KBr pellet, cm⁻¹): 1612(s), 1555(m), 1482(s), 1450(s), 1415(s), 1398(vs), 1252(s), 1223(m), 869(w), 821(m), 762(m), 705(w), 671(w), 645(w).

2.1.3. $[Cu_2(Hsal)_4(4,4'-bipy)]_n$ (3)

Crystals were grown using a method similar to **2**, but without a middle layer. *Anal.* Calc. for $C_{19}H_{14}NO_6Cu$: C, 54.88; H, 3.39; N, 3.37. Found: C, 55.03; H, 3.43; N, 3.47%. IR (KBr pellet, cm⁻¹): 1632(s), 1598(vs), 1485(m), 1464(s), 1416(w), 1390(vs), 1249(m), 1217(m), 866(w), 813(w), 765(m),705(w), 674(w), 634(w).

2.2. Crystallography

Single crystals of 1, 2, and 3 were prepared by the method described in the above procedures. All single crystals for crystallographic analysis were mounted on glass fibers. The crystal dimensions were $0.1 \times 0.3 \times 0.5$ mm for 1, $0.05 \times 0.3 \times 0.55$ mm for 2, and $0.2 \times 0.3 \times 0.3$ mm for 3. Measurements for all compounds were made on a Rigaku AFC 8R diffractometer with a CCD detector and graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Data were collected at room temperature (23 °C) for 1 and 2 and -100 °C for 3 to

a maximum 2θ value of 55.5 using ω scan. The 18845, 8321, and 27198 reflections for compounds 1, 2, and 3 were collected and 5948, 4887, and 2085 were unique reflections for 1, 2, and 3, respectively. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 35 mm. An empirical absorption correction based on azimuthal scans of several reflections was applied. Data were corrected for Lorentz and polarization effects. Crystal structures for 1, 2, and 3 were solved by direct methods SIR92 [8] and expanded using Fourier technique DIRDIF94 [9]. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Full-matrix leastsquares refinements based on 2911 for 1, 3687 for 2, and 1299 for **3** observed reflections $(I > 3.00\sigma(I))$ and the unweighted and weighted agreement factors of $R = \Sigma ||F_{o}| - |F_{c}|| \Sigma |F_{o}|$ and $R_{w} = [\Sigma w(|F_{o}| - |F_{c}|)^{2}/$ $\sum w |F_o|^2]^{1/2}$ were used. Variable parameters for compounds 1, 2, and 3 in the final cycle of full-matrix leastsquares refinements are 415, 370, and 279, respectively. The weighting scheme was based on counting statistics. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta / \lambda$, and various classes of indices showed no unusual trends. All calculations were performed using the TEXSAN crystallographic software package [10]. ORTEP graphs were reproduced using ORTEP-3 for WINDOWS [11]. Crystal data and details of

Table 1

Crystallographic data for {trans-[Cu(Hsal)₂(4,4'-bipy)](DMF)}_n (1), {cis-[Cu(Hsal)₂(4,4'-bipy)](2H₂O)}_n (2), and [Cu₂(Hsal)₄(4,4'-bipy)]_n (3)

	1	2	3
Formula	C ₂₇ H ₂₅ CuN ₃ O ₇	C24H22CuN2O8	C ₁₉ H ₁₄ CuNO ₆
М	567.06	529.99	415.87
Crystal system	monoclinic	triclinic	tetragonal
Space group	$P2_1/c$ (#14)	P1 (#2)	$I4_1cd$
a (Å)	13.689(4)	10.377(1)	13.9645(3)
b (Å)	11.158(3)	10.6890(4)	13.9645(3)
c (Å)	17.080(1)	11.026(1)	38.110(1)
α (°)	90	86.181(3)	90
β (°)	101.038(1)	70.2643(9)	90
γ (°)	90	88.837(1)	90
V (Å ³)	2560(1)	1148.6(1)	7431.7(4)
Ζ	4	2	16
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.471	1.532	1.487
F	1172	546	3392
λ (Å)	0.71069	0.71069	0.71069
$\mu ({\rm cm}^{-1})$	9.05	10.05	12.10
Crystal size (mm)	$0.1\times0.2\times0.3$	$0.05\times0.3\times0.55$	0.2 imes 0.2 imes 0.3
Crystal habit	Plate	prismatic	tetragonal
2θ (°)	55.5	55.5	55.5
N	5948	4887	2085
No. $(I > 3.0\sigma(I))$	2911	3687	1299
R	0.054	0.043	0.051
R _w	0.056	0.050	0.061

structure determinations for 1, 2, and 3 are summarized in Table 1.

3. Results and discussion

3.1. Syntheses of compounds 1, 2, and 3

Crystals of compounds 2 and 3 are stable overtime if kept in solution, while crystals of compound 1 become opaque, but they are stable overtime in air. Compounds 1 and 2 were obtained in different solvent systems (see Section 2.1). The formulae of compounds 1 and 2 are similar except for crystallized solvents (for 1, containing DMF and for 2, H₂O). Compound 1 was synthesized in water, methanol, and N,N'-dimethylformamide mixed solvent systems, while compounds 2 and 3 were synthesized in a methanol-water mixed solvent system. It is easy to distinguish compounds 1, 2, and 3 based upon their colors and crystal habits. Compound 1 is sky blue, 2 is dark blue, and 3 is green.

For the synthesis of compound 3, when two layers of solutions were put together without mixing them, a precipitate formed immediately at the interface of the two layers and after some days crystals of compound 3 were formed in the bottom layer.

Compounds 2 and 3 were synthesized using same solution concentrations and the same solvents in different layers. We did not observe changes for compounds 2 and 3 when kept in solution for 3 months.

3.2. Structural descriptions of complexes 1, 2, and 3

3.2.1. Description of the crystal structures

The ORTEP drawings of 1, 2, and 3 with atom numbering schemes are shown in Figs. 1-3. Views of networks of these three complexes are shown in Figs. 4-6. The 4,4'-bipy is disordered in compound 3, but it is not effected in comparison with the structural characteristics of compounds 1, 2 and 3. Selected bond lengths and angles for 1, 2, and 3 are given in Tables 2-4, respectively. Geometries of the copper atoms in these three compounds are distorted octahedral. The structure of compound 1 is constructed from a motif of two 1-D linear chains, which form a ladder network and the structure of compound 2 is constructed from a motif of a 1-D zig-zag network. The structure of compound 3 is composed of a 1-D dimer chain from a dimer motif. The bond length of Cu–N in compound 3 is longer than that of compound 2 or 3 (2.025 and 2.037 Å in 1; 1.987 and 1.995 Å in 2, and 2.133 Å in 3), but these Cu-N bond lengths are similar to these reported in reference [12]. In general, Cu–N bond lengths of polymers with a dimer motif are longer than that of ladder or zig-zag of 1-D and 2-D, or 3-D networks as reported elsewhere [6,13] and Table 8 of reference [12]. In compound 3 all salicylates have a bridging coordination mode and in compound 2 all salicylates are bidentately coordinated with copper. In compound 1 there are two kinds of coordination modes for salicylate. In compound 3 there are short Cu–O bond distances, shown in Tables 2–4 as compared with compounds 1 and 2 because of the Cu-··Cu interaction. The Cu-O bond lengths are



C(11) C(10) C(8) C(21) C(23) C(23) C(23) C(23) C(24) C(24) C(24) C(24) C(26) C

Fig. 1. ORTEP view of coordination environment in complex $\mathbf{1}$ with atom numberings.

Fig. 2. ORTEP view of coordination environment in complex 2 with atom numberings.



Fig. 3. ORTEP view of coordination environment in complex ${\bf 3}$ with atom numberings.

similar in compounds 2 and 3. In compound 1 the O(3)– H···O(2) hydrogen bond is stronger than that of O(6)– H···O(5) hydrogen bond in compound 2, but in compound 2 the two hydrogen bonds are the same. In compound 1 dihedral angles between ring planes of 4,4'bipy and salicylates are 77.4, 76.9, 81.4 and 84.0°. In compound 2 these dihedral angles between planes of



Fig. 4. Perspective view of 1-D ladder network of complex 1.



Fig. 5. Perspective view of 1-D zig-zag network of complex 2.



Fig. 6. Perspective view of 1-D linear network of complex 3.

Table 2 Selected bond lengths (Å) and angles (°) for compound 1

Bond lengths			
Cu(1) - O(1)	2.001(3)	Cu(1)–O(2)	2.651(4)
Cu(1)-O(4)	1.957(4)	Cu(1)-O(5*)	2.304(4)
Cu(1)-N(1)	2.037(3)	Cu(1)-N(2)	2.025(3)
Bond angles			
O(1)-Cu(1)-O(2)	54.5(1)	O(1) - Cu(1) - O(4)	146.9(1)
O(1)-Cu(1)-O(5*)	84.2(1)	O(1)-Cu(1)-N(1)	90.8(2)
O(1)-Cu(1)-N(2)	89.8(2)	O(2) - Cu(1) - O(4)	92.9(1)
O(2)-Cu(1)-O(5*)	137.9(1)	O(2)-Cu(1)-N(1)	97.8(2)
O(2)-Cu(1)-N(2)	85.2(2)	$O(4) - Cu(1) - O(5^*)$	128.9(1)
O(4) - Cu(1) - N(1)	88.0(2)	O(4) - Cu(1) - N(2)	93.3(2)
$O(5^*)-Cu(1)-N(1)$	89.3(2)	$O(5^*)-Cu(1)-N(2)$	87.6(2)
N(1)-Cu(1)-N(2)	176.7(2)		

* Symmetry operator: -x, -y, -z.

Table 3 Selected bond lengths (Å) and angles (°) for compound ${\bf 2}$

2.013(2)	Cu(1)–O(2)	2.423(3)
1.962(2)	Cu(1)–O(5)	2.549(2)
1.987(3)	Cu(1)-N(2)	1.995(2)
58.55(7)	O(1)-Cu(1)-O(4)	91.78(10)
95.27(8)	O(1)-Cu(1)-N(1)	90.5(1)
157.31(10)	O(2)-Cu(1)-O(4)	99.77(9)
146.11(8)	O(2)-Cu(1)-N(1)	98.55(10)
98.76(9)	O(4) - Cu(1) - O(5)	56.66(8)
159.79(9)	O(4) - Cu(1) - N(2)	92.01(10)
103.14(9)	O(5)-Cu(1)-N(2)	105.47(9)
93.6(1)		
	2.013(2) 1.962(2) 1.987(3) 58.55(7) 95.27(8) 157.31(10) 146.11(8) 98.76(9) 159.79(9) 103.14(9) 93.6(1)	$\begin{array}{ccccccc} 2.013(2) & Cu(1)-O(2) \\ 1.962(2) & Cu(1)-O(5) \\ 1.987(3) & Cu(1)-N(2) \\ \\ \hline \\ 58.55(7) & O(1)-Cu(1)-O(4) \\ 95.27(8) & O(1)-Cu(1)-N(1) \\ 157.31(10) & O(2)-Cu(1)-O(4) \\ 146.11(8) & O(2)-Cu(1)-N(1) \\ 98.76(9) & O(4)-Cu(1)-O(5) \\ 159.79(9) & O(4)-Cu(1)-N(2) \\ 103.14(9) & O(5)-Cu(1)-N(2) \\ 93.6(1) \\ \end{array}$

Table 4

Selected bond lengths (Å) and angles (°) for compound 3

Bond lengths			
Cu(1) - O(1)	1.928(7)	Cu(1) - O(3)	1.914(7)
Cu(1)-O(4)	2.041(6)	Cu(1)–O(6)	1.995(7)
Cu(1)-N(1)	2.133(3)		
Bond angles			
O(1)-Cu(1)-O(3)	92.8(3)	O(1)-Cu(1)-O(4)	163.8(2)
O(1)-Cu(1)-O(6)	87.7(3)	O(1)-Cu(1)-N(1)	99.6(3)
O(3)-Cu(1)-O(4)	87.8(3)	O(3)-Cu(1)-O(6)	170.3(2)
O(3)-Cu(1)-N(1)	93.6(3)	O(4) - Cu(1) - O(6)	89.1(3)
O(4)-Cu(1)-N(1)	96.5(3)	O(6)-Cu(1)-N(1)	95.8(3)

4,4'-bipy and salicylates are 3.9, 7.7, 89.9, and 98.6°. In compound **3**, dihedral angles between planes of 4,4'-bipy and salicylates are 10.9 and 74.8°.

3.2.2. Extension and compact nature of these structures

Distances between the two copper atoms connected by 4,4'-bipy in compounds **1**, **2**, and **3** are listed in Table 5. In compound **3** there is a longer Cu \cdots Cu separation of 11.31 Å than that of compounds **1** and **2** because of

Table 5 Cu···Cu distances (Å) separated by 4,4'-bipy and carboxylic groups in compounds 1, 2, and 3

Compound	Cu-N	Cu-bipy- Cu	Cu–O	Cu–carboxy– Cu
1	2.037, 2.025	11.16	1.957– 2.304	4.06
2	1.987, 1.995	11.04, 11.09	1.962– 2.549	
3	2.133	11.31	1.914– 2.041	2.66

the strong Cu-Cu interaction in the dimer motif. Consistently, the longer Cu···Cu distances are followed by longer Cu-N bond lengths. There are two types of Cu-Cu separations, 11.04 and 11.09 Å, in compound **2**.

From above structural information we conclude that there is a 1-D extension structure in compound 3 and there is a 1-D compact structure in compound 2. It would be very interesting to study these structural differences for compounds 1, 2, and 3 with regard to these different physiochemical properties.

3.2.3. Conformations of 4,4'-bipy in these three compounds

Conformations of 4, 4'-bipy in these three molecules are very different because of the intra- and intermolecular interactions. Dihedral angles between the two pyridine rings of 4,4'-bipy are listed in Table 6. In compound 2 the dihedral angle between two planes of pyridine rings is zero, they are co-planar. We can conclude that a larger dihedral angle between these two pyridine rings is followed by a longer $Cu \cdots Cu$ distance due to the 4,4'-bipy ring system.

3.2.4. Stacking effects in these compounds

In compound **3** there is no stacking effect between molecules because of the non-coplanar nature of two pyridine rings of 4,4-bipy. In compound **1** there is a stacking effect due to the bidentate salicylate and the bridging salicylate of another molecule, the dihedral angle and the distance of these two planes in these two salicylates are 168.24° and about 3.4 Å. In the compound **2** there is also a stacking effect between one bidentate salicylate and 4,4'-bipy from another molecule, the dihedral angle and the distance of these two

Table 6

The dihedral angles (°) between two pyridine rings of 4,4'-bipy in compounds 1, 2, and 3

Compound	Dihedral angles (°)
1	22.681
2	0.000
3	44.888

planes in salicylate and 4,4′-bipy are 7.72° and about 3.45 Å.

4. Conclusion

We have demonstrated that the reactions of $Cu_2(CH_3COO)_4 \cdot 2H_2O$, 4,4'-bipyridine, and salicylic acid, using the layered-solution approach and variable solvents, allows the isolation of three 1-D polymeric complexes with ladder, zig-zag, linear networks bearing a $[Cu(Hsal)_2(4,4-bipy)_n]$ motif. The $Cu \cdot Cu$ distances separated by 4,4'-bipy are different in these three compounds, which leads to a compact structure in compound **2** and an extended structure in compound **3** with varying conformations of 4,4'-bipy in three compounds. This effort is an example of crystal engineering aimed at design of the variable networks with functional properties, and is of benefit to develop chemistry of structural diversity.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 194214, 194215 and 194216 for compounds **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax:+44-1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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