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Novel 1D Copper(II) Helical Chain Formed by Weak Coordination-driven Self-assembly: Synthesis, Structure, and Magnetic Property

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A novel 1D copper(II) helical chain is constructed through the connection of tetranuclear copper(II) units $[Cu_4(L)(Py)_4]$ (H_8L＝*N*,*N'*-(BINOL-3,3'-dicarboxyl)-disalicylhydrazide, where BINOL is 1,1'-binaphthalenyl-2,2'-diol, py＝pyridine) by weak coordination-driven self-assembly, and characterized by IR, single crystal X-ray diffraction, thermogravimetric analysis, and X-ray power diffraction analysis. Interestingly, the helical chains are packed in an alternating left-(M) and right-handed (P) chirality, the orientation of the helices was determined by the axial chirality of the ligand. The complex shows antiferromagnetic interactions between the copper centers.

Keywords helical structures, copper, weak coordination-driven, axial chirality, magnetic property

Introduction

Over the last few years, considerable effort has been devoted to design and syntheses of new building blocks to construct helical structure especially chiral helical coordination polymers due to their aesthetically appealing topologies and potential applications in nonlinear optical materials, chiral recognitions, asymmetric catalysis and host-guest interactions.[1-9] The control of helicity at the supramolecular level via inducing conformation restrictions of molecules, formation of molecular hydrogen bonds, or coordination to metal ions is a particularly fascinating challenge.[10] Regarding the control of helicity, axially asymmetric 1,1'-binaphthyl backbone is an interesting building blocks.[11] Both Lin's and Hong's group have designed a variety of chiral bridging ligands based on atropisomeric 1,1'-binaphthyl framework and have constructed some novel helical metal-organic complexes with promising applications.[12-16] Interestingly, extensive investigations showed that binaphthyl-based materials and catalysts were often substituted at the 2-, 4-, 5- or 6-position to achieve additional molecular connecting points,[17-20] the 3-position of the binaphthyl scaffold has received much less attention.[21]

On the other hand, the *N*-acyl-salicylhydrazide ligands with multiple N, O coordination sites have been proven to be fruitful in the construction of fascinating polynuclear metal complexes with various applications, such as potential magnetic material, selective recognition, and asymmetric catalysis.[22-29] Very recently, we have constructed a novel interesting copper(II) complex[30] using a ligand, (*N*,*N'*-(2,6-pyridine-dicarboxyl)-disalicyl-hydrazide), which containes two salicylhydrazide groups. As part of our ongoing study of metal complexes constructed by two or more salicylhydrazide groups, introducing the *N*-acylsalicylhydrazide functional group in the 3-position of the binaphthyl scaffold as building blocks has particularly attracted our interest. We designed and synthesized a ligand containing bis-salicylhydrazide based binaphthyl framework, *N*,*N'*-(BINOL-3,3'-dicarboxyl)-disalicylhydrazide (H_8L), which features hinge-like ditopic with conformational and geometrical flexibility, where BINOL is 1,1'-binaphthalenyl-2,2'-diol. Herein, we present the synthesis and structure of one copper(II) complex with H_8L ligand, $[Cu_4(L)(Py)_4]\cdot 1.5DMF$ (**1**). A novel 1D helical chain was constructed with the aid of weak coordination-driven self-assembly. More interestingly, the helical chains are packed in an alternating left-(M) and right-handed (P) chirality, each chain is composed of only R_a or only S_a enantiomers ligand. The magnetic properties of the complex **1** were investigated.

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Experimental

Materials and general methods

All chemicals were used as obtained without further purification. 2,2'-Dihydroxy-[1,1']binaphthalenyl-3,3'-dicarboxylic acid (BINOL-3,3'-diacid) was prepared according to the literature method.[31] Infrared spectra were recorded as KBr pellets using a Nicolet 360 FT-IR spectrometer. Elemental analyses (C, H and N) were performed on a Vario EL analyser. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer in DMSO-d_6 with TMS as an internal standard. Thermogravimetric analyses were recorded with a Perkin-Elmer Pyris Diamond TG analyzer at a rate of 10 ℃/min from room temperature to 990 ℃ under a nitrogen atmosphere. The powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max 2200 diffractometer with Cu-Kα radiation. The magnetic susceptibility measurements were carried out on polycrystalline samples using a Quantum Design MPMS-5 SQUID magnetometer in the temperature range 2—300 K and magnetic field up to 5 T. Diamagnetic corrections were estimated from Pascal's constants.

Preparation of ligand (H_8L)

The mixture of 3.74 g (10 mmol) BINOL-3,3'-diacid and 50 mL $SOCl_2$ was refluxed in an 80 ℃ oil bath under nitrogen atmosphere for 10 h. Then the excess $SOCl_2$ was removed under vacuum. The crude carbonyl chloride, as a yellow foaming solid, was then dissolved in 30 mL dry THF and used in the next step immediately.

Triethylamine 2.9 mL (20 mmol) was added to 3.04 g (20 mmol) 2-hydroxy-benzoic acid hydrazide in 40 mL dry THF and the mixture was stirred in a -10 ℃ cool bath for 20 min. Then the crude carbonyl chloride prepared in the forward step was added to it dropwise and the mixture was stirred in the cool bath for another 1 h and then at room temperature for 48 h. Then crude product was deposited and filtrated. The solid was washing fully with water (20 mL×2) and THF (20 mL×2). The further purification could be carried out by reflux of the crude product in 40 mL mixture of THF and acetone for 20 min and hot filtration immediately. The yellow solid was collected and dry, yield 63%. m.p.>300 ℃; ^{1}H NMR (DMSO, 500 MHz) δ: 11.79 (s, 2H, NH), 11.58 (s, 2H, NH), 11.46 (s, 2H, Ar-OH), 10.89 (s, 2H, Ar-OH), 8.83 (s, 2H, ArH), 7.95—8.01 (m, 4H, ArH), 7.39—7.49 (m, 6H, ArH), 6.96—7.02 (m, 6H, ArH); ^{13}C NMR (DMSO, 125.77 MHz) δ: 168.43, 167.05, 158.79, 153.74, 135.85, 134.35, 129.72, 129.59, 129.13, 128.88, 126.79, 124.12, 124.03, 119.37, 117.43, 116.77, 115.94, 115.05; IR (KBr) v: 3217 (s), 1608 (s), 1561 (m), 1481 (s), 1454 (w), 1353 (m), 1307 (m), 1238 (w), 1212 (w), 1158 (m), 785 (w), 753 (s) cm^{-1}; ESI-MS: $M-H^-$ peak at m/z 641.10. Anal. calcd for $C_{36}H_{26}N_4O_8$: C 67.29, H 4.08, N 8.72; found C 67.53, H 4.15, N 8.99.

Preparation of $[Cu_4(L)(Py)_4]$•1.5 DMF (1)

H_8L (0.0322 g, 0.05 mmol) and $Cu(OAc)_2$•H_2O (0.0306 g, 0.15 mmol) were dissolved in 10 mL DMF, subsequently 0.5 mL pyridine was added. The mixture was stirred for 10 h at room temperature and then filtered. The filtrate was allowed to evaporate at room temperature, giving dark green block crystals of **1** suitable for single crystal X-ray diffraction after one month in 65% yield (based on Cu). IR data (KBr) v: 3430 (s), 1603 (s), 1583 (m), 1520 (s), 1449 (m), 1420 (m), 1366 (m), 1315 (s), 1257 (m), 1217 (m), 754 (s), 696 (s) cm^{-1}. Anal. calcd for $C_{60.5}H_{48.5}Cu_4N_{9.5}O_{9.5}$ (%): C 55.26, H 3.72, N 10.12; found C 55.07, H 3.98, N 10.44.

X-ray crystallography

Suitable single crystal of complex **1** was selected and mounted onto thin glass fibers, and the measurement was performed at 185(2) K using a Bruker CCDArea Detector with graphite-monochromated Mo-Kα radiation ($\lambda=0.71073$ Å). The structure was solved by direct methods using the SHELXS-97 program package and refined against F^2 by full-matrix least-squares methods with SHELXL-97[32,33] with anisotropic thermal parameters for all the non-hydrogen atoms except the disorder guest DMF. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms, except those bound to the disorder DMF. The crystallographic data are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Table 1 Crystal data and structure refinement parameters for complex **1**

Formula	$C_{121}H_{97}Cu_8N_{19}O_{19}$
Formula weight	2629.50
Temperature/K	185(2)
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	30.893(3)
b/Å	14.3503(12)
c/Å	25.076(2)
α/(°)	90
β/(°)	101.855(2)
γ/(°)	90
Z	4
V/Å^3	10879.7(16)
Density/(g•cm^{-3})	1.605
μ/mm^{-1}	1.613
F(000)	5360
Reflections collected	31868
Independent reflections	9524
R_{int}	0.0736
GOF on F^2	0.968
R_1, wR_2 ($I>2\sigma(I)$)	0.0539/0.1243
R_1, wR_2 (all data)	0.1123/0.1414

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**[a]

Cu(1)—O(1)	1.873(3)	Cu(2)—N(8)	1.977(4)	Cu(3)—O(4)	1.895(3)
Cu(1)—N(1)	1.869(4)	Cu(2)—O(6)	1.986(3)	Cu(3)—N(3)	1.979(5)
Cu(1)—O(3)	1.955(3)	Cu(3)—N(2)	1.872(4)	Cu(4)—N(5)	1.870(4)
Cu(1)—N(4)	1.983(4)	Cu(3)—O(2)	1.984(3)	Cu(4)—O(7)	1.952(4)
Cu(2)—N(6)	1.892(4)	Cu(3)—O(8A)	2.776	Cu(4)—N(7)	1.982(4)
Cu(2)—O(8)	1.913(4)	Cu(3B)—O(8)	2.776	Cu(4)—O(5)	1.865(4)
O(1)-Cu(1)-N(1)	92.24(15)	N(6)-Cu(2)-N(8)	175.93(19)	N(5)-Cu(4)-N(7)	170.44(18)
O(1)-Cu(1)-O(3)	172.15(14)	O(8)-Cu(2)-N(8)	92.33(18)	O(7)-Cu(4)-N(7)	94.58(17)
N(1)-Cu(1)-O(3)	82.17(15)	N(6)-Cu(2)-O(6)	81.19(16)	O(5)-Cu(4)-N(7)	92.14(17)
O(1)-Cu(1)-N(4)	92.38(15)	O(8)-Cu(2)-O(6)	172.87(15)	N(2)-Cu(3)-O(2)	81.24(15)
N(1)-Cu(1)-N(4)	168.00(16)	O(4)-Cu(3)-N(3)	92.75(17)	O(4)-Cu(3)-O(2)	170.66(15)
O(3)-Cu(1)-N(4)	94.18(15)	N(2)-Cu(3)-O(4)	91.52(16)	O(5)-Cu(4)-N(5)	92.25(16)
N(6)-Cu(2)-O(8)	91.68(17)	N(2)-Cu(3)-N(3)	174.64(17)	O(5)-Cu(4)-O(7)	171.66(15)
N(8)-Cu(2)-O(6)	94.80(17)	N(3)-Cu(3)-O(2)	94.17(16)	N(5)-Cu(4)-O(7)	81.85(16)

[a] Symmetry codes: A) $0.5-x$, $-0.5+y$, $0.5-z$; B) $0.5-x$, $0.5+y$, $0.5-z$; C) $-x, y$, $-z+0.5$.

Results and Discussion

The ligand *N,N'*-(BINOL-3,3'-dicarboxyl)disalicylhydrazide (H_8L) was synthesized by the acylation of racemic BINOL-3,3'-diacid and salicylhydrazide. The ligand contains twelve potential coordinating sites from two salicylhydrazide moieties and two phenol of the BINOL group, and might coordinate in a octa-anionic dodecadentate mode to metal ions. Indeed, the complex **1** was readily obtained in good yield by the reaction of H_8L with the $Cu(OAc)_2{\bullet}H_2O$ in a 1∶3 molar ratio under basic condition at room temperature. As depicted in Figure 1, the ligand uses all of its twelve coordinating atoms to coordinate with four copper ions in a μ_4-η^3∶η^3∶η^3∶η^3 mode. The same product was obtained when $Cu(ClO_4)_2{\bullet}6H_2O$ or $CuCl_2{\bullet}2H_2O$ were used instead of $Cu(OAc)_2{\bullet}H_2O$.

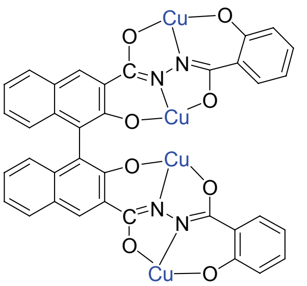

Figure 1 The coordination mode of H_8L ligand in **1**.

Structure description

The asymmetric unit of **1** contains three four-coordinated [Cu(1), Cu(2), Cu(4)] and one five-coordinated [Cu(3)] copper ions, one ligand, four coordinated pyridine molecules and one point five DMF solvent molecules as shown in Figure 2. Cu(1) and Cu(4) show similar binding mode, bound to one $O_{benzyl\text{-}acylamide}$ atom [O(3)/O(7)], one $N_{BINOL\text{-}acylamide}$ atom [N(1)/N(5)] and one $O_{BINOL\text{-}phenolic}$ atom [O(1)/O(5)] from one ligand and one nitrogen atom [N(4)/N(7)] of a pyridine molecule to form a slightly distorted square planar coordination polyhedron. Similarly, Cu(2) binds to one $N_{benzyl\text{-}acylamide}$ atom [N(6)], one $O_{BINOL\text{-}acylamide}$ atom [O(6)] and one $O_{phenolic}$ atom [O(8)] from one ligand and one nitrogen atom [N(8)] of a pyridine molecule to form a slightly distorted square planar coordination polyhedron. Cu(3) possesses a standard square pyramid geometry with one $N_{benzyl\text{-}acylamide}$ atom [N(2)], one $O_{BINOL\text{-}acylamide}$ atom [O(2)] and one $O_{phenolic}$ atom [O(4)] from one ligand and one nitrogen atom [N(3)] of a pyridine molecule in the equatorial plane, and one $O_{phenolic}$ atom [O(8A)] from the ligand of another tetranuclear unit at the apical position. The geometrical parameter τ is 0.066, $\tau=(\alpha-\beta)/60°$, in which β and α are the bond angles that involve *trans* donor atoms in the basal plane.[34] The length of the weak coordination bond Cu(3)—O(8A) is 2.776 Å, which is consistent with the reported copper(II) complexes.[35] Connected by the weak coordination of phenolic oxygen atoms [O(8) and O(8A)] with copper ions [Cu(3) and Cu(3A)], the tetranuclear unit forms one-dimensional helical chain along *b* direction as shown in Figure 3. Each helix contains two $[Cu_4(L)(Py)_4]$ motifs with a pitch of 14.35 Å. The heli-

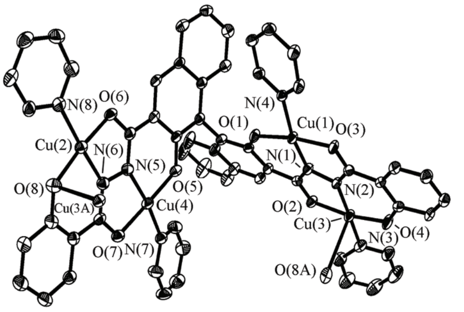

Figure 2 The ORTEP drawing of **1** with thermal ellipsoids set to 30% probability level. All H atoms and the DMF molecules are omitted for clarity.

cal chains are packed in an alternating left-(M) and right-handed (P) chirality in the overall structure (Figure 4). Interestingly, the right helical chain is composed of only S_a enantiomers and the left helical chain is composed of only R_a enantiomers, which demonstrate the orientation of the helices was determined by the axial chirality of the ligand. The aromatic rings are not stacked, van der Waals force contributes to the stabilization of the helical structure.

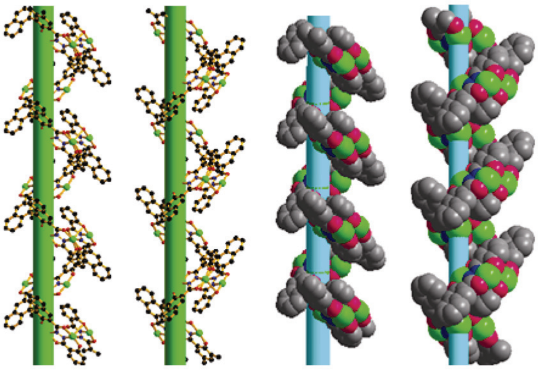

Figure 3 One dimensional helical chain viewed along the *b* direction, all H atoms and pyridine are omitted for clarity.

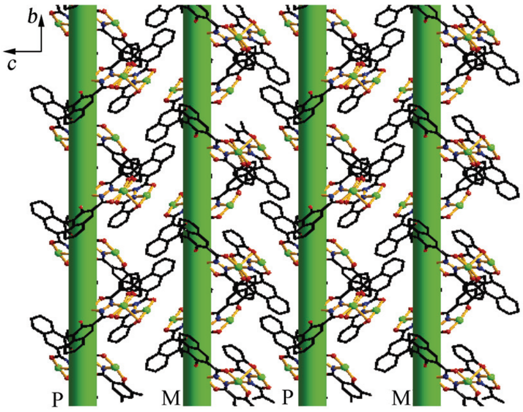

Figure 4 Alternately left-(M) and right-handed (P) helix array of **1** in *bc* plane.

Thermogravimetric analysis and PXRD

The thermogravimetric analysis (TGA) was carried out to examine the thermal stability of **1**. The TG curves for **1** show its decomposition in two stages (Figure S1). The first weight loss of 19.65% in the temperature range of 30—197 ℃ corresponds to the loss of guest DMF and two coordinated pyridine molecules (calcd 20.36%). Further heating leads to the final collapse of the tetranuclear skeleton by the decomposition of the ligand. In addition, the PXRD experiment is done in parallel beam mode, which is consistent with the simulated spectrum (Figure S2).

Magnetic properties

Magnetic susceptibility measurements were performed on microcrystalline samples of the compound at 0.1 T field in the temperature range 2—300 K. The value of product $\chi_m T$ is 1.64 $cm^3 \cdot K \cdot mol^{-1}$ at 300 K (Figure 5), which is slightly larger than the expected value of 1.50 $cm^3 \cdot K \cdot mol^{-1}$ for four noninteracting $S = 1/2$ Cu^{II} centers with a g value of 2.[36] Upon cooling, the $\chi_m T$ value decreases continuously, reaching a value of 0.0068 $cm^3 \cdot K \cdot mol^{-1}$ at 2.0 K, indicating the presence of an antiferromagnetic coupling.[37,38] The shape of the $\chi_m T$ vs. T plot indicates an overall, moderate antiferromagnetic coupling between the metal centers. The Curie tail in the low temperature susceptibility data reveals the presence of trace amount of paramagnetic impurities. The antiferromagnetic nature of complex is further supported by M vs. H plot at 2 K. The magnetization is 3.626 μ_B per Cu_4 formula unit at 5 T, which is smaller than the saturated value of four Cu(II) ions (the inset of Figure 5). Furthermore, the best linear fit according to the Curie-Weiss law $\chi_m = C/(T-\theta)$ in the temperature range of 120—300 K yields Curie constant of 2.957 $cm^3 \cdot K \cdot mol^{-1}$ and a Weiss constant of -232.485 K (Figure S3), which suggestes the presence of antiferromagnetic coupling in **1**. The magnetic interactions between the adjacent two dinuclear copper(II) centers in the Cu_4 formula unit are presumed to be very weak because the bridging binaphyl group can not transmit magnetic exchange effectively. Therefore, the temperature-variable magnetic susceptibility data can be described by the modified Bleaney-Bowers equation (1) for a dinuclear Cu^{II} ($S_1 = S_2 = 1/2$) system.[39,40]

$$\chi_m = [N_A \mu^2 g^2 / 3K_B(T-\theta)][1 + 1/3 \times \exp(-2J/K_B T)]^{-1} \times (1-\rho) + N_A \mu^2 g^2 / 4K_B T + N_a \quad (1)$$

where N_A is the Avogadro constant, μ the Bohr magneton, K_B the Boltzmann constant, g the g factor, and J the coupling constant. N_A and g have been fixed as 110×10^{-6} $cm^3 \cdot mol^{-1}$ and 2.20, respectively. The best data fits (solid red lines) with Eq. (1) for the complex **1** was shown in Figure 5. The calculated values are $2J = -122$ cm^{-1}, $g = 2.01$, $\theta = -3$ K, and $\rho = 0.015$, which show that there are antiferromagnetic interactions between the copper metal ions in the complex.[41]

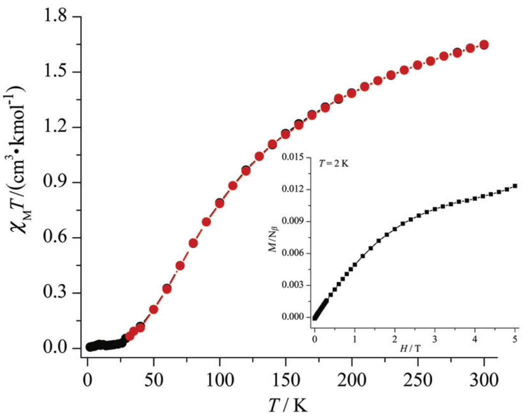

Figure 5 Temperature dependence of the magnetic susceptibility of **1** measured at 1000 Oe. The solid lines represent the theoretical fits (see text). Inset: the field dependence of the magnetization at 2 K.

Conclusions

In summary, the first ligand by introducing the *N*-acyl-salicylhydrazide multiple functional group in the binaphthyl scaffold, *N*,*N'*-(BINOL-3,3'-dicarboxyl)-disalicylhydrazide (H_8L), was synthesized. Reaction of the ligand with $Cu(OAc)_2•H_2O$ under conventional condition afforded a copper coordination polymer with tetranuclear copper(II) units $[Cu_4(L)(py)_4]$ as secondary building blocks. The connection of the tetranuclear units by weak coordination-driven self-assembly formed interesting helical chain, which are composed of only R_a or only S_a enantiomers in each case, namely the orientation of the helices was determined by the axial chirality of the ligand. The complex shows antiferromagnetic coupling interaction among the copper centers.

Supplementary material

TG curve, PXRD plot, $1/\chi_m$ vs. T plot and all spectra of new compounds (Figure S1—S7) are in the supporting information. CCDC-855713 contains the supplementary crystallographic data for complex **1**. The data can be obtained free of charge via the Internet at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12Union Road, Cambridge CB21EZ, UK. Email: deposit@ccdc.cam.ac.uk.

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