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Structural diversity of Cu(II) compounds of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and a series of aminobenzoic acid

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ABSTRACT

Five novel Cu(II) metal–organic coordination polymers, $[(CuL^1)_n]$ (**1**), $[Cu_2L^2_2(Py)_4]$ (**2**), $[Cu(HL^3)(DMF)_2]$ (**3**), $[Cu_6L^3_4(Py)_6 \cdot H_2O]_n$ (**4**), $[Cu_6L^3_4(Py)_8(C_{10}H_8N_2)_2 \cdot 8CH_3OH]_n$ (**5**) (H_2L^1 = N-2-hydroxy-naphthaldehyde-1-alkenyl-*o*-amino acid, H_2L^2 = N-2-hydroxy-naphthaldehyde-1-alkenyl-*m*-amino acid, H_2L^3 = N-2-hydroxy-naphthaldehyde-1-alkenyl-*o*-amino-terephthalic acid), have been synthesized and characterized by IR, elemental analysis, UV spectroscopy and single-crystal X-ray diffraction analyses. Complex **1** possesses helical chain structure, which are further assembled to form three-dimensional frameworks by $\pi\cdots\pi$ stacking interactions. Complex **2** and **3** exhibit dimeric and monomeric structure. Complex **4** is a novel two-dimensional layer structure based on two kinds of binuclear Secondary Building Units (SBUs), Cu_2O_2 and $Cu_2(CO_2)_4$. Complex **5** exhibits a distorted zigzag chain by the alternate connectivity of L and bpy molecules. This result shows that the position of carboxylate groups play an important role in the formation of supramolecular networks.

1. Introduction

Supramolecular coordination assemblies attract much interest in recent years, not only due to the potential applications in the areas including gas storage, molecular sieves, ion-exchange, catalysis, magnetism and optoelectronics, but their intriguing variety of architectures and topologies, such as molecular grids, bricks, herringbones, ladders, rings, boxes, diamondoids, honeycombs [1–4]. Exploring multi-topic ligands and suitable metal salts are important to the construction of these architectures. Schiff bases, one kind of the most widely used organic ligands, have been used as pigments and dyes, catalysts, intermediates in organic synthesis and polymer stabilizers. Coordination chemistry of these ligands is also interesting through the selection of suitable amine and aldehyde substituents with different steric and electronic functional groups, which may bring about subtle structural and functional variations. [5,6].

We are interested in the introduction of carboxylate groups into the Schiff bases. Up to now, a few Schiff base ligands with carboxylate groups have been reported [7,8], of which only one compound based on naphthaldehyde ligand was obtained [8]. Three different Schiff bases derived from the 2-hydroxy-1-naphthaldehyde and *o*-, *m*- and *o*-amino-terephthalic acid have been synthesized: H_2L^1 = N-2-hydroxy-naphthaldehyde-1-alkenyl-*o*-amino acid, H_2L^2 = N-2-hydroxy-naphthaldehyde-1-alkenyl-*m*-amino acid, H_2L^3 = N-2-hydroxy-naphthaldehyde-1-alkenyl-*o*-amino-terephthalic acid). Based on them, five novel Cu(II) coordination polymers, $[(CuL^1)_n]$ (**1**), $[Cu_2L^2_2(Py)_4]$ (**2**), $[Cu(HL^3)(DMF)_2]$ (**3**), $[Cu_6L^3_4(Py)_6 \cdot H_2O]_n$ (**4**), $[Cu_6L^3_4(Py)_8(C_{10}H_8N_2)_2 \cdot 8CH_3OH]_n$ (**5**), have been synthesized and characterized by IR, elemental analysis, UV spectroscopy and single-crystal X-ray diffraction analyses. Complex **1** possesses helical chain structure, which are further assembled to form three-dimensional frameworks by $\pi\cdots\pi$ stacking interactions. Complex **2** and **3** exhibit dimeric and monomeric structure, respectively. Complex **4** is a novel two-dimensional layer structure based on two kinds of binuclear SBUs (Secondary Building Units), Cu_2O_2 and $Cu_2(CO_2)_4$. Complex **5** exhibits a distorted zigzag chain by the alternate connectivity of Schiff base ligand and 4,4′-bipyridine molecules. This result shows that the positions of carboxylate groups play an important role in the formation of supramolecular networks.

2. Experimental

2.1. Material and measurements

All reagents and solvents are commercially available and used without further purification. The ligands were synthesized according to the literature [9]. Infrared spectra were recorded in the range 400–4000 cm^{-1} from KBr pellets on a Nicolet-5700 FT-IR spectrophotometer. Elemental analysis is (C, H and N) was carried out with a Perkin–Elmer 2400 II elemental analyzer. UV–visible spectral was performed on HP-8453 UV–visible spectrophotometer at

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room temperature. ^{1}H NMR spectra were obtained on a Varian Mercury Plus 400 MHz NMR spectrometer.

2.2. Synthesis of Schiff bases

An ethyl alcohol solution of 2-hydroxy-1-naphthaldehyde (10 mmol) was added to 10 mL of ethyl alcohol solution of sodium hydroxide and aminobenzoic acid (10 mmol). The mixed solution was refluxed under stirring for 4 h. The resulting precipitate was filtered and rinsed with ethyl alcohol and ethyl ether, and then dried in vacuum to give the ligands.

2.2.1. Synthesis of H_2L^1 (N-2-hydroxy-naphthaldehyde-1-alkenyl-o-amino acid)

Yellow crystals were obtained in the resulting ethyl alcohol solution over a period of two weeks. The crystals were collected by filtration rinsed and dried in vacuum. Yield: 57.6%. M.p. 277–278 °C. IR (KBr pellet: cm^{-1}): 3437(s, br), 3025(w), 2922(w), 1712(w), 1612 (vs), 1590(vs), 1543(m), 1484(w), 1457(w), 1366(vs), 1317(w), 1278(m), 1212(w), 1175(w), 1155(w), 760(m). Anal. Calc. (%) for $C_{18}H_{13}NO_3$ (Mw, 291.31): C 74.22, H 4.50, N 4.81. Found: C 74.32, H 4.58, N 4.56. ^{1}H NMR (DMSO-d_6, ppm): 15.12(s, 1H, —OH), 13.22(s, 1H, —COOH), 9.26(s, 1H, —CH=N), 6.78–8.25(m, 10H, 10-Ar—H).

2.2.2. Synthesis of H_2L^2 (N-2-hydroxy-naphthaldehyde-1-alkenyl-m-amino acid)

A yellow solid. Yield: 48.9%. M.p. 294–295 °C. IR (KBr pellet: cm^{-1}): 3438(s, br), 3056(w), 2921(w), 1698(m), 1619(vs), 1603 (m), 1589(w), 1545(m), 1495(w), 1460(w), 1352(s), 1314(w), 1292(m), 1218(w), 1167(w), 1142(w), 752(m), 739(w). Anal. Calc. (%) for $C_{18}H_{13}NO_3$(Mw, 291.31): C 74.22, H 4.50, N 4.81. Found: C 74.35, H 4.62, N 4.72. ^{1}H NMR (DMSO-d_6, ppm): 15.55(s, 1H, —OH), 12.94(s, 1H, —COOH), 9.65(s, 1H, —CH=N), 7.03–8.42(m, 10H, 10-Ar—H).

2.2.3. Synthesis of H_2L^3 (N-2-hydroxy-naphthaldehyde-1-alkenyl-o-amino-terephthalic acid)

A yellow solid. Yield: 62.5%. M.p. 317–318 °C. IR (KBr pellet: cm^{-1}): 3438(s, br), 3054(w), 2923(w), 1717(w), 1623(vs), 1605 (vs), 1546(m), 1493(w), 1428(w), 1361(m), 1312(w), 1275(w), 1215(w), 1163(w), 1141(w), 760(m), 746(m). Anal. Calc. (%) for $C_{19}H_{13}NO_5$ (Mw, 335.32): C 68.06, H 3.91, N 4.18. Found: C 68.13, H 4.02, N 4.12. ^{1}H NMR (DMSO-d_6, ppm): 14.99(s, 1H, —OH), 13.38(s, br, 2H, 2-COOH), 9.34(s, 1H, —CH=N), 6.86–8.28(m, 9H, 9-Ar—H).

2.3. Synthesis of the complexes

2.3.1. Synthesis of $[(CuL^1)_n]$ (**1**)

In a general synthesis procedure, an amount of $Cu(OAc)_2{\cdot}H_2O$ (0.1997 g, 1 mmol) was added to a stirred solution of DMF (10 mL) containing H_2L^1 (0.2913 g, 1 mmol). The mixed dark green solution was refluxed under stirring for 4 h. Green precipitates were filtered and dissolved in a mixture of DMF and pyridine. Dark green crystals were obtained over a period of two months through the diffusion of ethyl ether. Yield: 57.2%. IR (KBr pellet: cm^{-1}): 3438(s, br), 3062(w), 1620(m), 1598(m), 1588(w), 1574(m), 1536(s), 1487(m), 1382(s),

Table 1
Crystal data and structure refinement information for **1–5**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{36}H_{22}N_2O_6Cu$	$C_{56}H_{42}N_6O_6Cu_2$	$C_{25}H_{25}N_3O_7Cu$
Formula weight	705.64	1022.04	543.02
Space group	$P2_12_12_1$	P-1	P-1
a (Å)	7.255(2)	6.6850(17)	9.7672(15)
b (Å)	12.166(4)	10.3390(18)	11.0212(16)
c (Å)	16.001(5)	14.649(2)	11.6341(17)
α (°)	90.00	72.396(2)	85.126(2)
β (°)	90.00	86.436(3)	71.383(2)
γ (°)	90.00	74.180(2)	87.338(3)
V (Å^3)	1412.4(8)	1206.0(4)	1182.3(3)
Z	2	1	2
$D_{calcd.}$ (g cm^{-3})	1.659	1.407	1.525
μ (mm^{-1})	1.561	0.941	0.976
θ range	2.8–27.4	2.1–25.0	2.2–24.4
Index ranges	$-8 \leqslant h \leqslant 8$; $-14 \leqslant k \leqslant 13$; $-17 \leqslant l \leqslant 19$	$-10 \leqslant h \leqslant 10$; $12 \leqslant k \leqslant 11$; $-13 \leqslant l \leqslant 17$	$-11 \leqslant h \leqslant 10$; $-12 \leqslant k \leqslant 13$; $-13 \leqslant l \leqslant 7$
$R1$, w$R2$[a] [$I > 2\sigma(I)$]	0.0378; 0.0932	0.0925; 0.2058	0.0444; 0.1011
GOF	1.000	1.000	1.001
Complex	**4**	**5**	
Empirical formula	$C_{107}H_{76}N_{10}O_{22}Cu_6$	$C_{72}H_{64}N_8O_{14}Cu_3$	
Formula weight	2235.02	1455.93	
Space group	P-1	C 2/c	
a (Å)	13.3797(13)	26.558(3)	
b (Å)	14.0893(15)	16.5646(18)	
c (Å)	14.7212(16)	15.0372(12)	
α (°)	99.4020(10)	90.00	
β (°)	100.2600(10)	106.236(2)	
γ (°)	90.00	90.00	
V (Å^3)	2477.4(4)	6351.5(10)	
Z	1	4	
$D_{calcd.}$ (g cm^{-3})	1.498	1.523	
μ (mm^{-1})	1.343	1.072	
θ range	2.4–26.8	2.6–25.4	
Index ranges	$-14 \leqslant h \leqslant 15$; $-16 \leqslant k \leqslant 8$; $-17 \leqslant l \leqslant 17$	$-31 \leqslant h \leqslant 27$; $-16 \leqslant k \leqslant 19$; $-16 \leqslant l \leqslant 17$	
$R1$, w$R2$[a] [$I > 2\sigma(I)$]	0.0505; 0.1544	0.0648; 0.1663	
GOF	1.000	1.000	

[a] $R1 = \sum||F_o| - |F_c||/|F_o|$. w$R2 = [\sum w(\sum_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.