Chinese Chemical Letters Vol. 16, No. 9, pp 1255-1258, 2005 1255
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One-dimensional Copper(II) Complex Constructed with Nitrate Counter-anion as Bitopic Connector

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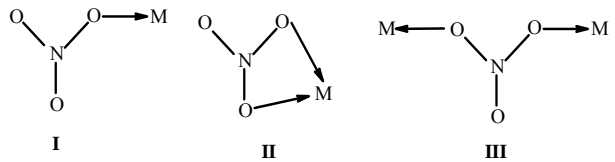
Abstract: Coordination polymer $\{[Cu(NPPCA)_3(NO_3)(H_2O)]\cdot NO_3\cdot H_2O\}_n$ **1** (NPPCA = N-(4′-nitrophenyl)-4-pyridinecarboxamide) has been synthesized by the reaction of NPPCA with copper(II) nitrate in ethanol–water solution and characterized by X-ray diffraction. **1** crystallizes in the monoclinic space, group $P2_1/n$, a = 17.341(6) Å, b = 6.744(2) Å, c = 34.555(12) Å, β = 100.493(6)°, V = 3974(2) Å^3, Z = 4. Each copper(II) ion has a distorted octahedral coordination geometry. Nitrate anion adopts the unusual coordination mode linking two adjacent copper(II) ions to form a one-dimensional coordination polymer and these chains are further linked by noncovalent interactions.

Keywords: Copper(II) complex, one-dimensional coordination polymer, bidentate nitrate, non-covalent interaction.

The design and synthesis of supramolecular structures has become an area of intense research in recent two decades. By carefully choosing the ions and ligands, frameworks with interesting and desirable properties can be created[1-2]. Essence of supramolecular chemistry is the self-assembly process of diversified interactions, such as metal-ligand coordination, hydrogen bonding, π-π stacking, *etc*. In contrast to the well-studied metal ions and ligands, there are relatively few examples about anionic function in the formation of supramolecular structure except a few reported anion-templated processes[3].

In some cases nitrate ions existed simply as counter-anions of the supramolecular network but in others as coordinated ligands. Nitrate ions as ligands show three coordination modes (**Scheme 1**).

Scheme 1



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Mode **I** (monodentate coordination) and **II** (bidentate coordination) are the most commonly observed coordination mode in which nitrate ions as blocking ligands that make appropriate coordination sites available for other ligands[4-6]. Herein we report the third mode (linking bidentate coordination) in **1**.

Amide-containing ligands have been used to generate some novel structures, some of them contain useful functions[7]. The crystals of ligand N-(4′-nitrophenyl)-4-pyridine-carboxamide (NPPCA) can form by utilizing several interactions. Compared to other analogs the nitro group will have additional hydrogen bonding interactions.

NPPCA was prepared by isonicotinoyl chloride hydrochloride, 4-nitroaniline and triethylamine in CH_2Cl_2 under low temperature according to literatural method[7b], yield 41%.

$\{[Cu(NPPCA)_3(NO_3)(H_2O)]\cdot NO_3\cdot H_2O\}_n$ **1** was synthesized by adding the solution of copper(II) nitrate hydrated (0.5 mmol) in H_2O (5 mL) into the solution of NPPCA (2 mmol) in ethanol (30 mL) slowly with stirring. After filtration, upon slow evaporation of the filtrate, blue plate-shaped crystals were obtained after several weeks. The crystals were filtered, washed with water and ethanol, dried in air, yield 75%.

The single-crystal X-ray diffraction study revealed that the structure of **1** is constructed from six-coordinate copper sites with distorted octahedral geometry which are linked to a one-dimensional chain[8]. The coordination sphere of Cu(II) is defined by three pyridyl nitrogen from three NPPCA ligands, one aquo oxygen forming a basal plane with Cu-N bond lengths of [Cu(1)-N(1) 2.010(3), Cu(1)-N(4) 2.024(3), Cu(1)-N(7) 2.016(3) Å] and [Cu(1)-O(16) 1.974(2) Å]. Two nitrate oxygen atoms are in two axial positions with long Cu-O bond distances of 2.476(3) Å for Cu(1)-O(10) and 2.517(3) Å for Cu(1)-O(11), respectively, giving a 4+2 environment [9] (**Figure 1**). Three of these ligands and the copper ion form a 'T' shape building block, bidentate nitrates connect them into one-dimensional chains. Copper-copper separation is 6.744 Å. The coordinated water, nitrate ligands and solvent water molecules, uncoordinated nitrate ions participate in five hydrogen bonds with average O–H···O contacts of 2.77 Å and N–H···O 3.02 Å. Couples of chains are hold together by the hydrogen bonds to form a one-dimensional dimer that act as a new unit (**Figure 2**).

Figure 1 ORTEP drawings of coordination environment of Cu(II) with 50% probability (uncoordinated water molecules and nitrate anions are omitted for clarity)

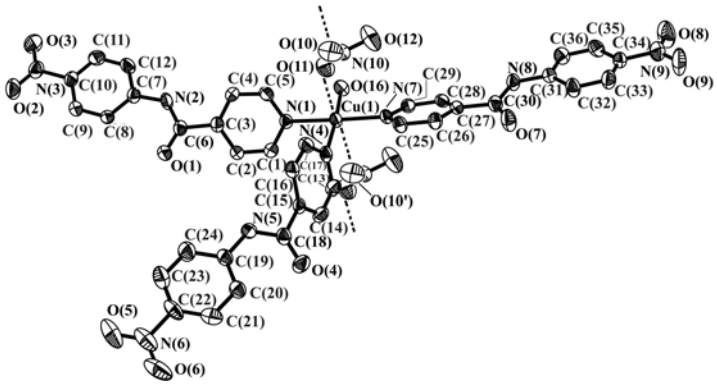


Figure 2 A dimer of chains with uncoordinated H_2O, NO_3^- showing inter-chain hydrogen-bonds

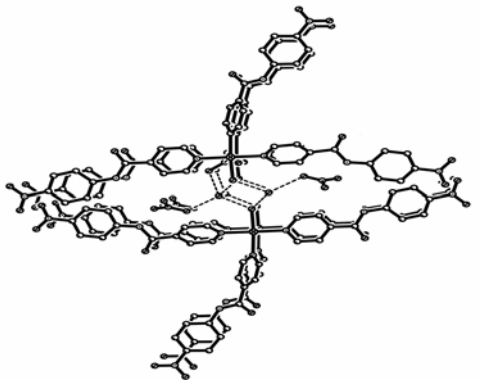
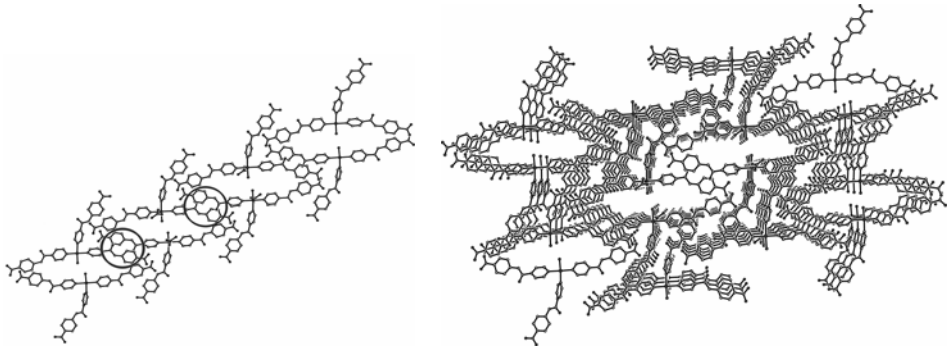


Figure 3 The formation of 3D supramolecular structure from 2D supramolecular structure



Left: the extended 2-D layer viewed from the *b*-axis (the interchain offset *π*-*π* interactions are indicated by a solid circle); right : 3-D structure with channels viewed along *b*-axis. Uncoordinated water molecules and nitrate anions are omitted for clarity.

There are offset π-π interactions involving benzamide groups between the chains with average inter-ring contacts of 3.64 Å. Therefore, adjacent dimers further connected by π-π stacking interactions which extend in *ac* plane to form a two-dimensional layer. These 2-D layers are linked into a 3-D network through hydrogen bands (**Figure 3**). Oxygen atoms of nitro group form hydrogen bonding with N-H group from adjacent layer [N(5)···O(3) (symmetry code: -x+1,-y+1,-z+1) 2.228 Å, N(5)-H(5A)···O(3) 149.7 °]. Stacked layers leave small channels, in which anions and water molecules are trapped.

Thermal gravimetric experiments showed that all H_2O can be removed, when **1** was heated, a gradual loss of 3.92 % of total weight between 95.7 ℃ and 117.3 ℃, corresponding to the loss of two water molecules per formula unit (expected 3.78 %). Above 117.3 ℃, no further weight loss up to 230.5 ℃ at which temperature the compound decomposed.

The structure was confirmed by elemental analysis and IR spectroscopy[10].

Acknowledgment

This project is supported by the Natural Science Foundation of Education Bureau of Liaoning Province, China.

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8. Crystal data for **1**: monoclinic, space group $P2_1/n$, with a=17.341 (6) Å, b=6.744 (2) Å, c=34.555 (12) Å, B=100.493 (6)°, V=3974 (3) Å^3, Z=4, D_c=1.593 g/cm^3, R1=0.0534, wR2= 0.1179 [I>2σ(I)]. Other crystallographic parameters have been deposited in the editorial office of CCL.
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10. NPPCA: Anal. Calcd. for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.63; H, 3.76; N, 16.93. IR (KBr, cm $^{-1}$): 3467s, 1667m, 1620m, 1600m, 1409m, 1335m, 849m, 760m; **1**: Anal.Calcd. for $C_{36}H_{31}Cu_1N_{11}O_{17}$: C, 45.36; H, 3.28; N, 16.16. Found: C, 45.59; H, 3.32; N, 15.78. IR (KBr, cm^{-1}): 3440s, 3347s, 1694m, 1620m, 1600m, 1557m, 1405m, 855m, 758m.

Received 8 November, 2004