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Metal-organic and supramolecular networks driven by 5-chloronicotinic acid: Hydrothermal self-assembly synthesis, structural diversity, luminescent and magnetic properties

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ABSTRACT

Four new crystalline solids, namely $[Co_2(\mu_2\text{-5-Clnic})_2(\mu_3\text{-5-Clnic})_2(\mu_2\text{-}H_2O)]_n$ (**1**), $[Co(5\text{-Clnic})_2(H_2O)_4]\cdot 2(5\text{-ClnicH})$ (**2**), $[Pb(\mu_2\text{-5-Clnic})_2(phen)]_n$ (**3**), and $[Cd(5\text{-Clnic})_2(phen)_2]\cdot 3H_2O$ (**4**) were generated by hydrothermal self-assembly methods from the corresponding metal(II) chlorides, 5-chloronicotinic acid (5-ClnicH) as a principal building block, and 1,10-phenanthroline (phen) as an ancillary ligand (optional). All the products **1**–**4** were characterized by IR spectroscopy, elemental analysis, thermogravimetric (TGA), powder X-ray diffraction (PXRD) and single-crystal X-ray diffraction. Their structures range from an intricate 3D metal-organic network **1** with the **3,6T7** topology to a ladder-like 1D coordination polymer **3** with the **2C1** topology, whereas compounds **2** and **4** are the discrete 0D monomers. The structures of **2** and **4** are further extended (0D→2D or 0D→3D) by hydrogen bonds, generating supramolecular networks with the **3,8L18** and **ins** topologies, respectively. Synthetic aspects, structural features, thermal stability, magnetic (for **1**) and luminescent (for **3** and **4**) properties were also investigated and discussed.

1. Introduction

In the past decades, a considerable attention was focused on the crystal engineering of metal-organic and supramolecular architectures, based on different carboxylic acid building blocks and assembled by covalent bonds and various non-covalent forces (strong and weak hydrogen bonds, π–π interactions, and halogen bonding) [1–15]. This research was primarily justified by a diversity of applications of the obtained compounds that span from gas sorption, magnetism, sensing and molecular recognition to photochemistry, catalysis, and medicinal chemistry [16–29].

The search for new or unexplored carboxylic acid building blocks toward the design of novel metal-organic and/or supramolecular network materials continues to be a particularly attractive research direction. Among a multitude of carboxylic acid ligands, spacers, or linkers that have already found a notable application in crystal engineering research, the use of some simple multifunctional *N*-heteroaromatic carboxylic acids has remained less explored. In particular, various derivatives of nicotinic acid (also known as niacin, vitamin B_3) represent an interesting but still little studied class of low-cost, water-soluble, bioactive, and versatile building blocks for the self-assembly generation of different metal-organic or supramolecular architectures with interesting structural and functional characteristics [30–35].

In pursuit of our recent interest in exploring various derivatives of nicotinic acid for the synthesis of metal-organic networks, low-dimensional coordination polymers, or discrete metal complexes [36–38], in the present work we focused our attention on 5-chloronicotinic acid (5-ClnicH) as a simple multifunctional building block for the generation of new coordination compounds. The selection of 5-ClnicH was governed by (i) an availability of pyridyl *N* and carboxylate *O* atoms for the coordination to a metal center, (ii) the presence of Cl-functionality that is capable of taking part in oxygen (or nitrogen)···Cl halogen bonding and related Cl···π and Cl···Cl interactions, (iii) its solubility and stability in water that allows to carry out aqueous-medium self-assembly syntheses, and (iv) an almost unexplored application of this carboxylic acid in coordination chemistry as attested by a search of the Cambridge Structural Database [38–41]. Hence, we report herein the hydrothermal self-assembly synthesis, full characterization, X-ray crystal structures, supramolecular and topological features, thermal stability and luminescent or magnetic properties of a new series of crystalline solids driven by 5-chloronicotinic

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acid (5-ClnicH) as a main building block and 1,10-phenanthroline (phen) as an optional ancillary ligand. The obtained products include a 3D network $[Co_2(\mu_2\text{-5-Clnic})_2(\mu_3\text{-5-Clnic})_2(\mu_2\text{-}H_2O)]_n$ (**1**), a 2D supramolecular network assembled from the $[Co(5\text{-Clnic})_2(H_2O)_4]\cdot 2(5\text{-ClnicH})$ (**2**) units, a 1D coordination polymer $[Pb(\mu_2\text{-5-Clnic})_2(phen)]_n$ (**3**), and a 3D supramolecular framework constructed from the $[Cd(5\text{-Clnic})_2(phen)_2]\cdot 3H_2O$ (**4**) blocks.

2. Experimental section

2.1. Materials and methods

All chemicals and solvents were of A.R. grade and used without further purification. Carbon, hydrogen, and nitrogen contents were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analyses (TGA) were performed under a N_2 atmosphere with a heating rate of 10 °C/min on a LINSEIS STA PT1600 thermal analyzer. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu-*K*α radiation ($\lambda = 1.54060$ Å), in which the X-ray tube was operated at 40 kV and 40 mA. Excitation and emission spectra were recorded for the solid samples on an Edinburgh FLS920 fluorescence spectrometer at room temperature. Magnetic susceptibility data were collected in the 2–300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis.

2.2. Synthesis of $[Co_2(\mu_2\text{-5-Clnic})_2(\mu_3\text{-5-Clnic})_2(\mu_2\text{-}H_2O)]_n$ (1)

A mixture of $CoCl_2\cdot 6H_2O$ (0.036 g, 0.15 mmol), 5-ClnicH (0.047 g, 0.3 mmol), NaOH (0.012 g, 0.3 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 $°C\,h^{-1}$. Pink needle-shaped crystals of **1** were isolated manually and washed with distilled water. Yield: 61% (based on Co salt). Anal. Calcd for $C_{24}H_{14}Cl_4Co_2N_4O_9$ (%): C 37.82, H 1.85, N 7.35. Found: C 37.98, H 1.83, N 7.29. IR (KBr, cm^{-1}): 1558s, 1522s, 1420w, 1398m, 1362s, 1262w, 1215w, 1148w, 1081w, 1040w, 910w, 863w, 837w, 821w, 764 w, 702m, 671w, 630w, 567w.

2.3. Synthesis of $[Co(5\text{-Clnic})_2(H_2O)_4]\cdot 2(5\text{-ClnicH})$ (2)

The preparation of **2** was similar to that of **1** except using a different amount of 5-ClnicH (0.094 g, 0.6 mmol). After being cooled to room temperature, pale yellow needle-shaped crystals were isolated manually and washed with distilled water. Yield: 65% (based on Co salt). Calcd for $C_{24}H_{22}Cl_4CoN_4O_{12}$ (%): C 37.97, H 2.92, N 7.38. Found: C 38.17, H 2.95, N 7.44. IR (KBr, cm^{-1}): 3494m, 3074m, 1719m, 1631s, 1589m, 1568w, 1429w, 1371s, 1325w, 1288m, 1180w, 1138w, 1112m, 1028w, 914w, 889w, 790w, 769w, 738w, 688m, 629w, 546w.

2.4. Synthesis of $[Pb(\mu_2\text{-5-Clnic})_2(phen)]_n$ (3)

A mixture of $PbCl_2$ (0.042 g, 0.15 mmol), 5-ClnicH (0.047 g, 0.3 mmol), phen (0.060 g, 0.30 mmol), NaOH (0.012 g, 0.3 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 $°C\,h^{-1}$. Colorless block-shaped crystals of **3** were isolated manually and washed with distilled water. Yield: 60% (based on Pb salt). Calcd for $C_{24}H_{14}Cl_2PbN_4O_4$ (%): C 41.15, H 2.01, N 8.00. Found: C 41.33, H 2.03, N 7.96. IR (KBr, cm^{-1}): 1589s, 1547m, 1513w, 1427w, 1375s, 1290w, 1187w, 1132w, 1093w, 1027w, 904w, 881w, 851w, 784m, 752m, 690w, 639w.

2.5. Synthesis of $[Cd(5\text{-Clnic})_2(phen)_2]\cdot 3H_2O$ (4)

The preparation of **4** was similar to that of **3** except using $CdCl_2\cdot H_2O$ instead of $PbCl_2$. After being cooled to room temperature, colorless block-shaped crystals were isolated manually and washed with distilled water. Yield: 55% (based on Cd salt). Anal. Calcd for $C_{36}H_{28}Cl_2CdN_6O_7$ (%): C 51.48, H 3.36, N 10.00. Found: C 51.27, H 3.41, N 9.93. IR (KBr, cm^{-1}): 3443w, 3054w, 1600s, 1552m, 1513m, 1426s, 1378s, 1344m, 1288m, 1220w, 1185w, 1141w, 1092m, 1050w, 1022m, 990w, 936w, 900w, 884w, 849s, 788m, 758s, 729s, 691m, 636w.

3. X-ray crystallography

The single-crystal data for compounds **1–4** were collected at 293(2) K on a Bruker APEX-II CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms (except for those bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations at the final stage of full-matrix least-squares refinement. The hydrogen atoms of the water molecules were located by difference maps and constrained to ride on their parent O atoms. All calculations were performed using the SHELXTL-97 system [42]. The details of the crystal parameters, data collections and refinement for **1–4** are summarized in Table 1 and selected bond lengths with the estimated standard deviations are listed in Table 2. Hydrogen bonds in crystal packing for the compounds **1–4** are listed in Table 3.

4. Results and discussion

4.1. Synthesis and characterization of compounds 1–4

Compounds **1** and **2** were synthesized by hydrothermal self-assembly reactions between cobalt(II) chloride and 5-chloronicotinic acid under the same reaction conditions (160 °C, 3 days, Scheme 1), but using different molar ratios of $CoCl_2\cdot 6H_2O$ and 5-ClnicH [i.e., 1:2 for **1** and 1:4 for **2**]. Compounds **3** and **4** were also generated in a similar manner, except using different metal chloride salts as a starting material (namely, $PbCl_2$ for **3** and $CdCl_2\cdot H_2O$ for **4**), as well as in the presence of 1,10-phenanthroline as an ancillary ligand. The selection of metal(II) (Co, Pb, and Cd) metal centers was governed by (i) a relatively easy crystallization behavior of the obtained products and their phase purity, (ii) a particular suitability of these metal ions for the hydrothermal self-assembly synthesis, (iii) a coordination diversity and versatility of these metal nodes [36–38,40], and (iv) interesting luminescent and/or magnetic properties of coordination polymers incorporating these metals [27,28,36–38,40]. The structural differences in the obtained products suggest that the assembly process is dependent on the molar ratio of a metal ion and a main building block, as well as on the type of metal ion and presence of an ancillary ligand. As a result, the obtained compounds vary from a 3D metal-organic network **1** and a 1D ladder-like coordination polymer **3** to distinct 0D compounds **2** and **4**. All the products were isolated as stable crystalline solids and were characterized by standard methods, namely by elemental analysis, IR spectroscopy, thermogravimetric analysis (TGA), single crystal and powder X-ray diffraction (PXRD)