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Synthesis and crystal structure of cadmium(II) coordination polymers with 3- and 4-pyridylacrylic acids

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ABSTRACT

Four new cadmium(II) coordination polymers, $[Cd_3(4\text{-Hpya})_4(SCN)_6(H_2O)_2]$ (**1**), $[Cd(4\text{-pya})(SCN)(H_2O)]\cdot H_2O$ (**2**), $[Cd(3\text{-Hpya})_2(SCN)_2]$ (**3**) and $[Cd(3\text{-pya})_2]$ (**4**), have been synthesized from appropriate Cd(II) salts and 4-pyridylacrylic acid (4-Hpya) or 3-pyridylacrylic acid (3-Hpya) in the presence of thiocyanate under similar hydrothermal conditions. The use of cadmium perchlorate as metal source leads to complexes (**1** and **3**) with 4-Hpya and 3-Hpya, while the use of cadmium acetate leads to complexes (**2** and **4**) with 4-pya^- and 3-pya^-. In **1** and **3**, the protonated ligands act as monodentate terminal ligands and lead to different 1D coordination chains with alternating *end-to-end* and *end-on-N* thiocyanate bridges (**1**) or with uniform *end-to-end* thiocyanate bridges (**3**). While 3-Hpya is in the normal carboxylic acid form in **3**, it is unusual and unprecedented that 4-Hpya in **1** takes the zwitterionic form with the proton attached to the pyridyl nitrogen. The proton in either compound plays an important role in assembling the chains into higher-dimensional networks via hydrogen bonds. On the other hand, the deprotonated ligands in **2** and **4** assume μ_2 and μ_3 multidentate bridging modes, respectively, and allow the formation of 2D layers with coexistent NCS^- and 4-pya^- bridges (**2**) or with only 3-pya^- bridges (**4**).

1. Introduction

The design and syntheses of multidimensional coordination polymers have been of increased interest recently in the fields of coordination chemistry and material science [1]. Based on the rich coordination chemistry of metal ions and organic ligands, a plethora of polymeric coordination networks with intriguing structures and properties have been achieved by way of crystal engineering [2] or serendipitous assembly [3]. The final structures of coordination polymers are dependent mainly upon the geometrical and electronic properties of the metal ions and the ligands, and also influenced by multiply synthetic factors, such as the counterions and the solvent systems [4]. The most extensively employed ligands are multidentate ligands with two or more neutral pyridyl groups (e.g., 4,4′-bipyridine, etc.) [5] or anionic carboxylate groups (e.g., benzenedicarboxylate, biphenyldicarboxylate) [6]. Mixed N- and O-donating ligands incorporating both pyridyl and carboxylate groups, such as 3- or 4-pyridylcarboxylic acid, 3- or 4-pyridylacrylic acid (3-Hpya, 4-Hpya), etc. [7], have also been explored. The interest in these bifunctional ligands has initially been evoked by the unsymmetrical bridging feature of the deprotonated ligands, which provides the possibility of designing extended solids with specific noncentrosymmetric topology and properties such as second order nonlinear optics (NLO) [8]. The unsymmetrical bridging modes are illustrated by 3-Hpya and 4-Hpya in Scheme 1, I–III. Another interesting feature of these ligands is that their carboxylic groups can form a dimeric motif through self-complementary hydrogen bonds, and thus the dimeric ligands can act as expanded bridges between metal ions (Scheme 1, IV). Taking advantage of this interesting feature, a series of two-dimensional (2D) open networks that can host different organic molecules have been synthesized by self-assembly in the presence of thiocyanate bridges. The studies have been focused on Ni(II)-SCN systems [9], and the self-assembly of these ligands with other metal ions in the presence of thiocyanate remains nearly unexplored [9]. Actually, thiocyanate is a highly versatile ambidentate ligand that can coordinate to metals through either nitrogen or sulfur, or both, and it has been used to synthesize a large number of coordination networks with interesting architectures and physical properties. The Cd(II)-SCN systems are of particular interest, because of the high adaptability of Cd(II) to both N- and S-bonding, as expected from the hard-soft acid-base concept [10,11].

With these considerations, we investigate the self-assembly of Cd(II) and 3- or 4-Hpya in the presence of thiocyanate. In this article, we report four Cd(II) coordination polymers synthesized from appropriate metal salts and 4-Hpya or 3-Hpya in the presence of thiocyanate ions: $[Cd_3(4\text{-Hpya})_4(SCN)_6(H_2O)_2]$ (**1**), $[Cd(4\text{-pya})(SCN)(H_2O)]\cdot H_2O$ (**2**), $[Cd(3\text{-Hpya})_2(SCN)_2]$ (**3**) and $[Cd(3\text{-pya})_2]$ (**4**).

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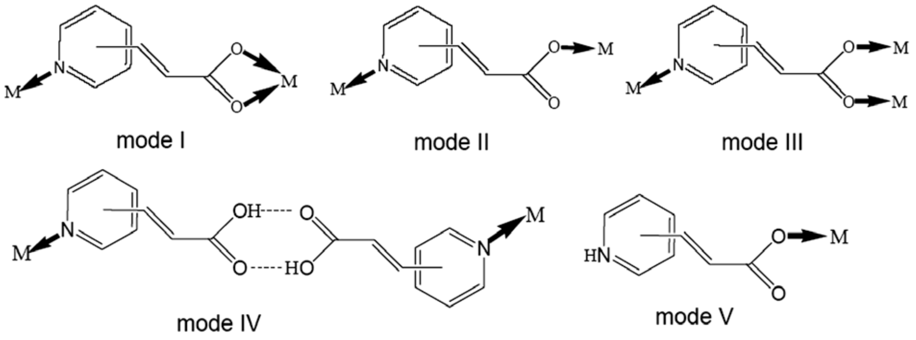

Scheme 1. The coordination modes of the 3-Hpya and 4-Hpya ligands.

2. Experimental

2.1. Materials and physical measurements

All the solvents and reagents for synthesis were commercially available and used as received. The ligands 4-pyridylacrylic acid and 3-pyridylacrylic acid were synthesized according to the literature methods [12]. Infrared spectra were recorded on a NEXUS 670 FT-IR spectrometer using the KBr pellets. Elemental analysis was carried out on an Elementar Vario El III elemental analyzer. X-ray powder diffraction (XRPD) measurements were performed on a Bruker D8 ADVANCE X-ray diffractometer.

2.2. Syntheses

2.2.1. [$Cd_3(4\text{-}Hpya)_4(SCN)_6(H_2O)_2$] (**1**)

A mixture of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.63 g, 1.5 mmol), 4-pyridylacrylic acid (0.15 g, 1 mmol) and NH_4SCN (0.23 g, 3 mmol) in water (3 mL) and ethanol (3 mL) was sealed in a Teflon-lined autoclave and heated at 110 °C. After 3 days of heating, the mixture was cooled slowly to room temperature, yielding colorless needle crystals in the 67% yield (based on 4-Hpya). IR (KBr pellet, cm^{-1}): 3360 (b), 3260 (b), 2117 (vs), 2000 (vs), 1669 (s), 1659 (s), 1631 (m), 1394 (s), 1216 (m), 959 (m), 831 (m), 731 (m). Anal. Calcd ($C_{38}H_{32}Cd_3N_{10}O_{10}S_6$,%): C, 34.62; N, 10.62; H, 2.45. Found (%): C, 34.35; N, 10.99; H, 2.75.

2.2.2. [$Cd(4\text{-}pya)(SCN)(H_2O)$]·$H_2O$ (**2**)

The reaction was carried out by a procedure similar to that for **1**, using $Cd(OAc)_2{\cdot}2H_2O$ (0.40 g, 1.5 mmol) instead of $Cd(ClO_4)_2{\cdot}6H_2O$. Colorless block crystals were obtained in the 55% yield (based on 4-Hpya). IR (KBr pellet, cm^{-1}): 3400 (b, s), 2117 (s), 2077 (s), 1645 (m), 1610 (s), 1537 (vs), 1411 (vs), 1240 (w), 1019 (w), 982 (m), 828 (m), 756 (m), 607 (m). Anal. Calcd ($C_9H_{10}CdN_2O_4S$,%): C, 30.34; N, 7.87; H, 2.84. Found (%): C, 30.59; N, 7.63; H, 3.22.

2.2.3. [$Cd(3\text{-}Hpya)_2(SCN)_2$] (**3**)

Colorless rod crystals of **3** were obtained by a method similar to that for **1**, using 3-Hpya. Yield, 52% (based on 3-Hpya). IR (KBr pellet, cm^{-1}): 3370 (b), 2100 (s), 1702 (s), 1636 (s), 1588 (m), 1415 (m), 1326 (s), 1292 (s), 1235 (m), 982 (w), 949 (m), 818 (w), 712 (m), 687 (m). Anal. Calcd ($C_{18}H_{14}CdN_4O_4S_2$%): C, 41.03; N, 10.63; H, 2.68. Found (%): C, 40.91; N, 10.60; H, 2.91.

2.2.4. [$Cd(3\text{-}pya)_2$] (**4**)

Colorless rod crystals of **4** were obtained by a method similar to that for **3**, using $Cd(OAc)_2{\cdot}2H_2O$ instead of $Cd(ClO_4)_2{\cdot}6H_2O$. Yield, 47% (based on 3-Hpya). IR (KBr pellet, cm^{-1}): 1645 (s), 1547 (vs), 1490 (m), 1433 (s), 1381 (vs), 1292 (m), 1269 (m), 1219 (m), 1031 (s), 949 (s), 891 (w), 818 (s), 720 (s), 646 (m). Anal. Calcd ($C_{16}H_{12}CdN_2O_4$,%): C, 47.02; N, 6.85; H, 2.96. Found (%): C, 46.63; N, 6.82; H, 3.16.

2.3. Crystal data collection and refinement

Diffraction intensity data were collected at 293 K on a Bruker APEX II diffractometer equipped with a CCD area detector and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the SADABS program [13]. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2, with all non-hydrogen atoms refined with anisotropic thermal parameters [14]. The hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. The hydrogen atoms attached to nitrogen (in **1**) and oxygen, except for the lattice water hydrogen atoms in **2**, were located from the difference maps. The lattice water molecule in **2** is disordered over two positions (O4 and O4′, the occupancies were refined to be 0.36 and 0.64, respectively), and we were unable to locate the hydrogen atoms. Crystallographic data are summarized in Table 1.

CCDC reference numbers 691386–691389 (**1**–**4**). See http://www.rsc.org/suppdata/ce/b4/bXXXX/ for crystallographic data in CIF or other electronic format.

3. Results and discussion

3.1. Synthesis

Compounds **1**–**4** were all prepared by the solvothermal reactions of appropriate ligands and cadmium(II) salts in the presence of NH_4SCN in aqueous ethanol (Scheme 2). For both 3- and 4-Hpya, the products are dependent upon the nature of the counterions of cadmium(II) salts, although the counterions are absent in the products. With cadmium perchlorate, the organic acids are not deprotonated and act as neutral ligands, while the use of cadmium acetate leads to deprotonation of the ligands. It is apparent that the weakly basic acetate ion is important in promoting the deprotonation. As will be shown below, the protonated ligands act as monodentate terminal ligands and lead to 1D chain coordination polymers with only thiocyanates as bridges (**1** and **3**), while the deprotonated ligands assume multidentate bridging modes and allow the formation of 2D coordination networks (**2** and **4**). Finally, the thiocyanate ion is absent in **4**, and we have found that the same compound can be obtained by the reaction of 3-Hpya and cadmium acetate in the absence of thiocyanates.

3.2. Infrared spectra and thermogravimetric analyses

The IR spectrum of **1** exhibits two strong bands at 2120 and 2000 cm^{-1}, which are associated with the ν(CN) stretching modes,