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Reactions of $[Cd(SCN)_2]$ and Isonicotinonitrile, Synthesis and X-ray Characterization of 1- and 3D Coordination Polymers, $[Cd(SCN)_2(pyCN)_n]$ (pyCN = isonicotinonitrile, n = 1, 2)

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Two adducts of $[Cd(SCN)_2]$ and isonicotinonitrile, $[Cd(SCN)_2(pyCN)_n]$ (pyCN = isonicotinonitrile, n = 1, 2), have been synthesized and characterized by X-ray diffraction analysis. The coordination environment of the cadmium atoms in both **1** and **2** is a distorted octahedron with a 2*S*4*N* coordination geometry. Compound **1** crystallizes via the SCN^- functionality, resulting in infinite linear chains. Compound **2** crystallizes via both SCN^- and isonicotinonitrile functionality, thus forming an infinite 3D framework material based on 22- and 8-membered rings.

Construction of supramolecular compounds through coordination chemistry is currently of great interest in research, the use of transition metal centers and coordination chemistry for directing the formation of complex structures has evolved into one of the most widely used strategies for organizing molecular building blocks into supramolecular arrays.[1–3] Network solids assembled by coordination is of fundamental interest. The attractiveness lies in the synthesis of materials with new and potentially useful properties such as magnetic, optical or mechanical properties.

A number of Lewis-base adducts of cadmium(II) thiocyanate, $[\{Cd(SCN)_2L_2\}_n]$ (where L = 2, 3, or 4-methylpyridine,[4] benzylamine,[5] dibenzylamine,[6,7] trialkylphosphine,[8] dmso,[9] hexamethylenetetramine,[10] thiosemicarbazide,[11] morpholine,[12] aniline,[13] imidazole[14] and *N*,*N*-dialkylethylenediamine[15]) have been reported. Most of the reported polymeric adducts exhibit infinite one-dimensional structures, with two SCN^- ions bridging the adjacent cadmium atoms. Few of them give two-dimensional (2D) planar structures,[15] none of them show three-dimensional (3D) networks among the known cadmiumthiocyanate adducts so far. Here in this paper we describe two new adducts of cadmiumthiocyanate and isonicotinonitrile, $[Cd(SCN)_2(pyCN)_2]$ (**1**), and $[Cd(SCN)_2(pyCN)]$ (**2**). Compound **1** is a common 1D coordination polymer, whereas **2** is a much more interesting 3D five-connected polymer, which is rare. Coordination polymer **2** represents the first example of 3D framework materials assembled by $[Cd(SCN)_2]$ and nitrogen ligands.

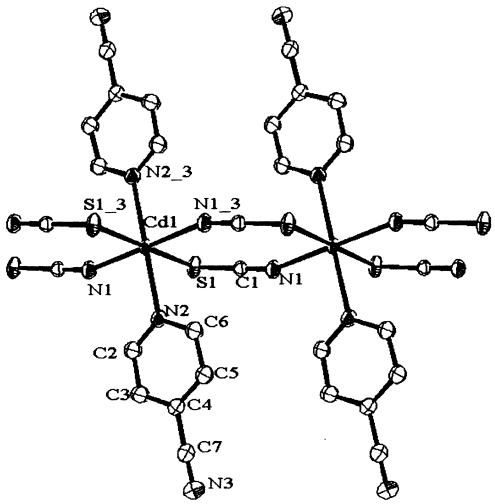

Fig. 1. ORTEP drawing of $[Cd(SCN)_2(pyCN)_2]$, (**1**) with atomic numbering scheme (ellipsoids at 50% probability).

The two compounds were prepared by mixing $[Cd(SCN)_2]$ and isonicotinonitrile in $EtOH/H_2O$. When one equivalent of isonicotinonitrile was employed, compound **1** and compound **2** were both formed, compound **2** being the major product. Compound **1** can be exclusively obtained by using 2 equivalents of isonicotinonitrile under similar conditions. The compositions of both **1** and **2** were determined by elemental analysis and confirmed further by X-ray diffraction analysis.

The structure of compound **1** with atom numbering schemes is shown in Fig. 1. The cadmium(II) atom is at the centre of symmetry, being 4*N*2*S* hexacoordinated in an octahedral geometry, as depicted in Fig. 1. Cadmium(II) atoms are bridged by two SCN^- ions, one of them is *S*-coordinate and the other one is *N*-coordinated to the same side of the metal atom, thus forming an infinite linear chain structure.

Each Cd atom is coordinated with two SCN^- sulfur atoms, two SCN^- nitrogen atoms, and two pyridyl nitrogen atoms, and each pair of the same donating atoms is in a *trans*-configuration. The cyano nitrogen atom of isonicotinonitrile remains uncoordinated. The Cd–S and Cd–N(NCS) bond distances are 2.7510(7) Å and 2.3005(19) Å, C–N–Cd and C–S–Cd angles are 159.51(18) and 96.93(8)° respectively. The Cd–N(pyridyl) separation is longer than that of Cd–N(NCS). These values are consistent with those of known thiocyanatocadmium complexes.[4–9] The S–C–N angles deviate slightly from, but are very close to, the ideal value of a linear configuration.

Unlike most of the $[Cd(SCN)_2L_2]$ complexes,[4–15] which show infinite zigzag chain alignment, the spatial arrangement of Cd···Cd in **1** exhibits a 1D infinite linear chain structure. As shown in Fig. 1, the linear chains consist of eight-membered rings of two cadmium atoms and two bridging SCN^- ligands. The infinite $[Cd(SCN)_2]$ chains are perfectly linear, with the Cd···Cd···Cd angle of 180°, and the Cd···Cd distance is 5.827(2) Å. The Cd···Cd distance matches other reported values in $[Cd(SCN)_2(mpy)_2]$ (mpy = 2-, 3-, and 4-methylpyridine).[4]

The structure of complex **2** is depicted in Fig. 2. Each cad-

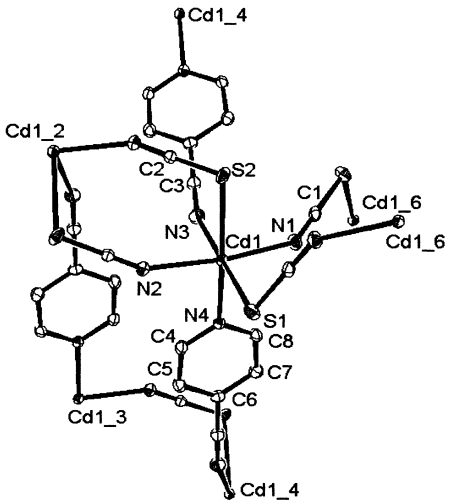

Fig. 2. 3D framework of **2** as viewed down the *b* axis. Hydrogen atoms are omitted for clarity.

mium(II) atom has a distorted octahedral coordination geometry, it links five adjacent cadmium atoms through SCN^- ions and isonicotinonitrile, in which one cadmium atom is doubly bridged by two SCN^- ions, and one pair of cadmium atoms is singly bridged by one SCN^- ion. And the other two cadmium atoms are bridged by isonicotinonitrile molecules. Thus a 3D framework is formed. The mean Cd–N and Cd–S bond distances are 2.319 Å and 2.6572 Å respectively; these bond lengths and angles are in the normal range. The adjacent Cd···Cd distances are 5.713 Å, 6.04 Å and 6.27 Å for $Cd(SCN)_2Cd$, Cd(SCN)Cd and $Cd(NCC_5H_4N)Cd$ respectively. Four cadmium atoms together with two isonicotinonitrile molecules, and two SCN^- ions form a 22-membered ring; two adjacent cadmium atoms (Cd1 and Cd1_2) and two SCN^- ions form eight-membered rings. These 22- and 8-membered rings held together and form the 3D networks.

In summary, we have successfully prepared two novel polymeric adducts of $[Cd(SCN)_2]$ and isonicotinonitrile by coordination-driven self-assembly. $[Cd(SCN)_2(pyCN)_2]$ exhibits a normal one-dimensional linear polymeric structure, whereas $[Cd(SCN)_2(pyCN)]$ gave a three-dimensional open-framework structure. The interesting open framework materials based on 22- and 8-membered mettallocyclic rings have been obtained. The characterization of the coordination polymer **2** illustrates that 3D networks can be obtained through the choice of suitable bidentate ligands. The size, shape of porous and channels may be tuned by adjusting the bridging ligands.

Experimental

Preparations of $[Cd(SCN)_2(pyCN)_2]$ (1). To a solution of $[Cd(SCN)_2]$ (1 mmol) in 10 mL of H_2O/EtOH (1:4) was added isonicotinonitrile (2 mmol). Upon standing colorless crystals were obtained. Yield: 87%. Anal. Calcd for $C_{14}H_8CdN_6S_2$%: C, 38.50; H, 1.85; N, 19.24%. Found: C, 38.22; H, 1.99; N, 18.96%.

Preparartion of $[Cd(SCN)_2(pyCN)]$ (2). $[Cd(SCN)_2]$ (1 mmol) was dissolved in 5 mL of H_2O/EtOH (1:4). A solution of isonicotinonitrile (1 mmol) in 3 mL of EtOH was added. Upon standing and cooling, colorless crystals were obtained. Yield: 42%. A small amount of **1** was also formed which was separated manually under microscope. Anal. Calcd for $C_8H_4CdN_4S_2$: C, 28.88; H, 1.21; N, 16.84%. Found: C, 28.45; H, 1.37; N, 16.45%.

Crystal Structure Determination. The single crystals of **1** and **2** were mounted on a glass fiber and placed on a Siemens SMART CCD diffractometer, equipped with graphite monochromatized Mo-$K\alpha$ radiation, λ = 0.71073 Å. The structures were solved by direct methods (SHELXS-97) and refined on all F^2 by the full-matrix least-squares using the procedure (SHELXL-97).[16] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at the calculated position. Crystallographic data: For **1**: $C_{14}H_8CdN_6S_2$, fw = 436.78, monoclinic, space group $P2_1/n$, a = 5.8271(10) Å, b = 17.886(3) Å, c = 8.6627(15) Å, β = 109.388(3)°, V = 851.7(3) Å^3, Z = 2, D_{calc} = 1.703 Mg/m^3, crystal size 0.11 × 0.11 × 0.42 mm, 5039 reflections collected, 1939 unique (R_{int} = 0.0379), Goodness-of-fit on F^2 = 1.040, $R1$ = 0.0298, $wR2$ = 0.0838 [$I > 2\sigma(I)$]. For **2**: $C_8H_4CdN_4S_2$, fw = 332.67, monoclinic, space group $C2/c$, a = 18.814(5) Å, b = 7.973(2) Å, c = 15.374(4) Å, β = 108.046(4)°, V = 2192.6(10) Å^3, Z = 8, D_{calc} = 2.016 Mg/m^3, crystal size 0.31 × 0.50 × 0.53 mm, 6198 reflections collected, 2470 unique (R_{int} = 0.0227), Goodness-of-fit on F^2 = 1.138, $R1$ = 0.0222, $wR2$ = 0.0601 [$I > 2\sigma(I)$].

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