A New Inclusion Compound Consisting of 2D Coordination Layers of $[Cd(SCN)_2]_\infty$ and Pillars of Isonicotinamide Dimers

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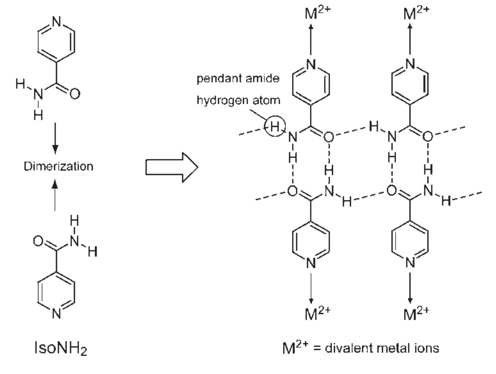
Self-assembly of Cd^{2+}, SCN^-, isonicotinamide (isoNH$_2$), and 9,10-dichloroanthracene gave a new inclusion compound formulated as $[Cd(SCN)_2(isoNH_2)_2]\cdot 1/2$(9,10-dichloroanthracene) (**1**). This inclusion compound consists of 2D coordination layers of $[Cd(SCN)_2]_\infty$ and pillars of isoNH$_2$ dimers. 9,10-dichloroanthracene molecules are included in zigzag channels.

Self-assembly of two soluble components with assistance of self-complementary hydrogen bonding is an efficient synthetic procedure for long building blocks. Its effectiveness has been substantiated by recent investigation reported by our group.[1] In that study, a long bidentate building block is constructed through carboxylic acid dimer formation of a pair of isonicotinic acid (isoH). Self-assembly of this isoH dimer with Ni^{2+} and SCN^- gives a 2D host layer formulated as $[Ni(SCN)_2(isoH)_2]_\infty$ (isoH system), which shows excellent inclusion ability for a variety of aromatic molecules.[2] In this study, we have employed isonicotinamide (isoNH$_2$) for a structural extension from the isoH system. As shown in Scheme 1, isoNH$_2$ can form head-to-head amide dimer through self-complementary pairwise N–H···O hydrogen bonding between amide functional groups.[3] This isoNH$_2$ dimer can serve as a bidentate building block with a linear structure similar to the isoH dimer.[4,5] We have envisaged that self-assembly of isoNH$_2$ with $M(SCN)_2$ (M = divalent metal ions with O_h coordination geometries[6]) gives new host systems. The presence of two amide hydrogen atoms of an isoNH$_2$ dimer that do not participate in the amide–amide dimer formation (pendant amide hydrogen atoms[5]) would affect overall crystal packing through N–H···O hydrogen bonding with adjacent dimers.[7]As a result, the crystal structures and inclusion properties of the new host systems would be distinct from those of the isoH system. Therefore, this structural extension is of considerable interest. We report herein the preparation and crystal structure of a new inclusion compound formulated as $[Cd(SCN)_2(isoNH_2)_2]\cdot 1/2$(9,10-dichloroanthracene) (**1**) synthesized based on the above concept.



Scheme 1.

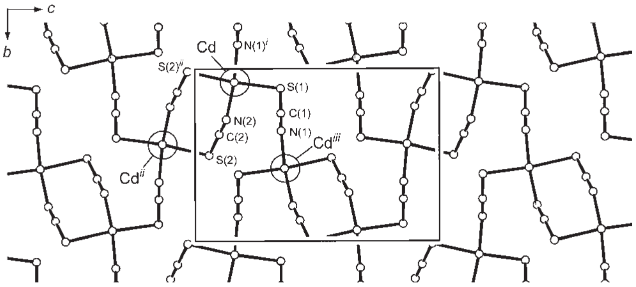


Figure 1. The framework of $[Cd(SCN)_2(isoNH_2)_2]_\infty$ 2D coordination layer. IsoNH$_2$ ligands and 9,10-dichloroanthracene guests are omitted for clarity. *i*, *ii*, and *iii* denote symmetry operations: *i* $(3/2 - x, -1/2 + y, 1/2 - z)$; *ii* $(3/2 - x, 1/2 - y, -z)$; *iii* $(3/2 - x, 1/2 + y, 1/2 - z)$.

In our preparative experiments using Ni^{2+} and Cd^{2+}, the latter afforded inclusion compound. Colorless crystals of **1** were obtained from a methanol solution containing Cd^{2+}, SCN^-, isoNH$_2$, and 9,10-dichloroanthracene after slow evaporation of the solvent at room temperature.[8]

X-ray structure determination of **1** revealed that it crystallized in the monoclinic crystal system with space group $C2/c$ (#15).[9] The crystal structure of **1** features a layered structure. Each layer (2D coordination layer) is composed of Cd^{2+} and SCN^- and spreads over the crystallographic *bc* plane. The framework of the layer is shown in Figure 1. The asymmetric unit contains one crystallographically independent Cd^{2+} ion with distorted octahedral coordination geometry and two crystallographically independent SCN^- ions. Four equatorial coordination sites of the Cd^{2+} ion are ligated by two nitrogen atoms of SCN^- ions and two sulfur atoms of SCN^- ions in trans configurations. Bond distances of Cd–N(1)^i, Cd–N(2), Cd–S(1) and Cd–S(2)^{ii} are 2.286(3), 2.304(3), 2.7081(9), and 2.7977(9) Å, respectively. All SCN^- ions adopt $\mu_{1,3}$ ambidentate coordination fashion. Cd and Cd^{iii} are connected by one SCN^- ion with a distance of 6.0507(3) Å, whereas Cd and Cd^{ii} are doubly connected by two SCN^- ions in anti parallel fashion with a distance of 5.8672(4) Å. Two isoNH$_2$ ligands are bonded to the remaining axial coordination sites of the Cd^{2+} ion via pyridyl nitrogen atoms with an average Cd–N distance of 2.355 Å.

Each isoNH$_2$ ligand forms head-to-head amide dimer with an isoNH$_2$ ligand of an adjacent layer through self-complementary pairwise N–H···O hydrogen bonding with an average N···O distance of 2.966 Å (Figure 2a), in accord with corresponding ones observed in other structures.[4,5,7] The resultant isoNH$_2$ dimers are significantly twisted with an dihedral angle of 41.8(1)° between the pyridine rings. The dimers serve as pillars and sustain the layered structure of **1**. An interlayer Cd···Cd

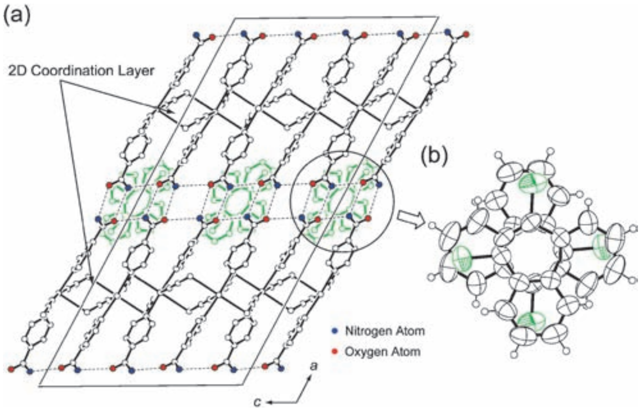


Figure 2. (a) Crystal structure of **1** viewed along the *b* axis. Hydrogen atoms are omitted for clarity. Broken lines show hydrogen bonds. (b) ORTEP diagram of 9,10-dichloroanthracene guest (50% probability level).

separation through an isoNH$_2$ dimer is 17.3631(8) Å.

As expected, the two pendant hydrogen atoms of each isoNH$_2$ dimer form two N–H···O hydrogen bonds with the amide oxygen atoms of adjacent isoNH$_2$ dimers with an average N···O distance of 2.926 Å to afford a hydrogen bond network extending along the *c* axis. Crystal structure viewed along the *a* axis is shown in Figure 3. IsoNH$_2$ dimers are arranged in zigzag fashion along the *c* axis to afford an isoNH$_2$ dimer wall.

Zigzag channels are formed between isoNH$_2$ dimer walls and are running along the *c* axis. In the channels, 9,10-dichloroanthracene guests are arranged in zigzag fashion (Figure 3). Interestingly, the 9,10-dichloroanthracene guests are in a structural disordered state (Figure 2b). The guest was found as an overlapped image of two molecules whose long molecular axes penetrating throughout the anthracene units of the 9,10-dichloroanthracene guests cross each other at almost right angles.

Guest accessible volume of the channel calculated by *PLATON* program[10] is 721.1 Å^3 per unit cell. In addition to this volume, the findings that the 9,10-dichloroanthracene molecules are included in the zigzag channels and are in the structural disordered state lead us to expect that other organic molecules whose sizes are similar to or smaller than that of 9,10-dichloroanthracene are included in this host. The detail survey on the inclusion property of the present host system is currently in progress.

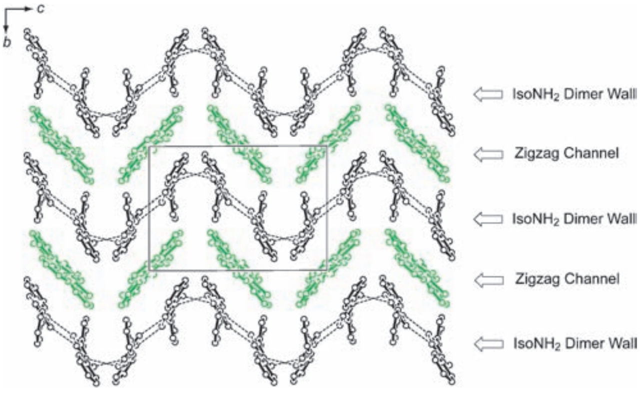


Figure 3. Crystal structure of **1** viewed along the *a* axis. Zigzag channels are formed between isoNH$_2$ dimer walls. 2D coordination layers and hydrogen atoms are omitted for clarity. Broken lines show hydrogen bonds.

The elongation of isoNH$_2$ by introducing a certain hydrocarbon unit, such as phenylene unit, between the pyridine ring and the amide functional group of isoNH$_2$ would result in the formation of a longer amide dimer. Self-assembly of Cd^{2+}, SCN$^-$, and this elongated amide dimer could give a host system permitting to include much larger organic molecules that cannot be included in the present host system. The possibility of this structural extension is currently in assessment.

In summary, we have developed a new inclusion compound formulated as [Cd(SCN)$_2$(isoNH$_2$)$_2$]$\cdot$1/2(9,10-dichloroanthracene) (**1**), featuring the layered structure of [Cd(SCN)$_2$]$_\infty$ and the pillars of the isoNH$_2$ dimers. IsoNH$_2$ dimers are connected with each other through N–H···O hydrogen bonding to form an isoNH$_2$ dimer wall. The 9,10-dichloroanthracene guests are included in the zigzag channels formed between the isoNH$_2$ dimer walls.

References and Notes

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8 Typical procedure for the preparation of **1**: to 50 mL of methanol suspended with CdCl$_2\cdot$2.5H$_2$O (0.19 g, 0.82 mmol), KSCN (0.16 g, 1.65 mmol) was added with vigorous stirring. After refluxing the solution for 1 h, isoNH$_2$ (0.20 g, 1.64 mmol) and 9,10-dichloroanthracene were added to the solution. Crystals of the inclusion compound were obtained after slow evaporation of the solvent over a period of a few weeks at room temperature. IR (KBr): 1701 (C=O), 2066 (C≡N), 2096 (C≡N). Anal. Calcd for $C_{21}H_{16}N_6O_2ClS_2Cd$: C, 42.29; H, 2.71; N, 14.09%. Found: C, 42.35; H, 2.77; N, 14.23%.

9 Crystal data for **1**: $C_{21}H_{16}N_6O_2ClS_2Cd$, $M = 596.4$, monoclinic, space group $C2/c$ (#15), $a = 33.277(2)$ Å, $b = 9.9276(4)$ Å, $c = 16.2019(2)$ Å, $\beta = 118.459(2)^\circ$, $V = 4705.7(6)$ Å^3, $Z = 8$, $D_{\rm calc} = 1.68$ g cm^{-3}, μ(Mo Kα) $= 1.251$ mm^{-1}, crystal size $0.60 \times 0.45 \times 0.10$ mm^3. A total of 11907 reflections ($1.4 < \theta < 29.9$) were processed of which 6663 were unique and significant with $I_{\rm net} > 2\sigma(I_{\rm net})$. Final residuals for $I_{\rm net} > 2\sigma(I_{\rm net})$ were $R_1 = 0.0384$ and $wR2 = 0.1115$ (GoF = 1.154) for 347 parameters. The maximum and minimum electron density residues found in the final differential Fourier synthesis were 0.642 and -0.878 e Å^{-3}, respectively CCDC.

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