

Synthesis and Structure of [(12C4)₂Cd][Cd₂(SCN)₆]. Formation of a Novel Tetragonal Net of Anionic Layered Structure of [Cd₂(SCN)₆]²⁻ Templated by the Square-Shaped Sandwich [(12C4)₂Cd]²⁺ Cation

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Design and syntheses of novel compounds with unusual and tailorable structures are important steps toward the discovery and fabrication of technologically useful materials.^{1–3} An example is our recent report of a new series of hybrid crystalline materials based on inorganic polymers with organic spacers (IPOS)⁴ of the general formula [H–G][M–L] where the cation [H–G] is a host(H)–guest(G) complex⁵ and the anion [M–L] is a metal(M)–ligand(L) polymer,⁶ as exemplified by the [(18C6)M][Cd(SCN)₃] (M⁺ = Na⁺, K⁺) compounds.⁴ In this particular system, the anionic [Cd(SCN)₃]⁻ complex forms one-dimensional (1-D) infinite polymeric zig-zag chains.⁷ More important, however, is the fact that the [(18C6)M]⁺ cations (monomeric for M⁺ = K⁺ and dimeric for M⁺ = Na⁺) cause the infinite [Cd(SCN)₃]⁻ chains to arrange in a parallel and an antiparallel manner, giving rise to acentric and centric space groups for M⁺ = K⁺ and Na⁺, respectively.⁴ The former exhibits nonlinear optical properties (second harmonic generation) while the latter does not. In this regard, the [(18C6)M]⁺ cations serve as the spacer/controller, dictating the crystal structure and symmetry, thereby giving rise to desirable properties. In order to extend the IPOS concept to two-dimensional (2-D) cadmium–thiocyanate polymers, we chose the combina-

tion of 12C4 and NH₄SCN in the reaction with CdSO₄, reasoning that a sandwich cation such as [(12C4)₂NH₄]⁺ may favor the formation of a layered structure. Indeed, we obtained a novel 2-D metal–thiocyanate coordination solid, formulated as [(12C4)₂Cd][Cd₂(SCN)₆] (**1**), which is reported herein. To our surprise, however, the title compound contains [(12C4)₂Cd]²⁺ (instead of [(12C4)₂NH₄]⁺) as the sandwich cation and [Cd₂(SCN)₆]²⁻ as the anionic 2-D polymeric network. The significance of the title compound lies in the fact that the [(12C4)₂Cd]²⁺ dication in **1** serves not only as the “spacer” and “controller” of the crystal packing, but also as a “template” for the formation of a novel two-dimensional (2-D) motif of a cadmium–thiocyanate coordination solid.¹¹

The title compound [(12C4)₂Cd][Cd₂(SCN)₆] (**1**) was prepared by dropwise addition, with vigorous stirring, of an aqueous solution of 12-crown-4 (12C4) to a mixture of CdSO₄ and NH₄SCN in water (molar ratio 1:4:32). Care must be taken to prevent supersaturation and/or precipitation during the reaction. Colorless square-plate crystals, measuring millimeters in size, formed within a few days (yield 21% based on 12C4).¹³ IR spectroscopy of **1** (CsI pellet)¹⁴ confirms the presence of coordinated 12C4 and SCN ligands. In particular, four ν(CN) peaks (see Figure S1 of Supporting Information) at 2129, 2094, 2070, and 2023 cm⁻¹ can be assigned to the various coordination types of SCN⁻ observed in the structure (*vide infra*). These four peaks are highly characteristic of, and can be used to identify, the particular 2-D structure of **1** described below.

Compound **1** crystallizes in the monoclinic unit cell with space group C2/c (*b* unique) and eight [(12C4)₂Cd][Cd₂(SCN)₆] per unit cell.¹⁵ There are two crystallographically independent¹⁶ [Cd₂(NCS)₂] dimers which are centered about the centers of symmetry situated at (1/4, 1/4, 0) (Cd1 and Cd1*) and (1/4, 1/4, 1/2) (Cd2 and Cd2*) and two independent [(12C4)₂Cd]²⁺ dications centered at Cd3 (1/2, 0.05, 3/4) and Cd4 (0, 0.03, 1/4), both of which reside on the 2-fold symmetry axes, as depicted in Figure 1a. The two Cd atoms within each [Cd₂(NCS)₂] dimer are separated by 3.72 (av) Å and bridged by two N atoms from two NCS groups (hereafter referred to as “bridging” NCS⁻ groups). The dimers are further linked by four additional SCN groups (hereafter referred to as “linkage” SCN⁻ groups) to other dimers to form a two-dimensional (2-D) layered structure of anionic

(11) While layered transition metal thiocyanate structures have been reported in the literature,^{10,12} the title structure represents an unprecedented 2-D motif. For example, a different type of 2-D polymeric structure was observed for RbCd(SCN)₃¹⁰ in which octahedral Cd(SCN)₄(NCS)₂ and Cd(NCS)₄(SCN)₂ groups are connected by Cd–SCN–Cd bridges to form layers with Rb⁺ ions residing in between the layers. Yet another example is the distinctly different tetragonal net found in CoHg₂(SCN)₆·C₆H₆¹² where Co(NCS)₆ octahedral groups are linked through S atoms by pairs of Hg atoms which are themselves bridged by two S atoms of two SCN ligands. The resulting layers are intercalated with benzene molecules.

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(13) Analysis by Midwest Microlab (Indianapolis, IN) of single crystals of [(12C4)₂Cd][Cd₂(SCN)₆] (FW = 1038.17). Calcd (found): C, 25.43 (25.50); H, 3.11 (3.09); N, 8.10 (8.07); S, 18.53 (18.50).

(14) The infrared (IR) spectrum was measured on a BIO-RAD FTS-40 spectrometer in the range of 4000–200 cm⁻¹.

(15) [(12C4)₂Cd][Cd₂(SCN)₆]: monoclinic, C2/c, *a* = 16.297(3) Å, *b* = 26.267(3) Å, *c* = 16.296(2) Å, β = 90.20(1)°, *V* = 6975(1) Å³, *Z* = 8. An asymmetric unit of 7288 data (2θ_{max} = 52°) was collected at ambient temperature using a Rigaku AFC7R diffractometer equipped with a rotating anode generator (Mo Kα radiation). An empirical ψ scan absorption correction was applied to the data (μ = 2.226 mm⁻¹). Structural solution by direct methods and anisotropic least-squares refinements (based on *F*) were performed with TeXsan package. This refinement (407 parameters) on 5818 independent reflections with *I* > 3σ converged at *R*₁ = 0.039 and *R*₂ = 0.041. See CIF files of Supporting Information for details.

(16) Had the two crystallographically independent [(12C4)₂Cd][Cd₂(SCN)₆] units become symmetry equivalent, the crystal system would have been tetragonal with cell dimension *a* = 11.523 Å, *c* = 26.267 Å, *V* = 3487 Å³, and *Z* = 4. The two most plausible space groups are *I4* and *I4*. However, isotropic refinements based on either space groups were unsuccessful, resulting in divergence and high discrepancy factors (*R*₁ > 0.25 vs *R*₁ = 0.09 for the correct space group¹⁵).

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(7) Although numerous metal complexes or coordination solids containing SCN ligands, bonded either through S (thiocyanate), N (isothiocyanate), or both (bridging), are known,^{6,8–12} we note that anionic cadmium thiocyanate complexes or coordination solids of the general formula [Cd_m(SCN)_n]^{2m-n} are rather rare. Most of them adopt one-dimensional (1-D) polymeric structures.^{4,8,9} To the best of our knowledge, there is only one previous example of two-dimensional (2-D) polymeric structures of anionic cadmium thiocyanate complexes, namely, RbCd(SCN)₃.¹⁰ Furthermore, all of these structures are based on monocadmium complexes (*m* = 1) as building blocks. Hence, the title compound represents the first example of a 2-D anionic cadmium thiocyanate polymeric structure with a dicadmium complex (*m* = 2) as the basic building block.

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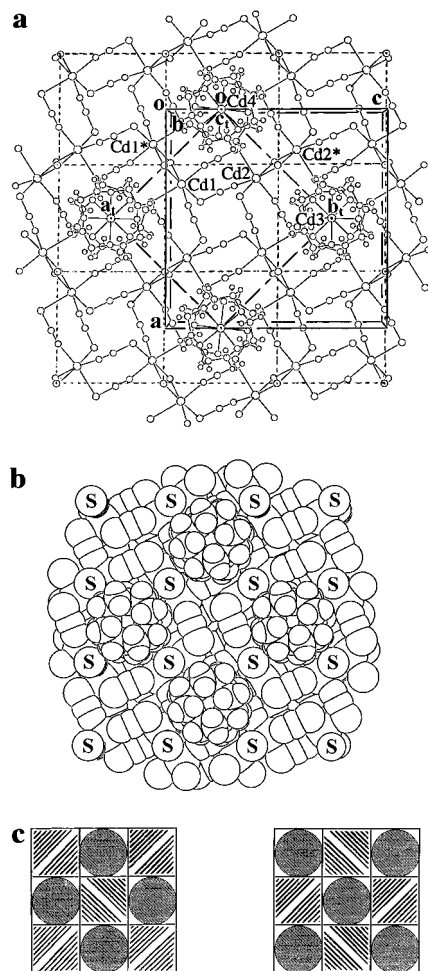


Figure 1. (a) Tetragonal motif of the layered structure of $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**). The crystallographic monoclinic unit cell is indicated by a , b , and c (solid lines) while the pseudotetragonal unit cell is by a_1 , b_1 , and c_1 (dashed lines). Note that $a_1 = b_1 = a/2^{1/2} = c/2^{1/2}$, and $c_1 = b$. Also indicated is the noncrystallographic square lattice ($a/2$, $c/2$), represented by dotted lines, of square holes created by the “dangling” sulfur atoms (see part b). (b) Space-filling model of one layer of $[(12C4)_2Cd][Cd_2(SCN)_6]$ with the “deep” holes (type A) filled with the $[(12C4)_2Cd]^{2+}$ dications. The sulfur atoms of the “bridging” NCS⁻ ligands are labeled to highlight the noncrystallographic square lattice (and the square holes) formed by these “dangling” S atoms. (c) Schematic “checker board” representations of adjacent layers of **1**. The “deep” (type A) and “shallow” (type B) holes are represented by white and shaded boxes, respectively. The $[(12C4)_2Cd]^{2+}$ dications are denoted by black circles. The stripes in the shaded boxes illustrate schematically the “herringbone” arrangement of the antiparallel “linkage” SCN⁻ ligands. The left figure corresponds to the space-filling model in part b. Note that the layers alternate and complement one another such that the $[(12C4)_2Cd]^{2+}$ dications in the “deep” holes of one layer protrude into the “shallow” holes of the adjacent layer (see text).

$[Cd_2(SCN)_6]^{2-}$ polymeric tetragonal nets (Figure 1a). The average Cd···Cd distance bridged by the linkage SCN⁻ ligands is 5.58 Å. The layers are perpendicular to the crystallographic b axis and centered at $y = 1/4$ and $3/4$ with an interlayer spacing of $b/2 = 13.14$ Å. The Cd atoms in the $[Cd_2(SCN)_6]^{2-}$ layers are octahedrally coordinated with two N atoms at 2.46 (av) Å from the “bridging” NCS⁻ ligands and two N atoms at 2.31 (av) Å and two S atoms at 2.69 (av) Å from the “linkage” SCN⁻ groups. The Cd atoms (Cd3 and Cd4) in each of the sandwich $[(12C4)_2Cd]^{2+}$ dications are coordinated with eight oxygens (average Cd–O distance, 2.39 Å) from two 12C4 ligands (see Figure S2 of Supporting Information). The two 12C4 ligands are staggered with respect to each other such that the dications conform to the idealized D_{4d} point group symmetry.

The four “linkage” SCN⁻ groups can be subdivided into two categories: in-plane SCN⁻ (labeled 2 and 4) and out-of-plane SCN⁻ ligands (labeled 1 and 3). (See Figures S2 and S3, Supporting Information.) The in-plane SCN⁻ groups form individual $[Cd_4(SCN)_4]$ squares which are bridged by four more “out-of-plane” SCN⁻ groups, two above and two below the plane, as depicted in Figure 1a,b. The resulting $[Cd_4(SCN)_8]$ squares are further linked by two “bridging” NCS⁻ (labeled 5 and 6) groups to give an intricate motif shown in the space-filling model in Figure 1b.

The most important feature of the structure is the square net, indicated by dotted lines in Figure 1a, formed by the “dangling” S atoms of the two bridging NCS⁻ groups (oriented parallel to the crystallographic b axis) within each $[Cd_2(NCS)_2]$ dimer, giving rise to a noncrystallographic sublattice ($a/2$, $c/2$). The space-filling model of such squares, which are in reality holes, is shown in Figure 1b. Half of these square holes (type A, hereafter referred to as “deep” holes) are filled with the $[(12C4)_2Cd]^{2+}$ dications. The other half (type B, hereafter referred to as “shallow” holes) are filled with two out-of-plane linkage SCN⁻ groups, arranged in an antiparallel fashion. The remaining spaces in these latter (type B) holes are occupied by the $[(12C4)_2Cd]^{2+}$ cations protruded from an adjacent layer. Within each layer, the “deep” holes (type A) and the “shallow” holes (type B) alternate like a checker board as depicted schematically in Figure 1c. The relative arrangement between the layers, however, is rather interesting. As a result of the crystallographic C-centering, the adjacent layers, with a spacing of $b/2 = 13.14$ Å, are shifted by $a/2$ and $b/2$. This implies that the “checker boards” complement one another with the “deep” holes of one layer being aligned with the “shallow” holes of an adjacent layer (see Figure 1c). In this regard, the structure may be likened to stacks of “eggs in cartons” with the $[(12C4)_2Cd]^{2+}$ dications as “eggs” and the tetragonal nets of the polymeric $[Cd_2(SCN)_6]^{2-}$ layers as “cartons”. The $[(12C4)_2Cd]^{2+}$ dications fit snugly into the complementary “deep” and “shallow” holes of adjacent layers.

A detailed examination of the crystal structure of **1** prompted us to propose a “templating mechanism” in which the organic cations serve as templates for the formation of the extended coordination solid structure, in a way similar to the formation of zeolite structures by organic template molecules.¹⁷ In other words, we believe that the square-shaped $[(12C4)_2Cd]^{2+}$ dication “induces” and/or “directs” the formation of the intricate quilt composed of various basic building units (*vide supra*) woven into the observed tetragonal motif of the anionic $[Cd_2(SCN)_6]^{2-}$ polymeric structure (Figure 1). In this context, the title compound also raises the question concerning the relative importance of the *shape selectivity vs charge specificity* of the cations in the formation of anionic $[Cd_m(SCN)_n]^{(2m-n)}$ polymers in general. Work is in progress to differentiate the role(s) played by each of these effects in the formation of the structures by utilizing cations of various size, shape, and charge, as well as by employing different $m:n$ ratios in the synthesis, with the hope of furthering the “template” hypothesis and opening up new and controllable routes to other anionic cadmium–thiocyanate compounds of tailorable structures and properties.

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Supporting Information Available: Figures S1–S3 and CIF tables listing crystallographic data (14 pages). See any current masthead page for ordering and Internet access instructions.

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