Anisotropic Templating Effect in the Formation of Two-Dimensional Anionic Cadmium−Thiocyanate Coordination Solids $[(12C4)_2Cd][Cd_2(SCN)_6]$ and $[(12C4)_2Cd][Cd_3(SCN)_8]$ with Checkerboard and Herringbone Patterns, Respectively

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Received April 7, 1998

This paper reports the syntheses, characterization, and structures of two new two-dimensional cadmium−thiocyanate coordination solids $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**) and $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**), where 12C4 denotes 12-crown-4, $C_8H_{16}O_4$. **1** crystallizes in a monoclinic unit cell, space group $C2/c$ with lattice parameters $a = 16.297(3)$ Å, $b = 26.267(3)$ Å, $c = 16.296(2)$ Å, $\beta = 90.20(1)°$, and $Z = 8$. **2** crystallizes in a monoclinic unit cell, space group $P2_1/n$ with lattice parameters $a = 11.604(7)$ Å, $b = 11.366(7)$ Å, $c = 15.736(4)$ Å, $\beta = 92.84(3)°$, and $Z = 2$. The structure of **1** exhibits a two-dimensional *tetragonal* motif consisting of Cd_2 units arranged in a checkerboard pattern with the dimeric $[Cd_2(SCN)_6]^{2-}$ complex as the building block. The crystal structure of **2** can be described as a two-dimensional *hexagonal* array of linear trimeric Cd_3 units arranged in a herringbone pattern with the $[Cd_3(SCN)_8]^{2-}$ complex as the building block. In both **1** and **2**, the $[(12C4)_2Cd]^{2+}$ dications are housed in cavities within and between the anionic cadmium−thiocyanate layers but with different orientations ("upright" in **1** and "sideways" in **2**) with respect to the cadmium−thiocyanate layers, giving rise to an anisotropic templating effect.

Introduction

Design and synthesis of novel compounds with unusual and tailorable structures are important steps toward the discovery and fabrication of technologically useful materials.[1−3] Recently we reported 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) complex[5] 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 $[Cd(SCN)_3{}^-]_\infty$ complex forms one-dimensional (1-D) infinite polymeric zigzag chains.[7] More important, however, is the fact that the $[(18C6)M]^+$ cations (monomeric for $M^+ = K^+$ and the dimeric for $M^+ = Na^+$) cause the infinite $[Cd(SCN)_3{}^-]_\infty$ chains to arrange in a parallel and antiparallel manner, giving rise to noncentrosymmetric and centrosymmetric space groups for $M^+ = K^+$ and Na^+, respectively.[4] The former exhibits efficient nonlinear optical effects (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. To extend the IPOS concept to two-dimensional (2-D) cadmium−thiocyanate polymers, we chose the crown ether with a smaller cavity size (such as 12C4) in combination with NH_4SCN and $CdSO_4$, reasoning that a sandwich dication such as $[(12C4)_2Cd]^{2+}$ may favor the formation of a layered (2-D) anionic cadmium−thiocyanate structure. Indeed, we obtained two different 2-D metal−thiocyanate coordination solids, formulated as $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**) and $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**), which are reported herein.

The title compounds are synthesized from 12-crown-4 (12C4, $C_8H_{16}O_4$), $CdSO_4$, and NH_4SCN. They both contain $[(12C4)_2Cd]^{2+}$ as the sandwich dication and a cadmium−thiocyanate complex, $[Cd_2(SCN)_6]^{2-}$ in **1** and $[Cd_3(SCN)_8]^{2-}$ in **2**, as the anionic layered coordination solids. The structure of **1**, which was communicated previously,[9] exhibits a 2-D *tetragonal* motif and consists of Cd_2 units arranged in a checkerboard pattern with the dimeric $[Cd_2(SCN)_6]^{2-}$ as the building block (Figure 1). We now wish to report, for the first time, the structure of a new coordination solid formulated as $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**), prepared with a different ratio of reactants. The crystal structure of **2** can be described as a 2-D *hexagonal* array of linear trimeric Cd_3 units arranged in a

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10.1021/ic980387v CCC: \$18.00 © 1999 American Chemical Society
Published on Web 02/06/1999

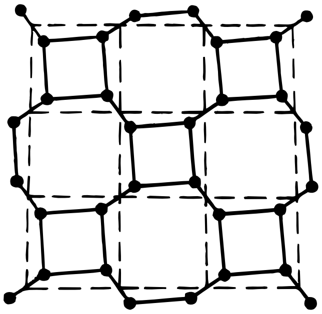

Figure 1. Tetragonal array of dicadmium Cd_2 units arranged in a checkerboard pattern in the layered structure of $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**). (Note that the Cd atoms are not bonded and that $[(12C4)_2Cd]^{2+}$ and SCN^{-} ligands are omitted for clarity.)

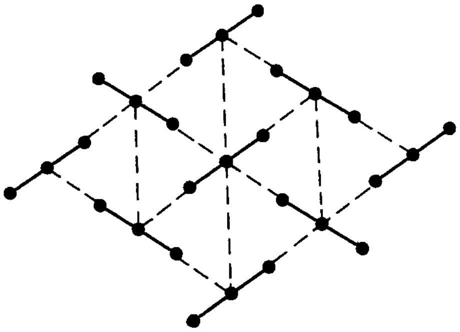

Figure 2. Hexagonal array of linear tricadmium Cd_3 units arranged in a herringbone pattern in the layered structure of $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**). (Note that the Cd atoms are not bonded and that $[(12C4)_2Cd]^{2+}$ and SCN^- ligands are omitted for clarity.)

herringbone pattern (Figure 2) with the $[Cd_3(SCN)_8]^{2-}$ complex as the building block. In both **1** and **2**, the $[(12C4)_2Cd]^{2+}$ dications are housed in cavities within and between the anionic cadmium−thiocyanate layers. As such, they serve not only as the "spacer" and "controller" of the crystal packing and symmetry but also as "templates" in the formation of these new 2-D motifs of cadmium−thiocyanate coordination solids. While other 2-D cadmium−thiocyanate coordination solids are known in the literature,[8] the most important finding of the present study is that the $[(12C4)_2Cd]^{2+}$ dications in the title structures exhibit different orientations ("upright" in **1** and "sideways" in **2**) with respect to the cadmium−thiocyanate layers, thereby giving rise to an anisotropic templating effect.

Experimental Section

Synthesis. All reagents were purchased from Aldrich Chemicals and were used without further purification. The purities of 12C4, $CdSO_4$, and NH_4SCN were 98%, 99%, and 98%, respectively. Triply distilled water was used in our study. The title compounds were prepared using similar procedures but with different ratios of reactants.[9] With vigorous stirring, 18 mL of an aqueous solution of 0.056 M 12-crown-4 (12C4) was added dropwise to a preformed mixture of 13.3 mL (for **1**) and 20 mL (for **2**) of 0.3 M aqueous solution of $CdSO_4$ and 32 mL (for **1**) or 24 mL (for **2**) of 1 M aqueous solution of NH_4SCN, respectively, over a period of 30 min. (The final 12C4:$CdSO_4$:NH_4SCN molar ratios were 1:4:32 for **1** and 1:6:24 for **2**.) Care must be taken to prevent supersaturation and/or precipitation during the addition. Colorless crystals, millimeters in size, were grown via slow evaporation. The morphology of the crystals can be described as square plates for **1** and truncated polyhedra for **2**. Yield: 78% for **1** and 85% for **2** calculated on the basis of 12C4. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Anal. Calcd (found) for $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**) (fw = 1038.17): C, 25.43 (25.50); H, 3.11 (3.09); N, 8.10 (8.07); S, 18.5 (18.5). Anal. Calcd (found) for $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**) (fw = 1266.69): C, 22.76 (22.86); H, 2.55 (2.50); N, 8.85 (8.83); S, 20.3 (20.6).

Table 1. Crystallographic Data for $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**)[a]

empirical formula	$Cd_4S_8N_8O_8C_{24}H_{32}$
fw	1266.69
space group	$P2_1/c$
a (Å)	11.604(7)
b (Å)	11.366(7)
c (Å)	15.736(4)
β (deg)	92.84(3)
V (Å^3)	2072(1)
Z	2
D_{calcd} (g cm^{-3})	2.029
μ (cm^{-1})	24.818
λ (Mo Kα, Å)	0.7107
T (°C)	25
$2\theta_{max}$	52
no. of obsd rflcns	2915 ($I > 3\sigma$)
no. of variables	346
R^b	0.030
$R_w{}^c$	0.031

[a] The corresponding table for $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**) can be found in ref 9 as Supporting Information. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

X-ray Crystallography. A colorless crystal of **1**, in the shape of a thin square plate and with dimensions of 0.20 mm × 0.13 mm × 0.20 mm, and a colorless crystal of **2**, in the shape of a truncated polyhedron and with dimensions of 0.18 mm × 0.22 mm × 0.20 mm, were selected and mounted on glass fibers with epoxy resin, respectively. Room-temperature (23 ± 2 °C) single-crystal X-ray diffraction data were collected on a Rigaku AFC7R diffractometer equipped with a rotating anode generator using monochromatized Mo Kα radiation (λ = 0.710 69 Å). The observed intensities were corrected for Lorentz and polarization effects. The empirical ψ scans absorption correction was applied to the data of **1** (μ = 22.26 cm^{-1}, transmission range = 0.757−0.999), whereas theoretical absorption correction, using the program DIFABS (μ = 24.82 cm^{-1}, transmission range = 0.961−1.050),[10] was applied to the data of **2**. Structure solution and refinements of both title compounds **1** and **2** were performed using the teXsan package of Molecular Structure Corporation.[11] Positions of the cadmium atoms and SCN^- ligands were obtained from direct methods, and atoms of 12C4 ligands were located via Fourier syntheses. In **1**, there are eight $[(12C4)_2Cd][Cd_2(SCN)_6]$ per unit cell (Z = 8). The structural analysis required the location of two cadmium atoms and six SCN^- ligands of $[Cd_2(SCN)_6]^{2-}$ and two cadmium atoms, eight oxygen atoms, and 16 carbon atoms of $[(12C4)_2Cd]^{2+}$ per asymmetric unit. In **2**, there are two $[(12C4)_2Cd][Cd_3(SCN)_8]$ per unit cell (Z = 2). The analysis of the structure required the location of two cadmium atoms and four SCN^- ligands of $[Cd_3(SCN)_8]^{2-}$ and one cadmium atom, eight oxygen atoms, and 16 carbon atoms of $[(12C4)_2Cd]^{2+}$ per asymmetric unit. Note that the $[(12C4)_2Cd]^{2+}$ dication in **2** is disordered due to crystallographic inversion symmetry (−1). In the final cycles of full-matrix least-squares refinement (based on F), anisotropic thermal parameters were used for all non-hydrogen atoms. Idealized hydrogen atom positions (C−H, 0.95 Å) of 12C4 were included in the calculations but not refined. For **1**, anisotropic refinement (407 parameters) on 5818 independent reflections with $I > 3\sigma(I)$ converged at R = 0.039 and R_w = 0.041. For **2**, anisotropic refinement (346 parameters) on 2915 independent reflections with $I > 3\sigma(I)$ converged at R = 0.030 and R_w = 0.031. Details of the crystallographic data for **2** are summarized in Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (U_{ij}) for **2** are listed in Table 2. Selected interatomic distances and bond angles, together with the estimated standard deviations, are given in Tables 3 and 4 for **1** and **2**, respectively. Other crystallographic and structural details are provided in the Supporting Information.

Physical Measurements. The infrared (IR) spectra were measured with a BIO-RAD FTS-40 spectrophotometer. IR of **1** and **2** (CsI pellet) showed the presence of coordinated 12C4 and SCN^- ligands. In

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Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (U_{eq}, Å^2) for $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**)[a]

	occupancy	x	y	z	U_{eq}[b]
Cd1	1.0	0.00388(3)	0.19064(3)	0.20652(2)	0.0299
Cd2	0.5	0.0000	0.0000	0.0000	0.0328
Cd3	0.5	1/2	1/2	0.0000	0.0337
S1	1.0	−0.0557(1)	0.3532(1)	0.09274(8)	0.0354
S2	1.0	−0.1797(1)	0.2221(2)	0.29958(9)	0.0510
S3	1.0	−0.1673(1)	0.0235(1)	0.11788(8)	0.0347
S4	1.0	0.3531(1)	0.0534(2)	0.1328(1)	0.0696
N1	1.0	0.0655(4)	0.0417(4)	0.2934(3)	0.0454
N2	1.0	−0.0728(4)	0.1636(4)	−0.0606(3)	0.0436
N3	1.0	0.1229(4)	0.3247(4)	0.2793(2)	0.0350
N4	1.0	0.1227(4)	0.1097(4)	0.1012(3)	0.0365
C1	1.0	−0.0616(4)	0.4631(4)	0.1614(3)	0.0323
C2	1.0	−0.1166(4)	0.2905(4)	0.3810(3)	0.0332
C3	1.0	−0.1391(4)	−0.0944(4)	0.1782(3)	0.0275
O1	0.5	0.3106(6)	0.4537(8)	0.0377(5)	0.0468
O2	0.5	0.4354(7)	0.3334(7)	−0.0802(5)	0.0485
O3	0.5	0.6181(6)	0.3263(7)	0.0379(5)	0.0407
O4	0.5	0.4939(6)	0.4468(7)	0.1551(4)	0.0380
O5	0.5	0.6729(7)	0.5938(8)	0.0590(6)	0.0615
O6	0.5	0.4540(7)	0.6855(8)	0.0592(5)	0.0548
O7	0.5	0.4135(6)	0.6078(8)	−0.1053(6)	0.0557
O8	0.5	0.6323(8)	0.5149(8)	−0.1068(6)	0.0638
C4	0.5	0.2191(5)	0.0864(4)	0.1153(3)	0.0351
C5	0.5	0.263(1)	0.377(2)	−0.024(1)	0.1073
C6	0.5	0.322(1)	0.290(1)	−0.055(1)	0.0793
C7	0.5	0.515(2)	0.235(1)	−0.080(1)	0.1038
C8	0.5	0.584(2)	0.217(1)	0.000(1)	0.0747
C9	0.5	0.640(1)	0.311(2)	0.1270(9)	0.0871
C10	0.5	0.549(1)	0.337(1)	0.1794(9)	0.0654
C11	0.5	0.379(1)	0.461(1)	0.1829(9)	0.0593
C12	0.5	0.289(1)	0.420(1)	0.1241(8)	0.0556
C13	0.5	0.646(1)	0.687(1)	0.1194(8)	0.0742
C14	0.5	0.547(2)	0.755(1)	0.078(1)	0.0781
C15	0.5	0.362(1)	0.735(1)	0.004(1)	0.0675
C16	0.5	0.393(1)	0.728(1)	−0.0880(9)	0.0642
C17	0.5	0.468(2)	0.590(2)	−0.1840(8)	0.0872
C18	0.5	0.602(1)	0.604(2)	−0.1694(9)	0.0940
C19	0.5	0.747(1)	0.541(1)	−0.0684(10)	0.0644
C20	0.5	0.758(1)	0.623(2)	0.006(1)	0.0749

[a] The corresponding table for $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**) can be found in ref 9 as Supporting Information. [b] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**)

	$[Cd_2(SCN)_6]^{2-}$		
Cd1	S1		2.647(2)
Cd1	S4		2.699(2)
Cd1	N2		2.263(5)
Cd1	N3		2.356(5)
Cd1	N5		2.375(5)
Cd1	N5		2.539(5)
Cd2	S2		2.690(2)
Cd2	S3		2.698(2)
Cd2	N1		2.335(5)
Cd2	N4		2.250(5)
Cd2	N6		2.467(5)
Cd2	N6		2.421(5)
S1	C1		1.656(7)
S2	C2		1.651(6)
S3	C3		1.661(6)
S4	C4		1.659(6)
S5	C5		1.628(7)
S6	C6		1.623(7)
N1	C1		1.157(8)
N2	C2		1.142(8)
N3	C3		1.152(8)
N4	C4		1.145(8)
N5	C5		1.158(9)
N6	C6		1.169(8)
	$[(12C4)_2Cd]^{2+}$		
Cd	O		2.387(4)
O	C		1.434(8)
C	C		1.507(9)
S1	Cd1	S4	92.92(5)
S1	Cd1	N2	92.6(1)
S1	Cd1	N3	91.0(1)
S1	Cd1	N5	172.5(1)
S1	Cd1	N5	91.1(1)
S4	Cd1	N2	171.1(1)
S4	Cd1	N3	88.7(1)
S4	Cd1	N5	87.2(1)
S4	Cd1	N5	84.7(1)
N2	Cd1	N3	98.2(2)
N2	Cd1	N5	86.4(2)
N2	Cd1	N5	88.2(2)
N3	Cd1	N5	96.4(2)
N3	Cd1	N5	173.2(2)
N5	Cd1	N5	81.4(2)
S2	Cd2	S3	94.26(5)
S2	Cd2	N1	86.6(1)
S2	Cd2	N4	171.7(1)
S2	Cd2	N6	86.1(1)
S2	Cd2	N6	87.2(1)
S3	Cd2	N1	93.1(1)
S3	Cd2	N4	93.0(1)
S3	Cd2	N6	90.7(1)
S3	Cd2	N6	171.7(1)
N1	Cd2	N4	97.0(2)
N1	Cd2	N6	172.0(2)
N1	Cd2	N6	95.1(2)
N4	Cd2	N6	89.8(2)
N4	Cd2	N6	85.1(2)
N6	Cd2	N6	81.2(2)
Cd1	S1	C1	102.4(2)
Cd2	S2	C2	94.6(2)
Cd2	S3	C3	101.8(2)
Cd1	S4	C4	93.9(2)
Cd2	N1	C1	137.8(5)
Cd1	N2	C2	161.0(5)
Cd1	N3	C3	136.8(5)
Cd2	N4	C4	161.5(5)
Cd1	N5	Cd1	98.6(2)
Cd1	N5	C5	125.2(4)
Cd1	N5	C5	134.3(4)
Cd2	N6	Cd2	98.8(2)
Cd2	N6	C6	129.9(4)
Cd2	N6	C6	129.7(4)
S1	C1	N1	176.6(6)
S2	C2	N2	179.3(6)
S3	C3	N3	175.4(6)
S4	C4	N4	179.9(6)
S5	C5	N5	179.6(5)
S6	C6	N6	179.3(5)

particular, four ν(C−N) peaks observed at 2129, 2094, 2070, and 2023 cm^{-1} for **1** and 2125, 2114, 2060, and 1995 cm^{-1} for **2** are highly characteristic of, and can be used to identify, the two different 2-D structures.

Solid-state ultraviolet and visible spectra were obtained with a Shimadzu UV-2100 spectrophotometer equipped with an Integrating Sphere assembly. The title compounds are transparent in the visible and ultraviolet region (between 220 and 900 nm).

Results

Synthesis. Compounds **1** and **2** are formed in aqueous solutions according to the following reactions:

$$2(12C4) + 3CdSO_4 + 6NH_4SCN \rightarrow [(12C4)_2Cd][Cd_2(SCN)_6]\ (\mathbf{1}) + 3(NH_4)_2SO_4 \quad (1)$$

$$2(12C4) + 4CdSO_4 + 8NH_4SCN \rightarrow [(12C4)_2Cd][Cd_3(SCN)_8]\ (\mathbf{2}) + 4(NH_4)_2SO_4 \quad (2)$$

According to these balanced equations, the ratio of 12C4 to Cd to SCN$^-$ ligands should be 2:3:6 for $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**) and 2:4:8 for $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**). However, the concentration ratio of the reactants used in the preparation of **1** and **2** may deviate from these values due to the limited solubilities of the product(s). In fact, as mentioned in the

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**)

	$[Cd_3(SCN)_8]^{2-}$	
Cd1	S1	2.641(2)
Cd1	S2	2.668(2)
Cd1	S3	3.038(2)
Cd1	N1	2.269(4)
Cd1	N3	2.320(4)
Cd1	N4	2.392(4)
Cd2	S3	2.764(2)
Cd2	N2	2.236(4)
Cd2	N4	2.428(4)
S1	C1	1.655(5)
S2	C2	1.640(5)
S3	C3	1.666(5)
S4	C4	1.610(6)
N1	C1	1.145(6)
N2	C2	1.152(6)
N3	C3	1.147(6)
N4	C4	1.160(6)
	$[(12C4)_2Cd]^{2+}$	
Cd	O	2.388(8)
O	C	1.43(2)
C	C	1.46(2)

S1	Cd1	S2	95.09(5)
S1	Cd1	S3	89.02(4)
S1	Cd1	N1	174.0(1)
S1	Cd1	N3	90.3(1)
S1	Cd1	N4	86.6(1)
S2	Cd1	S3	79.28(5)
S2	Cd1	N1	90.3(1)
S2	Cd1	N3	96.5(1)
S2	Cd1	N4	159.3(1)
S3	Cd1	N1	89.4(1)
S3	Cd1	N3	175.6(1)
S3	Cd1	N4	80.1(1)
N1	Cd1	N3	91.7(2)
N1	Cd1	N4	87.4(2)
N3	Cd1	N4	104.2(1)
S3	Cd2	S3	180.00
S3	Cd2	N2	86.7(1)
S3	Cd2	N2	93.3(1)
S3	Cd2	N4	85.3(1)
S3	Cd2	N4	94.7(1)
N2	Cd2	N2	180.00
N2	Cd2	N4	92.9(2)
N2	Cd2	N4	87.1(2)
N4	Cd2	N4	180.00
Cd1	S1	C1	95.9(2)
Cd1	S2	C2	98.9(2)
Cd1	S3	Cd2	84.45(5)
Cd1	S3	C3	97.8(2)
Cd2	S3	C3	100.4(2)
Cd1	N1	C1	159.4(5)
Cd2	N2	C2	149.2(4)
Cd1	N3	C3	153.0(4)
Cd1	N4	Cd2	108.2(2)
Cd1	N4	C4	122.6(4)
Cd2	N4	C4	122.5(4)
S1	C1	N1	177.7(5)
S2	C2	N2	178.5(5)
S3	C3	N3	177.9(5)
S4	C4	N4	178.8(5)

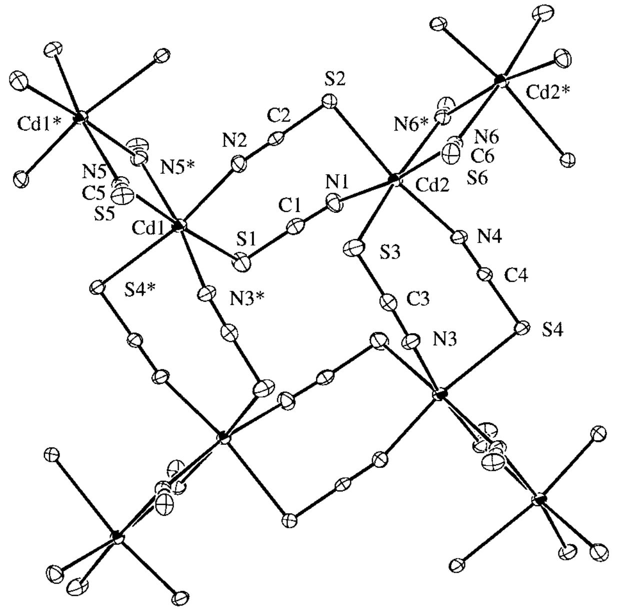

Figure 3. ORTEP diagram of $[Cd_2(SCN)_6{}^{2-}]_\infty$ layered structure in **1** (25% probability thermal ellipsoids). The symmetry-related atoms are labeled with asterisks. Each of Cd atoms is octahedrally coordinated with *cis*-S_2N_4.

Experimental Section, the relative amounts and concentrations of the reactants are important factors in avoiding the unwanted precipitation during the addition of the aqueous solution of 12C4. In an attempt to gain insights into the synthetic pathways and crystallization pattern, we have performed the reactions under various reaction conditions and characterized the products by crystal morphology and infrared spectroscopy. In a particular set of such experiments, the concentration of the 12C4 solution used was 0.056 M. The concentration of the $CdSO_4$ solution was systematically (stepwise) varied from 0.1 to 0.4 M, while that of the NH_4SCN solution was varied (again stepwise) from 0.4 to 1.0 M. It was found that, under these conditions, the product obtained is highly dependent upon the concentration ratio of the reactants. In particular, when the NH_4SCN:$CdSO_4$ concentration ratio is greater than 4, square-plate crystals of **1** are obtained. However, when the ratio is equal to or less than 4, truncated polyhedral crystals of **2** are formed. Consequently, in the synthetic procedures described in the Experimental Section, the ratios of 8 and 4 were used in the preparation of **1** and **2**, respectively.

Crystal Structure of $[(12C4)_2Cd][Cd_2(SCN)_6]$ (1): The Checkerboard Pattern. The crystal structure of **1** has been described by us in ref 9. The following highlights the important structural features, along with some new insights and/or relevant information needed in the comparison of the structures of **1** and **2**.

As portrayed in Figure 3, there are two crystallographically independent $[Cd_2(NCS)_2]$ dimers and two independent $[(12C4)_2Cd]^{2+}$ dications in **1**. The dimers are located at crystallographic inversion symmetries, whereas the dications conform to crystallographic 2-fold site symmetries. The two Cd atoms within each $[Cd_2(NCS)_2]$ dimer are separated by 3.72(av) Å and bridged by two N atoms from two NCS groups (referred to as "bridging" NCS^- groups with labels 5 and 6). The dimers are further linked by four additional SCN^- groups (referred to as "linkage" SCN^- groups: two "in-plane" SCN^- (labeled 2 and 4) and two "out-of-plane" SCN^- (labeled 1 and 3)) to other dimers to form an intricate 2-D layered structure of anionic $[Cd_2(SCN)_6{}^{2-}]_\infty$ polymeric tetragonal nets.[12]

The Cd atoms (Cd1 and Cd2) in the $[Cd_2(SCN)_6{}^{2-}]_\infty$ 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^-

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(12) The square-shaped $[Cd_4(SCN)_8]$ tetramers (see Figure 3), centered on crystallographic 2-fold symmetry axes along *b*, may also be considered as an alternative building block of the 2-D structure. The $[Cd_4(SCN)_8]$ "squares", each measuring approximately 8.15 × 8.15 Å^2 (i.e., *a*/2, *c*/2), are rotated by ca. 36° (or equivalently, 54°) with respect to the crystallographic *a* or *c* axis.

groups. The two sulfur atoms are in the *cis* configuration. Hence, the cadmium coordination spheres may be designated as *cis*-S_2N_4. As a result, there is one violation and two accordances of the *trans influence* (i.e., one "N *trans* to N" and two "S *trans* to N"). The two $[(12C4)_2Cd]^{2+}$ dications are ordered and conform to the idealized D_{4d} point group symmetry.

The tetragonal net of the metal framework of the anionic $[Cd_2(SCN)_6{}^{2-}]_\infty$ layers in **1** is depicted in Figure 1. The corresponding unit cell diagram (solid lines) can be found in Figure 1a of ref 9. As pointed out previously in ref 9, the "dangling" S atoms of the two bridging thiocyanate groups form a noncrystallographic square net ($a/2$, $c/2$), represented by dotted lines in Figure 1a of ref 9, creating approximately square holes. Half of these square holes (type A, referred to as "deep" holes) are filled with the $[(12C4)_2Cd]^{2+}$ dications, while the other half (type B, referred to as "shallow" holes) are filled with two out-of-plane linkage SCN^- groups, as portrayed in Figure 1b of ref 9.[13] Within each layer, the "deep" holes (type A) and the "shallow" holes (type B) alternate like a checkerboard, as shown schematically in Figure 1c (left) of ref 9. As a result of the crystallographic C-centering, the adjacent "checker board" layers complement one another, with the "deep" holes of one layer being aligned with the "shallow" holes of an adjacent layer (see Figure 1c (right) of ref 9). In this context, 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 $[Cd_2(SCN)_6{}^{2-}]_\infty$ layers as "cartons".[14]

Crystal Structure of $[(12C4)_2Cd][Cd_3(SCN)_8]$ (2): The Herringbone Motif. The crystal structure of **2** is best described as a layered anionic cadmium−thiocyanate complex consisting of interconnected linear tricadmium units (centered at Cd2 (0, 0, 0)), as illustrated in Figure 2. The basic building block of the layered structure is the $[Cd_3(SCN)_8]^{2-}$ complex, as portrayed in Figure 4. The sandwich $[(12C4)_2Cd]^{2+}$ dications are centered at Cd3 (1/2, 1/2, 0)) between the layers.

The unit cell diagram of compound **2** is depicted in Figure 5. The $[Cd_3(SCN)_8{}^{2-}]_\infty$ layers are perpendicular to the crystallographic a axis (see Figure 5) with all the Cd atoms residing on the same plane (at $x = 0$). The linear Cd_3 units are arranged in a herringbone pattern, with their centers forming a hexagonal array, as shown in Figure 2. This noncrystallographic, approximate hexagonal unit cell (designated by subscript h and indicated by dashed lines in Figure 5) is related to the crystallographic unit cell as follows: $a_h = (b - c)$, $b_h = (b + c)$, and $c_h = a$, with idealized dimensions of 19.412, 19.412, and 11.604 Å, respectively. It is apparent from Figure 2 that each linear Cd_3 unit is surrounded by six other linear Cd_3 units: two of them (in *para* positions) are parallel to the central unit, while the other four are oriented at an angle of 71.68°. Each of the latter four Cd_3 units is further linked to the central unit via three SCN^- ligands, thereby forming the 2-D net.

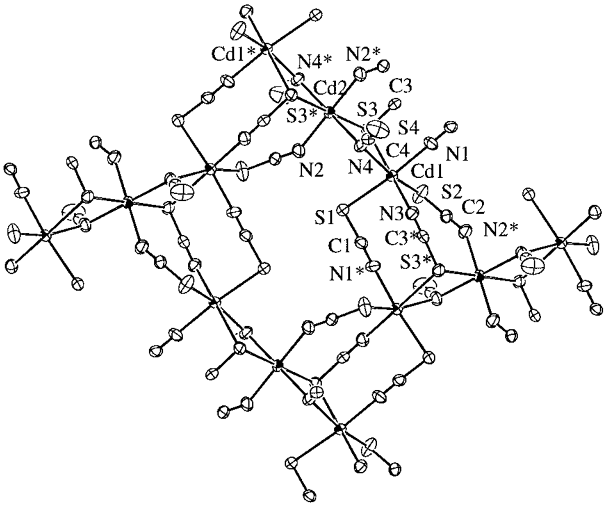

Figure 4. ORTEP diagram of $[Cd_3(SCN)_8{}^{2-}]_\infty$ layered structure in **2** (25% probability thermal ellipsoids). The symmetry-related atoms are labeled with asterisks. The central cadmium atoms (Cd2) of the tricadmium units are octahedrally coordinated with *trans*-S_2N_4 atoms, while the end ones (Cd1) atoms are octahedrally coordinated with *fac*-S_3N_3 atoms.

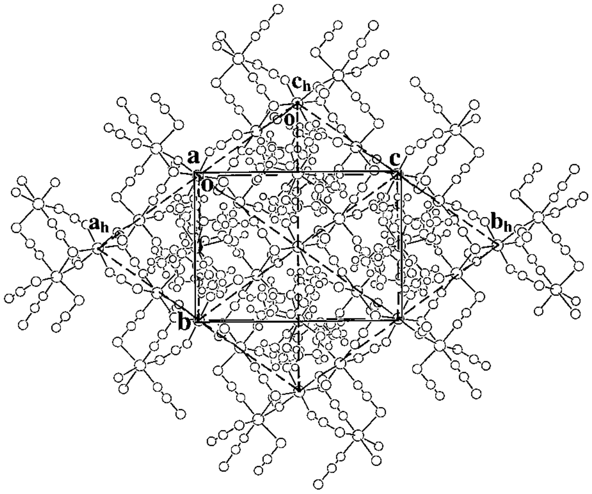

Figure 5. Unit cell diagram depicting the hexagonal motif of the layered structure of $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**). The crystallographic monoclinic unit cell is indicated by a, b, and c (solid lines), whereas the noncrystallographic hexagonal unit cell formed by the centers of the linear Cd_3 units (see Figure 2) are designated by a_h, b_h, and c_h (dashed lines). Note that $a_h = (b - c)$, $b_h = (b + c)$, $c_h = a$.

As portrayed in Figure 4, there are two crystallographically independent cadmium atoms in the $[Cd_3(SCN)_8]^{2-}$ unit: the central cadmium, Cd2, is located at an inversion center, while the end ones, Cd1 and Cd1*, are related by the same inversion symmetry. Cd1 is octahedrally coordinated with three S and three N atoms (in *fac* configuration, hereafter abbreviated as *fac*-S_3N_3), whereas Cd2 is octahedrally coordinated with two S and four N atoms, with the two sulfur atoms in *trans* configuration (hereafter designated as *trans*-S_2N_4). Within the Cd1 coordination sphere the S atoms are *trans* to the N atoms (S1 to N1, S3 to N3, and S2 to N4), in complete accord with the *trans* influence (S *trans* to N). In contrast, the configuration of the Cd2 coordination sphere violates the *trans* influence in that like atoms are *trans* to one another (i.e., S3 is *trans* to S3*, N2 to N2*, and N4 to N4*). The sandwich $[(12C4)_2Cd]^{2+}$ dication

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(13) The $[(12C4)_2Cd]^{2+}$ dications can be described as prolate objects with the long principal axis along the crystallographic b axis, with each $[(12C4)_2Cd]^{2+}$ cation protruding roughly 1/2 of its long axis into the "deep" hole (type A) of one $[Cd_2(SCN)_6{}^{2-}]_\infty$ layer and roughly 1/4 of the same axis into the "shallow" hole (type B) of an adjacent layer.

(14) Due to the fact that the $[Cd_2(NCS)_2]$ dimers are located at the crystallographic centers of symmetry, the layers are symmetrical on both sides insofar as the square arrangement of the bridging NCS^- groups are concerned. That is, along the crystallographic 2-fold rotational symmetry axes at $x = 0$ and $z = 1/4$ or 3/4, the arrangement of the holes is A·layer·A···B·layer·B···A·layer·A··· and so on. All the complementary interlayer voids of the type A···B are completely filled with $[(12C4)_2Cd]^{2+}$ dications. The S atoms of the bridging NCS^- groups of adjacent layers are aligned along the crystallographic b axis with S···S distances of ~4.4 Å. Taking 3.6 Å as the van der Waals distance between two sulfur atoms, there is a slight "exposed gap" of ~0.8 Å between the layers due to the bulk of the $[(12C4)_2Cd]^{2+}$ dications. Furthermore, the anionic $[Cd_2(SCN)_6{}^{2-}]_\infty$ layers are by no means planar. The slight corrugation of the layers creates complementary wavy layers.

Table 5. Comparisons of Average Cd−N and Cd−S Bond Lengths for the Various Types of Cadmium−Thiocyanate Coordinations in $[(12C4)_2Cd][Cd_2(SCN)_6]$ (**1**) and $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**)

cadmium−thiocyanate coordinations			average bond lengths (Å)	
			1	**2**
“bridging”	through nitrogen	Cd−N	2.451	2.410
“linkage”	in-plane	Cd−N	2.257	2.269
		Cd−S	2.680	2.641
	out-of-plane	Cd−N	2.346	
		Cd−S	2.673	
	out-of-plane/bridging through sulfur atom	Cd−N		2.320
		Cd−S		2.764, 3.038
	hybrid	Cd−N (in-plane)		2.236
		Cd−S (out-of-plane)		2.668

in **2** is centered at an inversion center and disordered due to the crystallographic inversion symmetry (−1), resulting in the point group symmetry of D_{4h} (instead of D_{4d} for the staggered configuration of the sandwich structure).

There are four crystallographically independent SCN^- ligands, exhibiting distinctively different bridging modes as portrayed in Figure 4. Adopting the terminology used in ref 9, the S(*n*)C(*n*)N(*n*) ligands, where $n = 1, 2, 3$, may be termed “linkage” thiocyanates, whereas S4C4N4 may be described as a “bridging” thiocyanate ligand (through N4) with a dangling sulfur atom (S4). However, unlike the structure of **1**, which has only two kinds (either in-plane or out-of-plane) of “linkage” SCN^- ligands, **2** has three types of linkage SCN^- ligands: the in-plane (S1C1N1), the out-of-plane (S3C3N3), and the peculiar hybrid (S2C2N2) consisting of in-plane (N2) and out-of-plane (S2) ligating atoms. Here “in” and “out” designate whether the ligating atom is “in” or “out” of the cadmium plane, respectively. Note that the sulfur atom, S3, of the out-of-plane linkage thiocyanate also serves as a doubly bridging ligand between two cadmium atoms (cf. Figure 4). Thus, the three Cd atoms within the linear Cd_3 unit are bridged by two nitrogen (N4) atoms from two “bridging” thiocyanates (N4C4S4) as well as two sulfur (S3) atoms from two “linkage” thiocyanates (S3C3N3) with Cd1···Cd2 distances of 3.90 Å. The latter are further coordinated to Cd1 of adjacent Cd_3 units. In fact, each linear Cd_3 unit is linked to four neighboring Cd_3 units via the three “linkage” thiocyanates: the in-plane S1C1N1, the hybrid (in/out-of-plane) S2C2N2, and the out-of-plane S3C3N3, with Cd2···Cd1* and Cd1···Cd1* distances of 5.81 and 5.85 Å, respectively. Note that the central Cd_3 unit is not linked to the two remaining neighboring Cd_3 units, which are of the same orientation (i.e. parallel), as per Figure 2.

The average Cd−N and Cd−S distances for the various types of thiocyanate coordination configurations in **1** and **2** are summarized in Table 5 for comparison. The following structural characteristics can be observed in both **1** and **2**. First, the Cd−N distances follow the trend in-plane (∼2.25 Å) < out-of-plane (∼2.35 Å) < bridging (∼2.45 Å). Second, the corresponding trend for the Cd−S distances is in-plane (∼2.65 Å) ∼ out-of-plane (∼2.65 Å) < bridging (2.76, 3.04 Å). It is apparent that the Cd−N bonds are much more sensitive than the Cd−S bonds to the configuration of the thiocyanate ligand with respect to the cadmium plane.

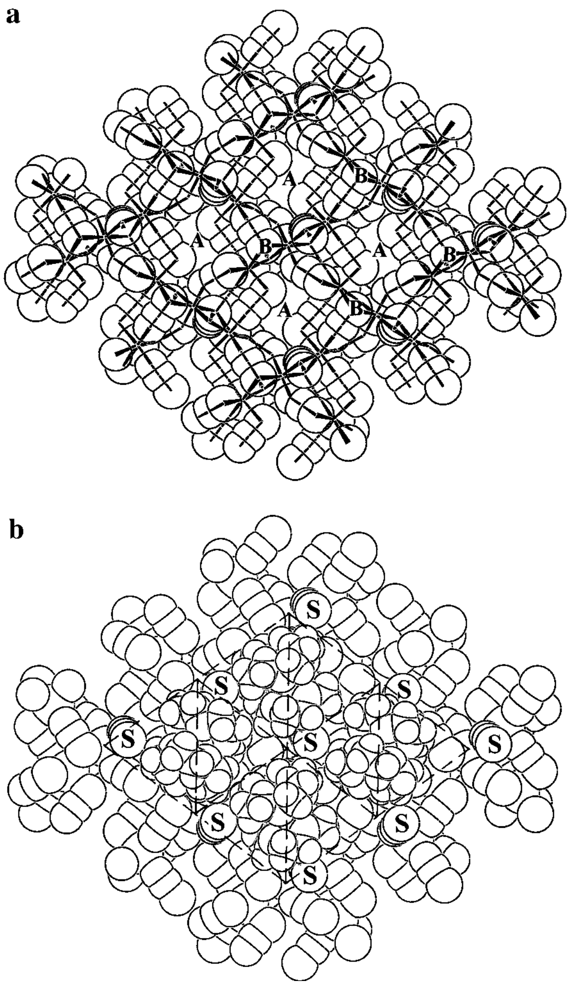

Figure 6. Space-filling diagrams (same view as Figure 5) of one layer of $[(12C4)_2Cd][Cd_3(SCN)_8]$ (**2**): (a) with the $[(12C4)_2Cd]^{2+}$ cations removed to expose the “deep” (type A) and the “shallow” (type B) holes; (b) with the $[(12C4)_2Cd]^{2+}$ dications. The sulfur atoms of the “bridging” (N4C4S4) ligands in b are labeled to highlight the highly distorted hexagonal net and the triangular holes created by these “dangling” S atoms. Also indicated is the noncrystallographic hexagonal unit cell formed by the linear Cd_3 units (dashed lines, same as in Figures 2 and 5). Note that the two hexagonal nets do not coincide (see text).

The space-filling model of **2** is portrayed in Figure 6a and b, with and without the $[(12C4)_2Cd]^{2+}$ dications, respectively. It can be seen that the “dangling” sulfur atoms (labeled as S in Figure 6b) of the “bridging” S4C4N4 ligands form a highly distorted hexagonal net of approximate dimensions $a_s = a_h/2$, $b_s = b_h/2$, and $c_s = c_h$, giving rise to highly distorted triangular holes. Here a_s, b_s, and c_s designate the highly distorted hexagonal network of “dangling” sulfurs (labeled as S in Figure 6b), whereas a_h, b_h, and c_h refer to the noncrystallographic hexagonal unit cell (dashed lines in Figures 2, 5, and 6b) of the metal framework mentioned above. Note that the *two hexagonal nets do not coincide*. Employing the same terminology used in the description of the structure of **1**, half of these triangular holes, which are filled with the $[(12C4)_2Cd]^{2+}$ dications, may be termed the “deep” (type A) holes. The other half, which are filled by the out-of-plane linkage S3C3N3 ligands, may be termed the “shallow” (type B) holes. The “deep” and “shallow” holes alternate within the same layer, as shown in Figure 6a. Taking into account the adjacent layers, the “deep” and “shallow” holes turn into highly distorted “octahedral” (type A) and “tetrahedral” (type B) holes, respectively, as depicted in the idealized schematic representation in Figure 7. The six dangling sulfurs, three from each of the neighboring layers (only one layer is shown), form “octahedral” (type A, solid circles) holes which encapsulate the $[(12C4)_2Cd]^{2+}$ dications with extensive hydrogen bonding. The “tetrahedral” (type B, shaded triangles) holes formed by four dangling sulfurs, three from one

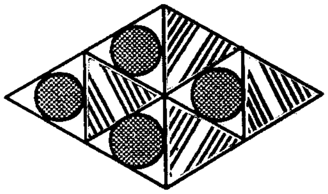

Figure 7. Schematic representation of one layer of the approximate hexagonal net of the "dangling" sulfur atoms (labeled with S in Figure 6b) of the $[Cd_3(SCN)_8{}^{2-}]_8$ layers in **2**. An approximately hexagonal close-packed (hcp) arrangement of the adjacent sulfur layers creates highly distorted octahedral holes which house the $[(12C4)_2Cd]^{2+}$ sandwich dications (solid circles) and tetrahedral holes which are filled with the out-of-plane linkage SCN^- (labeled S3C3N3 in Figure 3) ligands (shaded triangles). Note that the "octahedral" and "tetrahedral" holes correspond to the "deep" (type A) and "shallow" (type B) holes of individual layers shown in Figure 6a. The stripes in the shaded triangles illustrate schematically the orientations of the out-of-plane linkage thiocyanate ligands.

layer and one from the adjacent layer, are filled with the out-of-plane linkage SCN^- (labeled 3) ligands. In this regard, the arrangement of the dangling sulfur atoms may be likened to hexagonal close packing of spheres, producing one large octahedral hole and two smaller tetrahedral holes per sphere. Finally, we note that the layer spacing of 11.60 Å in **2** is significantly smaller than the corresponding value of 13.13 Å in **1** due to the fact that the dangling sulfur atoms of adjacent layers are intertwined in **2** but run "head on" in **1**.

Discussion and Conclusion

In summary, the $[(12C4)_2Cd]^{2+}$ dications in **1** and **2** serve not only as the "spacer" and "controller" of the crystal packing, but also as a "template" for the formation of the novel two-dimensional (2-D) motif of cadmium−thiocyanate coordination solids.[15] The interesting feature, demonstrated in this paper, is that the same $[(12C4)_2Cd]^{2+}$ dication template can arrange in two different orientations with respect to the cadmium−thiocyanate layers, giving rise to two distinctly different 2-D structures. Specifically, a comparison of the structures of **1** and **2** revealed that while the $[(12C4)_2Cd]^{2+}$ dications in **1** are oriented in the "upright" position, the $[(12C4)_2Cd]^{2+}$ dications in **2** are lying almost "sideways" with respect to the $[Cd_3(SCN)_8{}^{2-}]_\infty$ layers. More precisely, the 12C4 ligands of the $[(12C4)_2Cd]^{2+}$ dications (as represented by the least-squares planes passing through the oxygen atoms) make angles of 0° (upright) and 70.2(1)° (sideways) in **1** and **2**, respectively, with respect to the anionic cadmium−thiocyanate layers (as represented by the least-squares plane passing through the cadmium atoms), as depicted schematically in Figure 8. A systematic study of the effect of the cations of varying size, shape, and charge on the crystal structures of the resulting cadmium−thiocyanate coordination solids is under way in order to shed light on this anisotropic templating effect.

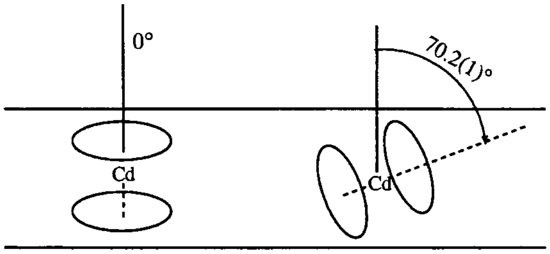

Figure 8. Schematic representation of the relative orientations of the $[(12C4)_2Cd]^{2+}$ dications with respect to the cadmium−thiocyanate layers: (a) "upright" (0°) in **1**; and (b) approximately "sideways" (70.2(1)°) in **2**.

Acknowledgment is made to the National Science Foundation (U.S.A.) for financial support of this research. We also thank H. Zang and N. Yang for their assistance in the collection of the X-ray diffraction data.

Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The use of (crown-ether)−(alkali-metal) complexes as templates in the synthesis of zeolite crystals is well established. See, for example: Delprato, F.; Delmotte, L.; Guth, J. L.; Huve, L. *Zeolites* **1990**, *10*, 546−552.