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Molecular Design and Crystal Engineering of a New Series of Inorganic Polymers Separated by Organic Spacers: Structures of $[(18C6)K][Cd(SCN)_3]$ and $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$

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Abstract: This paper reports the synthesis and structures of two key members, $[(18C6)K][Cd(SCN)_3]$ (**1**) and $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**2**), of a new *inorganic polymers* with *organic spacers* (IPOS) series with the general formula [H−G][M−L], where the organic cation $[H-G]^{q+}$ is a host (H)−guest (G) complex such as [(crown ether)−(alkali metal)]$^+$ and the inorganic anion $[M-L]^{q-}$ is a metal (M)−ligand (L) coordination polymer such as $[Cd(SCN)_3^-]_\infty$. **1** and **2** were prepared from 18C6, MSCN, and $CdSO_4$ where $M = K^+$ (for **1**) and Na^+ (for **2**), respectively. **1** crystallizes in an orthorhombic unit cell of $Cmc2_1$ space group symmetry with lattice parameters $a = 14.734(3)$ Å, $b = 15.304(2)$ Å, $c = 10.625(3)$ Å; $V = 2396(1)$ Å^3, and $Z = 4$. The structure was refined to $R_1 = 2.3\%$ for 878 independent reflections ($2\theta \leq 46°$) with $I > 3\sigma$. **2** crystallizes in a monoclinic unit cell of $P2_1/n$ space group symmetry with lattice parameters $a = 10.277(3)$ Å, $b = 10.915(5)$ Å, $c = 22.596(7)$ Å, $\beta = 111.48(5)°$; $V = 2359(5)$ Å^3, and $Z = 4$. The structure was refined to $R_1 = 3.7\%$ for 2415 independent reflections ($2\theta \leq 46°$) with $I > 3\sigma$. These crystals exhibit interesting physical properties such as nonlinear optical effects (NLO). The novel features of this particular IPOS series, as exemplified by the title compounds, as tailorable crystalline materials are (1) the anions form *isolated polymeric one-dimensional* zig-zag chains of $[Cd(SCN)_3^-]_\infty$ with *extended π-conjugation* system within the polymeric $-[M-S-C\equiv N]-M\cdots$ chain and high polarizabilities (which are important for NLO effects); and (2) the cationic host−guest complex [(18C6)M]$^+$ serves as a spacer/controller of the crystal structure and crystal symmetry. The most important characteristic of the IPOS system reported herein is that it allows concomitant but separate *molecular* and *crystal engineering* (i.e., design of molecular structures and crystal packings in two independent controls). A detailed analysis of the structures of **1** and **2** revealed *parallel* and *antiparallel* arrangements, respectively, of the infinite anionic $[Cd(SCN)_3^-]_\infty$ polymeric zig-zag chains; such arrangements are presumably dictated by the monomeric and dimeric host−guest [(18C6)M]$^+$ cations. General design strategies, in terms of symmetry control, as well as molecular and crystal engineering, in terms of electronic and stereochemical controls, are discussed. Furthermore, the structures of the title crystals may be considered as "crystal host−guest clathrates" in which the infinite anionic polymeric $[Cd(SCN)_3^-]_\infty$ chains form an approximate square motif, creating square channels which are filled by "molecular host−guest complexes" such as [(18C6)K]$^+$ (in **1**) or $[(18C6)_2Na_2(H_2O)_2]^{2+}$ (in **2**).

I. Introduction

One way to take advantage of the superior qualities of both *inorganic* and *organic* materials is to combine them in the same compound. One such hybrid system we have chosen is a new class of *inorganic polymers* with *organic spacers* (IPOS) with the general formula [H−G][M−L] where the organic cation $[H-G]^{q+}$ is a host (H)−guest (G) complex and the inorganic anion $[M-L]^{q-}$ is a metal (M)−ligand (L) coordination complex or polymer as illustrated schematically in Chart 1. Examples of each of these components are H = crown ethers, cryptands, etc.;[1−4] G = alkali metal, alkali-earth metals, etc.; M = transition metals; L = anionic ligands such as SCN$^-$, SeCN$^-$, TeCN$^-$, CN$^-$, halides, etc.[5]

This paper reports the synthesis and structures of two key members of this IPOS series, namely, $[(18C6)K][Cd(SCN)_3]$ (**1**) and $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**2**). These crystals exhibit interesting physical properties such as nonlinear optical effects (NLO).[6−12] A detailed analysis of the structures of **1** and **2** revealed parallel and antiparallel arrangements of the

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infinite anionic $[Cd(SCN)_3^-]_\infty$ chains, respectively. This, we believe, is caused by the ionic and van der Waals interactions of the one-dimensional anionic polymeric chains with the monomeric and dimeric host−guest (crown ether)−(alkali metal) cations. In this context, the title compounds represent first examples of the IPOS system in which one can exert substantial control over the crystal symmetry by tuning the stereochemistry of the molecular (cationic) host−guest complexes $[(18C6)M]^+$ ($M^+ = K^+$, Na^+), thereby dictating the arrangement of the anionic polymeric $[Cd(SCN)_3^-]_\infty$ chains and the formation of desirable crystal host−guest clathrate compounds.

It is hoped that a systematic study of the synthesis and structure of the IPOS system will not only lead to the discovery of new and interesting materials but also enable us to develop new strategies in materials fabrication at the *molecular engineering* level as well as to discover new patterns for crystallization at the *crystal engineering* level.[6−14] Finally, the structural principles and/or synthetic strategies developed in this paper may also be useful for other related systems.

II. Experiments

All starting materials (Aldrich Chemicals) used were of reagent grade. Triply distilled water was used in the preparation of the solutions.

Preparations and Physical Measurements. *$[(18C6)M]^+[Cd(SCN)_3]^-$ ($M = K^+$ (**1**); Na^+ (**2**)).* To a 0.2 M aqueous solution of $CdSO_4$ (10 mL) was added 3 equiv (6 mL) of a 1 M aqueous solution of MSCN. The solution mixture was stirred for an hour, and then 4 mL of a 0.5 M aqueous solution of the crown ether $C_{12}H_{24}O_6$ (18C6) was added in a dropwise manner. (Care must be taken to avoid supersaturation and formation of precipitates during the addition.) Colorless crystals suitable for X-ray diffraction study were grown from the solution mixture in a few days. Needle crystals measuring centimeters in length and millimeters in widths have also been grown from silica gel by one of us and reported elsewhere.[15] Spectroscopic and analytical results such as IR (indicating the presence of the bidentate SCN^- ligands and the presence of 18C6), X-ray photoelectron spectroscopy, X-ray powder diffraction, and elemental analysis can also be found in ref 15. Nonlinear optical measurements[15] for powder samples of **1** and **2** using the standard Kurtz and Perry[16] technique indicated that **1** exhibits nonlinear optical effect with a SHG coefficient equivalent to about 200 times that of quartz (or 10 times higher than that of ADP). No SHG effect was observed for **2**. The title compounds are *transparent* in the visible and ultraviolet region, making them useful hybrid NLO crystal materials.

Table 1. Summary of Crystal Data, Collection and Reduction of X-ray Diffraction Data, and Solution and Refinement of Structures of $[(18C6)K][Cd(SCN)_3]$ (**1**) and $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**2**)

	1	**2**
formula	$CdKS_3O_6N_3C_{15}H_{24}$	$CdNaS_3O_7N_3C_{15}H_{26}$
a, Å	14.734(3)	10.277(3)
b, Å	15.304(2)	10.915(5)
c, Å	10.625(3)	22.596(7)
β, deg		111.48(5)
V, Å^3	2396(1)	2359(5)
Z	4	4
space group	$Cmc2_1$	$P2_1/n$
ρ_{cal} (g cm^{-1})	1.64	1.67
λ (Å)[a]	0.7107	0.7107
T (°C)	23 ± 2	23 ± 2
$R(F_o)$[b]	0.023	0.037
$R_w(F_o)$[c]	0.026	0.041

[a] Graphite monochromator. [b] $R(F_o) = [\sum||F_o| - |F_c||/\sum|F_o|]$. [c] $R_w(F_o) = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2}$.

X-ray Crystallography. *(a) Collection and Reduction of X-ray Data.* A colorless needle shape crystal of **1** with dimensions 0.30 mm × 0.22 mm × 0.20 mm and a colorless plate shape crystal of **2** with dimensions 0.32 mm × 0.26 mm × 0.24 mm were selected and mounted on glass fiber with epoxy resin. Room-temperature (23 ± 2 °C) single-crystal X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å). The observed intensities were corrected for Lorentz, polarization, and absorption (ψ-scan) effects. Details of the crystal parameters and data collection for **1** and **2** are summarized in Table 1. Wilson plot of the data favored the acentric space group $Cmc2_1$ for **1** and the centric space group $P2_1/n$ for **2**. These space-group determinations were later confirmed by the successful solution and refinement of the structures.

(b) Solution and Refinement of the Structures. The crystal structures of both title compounds **1** and **2** were solved by using the Enraf-Nonius SDP package. Positions of the Cd, K, and SCN were obtained from direct methods, and 18C6 atoms were located via Fourier syntheses. In **1**, there are four $[(18C6)K]^+[Cd(SCN)_3]^-$ units per unit cell ($Z = 4$). Since the Cd^{2+} ion, one SCN^- ligand and the $[(18C6)K]^+$ cation in **1** are located on the crystallographic mirror along a, the analysis of the structure required the location of one Cd^{2+} ion, two SCN^- ligands, one K^+ cation, and four oxygen and six carbon atoms of the 18C6 ligand under $Cmc2_1$ space group. In **2**, there are four $[(18C6)Na(H_2O)]^+[Cd(SCN)_3]^-$ units per unit cell ($Z = 4$) or, in terms of the dimeric cations, two $[(18C6)_2Na_2(H_2O)_2][Cd(SCN)_3]_2$ units per unit cell. Since all atoms are in general positions, the structure analysis of **2** required the location of one Cd^{2+} ion, three SCN^- ligands, one Na^+ ion, one water molecule, and six oxygen and twelve carbon atoms of the 18C6 ligand. In the final cycles of least-squares refinement, anisotropic thermal parameters were used for all non-hydrogen atoms. Idealized hydrogen atom positions (C−H, 0.95 Å) were included in the calculations but not refined. Final $R_1 = [\sum(|F_o| - |F_c|/|F_o|] \times 100\%$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ values were 2.3% and 2.6% for 878 unique reflections with $I > 3\sigma(I)$ for **1**, and 3.7% and 4.1% for 2415 unique reflections with $I > 3\sigma(I)$ for **2**, respectively. The final difference map showed no peaks greater than 0.5 e/Å^3 except those close (<1.5 Å) to the Cd atoms. Selected interatomic distances and bond angles, together with the estimated standard deviations, are given in Table 2. Completed crystallographic and structural details are provided in the Supporting Information.

III. Results

(A) Syntheses. The title compounds were prepared according to the following reactions:

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Table 2. Selected Bond Lengths (Å) and Angles (deg) and Their Estimated Standard Deviations for $[(18C6)K][Cd(SCN)_3]$ (**1**) and $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**2**)

	1		
Cd−S1	2.703(2)	Cd−S2	2.760(2)
Cd−N1	2.286(7)	Cd−N2	2.317(5)
S1−C1	1.636(9)	S2−C2	1.658(6)
N1−C1	1.13(1)	N2−C2	1.14(1)
K−O1	2.901(8)	K−O2	2.876(5)
K−O3	2.872(5)	K−O4	2.846(7)
S1−Cd−S2	83.70(5)	S1−Cd−N1	174.6(2)
S1−Cd−N2	91.1(1)	S2−Cd−S2	89.43(5)
S2−Cd−N1	92.5(1)	S2−Cd−N2	174.2(1)
S2−Cd−N2	92.5(1)	N1−Cd−N2	92.9(2)
N2−Cd−N2	85.1(2)	Cd−S1−C1	92.6(3)
Cd−S2−C2	98.4(2)	Cd−N1−C1	158.8(6)
Cd−N2−C2	143.9(5)	S1−C1−N1	178.9(8)
S2−C2−N2	179.1(5)		
	2		
Cd−S1	2.744(2)	Cd−S2	2.753(2)
Cd−S3	2.698(2)	Cd−N1	2.378(5)
Cd−N2	2.305(7)	Cd−N3	2.274(5)
S1−C1	1.639(7)	S2−C2	1.657(7)
S3−C3	1.642(7)	N1−C1	1.16(3)
N2−C2	1.14(2)	N3−C3	1.15(3)
Na−O1	2.551(5)	Na−O1	2.929(6)
Na−O2	2.575(7)	Na−O3	2.603(8)
Na−O4	2.828(7)	Na−O5	2.631(8)
Na−O6	2.615(7)	Na−O7w	2.313(5)
S1−Cd−S2	96.74(6)	S1−Cd−S3	87.34(6)
S1−Cd−N1	173.8(2)	S1−Cd−N2	91.5(1)
S1−Cd−N3	89.5(1)	S2−Cd−S3	83.69(6)
S2−Cd−N1	89.1(2)	S2−Cd−N2	169.3(2)
S2−Cd−N3	89.1(2)	S3−Cd−N1	91.3(2)
S3−Cd−N2	90.0(2)	S3−Cd−N3	171.8(2)
N1−Cd−N2	82.4(2)	N1−Cd−N3	92.6(2)
N2−Cd−N3	97.6(2)	Cd−S1−C1	100.9(2)
Cd−S2−C2	101.7(3)	Cd−S3−C3	96.1(2)
Cd−N1−C1	146.2(3)	Cd−N2−C2	146.1(3)
Cd−N3−C3	156.9(3)	S1−C1−N1	179.1(4)
S2−C2−N2	179.5(5)	S3−C3−N3	178.8(4)
O1−Na−O1	73.5(1)	O1−Na−O7w	177.7(3)
O1−Na−O7w	105.4(2)	Na−O1−Na	106.5(2)

$$18C6 + 3KSCN + CdSO_4 \xrightarrow{H_2O} \underset{\mathbf{1}}{[(18C6)K][Cd(SCN)_3]} + K_2SO_4 \quad (1)$$

$$18C6 + 3NaSCN + CdSO_4 + H_2O \xrightarrow{H_2O} \underset{\mathbf{2}}{[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]} + Na_2SO_4 \quad (2)$$

Thiocyanate is an ambidentate ligand with two donor atoms. In accordance with Pearson's hard−soft acid−base concept,[17] the S atom of the SCN^- ligand, being a soft base, preferentially coordinates to the Cd^{2+} ion (with a d^{10} configuration) which may be considered as a soft acid. With proper stoichiometry, the ambidentate nature of the SCN^- ligand allows the formation of bridges between metal atoms which, in the present case, results in the formation of the anionic polymeric chain $[Cd(SCN)_3{}^-]_\infty$. The alkali metals, on the other hand, are preferentially coordinated by the oxygen atoms of the crown ethers 18C6 via size selectivity, giving rise to the cationic $[(18C6)M]^+$ ($M^+ = K^+$ (**1**), Na^+ (**2**)) complexes. The coexistence of the cationic host−guest complexes and the anionic inorganic polymeric chains in the solid state via ionic interactions gives rise to the IPOS systems. It should be mentioned that many examples of inorganic compounds which incorporate crown ether complexes of alkali metals can be found in the literature.[4g] Furthermore, a number of inorganic metal−thiocyanate complexes are also known to exhibit polymeric structures. For example, in $RbCd(SCN)_3$, octahedral Cd complexes are connected by Cd−S−C−N−Cd moieties to form two-dimensional arrays whereas the structure of $CsCd(SCN)_3$ is built up by Cd octahedra, linked in the same way, to form a three-dimensional framework.[5b] The low (one) dimensionality of the title compounds $[(18C6)M][Cd(SCN)_3]$ ($M^+{=}K^+$(**1**), Na^+(**2**)) is made possible by the cationic (crown ether)−(alkali metal) complexes acting as spacers (in between the chains) as well as controllers of the crystal structure (vide infra).

Chart 1. Four Components of the IPOS System

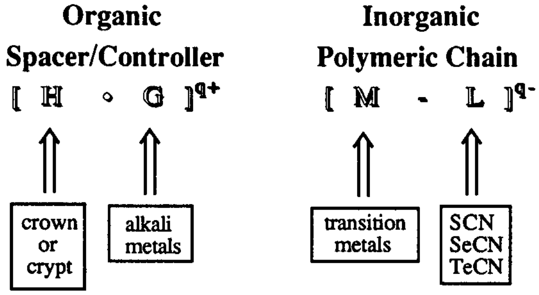
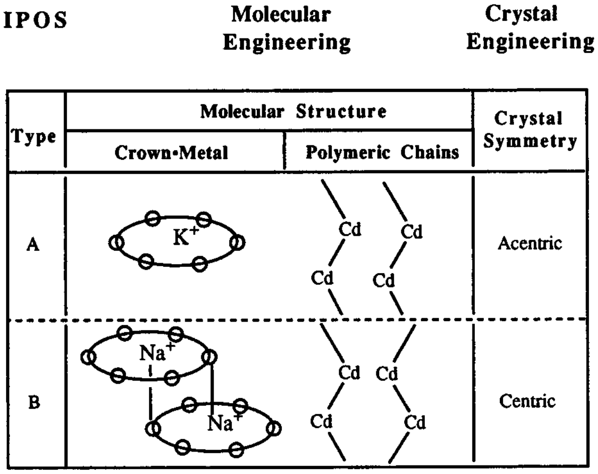


Chart 2. Molecular and Crystal Engineering of the IPOS System $[18C6{\cdot}M]^+[Cd(SCN)_3]^-$: Type A, $M = K^+$; Type B, $M = Na^+$



(B) Pattern of Crystallization. As shown in Chart 2, $[(18C6)M]^+[Cd(SCN)_3]^-$, where $M^+ = K^+$ and Na^+, crystallize in two different crystal systems which we shall refer to as types A and B, respectively. With the monomeric $[(18C6)K]^+$ monocation, as in **1**, the crystal adopts an acentric space group $Cmc2_1$ (type A). In contrast, the dimeric $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dication, as in **2**, tend to reside at crystallographic inversion centers, giving rise to centric space group $P2_1/n$ (type B).

The polymeric $[Cd(SCN)_3{}^-]_\infty$ chains in **1** (type A) are "parallel" to one another, as depicted in the crystal packing diagram Figure 1a. The corresponding chains in **2** (type B) are "antiparallel" and related by inversion centers, as depicted in the crystal packing diagram Figure 2a.

(C) Crystal Structures. *(a) [(18C6)K][Cd(SCN)3] (1).* The crystal structure of **1** is depicted in Figure 1a,b, as viewed along the crystallographic *a* (approximate) and *c* axes, respectively. There are four $[(18C6)K][Cd(SCN)_3]$ ($Z = 4$) per unit cell. The four Cd^{2+} atoms per unit cell are located at (0, −0.030, 0), (0, 0.030, 0.5), (0.5, 0.470, 0), and (0.5, 0.530, 0.5). As shown in Figure 1b, the former two Cd^{2+} atoms form a zig-zag chain along the 2_1 screw axis along the crystallographic *c* axis at $x = 0$, $y = 0$ while the latter two along the 2_1 axis along *c* at $x =$

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[17] Pearson, G. S. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 177.

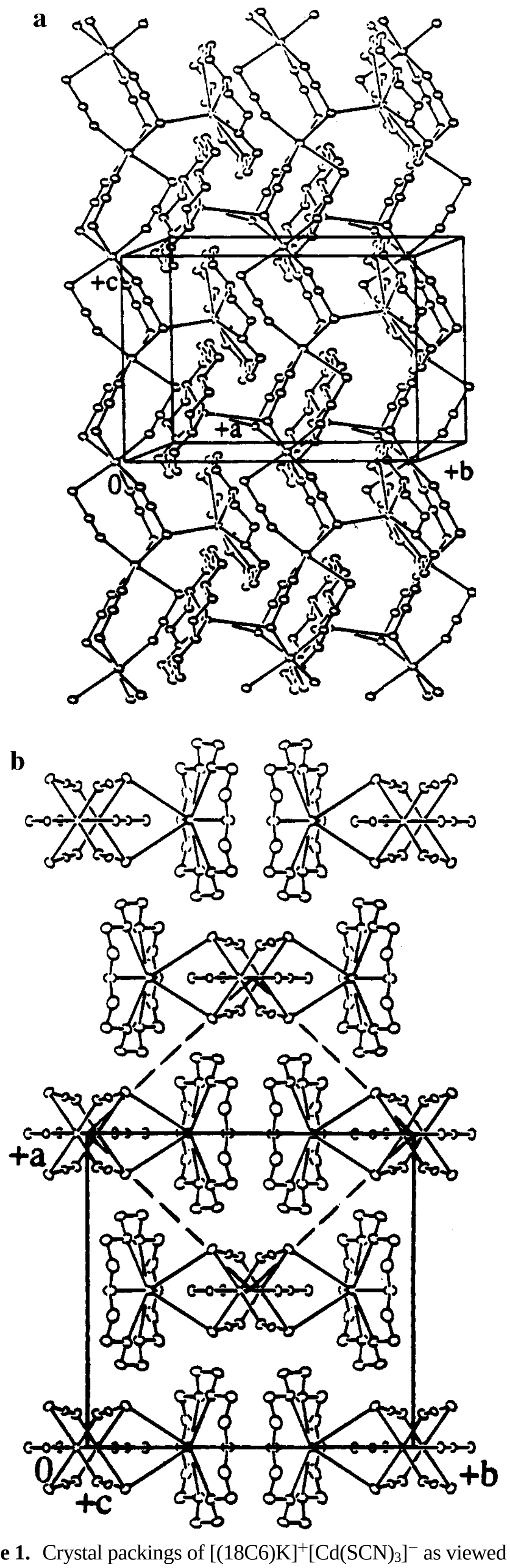


Figure 1. Crystal packings of $[(18C6)K]^+[Cd(SCN)_3]^-$ as viewed along (a) approximately the crystallographic *a* axis and (b) the crystallographic *c* axis. Note that the zig-zag $[Cd(SCN)_3{}^-]_\infty$ chains are "parallel" to one another and run along the crystallographic *c* axis.

$^1/_2$, $y = {}^1/_2$. These two chains are related by C-centering. There are no cadmium chains at 2_1 axis along *c* at $x = {}^1/_4$, $y = {}^1/_4$ or at $x = {}^3/_4$, $y = {}^3/_4$ (which are also related by C-centering).

The four $[(18C6)K]^+$ cations per unit cell are located at (0.5, 0.187, 0.190), (0.5, 0.813, 0.690), (0, 0.687, 0.190), and (0, 0.313, 0.690) which are also the coordinates of the K^+ cations.

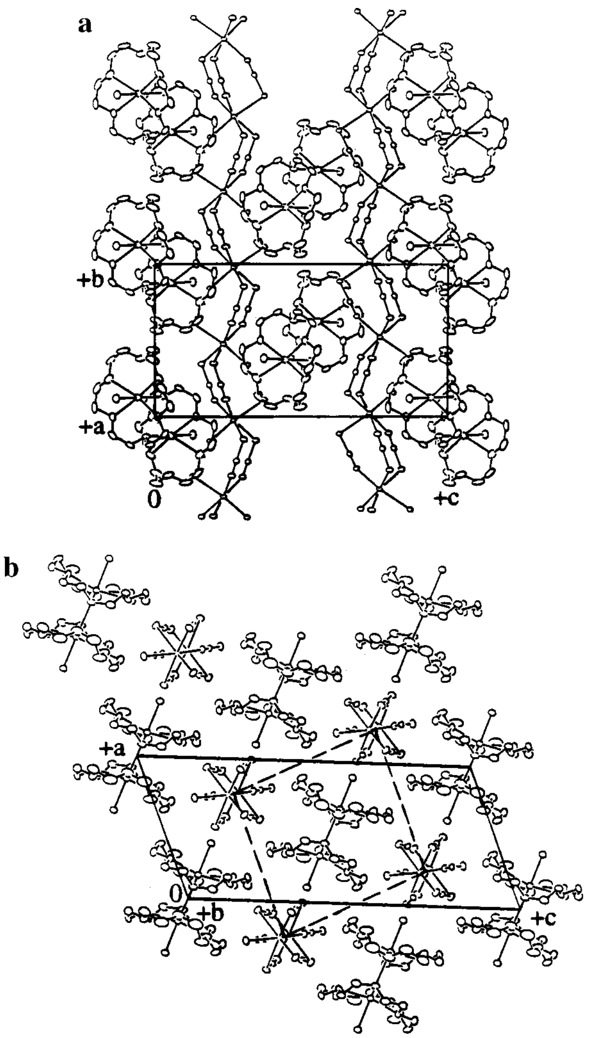


Figure 2. Crystal packings of $[(18C6)_2Na_2(H_2O)_2]_{1/2}{}^+[Cd(SCN)_3]^-$ as viewed along (a) the crystallographic *a* axis and (b) the crystallographic *b* axis. Note that the zig-zag $[Cd(SCN)_3{}^-]_\infty$ chains are "antiparallel" to one another and run along the crystallographic *b* axis.

The $[(18C6)K]^+$ cations fill the channels created by the infinite $[Cd(SCN)_3{}^-]_\infty$ chains (vide infra).

(b) $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ *(2).* The crystal structure of **2**, as depicted in Figure 2a,b viewed along the crystallographic *a* and *b* axes, respectively, can be described as infinite anionic chains of $[Cd(SCN)_3{}^-]_\infty$ separated by dimeric $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dications. There are four formula units $[(18C6)Na(H_2O)][Cd(SCN)_3]$ per unit cell. The four Cd^{2+} atoms per unit cell have coordinates of (0.235, 0.022, 0.733), (0.265, 0.522, 0.767), (0.735, 0.478, 0.233), and (0.765, 0.978, 0.267). The former two cadmium atoms form the zig-zag chain at $x = {}^1/_4$ and $z = {}^3/_4$, whereas the latter two constitute the zig-zag chain at $x = {}^3/_4$ and $z = {}^1/_4$. Hence, there are two infinite $[Cd(SCN)_3{}^-]_\infty$ chains per unit cell which wind around 2_1 axes along *b* direction.

As portrayed in Figure 2b, the dicationic dimers $[(18C6)_2Na_2(H_2O)_2]^{2+}$ in **2** reside at the crystallographic inversion centers. The four Na^+ ions per unit cell are located at (−0.167, 0.126, −0.056), (0.167, −0.126, 0.056), (0.333, 0.374, 0.444), and (0.667, 0.626, 0.556). The former two sodium atoms form a dimer at (0, 0, 0) whereas the latter two constitute the dimer at ($^1/_2$, $^1/_2$, $^1/_2$). The implication of this dimer formation in crystal engineering will be discussed later.

(**D**) **Host−Guest Cations.** Since the K^+ ion, with a diameter of 2.66 Å, is of the right size to fit into the 18C6 hole (cavity

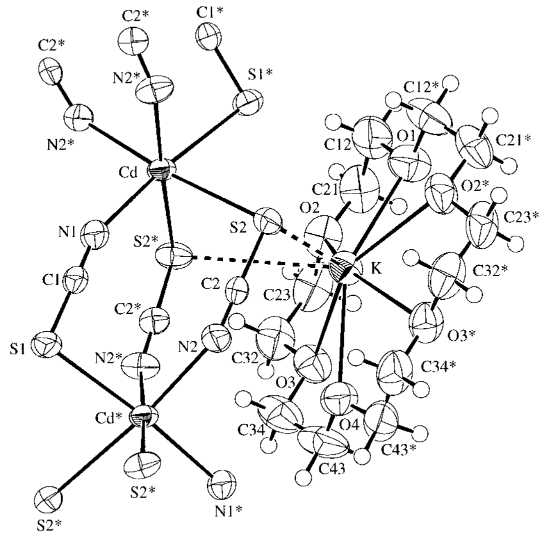


Figure 3. Pseudo-eight-coordinated K^+ ion forms six K−O bonds with the six oxygen atoms of 18C6 and two van der Waals contacts to two sulfur atoms of the anionic $[Cd(SCN)_3]^-$ chain (50% thermal ellipsoids).

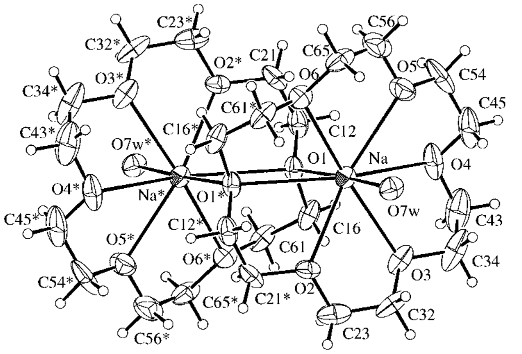


Figure 4. Dimeric $[(18C6)_2Na_2(H_2O)_2]^{2+}$ complex in which each Na^+ ion is eight-coordinated, forming six Na−O bonds with 18C6, one Na−O bond with one of the oxygen atoms of the other 18C6 and one Na−O_w bond with a water molecule (25% thermal ellipsoids).

diameter 2.67−2.86 Å), the $[(18C6)K]^+$ cation in **1** forms a 1:1 monomeric complex which is located on the mirror along *a*. The mirror bisects the $[(18C6)K]^+$ cation which is portrayed in Figure 3 (see also Figure S1(a),(b) of the Supporting Information for different views). The 18C6 ligand is crystallographically ordered with normal ethylene ($-CH_2CH_2-$) configuration. The six oxygen atoms form a six-membered ring which is virtually coplanar (see Table E of the Supporting Information). The central K^+ ion has six K^+−O bonds ranging from 2.846(7) to 2.901(8) Å and is 0.73 Å out of the average plane of the six oxygen atoms (Table E of the Supporting Information), presumably due to the interaction with the anionic $[Cd(SCN)_3^-]_\infty$ chains. In fact, as depicted in Figure 3, there are two van der Waals $K^+\cdots S$ contacts of 3.62 Å. In this context, the K^+ ions may be described as pseudo-eight-coordinated.

Since the Na^+ ion, with a diameter of 1.90 Å, is smaller than the cavity of 18C6, it instead forms a dimer with two terminal water molecules $[(18C6)_2Na_2(H_2O)_2]^{2+}$, as portrayed in Figure 4 (see also Figure S2(a),(b) of the Supporting Information for different views). It is obvious that the "mismatch" in the size of the Na^+ ion and the 18C6 hole causes the dimer formation. The centrosymmetric dimeric cations reside at the crystallographic center of symmetry (−1). Here the two 18C6 ligands are bent back (away from the center of the dimer), resulting in a "saddle" shape as portrayed in Figure S2(a) of the Supporting Information. The six oxygen atoms of each of the 18C6, however, adopt a "boat" shape (Figure S2(a),(b) and Table F of the Supporting Information). The central Na^+ ion has six Na^+−O bonds ranging from 2.551(5) to 2.828(7) Å and is 0.37 Å out of the average plane of four virtually planar oxygen atoms (O2, O3, O5, and O6) of 18C6. The remaining two oxygen atoms, O1 and O4, from the same 18C6 ligand are also 1.04 and 0.95 Å, respectively, out of the same plane and on the same side as the Na^+ ion, as depicted in Figure S2(b) of the Supporting Information. The Na^+ is further coordinated by one oxygen atom (O_1*) from the other 18C6 ligand with a Na^+−O_1* distance of 2.929(6) Å and a water molecule with a Na^+−O_w distance of 2.313(5) Å. As a result, each Na^+ ion is eight-coordinated; the local coordination can be described as a highly distorted hexagonal bipyramid with the O_1* and O_w occupying the axial positions (Figure 4).

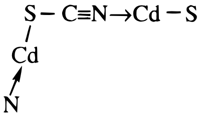
To the best of our knowledge, the observed 2:2 dimeric structure of the $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dication in **2** is a new form of $[(18C6)Na]^+$. It is distinctly different from that of the structure of the 1:1 monomer of $[(18C6)Na(H_2O)]^+(SCN)^-$ in which the Na^+ ion is coordinated by an incompletely coiled 18C6 ligand and a water molecule, rendering a highly distorted pentagonal-bipyramidal coordination of Na^+ with one oxygen atom from the 18C6 and the water molecule as the axial ligands.[4] It is also different from that of the 2:2 dimer of $[(18C6)Cs(SCN)]_2$ in which the big Cs^+ ions sit atop the 18C6 ligands and are bridged by two SCN^- ligands.[4] Further structural examples of crown ether−alkali metal complexes will be discussed in a later section.

(E) Infinite Anionic $[Cd(SCN)_3^-]_\infty$ Chains. The anionic $[Cd(SCN)_3^-]_\infty$ chains in **1** and **2** are very similar. In both structures, the Cd atoms are octahedrally coordinated with three nitrogen and three sulfur atoms, from six SCN^- ligands as illustrated in Figure 3 for **1** (for **2**, see Figure S3 of the Supporting Information). The trans influence dictates that the sulfurs are trans to the nitrogens. The three N−Cd−S angles average to 174.3° in **1** and 171.6° in **2**; both are very close to linearity. The Cd atoms form an infinite zig-zag chain of Cd atoms with Cd⋯Cd distances of 5.39 and 5.51 Å and Cd⋯Cd⋯Cd angles of 160.2° and 164.7° in **1** and **2**, respectively (see Chart 2). The zig-zag chains are "parallel" to one another and run along the crystallographic *c* axis in **1** but are "antiparallel" to one another and run along the crystallographic *b* axis in **2**. If we include the bridging thiocyanate ligands, there are three infinite zig-zag chains of $-[S-C{\equiv}N-Cd]_\infty-$winding around the crystallographic 2_1 axes along *c* (in **1**) or *b* (in **2**). The net result is three zig-zag $-[S-C{\equiv}N-Cd]_\infty-$ chains bundled around the central zig-zag Cd⋯Cd chain, with Cd atoms as knots (Figures 1a and 2a). These metal−thiocyanate chains make ~90° kinks at the sulfur atoms and ~20° bents at the nitrogen atoms, resulting in nearly collinear five-atom fragments S−C−N−Cd−S (see Table 2).

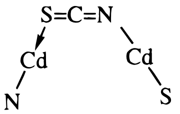
We shall describe the salient structural features of the $-[S-C{\equiv}N-Cd]_\infty-$ chains and their bonding implications, first using **1** as an example. In **1**, one of the three $-[S-C{\equiv}N-Cd]_\infty-$ chains (S1−C1−N1) lie in the crystallographic mirror plane along *a* (i.e., the *bc* plane) with Cd−S1−C1, S1−C1−N1, C1−N1−Cd, and N1−Cd−S1 angles of 92.6(3)°, 178.9(8)°, 158.8(6)°, and 174.6(2)°, respectively. The remaining two chains (S2C2N2 and S2*C2*N2*) are related by the same crystallographic reflection plane (see Figure 1a). The corresponding Cd−S2−C2, S2−C2−N2, C2−N2−Cd, and N2−Cd−S2 angles are 98.4(2)°, 179.1(5)°, 143.9(5)°, and 174.2(1)°, respectively (see Table 2).

The average S−C and C−N distances of 1.651 and 1.138 Å in **1** indicate a partial π-delocalization along the metal−

thiocyanate chains. This observation is consistent with the fact that the SCN$^-$ ligand is easily polarizable ($^-$S−C≡N ↔ S=C=N$^-$). The observed C−N−Cd angle of 158.8(6)° in **1** indicates that the bonding picture is somewhere between the following two limiting *canonical* forms I and II:

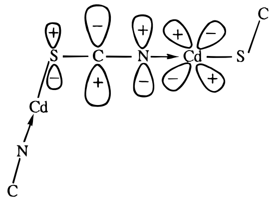


I

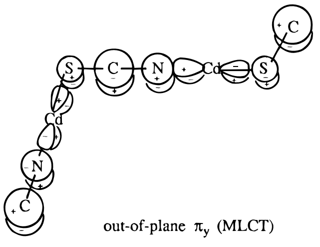


II

With only two exceptions, all Cd−S−C−N−Cd moieties in the chains are coplanar, indicating that descriptions I is more appropriate than description II. The exceptions are as follows: in **1**, plane Cd−S2−C2 makes an angle of 32.44° with plane C2−N2−Cd; and in **2**, plane Cd−S2−C2 makes an anlge of 20.08° with plane C2−N2−Cd. We note that the idealized angle between Cd−S−C and C−N−Cd planes in forms I and II should be 0° and 90°, respectively. Notice that there is a greater degree of partial π-delocalization along the chains in the canonical form I since there are two π-bonds (instead of one in II) in the C≡N moiety of the SCN$^-$ ligand and that the N→Cd bond is a dative bond which, by synergic effect, should enhance the metal-to-ligand π-back-donation (in addition to the ligand-to-metal σ- and π-donations). One component, the out-of-plane component, π_y, runs through the infinite $-(\mathrm{S{-}C{\equiv}N{-}Cd})_\infty-$ chain, while the in-plane component, π_x, is limited to the five-atom S−C≡N−Cd−S fragment as depicted below:



in-plane π_x (MLCT)



out-of-plane π_y (MLCT)

In fact, the observed C−N−Cd angle can be used as a gauge of the metal-to-ligand charge transfer (MLCT). In other words, as the C−N−Cd angle increases, the in-plane metal-to-ligand π-back-donation, π_x, increases and is maximized when the five-atom moiety S−C≡N−Cd−S becomes linear, thereby enhancing the partial π-delocalization along the infinite $-[\mathrm{S{-}C{\equiv}N{-}Cd}]_\infty-$ chains. Other expected changes in the molecular parameters (based upon these bonding considerations) include a shortening of the Cd−S and N−Cd bonds, a decrease in the Cd−S−C angle, and an increase in the C−N−Cd angle, as indeed observed experimentally.

The three $-[\mathrm{S{-}C{\equiv}N{-}Cd}]_\infty-$ chains are not identical in the title compounds. In **1**, the Cd−S1, S1−C1, and N1−Cd distances of 2.703(2), 1.636(9), and 2.286(7) Å are somewhat shorter than the Cd−S2, S2−C2, and N2−Cd distances of 2.760(2), 1.658(6), and 2.317(5) Å, respectively. Furthermore, the Cd−S1−C1 angle of 92.6(3)° is smaller than the Cd−S2−C2 angle of 98.4(2)°, whereas the C1−N1−Cd angle of 158.8(6)° is significantly larger than the C2−N2−Cd angle of 143.9(5)° (Table 2). These observations are indicative of a larger partial π-delocalization of the polymeric $-[\mathrm{S1{-}C1{\equiv}N1{-}Cd}]_\infty-$ chain in comparison with that of the $-[\mathrm{S2{-}C2{\equiv}N2{-}Cd}]_\infty-$ chains based on the above-mentioned bonding considerations (see in-plane π_x).

The same observations, and arguments, hold true for **2**. The average S−C and C−N distances of 1.646 and 1.15 Å, respectively, in **2**, indicate partial π-delocalization for all three chains. In contrast to **1**, however, all three $-[\mathrm{S{-}C{\equiv}N{-}Cd}]_\infty-$ chains in **2** are crystallographically independent. Interestingly though, one chain, $-[\mathrm{S3{-}C3{\equiv}N3{-}Cd}]_\infty-$, has shorter Cd−S3 and N3−Cd distances of 2.698(2) and 2.274(5) Å, respectively (in comparison with the corresponding average distances of 2.749 and 2.342 Å for the other two chains) and a smaller Cd−S3−C3 angle of 96.1(2)° (in comparison with the corresponding average value of 101.3° for the other two chains) and a larger C3−N3−Cd angle of 156.9(3)° (in comparison with the corresponding average value of 146.2° for the other two chains). Therefore, the $-[\mathrm{S3{-}C3{\equiv}N3{-}Cd}]_\infty-$ chain in **2** bears a striking resemblance to the $-[\mathrm{S1{-}C1{\equiv}N1{-}Cd}]_\infty-$ chain in **1** in that it exhibits a larger partial π-delocalization along the polymeric chain in comparison with the other two chains ($-[\mathrm{S1{-}C1{\equiv}N1{-}Cd}]_\infty-$ and $-[\mathrm{S2{-}C2{\equiv}N2{-}Cd}]_\infty-$ in **2**).

In short, the partial π-delocalization (in terms of both π-donation and π-back-donation) along the infinite $-[\mathrm{S{-}C{\equiv}N{-}Cd}]_\infty-$ chains, coupled with the highly polarizable “soft” metal such as Cd^{2+} ions, makes these cadmium−thiocyanate polymers highly promising candidates for nonlinear optical materials as we shall discuss next.

IV. Discussion

(1) Design Criteria for the IPOS Systems as Hybrid Materials. Before discussing the molecular and crystal engineering of the IPOS series, it is interesting to consider the design criteria of the IPOS system as a new class of, for example, nonlinear optical (NLO) materials.[6−12] The IPOS system reported here resembles the traditional inorganic and organic NLO materials in some aspects but differs in many others. For example, as described earlier, the title compounds possess desirable physical properties such as high melting points, excellent transparency in the entire visible and ultraviolet region, and a high second harmonic generation (SHG) coefficient[15] for **1** and no SHG effect for **2**, which is consistent with the observed acentric crystal structure of **1** and the centric crystal structure of **2** reported here. Furthermore, an intense metal-to-ligand charge-transfer (MLCT) band (or metal-mediated ligand $\pi \rightarrow \pi^*$ transition) has been observed at 220 nm (with a shoulder at 262 nm) in the solid-state electronic spectrum of the polymeric metal−thiocyanate system discussed here. Such transition is believed to be the origin of the NLO responses. In this paper, however, attention will be focused on the design strategies and crystal engineering of the IPOS system.

It is generally accepted that the molecular design rules for organic NLO materials are (1) highly delocalized, easily polarizable π systems; and (2) large asymmetry in electronic distribution caused by intramolecular donor−acceptor charge transfer.[6−12] Unfortunately, molecules with donor−acceptor groups on both ends of a highly polar molecule tend to couple head-to-tail in crystal packing, giving rise to *centrosymmetric* arrangement, and hence no second-order NLO responses.[18] Different counterions, however, can be used to avoid the formation of centric crystals. Such strategies have been successfully employed by Meredith, Marder, Cheng, Marks, Nakanishi, and others.[6−12] These strategies, though analogous

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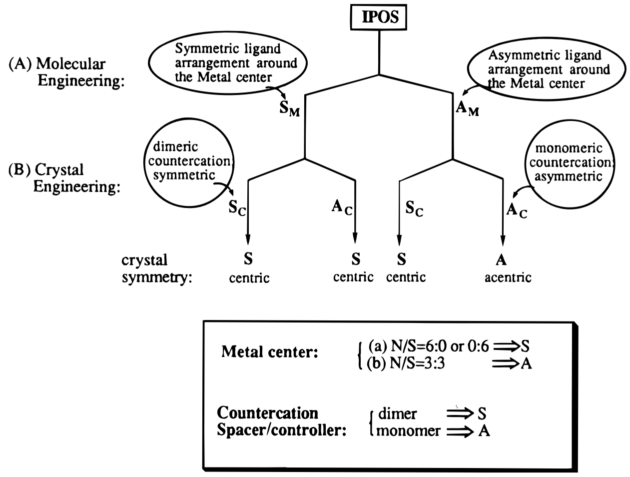
[18] The majority of organic NLO materials with large hyperpolarizabilities consist of a conjugated system containing a donor and an acceptor groups positioned at both ends of the conjugation.[9] However, the presence of polarising groups of this type usually causes the molecules to crystallize in a centrosymmetric space group and the NLO effect is reduced or lost. Furthermore, in one important nonlinear optical application which involves frequency doubling from a fundamental wavelength of 830 nm to a second harmonic of 415 nm, polar molecules of this type show a strong absorption either near UV or in the visible region of the spectrum, producing destructive absorption of the required wavelength.

Chart 3. Separate but Concomitant Controls in Molecular and Crystal Engineering



to ours in some respects, are different in many others. First, the role of the "host" matrix and the "guest" spacer/controller are reversed. While these researchers used organic host with inorganic counterions, we use inorganic host and organic counterions. Second, while their NLO responses stem from the organic host, the NLO effects of our IPOS system are due to the inorganic component. Third, the organic NLO used in their studies are molecular donor−acceptor charge−transfer compounds, whereas the inorganic NLO components of our IPOS system are polymeric metal−ligand complexes.

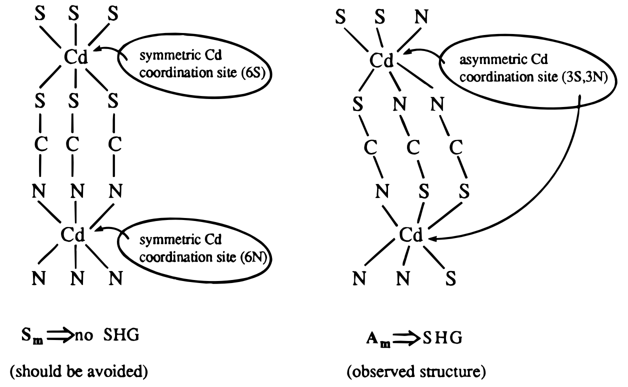
It should also be emphasized that the IPOS system reported in this paper satisfies all four "molecular design" criteria for organometallic NLO compounds advocated by Kanis, Ratner, and Marks.[7a,19] Namely, (1) the SCN^- ligand has a polarizable π system, (2) the Cd^{2+} ion has a closed-shell d^{10} configuration which is highly polarizable, (3) the hard nitrogen and the soft sulfur ligands are trans to one another, and (4) an intense MLCT transition has been observed at 220 nm (shoulder at 262 nm) for the title compounds. The key advantageous characteristic of the IPOS system over other organometallic compounds, however, is that the "molecular engineering" strategy of arranging hard and soft ligands trans to one another is automatically provided by the trans influence while "*crystal engineering*" is afforded by the "host−guest" cations which dictate crystal packing and crystal symmetry. Thus, the IPOS systems are highly promising hybrid (inorganic, organic, and polymeric) materials with tailorable molecular and crystal structures.

(2) Design Strategies: Symmetry Control. On the basis of the observed structures of $[(18C6)M]^+[Cd(SCN)_3]^-$ where $M^+ = K^+$ and Na^+, and their crystallization pattern, the following design strategies for acentric crystals can be formulated: (1) molecular engineering: avoid the symmetric (S_m) coordination around the metal; and (2) crystal engineering: avoid symmetric counterions (S_c) in the crystal packing, as illustrated in Chart 3. Here S and A refer to symmetric and asymmetric and the subscripts m and c refer to molecular and crystal engineering, respectively. The multiplication table is shown in Chart 4 (assuming $S = 0$ and $A = 1$). Details on the manipulation of S_m, A_m, S_c, and A_c will be discussed later. *The underlying principle here is to avoid or eliminate electronic and stereochemical factors that tend to give rise to centric crystals.*

Chart 4. Multiplication Table

c \ m	S_m	A_m
S_c	S	S
A_c	S	A

Chart 5. Molecular Engineering[a]



[a] Left: symmetrical ligand arrangements of 6S or 6N should be avoided. Right: asymmetrical ligand arrangements of 3S and 3N gives rise to NLO (SHG) properties.

(3) From Molecular to Crystal Engineering: Electronic and Stereochemical Controls. It is well recognized that the systematic design of new materials may be conceptually divided into two steps: *molecular engineering* wherein the electronic properties of the molecule are optimized and *crystal engineering* wherein crystallization in certain symmetry pattern (for example, an acentric space group for SHG effect) is achieved. The main problem, however, is that these two steps are generally not independent of each other. For instance, a compound whose molecular structure has been optimized for NLO properties by including a delocalized π-system to achieve a high hyperpolarizability tends to form centrosymmetric crystal structures because of dipole−dipole interactions, thereby nullifying the SHG effect.[14,18]

The IPOS series, as exemplified by the title compounds, allows concomitant but independent *molecular* and *crystal engineerings* in two separate controls, as illustrated in Chart 3. This feature is particularly useful in the optimization of their physical properties. Intuitively, we should have several levels of electronic and stereochemical controls over the crystal symmetry.

(A) Molecular Engineering: Inorganic Polymers (IP). We have chosen ligands such as SCN^- because of their high degree of *polarizability* which is crucial in the development of their nonlinear optical properties. Furthermore, the ambidentate SCN^- ligand, with a hard N atom and a softer S atom as donor atoms, tends to form polymeric chain structures with transition-metal ions (M).

At the first level, the formation of symmetric Cd coordination site (S_m) such as 6S or 6N (Chart 5, left) should be avoided as it would inevitably lead to centrosymmetric crystals.

For the present system, each Cd atom has 3S and 3N in its coordination sphere (Chart 5, right). The hard N atoms are trans to the softer S atoms owing to the trans influence, giving rise to an unsymmetrical Cd coordination (A_m) and hence highly asymmetrical electronic distribution about the Cd atoms. (Though not exhibited here, we should note that other asymmetric arrangements of three S and three N atoms around the Cd atoms are also possible.)

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(19) The four criteria for organometallic NLO compounds[7a] are (1) highly polarizable ligand π-system, (2) easily polarizable (i.e., weakly bound valence electrons) metal atoms, (3) asymmetric metal coordination so as to give rise to an asymmetric electronic distribution at the metal center (the "ideal" ligand environment being the arrangement of "hard" and "soft" ligands trans to one another), and (4) intense low-energy MLCT bands.

(B) Crystal Engineering: Organic Spacers/Controllers (OS). The crystal structures (Figures 1 and 2) of the $[(18C6)M]^+[Cd(SCN)_3]^-$ series are, to a large extent, controlled by the *cationic* [host−guest]$^+$ complexes. As illustrated schematically in Chart 2, the *monomeric* $[(18C6)K]^+$ cations cause the anionic $[Cd(SCN)_3{}^-]_\infty$ zig-zag chains to be parallel, resulting in an acentric space group and efficient SHG effects. In contrast, the *dimeric* $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dications cause the anionic $[Cd(SCN)_3]^-{}_\infty$ zig-zag chains to stack in an antiparallel fashion, resulting in a centric space group and hence the disappearance of the SHG effects. We therefore conclude that the host−guest alkali-metal cations play the role of organic spacers/controllers, dictating the arrangement of the $[Cd(SCN)_3{}^-]_\infty$ chains.

The host−guest chemistry refers to the binding of a wide variety of substrates in molecular cavities.[1−4,13] The binding of the cyclic crown ethers with metals can be categorized into at least four types, according to the *match* or *mismatch* of the metal ion with the size of the cavity of the crown ether: (I) monomeric structures with a host:guest ratio of 1:1; (II) dimeric structures with a host:guest ratio of 2:2; (III) a sandwhich structure with a host:guest ratio of 2:1; (IV) a two-nuclei structure with a host:guest ratio of 1:2. To enhance the possibility of forming an acentric space group, the monomeric host−guest complexes (host:guest = 1:1), of either a disklike, a partially coiled, or a coiled structure, such as those observed in $[(18C6)K][Cd(SCN)_3]$ (**1**, this work), $[(18C6)Na(H_2O)](SCN)$[4e], and [(dibenzo-30C10)K](I),[4d] respectively, should be used as cationic spacer/controller. To prevent the formation of centric space groups, symmetrical cationic host−guest molecules such as dimers (host:guest = 2:2) (e.g., those observed in $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**2**, this work) and $[(18C6)Cs(SCN)]_2$[4f]), sandwich complexes (host:guest = 2:1) (e.g., those observed in $[(benzo\text{-}15C5)_2K](I)$[4b]), or two-nuclei complexes (host:guest = 1:2) (e.g., those observed in $[(dibenzo\text{-}24C8)Na_2](o\text{-}O_2NC_6H_4O^-)_2$[4c]) should be avoided as these latter complexes have the tendency to form centrosymmetric structures. (For third-order harmonic generation, THG,[6e] however, such a restriction does not apply.)

(4) From Molecular Host−Guest Complexes to Crystal Host−Guest Clathrates. The infinite zig−zag $[Cd(SCN)_3{}^-]_\infty$ chains form an approximate square array, creating square channels which are filled by the $[(18C6)K]^+$ (in **1**) or $[(18C6)_2Na_2(H_2O)_2]^{2+}$ (in **2**) cations. The van der Waals diagram of one such square channel, together with the cations, is shown in Figure 5a,b for **1** and **2**, respectively. These square-channel motifs correspond to noncrystallographic “reduced cells” indicated by the dashed lines in Figures 1b and 2b, respectively. The weak ionic interactions between $[(18C6)K]^+$ ions and the sulfur atoms of the $[Cd(SCN)_3{}^-]_\infty$ chains cause the chains to be parallel in **1**, whereas the centrosymmetric nature of the $[(18C6)_2Na_2(H_2O)]^{2+}$ dimers render the chains antiparallel in **2**.

In this context, it occurs to us that there is a close parallel between the “molecular host−guest complexes” and “crystal host−guest lattices”. In other words, the cations, $[(18C6)K]^+$ or $[(18C6)_2Na_2(H_2O)_2]^{2+}$, of the title compounds may be regarded as molecular host−guest complexes where the “guest” alkali-metal ions, M^+, fit in the cavity of the crown ether “host” 18C6, whereas the crystal structures may be considered as “crystal host−guest clathrates” wherein the infinite $[Cd(SCN)_3{}^-]_\infty$ chains form an approximate square network of “host lattice”, creating square channels which are filled by the molecular host−guest complex cations. This embedding of “molecular host−guest complexes” as “guests” in a host lattice to form a “crystal host−guest clathrate” is rather interesting and may be considered as “host−guest” within “host−guest”.

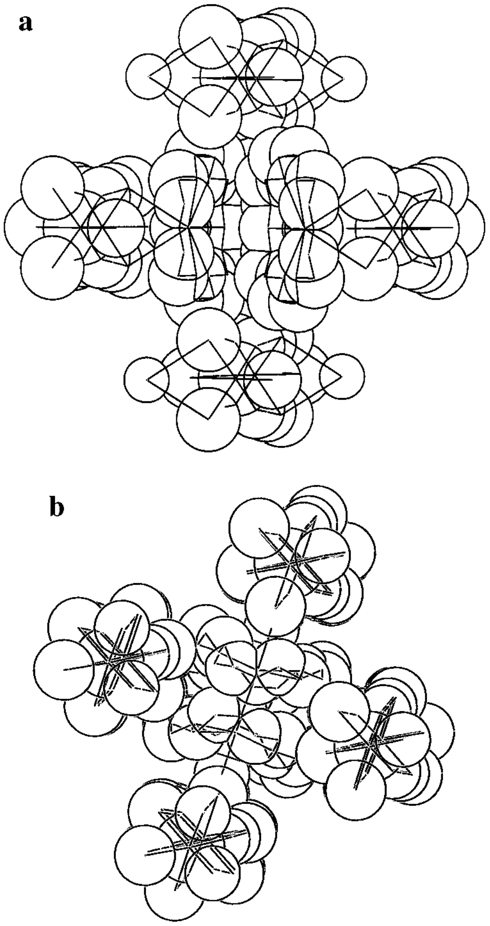

Figure 5. van der Waals diagrams of the anionic $[Cd(SCN)_3{}^-]_\infty$ chains in **1** and **2**, forming square channels housing the (crown ether)−(alkali metal) cations. Only one such square channel, consisting of segments of the chain, is shown. (a) In **1**, each square channel is filled with two $[(18C6)K]^+$ ions. The square channel motif corresponds to a noncrystallographic “reduced cell”, indicated by the dashed lines in Figure 1b, and is related to the crystallographic cell in the following manner: $\mathbf{a}' = (\mathbf{a} + \mathbf{b})/2$, $\mathbf{b}' = (\mathbf{a} - \mathbf{b})/2$, $\mathbf{c}' = \mathbf{c}$. (b) In **2**, each square channel is filled with one $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dimer. The square channel motif corresponds to a noncrystallographic “reduced cell”, indicated by the dashed lines in Figure 2b, and is related to the crystallographic cell in the following manner: $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = (\mathbf{a} + \mathbf{c})/2$.

V. Conclusions and Future Prospects

The IPOS concept combines the advantageous properties of inorganic, polymeric, and organic materials. It offers an excellent opportunity to synthesize *isolated* inorganic polymeric chains interspersed in an “organic medium” (and vice versa). The IPOS series, as exemplified by the title compounds, allows concomitant but separate *molecular* and *crystal engineering* (i.e., design of molecular structure and crystal packing in two independent controls).

The novel features of the IPOS series as tailorable crystal materials are (1) the anions form *isolated* (well-separated) *polymeric one-dimensional* zig-zag chains of $[Cd(SCN)_3{}^-]_\infty$; (2) the *extended π-conjugation* system within the polymeric $-[Cd-S-C{\equiv}N]-Cd\cdots$ chain, with the high polarizabilities of both the metal and the ligand, gives rise to NLO effects;[15] (3) the low dimensionality implies highly anisotropic physical properties; (4) low-lying π^* orbitals of the SCN^- ligands give rise to strong metal-to-ligand charge-transfer (MLCT) excitations (or metal-mediated ligand $\pi \rightarrow \pi^*$ transitions) which may be the origin of the nonlinear optical properties; (5) the cationic host−guest complex $[H-G]^+$ serves as a spacer/controller of the crystal structure and crystal symmetry; (6) Cd(II) d^{10} configuration gives rise to colorless crystals (transparent in the visible and ultraviolet region); (7) ionic salt $[H-G]^+[M-L]^-$ gives rise to relatively high melting point and good mechanical properties; (8) stoichiometric compounds of well-defined structures; (9) flexibility in design and fabrication; (10) large, high-quality crystals can be obtained for technological applications.

General design strategies, in terms of symmetry, electronic, and structural controls are also discussed. It is hoped that the structural principles deduced from the IPOS system will allow the development of new strategies for materials fabrication at the *molecular* level as well as to discover new patterns in crystallization at the *crystal* engineering level. The structures of the title compounds, **1** and **2**, may also be described as a "crystal host−guest clathrates" in which the infinite anionic polymeric $[Cd(SCN)_3]^-$ chains form an approximate square network, creating square channels which are filled by "molecular host−guest complexes" $[(18C6)K]^+$ (in **1**) or $[(18C6)_2Na_2(H_2O)_2]^{2+}$ (in **2**). Further development of this class of IPOS series as clathrate or inclusion compounds is in progress.

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Supporting Information Available: Tables of complete crystallographic and structural details and figures for $[(18C6)K][Cd(SCN)_3]$ (**1**) and $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**2**) (33 pages). See any current masthead page for ordering and Internet access instructions.

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