

Synthesis and Structure of [(DB24C8)Na][Cd(SCN)₃]. Formation of a Novel Linear Cd···Cd···Cd Chain with a *mer*-CdN₃S₃ Coordination Configuration and a New Coiled [(DB24C8)Na]⁺ Cation

Hong Zhang,^{*,†} Ximin Wang,[‡] David E. Zelmon,[†] and Boon K. Teo^{*,‡}

Materials Directorate, Air Force Research Laboratory (AFRL/MLPO), Wright-Patterson Air Force Base, Ohio 45433-7707, and Department of Chemistry (M/C 111), 845 West Taylor Street, University of Illinois at Chicago, Chicago, Illinois 60607

Received February 17, 2000

We report herein a novel coordination solid, [(DB24C8)Na][Cd(SCN)₃] (**6**) (DB24C8 denotes dibenzo-24-crown-8), which exhibits a new type of [Cd(SCN)₃]^{-∞} chain with two unusual stereochemical characteristics: (1) a *mer*-CdN₃S₃ coordination and (2) a *linear* Cd chain with a Cd···Cd···Cd angle of 180°. In addition, the [(DB24C8)Na]⁺ monocation adopts a new structural type—a coiled structure—for the combination of crown ether DB24C8 and alkali metal Na⁺. The title compound crystallizes in a monoclinic unit cell of *C2/c* space group symmetry with lattice parameters *a* = 16.110(8) Å, *b* = 20.380(5) Å, *c* = 11.01(1) Å, β = 119.87(3)°, and *Z* = 4. The arrangement of the [Cd(SCN)₃]^{-∞} chains in the crystal lattice in the title compound is approximately hexagonal, creating triangular channels which are filled with [(DB24C8)Na]⁺ monocations. It was previously reasoned by us that the coiled [(DB24C8)Na]⁺ monocation, which lacks inversion or mirror symmetries, should enhance the tendency for the formation of the noncentrosymmetric space group of the title crystal, making it a potential second-order nonlinear optical crystal. Interestingly, however, the title compound crystallizes in a centrosymmetric space group (*C2/c*) and gives rise to no second harmonic generation (SHG). Previously known [Cd(SCN)₃]^{-∞} chains adopt *fac*-CdN₃S₃ coordination and a zigzag Cd chain configuration with a Cd···Cd···Cd angle of 165°. The zigzag chains can align in either parallel or antiparallel fashion, resulting in efficient or no SHG effects, respectively. The linear Cd···Cd···Cd chain configuration observed in the title compound, on the other hand, makes it indistinguishable between parallel and antiparallel alignments. It is concluded that, to ensure the formation of noncentrosymmetric space groups, it is necessary to employ optically pure chiral cations as spacers and/or controllers. Furthermore, to enhance the nonlinear optical responses, [Cd(SCN)₃]^{-∞} chains with *fac*-CdN₃S₃ coordination and parallel alignments of the zigzag Cd chains should be used.

I. Introduction

Anionic cadmium thiocyanate coordination solids are relatively rare. One-dimensional (1-D) anionic cadmium thiocyanate polymeric chains,^{1,2} in particular, are of structural interest in that they form infinite columns arranged in either tetragonal or hexagonal arrays which create square or triangular channels, respectively, that can be filled with countercations of various sizes and shapes. For example, while the anionic [Cd(SCN)₃]^{-∞} chains in [(18C6)K][Cd(SCN)₃] (**1**)^{1a} and [(18C6)₂Na₂(H₂O)₂]_{1/2}[Cd(SCN)₃] (**2**)^{1a} are arranged in a tetragonal lattice, the anionic [Cd(SCN)₃]^{-∞} chains in [(12C4)₂Na][Cd(SCN)₃] (**3**),^{1b} [Et₄N][Cd(SCN)₃] (**4**),^{1c,2a} and [Me₄N][Cd(SCN)₃] (**5**)^{1c,2b} adopt a hexagonal arrangement. This intriguing structural difference can be rationalized in terms of the size, shape, and symmetry of the cations.

To date, the majority of the anionic [Cd(SCN)₃]^{-∞} (as well as their seleno analogues,^{1c} [Cd(SeCN)₃]^{-∞}) adopt a cadmium coordination sphere of *fac*-CdN₃S₃ with zigzag Cd chains (Cd···Cd···Cd angles averaging 165°). The alignment of the zigzag chains can be either parallel or antiparallel in their respective lattice. This latter characteristic has a profound influence on their physical properties (vide infra).

We report here a novel coordination solid, [(DB24C8)Na][Cd(SCN)₃] (**6**) (where DB24C8 denotes dibenzo-24-crown-8), which exhibits a new type of [Cd(SCN)₃]^{-∞} chain with two unusual stereochemical characteristics: (1) a *mer*-CdN₃S₃ coordination and (2) a *linear* Cd chain with Cd···Cd···Cd angles of 180°. The arrangement of the chains in the crystal lattice of the title compound **6** is approximately hexagonal, creating triangular channels which are filled with the relatively large [(DB24C8)Na]⁺ monocations. The [(DB24C8)Na]⁺ monocation adopts an unusual structure due to the fact that the alkali metal Na⁺ ion is too small to fit in the relatively large cavity of crown ether DB24C8. A previously known host–guest complex involving DB24C8 and Na⁺ is the two-nucleus 1:2 complex [(DB24C8)Na₂]²⁺ dication.^{3d} A coiled structure was reported for the combination of crown ether dibenzo-30-crown-10 (DB30C10) and alkali metal K⁺ as observed in the [(DB30C10)K]⁺ monocation.^{3b} Hence,

[†] Air Force Research Laboratory.

[‡] University of Illinois at Chicago.

- (1) (a) Zhang, H.; Wang, X.; Teo, B. K. *J. Am. Chem. Soc.* **1996**, *118*, 11813. (b) Zhang, H.; Wang, X.; Zhang, K.; Teo, B. K. *Inorg. Chem.* **1998**, *37*, 3490. (c) Zhang, H.; Zelmon, Z.; Price, G.; Teo, B. K. *Inorg. Chem.* **2000**, *39*, 1868.
 (2) (a) Kuniyasu, Y.; Suzuki, Y.; Taniguchi, M.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 179. (b) Taniguchi, M.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 424.

the coiled structure observed for the 1:1 complex [(DB24C8)-Na]⁺ monocation in the title compound **6** represents a new structural type for the combination of the crown ether DB24C8 and the Na⁺ ion.

The discovery of title crystal [(DB24C8)Na][Cd(SCN)₃] (**6**) as a new member of a series of inorganic polymer separated by organic spacers (IPOS) coordination solids^{1,4,5} is an outgrowth of our systematic study of the effects of cations of various sizes and shapes on the arrangement and the alignment of the anionic cadmium thiocyanate chains in the crystal lattice. In particular, it was previously reasoned by us that coiled crown ether monocations, which lack inversion or mirror symmetries, should enhance the tendency for the formation of noncentrosymmetric space groups, resulting in potential second-order nonlinear optical crystals.⁶ Interestingly, however, the title crystal **6** instead crystallizes in a centrosymmetric space group (*C2/c*) and gives rise to no second harmonic generation (SHG). A detailed analysis of the structure of **6** revealed that, distinct from the previous [Cd(SCN)₃]⁻_∞ zigzag chains with Cd···Cd···Cd angles of 165°,¹ the anionic cadmium thiocyanate polymer in **6** adopts a linear Cd···Cd···Cd chain configuration with Cd···Cd···Cd angles of 180°. Hence, it is indistinguishable between parallel and antiparallel alignments. On the basis of the present study, a new set of design criteria is formulated. As we shall see in this paper, to ensure the formation of noncentrosymmetric space groups for the IPOS system, it is necessary to employ optically pure chiral cations as spacers and/or controllers. In addition, to enhance the nonlinear optical (NLO) responses, the [Cd(SCN)₃]⁻_∞ chains must adopt the zigzag configuration and arrange in a parallel fashion.

Table 1. Crystallographic Data for [(DB24C8)Na][Cd(SCN)₃] (**6**)

empirical formula	CdNaS ₃ N ₃ O ₈ C ₂₇ H ₃₂	<i>Z</i>	4
fw	758.14	<i>T</i> (K)	296
space group	<i>C2/c</i> (no. 15)	<i>λ</i> (Å)	0.7107
<i>a</i> (Å)	16.110(8)	ρ_{calcd} (g cm ⁻³)	1.607
<i>b</i> (Å)	20.380(5)	μ (cm ⁻¹)	9.633
<i>c</i> (Å)	11.01(1)	<i>R</i> (<i>F</i> _o) ^a	0.041
β (deg)	119.87 (3)	<i>R</i> _w (<i>F</i> _o) ^b	0.043
<i>V</i> (Å ³)	3134(3)		

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

II. Experiments

(1) Preparations and Characterization. All reagents were purchased from Aldrich Chemicals and were used without further purification. Compound **6** was prepared as follows. With vigorous stirring, a solution of 0.45 g (1 mmol) of DB24C8 in 40 mL of acetonitrile was added dropwise to a preformed mixture of 0.26 g (1 mmol) of CdSO₄·3H₂O in 10 mL of water and 0.25 g (3 mmol) of NaSCN in 10 mL of water, over a period of 20 min. White precipitates slowly formed in the process. The solution was stirred for an hour after the completion of the addition. The white precipitate was then collected by filtration and washed several times with methanol. Yield: 0.56 g (74%). Single crystals suitable for X-ray diffraction study were obtained by recrystallization from aqueous solution. Anal. Calcd (Found) for [(DB24C8)Na][Cd(SCN)₃] (**6**) (fw = 758.14): C, 42.74 (42.67); H, 4.22 (4.21); N, 5.54 (5.51); S, 12.69 (12.86); Na, 3.03 (2.98); Cd, 14.82 (14.38).

(2) X-ray Crystallography. (a) Collection and Reduction of X-ray Data. A colorless needle crystal of the title compound **6**, with the dimensions 0.22 mm × 0.12 mm × 0.14 mm, was selected and mounted onto a glass fiber with epoxy resin. 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 K α radiation ($\lambda = 0.71069$ Å). The observed intensities were corrected for Lorentz, polarization, and empirical ψ scan absorption effects. The space group of *C2/c* (*b* unique) was defined by the systematic absences, and was later confirmed by the successful solution and refinement of the structure.

(b) Solution and Refinement of the Structure. Structural solution and refinements of compound **6** was performed using the teXsan package of Molecular Structural Corp. The systematic absences of the data are consistent with the space group *C2/c* or *Cc*. Wilson plots indicate the centrosymmetric space group *C2/c*. The positions of the cadmium and sodium atoms and the SCN⁻ ligands were obtained by direct methods, and the atoms of DB24C8 were located via Fourier syntheses. There are four [(DB24C8)Na][Cd(SCN)₃] molecules per unit cell (*Z* = 4). The asymmetric unit consists of half of the formula unit [(DB24C8)Na][Cd(SCN)₃]. The structural solution requires the location of one cadmium atom (which resides on the inversion center at (1/2, 0, 1/2)), two SCN⁻ ligands, one sodium atom (which is located at the 2-fold symmetry axis at (0, *y*, 3/4)), and four oxygen atoms and twelve carbon atoms of the DB24C8 ligand. One of the two crystallographically independent thiocyanide ligands, S2C2N2, also resides on the crystallographic 2-fold symmetry, making it 2-fold disordered with the C2 atom situated on the 2-fold axis at (1/2, *y*, 1/4). As a result, the occupancy factors of Cd, Na1, S2, C2, and N2 were fixed at 1/2. In the final cycles of full-matrix least-squares refinement (based on *F*), anisotropic thermal parameters were used for all non-hydrogen atoms. The idealized hydrogen atom positions of (C-H = 0.95 Å) were included in the calculations but not refined. Anisotropic/isotropic refinement (206 parameters) on 1947 independent reflections with *I* > 3 σ (*I*) converged at *R* = 0.041 and *R*_w = 0.043. The final difference map showed no peaks greater than 0.3 e/Å³ except four peaks (<0.6 e/Å³) close (<1.5 Å) to the Cd atom. Details of the crystallographic data are summarized in Table 1. Selected interatomic distances and bond angles, together with the estimated standard deviations, are given in Table 2. Complete crystallographic and structural details are provided in the Supporting Information.

- (3) (a) Dobler, M.; Dunitz, J. D.; Seiler, P. *Acta Crystallogr.* **1974**, *B30*, 2741. (b) Bush, M. A.; Truter, M. R. *J. Chem. Soc., Perkin Trans.* **1972**, 2, 345. (c) Dobler, M.; Phizackerley, R. P. *Acta Crystallogr.* **1974**, *B30*, 2748. (d) Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1975**, 2374. (e) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49. (f) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8 and references therein. (g) Stoddart, J. F. *Chem. Soc. Rev.* **1979**, *8*, 85 and references therein.
- (4) (a) Zhang, H.; Wang, X.; Zhu, H.; Xiao, W.; Teo, B. K. *J. Am. Chem. Soc.* **1997**, *119*, 5463. (b) Zhang, H.; Wang, X.; Zhu, H.; Xiao, W.; Teo, B. K. *Inorg. Chem.* **1999**, *38*, 886.
- (5) Zhang, H.; Wang, X.; Zhang, K.; Teo, B. K. *Coord. Chem. Rev.* **1999**, *183*, 157.
- (6) Understanding the structure–function relationship of crystalline materials is critical to the rational design and engineering of functional crystals. In fact, it is the symmetry that dictates the presence or absence of many physical responses of a crystal. For example, crystals with an inversion center cannot possess properties such as pyroelectricity, piezoelectricity, second-order nonlinear optical properties, etc.^{7–9} In other words, for these properties, it is important to design and grow crystals with noncentrosymmetric symmetries.
- (7) (a) Williams, D. J., Ed. *Nonlinear Optical Properties of Organic and Polymeric Materials*. *ACS Symp. Ser.* **1983**, *23*. (b) Marder, S. R.; Sohn, J. E.; Stucky, G. D., Eds. *Materials for Nonlinear Optics: Chemical Perspectives*. *ACS Symp. Ser.* **1991**, *455*. (c) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic: Orlando, 1987. (d) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecular and Polymers*; Wiley-Interscience: New York, 1991.
- (8) (a) Zhang, H.; Wang, X.; Zhang, K.; Teo, B. K. *J. Solid State Chem.* **2000**, *152*, 191. (b) Fischer, D. W.; Ohmer, M. C.; McCrae, J. E. *J. Appl. Phys.* **1997**, *81*, 3579. (c) Singh, N. B.; Henningsen, T.; Balakrishna, V.; Suhre, D. R.; Femelius, N.; Hopkins, F. K.; Zelmon, D. E. *J. Cryst. Growth* **1996**, *161*, 398.
- (9) (a) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10338. (b) Stucky, G. D.; MacDougall, J. E. *Science* **1990**, *247*, 669. (c) Meyer, F.; Bredas, J. L.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 2914. (d) Schwiebert, K. E.; Chin, D. N.; MacDonald, J. C. Whitesides, G. M. *J. Am. Chem. Soc.* **1996**, *118*, 4018. (e) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (f) Thalladi, V. R.; Brasselet, S.; Weiss, H.; Blaser, D.; Katz, A. K.; Carrell, H. L.; Boese, R.; Zyss, J.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 2563.

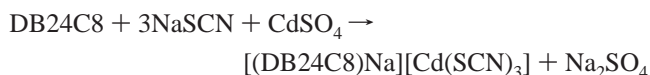
Table 2. Selected Bond Lengths (Å) and Angles (deg) for [(DB24C8)Na][Cd(SCN)₃] (**6**)

Cd1	Cd1	5.504	Cd1	Cd1	Cd1	180
Cd1	S1	2.737(2)	S1	Cd1	S1	180
Cd1	S2	2.764(4)	S2	Cd1	S2	180 ^a
Cd1	N1	2.360(5)	N1	Cd1	N1	180
Cd1	N2	2.23(2)	N2	Cd1	N2	180 ^a
S1	C1	1.639(6)	S1	Cd1	S2	95.8(1)
S2	C2	1.356(6) ^a	S1	Cd1	S2	84.2(1)
N1	C1	1.163(7)	S1	Cd1	N1	92.9(1)
N2	C2	1.47(2) ^a	S1	Cd1	N1	87.1(1)
Na1	O1	2.443(4)	S1	Cd1	N2	90.4(5)
Na1	O2	2.470(4)	S1	Cd1	N2	89.6(5)
Na1	O3	2.480(4)	S2	Cd1	N1	90.9(2)
Na1	O4	2.556(4)	S2	Cd1	N1	89.1(2)
O1	C3	1.436(7)	S2	Cd1	N2	173.5(5)
O1	C10	1.396(7)	N1	Cd1	N2	87.0(5)
O2	C4	1.432(7)	N1	Cd1	N2	93.0(5)
O2	C5	1.435(7)	Cd1	S1	C1	100.3(2)
O3	C6	1.437(7)	Cd1	S2	C2	103.1(4)
O3	C7	1.423(7)	Cd1	N1	C1	142.0(5)
O4	C8	1.438(6)	Cd1	N2	C2	128(1)
O4	C9	1.373(6)	S1	C1	N1	179.3(5)
C3	C4	1.501(9)	S2	C2	N2	175(1)
C5	C6	1.495(9)	O1	Na1	O2	67.1(1)
C7	C8	1.500(8)	O2	Na1	O3	67.5(1)
C9	C10	1.394(8)	O3	Na1	O4	66.6(1)
C9	C14	1.386(8)	O1	Na1	O4	63.7(1)
C10	C11	1.377(8)	O1	Na1	O1	95.5(2)
C11	C12	1.386(9)	O2	Na1	O2	139.8(2)
C12	C13	1.363(10)	O3	Na1	O3	85.4(2)
C13	C14	1.388(9)	O4	Na1	O4	148.9(2)

^a S2C2N2 is 2-fold disordered with the C2 atom residing on the 2-fold symmetry axis. The S2...N2* distance is 2.82(2) Å (not listed). Assuming S2–C2 of 1.639 Å (same as S1–C1), C2–N2 is calculated to be 1.184 Å.

III. Results and Discussion

(1) Syntheses. The title compound was prepared according to the following reaction:



The thiocyanate ion, SCN[−], is a linear pseudohalide. It is a highly versatile ambidentate ligand with two donor atoms that can coordinate to metals through either the nitrogen or the sulfur atoms or both.^{10–12} Cd(II) is interesting in that it exhibits both (S and N) bonding modes with the SCN[−] ligand as well as a variety of coordination numbers. With appropriate stoichiometry, the ambidentate nature of the SCN[−] ligand allows the formation of bridges between cadmium atoms, giving rise to the infinite anionic [Cd(SCN)₃][−] chains as observed in the title compound **6**. The alkali metal ion Na⁺ is coordinated by the oxygen atoms of the crown ether DB24C8, giving rise to the monocationic [(DB24C8)Na⁺] complex which has a crown ether:alkali metal = 1:1 ratio. The cationic organic–alkali metal complex ([DB24C8)Na⁺]) and the anionic inorganic polymeric chains ([Cd(SCN)₃][−]) are held together in the crystal by ionic interactions.

- (10) (a) *Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives*; Newman, A. A. Ed.; Academic Press: New York, 1975. (b) *Chemistry of Pseudohalides*; Golub, A. M., Kohler, H., Skopenko, V. V., Eds.; Elsevier: Amsterdam, 1986.
- (11) (a) Basolo, F. *Coord. Chem. Rev.* **1968**, *3*, 213. (b) Burmeister, J. L. *Coord. Chem. Rev.* **1968**, *3*, 225.
- (12) (a) Thiele, V. G.; Messer, D. Z. *Anorg. Allg. Chem.* **1980**, *646*, 255. (b) Gronbaek, R.; Dunitz, J. D. *Helv. Chim. Acta* **1964**, *47*, 1889–1897. (c) Cannas, M.; Carta, G.; Cvistini, A.; Marongiu, G. *J. Chem. Soc., Dalton Trans.* **1976**, 300.

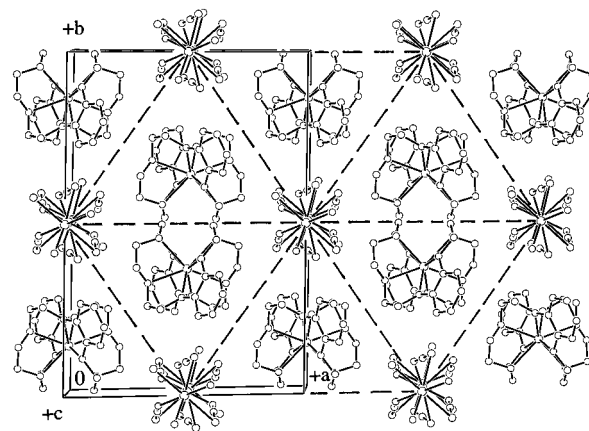


Figure 1. Crystal packing of [(DB24C8)Na⁺][Cd(SCN)₃][−] (**6**) as viewed along the crystallographic *c* axis. The anionic [Cd(SCN)₃][−] chains are arranged in an approximately hexagonal array (dashed lines), creating triangular channels which are filled with the [(DB24C8)Na⁺] cations. (The hydrogen atoms are omitted for clarity.) The crystallographic unit cell is represented by solid lines.

(2) Crystal Structure of 6. The title compound **6** crystallizes in a monoclinic unit cell (*b* unique) of dimensions *a* = 16.110(8) Å, *b* = 20.380(5) Å, *c* = 11.01(1) Å, and β = 119.87(3)° (*V* = 3134(3) Å³) and space group *C2/c* (*b* unique) with four [(DB24C8)Na][Cd(SCN)₃] molecules per unit cell (*Z* = 4). The asymmetric unit comprises half the formula unit [(DB24C8)Na][Cd(SCN)₃] with the Na⁺ and the Cd(II) ions located on crystallographic 2-fold and inversion symmetries, respectively. Furthermore, the carbon atom of one of the two crystallographically independent thiocyanide ligands, C2, also resides on a crystallographic 2-fold rotation symmetry. Selected bond lengths and angles are tabulated in Table 2. All bond lengths and angles are normal except S2–C2 and C2–N2. However, if we assume a linear configuration for the disordered S2–C2–N2 ligand and a S2–C2 bond length of 1.639 Å (same as S1–C1), the C2–N2 distance of 1.18 Å, which is close to the C1–N1 distance of 1.16(1) Å, can be calculated on the basis of the observed S2...N2 distance of 2.82(2) Å.

The crystal structure of **6**, viewed along the crystallographic *c* axis, as depicted in Figure 1, can be described as infinite anionic [Cd(SCN)₃][−] chains which run along the crystallographic *c* axis and are separated by the coiled [(DB24C8)Na⁺] cations. The dashed lines in Figure 1 depict a noncrystallographic approximate hexagonal arrangement of the [Cd(SCN)₃][−] chains, creating triangular channels which are filled with [(DB24C8)Na⁺] cations. The view along the crystallographic *b* axis, depicted in Figure 2 (with the cations omitted for clarity), depicts the relative arrangement of the linear [Cd(SCN)₃][−] chains as well as the intra- and interchain symmetries.

(a) Infinite Anionic [Cd(SCN)₃][−] Chains. As observed in all 1-D [Cd(SCN)₃][−] chains in IPOS systems reported so far,¹ the Cd atoms in the title compound **6** are octahedrally coordinated with three S and three N atoms. The difference, however, is that each Cd atom in **6** has a *mer*-CdN₃S₃ configuration with N2 *trans* to S2, N1 *trans* to N1*, and S1 *trans* to S1*, as depicted in Figure 3.¹³ As a result, there are two violations of the *trans* influence. To the best of our knowledge, this is the first time this type of coordination around the Cd atom has been observed in 1-D anionic cadmium thiocyanate [Cd(SCN)₃][−] chains. Adjacent Cd atoms are linked by three bridging SCN[−] ligands with a Cd...Cd distance of 5.504 Å

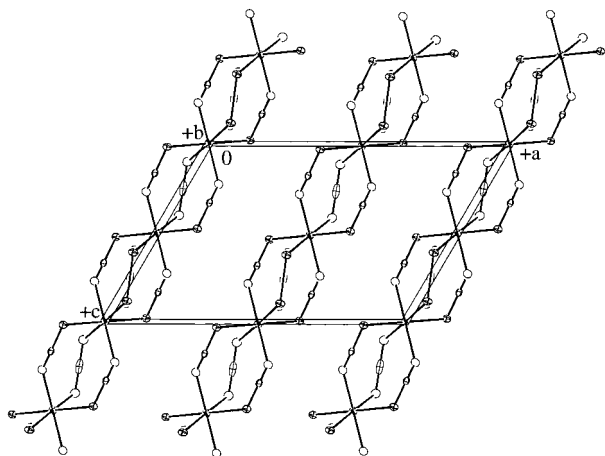


Figure 2. Alignment of the infinite linear anionic $[\text{Cd}(\text{SCN})_3]_\infty$ chains (20% thermal ellipsoids) in $[(\text{DB24C8})\text{Na}^+][\text{Cd}(\text{SCN})_3]_\infty$ (**6**) as viewed along the crystallographic b axis. The cationic $[(\text{DB24C8})\text{Na}^+]$ complexes are omitted for clarity. Note that only one component of the crystallographically disordered S2C2N2 , which is located on the 2-fold rotation symmetry axis, is shown.

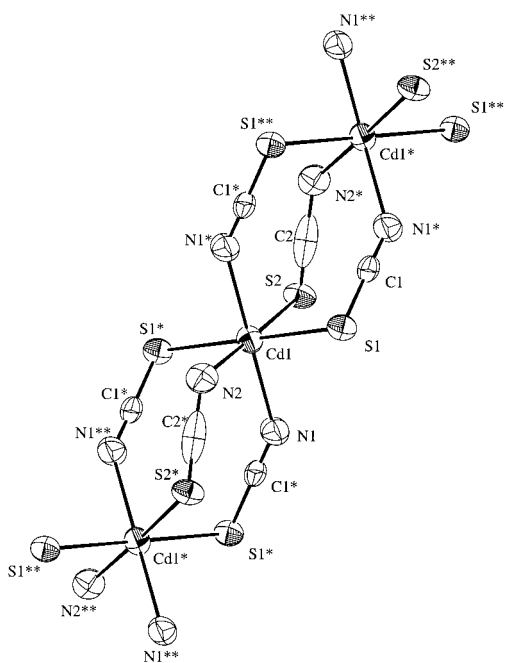


Figure 3. ORTEP diagram (50% thermal ellipsoids) of a segment of the infinite $[\text{Cd}(\text{SCN})_3]_\infty$ chains in $[(\text{DB24C8})\text{Na}^+][\text{Cd}(\text{SCN})_3]_\infty$ (**6**). Note that only one component of the crystallographically disordered S2C2N2 , which is located on the 2-fold rotation symmetry axis, is shown.

(which is half the crystallographic c axis), forming infinite $[\text{Cd}(\text{SCN})_3]_\infty$ chains.

We shall now compare the infinite $[\text{Cd}(\text{SCN})_3]_\infty$ chains in **6** with other similar chains observed in the IPOS series. Let us take the infinite $[\text{Cd}(\text{SCN})_3]_\infty$ chains in **1** and **2** as examples. In both structures, the Cd atoms are octahedrally coordinated with three N and three S atoms, from six SCN^- ligands. The S atoms are *trans* to the N atoms due to the *trans* influence, as shown in Figure 4a. As a result, the three zigzag $-\text{S}-\text{C}\equiv\text{N}-\text{Cd}$ chains wrapped around the central zigzag $\text{Cd}\cdots\text{Cd}\cdots\text{Cd}$ chain with a $\text{Cd}\cdots\text{Cd}\cdots\text{Cd}$ angle of 165° . Though the $\text{Cd}\cdots\text{Cd}$ distances of 5.50 \AA in **6** are similar to those observed in **1** and **2** (5.45 \AA), the Cd chains are perfectly linear with $\text{Cd}\cdots\text{Cd}\cdots\text{Cd}$ angles of exactly 180° , as depicted in Figures 2 and 4b. The spatial alignment of linear infinite $[\text{Cd}(\text{SCN})_3]_\infty$ chains

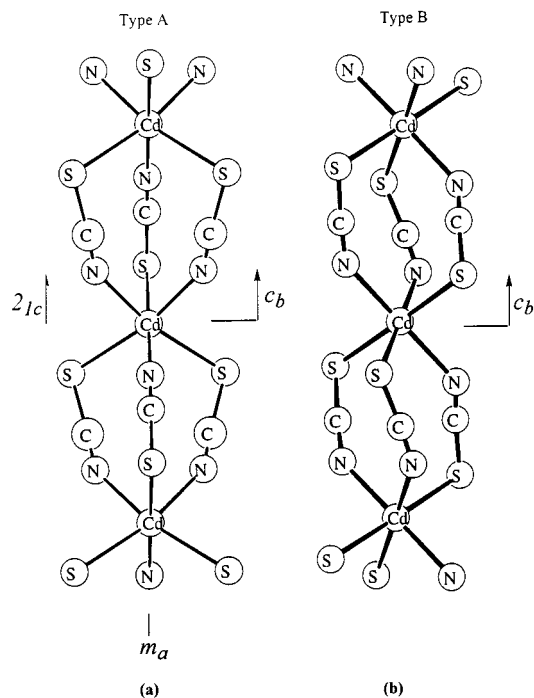


Figure 4. Two types of the infinite anionic $[\text{Cd}(\text{SCN})_3]_\infty$ chains, type A and type B, as exemplified by (a) $[(18\text{C6})\text{K}^+][\text{Cd}(\text{SCN})_3]_\infty$ (**1**) and (b) $[(\text{DB24C8})\text{Na}^+][\text{Cd}(\text{SCN})_3]_\infty$ (**6**), respectively. Type A has crystallographic $21c$, m_a , and c_b intrachain symmetries, whereas type B has c_b , -1 , and 2_b intrachain symmetries (see the text). For type B, only c_b is shown.

in **6** is thus indistinguishable between “parallel” and “antiparallel” (cf. Figure 6).

(b) Coiled $[(\text{DB24C8})\text{Na}^+]$ Cation. The binding of the crown ethers (host) with alkali metals (guest) can be generally categorized into seven classes, according to the host:guest ratio as well as the match or mismatch of the metal ion with the size of the cavity of the crown ether (see Figure 1 of ref 5). In the title compound **6**, where the cavity size of DB24C8 is significantly larger than the Na^+ ion, the host crown ether (DB24C8) wraps around the guest metal ion (Na^+) to form a “coiled” structure, as depicted in Figure 7, for the $[(\text{DB24C8})\text{Na}^+]$ monocation (with host:guest ratio of 1:1). The $[(\text{DB24C8})\text{Na}^+]$ monocation is chiral and resides on the crystallographic 2-fold rotation symmetry axis. The Na^+ ion is surrounded by eight oxygen atoms of DB24C8 with the Na^+-O bonds ranging from $2.443(4)$ to $2.556(4) \text{ \AA}$. The coordination around the Na^+ ion may be described as highly distorted triangular dodecahedron (cf. Figure 7b) with $\text{O1}-\text{Na}-\text{O1}^*$ and $\text{O3}-\text{Na}-\text{O3}^*$ angles of 90.5° (av) and $\text{O2}-\text{Na}-\text{O2}^*$ and $\text{O4}-\text{Na}-\text{O4}^*$ angles of 144.4° (av) (where the asterisks designate the 2-fold rotation symmetry related atoms). Consistent with this description, the $\text{O}(n)-\text{Na}-$

(13) Note that, under the centrosymmetric space group $C2/c$, the crystallographically disordered S2C2N2 , located on the 2-fold rotation symmetry axis, and the fact that the Cd atoms reside on the inversion symmetry make the distinction among *mer*- CdN_3S_3 , *trans*- CdN_2S_4 , and *trans*- CdS_2N_4 coordinations difficult. However, we believe that the cadmium coordination in **6** is *mer*- CdN_3S_3 (instead of an admixture of *trans*- CdN_2S_4 and *trans*- CdS_2N_4) by comparison with the closely related compounds **1–5**. Under the noncentrosymmetric sub space group Cc , the intrachain crystallographic symmetries -1 and 2_b , as well as the interchain crystallographic symmetries -1 and 21_b , vanish, thereby removing the 2-fold disorder of the S2C2N2 ligand. Therefore, it is possible, in theory, to refine an ordered structure under the noncentrosymmetric space group Cc . Attempts to do so, however, led to strong correlations among the thermal parameters (though the resulting structural parameters are very similar for the two space groups).

Table 3. Space Groups, Channels, Relative Alignments, and Intra- and Interchain Crystallographic Symmetries of Various IPOS Crystals [Cation][Cd(SCN)₃]⁻ Containing Infinite [Cd(SCN)₃]⁻_∞ Chains

compd	cation	space group	channel	alignment	intrachain crystallographic symmetry	interchain crystallographic symmetry
1	[(18C6)K] ⁺	<i>Cmc</i> 2 ₁	◇	⟨⟨	2 _{1c} , <i>m</i> _a , <i>c</i> _b	<i>C</i> , <i>b</i> _a , <i>n</i> _b , 2 _{1c}
2	[(18C6) ₂ Na ₂ (H ₂ O) ₂] ²⁺	<i>P</i> 2 ₁ / <i>n</i>	◇	⟨⟩	2 _{1b}	-1, <i>n</i> _b
3	[(12C4)Na] ⁺	<i>P</i> 2 ₁ / <i>n</i>	△	⟨⟩	2 _{1b}	-1, <i>n</i> _b
4	[Et ₄ N] ⁺	<i>Cmc</i> 2 ₁	△	⟨⟨	2 _{1c} , <i>m</i> _a , <i>c</i> _b	<i>C</i> , <i>b</i> _a , <i>n</i> _b , 2 _{1c}
5	[Me ₄ N] ⁺	<i>Pna</i> 2 ₁	△	⟨⟩	<i>a</i> _b	<i>n</i> _a , 2 _{1c}
6	[(DB24C8)Na] ⁺	<i>C</i> 2/ <i>c</i>	△		2 _b , -1, <i>c</i> _b	<i>C</i> , -1, <i>n</i> _b , 2 _{1b}

O(*n*+1) angles of the O(*n*)–Na–O(*n*+1) triangles range from 63.7(1)° to 67.5(1)°, with an average value of 66.2° (av). Here O(*n*) and O(*n*+1) represent oxygen atoms connected by ethylene groups (*n* = 1–4) except for O1 and O4, which are connected by the benzo groups. Finally, the presence of the two pairs of inversion symmetry related configurations of the chiral [(DB24C8)Na]⁺ monocation per unit cell (*Z* = 4) results in the formation of the centrosymmetric space group *C*2/*c*.

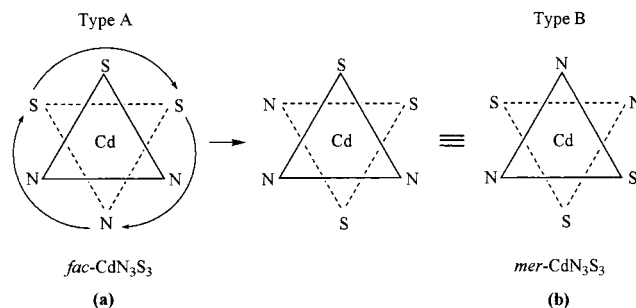
It should be pointed out that the same ligand DB24C8 was previously found to coordinate with two sodium ions, resulting in the two-nucleus complex [(DB24C8)Na₂][(o-O₂NC₆H₄O)₂] (cf. ref 5, Figure 1g).^{3d} The coiled structure was only observed in the crown ether of larger cavity with a larger potassium ion, as observed in dibenzo-30-crown-10 (DB30C10) and the potassium iodide complex [(DB30C10)K]I.^{3b} In this context, the coiled structure of the [(DB24C8)Na]⁺ monocation represents a new configuration for the DB24C8–Na⁺ host–guest complex.

(3) Comparison of Various Infinite [Cd(SCN)₃]⁻ Chains.

A comparative study of the stereochemical characteristics of various [Cd(SCN)₃]⁻_∞ chains in a variety of structures will not only bring out the commonalities and differences among them, but also provide important insights into the dramatic differences in their physical properties. Table 3 lists the space groups, arrangements of the [Cd(SCN)₃]⁻_∞ chains/columns, channels produced by the columns, alignment of the chains, intrachain symmetries that produce the infinite chains, and, finally, interchain symmetries that relate the adjacent chains. In the following discussion, we shall differentiate between precise crystallographic symmetries and approximate noncrystallographic symmetries regarding intra- and interchain symmetries. Only the former—precise crystallographic symmetries—are listed in Table 3. Furthermore, we tabulated only cadmium thiocyanate structures in Table 3 since they are the most studied. The same principles apply to the cadmium selenocyanate analogues.^{1c}

(a) Intrachain Symmetries. Despite the versatility of the [Cd(SCN)₃]⁻_∞ chains in crystallizing in a variety of crystal systems and space groups, resulting in different types of channels and relative alignments of the chains (see Table 3), there are, to the best of our knowledge, only two kinds of 1-D [Cd(SCN)₃]⁻_∞ chains. These two types, designated as A and B and exemplified by **1** and **6**, are portrayed in parts a and b, respectively, of Figure 4. The corresponding *fac*- and *mer*-CdN₃S₃ coordinations are depicted in parts a and b, respectively, of Figure 5.

The most common type, type A, is adopted by compounds **1**–**5**. It has a cadmium coordination sphere of *fac*-CdN₃S₃ (Figures 4a and 5a). All N atoms are *trans* to S atoms, thus conforming to the *trans* influence. The highest possible number of precise intrachain crystallographic symmetries is three, as exemplified in Figure 4a for compound **1**. Here, under space group *Cmc*2₁, the repeating [Cd(SCN)₃]⁻ units are related by 2_{1c}, and *c*_b while atoms within each repeat unit are related by

**Figure 5.** Interrelationship between *fac*- and *mer*-CdN₃S₃ coordination spheres. A 120° rotation of the bottom SSN triangle of *fac*-CdN₃S₃ (a) about the chain direction gives rise to the *mer*-CdN₃S₃ (b).**Table 4.** Point Group Representations of Precise Crystallographic and Approximate Noncrystallographic Intrachain Symmetries for 1-D [Cd(SCN)₃]⁻_∞ Chains^{a,b}

compd	type	<i>m</i>	<i>m</i> '	2
1	A	X	X	X
2	A	~	~	X
3	A	~	~	X
4	A	X	X	X
5	A	~	X	~

compd	type	-1	<i>m</i> '	2
6 ^c	B	X	X	X

^a The point group symmetry representations *m*, *m*', and 2 correspond to the mirror *m*, the glide planes, and the 2₁ screw axes in Table 3 under "intrachain crystallographic symmetry". Note that the three symmetry axes are mutually perpendicular (or approximately so if not precise crystallographic symmetries). ^b Precise crystallographic symmetries are marked by the symbol "X" and approximate symmetries by the symbol "~". ^c Note that the crystallographic symmetry 2_b in **6** is along the same direction (*b* axis) as the glide plane *c*_b. In **6**, the three intrachain crystallographic symmetries are -1, *c*_b, and 2_b as indicated by -1, *m*', and 2.

the *m*_a mirror. These three symmetry elements are along the three mutually perpendicular axes of the orthorhombic unit cell. The situation is the same for **4**, which also crystallizes in space group *Cmc*2₁. In **2** and **3**, the lowering of the crystal system from orthorhombic to monoclinic destroys the mirror and the glide planes, leaving intact only the 2₁ screw axis. However, a detailed examination of the structures of **2** and **3** revealed that the [Cd(SCN)₃]⁻_∞ chains still retain an approximate mirror symmetry and an approximate glide plane symmetry (both noncrystallographic), along the three mutually perpendicular (albeit approximately) directions. In **5**, the lowering of space group *Cmc*2₁ to its subgroup *Pna*2₁ (both are orthorhombic) eliminates the 2₁ screw axis and the mirror *m*. Once again, the [Cd(SCN)₃]⁻_∞ chains retain the two lost crystallographic symmetries in an approximate way. The foregoing discussion is summarized in Table 4. Here, for the sake of clarity, we reduce the space group symmetries to the corresponding point group representations (2₁ screw axis to 2, mirror and glide planes

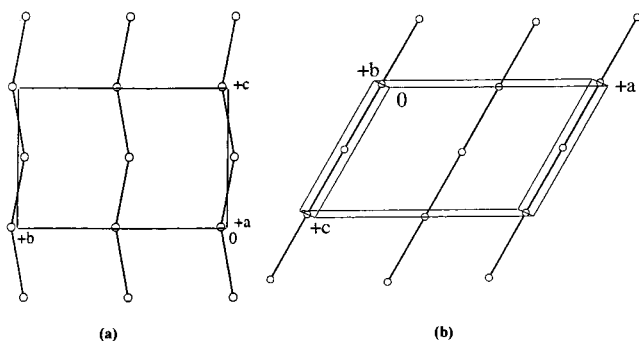


Figure 6. (a) Parallel alignment of zigzag cadmium chains (type A) as observed in $[(18C6)K^+][Cd(SCN)_3^-]$ (**1**). (b) Parallel alignment of linear cadmium chains (type B) as observed in $[(DB24C8)Na^+][Cd(SCN)_3^-]$ (**6**).

to m and m' , respectively). Precise symmetries are marked by the symbol "X" and approximate symmetries by "~".

Type B $[Cd(SCN)_3^-]_\infty$ chains are distinctly different. We believe it is observed, and reported here, for the first time in the title compound **6**. The coordination sphere of the Cd atoms can be described as *mer*- CdN_3S_3 . Two sulfurs (S1 and S1*) and two nitrogens (N1 and N1*) are *trans* to one another, as portrayed in Figures 3 and 4b and represented schematically in Figure 5b, thus violating the *trans* influence. Here the asterisks indicate atoms related by inversion symmetry. The remaining two coordination sites are occupied by the crystallographically disordered S2C2N2. This particular cadmium coordination (*mer*- CdN_3S_3) eliminates the 2_1 screw axis (along the chain direction) and, along with it, the mirror plane, m , which relates atoms within each $[Cd(SCN)_3^-]$ repeat unit. Instead, in **6**, there are two crystallographically imposed symmetries: the inversion center at $(1/2, 0, 1/2)$ and a 2-fold symmetry axis at $(0, 0, 3/4)$. The Cd atoms reside on the inversion symmetry. The C2 atom of the crystallographically disordered S2C2N2 is located on the 2-fold symmetry axis. Thus, the repeat $[Cd(SCN)_3^-]$ units in **6** are now related crystallographically by the glide plane, c_b , and the inversion center, while atoms within each repeat unit are related by the 2-fold rotation symmetry axis. The point group representations of the crystallographic symmetries in **6** are also indicated in Table 4.

It turns out that there are only two types of isomers for an octahedral MA_3B_3 coordination complex—*fac* and *mer*—as illustrated in Figure 5 for CdN_3S_3 . The *fac*- CdN_3S_3 and *mer*- CdN_3S_3 configurations are related by a relative rotation of approximately 120° of the two triangles (comprising S, S, N and N, N, S) about the chain axis, as illustrated in Figure 5.

Another important stereochemical difference of the two types of $[Cd(SCN)_3^-]_\infty$ chains listed in Table 3 is that type A $[Cd(SCN)_3^-]_\infty$ polymers have zigzag cadmium chains with average $Cd\cdots Cd\cdots Cd$ angles 165° (see Figure 6a for **1** as an example) while the cadmium chains in type B $[Cd(SCN)_3^-]_\infty$ polymers are exactly linear with $Cd\cdots Cd\cdots Cd$ angles of 180° (see Figure 6b for **6**). This difference has a profound influence on the relative alignment of the chains in the crystal, thereby impacting their physical properties (to be discussed later).

(b) Interchain Symmetries. Despite the simplicity in the classification of individual $[Cd(SCN)_3^-]_\infty$ chains (types A and B), their relative alignments as well as their arrangements (and the channels created) in a crystal exhibit a range of diversity as tabulated in Table 3. Crystallographically precise symmetry operations relating the adjacent chains are listed in the last column. It is apparent that, in space group $Cmc2_1$ (as observed

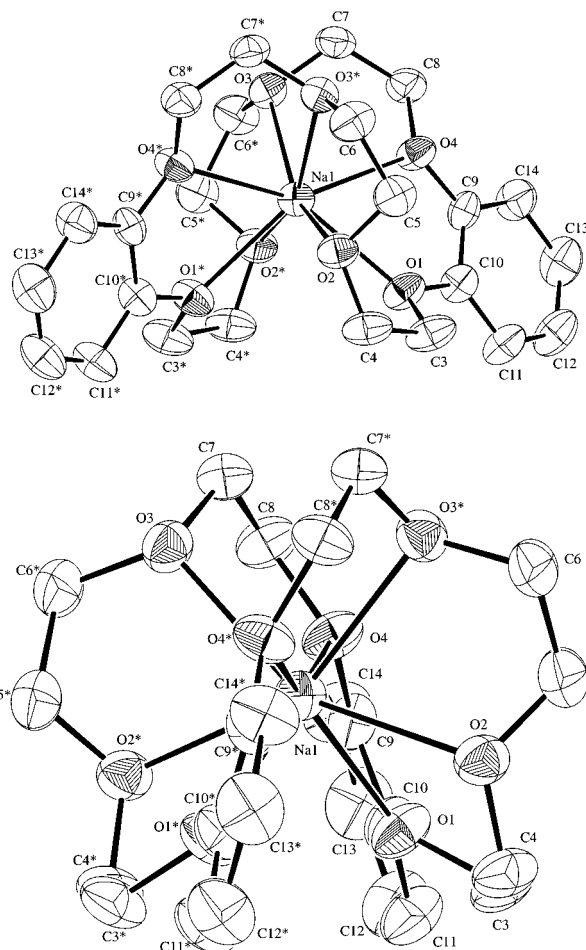


Figure 7. ORTEP diagrams (50% thermal ellipsoids) of the coiled $[(DB24C8)Na^+]$ monocation in two different views.

for **1** and **4**), the neighboring chains are related by the C -centering (as well as screw axis 2_{1c} and two glide planes, b_a and n_b). The implication of this interchain crystallographic symmetry is obvious: the adjacent zigzag chains must be aligned parallel to one another (see Figure 6a for **1**). In fact, the parallel alignment gives rise to SHG.^{1a} In contrast, the adjacent chains in **2** and **3** (space group $P2_1/n$) are related by inversion center -1 , as well as glide plane n_b , making their relative alignment antiparallel, and thus resulting in nullification of the SHG responses. Finally, we note that the adjacent (type A) chains in **5** are related by 2_{1c} and n_a . The lack of inversion symmetry in the crystal structure of **5** initially suggested that the neighboring chains might be aligned in a parallel fashion. Subsequent measurements revealed weak or no SHG response for **5**. An examination of the crystal structure of **5** revealed that the zigzag chains are aligned in an approximately antiparallel manner, which explains the lack of the SHG response. The antiparallel alignment in **5** was rationalized in terms of the small size of $(Me_4N)^+$ cations which are nested in the "pockets" formed by zigzag $[Cd(SCN)_3^-]_\infty$ chains.

As depicted in Figure 1 (unit cell packing diagram viewed along the crystallographic c axis) and listed in Table 3, the adjacent $[Cd(SCN)_3^-]_\infty$ chains in **6** are related by the crystallographic C -centering, the inversion symmetry -1 at $(1/4, 1/4, 0)$, the screw axis 2_{1b} at $(1/4, 0, 1/4)$, and the glide plane n_b at $(0, 1/4, 0)$. Unfortunately, as discussed earlier, the type B chains in **6** are perfectly linear (see Figure 6b), which makes the distinction between parallel and antiparallel alignments a moot

point. This is one of the reasons (others to be discussed in the following section) that the title compound **6** exhibits no SHG effects.

(4) Molecular and Crystal Engineering. (a) Molecular Engineering. The ambidentate XCN⁻ ligand (X = S, Se, Te), with a hard N atom and softer X atoms as donor atoms, tends to form polymeric structures with transition metal ions such as Cd(II).^{10–12} The asymmetric ligand arrangement and hence the highly asymmetric electronic distribution around the cadmium atoms are crucial in the realization of second-order nonlinear optical responses as exemplified by **1**.^{1a} With the *fac*-CdN₃S₃ configuration, the S atoms are *trans* to the N atoms, giving rise to highly asymmetric electronic distribution around the Cd atoms. This asymmetric electronic density distribution is highly desirable in the optimization of the second-order NLO effects. With the *mer*-CdN₃S₃ configuration, on the other hand, two pairs of like atoms are *trans* to one another (S to S and N to N), leaving only one unlike atom pair being *trans* to each other (S to N).¹³ This implies that the asymmetry in electron density distribution around the Cd atom is greatly reduced in comparison with that in the *fac*-CdS₃N₃ configuration. It is concluded, therefore, that, at the level of molecular engineering, the second-order NLO responses for the title compound **6** should be less than that observed for the *fac*-CdS₃N₃ complexes even in a noncentrosymmetric space group.

(b) Crystal Engineering. The spatial arrangement and the relative alignment (either parallel or antiparallel) of [Cd(SCN)₃]^{-∞} zigzag chains in the crystal structures of compounds **1–5** are, to a large extent, influenced by the countercations. In other words, the cations serve not only as spacers, filling in the voids between the chains, but also as controllers, dictating the alignment of the [Cd(SCN)₃]^{-∞} zigzag chains. In this regard, we previously reasoned that the coil structure of a cation such as [(DB24C8)Na]⁺ in the title compound **6** should enhance the tendency to form noncentrosymmetric crystals, making them potential candidates for such applications as SHG. Instead, the title crystal **6** adopts a centrosymmetric space group (*C2/c*) and gives rise to no SHG effects. This was, at first glance, a puzzle. A detailed analysis of this structure, as reported here, revealed the linear configuration of the [Cd(SCN)₃]^{-∞} chains, which results in the alignment of adjacent chains being indistinguishable between parallel and antiparallel. Furthermore, the presence of the two mirror-related configurations (*Z* = 4) of the chiral

cation [(DB24C8)Na]⁺ in **6** gives rise to the centrosymmetric space group *C2/c*, thereby nullifying the SHG effects.

IV. Conclusion

In summary, the title compound **6** reported in this paper represents a new IPOS compound with a novel crystal structure. It crystallizes in the centrosymmetric space group *C2/c*. The cadmium coordination may be described as *mer*-CdN₃S₃, which violates the *trans* influence in the Cd(II) coordination sphere.¹³ The [Cd(SCN)₃]^{-∞} chains are exactly linear and possess inversion symmetry, thereby nullifying second-order NLO effects. A detailed analysis of the structure of the title compound and its comparison with the closely related IPOS compounds **1–5**, discussed in this paper, revealed that the title compound crystallizes in the centrosymmetric space group owing to the presence of the two inversion-related configurations of the chiral [(DB24C8)Na]⁺ monocation. However, even under a noncentrosymmetric space group (such as the subgroup of *C2/c*, namely, *Cc*), the linear configuration of the [Cd(SCN)₃]^{-∞} chains and the *mer*-CdN₃S₃ coordination would probably give rise to weak NLO effects.

On the basis of the systematic structural studies presented here and elsewhere,^{1,4,5} we conclude that, to enhance the possibility of obtaining efficient NLO crystals of the IPOS systems, the following four criteria must be satisfied. First, the desirable cadmium coordination sphere is *fac*-CdN₃S₃ with highly polarizable, asymmetric electron distribution around the metal atom. Second, to ensure the formation of noncentrosymmetric crystals, optically pure chiral cations must be used as spacers. Third, the [Cd(SCN)₃]^{-∞} chains must adopt the zigzag configuration. And fourth, the zigzag chains must be aligned in a parallel fashion. Obviously, the first criterion relates to molecular engineering, whereas the remaining three relate to crystal engineering. Work is in progress to verify and/or further these design principles.

Acknowledgment. We thank Linda Collier (MLOC) of AFRL for her technical support. Acknowledgment is also made to the National Research Council (H.Z.) and National Science Foundation (B.K.T.) for financial support of this research.

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

IC0001762