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Crystal Engineering in [(12C4)$_2$Na][Cd(SCN)$_3$]: First Example of an Anionic Cadmium Thiocyanate Coordination Solid with a Sandwich [(12C4)$_2$Na]$^+$ Cation as Spacer/Controller, Resulting in a Hexagonal Arrangement of Antiparallel Zigzag [Cd(SCN)$_3{}^-$]$_\infty$ Chains

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This paper reports the synthesis, characterization, and structure of [(12C4)$_2$Na][Cd(SCN)$_3$] (**3**). The title compound **3** represents the first example of an anionic cadmium thiocyanate coordination solid in which a sandwich [(12C4)$_2$Na]$^+$ monocation serves as the spacer/controller, giving rise to a hexagonal array of antiparallel infinite zigzag [Cd(SCN)$_3{}^-$]$_\infty$ chains with the cations occupying the triangular channels. The title compound **3** crystallizes in a monoclinic unit cell of $P2_1/n$ space group symmetry with lattice parameters of 13.204(2) Å, 10.692(2) Å, 21.036(1) Å, 95.520(8)°, and $Z = 4$. A detailed comparison of the title structure (**3**) with that of [(18C6)$_2$Na$_2$(H$_2$O)$_2$]$_{1/2}$[Cd(SCN)$_3$] (**1**) and [(18C6)K][Cd(SCN)$_3$] (**2**) revealed that the *arrangement* and the *alignment* of the infinite anionic [Cd(SCN)$_3{}^-$]$_\infty$ zigzag chains are dictated by the *dimensions* and *symmetry*, respectively, of the cations. The infinite anionic [Cd(SCN)$_3{}^-$]$_\infty$ chains in **1** and **2** form an approximate tetragonal array, creating square channels which are filled with the dimeric [(18C6)$_2$Na$_2$(H$_2$O)$_2$]$^{2+}$ (in **1**) or with two monomeric [(18C6)K]$^+$ (in **2**) cations while the infinite anionic [Cd(SCN)$_3{}^-$]$_\infty$ chains in **3** adopt an approximate hexagonal arrangement with the triangular channels filled by the smaller [(12C4)$_2$Na]$^+$ cations (the *dimension* effect). The relative alignment (either parallel or antiparallel) of the anionic chains is dictated by the symmetry or approximate symmetry of the cations. Thus, both the dimeric cation in **1** and the sandwich cation in **3** give rise to antiparallel alignment of the anionic [Cd(SCN)$_3{}^-$]$_\infty$ chains with the centrosymmetric space group $P2_1/n$ whereas the disklike cation in **2** gives rise to parallel alignment of [Cd(SCN)$_3{}^-$]$_\infty$ chains with noncentrosymmetric space group $Cmc2_1$ (the *symmetry* effect).

Introduction

As part of our effort in the design and synthesis of inorganic polymers with organic spacer (IPOS) systems[1,2] involving cadmium thiocyanates,[3−7] we report herein the preparation, structure, and characterization of [(12C4)$_2$Na][Cd(SCN)$_3$]. A detailed comparison of the title structure with that of [(18C6)$_2$Na$_2$(H$_2$O)$_2$]$_{1/2}$[Cd(SCN)$_3$] (**1**)[1] and [(18C6)K][Cd(SCN)$_3$] (**2**)[1] revealed that the *arrangement* and the *alignment* of the infinite anionic [Cd(SCN)$_3{}^-$]$_\infty$ zigzag chains are dictated by the *dimensions* and *symmetry*, respectively, of the cations. In this context, the title compound represents our first successful attempt in utilizing a sandwich monocation (viz. [(12C4)$_2$Na]$^+$) as a spacer/controller in influencing the arrangement and alignment of the infinite anionic [Cd(SCN)$_3{}^-$]$_\infty$ chains in cadmium thiocyanate coordination solids.

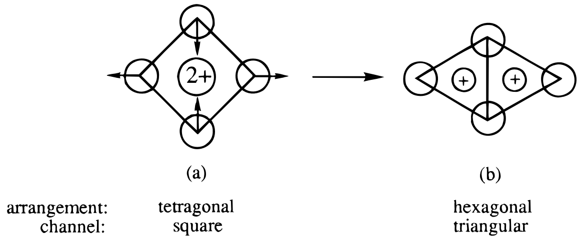

Figure 1. Schematic representation of the formal distortion of the arrangement of the infinite [Cd(SCN)$_3{}^-$]$_\infty$ chains (open circles) from tetragonal (a) to hexagonal (b) as viewed along the chain direction. Each square channel in (a), housing either a dimeric dication such as [(18C6)$_2$Na$_2$(H$_2$O)$_2$]$^{2+}$ in **1** or two monocations such as [(18C6)K]$^+$ in **2** per two [Cd(SCN)$_3$]$^-$ units, becomes two triangular channels, accommodating two sandwich monocations (one each) such as [(12C4)$_2$Na]$^+$ in **3**, again, per two [Cd(SCN)$_3$]$^-$ units.

The infinite anionic [Cd(SCN)$_3{}^-$]$_\infty$ chains in **1** and **2** form an approximate tetragonal array, creating square channels which are filled by the dimeric [(18C6)$_2$Na$_2$(H$_2$O)$_2$]$^{2+}$ (in **1**) or by two monomeric [(18C6)K]$^+$ (in **2**) cations as depicted schematically in Figure 1a. We reason that a smaller cation such as [(12C4)$_2$Na]$^+$ may lead to a different arrangement of the anionic [Cd(SCN)$_3{}^-$]$_\infty$ chains. Indeed, the infinite anionic [Cd(SCN)$_3{}^-$]$_\infty$ chains of the title compound [(12C4)$_2$Na][Cd(SCN)$_3$] (**3**) adopt an approximate hexagonal arrangement with the distorted triangular channels filled with the sandwich [(12C4)$_2$Na]$^+$ cations (see schematic representation in Figure 1b). The hexagonal array may be derived from the tetragonal arrangement

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† University of Illinois at Chicago.

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via a formal distortion as depicted in Figure 1. The control of the spatial arrangement of the anionic chains by the cations (due to their size and shape) may be termed the "dimension effect". As predicted,[1] the sandwich $[(12C4)_2Na]^+$ cation in **3** gives rise to an antiparallel alignment of the $[Cd(SCN)_3^-]_\infty$ zigzag chains in the crystal, resulting in a centrosymmetric space group ($P2_1/n$). The control of the relative alignment of the $[Cd(SCN)_3^-]_\infty$ zigzag chains and the symmetry of the crystal may be considered as the "symmetry effect". The stereochemical consequences and their impacts on the physical properties of these crystals such as nonlinear optical behavior will be discussed.

Experimental Section

Synthesis and Characterization. All reagents were used as purchased. The title compound $[(12C4)_2Na][Cd(SCN)_3]$ (**3**) was prepared by adding an aqueous mixture of 2 mL of 0.56 M 12-crown-4 (12C4, $C_8H_{16}O_4$)) and 35 mL of 2 M NaSCN to 35 mL of an aqueous solution of 0.5 M $CdSO_4$. (Care must be taken to avoid local supersaturation and/or precipitation during the addition.) Colorless prismatic crystals of **3**, measuring millimeters in size, were grown from the reaction mixture via solvent evaporation. **3** gave satisfactory elemental analysis (analysis by Midwest Microlab, Indianapolis, IN). Calcd (found) for $[(12C4)_2Na][Cd(SCN)_3]$ (fw = 662.06): C, 34.47 (34.54); H, 4.83 (4.83); N, 6.36 (6.33); S, 14.53 (14.78). The infrared (IR) spectrum of crystalline samples of **3** (CsI pellet) was measured with a BIO-RAD FTS-40 spectrophotometer. IR spectrum of **3** indicates the presence of the bidentate SCN^- ligands and the presence of 12C4. Nonlinear optical measurement using the standard Kurts and Perry powder technique[8] showed no SHG effect for **3**, consistent with the centrosymmetric space group $P2_1/n$. The title compound **3** is transparent in the visible and ultraviolet regions.

X-ray Crystallography. A colorless prismatic crystal of $[(12C4)_2Na][Cd(SCN)_3]$ (**3**) with dimensions of 0.12 mm × 0.20 mm × 0.14 mm was selected and mounted on a glass fiber with epoxy resin. Room-temperature (23 ± 2 °C) single-crystal X-ray diffraction data was 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. An empirical absorption correction (ψ-scan) was applied to the data (μ = 1.0353 mm^{-1}). A Wilson plot of the data favored the centrosymmetric space group $P2_1/n$, which was confirmed by the successful solution and refinement of the structure. Structural solution and refinements were performed using teXsan package of the Molecular Structural Corp. Positions of the Cd, Na, and SCN atoms were located via direct methods while the O and C atoms of the two 12C4 were obtained via successive Fourier syntheses. There are four formula units of $[(12C4)_2Na][Cd(SCN)_3]$ per unit cell ($Z = 4$), i.e., one per asymmetric unit. Since all atoms are in general positions, the structural analysis of **3** required the location of one Cd, three SCN ligands, one Na, and two 12C4 ligands. In the final cycles of full-matrix least-squares refinement, 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. Anisotropic refinements (317 parameters) on 4008 independent reflections ($2\theta_{max} = 52°$) with $I > 3\sigma(I)$ converged at $R = 0.066$ and $R_w = 0.099$. Details of the crystallographic data are summarized in Table 1. Fractional atomic coordinates, along with equivalent isotropic displacement parameters are listed in Table 2. Selected interatomic distances and bond angles, together with the estimated standard deviations, are given in Table 3. Completed crystallographic and structural details are provided in the Supporting Information.

Table 1. Crystallographic Data for $[(12C4)_2Na][Cd(SCN)_3]$ (**3**)

empirical formula	$CdNaS_3N_3O8C_{19}H_{32}$
fw	662.06
space group	$P2_1/n$
a (Å)	13.204(2)
b (Å)	10.692(2)
c (Å)	21.036(1)
β (deg)	95.520(8)
V (Å^3)	2956.0(6)
Z	4
D_{calc} (g cm^{-3})	1.703
μ (cm^{-1})	10.353
λ (Mo Kα, Å)	0.7107
T (°C)	25
$2\theta_{max}$ (deg)	52
R^a	0.066
$R_w{}^b$	0.099

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

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (U_{eq},[a] Å^2) for $[(12C4)_2Na][Cd(SCN)_3]$ (**3**)

	x	y	z	U_{eq}
Cd1	0.74569(3)	0.00213(3)	0.23007(2)	0.0459
S1	0.5812(1)	0.1298(1)	0.17284(10)	0.0609
S2	0.8966(1)	0.1287(2)	0.1787(1)	0.0691
S3	0.7356(1)	−0.1399(1)	0.11852(9)	0.0556
Na1	0.7754(2)	0.3271(3)	−0.1012(1)	0.0635
O1	0.8152(6)	0.179(1)	−0.1862(4)	0.1683
O2	0.7873(7)	0.429(1)	−0.2113(5)	0.1717
O3	0.9187(8)	0.476(1)	−0.0954(8)	0.1983
O4	0.9432(6)	0.2324(10)	−0.0724(6)	0.1973
O5	0.5956(7)	0.294(1)	−0.1447(4)	0.1860
O6	0.6611(7)	0.5210(9)	−0.0908(6)	0.1909
O7	0.7625(6)	0.378(1)	0.0094(4)	0.1502
O8	0.6962(7)	0.1488(9)	−0.0488(5)	0.1762
N1	0.8690(5)	−0.1343(5)	0.2786(3)	0.0716
N2	0.6336(5)	−0.1323(5)	0.2725(3)	0.0672
N3	0.7522(5)	0.1318(5)	0.3168(3)	0.0620
C1	0.6119(4)	0.2676(5)	0.2026(3)	0.0469
C2	0.8784(4)	0.2695(5)	0.2080(3)	0.0454
C3	0.7442(5)	−0.2725(5)	0.1556(3)	0.0422
C4	0.851(1)	0.225(1)	−0.2398(7)	0.1699
C5	0.784(2)	0.338(2)	−0.2514(8)	0.2078
C6	0.880(2)	0.490(2)	−0.2147(8)	0.2035
C7	0.883(2)	0.541(2)	−0.146(1)	0.2500
C8	1.0167(8)	0.415(2)	−0.0846(9)	0.2091
C9	1.008(1)	0.323(2)	−0.0513(9)	0.1956
C10	0.982(1)	0.153(1)	−0.122(1)	0.2041
C11	0.8828(9)	0.085(1)	−0.1588(9)	0.1696
C12	0.546(1)	0.416(2)	−0.1463(8)	0.2088
C13	0.565(1)	0.509(2)	−0.108(1)	0.2087
C14	0.684(2)	0.536(2)	−0.0212(9)	0.2475
C15	0.707(1)	0.468(2)	0.0293(7)	0.1899
C16	0.724(2)	0.310(2)	0.0483(7)	0.2265
C17	0.707(2)	0.177(2)	0.0123(7)	0.2608
C18	0.611(1)	0.124(2)	−0.088(1)	0.2660
C19	0.552(1)	0.193(2)	−0.1209(9)	0.2611

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results

Synthesis and Characterization. Our previous attempt to use a sandwich monocation such as $[(12C4)_2NH_4]^+$ led instead to the sandwich $[(12C4)_2Cd]^{2+}$ dication (due to the low binding affinity of 12C4 for NH_4^+), resulting in the formation of $[(12C4)_2Cd][Cd_2(SCN)_6]$ with a two-dimensional $[Cd_2(SCN)_6{}^{2-}]_\infty$ structure.[2] We reason that, by using a smaller cation such as Na^+, a stable sandwich monocation $[(12C4)_2Na]^+$ can be formed in situ which will induce the formation of $[(12C4)_2Na][Cd(SCN)_3]$ (**3**) with one-dimensional $[Cd(SCN)_3^-]_\infty$ chains. This is indeed observed in the title compound. The balanced equation for the reaction is as follows:

$$2\ 12C4 + 3NaSCN + CdSO_4 \xrightarrow{H_2O} [(12C4)_2Na][Cd(SCN)_3] + Na_2SO_4 \quad (1)$$

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[(12C4)_2Na][Cd(SCN)_3]$ (**3**)

Cd1−S1	2.743(2)	O3−C8	1.45(2)
Cd1−S2	2.718(2)	O4−C9	1.34(2)
Cd1−S3	2.788(2)	O4−C10	1.47(2)
Cd1−N1	2.346(6)	O5−C12	1.46(2)
Cd1−N2	2.304(6)	O5−C19	1.34(2)
Cd1−N3	2.286(6)	O6−C13	1.28(2)
S1−C1	1.637(6)	O6−C14	1.47(2)
S2−C2	1.653(6)	O7−C15	1.30(2)
S3−C3	1.617(6)	O7−C16	1.24(2)
Na1−O1	2.481(9)	O8−C17	1.31(2)
Na1−O2	2.58(1)	O8−C18	1.36(2)
Na1−O3	2.47(1)	N1−C1	1.140(7)
Na1−O4	2.458(9)	N2−C2	1.144(7)
Na1−O5	2.485(9)	N3−C3	1.175(7)
Na1−O6	2.586(10)	C4−C5	1.51(2)
Na1−O7	2.409(9)	C6−C7	1.54(3)
Na1−O8	2.48(1)	C8−C9	1.22(3)
O1−C4	1.36(2)	C10−C11	1.64(2)
O1−C11	1.43(2)	C12−C13	1.29(2)
O2−C5	1.29(2)	C14−C15	1.30(3)
O2−C6	1.40(2)	C16−C17	1.62(3)
O3−C7	1.32(3)	C18−C19	1.23(3)
S1−Cd1−S2	99.08(6)	S2−Cd1−N3	92.5(1)
S1−Cd1−S3	85.97(5)	S3−Cd1−N1	90.1(2)
S1−Cd1−N1	170.9(1)	S3−Cd1−N2	90.3(2)
S1−Cd1−N2	88.2(2)	S3−Cd1−N3	175.7(1)
S1−Cd1−N3	90.9(1)	N1−Cd1−N2	83.6(2)
S2−Cd1−S3	85.07(6)	N1−Cd1−N3	93.4(2)
S2−Cd1−N1	88.7(2)	N2−Cd1−N3	92.6(2)
S2−Cd1−N2	171.0(1)	Cd1−S1−C1	97.1(2)
Cd1−S2−C2	99.6(2)	C7−O3−C8	127(1)
Cd1−S3−C3	94.4(2)	Na−O4−C9	108.2(9)
O1−Na1−O2	65.5(4)	Na1−O4−C10	115.9(9)
O1−Na1−O3	103.4(4)	C9−O4−C10	113(1)
O1−Na1−O4	70.5(3)	Na1−O5−C12	107.2(9)
O1−Na1−O5	84.6(3)	Na1−O5−C19	113(1)
O1−Na1−O6	137.5(4)	C12−O5−C19	121(1)
O1−Na1−O7	151.5(4)	Na1−O6−C13	117(1)
O1−Na1−O8	87.6(4)	Na1−O6−C14	95.9(10)
O2−Na1−O3	70.1(4)	C13−O6−C14	113(1)
O2−Na1−O4	105.3(4)	Na1−O7−C15	124.8(10)
O2−Na1−O5	82.4(3)	Na1−O7−C16	125(1)
O2−Na1−O6	79.9(4)	C15−O7−C16	86(1)
O2−Na1−O7	142.0(4)	Na1−O8−C17	104(1)
O2−Na1−O8	142.0(4)	Na1−O8−C18	103(1)
O3−Na1−O4	65.5(4)	C17−O8−C18	130(1)
O3−Na1−O5	144.1(5)	Cd1−N1−C1	147.6(5)
O3−Na1−O6	86.0(3)	Cd1−N2−C2	145.9(5)
O3−Na1−O7	86.1(4)	Cd1−N3−C3	156.8(5)
O3−Na1−O8	145.8(5)	S1−C1−N1	177.3(6)
O4−Na1−O5	147.0(4)	S2−C2−N2	178.9(6)
O4−Na1−O6	146.0(4)	S3−C3−N3	178.1(6)
O4−Na1−O7	90.1(3)	O1−C4−C5	99(1)
O4−Na1−O8	89.0(3)	O2−C5−C4	121(1)
O5−Na1−O6	66.4(4)	O2−C6−C7	93(1)
O5−Na1−O7	103.5(3)	O3−C7−C6	123(2)
O5−Na1−O8	68.1(4)	O3−C8−C9	108(1)
O6−Na1−O7	69.0(4)	O4−C9−C8	119(1)
O6−Na1−O8	107.7(3)	O4−C10−C11	105(1)
O7−Na1−O8	70.9(4)	O1−C11−C10	108(1)
Na1−O1−C4	119.2(9)	O5−C12−C13	127(1)
Na1−O1−C11	109.1(8)	O6−C13−C12	112(1)
C4−O1−C11	109(1)	O6−C14−C15	139(1)
Na1−O2−C5	105(1)	O7−C15−C14	104(1)
Na1−O2−C6	111.9(9)	O7−C16−C17	104(1)
C5−O2−C6	107(1)	O8−C17−C16	130(1)
Na1−O3−C7	94(1)	O8−C18−C19	131(1)
Na1−O3−C8	112.9(10)	O5−C19−C18	114(1)

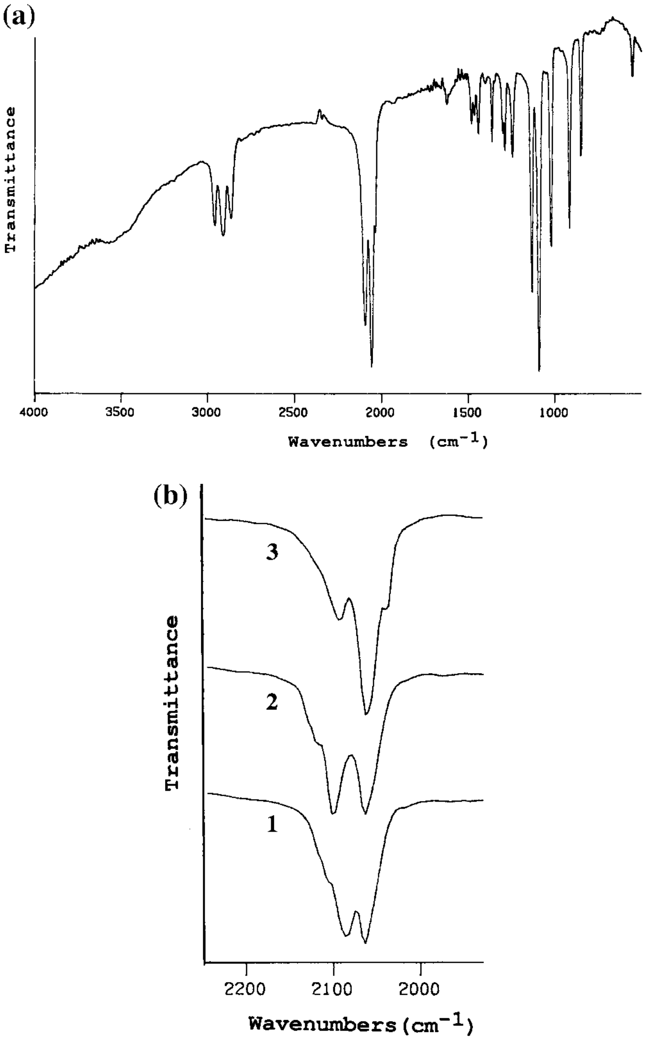

Figure 2. (a) Infrared spectrum (CsI pellet) of $[(12C4)_2Na][Cd(SCN)_3]$ (**3**). (b) Comparison of the ν(CN) stretching frequencies of the bridging thiocyanate ligands in $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**1**), $[(18C6)K][Cd(SCN)_3]$ (**2**), and $[(12C4)_2Na][Cd(SCN)_3]$ (**3**). These patterns are highly characteristic of, and hence can be used to identify, the one-dimensional anionic $[Cd(SCN)_3^-]_\infty$ zigzag chains in cadmium thiocyanate coordination solids.

The infrared spectrum of the title compound **3** exhibits coordinated 12C4 and bridging SCN$^-$ ligands as depicted in Figure 2a. In particular, the ν(C−N) peaks of the bridging SCN$^-$ are observed at 2107 (m) and 2069 (s) cm^{-1}. These IR frequencies are similar to those observed for **1** and **2** (see Figure 2b).[1] In fact, these peaks are highly characteristic of, and can be used to identify, the 1-D $[Cd(SCN)_3^-]_\infty$ chains.

Crystal Structure. The title compound $[(12C4)_2Na][Cd(SCN)_3]$ (**3**) crystallizes in the monoclinic unit cell of dimensions 13.204(2) Å, 10.692(2) Å, 21.036(1) Å, and 95.520(8)° (V = 2956.0(6) Å^3) and space group $P2_1/n$ (b unique), with four $[(12C4)_2Na][Cd(SCN)_3]$ per unit cell (Z = 4). Since all atoms reside on general positions, the asymmetric unit comprises one formula unit of $[(12C4)_2Na][Cd(SCN)_3]$. Selected bond lengths and angles are tabulated in Table 3. The $[(12C4)_2Na]^+$ cations in **3** adopt the sandwich structure of idealized D_{4d} symmetry (Figure 3a) with an average Na−O distance of 2.51 Å. The Cd atoms in **3** are octahedrally coordinated (Figure 3b) with three S and three N atoms (in *fac* configuration) with average Cd−S and Cd−N distances of 2.748 and 2.307 Å, respectively. The average Cd−S−C and Cd−N−C angles of 97.1 and 150.9°, respectively, are similar to those observed in **1** and **2**.[1] The SCN$^-$ ligands are virtually linear (178.2(av)°) with S−C and C−N bond lengths of 1.640(av) and 1.147(av) Å, respectively. The nitrogen atoms are trans to the sulfur atoms, in accordance with the trans influence. As in **1** and **2**, the Cd atoms form an

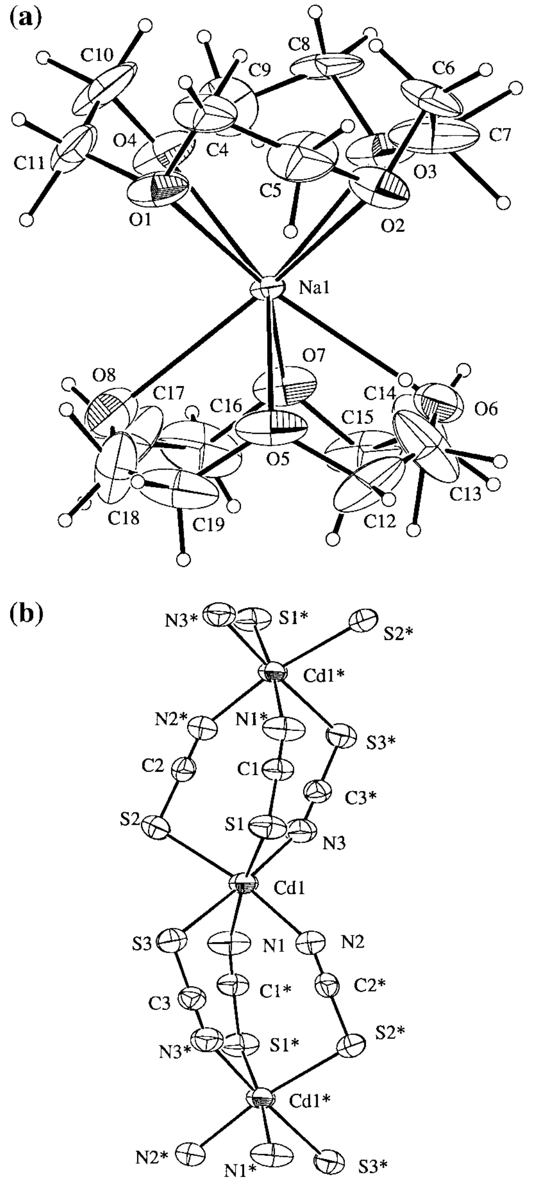

Figure 3. ORTEP drawings of (a) the $[(12C4)_2Na]^+$ sandwich cation which conforms to the idealized D_{4d} point group symmetry (10% thermal ellipsoids) and (b) the infinite anionic $[Cd(SCN)_3{}^-]_\infty$ zigzag chains (50% thermal ellipsoids).

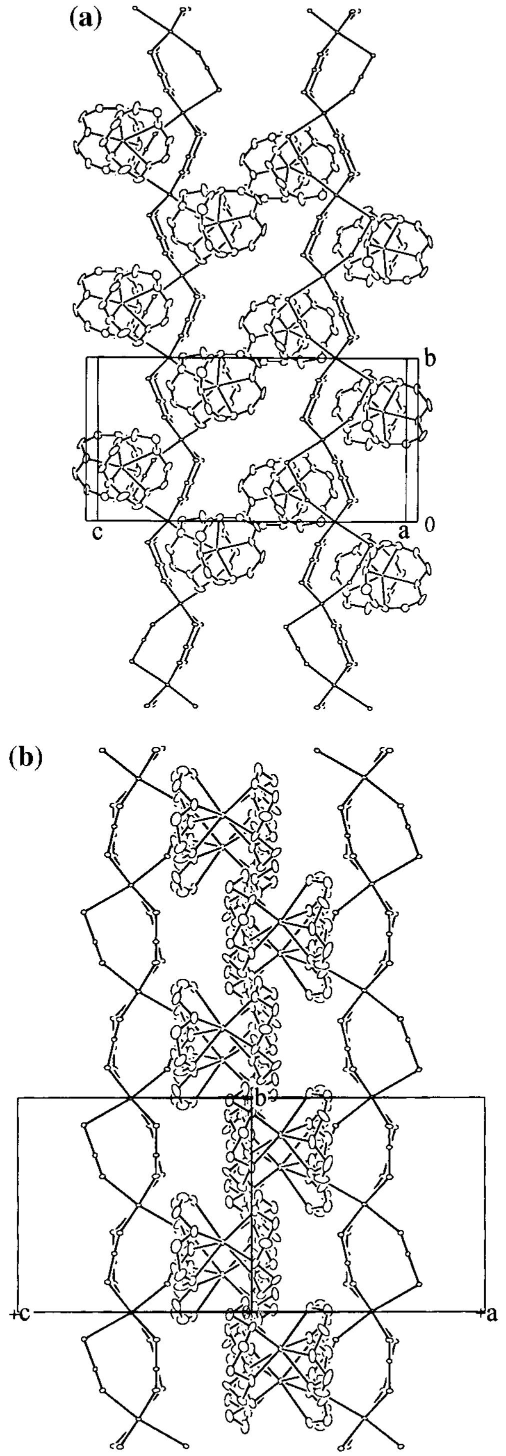

Figure 4. Crystal packing of $[(12C4)_2Na][Cd(SCN)_3]$ (**3**) as viewed along (a) the crystallographic *a* axis and (b) the crystallographic ($a + c$) axis (diagonal).

infinite zigzag chain with Cd···Cd distances of 5.41(av) Å and Cd···Cd···Cd angles of 162.2(av)°. The $[Cd(SCN)_3{}^-]_\infty$ chains run along the crystallographic *b* axis. The zigzag $[Cd(SCN)_3{}^-]_\infty$ chains and the dispositions of the sandwich $[(12C4)_2Na]^+$ cations in **3** are portrayed in Figure 4, in two different views. It can be seen that adjacent rows of zigzag chains are "antiparallel" to one another, resulting in the centrosymmetric space group $P2_1/n$. Furthermore, the two $[(12C4)_2Na]^+$ cations in two adjacent triangular channels are not at the same height with respect to the crystallographic *b* axis.

We shall now compare the crystal structures of $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**1**)[1] (Figure 5) and $[(12C4)_2Na][Cd(SCN)_3]$ (**3**) (Figure 6). As depicted in Figures 5 and 6, the infinite zigzag $[Cd(SCN)_3{}^-]_\infty$ chains in **1** and **3** form approximate tetragonal and hexagonal arrays, as viewed along the crystallographic *b* axis, creating square and triangular channels which are filled with the $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dications (in **1**) and $[(12C4)_2Na]^+$ cations (in **2**), respectively. The noncrystallographic (quasi) hexagonal unit cell (indicated by the dashed lines and designated by subscript *h* in Figure 6) is related to the crystallographic monoclinic unit cell (solid lines in Figure 6) as follows: $a_h = a$; $b_h = (-a + c)/2$; $c_h = b$. This pseudohexagonal arrangement gives rise to distorted triangular channels. The $[(12C4)_2Na]^+$ cations are located at centers of the triangular channels, lying sideways with the "width" (diameter) of the 12C4 rings aligned with one edge of the triangle (i.e., the $a_h + b_h$ direction). This is to be contrasted with the structure of **1** in which the $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dications are located at centers of the square channels created by the noncrystallographic pseudotetragonal array (indicated by subscript *t* in Figure 5) of the $[Cd(SCN)_3{}^-]_\infty$ chains. The lateral

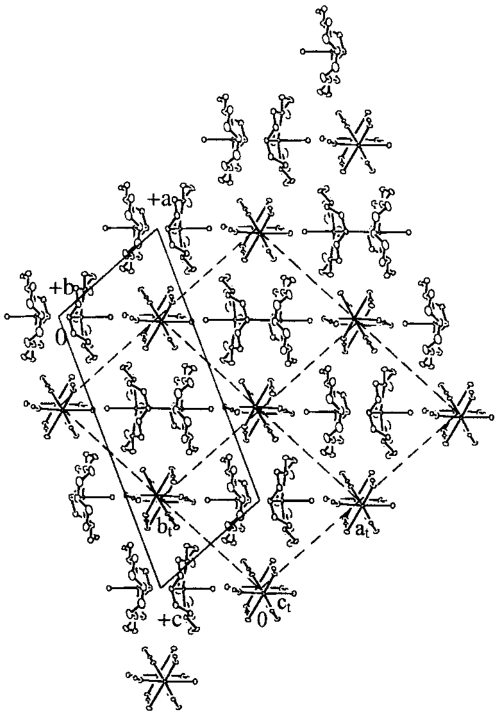

Figure 5. Crystal packing of $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**1**) (viewed along the crystallographic *b* axis; 10% probability thermal ellipsoids). Approximate tetragonal arrangement of zigzag $[Cd(SCN)_3^-]_\infty$ chains creates square channels filled with dimeric $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dications. The crystallographic monoclinic unit cell is indicated by *a*, *b*, and *c* (solid lines) while the noncrystallographic pseudotetragonal unit cell is indicated by a_t, b_t, and c_t (dashed lines) which are related to the crystallographic monoclinic unit cell as follows: $a_t = a$; $b_t = -(a + c)/2$; $c_t = b$.

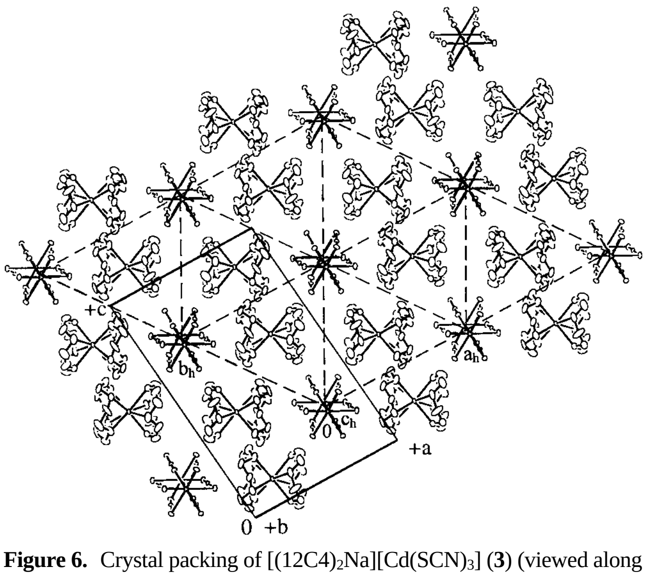

Figure 6. Crystal packing of $[(12C4)_2Na][Cd(SCN)_3]$ (**3**) (viewed along the crystallographic *b* axis; 10% probability thermal ellipsoids). Approximate hexagonal arrangement of zigzag $[Cd(SCN)_3^-]_\infty$ chains gives rise to triangular channels filled with the $[(12C4)_2Na]^+$ cations. The crystallographic monoclinic unit cell is indicated by *a*, *b*, and *c* (solid lines), while the noncrystallographic pseudohexagonal unit cell is indicated by a_h, b_h, and c_h (dashed lines) which are related to the crystallographic monoclinic unit cell as follows: $a_h = a$; $b_h = (-a + c)/2$; $c_h = b$.

dimensions or “width” of the 18C6 rings are oriented along the diagonal ($a_t + b_t$) of the pseudotetragonal cell. The fact that the diagonal of the square channels in **1** ($(2)^{1/2}a_t = (2)^{1/2} \times 10.227 = 14.53$ Å) is larger than the edge length of the triangular channels ($a_h = b_h = (a_h + b_h) = 13.20$ Å) in **3** is consistent with the difference in the lateral dimensions between 18C6 and 12C4.

Discussions

The approximate hexagonal arrangement of the $[Cd(SCN)_3^-]_\infty$ chains in $[(12C4)_2Na][Cd(SCN)_3]$ (**3**) can be conceptually derived from the approximate tetragonal motif in $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**1**) by a formal distortion (compression along the diagonal ($a_t + b_t$) direction and elongation along the diagonal ($a_t - b_t$) direction) as illustrated schematically in Figure 1. Each square channel (Figure 1a) becomes two triangular channels (Figure 1b).[9] The two $[(12C4)_2Na]^+$ monocations housed in two adjacent triangular channels in **3** correspond to a single dimeric $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dication in a square channel in **1**;[1] both are per two $[Cd(SCN)_3^-]$ units. We believe that this distortion is attributable to the smaller size of $[(12C4)_2Na]^+$ (in triangular channels) in comparison with the $[(18C6)_2Na_2(H_2O)_2]^{2+}$ dimer (in square channels). In other words, the *dimensions* of the cation dictate the spatial arrangement of the $[Cd(SCN)_3^-]_\infty$ chains. Furthermore, the *symmetry* of the cation plays an important role in influencing the alignment of the $[Cd(SCN)_3^-]_\infty$ chains. We shall discuss these two effects next.

(A) Cations as Spacers: Spatial Arrangements of the Anionic $[Cd(SCN)_3^-]_\infty$ Chains (Dimension Effect). The arrangement of the anionic $[Cd(SCN)_3^-]_\infty$ chains is to a significant extent dictated by the size and shape of the cations as illustrated schematically in Figure 1. In other words, the cations serve as spacers, filling in the voids between the chains. With large spherical shaped cations such as the dimeric $[(18C6)_2Na_2(H_2O)_2]^{2+}$ in **1** (Figure 5), tetragonal (or square) arrangement of the anionic $[Cd(SCN)_3^-]_\infty$ chains is favored.[1] With small cations such as $[(12C4)_2Na]^+$ in **3** (Figure 6), distorted hexagonal arrangement of the anionic $[Cd(SCN)_3^-]_\infty$ chains is observed. However, volume alone cannot explain why with $[(18C6)K]^+$ in **2** the anionic $[Cd(SCN)_3^-]_\infty$ chains also adopt the tetragonal arrangement.[1] In fact, $[(18C6)K]^+$ (which has a volume of 300 Å^3) is somewhat smaller than $[(12C4)_2Na]^+$ (which is estimated to have a volume of 345 Å^3). The difference between these two cations is the shape. Since the channels formed by the anionic $[Cd(SCN)_3^-]_\infty$ chains must have dimensions large enough to accommodate the cations, the disklike $[(18C6)K]^+$ cations, with a thickness of 4.0 Å and a diameter of 9.77 Å, require a tetragonal motif with an edge length of 10.62 Å and a diagonal dimension of $(2)^{1/2} \times 10.62$ Å $= 15.02$ Å. In fact, two $[(18C6)K]^+$ cations reside in each of the tetragonal channels (but at different heights with respect to the chain direction) with the lateral (diameter) dimension aligned with the diagonal of the square channel. This effect exerted by the cations on the spatial arrangement of the anionic $[Cd(SCN)_3^-]_\infty$ chains may be termed the “dimension effect”. This particular stereochemical characteristic persists in all the IPOS structures observed so far and can also be extended to cations of different sizes and shapes. For example, with relatively small, tetrahedral cations such as $(Me_4N)^+$ and

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[9] The volume of the square channels in **1** is given by, approximately, $a_t^2c_t = (10.277)^2 \times 10.915$ Å^3 $= 1152.8$ Å^3 whereas that of the triangular channels in **3** is, approximately, $(3)^{1/2}/4a_h^2c_h = (3)^{1/2}/4 \times (13.204)^2 \times 10.692$ Å^3 $= 807.18$ Å^3. It should be noted that, in theory, the square channels should have 2.31 times the volume of the triangular channels ($a_t^2c_t/((3)^{1/2}/4a_h^2c_h) = 4/(3)^{1/2} = 2.31$ assuming $a_t = a_h$ and $c_t = c_h$). In the present situation, an expansion of the pseudohexagonal axes in **3** ($a_h/a_t = 13.204$ Å$/10.277$ Å $= 1.285$) reduces this volume ratio substantially.

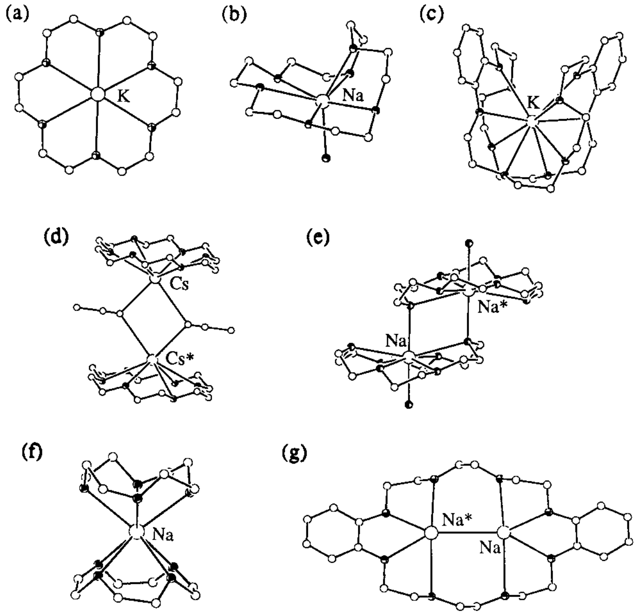

Figure 7. Representative examples of seven categories of the crown ether (host)−alkali metal (guest) structures: (a) disklike (host:guest = 1:1) as in $[(18C6)K][Cd(SCN)_3]$ (**2**);[1] (b) partially coiled (1:1) as in $[(18C6)Na(H_2O)](SCN)$;[20a] (c) coiled (1:1) as in [(dibenzo-30C10)K]I;[20b] (d) dimer (2:2) as in $(18C6)_2Cs_2(SCN)_2$;[20c] (e) dimer (2:2) as in $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**1**);[1] (f) sandwich (2:1) as in $[(12C4)_2Na][Cd(SCN)_3]$ (**3**); (g) two nuclei (1:2) as in [(dibenzo-24C8)Na_2][*o*-$O_2NC_6H_4O$]$_2$.[20d]

$(Et_4N)^+$, the $[Cd(SCN)_3^-]_\infty$ chains are also arranged in an approximate hexagonal array with the cations occupying the triangular channels in both $[Me_4N][Cd(SCN)_3]$ (**4**) and $[Et_4N][Cd(SCN)_3]$ (**5**).[5]

(B) Cations as Controllers: Alignment of the Zigzag $[Cd(SCN)_3^-]_\infty$ Chains (Symmetry Effect). While dimensions (size and shape) of the cations can account for the spatial arrangement of the anionic infinite $[Cd(SCN)_3^-]_\infty$ chains (serving as spacers), the relative alignment (either parallel or antiparallel) is determined by the symmetry or approximate symmetry of the cations and hence may be termed the "symmetry effect". For nonlinear optical effects[10−12] such as second harmonics generation (SHG), it is important to arrange the chains in a parallel fashion and to attain a noncentrosymmetric crystal symmetry.[1] From a crystal engineering point of view,[13−19] it means that one should choose cations which are less prone to reside on inversion centers ($\bar{1}$ symmetry) or are in itself less symmetrical in shape. In Figure 7, we categorize the binding of the crown ethers with alkali metals into seven classes, according to the match or mismatch of the metal ion with the size of the cavity of the crown ether, along with representative examples: (a) disklike (host:guest = 1:1) as in $[(18C6)K][Cd(SCN)_3]$ (**2**);[1] (b) partially coiled (1:1) as in $[(18C6)Na(H_2O)](SCN)$;[20a] (c) coiled (1:1) as in [(dibenzo-30C10)K]I;[20b] (d) dimer (2:2) as in $(18C6)_2Cs_2(SCN)_2$;[20c] (e) dimer (2:2) as in $[(18C6)_2Na_2(H_2O)_2][Cd(SCN)_3]$ (**1**);[1](f) sandwich (2:1) as in $[(12C4)_2Na][Cd(SCN)_3]$ (**3**); (g) two nuclei (1:2) as in [(dibenzo-24C8)Na_2][*o*-$O_2NC_6H_4O$]$_2$.[20d] To enhance the tendency of forming a noncentrosymmetric space group, the monomeric host−guest (1:1) complexes of either a disklike, a partially coiled, or a coiled structure, as portrayed in Figure 7a−c, should be used as cationic spacer/controller. To prevent the formation of centrosymmetric space groups, symmetrical cationic host−guest molecules such as dimeric structures (Figure 7d,e), sandwhich complexes (Figure 7f), or two-nuclei complexes (Figure 7g) should be avoided as these latter complexes have the tendency to form centrosymmetric structures. For example, cations of the dimeric structure $[(18C6)_2Na_2(H_2O)_2]^{2+}$ caused an antiparallel arrangement of the $[Cd(SCN)_3^-]_\infty$ chains whereas cations of the disklike structure $[(18C6)K]^+$ led to a parallel arrangement of the $[Cd(SCN)_3^-]_\infty$ chains, resulting in centrosymmetric and noncentrosymmetric space groups as observed in **1** and **2**, respectively.[1] In **3**, the sandwich $[(12C4)_2Na]^+$ monocation also favors an antiparallel arrangement of the $[Cd(SCN)_3^-]_\infty$ chains (though the cation itself conforms to D_{4d} sysmetry which lacks the inversion symmetry), resulting in a centrosymmetric space group ($P2_1/n$). Thus, as illustrated in Figure 4a, the cations are tucked snugly in the "pockets" of space formed by the "grooves" of adjacent antiparallel zigzag $[Cd(SCN)_3^-]_\infty$ chains. The grooves of the $[Cd(SCN)_3^-]_\infty$ chains are due to the "kinks" at the sulfur atoms (Cd−S−C of 97.1°) of the bridging SCN^- ligands.

The principle of alignment control (symmetry effect) by the cations also applies to $[Me_4N][Cd(SCN)_3]$ (**4**) and $[Et_4N][Cd(SCN)_3]$ (**5**)[5] mentioned previously. Here the tetrahedral $(Me_4N)^+$ and $(Et_4N)^+$ cations, which lack the inversion symmetry, give rise to noncentrosymmetric space groups $Pna2_1$ and $Cmc2_1$ for **4** and **5**, respectively. However, a detailed examination of these two latter structures indicates that the $[Cd(SCN)_3^-]_\infty$ chains in **4** and **5** are arranged in an antiparallel and parallel fashion, respectively. Hence, we caution that antiparallel alignment of the infinite metal thiocyanate chains (as in **4**) does not always give rise to a centrosymmetric space group. On the other hand, parallel alignment of the chains should always lead to a noncentrosymmetric space group (as in **2**, **5**, and in $[(dibenzo\text{-}24C8)Na][Cd(SCN)_3]$[21]).

Conclusion

In conclusion, the sandwich $[(12C4)_2Na]^+$ cation serves both as the spacer and as the controller of the arrangement (hexagonal) and alignment (antiparallel), respectively, of the infinite $[Cd(SCN)_3^-]_\infty$ zigzag chains in the coordination solid $[(12C4)_2Na][Cd(SCN)_3]$. The influence of the cation, due to its size

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(21) Since the submission of this paper, we have synthesized and structurally characterized a 1-D cadmium thiocyanate coordination solid with a coiled crown-ether−alkali-metal cation (similar to Figure 7c), namely, $[(dibenzo24C8)Na][Cd(SCN)_3]$. This compound, as predicted, has a parallel alignment of the infinite cadmium thiocyanate chains, giving rise to a noncentrosymmetric space group *Cc* (to be published).

and shape, on the spatial arrangement of the $[Cd(SCN)_3^-]_\infty$ chains may be termed the "dimension effect". The control of the relative alignment of the anionic chains as well as the crystal symmetry by the cation, owing to its geometry and symmetry, may be termed the "symmetry effect". Work is in progress to further assess the relative importance of the size, shape, symmetry, and charge of the cations in influencing the structure and properties of anionic cadmium thiocyanate coordination solids.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available. Access and/or ordering information is given on any current masthead page.

Note Added in Proof

Powder measurements on $[Et_4N][Cd(SCN)_3]$ (**5**) indicate, as predicted, that it exhibits efficient second-order nonlinear optical effect (submitted for publication).

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