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Syntheses and Structural Characterizations of the Three-dimensional Polymers $[(R_2Sn)_3\{Co(CN)_6\}_2{\cdot}X]$ (R = Vinyl, Propyl, Butyl; X = Solvent)

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Three coordination polymers with the general formula $[(R_2Sn)_3\{Co(CN)_6\}_2{\cdot}X]$, R = vinyl(**1**), butyl(**2**), and propyl (**3**), were synthesized and structurally characterized. The three compounds are homologues with similar cell dimensions. They all crystallize in space group $P6_3/mcm$ [**1**, $a = 13.034(1)$ Å, $c = 13.678(1)$ Å; **2**, $a = 13.741(1)$ Å, $c = 13.363(1)$ Å; **3**, $a = 13.477(1)$ Å, $c = 13.362(1)$ Å]. The structures are formed by linking R_2Sn units with distorted octahedral $Co(CN)_6$ fragments. Each tin atom is coordinated by four $Co(CN)_6$ units and adopts an octahedral SnN_4C_2 arrangement. Channels along the *c* axis are occupied by disordered alkyl groups. The channels have "bottlenecks" which in **1** prevent facile release of solvent molecules. No solvent molecules are found in **2** and **3**, since the channel space is occupied by the alkyl groups.

Introduction

Synthesis of novel microporous materials using both organic and inorganic components is an active research area.[1,2] We are studying the synthesis and crystal structures of organotin−cyanometalate coordination polymers.[3−6] Several compounds with the general formula $[(R_mSn^{IV})_x\{M(CN)_n\}_y]$ are known,[7−9] but few crystal[10−12] structures have been obtained. We have grown single crystals of several new and previously reported compounds and systematically studied the effects of the size and number of the R groups and the number of CN groups on the structures that are formed.

The structure of $[Co^{III}(CN)_6(Me_3Sn)_3]$[10,11] was the first obtained in the organotin−cyanometalate family of coordination polymers. This structure type has a framework containing large channels and shows intercrystalline reaction chemistry.[13−16] For example, $[(Fe^{III}Cp_2)(Me_3Sn)_3Fe^{II}(CN)_6]$[13] was synthesized by direct intercalation of $[Fe^{III}(CN)_6(Me_3Sn)_3]$ with ferrocene($Fe^{II}Cp_2$). The iron compound is isostructural with $[(Co^{III}Cp_2)(Me_3Sn)_3Fe^{II}(CN)_6]$.[17] The latter compound was prepared by direct reaction and its structure was determined by single-crystal X-ray diffraction. The crystal structures of the related compounds $[(Me_3Sn)_4Fe^{II}(CN)_6{\cdot}2H_2O{\cdot}C_4H_8O_2]$[18] and $[(Me_3Sn)_4Fe^{II}(CN)_6{\cdot}4H_2O]$[19] have also been determined. These compounds are bridged by Me_3Sn units in only two dimensions. The three-dimensional framework is formed by hydrogen bonds between the coordinated water molecules and the guest solvent molecules. The framework structure of $[CuCN{\cdot}Me_3SnCN{\cdot}0.5bpy]$,[20] contains both bridging Me_3Sn and 4,4′-bipyridine. $[(Me_3Sn)_2Ni(CN)_4(^nBu_4N)OH]$ and $[(R_4N)(Me_3Sn)_2Co(CN)_6{\cdot}H_2O]$ are examples of compounds with structures containing both bridging R_3Sn ligands and terminal R_3SnOH or R_3SnOH_2 groups.[21−23]

The choice of the R group determines the specific organotin−cyanometalate structure. For example, the framework of $[Co^{III}(CN)_6(Me_3Sn)_3]$ is defined by rings containing four cobalt atoms. In contrast, when R = Bu, the structure of $[\{(n\text{-}C_4H_9)_3Sn\}_3Co(CN)_6]$[5] contains three- and five-membered rings. When R = Ph, the compound $[(Ph_3Sn)_3Fe(CN)_6{\cdot}H_2O{\cdot}2CH_3CN]$[4] contains terminal $Sn{-}OH_2$ groups hydrogen bonded to one-sixth of the terminal CN groups. As expected, the topology of

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Table 1. Crystallographic data for **1**−**3**

	$[\{(C_2H_3)_2Sn\}_3\{Co(CN)_6\}_2\cdot X]$	$[\{(C_4H_9)_2Sn\}_3\{Co(CN)_6\}_2]$	$[\{(C_3H_7)_2Sn\}_3\{Co(CN)_6\}_2]$
formula	$C_{26}H_{22}Co_2N_{12}Sn_3$	$C_{36}H_{54}Co_2N_{12}Sn_3$	$C_{30}H_{42}Co_2N_{12}Sn_3$
fw	976.49	1128.84	1044.69
crystal size, mm^3	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.3	0.22 × 0.2 × 0.14
a (Å)	13.034(1)	13.741(1)	13.477(1)
c (Å)	13.678(1)	13.363(1)	13.362(1)
V (Å^3)	2012.4(2)	2185.1(2)	2101.6(2) 2
Z	2	2	2
space group	$P6_3/mcm$ (No. 193)	$P6_3/mcm$ (No. 193)	$P6_3/mcm$ (No. 193)
T, K	223	223	223
λ, Å	0.71073	0.71073	0.71073
ρ_{calc}, g/cm^{-3}	1.612	1.716	1.651
μ, cm^{-1}	26.73	24.74	25.65
$R(F)^a(I > 4\sigma(I))$	0.0198	0.0472	0.0190
w$R2(F^2)^b$	0.0551	0.1088	0.0570
A, B^b	0.018, 2.21	0.05, 33.04	0.0290, 2.61

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$.

the framework is also determined by the number of CN groups per metal atom, for example, in $[(^nBu_4N)(Et_3Sn)_2Cu(CN)_4]$,[12] $[(Me_3Sn)_4Mo(CN)_8]$,[3] and $[(Ph_3Sn)_2Ni(CN)_4\cdot Ph_3SnOH\cdot{\sim}0.8CH_3CN\cdot{\sim}0.2H_2O]$.[6]

The diorganotin−cyanometalates, $[(R_2Sn^{IV})_mM(CN)_n]$, have received less attention. The synthesis of $[(Bu_2Sn^{IV})_3\{Fe(CN)_6\}_2\cdot 4H_2O]$[9] has been reported, but the structure was not determined. Here we report new syntheses of the three 3-D coordination polymers $[(R_2Sn)_3\{Co(CN)_6\}_2\cdot X]$ (R = vinyl, propyl, and butyl) together with their X-ray crystal structures. We also compare them with other compounds in the organotin−cyanometalate family.

Experimental Section

$K_3[Co(CN)_6]$, $(C_2H_3)_2SnCl_2$, $(n\text{-}C_3H_7)_3SnCl$ (98%), and $(n\text{-}C_4H_9)_2SnCl_2$ (STREM Chemical Co.) were used as received. Methanol and tetrahydrofuran (THF) were dried over molecular sieves (4 Å). Infrared spectra were collected on a Galaxy FTIR 5000 series spectrometer using the KBr pellet method. Thermogravimetric analyses were carried out using a Du Pont Instruments 2000 thermal analyzer in a flowing oxygen atmosphere.

$K_3[Co(CN)_6]$ (0.136 g, 0.410 mmol) was dissolved in distilled water (10 mL) and placed in a 25 mL screw-capped tube. A 5 mL mixture of 1:1 water/THF was applied as a buffer layer and 10 mL of a THF solution of $(C_2H_3)_2SnCl_2$ (0.280 g, 1.149 mmol) was layered on top. Clear block crystals of $[\{(C_2H_3)_2Sn\}_3\{Co(CN)_6\}_2\cdot X]$ (**1**) were observed at the interface after 1 week of interdiffusion. The yield was 65% based on $K_3[Co(CN)_6]$.

The compound $[\{(C_4H_9)_2Sn\}_3\{Co(CN)_6\}_2]$ (**2**) was synthesized in a similar way. $K_3[Co(CN)_6]$ (0.109 g, 0.329 mmol) and $(C_4H_9)_2SnCl_2$ (0.200 g, 0.658 mmol) were dissolved in water and MeOH, respectively. The layer method was used as for **1** with a buffer layer of MeOH and water. Colorless, block crystals of **2** were formed in about 2−3 weeks. The yield was 98% based on $K_3[Co(CN)_6]$.

For **3**, $K_3[Co(CN)_6]$ (0.078 g, 0.235 mmol) and $(C_3H_7)_3SnCl$ (0.200 g, 0.706 mmol) were dissolved in water and THF, respectively. Then the THF solution was layered on top of the aqueous solution with a water/THF buffer layer in between. Colorless crystals were observed in the middle of the tube in about 3−4 weeks in two distinct shapes. The minor phase was prismatic column crystals with the composition $[\{(C_3H_7)_2Sn\}_3\{Co(CN)_6\}_2]$ (**3**). The major phase was colorless square plate crystals with the composition $[\{(C_3H_7)_3Sn\}_3\{Co(CN)_6\}]$ (**4**).

X-ray Crystallography. A colorless block crystal of **1** with approximate dimensions 0.4 × 0.3 × 0.3 mm was mounted in a random orientation on a Siemens SMART platform diffractometer equipped with a 1K CCD area detector.[24] The sample was placed in a stream of dry nitrogen gas at −50 °C. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using Mo Kα radiation and a narrow-frame method with scan widths of 0.30° in ω with an exposure time of 15 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on I was <1%. The data were integrated using the Siemens SAINT program,[25] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. An empirical absorption correction was applied on the basis of the entire data set using SADABS.[26] Redundant reflections were averaged. The Laue symmetry was determined to be 6/*mmm*. The structure of **1** was solved in hexagonal space group $P6_3/mcm$ using direct methods, and the structure refinement was carried out using the SHELXTL program package.[27] The asymmetric unit consists of $^1/_6$ $Co(CN)_6$ located on a crystallographic 3.2 site, and $^1/_4$ $(C_2H_3)_2Sn$ located about a *m*2*m* site. All non-hydrogen atoms were located and their positions refined by a series of least squares cycles and difference Fourier syntheses.

Data were collected for **2** with a colorless block crystal having dimensions 0.3 × 0.2 × 0.3 mm and for **3** with a colorless prismatic column crystal of dimensions 0.22 × 0.2 × 0.14 mm. The structures were both solved in space group $P6_3/mcm$ and refined as described for compound **1**. Crystallographic information for all three compounds can be found in Table 1. Bond distances and angles can be found in Table 2.

Results and Discussion

Synthesis. Interdiffusion of $Co(CN)_6^{3-}$ with either $(C_2H_3)_2Sn^{2+}$ or $(C_4H_9)_2Sn^{2+}$ gave single-phase samples of **1** and **2** in single crystal form in high yield. Crystalline samples of both **1** and **2** were also made by direct reaction. Their powder X-ray

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**3**

$[\{(C_2H_3)_2Sn\}_3\{Co(CN)_6\}_2\cdot X]$ (**1**)[a]			
Sn−C(11)	2.104(6)	Sn−C(21)	2.113(8)
Sn−N	2.284(2)	Co−C(1)	1.887(3)
N−C(1)	1.144(4)	C(11)−C(12)	1.22(2)
C(11)−C(13)	1.22(2)	C(21)−C(22)	1.22(2)
C(21)−C(23)	1.21(2)		
C(11)−Sn−C(21)	180.0(1)	C(11)−Sn−N	91.43(7)
C(21)−Sn−N	88.57(7)	C(1)−Co−C(1)#6	89.5(2)
C(1)#4−Co−C(1)#6	178.2(2)	C(1)−N−Sn	160.3(3)
N−C(1)−Co	177.4(3)	N−Sn−N#2	90.54(13)
C(12)−C(11)−Sn	126(2)	C(13)−C(11)−Sn	129.8(14)
C(22)−C(21)−Sn	128.8(11)	C(23)−C(21)−Sn	148(2)
$[\{(C_4H_9)_2Sn\}_3\{Co(CN)_6\}_2]$ (**2**)[b]			
Sn−C(11)	2.183(9)	Sn−C(21)	2.198(10)
Sn−C(31)	2.192(10)	Sn−N(1)	2.330(6)
Co−C(1)	1.887(7)	N(1)−C(1)	1.154(9)
C(11)−C(12)	1.53	C(12)−C(13)	1.50
C(13)−C(14)	1.48(3)	C(11)−C(12′)	1.497(10)
C(12′)−C(13′)	1.50	C(13′)−C(14′)	1.44(3)
C(13′)−C(14″)	1.45(3)	C(21)−C(22)	1.50
C(22)−C(23)	1.54	C(23)−C(24)	1.45(3)
C(31)−C(32)	1.50	C(32)−C(33)#3	1.39(5)
C(33)−C(34)	1.44(3)		
C(11)−Sn−C(31)	167.4(9)	C(11)−Sn−C(21)	164(3)
C(31)−Sn−C(21)	17(4)	C(11)−Sn−N(1)	91.2(2)
C(21)−Sn−N(1)	96(4)	C(31)−Sn−N(1)	101.2(10)
C(1)#4−Co−C(1)	94.3(4)	C(1)#5−Co−C(1)#6	174.6(5)
C(1)−N(1)−Sn	163.6(7)	N(1)−C(1)−Co	175.4(8)
N(1)#1−Sn−N(1)	84.7(3)	C(12)−C(11)−Sn	114(2)
C(13)−C(12)−C(11)	107.5	C(14)−C(13)−C(12)	153(3)
C(12′)−C(11)−Sn	125(3)	C(11)−C(12′)−C(13′)	103(5)
C(14′)−C(13′)−C(12′)	74(2)	C(14″)−C(13′)−C(12′)	129(6)
C(21)−C(22)−C(23)	112.5	C(24)−C(23)−C(22)	155(10)
C(31)#2−C(32)−C(33)#3	103(5)	C(34)−C(33)−C(32)	122(6)
$[\{(C_3H_7)_2Sn\}_3\{Co(CN)_6\}_2]$ (**3**)[c]			
Sn−C(11)	2.128(7)	Sn−C(21)	2.128(10)
Sn−N(1)	2.307(3)	Co−C(1)	1.890(3)
N(1)−C(1)	1.146(4)	C(11)−C(12)	1.51(2)
C(12)−C(13)	1.51(2)	C(11)−C(12′)	1.544(10)
C(12′)−C(13′)	1.545(10)	C(21)−C(22)	1.509(13)
C(22)−C(23)	1.521(13)		
C(21)−Sn−C(11)	167.6(6)	C(11)−Sn−N(1)	92.5(5)
C(21)−Sn−N(1)	75.3(3)	C(1)−Co−C(1)#6	176.9(2)
C(1)−Co−C(1)#7	92.3(2)	C(1)−N(1)−Sn	161.3(3)
N(1)−C(1)−Co	176.8(3)	N(1)#3−Sn−N(1)	93.7(2)
C(12)−C(11)−Sn	118.0(13)	C(13)−C(12)−C(11)	109(3)
C(12′)−C(11)−Sn	108(2)	C(11)−C(12′)−C(13′)	124(4)
C(22)−C(21)−Sn	116.9(7)	C(21)−C(22)−C(23)	110.0(11)

[a] Symmetry transformations used to generate equivalent atoms: #2, x, y, $-z + 1/2$; #4, $-y$, $-x$, $-z$; #6, x, $x - y + 1$, -z. [b] Symmetry transformations used to generate equivalent atoms: #1, x, y, $-z + 1/2$; #2 $x - y$, $-y$, $-z + 1/2$; #3, $x - y$, $-y$, z; #4, $-y + 1$, $-x + 1$, $-z$; #5, $-y + 1$, $x - y$, z; #6, $-x + y + 1$, y, $-z$. [c] Symmetry transformations used to generate equivalent atoms: #3, $-x$, $-x + y$, z; #6 $-y + 1$, $-x + 1$, $-z$; #7 $-x + y$, y, $-z$.

patterns matched the patterns simulated from single-crystal data. Single crystals of **2** were also obtained using other solvents such as THF, CH_3CN, acetone, EtOH, and DMF for $(C_4H_9)_2SnCl_2$.

Single crystals of **3** were obtained as a minor phase. The major phase was determined to be $[\{(C_3H_7)_3Sn\}_3\{Co(CN)_6\}]$ (**4**) by elemental analysis (Calcd (%): Sn 37.14, Co 6.15, C 41.33, N 8.76, H 6.62. Found (%): Sn 36.38, Co 6.19, C 41.77, N 8.66, H 7.00).

Crystals of **4** suitable for single-crystal X-ray diffraction have not yet been obtained. A structure determination of the minor phase **3** showed that it was isostructral with **1** and **2** with the composition $[\{(C_3H_7)_2Sn\}_3\{Co(CN)_6\}_2]$. Consequently we have included a discussion of its structure for comparison with **1** and **2**.

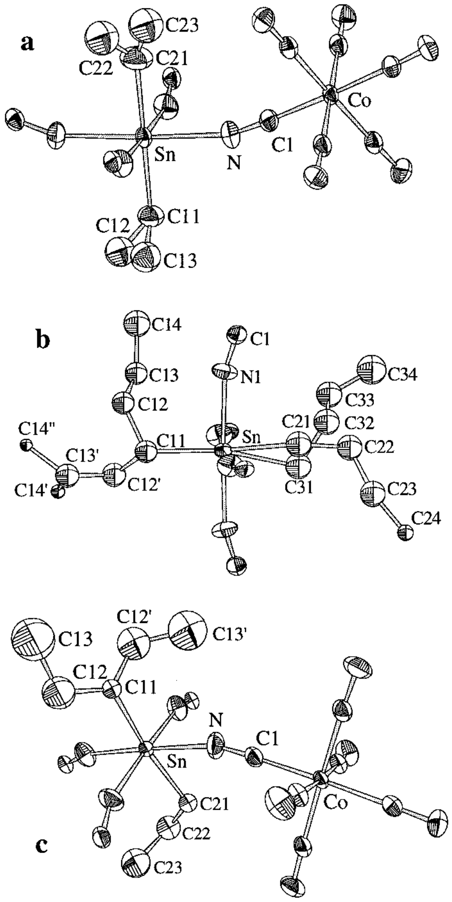

Figure 1. ORTEP drawings of local coordination environments of (a) **1**, (b) **2**, and (c) **3**, showing the disordered alkyl groups. Thermal ellipsoids are shown at 50% probability.

The presence of $(C_3H_7)_2SnCl_2$ as an impurity in $(C_3H_7)_3SnCl$ (98%) is probably a result of the methods used to synthesize $(C_3H_7)_3SnCl$.[28−30] Reaction of R_4Sn with $SnCl_4$ is the most widely used method to prepare both R_3SnCl and R_2SnCl_2.[28] The final product is controlled by the ratio of the starting materials and synthesis conditions. Alternatively, the synthesis of $(C_3H_7)_3SnCl$ by using metallic tin powder and an excess of alkyl chloride in the presence of a catalyst[29] may also lead to the formation of $(C_3H_7)_2SnCl_2$. R_2SnX_2 and R_4Sn can be formed by decomposition of R_3SnX on heating.[28] Similar results were obtained with other sources of $(C_3H_7)_3SnCl$.

Direct reaction of $(C_3H_7)_3SnCl$ with $K_3[Co(CN)_6]$ in water/THF gave a microcrystalline product of **4**, powder X-ray diffraction pattern of which was significantly different from the pattern simulated from the single-crystal data of **3**.

Structure. Figure 1 shows the local coordination environments of the compounds. Terminal carbons of the vinyl groups in **1** are disordered over two distinct positions (Figure 1a). The ratio of the occupancies is 3:2 for C13 to C12 and 2:1 for C22 to C23. The four C−C distances of the disordered vinyl groups were constrained to be equal and refined as a free variable.

The butyl groups of **2** are disordered over three distinct positions (Figure 1b), with unequal populations for each orientation (the ratio of the occupancies of C11 to C21 to C31 is 1:0.76:0.24). Rigid body refinement combined with distance

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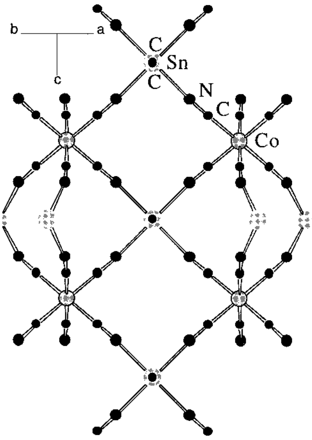

Figure 2. A view perpendicular to *c* axis, showing the coordination environments of Co and Sn atoms, with only the carbon atoms attached to Sn shown. These two carbons overlap with the Sn atoms in the projection.

constraints were applied. The carbon atoms of each butyl group were modeled as an ideal *n*-propyl group (C−C = 1.50 Å, C−C−C = 109.5°) with the C−C distance to the terminal carbon atom constrained to be 1.45 Å. The bond distances were made less than the ideal 1.54 Å in order to account for large thermal motion and/or minor static disorder. All Sn−C bond lengths were constrained to be 2.20 ± 0.03 Å. The disordered butyl group starts with C11 split into C12−C14 and C12′−C14′ with a 5:2 ratio, and the terminal carbon atom attached to C13′ is disordered over C14′ and C14″.

One of the propyl groups of **3** (Figure 1c) is disordered over two positions with approximately equal populations. The C−C distances in the structure were constrained to be equal and refined as a free variable, except for the C−C distances of the second position of the disordered propyl group, which were constrained to be 1.54 Å.

Compounds **1**, **2**, and **3** are homologues that crystallize in space group *P*63/*mcm* with similar cell dimensions. In all cases, every $Co(CN)_6$ group is connected through R_2Sn bridges to other $Co(CN)_6$ units to form a three-dimensional network. The Sn−N−C angles are bent significantly at the N atoms [160.3(3)° for **1**, 163.6(7)° for **2**, and 161.3(3)° for **3**]. The N−Sn−N angles are 90.5(2)°, 84.7(3)°, and 93.7(2)° for **1**, **2**, and **3**, respectively. The Sn−N distances [2.284(2), 2.330(6), and 2.307(3) Å for **1**, **2**, and **3**, respectively] are comparable to those found in other organotin compounds, e.g. $[\{(n\text{-}C_4H_9)_3Sn\}_3Co(CN)_6]$[5] (2.38 Å) and $[(Me_3Sn)_4Mo(CN)_8]$[3] (2.34 Å). The $Co(CN)_6$ units display a slightly distorted octahedral geometry with all the C−Co−C angles close to linear [178.2(2)°, 174.6(5)°, and 176.9(2)° for **1**, **2**, and **3**, respectively]. Each Sn atom is a vertex for four $Co(CN)_6$ units. The R_2SnN_4 units are octahedral with the alkyl C atoms in the axial positions. In compounds formed with R_3Sn^+ bridging groups, the Sn atoms always adopt a R_3SnN_2 trigonal-bipyramidal configuration.

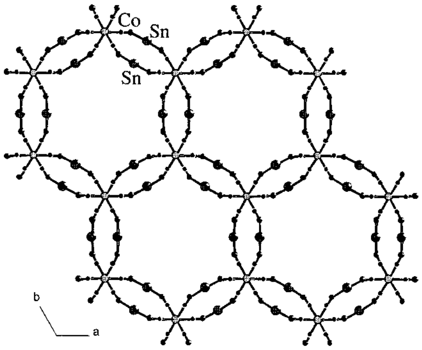

Figure 3. View of the frameworks along *c*, with alkyl groups and solvent molecules omitted.

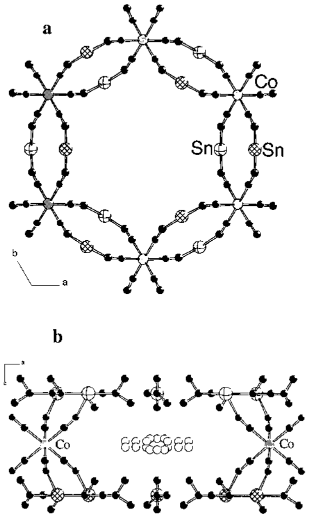

Figure 4. $[(Vinyl_2Sn)_3\{Co(CN)_6\}_2 \cdot X]$(**1**): (a) view of one ring, with alkyl groups and solvent molecules omitted. Sn atoms with the same shading are in the same plane perpendicular to *c*. (b) View of one ring perpendicular to the channel, showing the bottlenecks. Solvent molecules are shown as open circles.

The frameworks of **1**, **2**, and **3** are closely similar. Figure 2 is a view perpendicular to *c*, showing the coordination environments of Co and Sn atoms. The carbon atoms of the two alkyl groups overlap the Sn atoms in this projection. Alternate Sn atoms lie above and below the plane. Channels are formed along the *c* axis (see Figure 3), which are occupied by the alkyl groups bonded to the Sn atoms. The space group is centric and consequently the structure contains equal numbers of the two possible orientations of the tris(chelato)cobalt(III) fragment. In **1** solvent molecules are also found in the channel. For a particular ring (Figure 4a), all six Co atoms are in the same plane perpendicular to the *c* axis, and the Sn atoms that connect the $Co(CN)_6$ units together form two planes above and below the Co plane. In Figure 4a, the Sn atoms in the same plane are shown with the same shading. In the inner side of the channel, the distances between the Sn atoms that are in the same plane are 9.21, 10.04, and 9.66 Å for **1**, **2**, and **3**, respectively.

The channels in **1** are filled with both vinyl groups attached to Sn and solvent molecules. Figure 4b is a cross section of the channels perpendicular to *b* with disordered vinyl groups and solvent molecules shown. The empty circles in the middle of the ring are the solvent molecules. The solvent molecules in **1** are so heavily disordered that only two sites designated as carbon atoms were located. The X-ray data cannot distinguish between THF, water, or a mixture, but thermogravimetric analysis data suggest ~0.5 THF per formula unit. Three vinyl groups form "bottlenecks" 6.84 Å apart along the channel above and below the solvent molecules. The closest contact between terminal carbons of adjacent vinyl groups forming the same bottleneck is 3.5 Å. Removal of the solvent molecules from the framework is hindered by these bottlenecks. The distances between the solvent molecules and the double bonds of the vinyl groups are less than 3.42 Å. Some interaction between the lone pair electrons of the oxygen atoms from either THF or water with the double bonds is possible.

In **3**, the propyl groups replace the vinyl groups. Since the propyl groups occupy more space, solvent molecules are excluded from the channels. Figure 5 shows how the channels

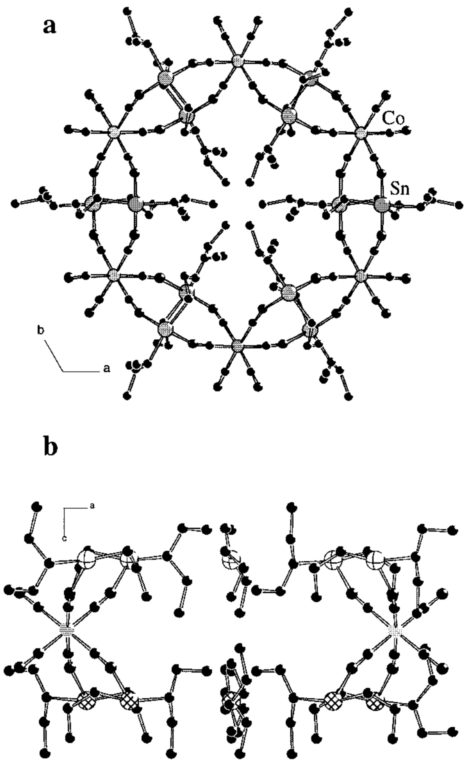

Figure 5. [(Propyl$_2$Sn)$_3${Co(CN)$_6$}$_2$] (**3**): (a) view of one ring along *c*. (b) cross section of one ring perpendicular to the channel.

are occupied by propyl groups. The distance between the two bottlenecks is 6.68 Å along *c*. No solvent molecules are found in the channels of **2**, and the butyl groups are severely disordered. The distance between the two bottlenecks is 6.68 Å, as found in **3**.

Other Characterizations. The IR spectra of **1** and **2** exhibit CN stretching bands at 2170 and 2154 cm^{-1}. As is observed in other organotin−cyanometalates,[4,10] the bands are both blue-shifted from that of $K_3Co(CN)_6$ (2118 cm^{-1}).[10] The TGA experiments were carried out in oxygen with a 3°/min flow rate. A slower rate of 1°/min, from 300 to 350 °C for **1** and from 280 to 320 °C for **2**, was used to avoid exothermic combustion.

Thermogravimetric oxidation of **1** was complete at 350 °C, and the residue was shown to be Co_3O_4 and SnO_2 by X-ray powder diffraction (found 55.79%, cal. 54.55%). The total weight loss indicated the presence of some solvent molecules. This was also apparent in the significant weight loss observed below 150 °C. The solvent loss occurs at temperatures significantly above the boiling points of THF (66 °C) and/or H_2O, suggesting that the bottlenecks hinder solvent thermal desorption. Thermogravimetric oxidation of **2** was also complete at 350 °C. The overall weight loss (51.31%) was in very good agreement with the value calculated (51.7%) for the oxidation of [{(C$_4$H$_9$)$_2$Sn}$_3${Co(CN)$_6$}$_2$].

Summary

Three coordination polymers with the general formula [(R$_2$Sn)$_3${Co(CN)$_6$}$_2$·X], R = vinyl, propyl and butyl, were synthesized and structurally characterized by single-crystal X-ray diffraction. The three compounds are homologues with similar cell dimensions. The frameworks are little effected by the size of the R groups, in contrast to the triorganotin−cyanometalates, where the size of the R group has a strong influence on the topology of the framework. The 3-D neutral networks are made up of bridging R_2Sn units and distorted octahedral $Co(CN)_6$ fragments. Each tin atom is coordinated by four $Co(CN)_6$ units and adopts an octahedral SnN_4C_2 arrangement. Channels along the *c* axis are occupied by disordered alkyl groups. The channels have bottlenecks which in **1** prevent facile release of solvent molecules. No solvent molecules are found in **2** and **3**, since the channel space is occupied by the alkyl groups.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of ([{(C$_2$H$_3$)$_2$Sn}$_3${Co(CN)$_6$}$_2$·X], [{(C$_4$H$_9$)$_2$Sn}$_3${Co(CN)$_6$}$_2$], and [{(C$_3$H$_7$)$_2$Sn}$_3${Co(CN)$_6$}$_2$]). This material is available free of charge via the Internet at http://pubs.acs.org.

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