

Syntheses and Structural Characterizations of Two Three-Dimensional Polymers:

 ${}^3_{\infty}[\{(n\text{-C}_4\text{H}_9)_3\text{Sn}\}_3\text{M}(\text{CN})_6]$ (M = Fe, Co)

Tianyan Niu, Jian Lu, Xiqu Wang, James D. Korp, and Allan J. Jacobson*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Received May 13, 1998

The three-dimensional coordination polymers $[\{(n\text{-C}_4\text{H}_9)_3\text{Sn}\}_3\text{M}(\text{CN})_6]$ (M = Fe, Co) were synthesized by slow interdiffusion of aqueous solutions of $\text{K}_3[\text{M}(\text{CN})_6]$ and THF solutions of $(\text{C}_4\text{H}_9)_3\text{SnCl}$. The structures were determined by single-crystal X-ray crystallography (M = Fe, cubic, $P4_132$, $a = 17.338(1)$ Å, $Z = 4$; M = Co, cubic, $P4_332$, $a = 17.260(1)$ Å, $Z = 4$). The compounds are examples of guest-free cyanide-bridged 3-D neutral networks and are composed of nearly planar Bu_3Sn units linked together with slightly distorted octahedral $\text{M}(\text{CN})_6$ fragments through the cyanide N atoms. Ignoring the butyl groups, each $\text{M}(\text{CN})_6$ octahedron is corner-shared with six neighbors through Sn, and each M atom is a vertex for three three-membered rings and fifteen five-membered rings. The butyl groups are disordered over three positions, with their trigonal arrangement preserved. The $[\{(n\text{-C}_4\text{H}_9)_3\text{Sn}\}_3\text{M}(\text{CN})_6]$ compounds crystallize in chiral space groups, and they are essentially isostructural enantiomers with similar cell dimensions.

Introduction

Compounds formed by coordination between metal cyanide anions and organotin cations can have large cavities in their extended lattices and therefore have potential for use in molecule separations. Various two- or three-dimensional polymers having the general formula $(\text{R}_3\text{Sn}^{\text{IV}})_n\text{M}(\text{CN})_{2n}$ ($n = 1\text{--}4$) have been prepared, some with guest molecules incorporated into the framework.^{1,2} A common feature of all compounds in this class are the polymeric $\text{M}\text{--}\text{C}\equiv\text{N}\text{--}\text{Sn}\text{--}\text{N}\equiv\text{C}\text{--}\text{M}$ chains which intersect to build up frameworks with various topologies. Anionic transition-metal cyano complexes with octahedral (Fe,³ Co,⁴ Ru,⁵ and Os⁵) tetrahedral (Cu),⁶ and square antiprismatic (Mo⁷ and W⁷) coordination environments have been studied in combination with R_3Sn^+ (R = methyl,⁴ ethyl,⁶ and phenyl³) cations. Of the $[(\text{R}_3\text{Sn}^{\text{IV}})_3\text{M}^{\text{III}}(\text{CN})_6]$ ($n = 3$) compounds, $[(\text{Me}_3\text{Sn}^{\text{IV}})_3\text{Co}^{\text{III}}(\text{CN})_6]$ has been fully studied, including the determination of its crystal structure.^{4,8} Crystal structures have also been reported for the analogous $[(\text{Me}_3\text{Pb}^{\text{IV}})_3\text{M}^{\text{III}}(\text{CN})_6]$ (M = Co, Fe) phases.⁸

$[(\text{R}_3\text{Sn}^{\text{IV}})_3\text{M}^{\text{III}}(\text{CN})_6]$ (M = Fe, Co) compounds with other R groups, including ethyl, propyl, and *n*-butyl, have also been reported.^{8,9} These coordination polymers were characterized

by IR, Raman, and Mössbauer spectroscopies, together with NMR, ESR,¹⁰ and X-ray powder diffraction studies.¹¹ However, all attempts to grow single crystals resulted in polycrystalline precipitates, which precluded complete structural understanding. In the present work, we have successfully grown single crystals of the two 3-D coordination polymers $[\{(n\text{-C}_4\text{H}_9)_3\text{Sn}^{\text{IV}}\}_3\text{M}(\text{CN})_6]$ (M = Fe, Co) and report their X-ray crystal structures. The structures of the polymers are compared with that of $[(\text{Me}_3\text{Sn})_3\text{Co}(\text{CN})_6]$ and with those of the other known organotin–cyanometalate structures.

Experimental Section

$\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Co}(\text{CN})_6]$, and $(n\text{-C}_4\text{H}_9)_3\text{SnCl}$ (Strem Chemical Co.) were used as received. Tetrahydrofuran (THF) was dried over molecular sieves (4 Å). Infrared data were collected on a Galaxy FTIR 5000 series spectrometer using the KBr pellet method. Thermogravimetric analyses were carried out by using a TA Instruments 2100 thermal analyzer in a flowing nitrogen atmosphere at a heating rate of 2 °C/min. All materials examined in this paper were analyzed on a JEOL JXA-8600 electron microprobe using wavelength-dispersive spectrometers. The probe has four WD spectrometers, allowing different elements to be analyzed simultaneously. Electron microprobe standards used were cassiterite (SnO_2) for Sn, ilmenite (FeTiO_3) for Fe, and pure metal for Co. Counting times were 60 s on the peaks and 30 s on each background. The accelerating voltage was 15 kV, and the sample current was 15 mA. Intensity data were reduced using the $\phi\rho Z$ matrix correction model of Bastin et al.¹²

$\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.063 g, 0.192 mmol) or $\text{K}_3[\text{Co}(\text{CN})_6]$ (0.063 g, 0.192 mmol) was dissolved in distilled water (10 mL), and the solution was placed in a 30 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 excess $(\text{C}_4\text{H}_9)_3\text{SnCl}$ (0.25 g, 0.576 mmol) was layered on top. Dark red crystals of $[\{(C_4H_9)_3Sn\}_3Fe(\text{CN})_6]$ (1) (yield based on Fe: 46.9%)

* To whom correspondence should be addressed. Tel: (713) 743-2785. Fax: (713) 743-2787. E-mail: ajacob@uh.edu.

- (1) Adam, M.; Brimah, A. K.; Fischer, R. D.; Fu, L. X. *Inorg. Chem.* **1990**, *29*, 1595.
- (2) Schwarz, P.; Siebel, E.; Fischer, R. D.; Apperley, D. C.; Davies, N. A.; Harris, R. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1197.
- (3) Lu, J.; Harrison, W. T. A.; Jacobson, A. J. *Inorg. Chem.* **1996**, *35*, 4271.
- (4) Yünlü, K.; Höck, N.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 879.
- (5) Eller, S.; Fischer, R. D. *Inorg. Chem.* **1990**, *29*, 1289.
- (6) Brimah, A. K.; Siebel, E.; Fischer, R. D.; Davies, N. A.; Apperley, D. C.; Harris, R. K. *J. Organomet. Chem.* **1994**, *475*, 85.
- (7) Lu, J.; Harrison, W. T. A.; Jacobson, A. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2557.
- (8) Behrens, U.; Brimah, A. K.; Soliman, T. M.; Fischer, R. D.; Apperley, D. C.; Davies, N. A.; Harris, R. K. *Organometallics* **1992**, *11*, 1718.
- (9) Yünlü, K. Dissertation, Universität Hamburg, 1983; p 107 ff.

- (10) Bonardi, A.; Carini, C.; Pelizzi, C.; Pelizzi, G.; Predieri, G.; Tarasconi, P.; Zoroddu, M. A.; Molloy, K. C. *J. Organometallic Chem.* **1991**, *401*, 283.
- (11) Apperley, D. C.; Davies, N. A.; Harris, R. K.; Brimah, A. K.; Eller, S.; Fischer, R. D. *Organometallics* **1990**, *9*, 2672.
- (12) Bastin, G. F.; Van Loo, F. J. J.; Heijligers, H. J. M. *X-ray Spectrosc.* **1984**, *13*, 91.

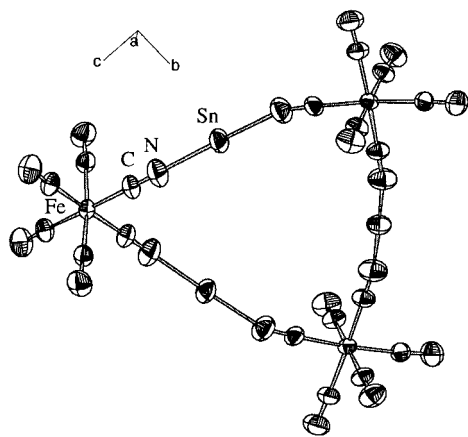


Figure 1. Metal atom coordination environments in **1** with thermal ellipsoids at 50% probability. The butyl groups are omitted for clarity.

were observed at the interface after 2 months of interdiffusion, while clear crystals of $[(C_4H_9)_3Sn]_3Co(CN)_6$ (**2**) (yield based on Co: 90.2%) formed in about 1 month.

X-ray Crystallography

For **1**, a dark red crystal having approximate dimensions $0.2 \times 0.2 \times 0.1$ mm was mounted in a random orientation on a Siemens SMART platform diffractometer equipped with a 1K CCD area detector.¹³ The sample was placed in a stream of dry nitrogen gas at -50 °C, and the radiation used was Mo K α monochromatized by a highly ordered graphite crystal. A hemisphere of data (1271 frames at 5 cm detector distance) were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 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,¹⁴ 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 based on the entire data set was applied using SADABS.¹⁵ Redundant reflections were averaged. The Laue symmetry was determined to be $m\bar{3}m$, and from the systematic absences noted the space group was shown to be either $P4_132$ or $P4_332$.

The structure of **1** (see Figure 1) was solved in the cubic space group $P4_132$ using direct methods, and the structure refinement was carried out using SHELX96.¹⁶ The asymmetric unit consists of $1/6$ $Fe(CN)_6$ located on a crystallographic 32 site and $1/2$ Bu_3Sn located about a 2-fold axis. All non-hydrogen atoms were located and their positions refined by a series of least-squares cycles and difference Fourier syntheses. The butyl groups of the Bu_3Sn moiety are quite heavily disordered over three distinct positions, with approximately equal populations for each orientation. Since there are only about $2e^-$ at any particular carbon site, it was necessary to use rigid-body refinement combined with mild distance constraints. Each butyl site was modeled as an ideal n -propyl group ($C-C = 1.50$ Å, $C-C-C = 109.5^\circ$) with a free-floating terminal carbon atom constrained to be about 1.45 Å away. 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. When the Sn-C distances were constrained to be equal but variable, they converged at a value close to 2.2 Å, and since this value was close to the average distance found in other Bu_3Sn systems,¹⁷ in the final refinement all Sn-C bond lengths were constrained to be approximately 2.20 Å. The terminal

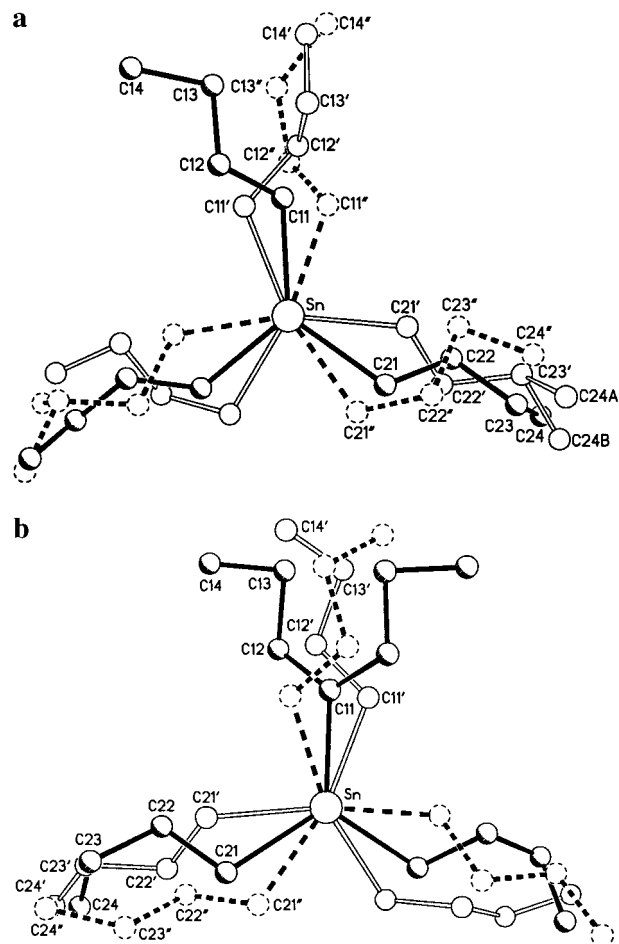


Figure 2. ORTEP drawings of the disordered Bu_3Sn fragments. Each of the disordered trigonal configurations is indicated by a different bond type (solid, hollow, or dashed): (a) **1**; (b) **2**. Only one orientation of the C(11), C(11'), and C(11'') groups is shown for **1**.

atom of the C(21') butyl group appears to be split over two different positions, C(24A) and C(24B) (See Figure 2). The correct absolute configuration and space group were determined by analysis of the Flack parameter.¹⁸ Selection of the correct enantiomer for **1** was unambiguous (Flack x parameter 0.01).

Data collection and refinement for **2** were carried out similarly. A colorless crystal with dimensions $0.1 \times 0.1 \times 0.1$ mm was used, and an empirical absorption correction was applied. The structure was determined and refined in space group $P4_332$ (Flack x parameter 0.03) using the SHELXTL program package.¹⁹ In **2**, the butyl groups are disordered over three distinct positions. Crystallographic information for both complexes can be found in Table 1.

Results and Discussion

Structure. Atomic coordinates and equivalent isotropic displacement parameters for **1** and **2** are listed in Tables 2 and 3, respectively. Selected bond distances and angles are given in Table 4.

Compounds **1** and **2** crystallize in the chiral space groups $P4_132$ and $P4_332$, respectively. They are essentially isostructural enantiomers with similar cell dimensions. We assume that there are equal amounts of both materials in both space groups,

(13) SMART, Version 4.05; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995.

(14) SAINT, Version 4.05; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995.

(15) SADABS: Siemens area detector absorption correction program; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995.

(16) Sheldrick, G. M. SHELXS-96 beta and SHELXL-96 beta, program package for structure solution and refinement; University Göttingen: Göttingen, Germany, 1996.

(17) For example: (a) Batchelor, R. J.; Einstein, F. W. B.; Jones, C. H. W.; Sharma, R. D. *Inorg. Chem.* **1988**, *27*, 4636. (b) Puff, H.; Breuer, B.; Gehrke-Brinkmann, G.; Kind, P.; Reuter, H.; Schuh, W.; Wald, W.; Weidenbruch, G. *J. Organomet. Chem.* **1989**, *363*, 265.

(18) Flack, H. D. *Acta crystallogr.* **1983**, *A39*, 876.

(19) Sheldrick, G. M. SHELXTL, Version 5.03; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995.

Table 1. Crystallographic Data for **1** and **2**

	$\{[(C_4H_9)_3Sn]_3Fe(CN)_6\}$	$\{[(C_4H_9)_3Sn]_3Co(CN)_6\}$
formula	C ₄₂ H ₈₁ FeN ₆ Sn ₃	C ₄₂ H ₈₁ CoN ₆ Sn ₃
fw	1082.05	1085.13
<i>a</i> , (Å)	17.338(1)	17.260(1)
<i>Z</i>	4	4
<i>V</i> , (Å ³)	5211.7(3)	5141.6(3)
space group	<i>P</i> 4 ₃ 2 (No. 213)	<i>P</i> 4 ₃ 2 (No. 212)
<i>T</i> , K	223	223
<i>λ</i> , Å	0.710 73	0.710 73
ρ_{calc} , g cm ⁻³	1.379	1.402
μ (Mo K α), cm ⁻¹	17.25	17.89
<i>R</i> ^a (<i>I</i> > 4 σ (<i>I</i>))	0.0378	0.0286
<i>wR</i> ^{2b}	0.0910	0.0866
<i>A</i> , <i>B</i> ^b	0.047, 3.07	0.0557, 1.9727

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

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Fe	3750	3750	3750	36(1)
Sn	6250	2785(1)	5285(1)	61(1)
N	5013(3)	3172(3)	4864(3)	72(1)
C(1)	4533(3)	3382(3)	4469(3)	48(1)
C(11)	6250	3677(4)	6177(4)	98(8)
C(12)	5957(34)	4446(11)	5936(27)	98(8)
C(13)	6156(35)	5036(10)	6537(24)	98(8)
C(14)	6153(62)	5741(40)	6131(63)	158(31)
C(11')	6351(47)	3924(20)	5826(34)	98(12)
C(12')	6318(32)	3927(39)	6691(33)	98(12)
C(13')	5567(35)	4271(41)	6950(30)	98(12)
C(14')	5987(68)	4699(80)	7532(61)	153(44)
C(11'')	6090(35)	3312(32)	6422(19)	117(10)
C(12'')	6769(21)	3812(28)	6613(33)	117(10)
C(13'')	6509(28)	4483(25)	7093(33)	117(10)
C(14'')	6045(67)	4386(73)	7763(68)	201(53)
C(21)	5823(17)	1592(8)	5377(15)	123(5)
C(22)	6007(19)	1158(15)	6102(14)	123(5)
C(23)	5513(16)	449(12)	6148(15)	123(5)
C(24)	6093(20)	-123(20)	6317(22)	147(12)
C(21')	5759(14)	1840(9)	5994(13)	109(5)
C(22')	6027(17)	1034(12)	5831(12)	109(5)
C(23')	5772(19)	509(8)	6470(16)	109(5)
C(24A)	4954(21)	347(44)	6507(45)	153(25)
C(24B)	5622(49)	-292(17)	6288(43)	143(22)
C(21'')	5998(25)	1586(9)	4976(17)	122(9)
C(22'')	5442(17)	1298(27)	5572(20)	122(9)
C(23'')	5784(24)	1398(22)	6361(17)	122(9)
C(24'')	5430(22)	703(18)	6671(21)	83(9)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

although this apparent case of spontaneous resolution has not been explored further. In both **1** and **2**, every M(CN)₆ group is connected through Bu₃Sn bridges to six other M(CN)₆ units, forming three infinite nonlinear chains which interlink into a three-dimensional network.

The butyl groups are disordered over three positions, with their trigonal arrangement preserved. C(11), C(21), and C(21)-#6 form the first trigonal orientation with C(11)-Sn-C(21) = 127.8(7)°, C(11)-Sn-C(21)#6 = 127.8(7)°, and C(21)-Sn-C(21)#6 = 104.5(2)°. The second orientation is composed of C(11'), C(21'), and C(21'')#6, and the third is C(11'') (C(11'')-#6 for **2**), C(21'') and C(21'')#6 (see Figure 2). Detailed angular information is given in Table 4.

Ignoring the butyl groups, the underlying 3-D -M-C≡N-Sn-N-C≡N- framework is quite intricate. Each M(CN)₆ octahedron is corner-shared with six neighbors through Sn, and each M atom is a vertex for three three-membered rings and fifteen five-

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Co	6250	6250	6250	28(1)
Sn	4721(1)	3750	7221(1)	50(1)
N	5152(2)	4995(2)	6825(2)	59(1)
C(1)	5544(2)	5484(2)	6614(2)	40(1)
C(11)	3828(4)	3750	6328(4)	119(5)
C(12)	4007(14)	4113(20)	5584(8)	119(5)
C(13)	3358(17)	3957(22)	5028(8)	119(5)
C(14)	3901(33)	3960(41)	4377(25)	181(21)
C(11')	3593(9)	3877(18)	6665(13)	102(5)
C(12')	3659(11)	4107(18)	5829(13)	102(5)
C(13')	2881(15)	4041(16)	5447(11)	102(5)
C(14')	3003(43)	3537(36)	4773(28)	200(23)
C(21)	5895(7)	3272(11)	7021(9)	109(3)
C(22)	6126(10)	3368(10)	6189(9)	109(3)
C(23)	6747(11)	2793(12)	5991(9)	109(3)
C(24)	7370(23)	3307(24)	6209(24)	182(14)
C(21'')	5632(6)	3224(8)	6457(8)	83(2)
C(22'')	6443(6)	3521(7)	6548(7)	83(2)
C(23'')	6956(5)	3155(10)	5950(8)	83(2)
C(24'')	7724(17)	3517(24)	6018(25)	180(14)
C(21''')	5914(9)	3401(23)	7479(17)	115(7)
C(22''')	6505(23)	3615(17)	6880(23)	115(7)
C(23''')	6956(21)	2908(23)	6651(21)	115(7)
C(24''')	7350(33)	2523(33)	6022(27)	144(16)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

$\{[(n-C_4H_9)_3Sn]_3Fe(CN)_6\}$ (1) ^a			
Fe-C(1)	1.950(5)	N-C(1)	1.138(7)
Sn-N	2.363(5)	Sn-C(11)	2.187(10)
Sn-C(11')	2.193(10)	Sn-C(11'')	2.191(10)
Sn-C(21)	2.203(9)	Sn-C(21')	2.219(9)
Sn-C(21'')	2.190(10)		
C(1)-Fe-C(1)#1	175.4(3)	C(1)-Fe-C(1)#2	87.4(3)
C(1)-Fe-C(1)#3	89.5(2)	C(1)-Fe-C(1)#5	93.8(3)
C(11)-Sn-C(21)	127.8(7)	C(11)-Sn-C(21)#6	127.8(7)
C(21)-Sn-C(21)#6	104(2)	C(11'')-Sn-C(21'')	117(2)
C(11')-Sn-C(21'')#6	128(2)	C(21')-Sn-C(21'')#6	114.9(10)
C(11'')-Sn-C(21'')	126(2)	C(11''')-Sn-C(21'')#6	118.9(14)
C(21'')-Sn-C(21'')#6	114.9(10)	C(1)-N-Sn	160.2(5)
N-C(1)-Fe	177.0(5)		
$\{[(n-C_4H_9)_3Sn]_3Co(CN)_6\}$ (2) ^b			
Co-C(1)	1.904(3)	N-C(1)	1.141(4)
Sn-N	2.375(3)	Sn-C(11)	2.178(10)
Sn-C(11')	2.182(10)	Sn-C(21)	2.215(9)
Sn-C(21')	2.244(8)	Sn-C(21'')	2.191(10)
C(1)-Co-C(1)#1	175.6(2)	C(1)-Co-C(1)#2	89.80(14)
C(1)-Co-C(1)#3	87.2(2)	C(1)-Co-C(1)#5	93.4(2)
C(11)-Sn-C(21)	122.5(4)	C(11)-Sn-C(21)#6	122.5(4)
C(21)-Sn-C(21)#6	115.1(9)	C(11')-Sn-C(21')	114.1(8)
C(11'')-Sn-C(21'')#6	124.6(11)	C(21'')-Sn-C(21'')#6	121.4(9)
C(11'')#6-Sn-C(21'')	124.6(11)	C(11'')#6-Sn-C(21'')#6	114.1(8)
C(21'')-Sn-C(21'')#6	121.4(9)	C(1)-N-Sn	161.3(3)
N-C(1)-Co	176.2(3)		

^a Symmetry transformations used to generate equivalent atoms: (#1) $-z + 3/4, -y + 3/4, -x + 3/4$; (#2) $-y + 3/4, -x + 3/4, -z + 3/4$; (#3) z, x, y ; (#4) y, z, x ; (#5) $-x + 3/4, -z + 3/4, -y + 3/4$; (#6) $-x + 3/4, z - 1/4, y + 1/4$. ^b Symmetry transformations used to generate equivalent atoms: (#1) $-y + 5/4, -x + 5/4, -z + 5/4$; (#2) z, x, y ; (#3) $-x + 5/4, -z + 5/4, -y + 5/4$; (#4) y, z, x ; (#5) $-z + 5/4, -y + 5/4, -x + 5/4$; (#6) $z - 1/4, -y + 3/4, x + 1/4$.

membered rings (see Figure 3). Each C≡N-Sn-N≡C moiety forms the side of one three-membered ring and five five-membered rings. The M(CN)₆ units display a slightly distorted octahedral geometry, and the Bu₃SnN₂ units are trigonal bipyramids, with cyanide N atoms in the axial positions. All

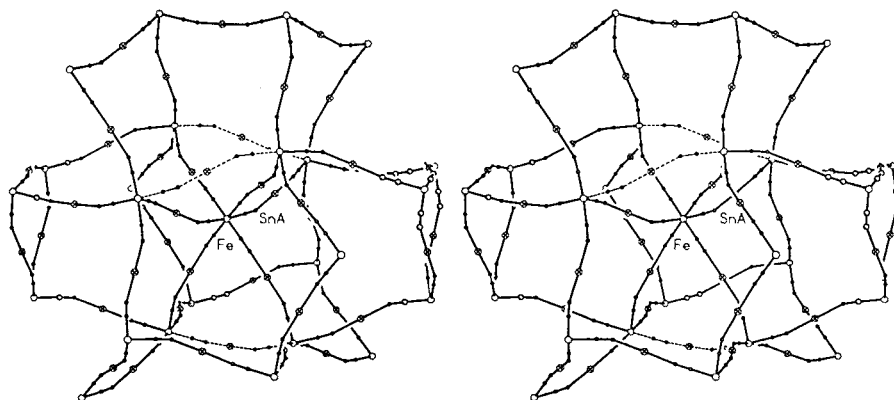


Figure 3. Stereoview of **1** with butyl groups omitted, showing the arrangement of five-membered and three-membered rings about a central Fe atom.

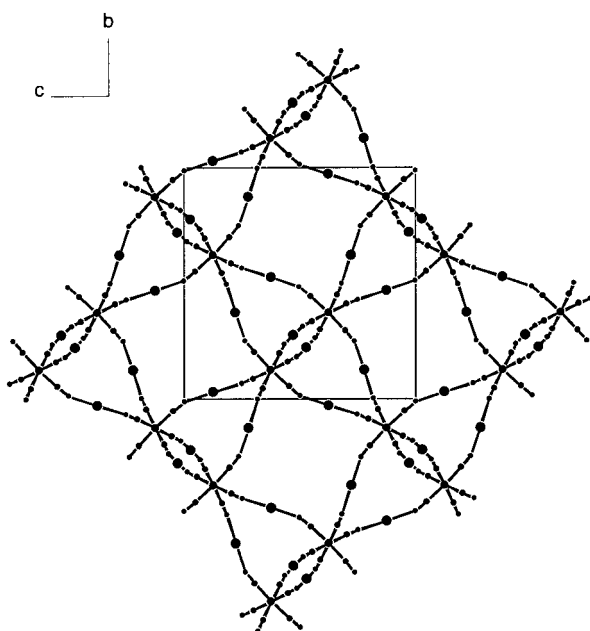


Figure 4. View of **1** along 100, with butyl groups omitted.

C–M–C sections within each chain are practically linear ($175.4(3)$ and $175.6(2)^\circ$ for **1** and **2**, respectively); however, the Sn–N–C angles are bent significantly at the N atoms ($160.1(5)^\circ$ for **1** and $161.3(3)^\circ$ for **2**). The Sn–N distances ($2.363(5)$ and $2.375(3)$ Å for **1** and **2**, respectively) are comparable to those found in other organotin compounds, e.g. $[(\text{Me}_3\text{Sn})_4\text{Mo}(\text{CN})_8]^{7-}$ (2.34 Å) and $[(\text{Ph}_3\text{Sn})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O} \cdot 2\text{CH}_3\text{CN}]^{3-}$ (2.33 Å). The three infinite M–C≡N–Sn–N≡C–M chains are crystallographically equivalent, whereas in $[(\text{Me}_3\text{Sn})_3\text{Co}^{\text{III}}(\text{CN})_6]^{4-}$ the three chains are different, with one-third of them nearly linear (C–N–Sn = 171 or 172°) and the rest bent at the N atom (157 or 146°). NMR studies suggest that the triethyltin compound $[(\text{Et}_3\text{Sn})_3\text{Co}^{\text{III}}(\text{CN})_6]$ has one unique type of chain.¹¹ In $[(\text{Me}_3\text{Sn})_4\text{M}(\text{CN})_8]^{7-}$ all M–C≡N–Sn–N≡C–M chains are crystallographically equivalent, with C–N–Sn angles of $163.7(5)$ and $166.0(9)^\circ$ for M = Mo and W, respectively.

In **1** and **2**, the three chains define various channels in the structure, which are filled by the butyl groups bonded to the Sn atoms. The channels along each of the principal axes have a width of about 8.8 Å, measured across the projection of opposing Sn atoms (see Figure 4). These channels are composed of spiral chains having either right-handed (4_1) or left-handed (4_3) chirality for the Fe or Co complex, respectively. Figure 5 shows the channels along the 111 (3-fold axis)

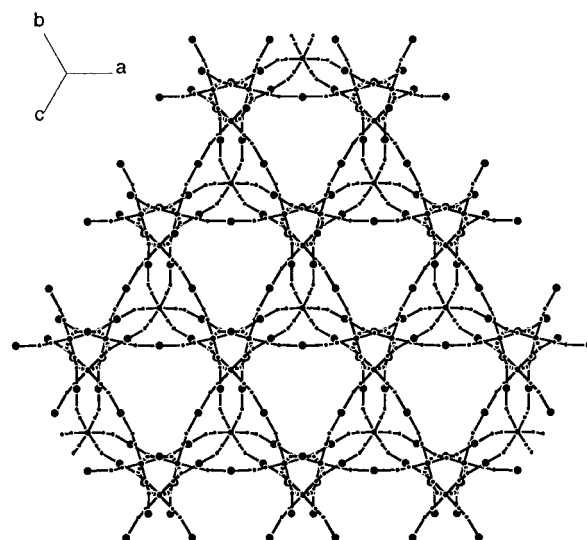


Figure 5. View of **1** along 111, with butyl groups omitted.

direction. These channels are defined by three sides of about 7.5 Å each as measured between the projections of the Sn atoms, giving a cylinder of 4.3 Å diameter. The arrangement of the channels is significantly different from those in similar complexes. Only one other covalently bonded 3-D framework is known containing an $\text{M}(\text{CN})_6$ unit, namely, $[(\text{Me}_3\text{M})_3\text{Co}(\text{CN})_6]$ (M = Sn, Pb)^{4,8} and the related compound $[(\text{Me}_3\text{M})_3\text{Fe}(\text{CN})_6 \cdot \text{CoCp}_2]$. Compounds **1** and **2** contain three- and five-membered rings, whereas in the previously reported structure type, the framework is defined by four-membered rings.

No solvent molecules are incorporated into the structures of **1** and **2**, indicating that the butyl groups occupy most of the space in the channels within the structure. The substantially different butyl ligand positions found in the disordered models (see Figure 2) probably arise from the different possible ways that butyl groups on adjacent tin atoms can be arranged to fill the channels (see Figure 6). It appears that the difference between the structures of the methyl- and butyltin compounds arises from the constraints imposed by packing the ligands within the framework defined by the M–CN–Sn bonds. Preliminary results suggest that R_3Sn compounds with other R groups, for example, ethyl and propyl, result in different framework connectivities.

Other Characterizations. The physical properties of **2**, including the NMR spectrum, have been reported elsewhere.¹¹ The IR spectrum of **1** exhibits two CN stretching bands from Fe–CN–Sn at 2135 and 2091 cm^{-1} , while the CN stretching frequency for **2** is observed at 2149 cm^{-1} (same as observed

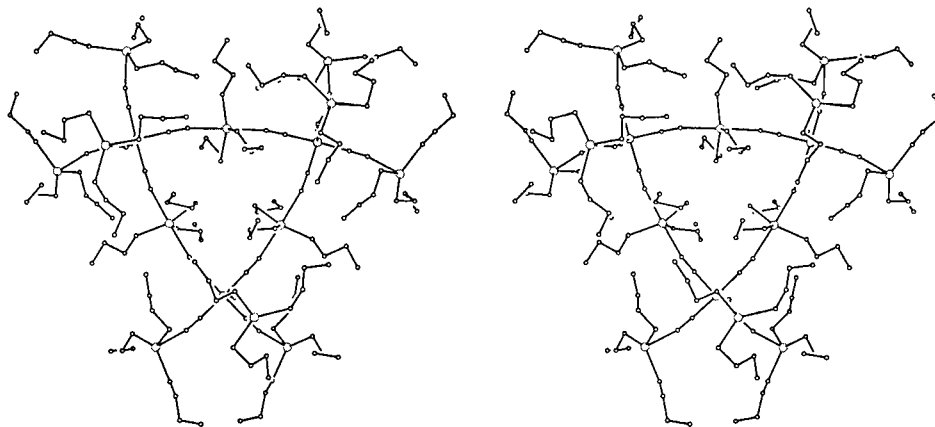


Figure 6. Stereoview of a single three-membered ring in **1** showing the staggered arrangement of the butyl groups. Only one orientation of each disordered butyl ligand is shown.

by Behrens et al.).⁸ Both major CN stretches (2135 and 2149 cm^{-1}) are blue-shifted from those of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Co}(\text{CN})_6$ (2105 and 2118 cm^{-1} , respectively),⁸ which is common in organotin–metal cyanide complexes.^{8,20} The lower CN stretching frequency observed for **1** (2091 cm^{-1}) may arise from partial reduction of the oxidation state of iron.¹⁰ Upon heating, the weight of compound **2** remains constant from 30 to ~ 250 °C. At 250 °C, total decomposition occurs, as reported by Bonardi.¹⁰ The thermal decomposition behavior of **1** is similar to that of **2**, except that decomposition begins at 150 °C and occurs over a wider temperature range. The ratios of Sn to Fe and Sn to Co were determined by electron microprobe analysis to be 2.88 and 2.99, respectively.

Conclusions

The two coordination polymers **1** and **2** are examples of guest-free cyanide-bridged 3-D networks $[(\text{R}_3\text{Sn})_n\text{M}(\text{CN})_{2n}]$. These 3-D neutral networks are composed of nearly planar Bu_3Sn units linked together with slightly distorted octahedral $\text{M}(\text{CN})_6$ fragments through the cyanide N atoms. Ignoring the butyl groups, each $\text{M}(\text{CN})_6$ octahedron is corner-shared with six neighbors through Sn, and each M atom is a vertex for three three-membered rings and fifteen five-membered rings. The butyl groups are disordered over three positions, with their trigonal arrangement preserved. Compounds **1** and **2** crystallize

in chiral space groups, and they are essentially isostructural enantiomers with similar cell dimensions.

Regarding Fischer's suggestion⁴ that increasing the steric bulk of the R group might force all C–N–Sn angles to become 180°, resulting in a marked expansion and simplification of the lattice, we do find that changing the R group from methyl to butyl results in a higher point group symmetry for the M atom. All three M–C \equiv N–Sn–N \equiv C–M chains are now uniform, and the C–N–Sn angles are closer to 180°. The connectivity of the 3-D lattice is changed, however, because of the steric requirements of the butyl groups. Further work is still needed in order to synthesize the ideal “super-Prussian-blue” structure, containing R_3Sn as the bridging unit.^{4,8,21}

Acknowledgment. We thank the National Science Foundation (Grant DMR-9214804) and the Robert A. Welch Foundation for support. This work used the MRSEC/TCSUH Shared Experimental Facilities supported by the National Science Foundation under Award No. DMR-9632667 and the Texas Center for Superconductivity at the University of Houston.

Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

IC980536+

(20) Shriver, D. F. *Struct. Bonding* **1966**, *1*, 32.

(21) Fukita, N.; Ohba, M.; Okawa, H.; Matsuda, K.; Iwamura, H. *Inorg. Chem.* **1998**, *37*, 842.