Synthesis and Crystal Structure of the Two-Dimensional Coordination Polymer $(Ph_3Sn)_3Fe(CN)_6 \cdot H_2O \cdot 2CH_3CN$

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Received January 24, 1996

Introduction

Coordination polymers formed with metal cyanides have been explored because of their potential as porous materials and as molecular-based ferromagnets.[1−11] The octahedral building blocks $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ have played an important role. The $Fe(CN)_6^{4-}$ complexes are found in extended lattices coordinated with Me_3Sn^+ units *via* Fe−C−N−Sn bonds,[1−7] while $Fe(CN)_6^{3-}$ has been used as a building block in forming bimetallic ferromagnets with other transition metal complexes.[8−11] In the microporous structures formed by metal cyanides with organotin compounds, structural information is crucial to understand the relationship between the framework topology and properties. Single-crystal structures of $(Me_3E)_3Co(CN)_6$ (E = Pb or Sn)[2] and $(Me_3Sn)_4M(CN)_8 \cdot n$THF (M = Mo, W)[3] revealed large empty channels enclosed by the 3D frameworks. Zeolite-like host−guest networks were also found for $[(CoCp_2)(Me_3Sn)_3Fe(CN)_6]$,[1] $(Me_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot C_4H_8O_2$,[12] $(Me_3Sn)_4Fe(CN)_6 \cdot 4H_2O$,[13] and $[(n\text{Bu}_4N)(Et_3Sn)_2Cu(CN)_4]$.[7] In all of the crystal structures reported so far, the organotin units are Me_3Sn^+ or Et_3Sn^+. The synthesis of other compounds containing R_3Sn^+ connectors was briefly noted in ref 2, but the crystal structures were not determined. Reactions of the sterically bulky Ph_3Sn^+ with $[(Ph_3P)_2N]_4Fe(CN)_6$ in attempts to form soluble, polynuclear species resulted instead in an ionic compound $[(Ph_3P)_2N]_2(Ph_3SnCl)_2Fe(CN)_4(dmso)_2$ containing two terminal Ph_3SnCl groups.[14] We have studied the reactions of Ph_3SnCl with $K_3Fe(CN)_6$ and $K_3Co(CN)_6$, and we report here the structure of $(Ph_3Sn)_3Fe(CN)_6 \cdot H_2O \cdot 2CH_3CN$ (**1**).

Table 1. Crystallographic Data for **1**

formula	$Sn_3Fe_1O_1N_8C_{64}H_{53}$	Z	8
fw	1362.09	T, K	223
space group	*Pbca* (No. 61)	λ, Å	0.710 73
a, Å	16.253(4)	ρ_{calcd}, g cm^{-3}	1.49
b, Å	21.746(7)	μ(Mo Kα), cm^{-1}	15.0
c, Å	34.389(7)	R,^{a} %	5.41
V, Å^3	12154(6)	R_w,^{b} %	4.46

^{a} $R = 100\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = 100[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w_i = 1/\sigma_i^2$.

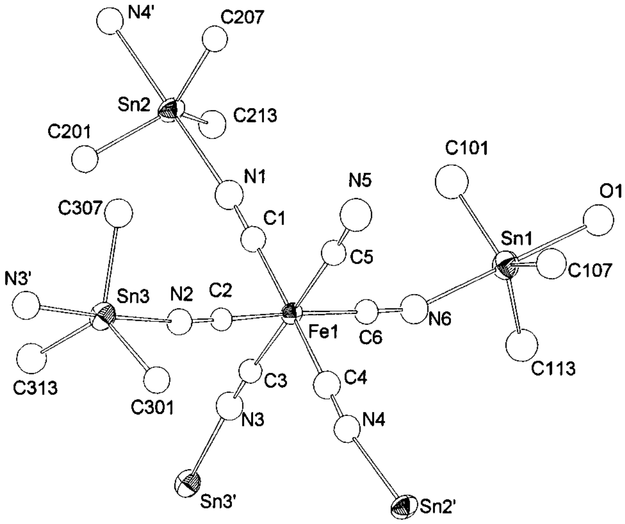

Figure 1. Local coordination of **1** with phenyl rings omitted.

Experimental Section

An acetonitrile solution of Ph_3SnCl was allowed to diffuse into an aqueous solution of $K_3Fe(CN)_6$ in a sealed tube. Small red rod-shaped crystals of **1** formed at the water/acetonitrile interface in about a week. The purity of the bulk material was checked by comparison of the X-ray powder diffraction data with the simulated pattern obtained using the single crystal structure. A similar reaction was carried out using $K_3Co(CN)_6$ in place of $K_3Fe(CN)_6$ and colorless rod-shaped crystals of **2** were formed at the interface. No crystals were formed when other solvents were used for Ph_3SnCl (e.g. ethanol, methanol, acetone, THF). **1** and **2** have similar X-ray powder diffraction patterns suggesting that they have the same structure and a single-crystal X-ray study of **2** gave a similar unit cell. **1** and **2** are insoluble in most solvents and are stable under water/acetonitrile. The IR spectrum of **1** exhibits two CN stretching bands from Fe−CN− at 2145 and 2087 cm^{-1}. The CN stretching frequencies for CH_3CN are observed at 2338 and 2295 cm^{-1}.

Crystal data for **1** are given in Table 1. A dark red, square column crystal, dimensions ~0.14 × 0.16 × 0.28 mm, was mounted on a thin pyrex fiber, and low temperature [−50(2) °C] intensity data were collected on a Siemens/Nicolet automated 4-circle diffractometer (graphite-monochromated Mo Kα radiation) in the *ω* scanning mode. Space group *Pbca* (No. 61) was uniquely determined from systematic absences. Initial heavy-atom positions (Fe, Sn) were located by using

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S0020-1669(96)00077-8 CCC: $12.00

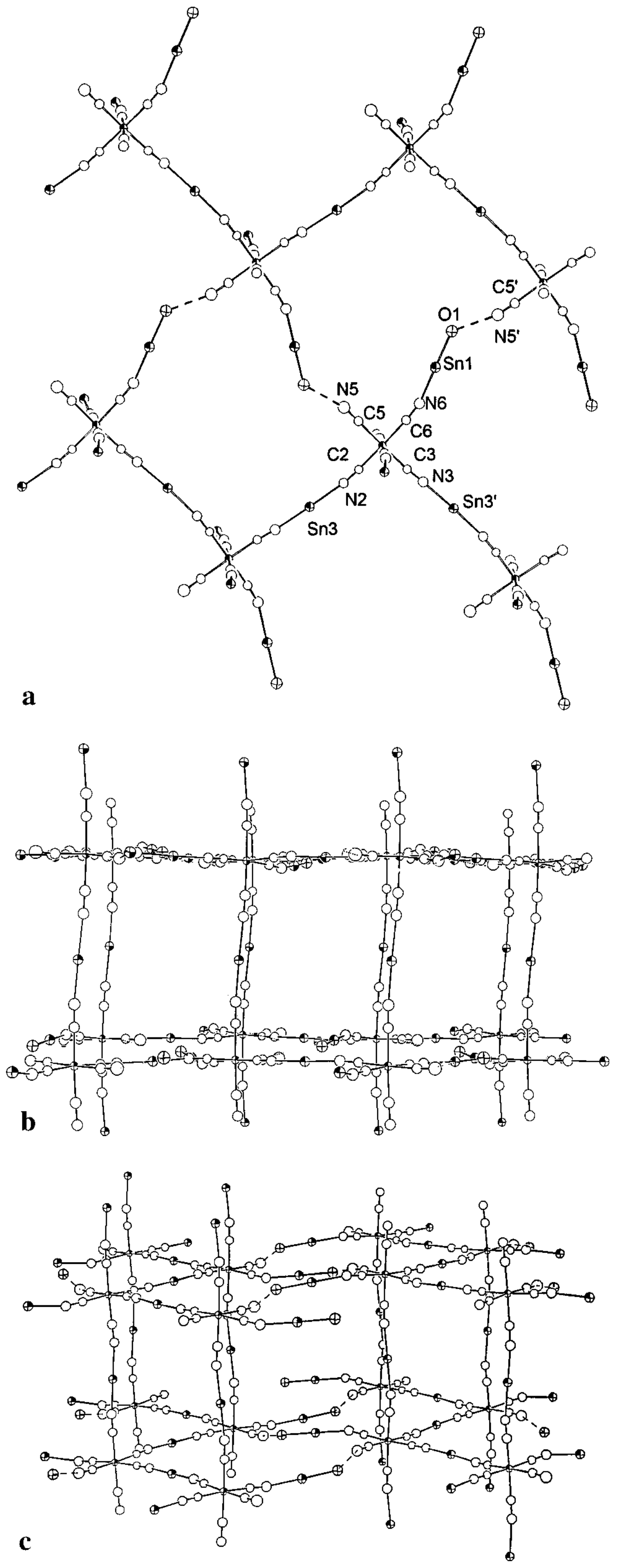

Figure 2. Views of the channels in **1** with phenyl rings and acetonitrile molecules removed (a) down the *b* axis showing the hydrogen bonds connecting the zigzag sheets along the *c*, (b) down the *c* axis revealing the almost rectanglar channels, (c) approximately along the *a* axis showing the two types of channels, one with and the one without hydrogen bonding. The hydrogen bonds are shown as dashed lines. All channels are occupied by phenyl groups and acetonitrile molecules.

the direct-methods program SHELXS-86,[15] and the other atom positions were located from repeated Fourier difference maps during the refinement (software: CRYSTALS[16]). The phenyl carbon atoms were stabilized by restraints [d(C−C) = 1.39(1) Å, θ(C−C−C) = 120(1)°] in the later refinement cycles.

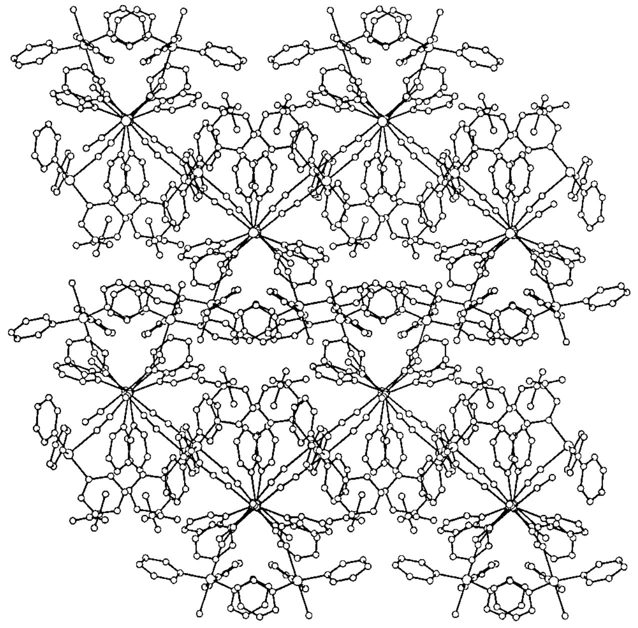

Figure 3. View of the structure of **1** down the *b* axis showing the phenyl rings and acetonitrile molecules.

Results and Discussion

Figure 1 shows the local coordination around the iron atom. The atomic coordinations for **1** are given in Table 2. Selected bond distances and angles are listed in Table 3. A three dimensional structure with all six nitrogen atoms from the Fe(CN)$_6$ unit coordinated to tin atoms is not possible because of steric interference between the bulky Ph$_3$Sn$^+$ groups. Thus, one of the CN groups bound to iron is not coordinated to a tin atom. Instead, its N atom is hydrogen bonded to the water molecule that is coordinated to a tin atom (the O(1)···N(5) distance is 2.82(2) Å). The average Sn−N distance in **1** is 2.33(1) Å, comparable to values reported in the literature.[1,14] The Sn−N−C angles are close to 180°, except for Sn(1)−N(6)−C(6) which is 159(1)°. This nonlinearity may arise because the water molecule bonded to Sn(1) is hydrogen bonded to N(5) (Figure 2) and to one of the acetonitrile molecules. There are three different types of infinite chains in the structure. A quasi-linear chain A, −(Sn(2)−N(1)−C(1)−Fe(1)−C(4)−N(4)−)$_\infty$, extends along the *b* axis. Chain A and a zigzag chain B, −(Sn(3)−N(2)−C(2)−Fe(1)−C(3)−N(3)−)$_\infty$ (see Figure 1), form a zigzag sheet. The zigzag sheets formed by chain A and chain B are stacked along the *c* axis, at a separation of half of the *c* axis, 17.19 Å. The zigzag chain C formed by hydrogen bonding, −(Sn(1)−N(6)−C(6)−Fe(1)−C(5)−N(5)···O(1)−)$_\infty$, connects the sheets into a 3D network (Figure 2a). The three chains define stuffed channels down different axes. The channels along the *b* axis have nominal dimensions of $c/2 \times a$ (17.2 Å × 16.3 Å) (Figure 2a), and the channels along the *c* axis are close to rectangular with the dimensions of $a/2 \times b/2$ (8.1 Å × 10.9 Å) (Figure 2b). There are two types of channels along the *a* axis. One involving hydrogen bonding ($(c - a)/2 \times b/2$) (9.1 Å × 10.9 Å), and the other one without hydrogen bonding ($a/2 \times b/2$) (8.1 Å × 10.9 Å) (Figure 2c). All of the channels are

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Table 2. Atomic Positional/Thermal Parameters for **1**

atom	*x*	*y*	*z*	U_{eq}[a]
Fe(1)	0.7330(1)	0.2327(1)	0.64677(6)	0.0192
Sn(1)	0.57300(7)	0.22859(7)	0.51254(3)	0.0337
Sn(2)	0.7432(1)	0.48239(6)	0.64811(3)	0.0283
Sn(3)	0.96744(7)	0.23621(6)	0.75718(3)	0.0291
N(1)	0.7330(9)	0.3773(7)	0.6433(4)	0.037(4)[b]
N(2)	0.8568(7)	0.2358(7)	0.7140(3)	0.030(3)[b]
N(3)	0.5812(8)	0.2407(6)	0.7016(3)	0.034(4)[b]
N(4)	0.7419(9)	0.0922(6)	0.6533(4)	0.033(4)[b]
N(5)	0.8785(8)	0.2322(8)	0.5887(4)	0.047(4)[b]
N(6)	0.6161(8)	0.2186(6)	0.5758(4)	0.037(4)[b]
O(1)	0.5284(6)	0.2403(5)	0.4484(3)	0.042(3)[b]
C(1)	0.733(1)	0.3227(8)	0.6443(5)	0.030(6)[b]
C(2)	0.8078(9)	0.2347(8)	0.6892(4)	0.023(4)[b]
C(3)	0.6403(9)	0.2384(8)	0.6825(4)	0.025(4)[b]
C(4)	0.737(1)	0.1456(8)	0.6504(5)	0.034(6)[b]
C(5)	0.8235(9)	0.2304(9)	0.6099(4)	0.029(4)[b]
C(6)	0.6581(9)	0.2247(8)	0.6036(4)	0.027(4)[b]
C(101)	0.599(1)	0.3246(5)	0.5161(5)	0.050(6)[b]
C(102)	0.6643(9)	0.3477(7)	0.5387(5)	0.049(6)[b]
C(103)	0.679(1)	0.4108(7)	0.5404(5)	0.063(7)[b]
C(104)	0.624(1)	0.4507(5)	0.5218(6)	0.072(7)[b]
C(105)	0.560(1)	0.4282(7)	0.4991(6)	0.093(8)[b]
C(106)	0.545(1)	0.3646(8)	0.4968(5)	0.077(7)[b]
C(107)	0.6674(8)	0.1681(7)	0.4923(4)	0.041(5)[b]
C(108)	0.741(1)	0.1623(7)	0.5132(4)	0.048(5)[b]
C(109)	0.8024(8)	0.1221(9)	0.4998(5)	0.078(8)[b]
C(110)	0.7896(9)	0.0877(8)	0.4658(5)	0.070(7)[b]
C(111)	0.715(1)	0.0917(7)	0.4464(4)	0.054(6)[b]
C(112)	0.6546(8)	0.1327(8)	0.4588(4)	0.047(6)[b]
C(113)	0.4540(8)	0.1933(7)	0.5236(5)	0.046(6)[b]
C(114)	0.397(1)	0.2296(6)	0.5436(5)	0.066(6)[b]
C(115)	0.3175(9)	0.2071(8)	0.5508(6)	0.078(8)[b]
C(116)	0.2962(8)	0.1478(8)	0.5389(6)	0.073(7)[b]
C(117)	0.353(1)	0.1123(6)	0.5186(6)	0.074(7)[b]
C(118)	0.431(1)	0.1353(7)	0.5108(5)	0.069(6)[b]
C(201)	0.762(1)	0.4749(6)	0.7092(3)	0.032(5)[b]
C(202)	0.803(1)	0.4240(6)	0.7253(4)	0.043(6)[b]
C(203)	0.817(1)	0.4217(6)	0.7656(4)	0.054(6)[b]
C(204)	0.786(1)	0.4677(7)	0.7898(3)	0.058(7)[b]
C(205)	0.746(1)	0.5188(7)	0.7738(3)	0.053(5)[b]
C(206)	0.736(1)	0.5227(6)	0.7333(4)	0.037(5)[b]
C(207)	0.8419(8)	0.4860(7)	0.6076(4)	0.030(5)[b]
C(208)	0.913(1)	0.4510(8)	0.6134(4)	0.063(7)[b]
C(209)	0.9793(9)	0.4554(8)	0.5874(5)	0.073(7)[b]
C(210)	0.9745(9)	0.4958(9)	0.5558(5)	0.070(7)[b]
C(211)	0.902(1)	0.5293(8)	0.5494(4)	0.067(7)[b]
C(212)	0.8359(8)	0.5248(7)	0.5753(5)	0.051(6)[b]
C(213)	0.6218(7)	0.4959(7)	0.6258(5)	0.035(5)[b]
C(214)	0.565(1)	0.4480(6)	0.6283(5)	0.055(6)[b]
C(215)	0.4834(9)	0.4579(7)	0.6163(6)	0.071(7)[b]
C(216)	0.4603(8)	0.5148(8)	0.6009(6)	0.079(7)[b]
C(217)	0.518(1)	0.5614(6)	0.5971(5)	0.062(7)[b]
C(218)	0.5985(9)	0.5527(6)	0.6106(5)	0.042(6)[b]
C(301)	0.987(1)	0.1403(5)	0.7494(5)	0.032(4)[b]
C(302)	1.022(1)	0.1053(7)	0.7794(4)	0.063(6)[b]
C(303)	1.034(1)	0.0417(7)	0.7744(4)	0.078(7)[b]
C(304)	1.012(1)	0.0139(5)	0.7394(5)	0.063(7)[b]
C(305)	0.980(1)	0.0491(7)	0.7091(4)	0.073(7)[b]
C(306)	0.967(1)	0.1126(7)	0.7143(4)	0.056(6)[b]
C(307)	1.024(1)	0.3015(6)	0.7195(3)	0.036(5)[b]
C(308)	1.0130(9)	0.2975(6)	0.6791(4)	0.028(5)[b]
C(309)	1.048(1)	0.3419(7)	0.6552(3)	0.059(6)[b]
C(310)	1.092(1)	0.3909(7)	0.6716(4)	0.053(6)[b]
C(311)	1.098(1)	0.3967(6)	0.7119(4)	0.057(6)[b]
C(312)	1.065(1)	0.3511(7)	0.7360(3)	0.037(5)[b]
C(313)	0.8888(7)	0.2657(8)	0.8037(4)	0.040(5)[b]
C(314)	0.8042(8)	0.2613(9)	0.7976(4)	0.053(6)[b]
C(315)	0.7502(7)	0.2803(9)	0.8268(5)	0.071(6)[b]
C(316)	0.7804(9)	0.3062(9)	0.8609(4)	0.074(7)[b]
C(317)	0.8650(9)	0.3114(9)	0.8667(4)	0.065(7)[b]
C(318)	0.9194(7)	0.2913(7)	0.8378(4)	0.048(6)[b]
C(10)	0.164(1)	0.370(1)	0.1677(7)	0.097(8)[b]
C(11)	0.140(1)	0.333(1)	0.1311(6)	0.063(7)[b]
C(12)	0.445(2)	0.387(1)	0.1216(7)	0.112(9)[b]
C(13)	0.379(2)	0.428(1)	0.1283(8)	0.12(1)[b]
N(11)	0.119(1)	0.3047(8)	0.1053(5)	0.070(6)[b]
N(12)	0.319(2)	0.458(1)	0.1237(6)	0.132(9)[b]

[a] U_{eq} (Å^2) = $(U_1U_2U_3)^{1/3}$. [b] U_{iso} (Å^2).

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

Distances

Fe(1)−C(1)	1.96(2)	Fe(1)−C(2)	1.90(1)	Fe(1)−C(3)	1.95(2)
Fe(1)−C(4)	1.90(2)	Fe(1)−C(5)	1.94(2)	Fe(1)−C(6)	1.93(2)
Sn(1)−N(6)	2.30(1)	Sn(1)−O(1)	2.34(1)	Sn(2)−N(1)	2.30(1)
Sn(2)−N(4)	2.41(1)	Sn(3)−N(2)	2.33(1)	Sn(3)−N(3)	2.33(1)
O(1)···N(5)	2.82(2)				

Angles

Sn(1)−N(6)−C(6)	158.7(13)	Sn(1)−O(1)···N(5)	136.1(5)
Sn(2)−N(1)−C(1)	172.9(14)	Sn(2)−N(4)−C(4)	170.6(13)
Sn(3)−N(2)−C(2)	172.4(11)	Sn(3)−N(3)−C(3)	174.3(13)

packed with the phenyl groups bonded to tin atoms and acetonitrile solvent molecules. A view of the channels along the *b* axis including the phenyl rings and acetonitrile molecules is shown in Figure 3.

Acknowledgment. This material is based in part on work supported by the Texas Advanced Research Program under Grant No. 003652−048. We also thank the Robert A. Welch Foundation for support of this work and Dr. James Korp for help with crystallography.

Supporting Information Available: Tables of crystallographic data, bond distances and angles, and anisotropic displacement parameters for iron and tin atoms (5 pages). Ordering information is given on any current masthead page.

IC960077H