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A Series of New Organotin−Cyanometalate Compounds Based on Triorganotin, Diorganotin, and Organooxotin Clusters

Guo-Hai Xu, Jian-Fang Ma,* Hai-Xia Yu, Shun-Li Li, Ying-Ying Liu, Jin Yang,
Zhong-Min Su, and Chun-Feng Shi

Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

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The reactions of sodium nitroprusside $[Na_2Fe(CN)_5NO\cdot 2H_2O]$ with organotin have been studied. Six new organotin−cyanometalate compounds, $[Ph_3Sn]_2[Fe(CN)_5NO]$ (**1**), $[Bz_3Sn]_2[Fe(CN)_5NO]$ ($Bz{=}C_6H_5\text{-}CH_2{-}$) (**2**), $[Bz_2Sn][Fe(CN)_5NO]$ (**3**), $[(Bz_3Sn)_2CN]_2[Fe(CN)_5NO]$ (**4**), $[Bz_2SnOSn(MeO)Bz_2]_2[Fe(CN)_5NO]\cdot 3CH_2Cl_2$ (**5**), and $[Bz_2SnOSn(EtO)Bz_2]_2[Fe(CN)_5NO]\cdot 3CH_2Cl_2$ (**6**), have been isolated in these reactions and characterized by the X-ray diffraction method. Each of compounds **1**, **2**, **3**, and **4** shows a 2D polymeric structure containing planar four-connected $[Fe(CN)_5NO]^{2-}$ anions. Compound **4** is the first organotin−cyanometalate compound containing a superlong $-CN-R_3Sn-CN-SnR_3-NC-$ spacer. Compounds **5** and **6** are the first examples of organotin−cyanometalate compounds of organooxotin clusters, in which the organooxotin clusters are bridged by cyanometalate anions to generate a novel 1D polymeric chain structure.

Introduction

The organometallic coordination polymers formed by organotin with metal cyanide have been of considerable interest due to their potential applications as porous materials.[1a,b] Several compounds with the general formula $(R_nSn^{IV})_x[M(CN)_m]_y$ are known.[1] Over the past few years, Niu et al. have 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. For instance, the coordination environments of anionic transition metal cyano complexes with octahedron (Fe,[1d] Co,[2a] Ru,[3] and Os[3]), tetrahedron (Cu),[2c] and square antiprism (Mo[1c] and W[1c]) structure have been studied in combination with bridging R_nSn^{4-n} ($n = 3$, R = methyl,[1c,2a,3] ethyl,[2c] and phenyl;[1d] $n = 2$, R = vinyl,[1f] propyl,[1f] butyl[1f]). A common feature of all compounds in this class is the polymeric $M-C{\equiv}N-Sn-N{\equiv}C-M$ chain, which intersects to build up frameworks with various topologies. In addition, the structure of $[CuCN\cdot Me_3SnCN\cdot 0.5bpy]$[4] (bpy = 4,4′-bipyridine) contains both bridging Me_3Sn^+ and bipy, while $[(Me_3Sn)_2Ni(CN)_4(^nBu_4N)OH]$ and $[(R_4N)(Me_3Sn)_2Co(CN)_6\cdot H_2O]$ compounds contain both bridging R_3Sn^+ ligands and terminal R_3SnOH or R_3SnOH_2 groups.[5] In principle, these supramolecular assemblies may behave as potential hosts of various appropriately functional molecules. Therefore, structural information is crucial to understand the relationship between the framework topology and properties. Furthermore, Fischer and co-workers[6] have shown that organometallic polymers of the type $\{(R_3Sn)_3{-}M(CN)_6\}_\infty$ are effective 3D host systems, being able to act as efficient ion exchangers and receptors for organic and organometallic cations. For example, $[(Fe^{III}Cp_2)(Me_3Sn)_3Fe^{II}(CN)_6]$[7] was synthesized by direct intercalation of $[Fe^{III}(CN)_6(Me_3Sn)_3]$ with ferrocene− $(Fe^{II}Cp_2)$. Despite the important role that organotin−cyanometalate compounds may play in host systems, the structurally characterized organotin−cyanometalate complexes are still rare and further research is necessary to enrich and develop this field.

In the organotin−cyanometalate family of coordination polymers, the octahedral building blocks $M(CN)_6^{3-}$ and $M(CN)_6^{4-}$ have played an important role. However, the analogous complexes based on the photochromic nitroprusside anion have not hitherto received any attention. Nitroprusside is currently used as a reversible inhibitor of a group of enzymes known as superoxide dismutases[8] and displays very interesting photoinduced transition to long-lived metastable states.[9] Studies[10] have

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* Corresponding author. E-mail: jianfangma@yahoo.com.cn. Tel: +86-431-5098620. Fax: +86-431-5684009.

(1) (a) Fischer, R. D.; Hanika-Heidl, H.; Ling, M.; Eckhardt, R. In *Nanoporous Crystals*; Laeri, F., Schüth, F., Simon, U., Wark, M., Eds.; Wiley-VCH: Weinheim (Germany), 2003; Chapter 12. (b) Niu, T. Y.; Lu, J.; Wang, X. Q.; Korp, J. D.; Jacobson, A. J. *Inorg. Chem.* **1998**, *37*, 5324. (c) Lu, J.; Harrison, W. T. A.; Jacobson, A. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2557. (d) Lu, J.; Harrison, W. T. A.; Jacobson, A. J. *Inorg. Chem.* **1996**, *35*, 4271. (e) Niu, T. Y.; Wang, X. Q.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1934. (f) Niu, T. Y.; Jacobson, A. J. *Inorg. Chem.* **1999**, *38*, 5346. (g) Siebel, E.; Fischer, R. D.; Davies, N. A.; Apperley, D. C.; Harris, R. K. *J. Organomet. Chem.* **2000**, *604*, 34. (h) Eckhardt, R.; Hanika-Heidl, H.; Fischer, R. D. *Chem.−Eur. J.* **2003**, *9*, 1795. (i) Hanika-Heidl, H.; Fischer, R. D. *Microporous Mesoporous Mater.* **2004**, *73*, 65.

(2) (a) Yünlü, K.; Höck, N.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 879. (b) Behrens, U.; Brimah, A. K.; Soliman, T. M.; Fischer, R. D.; Apperley, D. C.; Davics, N. A.; Harris, R. K. *Organometallics* **1992**, *11*, 1718. (c) Brimah, A. K.; Siebel, E.; Fischer, R. D.; Davies, N. A.; Apperley, D. C.; Harris, R. K. *J. Organomet. Chem.* **1994**, *475*, 85.

(3) Eller, S.; Fischer, R. D. *Inorg. Chem.* **1990**, *29*, 1289.

(4) Ibrahim, A. M. A.; Siebel, E.; Fischer, R. D. *Inorg. Chem.* **1998**, *37*, 3521.

(5) (a) Siebel, E.; Schwarz, P.; Fischer, R. D. *Solid State Ionics* **1997**, *285*, 101−103. (b) Schwarz, P.; Siebel, E.; Fischer, R. D.; Apperley, D. C.; Davies, N. A.; Harris, R. K. *Chem. Eur. J.* **1998**, *4* (5), 919. (c) Siebel, E.; Fischer, R. D.; Kopf, J.; Davies, N. A.; Apperley, D. C.; Harris, R. K. *Inorg. Chem. Commun.* **1998**, 346.

(6) (a) Eller, S.; Brandt, P.; Brimah, A. K.; Schwarz, P.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1263. (b) Adam, M.; Brimah, A. K.; Fischer, R. D.; Li, X. *Inorg. Chem.* **1990**, *29*, 1595. (c) Eller, S.; Adam, M.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1126.

(7) Brandt, P.; Brimah, A. K.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1521.

(8) Misra, H. P. *J. Biol. Chem.* **1984**, *259*, 12678.

(9) Gütlich, P.; et al. *Coord. Chem. Rev.* **2001**, *839*, 219−221.

(10) (a) Shyu, H. L.; Wei, H. H.; Wang, Y. *Inorg. Chim. Acta* **1997**, *258*, 81. (b) Mullica, D. F.; Hayward, P. K.; Sappenfield, E. L. *Inorg. Chim. Acta* **1995**, *237*, 111. (c) Chen, Z. N.; Wang, J. L.; Qiu, J.; Miao, F. G.; Tang, W. X. *Inorg. Chem.* **1995**, *34*, 2255. (d) Xang, K.; Xu, Y.; Wang, Z.; Jin, C.; You, X. *Trans. Met. Chem.* **2002**, *27*, 95. (e) Clemente-León, M.; Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Woike,

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shown that a great variety of discrete and extended structures can be obtained by the association of the nitroprusside anion with transition metal elements. In this work, nitroprusside has been chosen on the basis of the following considerations: (1) we want to further elucidate the number of CN groups in tuning the crystal structures of organotin−cyanometalates; (2) nitroprusside is already in use in medical practice to treat many different diseases thanks to the role of the nitric oxide released[11] and provides the organotin−cyanometalate family with potential application in medicinal chemistry. It is known that the organooxotin clusters, owing to their novel structures,[12] are suitable for the construction of supramolecular frameworks.[13] However, to date, no organotin−cyanometalate compounds containing an organooxotin cluster have been reported. We are interested in the investigation of organooxotin clusters serving as bridging units to construct organotin−cyanometalate polymers. We report herein six organotin−cyanometalate polymers of nitroprusside, namely, $[Ph_3Sn]_2[Fe(CN)_5NO]$ (**1**), $[Bz_3Sn]_2[Fe(CN)_5NO]$ (**2**), $[Bz_2Sn][Fe(CN)_5NO]$ (**3**), $[(Bz_3Sn)_2CN]_2[Fe(CN)_5NO]$ (**4**), $[Bz_2SnOSn(MeO)Bz_2]_2[Fe(CN)_5NO]\cdot 3CH_2Cl_2$ (**5**), and $[Bz_2SnOSn(EtO)Bz_2]_2[Fe(CN)_5NO]\cdot 3CH_2Cl_2$ (**6**).

Experimental Section

General Procedures. Bz_3SnCl,[14] Bz_2SnCl_2,[14] and 1,1′-(1,4-butanediyl)bis(imidazole)[15] were prepared by the literature methods. Other reagents were purchased from commercial sources and used without further purification.

All organotin chlorides were transformed into the corresponding nitrates by treating R_nSnCl_{4-n} ($n = 2, 3$) with stoichiometric amounts of $AgNO_3$ in MeOH or EtOH. After removal of the AgCl the filtrate was used for further reactions without additional treatment.

Synthesis of $[Ph_3Sn]_2[Fe(CN)_5NO]$ (1). $Na_2Fe(CN)_5NO\cdot 2H_2O$ (0.5 mmol 0.149 g) was dissolved in 5 mL of distilled water and placed in a 25 mL screw-capped tube. A mixture of 1:1 water/MeOH (5 mL) was applied as a buffer layer, and a methanol solution (5 mL) of Ph_3SnNO_3 (1 mmol) was layered on top. Red block crystals were obtained at the interface after one week. Yield: 78% based on $Na_2Fe(CN)_5NO\cdot 2H_2O$. Anal. Calcd for $C_{41}H_{30}ON_6Sn_2Fe$: C, 53.76; H, 3.30; N, 9.18. Found: C, 53.62; H, 3.41; N, 9.12.

Synthesis of $[Bz_3Sn]_2[Fe(CN)_5NO]$ (2). 2 was synthesized by a procedure similar to that used for **1** except that stoichiometric amounts of Bz_3SnNO_3 were used in place of Ph_3SnNO_3. Yield: 63% based on $Na_2Fe(CN)_5NO\cdot 2H_2O$. Anal. Calcd for $C_{47}H_{42}ON_6Sn_2Fe$: C, 56.45; H, 4.23; N, 8.40. Found: C, 56.48; H, 4.15; N, 8.61.

Synthesis of $[Bz_2Sn][Fe(CN)_5NO]$ (3). 3 was also synthesized by a procedure similar to that used for **1** except that stoichiometric amounts of $Bz_2Sn(NO_3)_2$ were used in place of Ph_3SnNO_3. Yield: 67% based on $Na_2Fe(CN)_5NO\cdot 2H_2O$. Anal. Calcd for $C_{19}H_{14}ON_6SnFe$: C, 44.15; H, 2.73; N, 16.26. Found: C, 44.11; H, 2.79; N, 16.21.

Synthesis of $[(Bz_3Sn)_2CN]_2[Fe(CN)_5NO]$ (4). A mixture of Bz_3SnNO_3 (1 mmol) and $Na_2Fe(CN)_5NO\cdot 2H_2O$ (0.5 mmol 0.149 g) in MeOH (10 mL) was sealed in a reaction vessel and allowed to stand in a freezer at 4 °C. Well-shaped red crystals were obtained after several weeks. Yield: 26% based on $Na_2Fe(CN)_5NO\cdot 2H_2O$. Anal. Calcd for $C_{91}H_{84}ON_8Sn_4Fe$: C, 59.52; H, 4.61; N, 6.10. Found: C, 60.02; H, 4.64; N, 6.16.

Synthesis of $[Bz_2SnOSn(MeO)Bz_2]_2[Fe(CN)_5NO]\cdot 3CH_2Cl_2$ (5). A white precipitate was obtained upon addition of 1,1′-(1,4-butanediyl)bis(imidazole) (0.25 mmol 0.095 g) to a solution of $Bz_2Sn(NO_3)_2$ (0.5 mmol) in methanol (10 mL) under stirring. The precipitate was filtered and dissolved in CH_2Cl_2 (5 mL). The solution was placed in a 25 mL screw-capped tube. A mixture of 1:1 $MeOH/CH_2Cl_2$ (5 mL) was applied as a buffer layer, and a solution of $Na_2Fe(CN)_5NO\cdot 2H_2O$ (0.5 mmol, 0.149 g) in methanol (5 mL) was layered on top. After 1 week orange crystals were obtained at the interface. Yield: 81% based on $Bz_2Sn(NO_3)_2$. Anal. Calcd for $C_{66}H_{68}O_5N_6Cl_6Sn_4Fe$: C, 44.82; H, 3.88; N, 4.75. Found: C, 45.01; H, 4.02; N, 4.90.

Synthesis of $[Bz_2SnOSn(EtO)Bz_2]_2[Fe(CN)_5NO]\cdot 3CH_2Cl_2$ (6). A white precipitate was obtained upon addition of 1,1′-(1,4-butanediyl)bis(imidazole) (0.25 mmol 0.095 g) to a solution of $Bz_2Sn(NO_3)_2$ (0.5 mmol) in ethanol (10 mL) under stirring. The precipitate was filtered and dissolved in CH_2Cl_2 (5 mL). The solution was placed in a 25 mL screw-capped tube. A mixture of 1:1 $EtOH/CH_2Cl_2$ (5 mL) was applied as a buffer layer, and a solution of $Na_2Fe(CN)_5NO\cdot 2H_2O$ (0.5 mmol, 0.149 g) in ethanol (5 mL) was layered on top. After 1 week orange block crystals were obtained at the interface. Yield: 74% based on $Bz_2Sn(NO_3)_2$. Anal. Calcd for $C_{68}H_{72}O_5N_6Cl_6Sn_4Fe$: C, 45.46; H, 4.04; N, 4.68. Found: C, 45.41; H, 4.00; N, 4.63.

Crystal Structure Determination and Physical Measurements. Experimental details of the X-ray analyses are provided in Table 1. Diffraction intensities for compound **4** were collected on a Rigaku RAXIS-RAPID image plate diffractometer, and diffraction intensities for the other five compounds were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Absorption corrections were applied using the multiscan technique.[16] The structures were solved by direct methods using SHELXS-97[17] and refined with full-matrix least-squares techniques using the SHELXL-97 program[18] within WINGX.[19] Analytical expression of neutral-atom scattering factors was employed, and anomalous dispersion corrections were incorporated.[20]

The FT-IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer.

Th.; Clemente-Juan, J. M. *Inorg. Chem.* **2001**, *40*, 87. (f) Soria, D. B.; Villalba, M. E. C.; Piro, O. E.; Aymonino, P. J. *Polyhedron* **2002**, *21*, 1767. (g) Bllouard, F.; Clemente-León, M.; Coronado, E.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J.; Woike, Th. *Polyhedron* **2001**, *20*, 1615. (h) Gómez, A.; Reguera, E.; Cranswick, L. M. D. *Polyhedron* **2001**, *20*, 165. (i) Kou, H. Z.; Wang, H. W.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Yan, S. P.; Huang, X. Y.; Wang, G. L. *Aust. J. Chem.* **1998**, *51*, 661. (j) Mullica, D. F.; Tippin, D. B.; Sappenfield, E. L. *Inorg. Chim. Acta* **1990**, *174*, 129.

(11) (a) Butler, A. R.; Megson, I. L. *Chem. Rev.* **2002**, *102*, 1155. (b) Kim, P. K. M.; Zamora, R.; Petrosko, P.; Billiar, T. R. *Int. Immunopharmacol.* **2001**, *1*, 1421. (c) Terwel, D.; Nieland, L. J. M.; Schutte, B.; Reutelingsperger, C. P. M.; Ramaekers, F. C. S.; Steinbusch, H. W. M. *Eur. J. Pharmacol.* **2000**, *400*, 19.

(12) (a) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190. (b) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1. (c) Tiekink, E. R. T. *Trends Organoment. Chem.* **1994**, *1*, 71.

(13) (a) Chandrasekhar, V.; Nagendran, S.; Bansal, S.; Cordes, A. W.; Vij, A. *Organometallics* **2002**, *21*, 3297. (b) Mehring, M.; Gabriele, G.; Hadjikakou, S.; Schürmann, M.; Dakternieks, D.; Jurkschat, K. *Chem. Commun.* **2002**, 834.

(14) Sisido, K.; Takeda, Y.; Kinugawa, Z. *J. Am. Chem. Soc.* **1961**, *83*, 538.

(15) Ma, J. F.; Yang, J.; Zheng, G. L.; Li, L.; Zhang, Y. M.; Li, F. F.; Liu, J. F. *Polyhedron* **2004**, *23*, 553.

(16) (a) Higashi, T. *ABSCOR*; Rigaku Corporation: Tokyo, Japan, 1995. (b) Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 1996.

(17) Sheldrick, G. M. *SHELXS-97*, A Program for Automatic Solution of Crystal Structure; University of Geottingen: Germany, 1997.

(18) Sheldrick, G. M. *SHELXL-97*, A Program for Crystal Structure Refinement; University of Geottingen: Germany, 1997.

(19) Farrugia, L. J. *WINGX*, A Windows program for Crystal Structure Analysis; University of Glasgow, UK, 1988.

(20) Cromer, T. *International Tables for X-ray Crystallography*; Kluwer Academic: Dordrecht, 1992; Vol. C.

Table 1. Crystal Data and Structure Refinements for Compounds 1−6

	1	**2**	**3**
empirical formula	$C_{41}H_{30}ON_6Sn_2Fe$	$C_{47}H_{42}ON_6Sn_2Fe$	$C_{19}H_{14}ON_6SnFe$
fw	915.94	1000.10	516.90
cryst size [mm]	0.268 × 0.121 × 0.120	0.697 × 0.077 × 0.120	0.206 × 0.176 × 0.064
cryst syst	monoclinic	orthorhombic	tetragonal
space group	*Cc*	*Pbca*	*P4/mmm*
a [Å]	14.491(3)	14.337(1)	7.590(5)
b [Å]	15.479(2)	21.939(2)	7.590(5)
c [Å]	17.360(3)	29.751(2)	9.307(5)
α [deg]	90	90	90
β [deg]	90.30(3)	90	90
γ [deg]	90	90	90
volume [$Å^3$]	3894(1)	9358(1)	536.2(6)
Z	4	8	1
R_{int}	0.0475	0.0730	0.0397
R1 [$I > 2\sigma(I)$]	0.0315	0.0510	0.0445
wR2 (all data)	0.0708	0.1414	0.1251

	4	**5**	**6**
empirical formula	$C_{91}H_{84}ON_8Sn_4Fe$	$C_{66}H_{68}O_5N_6Sn_4FeCl_6$	$C_{68}H_{72}O_5N_6Sn_4FeCl_6$
fw	1836.27	1768.57	1796.63
cryst size [mm]	0.312 × 0.309 × 0.116	0.172 × 0.064 × 0.064	0.358 × 0.161 × 0.082
cryst syst	tetragonal	triclinic	triclinic
space group	*P4/n*	$P\bar{1}$	$P\bar{1}$
a [Å]	19.886(3)	12.6316(8)	12.7533(8)
b [Å]	19.886(3)	13.3725(8)	13.4046(8)
c [Å]	10.595(2)	22.382(1)	22.421(1)
α [deg]	90	81.483(1)	81.961(1)
β [deg]	90	78.401(1)	77.693(1)
γ [deg]	90	79.649(1)	79.673(1)
volume [$Å^3$]	4190(1)	3618.6(4)	3663.5(4)
Z	2	2	2
R_{int}	0.1395	0.0633	0.0493
R1 [$I > 2\sigma(I)$]	0.0697	0.0976	0.0597
wR2 (all data)	0.1680	0.1833	0.1541

Cyclic voltammetry was performed using EG and GPAR model 273 potentiostats in a three-electrode cell with a purged N_2 gas inlet and outlet. The cell comprises a platinum wire working electrode, a platinum auxiliary electrode, and a Ag wire reference electrode. Current−potential curves were displayed on an IBM computer using model 270 electrochemical analysis software. The voltammograms of the compounds were obtained in DMF with ^{n}-Bu_4NClO_4 (0.1 M) as the electrolyte at a scanning rate of 100 mV s^{-1}.

Results and Discussion

Synthetic Aspects. The products of **1**, **2**, **3**, **5**, and **6** were synthesized by the diffusion of the solution of $Na_2[Fe(CN)_5NO]$ with the solution of the corresponding organotin nitrate. Solution diffusion is a general method to obtain cyanide-bridged bimetallic assemblies.[21] **4** is synthesized by a reaction in solution. In all cases, the syntheses should avoid light exposure, and the use of organotin nitrates instead of organotin chlorides is indispensable because of the low coordination ability of NO_3^-. Compounds **1**−**6** are insoluble in common solvents (e.g., H_2O, THF, C_6H_6, CH_3OH, and CH_2Cl_2).

X-ray Crystal Structures of Compounds 1−6. Selected bond distances and angles for **1**−**6** are listed in Table 2. The crystal structures of organotin−cyanometalates for triphenyl organotin were rarely reported.[1d] Compound **1** crystallizes in the non-centrosymmetric space group *Cc*. Part of the structure of compound **1** is shown in Figure 1a. Each $[Fe(CN)_5NO]^{2-}$ anion is connected to four $[Ph_3Sn]^+$ cations through its four equatorial CN^- groups, and each $[Ph_3Sn]^+$ cation is coordinated by two CN^- groups from two different $[Fe(CN)_5NO]^{2-}$ anions. $[Ph_3Sn]^+$ cations are bridged by $[Fe(CN)_5NO]^{2-}$ anions to form a 2D polymeric layer that contains 24-membered $Fe_4(CN)_8Sn_4$ heterocyclic rings (Figure 1b). Tin atoms show a *trans*-R_3SnN_2 trigonal bipyramidal coordination environment with three phenyl groups in equatorial positions (C6, C12, C18 for Sn1; C24, C30, C36 for Sn2) and two N atoms in axial positions (N1, N3A for Sn1; N2, N4A for Sn2). The axial−tin−axial angles are 177.0(1)° (N1−Sn1−N3A) and 174.5(1)° (N2−Sn2−N4A), which indicates that the structures are slightly distorted trigonal bipyramids. The average Sn−C bond length is 2.122 Å, and the longest and shortest Sn−C bond lengths are Sn1−C18 (2.127(4) Å) and Sn2−C24 (2.119(4) Å), respectively. The Sn−N distances [2.314(3)−2.375(3) Å] are comparable to those found in other related organotin compounds, e.g., $[(Me_3Sn)_4Mo(CN)_8]$[1c] (2.34 Å) and $[(Ph_3Sn)_3Fe(CN)_6{\cdot}H_2O{\cdot}2CH_3CN]$[1d] (2.33 Å). The geometry of $[Fe(CN)_5NO]^{2-}$ is in agreement with those of the previous studies.[22] The axial CN^- group that is *trans* to the NO group is not coordinated to the Sn atom. The Fe−C bond lengths range from 1.928 to 1.938 Å. The C−N bond lengths range from 1.132 to 1.156 Å. The Fe−N and N−O bond distances in $[Fe(CN)_5NO]^{2-}$ are 1.656 and 1.126 Å, respectively. These values are in accordance with the reported values for $Na_2Fe(CN)_5NO{\cdot}2H_2O$.[22]

For the $[Fe(CN)_6]^{3-}$ anion, each of the six CN^- groups can coordinate to the Sn atom. In the structure of $(Ph_3Sn)_3Fe(CN)_6{\cdot}H_2O{\cdot}2CH_3CN$,[1d] due to the steric repulsion between the bulky $[Ph_3Sn]^+$ groups, only five CN^- of the $[Fe(CN)_6]^{3-}$ anion coordinate to Sn atoms directly. The tin atoms act as both μ_2-bridging group $[Ph_3Sn]^+$ and terminal group $[Ph_3SnOH_2]^+$. $[Ph_3Sn]^+$ groups are connected by $[Fe(CN)_6]^{3-}$ anions through four

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[21] (a) Ohba, M.; Fukita, N.; Okawa, H.; Enoki, T.; Latour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11566. (b) Ohba, M.; Fukita, N.; Okawa, H. *J. Chem. Soc. Dalton Trans.* **1997**, 1733.

[22] Woike, T. H.; Imlau, M.; Angelov, V.; Schefer, J.; Delley, B. *Phys. Rev. B* **2000**, *61*, 249.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compounds 1−6[a]

	Compound **1**		
C1−N1	1.140(5)	C1−Fe1	1.938(4)
C2−N2	1.156(5)	C2−Fe1	1.928(4)
C3−N3	1.140(5)	C3−Fe1	1.928(4)
C4−N4	1.145(5)	C4−Fe1	1.938(4)
C5−N5	1.132(6)	C5−Fe1	1.937(4)
N1−Sn1	2.314(3)	N2−Sn2	2.336(3)
N3−Sn1#1	2.351(3)	N4−Sn2#2	2.375(3)
N6−O1	1.126(5)	N6−Fe1	1.656(4)
Sn1−N3#3	2.351(3)	Sn2−N4#4	2.375(3)
C1−N1−Sn1	157.3(3)	C2−N2−Sn2	161.6(3)
C3−N3−Sn1#1	161.8(3)	C4−N4−Sn2#2	156.4(3)
N1−Sn1−N3#3	177.02(13)	N2−Sn2−N4#4	174.50(12)
	Compound **2**		
C1−N1	1.136(6)	C1−Fe1	1.912(5)
C2−N2	1.143(6)	C2−Fe1	1.907(5)
C3−N3	1.134(6)	C3−Fe1	1.925(5)
C4−N4	1.142(6)	C4−Fe1	1.927(5)
C5−N5	1.126(7)	C5−Fe1	1.931(7)
N1−Sn1	2.304(5)	N2−Sn2	2.380(5)
N3−Sn1#1	2.351(5)	N4−Sn2#2	2.295(4)
N6−O1	1.118(6)	N6−Fe1	1.642(5)
Sn1−N3#3	2.351(5)	Sn2−N4#4	2.295(4)
C1−N1−Sn1	167.5(5)	C2−N2−Sn2	164.1(6)
C3−N3−Sn1#1	167.7(5)	C4−N4−Sn2#2	169.8(4)
N1−Sn1−N3#3	177.21(17)	N4#4−Sn2−N2	177.2(2)
	Compound **3**		
C1−N1	1.131(14)	C1−Fe1#1	1.975(9)
C1−Fe1	1.975(9)	C2−N2	1.16(3)
C2−Fe1	1.50(3)	C2−Fe1#1	2.31(3)
N1−Sn1	2.303(10)	Fe1−Fe1#1	0.808(6)
Fe1−C1#1	1.975(9)	Fe1−C1#2	1.975(9)
Fe1−C1#3	1.975(9)	Fe1−C2#1	2.31(3)
Fe1−N2′#1	2.31(3)	Sn1−N1#4	2.303(10)
Sn1−N1#5	2.303(10)	Sn1−N1#6	2.303(10)
C1−N1−Sn1	180.0(9)	N1#4−Sn1−N1	180.0
N1#4−Sn1−N1#5	90.0	N1−Sn1−N1#5	90.0
N1#4−Sn1−N1#6	90.0	N1−Sn1−N1#6	90.0
N1#5−Sn1−N1#6	180.0		
Compound **4**			
C22−N1	1.150(7)	C22−Fe1	1.922(6)
C23−N2	1.163(14)	C23−Fe1	1.925(11)
N1−Sn1	2.468(5)	N3−O1	1.112(11)
N3−Fe1	1.661(9)	N4−C24#1	1.112(11)
N4−N4#1	1.112(11)	N4−Sn1	2.293(5)
Fe1−C22#2	1.922(6)	Fe1−C22#3	1.922(6)
Fe1−C22#4	1.922(6)		
N2−C23−Fe1	180.000(1)	C22−N1−Sn1	146.9(5)
O1−N3−Fe1	180.000(2)	C24#1−N4−Sn1	177.5(8)
N4#1−N4−Sn1	177.5(8)	N4−Sn1−N1	178.3(2)

	Compound **5**		
C1−N1	1.140(12)	C1−Fe1	1.903(11)
C2−N2	1.140(13)	C2−Fe1	1.924(12)
C3−N3	1.146(14)	C3−Fe1	1.943(13)
C4−N4	1.170(15)	C4−Fe1	1.935(14)
C5−N5	1.138(14)	C5−Fe1	1.940(12)
N1−Sn1	2.272(9)	N2−Sn3	2.253(10)
N6−O5	1.142(11)	N6−Fe1	1.649(10)
O1−Sn1	2.005(6)	O1−Sn2	2.064(6)
O1−Sn2#1	2.140(7)	O2−Sn1	2.138(7)
O2−Sn2	2.164(6)	O3−Sn3	2.020(7)
O3−Sn4	2.061(7)	O3−Sn4#2	2.135(7)
O4−Sn3	2.133(7)	O4−Sn4	2.155(8)
Sn2−O1#1	2.140(7)	Sn4−O3#2	2.135(7)
C1−N1−Sn1	166.5(9)	C2−N2−Sn3	165.8(10)
Sn1−O1−Sn2	111.1(3)	Sn1−O1−Sn2#1	141.6(3)
Sn2−O1−Sn2#1	106.1(3)	Sn1−O2−Sn2	102.5(3)
Sn3−O3−Sn4	110.8(3)	Sn3−O3−Sn4#2	143.0(4)
Sn4−O3−Sn4#2	106.2(3)	Sn3−O4−Sn4	103.2(3)
O1−Sn1−O2	73.7(3)	O1−Sn1−N1	85.0(3)
O2−Sn1−N1	158.7(3)	O1−Sn2−O1#	173.9(3)
O1−Sn2−O2	72.0(3)	O1#1−Sn2−O2	145.8(2)
O3−Sn3−O4	73.5(3)	O3−Sn3−N2	84.8(3)
O4−Sn3−N2	158.4(3)	O3−Sn4−O3#2	73.8(3)
O3−Sn4−O4	72.3(3)	O3#2−Sn4−O4	145.9(3)
	Compound **6**		
C1−N1	1.148(9)	C1−Fe1	1.919(7)
C2−N2	1.139(9)	C2−Fe1	1.926(7)
C3−N3	1.135(10)	C3−Fe1	1.953(8)
C4−N4	1.142(11)	C4−Fe1	1.943(9)
C5−N5	1.146(10)	C5−Fe1	1.944(9)
N1−Sn1	2.258(6)	N2−Sn3	2.265(6)
N6−O5	1.135(8)	N6−Fe1	1.656(7)
O1−Sn1	2.143(4)	O1−Sn2	2.172(4)
O2−Sn1	2.014(4)	O2−Sn2	2.067(4)
O2−Sn2#1	2.134(4)	O3−Sn3	2.145(5)
O3−Sn4	2.156(6)	O4−Sn3	2.027(5)
O4−Sn4	2.059(5)	O4−Sn4#2	2.136(5)
Sn2−O2#1	2.134(4)	Sn4−O4#2	2.136(5)
C1−N1−Sn1	164.5(6)	C2−N2−Sn3	168.2(7)
Sn1−O1−Sn2	102.04(17)	Sn1−O2−Sn2	110.52(19)
Sn1−O2−Sn2#1	142.2(2)	Sn2−O2−Sn2#1	106.44(18)
Sn3−O3−Sn4	102.8(2)	Sn3−O4−Sn4	110.7(2)
Sn3−O4−Sn4#2	142.9(2)	Sn4−O4−Sn4#2	106.5(2)
O2−Sn1−O1	74.26(17)	O2−Sn1−N1	84.45(19)
O1−Sn1−N1	158.70(19)	O2−Sn2−O2#1	73.56(18)
O2−Sn2−O1	72.62(16)	O2#1−Sn2−O1	146.12(16)
O4−Sn3−O3	73.63(19)	O4−Sn3−N2	84.2(2)
O3−Sn3−N2	157.8(2)	O4−Sn4−O4#2	73.5(2)
O4−Sn4−O3	72.77(19)	O4#2−Sn4−O3	146.14(18)

[a] Symmetry codes. For **1** #1 $x - 1/2, y + 1/2, z$; #2 $x + 1/2, y + 1/2, z$; #3 $x + 1/2, y - 1/2, z$; #4 $x - 1/2, y - 1/2, z$. For **2** #1 $x - 1/2, y, -z + 1/2$; #2 $x - 1/2, -y + 1/2, -z$; #3 $x + 1/2, y, -z + 1/2$; #4 $x + 1/2, -y + 1/2, -z$. For **3** #1 $-x, -y, -z$; #2 $x, -y, -z$; #3 $-x, y, z$; #4 $-x + 1, -y + 1, -z$; #5 $x, -y + 1, -z$; #6 $-x + 1, y, z$. For **4** #1 $-x + 1, -y, -z$; #2 $-y + 1/2, x, z$; #3 $y, -x + 1/2, z$; #4 $-x + 1/2, -y + 1/2, z$. For **5** and **6**: #1 $-x + 2, -y + 2, -z + 1$; #2 $-x + 1, -y + 2, -z + 2$.

cis CN^- groups to form a 2D polymeric zigzag layer. One of the remaining CN^- groups is coordinated to a $[Ph_3SnOH_2]^+$ terminal group , and the other is hydrogen-bonded to the water molecule of $[Ph_3SnOH_2]^+$ from the adjacent layer. For compound **1**, the $[Fe(CN)_5NO]^{2-}$ anion contains five CN^- groups, and only four equatorial CN^- groups can coordinate to the Sn atoms. Thus a 2D polymeric structure of **1** was formed with the $[Fe(CN)_5(NO)]^{2-}$ anion acting as a planar four-connected node.

There have been no reports on the crystal structures of organotin−cyanometalates for tribenzyltin. Compound **2** shows a framework similar to that of **1** (Figure 2a). Compound **2** crystallizes in the centrosymmetric space group *Pbca*. Part of the structure of **2** is shown in Figure 2b. In **2**, the Sn−N bond lengths range from 2.295 to 2.380 Å. The C−N bond lengths range from 1.126 to 1.143 Å. The Fe−C bond lengths ranging from 1.907 to 1.931 Å are somewhat shorter than those of **1**. It should be noted that the C−N−Sn bond angles ranging from 164.1° to 177.2° are larger than those of **1**. In Fischer's opinion,[2a] the steric effect of the R group might force all C−N−Sn angles to become 180°, resulting in a marked expansion and simplification of the lattice. In this case, the replacement of the phenyl group by a benzyl group results in the increase of the C−N−Sn bond angles.

To the best of our knowledge, the crystal structures of diorganotin−cyanometalates have been reported only rarely.[1f,g] In order to illustrate the effect of the number of R groups of organotin on the framework, the crystal structure of compound **3** has been determined. Part of the structure of **3** is shown in Figure 3a. Compound **3** crystallizes in a highly symmetric space group *P*4/*mmm*. Both the Fe and Sn atoms lie at special positions, and the Fe atom is disordered over two positions. The positions of NO and the axial CN group of the $[Fe(CN)_5NO]^{2-}$ anion cannot be distinguished due to the disorder, and the benzyl

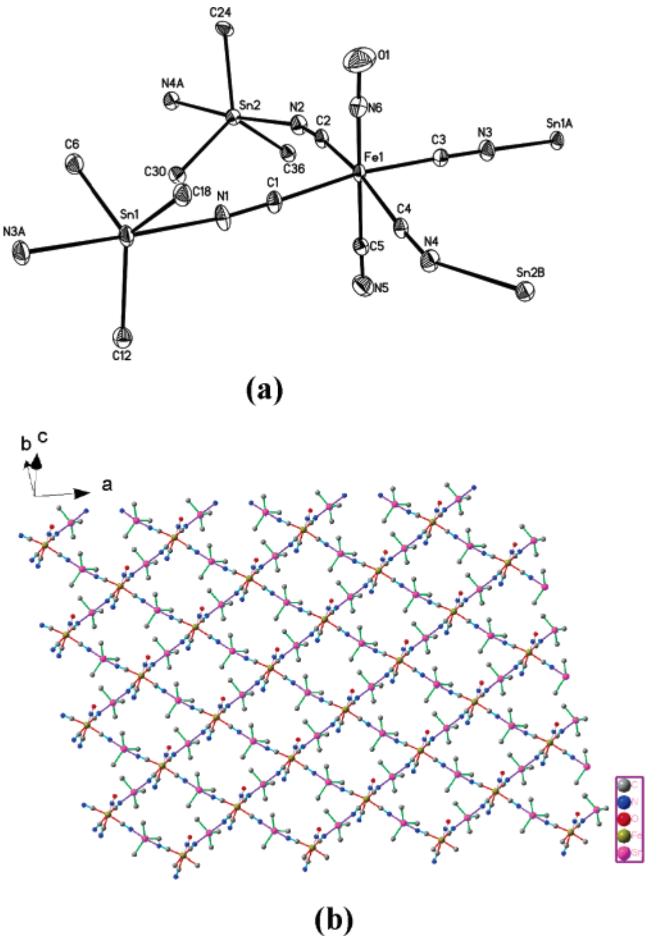

Figure 1. (a) Coordination environments of Sn and Fe in **1**. (b) View of the polymeric layer of **1**. (Phenyl rings are omitted for clarity except for the carbon atoms bonded to tin atoms.)

groups are also disordered. The four equatorial CN^- ligands are crystallographically equivalent, and their Fe—C, C—N, and N—Sn distances are 1.975, 1.131, and 2.303 Å, respectively. Like **1** and **2**, the $[Fe(CN)_5NO]^{2-}$ anion in **3** also coordinates to four tin atoms through four equatorial CN^- groups, showing a planar four-connected configuration. Each Bz_2Sn^{2+} cation is coordinated by four CN^- groups from four different $[Fe(CN)_5NO]^{2-}$ anions, showing an octahedral configuration of $[Bz_2SnN_4]$ with two benzyl groups at axial positions. Bz_2Sn^{2+} cations and $[Fe(CN)_5NO]^{2-}$ anions are connected to form a 2D polymeric layer containing 12-membered $Fe_2(CN)_4Sn_2$ rings (Figure 3b). In this 2D (4, 4) network, each of the Fe and Sn atoms acts as a planar four-connected node.

The crystals of compound **4** were obtained by a common solution reaction between Bz_3SnNO_3 and $Na_2Fe(CN)_5NO{\cdot}2H_2O$ in methanol. In compound **4**, two $[Bz_3Sn]^+$ cations are bridged by one CN^- anion to form a dimeric condensate of a $[Bz_3Sn{-}CN{-}SnBz_3]^+$ unit. Each $[Fe(CN)_5NO]^{2-}$ anion is connected to four dimeric condensates of $[Bz_3Sn{-}CN{-}SnBz_3]^+$ cations through its four equatorial CN^- groups, resulting in a 2D polymeric layer that contains 36-membered $Fe_4(CN)_{12}Sn_8$ rings (Figure 4a). The 2D polymeric network of **4** contains superlong spacers of [−CN—Bz_3Sn—CN—SnBz_3—NC−]. A related example containing superlong spacers of [−CN—Ag—CN—Ag—NC−] is already known.[23] As shown in Figure 4b, the four equatorial CN^- groups of the $[Fe(CN)_5NO]^{2-}$ anion are crystallographically equivalent, and their Fe—C, C—N, and N—Sn bond distances are 1.922, 1.150, and 2.468 Å, respectively. The Sn—N bond distance of **4** is longer than the normal length (about 2.33 Å) of the [−CN—Sn—NC−] spacer, but shorter than the value in $[(Me_3Sn)_3Fe^{III}(CN)_6{\cdot}4H_2O{\cdot}bpy]$.[1h] The C—N—Sn bond angle (146.9°) is much more significant than those found in compounds **1**−**3**, and an umbrella-like configuration appears (Figure 4b). The umbrella-like arrangement has already been described in a previous study.[1i] These umbrella-like units of **4** connect to each other by sharing the central CN^- anions of the dimeric condensates of $[Bz_3Sn{-}CN{-}SnBz_3]^+$ cations to form a polymeric layer structure (Figure 4a). The axial Fe—C, Fe—N, C—N, and N—O bond distances (1.925, 1.661, 1.163, and 1.112 Å, respectively) are longer than those of $Na_2Fe(CN)_5NO{\cdot}2H_2O$.[22] One unique feature of **4** is the superlong spacers of [−CN—Bz_3Sn—CN—SnBz_3—NC−]. To the best of our knowledge, this is the first example of the organotin−cyanometalate family that contains [−CN—Bz_3Sn—CN—SnBz_3—NC−] spacers. The central cyanide C—N bond distance of $[Bz_3Sn{-}CN{-}SnBz_3]^+$ cations (1.112 Å) is shorter than the CN^- ligands of the $[Fe(CN)_5NO]^{2-}$ anion. The positions of the C and N atoms of the central CN^- anion of $[Bz_3Sn{-}CN{-}SnBz_3]^+$ cations are mixed together due to the disorder. This central cyanide is possibly generated from the decomposition of the nitroprusside anion. It is known that the NO is easily detachable from the $Fe(CN)_5NO^{2-}$ group, especially photochemically. After the loss of the active substance NO, the remaining cyano ligands become labile and are subsequently released.[24]

Compounds **1**−**4** exhibit infinite 2D (4, 4) networks containing rectangular grids (Scheme 1). On the basis of the Fe⋯Fe or Fe⋯Sn distances, the approximate dimensions of the grids are 10.6 Å × 10.6 Å for **1**, 10.6 Å × 10.6 Å for **2**, 5.4 Å × 5.4 Å for **3**, and 16.0 Å × 16.0 Å for **4**. From the structures of **1** and **2**, it can be seen that the replacement of the phenyl groups by benzyl groups on the organotin has little effect on the overall structure. From the structures of **2** and **3**, the number of benzyl groups plays an important role in the construction of the grids (see grids **I** and **II**). In both of **2** and **3**, the $[Fe(CN)_5NO]^{2-}$ anion coordinates to four Sn atoms through four equatorial CN^- ligands, and Fe atom acts as a four-connected node. For **2**, the Sn atoms adopt a $[Bz_3SnN_2]$ trigonal-bipyramidal configuration, and the $[Bz_3Sn]^+$ cation acts as a tether, while for **3**, the Sn atoms adopt a $[Bz_2SnN_4]$ octahedral configuration and the $[Bz_2Sn]^{2+}$ cation acts as a planar four-connected node. For **4**, two $[Bz_3Sn]^+$ cations are bridged by one CN^- anion to form a long spacer $[Bz_3Sn{-}CN{-}SnBz_3]^+$, leading to the formation of large grids.

Furthermore, the coplanarity of the Fe and Sn atoms of one polymeric layer is significantly different for **1**−**4** (Figure 5). The coplanarity of the Fe and Sn atoms of one polymeric layer can be identified by the thickness of the layer of Fe and Sn atoms. The smaller the thickness is, the better the coplanarity is. For **1**, one face of the layer is composed of Fe atoms, and the other face is composed of Sn atoms; for **2**, both faces of the layer are composed of Sn atoms; for **3** and **4**, both faces of the layer are composed of Fe atoms. The thicknesses of the layers are 0.47 (**1**), 3.9 (**2**), 0.81 (**3**), and 7.6 Å (**4**), respectively. It is noteworthy that the polymeric layers of compounds **2** and **4** display beautiful sinusoidal ruffles (Figure 5), and the period of compound **4** (19.9 Å) is shorter than that of compound **2** (29.8 Å). Obviously, these differences are due to the existence

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(23) (a) Takayoshi, S.; Toschitake, I. *Chem. Lett.* **1994**, 821. (b) Takayoshi, S.; Hidetaka, Y.; Toschitake, I. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1665.

(24) Roychowdhury, S.; Komiyama, T.; Yukawa, Y.; Bhattacharyya, R. *Inorg. Chem. Commun.* **2004**, *7*, 1117.

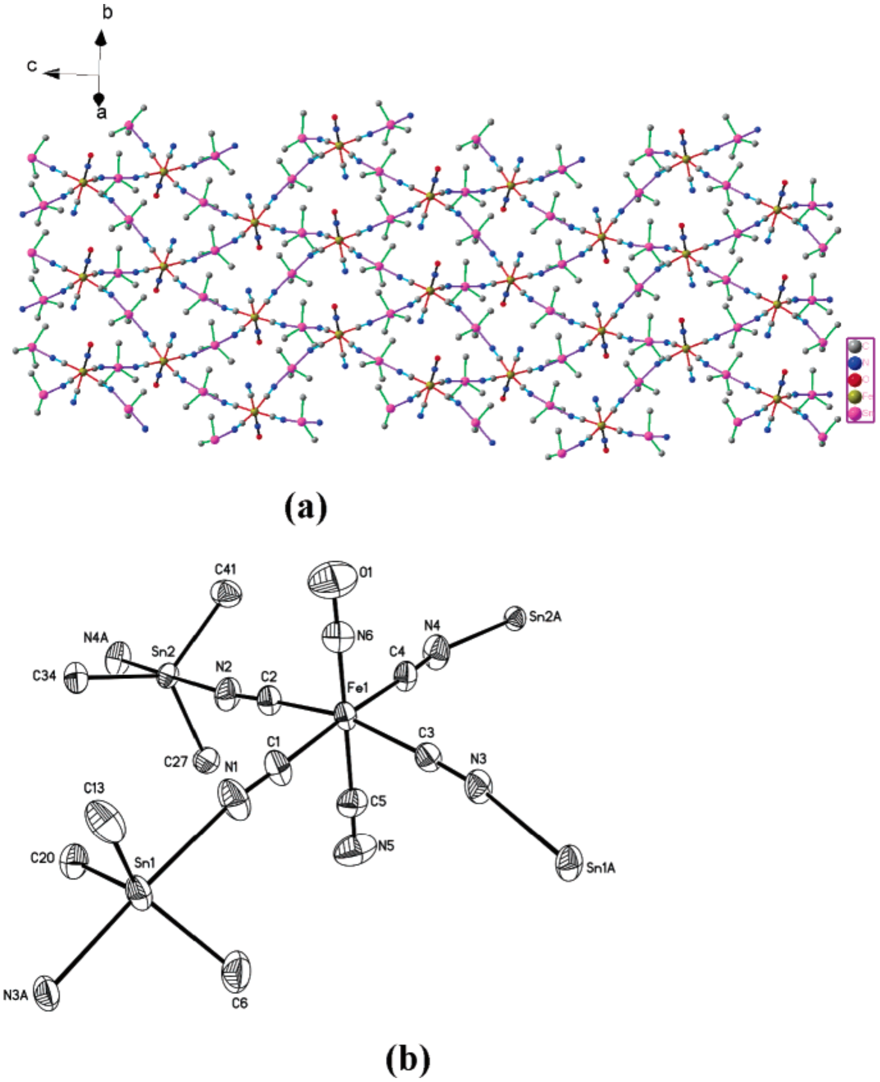

Figure 2. (a) View of the polymeric layer of **2**. (b) Coordination environments of Sn and Fe in **2**. (Benzyl groups are omitted for clarity except for the carbon atoms bonded to tin atoms.)

of the superlong spacers of [–CN–Bz_3Sn–CN–$SnBz_3$–NC–] in the framework of compound **4**. Interestingly, for **1**, NO groups of one polymeric layer lie on the same side of the layer; for **2**–**4**, NO groups of one polymeric layer lie on both sides of the layer. The average interlayer separations are 8.7 (**1**), 11.0 (**2**), 9.3 (**3**), and 10.6 Å (**4**), respectively.

Organooxotin clusters can be bridged by organic or inorganic spacers.[25] In our previous work,[26] a series of organooxotin cluster compounds, which are bridged by various inorganic or organic spacers, have been reported. Syntheses of new ligand-bridged organooxotin clusters can be expected to continue to attract considerable attention. For organooxotin cluster chemistry, organooxotin clusters bridged by inorganic spacers are reported very rarely.[25h] It is undoubtedly an interesting attempt to introduce organooxotin clusters into the organotin–cyanometalate family. In this work, compound **5** is successfully isolated and characterized crystallographically. **5** is the first compound where organooxotin clusters are bridged by cyanometalate anions to form a novel chain structure (Figure 6).

In the previous reports,[25i,j] dimeric tetraorganodistannoxane units bridged by organic anions have been found. In compound **5** (Figure 6), the similar organooxotin clusters are connected by $[Fe(CN)_5NO]^{2-}$ anions. Two *trans* equatorial CN^- ligands of the $[Fe(CN)_5NO]^{2-}$ anion coordinate to two *exo* tin atoms from two $[Bz_2SnOSn(RO)Bz_2]_2^{2+}$ clusters to form the 1D polymeric chain structure. All of the tin atoms show five-coordinated trigonal-bipyramidal configuration. According to the different coordination environments, the tin atoms can be divided into two types. Each of Sn1 and Sn3 is bonded to one μ_3-O^{2-} ion, one μ_2-RO^- group, and one CN^- group from the $[Fe(CN)_5NO]^{2-}$ anion, while each of Sn2 and Sn4 is bonded to two μ_3-O^{2-} ions and one μ_2-RO^- group. The C–N and Fe–C bond distances of the CN^- ligands bonded to tin atoms are somewhat shorter than those of the CN^- ligands uncoordinated

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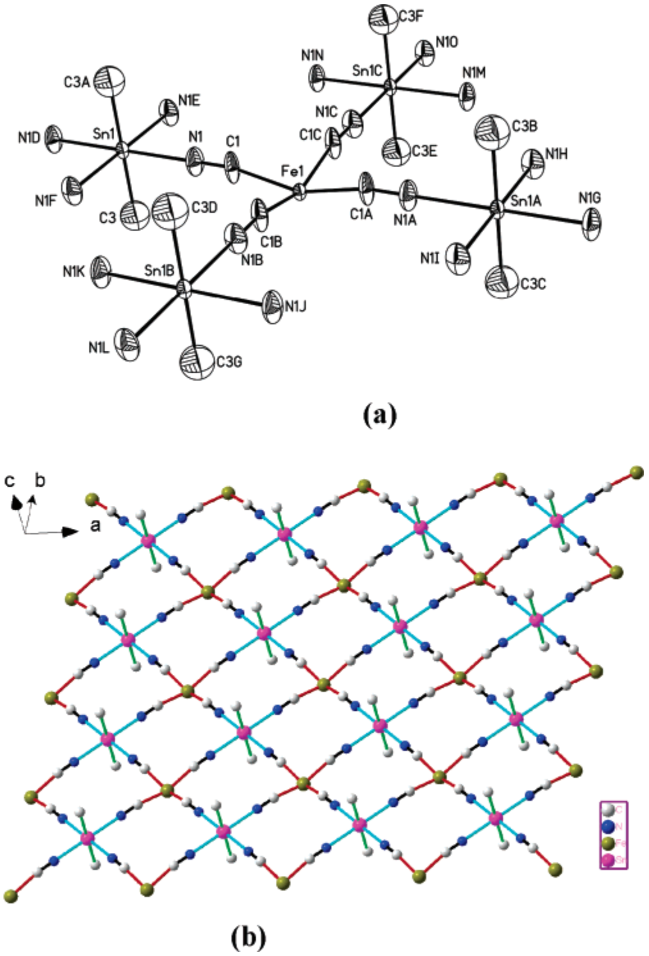
[25] (a) Dakternieks, D.; Jurkschat, K.; Schollmeyer, D.; Wu, H. *Organometallics* **1994**, *13*, 4121. (b) Mehring, M.; Schürmann, M.; Reuter, H.; Dakternieks, D.; Jurkschat, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1112. (c) Mehring, M.; Paulus, I.; Zobel, B.; Schürmann, M.; Jurkschat, K.; Duthie, A.; Dakternieks, D. *Eur. J. Inorg. Chem.* **2001**, 153. (d) Dakternieks, D.; Duthie, A.; Zobel, B.; Jurkschat, K.; Schürmann, M.; Tiekink, E. R. T. *Organometallics* **2002**, *21*, 647. (e) Mehring, M.; Schürmann, M.; Paulus, I.; Horn, D.; Jurkschat, K.; Orita, A.; Otera, J.; Dakternieks, D.; Duthie, A. *J. Organomet. Chem.* **1999**, *574*, 176. (f) Dakternieks, D.; Zobel, B.; Jurkschat, K.; Schürmann, M.; Tiekink, E. R. T. *Organometallics* **2003**, *22*, 1343. (g) Ma, C. L. Jiang, Q. Zhang, R. F. Wang, D. Q. *J. Chem. Soc., Dalton Trans.* **2003**, 2975. (h) Chandrasekhar, V.; Baskar, V.; Vittal, J. J. *J. Am. Chem. Soc.* **2003**, *125*, 2392. (i) Orita, A.; Xiang, J. N.; Sakamoto, K.; Otera, J. *J. Organomet. Chem.* **2001**, *624*, 287. (j) Xiong, R. G.; Zuo, J. L.; You, X. Z.; Fun, H. K.; Sundara, Raj, S. S. *Organometallics* **2000**, *19*, 4183.

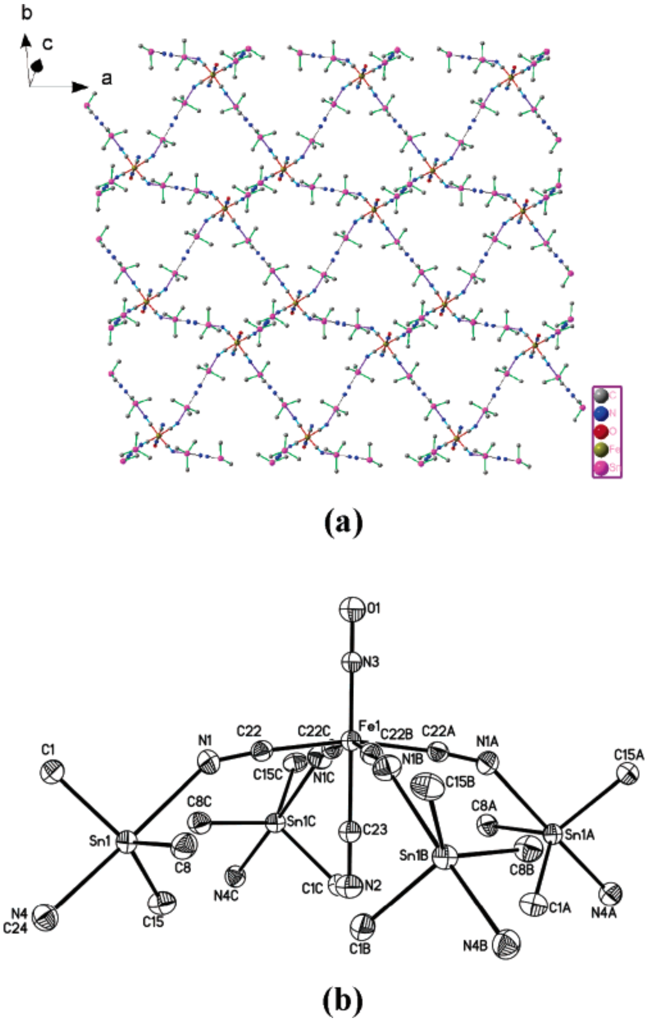
[26] Zheng, G. L.; Ma, J. F.; Yang, J.; Li, Y. Y.; Hao, X. R. *Chem.–Eur. J.* **2004**, *10*, 3761.



(a)

(b)

Figure 3. (a) Part of the structure of **3**. (b) View of the polymeric layer of **3**. (Benzyl groups are omitted for clarity except for the carbon atoms bonded to tin atoms.)



(a)

(b)

Figure 4. (a) View of the polymeric layer of **4**. (b) Coordination environments of Sn and Fe in **4**. (Benzyl groups are omitted for clarity except for the carbon atoms bonded to tin atoms.)

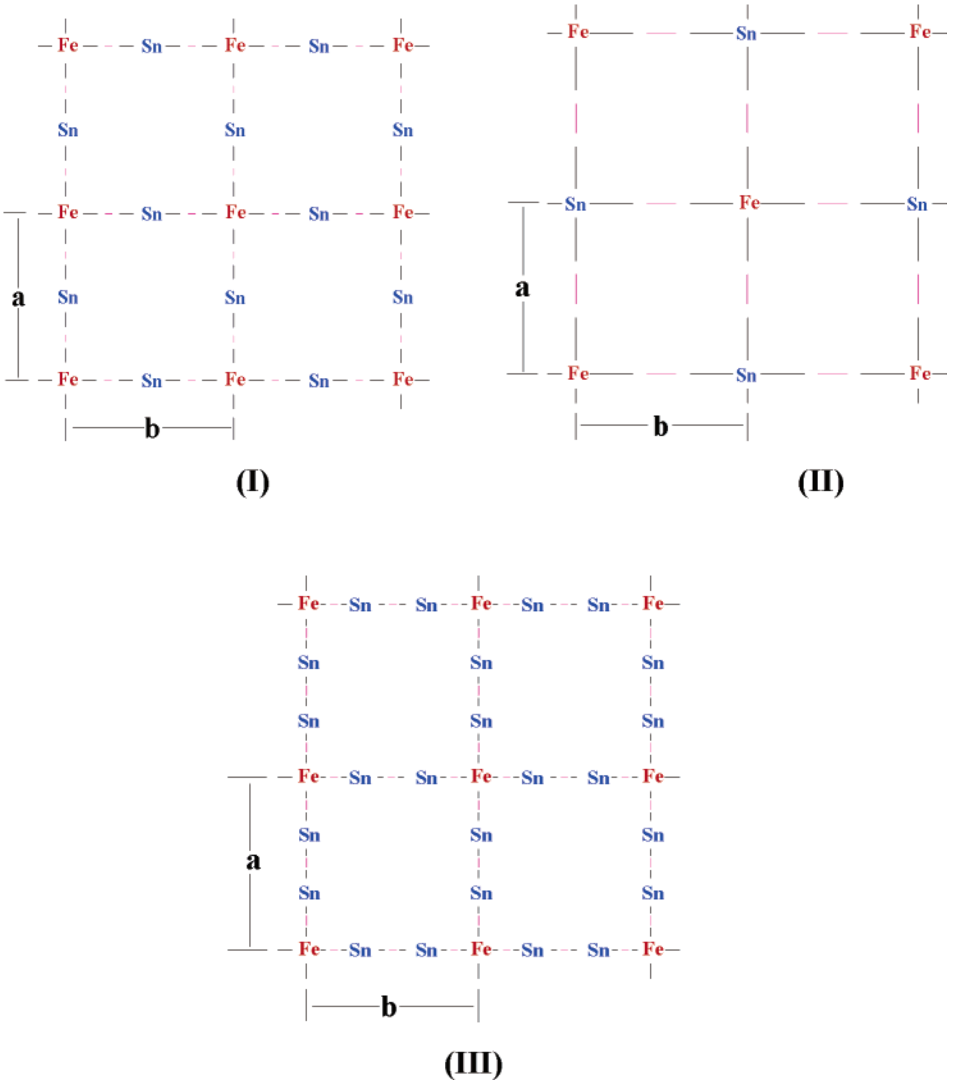
to tin atoms, which is in accordance with compounds **1**−**4**. The Sn−N distances (2.272 Å for Sn1−N1, 2.253 Å for Sn3−N2) are somewhat shorter than the distances observed in compounds **1**−**4**. The C−N−Sn bond angles are bent significantly at the N atoms (166.5° for C1−N1−Sn1, 165.8° for C2−N2−Sn3). The Sn and O atoms of the $[Bz_2SnOSn(MeO)Bz_2]_2^{2+}$ cluster are nearly coplanar, and the dihedral angle between the Sn−O planes of two adjacent clusters is 70.1°. This may be the suitable conformation through rotating around the N−Sn bond to minimize the steric hindrance between the adjacent $[Bz_2SnOSn(MeO)Bz_2]_2^{2+}$ clusters and the repulsion among the neighboring polymeric chains.

The organooxotin cluster of **5** contains MeO^- groups, and these MeO^- groups may be replaced by other RO^- groups through using other alcohols in the reaction. On the basis of this idea, ethanol was used instead of methanol, and compound **6** was successfully isolated. Compound **6** shows a very similar structure to that of **5**, and the structural difference is the replacement of MeO^- groups by EtO^- groups. Figures for the structure of **6** are given in the Supporting Information (Figures S1−S3).

Two related compounds containing dimeric tetraorganodistannoxane units, $\{[(TfO)Bu_2SnOSnBu_2OH]_2\}_n$[25i] (**7**) (TfOH = triflic acid) and $\{([Me_2Sn(VA)_{0.5}]_2O)_2 \cdot 2H_2O\}_n$ (**8**)[25j] (HVAH = 4-hydroxy-3-methoxybenzoic acid), have been reported. In comparison with **5** and **6**, the μ_2-OR groups are replaced by μ_2-OH groups for **7**, and each *exo* Sn atom of the dimeric tetraorganodistannoxane unit is bonded to two sulfonate O atoms, showing an octahedral geometry. In **8**, each VA^{2-} ligand affords one μ_2-oxygen atom of phenolato and one oxygen atom of carboxylate as a tridentate ligand. The RO− groups of **5** and **6** are replaced by the phenolato groups, and the carboxylate group plays the role of $[Fe(CN)_5NO]^{2-}$ anion. For **7** and **8**, dimeric tetraorganodistannoxane units act as four-connected nodes that are linked by the spacers TfO^- and VA^{2-} to form 2D polymeric (4, 4) networks, respectively, while for **5** and **6**, dimeric tetraorganodistannoxane units act as two-connected spacers that are joined by μ_2-$[Fe(CN)_5NO]^{2-}$ anions to form a 1D chain structure.

In comparison with **1**−**4**, compounds **5** and **6** exhibit a one-dimensional polymeric chain. A crenel-like arrangement appears when looking along the *a*-axis (Figure 6b). In **1**−**4**, each $[Fe(CN)_5NO]^{2-}$ anion coordinates to four $[R_3Sn]^+$ or $[R_2Sn]^{2+}$ groups through four equatorial CN^- ligands to form a 2D polymeric layer, while for **5** and **6**, since the $[Bz_2SnOSn(RO)Bz_2]_2^{2+}$ cluster is much bulkier than the $[R_3Sn]^+$ or $[R_2Sn]^{2+}$ group, each $[Fe(CN)_5NO]^{2-}$ anion coordinates to two $[Bz_2SnOSn(RO)Bz_2]_2^{2+}$ clusters through two *trans* equatorial CN^- ligands, and the 1D chain structure is formed. The voids in the structures of **5** and **6** are occupied by lattice CH_2Cl_2 molecules (Figure 6c). The 2D layers of **1**−**4** pack more closely than the 1D chains of **5** and **6**, and there are no solvent molecules in the structures of **1**−**4**.

Scheme 1. Three Types of Rectangular Grids: I for 1 and 2; II for 3; III for 4



In other polymeric structures reported for the octahedral building blocks $M(CN)_6^{3-}$ and $M(CN)_6^{4-}$,[1b,d,f] the structures are constructed through cyano nitrogen atoms either coordinating directly to tin atoms or hydrogen bonding to the solvent molecules that are coordinated to tin atoms. In contrast, the nitroprusside anion contains five cyanide ligands that may coordinate to tin atoms. As far as we know, a bridging NO group has never been reported to date for nitroprusside. For compounds **1**−**6**, the cyanide *trans* to NO of the nitroprusside anion does not coordinate to tin atoms, and the $[Fe(CN)_5NO]^{2-}$ anion coordinates to tin atoms through equatorial CN^- groups, resulting in the formation of infinite 2D layers and 1D chain structures. In the reported complexes of nitroprusside, the nitroprusside anion often coordinates through the CN group *cis* to NO, but the coordination through the CN group *trans* to NO is also reported.[10]

To better clarify the M−M connection in the crystal structures, the description in Table 3 is preferred to the more conventional formulas. In Fischer's opinion,[1a] the infinite "naked" [−M−CN−Sn−NC−] chains generating the SPB (super-Prussian blue) skeleton turn out to avoid linearity (i.e., they tend to be shortened) to minimize empty voids, while the volume demand of the groups coordinated to Sn and of guests will hold back this tendency. The net result of this interplay can be reflected by the variation of the formula volume, $V_f = N_F M_r/\rho_{calc} = 0.602 N_F V/Z$. The V_f values of compounds **1**−**4** are listed in Table 3.

The V_f values of compounds **1** and **2** containing exclusively [−M−CN−Sn−NC−] chains turn out to be lower than the V_f value of about 1000 Å^3 extrapolated for ideal super-Prussian blue (SPB) with strictly linear spacers.[1a] Inasmuch as each CH_2 fragment of a benzyl group in **2** may be considered as a pseudoguest of **1** (comprising 18 extra atoms in total), the V_f value of **2** comes closer to the extrapolated V_f value. Obviously, the free space available within the frameworks of **1** and **2** is too small to accommodate large guests. A still higher V_f value results for **4** with spacers longer than those of **1** and **2** and compares well with the value of $^3_\infty[Fe^{II}\{\mu\text{-}CNSn(Me_3)NC\}_2\text{-}\{\mu\text{-}CNSn(Me_3)O(H)H\cdots(diox)\cdots HO(H)Sn(Me_3)NC\}]$ (1360 Å^3), which contains a $[-M-CN-Sn-OH\cdots(C_4H_8O_2)\cdots HO-Sn-NC-]$ chain.[6b] Compound **3** is a heterometallic 2D PB coordination polymer that contains only the short CN^- spacers and two kinds of four-connected metal centers, Fe and Sn. This results in a very small V_f value for **3** (161 Å^3).

Electrochemistry Studies. Cyclic voltammograms of these compounds are similar to that of $[N(C_4H_9)_4]_2Fe(CN)_5NO$.[27] Cyclic voltammograms of compounds **1**, **2**, **3**, and **5** in $^nBu_4NClO_4$−DMF (Figure 7) show two waves in the vicinity of −0.9

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[27] Bowden, W. L.; Bonnar, P.; Brown, D. B.; Geiger, W. E. *Inorg. Chem.* **1977**, *16*, 41.

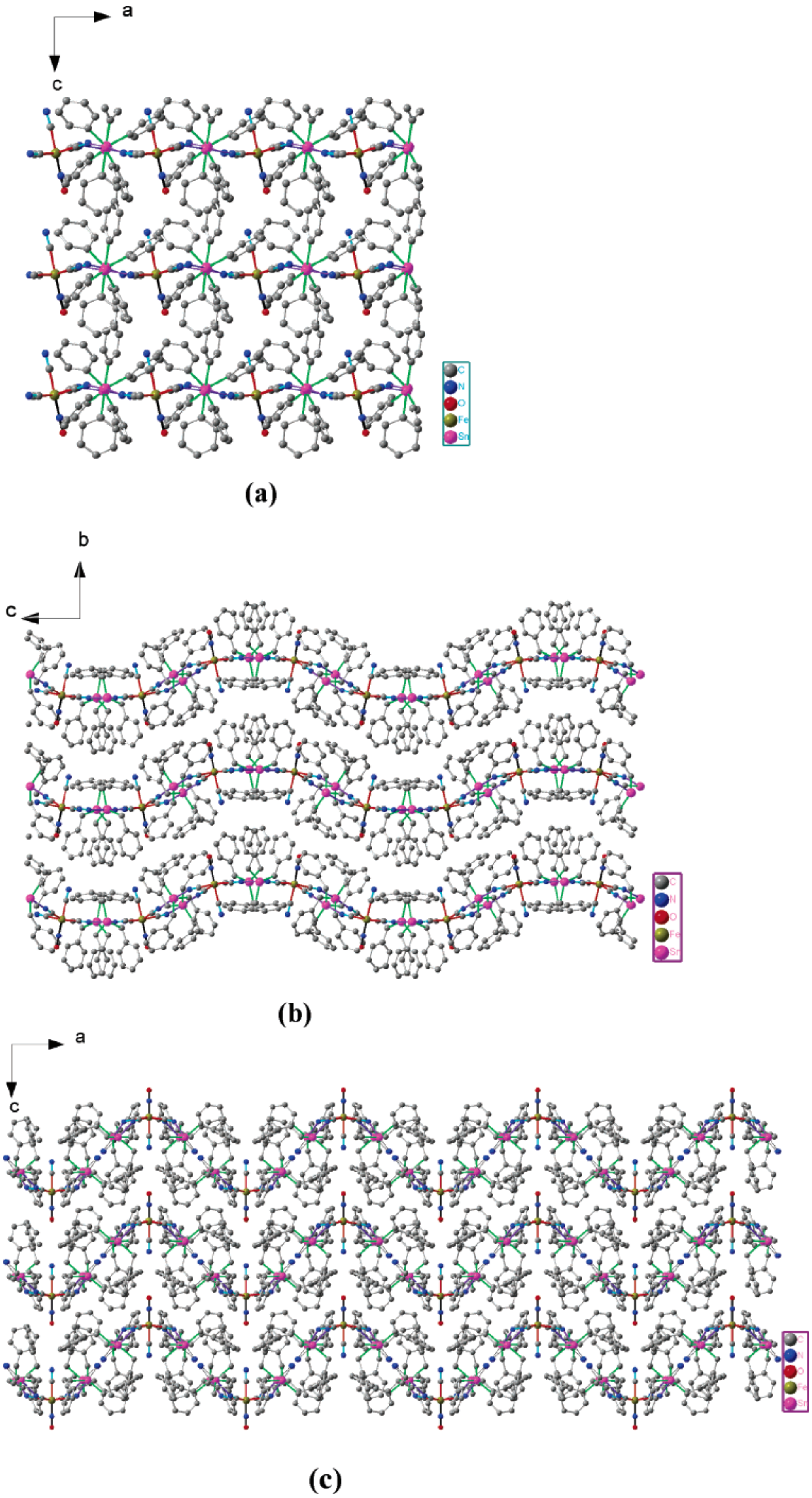

Figure 5. (a) View of layers of **1** along the *b*-axis. (b) View of layers of **2** along the *a*-axis. (c) View of layers of **4** along the *b*-axis. All the H atoms are omitted for clarity.

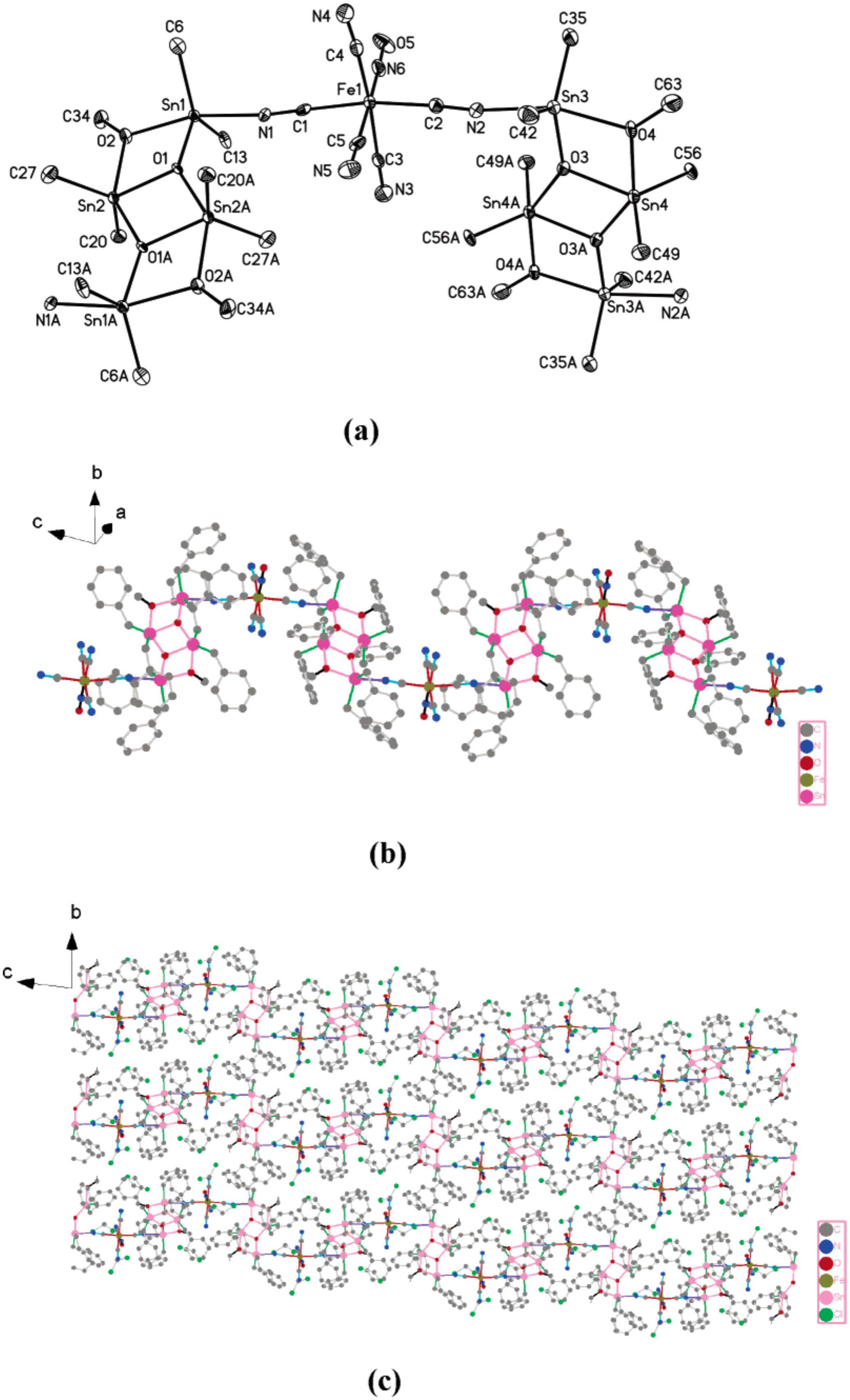

Figure 6. (a) Coordination environments of Sn and Fe in **5**. (Benzyl groups are omitted for clarity except for the carbon atoms bonded to tin atoms.) (b) View of the 1D polymeric chain of **5**. (c) Packing diagrams of **5**.

and −1.3 V. The results are consistent with the formulation that one electron is consumed in each wave. The irreversible peak with the $E_{1/2}$ value of −0.9 V assigned to the $Fe(CN)_5NO^{2-}/Fe(CN)_5NO^{3-}$ couple demonstrates that the lifetime of the reduced nitroprusside ion, $Fe(CN)_5NO^{3-}$, is very short. $Fe(CN)_5NO^{3-}$ transforms to $Fe(CN)_4NO^{2-}$ by rapid loss of cyanide. The quasireversible peak with the $E_{1/2}$ value of −1.3 V is assigned to the $Fe(CN)_4NO^{2-}/Fe(CN)_4NO^{3-}$ couple. The

Table 3. Formula Volumes, V_f, of Compounds 1−4

compound	formula	n_D	N_F[a]	V_f (Å ^{3})
1	$^2_\infty[\mathrm{Fe^{II}(CN)(NO)}\{\mu_2\text{-}\mathrm{CNSnPh_3NC}\}_2]$	2	1	586
2	$^2_\infty[\mathrm{Fe^{II}(CN)(NO)}\{\mu_2\text{-}\mathrm{CNSnBz_3NC}\}_2]$	2	1	704
3	$^2_\infty[\mathrm{Fe^{II}(CN)(NO)SnBz_2}(\mu_2\text{-}\mathrm{CN})_4]$	2	1	161
4	$^2_\infty[\mathrm{Fe^{II}(CN)(NO)}\{\mu_2\text{-}\mathrm{CNSnBz_3(NC)SnBz_3NC}\}_2]$	2	1	1261

[a] N_F: number of interpenetrating frameworks.

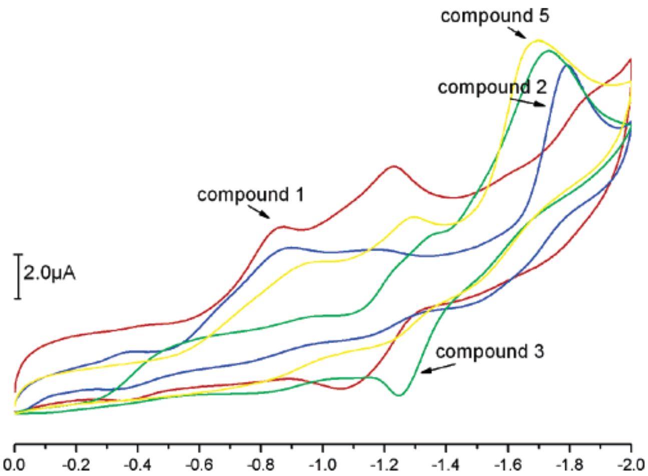

Figure 7. Cyclic voltammograms of compounds **1**, **2**, **3**, and **5** in N_2-saturated DMF solution containing $^n\mathrm{Bu_4NClO_4}$ (0.1 M) at a scan rate of 100 mV s^{-1} (vs Ag/AgCl).

appearance of an oxidation wave with an $E_{1/2}$ value of ca. −1.7 V suggests that the initial reduction product, $\mathrm{Fe(CN)_4NO^{3-}}$, decomposes in a further reaction. Coordination polymers of $[\mathrm{(R_3Sn)_3Fe(III)(CN)_6}]_n$ can form a CT guest−host system $[\mathrm{(G)}_x\mathrm{(R_3Sn)_3Fe(III)}_{1-x}\mathrm{Fe(II)}_x\mathrm{(CN)_6}]_n$ by oxidizing the guest molecules (G).[28] Attempts to encapsulate thiophene molecules within the present 2D coordination polymers failed, partly because the nitroprusside ion is a reductant with low oxidation potential (−0.9 V) and cannot oxidize the guest molecule thiophene.

Infrared Spectra. The IR spectra of **1**−**6** exhibit CN stretching bands in the range from 2146 to 2173 cm^{-1}. As is observed in other organotin−cyanometalates,[1b,f] the bands are all blue-shifted from that of $\mathrm{Na_2Fe(CN)_5NO{\cdot}2H_2O}$ (2143 cm^{-1}), in agreement with the bridging nature of cyano groups. Peaks ranging from 1932 to 1943 cm^{-1} are attributed to the NO stretching vibration of the $\mathrm{Fe(CN)_5NO^{2-}}$ anion, and the $\mathrm{CH_2}$ bands for **2**−**5** appear in the range 2956−3064 cm^{-1}.

Conclusion

In this work, the coordination chemistry of the photochromic nitroprusside anion, $[\mathrm{Fe(CN)_5NO}]^{2-}$, has been extended to its association with triorganotin, diorganotin, and organooxotin clusters. Six novel compounds have illustrated the ability of nitroprusside as a building block in tuning the topologies of a new subfamily of organotin−cyanometalate. We have first succeeded in introducing organooxotin clusters into the organotin−cyanometalate family. Given the large variety of organooxotin clusters, the scope of the further synthesis of other novel cyanometalate compounds based on organooxotin clusters appears to be very inspiring. In addition, the first organotin−cyanometalate containing superlong spacers of $-\mathrm{CN}-\mathrm{R_3Sn}-\mathrm{CN}-\mathrm{SnR_3}-\mathrm{NC}-$ has been obtained. Since the central $\mathrm{CN^-}$ anions of dimeric condensates of $[\mathrm{Bz_3Sn}-\mathrm{CN}-\mathrm{SnBz_3}]^+$ cations may be replaced by other bridging ligands, more new organotin−cyanometalates containing other additional anions can be expected.

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Supporting Information Available: Figures for the structure of compound **6**. X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM060157L

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(28) Ibrahim, M. S.; Werida, A. H.; Etaiw, S. E. H. *Transition Met. Chem.* **2003**, *28*, 585.