bottomed flask equipped with a reflux condenser and nitrogen inlet (gas adapter), glass stopper, stirbar, and rubber septum was charged with 0.73 g (1.72 mmol) of (μ-$Me_2C{=}CHC{=}O$)(μ-EtS)$Fe_2(CO)_6$ (**15d**) and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 mL of THF. After the reaction mixture had been stirred for 15 h at room temperature and then 4 h at reflux, the solvent was removed in vacuo to yield a red oil, which was dissolved in pentane/CH_2Cl_2 (4:1 v/v) and filtered through a thin pad of silicic acid. Removal of solvent left a red oil, which was purified by filtration chromatography. Pentane eluted two red bands. The first gave a red oil identified by its ^1H NMR spectrum to be a mixture of several products. The second band gave 0.13 g (0.30 mmol, 17%) of starting material, **15d**, identified by its ^1H NMR spectrum ($CDCl_3$; 250 MHz). Repurification of the first fraction by medium-pressure chromatography yielded two bands eluting in pentane. The first gave a red oil identified by its ^1H NMR spectrum ($CDCl_3$; 250 MHz) to be a mixture of 0.22 g (0.57 mmol, 33%) of (μ-σ,π-$HC{=}CMe_2$)(μ-EtS)$Fe_2(CO)_6$ (**16d**) and 0.12 g (0.31 mmol, 36% based on S) of (μ-EtS)$_2Fe_2(CO)_6$ (**11**).[18] The second gave 0.08 g (0.18 mmol, 11%) of starting material, **15d**, identified by its ^1H NMR spectrum ($CDCl_3$; 250 MHz). Analytically pure (μ-σ,π-$HC{=}CMe_2$)(μ-EtS)$Fe_2(CO)_6$ (**16d**; a slightly air-sensitive red oil) could be obtained by repeated medium-pressure chromatography of the first fraction (fractionation of the leading edge). Anal. Calcd for $C_{12}H_{12}Fe_2O_6S$: C, 36.40; H, 3.05. Found: C, 36.80; H, 3.14. ^1H NMR ($CDCl_3$; 250 MHz): δ 1.29 (t, J = 7.37 Hz, 3 H, $SCH_2C\mathit{H}_3$), 1.66 (s, 3 H, $HC{=}C(C\mathit{H}_3)_2$ endo), 1.77 (s, 3 H, $HC{=}C(C\mathit{H}_3)_2$ exo), 2.30 (q, J = 7.36 Hz, 2 H, $SC\mathit{H}_2CH_3$), 7.57 (s, 1 H, $\mathit{H}C{=}CMe_2$). ^{13}C NMR ($CDCl_3$; 100.5 MHz): δ 17.88 (q, J = 128.9 Hz, $SCH_2\mathit{C}H_3$), 24.76 (q, J = 128.1 Hz, $HC{=}C(\mathit{C}H_3)_2$ exo), 35.41 (t, J = 142.2 Hz, $S\mathit{C}H_2CH_3$), 36.10 (q, J = 128.6 Hz, $HC{=}C(\mathit{C}H_3)_2$ endo), 114.91 (s, $HC{=}\mathit{C}Me_2$), 153.31 (d, J = 143.5 Hz, $H\mathit{C}{=}CMe_2$), 208.86 and 210.09 (both s, Fe—CO).

(b) (μ-$CH_2{=}CHC{=}O$)(μ-EtS)$Fe_2(CO)_6$. In an experiment similar to that above, a THF solution containing 0.39 g (0.99 mmol) of (μ-$CH_2{=}CHC{=}O$)(μ-EtS)$Fe_2(CO)_6$ (**15a**) was stirred for 48 h at room temperature. Subsequently, the solvent was removed in vacuo, and the resulting red oil was purified by filtration chromatography. Pentane eluted an orange band, which gave 0.34 g (0.91 mmol, 92%) of (μ-σ,π-$HC{=}CH_2$)(μ-EtS)$Fe_2(CO)_6$ (**16a**),[11a] identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

(c) (μ-$PhCH{=}CHC{=}O$)(μ-EtS)$Fe_2(CO)_6$. In an experiment similar to that above, a THF solution containing 0.09 g (0.20 mmol) of (μ-$PhCH{=}CHC{=}O$)(μ-EtS)$Fe_2(CO)_6$ (**15b**) was stirred for 40 h at room temperature and then 1.5 h at reflux. Subsequently, the solvent was removed in vacuo and the resulting red oil was purified by filtration chromatography. Pentane eluted a pale yellow band, which was not collected. Pentane then eluted a red band, which gave 0.07 g (0.16 mmol, 82%) of (μ-σ,π-$HC{=}CHPh$)(μ-EtS)$Fe_2(CO)_6$ (**16b** (**6h′**)), identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

(d) (μ-$MeCH{=}CHC{=}O$)(μ-EtS)$Fe_2(CO)_6$. In an experiment similar to that in (a), a THF solution containing 0.44 g (1.07 mmol) of (μ-$MeCH{=}CHC{=}O$)(μ-EtS)$Fe_2(CO)_6$ (**15c**) was stirred for 17 h at room temperature, 1.5 h at reflux, and then 4 h more at room temperature. Subsequently, the solvent was removed in vacuo, and the resulting red oil was purified by filtration chromatography. Pentane eluted an orange band, which gave 0.40 g (1.04 mmol, 98%) of (μ-σ,π-$HC{=}CHMe$)(μ-EtS)$Fe_2(CO)_6$ (**16c**), identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

Acknowledgment. We are grateful to the National Science Foundation for generous support of this research.

Supplementary Material Available: A table of IR and EI mass spectra of new compounds (13 pages). Ordering information is given on any current masthead page.

High-Resolution Solid-State ^{119}Sn and ^{13}C NMR Studies of Novel Organotin(IV) Coordination Polymers Involving R_3Sn and $M(CN)_m$ Fragments

David C. Apperley, Nicola A. Davies, and Robin K. Harris*

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.

Abdul K. Brimah, Stefan Eller, and R. Dieter Fischer*

Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, FRG

Received February 13, 1990

The room-temperature solid-state ^{119}Sn and ^{13}C CP/MAS NMR spectra of seven well-defined coordination polymers have been examined and satisfactorily interpreted: $[(Me_3Sn)_3Co^{III}(CN)_6]_\infty$ (**1**), $[(Et_3Sn)_3Co^{III}(CN)_6]_\infty$ (**2**), $[(Et_3Sn)Au^{I}(CN)_2]_\infty$ (**3**), $[(Me_3Sn)_4Fe^{II}(CN)_6]_\infty$ (**4**), $[(Me_3Sn)_4Ru^{II}(CN)_6]_\infty$ (**5**), $[(Me_3Sn)_4Fe^{II}(CN)_6\cdot 2H_2O\cdot C_4H_8O_2]_\infty$ (**6**), and $[(Me_3Sn)_4Fe^{II}(CN)_6\cdot nH_2O]_\infty$ (**7**). Owing to the appearance of relatively sharp NMR signals, the information to be deduced from the solid-state NMR spectra greatly exceeds that to be gained by other spectroscopic techniques applicable to powders (e.g. IR, Raman, and Mössbauer spectroscopy) and X-ray powder diffractometry. In particular, the NMR spectra of **1**, **6**, and **7** match well with the results of recent single-crystal X-ray studies. The ^{119}Sn NMR spectra of the isostructural homologues **4** and **5** may be interpreted in terms of trigonal bipyramidally configured $Me_3Sn(NC...)_2$ fragments (of the polymeric framework) as well as of quasi-mobile Me_3Sn^+ ions.

Introduction

Recently, high-resolution solid-state ^{119}Sn CP/MAS NMR spectroscopy has been shown to be one of the most effective tools for the detection of even subtle details in the structural and/or electronic properties of organotin compounds.[1] Thus, ^{119}Sn CP/MAS NMR spectra fre-

0276-7333/90/2309-2672\$02.50/0

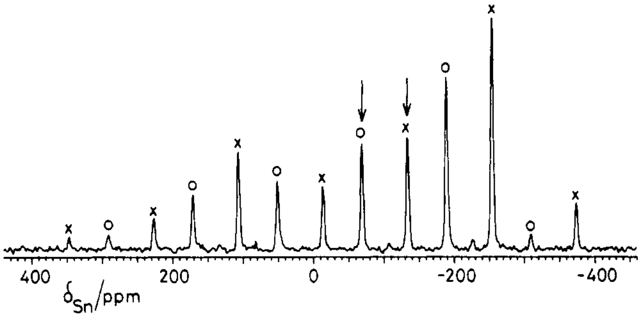


Figure 1. 111.9-MHz ^{119}Sn CP/MAS NMR spectrum of compound **6**, showing the two spinning-sideband manifolds (marked with circles and crosses). The center bands are indicated by the arrows. High-speed (13 500-Hz) magic-angle spinning was used. Other conditions: contact time 2.5 ms; relaxation delay 1 s; number of transients 44 200.

Table I. Solid-State ^{119}Sn NMR Data for the Organotin(IV) Coordination Polymers 1–7

	Sn1[a]			Sn2[a]		
compd	δ/ ppm	multiplet struct	I_{rel}	δ/ ppm	multiplet struct	I_{rel}
$[(Me_3Sn)_3Co(CN)_6]_\infty$ (**1**)	−88	quintet[b]	2	−118	quintet[c]	1
$[(Et_3Sn)_3Co(CN)_6]_\infty$ (**2**)	−75	quintet[b]		...	...	...
$[(Et_3Sn)Au(CN)_2]_\infty$ (**3**)	−64	none		...	...	...
$[(Me_3Sn)_4Fe(CN)_6]_\infty$ (**4**)	−108	none	1.0	46	none	>1
$[(Me_3Sn)_4Ru(CN)_6]_\infty$ (**5**)	−97	none	1.0	32	none	>1
$[(Me_3Sn)_4Fe(CN)_6\cdot 2H_2O\cdot C_4H_8O_2]_\infty$ (**6**)	−136	none	1	−73	none	1
$[(Me_3Sn)_4Fe(CN)_6\cdot nH_2O]_\infty$ (**7**)[d]	47	none				

[a] Numbering arbitrary. [b] Splitting arising from ^{119}Sn,^{14}N interactions ~127 Hz (but irregular). Such splitting depends on a number of factors, including ^{14}N quadrupole coupling constant and relaxation time. This would account for the fact that only broadening (rather than splitting) is seen for compounds **3–7**. [c] Poorly resolved. [d] At least two weaker center bands appear at −29 and −107 ppm.

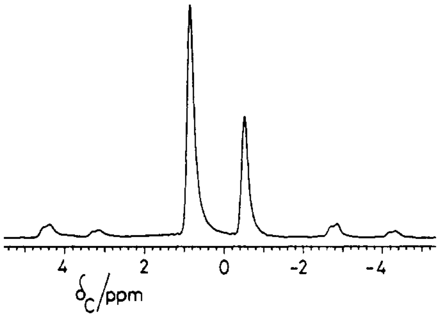


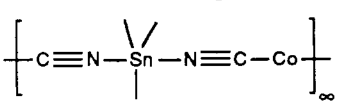
Figure 2. 75.4-MHz ^{13}C CP/MAS NMR spectrum of compound **1** (methyl region only), showing two signals of unequal intensity, together with tin satellite peaks. Spectrometer conditions: contact time 5 ms; relaxation delay 2 s; number of transients 1000; spinning speed 4120 Hz.

quently reflect features otherwise exclusively available from the results of single-crystal X-ray diffraction studies more closely than, for example, the concomitant ^{119m}Sn Mössbauer and IR/Raman spectra. The present contribution represents the first attempt to test the utility of solid-state ^{119}Sn NMR spectroscopy for an in-depth description of selected members of the rapidly growing new class of organotin(IV) coordination polymers $[(R_3Sn)_n{}^dM(CN)_{2n}]_\infty \equiv [^dM(\mu\text{-}CN\cdot R_3Sn\cdot NC)_n]_\infty$ with n = 2, 4, 6, and 8[2] as well as of some interesting derivatives thereof.[3,4] The polymeric nature of all these systems is due to the presence of trigonal-bipyramidal (tbp) $-C{\equiv}NSnN{\equiv}C-$ bridges between the single d-transition-metal ions $^dM^{n+}$, whose coordination numbers govern whether the polymeric network will be one-, two-, or three-dimensional. 3D systems of the type $[A(Me_3Sn)_3M^{II}(CN)_6]_\infty$ with M = Fe and Ru and A^+ = e.g. R_4N^+ (R = alkyl), $(C_5H_5)_2Co^+$, and even Me_3Sn^+ have most recently been shown to be effective new ion exchangers and chemical storage materials, respectively, of various organometallic and purely organic cations A^+.[3,4] The general mode of preparation, leading most frequently to polycrystalline precipitates, has so far precluded any systematic structural studies by single-crystal X-ray diffractometry. Thus, information on structural and electronic properties has to be collected by methods expressly designed for the examination of polycrystalline particles (e.g. Raman spectroscopy) or powders (e.g. X-ray powder diffractometry *and* solid-state NMR spectroscopy).

Results and Discussion

In the following, the room-temperature solid-state ^{119}Sn and ^{13}C NMR spectra of seven selected compounds will be described and appropriately discussed: $[(Me_3Sn)_3Co^{III}(CN)_6]_\infty$[2c] (**1**), $[(Et_3Sn)_3Co^{III}(CN)_6]_\infty$[2b] (**2**), $[(Et_3Sn)Au^{I}(CN)_2]_\infty$[2b] (**3**), $[(Me_3Sn)_4Fe^{II}(CN)_6]_\infty$[2b,3] (**4**), $[(Me_3Sn)_4Ru^{II}(CN)_6]_\infty$[3] (**5**), $[(Me_3Sn)_4Fe^{II}(CN)_6\cdot 2H_2O\cdot C_4H_8O_2]_\infty$[4] (**6**), and $[(Me_3Sn)_4Fe^{II}(CN)_6\cdot nH_2O]_\infty$[5] (**7**). While **1** and **2** belong to the fundamental type $[(R_3Sn)_n{}^dM(CN)_{2n}]_\infty$, **4** and **5** may be tentatively considered as members of the above-mentioned cation encapsulates $[A(Me_3Sn)_3{}^dM^{II}(CN)_6]_\infty$[3] with A ≡ Me_3Sn. Compound **6** may be best considered as a special derivative of **4** in that it serves as a host system for both water and dioxane molecules. Sample **7** has resulted after gentle drying of the crystalline compound $[(Me_3Sn)_4Fe^{II}(CN)_6\cdot 4H_2O]_\infty$ (**8**). A still "wet" crystal of **8** has been successfully examined by a single-crystal X-ray study.[5] So far, only **1** and **5** have also been subjected to detailed single-crystal X-ray studies, which have confirmed a polymeric nature.[2c,4] In accordance with the general expectation of local environments lacking tetrahedral or octahedral symmetry, the ^{119}Sn NMR spectra of all samples are rich in pronounced spinning sidebands (cf. Figure 1). Interpretation is made easier by the use of high MAS rates and a relatively low magnetic field. In Tables I and II, the most important data deduced from the solid-state ^{119}Sn and ^{13}C NMR spectra of **1–7**, respectively, are collected.

$[(Me_3Sn)_3Co^{III}(CN)_6]_\infty$ (1). One of the most significant structural features of **1**[2c] is the presence of two different



---

(1) (a) Lippmaa, E. T.; Alla, M. A.; Pehk, T. J.; Engelhardt, G. *J. Am. Chem. Soc.* **1978**, *100*, 1929. (b) Harris, R. K.; Packer, K. J.; Reams, P. *J. Magn. Reson.* **1985**, *61*, 564. (c) Harris, R. K.; Packer, K. J.; Reams, P. *Chem. Phys. Lett.* **1985**, *115*, 16. (d) Harris, R. K.; Mitchell, T. N.; Nesbitt, G. J. *Magn. Reson. Chem.* **1985**, *23*, 1080. (e) Komoroski, R. A.; Parker, R. G.; Mazany, A. M.; Early, T. A. *J. Magn. Reson.* **1987**, *73*, 389. (f) Harris, R. K.; Sebald, A.; Furlani, D.; Tagliavini, G. *Organometallics* **1988**, *7*, 388 and references therein. (g) Harris, R. K.; Sebald, A. *Magn. Reson. Chem.* **1989**, *27*, 81. (h) Gay, I. D.; Jones, C. H. W.; Sharma, R. D. *J. Magn. Reson.* **1989**, *84*, 501. (i) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294.

(2) See: (a) Uson, R.; Fornies, J.; Uson, M. A.; Lalinde, E. *J. Organomet. Chem.* **1980**, *185*, 359 (n = 2, M = Ag, Au; n = 4, M = Pd, Pt; n = 6, M = Fe). (b) Yünlü, K. Dissertation, Universität Hamburg, 1983, p 107 ff. (c) Yünlü, K.; Höck, N.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 879 (n = 4, M = Ni; n = 6, M = Fe, Co). (d) Eller, S.; Fischer, R. D. *Inorg. Chem.* **1990**, *29*, 1289 (n = 6, M = Ru). (e) Dülsen, S.; Yünlü, K.; Fischer, R. D. Unpublished results (n = 8, M = Mo, W).

(3) Eller, S.; Brandt, P.; Brimah, A. K.; Schwarz, P.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1263.

(4) Adam, M.; Brimah, A. K.; Li, X.-F.; Fischer, R. D. *Inorg. Chem.* **1990**, *29*, 1595.

(5) Behrens, U.; Brimah, A. K.; Fischer, R. D. Unpublished results.

Table II. Solid-State ^{13}C NMR Data for the Organotin(IV) Coordination Polymers 1–7^h

	C1, C1′ (Sn-bonded CH_3 or CH_2)			C2, C2′ (other C atoms)		
compd	δ/ppm^a	$\lvert{}^1J(^{119}Sn,^{13}C)\rvert$/Hz^b	I_{rel}	δ/ppm^a	I_{rel}	assign
$[(Me_3Sn)_3Co(CN)_3]_\infty$ (**1**)	0.8	550	2	ca. 132^c		CN
	−0.5	570	1			
$[(Et_3Sn)_3Co(CN)_6]_\infty$ (**2**)	11.7	500	1	ca. 134^c		CN
				10.3^{a,d}	1	CH_3
$[(Et_3Sn)Au(CN)_2]_\infty$ (**3**)	11.7	490	1	11.0^a	1	CH_3
$[(Me_3Sn)_4Fe(CN)_6]_\infty$ (**4**)	1.0	ca. 390	>1	ca. 175^c		CN
	4.4	ca. 460	1			
$[(Me_3Sn)_4Ru(CN)_6]_\infty$ (**5**)	1.4	ca. 435	>1	ca. 163^c		CN
	4.0	*g*	1			
$[(Me_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot C_4H_8O_2]_\infty$ (**6**)	0.8	540	1	ca. 174^c		CN
	2.2	*g*	<1	67.5^{a,e}		dioxane
$[(Me_3Sn)_4Fe(CN)_6 \cdot nH_2O]_\infty{}^f$ (**7**)	1.7	570		ca. 175^c		CN

^{a} Accuracy ca. ±0.2 ppm, with internal shift differences somewhat better. ^{b} Doublet, accuracy ca. ±10 Hz, except where otherwise noted. ^{c} Complex multiplet (see the text). ^{d} Doublet; $\lvert{}^2J(^{119}Sn,^{13}C)\rvert = 34 \pm 5$ Hz. ^{e} Singlet. ^{f} $0 < n < 4$. ^{g} Not observed. ^{h} The solid $[(C_5H_5)_2Co(Me_3Sn)_3Fe^{II}(CN)_6]_\infty$ shows two almost equally intense ^{13}C resonances with δ 3.8 (CH_3; $\lvert{}^1J(^{119}Sn,^{13}C)\rvert = 570$ Hz) and δ 86 (C_5H_5; sharp singlet).

chains with each Co atom as a joint member of three intersecting chains: While one-third of all chains are strictly linear, the other two-thirds display alternately two different Sn–N–C angles that are both smaller than 180° (i.e. 157.6 (2) and 146.5 (2)°). The appearance of *pairs* of relatively close-lying ^{119}Sn and ^{13}C NMR resonances (Figure 2) turns out to be in excellent accord with the X-ray results. From the relative intensities of the components of the ^{119}Sn NMR spectrum it appears that the resonance with δ −88 ppm (Sn1) is more intense by a factor of 2 than the signal with δ −118 ppm (Sn2) and could, hence, be attributed to Sn atoms of the more abundant zigzag chain. By corresponding arguments in view of the two ^{13}C resonances of the appropriate intensity ratio 1:2, the ^{13}C resonance at δ 0.8 ppm is assigned to the methyl carbon atom C1 of the nonlinear chain. It is, in principle, possible that the ^{13}C splitting arises from crystallographic nonequivalence of methyls in the distorted-trigonal-bipyramidal structure of the zigzag chains, combined with accidental overlap with the signal from methyls in linear chains, but this seems an unlikely alternative explanation. In view of three different CN groups in the asymmetric unit,[2c] but not because of notably different N–C and C–Co distances in **1**, three separate cyanide carbon resonance signals might in principle appear. This expectation cannot, however, be corroborated because the signals in question are weak and the fine structure is complex. Due to the absence of close-lying H atoms, cross polarization does not substantially improve the CN carbon signal intensities, and complicated splitting patterns might be expected to arise from coupling with the quadrupolar cyanide N and Co nuclei.[6] A single, broad solid-state ^{59}Co NMR signal with δ −225 ppm (relative to $K_3[Co(CN)_6]/H_2O$) has been reported earlier.[2c] In conclusion, it can be stated that **1** appears to be a very favorable condidate for solid-state NMR spectroscopy: both the ^{119}Sn and the ^{13}C NMR spectra reflect more valuable details with respect to the precise structure of **1** than the earlier reported[2c] IR, Raman, and ^{119m}Sn Mössbauer spectra in total.

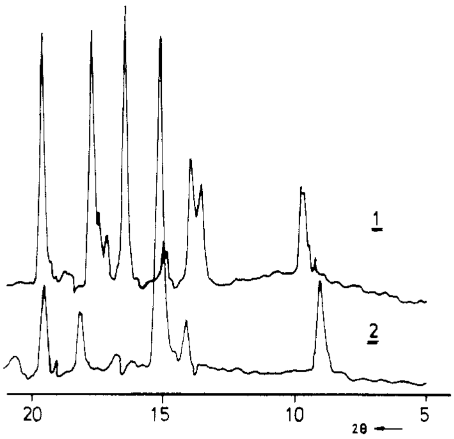
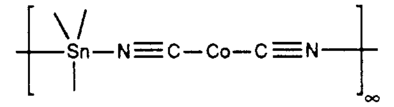


Figure 3. Debye–Scherrer X-ray powder diagrams of samples 1 and 2.

$[(Et_3Sn)_3Co^{III}(CN)_6]_\infty$ (2) and $[(Et_3Sn)Au^I(CN)_2]_\infty$ (3). Compound **2** belongs to a series of homologues of **1** in which R = Et, *n*-Pr, *n*-Bu, and Ph.[2b] All these polymers are white, are insoluble in H_2O as well as in most organic solvents, and display almost identical ν(CN) absorption frequencies (IR: one strong band at 2155 ± 10 cm^{-1}) and decomposition temperatures (345 ± 15 °C). While single crystals of **2** could not so far be obtained, the X-ray powder diagram (Debye-Scherrer) of **2** is seen to differ notably from that of **1** (Figure 3), suggesting a different 3D network of the interlinking



$$\left[-\!\!-Sn-N\equiv C-Co-C\equiv N-\!\!- \right]_\infty$$

chains. Concomitantly, the combined solid-state ^{119}Sn and ^{13}C NMR spectra differ considerably from those of **1**: First of all, the appearance of only one tin, as well as of one CH_2 and CH_3 carbon resonance, respectively, indicates the presence of one unique type of chain that could be either zigzag-shaped or linear. Although the larger space demand of an ethyl group (as compared with that of a methyl group) might favor the verification of the extremely voluminous "super Prussian blue" polymer that is expected to result from exclusively linear chains,[2c] a closer analysis of the Debye–Scherrer pattern of **2** rules out any cubic lattice framework. Moreover, the single ^{119}Sn NMR shift δ(Sn1) of **2** lies closer to δ(Sn1) than to δ(Sn2) of **1**. The Sn1 signals of both **1** and **2** can also be resolved (Figure 4) into quintets (somewhat better for **2** than for **1**), which probably result from the coupling of each tin with two quadrupolar nitrogen atoms (the splittings being somewhat unequal due to residual second-order effects). Sn2 of **1** does not show such a well-resolved multiplet. As δ(Sn1) of **1** has been tentatively assigned to the nonlinear chain (vide supra), δ(Sn1) of **2** might likewise be indicative of zigzag-shaped chains. The weak satellites of both ethyl carbon resonances resulting from ^{119}Sn,^{13}C coupling allow

---

(6) (a) Frey, M. H.; Opella, S. J. *J. Chem. Soc., Chem. Commun.* **1980**, 474. (b) Groombridge, C. J.; Harris, R. K.; Packer, K. J.; Say, B. J.; Tanner, S. F. *J. Chem. Soc., Chem. Commun.* **1980**, 175.

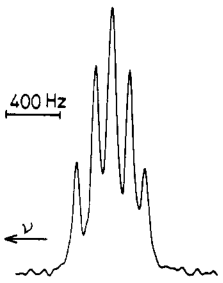
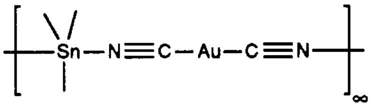


Figure 4. Expansion of the $n = -3$ spinning sideband in the 111.9-MHz ^{119}Sn CP/MAS NMR spectrum of compound **2**, illustrating the splitting caused by coupling (probably involving residual dipolar as well as scalar effects) to two neighboring ^{14}N nuclei. Spectrometer conditions: contact time 10 ms; relaxation delay 5 s; number of transients 1000; spinning speed 4500 Hz.

the assignment of the two ^{13}C shifts as given in Table II. When compared with the two methyl carbon resonances of **1**, both δ(C1) and the coupling parameter $J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ of **2** display notable alterations. The considerable high-frequency shift of δ(C1) could be due to some increased electron density of the CH_2 carbon atom arising from the donor character of the adjacent methyl group. The small high-frequency shift of δ(Sn1) of **2** relative to δ(Sn1) of **1** might consequently reflect a weak reduction of the Lewis acidity of Sn1 of **2**.

The ^{119}Sn and ^{13}C solid-state NMR spectra of the probably 1D polymeric compound $[(\mathrm{Et_3Sn})\mathrm{Au^I(CN)_6}]_\infty$ (**3**) turn out to be quite similar to those of **2** (Tables I and II). Major differences are only the lack of any multiplet structure of the Sn resonance and the absence of satellite signals of the methyl carbon resonances δ(C2). Although it cannot presently be decided whether the infinite



$$\left[-\mathrm{Sn}-\mathrm{N}\equiv\mathrm{C}-\mathrm{Au}-\mathrm{C}\equiv\mathrm{N}-\right]_\infty$$

chains are strictly linear or not, the actual δ(Sn) value of **3** might simply reflect a lower Lewis acidity of the d^{10} ion Au(+I) and not necessarily strong deviations from chain linearity. Hence, the correlation of a δ(Sn) value of -90 ppm with R_3SnN_2 fragments in nonlinear chains (vide supra) might still deserve a final clarification.

As a further statement it can be argued that the combined solid-state ^{119}Sn and ^{13}C NMR spectra of **2** are, together with the X-ray powder diagram, again more informative than the total results from vibrational spectroscopy. Although the actual structure of **2** cannot be given, the solid-state spectra clearly confirm different structures for **1** and **2** and are likely to stimulate further investigations of related members of the series $[(\mathrm{R_3Sn})_3\mathrm{Co^{III}(CN)_6}]_\infty$. Increased knowledge of the structural differences within this series might, moreover, be valuable for a better understanding of the rapidly decreasing thermal and photochemical stability of the members of the related series $[(\mathrm{R_3Sn})_3\mathrm{Fe^{III}(CN)_6}]_\infty$ as the size of R increases. The latter compounds are, however, less amenable to NMR spectroscopy because of their paramagnetism.

$[(\mathrm{Me_3Sn})_4\mathrm{M^{II}(CN)_6}]_\infty$ (4 (M = Fe) and 5 (M = Ru)). Although the sum of the formally nonbonding electron pairs on all cyanide N atoms and the number of Lewis acidic sites at the Sn atoms (i.e. usually two per R_3Sn^+) of **4** and its Ru homologue **5** do not match, **4** and **5** form surprisingly readily. Thus, precipitation of pure **4** and **5** takes place even under unfavorable stoichiometric conditions,[3] and the compound $[(\mathrm{NH_4})(\mathrm{Me_3Sn})_3\mathrm{Fe(CN)_6}]_\infty$ tends to reorganize:[7]

$$4[(\mathrm{NH_4})(\mathrm{Me_3Sn})_3\mathrm{Fe(CN)_6}]_\infty \xrightarrow[\text{or EtOH}]{\mathrm{H_2O}} 3[(\mathrm{Me_3Sn})_4\mathrm{Fe(CN)_6}]_\infty + 4\text{-}\mathrm{NH_4^+} + [\mathrm{Fe(CN)_6}]^{4-} \quad (1)$$

Thermally, **4** and **5** are about as stable as **1**–**3**. While the results of all non-NMR spectroscopic techniques are devoid of any clear evidence of the presence of two chemically different Me_3Sn groups, most recent preparative experiments have shown[3] that **4** and **5** easily undergo quantitative ion exchange of just one of the four Me_3Sn groups:

$$[(\mathrm{Me_3Sn})_4\mathrm{M(CN)_6}]_\infty \xrightarrow[-[\mathrm{Me_3Sn(H_2O)_2}]^+]{[\mathrm{A^+/H_2O}]} [\mathrm{A(Me_3Sn)_3M(CN)_6}]_\infty \quad (2)$$

$$\mathrm{A^+} = \text{e.g. } \mathrm{Et_4N^+} \text{ and } (\mathrm{C_5H_5})_2\mathrm{Co^+}$$

$$[(\mathrm{NH_4})(\mathrm{Me_3Sn})_3\mathrm{Fe(CN)_6}]_\infty \xrightarrow[-\mathrm{NH_4^+}]{[\mathrm{Me_3Sn(H_2O)_2}]^+/\mathrm{H_2O}} [(\mathrm{Me_3Sn})_4\mathrm{Fe(CN)_6}]_\infty \quad (3)$$

In fact, only the combined solid-state ^{119}Sn and ^{13}C NMR spectra of **3** and **4** account for these initially unexpected chemical reactions, confirming strongly the presence of Me_3Sn groups in two probably very different sites (Table I). While the δ(Sn1) values of the two isostructural samples, which give rise to superimposable X-ray powder diagrams, lie between the two δ(Sn) values of **1** and should thus straightforwardly be assigned to tbp-configured $\mathrm{Me_3Sn(NC)_2}$ bridges, their δ(Sn2) values are shifted by more than 100 ppm to higher frequency. The measured relative intensities of the two Sn resonances of compounds **4** and **5** are 2.7 and 2.1, respectively, but a number of experimental factors (such as cross-polarization efficiency and spinning-sideband spread) may have influenced these data. Nevertheless, the positions of δ(Sn2) of **4** and **5** tend to argue against a coordination number of 5 but could, in principle, be attributed to organotin moieties with the coordination number 4.[1] Most interestingly, the ^{119m}Sn Mössbauer spectra of both **3** and **4** display, even around ca. 200 K, only one (or two extremely close-lying) doublet with the common isomer shifts of R_3SnX systems.[8]

While the ^{13}C NMR spectra of **4** and **5** show complex signals from the cyanide carbon resonances (probably involving residual second-order effects), two pairs of methyl carbon signals of undoubtedly different intensity are clearly apparent. Yet, neither the methyl ^{13}C nor the ^{119}Sn resonances of **4** and **5** display any clearly resolved multiplet patterns, and little line broadening is observed. Interestingly, Wrackmeyer and co-workers[9] have very recently described some novel ion pairs of the general type $[\mathrm{MR_3}]^+[\mathrm{R'_3BC{\equiv}CR''}]^-$ (M = Pb, Sn), in which the R_3M cation adopts a side-on coordination to the C≡C bond. Correspondingly, the Me_3Sn groups of **4** and **5** with δ(Sn) positive may also be imagined to ride side-on to distinct C≡N bonds of the negatively charged polymer. The overall patterns of the spinning sidebands and the positions of the center bands for the ^{119}Sn spectra of **4** and **5** would not rule out this view. An alternative explanation of the high-frequency ^{119}Sn resonances in **4** and **5** could be based on the assumption of $[\mathrm{Me_3Sn(OH_2)}]^+$ cations inside the cavities of the polymers. Although there is no direct evidence of the presence of water molecules, it must be recalled that the samples used in this study were obtained as precipitates from aqueous solutions.[2b,c,3]

$[(\mathrm{Me_3Sn})_4\mathrm{Fe(CN)_6{\cdot}2H_2O{\cdot}C_4H_8O_2}]_\infty$ (6). Compound **6**, which resulted from an attempt to grow single crystals of

---

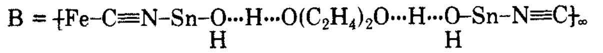
[7] Schwarz, P.; Fischer, R. D. Unpublished results.

[8] Depending on the computational fitting procedure used; cf. ref 3.

[9] Wrackmeyer, B.; Horchler, K.; Boese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1500; Personal communication.

4 from a water/dioxane solution, has turned out[4] to be an infinite 3D network of the two different chains

$A = \{Sn-N\equiv C-Fe-C\equiv N\}_\infty$



$B = \{Fe-C\equiv N-Sn-\underset{H}{O}\cdots H\cdots O(C_2H_4)_2O\cdots H\cdots \underset{H}{O}-Sn-N\equiv C\}_\infty$

In both chains, the Sn atoms are five-coordinated and give rise (Figure 1), in contrast to the "parent" system 4, to two ^{119}Sn resonances with negative δ values. As the more abundant chain A is, like chain B, also zigzag-shaped, the pronounced low-frequency resonance with $\delta(Sn2)$ −136 ppm must be attributed to a *non*linear chain. Since the relative intensities of the two tin resonances do not differ significantly, it might appear possible to correlate the signal at δ −73 ppm with the "less perfectly" realized tbp moiety ...$FeCNSnMe_3(OH_2)$... of chain B.[10] This admittedly still debatable view would, however, conflict with the above assignments of the high-frequency tin resonances of 1, 2, and 3 (−88, −75, and −64 ppm, respectively) with nonlinear chains in spite of probably more regular tbp moieties.

The complete ^{13}C NMR spectrum of 6 looks more complicated but indicates, as expected, two types of CH_3 groups. Only the resonance with δ 0.8 ppm displays $^{13}C,^{119}Sn$ coupling (with a *J* value typical of tbp-configured Me_3Sn derivatives: see Table II, footnote *h*). From the crystallographic results[4] three different cyanide ^{13}C resonances are expected. The signal appears to consist of three lines with additional splitting, but some of the complexity may arise from coupling effects to the quadrupolar ^{14}N nuclei.[6] As expected, the dioxane molecules, which are also anchored via hydrogen bridges, give rise to a singlet.

$[(Me_3Sn_4)Fe^{II}(CN)_6\cdot nH_2O]_\infty$ (7). While it has recently been possible to determine the X-ray structure of an incompletely dried single crystal of the composition $\{(Me_3Sn)_4Fe^{II}(CN)_6\cdot 4H_2O]_\infty$ (8),[5] even extremely careful drying of 8 has constantly led to white powders that are analyzed best for $n = 2$ (≡7). The residual H_2O molecules in 7 could be accommodated in various ways. For instance, a polymer exclusively based on type A chains (as in 6) with truncated *trans*-$\{H_2O\rightarrow SnN\equiv CFeC\equiv N\leftarrow SnOH_2\}$ chains B′ could have resulted. Another possiblity would be the polymeric host–guest system $[A(Me_3Sn)_3Fe^{II}(CN)_6]$ with isolated, tbp-configured $[Me_3Sn(H_2O)_2]^+$ cations as guests A.

According to a first view of the ^{119}Sn and ^{13}C NMR spectra of 7, this sample is likely to contain several components. Although the two ^{119}Sn resonances of compound 4 seem to reappear (Table I), the high-frequency signal at δ 47 ppm is unexpectedly intense, and at least one further resonance (δ −29 ppm) appears. A number of relatively intense signal groups occur in the CN range of the ^{13}C NMR spectrum, which feature might be reminiscent of the crystallographic finding that in the structure of pure 8 *all* cyanide N atoms seem to be involved in weak hydrogen bonds.[5] Both sample 7 and compound 4 show methyl ^{13}C resonances around δ 4.4 ppm, but the position of the dominant resonance of 7 (δ = 1.7 ppm) indicates the involvement of a new component.

Concluding Remarks

Although the combined ^{119}Sn and ^{13}C solid-state NMR spectra of each sample can be considered as highly informative in total, the essential "quality" of each individual spectrum appears to depend on different features. Thus, only the spectra of 1 and 2 display multiplet patterns for the ^{119}Sn and alkyl ^{13}C resonances. Whereas cyanide ^{13}C resonances are generally weak, compound 6 (along with some other samples not mentioned in this study) displays surprisingly pronounced signals in this region. There is a marked difference in the cyanide ^{13}C chemical shifts between compounds 1 and 2 on the one hand ($\delta(C) \sim 135$ ppm) and the remaining systems ($\delta(C) \sim 170$ ppm) on the other. The high value of the spectra of 4 and 5 results from the presence of two very differently coordinated Me_3Sn groups. Obviously, a still larger manifold of coordination polymers involving R_3Sn and $^dM(CN)_n$ building blocks has to be systematically inspected before a better understanding of these variations may result.

Experimental Section

All samples turned out to be air-stable and were prepared by following the reported procedures.[2b,c,3,4] Sample 7 was obtained after careful drying (ca. 40 °C, 6 h) of the initially well-shaped, but still moist, crystals of 8. The latter were grown within 3 days from an aqueous solution of Me_3SnCl and $K_4Fe(CN)_6$ (4:1) containing around 10% of glucosamine hydrochloride to inhibit the otherwise instantaneous precipitation of polycrystalline 4.[4,5] Anal. Calcd for $C_{18}H_{40}N_6O_2FeSn_4 \equiv (Me_3Sn)_4Fe(CN)_6\cdot 2H_2O$: C, 23.94; H, 4.46; N, 9.31; Fe, 6.18; Sn, 52.57. Found (by Dornis u. Kolbe, Mikroanalytisches Laboratorium, Mülheim, FRG): C, 23.94; H, 4.33; N, 9.32; Fe 6.26; Sn, 52.73. X-ray powder diffraction studies (Debye–Scherrer) were carried out on a Philips PW 1050 diffractometer (Cu Kα radiation, Ni filter).

The ^{119}Sn and ^{13}C solid-state NMR spectra were obtained at 111.9 and 75.4 MHz, respectively, with use of a Varian VXR 300 spectrometer in the cross-polarization mode with Doty Scientific probes (7-mm sample rotor). Contact times used varied between 1 and 10 ms; relaxation delays were in the range 1–5 s, and the number of transients for compounds 1–5 was between 120 and 2200 for ^{13}C (except for observation of CN signals for 4 and 5 when ~30 000 transients were accumulated) and between 260 and 10 000 for ^{119}Sn. The 90° pulse duration was ca. 4 μs, corresponding to Hartmann–Hahn matching at ca. 60 kHz. In the case of 6 a fast-spinning (5-mm sample rotor) probe was used, with spinning speeds between 9 and 14 kHz and correspondingly larger numbers of transients (30 000–45 000) to offset the smaller sample size. Chemical shifts are reported with the high-frequency-positive convention, in ppm with respect to the signals for $SnMe_4$ (for ^{119}Sn) and $SiMe_4$ (for ^{13}C). Center bands for ^{119}Sn were located by obtaining spectra at two different spinning speeds.

Acknowledgment. We acknowledge the Deutsche Forschungsgemeinschaft (FRG) and the Science and Engineering Research Council (U.K.) for financial support. We thank Dr. E. T. K. Haupt (Hamburg, FRG) for the NMR study of $[(C_5H_5)_2Co(Me_3Sn)_3Fe^{II}(CN)_6]_\infty$ (on a Bruker MSL-300 spectrometer) and Prof. B. Wrackmeyer (Bayreuth, FRG) for mentioning some unpublished results.

---

[10] Thus, the Sn–N and Sn–O distances are relatively short (2.149 Å) and long (2.448 Å), respectively, as compared with distances in genuine tbp systems (e.g. 2.317 and 2.295–2.326 Å[4]), and the Sn atom lies outside the plane of the three methyl carbon atoms (away from the N atom).