Organometallics 1993, 12, 3232-3240

Architecture of the Organometallic Ion Exchangers $[(Me_3Sn^{IV})_4M^{II}(CN)_6]_\infty$ (M = Fe, Ru, Os): A Combined Multinuclear Solid-State Magnetic Resonance and Infrared/Raman Spectroscopic Study

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Received December 29, 1992

With extensive use of the ^{15}N isotopomer, **1a**, of the organotin polymer $[(Me_3Sn)_4Fe(CN)_6]_\infty$ (**1**) and of variable-temperature solid-state ^{13}C NMR studies, the CP MAS ^{13}C, ^{15}N, and ^{119}Sn NMR spectra of the coordination polymers $[(Me_3Sn^{IV})_4M^{II}(CN)_6]_\infty$ with M = Fe (**1**), Ru (**2**), and Os (**3**) have been fully determined and optimally assessed. According to these measurements, the asymmetric unit involves *three* equally-abundant, nonequivalent CN ligands and *two* equally-abundant, nonequivalent Me_3Sn groups with six crystallographically different methyl C atoms. A structural model is proposed in which one type of N atom is bonded to *two* Sn atoms. Below −20 °C, each of the six CH_3 groups gives rise to an individual, sharp ^{13}C signal, while above room temperature rapid rotation of both Me_3Sn groups leads to two resonances. The vibrational spectra in the $\nu(SnC)$ and $\nu(CN)$ absorption ranges suggest the exclusive presence of trigonal planar Me_3Sn fragments and one significantly distorted (from O_h), albeit still centrosymmetric, $M(CN)_6$ unit (local symmetry: D_{4h} from IR/Ra: D_{2h} from NMR). From all spectroscopic findings, a three-dimensional network reminiscent of that of the polymeric acid $[H_4Fe(CN)_6]_\infty$ may be deduced. The preferred architecture, which also involves three-coordinate cyanide N atoms, $-CNSn_2$, contrasts with the known structures of polymeric $[(R_3Sn)_2CO_3]_\infty$ systems wherein both penta- and tetracoordinated Sn atoms coexist.

Introduction

In three preceding papers[1-3] we have demonstrated that high-resolution solid-state NMR spectroscopy is an exceedingly powerful tool for exploring structural details of novel polymeric organotin and -lead polymers of the general composition $[(R_3E)_nM(CN)_m{\cdot}pG{\cdot}qG']_\infty$, where R is an alkyl or aryl group, E = Sn or Pb, M is a group 8–10 transition metal, and G or G′ an occasionally present, uncharged or cationic, guest compound. While m is usually twice as large as n because each R_3E^+ cation tends to coordinate two cyanide N atoms of different $[M(CN)_m]^{q-}$ counteranions, m is smaller than $2n$ in the class of guest-free 3D polymers: $[(Me_3Sn^{IV})_4M^{II}(CN)_6]$ with Me = CH_3 and M = Fe, Ru, and Os (**1**–**3**).[3-5] Hence, the six cyanide N atoms of **1**–**3** may not straightforwardly be capable of creating trigonal bipyramidal (tbp) $Me_3Sn(NC)_2$ units with all *four* Me_3Sn^+ ions. Nevertheless, all members of the $[(Me_3Sn)_4M^{II}(Cn)_6]$ family are, like those of the type $[(Me_3Sn)_3M^{III}(CN)_6]$,[6a] thermally stable up to 350 °C and insoluble both in water (at pH ≤ 7) and in numerous organic solvents, typical exceptions being only exceedingly strong Lewis bases like dimethyl sulfoxide, dimethylformamide, etc.

The most outstanding chemical property of all $[(Me_3Sn)_4M(CN)_6]$ systems is their facile readiness to ion exchange:[4-6]

$$[(Me_3Sn)_4M(CN)_6] \xrightarrow[(H_2O)]{G^+} [(G^+)(Me_3Sn)_3M(CN)_6] + [Me_3Sn(aq)]^+ \quad (1)$$

Thus numerous, mainly organic or organometallic guest cations G^+ may be introduced quantitatively, and often within minutes, into suitable cavities of a negatively-charged host network by releasing at most one Me_3Sn^+ ion. This mode of heterogeneous ion exchange has, inter alia, led to host–guest systems involving electron receptors like $[methylviologen]^{2+}$ [5] and photosensitizers like $[Ru(bpy)_3]^{2-}$.[6b]

One of the driving forces of eq 1 is probably the $2n = m$ rule which is fulfilled by almost all resulting host–guest systems. Thus, according to our first solid-state NMR study,[1] only the $[(Me_3Sn)_4M(CN)_6]$ polymers (M = Fe, Ru) display, apart from one "well-behaved" (i.e. in view

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[1] Apperley, D. C.; Davies, N. A.; Harris, R. K., Brimah, A. K.; Eller, S.; Fischer, R. D. *Organometallics* **1990**, *9*, 2672.

[2] Behrens, U.; Brimah, A. K.; Soliman, T. M.; Fischer, R. D.; Apperley, D. C.; Davies, N. A.; Harris, R. K. *Organometallics* **1992**, *11*, 1718.

[3] Apperley, D. C.; Davies, N. A.; Harris, R. K.; Eller, S.; Schwarz, P.; Fischer, R. D. *Chem. Commun.* **1992**, 740.

[4] Eller, S.; Brandt, P.; Brimah, A. K.; Schwarz, P.; Fischer, R. D. *Angew Chem.* **1989**, *101*, 1274; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1263.

[5] Eller, S.; Adam. M.; Fischer, R. D. *Angew. Chem.* **1990**, *102*, 1157; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1126.

[6] (a) with M = Co, Rh, Ir: Eller, S.; Siebel, E.; Schwarz, P.; Fischer, R. D. Unpublished results. (b) Eller, S. Doctoral Dissertation, Universität Hamburg, 1992.

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of tbp-configured $Me_3Sn(NC)_2$ fragments) ^{119}Sn resonance at $\delta < -90$ ppm, a second ^{119}Sn resonance at $\delta > +25$ ppm which has been ascribed to one less-tightly anchored, and hence more readily exchangeable, Me_3Sn^+ ion.[7] So far, however, no satisfactory description of the supramolecular architecture of the three isostructural (as suggested by their practically superimposable X-ray powder diffractograms) homologues with M = Fe, Ru, and Os has been presented. All attempts to grow single crystals suitable for X-ray studies have so far ended up either with the formation of microcrystalline powders of the expected chemical composition or—in the presence of several Lewis bases inhibiting spontaneous precipitation—with the generation of well-crystallizing, but initially unexpected, host–guest derivatives, $[(Me_3Sn)_4Fe^{II}(CN)_6{\cdot}2H_2O{\cdot}qG']$. According to successful single-crystal X-ray studies of the products with G′ = dioxane (*q* = 1)[8] and water (*q* = 2),[9] two H_2O molecules may play the role of missing cyanide N atoms in establishing (pseudo-)tbp-configured $\{Me_3Sn(NC)OH_2\}$ units. A corresponding situation has, moreover, been found in the case of two G′-free (i.e. *q* = 0) organo*lead* polymers, $[(Me_3Pb)_4M(CN)_6{\cdot}2H_2O]$ (M = Fe, Ru).[10]

Most recently, we have noted briefly[3] that the methyl ^{13}C NMR spectra of polycrystalline, anhydrous $[(Me_3Sn)_4M(CN)_6]_\infty$ undergo dramatic changes with temperature. This observation, along with the results of a 2D-EXSY experiment has encouraged us to aim (even without ancillary X-ray data) at a more satisfactory description of the nature of the 3D network by making optimal use of the results of multinuclear solid-state magnetic resonance and vibrational (infrared and Raman) spectroscopy. The present study is devoted to this task. Of particular value has been the preparation of a highly ^{15}N-enriched isotopomer of **1**. This sample (**1a**) was expected to circumvent the usual difficulties resulting from the predominance of the strongly quadrupolar ^{14}N nuclei in natural nitrogen.

Solid-State NMR Spectroscopy of 1–3

Methyl ^{13}C NMR. A careful reexamination of the CP MAS ^{13}C NMR spectra of the two previously studied $[(Me_3Sn)_4M(CN)_6]$ systems with M = Fe (**1**) and Ru (**2**)[1] including now the highly ^{15}N-enriched "isotopomer" **1a** of **1**, as well as the Os homologue **3** of **1** and **2**, has unambiguously confirmed that above ca. 20 °C no more than two comparatively broad, and practically equally intense, singlets appear in the methyl carbon resonance region. Yet, in strong contrast to the polymers $[(Me_3E)_3M(CN)_6]_\infty$ fulfilling the $2n = m$ rule,[2,6a] the ^{13}C NMR spectra of **1**–**3** change their appearance strongly, and reversibly, on cooling, displaying between −40 and −60 °C *six* rather sharp, and practically equally intense, singlets in the region $-5 < \delta(^{13}C) < +10$ ppm (Figure 1b). The conclusion that the lattices of **1**–**3** involve no more than two nonequivalent Me_3Sn units whose six crystallographically different methyl groups become setwise equivalent around room temperature owing to (on the NMR time scale) rapid rotation about their individual trigonal axes has been fully substantiated by a recent 2D-EXSY experiment[3] on a sample of **1**. Thus three low-temperature ^{13}C singlets could be distinctly assigned to each of the two Me_3Sn units. In Table I the individual low-temperature shifts of **1**–**3** are listed along with the calculated averages of the two respective $\delta(^{13}C)$ triplets for the case of rapid site exchange. A rather satisfactory correlation of the calculated averages (for −60 °C) and the dynamically averaged values (at +40 °C) is obtained. As there is no degeneracy of two low-temperature ^{13}C lines (of either set), crystallographic mirror planes bisecting an Sn atom and just one of its methyl C atoms can be ruled out.

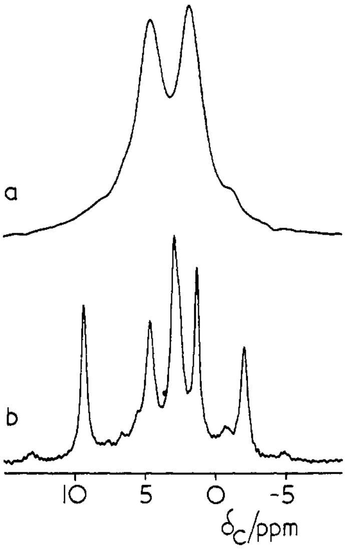

Figure 1. Carbon-13 CP MAS NMR spectra at 75.4 MHz of $[(Me_3Sn)_4Os(CN)_6]_\infty$ (methyl region only): (a) at 40 °C (300 transients, spin rate 4.18 kHz); (b) at −40 °C (650 transients, spin rate 4.09 kHz). In each case the contact time was 1 ms and the recycle delay 2 s. The line width of the signal at $\delta = 9.3$ ppm in (b) is 37 ± 5 Hz. Some ^{119}Sn satellites are clearly visible in (b).

Table I. Solid-State NMR Data (^{13}C and ^{119}Sn) for 1–3

sample	$\delta(^{13}C)$/ppm; $\lvert ^1J(^{119}Sn,^{13}C)\rvert$/Hz −60 °C[a]	 +40 °C[b]	$\delta(^{119}Sn)$/ppm room temp
1	**+8.9**; 590	+4.3; 550[e,f]	−108
	+3.8	(+4.3)	
	+2.8		
	+1.5[c]	+1.2; 430[e,f]	+46
	−2.5; 410	(+1.0)	
2	**+9.2**; 570		−97
	+4.4	+4.3; 470[e]	
	+2.8	(+4.5)	
	+2.4		+32
	+1.4	+1.4; 440[e]	
	−2.1; 440	(+1.6)	
3	**+9.2**; 550[d]		−94
	+4.6	+4.4; 560[e]	
	+2.8	(+4.4)	
	+2.5		+26
	+1.2	+1.7; 440[e]	
	−2.2; 430[d]	(+1.6)	

[a] Boldfaced: one of the two Me_3Sn groups (for **1** confirmed by 2D NMR spectrum[3]). [b] In parentheses arithmetic means of the two low-temperature triplets (first column). [c] Resolved by 2D NMR[3] into resonances at +1.7 and +1.3 ppm). [d] Determined at −40 °C. [e] Determined from deconvoluted 40 °C spectra. [f] Better-quality spectra of the dioxane derivative **1b** than obtained previously[1] enable us to determine the value of $\lvert J(^{119}Sn, ^{13}C)\rvert$ for *both* resonances as 570 Hz for the high-frequency signal and 520 Hz for the lower-frequency resonance.

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[7] R_3Sn derivatives with a formal coordination number (of Sn) of 3 are, however, likely to give rise to ^{119}Sn chemical shifts between +150 and +360 ppm: Lambert, J. B.; Kuhlmann, B. *Chem. Commun.* **1992**, 931.

[8] Adam, M.; Brimah, A. K.; Fischer, R. D.; Li, X.-F. *Inorg. Chem.* **1990**, *29*, 1595.

[9] Behrens, U.; Brimah, A. K.; Fischer, R. D. *J. Organomet. Chem.* **1991**, *411*, 325.

[10] Brimah, A. K. Doctoral Dissertation, Universität Hamburg, Germany, 1991.

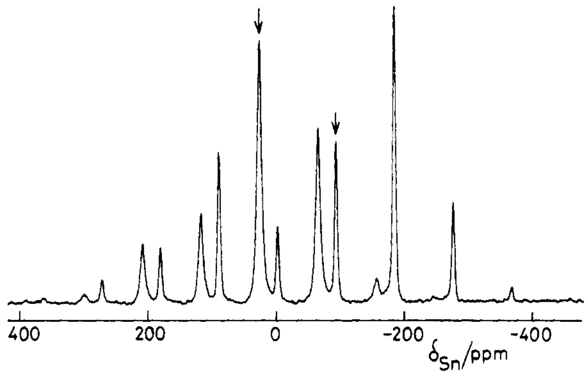

Figure 2. Tin-119 CP MAS NMR spectrum at 111.9 MHz of $[(Me_3Sn)_4Os(CN)_6]_\infty$, with the centerband signals indicated by vertical arrows; spin rate 10.26 kHz, 15 800 transients. The contact time was 3 ms and the recycle delay 1 s. The line width of the signal at δ = 26 ppm is 930 ± 50 Hz.

In contrast to a previous view,[1] the measurement of a strict 1:1 proportion of the two nonequivalent Me_3Sn units in **1**–**3** now rules out any structural model based upon a 1:3 proportion of only one, comparatively mobile, and chemically exchangeable,[4,5] Me_3Sn^+ "guest" cation.[7] Thus, in spite of the remarkable ion exchange properties of **1**–**3** (involving Me_3Sn^+ ions), NMR spectroscopy is not consistent with any translatory mobility of Me_3Sn^+ ions along the internal, probably channel-like[2] cavities of the network. Correspondingly, the electric conductivity of **1** at room temperature has been found[11] to be lower than 10^{-10} S·cm^{-1}.

^{119}Sn NMR. Room-temperature CP MAS ^{119}Sn NMR spectroscopy of **1a** has resulted in the same two-centerband feature as already described[1] for **1** (Table I). A corresponding ^{119}Sn spectrum is, moreover, displayed by the so-far-unreported polymer **3** (M = Os) and illustrated in Figure 2. The line widths of **1a** remain almost as broad as for **1**–**3**, suggesting that the nuclear quadrupole moment of ^{14}N is not responsible for the actual line broadening. Even in the case of **1a** the signals remain too broad to reveal any multiplet patterns due to ^{119}Sn–^{15}N coupling. The high-frequency signals are in each case substantially broader than those at low frequency, suggesting an unusual environment for Sn for the former. Careful variation of the spectrometer conditions for these systems shows that the intensity ratio of the two resonances (integrated over the relevant spinning sidebands) lies close to 1:1. While the high-frequency resonances of **1**–**3** remain difficult to interpret unambiguously (vide infra), one clear result of the ^{119}Sn spectra in total is that the number of ^{119}Sn centerbands agrees perfectly with the number of nonequivalent Me_3Sn units as reflected by the methyl ^{13}C NMR spectra.

According to the methyl ^{13}C NMR results, the two Me_3Sn units differ also essentially in their ^{119}Sn–^{13}C coupling parameters (Table I). The higher J values (of >500 Hz) should be ascribed to the Me_3Sn units with the negative $\delta(^{119}Sn)$ shift, indicating clearly tbp-configured $Me_3Sn(NC)_2$ fragments. A combination of the lower coupling constant $|^1J(^{119}Sn,^{13}C)|$ (of ca. 430 Hz) with the positive ^{119}Sn shift would not rule out that **1**–**3** involve nonbridging, pseudotetrahedral (pth) Me_3SnNC units. The presence of both tbp- and pth-configured R_3SnO_n (n = 2 or 1) units has been confirmed by crystallography and by CP MAS NMR for two 1D polymeric carbonates, $[(R_3Sn)_2CO_3]_\infty$[12a] (R = Me and Bu^i), which do not obey the $2n = m$ rule either. However, while in the lattices of the carbonates the pth-configured Sn atom can hardly approach any oxygen atom of the polymeric backbone, we have demonstrated previously that, e.g., the 3D network of $[(Me_3Sn)_3Co(CN)_6]_\infty$ contains pairs of N atoms (of different chains) that would appear spatially suitable to trap an additional Me_3Sn unit.[2] In this paper, a number of additional arguments in favor of structural alternatives in which *all* Me_3Sn groups of **1**–**3** would be tbp- or at least quasi-tbp-configured will be discussed.

Table II. Solid-State NMR Data (^{119}Sn Only) of Several Derivatives of 1 and 2 and One Example with Oxygen Atoms Instead of Nitrogen

compound	solid-state δ(Sn)/ppm			ref
$[(Me_3Sn)_4Fe^{II}(CN)_6]$ (**1a**)		−108 (1)	+46 (1)	1, 4[a]
$[(Me_3Sn)_4Fe^{II}(CN)_6{\cdot}2H_2O{\cdot}C_4H_8O_2]$ (**1b**)		−136 (1)	−73 (1)	1, 8[a]
$[(Et_4N^+)(Me_3Sn)_3Fe^{II}(CN)_6]$	−181 (1)	−158 (2)		4[a]
$[\{(C_5H_5)_2Co^+\}(Me_3Sn)_3Fe^{II}(CN)_6]$	−189 (1)	−139 (2)		6a[a]
$[(MV^{2+})_{0.5}(Me_3Sn)_3Ru^{II}(CN)_6]$	−173 (1)	−144 (1)	−104 (1)	5[a]
$[(Me_3Sn)_2MoO_4]$			+47.5	13b[a,b]

[a] Approximate relative intensity in parentheses; all signals are devoid of satellites and multiplet splitting, respectively. [b] $^1J(^{119}Sn,^{13}C)$ = 488 Hz.

The data of Table II (apart from the $\delta(^{119}Sn)$ values of **1b**, none of these data has been published earlier) demonstrate that the $\delta(^{119}Sn)$ values of all Me_3Sn units reflect an increased shielding both when Lewis-basic guest molecules are present in **1** and occasionally when one of the four Me_3Sn^+ ions of **1** or **2** is substituted by a noncovalently encapsulated guest cation. Most of the δ values of the derivatives of **1** (and **2**) are notably more negative than those of the polymers $[(R_3Sn)_3Co(CN)_6]_\infty$ with R = Me, Et, and Bu^n.[2] On the other hand, numerous examples of clearly tbp-configured R_3Sn derivatives with oxygen atoms in the axial positions have become known whose $\delta(^{119}Sn)$ values are strongly positive.[13a]

^{15}N NMR. The quality of the ^{15}N NMR spectrum of **1** is improved considerably by ^{15}N enrichment (Figure 3). Thus three centerbands of equal intensity are found in the spectrum of **1a**, suggesting, in view of the appearance of likewise three cyanide ^{13}C centerbands (vide infra), the presence of three crystallographically different CN groups. One of the three ^{15}N signals (signal N(1)) differs notably from the other two by its substantially increased ^{15}N shielding and line width. This is also the case for compounds **2** and **3** (Table III), though the shifts move to lower frequency for these systems, as expected from the data for $K_4[M(CN)_6]$.

Table III presents a survey of the $\delta(^{15}N)$ values of some selected complexes involving cyanide ligands of terminal and/or bridging functionality. Cyanide ^{15}N shifts more negative than ca.-140 ppm (relative to solid NH_4NO_3), depending on the metal, have been observed for isocyanides and metal-coordinated isothiocyanate ligands and, more recently, also for some samples involving MCN···H···NCM

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[11] Brandt, P. Doctoral Dissertation, Universität Hamburg, Germany, 1991.

[12] (a) Kümmerlen, J.; Sebald, A.; Reuter, H. *J. Organomet. Chem.* **1992**, *427*, 309. (b) The polymer $[(Et_3Sn)_2CO_3]_\infty$ displays a more pronounced temperature dependence between +30 and −40 °C: Haupt, E. T. K.; Kaphahn, M. Unpublished results.

[13] (a) see: Kümmerlen, J.; Sebald, A. *J. Am. Chem. Soc.* **1993**, *115*, 1134. (b) Behrens, U.; Brimah, A. K.; Yünlü, K.; Fischer, R. D. *Angew. Chem.* **1993**, *105*, 117; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 82.

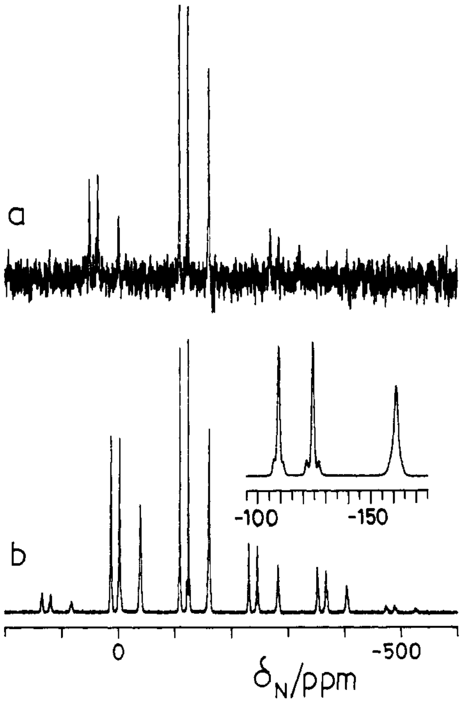
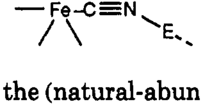


Figure 3. Nitrogen-15 CP MAS NMR spectra at 30.4 MHz of $[(Me_3Sn)_4Fe(CN)_6]_\infty$: (a) with natural-abundance ^{15}N (contact time 3 ms, recycle delay 1 s, spin rate 4.85 kHz, 70 000 transients); (b) with isotopically-enriched ^{15}N (contact time 8 ms, recycle delay 5 s, spin rate 2.54 kHz, 800 transients). The inset in (b) gives the centerband region in expanded scale to show the ^{119}Sn satellites. The widths of the two high-frequency resonances are 35 ± 2 Hz whereas that of the low-frequency signal is 67 ± 2 Hz.

and MCN···HOH bridges. The 3D polymers $[(Me_3Pb)_4M(CN)_6{\cdot}2H_2O]$ (**4a** and **4b**) have been found to contain the latter type of hydrogen bridges, too,[10] but tend to transform (possibly as a result of rapid sample spinning), into partially "anhydrous" derivatives.[14] This suggestion is based on the appearance of $\delta(^{15}N)$ values more negative than −140 ppm: According to our present experience, terminal cyanide ligands usually give rise to $\delta(^{15}N)$ values more positive than −110 ppm, while the $\delta(^{15}N)$ of polymeric $[MCN{\cdots}ER_3{\cdots}NC-]_n$ chains (with two-coordinate N atoms) appear between −110 and −140 ppm.[2] Cyanide ^{15}N shifts between ca. −140 and −170 ppm might be more characteristic of three-coordinate N atoms in multiple-bridging cyanide groups than of, e.g., isocyanide ligands. Following this hypothesis, resonance N(1) in the ^{15}N spectrum of **1a** could be tentatively assigned to fragments involving three-coordinate N atoms of the type



(E: Sn or Pb) (2)

As expected, the (natural-abundance) ^{15}N NMR spectrum of the thermally quite stable, and structurally well-understood,[8] derivative of 1, $[(Me_3Sn)_4Fe(CN)_6{\cdot}2H_2O{\cdot}C_4H_8O_2]$ (**1b**), which contains essentially two-coordinate N atoms (ignoring here any potential O–H···N bonding), is devoid of any low-frequency signals beyond −130 ppm (Table III): Two signals are seen, the high-frequency one being twice the intensity of the other. The crystal structure predicts three nonequivalent cyanide groups, so it would seem there is some accidental degeneracy. The cyanide ^{13}C spectrum of **1b** bears this out (see below).

The two coupling parameters, $|^1J(^{119}Sn, ^{15}N)|$ deduced from the satellites of the signals N(2) and N(3) of **1a** (of 121 and 166 Hz) match in magnitude the data reported recently[2] for $[(R_3Sn)_3Co(CN)_6]_\infty$ systems with R = Me, Et, and Bu^n (Table IV). While corresponding $|^1J(^{119}Sn, ^{15}N)|$ values of dissolved (i.e. nonpolymer R_3SnNCS (R = alkyl)) seem to be even larger, the known[16a–d] $^1J(^{119}Sn, ^{15}N)$ values of various, probably pth-configured Me_3Sn amides are surprisingly small (ranging from +9.5 to −41.4 Hz). The $^1J(^{119}Sn, ^{15}N)$ values of several triorganotin(IV) oxinates and thioxinates are, moreover, discussed in ref 16e. Resolution problems do not allow the clear observation of any satellite lines for the N(1) signal at −161 ppm.

Cyanide ^{13}C NMR. The cyanide ^{13}C NMR spectrum of 1 is also strongly improved by the almost quantitative ^{15}N enrichment in sample **1a**. Thus three equally intense cyanide centerbands appear as clean singlets in the spectrum of **1a**, while the spectrum of 1 displays essentially three 2:1 doublets characteristic of second-order effects originating from the quadrupolar ^{14}N nucleus owing to internuclear $^{13}C–^{14}N$ coupling (Figure 4). The weighted average positions of the doublets of 1 (Table V) correlate well with the peaks of the three singlets of **1a**. Moreover, the (natural-abundance) ^{13}C NMR spectrum of solid $[(Me_3Sn)_4Fe(CN)_6{\cdot}2H_2O{\cdot}C_4H_8O_2]$, **1b**, which is expected from the known crystal structure to display three cyanide carbon resonances,[8] gives rise to three multiplets strongly reminiscent of those of 1. The cyanide ^{13}C chemical shifts of 1–3 relate sensibly to the $\delta(^{13}C)$ values reported for the corresponding $[M(CN)_6]^{4-}$ anions dissolved in D_2O[18] (Table V), being in the order $\delta(1) > \delta(2) > \delta(3)$. The possibly "alloyed" solid 5 (vide infra) gives rise to essentially four, somewhat broader, center bands whose maxima could be matched with those of 1 and/or 2. None of the ^{13}C signals for **1a** is observably split due to coupling with their adjacent ^{15}N nuclei ($|^1J(^{15}N,^{13}C)|$ of $K_4[Fe(^{13}C^{15}N)_6]$: 6.8 Hz[17]).

NMR of Some Derivatives of 1 and 2

One potential "derivative" of 1 *and* 2 is the polymer $[(Me_3Sn)_4Fe_{0.5}Ru_{0.5}(CN)_6]$,[5] 5, which may have an alloyed nature. Its X-ray powder diagram and vibrational spectra in the ν(CN) absorption range (Table VI) would, however, also admit the assumption of a simple 1:1 mixture of polycrystalline 1 and 2. Arguments in favor of an alloyed

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[14] For instance, a sample of **4b** has displayed more than four ^{15}N resonances (Table III) although the asymmetric unit involves only three different N atoms[10] (Harris, R. K.; et al. Unpublished results).

(15) (a) Bär, E.; Fuchs, J.; Rieger, D.; Aguilar-Parrilla, F.; Limbach, H.-H.; Fehlhammer, W. P. *Angew. Chem.* **1991**, *103*, 88; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 88. (b) Witanowski, M.; Stefaniack, L.; Webb G. A. *Ann. Rep. NMR Spectrosc.* **1981**, *11B*, 72 (Table 108).

(16) (a) Wharf, I. *Inorg. Chim. Acta* **1989**, *159*, 41. (b) Molloy, K. C.; Quill, K.; Blunden, S. J.; Hill, R. *J. Chem. Soc., Dalton Trans.* **1986**, 875. (c) Blunden, S. J.; Cusack, P. A.; Gillies, D. G. *J. Magn. Reson.* **1984**, *60*, 114. (d) Wrackmeyer, B.; Horchler, K. *Annu. Rep. NMR Spectrosc.* **1990**, *22*, 249. (e) Lycka, A.; Holecek, J.; Schneider, B.; Straka, J. *J. Organomet. Chem.* **1990**, *389*, 29.

(17) Sano, M.; Yoshikawa, Y.; Yamatera, H. *Inorg. Chem.* **1982**, *21*, 2521.

(18) Pesek, J. J.; Mason, W. R. *Inorg. Chem.* **1979**, *18*, 924.

Table III. Survey of $\delta(^{15}N)$ Values of Various Systems Involving Terminal and Bridging CN Units [Data from Solid-State Spectra Unless Denoted by Footnote *c* (and for Pr^{n}NC)]

sample	$\delta(^{15}N)$/ppm				ref
$[Pr^n_4N][Cr(CN)(CO)_5]^{a,b}$		–83			15a
$[Et_4N]_3[Co(CN)_6]$		–89.8			2
$K_4[Fe(CN)_6]^{a,c}$		–95.9			17
$K_4[Ru(CN)_6]^{a,c}$		–105			17
$K_4[Os(CN)_6]^{a,c}$		–117			17
$[(Me_3Sn)_3Co(CN)_6]_\infty{}^d$	–116	–119	–123		2
$[(Bu^n_3Sn)_3Co(CN)_6]_\infty$		–118			2
$[(Me_3Pb)_3Co(CN)_6]_\infty{}^d$		–124			2
$[H_3Co(CN)_6]_\infty{}^d$			–134		2
$[(Me_3Sn)_4Fe(CN)_6{\cdot}2H_2O{\cdot}C_4H_8O_2]_\infty$	–116^g	–125			present paper, 1, 8
$[\{(C_5H_5)_2Co\}(Me_3Sn)_3Fe(CN)_6]^{a,d}$	–112	–121	–123		present paper
$[(Me_3Sn)_4Fe(CN)_6]_\infty{}^a$	–109	–124		–161.2^f	present paper
$[(Me_3Sn)_4Ru(CN)_6]_\infty$	–118	–136		–166^f	present paper
$[(Me_3Sn)_4Os(CN)_6]_\infty$	–126	–144		–172^f	present paper
$[(Me_3Pb)_4Fe(CN)_6{\cdot}2H_2O]_\infty{}^d$	–119	–132	–146		14
$[(Me_3Pb)_4Ru(CN)_6{\cdot}2H_2O]_\infty{}^{d,e}$	–127	–131		–158	14
$[Ph_4As][\{(CO)_5Cr(CN)\}_2H]^{a,b,d}$				–163	15a
Pr^{n}NC				ca. –200	15b
$(Bu^n_4N)_2[Zn(NCS)_4]$				ca. –217	15b
$(CO)_5Cr(CNH)^{a,b}$				–221	15a

[a] ^{15}N-enriched sample. [b] $\delta(^{15}N)$ readjusted from data with NH_4Cl as standard. [c] Solution (D_2O) spectrum; standard $Na^{15}NO_3$. [d] X-ray structure available. [e] Four weaker resonances appear between –129 and –164 ppm. [f] Resonance denoted as N(1) in the text. [g] Double the intensity of the other peak.

Table IV. Survey of Data for the Nuclear Coupling Constant $|^1J(^{15}N,^{119}Sn)|$ of Solid or Dissolved Samples Involving CN Groups

sample	$|^1J(^{119}Sn,^{15}N)|$/Hz	ref
$[(Me_3Sn)_4Fe(CN)_6]_\infty{}^{a,c}$	120,^{d,g} 170^{d,h}	present paper
$[\{(C_5H_5)_2Co\}(Me_3Sn)_3Fe(CN)_6]^{a-d}$	143, 171, 187	present paper
$[(Bu^n_3Sn)_3Co(CN)_6]_\infty{}^a$	150	2
$[(Et_3Sn)_3Co(CN)_6]_\infty{}^a$	180^e	1
$[(Me_3Sn)_3Co(CN)_6]_\infty{}^a$	ca. 160^e	1
$(C_6H_{11})_3SnNCS^b$	190.6^{e,f}	15b
$Bu^n_3SnNCS^b$	307^d	ftn 1 of ref 15c

[a] Solid sample (values given to ±5 Hz). [b] Solution spectra. [c] ^{15}N-enriched. [d] From ^{15}N spectrum only. [e] From ^{119}Sn spectrum (recalculated from $|^1J(^{119}Sn,^{14}N)|$). [f] From ^{14}N spectrum, also. [g] Signal N(2) (see the text). [h] Signal N(3) (see the text).

nature have so far been based on the visible absorption spectrum of the polymeric charge-transfer ion-"pair": $[(MV^{2+})_{0.5}(Me_3Sn)_3Fe_{0.5}Ru_{0.5}(CN)_6]$ (MV = methylviologen), obtained from **5** by ion exchange (i.e. replacement of one Me_3Sn^+ by 0.5 MV^{2+} according to eq 1).[5] For a statistical distribution of Fe and Ru atoms, each of the two nonequivalent Me_3Sn units (vide supra) should reside in one of the *three* environments I–III. Ideally, resolved

$$-\mathbf{Fe}\text{-CN}\cdots\underset{\text{I}}{\text{Sn}}\cdots\text{NC-}\mathbf{Fe}- \qquad -\text{Ru-CN}\cdots\underset{\text{II}}{\text{Sn}}\cdots\text{NC-}\mathbf{Ru}-$$
$$-\mathbf{Fe}\text{-CN}\cdots\underset{\text{III}}{\text{Sn}}\cdots\text{NC-}\mathbf{Ru}- \tag{3}$$

low-temperature ^{13}C NMR spectra of **5** would thus display twelve methyl carbon resonances practically coincident with those of pure **1** and **2** and, in addition, two extra sets of three signals, A(III) and B(III), attributable to Me_3Sn units in the alloyed environment III. In view of the proximity of most methyl carbon resonances (cf. Table I), however, numerous signals are expected to overlap. So far only the relatively isolated resonance around –2.3 ppm (cf. Table I) could in the spectrum of **5** be resolved into two lines (–60 °C: –2.7 and –2.2 ppm) while all other bands are just significantly more broadened. The two lines mentioned can be reasonably ascribed to I and II, respectively. The ^{15}N spectrum clearly shows six lines of approximately equal intensity at the positions expected for the NC–Ru and NC–Fe environments. For ^{15}N III is not expected to give signals at positions significantly different from those of I and II. The spectroscopic findings thus favor the admittedly surprising assumption that microcrystallites of pure **1** and **2** have resulted simply on addition of Me_3SnCl to a $K_4[Fe(CN)_6]/K_4[Ru(CN)_6]$ solution.

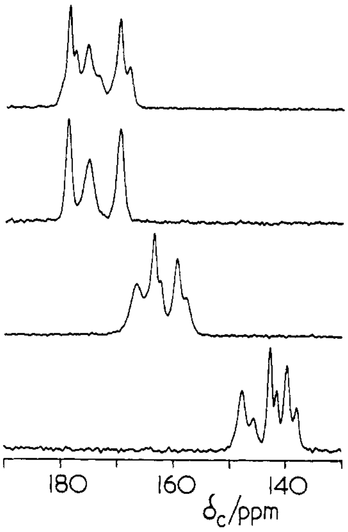

Figure 4. Carbon-13 CP MAS NMR spectra (cyanide region only) at 75.4 MHz of $[(Me_3Sn)_4M^{II}(CN)_6]_\infty$ with (top-to-bottom) M = Fe (CT 3 ms, RD 2 s, SR 4.6 kHz, NT 28 320), M = Fe (compound isotopically enriched in ^{15}N, CT 8 ms, RD 2 s, SR 4.9 kHz, NT 4600), M = Ru (CT 2.5 ms, RD 1 s, SR 5.0 kHz, NT 52 800), M = Os (CT 7 ms, RD 1 s, SR 5.03 kHz, NT 52 400). For the isotopically-enriched compound the line widths (high to low frequency) are 86, 157, and 102 ± 5 Hz. [CT ≡ contact time: RD ≡ recycle delay: SR ≡ spin rate: NT ≡ number of transients.]

For a satisfactory CP MAS NMR study, the extremely labile host–guest system $[(Me_3Sn)_4Fe(CN)_6{\cdot}4H_2O]$ (G and G′ = H_2O), whose crystal structure could only be determined[9] in selecting a pristine, undried crystal, had to be dried extremely carefully.[1] While the elemental analysis of this homogeneously powdered material (**1c**) had sug-

Table V. Chemical Shifts of the Cyanide Carbon (^{13}C) Atoms of 1–3 and Several Related Systems

sample	$\delta(^{13}C)$/ppm			
$K_4[Fe(CN)_6]^a$		177.2		
$[(Me_3Sn)_4Fe(CN)_6]^d$	178.4	174.8		169.1
$[(Me_3Sn)_4Fe(CN)_6]^b$	178.9	175.2		169.6
$[(Me_3Sn)_4Fe(CN)_6{\cdot}2H_2O{\cdot}C_4H_8O_2]^d$	177.1	172.6		167.5
$[\{(C_5H_5)_2Co\}(Me_3Sn)_3Fe(CN)_6]^b$	179.5	175.0		166.4
$K_4[Ru(CN)_6]^a$		162.3		
$[(Me_3Sn)_4Ru(CN)_6]^d$	165.8	163.1		158.8
$K_4[Os(CN)_6]^a$		142.5		
$[(Me_3Sn)_4Os(CN)_6]^d$	147.1	142.4		139.2
$[(Me_3Sn)_4Fe_{0.5}Ru_{0.5}(CN)_6]^{c,e}$	177.4	168.8	162.6	158.0

[a] ^{13}C-enriched sample, dissolved in D_2O.[18] [b] ^{15}N-enriched sample (**1a**). [c] Potentially "alloyed" sample **5**. [d] Data given are the weighted averages of the 2:1 doublets caused by second-order effects of coupling to ^{14}N. [e] Peak maxima given since the effects of ^{14}N are unclear.

Table VI. Vibrational Frequencies (in cm^{-1}) of all ν(CN) and ν(SnC) Bands Observed in the Infrared (Boldfaced Numbers) and Raman Spectra of 1–3, 1a, and 5

	1	1a	2	3	5
ν(CN)	**2045** (s)	**2021** (s)[a]	**2055** (s)	**2035** (s)	**2045, 2055**
	2067 (m)	2039 (m)	2070 (m)	2066 (m)	2065, 2070
	2073 (s)	**2044** (s)[b]	**2090** (s)	**2073** (s)	**2075, 2090**
	2088 (s)	2060 (s)		2096 (s)	2089, 2101
	2128 (s)	2101 (s)	2145 (s)	2150 (s)	2130, 2145
$\nu(SnC)_{sym}$	520 (s)	521 (s)	518 (s)	518 (s)	518 (s)
$\nu(SnC)_{as}$	552 (m)	550 (m)	548 (m)	553 (m, br)[c]	554 (m, br)
	553 (m)	**552** (m)	**553** (m)	**554** (m, br)	**555** (m, br)

[a] Calculated (see the text): 2019 cm^{-1}. [b] Calculated (see the text): 2043 cm^{-1}. [c] See also Figure 5.

gested the composition $(Me_3Sn)_4Fe(CN)_6{\cdot}2H_2O$ which would match with that of the crystallographically confirmed organolead homologues $[(Me_3Pb)_4M(CN)_6{\cdot}2H_2O]$ with M = Fe (**4a**) and Ru (**4b**), the major signals in the ^{119}Sn, ^{13}C, and ^{15}N spectra of **1c** (including the methyl ^{13}C resonances down to −60 °C) all matched those of the anhydrous compound **1**. Lower-intensity resonances (e.g. at −30 and −138 ppm in the ^{119}Sn spectrum) probably indicate the presence of a true hydrate (assumed to be the tetrahydrate revealed by X-ray studies).

These findings suggest that modest drying, along with rapid sample spinning, triggers the loss of incorporated water. Correspondingly, attempts to convert pure **1–3** into isolable "adducts" involving H_2O, NH_3, or $NCCH_3$ molecules as extra ligands (or "guests") have so far been unsuccessful, suggesting that all five coordination sites of the "excess" Me_3Sn^+ ions in **1** appear to be "satisfied".

Surprisingly, the main ^{119}Sn and (natural-abundance) ^{15}N NMR spectra of another, apparently even crystalline, derivative of **1** (sample **1d**) grown from Me_3SnCl and $K_4[Fe(CN)_6]$ in aqueous solution in the presence of D-(+)-glucose (which compound was, in its cyclic form, initially expected to mimic the dioxane of **1b**[8] as a corresponding guest) turn out again to be identical with the ^{119}Sn and ^{15}N spectra of **1**. Although the ^{13}C spectrum of **1d** does display several comparatively weak resonances typical of glucose, the notably more intense methyl carbon resonances of **1d** are similar to those of pure **1**. The elemental analysis of **1d** agrees better with a composition corresponding to that of **1**, although the ^{119}Sn spectrum contains weak spinning patterns centered at −30 and −138 ppm, i.e. as found for the hydrate component of **1c**. Solid-state NMR monitoring may thus eventually even be helpful in detecting viable routes to prepare crystalline guest-free **1** of sufficient X-ray quality.

Vibrational Spectroscopy

The relative wealth of information available from the solid-state NMR results contrasts with the rather limited information to be drawn from the ^{119m}Sn and ^{57}Fe Mössbauer spectra of **1**[19] which are essentially in favor of tbp-configured Me_3Sn derivatives. More valuable insights are based on vibrational (i.e. IR and Ra) spectroscopy, mainly in the absorption ranges of the ν(SnC) and ν(CN) vibrations (i.e. around 500–600 and 2000–2200 cm^{-1}, respectively). The strict absence of the symmetric vibration, $\nu(SnC)_{sym}$, in the IR spectra (Table VI), and the relatively low intensity of the asymmetric vibration, $\nu(SnC)_{as}$, in the Ra spectra, advocate an exclusive presence of trigonal planar Me_3Sn units (local symmetry: D_{3h}), plausibly owing to their axial anchoring to *two* cyanide N atoms. In the presence of terminal $CNSnMe_3$ ligands with pth configuration around the Sn atoms, at least one $\nu(SnC)_{sym}$ vibration should be observable both in the Ra and the IR spectrum. This is apparently not the case, nor do the spectra offer any convincing evidence of *two* chemically nonequivalent tbp-configured Me_3SnN_2 units, although the IR and Ra bands of the asymmetric (i.e. *doubly* degenerate in D_{3h}) $\nu(SnC)_{as}$ vibration tend to look like a doublet (Figure 5). As the exclusively Ra-active band of the nondegenerate $\nu(SnC)_{sym}$ vibration shows no evidence of splitting, the doubling of the asymmetric vibration may rather be due to the actual nonequivalence of the three methyl groups of each Sn atom (vide supra), thus reflecting departure from 3-fold symmetry. The Me_3Sn groups of the alloyed polymer **5** do not reveal any more complex a nature by an increased number of ν(SnC) bands.

As a general consequence of essentially covalent $M{-}C{\equiv}N{\rightarrow}M'$ bridging, the ν(CN) bands of **1–3** (Table VI) occur usually at higher wavenumbers than the bands of genuine salts of the corresponding $[M^{II}(CN)_6]^{4-}$ anions (cf. Table VII). The experimental wavenumbers of the $\nu(C^{15}N)$ bands of **1a** compare well with the corresponding calculated data, making use of the wavenumbers of **1** and of the standard equation of the diatomic oscillator. The alloyed polymer **5** displays two sets of ν(CN) bands, each of which is reminiscent of a "pure" $M(CN)_6$ unit with M = Fe or Ru (Table VI).

Interestingly, there is no coincidence in wavenumber of any pair of IR- and Ra-active ν(CN) bands, suggesting local *centro*symmetry for all $M(CNSn{\cdots})_6$ fragments of **1–3** and **5**. The more intense IR band even tends to split into two close-lying components (Figure 6). From the three centrosymmetric subgroups of O_h to be in question, D_{4h}, D_{3d}, and D_{2h}, the first two would not corroborate the IR/Ra results (see Figure 6) and the unequivocal NMR spectroscopic evidence of *three* nonequivalent CN ligands. The combination of NMR and vibrational evidence is required to reach the conclusion that in each $M(CNSn{\cdots})_6$ unit the pairwise equivalent cyanide groups occupy mutually trans orientations.

Interestingly, the spectra of the crystallographically well explored[21] ion exchange product with $Bu^n{}_4N^+$, $[(Bu^n{}_4N)_{0.5}(Me_3Sn)_{3.5}Fe(CN)_6{\cdot}H_2O]_\infty$ (**6**), give rise to five IR- and six

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(19) See footnote 16 of ref 4. Unlike for, e.g., $[(Ph_3Sn)_3Fe^{III}(CN)_6]$[20a] and $[H_4Fe^{II}(CN)_6]$,[20b] the absence of any quadrupole splitting of the ^{57}Fe Mössbauer signal of **1** suggests the presence of six comparatively similar ligands.

(20) (a) Bonardi, A.; Carini, C.; Pelizzi, C.; Pelizzi, G.; Predieri, G.; Tarasconi, P.; Zoroddu, M. A.; Molloy, K. C. *J. Organomet. Chem.* **1991**, *401*, 283. (b) Garg, A. N.; Goel, P. S. *J. Inorg. Nucl. Chem.* **1969**, *31*, 697.

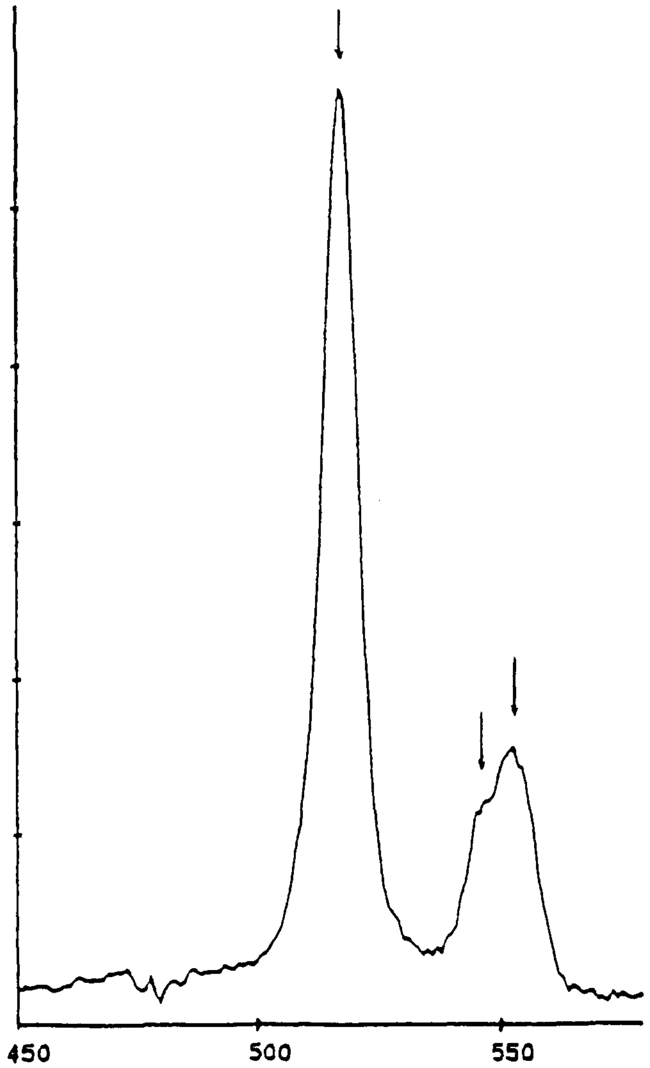

Figure 5. Raman spectrum of polymer **3** in the Sn–C stretching region.

Ra-active bands, pairwise coinciding in wavenumber (Table VII). The crystallographic results actually confirm the presence of only one Fe(CNSn···)$_6$ unit with six nonequivalent CNSn··· ligands. In view of this agreement the IR and Ra data for **1**–**3** and **5** are also likely to reflect essential symmetry-related information. For fragments involving genuine isocyanide ligands, Me$_3$Sn–N≡C—Fe—C≡N–SnMe$_3$, imaginable in view of the positive $\delta(^{119}\mathrm{Sn})$ value and a comparatively small coupling constant, $|^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})|$ (of **1**, vide supra), ν(CN) values >2110 cm^{-1} might be expected.[22]

The knowledge of absorptions attributable to ν(SnN) vibrations would be particularly valuable for a closer specification of the actual anchoring of the "excess" Me$_3$Sn units. However, such bands could so far not be identified with certainty.[23] Nevertheless, some interesting features have become apparent in the usual absorption range of the ν(MC) and δ(MCN) vibrations (i.e. ca. 300–500 cm^{-1}) and are currently being investigated in more detail.

Architecture of the 3D Polymers 1–3

The spectroscopic findings of major relevance for a more detailed understanding of the potential 3D network of **1**–**3** can be summarized as follows: (a) Each M(CN)$_6$ unit involves three nonequivalent CN ligands whose spatial arrangement corresponds to local D_{2h} symmetry. (b) Each formula unit contains *two* equally abundant sets of probably tbp-configured Me$_3$Sn units. (c) Two of the six N atoms of each M(CN)$_6$ unit are likely to adopt the coordination number 3, suggesting an anchoring of two not necessarily equal Me$_3$Sn units to each of these N atoms. Statement c appears to deserve a special comment since it deprives priority from construction patterns involving one nonbridging fragment Me$_3$SnN≡C—Fe—C≡N—SnMe$_3$. Interestingly, the well-confirmed (both by X-ray[24a] and neutron[24b] diffraction) crystal structure of the polymers $(\mathrm{H_4Fe^{II}(CN)_6})_\infty$ and $[\mathrm{D_4Fe^{II}(CN)_6}]_\infty$ where the four Me$_3$Sn$^+$ ions of **1**–**3** are formally substituted by four H$^+$ and D$^+$ ions, respectively, fulfills all of the spectroscopically deduced structural essentials of **1**–**3** (Figure 7). Thus each Fe(CN)$_6$ octahedron involves three crystallographically different N atoms that reside pairwise in trans positions (in Figure 7: N(1)/$\bar{\mathrm{N}}$(1), N(2)/$\bar{\mathrm{N}}$(2), and N(3)/$\bar{\mathrm{N}}$(3)). The atoms N(1) and $\bar{\mathrm{N}}$(1) of each Fe(CN)$_6$ unit function as bridgeheads of *two* hydrogen bridges, while all other N atoms are involved in just one ordinary N—H···N′ linkage. In analogy to our postulate of two different Me$_3$Sn bridges in **1**–**3**, no more than two nonequivalent hydrogen bridges (1:1) exist in $[\mathrm{H_4Fe(CN)_6}]_\infty$, which differ considerably both in "shape" and in their overall N···N′ distances:[24]

$$\text{bridge 1: N(1)–H(1), 1.45; H(1)–}\bar{\text{N}}\text{(3′), 1.23 Å; N(1)–H(1)–N(3′), 173°}$$

$$\text{bridge 2: N(1)–H(2), 1.81; H2–N(2′), 1.11 Å; N(1)–H(2)–N(2′), 148°} \quad (4)$$

All Me$_3$Sn units would thus have in common that they were anchored to one two- and one three-coordinate N atom. Alternatively, a model could be envisioned in which half of the Me$_3$Sn units would interact exclusively with three-coordinate N atoms and the other half with two-coordinate N atoms only. The actual structure of [H$_4$Fe(CN)$_6$] would make this polymer a suitable model for the 3D network of **1**–**3**, provided that (a) one cyanide N atom might also be capable of coordinating two different Me$_3$Sn units and (b) that the resulting -CN–Sn···NC bridges would differ appreciably in strength and symmetry to account for the two rather different $\delta(^{119}\mathrm{Sn})$ values.

Vahrenkamp et al. have demonstrated in 1990[25] that two separate d transition metal atoms may actually be bonded to one cyanide nitrogen atom of a given ^{d}M–C N functionality. We are, moreover, aware of two structures in which a nitrogen atom belonging to a cyanide-like unit is linked with *two* Me$_3$Sn groups. One is the polymeric cyanamide, $[(\mathrm{Me_3Sn})_2\mathrm{N_2C}]_\infty$, whose N atoms are exclusively three-coordinate, leading to a 3D network (a) with symmetrical bridges throughout (N–Sn = 2.48 Å[26]). The second example is the polymer $[\mathrm{Me_3SnNCO{\cdot}Me_3SnOH}]_\infty$

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(21) Schwarz, P.; Eller, S.; Soliman, T. M.; Fischer, R. D.; Davies, N. A.; Apperley, D. C.; Harris, R. K. To be published.

(22) Bär, E.; Fehlhammer, W. P. *J. Organomet. Chem.* **1988**, *353*, 197.

(23) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; J. Wiley: New York, 1986; pp 272–282.

(24) (a) Pierrot, M.; Kern, R.; Weiss, R. *Acta Crystallogr.* **1966**, *20*, 425. (b) Pierrot, M.; Kern, R. *Acta Crystallogr.* **1969**, *B25*, 1685.

(25) Oswald, B.; Powell, A. K.; Rashwan, F.; Heinze, J.; Vahrenkamp, H. *Chem. Ber.* **1990**, *123*, 243.

(26) Forder, R. A.; Sheldrick, G. M. *Chem. Commun.* **1970**, 1023.

Table VII. Comparison of the ν(CN) Vibrations (IR and Ra, in cm^{-1}) of Four Different Compounds Containing a M^{II}(CN)$_6$ Fragment

compound	Raman			infrared		
$(Et_4N)_4[Ru(CN)_6]$		2083 (m)	2045 (s)	2070 (m, sh)	2060 (s)	2040 (m, sh)
$[(Me_3Sn)_4Ru(CN)_6]$	2145 (s)	2070 (m)		2090 (s)		2055 (s)
$[(Et_4N)(Me_3Sn)_3Fe(CN)_6]$	2120 (s)	2081 (s)	2071 (m)	2065 (s)		2052 (s)
$[(Bu^n{}_4N)_{0.5}(Me_3Sn)_{3.5}Fe(CN)_6{\cdot}H_2O]$[21]	2130 (s)	2100 (s)	2095 (m)	2130 (w)	2095 (m)	2065 (s)
	2065 (w)	2045 (s)	2026 (m)	2045 (s)	2026 (m)	

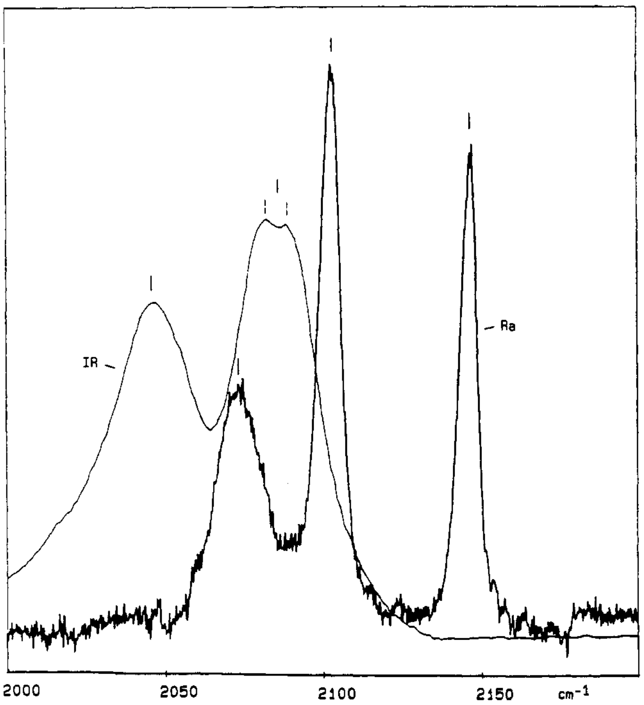
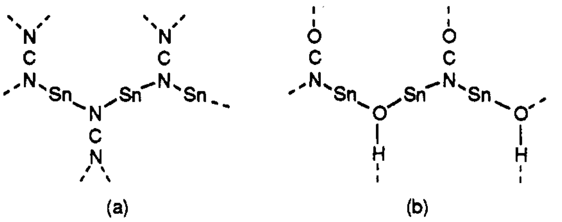


Figure 6. Infrared and Raman spectra of **2** in the ν(CN) range (the reproducible, weak splitting of one of the IR bands has not been considered in Table VI).



(5)

which involves zigzag chains of the type (b) with strongly alternating Sn–N bond lengths (i.e. of 2.43(5) and 2.75(5) Å[27]). The latter value represents the longest Sn–N distance so far reported and contrasts drastically with the Sn–N distance of 2.15(6) Å in the likewise polymeric solid Me$_3$SnNCS.[28] Sn–N distances of ca. 2.5 Å are, however, not uncommon.[29] In view of an estimated Sn···N van der Waals distance[27] of 3.7 Å but in contrast to an (early) assumption of essentially ionic Me$_3$Sn$^+$ and CN$^-$ components in polymeric [Me$_3$SnCN]$_\infty$ (Sn–N and Sn–C, 2.49 Å[30]),[31] rather long, still "bonding" Sn–N distances may in fact be expected.

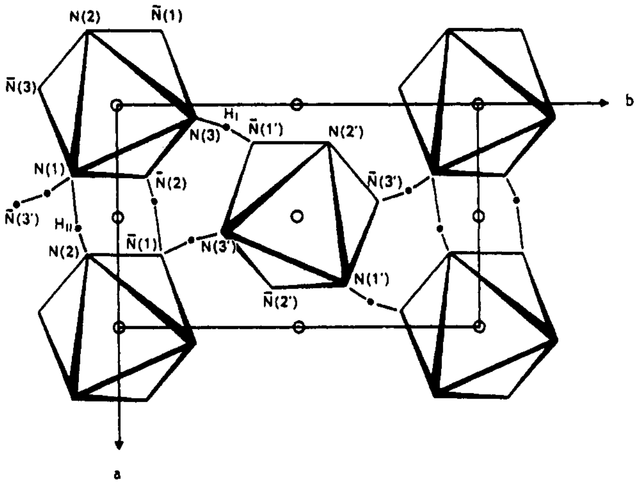
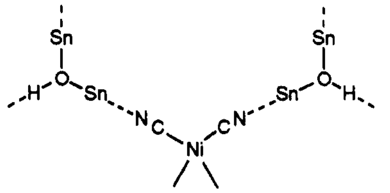


Figure 7. View of the three-dimensional network of [H$_4$Fe(CN)$_6$]$_\infty$ (following ref 26b). The trans-standing atoms N(1) and Ñ(1) of each Fe(CN)$_6$ unit are bridgeheads of *two* hydrogen bridges.

Solid-state ^{119}Sn NMR results on bridging Me$_3$Sn units with unusually long Sn–N bonds are so far only available for the 2D polymer [(Bu$^n{}_4$N)$_2${(μ-OH)(Me$_3$Sn)$_2$}$_2${(μ-NC)$_2$Ni(CN)$_2$}$_2$] whose anionic network contains fragments of the type



(6)

displaying Sn–N distances of 2.529(6) and 2.546(6) Å.[32a] Two (of the three observed) ^{119}Sn resonances have values of −33.5 and −42.3 ppm.[32b] The aforementioned polymer **6** shows one ^{119}Sn resonance at +6 ppm, due probably to a very unsymmetrical CN–Sn···OH$_2$ bridge with an unusually long Sn–O distance (Sn–N; 2.187 Å; Sn–O, 2.664 Å).[21] Thus, even positive δ(^{119}Sn) values could in fact be envisaged for (psuedo-)tbp-configured –CN···Sn···NC– bridges involving one long (≥2.5 Å) and one only slightly shorter (≥2.3 Å) Sn···N bond. While further experimental experience is undoubtedly highly desirable, we wish to point out in concluding that the well-confirmed evidence of *two equally*-abundant Me$_3$Sn units in the title compounds advocates, simply for topological reasons, a supramolecular architecture involving *all* its Me$_3$Sn groups in bridging positions. Infinitely weak Sn(2)···N(1) interactions cannot, however, be strictly ruled out.[36]

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(27) Hall, J. B.; Britton, B. *Acta Crystallogr.* **1972**, *B28*, 2133.

(28) Forder, R. A.; Sheldrick, G. M. *J. Organomet. Chem.* **1970**, *21*, 115.

(29) See: Basseth, C.; Bajue, S. A.; Bramwell, F. B. *Abstr. Pap.—Am. Chem. Soc.* **1992**, 203rd, INORG 536; *Abstr. Pap.—Am. Chem. Soc.* **1992**, 204th, INOR 254.

(30) Schlemper, E. O.; Britton, D. *Inorg. Chem.* **1966**, *5*, 507.

(31) We have found a δ(^{119}Sn) value of −144 ppm (not reported earlier) which appears to be fully consistent with the usual behavior of nonionic, tbp-configured Me$_3$Sn derivatives.

(32) (a) Soliman, T. M.; Etaiw, S. E. H.; Fendesak, G.; Fischer, R. D. *J. Organomet. Chem.* **1991**, *415*, C1. (b) Third δ(^{119}Sn) value −67.6 ppm: Harris, R. K.; Apperley, D. C.; Davies, N. A.; Kopf, J.; Fischer, R. D. Manuscript in preparation.

Experimental Section

The earlier-reported organotin polymers $[(Me_3Sn)_4M(CN)_6]$ with M = Fe and Ru (**1**, **2**), including the potentially alloyed species $[(Me_3Sn)_4Fe_{0.5}Ru_{0.5}(CN)_6]$ (**5**), as well as the water/dioxane adduct of **1**. $[(Me_3Sn)_4Fe(CN)_6{\cdot}2H_2O{\cdot}C_4H_8O_2]$ (**1b**), were prepared according to refs 4, 5, 8, and 31. Anal. Calcd for **1**/**2** = $C_{18}H_{36}N_6MSn_4$ (M: Fe/Ru): C, 24.93/23.69; H, 4.18/3.98; N, 9.69/9.21; Sn, 53.64/52.04. Found: C, 24.81/23.64; H, 4.01/3.93; N, 9.86/9.13; Sn, 52.82/50.68. ^{15}N-enriched $K_4[Fe(CN)_6]{\cdot}3H_2O$ was obtained by refluxing 0.20 g (2.23 mmol) of green $Fe(OH)_2$[32] with 1.1 g (16.64 mmol) of $KC^{15}N$ (99% Medgenix GmbH Germany) in ca. 35 mL of N_2-conditioned H_2O for 2 h. After filtration and addition of ca. 30 mL of EtOH to the filtrate, a light precipitate was isolated, subsequently redissolved in H_2O, and precipitated once more by adding EtOH. After washing with small portions of cold H_2O/EtOH (1:1) and drying in vacuo, 0.35 g of pure $K_4[Fe(C^{15}N)_6]{\cdot}3H_2O$ (yield: 36.7%) was obtained. A 0.2-g (0.47-mmol) amount of this product was dissolved in 30 mL of H_2O; this solution was united with a solution of 0.583 g (2.92 mmol) of Me_3SnCl (Merck-Schuchardt) in 30 mL of H_2O. The white precipitate of **1a** (0.35 g; yield: 86%) was dried in vacuo after filtration. Anal. Calcd for $C_{18}H_{36}{}^{15}N_6FeSn_4$: C, 24.76; H, 4.16; N, 10.31. Found: C, 24.61; H, 4.17; N, 9.69. The polymer $[(Me_3Sn)_4Os(CN)_6]$ (**3**) was prepared by adding a solution of 0.43 g (2.15 mmol) of Me_3SnCl in 10 mL of H_2O to a solution of 0.30 g (0.54 mmol) of $K_4[Os(CN)_6]{\cdot}3H_2O$ (prepared according to ref 33) in 10 mL of H_2O. After filtration, washing with cold H_2O, and drying in vacuo (3 h), 0.49 g of pure **3** (yield: 91%; dec temp >360 °C) was obtained. Anal. Calcd for $C_{18}H_{36}N_6OsSn_4$: C, 21.59; H, 3.62; N, 8.39; Sn, 47.41. Found: C, 21.06; H, 3.60; N, 7.99; Sn, 46.38. Compounds **1** and **2** (and, for comparison, **4a** and **6**), were also analyzed for oxygen; while the absence of O (and hence of H_2O) in **1** and **2** was indicated. Samples **4a** and **6** each contained oxygen corresponding to one H_2O molecule per Fe atom. Spontaneous precipitation of **1** was inhibited by mixing the solutions of 0.27 g (0.63 mmol) of $K_4[Fe(CN)_6]$ in 30 mL of H_2O and of 10 g (55.5 mmol) of D-(+)-glucose in 50 mL of H_2O. A solution of 0.5 g (2.5 mmol) of Me_3SnCl in 30 mL of H_2O was added dropwise to the stirred $K_4[Fe(CN)_6]$/glucose solution, avoiding any early turbidness. After 2 days, at a temperature of ca. 4 °C, ca. 0.46 g of colorless crystals was obtained (corresponding to a yield of the initially expected 1:1 adduct with glucose of 70%). Anal. Calcd for $[(Me_3Sn)_4Fe(CN)_6{\cdot}glucose]$ = $C_{24}H_{48}N_6O_6FeSn_4$: C, 27.53; H, 4.62; N, 8.03. Found: C, 24.81; H, 4.44; N, 8.89. IR ν(CN): 2060, 2080; Ra 2064, 2087, 2126. ν(SnC): IR 555; Ra 519, 553 cm^{-1}. The NMR sample originating after extremely careful drying from authentic $[(Me_3Sn)_4Fe(CN)_6{\cdot}4H_2O]$[9] was identical with that mentioned in ref 1.

Infrared spectroscopic measurements were carried out mainly on the Perkin-Elmer (PE) FT-IR-1720 instrument, with occasional use of the PE spectrometers 325 and 577. Raman spectra were run on the Ramanov U-1000 spectrometer of Jobin Yvon. Debye Scherrer X-ray diffraction studies (e.g. of **1**–**3** and **5**) were carried out on the Philips powder diffractometer PW 1050 (Cu, Kα, Ni filter). All four polymers turned out to be isostructural.

The ^{15}N, ^{13}C, and ^{119}Sn solid-state NMR spectra were obtained at 30.4, 75.4, and 111.9 MHz, respectively, using a Varian VXR 300 spectrometer in the cross-polarization mode with Doty scientific probes and high-power proton decoupling. For ^{15}N and ^{13}C 7-mm-o.d. rotors were employed, with typical MAS speeds in the range 4–5 kHz, whereas for ^{119}Sn 5-mm-o.d. rotors with MAS rates of 10–13 kHz were generally used. For the cross-polarization stage, contact times in the range 1–10 ms and relaxation delays of 1–2 s were found to be appropriate. Some ^{119}Sn spectra were obtained without cross-polarization. In general, many transients (10 000–60 000) were acquired for each spectrum, though for ^{13}C this was only necessary to obtain good sensitivity for the cyanide carbon signals. Such sensitivity also required relatively high contact times. Centerbands for ^{119}Sn were determined by recording spectra at two different spinning speeds (see Figure 2). Chemical shifts are reported with the high-frequency-positive convention, in ppm with respect to the signals for solid NH_4NO_3 (nitrate line), $SiMe_4$, and $SnMe_4$ for ^{15}N, ^{13}C, and ^{119}Sn, respectively.

The ambient probe temperature is ca. 23 °C. CP MAS spectra above room temperature were obtained using heated dry air as the spin gas. Below room temperature nitrogen gas was used, cooled using liquid nitrogen and subsequently heated to maintain a controlled temperature. A thermocouple situated close to the sample measured the temperature, which was stable to ±1 °C. Temperatures quoted are nominal (i.e. uncalibrated).

Acknowledgment. We thank the U.K. Science and Engineering Council for access to the Varian VXR 300 spectrometer under the national solid-state NMR service arrangements. We are also grateful for financial support from the British Council and the DAAD (Bonn) under the ARC Programme, which enables the international collaboration to take place. Dr. K. B. Dillon is thanked for a number of helpful discussions. A.K.B. and (in part) P.S. and S.E. wish to thank the Deutsche Forschungsgemeinschaft, Bonn, for financial support. The Fonds der Chemischen Industrie, Frankfurt/M., has enabled us to purchase the ^{15}N-enriched KCN.

OM920831G

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(33) Yünlü, K. Doctoral Dissertation, Universität Hamburg, Germany, 1983; p 109.

(34) Prepared by adding solid KOH to a solution of $Fe^{II}SO_4$ in N_2-conditioned H_2O, filtration, washing (H_2O), and drying in vacuo.

(35) Krauss, F.; Schrader, G. *J. Prakt. Chem.* **1928**, *119*, 282.

(36) Note added in proof: Another new polymer violating the $2n = m$ rule, but devoid of ion-exchanging properties, is the recently studied species $[(Me_3Sn)_6\{Fe(CN)_5\}_2(\mu\text{-}L)]$ (L = pyrazole), with $\delta(^{119}Sn) = -153.5$ and $+71.5$ ppm.[6b]