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Journal of Organometallic Chemistry 534 (1997) 187–194

Journal of Organometallic Chemistry

Novel organotin-functionalized, polymeric transition metal cyanides: from Me_3Sn- to $Me_2Sn(CH_2)_3SnMe_2$ spacers

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Received 15 October 1996

Abstract

The two new compounds $[\{Me_2Sn(CH_2)_3SnMe_2\}_{1.5}Co(CN)_6]$, **1**, and $[\{Me_2Sn(CH_2)_3SnMe_2\}_2Mo(CN)_8]$, **2**, have been prepared and compared with their notional 'parent' systems $[(R_3Sn)_3Co(CN)_6]$ (R = Me, Et, ^nBu) and solvent-free $[(Me_3Sn)_4M(CN)_8]$ (M = Mo, W) respectively. Results of extensive spectroscopic (i.e. IR/Raman as well as multinuclear CP MAS NMR) studies and of X-ray powder diffractometry suggest that the crystal structures of **1** and **2** involve three-dimensional networks notably different from those of their 'parent' systems. The probably regular, pairwise linkage of two $CNSnMe_2CH_2$ ligand fragments by a third CH_2 group even appears to 'improve' the local symmetry of the respective $\{M(CN)_k\}$ building block ($k = 6$ or 8) and simplifies the corresponding asymmetric units.
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Keywords: Cyanide; Cobalt; Tin; Molybdenum; Polymer; Nuclear magnetic resonance

1. Introduction

Since about 1990, our interest has been focused on structural aspects of polymeric metal cyanides involving bridging units of the type $[M–CN–ER_3–NC]_\infty$ (E = Sn, Pb; R = alkyl, aryl) making concerted use of solid-state NMR techniques [1] and X-ray diffractometry. While the first X-ray study of an $[(Me_3Sn)_{n/2}M(CN)_6]$ system dates back to 1985 ($n = 6$, M = Co [2]), the crystal structures of corresponding polymers with $n = 8$, M = Mo and W have been reported only recently [3]. Until now, exclusively mononuclear spacers SnR_3 with R = Me, Et, ^nBu [4] and ^nPr, Ph [5] have been employed. Here we describe the two new polymers $[\{Me_2Sn(CH_2)_3SnMe_2\}_{1.5}Co(CN)_6]$, **1**, and $[\{Me_2Sn(CH_2)_3SnMe_2\}_2Mo(CN)_8]$, **2**, containing the binuclear $Me_2Sn(CH_2)_3SnMe_2$ spacer instead of one pair of $SnMe_3$ groups. **1** and **2** may be considered as formal analogues of the known compounds $[(Me_3Sn)_3Co(CN)_6]$, **3** [1,2,4], and $[(Me_3Sn)_4M(CN)_8]$ with M = Mo (**4**) and W (**5**), only previously known as solvates [3], respectively. Each $–(CH_2)_3–$ chain within the new spacer will interlink two close-lying, separate $\{M–CN–Sn–NC\}_\infty$ chains of the polymeric metal cyanide, which one expects to lead to more constrained, and rigid, 3D-frameworks than in the case of the Me_3Sn spacer. As long as crystallographic results on single crystals are not available, multinuclear solid-state magnetic resonance and vibrational spectroscopy as well as X-ray powder diffractometry should allow valuable insights into the architectures of **1** and **2**, and help in the detection of possible deviations from the well-documented structures of **3** and **4** respectively.

2. Preparation and general properties of 1 and 2 as well as of solvent-free 4 and 5

The mode of preparation of the two novel polymers **1** and **2** resembles strongly that of their Me_3Sn-containing analogues **3** [4] and **4** [6]. In both cases the aqueous solutions of $ClMe_2Sn(CH_2)_3SnMe_2Cl$, **6**, and

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PII S0022-328X(96)06923-9

$K_3[Co(CN)_6]$ or $K_4[Mo(CN)_8] \cdot 2H_2O$ are mixed in the appropriate stoichiometric proportions:

$$1.5\,\mathbf{6} + K_3[Co(CN)_6] \xrightarrow{H_2O} 3KCl + \mathbf{1}\downarrow \text{ (white)} \quad (1a)$$

$$2\,\mathbf{6} + K_4[Mo(CN)_8] \cdot 2H_2O \xrightarrow{H_2O} 4KCl + \mathbf{2}\downarrow \text{ (yellow)} \quad (1b)$$

1 and **2** precipitate spontaneously and the results, after washing and drying, are analytically pure. While both products are practically insoluble in water (at neutral pH) and common organic solvents, clear solutions are readily obtained in alkaline aqueous media (of pH > 8). **1** and **2** give rise to X-ray powder diffractograms (XRP) consisting of relatively sharp reflections, indicating a polycrystalline nature. In Fig. 1 the XRP of **1** is compared with that of **3**. Although close similarity is neither expected nor actually displayed, the relative simplicity of the XRP of **1** is surprising. The pyknometric density determined in dioxane of $1.75\,g\,cm^{-3}$ leads to a formula volume of $413.96\,cm^3\,mol^{-1}$ which is significantly smaller than that of **3** [4].

A potentially hybrid-like (with respect to **1** and **3**) polymer **1a** was obtained by co-precipitation from **6**, Me_3SnCl and $K_3[Co(CN)_6]$ in the molar ratio 1:1:1. Both the elemental analysis and the solution (D_2O/NaOD) ^1H NMR spectrum agree with the anticipated composition $[(Me_3Sn)\{Me_2Sn(CH_2)_3SnMe_2\}Co(CN)_6]$ (**1a**), and the X-ray powder diffractogram is not in favour of an alternative description as a 2:1 mixture of **1** and **3** (Fig. 1).

Unlike the two tetrahydrofuran (THF)-containing derivatives of **4** and **5**, **4** · *n*THF and **5** · *m*THF respectively, so far described (e.g. $n = 1.61$ [3]), solvent-free

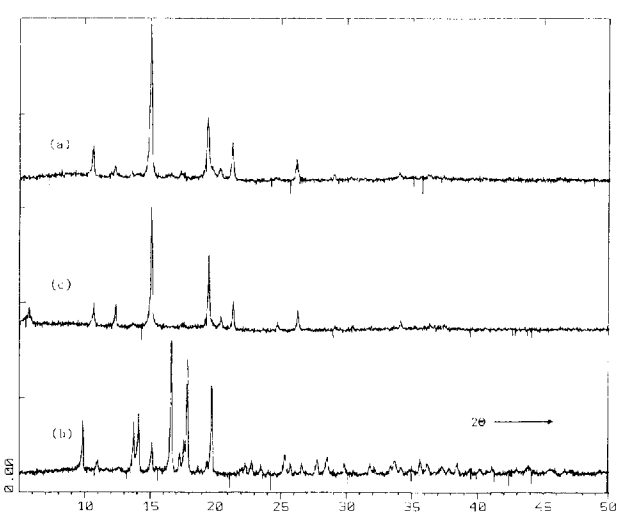

Fig. 1. X-ray powder diffractograms of **1** (a), **3** (b) and **1a** (c).

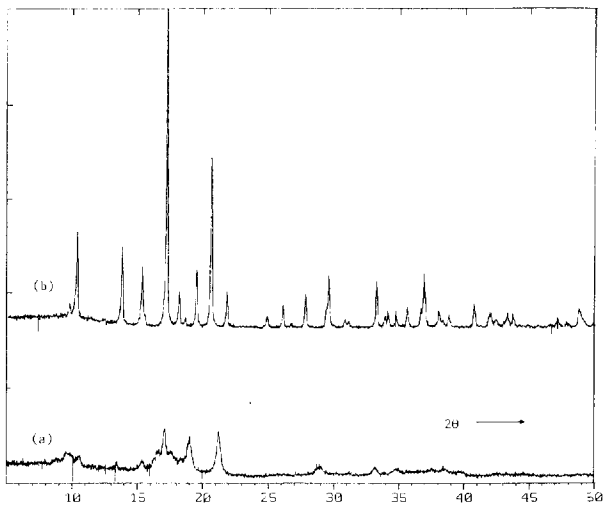

Fig. 2. X-ray powder diffractograms of **2** (a) and **4** (b).

4 and **5** were likewise prepared by precipitation from aqueous solution:

$$4Me_3SnCl + K_4[M(CN)_8] \cdot 2H_2O \quad (M = Mo \text{ or } W) \xrightarrow{(H_2O)} 4KCl + \mathbf{4}\downarrow \text{ or } \mathbf{5}\downarrow \quad (2)$$

The X-ray powder diffractogram of **4** shown in Fig. 2 indicates that again polycrystalline particles result even on spontaneous precipitation. The XRP of **2** differs strongly from that of **4**. Although the sample of **2** gave rise throughout to broader and less-pronounced reflections than that of **4**, it is evident that the actual number of well-isolated reflections is lower than in the XRP of **4**.

Extensive attempts to grow single crystals suitable for crystallographic studies from aqueous solutions have led in the case of **4** only to strongly disordered crystals, but most probably of the same space group as reported for **4** · *n*THF [3]. After suspension of **4** and **5** in THF, and subsequent drying, only the solvent-free compounds were recovered. The precursor $ClMe_2Sn(CH_2)_3SnMe_2Cl$, **6**, of the $Me_2Sn(CH_2)_3SnMe_2$ spacer was prepared according to Refs. [7,8]. The ^1H NMR spectrum of **6** in D_2O/NaOD looks very similar to the spectra of **1** and **2** under corresponding conditions (see Section 6).

3. Vibrational spectra

The most informative ranges of the infrared (IR) and Raman (Ra) spectra of all polymers considered are those of their ν(CN) and ν(SnC) vibrations. The ν(CN) spectra of **1** turn out to be very similar to those of **3** (see Table 1), suggesting that the $\{Co(CN)_6\}$ unit in **1** experi-

Table 1
Selected infrared and Raman data of **1–5** and **1a**

Compound	No.	ν(CN) (cm^{-1})			ν(SnC) (cm^{-1})			
		IR	Raman		IR	Raman		
$[\{Me_2Sn(CH_2)_3SnMe_2\}_{1.5}Co(CN)_6]$	**1**	2157	2173	2191	552	512	525	550 [a]
$[(Me_3Sn)\{Me_2Sn(CH_2)_3SnMe\}Co(CN)_6]$	**1a**	2157	2168	2190	553	514sh	523	548 [a]
$[(Me_3Sn)_3Co(CN)_6]$	**3** [b]	2157 2175sh	2180 2170sh	2195	554		524	556 [a]
$[\{Me_2Sn(CH_2)_3SnMe_2\}_2Mo(CN)_8]$	**2**	2136	2146 [c]	2173 [c]	552	505	527	551 [a]
$[(Me_3Sn)_4Mo(CN)_8]$	**4**	2140	2153	2173	554 517 [d]		520 [e]	555 [a]
$[(Me_3Sn)_4W(CN)_8]$	**5**	2123	[e]		552 510 [d]			

[a] Weak/medium intense band, assigned to the IR-active, unsymmetric ν(SnC) mode.
[b] Data from Ref. [2].
[c] Medium intense, very broad signal.
[d] Very weak signal, assigned to one of the Ra-active, symmetric ν(SnC) modes.
[e] Spectral quality unsatisfactory.

ences almost ideal local O_h symmetry. The crystallographically confirmed presence of negligibly distorted $\{Co(CN)_6\}$ octahedra in **3** [4] matches well with the appearance of one IR-active and two Ra-active bands, apart from one barely detectable, additional shoulder in the IR/Ra spectra. Actually, one IR-active (t_{1u}) and two Ra-active bands (a_{1g}, e_g) are expected for ideal O_h symmetry. Interestingly, no additional ν(CN) band (or shoulder) is detectable in the spectra of **1**. This feature is reminiscent of the results for related $[(R_3Sn)_3Co(CN)_6]$ systems with R = Et and ^nBu [4], which are in fact likely to be of higher symmetry than **3** (vide infra).

The Ra-active ν(SnC) vibrations of **1** reflect clearly the presence of two non-identical Sn–C bonds (i.e. Sn–CH_3 and Sn–CH_2–) in that here two stretching modes have become active. A third, considerably weaker, Ra band (at 550 cm^{-1}) is assigned to one of the antisymmetrical (with respect to the SnC_3 fragment) stretching modes which appears more clearly in the IR spectrum at 552 cm^{-1}.

Surprisingly, the ν(CN) spectra of **4** and **5** are poorer in signals than expected for square antiprismatic (D_{4d}) $\{M(CN)_8\}$ units as found crystallographically for **4** · nTHF and **5** · mTHF [3]. While group theoretical considerations predict two IR-active (b_2, e_1) and three Ra-active (a_1, e_2, e_3) ν(CN) modes, the experimental spectra of **4** and **5** would match better with cubic symmetry (expected for IR/Ra: t_{1u}/a_{2g}, t_{2g}). In contrast to the IR spectra of the THF-containing samples [3], those of neat **4** and **5** do not even display traces of additional ν(CN) bands around 2105 cm^{-1}. Interestingly, the more salt-like compound $Tl_8[Mo(CN)_8]$ whose anion is likewise square antiprismatic is also reported [9] to give rise to one single IR-active ν(CN) band (at 2078 cm^{-1}) only.

Compound **2** joins its quasi-homologues **4** and **5** in displaying a total of no more than three different ν(CN) bands, and **1** in showing three different ν(SnC) bands (the weak Ra line at 551 cm^{-1} being attributed, as is the intense IR band at 552 cm^{-1}, to the asymmetric vibration). From these spectroscopic features, it may at least be deduced that substitution of two Me_3Sn units by one $Me_2Sn(CH_2)_3SnMe_2$ group does not affect the comparatively high local symmetries of the respective $M(CN)_n$ fragments (for $n = 6$ or 8) in the well-known 'parent' systems.

4. Solid-state NMR spectra

The solid-state NMR spectra of all compounds considered in Table 2 are consistent with the assumption of diamagnetic samples of the structures as proposed. Strictly cubic $\{M^{IV}(CN)_8\}$ units (M = Mo, W), which should be paramagnetic owing to the presence of two d-electrons in the then doubly generate e_g orbital pair, may therefore be ruled out also for the solvent-free polymers **2**, **4** and **5** (vide supra). The multinuclear (^{13}C, ^{15}N, ^{119}Sn) magnetic resonance patterns of **4** and **5** turn out to be very simple in that only one methyl carbon, one cyanide carbon, one cyanide nitrogen and one tin resonance occurs for each compound. Assuming, as usual, rapidly (on the NMR time scale) rotating Me_3Sn propellers making all methyl carbon atoms of a distinct Me_3Sn group chemically equivalent, the experimentally found resonance patterns of **4** (Fig. 3) and **5** predict asymmetric units strictly consistent with those determined crystallographically for the two THF-containing derivatives **4** · nTHF and **5** · mTHF [3].

The new polymer **2** resulting formally from **4** after replacement of all its Me_3Sn groups by an equivalent in $Me_2Sn(CH_2)_3SnMe_2$ spacers, presents a multinuclear resonance pattern, Figs. 4 and 5, similar to those of the

Table 2
Collection of CP MAS solid-state NMR data for **1–6** and **1a**

Nucleus[13]	**1**	**1a**	**3** [a]	**7** [a]	**2**	**4**	**5**	**6**
C	−0.7 [b]	−1.2, 1.3, 4.6	−0.5(570) [c]	11.7(500)	−0.1 [b]	−0.1(500)	−0.2(550) [c]	−0.3
	21.8 [d]	22.4, 23.7	0.8(550) [e]	10.3	22.9 [b]			0.6, 3.0
	26.2 [d]	26.8						23.6, 25.7
	ca. 131 [b]	ca. 131 [b]	ca. 132	ca. 134	147	147/145 [k]	140	
^{15}N [f]			−116					
	−121 [g]	−119	−119	−119	−114	−115	−117	
			−123					
^{119}Sn		−84	−88 [j]	−75 [j]	−105	−110	−111 [h]	175 [i]
	−102	−108	−118 [j]					
^{59}Co	−211 [b]	−243 [b]	−244	−234				

[a] Data from Ref. [4] (**7** = $[(Et_3Sn)_3Co(CN)_6]$).
[b] Broad signal.
[c] Impurity at 4.5 ppm.
[d] Splits into three singlets (21.7; 22.7; 26.6 ppm) at +80 °C, but merges into one broad singlet (ca. 22.4 ppm) at −80 °C.
[e] Splits into two singlets (0.44; 0.73 ppm) at −60 °C.
[f] Of natural abundance.
[g] Line width 206 Hz, with 50% ^{15}N-enrichment: δ −128 ppm; $\Delta_{1/2}$ 118 Hz.
[h] Impurity at 24.2 ppm.
[i] Resolvable into four components.
[j] Multiplets from coupling to ^{14}N.
[k] 2:1 doublet from coupling to ^{14}N.

'parent' systems **4** and **5**. The two CH_3 groups on each Sn atom give rise to only one ^{13}C singlet, in spite of restricted rotation about each N–Sn–N axis in **5**, and the three CH_2 groups of each spacer display only one comparatively broad, additional ^{13}C signal, Fig. 5(a). It is noted here in passing that the solid-state spectra (^{13}C and ^{119}Sn) of $ClMe_2Sn(CH_2)SnMe_2Cl$ (**6**) give somewhat better resolution than for the polymers and show at least three methyl and two methylene ^{13}C signals as well as one ^{119}Sn resonance which is resolvable into four components, Fig. 5(c) and (d) (possibly arising from coupling to quadrupolar $^{35/37}$Cl). The average

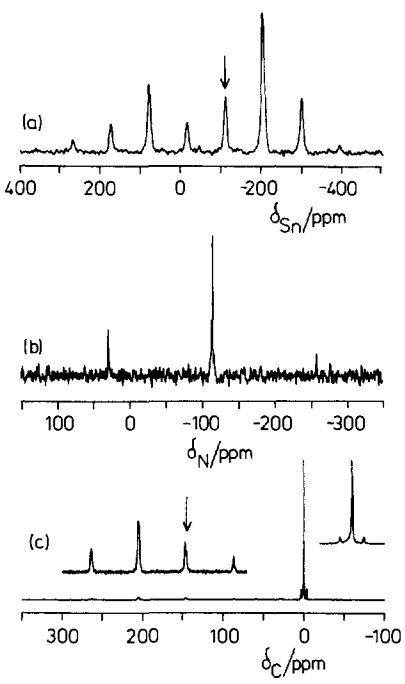

Fig. 3. CPMAS spectra of $(Me_3Sn)_4Mo(CN)_4$, **4**: (a) ^{119}Sn; (b) ^{15}N; (c) ^{13}C. The centre bands for (a) and for the ^{13}C cyanide resonance in (c) are indicated by vertical arrows. Contact times of 9 ms and recycle delays of 2 s were used for all three spectra. Spin rates were 10.6 kHz (a), 4.40 kHz (b) and 4.45 kHz (c), while the number of transients acquired were 1000 (a), 27000 (b) and 3500 (c).

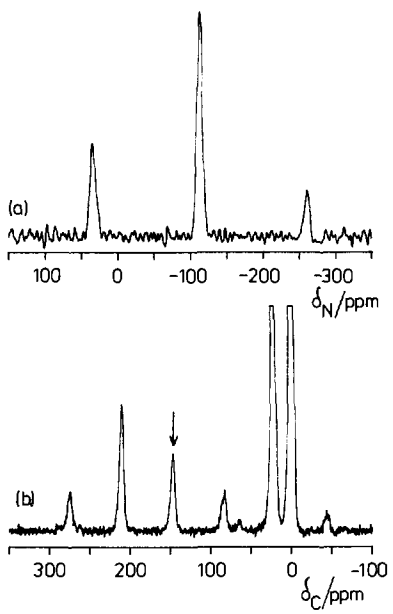

Fig. 4. CPMAS spectra of $\{Me_2Sn(CH_2)_3SnMe_2\}_2Mo(CN)_8$, **2**: (a) ^{15}N; (b) ^{13}C. The centre band of the cyanide resonance for (b) is indicated by a vertical arrow. Spectrometer operating conditions: contact time 10 ms (a) and 5 ms (b); recycle delay 1 s; number of transients 56300 (a) and 1500 (b); spin rate 4.56 kHz (a) and 4.83 kHz (b).

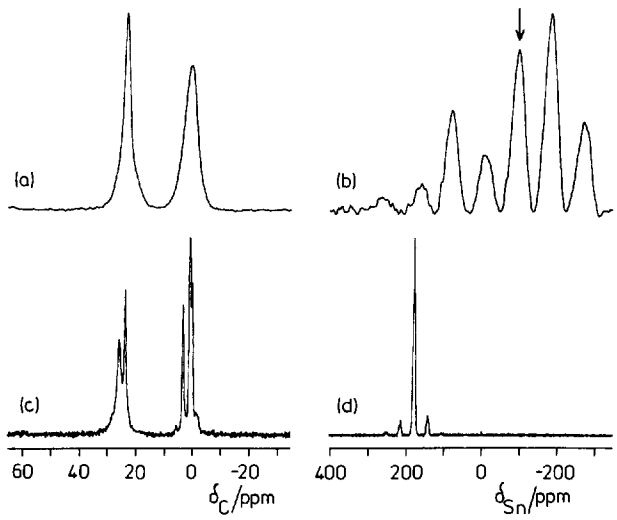

Fig. 5. CPMAS spectra of $\{Me_2Sn(CH_2)_3SnMe_2\}_2Mo(CN)_8$, **2**, and the corresponding free spacer precursor $ClMe_2Sn(CH_2)_3SnMe_2Cl$, **6**: (a) ^{13}C of **2** (at expanded scale, CH_2 and CH_3 regions only); (b) ^{119}Sn of **2**; (c) ^{13}C of **6**; (d) ^{119}Sn of **6**. The centre band for (b) is indicated by a vertical arrow. Spectrometer operating conditions for (b), (c) and (d) respectively: contact time 10, 1 and 10 ms; recycle delay 1, 10 and 20 s; number of transients 35000, 84 and 92; spin rate 9.95, 4.42 and 4.12 kHz. See the caption to Fig. 4 for the conditions for (a).

^{119}Sn chemical shift of the free spacer is almost 300 ppm to high frequency of the ^{119}Sn singlet of **2**, in accordance with the expectation that the coordination number of all tin atoms changes from 4 (for **6**) to 5 (for **2**).

The ^{13}C spectrum of compound **1** containing the same dinuclear organotin spacer as **2** resembles the ^{13}C spectrum of **3** with the exception that at room temperature **1** displays two methylene resonances. These signals merge into one broad band below ca. −40 °C, but split into three singlets above ca. +80 °C. Moreover, the cyanide carbon resonance of **1** is very broad, probably owing to unresolved coupling to the adjacent quadrupolar ^{59}Co nucleus. The same is true in the case of all 'parent' systems of **1** involving one $\{Co(CN)_6\}$ building block. The most suitable representatives of the $[(R_3Sn)_3Co(CN)_6]$ family for comparison with **1** in view of its multinuclear solid-state magnetic resonance behaviour (^{13}C, ^{15}N, ^{59}Co, ^{119}Sn) are those with R = Et (**7**) and ^{n}Bu rather than Me, since the lattice of $[(Me_3Sn)_3Co(CN)_6]$ (**3**) was found to involve three crystallographically different Me_3Sn units and six non-equivalent CN groups [4]. As the rather complicated architecture of **3** is in fact partially reflected by its NMR spectra, the simpler spectra of the homologues with R = Et and ^{n}Bu should indicate, like those of **1**, a considerably simpler asymmetric unit. Most significant is the appearance of only one cyanide ^{15}N and one ^{119}Sn resonance.

The potential hybrid (or 'alloyed') system **1a** displays only one broad ^{59}Co resonance (like **1** and **3**), but two ^{119}Sn resonances (like **3**). While these NMR results as such would not lead to a convincing decision in favour of or against one distinct species, they appear compatible with the X-ray powder diffractogram, suggesting that pure **3** is most probably absent.

5. Discussion

The X-ray powder diagrams of **1** and **3**, and of **2** and **4**, respectively, differ significantly in that those of both **1** and **2** imply a simpler architecture than their Me_3Sn-containing 'parent' systems. The spectroscopic results (i.e. both the vibrational and solid-state NMR spectra) for **1** and **2** appear to be consistent with relatively high local symmetries of the $M(CN)_n$ ($n = 6$ or 8) and Me_3Sn building blocks of **3** and **4** respectively. In particular, the multinuclear CP MAS magnetic reso-

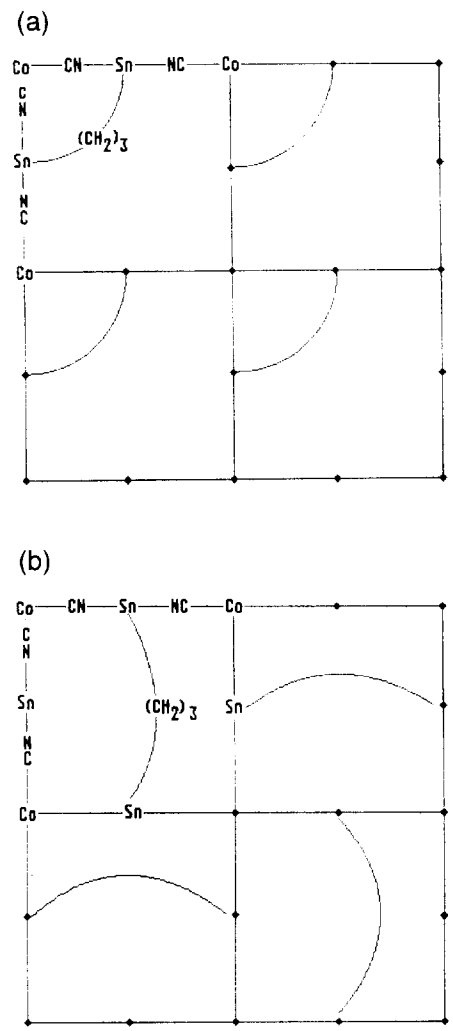

Fig. 6. Pairwise connection of two adjacent (a) and two non-adjacent (b) tin atoms in **1** (schematic view in two dimensions only).

nance spectra of **2** predict an asymmetric unit involving, like that of **4** [3], only one distinct CN group, as well as one Sn atom and, at most, three non-equivalent aliphatic C atoms. The asymmetric unit to be expected for **1** should be even simpler than that known for **3** [1] in that none of the chemically different atoms (i.e. cyanide C and N, α- and β-methylene C, methyl C, Sn) experience a variety of environments.

Making use of simple structural models based on those of **3** and **4** in which at least all d-transition metal atoms (i.e. Co or Mo) would adopt their crystallographically determined positions, it turns out to be impossible to arrive at the NMR spectroscopically predicted, surprisingly simple asymmetric units for **1** and **2**, even after exhaustive but unsatisfactory attempts to distribute all $-(CH_2)_3-$ linkages between structurally suitable pairs of $CNSnMe_2$ fragments. A corresponding result was obtained when the Co atoms of **1** were tentatively assumed to occupy the positions of a cubic face-centred lattice (ideal 'Super-Prussian Blue' system) built up of three identical, linear $\{CO-CN-Sn-NC\}_\infty$ chains (along each of the three Cartesian coordinates). Obviously, the rather long 'Co · · · Co distance' of at least 10 Å will preclude bridging of two non-adjacent tin atoms (Fig. 6).

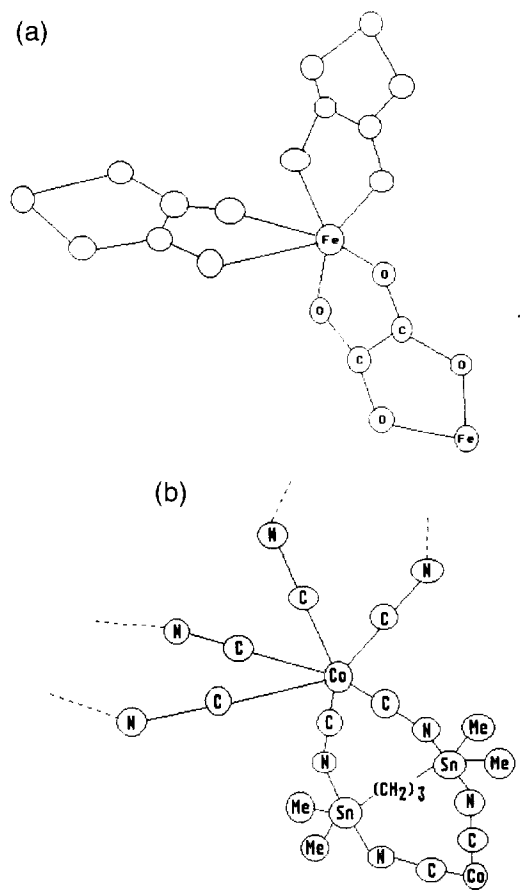

Fig. 7. (a) Coordination of Fe^{2+} in $^3_\infty[Fe_2(C_2O_4)_3^{2-}]$ according to Ref. [10]; (b) possible coordination of Co^{3+} in **1** anticipating a three-connected framework.

For the moment, however, it cannot be ruled out that the somewhat more pronounced broadening of the NMR signals for **1** and **2** (as compared with the spectral features of their 'parent' systems) may account for just moderately varying, non-equivalent environments of the difficult nuclei in question. We wish to point out here briefly that for **1** in principle another structural approach might appear feasible. In close analogy to the recently reported [10] three-connected, three-dimensional anionic framework: $^3_\infty[Fe^{II}_2\mu\text{-}(C_2O_4)_3]^{2-}$ (Fig. 7(a)) a corresponding 3D-network is imaginable in which each oxalate bridge is replaced by an $[\{Me_2Sn(NC)_2\}_2(CH_2)_3]^{2-}$ dianion (Fig. 7(b)). With C–Co–C′ angles of 90° and Co–C–N angles of 180°, the C–N–Sn angle of this bridge would then have to decrease down to 135°, with an Sn · · · Sn′ distance of ca. 4.3 Å. While in the structure of **3** a C–N–Sn angle of 134° is one of the most acute ones so far detected [4], a non-bonding Sn · · · Sn′ distance of even less than 4.2 Å has recently been found in a derivative of **6** [8]. This three-connected structural model would, however, require a larger formula volume than e.g. the six-connected framework of **3**, which expectation is not fulfilled by the comparatively small density-based formula volume of **1** (vide supra).

Corresponding structural considerations of **2** would be based on a variety of four-connected networks. The most symmetrical, and most spacious one, involving a diamondoid framework, should, however, require a strictly cubic $Mo(CN)_8$ arrangement and would thus be expected to be paramagnetic.

6. Experimental section

The dinuclear organotin compound $ClMe_2Sn(CH_2)_3SnMe_2Cl$ (**6**) was prepared following mostly Ref. [7]. Accordingly, the precursor of **6**, $MeSn(CH_2)_3SnMe_3$, was obtained as a colourless, clear liquid (yield 61%), provided that during this preparation the decomposition of hexamethyldistannane was controlled carefully, monitored by ^1H NMR. Even without distillation, our final ^1H NMR data compared well with those published [8]. Found ($CDCl_3$): δ 0.04 ppm, s, 18H, $^2J(^{119}Sn,^1H) = 51$ Hz (CH_3); δ 0.85 ppm, t, 4H (α-CH_2); δ 1.72 ppm, q, 2H (β-CH_2). In contrast to Refs. [7,8], the mixture of **6** and Me_3SnCl resulting from the subsequent step was not recrystallized. Instead, all Me_3SnCl was successfully removed, and recovered for further use, by vacuum sublimation at room temperature. The dirty-white residue was then sublimed in vacuo at 110 °C, affording after resublimation white, polycrystalline **6** (m.p. 81 °C; final yield 65%). Anal. Found: C, 20.84; H, 4.39. $C_7H_{18}Cl_2Sn_2$ Calc.: C,

20.48; H, 4.42% (no data in Refs. [7,8]). Again, the ^{1}H NMR spectrum compares well with the published one. Found ($CDCl_3$): δ 0.69 ppm, s, 12H, $^2J(^{119}Sn,^1H)$ = 54 Hz (CH_3); δ 1.42 ppm, t, 4H, $^2J(^{119}Sn,^1H)$ = ca. 60 Hz (α-CH_2); δ 2.11 ppm, q, 2H, $^3J(^{119}Sn,^1H)$ = ca. 66 Hz (β-CH_2). ^{1}H NMR in neat D_2O: δ 9.07 ppm, s, 12H, $^2J(^{119}Sn,^1H)$ = 44 Hz (CH_3); δ 5.59 ppm, t, 4H, $^2J(^{119}Sn,^1H)$ = 62 Hz (α-CH); δ 6.28 ppm, quint, 2H, $^3J(^{119}Sn,^1H)$ = 68 Hz (β-CH_2). ^{1}H NMR in D_2O/NaOD: δ 0.53, s, 12H, $^2J(^{119}Sn,^1H)$ = 65 Hz (CH_3); δ 1.37 ppm, t, 4H, $^2J(^{119}Sn,^1H)$ = 64 Hz (α-CH_2); δ 2.16 ppm, quin, 2H, $^3J(^{119}Sn,^1H)$ = ca. 104 Hz (β-CH_2).

Preparation of $[\{Me_2Sn(CH_2)_3SnMe_2\}_{1.5}Co(CN)_6]$ (**1**): during 10 min, an almost saturated aqueous solution of 4.25 g (10.4 mmol) of **6** was dropped under stirring into an almost saturated aqueous solution of 2.29 g (6.9 mmol) of $K_3[Co(CN)_6]$. After filtration and drying in vacuo, 4.72 g (6.4 mmol) of pure **1** was isolated (yield 92.8%). Anal. Found: C, 26.98; H, 3.67; N, 11.18. $C_{16.5}H_{27}N_6CoSn_3$ Calc.: C, 27.35; H, 3.76; N, 11.60%. Decomposition temperature ca. 315 °C (colour change via grey to black). ^{1}H NMR in D_2O/NaOD: δ 0.22 ppm, s, 12H, $^2J(^{119}Sn,^1H)$ = 63 Hz (CH_3); δ 1.07 ppm, t, 4H, $^2J(^{119}Sn,^1H)$ = 61 Hz (α-CH_2); δ 1.87 ppm, quint, 2H, $^3J(^{119}Sn,^1H)$ = 85 Hz (β-CH_2).

Polymer **3**, $[(Me_3Sn)_3Co(CN)_6]$, was prepared as described in Ref. [4], and polymer **1a**, $[(Me_3Sn)\{Me_3Sn(CH_2)_3SnMe_2\}Co(CN)_6]$ correspondingly by adding an aqueous solution of Me_3SnCl and **6** (1:1) to an aqueous solution of the corresponding equivalent of $K_3[Co(CN)_6]$. Yield 94%. Anal. Found: C, 26.54; H, 3.77; N, 11.50. $C_{16}H_{27}N_6CoSn_3$ Calc.: C, 26.79; H, 3.79; N, 11.69%. ^{1}H NMR (D_2O/NaOD): δ 0.61 ppm, s (broad, unsymm.), 21H (CH_3); δ 1.23 ppm, t, 4H (CH_2); δ 2.08 ppm, quin, 2H (CH_2). The infrared spectrum of **1a** equals strongly that of **1** (Table 1).

Polymer **2**, $[\{Me_2Sn(CH_2)_3SnMe_2\}_2Mo(CN)_8]$, was prepared as for **1** from 260 mg (0.63 mmol) of $K_4[Mo(CN)_8] \cdot 2H_2O$. Here, the solution of the latter was added to the solution of the former. Yield 220 mg (0.22 mmol = 74%). Anal. Found: C, 27.01; H, 4.47; N, 11.83. $C_{22}H_{36}N_8MoSn_4$ Calc.: C, 26.87; H, 3.69; N, 11.39%. Colour change towards black at 288 °C.

The polymers **4** and **5**, $[(Me_3Sn)_4M(CN)_8]$ with M = Mo and W, respectively, were obtained by adding dropwise, under an atmosphere of pure N_2, concentrated aqueous solutions of $K_4[M(CN)_8] \cdot 2H_2O$ to the clear aqueous solution of Me_3SnCl in the molar ratio 1:4. The spontaneously formed yellow precipitates were washed with N_2-conditioned H_2O and dried in vacuo. Anal. Found for **4**: C, 24.77; H, 3.85; N, 10.57; Mo, 10.13; Sn, 49.66. $C_{20}H_{36}N_8MoSn_4$ Calc.: C, 25.03; H, 3.75; N, 11.68; Mo, 10.01; Sn, 49.52%. Anal. Found for **5**: C, 21.29; H, 3.58; N, 8.72. $C_{20}H_{36}N_8WSn_4$ Calc.: C, 22.93; H, 3.44; N, 10.07%.

For pyknometric density measurements, dioxane had turned out to be optimal out of a series of different solvents examined. X-ray powder diffractograms were obtained on a Philips PW 1050 instrument (with Cu Kα, Ni filter), and infrared spectra on a Perkin Elmer (FT) IR 1720 spectrometer. Raman spectroscopy was carried out on a Jobin Yvon instrument Ramanov U-1000. Either a Varian Gemini -200 BB or a Bruker AM 360 spectrometer was used for the ^{1}H solution NMR studies.

The ^{13}C, ^{119}Sn, ^{15}N and ^{59}Co solid-state NMR spectra were recorded using Varian (VXR 300 for **4**, **5** and **6**, Unity Plus 300 for all other samples) spectrometers at frequencies of 75.4, 111.9, 30.4 and 71.1 MHz respectively. A cross-polarisation experiment with high-power ^{1}H decoupling was used for all spectra except ^{59}Co. All of the ^{13}C and ^{15}N spectra, and the ^{119}Sn spectrum of **6**, were recorded using a Doty Scientific probe with 7 mm o.d. rotors at spin rates of 4 to 5 kHz. All other ^{119}Sn spectra were recorded using a Doty Scientific probe with 5 mm o.d. rotors at spin rates of ca. 10 to 12 kHz. Recycle delays of 1 or 2 s were used for all samples except **6**, where longer times of 10 s for the ^{13}C and 20 s for the ^{119}Sn spectra were used. Contact times of 1 to 10 ms were used for all samples. Cobalt-59 spectra were obtained by direct polarisation using the 7 mm o.d. rotors spinning at 4 to 5 kHz. Pulse angles of ca. 25° with recycle delays from 0.5 to 1.0 s were utilized. Chemical shifts are reported, with the high-frequency positive convention, in ppm relative to the signals for $SiMe_4$, $SnMe_4$ and NH_4NO_3 (nitrate line), for ^{13}C, ^{119}Sn and ^{15}N respectively.

Acknowledgements

R.D.F. and J.-U.S. gratefully appreciate financial support by the Deutsche Forschungsgemeinschaft (Program "Nanoporous Crystals"), and R.E. would like to express his deep gratitude to the research team at Durham for their hospitality. The extensive CP MAS NMR work was supported by the UK EPSRC (through the National Solid-State NMR Service based at Durham).

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