

# Towards organometallic zeolites: spontaneous self-assembly of $\text{Et}_3\text{SnCN}$ , $\text{CuCN}$ and $(^n\text{Bu}_4\text{N})\text{CN}$ to supramolecular $[(^n\text{Bu}_4\text{N})(\text{Et}_3\text{Sn})_2\text{Cu}(\text{CN})_4]$

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(Received February 9, 1994)

## Abstract

Spontaneous self-assembly of  $\text{Et}_3\text{Sn}^+$ ,  $^n\text{Bu}_4\text{N}^+$  and  $[\text{Cu}(\text{CN})_4]^{3-}$  ions in  $\text{H}_2\text{O}$  affords white, crystalline  $[(^n\text{Bu}_4\text{N})(\text{Et}_3\text{Sn})_2\text{Cu}(\text{CN})_4]_\infty$  (7). A single-crystal X-ray study has confirmed the formation of a negatively charged, three-dimensional host framework with wide and parallel, interior channels occupied by well-ordered  $^n\text{Bu}_4\text{N}^+$  guest cations. 7: Tetragonal I-lattice,  $I4_322$ ;  $a$ ,  $b = 14.360(2)$ ,  $c = 40.003(6)$  Å; cell volume =  $8249(2)$  Å<sup>3</sup>,  $Z = 8$ ;  $wR2 = 0.1145$ ;  $wR2'$  (all data) = 0.1355. The title compound has, moreover, been characterized by IR/Raman ( $\nu(\text{CN})$ ) and MAS solid-state NMR spectroscopy (<sup>13</sup>C, <sup>119</sup>Sn). The NMR features are consistent with requirements based on the asymmetric unit. Even modest variations of the organic groups belonging to the 3D-framework, and of the template,  $\text{R}_4\text{N}^+$ , respectively, have been shown to afford 'derailed' assemblies of distinctly different stoichiometries, and/or spectroscopic properties, from  $[(\text{R}_4\text{N})(\text{R}'_3\text{Sn})_2\text{Cu}(\text{CN})_4]$ .

**Key words:** Tin; Copper; Cyanide; Polymer; Nuclear magnetic resonance; Crystal structure

## 1. Introduction

Even rather simple  $\text{AB}_2$  systems like  $\text{Cu}_2\text{O}$  or  $\text{M}(\text{CN})_2$  ( $\text{M} = \text{Zn}, \text{Cd}$ ) are known to prefer a comparatively compact, "super-diamondoid" lattice which consists of two individual, ideally interpenetrating, diamond-like 3D frameworks [1,2]. Accordingly, recent efforts to verify more complex, supramolecular aggregates of potentially "diamondoid" architecture in which two adjacent tetrahedral centres would be separated from each other by more than 5 Å (*e.g.* for  $\text{Zn}(\text{CN})_2$ ,  $D = 5.11$  Å [2]) have most frequently also led to "super-diamondoid" lattices built up of at least two, and up to now, maximally seven [3] equivalent, interpenetrating subframeworks [4–6\*]. Obviously, the relatively large volume of each "empty", adamantane-like unit (*c.f.* Fig. 1) within a diamondoid lattice is for  $D \geq 3.0$  Å thermodynamically disfavoured [6]. The recently described organometallic aggregate:  $[(\text{Me}_3\text{Sn})_2\text{MoO}_4]_\infty$  (1) ( $D = 7.4$  Å), circumvents, on the other hand, the

formation of a "super-diamondoid" lattice adopting instead a more compact, layered structure with, nevertheless, tetrahedral  $\text{MoO}_4$  units and non-linear  $\{\text{Mo}-\text{O}-\text{Sn}-\text{O}\}_\infty$  chains [7].

The most straightforward strategy to reduce, or even to fully exclude, lattice interpenetration makes use of encapsulation of uncharged or ionic guests (*i.e.* of "templates") into the adamantanoid cavities [2,4,5]. Examples of such diamond-like frameworks hosting only one, sterically appropriate, guest component range from  $\text{KH}_2\text{PO}_4$  [8\*] to *e.g.*  $[\text{Cd}(\text{CN})_2 \cdot \text{CMe}_4]$  (uncharged guest;  $D = \text{ca. } 5.5$  Å [9]) and  $[(\text{NMe}_4)\text{Cu}^{\text{I}}\text{Zn}^{\text{II}}(\text{CN})_4]$  (2), respectively (cationic guest;  $D = 5.03$  Å [2]). One fairly outstanding example both in view of the magnitude of  $D$  (8.85 Å) and the actual number of guest molecules is the "composite"  $[\text{Cu}^{\text{I}}(4,4',4'',4'''\text{-tetracyanotetraphenylmethane})\text{BF}_4 \cdot 7,7\text{C}_6\text{H}_5\text{NO}_2]$  (3) with at least 7,7 nitrobenzene molecules along with one  $\text{BF}_4^-$  anion per formula unit [2,4]. The main objective

\* Reference number with asterisk indicates a note in the list of references.

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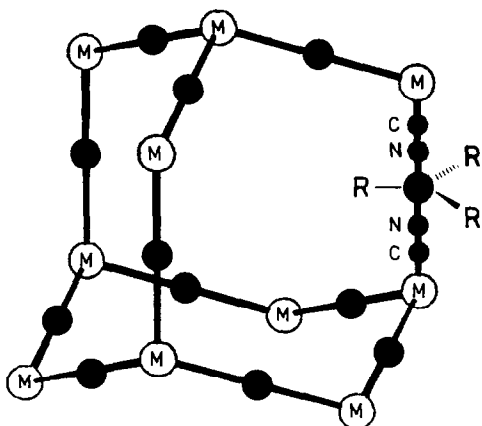


Fig. 1. Schematic view of a hypothetical adamantane-like  $M_{10}(R_3E(CN)_2)_{12}$  cage.

of the present contribution has been to investigate whether appropriately templated organometallic host-guest systems similar to 1 of the type:  $[G^+(R_3E^{IV})_2Cu^I(CN)_4]_\infty$  with  $\{Cu-CN-E-NC\}_\infty$  chains and  $D$ -values around  $10 \text{ \AA}$  ( $G^+$  = template,  $E = Sn$  or  $Pb$ ) may, due to appropriately dimensioned  $R$  and  $G^+$ , respectively, likewise be forced to crystallize as non-interpenetrating, three-dimensional networks.

Our recent exploration of corresponding aggregates involving  $R_3E^+$  and  $M(CN)_6^{m-}$  ions ( $M = Fe, Co$  etc.;  $m = 3$  or  $4$ ) as building blocks, has shown that 3D-frameworks of infinite, albeit frequently non-linear  $\{M-CN-E-NC\}_\infty$  chains with  $M \cdots M$  distances (*i.e.*  $D$ ) of  $\geq 10 \text{ \AA}$  are formed whenever both  $R_3E^+$  and  $M(CN)_6^{m-}$  ions come together in aqueous solution [10].

## 2. Preparation of $[(^nBu_4N)(Et_3Sn)_2Cu(CN)_4]$ (7)

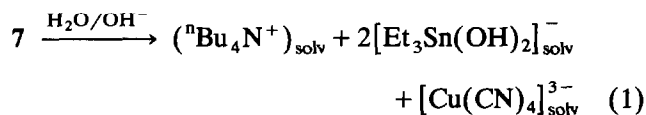
In Fig. 1 the architecture of one adamantanoid building block out of an infinitely extended, assumedly diamondoid,  $[(R_3Sn)_2M(CN)_4^q]_\infty$  framework ( $q = 0$  or  $1$ ) is shown. Obviously, the large volume of each "empty"  $M_{10}$  cage strongly advocates a preference of either multi-connected, "super-diamondoid" networks or of alternative "structural derailments" (as *e.g.* in the case of 1). Not too surprisingly, a guest-free ( $q = 0$ ) product  $[(Me_3Sn)_2Zn(CN)_4]$  (4), was not obtained; re-

action of  $Me_3SnCl$  and  $K_2[Zn(CN)_4]$  (2:1) in aqueous solution or liquid  $NH_3$  affords instead a precipitate of the unforeseen composition  $[(Me_3Sn)Zn(CN)_3]$  (5) (*vide infra* [11]). Moreover, attempts to arrive at a host-guest (*i.e.* a templated) system,  $[G^+(R_3Sn)_2Cu(CN)_4]$ , with  $G^+ = ^nBu_4N^+$  and  $R = Me$ , did not lead to a product of the envisaged stoichiometry either; instead, a similar polymeric precipitate,  $[(^nBu_4N)(Me_3Sn)Cu_2(CN)_4]$  (6), was isolated. However, after replacement of all methyl ligands by slightly more space-demanding ethyl groups, the first product 7 of the desired elemental composition (*i.e.*  $Sn/Cu = 2:1$ ) was obtained (Scheme 1).

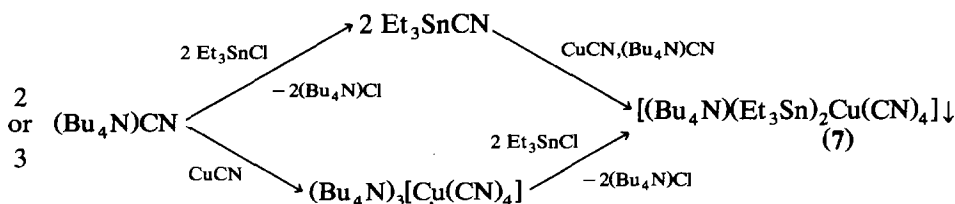
As  $Et_3SnCN$  may, like  $Me_3SnCN$  [11], be obtained from the corresponding halides and  $CN^-$  ions even in aqueous solution, route (a) of Scheme 1 is viable either in two separate, subsequent steps or in a one-pot-reaction (from  $Et_3SnCl$ ,  $(^nBu_4N)CN$  and  $CuCN$ ).

The second step of route (a) may be considered as a heterogeneous "remodelling" reaction of two already polymeric educts ( $Et_3SnCN$  and  $CuCN$ ) and one genuine salt into the unique, "supramolecular" aggregate 7. Generally, route (b) whose final step involves only soluble educts affords 7 in higher yields and better analytical purity than route (a) as a white, polycrystalline solid. Addition of a concentrated solution of  $Et_3SnCl$  in acetone (instead of  $H_2O$ ) to a dilute aqueous solution of  $(^nBu_4N)_3[Cu(CN)_4]$  leads after several days to well-shaped crystals of 7 of satisfactory X-ray quality.

While solid 7 is completely air-stable (decomp. temp.  $235^\circ C$ ), its preparation should be carried out under an inert atmosphere. Thus, even in the presence of little  $CO_2$  (as commonly present in air), crystals of both 7 and a second product could be distinguished. The by-product turned out to be (polymeric)  $(Et_3Sn)_2CO_3$  [12\*]. In alkaline  $H_2O$  ( $pH \geq 8$ ), 7 dissolves quantitatively, like the majority of polymeric  $R_3Sn^{IV}$  derivatives (eqn. 1):



$^1H$  NMR spectroscopy of 7 dissolved in alkaline  $D_2O$  (prepared by dissolving a little  $Na$  in pure  $D_2O$ ; *cf.* eqn. (1)) has turned out to be a helpful technique to



Scheme 1. Route (a)/(b): upper/lower equation.

TABLE 1.  $\nu(\text{CN})$  vibrations (infrared and Raman; maxima in  $\text{cm}^{-1}$ ) of several cyanides of Zn, Co and Sn

Sample	IR	Ra
$\text{Zn}(\text{CN})_2$	2215	2218
$(\text{Et}_4\text{N})_2[\text{Zn}(\text{CN})_4]$	2150	2136
$[(\text{Me}_4\text{N})\text{Zn}^{\text{II}}\text{Cu}^{\text{I}}(\text{CN})_4]$	2130	2132, 2156
$\text{Me}_3\text{SnCN}$	2160	2160
$\text{Ph}_3\text{SnCN}$	2155 [15a]	2165
$(\text{Me}_3\text{Sn})\text{Zn}(\text{CN})_3$ ( <b>5</b> )	2160, 2180, 2210	2166, 2183, 2214
$(\text{Ph}_3\text{Sn})_2\text{Zn}(\text{CN})_4$ ( <b>8</b> )	2160, 2200	2163
$[(\text{Ph}_3\text{Sn})_3\text{Co}(\text{CN})_6]$ ( <b>9</b> )	2152	2166, 2184
$[(\text{Me}_3\text{Sn})_3\text{Co}(\text{CN})_6]$	2158	2180, 2195 [10c]

easily determine the relative abundance of (Sn-bonded) ethyl and (N-bonded) n-butyl protons, and hence the actual ratio,  $[\text{C}_2\text{H}_5]/[\text{C}_4\text{H}_9]$ .

Following route (b) of Scheme 1, some additional host-guest aggregates could be prepared [13] whose C/H/N analyses suggest a formation of  $[\text{A}(\text{R}_3\text{Sn})_2\text{Cu}(\text{CN})_4]$  systems (e.g. with  $\text{A} = {}^n\text{Bu}_4\text{N}$  and  $\text{R} = {}^n\text{Bu}$ , or with  $\text{A} = \{\text{K} \cdot \text{cryptand}\}$  and  $\text{R} = \text{Me}, \text{Et}, {}^n\text{Bu}, \text{Ph}$ ). Since a number of them are even likely to crystallize, their detailed description is deferred to the advent of some crystallographic results.

As another guest-free species, a precipitate analysing as  $(\text{Ph}_3\text{Sn})_2\text{Zn}(\text{CN})_4$  (**8**) was obtained from  $\text{Ph}_3\text{SnClO}_4$  and  $(\text{Et}_4\text{N})_2[\text{Zn}(\text{CN})_4]$  (2:1) and characterized mainly by vibrational and solid-state NMR spectroscopy (*vide infra*).

### 3. Vibrational spectroscopy, focusing on the $\nu(\text{CN})$ vibrations

In Tables 1 and 2, the experimental  $\nu(\text{CN})$  frequencies of a number of complex zinc(II) and copper(I) cyanides, respectively, of some relevance for the identification and characterization of related polymers with bridging cyanide ligands, are listed. Evidently, the  $\nu(\text{CN})$  frequencies of the  $[\text{Zn}(\text{CN})_4]^{2-}$  anion with exclusively terminal cyanide ligands not only exceed those

of the corresponding  $[\text{Cu}(\text{CN})_4]^{3-}$  unit, but, moreover, of several copper(I) cyanides with bridging CN ligands. Consequently, the rather low  $\nu(\text{CN})$  frequencies of the diamondoid polymer **2** [2] (which have not been reported in [2]) clearly indicate the presence of bridges exclusively of the type,  $\text{Cu}-\text{CN} \rightarrow \text{Zn}$ . This notable information which is not immediately available from the crystallographic results [2] has also been deduced recently from a CP MAS solid-state NMR study involving the nuclei  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{65}\text{Cu}$  [14]. Product **5** (*vide supra*) displays not only more IR- and Ra-active  $\nu(\text{CN})$  bands than expected for a regular diamondoid system (like e.g. **2**), but also one absorption more (both in IR and Ra) than for a simple 1:2 mixture of  $\text{Zn}(\text{CN})_2$  and  $\text{Me}_3\text{SnCN}$ . Pure  $\text{Me}_3\text{SnCN}$  may be removed from **5** incompletely either by vacuum sublimation (*ca.* 200°C; neat  $\text{Me}_3\text{SnCN}$  already sublimates at 80°C) or by extraction with EtOH [11], whereafter only the  $\nu(\text{CN})$  band typical of pure  $\text{Me}_3\text{SnCN}$  is absent in the IR spectrum of the residue. Similarly, the spectra of product **8**, whose elemental analysis would match a guest-free “(super-)diamondoid” system (*cf.* Fig. 1), display exclusively  $\nu(\text{CN})$  bands at wave numbers almost coincident with those of pure  $\text{Ph}_3\text{SnCN}$  [15]. The last two entries of Table 1 suggest that, on the other hand, the probably genuine 3D-polymer **9** [16] gives rise to a total of three  $\nu(\text{CN})$  bands whose wave numbers differ significantly from those of  $\text{Ph}_3\text{SnCN}$  and (polymeric)  $\text{Co}(\text{CN})_3$  (*ca.* 2200  $\text{cm}^{-1}$  [17\*]), but approach closely those of its structurally well-understood homologue  $[(\text{Me}_3\text{Sn})_3\text{Co}(\text{CN})_6]$  [10c].

The data of Table 2 indicate that the  $\nu(\text{CN})$  frequencies of the anticipated  $\text{Cu}-\text{CN} \rightarrow \text{Sn}$  bridges in **7** and several related systems lie quite close to those of the “free”  $[\text{Cu}(\text{CN})_4]^{3-}$  ion, while polymers with  $\text{Cu}-\text{CN} \rightarrow \text{Cu}$  bridges like  $\text{CuCN}$  and  $\text{K}[\text{Cu}(\text{CN})_2]$  display  $\nu(\text{CN})$  values at least 40  $\text{cm}^{-1}$  higher. Even the  $\nu(\text{CN})$  data of compound **2** (Table 1) exceed those of **7** significantly, suggesting comparatively weak  $\text{CN} \rightarrow \text{Sn}$  donor bonds in **7**. Somewhat surprisingly, the  $\nu(\text{CN})$  spectra of **7** and the “derailment” product **6** do not differ

TABLE 2.  $\nu(\text{CN})$  vibrations (infrared and Raman; maxima in  $\text{cm}^{-1}$ ) of several  $\text{Cu}^{\text{I}}$  cyanides.

Sample	IR	Ra
$\text{CuCN}$	2155	2160
$\text{K}[\text{Cu}(\text{CN})_2]$	2085, 2105 [18]	2091, 2112 [18]
$({}^n\text{Bu}_4\text{N})[\text{Cu}(\text{CN})_2]$	2190, 2210 [19]	Not determined
$\text{K}_3[\text{Cu}(\text{CN})_4]$	2076 (soln.)	2081, 2093 [18b,20]
$(\text{Et}_4\text{N})_3[\text{Cu}(\text{CN})_4]$	2085	Ra silent
$[\text{BCu}(\text{CN})_4]$	2135sh, 2165 [21]	
$[({}^n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})\text{Cu}_2(\text{CN})_4]$ ( <b>6</b> )	2112	2117, 2136, 2173
$[({}^n\text{Bu}_4\text{N})(\text{Et}_3\text{Sn})_2\text{Cu}(\text{CN})_4]$ ( <b>7</b> )	2104br	2118, 2131br

TABLE 3. Summary of crystal data and details of data collection and refinement for 7

Empirical formula	C <sub>32</sub> H <sub>66</sub> CuN <sub>5</sub> Sn <sub>2</sub>
Formula weight	821.82
Temperature (K)	293 (2)
Crystal system	Tetragonal-I-Lattice
Space group	I4 <sub>3</sub> 22
Unit cell dimensions	
<i>a</i> , <i>b</i> (Å)	14.360(2)
<i>c</i> (Å)	40.003(6)
α, β, γ (°)	90
Volume (Å <sup>3</sup> )	8249(2)
<i>Z</i>	8
Density (calcd.) (mg m <sup>-3</sup> )	1.323
Radiation (Mo-Kα) (Å)	0.71073
μ (mm <sup>-1</sup> )	1.737
<i>F</i> (000)	3376
θ-range (°)	2.5–25.00
Reflections collected	4147
Independent reflections	3650 ( <i>R</i> (int) = 0.0319)
Data/restraints/parameters	3648/21/227
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.136
Final <i>R</i> indices [ <i>I</i> > σ2( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0594, <i>wR</i> <sub>2</sub> = 0.1145
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0995, <i>wR</i> <sub>2</sub> = 0.1355
Absolute structure parameter	0.01(6)
Extinction coefficient	0.00161(10)
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.286 and -0.367
Diffractometer	Syntex P2 <sub>1</sub>

considerably. The tributyltin homologue of 7 displays  $\nu(\text{CN})$  spectra quite similar to those of 7 although the greater space demand of its *n*-butyl ligands might lead to a different crystal structure. Interestingly, the solid material [BCu(CN)<sub>4</sub>] which has been assumed to adopt a Zn(CN)<sub>2</sub>-like super-diamondoid structure [21], gives rise, in sharp contrast to *e.g.* 2 and 7, to at least two IR-active  $\nu(\text{CN})$  bands, suggesting both Cu–CN → B and B–CN → Cu bridges and, hence, distorted E(CN)<sub>4</sub> tetrahedra (E = Cu or B).

#### 4. Crystal structure of [(<sup>n</sup>Bu<sub>4</sub>N)(Et<sub>3</sub>Sn)<sub>2</sub>Cu(CN)<sub>4</sub>] (7)

A carefully selected crystal of 7 was subjected successfully to a complete crystallographic X-ray study at room temperature. Parameters of major relevance for this study are collected in Table 3. Figure 2 presents a view of the unit cell of 7. Due to the presence of <sup>n</sup>Bu<sub>4</sub>N<sup>+</sup> cations (not shown in Fig. 2), an obviously negatively charged, three-dimensional, {(Et<sub>3</sub>Sn)<sub>2</sub>Cu(CN)<sub>4</sub>}<sup>-</sup> framework is realized. The basic framework is, however, non-cubic and hence packed more compactly (*vide infra*) without any lattice interpenetration. Two non-equivalent, non-linear chains, A and B, of equal abundance, whose four-coordinate Cu atoms serve as

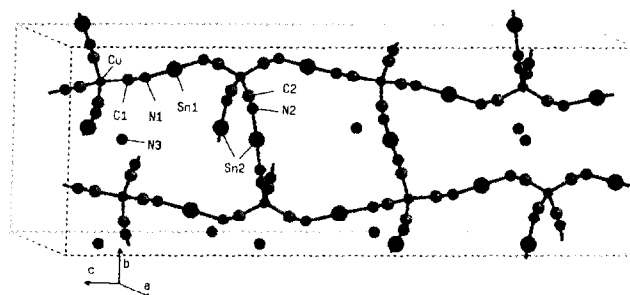
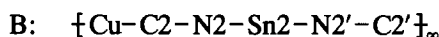
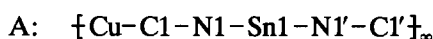


Fig. 2. Unit cell with atomic numbering scheme of 7. C<sub>2</sub>H<sub>5</sub> ligands and (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N (except N3) cations have been omitted for clarity.

crossover points of one type A and one type B chain, may be seen:



Selected interatomic distances and bond angles are listed in Table 4. While the C–N–Sn angles of both chains are substantially smaller than 180°, the corresponding C–Cu–C' angles are smaller and larger, respectively, than 109.5° (Table 4).

The site symmetry of the Cu atom is notably distorted (from *T<sub>d</sub>* to *C<sub>2v</sub>*) so that the lattice in total adopts tetragonal symmetry. This feature becomes more apparent when the structure is viewed along its *c*-axis. Then, the trace of each A-chain gives rise to the cluster-like pattern of atoms depicted in Fig. 3. These “clusters” are seen to be interlinked by the B-chains, giving rise to a tetragonal network as shown in Fig. 4. Note that in this perspective, *e.g.* all Sn2 and N3 atoms met by the dotted line on the bottom of Fig. 2 merge, in Figs. 3 and 4, to essentially one sphere (representing most frequently the uppermost Sn2 atom). The perspective of Fig. 5 where *c* is no longer strictly perpendicular to the paper plane helps to show that the strong tetragonal distortion of the initially envisioned

TABLE 4. Selected interatomic distances (Å) and bond angles (°) in crystalline 7 with e.s.d.s in parentheses

Sn(1)–N(1)	2.327(8)	C(1)–N(1)	1.129(10)
Sn(2)–N(2)	2.340(7)	C(2)–N(2)	1.144(9)
Cu(1)–C(1)	1.965(9)	N(3)–C(11)	1.528(10)
Cu(1)–C(2)	1.967(8)	N(3)–C(21)	1.535(10)
N(1)–Sn(1)–N(1)′	178.8(6)	C(11)–N(3)–C(11)	111.1(10)
N(2)–Sn(2)–N(2)′	178.0(4)	C(12)–C(11)–N(3)	116.1(7)
C(1)–N(1)–Sn(1)	163.9(10)	C(22)–C(21)–N(3)	114.6(7)
C(2)–N(2)–Sn(2)	149.3(7)	C(21)–N(3)–C(21)′	111.6(10)
C(1)–Cu(1)–C(2)	105.4(4)	C(1)′–Cu(1)–C(1)	106.0(6)
N(1)–C(1)–Cu(1)	173.9(9)	C(1)–Cu(1)–C(2)′	107.5(4)
N(2)–C(2)–Cu(1)	167.2(7)	C(2)′–Cu(1)–C(2)	123.8(4)

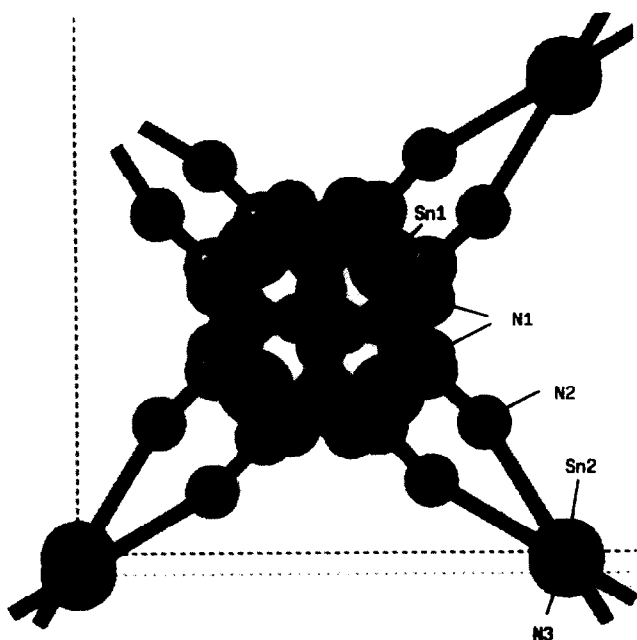


Fig. 3. Perspective of essentially one type-A chain of 7 ignoring the atoms N2, N3 and Sn2; view along  $c$  (green, Cu; red, Sn; blue, N; grey, C).  $C_2H_5$  and  $n-C_4H_9$  groups have been omitted for clarity.

diamondoid lattice leads, nevertheless, to a very open framework with straight, unusually wide channels parallel to  $c$ .

While the ethyl groups of both crystallographically different  $Et_3Sn$  units turn out to have high thermal

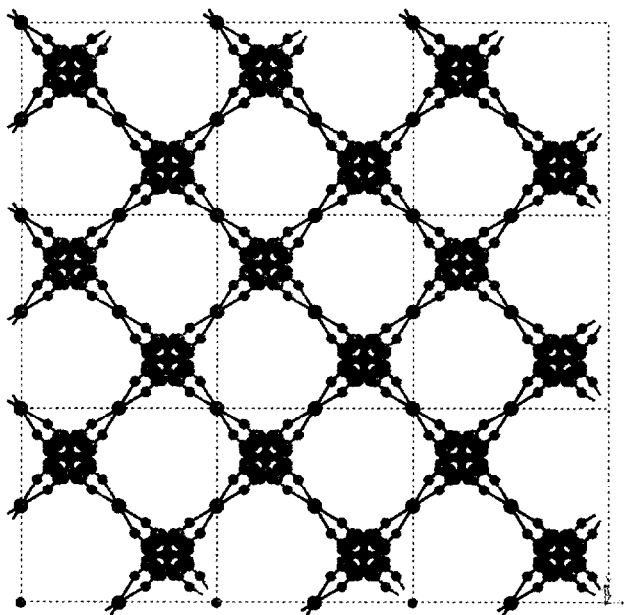


Fig. 4. View along  $c$  through the lattice of 7 (three unit cells). Ethyl and butyl groups are not shown.

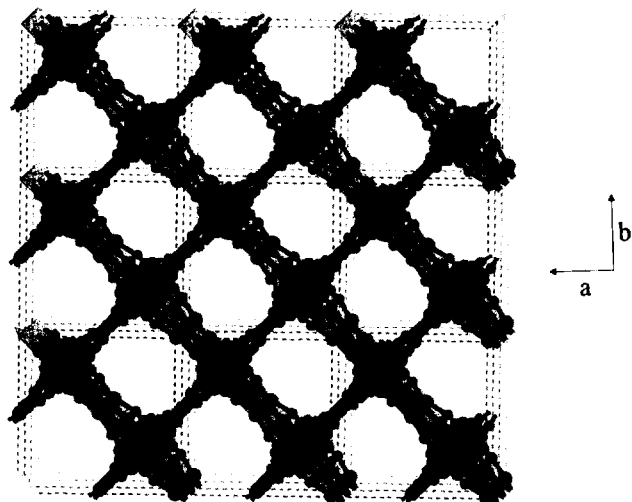


Fig. 5. Visualization of the wide, parallel channels of 7 (almost parallel to  $c$ ; see the text). Ethyl and butyl groups are not shown.

parameters, all carbon atoms of the  ${}^nBu_4N^+$  guest cation display practically unique positions. Thus, Fig. 6 illustrates that each quaternary N3 atom directs two of its  $n$ -butyl groups into one channel and the other two into an adjacent one [22\*]. Figure 6, moreover, demonstrates that the  ${}^nBu_4N^+$  cation behaves as an almost ideal space-filling template for the respective channels. Notable deviations of several bond angles of the  ${}^nBu_4N^+$  ion from  $109.5^\circ C$  (Table 4) indicate a somewhat flattened configuration, probably due to non-

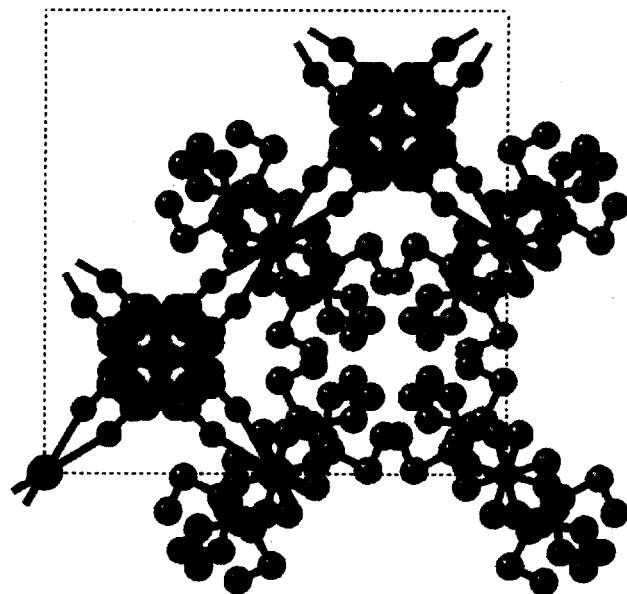


Fig. 6. Visualization of the  $n$ -butyl carbon atoms (of the  ${}^nBu_4N^+$  guest cations) in 7. Same view and colours as in Fig. 3; all ethyl carbon atoms are omitted.

negligible steric interaction with the Sn-bonded ethyl groups.

The  $\text{Cu}(\text{CN})_4$  unit of **7** displays not only non-tetrahedral C–Cu–C' angles (*vide supra*, Table 4), but also Cu–C distances notably elongated with respect to those of **2** (1.877 Å [2]) and  $\text{K}[\text{Cu}(\text{CN})_2]$  (1.916 and 1.922 Å [18]). A Cu–N distance of 2.052 has been reported for  $\text{K}[\text{Cu}(\text{CN})_2]$ . The presence of Sn–CN–Cu bridges in **7** may, nevertheless, be ruled out since various unusual spectroscopic effects to be expected in this case do not occur. The Cu–C2–N2 angle of 167.2(7)° of **7** which is even smaller than the smallest Cu–C–N angle reported for  $\text{K}[\text{Cu}(\text{CN})_2]$  (172.5° [18]) may also be considered as indicative of substantial steric constraints. The two Sn–N distances of about 2.33 Å are not uncommon for polymers built up of  $\{\text{M}-\text{CN}-\text{Sn}-\text{NC}\}$  chains with  $\text{M} = \text{Fe}$  or  $\text{Co}$  [10], as are the strongly reduced (from 180°) C–N–Sn angles. The two N–Sn–N' angles remain as usual close to 180°.

Although potentially diamondoid systems tend to undergo tetragonal distortions [3–5], the structure of the basic 3D-framework of **7** is unprecedented. The "space-filling interplay" of its ethyl and n-butyl groups is likely to cause a delicate balance of the structure actually observed involving numerous relatively unfavourable bond angles and distances, and less compact structural alternatives. The *D*-value of **7** (shortest intra-chain [23\*]  $\text{Cu} \cdots \text{Cu}$  distance) of 10.01 Å even exceeds that of **3** (*vide supra*) and is only shorter than in some aggregates with several hydrogen-bonded spacers [3,5].

## 5. Solid-state NMR spectroscopy

The  $^{119}\text{Sn}$  MAS NMR spectrum of **7** shows two centreband signals, at chemical shifts –114 and –136 ppm, each with a spinning sideband manifold covering a range of *ca.* 600 ppm, as is usual for trigonal bipyramidal tin with three equatorial alkyl groups and axial nitrogen atoms (of cyanide ligands). The higher-frequency signal has apparently a substantially higher intensity, but this may be a reflection of the experimental conditions: only a limited amount of sample was available and a large number of transients (57 000) was necessary, so that the recycle delay for the pulses was kept low (1 s) and the signals may be differentially saturated. The crystal structure predicts two  $^{119}\text{Sn}$  NMR signals of equal intensity. Both signals occur at lower frequencies than those of analogous polymers reported earlier [24], *viz.*  $[(\text{Et}_3\text{Sn})_3\text{Co}(\text{CN})_6]$ ,  $\delta(\text{Sn})$  –75 ppm, and  $[(\text{Et}_3\text{Sn})\text{Au}(\text{CN})_2]$ ,  $\delta(\text{Sn})$  –64 ppm. Since linear  $\{\text{Cu}-\text{CN}-\text{Sn}-\text{NC}-\text{Cu}\}$  chains are not found in **7**, one possible reason for the variation in  $\delta(\text{Sn})$  might be the higher negative charge of

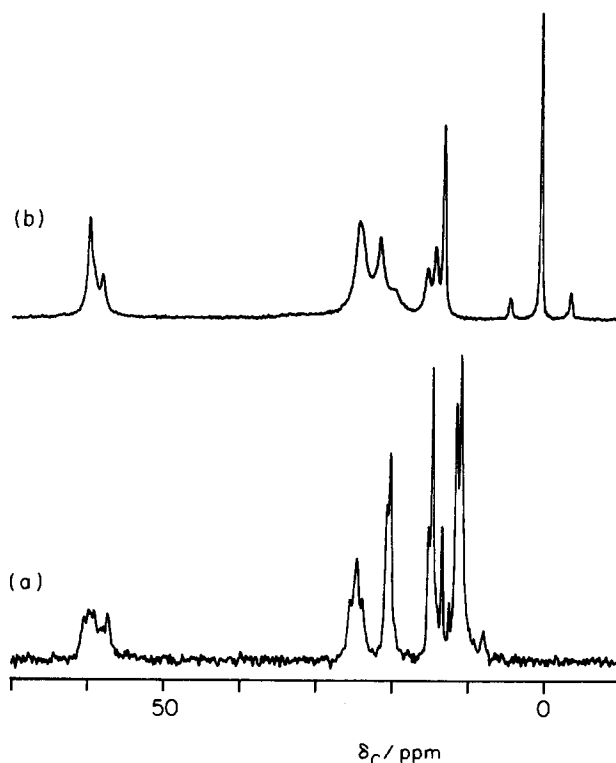


Fig. 7. Carbon-13 CPMAS spectra at 75.4 MHz of (a)  $[(^n\text{Bu}_4\text{N})(\text{Et}_3\text{Sn})_2\text{Cu}(\text{CN})_4]$  and (b)  $[(^n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})\text{Cu}_2(\text{CN})_4]$ . The cyanide resonances are omitted (off-scale). Experimental conditions: contact time 5 ms, recycle delay 1–0 s, number of transients 1000; spinning rate 4.5–4.8 kHz.

the  $\text{Cu}(\text{CN})_4^{3-}$  anion per  $\text{Et}_3\text{Sn}$  unit (*i.e.* –1.5 for **7**, as compared with –1.0 for the two other  $\text{Et}_3\text{Sn}$  derivatives). Correspondingly, the  $\delta(\text{Sn})$  values of the host-guest systems:  $[\text{A}(\text{Me}_3\text{Sn})_3\text{Fe}^{\text{II}}(\text{CN})_6]$  (*e.g.* for  $\text{A}^+ = (\text{C}_5\text{H}_5)_2\text{Co}^+$ ,  $\delta(\text{Sn})$  –139 and –189 ppm [25]) differ from those of  $[(\text{Me}_3\text{Sn})_3\text{Co}^{\text{III}}(\text{CN})_6]$  ( $\delta(\text{Sn})$  –88 and –118 ppm [10c,24]).

The crystallographic data give an asymmetric unit which contains two non-equivalent cyanide ligands, two butyl chains and five ethyl groups. However, the large temperature factors for the ethyl groups suggest substantial mobility, which is expected to reduce the complexity of the  $^{13}\text{C}$  NMR spectrum. The observed CPMAS spectrum (Fig. 7(a)) is consistent with this situation, although it is not possible at present to make definitive assignments. The spectrum is indeed complicated, and is confused by the expected proximity of  $\text{Et}_3\text{Sn}$  peaks to some of those for the butyl groups. However, there would appear to be substantially fewer of the former (in the region near  $\delta(\text{C})$  10 ppm) than the 10 expected on the basis of the X-ray results, so motional averaging is likely. Rapid internal rotation of equatorial trialkyl groups about an N–Sn–N axis in the solid state has now been well documented [26]. The

TABLE 5. Survey of  $\delta(^{119}\text{Sn})$  and  $\delta(^{13}\text{C})$  values of the title compound 7 and several related systems

Compound	$\delta_{\text{Sn}}$ (ppm)	$\delta_{\text{C}}$ (ppm) <sup>a</sup>
$(^n\text{Bu}_4\text{N})(\text{Et}_3\text{Sn})_2\text{Cu}(\text{CN})_4$ (7)	-114, -136 (1.6:1)	151
$(^n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})\text{Cu}_2(\text{CN})_4$ (6)	-166	157, 151, 139
$(\text{Me}_3\text{Sn})\text{Zn}(\text{CN})_3$ (5)	-66, -139	ca. 144; ca. 137 (complex)
$(\text{Ph}_3\text{Sn})_2\text{Zn}(\text{CN})_4$ (8)	-238	145, 144 (weak) <sup>b</sup>
$\text{Me}_3\text{SnCN}$	-143	135, 132 (2:1)
$\text{Zn}(\text{CN})_2$		142

<sup>a</sup> For the cyanide resonances. <sup>b</sup> Phenyl resonances at 139, 138, 137, 130 and 128 ppm.

cyanide  $^{13}\text{C}$  resonance of 7, not shown in Fig. 7(a), consists of a single broad band at  $\delta(\text{C}) -151$  ppm.

We have obtained solid-state spectra of a number of compounds relevant to the discussion of 7, and some of these results are reported in Table 5. The polymeric copper compound 6 gave a clean  $^{119}\text{Sn}$  MAS spectrum consisting of a single spinning sideband manifold, with the centreband at  $\delta(\text{Sn}) -166$  ppm (notably to lower frequency than those of 7). The  $^{13}\text{C}$  CPMAS spectrum (Fig. 7(b)) clearly showed the existence of a single type of methyl group for the  $\text{Me}_3\text{Sn}$  unit (presumably because of motional averaging), at  $\delta(\text{C}) 0.7$  ppm (with tin satellites). The rest of the  $^{13}\text{C}$  spectrum is more complex, indicating non-equivalence of some of the butyl groups. The cyanide region has three signals, probably due, in part, to second order effects arising from dipolar coupling to the quadrupolar  $^{14}\text{N}$  nucleus [25,26b].

The other "derailment" product, 5, gives rise to two  $^{119}\text{Sn}$  centrebands with an intensity ratio 1:1 with chemical shifts  $\delta(\text{Sn}) -66$  and  $-139$  ppm. The latter is very close to the shift for  $\text{Me}_3\text{SnCN}$ , supporting the speculation about the presence of relatively "free"  $\text{Me}_3\text{SnCN}$  moieties in 5 in addition to some "in-built"  $\text{Me}_3\text{Sn}$  (as deduced from the vibrational spectra, *vide supra*). Further evidence for this suggestion is obtained from the  $^{13}\text{C}$  chemical shifts for the cyanide groups of 5,  $\text{Zn}(\text{CN})_2$  and  $\text{Me}_3\text{SnCN}$  (see Table 5). The  $^{13}\text{C}$  spectrum of 5 contains two methyl signals, at  $\delta(\text{C}) 0.3$  and  $-1.6$  ppm.

The appearance of only one  $^{119}\text{Sn}$  centreband, one methyl  $^{13}\text{C}$  signal ( $\delta(\text{C}) -1.1$  ppm) and one cyanide carbon 2:1 doublet for neat  $\text{Me}_3\text{SnCN}$  supports the view that there are regular  $\text{Sn}-\text{CN}-\text{Sn}-\text{CN}$  chains with rapidly rotating  $\text{Me}_3\text{Sn}$  units in this compound. Note that no definite answer about the ordering of the Sn, C and N atoms within this 1D polymer is available from the X-ray study [27]. The second zinc-containing product, 8, gives a single  $^{119}\text{Sn}$  centreband, at  $\delta(\text{Sn}) -238$  ppm, with spinning sidebands spread over a smaller range (ca. 400 ppm) than for the other compounds reported here.

## 6. Experimental section

The title compound 7 ( $(^n\text{Bu}_4\text{N})(\text{Et}_3\text{Sn})_2\text{Cu}(\text{CN})_4$ ) precipitated, under a dry  $\text{N}_2$  atmosphere, as fine, colourless, needle-like crystals about 3 h after the addition of a solution of 1.2 g (5 mmol) of  $\text{Et}_3\text{SnCl}$  in ca. 30 ml of  $\text{H}_2\text{O}$  (plus a few drops of acetone) to a clear aqueous solution of  $(^n\text{Bu}_4\text{N})_3[\text{Cu}(\text{CN})_4]$ . The latter was prepared by dissolving 0.224 g (2.5 mmol) of  $\text{CuCN}$  in a solution of 2.0 g (7.5 mmol) of  $(^n\text{Bu}_4\text{N})\text{CN}$  in 45 ml of  $\text{H}_2\text{O}$ . Yield, after filtration, repeated washing with water/acetone and drying at  $40^\circ\text{C}$  (ca. 3 h) was 1.87 g (91%) based upon  $\text{CuCN}$ . Elemental anal. Found: C 46.88, H 8.15, N 8.42, Cu 7.59, Sn 29.06  $\text{C}_{32}\text{H}_{66}\text{N}_5\text{CuSn}_2$  calcd.: C 46.77, H 8.09, N 8.52, Cu 7.73, Sn 28.88%. IR/Ra:  $\nu(\text{SnC}) 527/530, 495\text{ cm}^{-1}$ ;  $\nu(\text{CuC}) 404\text{ cm}^{-1}$ . Pure  $(^n\text{Bu}_4\text{N})_3[\text{Cu}(\text{CN})_4]$  could not be obtained as a dry powder from its aqueous solution.

Product 6 ( $(^n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})\text{Cu}_2(\text{CN})_4$ ) (stoichiometric reaction): a solution of 0.49 g (2.5 mmol) of  $\text{Me}_3\text{SnCl}$  in 35 ml of  $\text{H}_2\text{O}$  was added to a clear prepared *in situ* solution of 5 mmol of  $(^n\text{Bu}_4\text{N})[\text{Cu}(\text{CN})_2]$  (cf. also ref. 19) in 40 ml of  $\text{H}_2\text{O}$  (from 1.34 g of  $(^n\text{Bu}_4\text{N})\text{CN}$  and 0.45 g of  $\text{CuCN}$ ). Precipitation of colourless microcrystals after ca. 8 h yielded, after filtration, repeated washing with  $\text{H}_2\text{O}$  and drying at  $40^\circ\text{C}$ , 1.47 g (92.5%) based upon  $\text{Me}_3\text{SnCl}$ . Decomp. temp.  $260^\circ\text{C}$ ; elemental anal. Found: C 43.31, H 7.13, N 10.90, Cu 19.90, Sn 18.75.  $\text{C}_{23}\text{H}_{45}\text{N}_5\text{Cu}_2\text{Sn}$  calcd.: C 43.34, H 7.12, N 10.99, Cu 19.94, Sn 18.62%. IR/Ra:  $\nu(\text{SnC}) 552/553, 519\text{ cm}^{-1}$ ;  $\nu(\text{CuC}) 412\text{ cm}^{-1}$ .

Product 5 ( $(\text{Me}_3\text{Sn})\text{Zn}(\text{CN})_3$ ) (attempted preparation of  $(\text{Me}_3\text{Sn})_2\text{Zn}(\text{CN})_4$  (4)): a solution of 0.295 g (1.2 mmol) of  $\text{K}_2[\text{Zn}(\text{CN})_4]$  in 25 ml of  $\text{H}_2\text{O}$  was added slowly under stirring to a clear solution of 0.49 g (2.5 mmol) of  $\text{Me}_3\text{SnCl}$  in 35 ml of  $\text{H}_2\text{O}$ . The white polycrystalline precipitate (formed with a delay of a few minutes) was washed with cold  $\text{H}_2\text{O}$ , isolated and dried *in vacuo* ( $50^\circ\text{C}$ ). The resulting fine powder sticks notably to the glass walls and is completely soluble (unlike pure  $\text{Zn}(\text{CN})_2$ ) in DMF and DMSO. Elemental anal. Found: C 24.0, H 3.2, N 20.0, Zn 18.8, Sn 33.9.  $\text{C}_6\text{H}_9\text{N}_3\text{ZnSn}$  calcd.: C 23.4, H 2.9, N 13.7, Zn 21.3, Sn 38.6%. IR:  $\nu(\text{ZnC}) 460\text{ cm}^{-1}$ ; Ra  $\nu(\text{SnC})$ : 518s, 552m  $\text{cm}^{-1}$ .

Product 8 ( $(\text{Ph}_3\text{Sn})_2\text{Zn}(\text{CN})_4$ ): a solution of 1.1 g (5.0 mmol) of  $\text{AgClO}_4$  in 10 ml of acetone was added to a solution of 1.9 g (5 mmol) of  $\text{Ph}_3\text{SnCl}$  in 20 ml of acetone. The clear filtrate (after removal of precipitated  $\text{AgCl}$ ) was added to a solution of 1.6 g (2.5 mmol) of  $(^n\text{Bu}_4\text{N})_2[\text{Zn}(\text{CN})_4]$  in 15 ml of acetone. The instantaneously resulting precipitate gave rise, after filtration and careful washing with acetone, to a white, air-stable powder (decomp. temp.  $283^\circ\text{C}$ ). Yield 2.13 g

(98%) based upon  $\text{Ph}_3\text{SnCl}$ . Elemental anal. Found: C 51.57, H 3.69, N 6.55, Zn 7.61, Sn 27.80.  $\text{C}_{40}\text{H}_{30}\text{N}_4\text{ZnSn}_2$  calcd.: C 55.26, H 3.48, N 6.44, Zn 7.50, Sn 27.30%. Compound **8** was insoluble in water, alcohols and diluted mineral acids, but soluble in DMSO.

$(^n\text{Bu}_4\text{N})_2[\text{Zn}(\text{CN})_4]$ : 1.3 g (10 mmol) of pure  $\text{Zn}(\text{CN})_2$  were dissolved at ca. 30–40°C in an aqueous solution of 6.0 g (20 mmol) of  $(^n\text{Bu}_4\text{N})\text{CN}$  in 50 ml of  $\text{H}_2\text{O}$ . The colourless, viscous oil resulting after filtration and solvent evaporation was redissolved in a little absolute THF. After complete removal of THF under vacuum, 5.9 g of a white, dry powder remained (yield 90%); (decomp. temp. 102°C). Elemental anal. Found: C 65.81, H 10.43, N 12.57.  $\text{C}_{36}\text{H}_{72}\text{N}_6\text{Zn}$  anal.: C 66.08, H 11.09, N 12.84%. Pure  $\text{Zn}(\text{CN})_2$  was prepared from  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (25 g in 250 ml of  $\text{H}_2\text{O}$ ) and KCN (9.3 g in 125 ml of  $\text{H}_2\text{O}$ ).

The compounds  $\text{Me}_3\text{SnCl}$ ,  $\text{Et}_3\text{SnCl}$ ,  $\text{Ph}_3\text{SnCl}$ ,  $(^n\text{Bu}_4\text{N})\text{CN}$ ,  $(\text{Et}_4\text{N})\text{CN}$  and  $\text{CuCN}$  were purchased from commercial suppliers. 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.

The single crystal of **7** selected for a crystallographic X-ray analysis (*vide supra*) was positioned in a Lindemann glass capillary. Details of relevance for the data collection on a four-circle Syntex P2<sub>1</sub> diffractometer are given in Table 3. The structure was solved by means of three-dimensional Patterson techniques and refined by least-square methods to an  $R$ -value,  $wR_2$ , of 11.45% [28] (applying SHELXS-86 [29] and SHELXL-93 [30]). The "conventional"  $wR$ -value (without inclusion of H-atoms) was 5.37%. Anisotropic thermal parameters were assigned to all non-H atoms. Positional parameters are listed in Table 6. Due to the very high thermal parameters of all ethyl carbon atoms, all interatomic parameters of the two crystallographically different  $\text{Et}_3\text{Sn}$  units were fixed to Sn–C (2.085 Å) and C–C (1.497 Å). Moreover, the Sn–C (methyl) distances Sn1–C32, Sn1–C42, Sn1–C52, Sn2–C62 and Sn2–C72 were fixed to 3.085 Å. Further details of the crystal structure investigation are available on request from the authors (R.D.F./E.S.). Appropriate data deposition will take place as soon as a concerted low-temperature X-ray study and solid-state NMR investigation (involving also a  $^{15}\text{N}$ -enriched sample) have been carried out. Visualization of various structural perspectives were obtained by means of the CERius software of Molecular Simulations Inc.

The  $^{13}\text{C}$  and  $^{119}\text{Sn}$  solid-state NMR spectra were obtained at 75.4 and 119.9 MHz, respectively, using a Varian VXR 300 spectrometer in the cross-polariza-

TABLE 6. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **7**.  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Sn(1)	5000	5000	6177(1)	126(1)
Sn(2)	3176(1)	8176(1)	7500	87(1)
Cu(1)	2500	7743(1)	6250	65(1)
C(1)	3584(7)	6920(6)	6201(2)	98(3)
N(1)	4159(7)	6385(6)	6183(3)	145(4)
C(2)	2682(6)	8388(5)	6679(2)	76(2)
N(2)	2796(6)	8598(5)	6952(2)	106(3)
C(31)	4566(17)	4795(28)	6662(4)	380(50)
C(32)	3564(24)	4525(73)	6697(10)	636(107)
C(41)	4342(16)	4733(23)	5730(5)	591(139)
C(42)	3303(16)	4670(28)	5752(10)	370(42)
C(51)	6180(13)	5784(17)	6258(10)	479(66)
C(52)	6290(17)	6597(28)	6027(21)	1406(326)
C(61)	2162(4)	7162(4)	7500	404(29)
C(62)	1481(14)	7229(21)	7782(5)	398(43)
C(71)	4466(10)	7834(19)	7312(4)	477(27)
C(72)	4909(18)	7002(20)	7471(6)	490(49)
N(3)	0	0	6433(2)	91(3)
C(11)	848(6)	224(6)	6217(2)	103(3)
C(12)	764(7)	1059(8)	5996(3)	139(5)
C(13)	1667(9)	1204(10)	5816(4)	196(8)
C(14)	1695(15)	2056(14)	5600(5)	293(14)
C(21)	–268(6)	843(7)	6649(2)	105(4)
C(22)	492(7)	1191(9)	6872(3)	145(5)
C(23)	125(11)	1980(10)	7079(4)	189(7)
C(24)	815(12)	2368(14)	7322(4)	224(10)

tion mode with Doty scientific probes and high-power proton decoupling. For  $^{13}\text{C}$ , 7 mm o.d. rotors were employed, with typical MAS speeds in the range 4–5 kHz, whereas for  $^{119}\text{Sn}$ , 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  $^{119}\text{Sn}$  spectra were obtained without cross-polarization. In general, many transients (10 000–60 000) were acquired for each spectrum, although for  $^{13}\text{C}$  this was only necessary to obtain good sensitivity for the cyanide carbon signals. Such sensitivity also required relatively high contact times. Centrebands for  $^{119}\text{Sn}$  were determined by recording spectra at two different spinning speeds. Chemical shifts are reported with the high-frequency positive convention, in ppm with respect to the signals for  $\text{SiMe}_4$  ( $^{13}\text{C}$ ) and  $\text{SnMe}_4$  ( $^{119}\text{Sn}$ ). The ambient probe temperature was ca. 23°C.

## 7. Conclusions

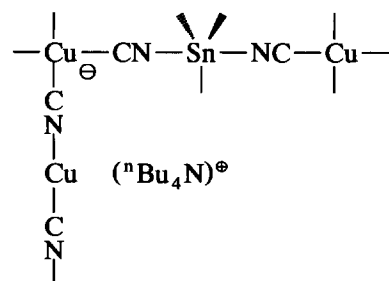
The foregoing presentation of the title compound **7**, as well as of several related organotin(IV) polymers, has shown that it is possible, albeit under certain limiting conditions, to arrive at three-dimensional, negatively charged frameworks of the type  $\{(\text{R}_3\text{Sn}^{\text{IV}})_2\text{Cu}^{\text{I}}\}$ .



(CN)<sub>4</sub><sup>-</sup> built up of distorted-tetrahedral Cu(CN)<sub>4</sub> and trigonal bipyramidal R<sub>3</sub>Sn(NC)<sub>2</sub> units via Cu–CN → Sn bridges. Obviously, the size and shape of the ligand R, as well as of the necessary counteraction (and template), A<sup>+</sup>, play an essential role for the verification and the actual structure of the envisaged host-guest system [A(R<sub>3</sub>Sn)<sub>2</sub>Cu(CN)<sub>4</sub>]. In the case of **7**, the dimensions of A<sup>+</sup> = <sup>n</sup>Bu<sub>4</sub>N<sup>+</sup> and R = Et preclude the formation of non- or multiply-interpenetrating, diamondoid host frameworks, nor is a layered structure with the guest cations in the interlayer sections preferred here, in possible analogy to **1**. The experimental formula volume, V/Z, of **7** turns out to be only one-third of the calculated formula volume of the hypothetical isomer with an ideal, diamondoid framework (devoid of interpenetration). Most generally, lattice compactness appears to be a primary requirement. Homologues of **7** with more voluminous components R and/or A<sup>+</sup> are thus likely to prefer frameworks closer to, or ultimately equivalent with, those involving adamantoid cages (cf. Fig. 1).

In view of the large structural variety of known aluminosilicate-based zeolites, A<sub>x</sub>Al<sub>x</sub>Si<sub>1-x</sub>O<sub>4</sub> (1 > x > 0), some formal analogy appears with potential derivatives of **7** of the general composition: [A<sub>x</sub>(R<sub>3</sub>E<sup>IV</sup>)<sub>2</sub>Cu<sup>I-II</sup>Zn<sup>I-II</sup><sub>1-x</sub>(CN)<sub>4</sub>] with E = Sn or Pb. The title compound **7** might thus be considered as a forerunner of "organometallic zeolites". First results of extended work in our laboratory in adopting different ligands R and guest/template cations A<sup>+</sup> appear promising in view of finding access to the more zeolite-like Cu<sup>I</sup>/Zn<sup>II</sup> systems. Nevertheless, it should be kept in mind that for x < 1, a distinct number (1 - x) of empty M<sub>10</sub> cages of "destabilizing nature" must be expected. On the other hand, compounds **2** and **3** mentioned in the Introduction are encouraging examples with x = 0.5.

In spite of the high validity of solid-state NMR and other spectroscopic techniques, the unambiguous identification of any potential "organometallic zeolite" will usually be difficult in the absence of a successful single-crystal X-ray study. For product **6**, a polymeric framework according to Scheme 2 may be suggested from the NMR and IR/Ra spectroscopic results. Yet,



Scheme 2.

even in this case access to single crystals and/or further spectroscopic studies involving e.g. samples with <sup>15</sup>N-enriched cyanide ligands, and <sup>63</sup>Cu NMR or NQR, would appear highly desirable.

### Acknowledgment

A.K. Brimah and R.D. Fischer are grateful to the Deutsche Forschungsgemeinschaft for financial support during an early stage of this work. Miss K. Rechter and Mr. R. Hinck are thanked for valuable preparative work, and Professor U. Behrens and Dr. O. Greis (T.U. Hamburg-Harburg), for a number of helpful discussions concerning the structural studies. The UK Science and Engineering Council is thanked for access to the Varian VXR 300 spectrometer under the national solid-state NMR service arrangements. The British Council and the DAAD (Bonn), under the ARC programme, enabled the bilateral cooperation.

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