

# Polymeric [(Me<sub>3</sub>Sn)<sub>3</sub>Rh(SCN)<sub>6</sub>]: A Novel "Super-Prussian-Blue" Derivative Containing the Nonlinear -SCN-Sn-NCS- Spacer

Eric Siebel and R. Dieter Fischer\*

Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday

**Abstract:** The new coordination polymer [(Me<sub>3</sub>Sn<sup>IV</sup>)<sub>3</sub>Rh<sup>III</sup>(SCN)<sub>6</sub>] =  $\frac{3}{x}$ [Rh{ $\mu$ -(SCNSnMe<sub>3</sub>NCS)}<sub>3</sub>] (**5**) is readily accessible by straightforward self-assembly of [Rh(SCN)<sub>6</sub>]<sup>3-</sup> and (dehydrated) {Me<sub>3</sub>Sn}<sub>aq</sub><sup>+</sup> ions. The architecture of **5** is strongly reminiscent of "super-Prussian-blue" systems reported earlier: there is a three-dimensional (3-D) framework in-

volving {Rh<sub>8</sub>} pseudocubes as the basic building blocks, the Rh<sup>3+</sup> ions being held apart by novel, nonlinear {SCN-SnMe<sub>3</sub>-NCS} spacers (*d*(Rh···Rh) = 1.27 nm).

The complete lattice consists of *two* equivalent and independent, ideally interwoven 3-D frameworks. Three homologues of **5** with slightly modified R<sub>3</sub>Sn units (R = Et, *n*Pr and *n*Bu) have been prepared as well, but display X-ray powder diffraction patterns notably different from that of **5**.

## Keywords

coordination polymers · Prussian blue · rhodium · structure elucidation · tin

## Introduction

The history of Prussian blue (PB) and closely related polymeric metal cyanides is rich in remarkable landmarks.<sup>[1]</sup> Interestingly, at least four years before the first presentation of the architecture of "real" PB,<sup>[2]</sup> Pauling and Pauling had already deduced the structure of the first "super-PB" systems from reported X-ray powder diffractogram (XRP) data.<sup>[3]</sup> According to their analysis, crystalline Ag<sub>3</sub>[Co(CN)<sub>6</sub>] (**1**) should consist of three equivalent and independent, ideally interwoven "super-PB" frameworks (Figure 1) with {CN-Ag-NC} instead of {CN} spacers between two transition-metal ions. This hitherto unquestioned view<sup>[4]</sup> is further supported by more recent studies of single crystals of the related compounds {K<sup>+</sup>c Au<sub>3</sub>[Co<sup>II</sup>(NC)<sub>6</sub>]<sup>-</sup>} (**2**)<sup>[5]</sup> and {Rb<sup>+</sup>c Ag<sub>3</sub>[Cd<sup>II</sup>(NC)<sub>6</sub>]<sup>-</sup>} (**3**).<sup>[6]</sup> In spite of the interpenetration of three {M<sub>8</sub>} pseudocubes in **1–3** (M = Co or Cd), sufficient space remains for the alkali guest cations to reside in straight channels along one body diagonal of the pseudocubes.<sup>[6]</sup> We first showed in 1985<sup>[7]</sup> that by the formal replacement of each Ag<sup>+</sup> ion of **1** (Figure 1) by a planar Me<sub>3</sub>Sn<sup>+</sup> fragment as spacer, lattice interpenetration is circumvented. The resulting organotin(IV) polymer [(Me<sub>3</sub>Sn)<sub>3</sub>Co(CN)<sub>6</sub>] =  $\frac{3}{x}$ [Co{ $\mu$ -(CNSnMe<sub>3</sub>NC)}<sub>3</sub>] (**4**) adopts an unprecedented type of spacious, three-dimensional (3-D) framework devoid of any pseudocubes as basic structural building blocks.<sup>[7, 8]</sup> After the recent demonstration<sup>[9]</sup> that the related

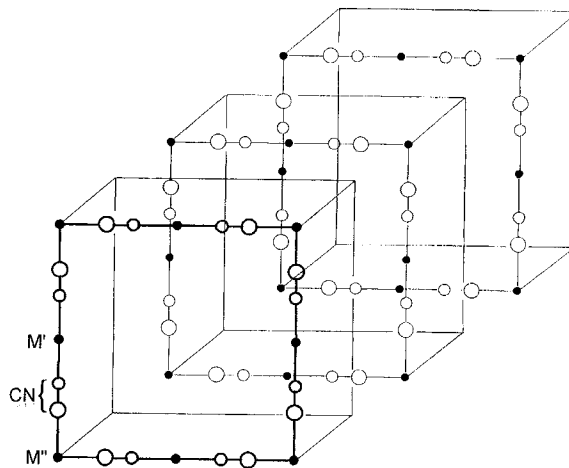


Figure 1. Simplified view of the interpenetrating, triple framework structure of the "super-Prussian-blue" systems **1**, **2**, and **3** (the alkali guest cation of **2** and **3** is omitted). M' = Ag, Au; M = Co, Cd.

negatively charged  $\frac{3}{x}$ [Fe<sup>II</sup>{ $\mu$ -(CNSnMe<sub>3</sub>NC)}<sub>3</sub>]<sup>-</sup> lattice displays intraframework channels wide enough to host, inter alia, metallocene cations, we wish to report here the synthesis and the crystal structure of the novel coordination polymer [(Me<sub>3</sub>Sn)<sub>3</sub>Rh(SCN)<sub>6</sub>] =  $\frac{3}{x}$ [Rh{ $\mu$ -(SCNSnMe<sub>3</sub>NCS)}<sub>3</sub>] (**5**), wherein the spacer is elongated by two sulfur atoms.

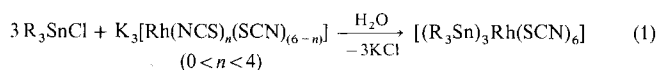
## Results and Discussion

Our intention to replace the "super-PB" spacers {NC-M'-CN} or {CN-M'-NC} (M' = Ag, Au) adopted so far with an obviously longer {SCN-Sn-NCS} tether would require the

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choice of a transition-metal ion able to coordinate the relatively soft<sup>[10]</sup> sulfur site of the thiocyanate ion. Trivalent rhodium was chosen in view of promising reports by Preetz et al.,<sup>[11]</sup> who succeeded in separating the salts of various linkage isomers of the complex type  $[\text{Rh}(\text{NCS})_n(\text{SCN})_{6-n}]^{3-}$  ( $n = 0-4$ ) from each other. To verify the situation for  $n = 0$ , we speculated on an ancillary activity of the triorganotin ion, which was expected to make only the sulfur atoms available for the rhodium ions, owing to its well-known preference for the nitrogen site of the  $\text{NCS}^-$  anion.<sup>[12]</sup>

Actually, analytically pure, air-stable products of the anticipated composition  $[(\text{R}_3\text{Sn})_3\text{Rh}(\text{SCN})_6]$  with  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $n\text{Pr}$  and  $n\text{Bu}$  (**5-8**) were readily accessible as red or orange precipitates according to Equation (1), where  $\text{R} = \text{Me}$  (**5**),  $\text{Et}$  (**6**),  $n\text{Pr}$



(**7**) or  $n\text{Bu}$  (**8**). Sparing solubility in common solvents and high thermal stability, without evidence of melting up to at least 250 °C, are indicative of the formation of coordination polymers. Only one  $\nu(\text{CN})$  band for each is detectable in the infrared (IR) spectra (Table 1), with frequencies significantly higher than for  $\text{K}_3[\text{Rh}(\text{SCN})_6]$  (2098  $\text{cm}^{-1}$ <sup>[11]</sup>) and polymeric  $[\text{Me}_3\text{SnNCS}]$  (2050–2090  $\text{cm}^{-1}$ <sup>[13]</sup>). Mixtures of different linkage isomers would be expected to display more than one  $\nu(\text{CN})$  band.<sup>[11]</sup> Centrosymmetric  $\{\text{RhS}_6\}$  fragments may be deduced for **5** from

Table 1. Selected spectroscopic (IR, <sup>13</sup>C NMR) data, experimental densities ( $\rho_{\text{exp}}$ ) and formula volumes ( $V_f$ ) of **5-8**.

Quantity	<b>5</b> (R = Me)	<b>6</b> (R = Et)	<b>7</b> (R = <i>n</i> Pr)	<b>8</b> (R = <i>n</i> Bu)
$\nu(\text{CN})$ ( $\text{cm}^{-1}$ )	2120 ss [a]	2118 ss	2116 ss	2117 ss
$\nu(\text{SnC})$ ( $\text{cm}^{-1}$ )	566 m	525 m	512 m	510 m
$\rho_{\text{exp}}$ ( $\text{g cm}^{-3}$ )	1.98	1.64	1.52	1.36
$V_f$ ( $\text{cm}^3$ ) [b]	499	652	786	971
$\delta(^{13}\text{C}_\alpha)$	2.02 [c]	11.3 br	19.1	19.7
$\delta(^{13}\text{C}_\beta)$		10.6	20.1	29.1
$\delta(^{13}\text{C}_\gamma)$			22.8	27.7 [d,e]
$^1J(^{119}\text{Sn}, ^{13}\text{C}_\alpha)$ (Hz)	512	493	[f]	513

[a] Raman band of **5**: 2127  $\text{cm}^{-1}$ . [b]  $V_f = \rho_{\text{exp}}/M_r$ . [c]  $\delta(^{13}\text{C})$  of NCS group of **5** = 122.3. [d]  $\delta(^{13}\text{C})$  of **8** = 14.2. [e] The assignment of  $\delta(^{13}\text{C})$  follows ref. [24]. [f] Suitable satellites of <sup>13</sup>C<sub>α</sub> resonance to determine <sup>1</sup>J(<sup>119</sup>Sn, <sup>13</sup>C) not detectable.

**Abstract in German:** Die Selbstorganisation von  $[\text{Rh}(\text{SCN})_6]^{3-}$ - und dehydratisierten  $\{\text{Me}_3\text{Sn}\}_{\text{aq}}^+$ -Ionen führt zu dem neuartigen Koordinationspolymer  $[(\text{Me}_3\text{Sn}^{\text{IV}})_3\text{Rh}^{\text{III}}(\text{SCN})_6] = {}_3[\text{Rh}\{\mu-(\text{SCNSnMe}_3\text{NCS})\}_3]$  (**5**), dessen Architektur deutlich an die bereits bekannter „Super-Berlinerblau“-Systeme erinnert.  $\{\text{Rh}_8\}$ -Quasiwürfel bilden die Grundbausteine eines dreidimensionalen (3-D) Netzwerks, dessen  $\text{Rh}^{3+}$ -Ionen durch relativ lange, nichtlineare  $\{\text{SCN}-\text{SnMe}_3-\text{NCS}\}^-$ -Spacer miteinander verknüpft sind ( $d(\text{Rh}\cdots\text{Rh}) = 1.27 \text{ nm}$ ). Das vollständige Gitter umfaßt zwei äquivalente und voneinander unabhängige 3-D-Netzwerke, deren  $\{\text{Rh}_8\}$ -Quasiwürfel optimal ineinander geschachtelt sind. Drei Homologe von **5** mit leicht modifizierten  $\text{R}_3\text{Sn}$ -Einheiten ( $\text{R} = \text{Et}$ ,  $n\text{Pr}$ , und  $n\text{Bu}$ ) werden ebenfalls hergestellt und näher beschrieben: Ihre Röntgenpulverdiagramme weichen signifikant von dem von **5** ab.

the appearance of two pairs of nonsuperimposable  $\nu(\text{RhS})$  bands in the IR and Raman (Ra) spectra (IR: 276 m, 282 m, Ra: 238, 258  $\text{cm}^{-1}$ ).

The structure analysis of a single crystal of **5** confirms the presence of quasioctahedral  $\{\text{RhS}_6\}$  units of local  $D_{2d}$  symmetry and, moreover, a closer resemblance to the above-mentioned “super-PB” systems **1-3** than to **4**. Thus,  $\{\text{Rh}_8\}$  pseudocubes result from the periodic cross-linking of almost linear  $\text{Rh}\cdots\text{Sn}\cdots\text{Rh}\cdots\text{Sn}$  chains with a  $\text{Rh}\cdots\text{Rh}$  separation of 1.27 nm and  $\text{Rh}-\text{Rh}'-\text{Rh}''$  angles of 87.22(1) and 92.78(2)°. When the thiocyanato bridges are accounted for as well, obviously nonlinear chains of the general pattern  $[\text{Rh}-\text{S}1-\text{C}1-\text{N}1-\text{Sn}-\text{N}2-\text{C}2-\text{S}2]_{\infty}$  become apparent (Figures 2 and 3).

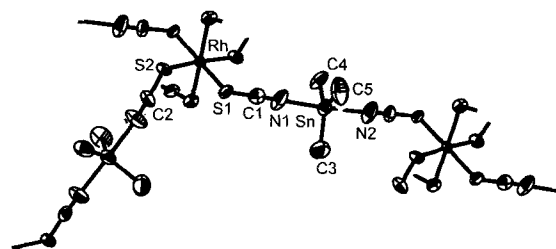


Figure 2. ORTEP plot of one representative zigzag chain of **5** and parts of its immediate surroundings.

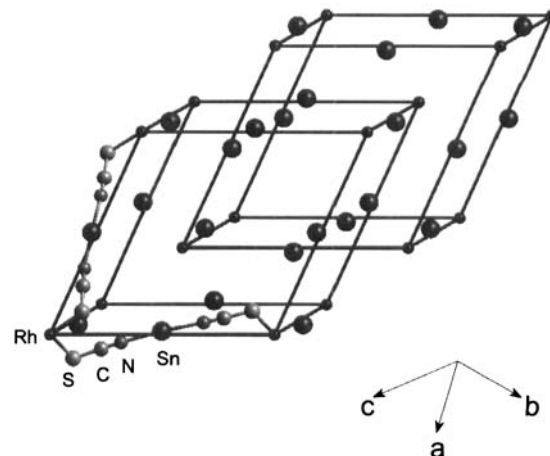


Figure 3. Simplified view of the interpenetrating double framework structure of **5**: NCS bridges are shown only between four Sn–Rh pairs, and all CH<sub>3</sub> groups are omitted for clarity (the direct lines between the Rh and Sn atoms do not correspond to chemical bonds).

The considerable elongation of the  $\text{Rh}\cdots\text{Rh}$  distance relative to the shortest  $\text{Co}\cdots\text{Co}$  distance in **4**<sup>[7,81]</sup> (ca. 0.94 nm) would favour framework interpenetration, while the pronounced kinks at the sulfur atoms (for the values of the  $\text{Rh}-\text{S}-\text{C}$  angles see Table 3) and the space-demanding tin-bonded methyl groups are more likely to counteract that tendency. It should be noted that the slightly smaller  $\text{Hg}-\text{S}-\text{C}$  angles of polymeric  $[\text{Co}-\text{Hg}(\text{SCN})_4]$  (97.3(5)°)<sup>[14]</sup> do prevent framework interpenetration in this potentially diamondoid 3-D system.

Actually, **5**, unlike **1-4**, displays a “super-PB”-like lattice built up of two equivalent, ideally interwoven frameworks (Figure 3). A perspective of the complete structure viewed along its crystallographic  $c$  axis (that is, along one body diagonal of the pseudocubes, Figure 4) suggests comparatively compact

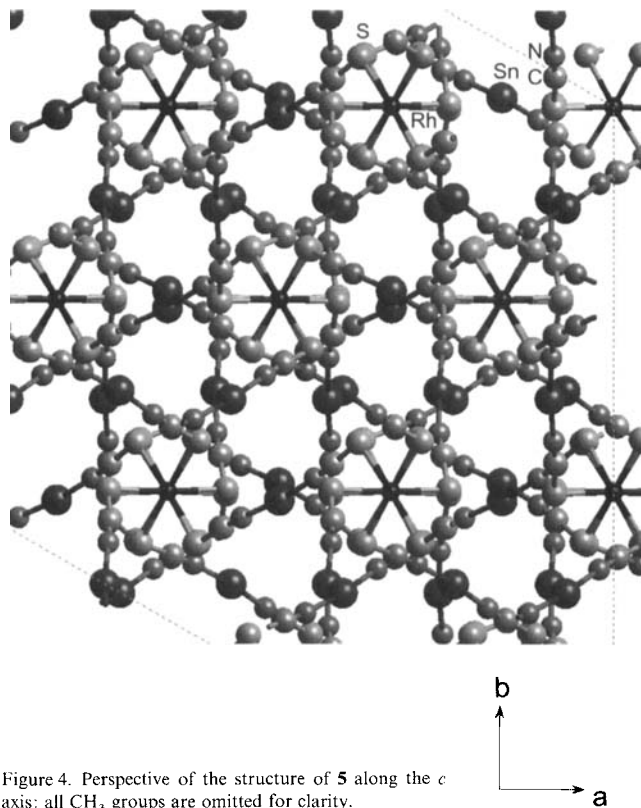


Figure 4. Perspective of the structure of **5** along the *c* axis: all  $\text{CH}_3$  groups are omitted for clarity.

packing, as the channels corresponding to those hosting the alkali guest cations of **2** and **3**<sup>[15]</sup> have to accommodate the tin-bonded methyl groups. As would be expected for the mutual interpenetration of two spacious frameworks, the crystallographic formula volume  $V_f$  of **5** (ca.  $500 \text{ cm}^3 \text{ mol}^{-1}$ ) exceeds that of **4** ( $460 \text{ cm}^3 \text{ mol}^{-1}$ ) by only 8.7%, but the  $V_f$  values of the *trireticulate* “super-PB” systems **1–3** ( $184\text{--}218 \text{ cm}^3 \text{ mol}^{-1}$ ) by at least 130% (for **3**).

As the experimental X-ray powder diffractogram (XRP) of **5** agrees well with the calculated one (Figure 5), the crystallo-

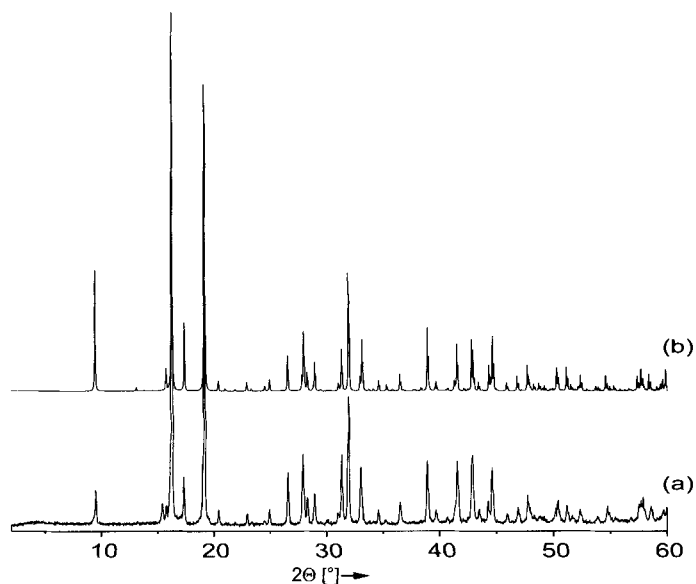


Figure 5. Experimental (a) and calculated (b) X-ray powder diffractograms of **5**.

graphically determined asymmetric unit should likewise be reflected by the CPMAS (CP = cross-polarisation; MAS = magic-angle spinning) solid-state  $^{13}\text{C}$  NMR spectrum of finely ground polycrystalline **5**. However, although three nonequivalent  $\text{CH}_3$ - and two different NCS units are present, only one methyl and one thiocyanate carbon resonance appear down to  $-30^\circ\text{C}$ . Rapid (on the NMR timescale) rotation of the  $\text{Me}_3\text{Sn}$  units about their N-Sn-N axes must account for this discrepancy. Similar deviations of solid-state NMR features from results of X-ray diffraction studies have been observed earlier in closely related cases, because these two techniques refer to very different timescales.<sup>[8, 9a, 16]</sup>

Interestingly, the XRP's of **6–8** [see Equation (1) and Figure 6] look quite different from that of **5**. Since the density-based

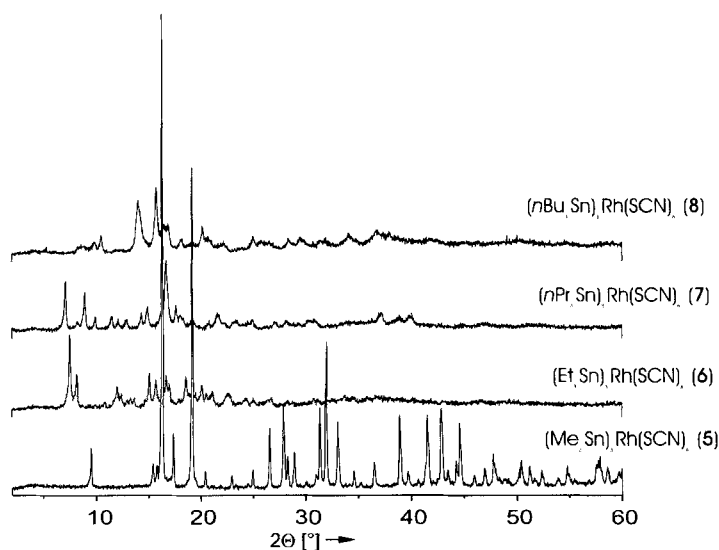


Figure 6. Experimental X-ray powder diffractograms of **5** and **6–8**.

formula volumes  $V_f$  of **5–8** increase gradually with the space demand of the tin-bonded group R (Table 1), changes of the framework architecture are likely to result as the volume of R increases. Actually, some of the intraframework voids of **5**, depicted in Figure 7, might be too narrow to accommodate  $\text{R}_3\text{Sn}$  units with R larger than Me, since the van der Waals spheres of the closest-lying methyl C and thiocyanato S atoms are not far from overlapping. For instance, we have found the following relatively short (but still nonbonding) distances (in pm):  $\text{S1}\cdots\text{C4}$ , 389.8;  $\text{S1}\cdots\text{H(4C)}$ , 318.6;  $\text{S2}\cdots\text{H(4B)}$ , 318.7. On the other hand,  $V_f$  does not increase abruptly, nor does it reach values about twice as large as  $V_f$  of **5**, so that a transition to a framework devoid of interpenetration seems unlikely. We have, moreover, observed a corresponding increase of  $V_f$  when R was varied within different series of coordination polymers of the type  $[(\text{R}_3\text{Sn})_3\text{M}(\text{CN})_6]$  with  $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ , where lattice interpenetration may be strictly ruled out (Table 2). The CPMAS  $^{13}\text{C}$  NMR spectra of **6–8** suggest that, owing to the anticipated moderate lattice expansion, rapid  $\text{R}_3\text{Sn}$  rotation again takes place, since just one signal is found for each of the non-equivalent carbon atoms in the  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -positions of R (Table 1).

Recently, the first complete description of a successful single-crystal X-ray study of a genuine salt of the  $[\text{Rh}(\text{SCN})_6]^{3-}$  ion,

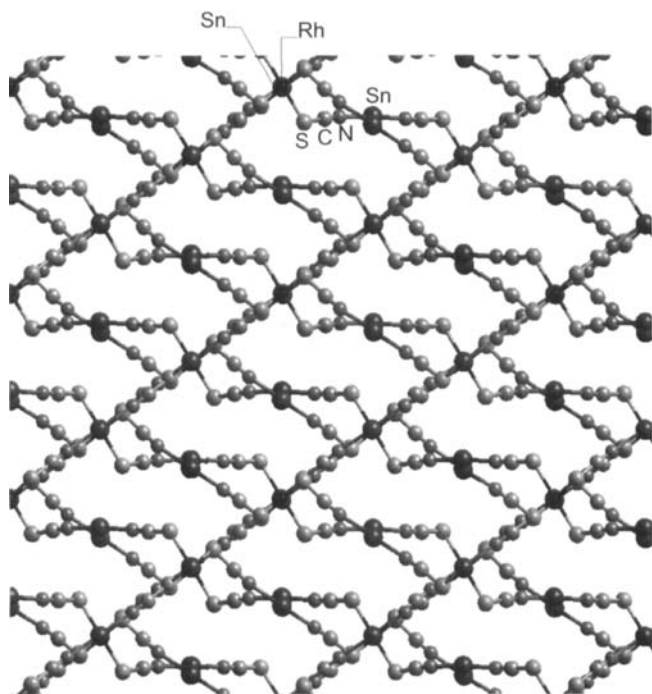


Figure 7. Perspective of the structure of **5** along the *a* axis, depicting the space actually available for the organic groups R of the organotin(IV) fragment. The CH<sub>3</sub> groups are omitted for clarity.

Table 2. Formula volumes  $V_f$  of various [(R<sub>3</sub>Sn)<sub>3</sub>M(CN)<sub>6</sub>] systems, calculated from pyknometric density values.

M	R = Me	R = Et	R = <i>n</i> Pr	R = <i>n</i> Bu
Co	460	603	705	798
Rh	436	573	711	836
Ir	431	543	680	654

[P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sub>3</sub>[Rh(SCN)<sub>6</sub>] (**9**), has appeared.<sup>[17]</sup> A selection of corresponding bond lengths and bond angles for **5** and **9** is listed for comparison in Table 3. Apart from the higher local symmetry of the {Rh(SCN)<sub>6</sub>} unit in **5**, most of the parameters considered adopt very similar values. On the other hand, the framework structure of **5** involves strict coplanarity of each of the three *trans*-oriented pairs of SCN ligands, while the [P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sup>+</sup> counteranions of **9** apparently force all *trans*-NCS–Rh–SCN fragments to adopt dihedral angles markedly different from 0°. The structural parameters of the {Me<sub>3</sub>SnN<sub>2</sub>} units of **5** compare well with those of **4**, for example (Table 3).

Interestingly, experimental access to genuine salts A<sub>3</sub>[Rh(SCN)<sub>6</sub>] (with all-S-bonded thiocyanate) is less straightforward than that to the new coordination polymers [(R<sub>3</sub>Sn)<sub>3</sub>Rh(SCN)<sub>6</sub>]. While for the preparation of the former considerable effort to separate the various linkage isomers [Rh(NCS)<sub>*n*</sub>(SCN)<sub>6-*n*</sub>]<sup>3-</sup> (e.g. by ion-exchange chromatography<sup>[11]</sup>) is inevitable, and severely reduces the yield of the desired isomer with *n* = 0, all coordination polymers can be obtained in yields of up to 90% without applying any separation technique. The most reasonable explanation of this result is that the initially hydrated Lewis acid R<sub>3</sub>Sn<sup>+</sup> strongly facilitates the

Table 3. Comparison of selected structural data (bond lengths in pm; bond angles in °) for **5** and **9**.

	<b>5</b>	<b>9</b> <sup>[17]</sup> or <b>4</b> <sup>[8]</sup>		<b>5</b>	<b>9</b> <sup>[17]</sup> or <b>4</b> <sup>[8]</sup>
Rh–S1	241.9(6)	239.6(6) to	Rh–S1–C1	109.9(6)	110.5(7) to
Rh–S2	235.1(5)	234.8(5) [a]	Rh–S2–C2	106.8(5)	107.9(5) [a]
S1–C1	161.4(14)	159(5) to	S1–C1–N1	174(2)	172(2) to
S2–C2	164(2)	166(2) [a]	S2–C2–N2	178(2)	177.4(14) [b]
C1–N1	114(2)	111(2) to	C1–N1–Sn	179(2)	134(3) to
C2–N2	115(2)	116(2) [b]	C2–N2–Sn	172(2)	172(4) [a]
Sn–N1	235(2)	220(2) to	N1–Sn–N2	175.5(6)	170(1) to 175(1) [c]
Sn–N2	237.4(13)	253(3) [a]	C3–Sn–C4	125.0(10)	
Sn–C3	209(2)		C3–Sn–C5	118.3(9)	
Sn–C4	211.5(14)		C4–Sn–C5	116.6(10)	
Sn–C5	205(3)		N1–Sn–C3	92.7(8)	
			N1–Sn–C4	88.9(6)	
			N1–Sn–C5	90.4(8)	

[a] Six different values. [b] Five different values. [c] Three different values.

conversion of all linkage isomers still involving Rh–N bonds into the all-(Rh–S)-containing [(SCN)<sub>6</sub>]<sup>3-</sup> isomer, because all nitrogen ends of the NCS<sup>-</sup> ions are efficiently captured by the likewise acidic but “harder” (than Rh<sup>3+</sup>)<sup>[10]</sup> tin sites.<sup>[24]</sup>

## Conclusion and Outlook

The present contribution describes the first successful attempt to expand the spacer of a “super-PB” system from the now familiar pentaatomic {CN–M–NC} unit to the notably longer, albeit nonlinear, heptaatomic {SCN–M–NCS} tether.<sup>[18]</sup> We consider the remarkably facile synthesis of the compounds **5–8**, based upon the excellent nitrogen-acceptor role of the {R<sub>3</sub>Sn<sup>+</sup>} cation, as encouraging for diverse related future explorations. For instance, with appropriately chosen guest cations A<sup>+</sup>, novel host–guest systems of the type [(A<sup>+</sup>)(R<sub>3</sub>Sn)<sub>3</sub>M<sup>II</sup>(SCN)<sub>6</sub>]<sup>-</sup> might be designed wherein a sufficiently large guest cation (or “structure director”) A<sup>+</sup> would prevent interpenetration in the framework. One first example of a “super-PB” system hosting both a voluminous metal complex together with some benzene molecules has briefly been mentioned.<sup>[19]</sup>

In view of the specific structural motif of **5**, we wish to point out that the number of interwoven frames based on octahedral centres (“ $\alpha$ -polonium-type” structures) so far known is still very limited: of a total of seven examples reported so far,<sup>[3, 5, 6, 20–22]</sup> only three<sup>[20–22]</sup> involve bireticular lattices.

## Experimental Section

**General methods:** Manipulation in an inert gas atmosphere was not necessary. Infrared spectra were obtained on a Perkin Elmer IR-1720 spectrometer, and Raman spectra on a Jobin Yvon U-1000 instrument equipped with a 514 nm Ar laser. CPMA S <sup>13</sup>C solid-state NMR spectra were recorded on a Bruker MSL-300 spectrometer operating at 75.47 MHz, and X-ray powder diffractograms on a Philips X'PERT instrument (Cu<sub>K $\alpha$</sub>  irradiation, Ni filter). The crystallographic single-crystal X-ray study was carried out on a Syntex P2<sub>1</sub> four-circle diffractometer. Pyknometric density measurements were conducted at 25 °C with 25 mL pyknometers (DIN 12797), freshly distilled dioxane and at least 0.7 g of the suspended samples per measurement.

**Preparation of tris(trimethyltin)hexakis(thiocyanato)rhodate(III) (5):** In a combination of procedures described in refs. [11] and [23], a mixture of RhCl<sub>3</sub>·H<sub>2</sub>O (3.0 g, 11.4 mmol), KSCN (6.0 g, 61.7 mmol) and H<sub>2</sub>O (80 mL)

was converted slowly, under continuous stirring at temperatures around 100 °C, into a viscous crystalline paste. H<sub>2</sub>O (ca. 50 mL) was added and then evaporated twice. The residue obtained after extraction with absolute EtOH, filtration and solvent evaporation was dissolved in an aqueous solution of KSCN (1.5 M, 210 mL) while being stirred for 6 h at 60 °C. This solution contained about 24.5 mg [(Rh(SCN)<sub>6</sub>]<sup>3-</sup> per mL and was stored in a refrigerator. To prepare **5**, a concentrated aqueous solution of Me<sub>3</sub>SnCl (478 mg, 2.4 mmol) was added to 15 mL of the above stock solution containing about 367 mg (0.8 mmol) of [Rh(CN)<sub>6</sub>]<sup>3-</sup>. Each of the homologues **6–8** of **5** was prepared correspondingly. The coordination polymer usually precipitated in high yields as a red, polycrystalline material. Filtration, washing with a little H<sub>2</sub>O and drying in vacuo led to analytically pure products. Yields of **5–8** (relative to [Rh(SCN)<sub>6</sub>]<sup>3-</sup>): **5**, 85, 94, 87, 97%. Compound **5**, C<sub>15</sub>H<sub>27</sub>N<sub>6</sub>S<sub>6</sub>Sn<sub>3</sub>Rh (942.77): calcd C 19.11, H 2.88, N 8.91, Sn 37.77; found C 19.10, H 2.64, N 8.90, Sn 37.46%. Compound **6**, C<sub>24</sub>H<sub>45</sub>N<sub>6</sub>S<sub>6</sub>Sn<sub>3</sub>Rh (1068.85): calcd C 26.96, H 24.24, N 7.86, Sn 33.31; found C 27.19, H 4.26, N 7.42, Sn 35.50%. Compound **7**, C<sub>33</sub>H<sub>63</sub>N<sub>6</sub>S<sub>6</sub>Sn<sub>3</sub>Rh (1195.01): calcd C 33.16, H 5.31, N 7.03, Sn 29.80; found C 33.58, H 5.47, N 6.49, Sn 32.58%. Compound **8**, C<sub>42</sub>H<sub>81</sub>N<sub>6</sub>S<sub>6</sub>Sn<sub>3</sub>Rh (1321.16): calcd C 38.18, H 6.17, N 6.36, Sn 26.95; found C 39.24, H 6.06, N 5.50, Sn 26.45%.

**X-ray crystallography:** Small, red single crystals of **5** crystallized from the filtrate obtained after the work-up of the main amount of **5** (see above) when it was kept for one month at about 5 °C. Crystal data for **5**: C<sub>15</sub>H<sub>27</sub>N<sub>6</sub>S<sub>6</sub>Sn<sub>3</sub>Rh, *M<sub>r</sub>* = 942.77 g mol<sup>-1</sup>, rhombohedral, *R*3*c* (No. 161); *a* = *b* = 13.441(2) × 10<sup>2</sup>, *c* = 30.557(6) × 10<sup>2</sup> pm, *γ* = 120°, *V* = 4780.8(14) × 10<sup>6</sup> pm<sup>3</sup>, *Z* = 6, *ρ*<sub>calc</sub> = 1.965 g cm<sup>-3</sup> (*ρ*<sub>exp</sub>: see Table 1), *F*(000) = 2700; *T* = 293 K, *2θ* range: 3.03 to 27.58°. For *R*(int) = 0.0626, 2448 symmetry-independent reflections (total: 2542) were collected; data/restraints/parameters: 2448/1/98, structure solution SHELXS, (SHELXTL PLUS (VMS), V4.2), refinement against |*F*<sup>2</sup>| with *R*1 = 0.0649 and *wR*2 = 0.1428 (*I* > 2σ) (SHELXL-93); absorption correction by DIFABS (PLATON 94); *μ* = 3.24 mm<sup>-1</sup>, min./max. transmission = 0.63/1.293. Powder diagram simulated with CERIUS 3.2 (MSI); *2θ* range 5–50°. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406417.

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- [1] a) A. Ludi, *Chem. Unserer Zeit* **1988**, 22, 123–127; b) K. R. Dunbar, R. A. Heintz, in *Prog. Inorg. Chem.*, Vol. 45 (Ed.: K. D. Karlin), Wiley, New York, **1997**, pp. 283–391.
- [2] That is, of Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>·14H<sub>2</sub>O: a) H. J. Buser, A. Ludi, W. Petter, D. Schwarzenbach, *J. Chem. Soc. Chem. Commun.* **1972**, 1299; b) H. J. Buser, D. Schwarzenbach, W. Petter, A. Ludi, *Inorg. Chem.* **1977**, 16, 2704–2710.
- [3] L. Pauling, P. Pauling, *Proc. Nat. Acad. Sci. USA* **1968**, 60, 362–367.
- [4] A. Ludi, H. U. Güdel, *Helv. Chim. Acta* **1968**, 51, 1762–1765.
- [5] S. C. Abrahams, J. L. Bernstein, R. Liming, F. T. Eisenmann, *J. Chem. Phys.* **1980**, 73, 4585–4590.
- [6] B. F. Hoskins, R. Robson, N. V. Y. Scarlett, *J. Chem. Soc. Chem. Commun.* **1994**, 2025–2026.
- [7] K. Yünlü, N. Höck, R. D. Fischer, *Angew. Chem.* **1985**, 97, 863–864; *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 879–881.
- [8] U. Behrens, A. K. Brimah, T. M. Soliman, R. D. Fischer, D. C. Apperley, N. A. Davies, R. K. Harris, *Organometallics* **1992**, 11, 1718–1726.
- [9] a) P. Schwarz, E. Siebel, R. D. Fischer, D. C. Apperley, N. A. Davies, R. K. Harris, *Angew. Chem.* **1995**, 107, 1311–1313; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 1197–1199; b) P. Brandt, A. K. Brimah, R. D. Fischer, *ibid.* **1988**, 100, 1578–1580 and **1988**, 27, 1521–1522.
- [10] See: R. G. Pearson, *J. Am. Chem. Soc.* **1963**, 85, 3533–3539.
- [11] H. H. Fricke, W. Preetz, *Z. Anorg. Chem.* **1983**, 507, 12–22.
- [12] R. A. Forder, G. M. Sheldrick, *J. Organomet. Chem.* **1970**, 21, 115–122.
- [13] V. Peruzzi, G. Tagliavini, R. E. Hester, *J. Organomet. Chem.* **1973**, 56, 185–192.
- [14] a) J. C. Jeffrey, K. M. Rose, *Acta Crystallogr. B* **1968**, 24, 653–662; b) in polymeric [Me<sub>3</sub>SnNCS] the Sn-S-C angle amounts likewise to 97° (ref. [12]); c) generally, even simple AB<sub>2</sub> systems have a pronounced tendency to undergo lattice interpenetration.
- [15] See, for comparison, Figure 2 of ref. [6].
- [16] P. Schwarz, S. Eller, E. Siebel, T. M. Soliman, R. D. Fischer, D. C. Apperley, N. A. Davies, R. K. Harris, *Angew. Chem.* **1996**, 108, 1611–1614; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1525–1527.
- [17] J.-U. Vogt, O. Haackel, W. Preetz, *Z. Anorg. Allg. Chem.* **1995**, 621, 1033–1036.
- [18] Some coordination polymers (of different architecture) involving even octaatomic {CN-Ag-CN-Ag-CN}⁻ bridges have recently been reported (ref. [22]).
- [19] See: T. Iwamoto in *Comprehensive Supramolecular Chemistry*, Vol. 6 (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Pergamon, Oxford, **1996**, p. 687.
- [20] H. Schäfer, H. G. von Schnering, K. J. Niehues, H. G. Nieder-Vahrenholz, *J. Less-Common Met.* **1965**, 9, 95–104.
- [21] J. Zhang, J. D. Corbett, *Inorg. Chem.* **1991**, 30, 431–435.
- [22] T. Soma, H. Yuge, T. Iwamoto, *Angew. Chem.* **1994**, 106, 1746–1748; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1665–1666.
- [23] A. Botar, E. Blasius, G. Klemm, *Z. Anorg. Allg. Chem.* **1979**, 449, 174–176.
- [24] T. N. Mitchell, *J. Organomet. Chem.* **1973**, 59, 189–197.