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### Supramolecular Self Assembly of $[\text{Cu}(\text{CN})_4]^{3-}$ Ions with Cationic $\{\text{Ph}_3\text{Sn}\}$ Units in the Presence of Neutral Bidentate Ligands

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## Supramolecular Self Assembly of $[\text{Cu}(\text{CN})_4]^{3-}$ Ions with Cationic $\{\text{Ph}_3\text{Sn}^+\}$ Units in the Presence of Neutral Bidentate Ligands

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*The supramolecular interplay of the  $\text{Ph}_3\text{Sn}^+$  unit and the  $[\text{Cu}(\text{CN})_4]^{3-}$  ion with either 4,4'-bipyridine (bpy), trans-1,2-bis(4-pyridyl)ethene (tbpe), 1,2-bis(4-pyridyl)ethane (bpe), pyrazine (pyz), or methylpyrazine (mepyz) as bidentate ligands in presence of  $\text{H}_2\text{O}$  has been investigated for the first time. The products obtained have the general formula  $[(\text{Ph}_3\text{Sn})_3\text{Cu}(\text{CN})_4 \cdot \text{L} \cdot \text{XH}_2\text{O}]$ , where L is a bidentate ligand and  $X = 0-2$ .  $\text{H}_2\text{O}$  molecules are usually coordinated to tin atoms and are involved in two significant  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bonds, wherein the nitrogen atoms belong either to the bidentate ligand or the M-coordinated cyanide ligands. The structures of these supramolecular coordination polymers were investigated by elemental analysis, X-ray powder diffraction, and IR, mass, and NMR spectra.*

**Keywords** Bidentate ligands; copper(I) cyanide; supramolecular; triphenyltin(IV) compounds

## INTRODUCTION

Great interest has been focused on using the molecular building block approach to generate microporous solids with three-dimensional-organic,<sup>1–3</sup> metal-organic<sup>4–6</sup> and inorganic<sup>7</sup> frameworks. Strategies for the construction of these solids have utilized hydrogen bonding interactions, metal-ligand coordination, and metal-cluster co-polymerization reactions to link their molecular components.

It is well known that the binary adduct  $[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6]$  can readily be converted into ternary adducts of the type  $[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6 \cdot n\text{L}]$ , where L is either bipyridine or dioxane.<sup>8–10</sup>

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The five atom metal connector, or spacer,  $-\text{CN} \rightarrow \text{Sn} \leftarrow \text{NC}-$  (spacer I) usually results by rapid self assembly when dissolved  $[\text{M}(\text{CN})_m]^{n-}$  ions meet hydrated  $\text{R}_3\text{Sn}^+$  ions. The somewhat modified host-guest system  $[(\text{Ph}_3\text{Sn})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O} \cdot \text{MeCN}]^8$  contains both spacer I and the seven-atom spacer:  $-\text{CN} \dots \text{HO}(\text{H}) \rightarrow \text{Sn} \leftarrow \text{NC}-$  (spacer II). Also, the coordination of tin atoms to the nitrogen atom of the ligand was recognized in the compound  $[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O} \cdot 3/2\text{bpy}]^9$  that was found to contain a new type of spacer:  $-\text{CN} \rightarrow \text{Sn} \leftarrow \text{N}(\text{bpy})\text{N} \rightarrow \text{Sn} \leftarrow \text{NC}-$  (spacer III). On the other hand, the guest free system,  $[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O} \cdot \text{dioxane}]^{10}$  contains both spacer I and a notably more extended spacer IV:  $-\text{CN} \rightarrow \text{Sn} \leftarrow \text{OH}(\text{H}) \cdots \text{L} \cdots \text{HO}(\text{H}) \rightarrow \text{Sn} \leftarrow \text{NC}-$  (with  $\text{L} = \text{dioxane}$ ).

Similarly, compounds of the more recently studied type,  $[\text{CuCN} \cdot 3\text{R}_3\text{SnCN}] = [(\text{R}_3\text{Sn})_3\text{Cu}(\text{CN})_4]^{11}$  might be able to add either two monodentate bases or one bidentate ligand. The self-assembly reactions of  $[\text{Cu}(\text{CN})_4]^{3-}$  as building blocks with  $\text{Me}_3\text{Sn}^+$  groups in the presence of bidentate ligands (bpe, tbpe, bpy, or pyz) affords the new Supramolecular Coordination Polymers (SCPs).<sup>12-14</sup>

The current study deals with the self assembly of the tetrahedral  $[\text{Cu}(\text{CN})_4]^{3-}$  building blocks and the trigonal planar  $[\text{Ph}_3\text{Sn}]$  connecting unit in the presence of bidentate ligands such as bpy, tbpe, bpe, pyz, and mepyz. The products have the formula  $[(\text{Ph}_3\text{Sn})_3\text{Cu}(\text{CN})_4 \cdot \text{L} \cdot \text{X} \cdot \text{H}_2\text{O}]$ ;  $\text{L} = \text{bpy}$ ,  $\text{X} = 0$  for **1**;  $\text{L} = \text{pyz}$ ,  $\text{x} = 1$  for **2**,  $\text{L} = \text{mepyz}$ ,  $\text{X} = 1$  for **3**;  $\text{L} = \text{tbpe}$ ,  $\text{X} = 2$  for **4**; and  $\text{L} = \text{bpe}$ ,  $\text{X} = 0$  for **5**.

## RESULTS AND DISCUSSION

### Infrared Spectra

The IR spectra of the SCPs **1**, **4**, and **5** exhibit only one strong band for  $\nu_{(\text{CN})}$  in the range of 2092 to 2112  $\text{cm}^{-1}$ , whereas the spectra of the SCPs **2** and **3** display two bands at 2084–2112  $\text{cm}^{-1}$  and 2081–2112  $\text{cm}^{-1}$ , respectively (Table I). The presence of these two bands for the CN group may be assigned to different force constants of the different bridging CN groups or to the presence of bridging and nonbridging (terminal) CN groups. Generally, the position of these bands reflects the covalent nature of the  $\text{Cu}-\text{C} \equiv \text{N} \rightarrow \text{Sn}$  bridging unit because they usually occur at higher wavenumbers than  $\nu_{(\text{CN})}$  bands of the corresponding salt,  $\text{K}_3[\text{Cu}(\text{CN})_4]$ .<sup>17</sup> On the other hand, these frequencies appear at relatively close positions to those of the salt, and this confirms the presence of the nonlinear bridging CN groups.<sup>11,18,19</sup>

The presence of the aromatic systems (phenyl and bidentate ligands) was confirmed by the presence of weak broad bands in the region of

**TABLE I** IR Spectral Data of SCPs **1–5**. **s** = Strong, **m** = Medium, **w** = Weak

Comp.	$\nu_{\text{(CH)}}$ (arom.)	$\nu_{\text{(CH)}}$ (aliph.)	$\nu_{\text{(CN)}}$	$\nu_{\text{(C=C)}}$		$\delta_{\text{(C-H)}}$ (aliph.)	$\gamma_{\text{(C-H)}}$ (arom.)	$\nu_{\text{(Sn-C)}}$	$\nu_{\text{(Cu-C)}}$
<b>1</b>	3048 m 2989 w 2926 w	—	2095 s	1595 m 1480 m	1531 w 1427 s	—	728 s 694 s	570 w	452 s
<b>2</b>	3047 m 2985 m	—	2112 s 2084 s	1577 w 1478 m	1520 w 1425 s	—	727 s 693 s	570 sh	451 s
<b>3</b>	3026 m 3047 m	2924 w 2850 w	2112 s 2081 s	1578 m 1427 s	1477 m	1382 m	727s 694 s	570 sh	451 s
<b>4</b>	3048 m 3065 m	2918 w 2853 w	2112 s	1581 s 1479 m	1501 s 1427 s	—	730 s 694 s	570 sh	450 s
<b>5</b>	3047 m 3065 m	2989 w 2924 w	2109 s	1603 s 1480 m	1515 w 1427 s	—	730 s 696 s	550 m	452 s

2926–3065  $\text{cm}^{-1}$ , these bands were assigned to  $\nu_{\text{(CH)}}$  vibrations. The aromatic rings' stretching vibrations appear as medium-intense bands in the region of 1425–1605  $\text{cm}^{-1}$ . In addition, the strong bands in the region of 693–730  $\text{cm}^{-1}$  are due to wagging vibrations,  $\gamma_{\text{(CH)}}$ , of the aromatic rings (Table I).

The vibrational spectra of the SCPs **1–5** show the band due to the asymmetric stretching vibrations of Sn–C bonds in the region of 540–570  $\text{cm}^{-1}$ . The presence of this band indicates that the  $\text{Ph}_3\text{Sn}$  group plays the role of linking  $[\text{Cu}(\text{CN})_4]^{3-}$  building blocks and acts as a connecting unit, to form three-dimensional-networks. The absence of the symmetric stretching vibration band of the Sn–C bond,  $\nu_{\text{(Sn-C) sym}}$ , of these SCPs advocate an exclusive presence of trigonal planar  $\text{Ph}_3\text{Sn}$  units, which are axially anchored to two cyanide N atoms forming trigonal bipyramidal (tbp) configured  $\text{Ph}_3\text{Sn}(\text{NC})_2$  units.<sup>11</sup> In addition, the IR spectra of these SCPs exhibit a medium band due to the stretching vibrations of Cu–C bonds around 450  $\text{cm}^{-1}$ .

## THERMOGRAVIMETRIC ANALYSIS

The thermal decomposition of the SCPs **1–5** usually starts by the loss of eventual water molecules between 70–100°C, followed by the loss of the bridging bidentate ligand between 120–220°C, and finally the loss of two molecules of  $\text{Ph}_3\text{SnCN}$  between 210–340°C. The loss of the coordinated water molecules at this low temperature range is well known to occur in many early reported organotin and organolead SCPs.<sup>9,10,20</sup> In the present study, the water molecules may be coordinated through their oxygen atoms to tin atoms of  $\text{Ph}_3\text{Sn}$  connecting units. The molecular

**TABLE II Thermogravimetric Analysis Data of SCPs 1–5. All Residues Are Stable Until 800°C Under a Nitrogen Atmosphere**

Comp.	First step		Second step		Third step		Residue
	Trans. temp.	$\Delta m$ % obs.(cal.)	Trans. temp.	$\Delta m$ % obs.(cal.)	Trans. temp.	$\Delta m$ % obs. (cal.)	$\Delta m$ % obs.(cal.)
<b>1</b>	130–200	10.4 (11.3)	210–340	55.1 (54.7)	–	–	33.7 (33.8)
<b>2</b>	70–90	1.2 (1.36)	120–180	5.8 (6.07)	200–310	57 (57.1)	36.0 (35.3)
<b>3</b>	70–90	1.3 (1.35)	130–180	7.3 (6.97)	200–320	56 (55.8)	35.4 (35.0)
<b>4</b>	70–100	2.5 (2.5)	130–140	12 (12.5)	210–330	53 (52.4)	32.5 (32.4)
<b>5</b>	140–230	14 (13.4)	240–330	54 (53.6)	–	–	32.0 (33.2)

weight of the residue obtained after complete decomposition of these compounds corresponds to the formula,  $[(\text{Ph}_3\text{Sn})\text{Cu}(\text{CN})_2]$ , which was found to be stable at high temperatures up to 800°C.<sup>11</sup> Thermogravimetric data of these SCPs with the different steps are illustrated in Table II.

## Mass Spectra

These SCPs usually undergo thermal decomposition in the ion source leading to the formation of their original components. Then each one of these components undergoes ionization and fragmentation as if it was present alone. The decomposition of these SCPs leads to the volatility of triphenyltin cyanide and the bidentate ligands.

The most important observation in the mass spectra of the SCPs **1–5** is that they are nearly similar except for the peaks arising from the bipodal ligands. This observation is predictable because these SCPs have similar structures and the same connecting unit,  $\text{Ph}_3\text{Sn}$ . Each mass spectrum displays more than 16 peaks. The base peak, in the spectra of all 5 SCPs, is at  $m/z$  154 and it corresponds to the  $(\text{C}_6\text{H}_5)_2^+$  radical ion. Also, they show the ion peak of the phenyl ion ( $m/z$  77) and its fragment ion  $\text{C}_4\text{H}_3^+$  ( $m/z$  51). The spectra also display the peaks of the  $\text{PhSnCN}^+$  radical ion and its fragment ions. Also, the mass spectra of the SCPs **1–5** display the peaks characteristic of the bidentate ligands; bpy ( $m/z$  156), pyz ( $m/z$  80), mepyz ( $m/z$  94), tbpe ( $m/z$  182), and bpe ( $m/z$  184). For instance, the mass spectrum of SCP **3** is interpenetrated in Table III.

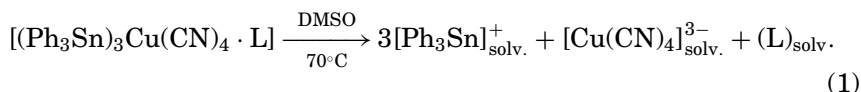
## NMR Spectra

The  $^1\text{H}$ -NMR spectra of **1–5** are shown in Figure 1, whereas the  $^{13}\text{C}$ -NMR spectra of compounds **1**, **2**, and **4** are illustrated in Table IV. The

**TABLE III Interpretation of the Mass Spectrum of SCP 3**

m/z(%)	Ion
28 (3%)	$\text{N}_2^+, \text{C}_2\text{H}_4^+$
40 (3%)	$\text{C}_3\text{H}_4^+$
51 (13%)	$\text{C}_4\text{H}_3^+$
67 (7%)	$\text{C}_4\text{H}_5\text{N}^+$
77 (24%)	$\text{C}_6\text{H}_5^+$
94 (10%)	$[\text{Mepyz}]^+$
120 (28%)	$\text{Sn}^+$
154 (100%)	$(\text{C}_6\text{H}_5)_2^+$
197 (25%)	$\text{PhSn}^+$
146 (9%)	$\text{SnCN}^+$
213 (2%)	$\text{PhSnOH}^+$
274 (14%)	$\text{Ph}_2\text{Sn}^+$
300 (31%)	$\text{Ph}_2\text{SnCN}^+$
351 (8%)	$\text{Ph}_3\text{Sn}^+$
377 (3%)	$\text{Ph}_3\text{SnCN}^+$
485 (1%)	$\text{PhSn}-\text{O}-\text{Sn}(\text{Ph}_2)^+$
561 (0.5%)	$(\text{Ph}_2\text{Sn})_2\text{O}^+$
639 (2%)	$\text{Ph}_2\text{Sn}-\text{O}-\text{Sn}(\text{Ph}_3)^+$
716 (0.5%)	$(\text{Ph}_3\text{Sn})_2\text{O}^+$

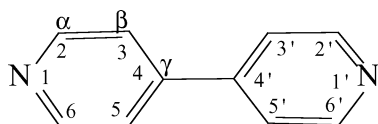
degradation of the SCPs under investigation, upon dissolution, may be represented by Eq. (1). Scheme 1 shows the numbering of the aromatic heterocyclic bases.



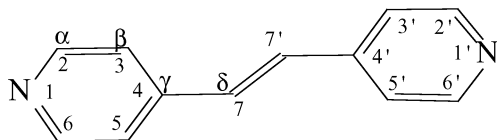
The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the SCPs under investigation display the same bands characteristic of the phenyl and cyanide groups. The  $^1\text{H}$ -NMR spectra of **1–5** display broad multiplet bands at  $\delta = 7.34$ – $7.93$  ppm that are due to the protons of  $\text{Ph}_3\text{Sn}$  connecting units.<sup>21</sup>  $^{13}\text{C}$ -NMR spectra of these SCPs, in the cyanide region, consist of a single

**TABLE IV  $^{13}\text{C}$ -NMR Data of SCPs **1**, **2**, and **4**. b-c = Broad-Complex, d = Doublet, m = Multiplet, s = Singlet**

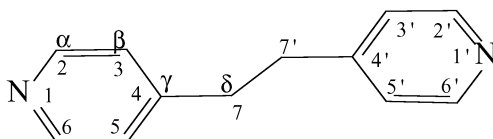
Compound	$\delta$ (Ph-Sn)	$\delta$ (CN)	$\delta$ (Ligand)
<b>1</b>	129 (b-c)	136 (s)	122 (s), 142 (s), 151 (s)
<b>2</b>	129 (b-c)	136 (s)	146 (s)
<b>4</b>	129 (b-c)	136 (s)	122 (s), 144 (s), 132 (s), 151 (s)



4,4'-Bipyridine



Trans-1,2-bis(4-pyridyl)ethylene



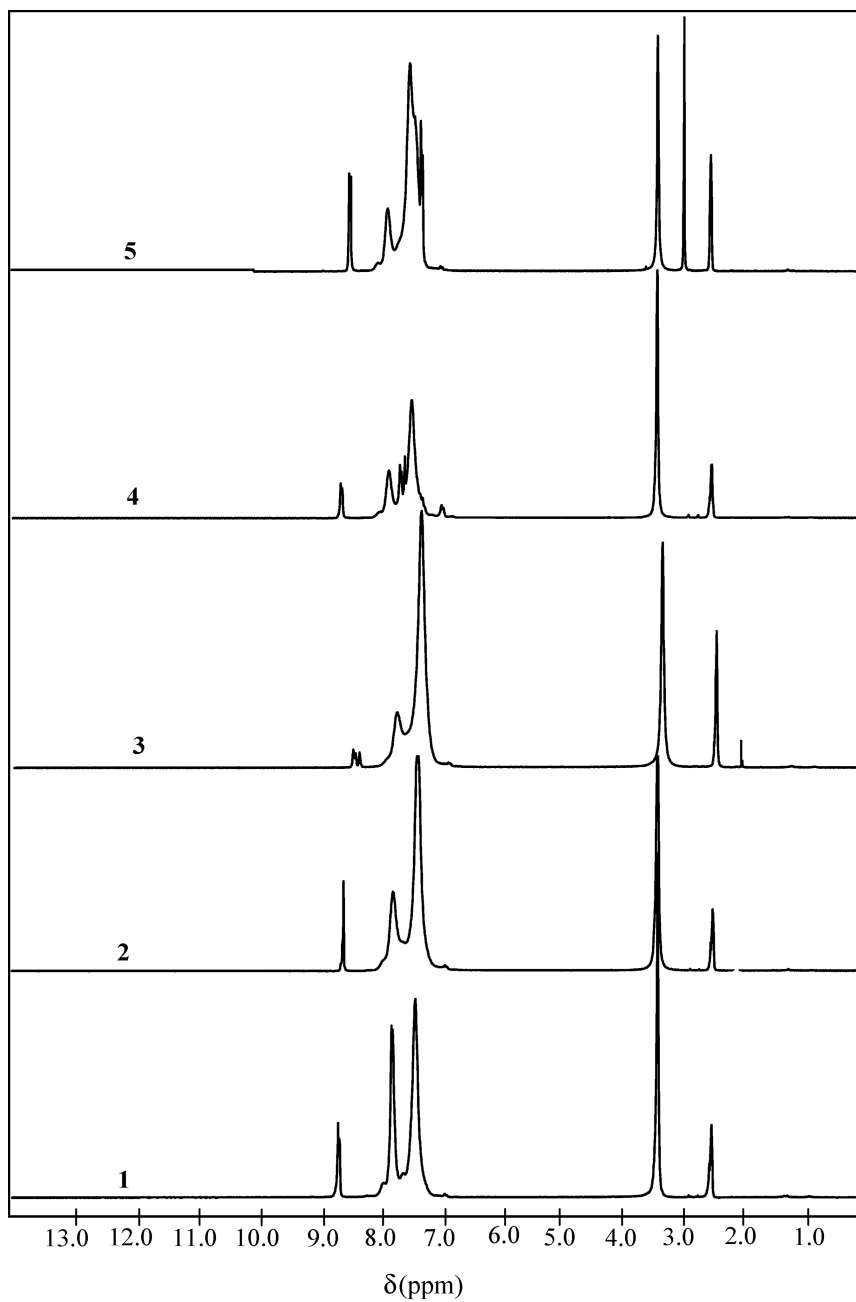
1,2-bis(4-pyridyl)ethane

**SCHEME 1** Atomic numbering scheme of bipodal ligands.

band at  $\delta = 136$  ppm. The broad complex bands at  $\delta = 129$  ppm, in the  $^{13}\text{C}$ - spectra of these compounds, were assigned to the phenyl groups.<sup>18</sup>

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the SCPs under investigation display different spectral bands due the presence of different bidentate ligands. The  $^1\text{H}$ -NMR spectrum of SCP **1** displays two doublets for bpy.<sup>22</sup> The first doublet at  $\delta = 8.70$  ppm was assigned to  $\text{H}_{2,6}$  &  $\text{H}_{2,6'}$ , whereas the second doublet at  $\delta = 7.80$  ppm was assigned to  $\text{H}_{3,5}$  &  $\text{H}_{3',5'}$ . The last doublet was coincident with the broad band of the protons of the phenyl groups. The bpy ligand gives rise to three singlet bands in the  $^{13}\text{C}$  spectrum, at  $\delta = 122$ , 142, and 151 ppm. These bands were assigned to  $\alpha$ ,  $\gamma$ , and  $\beta$  carbon nuclei, respectively.<sup>23</sup>

The  $^1\text{H}$ -NMR spectrum of **2** is similar to that of **1**. However, it displays only one singlet band for the pyz ligand at  $\delta = 8.63$  ppm<sup>22</sup>. The  $^{13}\text{C}$ -NMR spectrum of this compound, shows one singlet band for the pyz ligand at  $\delta = 146$  ppm.<sup>23</sup> The  $^1\text{H}$ -NMR spectrum of **3** shows three singlet bands at  $\delta = 8.42$ – $8.52$  ppm that were assigned to the protons of mepyz

**FIGURE 1**  $^1\text{H}$ -NMR spectra of the SCPs 1–5.

ring. The methyl group of this ligand displays a weak singlet band at  $\delta = 2.05$  ppm.

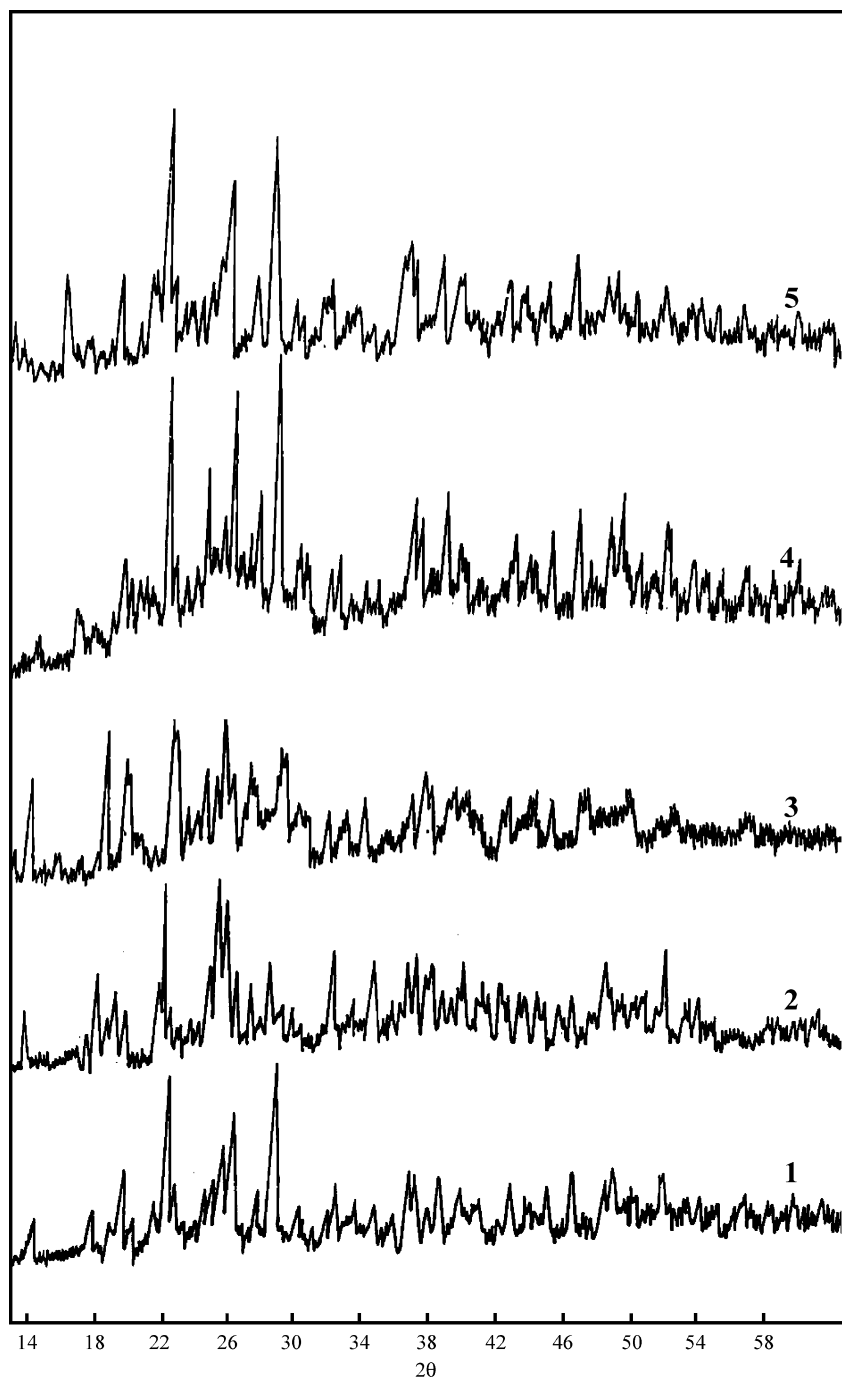
The  $^1\text{H}$ -NMR spectrum of **4** displays three distinct bands for *tbpe*.<sup>22</sup> The first doublet at  $\delta = 8.57$  ppm was assigned to  $\text{H}_{2,6}$  and  $\text{H}_{2',6'}$ , whereas the second doublet at  $\delta = 7.57$  ppm was assigned to  $\text{H}_{3,5}$  and  $\text{H}_{3',5'}$ . The latter doublet coincides with the band of the phenyl group protons. The third band appears as a singlet at  $\delta = 6.93$  ppm and was assigned to  $\text{H}_7$ ,  $\text{H}_{7'}$ . In the  $^{13}\text{C}$ -spectrum of **4**, there are four bands at  $\delta = 122$  ppm for  $\beta$  carbon nuclei,  $\delta = 144$  ppm for  $\gamma$  carbon nuclei,  $\delta = 151$  ppm for  $\alpha$  carbon nuclei, and  $\delta = 132$  ppm for the olefinic carbon nuclei.<sup>23</sup>

The  $^1\text{H}$ -NMR spectrum of **5** displays three distinct bands for *bpe*.<sup>22</sup> The doublet at  $\delta = 8.41$  ppm was assigned to  $\text{H}_{2,6}$  and  $\text{H}_{2',6'}$ , but the doublet at  $\delta = 7.23$  ppm was assigned to  $\text{H}_{3,5}$  and  $\text{H}_{3',5'}$ . The  $-\text{CH}_2-\text{CH}_2-$  group gives rise to one singlet band at  $\delta = 2.91$  ppm.

## Proposed Structures of the Supramolecular Coordination Polymers 1–5

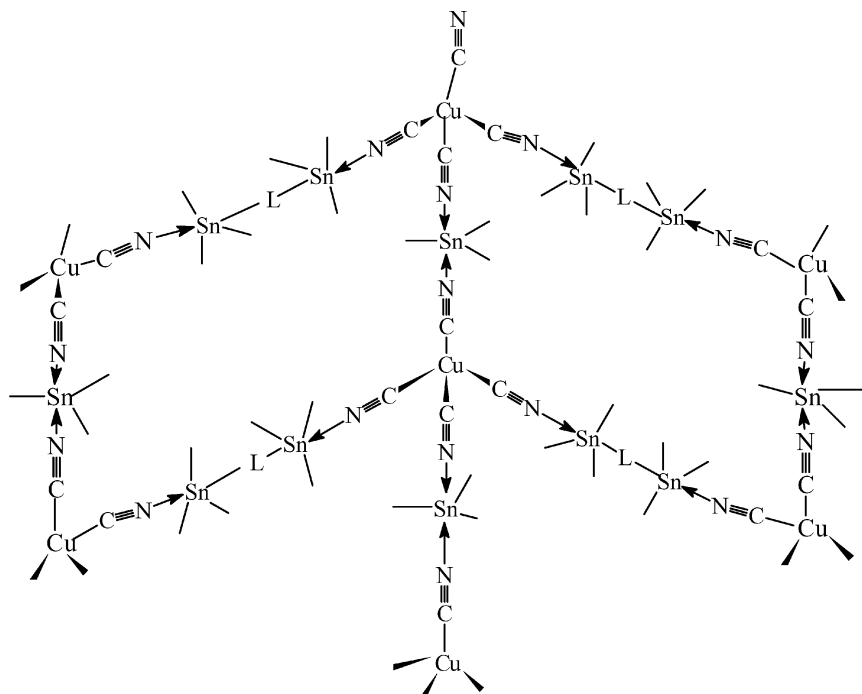
The SCPs **1–5** gave rise to satisfactory X-ray powder diffraction patterns with pronounced and sharp reflections that reflect the crystalline nature of these SCPs. According to Figure 2, there is good similarity between the X-ray powder diffraction patterns of **1–5**. The latter finding reflects the fact that SCPs **1–5** have similar structures with the differences being due to the different bidentate ligands and water content.

The tin atoms are pentacoordinated with a *tbp* configuration  $\{\text{Ph}_3\text{Sn}(\text{XX}')\}$ ;  $\text{X} = \text{X}' = \text{CN}$ , a bidentate ligand or  $\text{H}_2\text{O}$ . These groups are used as connecting units between  $\text{Cu}(\text{I})$  ions yielding an infinite three-dimensional-framework. In these three-dimensional networks, the four-coordinate copper(I) sites are interconnected by a variety of nonlinear spacers. The presence of these nonlinear spacers was confirmed by IR spectra that display  $\nu_{\text{CN}}$  at higher frequencies than those of the genuine salt anion,  $[\text{Cu}(\text{CN})_4]^{3-}$ . Also, the absence of the band of the asymmetric stretching of “ $\text{Sn}-\text{C}$ ” bonds indicates the presence of trigonal planar  $[\text{Ph}_3\text{Sn}]$  units and confirms the bridging nature of these groups. The SCPs may have one or more of the spacers:  $-\text{C}\equiv\text{N}\rightarrow\text{Sn}(\text{Ph}_3)\leftarrow\text{N}\equiv\text{C}-$  (I),<sup>14,24</sup>  $-\text{C}\equiv\text{N}\rightarrow\text{Sn}(\text{Ph}_3)\leftarrow\text{O}(\text{H})-\text{H}\cdots\text{N}\equiv\text{C}-$  (II),<sup>8</sup>  $-\text{C}\equiv\text{N}\rightarrow\text{Sn}(\text{Ph}_3)-\text{N}(\text{L})\text{N}-\text{Sn}(\text{Ph}_3)\leftarrow\text{N}\equiv\text{C}-$  (III),<sup>9</sup> and  $-\text{C}\equiv\text{N}\rightarrow\text{Sn}(\text{Ph}_3)\leftarrow\text{O}(\text{H})\text{H}\cdots\text{N}(\text{L})\text{N}\cdots\text{H}(\text{H})\text{O}\rightarrow\text{Sn}(\text{Ph}_3)\leftarrow\text{N}\equiv\text{C}-$  (IV)<sup>9</sup> (L is a bidentate ligand). Two or more of these spacers may combine to give rise to more complicated ones. Unfortunately, crystals suitable for X-ray single crystal analysis could not be obtained for any member of this class. Hence the actual structures of these compounds can not be



**FIGURE 2** X-ray powder diffraction of the SCPs 1–5.

defined categorically, but these structures may be predicted by comparison with the similar previously reported compounds. The structure of **1** and **5** may be considered as a three dimensional-framework in which Cu atoms are interconnected by both spacer I and spacer III. Scheme 2

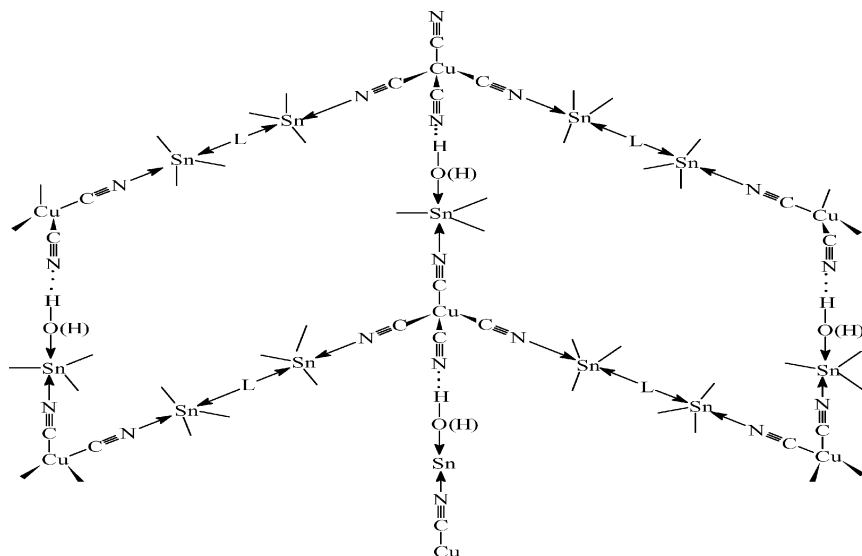


**SCHEME 2** Schematic representation of the hypothetical structure of **1** (or **5**), where L = 4,4'-bpy or bpe.

shows the schematic representation of the hypothetical structure of the latter two SCPs. The structure of **4** is similar to those of **1** and **5**, but the spacer III is replaced by spacer IV due to the insertion of two water molecules. Hence, the structure of **4** may be considered as a three-dimensional-network in which Cu(I) ions are interconnected by two different spacers, spacer I and spacer IV. The structure of **4** is similar to that of the well-known SCP  $[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6 \cdot \text{dioxane} \cdot 2\text{H}_2\text{O}]$ .<sup>10</sup> The structure of the latter compound may be described as an infinite three-dimensional-network of two different nonlinear chains, which are interlinked by their joint, octahedrally coordinated Fe atoms.

Thermogravimetric analyses of SCPs **2** and **3** clearly indicate the presence of only one water molecule in each polymer. This water molecule was lost in the temperature range 70–100°C. Thus, SCPs **2**

and **3** may have slightly different structures from those mentioned previously. Their frameworks may be similar to those of **1** and **5**, but one of the spacers present is slightly elongated due to insertion of one water molecule. The structures of both SCPs may be considered as three-dimensional-networks built up of tetrahedral four-coordinate Cu(I) ions that are interconnected by both spacer II and spacer III (Scheme 3).



**SCHEME 3** Schematic representation of the hypothetical structure of **2** (or **3**), where L = pyz or mepyz.

### Uptake of Gaseous $\text{NO}_2$ by SCPs 1–5

The three-dimension-networks of the SCPs **1–5** contain cavities that may act as hosts for many guest molecules. The ability of these SCPs to accommodate guest molecules was characterized by  $\text{NO}_2$  gas uptake. The reaction with  $\text{NO}_2$  runs spontaneously at ambient conditions. A mixture of  $\text{NaNO}_2$  and  $\text{AcOH}$  was used as a source of  $\text{NO}_2$  gas, which was allowed to interact with the powdered SCPs for a long time (ca. 6 h). The products were characterized by elemental analysis, IR, and magnetic moment measurements (Table V). All 5 SCPs are able to absorb  $\text{NO}_2$  gas followed by a change of color. The elemental analysis shows that these SCPs absorb one  $\text{NO}_2$  molecule per copper ion. The products, after the reaction with  $\text{NO}_2$ , exhibit paramagnetism due to the oxidation of Cu(I) to Cu(II) (Table V). Hence,  $\text{NO}_2$  is reduced to  $\text{NO}_2^-$  ions,

**TABLE V** General Characterization of the SCPs 1–5 After the Reaction With NO<sub>2</sub> Gas

Compound	Color	C %	H %	N %	$\nu\text{NO}_2^-$ (cm <sup>-1</sup> )	$\mu_{\text{eff}}$
		Cal. (found)	Cal. (found)	Cal. (found)		
<b>1</b> NO <sub>2</sub>	Green	57.5 (56.9)	3.7 (3.6)	6.9 (6.6)	1288	1.80
<b>2</b> NO <sub>2</sub>	Red	54.6 (54.0)	3.7 (3.9)	7.1 (6.9)	1288	1.3
<b>3</b> NO <sub>2</sub>	Green	54.9 (54.6)	3.5 (3.9)	7.1 (6.8)	1287	1.2
<b>4</b> NO <sub>2</sub>	Green	56.7 (55.5)	4.0 (3.5)	6.6 (6.9)	1289	1.87
<b>5</b> NO <sub>2</sub>	Grey	58.0 (56.9)	3.9 (4.0)	6.7 (6.5)	1288	2.3

and this was confirmed by IR spectra that show the band of the NO<sub>2</sub><sup>-</sup> anion at 1288 cm<sup>-1</sup>.

## EXPERIMENTAL

### Materials

K<sub>3</sub>[Cu(CN)<sub>4</sub>] was prepared according to the method described in the literature.<sup>15,16</sup> All other materials and solvents were received from Aldrich Chemicals Company and were used without further purification.

### Preparation of the SCPs 1–5

#### General Method

A solution of 180 mg (0.62 mmol) of K<sub>3</sub>[Cu(CN)<sub>4</sub>] in 10 mL of water was being added dropwise, with stirring, to a mixture of 0.63 mmol of the bidentate ligand in 10 mL of acetonitrile and 731 mg (1.9 mmol) of Ph<sub>3</sub>SnCl in 10 mL of acetonitrile. The precipitates were washed by water and acetonitrile. All preparations were carried out in the presence of air, and all the new compounds reported have been proven to be stable in air.

[(Ph<sub>3</sub>Sn)<sub>3</sub>Cu(CN)<sub>4</sub>·bpy], **1**: Yield: 0.615 g (72.2%); Color: yellow; anal. calcd. for C<sub>68</sub>H<sub>53</sub>N<sub>6</sub>CuSn<sub>3</sub>: C, 59.9; H, 4.0; N, 6.1; found: C, 59.9; H, 4.2; N, 5.9.

[(Ph<sub>3</sub>Sn)<sub>3</sub>Cu(CN)<sub>4</sub>·pyz·H<sub>2</sub>O], **2**: Yield: 0.724 g (88.7%); Color: yellow; anal. calcd. for C<sub>62</sub>H<sub>51</sub>N<sub>6</sub>OCuSn<sub>3</sub>: C, 56.6; H, 3.9; N, 6.3; found: C, 56.6; H, 4.3; N, 5.5.

[(Ph<sub>3</sub>Sn)<sub>3</sub>Cu(CN)<sub>4</sub>·mepyz·H<sub>2</sub>O], **3**: Yield: 0.692 g (82.0%); Color: yellow; anal. calcd. for C<sub>63</sub>H<sub>53</sub>N<sub>6</sub>OCuSn<sub>3</sub>: C, 56.8; H, 4.0; N, 6.3; found: C, 56.3; H, 4.2; N, 5.7.

$[(\text{Ph}_3\text{Sn})_3\text{Cu}(\text{CN})_4 \cdot \text{tbp} \cdot 2\text{H}_2\text{O}]$ , **4**: Yield: 0.700 g (77.3%); Color: yellow; anal. calcd. for  $\text{C}_{70}\text{H}_{59}\text{N}_6\text{O}_2\text{CuSn}_3$ : C, 58.5; H, 4.1; N, 5.8; found: C, 58.9; H, 4.7; N, 5.8.

$[(\text{Ph}_3\text{Sn})_3\text{Cu}(\text{CN})_4 \cdot \text{bpe}]$ , **5**: Yield: 0.769 g (87.6%); Color: yellow; anal. calcd. for  $\text{C}_{70}\text{H}_{57}\text{N}_6\text{CuSn}_3$ : C, 59.9; H, 4.1; N, 5.9; found: C, 59.7; H, 4.5; N, 5.4.

## Characterization

Microanalyses were carried out with a Perkin-Elmer 2400 automatic elemental analyzer. IR spectra were obtained on a Bruker Vector 22 spectrophotometer using KBr discs. Mass spectrometry data were measured with a Finnigan MAT 8222. The X-ray powder diffraction patterns were recorded using a Philips PW-129 (Cu K radiation using Ni filter). NMR spectra were recorded on a Bruker DPX 200 spectrometer using  $\text{DMSO-d}_6$  as a solvent. Thermogravimetric analyses were carried out on a Shimadzu AT 50 thermal analyzer (under  $\text{N}_2$  atmosphere). The magnetic susceptibility was determined with a Johnson-Matthey susceptometer.

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