Bimetallic multidimensional supramolecular coordination polymers containing triphenyltin cation and CuCN

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ABSTRACT

The reaction of $K_3[Cu(CN)_4]$ in H_2O with a solution of Ph_3SnCl and 4-methylpyrimidine (mpym) in acetonitrile affords, at room temperature, the white powder $[(Ph_3Sn)_3Cu(CN)_4.mpym \cdot H_2O]$, **II**, precipitating in the mother liquor and colourless platelet crystals $[(Ph_3Sn)_2Cu(CN)_3]$, **I**, which was obtained from the filterate after two days. The copper site in **I** assumes distorted trigonal plane geometry. The network structure of **I** is constructed via 3D-puckered layers constructed of infinite parallel $[CuCN-(\mu-Ph_3Sn)-CN]$ chains forming waves where the $CNSnPh_3$ fragments locate the peak and bottom positions of the waves as side arms. The 2D-layers are connected by hydrogen bonds and $\pi-\pi$ stacking. This is the first example for a Cu-coordination polymer containing the tetrahedral and bipyramidal configured tin atoms. The pyramidal tetrahedral $[Cu(CN)_4]^{3-}$ anion, in **II**, are interconnected by two kinds of nanometer spacers; $-C\equiv N \rightarrow Sn(Ph_3) \leftarrow O(H)H...N\equiv C-$ and $-C\equiv N \rightarrow Sn(Ph_3)-N(mpym)N-Sn(Ph_3) \leftarrow N\equiv C-$ creating super-Prussian blue 3D-network structure.

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1. Introduction

In the past few years, there has been considerable interest in the design and elaboration of multidimensional Cu(I) coordination polymers prepared by conventional solution routes or by the less conventional solvothermal techniques. The products should be either the $[(Cu)_n(CN)_m xL]$ complexes [1–7] or the organotin–copper(I) containing polymers [8–12]. The organometallic family $[(R_3E)_3M(CN)_6]\equiv[M\mu-(CNE(R_3)NC)_3]$ with R = alkyl and E = Sn or Pb was considered as super-prussian blue derivatives [11] which are related to zeolites. Few examples of zeolite-like polymeric copper cyanides involving the charged bipodal ligands and the likewise rod-like anionic $[CN.Sn(R_3)-NC]-$ acting as a nanometer-sized spacer ligand, are known [8–12]. The zeolite-like $[(Bu_4N)(Et_3Sn)_2Cu(CN)_4]$ was obtained by using Et_3SnCl [8], while the different $[(Bu_4N)(Me_3Sn)Cu_2(CN)_4]$ was exclusively formed by using Me_3SnCl [11]. The $(Bu_4N)^{4-}$ fragments act as guest ions. On the other hand, planar sheets involving both 4- and 24- atomic rings are interlinked in $[CuCN \cdot Me_3Sn \ 0.5bpy]$ by almost perpendicular bpy pillars to generate a very voluminous 3D-framwork [9]. The novel supramolecular assembly $[CuCN \cdot Me_3SnCN \cdot pyz]$ contains the basic building blocks constructed of distorted adamandoid Cu_{10} cages with Cu...Cu edges of 10.795 Å [10]. While $[CuCN \cdot Me_3SnCN \cdot 0.5bpe]$ and $[CuCN \cdot Me_3SnCN \cdot 0.5bpeH_2]$ display layered structures with rhombic $[Cu_2(\mu-CN)_2]$ motif as basic building block. On the other hand, $[CuCN \cdot Me_3SnCN \cdot cpy]$ crystallizes in a distorted-diamondoid structure $^3_\infty\{Cu[\mu-CNSn(Me)_3NC] \mu-cpy\}$ with four equivalent and independent, interlocking frameworks [12]. These coordination polymers contain alkyl tin fragments while there are no any derivatives containing the ph_3Sn fragments due to the difficulty for obtaining single crystals. In a trial to extend this work to obtain new zeolite-like coordination polymers containing ph_3Sn fragments, different bipodal ligands are used including mpym. Powder products are usually obtained while mpym gives the colourless platelet crystals $[(Ph_3Sn)_2Cu(CN)_3]$, **I**, and the crystalline $[(Ph_3Sn)_3(CN)_4mpym \cdot H_2O]$, **II**.

2. Experimental

$K_3[Cu(CN)_4]$ was prepared following the literature procedures [13,14]. Triphenyltin chloride, mpym and solvents were purchased from Aldrich, Merck or Fluka and used without further purification.

2.1. Synthesis of $[(Ph_3Sn)_2Cu(CN)_3]$, **I** and $[(Ph_3Sn)_3Cu(CN)_4 \cdot mpym \cdot H_2O]$, **II**

A solution of 90 mg (0.31 mmol) of $K_3[Cu(CN)_4]$ in 5 ml H_2O was added dropwise with stirring to a solution of 366 mg (0.95 mmol)

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of Ph$_3$SnCl and 29 mg (0.31 mmol) of mpym in 10 ml acetonitrile. A white precipitate of **II** was formed at once. After filtration, subsequent washing with water and acetonitrile and overnight drying, 223 mg (54.4% referred to K$_3$[Cu(CN)$_4$]) of the white precipitate, **II**, was obtained. Decomposition temperature is 190 °C. Elemental analysis data for C$_{63}$H$_{53}$N$_6$Sn$_3$·CuO are: Anal. Calc. C, 56.89; H, 3.98; N, 6.30; Cu, 4.78 and Found C, 56.43; H, 4.12; N, 5.96; Cu, 4.63%.

The colourless solution of the filtrate was kept at room temperature, where after two days, colourless platelet crystals started growing from that filtrate. After filtration, washing with water and acetonitrile and overnight drying, 55 mg (21% referred to K$_3$[Cu(CN)$_4$]) of **I** was obtained. Decomposition temperature is 180 °C. TGA thermogram of **I** exhibits three steps corresponding to the release of one Ph$_3$Sn unit and three cyanide groups in the temperature range of 180–270 °C, and three Phenyl groups in the temperature range 270–400 °C, with the formation of mixed metals Cu + Sn in the temperature range of 410–470 °C. The residue obtained after complete thermolysis (over 600 °C) of **I** is coincident with 0.5Sn +0.5(SnO$_2$) + Cu [observed mass = 23.99% (201.74 g mol^{-1}), calculated mass = 23.57% (198.25 g mol^{-1})].

IR spectrum of **I** $\nu_{(C\equiv N)}$ 2113 cm^{-1}, $\nu_{(C=C)}$ phenyl 1578 and 1481 cm^{-1} $\nu_{(Sn-C)}$ 550 cm^{-1} and $\nu_{(Cu-C)}$ 405 cm^{-1}. ^{1}H NMR spectrum of **I** displays only two broad multiplet peaks at 7.45 and 7.76 ppm due to the protons of the phenyl groups indicating the presence of the ph$_3$Sn units and the absence of the mpym ligand. The ESI$^+$ mass spectrum of **I**, exhibits the base peak at m/z 351 corresponding to the Ph$_3$Sn$^+$ isotopomer of the molecular ion. The interpretation of the positive and negative ion polarity mass spectra for the SCP **I** was listed in Table 1 indicating its polymeric nature. Elemental analysis data for C$_{39}$H$_{30}$N$_3$Sn$_2$Cu; are Anal. Calc. C, 55.65; H, 3.56; N, 4.99; Cu, 7.55 and Found C, 55.38; H, 3.46; N, 5.27; Cu, 7.39%.

2.2. Physical measurements

Microanalyses (C, H, N) were carried out with a Perkin–Elmer 2400 automatic elemental analyzer, while copper was determined using Perkin–Elmer 2380 atomic absorption spectrometer. Infrared spectra were recorded on a Bruker Vector 22 spectrophotometer as KBr discs in the range of 400–4000 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker DPX 200 spectrometer, using DMSO-d_6 as a solvent. Mass spectra were recorded on Finnigan MAT SSQ 7000 spectrometer. The thermogravimetric analyses were carried out on TGA-50 H thermal analyzer (under N$_2$ atmosphere), in the range of 25 °C to 800 °C at a heating rate 20 °C/min using 0.3–2 mg of the samples. X-ray powder diffraction patterns were recorded using a Diang Corporation diffractometer equipped with Co Kα radiation, tube operated at 45 Kv, 9 mA and single crystal X-ray diffraction measurements were carried out on a Kappa CCd Enaraf Nonius FR 90 four circle goniometer with graphite monochromatic Mo Kα

Table 1
Interpretation of the mass spectra of the positive and negative ion polarity (ESI$^+$) and (ESI$^-$), respectively for [(Ph$_3$Sn)$_2$Cu(CN)$_3$], **I**.

Ion	m/z	Ion	m/z
Sn$^+$	120	(Ph$_3$Sn)$_2$O$^+$	717
PhSn$^+$	197	[(Ph$_3$Sn)$_2$Cu(CN)$_2$]$^+$	817
Ph$_2$Sn$^+$	274	[(Ph$_3$Sn)$_2$Cu$_2$(CN)$_3$]$^+$	905
Ph$_3$Sn$^+$	351	[(Ph$_3$Sn)$_2$Cu(CN)$_3$PhSnCu(CN)$_2$]$^+$	1154
Ph$_3$SnCN$^+$	377	[(Ph$_3$Sn)$_2$Cu(CN)$_3$Ph$_3$SnPh$_2$SnCu(CN)$_2$]$^+$	1579
[Ph$_2$SnCu(CN)$_2$]$^+$	392	Cu$_6$(CN)$_7^-$	562
Cu(CN)$_2^-$	115	Cu$_7$(CN)$_8^-$	652
Cu$_2$(CN)$_3^-$	204	Cu$_8$(CN)$_9^-$	741
Cu$_3$(CN)$_4^-$	295	Cu$_9$(CN)$_{10}^-$	830
Cu$_4$(CN)$_5^-$	384	Cu$_{10}$(CN)$_{11}^-$	921
Cu$_5$(CN)$_6^-$	473		

radiation [λ Mo Kα] = 0.71073 Å]. The well developed crystal of **I** was mounted on glass fibers, and the measurements were made at 25 ± 2 °C. The structure was solved using direct-methods and all of the non-hydrogen atoms were located from the initial solution or from subsequent electron density difference maps during the initial stages of the refinement. After locating all of the non-hydrogen atoms in each structure the models were refined against F^2, first using isotropic and finally anisotropic thermal displacement parameters unless otherwise stated. The positions of the hydrogen atoms were then calculated and refined isotropically, and a final cycle of refinements was performed. The refinement of the structure of **I** was performed anisotropically for the non-hydrogen atoms giving R factor 0.058. However, it was observed that the carbon atoms of the phenyl groups are not stable due to their large temperature factors suggesting substantial mobility. So, the structure of **I** was refined anisotropically for the heavy metals (Sn and Cu) and the cyanide groups while the atoms of the phenyl groups were refined isotropically giving R factor 0.065. The structure in this case is stable at room temperature. This observation supports the opinion that the phenyl groups attached to the tin atoms act freely in the structure because they are not connected to any atom in the lattice giving rise to high amplitude of displacement factor. On the other hand, all cyanide atoms are ordered since the nitrogen ends are coordinated to the Sn atoms.

3. Results and discussion

The crystals of **I** were found to have the chemical formula $^3_\infty$[Cu(CN)$_3$-μ-(Ph$_3$Sn)Ph$_3$Sn] which is quite different than the molecular formula and the structure of the white powder **II** (vide infra). The crystal data and structure refinement parameters of **I** are summarized in Table 2.

The ORTEP plot of **I** shows one copper (I) site coordinated to the ordered cyanide groups representing the building blocks of the structure of **I**, Fig. 1. The copper site assumes distorted trigonal plane (TP-3) geometry with angles approximately equal to 360°, Table 3. These Cu(CN)$_3$ building blocks are bridged by one Ph$_3$Sn(1) unit while the other Ph$_3$Sn(2) unit is only bonded to the nitrogen end of the N(9)≡C(49) group. Thus, the copper atom is coordinated to the carbon ends of the cyanide groups while the tin atoms are coordinated to the nitrogen ends of the cyanide groups. The Sn(I)

Table 2
Crystal data and structure refinement parameters of **I**.

|	
Empirical formula	C$_{39}$H$_{30}$N$_3$CuSn$_2$
Formula weight (g mol^{-1})	841.616
Temperature (K)	298
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pca2_1$
a (Å)	26.1038(10)
b (Å)	9.5374(3)
c (Å)	15.3152(4)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3); Z	3812.9 (2)/4
ρ calc. (Mg m^{-3})	1.466
Absorption coefficient (mm^{-1})	1.88
$F(000)$	1656
Reflections collected/unique	5096/1910
R int	0.033
Data/restraints/parameters	1910/0/266
Goodness-of-fit on F^2	4.476
R indices [$I > 3\sigma(I)$]R^1/wR^2	0.065/0.147
$W = 1/s^2(F_0^2) + 0.1000 \times F_0^2)$	
R indices (all data)	0.091/0.152
Largest difference peak and hole	1.61/−0.80 e Å^3
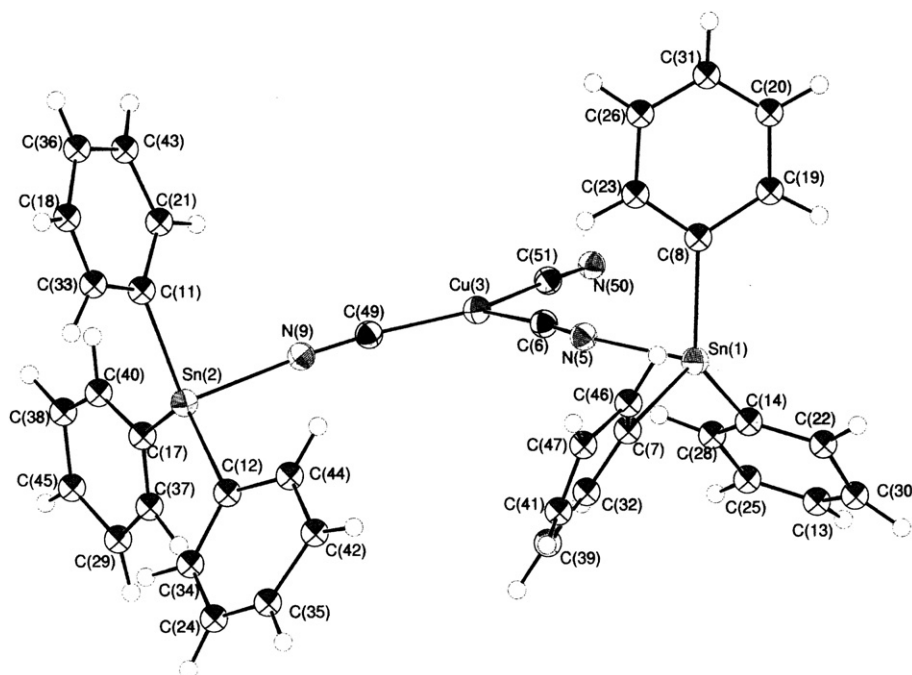
Fig. 1. Perspective view of the asymmetric unit of **I**, showing the atom labeling scheme and 50% thermal ellipsoids.

atom forms trigonal bipyramidal (TBPY-5) configuration where the three phenyl groups occupy the corners of a distorted TP-3, while the two cyanide groups occupy axial positions, Table 3. The angles of these cyanide groups at the axial positions defined by the TP-3 of Sn(1) site deviate slightly from the ideal value of 90° and consequently the angle of N(5)−Sn(1)−N(5) equals to 176.5°. The Ph$_3$Sn (1) fragment connects the Cu(CN)$_3$ building blocks forming corrugated 1D-Polymeric chain with Cu$_9$N$_9$Sn$_2$(ph$_3$) fragments located on both sides of the chain as side arms, Fig. 2. The Sn(2) atom is coordinated to the three phenyl rings and the nitrogen end of one cyanide group; N(9)−C(49), forming pseudo tetrahedral (PT-4) structure, Table 3. Also, it was observed that the bond lengths of the TP-3 assumed by the Sn(1) site are more or less equal, 2.104−2.147 Å, while the axial bonds suffer elongation giving Sn(1)−N(5) = 2.242 Å and Sn(1)−N(50) = 2.316 Å, the case which supports the TBPY-5-configured structure of the Sn(1) site. On the other hand, all the bond lengths of the PT-4 configured structure of the Sn(2) site are nearly equal supporting the PT-4 configured structure of the Sn(2) site, Table 3. Thus, the two tin atoms in the structure of **I** are

chemically and crystallographically different. This is the first example for a Cu-coordination polymer containing the PT-4 configured and the TBPY-5-configured tin atoms as far as we know. It is worth mentioning that the argument of presence of non bridging PT-4 configured R$_3$SnNC units in the structure of some organotin-cyano metallate polymers like [(Me$_3$Sn)$_4$M(CN)$_6$]; M = Fe, Ru or Os, could not be ruled out by solid state ^{13}C and ^{119}Sn NMR spectra [15]. However, the presence of both PT-4 and TBPY-5-configured R$_3$SnO$_n$ (n = 2 or 1) units has been confirmed by crystallography and by solid state NMR for two ID-polymeric carbonates [(R$_3$Sn)$_2$Co$_3$]$_\infty$, R = Me and Bu [16]. The phenyl rings occupying the positions of TP-3 and of PT-4 formed by the Sn(1) and Sn(2) atoms, respectively, are crystallographically equivalent

Table 3
Selected bond lengths (Å) and bond angles (°) for **I**.

|			
Sn(1)−N(5)	2.242(7)	N(5)−Sn(1)−C(7)	89.6(3)
Sn(1)−C(7)	2.137(7)	N(5)−Sn(1)−C(8)	87.6(3)
Sn(1)−C(8)	2.104(8)	N(5)−Sn(1)−C(14)	92.3(3)
Sn(1)−C(14)	2.146(7)	N(5)−Sn(1)−N(50)	176.5(3)
Sn(1)−N(50)	2.316(7)	C(7)−Sn(1)−C(8)	113.6(3)
Sn(2)−N(9)	2.172(8)	C(7)−Sn(1)−C(14)	118.5(3)
Sn(2)−C(11)	2.132(9)	C(7)−Sn(1)−N(50)	92.4(3)
Sn(2)−C(12)	2.157(9)	C(8)−Sn(1)−C(14)	127.9(3)
Sn(2)−C(17)	2.075(8)	C(8)−Sn(1)−N(50)	89.0(3)
Cu(3)−C(6)	2.056(10)	C(14)−Sn(1)−N(50)	89.3(3)
Cu(3)−C(49)	1.866(10)	N(9)−Sn(2)−C(11)	94.1(3)
Cu(3)−C(51)	1.969(11)	N(9)−Sn(2)−C(12)	95.1(3)
N(4)−C(6)	1.104(10)	N(9)−Sn(2)−C(17)	101.6(3)
N(9)−C(49)	1.199(10)	C(11)−Sn(2)−C(12)	120.4(3)
C(11)−Sn(2)−C(17)	115.2(3)	C(12)−Sn(2)−C(17)	120.2(3)
C(6)−Cu(3)−C(49)	122.1(3)	C(49)−Cu(3)−C(51)	128.7(3)
C(6)−Cu(3)−C(51)	108.8(3)	Cu(3)−C(6)−N(5)	173.0(3)
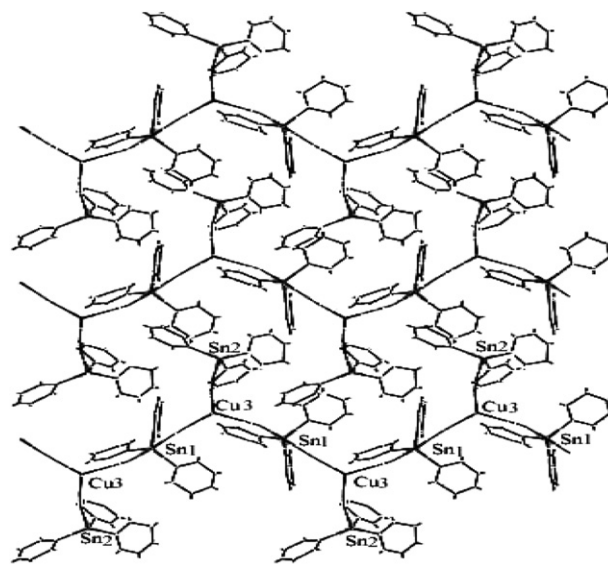
Fig. 2. A view of portion of the network structure of **I**, showing the arrangement of some phenyl groups into the wide channels of **I**. Hydrogen atoms are omitted for clarity.

around room temperature owning to rapid rotation about their individual trigonal axes. This conclusion is further substantiated by the previous solid state ^{13}C NMR [15] and 2D-EXSY [17] studies which confirmed the rapid rotation of the alkyl groups (on the NMR time scale) about their individual trigonal axes. It is, also, observed that the angles of C(6)−Cu(3)−C(49),C(49)−Cu(3)−C(51) and C(6)−Cu(3)C(51) forming the distorted TP-3 trigonal plane geometry of Cu(I) site have the values 122.1°, 128.7° and 108.8°, respectively. This situation results to decrease the steric hindrance between the phenyl groups of both tin atoms [Sn(l) and Sn(2)] and consequently the Ph$_3$Sn(2) unit seems to locate far away the {Ph$_3$Sn(l) NC−Cu−CN Ph$_3$Sn(l)}$_\infty$ fragment.

The cyanide bond lengths are in the normal range of 1.1160−1.1910 Å, Table 3. The CN−Cu and the CN−Sn angles deviate from 180° usually acquired by the CN−M angle being in the range of 162−172.1°. As a result of the values of these angles, the structure of **I** gives rise to comparatively compact 3D-puckered chains of infinite extension in the bc-plane, Fig. 2. The network structure of **I** is constructed via puckered chains constructed of infinite [CuCN-µ-(Ph$_3$Sn)−CN] units. These infinite puckered chains are parallel forming waves where the CNSn(2)Ph$_3$ fragments locate the peak and bottom positions of the waves as side arms. In between these parallel puckered chains, there are channels wide enough to accommodate the bulky phenyl groups, Fig. 2. The phenyl groups are arranged face-to-face causing stabilization of the 2D-network structure by π−π stacking (3.0 Å) as well as H-bonds between the H-atoms of the phenyl rings and the π-cloud of another phenyl ring in the neighboring layer and between H-atoms and the cyanide groups, Table 4.

3.1. Spectral characterization and structure of **II**

As single crystals of **II** were not obtained so far. Several experimental techniques were used to accomplish a definitive characterization of its structure. The presence of ternary adducts; Ph$_3$Sn cation, cyanide groups and mpym in the structure of **II** was confirmed by elemental analysis, TGA and spectroscopic methods. Consulting the IR spectrum of **II**, Table 5, and that of **I** (vide supra) indicates that they contain the Ph$_3$Sn and CuCN fragments. In consequence of bridging the tetrahedral Cu(CN)$_4$ building blocks by the Ph$_3$Sn units via an essential covalent Cu−C≡N→Sn bond, one can realize the presence of $\nu_{C \equiv N}$ band (2111 cm^{-1}) at higher wavenumbers than the band of the genuine salt of the corresponding [Cu(CN)$_4$]$^{3-}$ anion (2076 cm^{-1}) [18], which contains non-bridged cyanide groups. In addition, the stretching frequencies much higher than those of the genuine salts; K$_3$[Cu(CN)$_4$] and [(^{n}Bu$_4$N)$_3$Cu(CN)$_4$], have been assigned to linear bridging between metal centers, while frequencies near those of the salts are associated with terminal or non-linear bridging CN groups [8,19,20]. It is also worth mentioning that the cyanide band of **II** locates at more or less the same position as that of the prototype **I**. On the other hand, the IR spectrum of **II** exhibits a broad band at 3447 cm^{-1} corresponding to ν_{OH} of the water molecule. The broadening of this band indicates participation of the water molecules in hydrogen bonds while TGA indicated coordination of the water molecules to some tin atoms as they release at temperature above 160 °C (vide infra). Also the IR

Table 4
Selected hydrogen bond lengths (Å) for **I**.

N(5)−H(23)	2.858(7)	C(20)−H(21)	2.924(12)
N(5)−H(28)	2.507(7)	C(42)−H(18)	2.979(11)
N(5)−H(29)	2.804(6)	N(50)−H(19)	2.865(8)
N(9)−H(21)	2.821(7)	C(51)−H(22)	2.999(8)
C(6)−H(28)	2.618(9)	−	−

Table 5
Wavenumbers of the different vibrational modes of the SCP **II**.

Peak, cm^{-1}	Assignment	Peak, cm^{-1}	Assignment	Peak, cm^{-1}	Assignment
3447b 3136w	ν_{H_2O} ν_{CH_2} (pym)	1648 m 1598w 1577w 1544w 1516m	δ_{H_2O} $\nu_{C=C}$	1189w 857w 680w	ν_{C-N} γ_{CH} (mpym)
3064m 3047m	ν_{CH} (aromatic)	1480s	$\nu_{C=C}$ (Ph)	729s 694s	γ_{CH} (Ph)
2932m 2860m	ν_{CH} (m)	1438w	δ_{CH} (mpym)	541b	ν_{Sn-C}
2111s	$\nu_{C \equiv N}$	1428s 1334m	δ_{CH} (Ph)	451s	Vib. of Ph ring
1956w 1883w 1815w 1771w 1705m	Overtones and combinations of the phenyl groups	1391 m	δ_{CH} (mpym)	413w	ν_{Cu-C}

Pym = pyrimidine, m = methyl, ph = phenyl, mpym = methylpyrimidine, b = broad, s = strong, m = medium and w = weak.

spectrum of **II** shows the characteristic bands of mpym, Table 5, which are absent in the IR spectrum of **I**. These data indicate that the structure of **II** contains non-linear chains constructed by the Cu(CN)$_4$ building blocks bridged by the [Ph$_3$Sn←OH$_2$] or the [Ph$_3$Sn←mpym→Ph$_3$Sn] spacers. The broad band at 541 cm^{-1} due to asymmetric ν_{Sn-C} advocates the presence of trigonal plane Ph$_3$Sn units owing to their axial anchoring to two cyanide nitrogen atoms. The presence of mpym in the network structure of **II** is supported by the medium and weak bands at 3136 cm^{-1} ($\nu_{CH(pym)}$), 2932 and 2860 cm^{-1} ($\nu_{CH(m)}$), 1598, 1544 and 1516 cm^{-1}($\nu_{C=C}$), 1438, 1391 cm^{-1} (δ_{CH}), 1261 cm^{-1}(ν_{C-N}), 857 and 680 cm^{-1} (γ_{CH}).

The ^{1}H NMR spectrum of **II** shows two broad overlapping peaks at 7.92 and 7.96 ppm corresponding to the aromatic protons of mpym, while the methyl protons absorb at 2.05 ppm. This assignment was supported by consulting the ^{1}H NMR spectrum of mpym, which exhibits sharp singlet, two doublets and one broad singlet at 8.95, 8.60, 7.45 and 2.30 ppm corresponding to H(2), H(6), H(5) and CH$_3$, respectively. The peaks are shifted upfield supporting the participation of mpym in the formation of **II**. The ^{1}H NMR spectrum of **II** exhibits also, three broad peaks at 7.45, 7.76 and 7.78 ppm due to the absorption of the phenyl protons. These peaks are different in shape and position than those observed in the ^{1}H NMR spectrum of Ph$_3$SnCl which appear as well resolved multiplets in the range of 6.2−8.5 ppm. This observation indicates participation of the Ph$_3$Sn units in the formation of the structure of **II.** In addition to the peaks due to mpym and the Ph$_3$Sn units, a weak broad peak appears at 8.15 ppm corresponding to a water molecule. This peak disappears on deuteration by D$_2$O. This down field chemical shift indicates the coordination of the water molecules and the presence of strong intramolecular hydrogen bonding between the water protons and the cyanide nitrogen atoms. Thus, ^{1}H NMR spectra of mpym, Ph$_3$SnCl and **II** support the presence of mpym, Ph$_3$Sn units and H$_2$O in the structure of **II**.

The mass spectrum of **II** exhibits the base peak at m/z = 351 corresponding to ph$_3$Sn$^+$ isotopomer of the molecular ion. The interpretation of the positive ion and negative ion polarity mass spectra for **II** is listed in Table 6. The most important ion peak appears at m/z = 1584 corresponding to [(Ph$_3$Sn)$_3$Cu(CN)$_3$(mpym)Cu−C≡N...H$_2$O→SnPh$_3$]$^+$ which supports the participation of mpym and the water molecule in the formation of the network structure of **II**. On the other hand, the ESI$^-$ mass spectrum of **II** displays more than eleven peaks of [Cu$_n$(CN)$_{n+1}$]$^-$ units, where the base peak observed at m/z = 564 corresponds to [Cu$_6$(CN)$_7$]$^-$ isotopomer of the molecular ion, indicating the polymeric nature of the Cu(CN)$_4$ building blocks.

Table 6
Interpretation of the mass spectra of the positive and negative ion polarity (ESI$^+$) and (ESI$^-$), respectively for [(Ph$_3$Sn)$_3$Cu(CN)$_4$·mpym·H$_2$O], **II**.

| Ion	m/z	Ion	m/z
Sn$^+$	120	[Ph$_3$SnCu(CN)$_2$mpym]$^+$	561
PhSn$^+$	197	[(Ph$_3$Sn)$_2$CuCNmpym]$^+$	886
Ph$_2$Sn$^+$	274	[(Ph$_3$Sn)$_2$Cu$_2$(CN)$_3$mpym]$^+$	1001
Ph$_3$Sn$^+$	351	[(Ph$_3$Sn)$_3$Cu(CN)$_3$]$^+$	1194
(Ph$_3$Sn)$_2$OH$_2^+$	719	[(Ph$_3$Sn)$_3$Cu(CN)$_3$mpymCuCNPhSnOH$_2$]$^+$	1584
Cu(CN)$_2^-$	115	Cu$_7$(CN)$_8^-$	652
Cu$_2$(CN)$_3^-$	206	Cu$_8$(CN)$_9^-$	741
Cu$_3$(CN)$_4^-$	295	Cu$_9$(CN)$_{10}^-$	830
Cu$_4$(CN)$_5^-$	384	Cu$_{10}$(CN)$_{11}^-$	921
Cu$_5$(CN)$_6^-$	473	Cu$_{11}$(CN)$_{12}^-$	1010
Cu$_6$(CN)$_7^-$	564		

3.2. Thermogravimetric analysis of **II**

The thermogram shows the first step at 160–280 °C, which corresponds to the decomposition of 1.5(Ph$_3$SnCN) and the mpym molecule as well as the releasing of the interlayer water molecule [observed $\Delta m = -50.90\%$ (676.32 g mol^{-1}), calculated $\Delta m = -50.84\%$ (675.55 g mol^{-1})]. This step indicates that the water molecule is coordinated to some tin atoms O→Sn and may form hydrogen bonding with the cyanide group. The weight loss in the second step at 300–400 °C, is due to the loss of ½ Ph$_3$SnCN [observed $\Delta m = -14.22\%$ (188.97 g mol^{-1}), calculated $\Delta m = -14.14\%$ (187.85 g mol^{-1})]. The residue at 400–640 °C was Ph$_3$SnCu(CN)$_2$ which was found to be stable at higher temperatures [19] under dry pure nitrogen atmosphere [observed mass = 34.87% (463.34 g mol^{-1}), calculated mass = 35.01% (465.25 g mol^{-1})]. At higher temperatures over 750 °C and in the presence of the contaminated oxygen, **II** undergoes complete decomposition and oxidation to give the final product of mixed oxides. The molecular weight of the residue obtained after complete thermolysis of **II** is coincident with 2(SnO$_2$) + Cu$_2$O [observed mass = 34.00% (451.74 g mol^{-1}), calculated mass = 33.45% (444.5 g mol^{-1})]. Consulting the thermogravimetric data of **II**, leads to the conclusion that the structure of **II** contains the ternary adducts;

Ph$_3$Sn units, CuCN fragments and the bipodal base; mpym as well as the interlayer H$_2$O.

The X-ray powder diffractograms of (**I** and **II**) which are the products of the same ternary adducts, are very rich in sharp discrete lines. They are quite different exhibiting different 2θ values and different lattice constants. Thus, **I** and **II** are chemically and structurally different. The structure of **II** contains the PT-4 [Cu(CN)$_4$]$^{3-}$ anion which is considered the main building block in construction of growing number of coordination polymers [8,11]. It can bridge the ph$_3$Sn cations in much the same fashion that CN$^-$ anions do, except that the greater complexity of the [Cu(CN)$_4$]$^{3-}$ ion leads to three-dimensional polymers. Now, the point is investigating the role of mpym and the water molecule that should act either as guest molecules in the cavities of the three-dimensional framework of the [(Ph$_3$Sn)$_3$Cu(CN)$_4$] fragment, or as coordinated spacers to provide wide enough space to accommodate the bulky phenyl groups. Regarding the first case, it is well known that no coordination polymer is directly obtained as a material with empty cavities (pores) large enough for guest incorporation since nature tends to avoid empty space. Also, the guest molecules can be seen as templates which are not covalently bond to the framework and could, in principle, be removed if they are neutral.

In the case of **II** the nine phenyl groups per molecule acquire wide space for incorporation and also, to avoid steric hindrance which should arise between the phenyl groups of other molecules. In the network of **II**, mpym and H$_2$O could not be removed either chemically or by heating up to 160 °C. TGA analysis provides the decomposition of **II** at 160 °C, and shows that mpym and H$_2$O are released along with 1.5(Ph$_3$SnCN) in the temperature range 160–280 °C. Thus, mpym and H$_2$O can be considered as coordinated spacers in the network structure of **II** to provide cavities wide enough for the bulky phenyl rings. Thus, the structure of **II** is built up of PT-4 [Cu(CN)4]$^{3-}$ building blocks that are interconnected by the (Ph$_3$Sn) cations which acquire TBPY-5-configured structure. The four-coordinate copper(I) sites are interconnected by two kinds of non-linear spacers; $-C\equiv N\rightarrow Sn(Ph_3)\leftarrow O(H)-H...N\equiv C-$ and $-C\equiv N\rightarrow Sn(Ph_3)-N(mpym)N-Sn(Ph_3)\leftarrow N\equiv C-$, Scheme 1. The
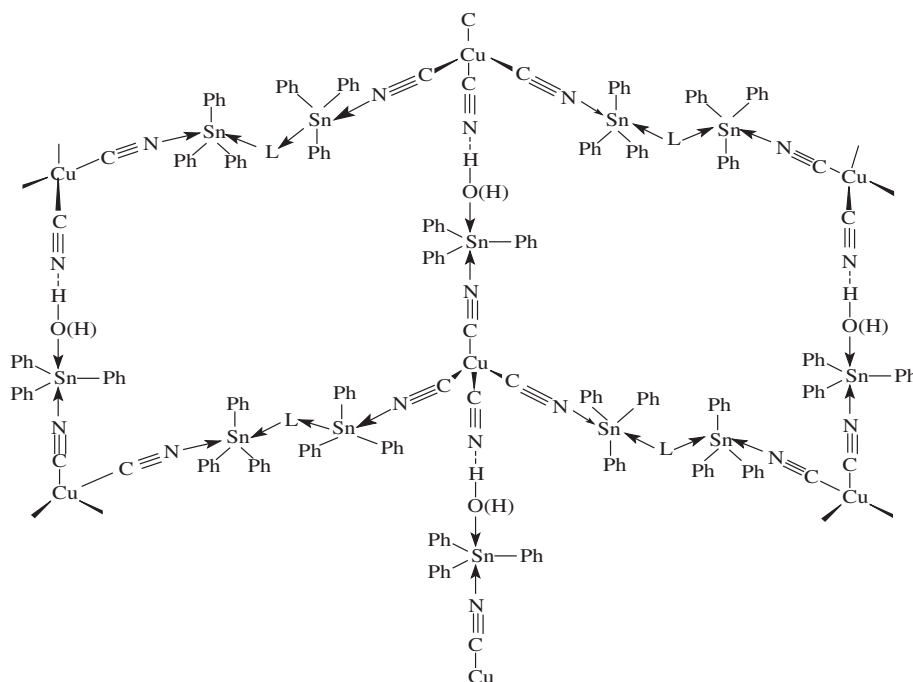
Scheme 1. Schematic representation of the proposed structure of the SCP **II**; L = (mpym).

presence of these non-linear spacers was confirmed by IR spectrum that display $\nu_{C\equiv N}$ at higher frequencies than those of the genuine salt anion, $[Cu(CN)_4]^{3-}$. Also, the presence of the band of the asymmetric stretching of Sn–C bonds indicates the presence of TBPY-5 Ph$_3$Sn units and confirms the bridging nature of these groups. It is a matter of fact that the actual structure of **II** cannot be defined categorically, but its structure was predicated by comparison with the prototype, early reported, compounds [21,22].

Appendix A. Supplementary data

CCDC 773506 contains the supplementary crystallographic data for **I**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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