Construction of supramolecular copper architecture via tetrahedral Cu(CN)$_4$ building blocks and trigonal bipyramidal [R$_3$Sn] connecting units

Amany M.A. Ibrahim

Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

Abstract

The self assembly of the pyramidal tetrahedral Cu(CN)$_4$ building blocks, the trigonal bipyramidal [R$_3$Sn] connecting units and the guest–template–cations leads to the construction of new types of non-interpenetrating polymeric networks. Twelve polymers have been prepared, most of them, according to the desired stoichiometry while polymers **9–12** represent binuclear copper compounds. These polymers are formed when no suitable space-demanding alkyl groups are used. The structures of the polymers under investigation were confirmed by elemental analysis, IR and Raman spectra, thermal analysis and NMR spectroscopy. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Supramolecular compounds; Copper; Tin; Cyanide

1. Introduction

A great interest has focused on using the molecular building block approach to generate microporous solids with 3D-organic [1], metal–organic [2], and inorganic [3] frameworks. Strategies for the construction of these solids have utilized hydrogen-bonding interactions metal-ligand coordination, and metal-cluster copolymerization reactions to link their molecular components. Recently, self-assembly of functionalised building blocks (e.g. Pt(CN)$_4^{2-}$, tetrahedral metal centres; metal = Zn, Cu, Cd,..., [Co(CN)$_6$]$^{3-}$ and [Fe$^{III/II}$(CN)$_6$]$^{3-/4-}$) and connecting units (e.g. tetrahedral Cu^I units, linear cyanide bridges, rod-like 4,4′-bipyridine (bpy) and (R$_3$Sn)$^+$ or (R$_3$Pb)$^+$) [4–7], leads to the construction of new types of infinite frameworks which may have interesting and useful properties with applications in areas such as ion exchange, molecular sieves and zeolite-like catalysis [8–12].

The spontaneous assembly of the non-interpenetrating diamond-like array consisting of tetrahedral metal centres interconnecting by linear bridges had been successfully obtained by bringing together in an aqueous solution the components Zn^{2+}, Cu$^+$, CN$^-$ and NMe$_4^+$ [13] forming frameworks consisting of equal numbers of inter-connecting square planar and tetrahedral centres. Also, a single-crystal X-ray study of polymer [(^{n}Bu$_4$N)(Et$_3$Sn)$_2$Cu(CN)$_4$]$_\infty$ has confirmed the formation of a negatively charged, three-dimensional host framework with wide channels (with D-value of 10.01 A°) occupied by well ordered Bu$_4$N$^+$ guest cations [14] which behave as an ideal space-filling template for the respective channels. On the other hand, single crystals of the ternary adducts of the general type [CuCN–L–R$_3$Sn CN] [L = pyrazine (pyz), R = Me (**1**); L = 4,4′-bpy, R = Et (**2**); L = bpy, R = Me (**3**)] have, very recently, been investigated [15,16]. The X-ray studies of the adducts (**1**) and (**2**) confirm the tetracoordination of Cu$^+$ ions, as simultaneous components of cross-linked chains of the type [–Cu–CN–Sn–NC–] and [–Cu–L–]$_\infty$. On the other hand, the architecture of (**3**) contains binuclear, practically, planar Cu$_2$(CN)$_4$

Table 1
Elemental analysis, colour and decomposition temperature of the supramolecular Cu^I-cyanides

No.	Compound	Colour	Decomp. T°C	Elemental analysis calc./(found)%				
				C	H	N	Cu	Sn
1	[(^{n}Bu$_4$N)$_3$Cu(CN)$_4$]$_n$	Faint yellow	[a]	69.78 (69.6)	12.16 (12.23)	10.95 (10.81)	7.10 (7.06)	— —
2	[(Me$_3$Sn)$_3$Cu(CN)$_4$]$_n$·2H$_2$O	White	127	22.46 (22.30)	4.49 (4.25)	8.10 (8.50)	9.14 (9.34)	51.23 (50.66)
3	[(Et$_3$Sn)$_3$Cu(CN)$_4$]$_n$·2H$_2$O	White	94	32.17 (31.84)	6.01 (5.98)	6.82 (6.49)	7.73 (7.55)	43.36 (43.12)
4	[(^{n}Bu$_3$Sn)$_3$Cu(CN)$_4$]$_n$	Colourless liquid	[a]	46.29 (46.25)	7.86 (7.95)	5.39 (5.21)	6.12 (6.10)	34.31 (34.23)
5	[Ph$_3$Sn)$_3$Cu(CN)$_4$]$_n$·2H$_2$O	White	105	55.56 (55.69)	3.94 (3.93)	4.46 (4.05)	5.06 (5 00)	28.40 (28.32)
6	[(^{n}Bu$_4$N)(Et$_3$Sn)$_2$Cu(CN)$_4$]$_n$	White	235	46.77 (46.75)	8.09 (8.10)	8.52 (8.48)	7.73 (7.64)	28.88 (28.96)
7	[(^{n}Bu$_4$N)(^{n}Bu$_3$Sn)$_2$Cu(CN)$_4$]·H$_2$O	White	190	52.41 (52.41)	9.19 (8.81)	6.94 (6.47)	6.30 (6.40)	23.54 (23.38)
8	[(Ph$_4$As)(^{n}Bu$_3$Sn)$_2$Cu(CN$_4$]$_n$	White	150	55.22 (55.13)	6.59 (6.10)	4.95 (4 04)	5.62 (5.59)	20.99 (20.80)
9	[(Me$_3$SbOH)(Me$_3$Sn)Cu$_2$(CN)$_4$]$_n$·H$_2$O	White	255	20.12 (19.80)	3.54 (3.43)	9.38 (9.60)	21.29 (21.50)	19.89 (20.10)
10	[(Ph$_3$SbOH)(Ph$_3$Sn)CU$_2$(CN)$_4$]$_n$·2H$_2$O	White	240	48.66 (48.72)	3.57 (3.38)	5.67 (5 6l)	12.86 (12.38)	12.02 (12.01)
11	[(MV^{2+})$_{0.5}$(Et$_3$Sn)Cu$_2$(CN)$_4$]$_n$·H$_2$O	Brown	220	35.05 (35.16)	4.41 (3.82)	12.77 (12.80)	23.18 (23.10)	21.65 (21.46)
12	[(^{n}Bu$_4$N)(Me$_3$Sn)Cu$_2$(CN)$_4$]$_n$	Colourless crystals	260	43.34 (43.30)	7.12 (7.13)	10 99 (10.90)	19.94 (19.90)	18.62 (18.61)

[a] Liquid at room temperature (ca. 18°C).

units which are cross-linked in the lattice, and the Cu–N (4,4'-bpy) bonds are oriented almost perpendicular to this plane. The Cu–Cu distance (2.62 nm) exceeds only slightly that of elemental copper (2.55 nm). These successful X-ray studies lead to the possible synthesis of several tailor made non-interpenetrating organotin(IV) polymers.

The present study deals with the synthesis of organotin polymers having metal–organic open frameworks with extended channels. The study, has also investigated the role of the size and shape of the ligand R as well as of the necessary counter cation, template, G$^+$. All these factors play an essential role for the verification and the actual structure of the host–guest system [G$^+$(R$_3$Sn)$_2$Cu(CN)$_4$]$_\infty$.

2. Experimental

The compounds Me$_3$SnCl, Et$_3$SnCl, ^{n}Bu$_3$SnCl, Ph$_3$SnCl, Ph$_4$AsCl, Me$_3$SbBr$_2$, MVCl$_2$, ^{n}Bu$_4$NCN, CuCN, KCN and the solvents were purchased from commercial suppliers.

In spite of the compounds **2–12** being air stable, Table 1, they should be prepared under a dry nitrogen atmosphere to avoid the formation of (R$_3$Sn)$_2$CO$_3$ as a by-product due to the high reactivity of R$_3$SnCl towards CO$_2$ even in the presence of any little amounts as

commonly present in air [14]. On the other hand, the compound **1** might be prepared and stored under a dry nitrogen atmosphere. This compound could be obtained as a liquid pure sample from its aqueous solutions. However, a clear prepared in-situ solution of the desired quantity of the compound has been obtained for further preparations.

[(^{n}Bu$_4$N)$_3$Cu(CN)$_4$]$_n$, **1**: 0.225 g (2.5 mmol) of CuCN was dissolved under nitrogen atmosphere in a solution of 2.025 g (7.5 mmol) of [(^{n}Bu$_4$N) CN in 45 ml of H$_2$O. After 1 h a faint yellow liquid was formed, then separated and stored under nitrogen.

[(Me$_3$Sn)$_3$Cu(CN)$_4$·2H$_2$O)]$_n$, **2**: A solution of 100 mg (0.351 mmol) of K$_3$[Cu(CN)$_4$] in 5 ml H$_2$O was added to a solution of 210 mg (1.053 mmol) of Me$_3$SnCl in 5 ml H$_2$O. White crystals were obtained, washed with H$_2$O, filtered off and dried from water overnight under vacuum.

[(Et$_3$Sn)$_3$Cu(CN)$_4$]$_n$·2H$_2$O, **3**: A solution of 210 mg (0.737 mmol) of K$_3$[Cu (CN)$_4$] in 2 ml H$_2$O was added to a solution of 533.6 mg = 0.37 ml (2.211 mmol) of Et$_3$SnCl in 5 ml H$_2$O. A white powder precipitate was readily formed, filtered off, washed by water and dried overnight under vacuum. The yield was 538 mg (93%) based upon Et$_3$SnCl.

[^{n}Bu$_3$Sn)$_3$Cu(CN)$_4$]$_n$, **4**: A solution of 100 mg (0.351 mmol) of K$_3$[Cu(CN)$_4$] in 2 ml H$_2$O was added to a solution of 343.7 mg ca. 0.28 ml (1.053 mmol) of

Table 2
Infrared spectra (in cm^{-1}) of the supramolecular Cu^I-cyanides

Compound no.	ν_{H_2O} δ_{H_2O}	ν_{CH}	ν_{CN}	$\nu_{C=C}$ *$\nu_{C=N}$	δ_{CH}	ν_{CH}	ν_{C-N}	ν_{Cu-C}	ν_{Sn-C}	ν_{Sb-C}
1	—	2960, 2930 2874	2082 2076	—	1474, 1381 1465, 1398	883 739	1241 1167	416 362	—	—
2	3520 1640	2994, 2917 2870	2111			785	— 370	418	550	—
3	3500 1620	2966, 2947 2869, 2825	2109	—	1457, 1378	956 683	—	421 375	524	—
4	—	2956, 2921 2872, 2856	2112	—	1464, 1377	878 748	—	420 373	560	—
5	3500 1620	3064, 3054 3045, 3024	2111	1579 1481	1428, 1331	766 694	—	418 368	557	—
6	—	2964, 2932 2872, 2835	2106	—	1482, 1381	884 685	1250 1170	409 360	527	—
7	3450 1616	2957, 2922 2872, 2856	2111	—	1465, 1378	881 737	1238 1160	409 355	522	—
8	—	3080, 3061 2955, 2924 2869	2109	1581, 1525 1483	1439, 1337 1455, 1374	877, 868 740, 688	—	412 356	518	—
9	3536 1629 3280[a]	2998, 2918 2882	2117	—	1430, 1383	861, 792		414 368	554	580
10	3436 1637	3070, 3049	2116 2045	1608, 1526 1481	1460, 1375	731, 691	—	407 356	564	585
11	3480 1620	3081, 3045 2948, 2929 2869	2112	1562, 1508 *1637	1431, 1328 1445, 1377	881, 850 795, 737	1269 1184	417 362	572	—
12	—	2968, 2937 2877	2144 2082	—	1465, 1380	790 742	1240 1162	412 —	552	—

° ν_{OH}.

^{n}Bu$_3$SnCl in 10 ml 2:1 acetone/water mixture. Two phases were obtained after 2 h. The reaction was left for 48 h and then the liquid phase of [^{n}Bu$_3$Sn)$_3$Cu(CN)$_4$] was isolated.

[(Ph$_3$Sn)$_3$Cu(CN)$_4$]·2H$_2$O]$_n$, **5**: A solution of 100 mg (0.351 mmol) of K$_3$[Cu(CN)$_4$] in 2 ml H$_2$O was added to 406 mg (1.053 mmol) of Ph$_3$SnCl in 12 ml 2:1 acetone/water mixture. A white crystalline precipitate was formed at once. The reaction was left for 24 h and then filtered off, washed with water/acetone mixture and dried overnight under vacuum. The yield was 385 mg (90%) based upon Ph$_3$SnCl.

[(Bu$_4$N)(Et$_3$Sn)$_2$Cu(CN)$_4$]$_n$, **6**: It was precipitated under a dry nitrogen atmosphere as fine white crystals using three different methods: (1) addition of a solution of 1.2 g (5 mmol) of Et$_3$SnCl in 30 ml of H$_2$O/acetone mixture to a clear aqueous solution of [(Bu$_4$N)$_3$Cu(CN)$_4$]. (2) addition of the solutions of 0.81 (3 mmol) of (Bu$_4$N)CN in H$_2$O, 0.48 (2 mmol) Et$_3$SnCl in H$_2$O/acetone mixture and 0.09 g (1 mmol) of CuCN; (3) addition of the solutions of 0.16 g (1 mmol) of CuSO$_4$ in H$_2$O, 0.27 g (1 mmol) of (Bu$_4$N)CN in H$_2$O, 0.48 g (2 mmol) Et$_3$SnCl in H$_2$O/acetone mixture and an excess of KCN (more than 3 mmol) in H$_2$O. Yield after filtration, repeated washing with water/acetone

and drying at 40°C (ca. 3 h) was (ca. 91%). The second route gives the best results and yield.

[(^{n}Bu$_4$N)(^{n}Bu$_3$Sn)$_2$Cu(CN)$_4$]$_n$·H$_2$O, **7**: Fine white crystals were obtained after the addition of a solution of 1.63 g (5 mmol) of ^{n}Bu$_3$SnCl in 20 ml of acetone–water mixture to a clear in-situ prepared aqueous solution of (2.5 mmol) of (^{n}Bu$_4$N)$_3$Cu(CN)$_4$. The yield finally obtained after filtration, repeated washing with water/acetone and drying at 40°C was 3.29 g (92%) based upon CuCN.

[(Ph$_4$As)(Bu$_3$Sn)$_2$Cu(CN)$_4$]$_n$, **8**: It was prepared by two methods. The first method includes the addition of a clear in-situ prepared solution of (1 mmol) of (^{n}Bu$_4$N)$_3$Cu(CN)$_4$ to a solution of 0.42 g (1 mmol) of Ph$_4$AsCl in 5 ml 2:1 acetone/water solvent and thenafter to this solution, a solution of 0.65 g (2 mmol) of Bu$_3$SnCl in acetone was added. The white precipitate was filtered off, washed several times with water/acetone and then dried under vacuum overnight at room temperature. The yield was 1.06 g (93%) based upon Ph$_4$AsCl. The second method of preparation includes the addition of 0.09 g (1 mmol) solid CuCN to a solution of 0.42 g (1 mmol) of Ph$_4$AsCl in 5 ml H$_2$O/ acetone mixture under dry nitrogen atmosphere, to a solution of 0.65 g (2 mmol) of Bu$_3$SnCl in acetone and
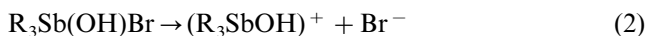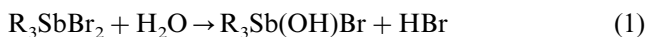
Table 3
Raman spectra (in cm^{-1}) of the supramolecular Cu^I-cyanides

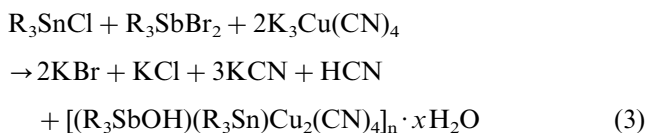| Compound	1	2	3	5	6	7	8	9	10	12	Band assignment
		2127	2141	2140	2134	2134		2174	2170	2173	$\nu(CN)$
	2094	2118	2136		2119		2129	2136	2116	2130	$\nu(CN)$
	2088	2095	2121	2121		2119	2116	2122	2094	2116	$\nu(CN)$
		478	525	537	598	598	597	554	540	553	$\nu_{asym}(Sn-C)$
		455	495	510	514	514	512	522	510	519	$\nu_{sym}(Sn-C)$
							617				$\nu_{asym}(As-C)$
							497				$\nu_{sym}(As-C)$
								583	624		$\nu_{asym}(Sb-C)$
								535	614		$\nu_{sym}(Sb-C)$
		265	266	265	263	272	270	263	265	265	$\nu(Cu-C)$

Compound **11** is Raman silent.

then a solution of KCN in H_2O was added in excess (more than 3 mmol). The white precipitate was filtered off, washed with H_2O and then dried under vacuum. The yield was 1.02 g (90%) based upon Ph_4AsCl.

$[(R_3SbOH)(R_3Sn)Cu_2(CN)_4]_n \cdot xH_2O$; R = Me, **9** or Ph, **10**: Many attempts were made to obtain the host–guest (i.e. a template) system $[(R_3Sb)(R_3Sn)Cu(CN)_4]$. However, the reactions did not lead to the products of the required stoichiometry, instead the polymeric precipitates $[(R_3SbOH)(R_3Sn)Cu_2(CN)_4]_n \cdot xH_2O$ (R = Me or Ph) were isolated. This could be due to the presence of water which may lead to hydrolysis of R_3SbBr_2 according to the following equations:

$$R_3SbBr_2 + H_2O \rightarrow R_3Sb(OH)Br + HBr \qquad (1)$$

$$R_3Sb(OH)Br \rightarrow (R_3SbOH)^+ + Br^- \qquad (2)$$

The overall reaction to obtain **9** or **10** is:

$$R_3SnCl + R_3SbBr_2 + 2K_3Cu(CN)_4$$
$$\rightarrow 2KBr + KCl + 3KCN + HCN$$
$$+ [(R_3SbOH)(R_3Sn)Cu_2(CN)_4]_n \cdot xH_2O \qquad (3)$$

On the other hand, many trials were made to isolate the required templated system by using acetonitrile or dry methanol as a solvent, unfortunately, very few drops of water must be added to dissolve $K_3[Cu(CN)_4]$ and R_3SbBr_2. The same polymers **9** and **10** were isolated. The reaction was carried out by adding a solution of 0.4 g (2 mmol) of Me_3SnCl in 4 ml MeOH to a solution of 0.65 g (2 mmol) of Me_3SbBr_2 in 4 ml MeOH and two drops H_2O. To this mixture, a solution of 1.14 g (4 mmol) of $K_3[Cu(CN)_4]$ in 5 ml MeOH and few drops of H_2O to dissolve the salt were added dropwise with continuous stirring. A white crystalline precipitate was formed which was filtered off end dried under vacuum overnight. The yield was 1.05 g (91%) based upon Me_3SbBr_2. The polymer **10** was prepared following the same procedure giving a yield of 1.67 g (88%) based upon Ph_3SbBr_2.

$[(MV^{2+})_{0.5}(Et_3Sn)Cu_2(CN)_4]_n \cdot H_2O$, **11**: A solution of 0.75 g (2 mmol) of $K_3[Cu(CN)_4]$ in 5 ml H_2O was added slowly under stirring to a solution of 0.77 g (3 mmol) of $MVCl_2$ in 5 ml H_2O. The resulting brown solution was evaporated at 100°C till dryness and then the residue was dissolved in $H_2O/NaOH$ solution. To this solution, a solution of 0.48 (2 mmol) of Et_3SnCl in 4 ml acetone was added to yield a brown precipitate which was filtered off, washed with H_2O/acetone mixture and dried overnight under vacuum. The yield was 0.95 g (87%) based upon Et_3SnCl.

$[(Bu_4N)(Me_3Sn)Cu_2(CN)_4]_n$, **12**: Colourless micro crystals was obtained by the addition of 0.45 g (5 mmol) of solid CuCN to a 1.34 g (5 mmol) of $(Bu_4N)CN$ in 40 ml H_2O followed by the addition of a solution of 0.49 g (2.5 mmol) of Me_3SnCl in 35 ml H_2O. The yield after filtration, washing with H_2O then drying at 40°C under vacuum, is 1.47 g (92.5%) based upon Me_3SnCl.

Colours, decomposition temperature and elemental analyses of these polymers are given in Table 1. The elemental analysis was performed with a Heraeus elemental analyser and a Perkin Elmer 2400 automatic elemental analyser. The metal analysis was carried out using a Perkin Elmer 2380 atomic absorption spectrophotometer. IR spectra were recorded using the Perkin Elmer PE 577 instrument as KBr discs. Raman spectra were run on the Rmanov U-1000 spectrometer of Jobin Yvon. The NMR spectra were measured on the Bruker MSL 300-spectrometer. The thermal gravimetric analysis (TGA) was carried out using Schimadzu AT 50 thermal analyzer.

3. Results and discussion

In a trial for preparing the host–guest systems (i.e. a template) $[G^+(R_3Sn)_2Cu(CN)_4]$, the addition of $(^nBu_4N)CN$ and Me_3SnCN or Me_3SnCl to CuCN in H_2O should lead to the polymer

Table 4
NMR spectra[a] of the supramolecular Cu^I-cyanides

Compound[b]	δ-(ppm)					Relative intensity of R/G$^+$ signals	Relative no. of protons R/G$^+$
	Me–Sn	Me–Sb	Et–Sn	Bu	Ph		
1				3.24			
2	0.68						
3			1.43				
4				3.30			
5					6.7		
6			1.12	3.18		5.9:6.7	30:36
7				3.12, 3.3		5.4:3.7	54:36
8				3.13	7.53	3.9:14	54:20
9	0.60	1.93				5:5.3	9:9
10					6.8–7.6	2.5:2.8	15:15
12	0.65			3.35		2.0:7.9	9:36

[a] The signals due to the water molecules appear at 4.8–5.1 ppm.
[b] Compound 11 does not dissolve in DONa.

[$^nBu_4N)(Me_3Sn)_2Cu(CN)_4$]. This polymer was not to be formed and instead the white polymer [$^nBu_4N)(Me_3Sn)Cu_2(CN)_4$] was obtained. After the replacement of the methyl ligands by a more space-demanding ethyl groups, the desired polymeric host–guest system of the composition [$(Bu_4N)(Et_3Sn)_2Cu(CN)_4$] was obtained [14]. Starting with this compound, the template cation Bu_4N^+ was replaced by the cation Et_4N^+ following the same procedure, the compound [$(Et_4N)(Et_3Sn)_2Cu(CN)_4$] could not also be obtained. Another trial was made to precipitate this compound by substitution according to the following reaction;

$$3Et_4NCN + CuCN \xrightarrow{H_2O} (Et_4N)_3Cu(CN)_4 \qquad (4)$$

$(Et_4N)_3Cu(CN)_4$
$+ 2Et_3SnCl$ (1:2 H_2O/acetone)/mixture) No ppt (5)
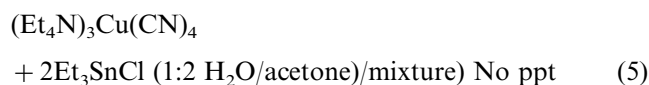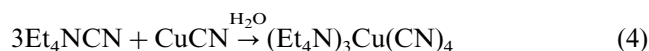
In this case, no product was obtained. In addition, the replacement of the trimethyltin or Bu_4N ligands by the triethyltin or (MV^{2+}) ligands, respectively, gave the polymers 3, 11. This indicates that the formation of such crystalline Cu^I cyanide complexes as non-interpenetrating, three dimensional networks depends on the suitable choice of the space-dimensional alkyl groups and the guest, template, systems. The right choice of these systems which act as the functionalised building blocks, the connecting units and the template leads directly to the formation of [$G^+(R_3Sn)_2Cu(CN)_4$] independent of the starting materials or the reaction pathway. As an example, irrespective of the fact that compound 6 was prepared by two routes using Cu^I compounds, it could also be obtained by direct co-precipitation on adding $CuSO_4$ to 2:1 acetone–water solution of Et_3SnCl followed by the addition of ($^nBu_4N)CN$ in H_2O. In such case the cyanide ions reduce Cu^{II} to Cu^I giving the white crystalline polymer [$(Bu_4N)(Et_3Sn)_2CU(CN)_4$]$_\infty$.

3.1. IR and Raman spectra

The IR and Raman spectra of the supramolecular polymers 1–12 are given in Tables 2 and 3. The IR spectra of the polymers 5, 8, 10 reveal the bands characteristic to the phenyl rings while the IR spectrum of polymer 11 shows the bands corresponding to the vibrations of the guest cation MV^{2+}. The presence of the water molecules in the polymers 2, 3, 5, 7, 9, 11 was supported by the appearance of a broad band at 3500 cm^{-1} and a medium one at 1616–1640 cm^{-1} while the characteristic bands due to ν_{OH} (polymers 9, 10) are observed at 3280 and at 3436 cm^{-1}, respectively. Also, the IR spectra reveal the bands corresponding to the alkyl groups of the connecting units and the guest cations. The presence of two distinct IR bands for every mode of vibrations of the C–H bonds of the alkyl or the phenyl groups suggests the different roles of these groups. The (R_3Sn) units could form bridges between the tetrahedral building blocks [$Cu(CN)_4$]$^{3-}$ through directed coordinate bond between the nitrogen and the tin atoms while the R groups (R = alkyl or phenyl) of the space-filling template are directed to two adjacent channels [14].

The Raman spectra of these supramolecular polymers exhibit two or three ν_{C-N} frequencies in the region 2088–2175 cm^{-1}, Table 3. On the other hand, the IR spectra of the compounds 1, 10 and 12 display two ν_{C-N} bands at 2076–2082, 2116–2045 and 2114–2082 cm^{-1}, respectively, while those of the other polymers show one ν_{C-N} band at 2106–2117 cm^{-1}. The frequencies of the cyanide bond vibrations are dependent on the changes in the bond order of the Cu–C bond, as
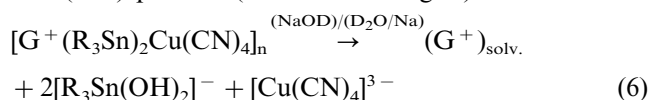
well as the way the cyanide groups are arranged around the copper ions and also the way they should be inter-connected together. The Raman and IR-v_{C-N} values of the polymers **1–8** are in consistence with those of the compounds containing the free $[Cu(CN)_4]^{3-}$ via, $K_3Cu(CN)_4$ (IR $v_{C-N} = 2076$ cm^{-1}, Raman (Ra.) $v_{C-N} = 2093$ and 2081 cm^{-1}) [17,18] and $(Bu_4N)_3Cu(CN)_4$, indicating the pyramidal tetrahedral (pth) structure [19]. These C–N frequencies are much lower than those of the polymers with [–Cu–CN–Cu–] bridges like CuCN (IR $v_{C-N} = 2155$ cm^{-1}, Ra. $v_{C-N} = 2160$ cm^{-1}) and $(Bu_4N)Cu(CN)_2$ which showed a double cyanide band at 2190 and 2210 cm^{-1} [20], similar to what was described [21] for potassium dicyanocoprrate. This lowering in vibration frequency of the cyanide groups suggests the formation of the nonlinear chains [–Cu–C≡N–Sn–N≡C–Cu–] [14]. On the other hand, the v_{C-N} values of the polymers, **9,10** and **12** are higher than the others, that seems to be more related to those containing [–Cu–CN–Cu–] bridge. This argument was further

supported by the presence of the three Raman v_{C-N} bands around 2116, 2130 and 2173 cm^{-1} corresponding to the absorption of the $Cu(CN)_4$ building blocks and the [–Cu–CN–Cu–] bridges.

The vibrational, IR and Raman spectra show the bands due to stretching vibrations of M–C bonds; M=Sn, As, Sb, and Cu, in the region 250–600 cm^{-1}, Tables 2 and 3. The appearance of these bands is a further support of the presence of the connecting units and template groups. The v_{Sn-C} absorptions exhibit wavenumbers quite close to those of trigonal bipyramidal (tbp) configured $R_3Sn(NC)_2$ units. The absence of the symmetric vibrations $v_{(Sn-C)sym}$ in the IR spectra and the relatively low intensity of the asymmetric vibrations $v_{(Sn-c)asym}$ in the Raman spectra advocate an exclusive presence of trigonal planar R_3Sn owing to their axial anchoring to two cyanide N atoms.

3.2. NMR-spectra

The ^{1}H-NMR-spectroscopy of the compounds **1–10** and **12** dissolved in alkaline D_2O prepared by dissolving a tiny piece of sodium in pure D_2O, Eq. (6), was found out to be a helpful technique to easily determine the relative abundance of (Sn-bonded) alkyl or phenyl (R) and (G$^+$) protons (Table 4 and Fig. 1).

$$[G^+(R_3Sn)_2Cu(CN)_4]_n \xrightarrow{(NaOD)/(D_2O/Na)} (G^+)_{solv.}$$
$$+ 2[R_3Sn(OH)_2]^- + [Cu(CN)_4]^{3-} \quad (6)$$

The NMR-spectra of the compounds **2**, **9** and **12** show a singlet at 0.6–0.68 ppm corresponding to the Me–Sn protons while the Me–Sb protons absorb at 1.93 ppm. The NMR-spectra of the Et–Sn protons appear as an intense doublet centered at 1.12–1.43 ppm. A multiplet appears in the range of 3.12–3.35 ppm corresponding to the n-butyl protons while the phenyl protons absorb at 6.7–7.6 ppm. Also, a very intense broad signal appears at 4.8–5.1 ppm corresponding to the protons of the water molecules (not indicated in Fig. 1). On the other hand, compound **11** is insoluble in DONa solution. The presence of these NMR signals is a further conformation of the structure of these non-interpenetrating organotin polymers. In addition, the relative intensity of R/G$^+$ signals are in good agreement with the relative number of the protons of R and G$^+$ groups, Table 4.

3.3. Thermal gravimetric analysis

The polymers **9** and **6** are stable until 160°C while the other polymers exhibit stability until 70–80°C. The TG curves of polymers **2**, **3**, **5**, **7**, **9**, **10** and **11** indicate the presence of lattice water molecules which are removed in the temperature range 80–170°C (Table 5 and Fig. 2). The second transition of these polymers and the first
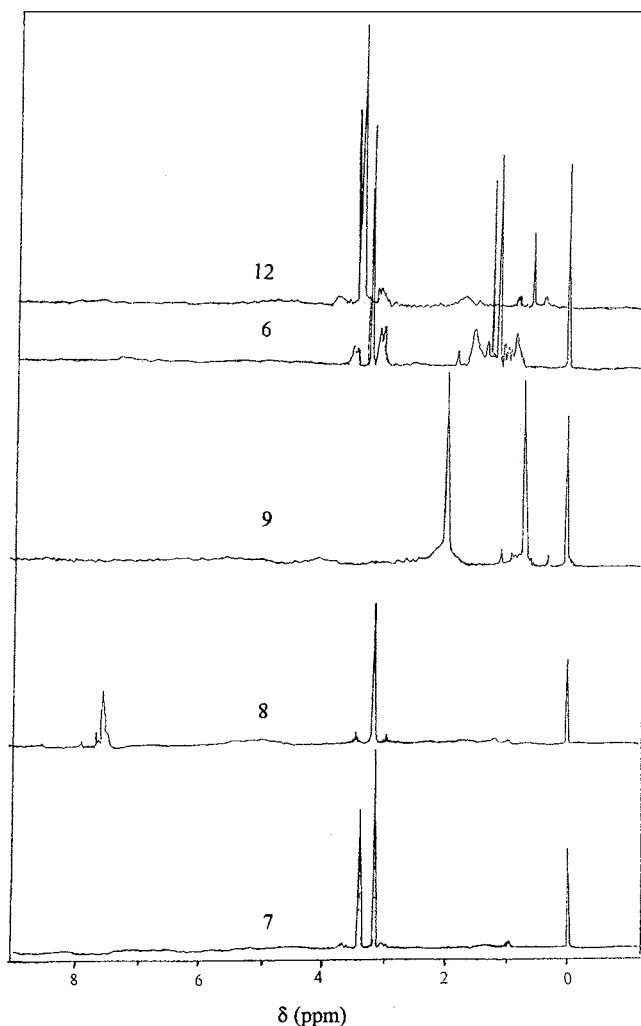

Fig. 1. The NMR spectra of some of the supramolecular Cu^I-cyanides.

Table 5
Thermal gravimetric analysis data of the supramolecular Cu^I-cyanides

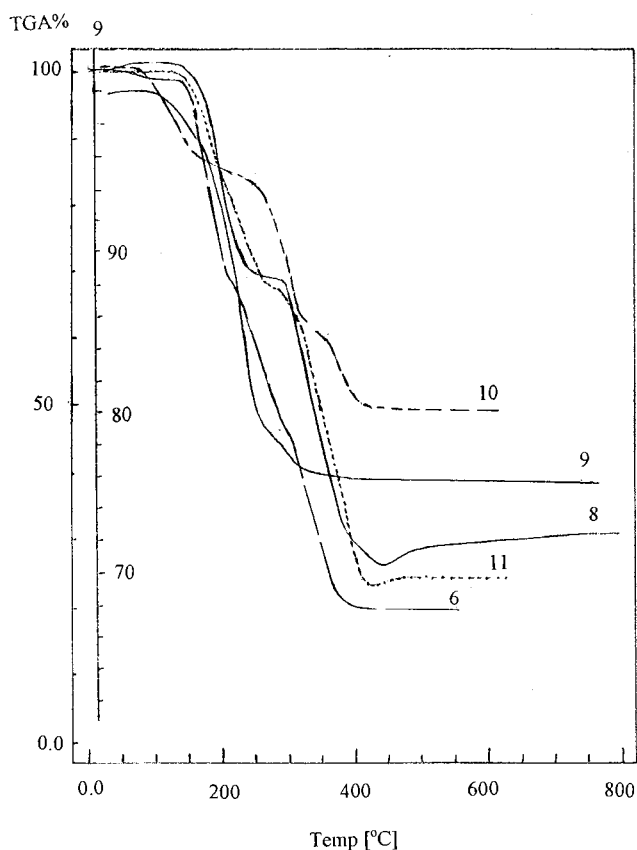| Compound	MW (g mol^{-1})	Transitions (temperature range (°C) and wt% loss)				Total trans.	MW of residue
		A	B	C	D		
1	895.02	19–230	230–410	—	—	25–600	76
		60	31.5			91.5	
2	694.60	100–160	165–220	250–420	—	25–650	172.49
		5.2	27.5	38.3		71.0	
3	821.30	90–150	150–208	208–290	290–390	23–500	130.0
		4.38	57.24	18.97	3.58	84.17	
4	1037.78	20–180	180–400	—	—	20–600	129.5
		28.0	59.52			87.52	
5	1253.69	80–140	180–290	290–380	—	25–500	457.59
		3.0	43.3	17.2		63.5	
6	821.874	150–250	250–400	—	—	20–600	180.8
		33.0	45.0			78.0	
7	1008.19	80–140	140–220	220–300	300–400	25–500	201.64
		1.8	29.4	28.8	20.0	80.0	
8	1131 07	70–320	320–370	—	—	25–550	130.07
		65.0	20.0			88.5	
9	596.83	150–250	250–600			29–800	155.17
		30.0	44.0			74.0	
10	987.26	100–170	170–260	260–320	—	24–750	753.28
		3.7	18.0	2.0		23.7	
11	548.186	80–150	150–230	230–320	320–415	20–600	273.54
		11.6	3.4	21.0	14.1	50.1	
12	637.445	90–220	255–410	—	—	30–650	184.86
		26.0	45.0			71.0	

Fig. 2. The TGA curves of some of the supramoecular Cu^I-cyanides.

one of the other polymers correspond to the loss of the guest cation and one cyanide ion. The next transitions correspond to the loss of at least one connecting unit and one cyanide ion followed by complete decomposition of the polymer. The loss of the guest cyanide molecule was confirmed by carrying out elemental analysis of the residue obtained at 240°C, compound **13**, for the polymer **6** and at 220°C, compound **14**, for the polymer **12**, Table 6. On the other hand, the IR spectra of the final decomposition products of the polymers, except those of the polymers **5** and **10**, indicate the absence of the cyanide ligands as well as the guest and the connecting units. The second and the third transitions of the polymer **5** look like one transition with an inflection at 290°C. They correspond to the loss of two Ph_3SnCN units. The final product obtained at 500°C was the polymer $[(Ph_3Sn)Cu(CN)_2]$, **15**, according to the IR-spectrum ($v_{CN} = 2175$, 2195 cm^{-1}), Fig. 3, and elemental analysis, Table 6.

The polymer **10** loses the interlayer water molecules at the temperature range 100–170°C followed by loss of $(Ph_3Sb)_{0.5}$ units and the OH group at the temperature range 170–320°C. The residue obtained at 320°C is thermally stable up to 750°C and has the structure $[(Ph_3Sb)_{0.5}(Ph_3Sn)Cu_2(CN)_4]$, **16**, according to the IR-spectrum ($v_{CN} = 2170$, 2130 cm^{-1}), Fig. 3, and elemental analysis, Table 6.

Table 6
Elemental analysis and colour of the compounds obtained by thermal synthesis

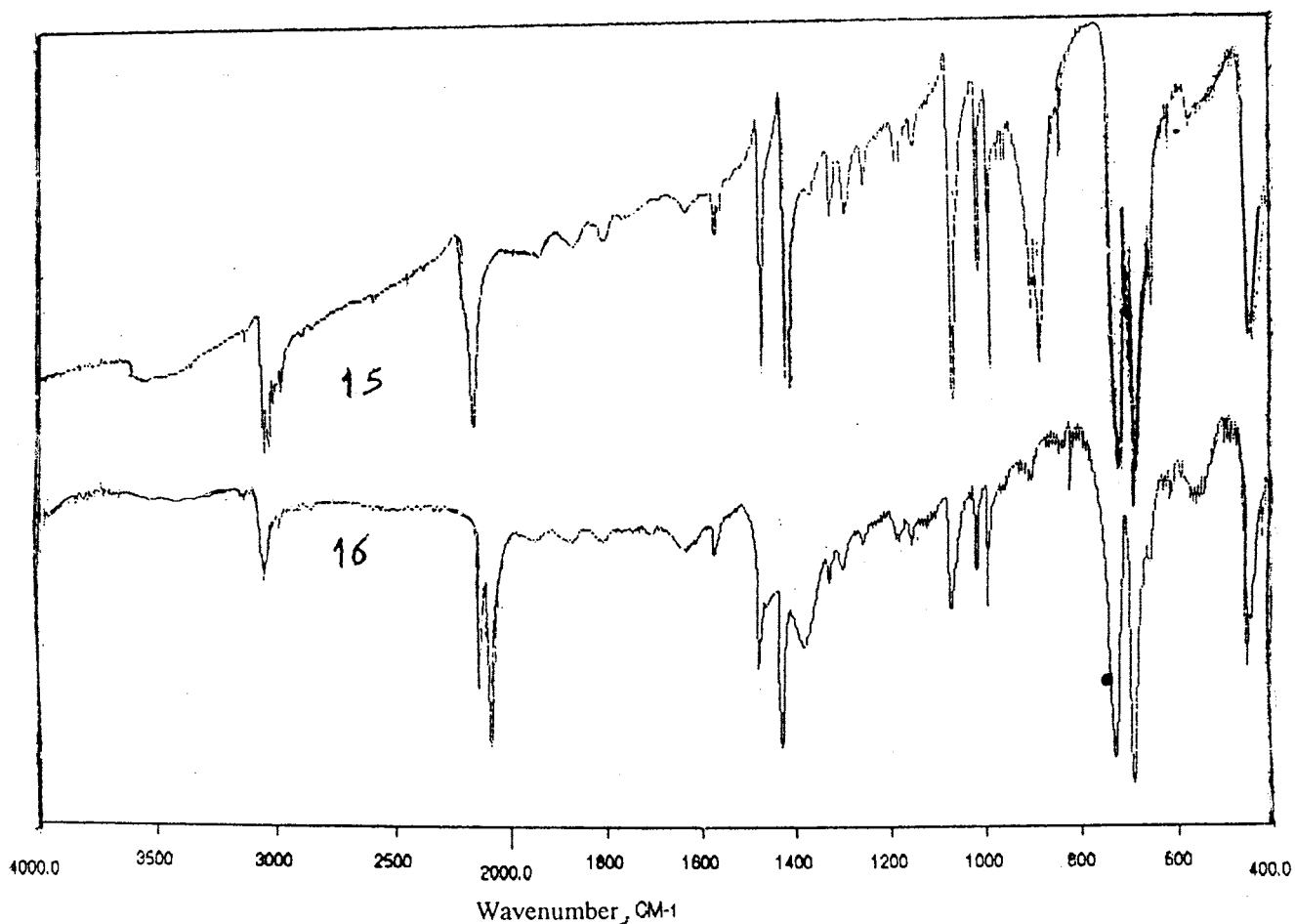| No.	Compound	Colour	Elemental analysis calc./(found) %			
			C	H	N	Cu
13	$(Et_3Sn)_2Cu(CN)_3$	White	35.54 (34.12)	5.46 (5.18)	7.62 (5.96)	11.48 —
14	$(Me_3Sn)Cu_2(CN)_3$	White	19.52 (18.73)	2.45 (2.40)	11.43 (10.16)	34.42 —
15	$(Ph_3Sn)Cu(CN)_2$	White	51.57 (50.12)	3.24 (3.62)	6.04 (5.18)	13.64 (12.43)
16	$[(Ph_3Sb)_{0.5}(Ph_3Sn)Cu_2(CN)_4]$	White	49.12 (49.70)	2.99 (2.78)	7.42 (6.23)	16.76 (15.34)

Fig. 3. The IR spectra of the polymers **15** and **16**.

4. Discussion

The organotin–copper polymers under investigation may be classified into three structural categories. The first category includes the polymers $[(R_3Sn)_3Cu(CN)_4]_n \cdot xH_2O$, **2–5**, where $x = 0$ or 2. The copper atom is coordinated to four cyanide ligands forming distorted pth configured building blocks which are connected by tbp configured $R_3Sn(NC)_2$ units. The size and shape of the ligand R do not play any role in the self assembly of this category of polymers. Unfortunately, the actual structure of the polymers could not be predicted obviously without a single-crystal X-ray study. The significance of the presence of the water molecules in the lattice is not quite clear at the present time nor the unbridged (R_3Sn) groups. It is supposed that only two of the three Sn atoms may reach penta-coordination while the third one should have pth

configuration, which in this case might add monodentate or bidentate bases (L) to form tbp configuration. On adding pyz or bpy to these polymers no reaction was obtained. However, on adding the starting materials, R_3SnCl to pyz or bpy and thenafter to $K_3Cu(CN)_4$, unexpectedly, ternary adducts of the general composition $[CuCN-L_x-R_3SnCN]$ $x = 0.5$ or 1, were obtained [15,16]. The polymers **6–8**, category 2, are isostructural with the well structurally characterised polymer $[(^nBu_4N)(Et_3Sn)_2Cu(CN)_4]_\infty$; as indicated by X-ray powder diffraction, IR and Raman spectra. These polymers are formed via negatively charged 3D frameworks of the type $[(R_3Sn)_2Cu(CN)^{4-}]_\infty$, built up of distored pth $[Cu(CN)_4]$ building blocks connected by tbp configured $R_3Sn(NC)_2$ units via $-[Cu-CN-Sn-NC-]$ bridges. The size and shape of the ligand R as well as the template G^+ play an essential role for the self assembly of these non interpenetrating 3D-host–guest polymers. The polymers **9–12** of the general composition $[(G^+)(R_3Sn)Cu_2(CN)_4]_n$ represent the third category. The present findings demonstrate that the actual structure of this class, of polymer appear to be neither straightforward synthetically nor can their structures correctly be predicted without a single-crystal X-ray study. All attempts to grow single crystals suitable for X-ray studies, have so far ended up with the formation of microcrystalline powders of the expected chemical composition.

The polymers $[(Ph_3Sn)Cu(CN)_2]$ and $[Ph_3Sb)_{0.5}(Ph_3Sn)Cu(CN)_4]$, obtained thermally at 500 and 320°C, respectively, were investigated by IR spectra and elemental analysis. However, these results show that thermal synthesis is a viable route to obtain supramolecular polymers having components that are not generally observed.

References

[1] (a) D. Venkataraman, S. Lee, I. Zhang, J.S. Moore, Nature 371 (1994) 591. (b) X. Wang, M. Simard, J.D. Wuest, J. Am. Chem. Soc. 116 (1994) 1219. (c) M.R. Ghadiri, J.R. Granja, R.A. Milligan, D.E. McRee, N. Khazanovich, Nature 366 (1993) 324.

[2] (a) O.M. Yaghi, D.A. Richardson, G. Li, C.E. Davis, T.L. Groy, Mater. Res. Soc. Symp. Proc. 371 (1994) 15. (b) O.M. Yaghi, G. Li, Angew. Chem. Int. Ed. Engl. 34 (1995) 207. (c) K.M. Park, T. Iwanoto, J. Chem. Soc. Chem. Commun. (1992) 72.

[3] O.M. Yaghi, Z. Sun, D.A. Richardson, T.L. Gray, J. Am. Chem. Soc. 116 (1994) 807.

[4] R. Robson, B.F. Abrahams, S.R. Batlen, R.W. Gable, B.F. Hoskins, J. Liu, in: T. Bein (Ed.), Supramolecular Architecture Symposium Series. No. 499, ACS Washington, DC, 1992, p. 256, and refs. therein.

[5] U. Behrens, A.K. Brimah, T.M. Soliman, R.D. Fischer, D.C. Apperley, N. Davis, R.K. Harris, Organometallics 11 (1992) 1718.

[6] D.C. Apperley, N.A. Davis, R.K. Harris, A.K. Brimah, S. Eller, R.D. Fischer, Organometallics 9 (1990) 2672.

[7] S. Eller, P. Schwarz, A.K. Brimah, R.D. Fischer, D.C. Apperley, N.A Davis, R.K. Harris, Organometallics 12 (1993) 2332.

[8] B.F. Hoskins, R. Robson, J. Am. Chem. Soc. 112 (1990) 1546 and refs. therein.

[9] J. Kim, D. Whang, J.I. Lee, K. Kim, J. Chem. Soc. Chem. Commun. (1993) 1400.

[10] (a) S. Eller, P. Brandt, Abdul K. Brimah, P. Schwarz, R.D. Fischer, Angew Chem. 101 (1989) 1274. (b) S. Eller, P. Brandt, Abdul K. Brimah, P. Schwarz, R.D. Fischer, Angew Chem. Int. Ed. Engl. 28 (1989) 1263.

[11] W.E. Prout, E.R. Russell, H.J. Groh, J. Inorg. Nul. Chem. 27 (1965) 473.

[12] Y. Murakami, A. Tijima, J.W. Ward (Eds.), New Developments Zeolite Science and Technology, Kodansha, Tokyo, 1986.

[13] J.W. Ward, J. Catal. 11 (1968) 238.

[14] A. K. Brimah, E. Siebel, R.D. Fischer, N.A. Davis, D.C. Apperley, R.K. Harris, J. Organomet. Chem. 475 (1994) 85.

[15] A.M.A. Ibrahim, E. Siebel, R.D. Fischer, First International Conference on Basic Science and Advanced Technology, Assiut, Egypt, 1996.

[16] A.M.A. Ibrahim, E. Siebel, R.D. Fischer, Inorg. Chem. (to be published).

[17] M.J. Reisfeld, L.H. Jones, J. Mol. Spectrosc. 18 (1965) 222 and refs. therein.

[18] H. Poulet, J.P. Mathieu, Spectrochim. Acta 1S (1959) 932.

[19] L.H. Jones, J. Chem. Phys. 19 (1958) 463.

[20] M. Nilson, Acta Chem. Scand. B36 (1982) 125.

[21] (a) W.R. Mason, J. Am. Chem. Soc. 95 (1973) 3573. (b) W.R. Mason, J. Am. Chem. Soc. 98 (1976) 5182.