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Synthesis and Structural Characterization of Self-Assembly Products Containing $[Fe(CN)_6]^{4-}$ Building Blocks with Cationic $\{R_3Sn\}^+$ Fragments in the Absence or Presence of a Bidentate Uncharged Ligand {2L}

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Spontaneous self-assembly of $[Fe(CN)_6]^{4-}$ and R_3Sn^+ ions (R = Me, n-Bu or Ph) in the absence or presence of uncharged bidentate ligands (such as dioxane (diox), methylpyrazine (Mepyz), or 4,4′-bipyridine (bpy)) affords white precipitates. The products with the general composition $[(R_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot 2L]$; 2L = diox, Mepyz or bpy, have been obtained as host-guest polymeric architecture. The new compounds have been compared with their hydrated systems $[(Me_3Sn)_4Fe(CN)_6 \cdot xH_2O]$; x = 2 or 4 and with the water-free $[(Me_3Sn)_4Fe(CN)_6]$. Results of extensive spectroscopic investigations (IR studies and X-ray powder diffractometry) suggest that the architecture of the novel host-guest systems involve three-dimensional networks, notably different from those of their parent system (containing four H_2O molecules). These compounds show no ion-exchange activity towards NH_4^+ cations and are affected by moderate temperature. Also, these 3D-host-guest polymeric systems exhibit a high sensitivity to pH of the media.

Key words: self-assembly, uncharged ligand, 3D-host-guest polymeric systems

Organometallic polymeric metal cyanides, involving quasi-linear μ-CN linked repeat units, have attracted considerable interest in recent years, because they act as zeolite-like host systems for numerous guest ions [1,2]. These polymeric metal cyanides may adopt two- or three-dimensional (2D or 3D) framework structures [3], and hetero (bi) metallic polymers may even share several characteristic properties with zeolites. These zeolite-like polymeric metal cyanides involve the classical M-CN-M′ bridge, and usually guest cations (G^+) [4]. The preparation of these polymeric metal cyanides is generally based upon the reaction of salts containing $[Fe(CN)_6]^{4-}$ building blocks and water-soluble R_3ECl (R = alkyl or aryl and E = Sn or Pb) forming $Fe\text{-}CN{\rightarrow}E(R)_3{\leftarrow}NC\text{-}Fe$ fragments [5]. The structures involve a symmetric unit with three-equally abundant, nonequivalent CN ligands and two-equally abundant, nonequivalent R_3E group with six-crystallographically different alkyl C-atoms. In the presence of one or more H_2O molecules within the chains of these compounds, it is frequently inserted spontaneously into N→Sn bond affording frameworks involving $CN{\rightarrow}Sn(R)_3{\leftarrow}O(H)\text{-}H\ldots NC\text{-}$ fragments [1,5–7]. On the other hand, uncharged molecules (like dioxane, pyrazine, 4,4′-bipyridine, or trans-bipyridyl-ethylene) are good candidates as molecular building blocks, due to their rod like rigidity and length.

In the polymeric structures, which contain uncharged ligands, several factors influence the specific framework structure [8–11]. For example, in the family of the compounds containing $[Fe(CN)_6]^{4-}$ building blocks and R_3Sn^+ connecting units, tin-coordinated H_2O molecules tend to generate hydrogen bonds with uncharged acceptor ligands forming extended lattice fragments *via* $-CN \rightarrow Sn(Me)_3 \leftarrow O(H)$-$-H...C_4H_8O_2...H$-$(H)O \rightarrow Sn(Me)_3 \leftarrow NC$- structure [12]. In this case, both hydrogen atoms of a tin-coordinated water molecule may be involved in the fixation of various bridge heads and guest atoms, respectively. The $[Fe(CN)_6]^{4-}$ building blocks within the chains of these compounds are extensively investigated as outer-sphere redox reactions [13–15]. In addition, this family of the polymeric cyanide, containing at least two metals, has turned out to be a suitable precursor to prepare well-defined oxides and inter-metallic phases at comparatively low temperature [16,17].

The present study has been developed to synthesis and to characterize novel 3D host-guest polymeric systems. The self-assembly reaction of $[Fe(CN)_6]^{4-}$ building blocks, cationic $\{R_3Sn\}^+$ units with uncharged bidentate ligand {2L} affords the build-up of 3D-systems, that even appear to receive notable stabilization on incorporation of secondary guests "guests of guests" units into their primary chains and cycles. The chemical and spectroscopic properties of the novel 3D-host guest $[(R_3Sn)_4Fe^{II}(CN)_6 \cdot 2H_2O \cdot 2L]$ (R = Me, n-Bu or Ph and 2L = diox, Mepyz or bpy) are compared with the homologues $[(Me_3Sn)_4Fe(CN)_6 \cdot xH_2O]$ ($x = 0.0$, 2.0 or 4.0).

EXPERIMENTAL

Materials and instrumentation: All reagents were obtained from Aldrich and used as received. Elemental analyses were performed using a Perkin-Elmer 2400 automatic analyzer. Mass spectra were recorded on a Finnigan MAT 8200 spectrometer. Infrared spectra were recorded as KBr-pellets in the range 4000–200 cm^{-1} using a Perkin-Elmer SP 1430 spectrophotometer. The X-ray powder diffraction was recorded at room temperature using a Phillips PW-1729 X-ray powder diffractometer (CuK_α; Ni-filter). Thermogravimetric data were collected on a Shimadzu TGA-50 thermal analyzer.

Preparation of host-guest polymeric containing $[Fe(CN)_6]^{4-}$ building blocks: The spontaneous precipitation of anhydrous/hydrous 3D-polymeric systems **1**–**3** from solutions containing both $Me_3Sn \cdot aq^+$ and $[Fe(CN)_6]^{4-}$ ions takes place in the absence of acceptor ligands [1,5,6,18].

$$4\,Me_3SnCl + K_4[Fe(CN)_6] \rightarrow [(Me_3Sn)_4Fe(CN)_6 \cdot xH_2O] + 4\,KCl \qquad (1)$$

$x = 0.0$ (system **1**), 2.0 (system **2**), or 2.0 (system **3**). An aqueous solutions of $K_4[Fe(CN)_6]$ (25 ml, 1 mmol) was added carefully to a solution of Me_3SnCl (4 mmol). The products **1**–**3** were filtered off, followed by extended drying in vacuum at room temperature. The structures of **1**–**3** were characterized by elemental analysis. These systems are reported here for comparison with the novel prepared 3D-polymeric systems **4**–**12**.

The precipitation of the novel host-guest 3D-polymeric systems $[(R_3Sn)_4Fe^{II}(CN)_6 \cdot 2H_2O \cdot 2L]$ (R = alkyl or aryl and 2L = diox, Mepyz or bpy) takes place following similar procedures but in the presence of acceptor ligands.

$$4\,R_3Sn \cdot aq^+ + [Fe(CN)_6]^{4-} + 2L \rightarrow [(R_3Sn)_4Fe^{II}(CN)_6 \cdot 2H_2O \cdot 2L]$$

R = alkyl or aryl and 2L = diox, Mepyz or bpy (2)

$[(R_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot diox]$; R = Me **4**, n-Bu **5** or Ph **6** and diox = dioxane. An aqueous solution of $K_4[Fe(CN)_6]$ (25 ml, 1 mmol) and 40 ml of dioxane were added carefully to R_3SnCl (4 mmol) soluble in 10 ml of dioxane. After complete precipitation, the products were filtered off, washed with cold water and dried under vacuum. The structures of **4–6** were characterized by elemental analysis.

$[(R_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot Mepyz]$; R = Me **7**, n-Bu **8** or Ph **9** and Mepyz = methylpyrazine. A procedure analogous to that employed for the last compounds was followed. 1 mmol of $K_4[Fe(CN)_6]$, and 1 mmol of Mepyz soluble in 40 ml acetone were added carefully to 4 mmol of R_3SnCl soluble in 10 ml of acetone solution of Mepyz. The products were filtered off, washed with cold water and dried under vacuum. The structures of **7**–**9** were characterized by elemental analysis.

$[(R_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot bpy]_n$; R = Me **10**, n-Bu **11** or Ph **12** and bpy = 4,4′-bipyridine. 1 mmol of $K_4[Fe(CN)_6]$, and 1 mmol of bpy soluble in 40 ml acetone were added carefully to 4 mmol of R_3SnCl soluble in 10 ml of acetone solution of bpy. The products were filtered off, washed with cold water and dried under vacuum. The structures of **10**–**12** were characterized by elemental analysis.

The self-assembly reactions of the host-guest 3D-polymeric systems **1**–**12** depend on the chain-propagating CN→Sn bonds which are energetically superior to the O_{water}→Sn bonds present in the $R_3Sn \cdot aq^+$ ions [19]. Their compositions are given in Table 1. The 3D-polymeric systems **1**–**12** are practically insoluble in most organic solvents (exceptions: DMF, DMSO and H_2O at pH values ≤ 7).

Table 1. The composition, number of water molecules (x), number of acceptor ligands (2L), colours, and molecular weight for the host-guest polymeric systems involving $[Fe(CN)_6]^{4-}$ building blocks.

No.	Composition	x (H_2O)	2L (guest)	Colours	MW (g mol^{-1})
1	$[(Me_3Sn)_4Fe(CN)_6]$	0.00	0.00	White	866.8
2	$[(Me_3Sn)_4Fe(CN)_6 \cdot 2H_2O]$	2.0	0.00	White	902.8
3	$[(Me_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot 2H_2O]$	2.0	2.0	White	938.8
4	$[(Me_3Sn)_4Fe(CN)_6 2H_2O \cdot diox]$	2.0	1.0	White	990.8
5	$[(n\text{-}Bu_3Sn)_4Fe(CN)_6 2H_2O \cdot diox]$	2.0	1.0	White	1494.8
6	$[(Ph_3Sn)_4Fe(CN)_6 2H_2O \cdot diox]$	2.0	1.0	White	1732.8
7	$[(Me_3Sn)_4Fe(CN)_6 2H_2O \cdot Mepyz]$	2.0	1.0	Faint yellow	996.8
8	$[(n\text{-}Bu_3Sn)_4Fe(CN)_6 2H_2O \cdot Mepyz]$	2.0	1.0	White	1500.8
9	$[(Ph_3Sn)_4Fe(CN)_6 2H_2O \cdot Mepyz]$	2.0	1.0	White	1740.8
10	$[(Me_3Sn)_4Fe(CN)_6 2H_2O \cdot bpy]$	2.0	1.0	Faint yellow	1058.3
11	$[(n\text{-}Bu_3Sn)_4Fe(CN)_6 2H_2O \cdot bpy]$	2.0	1.0	White	1562.3
12	$[(Ph_3Sn)_4Fe(CN)_6 2H_2O \cdot bpy]$	2.0	1.0	White	1802.3

RESULTS AND DISCUSSION

The mass spectra, except **1**–**3**, of the novel host-guest systems are difficult to interpret. The molecular ion is not valid, due to the fact that the compounds decompose readily, thermal decomposition or hydrolysis of the samples in the ion source leads to the non-detection of the molecular ion of the samples [20]. The spectra of these systems show that the highest mass fragment corresponded to CN bridge (m/z 26–28). Also, the mass fragmentation patterns indicate the presence of the tbp-connecting alkyl- or aryl-tin units. These groups exhibit three types of fragmentation in the region m/z 133–197, 146–272, and 165–351 corresponding to RSn, R_2Sn, and R_3Sn (R = Me, n-Bu or Ph), respectively. In addition, the presence of uncharged guest molecules is confirmed by the appearance of the intense peaks in the region m/z 84–156.

X-ray powder diffraction (XRD): The 3D-polymeric systems **1**–**12** display satisfactory XRD patterns with numerous pronounced and sharp reflections (Fig. 1). In systems **1**–**3**, iron is coordinated octahedrally (not strictly octahedral, but centro symmetric) [1] by six cyanide groups that are linked to trimethyl tin units. Two kinds of tin atoms exist with equal crystallographic occurrence; trigonal-bipyramidal coordinated CN-Me_3Sn-NC units and terminal tetrahedrally configured CN-SnMe_3 units. In the presence of water molecules, one pair of trans-oriented CN-ligands

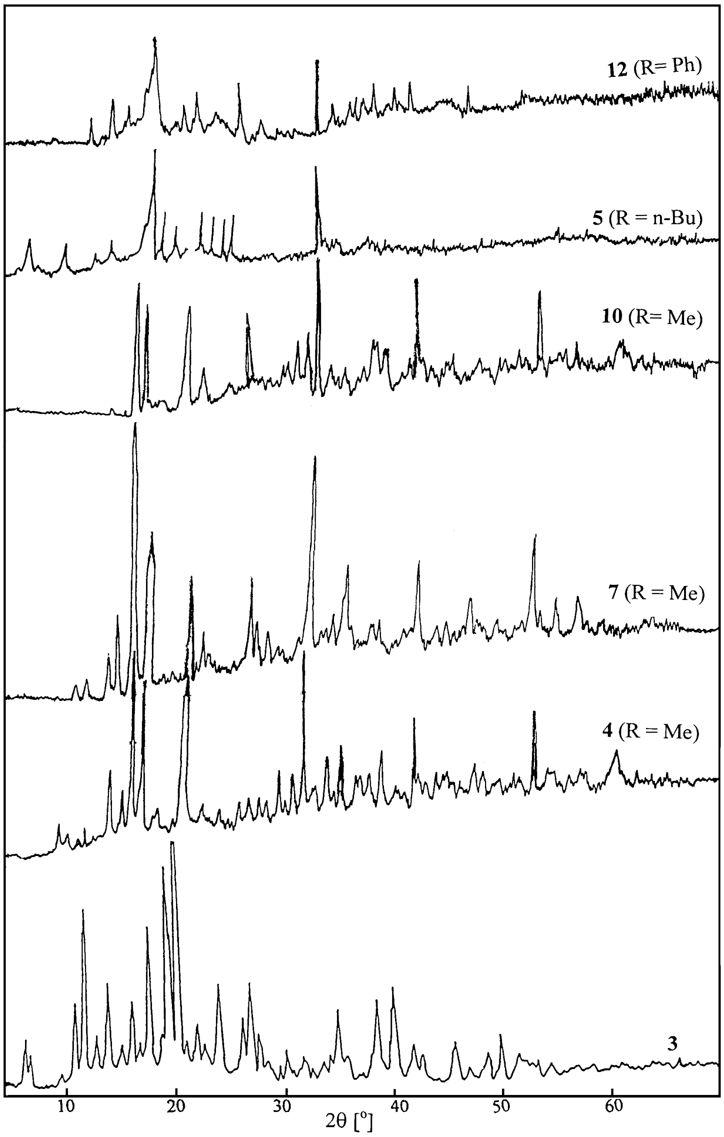


Figure 1. X-ray powder diffractograms of the some 3D-polymeric systems.

carries $Me_3Sn \cdot OH_2$ groups [1], while the infinite layers result from the intersection of [-Fe-CN-Sn-NC-] chains [6]. The structures **4**–**12** consist of the octahedral $[Fe(CN)_6]^{4-}$ building blocks, trigonal-bipyramidal Sn-coordinated and terminal tetrahedrally Sn-coordinated (similar to those of system **1**). Also, these polymeric systems consist of trans-oriented CN-ligands carries R_3SnOH_2, R = alkyl or aryl (similar to those of systems **2** and **3**). The new structures of **4**–**12** arise from the replacement of two water molecules (from four in system **3**) by an acceptor ligand {2L}. In this case, tin-coordinated H_2O molecules tend to form hydrogen bonds with the acceptors {2L} leading to more extended chains; $[CN \rightarrow Sn(R_3) \leftarrow O(H)\text{-}H..2L..H\text{-}(H)O \rightarrow Sn(R_3) \leftarrow NC]$. Both hydrogen atoms of a tin-coordinated H_2O molecule may be involved in the fixation of various bridgeheads and guest atoms [6,12]. The XRD of the compounds containing R = Me, n-Bu or Ph look quite different due to the density of polymeric systems, which increases gradually with the space demand of the tin-bonded R-group. The presence of R larger than Me leads to decrease in 2θ. This may be due to the narrow of the n-Bu or Ph groups, since the van der Waals spheres of the closest-lying C of the n-Bu or Ph and N of the cyanide groups are not far from overlapping [21].

Infrared spectra: The anhydrous/hydrate systems **1**–**3**, in the absence of {2L}, display just two or three IR-active $\nu(CN)$ bands in the range from 2025 to 2080 cm^{-1} (Table 2). The $\nu(CN)$ frequencies of novel host-guest 3D-polymeric systems **4**, **7**, and **10** give rise to only one IR-active band. Under high resolution within the $\nu(CN)$ range, the IR spectra of **5**, **6**, **8**, **9**, **11**, and **12** show two bands at 2036–2088 cm^{-1}. These $C \equiv N$ frequencies are much higher than those of the genuine salts of the corresponding $[Fe^{II}(CN)_6]^{4-}$ anion (Table 2). This enhanced in $\nu(CN)$ suggests the presence of anticipated $Fe\text{-}C \equiv N \rightarrow Sn$ bridges [22,23]. Also, the presence of two and/or three IR-active bands are due to the nonequivalent CN ligands. Moreover, the $\nu(Fe–C)$ frequencies of all systems at 442–459 cm^{-1} reflect clearly the presence of the octahedral $[Fe(CN)_6]^{4-}$ building blocks (Table 2 and Fig. 2).

Table 2. Infrared spectra (in cm^{-1}) of polymeric systems involving $[Fe(CN)_6]^{4-}$ building blocks.

No.	$\nu(CN)$	$\nu(H_2O)$, $\delta(H_2O)$	$\nu(CH)$	$\delta(CH)$	$\gamma(CH)$	$\nu(Fe^{II}–C)$	$\nu(Sn–C)$	$\nu(2L)$*
$K_4[Fe(CN)_6]$	2025, 2043							
1	2025, 2050, 2075	–	2918	1400	787	451	553	–
2	2050, 2075, 2080	3421, 1620	2918	1438	793	451	553	–
3	2051, 2075	3436, 1630	2918	1440	790	451	553	–
4	2046	3438, 1626	2918	1458	790	452	551	1120, 1197
5	2052, 2088	3425, 1630	2921	1456	697	445	516	1076, 1166
6	2045, 2085	3436, 1632	2920	1381	860	445	592	1072, 1189
7	2069	3436, 1632	2918	1520	788	451	551	1477
8	2047, 2087	3427, 1630	2920	1456	695	442	516	1666
9	2046, 2084	3426, 1629	2921	1375	729	445	585	1633
10	2067	3435, 1628	2917	–	786	451	551	1613
11	2036, 2079	3429, 1627	2919	1454	–	459	516	1600
12	2052, 2080	3427, 1627	2923	1396	730	446	585	1476, 1600

* 2L = diox, Mepyz or bpy.

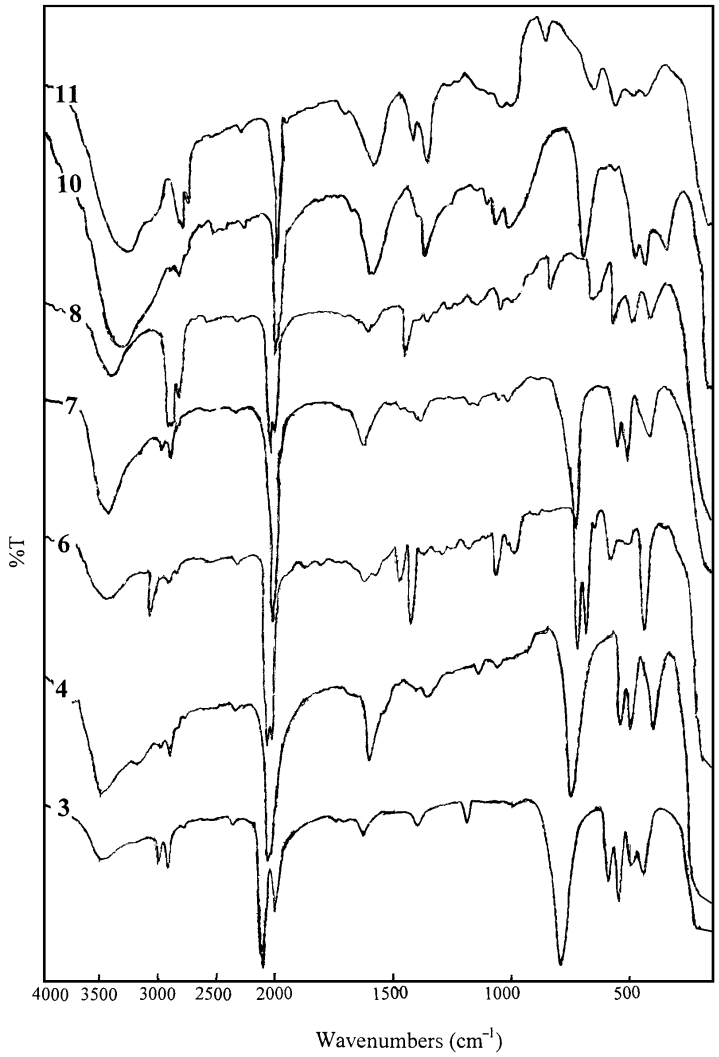


Figure 2. Infrared spectra of the seven 3D-polymeric samples.

The IR-active ν(Sn–C) vibrations of all 3D-polymeric systems reflect clearly the presence of one antisymmetric vibration Sn–C bond (*i.e.* Sn–R; R = alkyl or aryl). Absence of the symmetric vibration of $\nu(\text{Sn–C})_{\text{sym}}$ in the spectra advocate an exclusive presence of trigonal planar R_3Sn units owing to their axial anchoring to two cyanide N atoms [5]. The Sn–C band is similar to the stretching vibrations of the corresponding salts (*ca.* 554, 516, and 592 cm^{-1} for Me_3SnCl, n-Bu_3SnCl and Ph_3SnCl, respectively) [22–24]. Also, the main bands for R_3Sn (R = Me or n-Bu) are at 2919–2921 (C–H valence), 1454–1520 (CH_3 deformation), and 695–790 cm^{-1} (C–H rocking). On the other hand, the spectra of **6**, **9** and **12** display bands at

2920–2923, 1375–1396, and 729–860 cm^{-1} characteristic for different vibration modes of C–H. The R_3Sn^+ units could form bridges between the octahedral building blocks $[Fe(CN)_6]^{4-}$ through directed coordinate bond [25].

The presence of the acceptor guest molecules (diox, Mepyz or bpy) in the 3D-polymeric systems **4**–**12** are indicated by a number of IR absorption bands at 1072–1197 (diox), 1477–1666 (Mepyz), and 1476–1613 cm^{-1} (bpy). Moreover, the presence of nonremovable H_2O molecules (at least after prolonged drying in vacuum) in **2**–**12** was confirmed by the elemental analyses and by relatively intense and sharp ν(OH)- as well as δ(OH)-absorptions in the IR spectra (at 3350–3438 cm^{-1} and 1626–1635 cm^{-1}, respectively). The H_2O frequencies increase gradually with extending the coordinative $Sn–(OH_2)_2–Sn$, and $Sn–(OH_2)_2 \cdot 2L–Sn$ ($2L = H_2O$, diox, Mepyz or bpy) bonds. This indicates the presence of the regular bridges.

Thermogravimetric analysis: The thermolysis of $[(Me_3Sn)_4Fe(CN)_6 \cdot 2H_2O]$ (**2**) takes place in three steps. Within the first step, from room temperature to 120°C, two water molecules of crystal lattice and one molecule of trimethyl tin cyanide are released. Between 200 and 230°C, one Me_3SnCN molecule per formula unit is released, so that an intermediate formula $(Me_3Sn)_2Fe(CN)_4$ results [17,26]. After that the compound exhibits thermal stability to about 250°C when it undergoes complete decomposition, leading to the final nanocrystalline decomposition product Fe_2O_3 and SnO_2 [17,26] (Fig. 3).

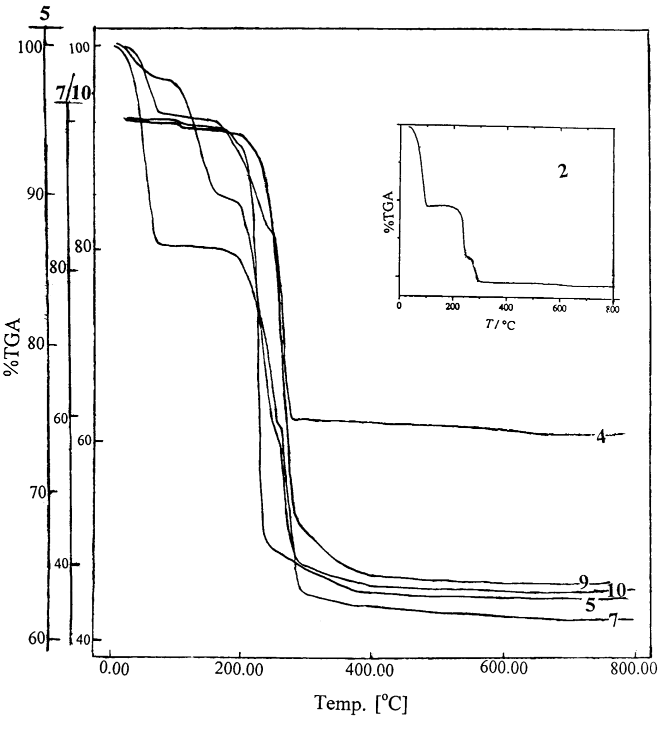


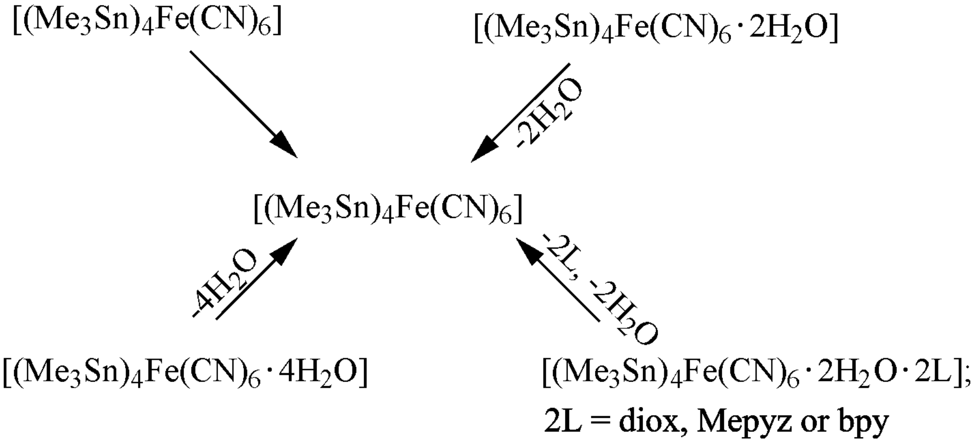
Figure 3. The thermolysis (TG-curves) for the 3D-polymeric systems **2**, **4**, **5**, **7**, **9** and **10**.

The samples **4**, **7** and **10** (R = Me) lost weights corresponding to water molecules around 76°C. The hydrogen-bonded water molecule of related systems are actually lost in this temperature range [1,17]. On further heating, the three samples lost weights between 76–234°C corresponding to one guest molecule. Thereafter, one decomposition step for these compounds can be distinguished at 237–290°C due to releasing of one molecule from Me_3SnCN per formula units. The trimethyl tin cyanide molecules are good volatile leaving groups, similar to trimethyl silyl halogenide groups [27,28]. The other two samples **5** (R = n-Bu) and **9** (R = Ph) decompose in two well-defined steps. This change may be due to the presence of less volatile n-butyl- or phenyl-tin groups. In the first step, the samples lost weight corresponding to water molecules until 108°C. This step followed by a loss in mass due to releasing of one guest molecule and two R_3SnCN units (R = n-Bu or Ph) per formula units. These systems suffer further decomposition at higher temperature (800°C) yielding the final decomposition mixed oxide products [17,26] (Fig. 3 and Table 3). The reaction temperature of these polymeric systems indicate that the systems containing n-Bu- or Ph-connecting units are more thermal stable than those Me-connecting units. Also, these polymeric systems are suitable precursors to oxidic and metallic products at ambient temperature. Whereas, classical routes to prepare these oxides take place at higher temperature for several days. The reason for this behaviour is probably the easy release of volatile reaction products like $(CN)_2$ or R_3SnCN, which play bridging functions in the coordination polymers so that their elimination can be accomplished easily.

Table 3. Thermogravimetric analysis data of some host-guest polymeric systems.

Compound	Transitions (temperature range (°C) and wt % loss)			
	A	B	C	D
2	24–120 24.6	200–240 21.7	Oxide product	–
4	24–76 3.2	76–234 8.9	234–279 19.9	Oxide product
5	21–107 1.8	107–250 48.4	Oxide product	–
7	26–68 3.1	68–240 8.5	240–290 18.8	Oxide product
9	20–108 2.3	108–287 45.0	Oxide product	–
10	26–68 3.6	68–237 16.1	237–265 17.8	Oxide product

Effect of moderate heating at ca. 70°C: The 3D-polymeric system **1** (x = 0.0) dried at *ca.* 70°C at ambient pressure for one day has led to the same composition. The drying 0.15 g of the hydrate 3D-polymeric systems **2** and **3** at elevated temperature (60–70°C) for one day leads to reducing the weight to ≈ 0.13 g due to the formation of completely anhydrous homologues of **1** (Scheme 1). The most significant changes take place in the ν(CN) frequencies (Fig. 2 and Table 2). The anhydrous 3D-polymeric system displays three IR-active ν(CN) bands that are still present in the same region after heating. Two hydrate 3D-polymeric systems **2** and **3** after drying exhibit three IR-active ν(CN) bands at the same region. This indicates the formation of anhydrous homologues **1** under the effect of moderate heating. When 0.1 g of the three novel host-guest 3D-polymeric systems **4**, **7**, and **10** are dried at *ca*. 70°C for one day, the water and guest molecules are removed and the weights reduced to $\approx$ 0.08 g. The weight loss is due to the formation of the anhydrous homologues **1** as reflected from the elemental analyses and IR spectra of these products. The two intense bands corresponding to the stretching vibrations of the water and guest molecules (at 3435–3438, 1626–1632, and 1120–1613 cm^{-1}, respectively) disappear completely after moderate heating.



Scheme 1. Comparison of four different compositions of the 3D-polymeric systems (loss of water and guest molecules at 60–70°C)

The 3D-polymeric systems as ions exchangers: The layered 3D-polymeric systems **1**–**3** contain, per formula unit, two trans-oriented, terminal $CNSnMe_3$ groups [2], which are known to exchange exactly one Me_3Sn^+ unit by an organic or organometallic guest cation [2,18,29]. For instance, suspensions of **1** in aqueous solution of NH_4Cl leads to the likewise insoluble host-guest $[(NH_4^+)(Me_3Sn)_3Fe(CN)_6]$ $\mathbf{1_a}$ system after prolonged stirring (*ca.* 6 hrs). Elemental analysis of $\mathbf{1_a}$ is C, 24.9; H, 4.3; N, 13.6 (calculated) and C, 24.5; H, 4.1; N, 13.3 (found):

$$\underset{\text{insoluble }\mathbf{1}}{[(Me_3Sn)_4Fe(CN)_6]} + (NH_4^+/H_2O) \rightarrow \underset{\text{insoluble }\mathbf{1_a}}{[(NH_4^+)(Me_3Sn)_3Fe(CN)_6]} + \underset{\text{soluble}}{Me_3Sn\cdot aq^+} \quad (3)$$

Suspension of the systems **4**, **5**, or **6** in aqueous NH_4Cl solutions do not undergo ion-exchange reactions, even upon prolonged stirring, as indicated from the elemental analyses and IR spectra of the obtained products after drying. The most important spectral information of $\mathbf{1_a}$ and the 3D-polymeric host-guest systems **4**–**6** after reaction with NH_4Cl are those of ν(CN), ν(Sn–C) and $\nu(NH_4)$ vibrations. The spectra of $\mathbf{1_a}$ gave rise to at least two extra bands at 3247 and 1415 cm^{-1} as a result of present NH_4^+ cations within the channels of **1**, whereas the spectra of the 3D-polymeric systems **4–6** do not show any changes in this region. In addition, the spectra of $\mathbf{1_a}$, and **4–6** in the ν(CN) and ν(Sn–C) region were still unchanged indicating the presence of the 3D-polymeric architecture. The 3D-polymeric system **1** undergoes facile exchange of just one Me_3Sn^+ ion (per formula unit) by a large variety NH_4^+ guest cations (Eq. 3). This reaction resembles a nonreversible ion-exchange process, while the reductance of the host-guest 3D-polymeric systems to undergo ion-exchange indicates that the notably "loose" fourth R_3Sn^+ ions become effectively immobilized in chains [12] and thus ion-exchange are not possible under these conditions. Moreover, the specific affinity of $\{R_3Sn^+\}$ fragment towards H_2O and acceptor ligand 2L must be appropriately balanced in view of the presence or absence of ion-exchange ability. The potential ability of N atoms incorporated into -Fe-C≡N→Sn←N≡C-Fe- chains to take part in hydrogen bonding with H_2O and 2L could promote a cleavage of N→Sn bonds.

Illumination-pH effects on the 3D-polymeric systems: The base hydrolysis of the 3D-polymeric systems can be studied by dissolving 0.01 g of **1**, **4**, **7**, or **10** in 0.1 M NaOH. The four samples are completely dissolved under the influence of a strong alkaline media. The Me_3Sn^+ tbp-configuration is attracted electrostatically to the negative OH^- group. This is similar to the attraction of OH^- group to H^+ ions forming water molecule:

$$[(Me_3Sn)_4Fe(CN)_6 \cdot xH_2O \cdot 2L] + 8\,OH^- \Leftrightarrow 4\,[Me_3Sn(OH)_2]^- + [Fe(CN)_6]^{4-} + 2L$$

1 (x = 0.0; 2L = 0.00) and **4**, **7** or **10** (x = 2; 2L = diox, Mepyz or bpy) (4)

Thereafter, 0.1 M HCl is slowly added to the soluble samples **1**, **4**, **7** or **10**. When the pH value is reduced to ≈ 5.3 to 5.8, the soluble compounds precipitate again (Fig. 4). The reaction of the polymeric systems in alkaline media is reversible "reorganization". When added HCl, the H^+ ions react with OH^- groups of the alkaline media and the self-assembly takes place forming the 3D-polymeric architecture. The insoluble white products were filtered off, washed with cold water and dried under vacuum. These products were examined by elemental analysis and vibrational spectra, which indicate the formation of the same composition host-guest 3D-polymeric systems **1**, **4**, **7** or **10**.

Commonly Fe^{II}-complexes may be oxidized to Fe^{III}- or $Fe^{II}Fe^{III}$-complexes under the effect of NO_2 gas which is a fairly strong oxidizing agent, E^0 = 1.07 V, in aqueous solution [15]. Conversely at room temperature, the reaction of **1** or **4** in a steam of NO_2 gas display mixed valence 3D-polymeric systems. The IR spectra of **1** and **4** exhibit strong band at 2146–2147 cm^{-1} corresponding to the stretching vibrations of $[Fe^{III}(CN)_6]^{3-}$ building blocks and a medium band at 2088–2089 cm^{-1} corresponding to the stretching vibrations of the $[\text{-}Fe^{II}(CN)_6]^{4-}$ building blocks (Fig. 5). Further work on this subject is in progress.

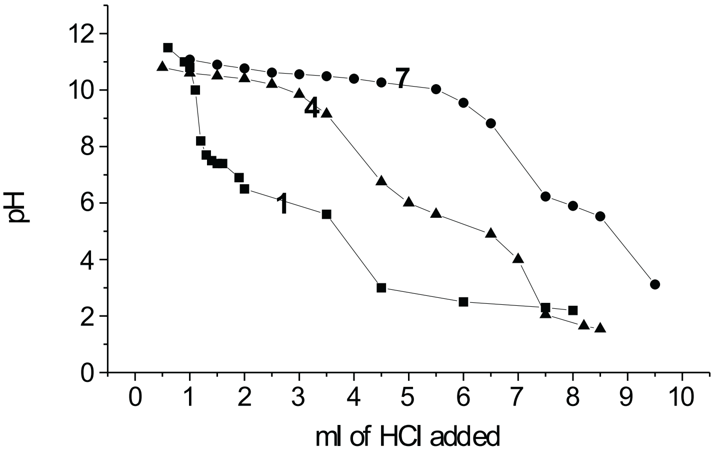


Figure 4. pH-titration curves for the 3D-polymeric systems **1**, **4**, and **7** ([HCl] = 0.1 M).

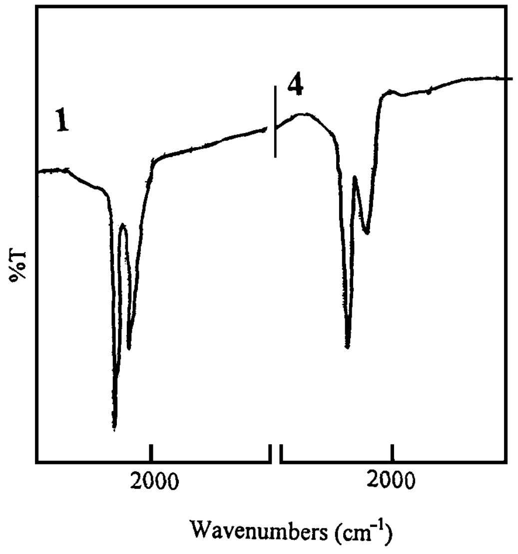


Figure 5. Infrared spectra in the ν(CN) absorption range of the 3D-polymeric systems **1** and **4**.

CONCLUSIONS

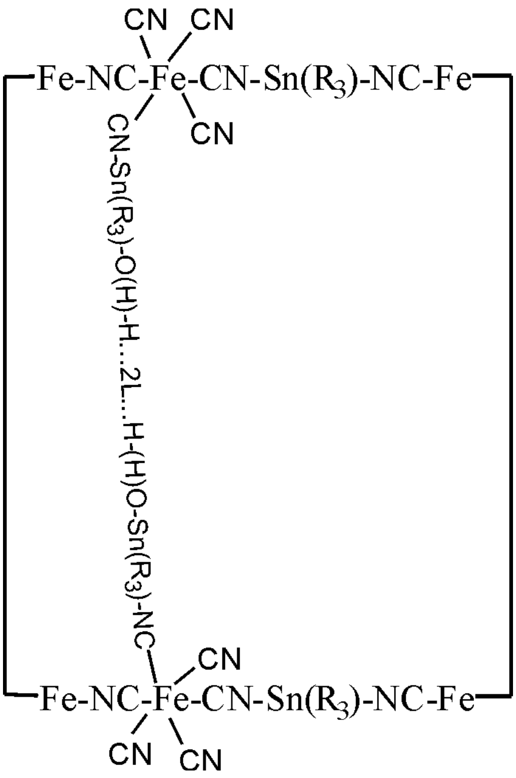
The self-assembly reactions between the salts containing $[Fe(CN)_6]^{4-}$, cationic R_3Sn^+ units and uncharged ligand {2L} yield novel host-guest systems, which have specific characterizations. In these systems, tin-coordinated H_2O molecules tend to generate hydrogen bonds with acceptors {2L}, leading to considerably more extended fragment,

$$\text{-CN}\rightarrow\text{Sn}(\text{R}_3)\leftarrow\text{O(H)-H...NC-} + 2\text{L} \rightarrow$$

$$\text{-CN}\rightarrow\text{Sn}(\text{R}_3)\leftarrow\text{O(H)-H..2L..H-(H)O}\rightarrow\text{Sn}(\text{R}_3)\leftarrow\text{NC-}$$

2L = diox, Mepyz or bpy (5)

The simple structure model may be described as infinite 3D-networks of two different chains, that are interlinked by their joint, octahedral coordinated Fe atoms. The acceptor ligands {2L} are incorporated into one (from two) chain to take part in hydrogen bonding with H_2O molecules (Scheme 2).



Scheme 2. Possible coordination of Fe^{II} in 3D-host guest polymeric systems **4**–**12**.

The presence of ligand bridges is important for the supramolecular architecture for the resulting spectroscopic properties, and for the ion-exchange activity. The specific affinity of an R_3Sn^+ unit towards H_2O and/or 2L molecules must be appropriately balanced in view of the presence or absence of ion-exchange activity.

The cleavage of terminal N→Sn bonds (then facilitating eventual ion-exchange) may be more difficult in the presence of H_2O and {2L} molecules, due to the fixation of various bridge heads.

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