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The Organotin(IV) Coordination Polymer $((Me_3Sn)_4Fe(CN)_6\cdot 2H_2O\cdot C_4H_8O_2)_\infty$: A Three-Dimensional Host–Guest Network Involving "Cascade-Type" Guests

Macro- or polycyclic Lewis *base* receptors[1] require an appropriate disposition of Lewis acidic centers over the respective organic rings. Frequently, after the anchoring of at least two metal ions to selected N and/or O atoms of the ring as "primary guests", the still remaining coordinative unsaturation of the metal ion admits the subsequent fixation of charged or uncharged donors as "secondary guests" (or "guests of guests").[2] Alternatively, single intrinsic ring sites may be made Lewis acidic, as has been demonstrated e.g. for built-in $Sn^{IV}Cl_2$ moieties.[3] We wish to describe here an essentially inorganic polymer that makes similar use of organotin(IV) units as primary acidic centers, as well as of hydrogen bonding, to build up a three-dimensional host–guest system that even appears to receive notable stabilization from the incorporation of "guest of guest"[2] (or "cascade-type guest") units into its primary chains and cycles, respectively.

While the recently reported,[4] anhydrous coordination polymers $((Me_3Sn)_4M^{II}(CN)_6)_\infty$ (M = Fe (**1a**), Ru (**1b**)) precipitate instantaneously from aqueous solutions of $K_4(M(CN)_6)$ and Me_3SnCl, the otherwise preferred[4] formation of (invariably microcrystalline) **1** is inhibited in the presence of various organic Lewis bases, yet in the case of some bi- or polydentate bases, surprisingly large, and well-formed, crystals grow from the modified solutions within a few days in yields of up to 70%. The Debye–Scherrer powder pattern of the crystalline product **2** obtained from $K_4(Fe(CN)_6)$ and Me_3SnCl in water/1,4-dioxane[5a] differs clearly from that of **1a**, and the appearance of signals characteristic of both $C_4H_8O_2$ and H_2O in the mass spectrum of **2** suggests the formation of an unforeseen host–guest system. Unlike the rather insignificant elemental analysis,[5b] the result of a crystallographic single-crystal X-ray study of **2**[6] has ascertained the composition "$(Me_3Sn)_4Fe(CN)_6\cdot 2H_2O\cdot C_4H_8O_2$": The actual crystal structure depicted in Figure 1 may be described as an infinite, three-dimensional network of two different nonlinear chains A and B that are interlinked by their joint, octahedrally coordinated Fe atoms. The repeating units of the two chains extend by the patterns

chain A:
$$-(\mathrm{Sn2{-}N1{-}C1{-}Fe{-}C1{-}N1{-}Sn2{-}N3{-}C3{-}Fe{-}C3{-}N3{-}})_\infty$$

chain B:
$$-(\mathrm{Sn1{-}O1{\cdots}O2(C_2H_4)_2O2{\cdots}O1{-}Sn1{-}N2{-}C2{-}Fe{-}C2{-}N2{-}})_\infty$$

Each $O2(C_2H_4)_2O2$ fragment corresponds to a dioxane molecule, and each O1 atom to one probably hydrogen bonded water molecule. The $Me_3Sn(NC)_2$ units of chain A (Sn2–N1 = 2.374 (8), Sn2–N3 = 2.285 (9) Å; averaged angle C(Me)–Sn2–N1 = 89.5°) are essentially trigonal bipyramidal (tbp), whereas the $Me_3Sn(NC)O$ units of chain B turn out to be notably distorted (Sn1–N2 = 2.160 (9), Sn1–O1 = 2.451 (8) Å; averaged angles C(Me)–Sn1–N2 = 94.2, C(Me)–Sn1–O1 = 85.8°). While the Sn–N distance in chain B is shorter than that in chain A and the earlier described[7] polymer $((Me_3Sn)_3Co(CN)_6)_\infty$, the Sn–O distance exceeds those of the tbp-configured $((n\text{-}Bu)_3Sn(OH_2)_2)^+$ cation (2.295 (4) and 2.326 (5) Å).[8] The O1–O2 distance of 2.779 Å matches best with the relatively long O···O separations of hydrogen bonds in liquid H_2O[9a] and water clathrates.[9b] The unexpectedly short O1–N1 distance of 3.122 Å does not rule out the possibility of additional hydrogen bonds between each water molecule and a distinct cyanide N atom.[10] The Fe–C and C–N distances compare well with those of the polymeric (via N···H···N

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(1) See: (a) Lehn, J.-M. *Angew. Chem.* **1988**, *100*, 91; *Angew Chem., Int. Ed. Engl.* **1988**, *27*, 89. (b) Schmidtchen, F. P. *Nachr. Chem., Tech. Lab.* **1988**, *36*, 8.

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(5) (a) Colorless crystals of **2** were grown within 2–3 days at 4 °C from a solution obtained as follows. A clear solution of 0.27 g (0.63 mmol) $K_4(Fe(CN)_6)$ in 25 mL of H_2O and 40 mL of $C_4H_8O_2$ was added carefully to a solution of 0.5 g (2.5 mmol) of $(CH_3)_3SnCl$ in 10 mL of $C_4H_8O_2$. Yield after filtration, washing with cold H_2O, and short drying at 40 °C: 0.45 g (72%). (b) Elemental analyses calculated for **2**, $C_{22}H_{48}N_6O_4FeSn_4$ (viz. **3a**, $C_{18}H_{36}N_6FeSn_4$): C, 26.66 (24.93); H, 4.88 (4.18); N, 8.48 (9.69); Fe, 5.63 (6.44); Sn, 47.89 (54.74). Found: C, 24.68; H, 4.60; N, 9.78; Fe, 6.26; Sn, 50.95.

(6) $(Me_3Sn)_4Fe(CN)_6\cdot 2H_2O\cdot C_4H_8O_2$ (**2**) crystallizes in the monoclinic space group $P2_1/n$, with $a = 13.242$ (2) Å, $b = 11.396$ (2) Å, $c = 13.322$ (3) Å, $\beta = 101.37$ (1)°, $\delta_c = 1.46$ g·cm^{-3}, and $Z = 2$. The structure was solved by automated Patterson methods (SHELX-86) for 2517 numerically absorption corrected reflections with $|F_o| > 4\sigma(F_o)$, and refined to $R = 0.051$ and $R_w = 0.053$. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically with fixed C–H bond lengths of 0.96 Å. Data were collected at 22 °C on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.709\,261$ Å).

(7) Yünlü, K.; Höck, N.; Fischer, R. D. *Angew. Chem.* **1985**, *97*, 863; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 879.

(8) Davies, A. G.; Goddard, J. P.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1983**, 597.

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(10) Interestingly, the most recently determined X-ray structure of the 3D polymer $(Me_3Sn)_4Fe(CN)_6\cdot 4H_2O$, in which each dioxane molecule of **2** is formally replaced by two water molecules, displays well-confirmed $O(H_2O)\cdots N(CN)$ hydrogen bonds with O–N distances of 2.972 and 3.052 Å: Behrens, U.; Brimah, A. K.; Fischer, R. D. Unpublished results.

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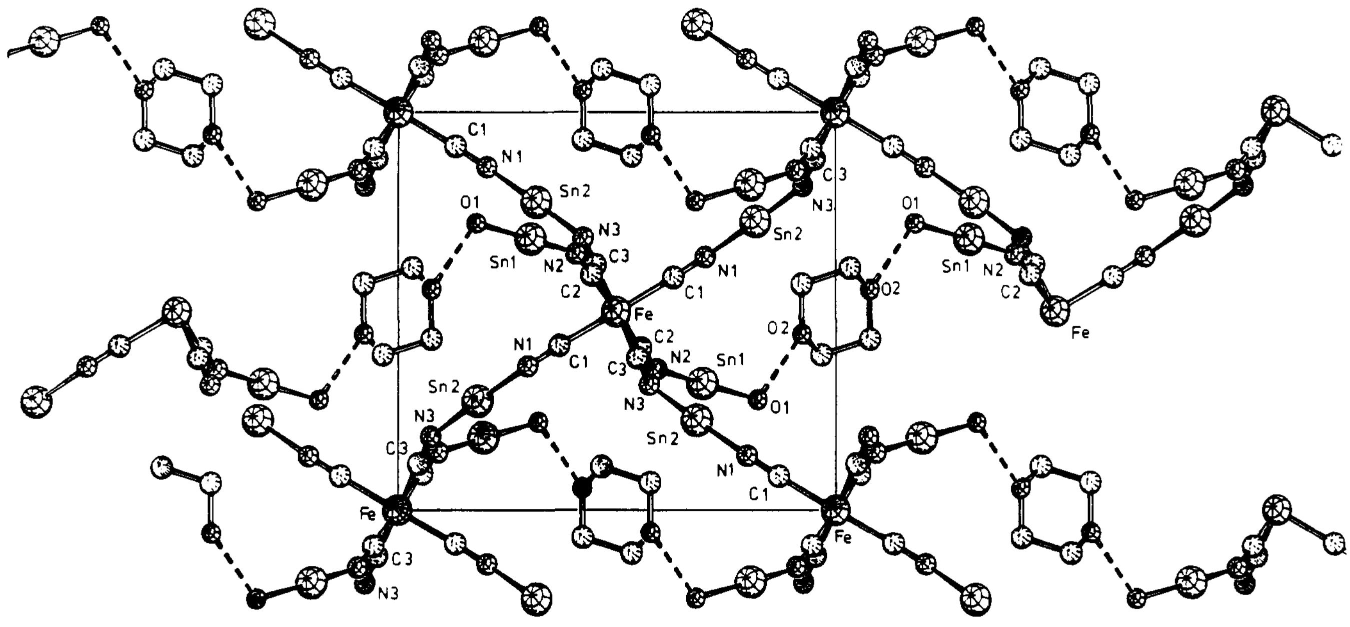


Figure 1. SCHAKAL[16] plot of **2**.[17] The dotted lines indicate the more essential water-to-dioxane hydrogen bridges.

bridges) complex $H_4Fe(CN)_6$[11] (Fe–C(average) = 1.89, C–N(average) = 1.15 Å): chain A, Fe–C1 = 1.917 (9), Fe–C3 = 1.923 (10), C1–N1 = 1.137 (11), C3–N3 = 1.136 (12) Å; chain B, Fe–C2 = 1.894 (10), C2–N2 = 1.164 (12) Å. All iron atoms and midpoints of dioxane molecules lie on centers of symmetry, which feature is only partially reflected by the infrared and Raman spectra in the ν(CN) absorption range of **2**.[12] The nonlinearity and the specific coiling of both chains may result from a reasonable compromise in view of the tendency to reach an optimal space filling for A (angles C1–N1–Sn2 = 148.2, C3–N3–Sn2 = 159.2°; dihedral angle[13] C1–N1–Sn2–N3–C3 = 73.6°) and B (angles C2–N2–Sn1 = 157.4, Sn1–O1–O2 = 137.6°; dihedral angle[13] C2–N2–Sn1–O1–O2 = 33.2°). Initial experiments have shown that the monosaccharides glucose, fructose, and mannose also inhibit the precipitation of **1**, suggesting that the building block of chain B, HO···H···O$(C_2H_4)_2$O···H···OH, may be replaced by a probably cyclized sugar molecule.

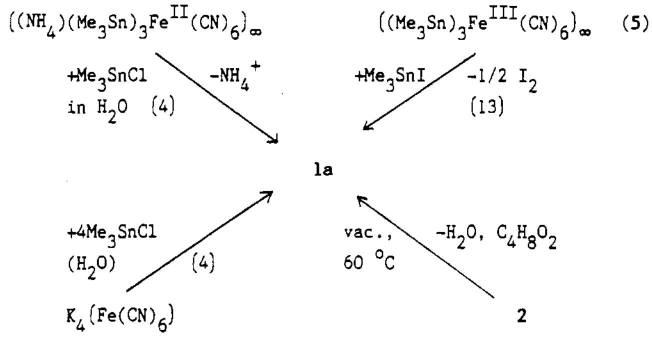
All (H_2O and $C_4H_8O_2$) guest molecules of **2** may be quantitatively removed under high vacuum at temperatures around 60 °C. According to its elemental analysis, X-ray powder pattern, and chemical behavior, the remaining white solid **3** turns out to be identical with authentic **1a**. For example, both **3** *and* **1a**,[4] but not **2**, quickly exchange Me_3Sn^+ for Et_4N^+ ions when exposed to an aqueous solution of Et_4NCl:

$$\underset{\mathbf{1a}\text{ or }\mathbf{3}}{((\mathrm{Me_3Sn})_4\mathrm{Fe(CN)_6})_\infty} \xrightarrow[-(\mathrm{Me_3Sn(H_2O)_2})^+]{(\mathrm{Et_4N})^+/\mathrm{H_2O}} \underset{\mathbf{4}}{((\mathrm{Et_4N})(\mathrm{Me_3Sn})_3\mathrm{Fe(CN)_6})_\infty} \quad (1)$$

The reluctance of the new host guest system **2** to undergo ion exchange when suspended in a dioxane-free aqueous solution of Et_4NCl for at least 6 h indicates that the notably "loose" fourth Me_3Sn^+ ion of **1a**[4] (cf. eq 1) becomes effectively immobilized in chain B of **2**.

Although **1a** may now be prepared via four different routes (Scheme I),[18] two educts of which have also structurally been characterized (i.e. **5** and **2**), the exact structure of **1** may still not be predicted with certainty.[14] The formation of **2** described above suggests that X-ray quality single crystals of **1a** (and likewise of **1b**) might grow best from solvent/inhibitor combinations that would lower the equilibrium concentration of exclusively hydrated Me_3SnCl (i.e. of $(Me_3Sn(OH_2)_2)^+$ ions) strongly, but not totally, allowing thus a sufficiently slow precipitation rate of **1**, which would, nevertheless, exceed notably the relative precipitation rates of all other possible products. Corresponding experiments in this direction are presently underway.

Scheme I. Comparison of Four Different Preparative Routes to **1a** (Ion Exchange, Solid-State Redox Reaction, Liberation of Guest Molecules, and Precipitation from Solution)[18]



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Supplementary Material Available: Listings of positional and displacement parameters and selected bond distances and angles and a figure showing an ORTEP plot of two asymmetric units of $(Me_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot C_4H_8O_2$ (5 pages); a listing of observed and calculated

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(11) Pierrot, M.; Kern, R.; Weiss, R. *Acta Crystallogr.* **1966**, *20*, 425.

(12) ν(CN) bands of **2** (in cm^{-1}): infrared, 2080 vs, 2045 s; Raman, 2131 s, 2087 vs, 2064 s.

(13) Angles spanned by the vector pairs N1→C1/N3→C3 and N2→C2/O1→O2, respectively.

(14) Brimah, A. K.; Fischer, R. D. To be submitted for publication.

(15) See, e.g., footnotes 15 and 16 of ref 4a as well as refs 4b and 10.

(16) Keller, E. A FORTRAN Program for the Graphic Representation of Molecules and Crystallographic Models. Universität Freiburg, Freiburg, FRG, 1986.

(17) To present an optimal impression of the 3D network, more than one asymmetric units have been considered. For clarity, all hydrogen and CH_3 carbon atoms have been omitted, and instead of a common ORTEP presentation, the SCHAKAL plot[16] with constant radii (for each element) has been preferred.

(18) Most recently, the compound $((NH_4)(Me_3Sn)_3Fe^{II}(CN)_6)_\infty$ has been shown to also rearrange to **1a** (and to dissolved $(NH_4)_3(Fe(CN)_6)$) when simply suspended in H_2O. The new polymer $(Me_3Sn)_4Fe^{II}(CN)_6 \cdot 4H_2O$[10] may be converted into **1a** essentially like **2**.

structure factors (15 pages). Ordering information is given on any current masthead page.

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Cyclic Voltammetry of Imidazolemicroperoxidase-8: Modeling the Control of the Redox Potential of the Cytochromes

A number of cytochromes have midpoint redox potentials that are strongly dependent upon pH; these include the bacterial cytochromes c_2[1,2] and both cytochrome b-562[3] and the cytochrome d terminal oxidase complex of *Escherichia coli*.[4] NMR and other spectroscopic evidence has shown, at least for the cytochromes c_2, that the redox potential is controlled by the state of ionization of a heme propionate or a noncoordinated imidazole of a His residue in close proximity to the iron porphyrin.[1] This provides an example of how proteins couple changes at one site (±e$^-$ at Fe) to changes at another site (±H$^+$ at an ionizable functional group), an effect that may be relevant, for example, to the proton-pumping activity of various components of the respiratory chain and physiological control of electron transport.[4-8]

We report here that the midpoint potential of the imidazole complex of the heme octapeptide from cytochrome *c*, microperoxidase-8 (MP8)[9-11] (Figure 1), determined by direct dc cyclic voltammetry at a glassy-carbon electrode, is strongly pH dependent and models these pH-linked redox effects in the cytochromes. The redox potential is controlled by at least five ionizations, three in the oxidized and two in the reduced heme peptide. We suggest that a heme propionate, the terminal amino group of the polypeptide, and the imino N atom of coordinated imidazole are the ionizing groups responsible.

The strong susceptibility of aquo-MP8 to dimerization in aqueous solution[9] makes a study of its electrochemical behavior problematic. A cyclic voltammetry investigation of the related heme undecapeptide, MP11,[12] yielded results that were apparently independent of MP11 concentration (0.1–1 mg/mL, i.e., 50–500 μM); with MP8, this would mean only 25%–9% monomer would be present in aqueous solution.[9] We therefore chose to perform our electrochemical experiments with MP8 in the presence of saturating concentrations of imidazole (0.15 M; the binding constant is 2.82 × 10^4 [10]). Successive dilutions of imidazole-MP8 were performed with buffered 0.15 M imidazole (0.1 M CAPS, pH = 10.2; μ = 1.0 M (KCl); 25 °C) to produce solutions with [MP8] = 1.2 mM to 80 nM, which were monitored at 527 nm in 0.1-, 1.0-, and 10.0-cm path-length cells. The complex obeys Beer's law over the entire concentration range (ϵ = 8540 ± 5 M^{-1} cm^{-1}). Observed effects are therefore strictly attributable to a monomeric complex in aqueous solution.

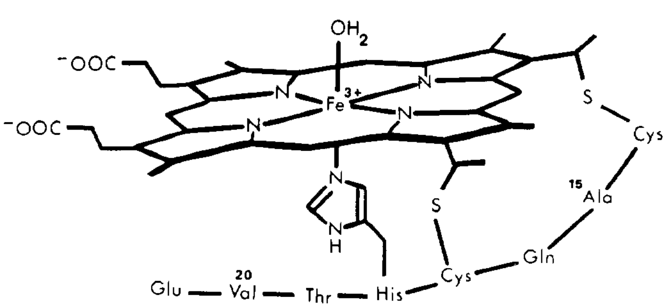

Figure 1. The heme octapeptide, microperoxidase-8 (MP8), obtained from proteolytic degradation of horse heart cytochrome *c*. The amino acid residue numbering is that of the parent protein.

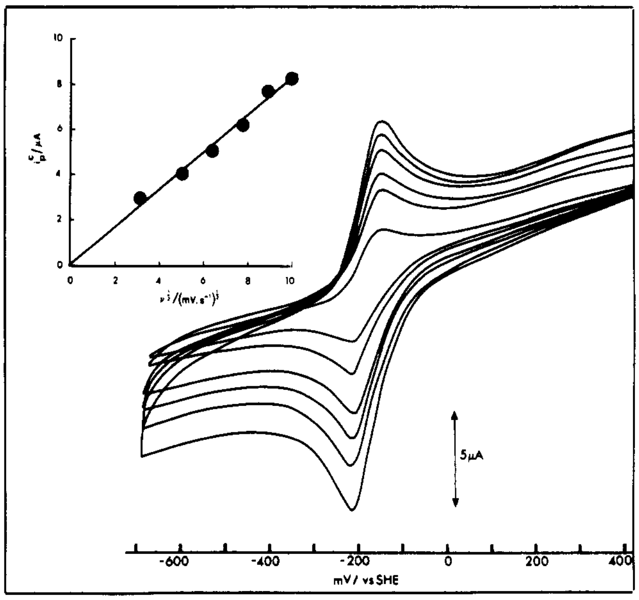

Figure 2. Cyclic voltammetry of MP8 (0.978 mM) is 0.15 M imidazole (μ = 1.0 M (KCl); 25 °C) on a glassy-carbon electrode, pH = 7.0, vs SHE. Sweep rates (mV s^{-1}): (a) 100; (b) 80; (c) 60; (d) 40; (e) 25; (f) 10. The inset shows a plot of peak cathodic currents as a function of (scan rate)$^{1/2}$. The slope gives the diffusion coefficient, D_0.[13]

MP8 was prepared as previously described.[9] Spectra were recorded on a Cary 2300 spectrophotometer fitted with thermostated cell holders. Cyclic voltammetry experiments were conducted on 3 mL of 0.978 mM MP8 in the presence of 0.15 M imidazole at 25 °C (μ = 1.0 M (KCl)) under N_2 by using a MINTEK Potential-GalvanoStat instrument (Council for Mineral Technology, Randburg, South Africa) operating in the potentiostat mode with a 3.0-mm-diameter glassy-carbon working electrode, a Ag/AgCl reference electrode, and a Pt-plate counter electrode. The electrode surface was manually polished on a polishing gauze with diamond powder slurry followed by sonication to produce a black mirrorlike surface. pH was adjusted by judicious addition of concentrated HCl or saturated KOH and measured with a Metrohm 605 pH meter and a microcombination glass electrode calibrated aganst standard buffers.

Voltammograms obtained at pH 7.0 are shown in Figure 2. The peak anodic to peak cathodic current ratio was 0.85 ± 0.06

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