Table I. Resonance Raman Band Positions, Iron Coordination Numbers, and $\mathrm{C_t}$–N Distances in Ferric Heme Proteins and Model Systems[a]

compd	ref	band II, cm^{-1}	band IV, cm^{-1}	coord no.	$\mathrm{C_t}$–N, Å
	High Spin				
chlorhemin	9	1495	1572	5	2.03
$\mathrm{Fe(PPIXDME)(SArNO_2)}$	this work	1490	1572	5	2.03
P-450 (rat, LM)	16c	1490	1578	5	2.03
P-450 (rabbit, LM)	16b		1571	5	2.03
P-450 (cam, bacteria)	16a	1488	1570	5	2.04
HRP native	18, 19	1500	1575	5	2.02
cytochrome *c*'	20, 21	1500	1578	5	2.02
$\mathrm{(Me_2SO)_2Fe(PPIX)}$	5	1475	1560	6	2.06
$\mathrm{(Me_2SO)_2Fe(OEP)}$	5	1481	1563	6	2.06
fluoride HRP	18, 19	1482	1555	6	2.06
MetHb	5	1481	1561	6	2.06
	Low Spin				
$\mathrm{(Im)_2Fe(MP)}$	9, 11	1505	1584	6	2.00
cyanide HRP	18	1497	1590	6	2.01
cytochrome *c*	12a	1506	1585	6	2.00
P-450 (rat, LM)	16c, 22	1505	1580	6	2.00
P-450 (rabbit, LM)	16b	1502	1585	6	2.01
P-450 (cam, bacteria)	16a	1502	1581	6	2.01

[a] For abbreviations, see ref 1.

thiolate sulfur coordinated in the 5th coordination position, mainly on the basis of spectral studies of model compounds.[14] Among those model substances, the $\mathrm{Fe(PPIXDME)(SArNO_2)}$[1] gives the closest approach to the optical, EPR, and Mössbauer spectral properties of high-spin (HS)[1] ferric cytochrome P-450.[15] Because the question of possible hexacoordination in high-spin ferric heme proteins is still a subject of discussion[5-8,13c] the possibility of proving the iron pentacoordination in HS P-450[1] by RR spectroscopy using the reasoning quoted above is, in the absence of direct crystallographic data, attractive.

To this purpose we have measured the RR spectrum of $\mathrm{Fe(PPIXDME)(SArNO_2)}$ as a pentacoordinated HS model compound with a thiolate axial ligand and compared it with that of HS P-450 reported by us and other authors.[16] The RR spectra of HS P-450 from rat liver microsomes[16c] and of the model compound are displayed in Figure 1; the positions of important RR bands (II and IV) of various HS and LS heme proteins and model substances are summarized in Table I. The comparison of the values shows clearly that the HS P-450 is similar to the $\mathrm{Fe(PPIXDME)(SArNO_2)}$ and behaves like a five-coordinated HS iron(III) heme protein.

The average values of the $\mathrm{C_t}$–N distance, calculated according to the above-mentioned relationship, are also included in Table I. The distance of 2.03 Å, found for both HS P-450 and $\mathrm{Fe(PPIXDME)(SArNO_2)}$, is somewhat greater than that determined for the latter compound by crystallographic analysis (2.017 Å).[15] This slight discrepancy observed with nonplanar hemes was discussed in the original paper.[5] The calculated $\mathrm{C_t}$–N distance for cytochrome P-450 fits also well to the family of pentacoordinated HS hemes.[5,9,18-21] The average $\mathrm{C_t}$–N values for LS P-450 correspond well to the value of 2.00 Å, found by Cramer et al.[17] for rabbit LS P-450 with an extended X-ray absorption fine-structure technique (EXAFS).

The results presented thus give a strong support to the hypothesis of thiolate ligation in P-450 and iron pentacoordination in high-spin ferric P-450, which is the crucial point for understanding the P-450 enzyme mechanism because of low-spin/high-spin equilibrium modulation caused by binding of substrate. Moreover, the resonance Raman data also supply a reasonable estimate of the porphyrin ring radius in this heme protein.

Acknowledgment. This work was supported partly by agreement between Charles University, Prague, and Jagellonian University, Cracow.

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An Organosilicon Polymer That Is Derived from a Mineral and Is at Least Partly Ladderlike and Inherently Fibrous

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We report herein a polymer that is at least partly ladderlike and inherently fibrous. This polymer is a siloxane and has pendent trimethylsilyl and silanol groups. The route used to make it involves the synthesis of a silicate containing the polymeric ladder ion shown in Figure 1a and then the silylation of this ion.

The silicate which has been employed the most for the synthesis of this polymer is litidionite, $\mathrm{NaKCuSi_4O_{10}}$. A drawing showing the specific structural arrangement of the ladder ion in this silicate[1] is presented in Figure 1b.

The litidionite was made by placing a disk of a sodium–potassium–copper glass of appropriate stoichiometry on a thin bed of previously prepared and powdered litidionite and then heating this assemblage. It was also made by sintering a mixture of $\mathrm{Na_2CO_3}$, $\mathrm{K_2CO_3}$, CuO, and $\mathrm{SiO_2}$ having the appropriate stoichiometry.[2-5]

Because of the nature of these procedures, it is apparent that the processes occurring in them which lead to the formation of the silicate ion are mainly ion migration processes. In the devitrification procedure these processes are probably integral parts of the crystallization process. In the sintering procedure this is certainly the case.

The silylated polymer was prepared from the litidionite by exposing a piece of it to a stirred mixture of trimethylchlorosilane, water, and dioxane. The polymer was also prepared by using mixtures of trimethylchlorosilane, water, and acetone or tetrahydrofuran and using powdered instead of lump litidionite.[6] It was purified by washing and density separation techniques.

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(3) Natural litidionite occurs in exceedingly tiny amounts in association with a blue glass found in the crater of Mt. Vesuvius: Zambonini, F. "Mineralogia Vesuviana"; S.I.E.M.: Naples, 1935; p 435.

(4) It is likely that the devitrification procedure parallels the process leading to natural litiodionite.

(5) The sintering procedure is similar to that used to make cuprorivaite, $\mathrm{CaCuSi_4O_{10}}$: Pabst, A. *Acta Crystallogr.* **1959**, *12*, 733.

(6) These procedures are patterned after earlier mineral silylation and germylation procedures. See, for example: (a) Lentz, C. W. *Inorg. Chem.* **1964**, *3*, 574. (b) Frazier, S. E.; Bedford, J. A.; Hower, J.; Kenney, M. E. *Ibid.* **1967**, *6*, 1693. (c) Calhoun, H. P.; Masson, C. R. *J. Chem. Soc., Chem. Commun.* **1978**, 560.

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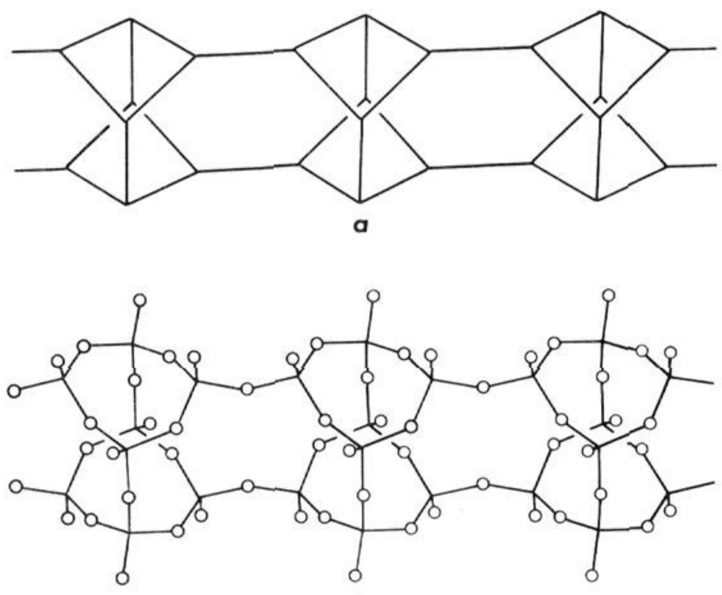

Figure 1. (a) Framework of ladder silicate ion employed. Junctions represent silicon atoms and pendent oxygen atoms, lines represent bridging oxygen atoms. (b) ORTEP drawing of silicate ion in litiodionite based on the data of Martin Pozas, Rossi, and Tazzoli. Junctions represent silicon atoms; circles represent oxygen atoms.

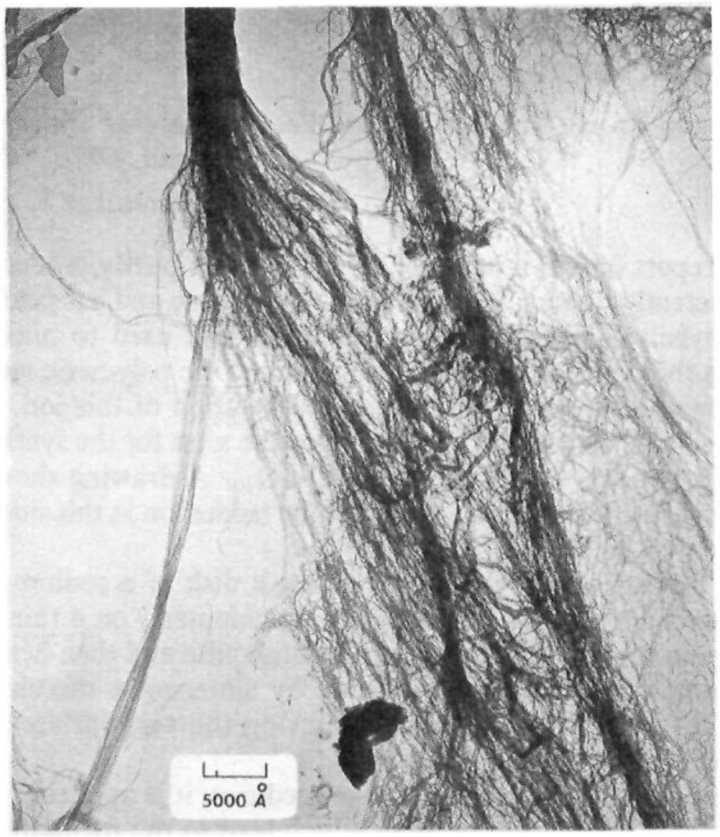

Figure 2. Transmission electron micrograph of the polymer.

The polymer is waxy and is insoluble in a wide range of organic solvents. However, it forms a gellike material with solvents such as dioxane and chloroform. When purified it is a very pale blue.

It gives an infrared spectrum showing $Si(CH_3)_3$, SiOH, and SiOSi bands[7] and a Si $2p_{3/2}$ X-ray photoelectron spectrum showing overlapping $SiOC_3$ and SiO_4 peaks. Micrographs of it show fibers that are limp and have very small diameters, Figure 2. Fibers with diameters of 40–60 Å are commonly seen. A few with diameters somewhat above 20 Å are seen.

One sample of the polymer yielded an analysis showing 14.08% C, 3.47% H, and 38.93% Si and gave an Si $2p_{3/2}$ X-ray photoelectron spectrum with $SiOC_3$ and SiO_4 peaks having areas with a ratio 27:73. It yielded K $1s_{1/2}$, Na $1s_{1/2}$, and Cu $2p_{3/2}$ spectra giving evidence for a small amount of potassium but no evidence for sodium or copper. The sample yielded a differential thermal analysis thermogram in air having a very small endotherm at 326 °C and a large exotherm beginning at $\sim$415 °C (decomposition). It gave a differential scanning calorimetry thermogram under helium which showed no transitions between -153 and 267 °C. An X-ray powder pattern of it had a strong broad Bragg angle peak at 13.5 Å and a weak broad one at 4.86 Å.

On the basis of the procedures used to make the polymer and on the basis of its properties, it appears that some of the fibers in the polymer have a framework consisting of a ladder that is like the one in the parent silicate ion except for the presence of additional internal cross-links and that the rest have frameworks made of ladders of this type which are sparingly joined by oxygen bridges.[8] It further appears that in the sample of the polymer subjected to elemental analysis approximately 37% of the backbone silicon atoms carry silyl groups. In addition it seems probable that the glass transition temperature of the polymer is below −153 °C.

Because fibers are inherent in this polymer and because they are so small, it is of considerable interest.[9,10] Moreover, this polymer is at least in part a ladder polymer (while another organosilicon polymer has been reported to be a ladder polymer,[11] it is now known not to be so[12]). The polymer is also of interest because it is derived from a precursor that is an integral part of a crystalline species and thus one that has very great regularity and very high molecular weight.

Acknowledgment. We gratefully acknowledge support of this work by Dow Corning Corporation and B. F. Goodrich Corporation Fellowships and by the Office of Naval Research.

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Photo-CIDNP Study of Adenosine 5′-Monophosphate. Pair-Substitution Effects due to Cation Radical Deprotonation

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The dye-sensitized generation of nuclear spin polarization in amino acid residues has been very useful in probing the surface structure of proteins.[1-3] Recently we found that nucleic acid bases can be polarized as well by making use of a cyclic reaction scheme similar to that employed in the case of amino acids. These effects are likely to be useful in elucidating structural features of nucleotides and their interactions with other molecules, like nucleotide binding proteins. Photo-CIDNP was observed in 5′-AMP and 5′-GMP in the presence of 3-(carboxymethyl)lumiflavin.[4] Unlike

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