found in Co[24] and Mn[9a] carboxylates, but rarely observed for Fe.[25] Low-temperature ESR studies[17,18] of **1** in frozen pyridine solution and of solid **2** reveal characteristic features of Mn(II) and Co(II), respectively. Integration of the ESR signal confirms that **1** contains 1.0 ± 0.1 Mn atoms per molecule. The μ_{eff} vs T plot for **1** indicates antiferromagnetic exchange coupling and a ground state with $S_T \leq 1$.

In conclusion, formal fusion of two $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$ fragments in the presence of a divalent heterometal has yielded the largest soluble polyiron oxo-hydroxo compounds to date. Further growth of the polymetal oxo-hydroxo core of **1** and **2** can be envisioned by repeating the steps outlined in Scheme I. This process allows the derivation of a general formula, $M_nFe_{5n+11}O_{4n+6}(OH)_{4n+6}(O_2CPh)_{5n+15}$, $n = 0, 1, 2$, etc., predicting the stoichiometry of higher members of this series. Attempts to synthesize such compounds, and to relate them to biological and mineralogical iron, are currently in progress.

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Supplementary Material Available: Table of atomic positional and thermal parameters for $2 \cdot 17CH_3CN$ (10 pages). Ordering information is given on any current masthead page.

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Organolithic Macromolecular Materials Derived from Vinyl-Functionalized Spherosilicates: Novel Potentially Microporous Solids

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Organolithic macromolecular materials (OMM's) are substances containing both silicate and organic components, with a definite chemical relationship between the two.[1,2] The structure of the organic component is well defined but that of the silicate component is usually undefined. One way of achieving some degree of control over the structure of the latter is to use a variant of the Lentz trimethylsilylation technique[3] to attach organosilicon moieties to the free $\equiv SiO^-$ groups of a silicate of known structure. The structure of the silicate component of the materials thus obtained is similar to the structure of the silicate used as the starting material.[4] One of the limitations of this method, when applied to the synthesis of macromolecular materials, is that the silicate structures are not entirely stable under the reaction conditions and hence the resultant material is not structurally well defined.

An alternative route has allowed us to synthesize an OMM that contains spherosilicate moieties $[Si_{10}O_{25}]$, with well-defined pentagonal prismatic structures, that are cross-linked at the vertices by organosilicon moieties whose structure is $(Si(CH_3)_2CH_2CH_2Si(CH_3)_2C_6H_4O_{0.5})_2$. The repeating unit of this OMM is actually the tetravalent unit $O_{3/2}SiOSi(CH_3)_2CH_2CH_2Si(CH_3)_2C_6H_4O_{1/2}$. However, the OMM has a more ordered structure than is suggested by this formula because the synthesis is begun with a polyreactive oligomer of known structure.

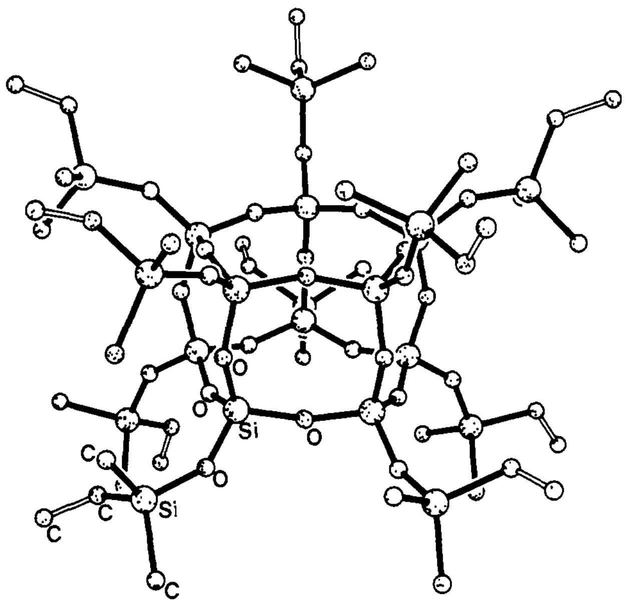

Figure 1. Ball-and-stick representation of the structure of $[Si_{20}O_{25}](Si(CH_3)_2(CHCH_2))_{10}$.

This material can be expected to be microporous because "geometric factors limit the density with which corner-linked "polyhedra" can fill space".[5] This principle has been the basis on which several approaches have been made to the synthesis of purely inorganic,[5] purely organic,[6] and also organometallic[7] microporous materials.

The synthesis of the OMM begins with a hydridospherosiloxane, $H_{10}Si_{10}O_{15}$ (**1**), which is obtained from a mixture of $(HSiO_{1.5})_n$ species prepared by a scarce-water hydrolysis of $HSiCl_3$[8,9] and can be converted to a vinyl-functionalized spherosilicate, $[Si_{10}O_{25}](Si(CH_3)_2(CHCH_2))_{10}$ (**2**), whose structure is shown in Figure 1. This conversion of **1** to **2** is effected by using the reagent $(CH_3)_3NO \cdot ClSi(CH_3)_2(CHCH_2)$.[10]

Compound **2**, which is a polyreactive oligomer, is then allowed to react with a stoichiometric amount of the bifunctional compound $(HSi(CH_3)_2C_6H_4O_{0.5})_2$ (**3**) in the presence of a catalyst, $PtCl_2(C_6H_5CN)_2$.[11] The long rigid central portion of **3** increases the likelihood that the two terminal $\equiv SiH$ groups will react with the $\equiv SiCH{=}CH_2$ groups on separate spherosilicate cores.[12] The resultant solid is a hard, clear, resilient, thermally stable[13] material that absorbs >50% by weight of tetrahydrofuran (THF). ^{13}C CP/MAS and ^{29}Si CP/MAS spectra of the solvent-swollen solid[14]

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(11) $PtCl_2(C_6H_5CN)_2$ was used as a solution in THF (250 μg of Pt/mL). Typical reaction procedure is as follows: **2** (0.204 g) + **3** (0.2 mL) + catalyst solution (0.25 mL); reaction time 2 days, under N_2; solvent allowed to evaporate slowly and the large chunks of solid material washed with several milliliters of THF.

(12) Two adjacent vertices of a spherosilicate unit cannot be cross-linked because they are too close to each other. Alternate pairs of vertices could be cross-linked but steric interference of bulky $\equiv Si(CH_3)_2(CHCH_2)$ substituents on intervening vertices makes this unlikely.

(13) Density (Hg displacement, 1 atm of pressure) 1.01 g/mL. TGA measurements (30-800 °C, 20 °C/min) show a 5% loss in weight by 110 °C (solvent desorption) and then no change in weight till the temperature reaches 350 °C.

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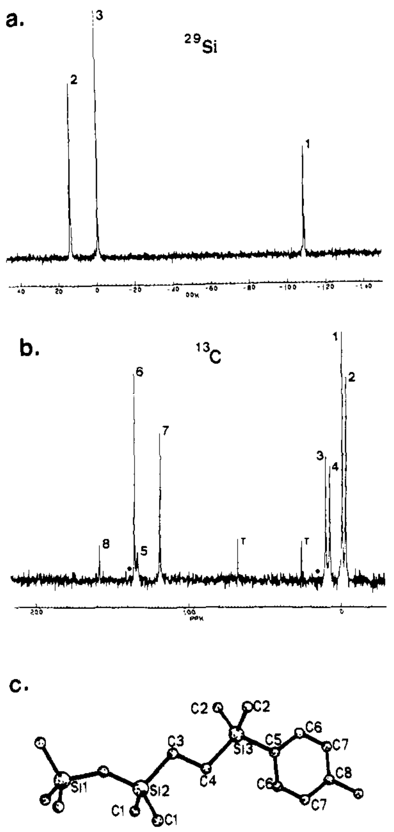

Figure 2. (a) ^{29}Si CP/MAS 59.6-MHz NMR spectrum of the OMM. (b) ^{13}C CP/MAS 75.5-MHz NMR spectrum of the OMM. The peaks labeled T are assigned to tetrahydrofuran. The stars are directly over the positions of the missing peaks mentioned in notes 15 and 17. (c) Ball-and-stick drawing of the repeating unit of this OMM. The atom numbers correspond to peak numbers in a and b. Unlabeled atoms are oxygen atoms.

indicate that the cross-linking reaction has gone almost to completion[15] and the spherosilicate cores have retained their structural integrity.[16] The addition of the $\equiv$SiH groups in **3** across the $\equiv$SiCH=CH$_2$ groups in **2** seems to have exclusively generated $\equiv$SiCH$_2$CH$_2$Si$\equiv$linkages.[17] These two spectra are shown in parts a and b of Figure 2, respectively. They seem to suggest that the OMM is crystalline; however, XRD traces show that it is amorphous.

The ^{13}C CP/MAS NMR spectrum of the OMM recorded at room temperature after most of the THF has evaporated shows only broad resonances, but at 100 °C the ones assigned to the methyl and methylene carbons are considerably narrower. This behavior is consistent with the fact that the material is not microporous, which was determined experimentally by low-temperature argon adsorption measurements.[18] This result could be explained as being due to the interpenetration of two or more porous networks, as is observed in crystalline adamantane-1,3,5,7-tetracarboxylic acid.[19]

We are currently engaged in a search for a way to control the secondary structure of the OMM by the use of templating additives and by varying the structure of the cross-linking groups, so that the potential of permanent microporosity is realized.

Acknowledgment. This work was supported by the Department of Chemistry at Virginia Polytechnic Institute and State University.

Supplementary Material Available: Spectral and analytical data for **2** and IR and NMR spectra, TGA thermograms, and Ar adsorption isotherm of the OMM (16 pages). Ordering information is given on any current masthead page.

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(14) ^{13}C CP/MAS (external standard = glycine; 75.5 MHz) δ -3.4^2, -1.0^1, 7.1^4, 9.8^3, 25.6^T, 67.4^T, 118.4^7, 133.1^5, 135.2^6, 158.0^8. ^{29}Si CP/MAS (external standard = M$_8$Q$_8$, 59.6 MHz) δ -109.1^1, -0.9^3, 13.5^2. Superscripts on chemical shift values refer to peak identifiers in Figure 2.

(15) >95% based on absence of a peak at ca. 138 ppm from unreacted $\equiv$SiCH=CH$_2$ groups.

(16) Only one sharp line can be seen in the Q^4 region.

(17) The alternative mode of addition generates a $\equiv$SiCH(CH$_3$)Si$\equiv$ linkage. The CH$_3$ carbon in this group should appear in the 10–15 ppm region of the ^{13}C NMR spectrum.

(18) Ar adsorption at 87 K, total uptake 0.0033 mL/g. Measurements were made on an Omnisorb 100 dynamic flow adsorption apparatus.

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Quinone-Functionalized Liposomes. Biomimetic Assemblies from a Phosphatidylcholine Anthraquinone

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Respiratory energy transduction involves the transport of electrons and protons across the inner mitochondrial membrane by the lipophilic molecule ubiquinone.[1] Questions concerning the motion and mode of action of ubiquinone[2] within this phospholipid bilayer membrane have prompted us to initiate a study of the redox and transport properties of quinone-functionalized liposomes (vesicles).[3-5] We report herein that we have synthesized the first agent necessary to prepare these biomembrane models. DPPC-AQ, an anthraquinone-containing dipalmitoylphosphatidylcholine (DPPC), is the first example of a quinone-functionalized phospholipid. Quinone-functionalized liposomes can be prepared by sonic dispersion of mixtures of DPPC-AQ and simple phospholipids (e.g., DPPC). Spectrophotometric titrations and kinetics experiments indicate that the DPPC-AQ amphiphiles can be reduced upon addition of external, aqueous S$_2$O$_4^{2-}$ or BH$_4^-$.

DPPC-AQ was prepared from L-α-dipalmitoylphosphatidyl-*N*,*N*-dimethylethanolamine (DPP–DMEA)[6] and 2-(bromomethyl)anthraquinone[7] as shown in Scheme I. After 16 h at 60 °C the reaction mixture was filtered and separated by flash chromatography on SiO$_2$ with CHCl$_3$/MeOH/H$_2$O (79:20:1, then 65:25:4) as the eluent. Extraction of a CHCl$_3$ solution of the phospholipid with aqueous EDTA to remove metal ions and precipitation with cold acetone[8] yielded pure material in 40–50% yield. The 300 MHz ^{1}H NMR spectrum of DPPC–AQ in CDCl$_3$ (Figure 1) reveals the expected aromatic resonances from 7.3 to 8.4 ppm, the glycerol and choline resonances between 3.4 and 5.2 ppm, and the acyl chain resonances from 0.8 to 2.2 ppm.

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