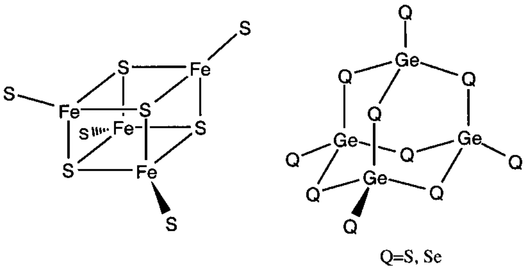
Supramolecular Assembly of Hexagonal Mesostructured Germanium Sulfide and Selenide Nanocomposites Incorporating the Biologically Relevant Fe_4S_4 Cluster[**]

Pantelis N. Trikalitis, Thomas Bakas,
Vasilios Papaefthymiou, and Mercouri G. Kanatzidis*

The design and construction of open-framework materials with mesoscale characteristics (20–200 Å) has been profoundly influenced by the use of organized surfactant assemblies as templating media.[1] Whereas the overwhelming majority of systems are oxides, only a few reports exist that describe nonoxidic mesostructured nanocomposites[2–4] which are now attracting great interest.[5–7] Recently, we[3, 8] and others[4, 9] demonstrated that nonoxidic mesostructured networks form by the binding of divalent metal ions with tetrahedral $[Ge_4Q_{10}]^{4-}$ (Q = S, Se) clusters in the presence of appropriate surfactants. These clusters (see Scheme 1) bind metal ions in tetrahedral arrangements that can give rise to diamondoid frameworks. On the other hand the functional implications of solid-state materials with biological attributes are not yet explored, but they are many and far-reaching. In this context the introduction of metallo-bioinorganic active sites to nonbiological inorganic matrices has not been previously described. Fe/S clusters are exceptional and ubiquitous in biological systems as they provide a major part of the foundation for electron transfer, catalytic, and enzymatic processes in living organisms.[10, 11] These clusters are some of the most studied entities in chemistry and biology. They can be readily synthesized as pure discrete species in high yield.[12, 13] Many proteins such as ferredoxins and hydrogenases contain Fe/S clusters and exploit their redox properties. Arguably, the cubane geometry is the most pervasive structural arrangement in biological cluster chemistry, and consists of a core of four iron and four sulfur atoms distributed over alternating vertices of a cube (see Scheme 1). Thus, it would be interesting to incorporate it as a functional unit into materials.



Scheme 1.

Here we report a rational approach, using the supramolecular assembly of adamantane $[Ge_4Q_{10}]^{4-}$ (Q = S, Se) clusters with substitutionally labile $[Fe_4S_4Cl_4]^{2-}$ clusters templated by cationic surfactant molecules to produce novel hexagonal mesophases built with the biologically relevant $[Fe_4S_4]$ core (Fe4S4-MSU-1 for $[Ge_4S_{10}]^{4-}$) and (Fe4S4-MSU-2 for $[Ge_4Se_{10}]^{4-}$). The preferred coordination geometry of the $[Fe_4S_4]$ core is tetrahedral and is well suited to form three-dimensional frameworks when combined with other linking anions which also prefer tetrahedral binding, for example the $[Ge_4Q_{10}]^{4-}$ (Q = S, Se) clusters. These structures have parallel pore tunnels with separations of ~35 Å and could provide the architectural and conceptual framework for exploring and understanding a new class of materials at the interface of materials science and bioinorganic chemistry. The inclusion of well-studied protein active sites in extended solid-state frameworks represents an important step towards achieving useful and functional interfaces between biological and materials chemistry.

Supramolecular assembly of adamantane $[Ge_4S_{10}]^{4-}$ and $[Ge_4Se_{10}]^{4-}$ clusters, in a nonaqueous medium, with substitutionally labile $[Fe_4S_4Cl_4]^{2-}$ clusters[14, 15] in the presence of a cationic surfactant resulted in the formation of novel mesophases containing $[Fe_4S_4]^{2+}$ cores. Metathesis reactions between $[Ge_4S_{10}]^{4-}$ or $[Ge_4Se_{10}]^{4-}$ and $[Fe_4S_4Cl_4]^{2-}$ in the presence of cetylpyridinium (CP) bromide, in formamide/dimethylformamide (DMF) mixtures gave ordered hexagonal mesostructured CP-$[Fe_4S_4]/(Ge_4S_{10})$ and CP-$[Fe_4S_4]/(Ge_4Se_{10})$ materials. These materials, referred to as Fe4S4-MSU-1 and Fe4S4-MSU-2, respectively, are dark brown and have a reproducible and consistent composition. The samples were analyzed with energy-dispersive spectroscopy (EDS) in a scanning electron microscope and showed only Fe, S, Ge, and Se (Figure 1 a). Combined with C, H, N analyses we obtain the empirical formulae $(CP)_3Fe_4S_4Ge_4S_{10+\delta}$ for Fe4S4-MSU-1 and $(CP)_{3.4}Fe_4S_4Ge_4Se_{10+\delta}$ for Fe4S4-MSU-2.[16]

The mesostructured nature of Fe4S4-MSU-1 and Fe4S4-MSU-2 is evident in the powder X-ray diffraction patterns that show strong diffraction peaks at very low scattering angles (Figure 1 b). These are analogous to those of the hexagonal mesoporous silica phases.[17] We index the three reflections for Fe4S4-MSU-1 at 34.2, 19.5, and 17.3 Å as (100), (110), and (200), respectively, with a hexagonal lattice parameter of $a_H = 39.5$ Å. The corresponding values for Fe4S4-MSU-2 are 34.9, 20.6, and 18.5 Å with $a_H = 40.3$ Å. As with the conventional mesostructured oxides,[18] we do not observe Bragg diffraction peaks at wide angles, suggesting that the inorganic walls of Fe4S4-MSU-1 and Fe4S4-MSU-2 lack long-range order. Nevertheless, these materials exhibit well-defined diffuse scattering at $2\theta > 10°$ consistent with the presence of short-range local order in the wall structure.

Thermal gravimetric analyses (TGA) of Fe4S4-MSU-X materials show that they lose all their surfactant molecules between 200 and 500 °C (Figure 1 c). The first weight loss step occurs at ~250 °C which corresponds to the removal of the pyridine head group (identified by mass spectrometry). This is

---

[*] Prof. M. G. Kanatzidis, Dr. P. N. Trikalitis
Department of Chemistry, Michigan State University
East Lansing, MI 48824-1322 (USA)
Fax: (+1) 517-353-1793
E-mail: kanatzid@cem.msu.edu

Dr. T. Bakas, Prof. V. Papaefthymiou
Department of Physics
University of Ioannina (Greece)

[**] Financial support from the National Science Foundation (CHE 99-03706, Chemistry Research Group) is gratefully acknowledged. Part of this work was carried out using the facilities of the Center for Electron Optics of Michigan State University.

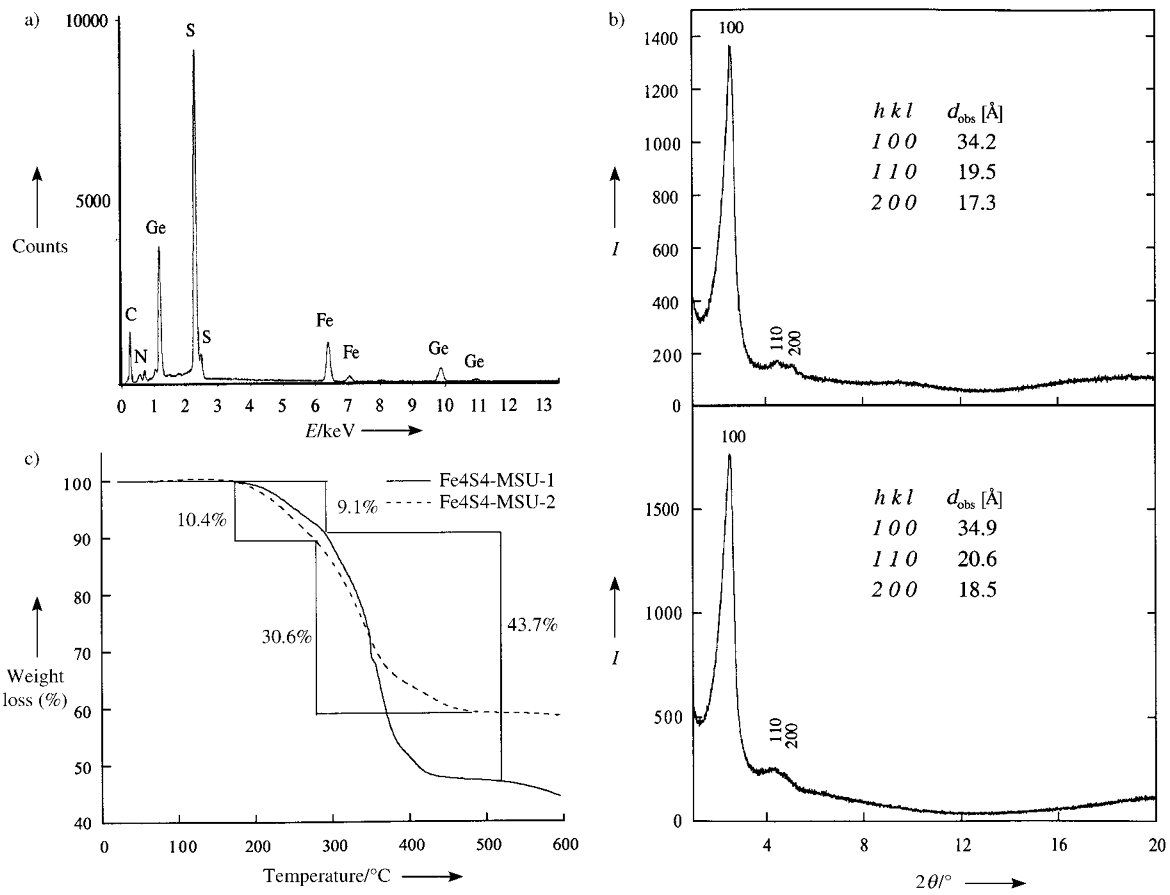


Figure 1. a) Typical energy-dispersive X-ray fluorescence spectrum showing the presence of C, N, Fe, Ge, and S elements in Fe4S4-MSU-1. The absence of elements associated with the counterions of the starting reagents (e. g. Br, Cl, and P of Ph_4P^+) is evident. b) X-ray scattering ($Cu_{K\alpha}$ radiation) from Fe4S4-MSU-1 (top) and Fe4S4-MSU-2 (bottom). Peaks are indexed to a hexagonal cell. I = intensity. c) Corresponding thermal gravimetric analysis (TGA) data. Experiments were performed under nitrogen flow with a heating rate of 10 deg min^{-1}.

followed by a second step from 250 to 500 °C, which is associated with the loss of the long hydrocarbon chain. The weight loss values are in good agreement with the elemental C, H, N analyses. At 500 °C the materials decompose to amorphous GeS_2 and FeS_x.

High-resolution transmission electron micrographs (HRTEM) of Fe4S4-MSU-1 and Fe4S4-MSU-2 reveal a strikingly regular hexagonal organization of the inorganic framework pores (Figure 2), which resemble those obtained for hexagonal mesoporous oxides (MCM-41)[17] and cetyltrimethylammonium (CTA)/$M_2Ge_4S_{10}$.[9] Overall, the samples appear homogeneous. The dimensions of the channels and the presence of hexagonal order are consistent with the X-ray diffraction results. The width of the channels in Figure 2 is roughly 24–26 Å. The hexagonal domains are very large (> 400 nm) in both Fe4S4-MSU-1/2 and often span the length of entire particles.

The existence of the $[Fe_4S_4]$ core in these mesostructures was confirmed with Mössbauer spectroscopy. The Mössbauer spectrum of Fe4S4-MSU-1 at 85 K (Figure 3 a) shows two closely spaced quadrupole doublets (equal areas) with an isomer shift δ of 0.47 and 0.45 mm s^{-1} and a quadrupole splitting ΔE_q of 1.14 and 0.84 mm s^{-1}, respectively. The parameters for Fe4S4-MSU-2 are $\delta = 0.50/0.47$ mm s^{-1} and $\Delta E_q = 0.66/1.14$ mm s^{-1}, respectively. These are typical values for $[Fe_4S_4]^{2+}$ cores in asymmetric environments both in ferredoxins[19, 20] and synthetic model compounds.[21, 22]

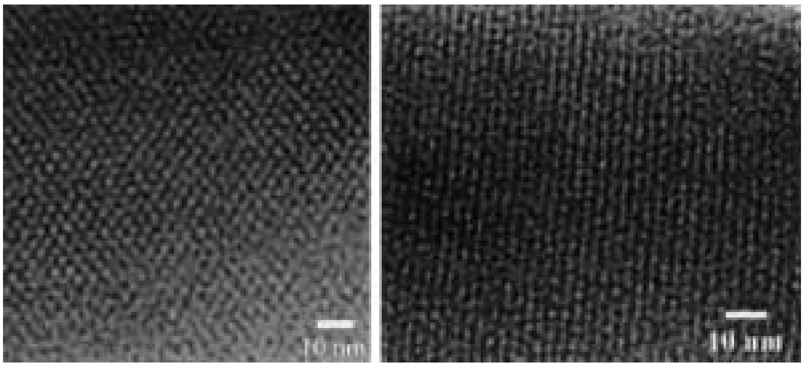


Figure 2. TEM images of Fe4S4-MSU-1; view down the tunnels (left; [001] direction) and view perpendicular to the tunnel axis (right; [100] direction), showing the parallel organization and straight character of the tunnels. TEM samples were prepared by suspending the precipitate in diethyl ether, then casting on a holey carbon grid. High-resolution transmission electron micrographs were acquired with a JEOL 120CX instrument equipped with a CeB_6 filament.

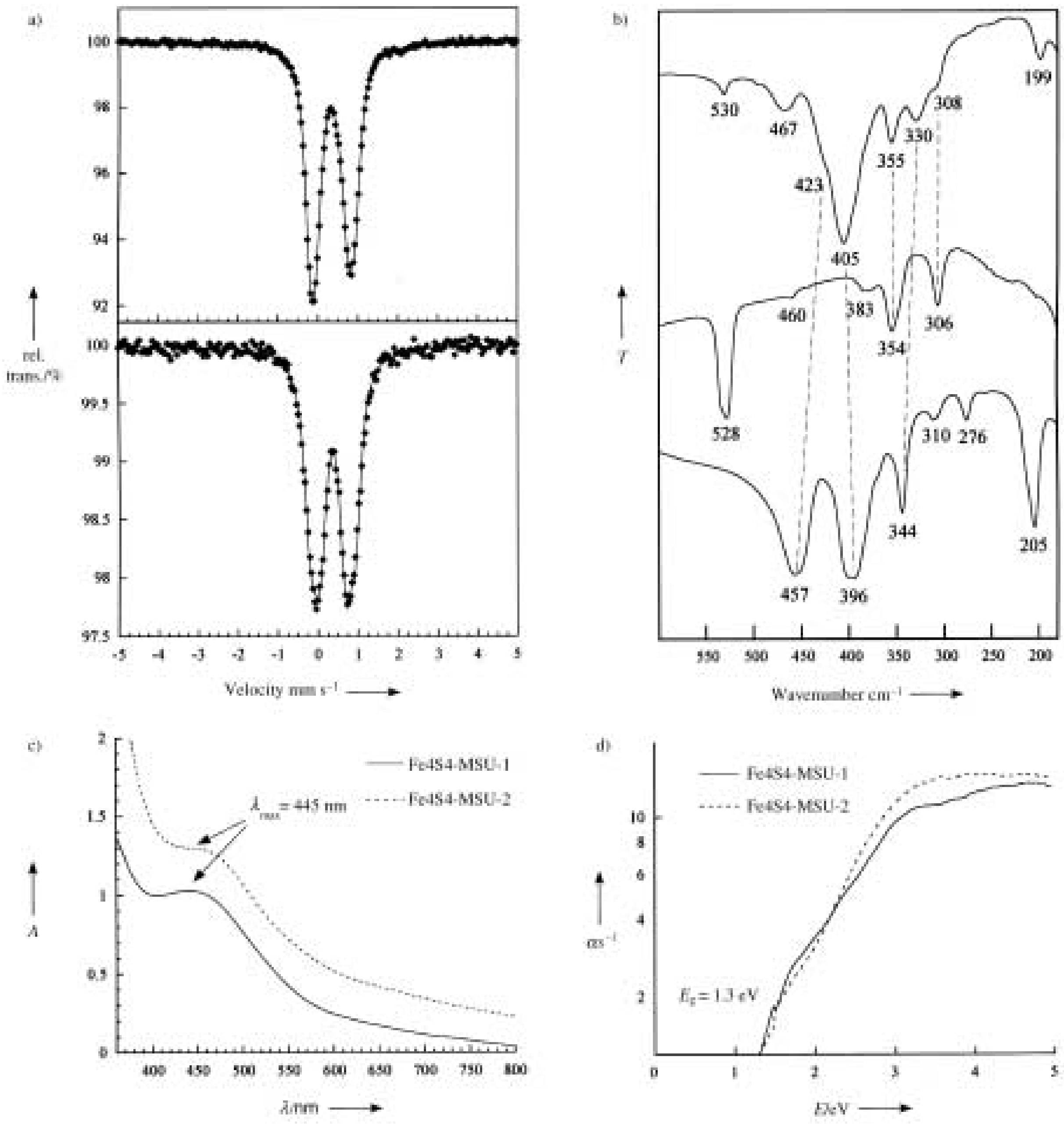


Figure 3. a) ^{57}Fe Mössbauer spectra of Fe4S4-MSU-1 (top) and Fe4S4-MSU-2 (bottom) at 85 K. The solid lines are least-squares fits for the δ and ΔE_q parameters quoted in the text. rel. trans. = relative transmission. b) Infrared spectra of Fe4S4-MSU-1 (top), $(Ph_4P)_2Fe_4S_4Cl_4$ (center; the strong peak at 528 cm^{-1} is from the Ph_4P^+ cation), and $(Me_4N)_4Ge_4S_{10}$ (bottom). The spectra were taken as pressed CsI pellets. T = transmittance. c) UV/Vis spectrum in DMF of the $[Fe_4S_4(SPh)_4]^{2-}$ cluster extracted from Fe4S4-MSU-1 and Fe4S4-MSU-2 upon reaction with excess PhS$^-$ or PhSH showing the characteristic λ_{max} at ~445 nm (13, 20). A = absorbance. d) Typical electronic absorption spectra of Fe4S4-MSU-1 and Fe4S4-MSU-2. E = energy.

The far-IR spectrum of Fe4S4-MSU-1 shows characteristic bands at 467 (m), 423 (m,sh), 405 (vs), 355 (s), 330 (m), 308 (m), and 199(m) cm^{-1}, respectively (Figure 3b). Those at 467, 423, 405, 330, and 199 cm^{-1} correspond to the modes of the adamantane $[Ge_4S_{10}]^{4-}$ cluster, whereas those at 355 and 308 cm^{-1} are due to the internal modes of the Fe_4S_4 cluster. The terminal Ge–S stretching modes in the free $[Ge_4S_{10}]^{4-}$ occurring at 457 and 344 cm^{-1} (Figure 3b top) shift to lower frequencies at 423 and 330 cm^{-1} in Fe4S4-MSU-1 due to Fe ligation. The strong peak at 396 cm^{-1} in the free $[Ge_4S_{10}]^{4-}$ is due to modes internal to the Ge_4S_6 core and is not significantly affected; it occurs at 405 cm^{-1} in Fe4S4-MSU-1. Fe4S4-MSU-2 shows bands at 386 (m), 352 (vs), 321 (m, sh), 307 (vs), 284 (s), 255 (w), 227 (w), and 202 (w) cm^{-1}, respectively. The bands at 321, 284, originate from the $[Ge_4Se_{10}]^{4-}$ cluster,[23] whereas those at 352 and 307 cm^{-1} are due to Fe_4S_4 cluster.

The presence of Fe_4S_4 clusters in these materials was independently determined by the excision method used to identify them in proteins.[24, 25] This involves cluster extraction from the protein by ligand exchange with excess thiol (e.g. PhSH). When Fe4S4-MSU-1 and Fe4S4-MSU-2 were treated with excess PhSH (or PhS$^-$; 4–8 equiv) in DMF they dissolved promptly, indicating ligation and subsequent excision of the $[Fe_4S_4]^{2+}$ core from the framework according to

0044-8249/00/11224-4734 $ 17.50+.50/0

Equation (1). The brown solution obtained displayed a UV/Vis spectrum with an absorption maximum at 445 nm (Figure 3c). This is characteristic of the presence of the molecular $[Fe_4S_4(SPh)_4]^{2-}$ cluster.[15, 26] The latter species was also identified by its NMR spectrum from the characteristic *ortho*-, *meta*-, and *para*-H resonances of the SPh ligands which occur at $\delta = 5.84$, 8.25, and 5.15, respectively.[27]

$$(C_{16}H_{33}Py)/(Fe_4S_4)/(Ge_4Q_{10}) + 4\,KSPh \longrightarrow [Fe_4S_4(SPh)_4]^{2-} + C_{16}H_{33}Py^{+} + 4\,K^{+} + [Ge_4Q_{10}]^{4-} \quad (1)$$

The optical absorption properties of these materials suggest that they are medium band-gap semiconductors. The electronic spectra show clearly defined energy gaps at 1.3 eV for both Fe4S4-MSU-1 and Fe4S4-MSU-2 (see Figure 3d). These gaps are in the same range as those of many important semiconductors such as GaAs (1.54 eV) and CdTe (1.45 eV).

The construction of mesostructured chalcogenide phases that embody the biological Fe_4S_4 center has been demonstrated by using a templated assembly process. Based on the above results we surmise that the inorganic frameworks (Figure 4) of Fe4S4-MSU-1 and Fe4S4-MSU-2 resemble those of MCM-41 and $CTA/M_2Ge_4S_{10}$. The approach described here clearly points to a pathway for generating stable hybrid systems with combined biological and abiological characteristics. Such hybrid structures may find applications in shape-selective electro- and photocatalysis, artificial photosynthesis, and biosensors, particularly those based on enzymatic processes related to Fe_4S_4 centers.[28] As part of a rigid framework, Fe_4S_4 clusters are expected to be stable in more reactive oxidation states, for example $[Fe_4S_4]^{1+/3+}$. These states are readily found in proteins but are difficult to stabilize in molecules in solution. The combination of elegant, naturally refined catalytic sites with the robustness and diversity of extended solid-state systems could engender a new class of biologically inspired materials with unique or multiple functionality. Particularly intriguing, for example, would be materials incorporating the $MoFe_7S_9$-cofactor[29] of nitrogenase, an important nitrogen-fixing enzyme, that may be rendered capable of similar activity.

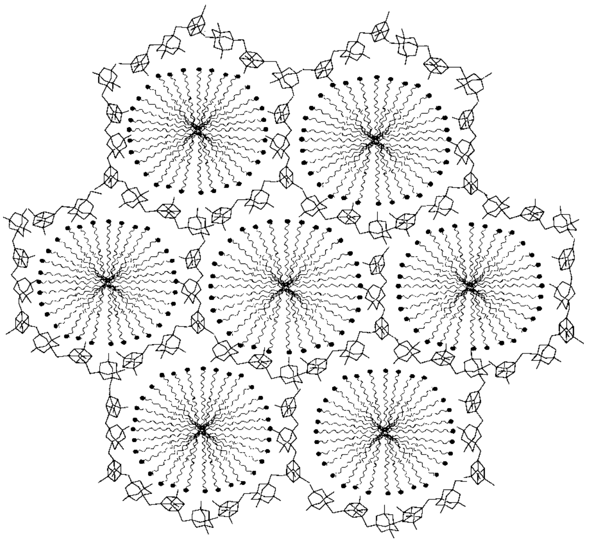


Figure 4. Schematic representation of the constituents of the hexagonal framework in which Fe_4S_4 cores are linked with $[Ge_4Q_{10}]^{4-}$ clusters around the surfactant counterions.

Experimental Section

Methods: ^{57}Fe Mössbauer spectra were obtained at 85 K. A constant acceleration spectrometer was used to move a ^{57}Co (Rh) source kept at 300 K. The spectrometer was calibrated with α-Fe, and isomer shift values are given relative to α-Fe at 300 K. Optical absorption spectra were obtained at ~300 K with a Shimadzu UV-3101PC double beam, double monochromator spectrophotometer equipped with an integrating sphere. For details see T. J. McCarthy, S.-P. Ngeyi, J.-H. Liao, D. DeGroot, T. Hogan, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **1993**, *5*, 331–340.

Typical synthetic procedure: Fe4S4-MSU-1: Cetylpyridinium bromide monohydrate (4.00 g, 10 mmol) and $K_4Ge_4S_{10}$ (0.767 g, 1 mmol) were dissolved in formamide (20 mL) at 75 °C to form a colorless solution. To this $(Ph_4P)_2Fe_4S_4Cl_4$ (0.883 g, 1 mmol) dissolved in DMF (10 mL) was added dropwise under stirring over a period of 2 min. The deep brown precipitate formed immediately and was aged for 24 h. It was then filtered, washed with warm water, and dried under vacuum. Approximately 1.5 g of product was obtained (yield >80 % based on $K_4Ge_4S_{10}$). The procedure is similar in the case of Fe4S4-MSU.

Received: September 4, 2000 [Z15759]

---

[1] C. T. Kresge, M. E. Leonowicz, W. J. Roth, W. J. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.

[2] P. V. Braun, P. Osenar, S. I. Stupp, *Nature* **1996**, *380*, 325.

[3] K. K. Rangan, S. J. L. Billinge, V. Petkov, J. Heising, M. G. Kanatzidis, *Chem. Mater.* **1999**, *11*, 2629.

[4] M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *397*, 681.

[5] C. L. Bowes, G. A. Ozin, *Adv. Mater.* **1996**, *8*, 13.

[6] J. B. Parise, *Science* **1991**, *251*, 293.

[7] H. Ahari, R. L. Bedard, C. L. Bowes, T. Jiang, A. Lough, G. A. Ozin, S. Petrov, D. Young, *Adv. Mater.* **1995**, *7*, 375.

[8] M. Wachhold, K. K. Rangan, M. F. Thorpe, S. J. L. Billinge, V. Petkov, J. Heising, M. G. Kanatzidis, *J. Solid State Chem.* **2000**, *152*, 21; K. K. Rangan, P. Trikalitis, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2000**, *122*, 10230.

[9] M. J. MacLachlan, N. Coombs, R. L. Bedard, S. White, L. K. Thompson, G. A. Ozin, *J. Am. Chem. Soc.* **1999**, *121*, 12005.

[10] H. Beinert, R. H. Holm, E. Münck, *Science* **1997**, *277*, 653.

[11] H. Beinert, *J. Biol. Inorg. Chem.* **2000**, *5*, 2.

[12] R. H. Holm, P. Kennepohl, E. I. Solomon, *Chem. Rev.* **1996**, *96*, 2239, and references therein.

[13] M. G. Kanatzidis, N. C. Baenziger, D. Coucouvanis, A. Simopoulos, A. Kostikas, *J. Am. Chem. Soc.* **1984**, *106*, 4500.

[14] R. W. Johnson, R. H. Holm, *J. Am. Chem. Soc.* **1978**, *100*, 5338.

[15] D. Coucouvanis, M. G. Kanatzidis, E. Simhon, N. C. Baenziger, *J. Am. Chem. Soc.* **1982**, *104*, 1874.

[16] Fe4S4-MSU-1 (%): C 40.25, H 6.06, N 2.18; EDS analysis: Fe:Ge:S 0.9:1:4; Fe4S4-MSU-2 (%): C 33.72, H 5.51, N 1.85; EDS analysis: Fe:S:Ge:Se 0.8:0.9:1:2.5.

[17] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K.D. Schmitt, C. T.-W. Chu, D. H. Olsen, E. W. Shepard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834.

[18] T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli, O. M. Yaghi, *Chem. Mater.* **1999**, *11*, 2633.

[19] R. Cammack, D. P. E. Dickson, C. E. Johnson in *Iron–Sulfur Proteins, Vol. III* (Ed.: W. Lovenberg), Academic Press, New York, **1977**, p. 283.

[20] W. H. Orme-Johnson, N. R. Orme-Johnson in *Metal Ions in Biology, Vol. 4* (Ed.: T. G. Spiro), Wiley, New York, **1982**, p. 67.

[21] R. H. Holm, J. A. Ibers in *Iron–Sulfur Proteins, Vol. III* (Ed.: W. Lovenberg), Academic Press, New York, **1977**, p. 206.

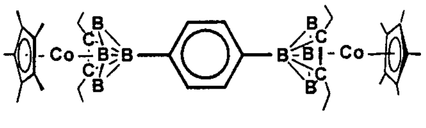
[22] V. Papaefthymiou, M. M. Millar, E. Münck, *Inorg. Chem.* **1986**, *25*, 3010.
[23] The $K_4Ge_4Se_{10}$ exhibits bands at 318 (vs), 282 (vs), 255 (s, sh), and 208 (w) cm^{-1}.
[24] L. Que, R. H. Holm, L. E. Mortenson, *J. Am. Chem. Soc.* **1975**, *97*, 463.
[25] W. O. Gillum, L. E. Mortenson, J.-S. Chen, R. H. Holm, *J. Am. Chem. Soc.* **1977**, *99*, 584.
[26] R. B. Frankel, T. Herskovitz, B. A. Averill, R. H. Holm, P. J. Krusic, W. D. Phillips, *Biochem. Biophys. Res. Commun.* **1974**, *58*, 974.
[27] R. H. Holm, W. D. Phillips, B. A. Averill, J. J. Mayerle, T. Herskovits, *J. Am. Chem. Soc.* **1974**, *96*, 2109.
[28] T. A. Rouault, R. D. Klausner, *Trends Biochem. Sci.* **1996**, *21*, 174.
[29] J. S. Kim, D. C. Rees, *Nature* **1992**, *360*, 553.

Benzene-Centered Tri- and Tetrametallacarborane Sandwich Complexes[**]

Martin Bluhm, Hans Pritzkow, Walter Siebert,[*] and Russell N. Grimes[*]

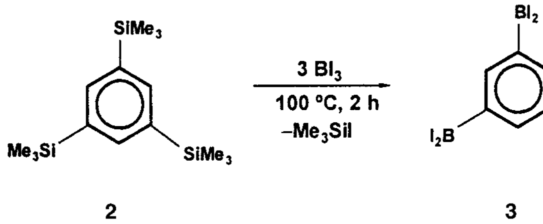
The special steric and electronic properties of polyhedral borane and carborane clusters—notably their three-dimensional geometry and electron delocalization (aromatic character)—are being employed to advantage in the construction of novel molecular architectures for use in a variety of projected applications in materials synthesis, microelectronics, optics, and medicine.[1] In recent work some remarkable compound types have been produced in which boron clusters serve as scaffolds or templates for attachment of organic moieties; examples include $(1,7\text{-}C_2B_{10}H_{10})_nHg_n$ "anti-crowns" ($n = 3$, 4),[1d, 2] peralkylated carboranes that mimic spherical hydrocarbons, [3] and benzene-*m*-carboranyl macrocycles.[4]

This paradigm can be reversed: Hydrocarbons may serve as frameworks for attachment of multiple boron clusters. If an aromatic system such as benzene is employed as a linchpin connecting several metallaboron units, one might prepare polynuclear, electron-delocalized, mixed-valence systems that are not only interesting from a fundamental perspective, but may also have practical potential as precursors or models for new kinds of electronically tailorable organometallic compounds. Although 1,3,5-tris(carboranyl)benzene derivatives incorporating icosahedral 1,2- or 1,12-C_2B_{10} polyhedra have been reported,[5] no corresponding metallaborane or metallacarborane species (i.e., having metal atoms in the polyhedral framework) have been described; to our knowledge, the closest known metal system is the dimetallic 1,4-bis(7-cobaltacarboranyl)benzene complex **1** (B = BH, B), which was recently prepared in one of our laboratories.[6] In contrast, a number of benzene-centered trinuclear organometallic compounds of the type $1,3,5\text{-}C_6H_3(XML_n)_3$ have been synthesized,[7] in which transition metals M are linked to benzene through groups X (e.g. alkynyl). Here we report the designed synthesis of the first metallacarborane systems of this class.



1

The approach utilized boron-recapping ("recapitation") of *nido*-$[1,2,3\text{-}Cp^*Co(2,3\text{-}Et_2C_2B_3H_3)]^{2-}$ ($Cp^* = C_5Me_5$), a method recently developed in our groups for preparing mono- or dimetallic species bearing substituents at the apex [B(7)] boron atom.[6, 8] In the present work, we required a suitable trifunctional benzene derivative as a precursor to the desired metal complexes. Accordingly, 1,3,5-tris(diiodoboryl)benzene (**3**), previously prepared but not isolated,[9] was generated from the corresponding tris(trimethylsilyl)benzene as shown in Scheme 1 and isolated in 30% yield as a colorless, air-sensitive solid. Treatment of $Li_2[Cp^*Co(2,3\text{-}Et_2C_2B_3H_3)]$ (**4**) with one-third molar equivalent of **3** in toluene at 0 °C gave the target compound $[\{Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7)\}_3C_6H_3]$ (**5**) as a moderately air-stable yellow complex in 46% yield (Scheme 2).



Scheme 1. Synthesis of **3**.

Characterization of **5** by multinuclear NMR and IR spectroscopy as well as mass spectrometry supports the trigonally symmetric geometry shown (the rotamer depicted is arbitrary), and the solid-state structure has been confirmed by X-ray crystallography (Figure 1).[10] With the exception of the benzene ring (see the figure caption), the bond lengths and angles are normal, and the metal atoms and apical boron atoms are coplanar with the benzene ring. A notable feature of the ^1H NMR spectrum of **5** is the strong upfield shift of the aromatic benzene resonances ($\delta = 5.92$ in $CDCl_3$ versus 7.51 for benzene itself), reflecting the electron-donating character of the carborane ligand (for comparison, the corresponding

---

[*] Prof. Dr. R. N. Grimes, Dr. M. Bluhm
Department of Chemistry
University of Virginia
Charlottesville, VA 22901 (USA)
Fax: (+1) 804-924-3710
E-mail: rng@virginia.edu
Prof. Dr. W. Siebert, Dr. H. Pritzkow
Anorganisch-chemisches Insititut der Universität
Im Neuenheimer Feld 276
69120 Heidelberg (Germany)
Fax: (+49) 6221-54-5609
E-mail: ci5@ix.urz.uni-heidelberg.de

[**] Organotransition-Metal Metallacarboranes, part 56. This work was supported in part by the National Science Foundation (grant CHE 9980708 to R.N.G.) and the Deutsche Forschungsgemeinschaft (SFB 247, to W.S. for M.B.). Part 55: T. Dodge, M. A. Curtis, J. M. Russell, M. Sabat, M. G. Finn, R. N. Grimes, *J. Am. Chem. Soc.* **2000**, *122*, 10573.