the p† orbitals of thiolate sulfur with the $a_{2u}(\pi)$ orbital of the ferrous porphyrin that is believed to cause the unique spectral characteristics of the CO-ligated adduct.[25] The shortening of the Fe–S_{ax} bond upon deprotonation of the ligated thiol can also be explained by electrostatic considerations.

The other hexacoordinate complexes, FeOEP(THT)(CO) and FeOEP(MeSSMe)(CO), serve as models for methionine and cystine axial ligation in heme proteins and are structurally characterized for the first time herein. The structural properties of both complexes are similar to those of FeOEP(PrSH)(CO) and distinct from those of FeOEP(SPr)(CO)$^-$. Also, only one of the structurally equivalent sulfur atoms in the disulfide-containing complex was found to be bound to the iron. These observations are not altogether unexpected since the sulfur atoms in PrSH, THT, and MeSSMe are all uncharged, are presumably sp^3-hybridized, and are poor π-donors; thus, their bonding to FeOEP(CO) should be similar. The Fe–S_{ax} distance in the THT-ligated ferrous porphyrin with CO as the trans ligand is somewhat longer than those of the analogous complexes in which imidazole (2.31 Å)[8] and THT (2.336 Å)[8] are trans. This can be explained by the greater interaction of the d_π orbitals of the iron with CO (π-acceptor) than with either imidazole or THT (σ-donors), thus reducing the electron density in the iron-to-trans ligand bond. A similar lengthening of the Fe–L_{ax} bond trans to a π-acceptor has been noted upon replacement of 1-methylimidazole[26] with O_2[24] in Fe(porphyrin)(1-methylimidazole)(L) and piperidine[27] for NO[28] in Fe(porphyrin)(piperidine)(L) complexes.[29]

These results suggest the existence of two distinct structural categories for sulfur-donor-ligated, hexacoordinate Fe(porphyrin)(RSY)(CO) complexes (R is an alkyl moiety). When the Y group is H, R, or SR (thiol-like), the ligated sulfur is present as an uncharged σ-donor ligand, resulting in a Fe–S_{ax} distance of 2.40 Å or greater. When the Y group is absent (thiolate), the ligated sulfur is present as an anionic π-donor ligand that is able to more extensively interact with the molecular orbitals of the iron, causing a Fe–S_{ax} bond length contraction to ~2.33 Å. These results are of particular importance in the structural analysis of sulfur-donor-ligated heme proteins. In the past, it was not possible to use EXAFS to distinguish the kind of sulfur ligand bound to ferrous iron, only its distance and number. With the present findings, assignment of the nature of the axial ligand trans to CO as being either thiolate or thiol-like can be made with greater certainty. In the case of the CO adduct of P-450, axial ligation by a sulfur donor other than cysteinate can be completely ruled out on the basis of its Fe–S_{ax} distance, thus confirming the previous conclusion from spectral data.[11] Identification of the sulfur donor in heme proteins such as cytochrome c_1[31] and hemoprotein H-450,[32] which have been proposed to contain sulfur donor axial ligands, should now be possible on the basis of EXAFS measurements of their ferrous–CO adducts.[33] Inspection of the data for ferrous–O_2 complexes[7,9] (Table I) reveals a similar difference of ~0.1 Å in the Fe–S_{ax} bond distance for thiolate and non-thiolate (thioether) sulfur donors.[34]

In summary, the length of the Fe–S_{ax} bond trans to CO in hexacoordinate Fe^{2+}OEP(CO)(sulfur donor) complexes has been found to fall into two distinct groups (2.33 and 2.40–2.41 Å) depending on the nature of the sulfur donor (thiolate and non-thiolate, respectively). The Fe(II)–S_{ax} distances in the thiol-, thioether-, and disulfide-ligated ferrous–CO complexes (models for cysteine, methionine, and cystine ligation, respectively) are significantly longer (up to 0.10 Å) than those in other sulfur-donor-containing ferrous porphyrin complexes, with the exception of a thioether/O_2 ferrous porphyrin;[9] the Fe(II)–S bond length depends on either the protonation state (thiolate vs. thiol-like) of the sulfur donor or the trans axial ligand (CO or O_2 vs. imidazole and thioether). These results substantially expand the database of Fe(II)–S_{ax} bond lengths in ferrous porphyrin complexes. Identification of sulfur donor ligands as either thiolate or non-thiolate in ferrous-CO heme protein complexes using Fe(II)–S_{ax} distances determined from EXAFS analysis can now be accomplished with greater certainty.

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Registry No. FeOEP(SPr)$^-$, 104241-88-5; FeTPP(SEt)$^-$, 72344-95-7; FeOEP(SPr)(CO)$^-$, 104241-89-6; FeTPP(SEt)(CO)$^-$, 104241-90-9; FeTpivPP(SC_6HF_4)(O_2)$^-$, 86124-04-1; FeOEP(PrSH)(CO), 104241-91-0; FeOEP(THT)(O_2), 104241-92-1; FeTpivPP(THT)(O_2), 59041-09-7; FeOEP(MeSSMe)(CO), 104241-93-2; FeTPP(THT)$_2$, 70948-65-1; FeTPP(C5Im)(THT), 70948-63-9; Fe, 7439-89-6; S, 7704-34-9.

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(33) The complexes studied herein are structurally unconstrained. Assuming that the strain on axial bond lengths in heme proteins is less than 0.04 Å (see ref 24b), the proposed distinction of sulfur donor types based on EXAFS measurements should be feasible.

(34) Note added in proof: The ferrous–dioxygen adducts of cytochrome P-450-CAM and of chloroperoxidase have been structurally characterized for the first time by using EXAFS spectroscopy (Dawson, J. H.; Kau, L.-S.; Penner-Hahn, J. E.; Sono, M.; Eble, K. S.; Bruce, G. B.; Hager, L. P.; Hodgson, K. O. *J. Am. Chem. Soc.*, in press). Both contain an axial sulfur atom trans to dioxygen with an Fe–S bond length of 2.37 Å and have Fe–N_p bond distances of 2.00 Å; these values are extremely similar to those reported by Weiss and co-workers for a thiolate/O_2-ligated ferrous heme model complex (Table I).

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1,12-Bis(hydroxymethyl)decahydrododecaborate(2–) and $B_{12}H_{10}(CH_2X)_2^{2-}$ and $B_{12}H_{10}(CH_2L)_2$ Derivatives

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Carbonyl-substituted closo polyhedral boranes with B_{10} and B_{12} cages are important classes of derivatives capable of transformation to cyanide, amide, keto, ester, amine, etc. functions.[1] Only the perchloro B_{10} dicarbonyl, however, has been reduced to the hy-

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Table I. Analyses and Infrared Data for $B_{12}H_{10}(CH_2X)_2$ Derivatives

	anal.								
	% C		% H		% N		% other		
compd	calcd	found	calcd	found	calcd	found	calcd	found	infrared data,[a] cm^{-1}
$Cs_2B_{12}H_{10}(CH_2OH)_2$	5.1	5.9	3.4	3.6			27.7 (B)	26.2 (B)	3580 s, 2530 sh, 2510 s, 2490 s, 2465 s, 2450 s, 1370 sh, 1360 m, 1260 m, 1190 m, 1075 w, 1055 w, 1020 w, 940 s, 920 m, 750 w, 740 w
$Cs_2B_{12}H_{10}(CH_2I)_2$	3.5	3.5	2.0	2.0			18.9 (B) 36.9 (I)	16.1 (B) 37.8 (I)	2510 sh, 2490 s, 2300 sh, 1410 w, 1160 w, 1130 w, 1085 w, 1070 w, 1050 w, 995 w, 740 w
$Cs_2B_{12}H_{10}(CH_2N_3)_2$	4.6	4.6	2.7	2.7	16.2	12.9			2500 s, 2400 sh, 2350 sh, 2130 s, 2070 sh, 1320 w, 1310 w, 1230 m, 1060 m, 995 w, 860 m, 750 m, 740 sh
$Cs_2B_{12}H_{10}(CH_2SCN)_2$	8.7	9.0	2.5	2.5	5.1	5.0			2510 sh, 2500 s, 2190 s, 1410 w, 1060 w, b, 985 m, 740 w
$B_{12}H_{10}[CH_2N(CH_3)_3]_2$	33.6	32.6	11.2	10.3	9.8	9.4			3025 sh, 2500 s, 1480 m, sh, 1420 w, 1415 w, 1050 w, 1010 w, 980 w, 900 m, 740 w
$B_{12}H_{10}[CH_2N(CH_3)_2H]_2$	27.9	27.8	10.9	11.2	10.8	10.6			3200 s, 3050 w, 2510 sh, 2500 s, 1425 w, 1410 w, 1170 w, 1130 w, 1060 w, 1050 sh, 1010 w, 950 m, 925 w, 740 w
$B_{12}H_{10}[CH_2N(CH_3)_2CO_2C_2H_5]_2$	35.8	33.2	9.0	9.3	7.0	6.2			3060 w, 2520 s, 2495 s, 1810 s, 1480 m, 1420 w, 1375 m, 1240 s, 1225 msh, 1205 w, 1150 w, 1105 w, 1060 w, 1025 w, 945 m, 910 w, 900 w, 885 m, 865 w, 815 w, 760 w
$B_{12}H_{10}[CH_2N(CH_3)_2CH_2CO_2C_2H_5]_2$	39.1	39.2	9.4	9.7	6.5	7.2			3010 sh, 2510 s, 1770 s, 1480 sh, 1460 s, 1425 w, 1330 w, 1230 m, 1200 m, 1150 w, 1125 w, 1040 m, 1020 w, 995 w, 900 m, 875 w, 775 w, 740 w
$B_{12}H_{10}[CH_2N(CH_3)_2C(CH_3)HCO_2C_2H_5]_2$	41.9	40.8	9.7	10.1	6.1	6.1			

[a] Run as mineral oil mulls. Very weak absorptions and those masked by mineral oil peaks are not reported. Abbreviations: s = strong, m = moderately strong, w = weak, b = broad, sh = shoulder.

droxymethyl derivative (by using sodium borohydride.)[2] Reduction of the B_{12} 1,12-dicarbonyl is herein reported, along with a novel isolation of the bis(hydroxymethyl)-substituted anion from a lake of aluminum hydroxide.

Reduction proceeds in rigorously dried glyme (1,2-dimethoxyethane) with excess lithium aluminum hydride at room temperature. Isolation makes use of an interesting property of hydroxylated $B_{12}H_{12}^{2-}$ anions toward the cation $Ph_3PCH_3^+$ that permits the almost completely water-insoluble $Ph_3PCH_3^+$ salt to be metathesized quantitatively to the Cs^+ salt by dry methanolic CsF.[3] Isolated yields of $Cs_2B_{12}H_{10}(CH_2OH)_2$ exceed 95%. Some interaction of the hydroxyl function, presumedly with the phosphorus atom of the phosphonium cation, is evidenced by disappearance of the normally sharp OH infrared absorptions at 3580, 1260, and 1190 cm^{-1} of the Cs^+ salt.

Several derivatives paralleling those reported for $B_{10}Cl_8(CH_2OH)_2^{2-}$ were subsequently synthesized. Replacement of OH by iodide was facile. Tosylates could not be isolated, since they reacted readily with donor solvent to give $B_{12}H_{10}(CH_2L)_2$ products. (Without a basic solvent no reaction was observed.) Conversions of 90% of the hydroxymethyl into iodomethyl were realized by heating $B_{12}H_{10}(CH_2OH)_2^{2-}$ in 57% hydriodic acid at 40–50 °C. A number of anionic and neutral nucleophiles in turn were used to displace iodide from the iodomethyl derivative, to make $B_{12}H_{10}(CH_2X)_2^{2-}$ ($X = CN^-, SCN^-, N_3^-$) and $B_{12}H_{10}(CH_2L)_2$ ($L = PMe_3$, py, NMe_3, NMe_2H, NH_3, PPh_3). Reaction was accomplished by contact of the cesium salt with the nucleophile neat or in warm aqueous solution. Care in crystallization is required since the iodide is less soluble than the derived salts, so addition of CsF was made in incremental amounts to force precipitation. Recrystallization was effected from hot water. Infrared spectra were used to monitor purification.

Second-generation derivatives of $B_{12}H_{10}(CH_2NMe_2H)_2$ were also obtained by proton abstraction with butyllithium followed by reaction with organic halides, to make $B_{12}H_{10}(CH_2NMe_2Y)_2$ ($Y = CH_3$, CH_2CO_2Et, CH_2CONH_2, $CH(CH_3)CO_2Et$, CO_2Et). These charge-compensated derivatives have a small solubility in polar organic solvents.

Attempts were made to prepare the cage-halogenated hydroxymethyl anions to learn if halogen substitution reduces the electron release from the closo cage enough to permit isolation of a less reactive tosylate. Knoth reports chemistry of analogous $B_{10}Cl_8(CH_2OH)_2^{2-}$ but not that of the unhalogenated anion.[2] In our study, chlorination of the hydroxymethyl cage anion in acetonitrile led to oxychlorination to the carboxylic acid derivative $B_{12}Cl_{10}(CO_2H)_2^{2-}$, which could not then be reduced by lithium aluminum hydride in glyme.

Experimental Section

Samples of 1,12-$B_{12}H_{10}(CO)_2$ were obtained from Du Pont. 1,2-Dimethoxyethane, ether, and tetrahydrofuran (THF) were purified by distillation from lithium aluminum hydride and stored in metal cylinders under nitrogen or autogeneous pressure. Acetonitrile was distilled from phosphorus pentoxide and stored over calcium hydride. Other reagents were of commercial grade. Infrared data and NMR data are obtained on Perkin-Elmer 237B and Varian A60A instruments, respectively. Chemical analyses were obtained from Schwarzkopf Microanalytical Laboratory (Woodside, NY), Bernhardt Microanalytical Laboratory (Mulheim, FRG), and Peninsular ChemResearch (Greenville, FL). Characterization data for various new cage derivatives are collected in Table I.

1,12-$B_{12}H_{10}(CH_2OH)_2^{2-}$. Under nitrogen atmosphere a solution of 0.59 g (3.0 mmol) of 1,12-$B_{12}H_{10}(CO)_2$ in about 50 mL of dried glyme (If glyme is not rigorously dried, the reaction fails.) was added via syringe to a stirred suspension of 0.46 g (12 mmol) of lithium aluminum hydride

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(2) Knoth, W. H. *J. am. Chem. Soc.* **1967**, *89*, 4850.

(3) Riley, M. D. Ph.D. Dissertation, University of South Dakota, 1970.

contained in a two-necked, 250-mL round-bottomed flask. Immediate exothermic reaction produced a thick, crusty slurry that had to be mechanically broken at intervals during 2 h of stirring. After a period of reflux for 2 h, the reaction mixture was cooled and excess hydride destroyed by addition of 20 mL of 2-propanol followed by 25 mL of water. The voluminous solid was separated by vacuum filtration and the filtrate concentrated to 50 mL under vacuum. The solid was stirred with 250 mL of water and the 50 mL of filtrate in an open beaker by using a magnetic stirring bar. After 12 h of stirring, the solid was separated from the mixture by vacuum filtration and discarded. The filtrate was reduced under vacuum to 50 mL in a film evaporator and treated with 2.5 g (7 mmol) of triphenylmethylphosphonium bromide. The resulting precipitate of $Ph_3PCH_3^+$ salt was dried under vacuum and metathesized to the cesium salt by stirring in 25 mL of methanol containing 1.5 g (10 mmol) of CsF. The resulting solid was collected by filtration and dried to give 1.3 g (95%) of $Cs_2B_{12}H_{10}(CH_2OH)_2$.

$\mathbf{B_{12}H_{10}(CH_2I)_2^{2-}}$. $Cs_2B_{12}H_{10}(CH_2OH)_2$ was stirred in 57% aqueous HI (in proportion of 10 mL/g of cesium salt) under nitrogen in a closed vessel in the dark for 8 h. The mixture was evaporated to dryness on a vacuum line. The residue was stirred with a small portion of aqueous CsF solution, filtered out, washed with small portion of water, and dried under high vacuum. The product showed no trace of the intense OH absorption in the infrared spectrum. A small sample was converted back to the original hydroxymethyl derivative by stirring with 10% aqueous sodium hydroxide for 1 h at 80 °C.

$\mathbf{B_{12}H_{10}(CH_2SCN)_2^{2-}}$. $Cs_2B_{12}H_{10}(CH_2I)_2$, 98 mg (0.14 mmol), and 0.80 g (8.2 mmol) of potassium thiocyanate were heated into solution at 80 °C for 2 h. Crystals collected on cooling to room temperature and the crops collected by addition of 0.5 g of CsF and cooling to −22 °C were combined and recrystallized from hot water; 33 mg, 30% yield.

$\mathbf{B_{12}H_{10}(CH_2N_3)_2^{2-}}$ was prepared in a similar way using sodium azide, and the product was identified by the strong infrared absorption characteristic of azide at 2103 cm^{-1}. Deviation of nitrogen analysis appears to be a problem of analysis (vide infra) rather than one of identification of product.

$\mathbf{B_{12}H_{10}(CH_2N(Me_2H)_2/B_{12}H_{10}(CH_2Nuc)_2}$. $Cs_2B_{12}H_{10}(CH_2I)_2$, 0.55 g (0.80 mmol), and Me_2NH (20 mmol) were allowed to mix with continuous stirring (magnetic bar) in a sealed ampule at room temperature for 2 h. Evaporation of volatiles under vacuum left a residue, which was washed in water and recrystallized from hot acetonitrile; 0.13 g, 63% yield. In similar ways or with acetonitrile or methanol solvents, other nucleophilic displacements were carried out with PPh_3, PMe_3, and NH_3. These products analyzed low for carbon and hydrogen because of analytical difficulties investigated in some detail for the dimethylamine derivative:

		anal., %		
		C	H	N
calcd for $B_{12}H_{10}(CH_2NMe_2H)_2$		27.9	10.9	10.8
found	lab A	19.7	8.0	6.3
	lab A with V_2O_5	35.7	8.5	7.8
	lab A with V_2O_5/WO_3	21.3	8.4	6.0
	lab B	24.5	10.2	11.3
	lab C	27.8	11.2	10.6

$\mathbf{B_{12}H_{10}(CH_2NMe_2Y)_2}$. $B_{12}H_{10}(CH_2NMe_2H)_2$, 68 mg (0.26 mmol), was stirred with 10 mL of THF at −78 °C while 5.6 mmol of *n*-butyllithium in hexane was added. The amount of insoluble material markedly decreased, and the mixture took on a yellow coloration. No attempt was made to isolate the presumed intermediate $B_{12}H_{10}(CH_2NMe_2)_2^{2-}$ salt. Addition of 0.3 mL of ethyl chloroformate and warming to 45 °C dissipated the color and produced a white solid. Collection of the solid by filtration, washing with ether and then water, and recrystallization from hot acetonitrile gave 85 mg (89%) of $B_{12}H_{10}(CH_2NMe_2CO_2Et)_2$. Treatment of the lithium salt with ethyl chloroacetate gave 32% $B_{12}H_{10}(CH_2NMe_2CH_2CO_2Et)_2$, and treatment with ethyl 2-bromopropionate gave 61% $B_{12}H_{10}[CH_2NMe_2C(CH_3)HCO_2Et]_2$. When the lithium salt was treated with methyl iodide, the product was identical by infrared analysis with that obtained from the iodomethyl derivative and trimethylamine, supporting assignment as $B_{12}H_{10}(CH_2NMe_3)_2$.

For only two compounds was the limited solubility in common solvents sufficient for proton magnetic resonance. A doublet PCH_3 peak at 1.69 ppm (J = 15 Hz) was observed for $B_{12}H_{10}[CH_2P(CH_3)_3]_2$ in dimethyl-d_6 sulfoxide. The four resonances observed for $B_{12}H_{10}[CH_2NMe_2C(CH_3)HCO_2Et]_2$ were assigned: 0.99 ppm triplet (J = 7 Hz) and 3.96 ppm quartet (J = 7 Hz) for ethyl; 1.22 ppm doublet (J = 7 Hz) for CCH_3; 2.82 ppm doublet (J = 6 Hz) for $N(CH_3)_2$.

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Registry No. 1,12-$B_{12}H_{10}(CO)_2$, 12541-42-3; $Cs_2B_{12}H_{10}(CH_2OH)_2$, 104375-56-6; $Cs_2B_{12}H_{10}(CH_2I)_2$, 104393-04-6; $Cs_2B_{12}H_{10}(CH_2SCN)_2$, 104375-57-7; $Cs_2B_{12}H_{10}(CH_2N_3)_2$, 104375-58-8; $B_{12}H_{10}[CH_2N(CH_3)_2H]_2$, 104375-59-9; $B_{12}H_{10}[CH_2N(CH_3)_2CO_2C_2H_5]_2$, 104375-60-2; $B_{12}H_{10}[CH_2N(CH_3)_2CO_2C_2H_5]_2$, 104375-61-3; $B_{12}H_{10}[CH_2N(CH_3)_2C(CH_3)HCO_2C_2H_5]_2$, 104375-62-4; $B_{12}H_{10}[CH_2N(CH_3)_3]_2$, 104375-63-5; $B_{12}H_{10}[CH_2P(CH_3)_3]_2$, 104375-64-6.

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Use of Infrared Spectroscopy To Study Incorporation of Trivalent Elements into Molecular Sieve Gels

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Numerous factors are critical for crystallization of the zeolite molecular sieve materials but an additional factor results from the differing behavior of the aluminum-replacing or silicon-replacing elements under conditions necessary for crystallization of non-aluminosilicate molecular sieves.[1,2] We have applied infrared spectroscopy to the examination of the gels used in crystallizing these non-zeolite materials. Gels containing iron and gallium in place of aluminum were investigated in order to determine the conditions necessary for successful incorporation of these elements into the gel before further attempting to crystallize a specific molecular sieve structure. The region between 500 and 900 cm^{-1}, associated with the symmetric stretching vibrations of the Si–O–Si and Si–O–T groups, was monitored in these studies. T denotes the trivalent elements, aluminum, gallium, or iron. These stretching vibrations are sensitive to metal incorporation.[3]

Shown in Figure 1 are the infrared spectra of metallosilicate gels where successful incorporation of the elements gallium and iron was obtained. The Si–O–T symmetric stretching vibration (B in Figure 1) occurs at a position consistent with the difference in mass of these two elements. The Si–O–Fe symmetric stretching vibration (Figure 1b) appears at 656 cm^{-1} and the Si–O–Ga vibration (Figure 1c) appears at 611 cm^{-1} in these gels. In comparison, for the aluminosilicate gel (Figure 1a), a broad band appears around 730 cm^{-1}. The Si–O–Si and Si–O–Al vibrations in the aluminosilicate gel are thought to mix due to the similar mass of silicon and aluminum.[3] The vibration due to the Si–O–Si oscillator for the ferri- and gallosilicate gels occurs near 770 cm^{-1}, separate from the Si–O–T vibration since the T atom for these two gels are significantly different in mass relative to silicon.

The success of this technique in identifying the correct conditions of metal incorporation for non-zeolite molecular sieve crystallization is confirmed through the successful crystallization of these gels. A new molecular sieve ferrisilicate with the sodalite structure was prepared from the gel whose infrared spectrum in shown in Figure 1b. This is described elsewhere.[4] The infrared symmetric stretching vibrations of this crystalline material are identical with that of the gel shown in the figure. The presence of the Si–O–Si vibration is observed in both the gel and the final crystalline phase as a silica-rich ferrisilicate analogue of sodalite was prepared. The SiO_2/Fe_2O_3 ratios for the gel and crystalline phase are 13 and 11, respectively, indicating that all of the iron is incorporated into the structure.

We have also used infrared spectroscopy to observe changes that occur upon aging a metallosilicate gel. Figure 2 shows the

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