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Hydrosulfide (HS⁻) Coordination in Iron Porphyrinates

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Abstract

Recent reports of potential physiological roles of hydrogen sulfide have prompted interest in heme-sulfide interactions. Heme-H₂S and/or heme-HS⁻ interactions could potentially occur during endogenous production, transport, signaling events, and catabolism of H₂S. We have investigated the interaction of the hydrosulfide ion (HS⁻) with iron porphyrinates. UV-vis spectral studies show the formation of [Fe(Por)(SH)]⁻, [Fe(Por)(SH)₂]²⁻, and the mixed ligand species [Fe(Por)(Im)(SH)]⁻. UV-vis binding studies of [Fe(OEP)] and [Fe(Tp-OMePP)] (OEP = octaethylporphyrinate, Tp-OMePP = tetra-*p*-methoxyphenylporphyrinate) with HS⁻ allowed for calculation of formation constants and extinction coefficients of the mono- and bis-HS⁻ complexes. We report the synthesis of the first HS⁻ bound iron(II) porphyrin compounds, [Na(222)][Fe(OEP)(SH)]·0.5C₆H₆ and [Na(222)][Fe(Tp-OMePP)(SH)]·C₆H₅Cl (222 = kryptofix-222). Characterization by single-crystal X-ray analysis, mass spectrometry, and Mössbauer and IR spectroscopy are all consistent with that of known sulfur-bound high-spin iron(II) compounds. The Fe–S distances of 2.3929(5) and 2.3887(13) Å are longer than all reported values of [Fe^{II}(Por)(SR)]⁻ species. An analysis of porphyrin non-planarity for these derivatives and for all five-coordinate high-spin iron(II) porphyrinate derivatives with an axial anion ligand is presented. In our hands, attempts to synthesize iron(III) HS⁻ derivatives led to iron(II) species.

Introduction

Hydrogen sulfide (H₂S) has recently been recognized as a third possible gasotransmitter, along with NO and CO, and may play a role in vasodilation, blood pressure regulation and neurological health.^{1–5} Previously known H₂S biology consisted of its malodor and ability to inhibit cytochrome *c* oxidase.⁶ However, the interaction of H₂S with mitochondrial cytochrome *c* oxidase is concentration dependent.⁷ Endogenously produced hydrogen sulfide has been linked to hippocampal long-term potentiation⁸ as well as neurological disorders such as Down Syndrome and Alzheimer's disease.⁹ The prospect of suspended animation in animals and humans is yet another facet of H₂S biology. When mice were exposed to 80 ppm H₂S, they had sequential drops in metabolic rate and core body temperature, similar to those observed in animals during the onset of hibernation.¹⁰ After H₂S treatment was stopped, vital signs returned

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Supporting Information **Available.** A discussion of hydrosulfide hydrogen atom assignment in the X-ray crystal structures, further validation of sulfur ligation and experimental details of UV-vis binding studies. Figure S1, an ORTEP drawing of anion **2** of [Na(222)][Fe(OEP)(SH)], Figure S2 gives a plot of the asymmetric unit of structure for [Na(222)][Fe(OEP)(SH)]·0.5C₆H₆, Figure S3 gives a thermal ellipsoid plot for [Fe(Tp-OMePP)(SH)]⁻, Figure S4 is a UV-vis plot of reactions of [Fe^{II}(TMP)] with HS⁻, Figure S5, mean plane diagrams for [Na(222)][Fe(OEP)(SH)], Figure S6 gives mean plane diagrams for [Fe(Tp-OMePP)(SH)]⁻, and Figure S7, detailing reaction products with SH⁻ and Fe(III). Complete crystallographic information for [Na(222)][Fe(OEP)(SH)]·0.5C₆H₆ is listed in Tables 1–6, and that for Na(222)[Fe(Tp-OMePP)(SH)]·C₆H₅Cl is listed in Tables 7–S12. Crystallographic data is available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

to normal, and no long-term functional or behavioral abnormalities were observed. This has prompted speculation into the use of H₂S as a means to improve post-surgery and post-trauma recovery.¹¹

Hydrogen sulfide is produced endogenously in mammals by two enzymes. Cystathionine γ -lyase (CSE) is the primary source of physiological H₂S in the mammalian cardiovascular system (CVS)¹² and cystathionine β -synthase (CBS) in the central nervous system.¹³ The endogenous H₂S levels in mammalian tissues is about 15 nM,² allowing for localized high intracellular gas concentrations like those observed in NO signaling wherein tissue function is altered upon nM fluctuations.¹⁴ At the biological pH of 7.4, dissolved hydrogen sulfide, $pK_a = 6.9$, is partially deprotonated; the HS⁻:H₂S ratio is 3:1, so one or more sulfide species could act as ligands to receptor proteins. Neither the binding species nor receptors for potential sulfide-protein interactions associated with the aforementioned phenomena has been identified, however, reactions of H₂S with heme proteins have been investigated for quite some time.

In 1933, Keilin¹⁵ reviewed the previous work on H₂S-heme-protein studies, starting with the 1866 report by Hoppe-Seyler¹⁶ of a green compound that formed irreversibly upon contact of methemoglobin with H₂S in the presence of oxygen. Haurowitz¹⁷ was able to obtain a molecule that he called "sulpho-hemoglobin" with an absorption band at 618 nm that is clearly a porphyrin-based compound. The irreversible product was later suggested to be sulfhemoglobin wherein the elements of H₂S add across a β - β double bond of a pyrrole.¹⁸ Subsequent NMR studies more firmly established structures of the covalently-modified sulfur-containing pyrrole of protoporphyrin IX.¹⁹ This modified pyrrole chemistry accounts for reports of patients exhibiting green blood and reduced oxygen transport after ingestion of certain sulfur containing compounds.²⁰

Direct interaction of sulfide with the iron center is also known. In Keilin's 1933 paper,¹⁵ he also presented data that demonstrated that a new red product could be formed by the anaerobic reaction of H₂S with methemoglobin; this is commonly believed to be a coordination complex of the iron(III) porphyrin with sulfide. Neuroglobin, a highly preserved heme enzyme that occurs throughout the human central nervous system, regulates oxygen, and perhaps sulfide as it has been shown, *in vitro*, to bind hydrogen sulfide quite tightly.²¹ However, the best-understood interactions of heme proteins with H₂S are found in marine organisms that inhabit sulfide-rich environments.²²

The most studied of these systems are the proteins from the clam *Lucina pectinata* that has several different gill hemoglobins, of which hemoglobin I in its ferric form binds sulfide. The function of HbI²³ is apparently sulfide delivery to a symbiotic sulfide-oxidizing bacterium. Kraus and Wittenberg²⁴ have measured EPR spectra of the anaerobically formed complexes of H₂S with whale myoglobin (Mb) and *Lucina pectinata* hemoglobins I and II (HbI and HbII). The EPR spectra are consistent with low-spin iron(III) complexes. The crystal structure of HbI-sulfide was reported by Rizzi et al.²⁵ in 1996; however complete ligand identity and iron oxidation state cannot be verified from the 1.9 Å resolution data. A very recent report suggests that H₂S, at high concentrations, will reduce the ferric HbI species.²⁶ There are a few other reports of heme-protein-H₂S interactions in the literature. An optical spectral study of gill tissue from the bivalve mollusk *Solemya velum* led Doeller et al. to conclude that in this case, hemoglobin must be converted from the ferrous to the ferric state prior to sulfide binding.²⁷ The giant hemoglobin of *Oligobranchia mashikoi* can transport oxygen and sulfide simultaneously.²⁸

These intriguing results for heme proteins prompted us to investigate iron porphyrinates with the hydrosulfide anion as a possible ligand. We first note that transition metal complexes with hydrosulfide or hydrogen sulfide as a ligand are rare. English et al.²⁹ reported the synthesis of

an iron(III) species $[\text{Fe}(\text{Tp-OMePP})(\text{SH})]$ using $\text{S} + \text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$ (an unusual source of HS^-). The room temperature X-ray structure revealed a single axial atom at 2.30 Å from iron, but without any evidence for a hydrogen atom. There is, however, a report of a failure to reproduce this preparation.³⁰ Cai and Holm³¹ reported the transient formation of a species they believed to be $[\text{Fe}^{\text{III}}(\text{OEP})(\text{SH})]$ from the reaction of H_2S and $[\text{Fe}^{\text{III}}(\text{OEP})]_2\text{O}$. The identification was based on an observed ^1H NMR meso-H shift of -50.0 ppm, but the complex quickly reduced to $[\text{Fe}^{\text{II}}(\text{OEP})]$. Also reported in this work was $[\text{Fe}_4\text{S}_4(\text{LS}_3)\text{-S-Fe}(\text{OEP})]^{2-}$, $\text{LS}_3 = 1,3,5\text{-tris}[(4,6\text{-dimethyl-3-mercaptophenyl})\text{-thio}]\text{-2,4,6-tris(p-tolylthio)benzene(3-)}$, which contains an Fe–S–Fe bridge and is an analogue of certain assimilatory sulfite and nitrite reductases. Other (nonbiological) transition metal hydrosulfide complexes of known structure include $[\text{RhCl}(\text{H})(\text{SH})(\text{P}(\text{Ph}_3)_2)_2]$ and $[\text{IrCl}(\text{H})(\text{SH})(\text{CO})(\text{P}(\text{Ph}_3)_2)_2]$,³² $[\text{Mn}^{\text{III}}(\text{oespz})(\text{SH})]$,³³ $[\text{Co}(\text{cyclam})(\text{SH})]_n[\text{ClO}_4]_n$ and $[\text{Ni}(\mu\text{-SH})(\text{cyclam})]_2[\text{Ni}(\text{SH})_2(\text{cyclam})][\text{ClO}_4]$,³⁴ *trans*- $[\text{Rh}(\text{SH})(\text{CO})(\text{P}(\text{Ph}_3)_2)]$,³⁵ and *trans*- $[\text{M}(\text{SH})_2(\text{dmpe})_2]$; $\text{M} = \text{Cr}, \text{Fe}$.³⁶ For hydrogen sulfide there are just six structures, all of which are Ru^{II} complexes.^{37,38,39} One of these, $[\text{Ru}(\text{IMes})_2(\text{CO})(\text{H}_2\text{S})\text{H}_2]$, is air stable, and forms a 16-electron species $[\text{Ru}(\text{IMes})_2(\text{CO})(\text{SH})_2]$ upon treatment with H_2S .³⁷

We report the binding of HS^- to three iron(II) porphyrins, $[\text{Fe}(\text{OEP})]$, $[\text{Fe}(\text{Tp-OMePP})]$ and $[\text{Fe}(\text{TMP})]$ that was followed spectrophotometrically, as well as the reaction of $[\text{Fe}(\text{TMP})(1\text{-MeIm})_2]$ with HS^- . We have been able to synthesize iron(II) derivatives and report the crystal structures of two hydrosulfido iron(II) porphyrinates, $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]\cdot 0.5\text{C}_6\text{H}_6$ and $[\text{Na}(222)][\text{Fe}(\text{Tp-OMePP})(\text{SH})]\cdot \text{C}_6\text{H}_5\text{Cl}$, both are five coordinate and high spin. Attempts to synthesize analogous iron(III) compounds were unsuccessful; in our hands HS^- reduces iron(III) porphyrinates. $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]\cdot 0.5\text{C}_6\text{H}_6$ was further characterized by far-IR, mass spectrometry and Mössbauer analysis. Most aspects of the two iron(II) complexes are similar to those of other five-coordinate anionic iron(II) porphyrinates and comparisons are provided.

Experimental

General Information

All manipulations for the preparation of the iron(II) five-coordinate porphyrin derivatives were carried out under argon using a double-manifold vacuum line, Schlenkware and cannula techniques. Benzene and hexanes were distilled over sodium benzophenone. Chlorobenzene was stirred over concentrated sulfuric acid, washed with a dilute Na_2CO_3 solution, dried with Na_2SO_4 and then distilled over P_2O_5 . Octaethylporphyrin (H_2OEP) was synthesized from formaldehyde and 3,4-diethylpyrrole.⁴⁰ $[\text{Fe}(\text{OEP})\text{Cl}]$ was prepared according to a modified Adler preparation,⁴¹ and $[\text{Fe}(\text{OEP})]_2\text{O}$ was prepared from $[\text{Fe}(\text{OEP})\text{Cl}]$. $[\text{Fe}(\text{Tp-OMePP})]_2\text{O}$ and $[\text{Fe}(\text{TMP})(\text{OH})]$ were also prepared by the same general procedure. All other chemicals were used as received from Aldrich or Fisher.

Mössbauer measurements were performed on a constant acceleration spectrometer from 4.2 K to 300 K with optional small field and in a 9 T superconducting magnet system (Knox College). Samples for Mössbauer spectroscopy were prepared by immobilization of the crystalline material in Apiezon M grease.

Anhydrous NaHS

Anhydrous sodium hydrosulfide was prepared by a method described in *Inorganic Substances Handbook* with minor modifications.⁴² In a dry box, each side of a 1 g cube of sodium was shaved to shiny surface. The resulting cube was cut in half, and each half was pressed into a 1.5 mm thin sheet using a spatula. If the sheets are not sufficiently thin, the interior sodium may be inaccessible for the reaction. The sheets were loosely rolled around the spatula, and

placed in a Schlenk tube. At the Schlenk line, 15 mL of benzene was added, and the mixture was stirred under an H₂S atmosphere for 2 days. The head gas was replaced several times with fresh H₂S during the reaction. Benzene was removed under vacuum, and the white powder NaHS was collected and stored under inert conditions. Solid NaHS is sparingly soluble in benzene or chlorobenzene. At higher concentrations, the dissolution of the NaHS-kryptofix mixture in chlorobenzene required 24 h of stirring. The resulting solution had a light blue tint, consistent with the possible presence of small amounts of polysulfide ions such as S₃²⁻.

[Na(222)][Fe(OEP)(SH)]·0.5C₆H₆

Standard Schlenk procedures were followed. 50 mg (0.04 mmol) [Fe(OEP)]₂O was placed in a Schlenk flask to which 10 mL benzene and 1.0 mL ethanethiol was added. The mixture was stirred for 2 h at 60 °C then 16 h at 25 °C. Benzene and ethanethiol were removed under vacuum. The flask containing a purple powder was transferred into a dry box where 5 mg (0.09 mmol) of NaHS and 34 mg (0.09 mmol) of Kryptofix(222) were added. The flask was removed from the dry box and Schlenk procedures were resumed. Ten milliliters of benzene was added, followed by stirring at 60 °C for 1 h. The mother liquor was divided evenly between four 7-mm ID glass tubes by cannula transfer. A layer of 7 mL hexanes was added to each tube. The tubes were flame sealed under slight vacuum and stored in the dark. Hexagonal pill-shaped crystals were harvested after three weeks. Yields from the tube reactions were about 42%. Large scale preparations were not attempted. For Mössbauer spectroscopy, the same procedure was followed except that the hexanes and mother liquor were mixed together to cause immediate precipitation of the product which was recovered by filtration and drying under vacuum.

[Na(222)][Fe(Tp-OMePP)(SH)]·C₆H₅Cl

To a Schlenk flask, 40 mg (0.025 mmol) [Fe(Tp-OMePP)]₂O, 12 mL chlorobenzene and 1.0 mL ethanethiol were added. The mixture was stirred for 2 h at 60 °C then 16 h at 25 °C. Chlorobenzene and ethanethiol were removed under vacuum. The flask containing a purple powder was transferred to a dry box where 4.5 mg (0.08 mmol) NaHS and 32 mg (0.09 mmol) Kryptofix(222) were added. After removing the flask from the dry box, Schlenk procedures were resumed and 12 mL chlorobenzene were added. This slurry was stirred at near boiling for 1 h in an oil bath until a brown-green solution resulted. Stirring and heating were terminated, and the reaction vessel remained undisturbed in the oil bath for 40 h. Purple needle-like crystals were collected by filtration of the reaction solution and were washed with hexanes. The yield was approximately 30%.

X-Ray Crystallographic Studies

For [Na(222)][Fe(OEP)(SH)]·0.5C₆H₆, a crystal was placed in inert oil to reduce air exposure and cut by razor blade to 0.5 × 0.4 × 0.3 mm. Crystal data were collected and integrated using a Bruker Apex system, with graphite monochromated Mo-K_α radiation ($\lambda = 0.70173 \text{ \AA}$) at 100 K (700 Series Oxford Cryostream). The program SADABS⁴³ was applied for absorption corrections. The structure was solved by direct methods in SHELXS-97⁴³. All structures were refined using SHELXL-97⁴³. All non-hydrogen atoms were found after successive full-matrix least-squares refinement cycles on F^2 then refined with anisotropic thermal parameters. Most hydrogen atom positions were idealized with a riding model and fixed thermal parameters [$U_{ij} = 1.2U_{ij(eq)}$ or $1.5U_{ij(eq)}$] for the atom to which they are bonded. The exceptions are the sulfur bound hydrogens which were refined freely, with and without constraints for comparison. For [Na(222)][Fe(Tp-OMePP)(SH)]·C₆H₅Cl, disorder was found in one peripheral (*p*-methoxyphenyl group with two orientations, three ethylene groups of the 222; three positions of the chlorobenzene solvate around an inversion center were required for a

complete description. The sulfur bound hydrogen atom in this case was refined freely, without constraints.

Mass Spectroscopy

In a dry box, isolated crystals of $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]\cdot 0.5\text{C}_6\text{H}_6$ with a combined mass of ~ 1 mg were dissolved in 500 μL of THF. The solution was drawn into an air-tight syringe, removed from the dry box and injected into a JEOL AX505HA triple quadrupole mass spectrometer with electrospray sample ionization and time of flight detection. Both negative and positive ion mode spectra were collected for $m/z = 0$ to 2000.

Infrared Spectroscopy

Infrared spectra were collected on a Nicolet Nexus 670 FT-IR with 2 cm^{-1} resolution equipped with EZ Omnic E.S.P. version 5.2a software. Mid-IR spectra were collected from KBr pellets and far-IR from CsI pellets. All pellets were prepared in a dry box then analyzed immediately. The CsI pellet was analyzed again after 24 h of air exposure for $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]\cdot 0.5\text{C}_6\text{H}_6$. A far-IR spectrum was also collected on a similarly prepared, Fe^{57} enriched crystalline sample of $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]\cdot 0.5\text{C}_6\text{H}_6$.

UV-vis Binding Studies

Binding studies of HS^- in the form of solutions of $\text{Na}(222)\text{HS}$ were carried out by reaction of $[\text{Fe}(\text{OEP})]$, $[\text{Fe}(\text{Tp-OMePP})]$, or $[\text{Fe}(\text{TMP})]$ in order to determine the stoichiometry, bonding constants, and spectral properties. Displacement reactions of $[\text{Fe}(\text{TMP})(1\text{-MeIm})_2]$ with $\text{Na}(222)\text{HS}$ were also performed. Complete experimental details are given in the Supporting Information.

Results

The interaction of the HS^- ion with iron(II) porphyrinates has been established by a series of UV-vis observations on solutions of iron(II) porphyrinates with varying amounts of added NaHS . These data were interpreted as demonstrating the formation of both five-coordinate $[\text{Fe}(\text{Por})(\text{HS})]^-$ and six-coordinate $[\text{Fe}(\text{Por})(\text{HS})_2]^{2-}$.

Two different five-coordinate $[\text{Fe}(\text{Por})(\text{HS})]^-$ derivatives have been crystallized and structurally characterized. Both are five-coordinate high-spin species with an axial hydrosulfide ligand. Brief crystallographic data and intensity information is given in Table 1. $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]\cdot 0.5\text{C}_6\text{H}_6$ crystallizes with two porphyrin anions, two sodium cryptand cations and a benzene solvate molecule in the asymmetric unit of structure. The independent porphyrinate anions in the asymmetric unit will be referred to as **1** and **2**. Thermal ellipsoid plots of the two anions are given in Figures 1 and S1. A diagram of the contents of the asymmetric unit of structure are given in Figure S2. A similar five-coordinate species was also found for $[\text{Na}(222)][\text{Fe}(\text{Tp-OMePP})(\text{SH})]\cdot \text{C}_6\text{H}_5\text{Cl}$ and a thermal ellipsoid plot of the porphyrinate anion is presented in Figure S3. Complete lists of bond distances and angles for all species are given in the Supporting Information.

The OEP complex has also been characterized by electrospray mass spectroscopy, far-IR and Mössbauer spectroscopy. As shown in Figure 2, the negative-ion mode mass spectrum for $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]\cdot 0.5\text{C}_6\text{H}_6$ exhibits a series of peaks, $m/z = 619.3$, 621.3 , 622.3 and 623.3 , with relative peak heights similar to the natural abundance isotopic distribution for $[\text{Fe}(\text{OEP})(\text{SH})]^-$, as shown by the red bars. Also shown in Figure 2 for comparison are the expected isotopic variant m/z and relative intensities for $[\text{Fe}(\text{OEP})(\text{Cl})]^-$ as blue bars. Mössbauer spectra for $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]$, measured from 25 to 200 K, were consistent with the high-spin iron(II) state assigned to the complexes.

Discussion

Spectral Studies

The UV-vis spectra of $[\text{Fe}^{\text{II}}(\text{Tp-OMePP})]$ with varied concentrations of HS^- exhibit large spectral changes consistent with the formation of new species. The complex changes are illustrated in the top panel (A) of Figure 3. The Soret peak at 420 nm in the initial spectrum has a modest shoulder at 444 nm. This shoulder markedly increases in intensity and becomes a sharp peak at 447 nm with maximum intensity at an HS^-/Fe ratio near 2.5. The initial 420 nm peak drops substantially in intensity with increasing HS^- concentration until it has approximately half the intensity of the 447 peak and is slightly shifted to 423 nm at an HS^-/Fe ratio near 2.5. Increasing HS^- concentrations lead to the final position of the Soret band at 419 nm along with a less intense band at 454 nm. The Q band region for $[\text{Fe}^{\text{II}}(\text{Tp-OMePP})]$ displays commensurate spectral changes on increasing HS^- concentrations. The Q band region starts with a broad peak at ~ 543 nm with two shoulders to the red. The shoulders gradually grow into resolved peaks at 584 and 628 nm at the highest HS^-/Fe ratios with intermediate peaks seen at 576 and 617 nm at a HS^-/Fe ratio near 2.5. The initial peak at 543 nm decreases in intensity and shifts slightly to the red. The spectral changes over the lower and higher HS^- concentration ranges are shown as panels B and C, respectively, in Figure 3. These spectral changes clearly demonstrate that the reaction of $[\text{Fe}^{\text{II}}(\text{Tp-OMePP})]$ with HS^- leads to more than one new species. The two species are most probably identified as $[\text{Fe}^{\text{II}}(\text{Tp-OMePP})(\text{SH})]^-$ and $[\text{Fe}^{\text{II}}(\text{Tp-OMePP})(\text{SH})_2]^{2-}$ as shown in the equations below

Formation constants were calculated using least-squares fits for the spectral data;⁴⁴ the data are summarized in Table 2.

The reaction of $[\text{Fe}^{\text{II}}(\text{OEP})]$ with HS^- gave equally complex spectra (shown in the top panel of Figure 4) and point to the formation of the same species as in the *Tp-OMePP* system. The broad Soret peak of $[\text{Fe}^{\text{II}}(\text{OEP})]$ at 384 nm splits into two sharper peaks as the HS^-/Fe ratio is increased from 0.0 to 1.5. Upon further ligand addition, the two Soret peaks at 384 and 410 nm coalesce into a single peak at 397 nm, which intensifies slightly at the highest HS^- levels. Further, a shoulder on the high wavelength side of the Soret peak in the initial spectrum becomes gradually more prominent with increasing $[\text{HS}^-]$ until in the limiting spectrum (HS^-/Fe ratio at 9.6) it is a nearly resolved peak at ~ 439 nm. The Q band region again shows commensurate changes with increasing HS^- additions. The Q band region in $[\text{Fe}^{\text{II}}(\text{OEP})]$ has two peaks at 529 and 562 nm. The lower energy band intensifies to a maximum at a HS^-/Fe ratio of 1.5; further addition of HS^- causes the two peaks to gradually coalesce into a single peak at 554 nm at the highest concentrations of HS^- . The spectral changes over the lower and higher HS^- concentration ranges are shown as panels B and C, respectively, in Figure 4. Formation constants were again calculated using least-squares fits for the spectral data and values are summarized in Table 2. The spectral changes observed during the reaction of $[\text{Fe}^{\text{II}}(\text{TMP})]$ with HS^- (given in Figure S4 of the SI) are quite similar to those of $[\text{Fe}^{\text{II}}(\text{Tp-OMePP})]$, with only small differences in wavelength maxima and relative intensity as shown in Table 2.

The spectral changes observed in the reaction of $[\text{Fe}^{\text{II}}(\text{TMP})(1\text{-MeIm})_2]$ with HS^- also indicate the formation of a new species. When a solution of $[\text{Fe}^{\text{II}}(\text{TMP})(1\text{-MeIm})_2]$ was reacted with increasing levels of HS^- , a large increase of the Soret band is observed as the HS^-/Fe ratio is

increased from 0.0 to 1.2, followed by a rapid decrease as the HS^-/Fe ratio is increased from 1.2 to 4.7. The limiting spectrum shown in Figure 5 is strikingly similar to the limiting spectrum from the reaction of $[\text{Fe}^{\text{II}}(\text{TMP})]$ with HS^- (Figure S4), consistent with a common final species. We suggest that the species responsible for the intense Soret peak at the HS^-/Fe ratio of 1.2 is $[\text{Fe}^{\text{II}}(\text{TMP})(\text{SH})(1\text{-MeIm})]^-$, and that further additions of HS^- results in the formation of $[\text{Fe}^{\text{II}}(\text{TMP})(\text{SH})_2]^{2-}$.

Synthesis

The strong evidence for the existence of $[\text{Fe}^{\text{II}}(\text{Por})(\text{SH})]^-$ and $[\text{Fe}^{\text{II}}(\text{Por})(\text{SH})_2]^{2-}$ led us to attempt their synthesis for further characterization. Crystallization experiments with the OEP and *TP*-OMePP derivatives yielded crystals of the five-coordinate species, $[\text{Na}(222)][\text{Fe}^{\text{II}}(\text{Por})(\text{SH})]$, with the HS^-/Fe ratio ranging from 1.2 to 2.0 in the crystallizing solvent. Crystallization from solutions with the HS^-/Fe ratio of 5.0, near the solubility-imposed maximum, again yield the five-coordinate species. The lower solubility of the five-coordinate species, and/or instability of the doubly charged bis- HS^- adduct may preclude isolation of $[\text{Fe}^{\text{II}}(\text{Por})(\text{SH})_2]^{2-}$ as a solid. Similar results were obtained for bulk preparations where only the five-coordinate species were obtained. All attempts to prepare mixed ligand species were unsuccessful.

Attempts to prepare iron(III) species also were not successful; the SH^- ligand reduced all iron (III) porphyrinates used. In our attempts to prepare $[\text{Fe}^{\text{III}}(\text{Por})(\text{SH})]$ species, we reacted $[\text{Fe}(\text{Por})(\text{OCIO}_3)]$, $\text{Por} = \text{OEP}$ or *TP*-OMePP, with NaHS in chlorobenzene in the presence of (222) to aid in solubilizing NaHS. In all cases, mixtures of $[\text{Fe}(\text{Por})(\text{SH})]^-$ and $[\text{Fe}(\text{Por})(\text{SH})_2]^{2-}$ were obtained. Spectra obtained from these synthetic procedures were similar to those obtained from the reaction of $[\text{Fe}^{\text{II}}(\text{Por})]$ with SH^- as shown in Figure S7. This is in contrast to the earlier report of the preparation of the low-spin iron(III) derivative $[\text{Fe}(\text{TP-OMePP})(\text{SH})]$.²⁹ A certain ambiguity is associated with this complex as no direct evidence for the hydrogen atom of HS^- was obtained and neither was an Fe–S stretch observed. However, the physical properties of $[\text{Fe}(\text{TP-OMePP})(\text{SH})]$ were consistent with an axially symmetric low-spin iron(III) species and include Mössbauer, EPR, NMR and magnetic susceptibilities. The low-spin state seems unexpected. Reduction, but rather slow reduction of $[\text{Fe}^{\text{III}}(\text{TP-OMePP})(\text{SH})]$ on standing in toluene or benzene solution was noted. It is possible that environmental factors play a significant role in this reduction. The apparent ease of reduction of Fe(III) porphyrinates to Fe(II) in reactions with hydrosulfide lead us to believe that the stability of the reported sulfide-bound iron(III) heme proteins results from either a specialized (low polarity) protein environment or from the protein allowing only limited access to the binding site that deters reduction at low concentrations of sulfide species.

Far-IR spectra gave $\nu_{\text{Fe-S}} = 344 \text{ cm}^{-1}$ in $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]$; the peak shifted to 340 cm^{-1} in the ^{57}Fe isotopomer, confirming the participation of iron in the vibration. The analogous peak in $[\text{Na}(222)][\text{Fe}(\text{TP-OMePP})(\text{SH})]$ was found at 337 cm^{-1} . Exposure of the original pellet to air for 24 h led to the disappearance of the 344 cm^{-1} Fe–S peak. The IR stretch of the SH group was not observed for either porphyrin complex; the band is typically weak but has been previously reported at 2550 cm^{-1} for $[\text{Fe}(\text{SH})_2(\text{dmpe})_2]$.³⁶ The electrospray mass spectrum, described earlier, clearly demonstrates that the axial ligand is not chloride, a common possible impurity in the iron(II) systems.

Mössbauer Spectra

Mössbauer spectra for $[\text{Na}(222)][\text{Fe}^{\text{II}}(\text{OEP})(\text{SH})] \cdot 0.5\text{C}_6\text{H}_6$ were collected between 25 and 200 K in a 500 G magnetic field. The spectra consist of two peaks that broaden with decreased temperature. Shoulders are clearly evident in the 25 K spectrum consistent with two quadrupole doublets as shown in Figure 6. The data can be fit to four, equal area, overlapped Lorentzian

lines for each temperature; values of the fits are provided in Table 3. The two quadrupole doublets are designated as “a” and “b.” At 25 K, the quadrupole splitting (ΔE_Q) values are 2.81 and 2.14 mm/s with corresponding isomer shifts (δ_{Fe}) of 0.95 and 0.89 mm/s. Some temperature dependence was observed; ΔE_Q values are 2.62 and 2.09 mm/s with corresponding δ_{Fe} values of 0.92 and 0.89 mm/s at 200 K.

The observed ΔE_Q and δ_{Fe} values are strongly consistent with known high-spin iron(II) porphyrin complexes.⁴⁵ Isomer shift values are far too large to be consistent with iron(III) species. Table 4 compares the Mössbauer parameters of iron sites “a” and “b” with other high-spin iron(II) porphyrinates, four-coordinate iron(II) species as well as some iron(III) compounds.^{46–56} The most comparable species are those with axial thiolates as the ligand; $[Fe^{II}(TpivPP)(SC_2H_5)]^-$ has $\Delta E_Q = 2.18$ mm/s and $\delta_{Fe} = 0.83$ mm/s and $[Fe^{II}(TpivPP)(SC_6HF_4)]^-$, $\Delta E_Q = 2.38$ mm/s and $\delta_{Fe} = 0.83$ mm/s. Other iron(II) compounds, with nitrogen or oxygen as anionic axial ligands have slightly higher δ_{Fe} values, but significantly larger ΔE_Q values; some representative examples are $[Fe(TPP)(2-MeIm^-)]^-$ with $\Delta E_Q = 3.60$ mm/s and $\delta_{Fe} = 1.00$ mm/s, and $[Fe(TPP)(OC_6H_5)]^-$ with $\Delta E_Q = 4.01$ mm/s and $\delta_{Fe} = 1.03$ mm/s. Four-coordinate iron(II) compounds have significantly lower δ_{Fe} values, 0.52 and 0.62 mm/s for $[Fe(TPP)]$ and $[Fe(OEP)]$, respectively. Possible reasons for the appearance of two Mössbauer distinguishable sites in crystalline $[Na(222)][Fe^{II}(OEP)(SH)] \cdot 0.5C_6H_6$ will be discussed subsequently.

Structures of the $[Fe^{II}(\text{Por})(SH)]^-$ anions

The asymmetric unit of crystalline $[Na(222)][Fe^{II}(OEP)(SH)] \cdot 0.5C_6H_6$ contains two square-pyramidal anions with hydrosulfide as the axial anionic ligand as shown in Figures 1 and S1. The two anions will be referred to as anion **1** and anion **2**. The two porphyrin moieties do have some small, but significant, differences in their coordination geometry. The average Fe–N_p distances are consistent with high-spin iron(II) complexes: 2.1192(13) Å for anion **1** and 2.1081(14) Å for anion **2**.^{57, 58} The Fe–S distances of 2.3929(5) and 2.3830(5) Å for **1** and **2**, respectively, are reasonable; longer than the 2.340(5) Å Fe–Cl of $[Fe^{II}(TPP)(Cl)]^-$,⁵⁹ and shorter than the 2.434(2) Å Fe–Br of $[Fe^{II}(TpivPP)(Br)]^-$.⁶⁰ Known Fe^{II}–thiolate values: 2.360(2) Å in $[Fe^{II}(TPP)(SC_2H_5)]^-$,⁶¹ and 2.324(2) Å in $[Fe^{II}(TpivPP)(SC_2H_5)]^-$,⁶² are slightly shorter than the Fe–SH values. These data are summarized in Table 5. Also included in the table are other $[Fe^{II}(\text{Por})X]$ complexes with singly charged anionic ligands,^{63, 64} and related $[Fe^{III}(\text{Por})(SR)]$ complexes.^{66, 67}

The atom displacements of the iron and the core atoms from the 24-atom and 4-nitrogen atom mean planes of $[Fe^{II}(OEP)(SH)]^-$ are given in Figures 7 (anion **1**) and S5 (anion **2**). Also displayed on these formal diagrams are the averaged values of bond distance and angles in each of the cores; the agreement between the two cores is very good. The iron atom displacements from the four-nitrogen planes (ΔN_4) of 0.55 Å and 0.52 Å for **1** and **2** are consistent with the iron(II) anionic complexes, notably 0.53 Å of $[Fe^{II}(TPP)(Cl)]^-$,⁵⁹ the 0.49 Å of $[Fe^{II}(TpivPP)(Br)]^-$,⁶⁰ and the 0.52 Å of $[Fe^{II}(TPP)(SC_2H_5)]^-$.⁶¹

Interestingly, the porphyrin core conformations of anions **1** and **2** of $[Fe^{II}(OEP)(SH)]^-$ have some substantial differences. The plots of the iron atom displacements from the two mean planes of Figures 7 and S5 clearly show that both anions have domed cores but otherwise differ in the patterns of atom displacements. Clearly additional, but distinct, distortions from nonplanarity are present in the two anions. The differences for the two anions in the asymmetric unit occurs despite identical composition in a common lattice. The different types of distortions have been categorized as ruffling, doming, saddling, waving and propeller and may be simultaneously present in a porphyrin core to varying degrees.^{68, 69} The deformations can be differentiated using the Normal-Coordinate Structural Decomposition (NSD) procedure, a method to calculate the contribution from each type of distortion.⁷⁰ Results from the NSD

analysis for the two $[\text{Fe}^{\text{II}}(\text{OEP})(\text{SH})]^-$ anions along with a number of additional high-spin iron (II) porphyrinates coordinated by an anionic axial ligand are presented in Table 6. The table makes clear that although both $[\text{Fe}^{\text{II}}(\text{OEP})(\text{SH})]^-$ anions have a substantial doming component, the differing distortion is that anion **1** core has a ruffling component whereas anion **2** core has a large saddling component. The overall difference in the core conformations probably leads to the modest difference in the Fe–N_p bond distances.

As has been noted previously, the Mössbauer spectrum of crystalline $[\text{Na}(222)][\text{Fe}^{\text{II}}(\text{OEP})(\text{SH})]\cdot 0.5\text{C}_6\text{H}_6$ displayed two overlapping quadrupole doublets. The most likely explanation for the two signals is that the conformational differences are driving modest differences in the electronic distribution that is revealed in the quadrupole splitting values. Although we have no way of unambiguously associating a particular conformation with the quadrupole splitting, we think that anion **1** with its slightly longer Fe–N_p bond distances is to be associated with the larger quadrupole doublet (“a”). This issue is difficult to study since any rigorous evaluation requires samples with identical composition, but differing core conformations. We carefully studied the crystal packing pattern to see if differing environments of the HS[−] ligand could be the cause of the differing physical properties of the two anions. Significant differences are not apparent (See Figure S2).

Table 6 also gives the results of the NSD analysis for a number of additional high-spin iron(II) porphyrinates with anionic axial ligands. All of these anionic species are seen to display significant core doming, moreover, all have at least one other significant core distortion mode. This is reflected in the large values of D_{oop} (a measure of total displacements, Table 6). Note that none of these complexes are derivatives with peripheral crowding designed to induce significant nonplanar distortions. A similar analysis has been done for high-spin iron(II) porphyrinates with (neutral) imidazole as the axial ligand.⁷¹ These two systems provide some interesting comparisons. Although the imidazole derivatives also frequently display core doming, the magnitude is, on average, only 3/4 that of the anionic species. Moreover, the total distortion value D_{oop} is also only about 60% in the imidazole-ligated species. These differences are consistent with the idea that there are two distinct $S = 2$ states for high-spin iron porphyrinate derivatives that are characterized by, *inter alia*, apparent differences in the size of the iron center.⁵⁹

The X-ray structure of a second hydrosulfide derivative, $[\text{Fe}(\text{Tp-OMePP})(\text{SH})]^-$, has also been determined. The coordination geometry for this complex is similar to that of its OEP analog, with an Fe–S bond distance of 2.3887(13) Å, and an average Fe–N_p distance of 2.108(5) Å. Table 7 details the coordination site geometry, and Table 5 compares the geometry of $[\text{Fe}(\text{Tp-OMePP})(\text{SH})]^-$ to the OEP analog and to related porphyrin complexes. The displacements of all porphyrinate atoms from 24-atom mean plane and the 4-nitrogen plane are presented in Figure S6. Although the porphyrin core is less domed than in the OEP species, it is still strongly distorted as shown in Table 6, with unusually large *wav* (*x,y*) components. A complete description the treatment of hydrogen atoms of the HS[−] ligand in the two complexes are given in the Supporting Information. A comparison of the Fe–S–H geometries with those of thiolates (Table 7) show strong similarities.

Summary

This work clearly shows that HS[−], the most abundant form of H₂S at physiological pH, can act as a good ligand in iron porphyrinate systems and that the combination of heme proteins and the HS[−] ligand could have a significant place in heme biological systems. The observed reducing power of HS[−] with isolated hemes strongly suggests that heme proteins coordinating to sulfide ligands in the iron(III) oxidation state must have either specialized (low polarity) environments or must allow only limited access to the HS[−]/S^{2−} binding site. There are no equivalent restrictions for the iron(II) species. Solution UV-vis spectral investigations show

stability for three distinct iron(II) species $[\text{Fe}(\text{Por})(\text{SH})]^-$, $[\text{Fe}(\text{Por})(\text{SH})_2]^{2-}$, and a mixed ligand species $[\text{Fe}(\text{Por})(\text{SH})(\text{Im})]^-$. The five-coordinate species, $[\text{Fe}(\text{Por})(\text{SH})]^-$, are the first hydrosulfido iron(II) porphyrinate compounds to be synthesized, isolated, and characterized by single-crystal structure determinations, infrared and Mössbauer spectroscopy, and mass spectrometry. Results from all analyses are consistent with high-spin iron(II) with iron-bound sulfur. Physical properties are most similar to those of other high-spin iron(II) porphyrinates with axial anionic ligands. Solution binding studies yield values for formation constants that are comparable to those of imidazoles. Extinction coefficients and peak maxima for hydrosulfido metalloporphyrin complexes have been reported. Porphyrin core conformations for the $[\text{Fe}(\text{Por})(\text{SH})]^-$ species were analyzed by NSD and compared for all iron(II) species with anionic ligands. The OEP complexes may display larger contributions from doming than those of related iron(II) species.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References and Notes

1. Abe K, Kimura H. *J Neurosci* 1996;16:1066. [PubMed: 8558235]
2. Furne J, Saeed A, Levitt MD. *Am J Physiol Regul Integr Comp Physiol* 2008;295:R1479. [PubMed: 18799635]
3. Olson KR, Dombrowski RA, Russell MJ, Doellman MM, Head AK, Whitfield NL, Madden JA. *J Exp Biol* 2006;209:4011. [PubMed: 17023595]
4. Hosoki R, Matsuki N, Kimura H. *Biochem Biophys Res Commun* 1997;237:527. [PubMed: 9299397]
5. Mustafa AK, Gadalla MM, Snyder SH. *Science Signaling* 2009;2:re2. [PubMed: 19401594]
6. Wever R, Van Gelder BF, Dervartanian DV. *Biochim Biophys Acta* 1975;387:189. [PubMed: 164940]
7. Cooper CE, Brown GC. *J Bioenerg Biomembr* 2008;40:533. [PubMed: 18839291]
8. Billaut-Laden I, Allorge D, Crunelle-Thibaut A, Rat E, Cauffiez C, Chevalier D, Houdret N, Lo-Guidice J, Broly F. *Toxicology* 2006;225:1. [PubMed: 16790311]
9. Kamoun P. *Amino Acids* 2004;26:243. [PubMed: 15221504]
10. Blackstone E, Morrison M, Roth MB. *Science* 2005;308:518. [PubMed: 15845845]
11. Leslie M. *Science* 2008;320:1155. [PubMed: 18511669]
12. Yang G, Wu L, Jiang B, Yang W, Qi J, Cao K, Meng Q, Mustafa A, Mu W, Zhang S, Snyder S, Wang R. *Science* 2008;322:587. [PubMed: 18948540]
13. Eto K, Kimura H. *J Neurochem* 2002;83:80. [PubMed: 12358731]
14. Simonsen U, Wadsworth RW, Buus NH, Mulvany MJ. *J Physiol* 1999;316:271. [PubMed: 10066940]
15. Keilin D. *Proc R Soc Lond Ser B Biol Sci* 1933;133:393.
16. Hoppe-Seyler F. *Zentralbl Med Wiss* 1866;4:436.
17. Haurowitz F. *Z Physiol Chem* 1926;151:130.
18. (a) Berzofsky JA, Peisach J, Blumberg WE. *J Biol Chem* 1971;246:3367. [PubMed: 4324899] (b) Berzofsky JA, Peisach J, Horecker BL. *J Biol Chem* 1972;247:3783. [PubMed: 5033390]
19. (a) Chatfield MJ, La Mar GN, Lecomte JTJ, Balch AL, Smith KM, Langry KC. *J Am Chem Soc* 1986;108:710. (b) Chatfield MJ, La Mar GN, Kauten RJ. *Biochemistry* 1987;26:6939. [PubMed: 3427054]
20. Wu C, Kenny MA. *Clinical Chemistry* 1997;43:162. [PubMed: 8990240]

21. Brittain T, Yosaatmadja Y, Henty K. IUBMB Life 2008;60:135. [PubMed: 18380003]
22. Weber RE, Vinogradov SN. Physiol Rev 2001;81:569. [PubMed: 11274340]
23. The following abbreviations are used in this paper: HbI, hemoglobin I from *Lucina pectinata*; OEP, dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; Tp-OMePP, dianion of *meso*-tetrapara-methoxyphenylporphyrin; TPP, dianion of *meso*-tetraphenylporphyrin; TMP, dianion of *meso*-tetramesitylporphyrin; TpivPP, dianion of *a,a,a,a*-tetrakis(*o*-pivalamidophenyl)porphyrin; Proto IX DME, dianion of protoporphyrin IX; Por, generalized porphyrin dianion; 222, 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]-hexacosane; Im, generalized imidazole; HIm, imidazole; 2-MeHIm, 2-methylimidazole; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazolate; cyclam, 1,4,8,11-tetraazacyclotetradecane; oespz, 2,3,7,8,12,13,17,18-octakis(ethylsulfanyl)-5,10,15,20-tetraazaporphyrinate dianion; dmpe, 1,2-bis(dimethylphosphino)ethane; IMes, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.
24. Kraus DW, Wittenberg JB, Jing-Fen L, Peisach J. J Biol Chem 1990;265:16054. [PubMed: 2168877]
25. Rizzi M, Wittenberg JB, Coda A, Ascenzi P, Bolognesi M. J Mol Biol 1996;258:1. [PubMed: 8613980]
26. Pietra R, Lewis A, Leon RG, Casabona G, Kiger L, Yeh S, Fernandez-Alberti S, Marden MC, Cadilla CL, Lopez-Garriga J. Biochemistry 2009;48:4881. [PubMed: 19368335]
27. Doeller JE, Kraus DW, Colacino JM, Wittenberg JB. Biol Bull 1988;175:388.
28. Numoto N, Nakagawa T, Kita A, Sasayama Y, Fukumori Y, Miki K. Proc Natl Acad Sci USA 2005;102:14521. [PubMed: 16204001]
29. English DR, Hendrickson DN, Suslick KS, Eigenbrot CW, Scheidt WR. J Am Chem Soc 1984;106:7258.
30. Balch AL, Cornman CR, Safari N, Latos-Grażyński L. Organometallics 1990;9:2420.
31. Cai L, Holm RH. J Am Chem Soc 1994;116:7177.
32. Muetting AM, Boyle P, Pignolet LH. Inorg Chem 1984;23:44.
33. Ricciardi G, Bencini A, Belviso S, Bavaso A, Lelj F. J Chem Soc, Dalton Trans 1998:1985.
34. Pleus RJ, Waden H, Saak W, Haase D, Pohl S. J Chem Soc, Dalton Trans 1999:2601.
35. Gaffney TR, Ibers JA. Inorg Chem 1982;21:2851.
36. Arif AM, Hefner JG, Jones RA, Koschmieder SU. J Coord Chem 1991;23:13.
37. Chatwin SL, Diggle RA, Jazzar RF, MacGregor SA, Mahon MF, Whittlesey MK. Inorg Chem 2003;42:7695. [PubMed: 14632475]
38. Mudalige DC, Ma ES, Rettig SJ, James BR, Cullen WC. Inorg Chem 1997;36:5426.
39. Sellman D, Lechner P, Knoch F, Moll M. J Am Chem Soc 1992;114:922.
40. Milgram BC, Eskildsen K, Richter SM, Scheidt WR, Scheidt KA. J Org Chem 2007;72:3941. [PubMed: 17432915]
41. (a) Adler AD, Longo FR, Kampus F, Kim J. J Inorg Nucl Chem 1970;32:2443. (b) Buchler, JW. Porphyrins and Metalloporphyrins. Smith, KM., editor. Elsevier Scientific Publishing; Amsterdam, The Netherlands: 1975. Chapter 5
42. Lidin, RA. Inorganic Substances Handbook. Begel House Inc.; New York: 1996. p. 284
43. Sheldrick GM. Acta Crystallogr, Sect A 2008;A64:112. [PubMed: 18156677]
44. Legget, DJ. SQUAD: Stability Quotients from Absorbance Data. In: Legget, DJ., editor. Computational Methods for the Determination of Formation Constants. Plenum Press; New York: 1996. p. 159-217. Modern Inorganic Chemistry Series
45. Debrunner, PG. Mössbauer Spectroscopy of Iron Porphyrins. In: Lever, ABP.; Gray, HB., editors. Iron Porphyrins, Part 3. VCH Publishers Inc.; New York: 1983. Chapter 2
46. Nasri H, Fischer J, Weiss R, Bill E, Trautwein A. J Am Chem Soc 1987;109:2549.
47. Schappacher M, Weiss RR, Montiel-Montoya R, Gonser U, Bill E, Trautwein A. Inorg Chim Acta 1983;78:L9.
48. Hu C, Noll BC, Schulz CE, Scheidt WR. J Am Chem Soc 2005;127:15018. [PubMed: 16248628]
49. Shaevitz BA, Lang G, Reed CA. Inorg Chem 1988;27:4607.
50. Bominaar EL, Ding X, Gismelseed A, Bill E, Winkler H, Trautwein AX, Nasri H, Fisher J, Weiss R. Inorg Chem 1992;31:1845.

51. Collman JP, Hoard L, Kim N, Lang G, Reed CA. *J Am Chem Soc* 1975;97:2676. [PubMed: 166106]
52. Hu C, Noll BC, Schulz CE, Scheidt WR. *Inorg Chem* 2007;46:619. [PubMed: 17257003]
53. Strauss SH, Silver ME, Long KM, Thompson RG, Hudgens RA, Spartalian K, Ibers JA. *J Am Chem Soc* 1985;207:4207.
54. Maricondi C, Straub DK, Epstein LM. *J Am Chem Soc* 1972;94:4157. [PubMed: 5036643]
55. Moss TH, Bearden AJ, Caughey WS. *J Chem Phys* 1969;51:2624. [PubMed: 4309550]
56. Tang SC, Koch S, Papaefthymiou GC, Foner S, Frankel RB, Ibers JA, Holm RH. *J Am Chem Soc* 1976;98:2414. [PubMed: 177476]
57. Scheidt WR, Reed CA. *Chem Rev* 1981;81:543.
58. Scheidt, WR. Systematics of Porphyrins and Metalloporphyrins. In: Kadish, KM.; Smith, KM.; Guillard, R., editors. *The Porphyrin Handbook*. Vol. 3. Academic Press; San Diego, CA: 2000. p. 72-73.
59. Hu C, Sulok CD, Paulat F, Lehnert N, Zatsman AI, Hendrich MP, Schulz CE, Scheidt WR. manuscript in preparation.
60. Nasri, H. PhD Thesis. University of Louis Pasteur; Strasbourg, France: 1987.
61. Caron C, Mitschler A, Riviere G, Ricard L, Schappacher M, Weiss R. *J Am Chem Soc* 1979;101:7401.
62. Schappacher M, Ricard L, Weiss RR, Montiel-Montoya R, Bill E, Trautwein AX. *Inorg Chem* 1989;28:4639.
63. Nasri H, Ellison MK, Shaevitz B, Gupta GP, Scheidt WR. *Inorg Chem* 2006;45:5284. [PubMed: 16813390]
64. Mandon D, Ott-Woelfel F, Fischer J, Weiss R, Bill E, Trautwein AX. *Inorg Chem* 1979;101:2442.
65. Tang SC, Koch S, Papaefthymiou GC, Foner S, Frankel RB, Ibers JA, Holm RH. *J Am Chem Soc* 1976;98:2414. [PubMed: 177476]
66. Miller KM, Strouse CE. *Acta Crystallogr, Sect C* 1984;C40:1324.
67. Miller KM, Strouse CE. *Inorg Chem* 1984;23:2395.
68. Scheidt WR, Lee YJ. Recent Advances in the Stereochemistry of Metallotetrapyrroles. *Struct Bonding* (Berlin) 1987;64:1–70.
69. Shelnutt JA, Song X, Ma J, Jia A, Jentzen W, Medforth CJ. *Chem Soc Rev* 1998;27:31.
70. Sun, L.; Shelnutt, JA. Program is available via the internet at <http://jasheln.unm.edu>
71. See Table 3 of Hu C, An J, Noll BC, Schulz CE, Scheidt WR. *Inorg Chem* 2006;45:4177. [PubMed: 16676979]

Figure 1.

Thermal ellipsoid plot (50% probability ellipsoids) of anion **1** in [Na(222)][Fe(OEP)(SH)]·0.5C₆H₆ at 100 K. In this and other figures and tables the following atom naming convention has been used: *Q*(*n*), *Q*(*ny*) and *Q*(*nyy*), where *Q* is the atom type, *n* refers to anion **1** or **2** and *y* or *yy* are further numbers and letters needed to completely specify the atom. Thus similar atoms in the two anions have the same name except for the digit *n*. Hydrogen atoms (except at S) are omitted for clarity.

Figure 2.

Negative ion mode mass spectrum of $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})]$ with overlays of calculated m/z , $z=1$, for the four most abundant isotopic variants of $[\text{Fe}(\text{OEP})(\text{SH})]^-$ (red) and $[\text{Fe}(\text{OEP})(\text{Cl})]^-$ (blue). Bar heights are proportional to their calculated relative occurrence.

Figure 3.

UV-visible molar absorptivity plots of chlorobenzene solutions of $[\text{Fe}(\text{Tp-OMePP})]$ with varied HS^-/Fe ratios. Concentration of $[\text{Fe}(\text{Tp-OMePP})]$ ranged from 0.085 to 0.073 mM with concentration of HS^- adjusted according to the ratios reported in the Figure. Decrease in $[\text{Fe}(\text{Tp-OMePP})]$ concentration is due to dilution incurred upon ligand addition. Panel A shows a selection of spectral traces from the complete range of HS^-/Fe ratios explored, panel B shows results from the lower HS^- concentrations, and panel C from the highest HS^- concentrations. Note that for reasons of clarity, the concentration color coding is distinct in each panel. From 500 to 700 nm, plots are shown both at regular scale and magnified 5 $\times$.

Figure 4.

UV-visible molar absorptivity plots of chlorobenzene solutions of [Fe(OEP)] with varied $\text{HS}^-:\text{Fe}$ ratios. Concentration of [Fe(OEP)] ranged from 0.113 mM to 0.088 mM with concentration of HS^- adjusted according to the ratios reported in the Figure. Decrease in [Fe(OEP)] concentration is due to dilution incurred upon ligand addition. Panel A shows a selection of spectral traces from the complete range of $\text{HS}^-:\text{Fe}$ ratios explored, panel B shows results from the lower HS^- concentrations, and panel C from the highest HS^- concentrations. Note that for reasons of clarity, the concentration color coding is distinct in each panel. From 500 to 700 nm, plots are shown both at regular scale and magnified $5\times$.

Figure 5.

UV-visible molar absorptivity plots of chlorobenzene solutions of [Fe(TMP)] with varied Fe: 1-Melm: HS⁻ ratios. Concentration of [Fe(TMP)] ranged from 0.069 mM to 0.053 mM while 1-Melm ranged from 0.36 mM to 0.28 mM and HS⁻ was adjusted according to the ratios reported in the Figure. Decrease in [Fe(TMP)] concentration is due to dilution incurred upon ligand addition. From 500 to 700 nm, plots are shown both at regular scale and magnified 5×.

Figure 6. Mössbauer spectrum of $[\text{Na}(222)][\text{Fe}(\text{OEP})(\text{SH})] \cdot 0.5\text{C}_6\text{H}_6$ at 25 K with magnetic field of 500 Gauss. The experimental data and the deconvolution of the spectrum into two equal-area doublets is shown.

Figure 7.

Mean plane diagrams for anion 1 of [Na(222)][Fe(OEP)(SH)]·0.5C₆H₆. The values of the atomic displacements from 24-atom (top) and 4-nitrogen (bottom) mean planes are given in units of 0.01 Å. Also entered on the diagrams are mean porphyrin core bond lengths in Å and mean bond angles in degrees.

Table 1

Brief Crystallographic Data and Data Collection Parameters

	[Na(222)][Fe(OEP)(SH)]·0.5C ₆ H ₆	[Na(222)][Ee(Tp-OMePP)(SH)]·C ₆ H ₅ Cl
formula	[C ₃₆ H ₄₅ FeN ₄ S] ⁺ , [C ₁₈ H ₃₆ N ₂ NaO ₆] ⁺ ·0.5C ₆ H ₆	[C ₄₈ H ₃₇ FeN ₄ O ₄ S] ⁺ , [C ₁₈ H ₃₆ N ₂ NaO ₆] ⁺ ·C ₆ H ₅ Cl
FW, amu	1060.21	1333.75
<i>a</i> , Å	21.9682(4)	12.3987(5)
<i>b</i> , Å	23.7269(4)	25.3197(10)
<i>c</i> , Å	24.1203(6)	21.7450(8)
β , deg	116.676(1)	95.392(2)
<i>V</i> , Å ³	11234.2(4)	6796.2(5)
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	8	4
<i>D</i> _c , g/cm ³	1.254	1.304
<i>F</i> (000)	4552	2808
μ , mm ⁻¹	0.367	0.361
crystal dimensions, mm	0.47 × 0.39 × 0.34	0.33 × 0.13 × 0.12
radiation	MoK α , λ = 0.71073 Å	MoK α , λ = 0.71073 Å
temperature, K	100(2)	100(2)
total data collected	398321	90934
absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
unique data	37293 (<i>R</i> _{int} = 0.046)	11972 (<i>R</i> _{int} = 0.044)
unique obsd data [<i>I</i> > 2 σ (<i>I</i>)]	27137	8963
refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.1118	<i>R</i> ₁ = 0.0691, <i>wR</i> ₂ = 0.1934
final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0761, <i>wR</i> ₂ = 0.1346	<i>R</i> ₁ = 0.0922, <i>wR</i> ₂ = 0.2164

Table 2
Formation Constants and Derived $\lambda_{max}(\log \epsilon)$ Values for Hydrosulfido Porphyrinate Complexes.

Complex	stability constant	Soret ^a	Q-band ^a
[Fe(OEP)(SH)] ⁻	5.0±0.2 ^b	380(4.84)	528(4.07)
[Fe(OEP)(SH) ₂] ²⁻	10.4±0.2 ^c	397(4.89)	552(4.17)
[Fe(Tp-OMePP)(SH)] ⁻	4.7±0.4 ^b	428(4.81)	543(4.07)
[Fe(Tp-OMePP)(SH) ₂] ²⁻	8.7±0.4 ^c	418(4.98)	585(4.03)
[Fe(TMP)(SH)] ⁻	4.6±0.7 ^b	421(5.36)	542(4.38)
[Fe(TMP)(SH) ₂] ²⁻	9.2±0.4 ^c	416(4.90)	584(4.12)
			656(3.64)

^a nm.

^b $\log K_1, K_1 = [\text{Fe(Por)(SH)}^-]/[\text{Fe(Por)}][\text{SH}^-]$.

^c $\log \beta_2, \beta_2 = [\text{Fe(Por)(SH)}_2^{2-}]/[\text{Fe(Por)}][\text{SH}^-]^2$

Table 3Mössbauer Parameters for [Na(222)][Fe(OEP)(SH)]·0.5C₆H₆

Iron Site	ΔE_Q^a	δ_{Fe}^a	Γ^b	T ^c
a	2.81	0.95	0.66	25
a	2.86	0.96	0.68	50
a	2.62	0.90	0.58	100
a	2.62	0.92	0.52	200
b	2.14	0.89	0.36	25
b	2.13	0.90	0.37	50
b	2.13	0.93	0.37	100
b	2.09	0.89	0.38	200

^a mm/s.^b FWHM, mm/s.^c K.

Table 4

Mössbauer parameters for Relevant Iron(II) and -(III) Porphyrinates

Complex	ΔE_Q^a	δ_{Fe}^a	Γ^b	T^c	ref.
Iron(II)					
[Fe(OEP)(SH)] ⁺ , site "a"	2.82	0.95	0.66	25	tw ^d
[Fe(OEP)(SH)] ⁺ , site "b"	2.13	0.89	0.36	25	tw ^d
[Fe(TpivPP)(SC ₂ H ₅)] ⁺	+2.18 ^e	0.83	0.30	4.2	48
[Fe(TpivPP)(SC ₆ H ₄)] ⁺	2.38	0.83	0.32	4.2	47
[Fe(TpivPP)(Cl)] ⁺	4.36	1.01	0.31	77	47
[Fe(TPP)(OC ₆ H ₅)] ⁺	+4.01 ^e	1.03	0.25	4.2	49
[Fe(TpivPP)(O ₂ CCH ₃)] ⁺	+4.25 ^e	1.05	0.30	4.2	50
[Fe(TpivPP)(OCH ₃)] ⁺	3.67	1.03	0.40	4.2	46
[Fe(TpivPP)(OC ₆ H ₅)] ⁺	3.90	1.06	0.38	4.2	46
[Fe(OEP)(2-Melm ⁺)] ⁺	+3.71 ^e	1.00	0.29	4.2	48
[Fe(TPP)(2-Melm ⁺)] ⁺	+3.60 ^e	1.00	0.33	4.2	48
[Fe(TPP)] (42d)	1.51	0.52	NR ^f	4.2	51
[Fe(TPP)] (PT)	2.21	0.57	NR ^f	20	52
[Fe(OEP)]	1.71	0.62	NR ^f	4.2	53
Iron(III)					
[Fe(TPP)(Cl)]	0.46	0.41	NR ^f	4.2	54
[Fe(TPP)(Br)]	0.72	0.45	NR ^f	4.2	54
[Fe(OEP)(SC ₆ H ₅)]	0.31	0.49	NR ^f	4.2	56

^a mm/s.

^b FWHM, mm/s.

c_K . $d_{\text{this work}}$. e sign of ΔE_Q experimentally defined. f not reported.

Table 5
Selected Distances (Å) and Angles (deg) for Iron(II) Porphyrinates with Anionic Ligands.

Complex	$\angle \text{Fe-N}_p > ab$	Fe-L ^b	Fe-S-R ^c	$\Delta N_p^b, d$	ref.
Iron(II) Complexes:					
[Fe(OEP)(SH)] ⁺ , Fe(1)	2.1192(13)	2.3929(5)	98.5(10) ^e	0.55	tw
[Fe(OEP)(SH)] ⁺ , Fe(2)	2.1081(14)	2.3830(5)	100.2(15) ^e	0.52	tw
[Fe(TpOMePP)(SH)] ⁺	2.108(5)	2.3887(13)	106.(2) ^e	0.52	tw
[Fe(TPP)(SC ₂ H ₅)] ⁺	2.096(4)	2.360(2)		0.52	61
[Fe(TpivPP)(SC ₂ H ₅)] ⁺	2.074(10)	2.324(2)	106.64	0.44	62
[Fe(TpivPP)(OC ₆ H ₅)] ⁺	2.114(2)	1.937(4)		0.56	46
[Fe(TpivPP)(O ₂ CCH ₃)] ⁺	2.107(2)	2.034(3)		0.55	46
[Fe(TpivPP)(NO ₃)] ⁺	2.070(16)	2.069(4)		0.42	63
[Fe(TpivPP)(2-Melm ⁺)] ⁺	2.11(2)	2.002(15)		0.52	64
[Fe(TPP)(Cl)] ⁺	2.1161(11)	2.3400(5)		0.56	59
[Fe(TpivPP)(Cl)] ⁺	2.108(15)	2.301(2)		0.53	47
[Fe(TpivPP)(Br)] ⁺	2.094(3)	2.434(3)		0.49	60
[Fe(TpivPP)(I)] ⁺	2.079(2)	2.712(1)		0.40	60
Iron(III) Complexes:					
[Fe(Tp-OMePP)(SH)] ⁺	2.0155(19)	2.2928(27)	NA	0.33	29
[Fe(Proto IX DME)(SC ₆ H ₄ NO ₂)]	2.064(18)	2.324(2)	100.4(2)	0.43	65
[Fe(OEP)(SC ₆ H ₅)]	2.057(6)	2.299(3)	102.5(3)	0.47	66
[Fe(TPP)(SC ₆ HF ₄)]	2.058(2)	2.298(5)	103.7	0.40	67

^a Average Fe-N_p distance.

^b Value in Å.

^c Value in degrees.

^d Iron displacement from the four nitrogen plane.

$e_R = H.$ $f_{\text{Low Spin.}}$

Table 6

Out-of-Plane Displacements ($\text{\AA}$) of the Minimal Basis for the X-ray Crystal Structures of Five-coordinate, High-Spin Iron(II) Porphyrinates

porphyrin	D_{oop}^a	δ_{oop}^b	sad	ruf	dom	wav(x)	wav(y)	pro	ΔN_4^c	Δ^d	ref
[Fe(OEP)(SH)] ⁺ , Fe(1)	0.526	0.015	0.016	-0.207	-0.481	0.019	-0.014	0.035	0.55	0.70	tw
[Fe(OEP)(SH)] ⁺ , Fe(2)	0.514	0.012	0.324	-0.001	-0.393	-0.049	0.041	-0.003	0.52	0.64	tw
[Fe(Tp-OMePP)(SH)] ⁻	0.444	0.024	-0.316	0.090	-0.203	0.181	0.122	-0.009	0.52	0.59	tw
[Fe(OEP)(2-MeIm ⁺)] ⁻	0.772	0.005	-0.511	0.497	-0.261	0.109	-0.090	0.032	0.56	0.65	48
[Fe(TpivPP)(2-MeIm ⁺)] ⁻	0.613	0.018	0.205	0.420	-0.365	-0.154	-0.012	-0.012	0.53	0.65	64
[Fe(TpivPP)(NO ₃)] ⁻	0.574	0.012	-0.081	0.528	-0.207	-0.012	0.033	-0.001	0.55	0.65	63
[Fe(TpivPP)(O ₂ CCH ₃)] ⁻	0.582	0.008	-0.077	0.505	-0.277	0.028	0.006	0.020	0.55	0.65	50
[Fe(TpivPP)(OC ₆ H ₅)] ⁻	0.443	0.013	-0.058	0.387	-0.176	0.049	-0.100	0.003	0.57	0.63	46
[Fe(TpivPP)(SC ₂ H ₅)] ⁻	0.542	0.017	0.228	0.396	-0.290	-0.018	0.018	-0.005	0.44	0.54	62
[Fe(TPP)(2-MeIm ⁺)] ⁻	0.666	0.005	-0.536	0.080	-0.301	0.019	-0.242	-0.016	0.56	0.66	48
[Fe(TPP)(Cl)] ⁻	0.649	0.009	-0.335	-0.359	-0.398	0.098	-0.106	-0.013	0.56	0.69	59

^a Observed total distortion.

^b The mean deviations.

^c Displacement of iron from the mean plane of the four pyrrole nitrogen atoms.

^d Displacement of iron from the 24-atom mean plane.

Table 7

Selected Bond Distances and Angles for [Na(222)][Fe(Por)(SH)].

Por	Fe-N ^a	Fe-S ^a	S-H ^a	N-Fe-N ^b	Fe-S-H ^b
OEP, Fe(1)	2.1148(13)	2.3929(5)	1.31(2)	86.18(5)	98.8(12)
	2.1172(13)			86.15(5)	
	2.1219(13)			86.35(5)	
	2.1231(13)			86.65(5)	
OEP, Fe(2)	2.0976(13)	2.3830(5)	1.23(2)	87.50(5)	100.3(15)
	2.1073(14)			86.00(5)	
	2.1136(14)			86.47(5)	
	2.1138(14)			86.32(5)	
Tp-OMePP	2.105(3)	2.3887(13)	1.36(5)	86.61(12)	106.(2)
	2.105(3)			86.06(12)	
	2.108(3)			86.19(12)	
	2.116(3)			87.00(12)	

^aValue in angstroms.^bValue in degrees.