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Weak coordination of H₂S to the solid-state ferrous porphyrin complexes with diatomic

molecules. Characterization of 6-coordinate adducts at low temperature.

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Abstract.

The interaction of hydrogen sulfide (H_2S) with ferrous porphyrin five coordinate complexes bearing CO and O₂ (L) wasstudied at low temperatures in sublimated porphyrin layers using electronic and infrared absorption spectroscopy. Upon addition of H₂S to a cryostat containing Fe(II)(TPP)(L) (TPP is *meso*-tetraphenyl-porphyrinato dianion) at low temperatures, the spectral changes were observed that are consistent with H₂S binding in axial position trans to the diatomic ligand. Density functional theory (DFT) computational analysis also supports formation of the six-coordinate adducts. These complexes are stable only at very low temperature and dissociate upon warming. The stretching frequencies of diatomic ligands in the six-coordinate adducts were recorded and compared with those, known for the other thiol and thioether ligands.

Keywords.

Ferrous porpyrin; Dioxyden and carbonyl complexes; Hydrogen sulfide binding; FTIR and UVvis spectroscopy; DFT computations

Introduction

Hydrogen sulfide (H₂S) is an endogenously produced biological signaling molecule, which has been considered as a third gasotransmitter after carbon monoxide (CO) and nitric oxide (NO) [1]. Over the last two decades H₂S interaction with bioinorganic targets has been under active investigation and it is widely accepted now, that hydrogen sulfide is involved in a variety of physiological functions including smooth muscle relaxation, neurotransmission and vasoregulation [2-4]. It has also been shown that H₂S can be cytoprotective against the oxidative stress [5, 6]. Concurrent with substantial interest in the biological roles of hydrogen sulfide, new methods for H₂S quantification and detection are rapidly emerging [7-9]. H₂S is produced in the mammalian cardiovascular and central nervous system by cystathionine y-lyase and cystathionine β -synthase respectively [10, 11]. Similar to NO and CO the hydrogen sulfide functions through interaction with heme proteins. However, in contrast to these, hydrogen sulfide exists in different protonation states under physiological conditions (approximate molar ratio H_2S : $HS^- \sim 1$: 3), thus both species, heme iron- H_2S and heme iron- HS^- could potentially occur upon interaction with active centers of biological targets. One of the best studied systems, in which heme iron reversibly binds sulfide, is the HbI center of the Lucina Pectinata clam found in sulfide-rich mangrove swamps. This protein is responsible for delivering hydrogen sulfide to the living inside the gill of the clam bacteria, which oxidize H_2S in the presence of oxygen [12, 13]. Upon coordination, the hydrogen sulfide can form a stable low spin Fe(III)(HS⁻) complex or an unstable Fe(II)(SH₂) which rapidly dissociates to produce the ferrous iron Fe(II) [14, 15]. The possibility of the heme iron to transport oxygen and sulfide simultaneously has been suggested

for extracellular hemoglobins of the marine beard worm *Oligobrachia mashikoi* (Pogonophora) [16, 17] and the deep sea animal *Riftia pachyptila* (Vestimentifera) [18].

Different model bioinorganic transition metal complexes were used to probe the reactivity of H₂S/HS⁻. Pluth and coworkers have studied the interaction of H₂S and HS⁻ with zinc(II) and cobalt(II) phthalocyanine (Pc) complexes and showed that both complexes reacted with HS⁻, but not H₂S. [19]. The same authors have later reported H₂S/HS⁻ reactivity with series of ferrous and ferric FeTPP, and protected picket-fence Fe(TpivPP) complexes at ambient conditions. H₂S complexation was not detected, while ligation by an equivalent of HS⁻ was revealed for picket-fence and tetraphenyl porphyrin systems [20]. Scheidt and coworkers investigated the interaction of the hydrosulfide ion (HS⁻) with iron porphyrinates (octaethylporphyrinate and tetra-p-methoxyphenylporphyrinate) and showed the formation of $[Fe(Por)(SH)]^{-}$, $[Fe(Por)(SH)_2]^{2-}$, and the mixed-ligand species $[Fe(Por)(Im)(SH)]^{-}$ (Im = Imidazole) [21]. Tonzetich and coworkers have reported the reactivity of iron(III) porphyrinates containing silanethiolate ligands with several biologically relevant small molecules including H₂S [22]. Recent report from the same group described reactivity and binding constants determination for hydrosulfide adducts [Fe(Por)(SH)] of several tetraarylporphyrins [23]. Strianese and Pellecchia, published the series of papers providing evidence that reactions of hydrogen sulfide with Cu- and Zn porphyrin complexes leads to stabilization of the resulting hydrosulfide complexes [24-26]. These studies show that the model complexes do not bind H₂S in the ambient temperature solutions. In contrast, HS⁻ acts as a good ligand forming hydrosulfide complexes.

A less studied aspect of sulfide biochemistry is the potential of neutral H_2S to coordinate with bio-inspired metal centers. There are only few H_2S ligated transition-metal complexes

reported until today. Among them ruthenium complexes, which are able to reversibly coordinate H_2S under anaerobic conditions [27-30]. The air stable [Ru(IMes)₂(CO)(H₂S)H₂] complex was obtained by addition of H₂S gas to the initial [Ru(IMes)₂(CO)(EtOH)H₂] (IMes 1,3-bis(2, 4, 6 trimethylphenyl)imidazol-2-ylidene) [31]. Bubbling H₂S through a tetrahydrofuran solution of $[Sn^{IV}(PPIX)(THF)_{1-2}]^{2+}$ (PPIX- protoporphyrin IX) produced a bathochromic shift in the Soret band that is believed to be consistent with ligand coordination to form $[Sn^{IV}(PPIX)(H_2S)]^{2+}$ [32]. Recently, Galardon and co-workers reported a structure of hydrogen sulfide iron(II) complex, which was stabilized by an intramolecular hydrogen bond. The starting complex [(L)Fe]·BPh₄, in which iron(II) coordinated to the five nitrogen donors and to the oxygen of a carboxamidato group, reacted with hydrogen sulfide in dichloromethane or acetonitrile to give the H₂S ligated derivative [33]. To the best of our knowledge, the studies by Collman and co-workers using a cytochrome c oxidase (CcO) model, is the only investigation, which shows that heme-iron of both ferrous Fe-only and Fe-Cu binuclear site complexes (containing distal histidine) are able to coordinate the hydrogen sulfide, although mass spectroscopic studies revealed two H₂S molecules at the iron site, possibly hydrogen bounded [34].

Motivated by the growing interest in the biochemical functions of hydrogen sulfide and lack of the detailed information on the H_2S ligated synthetic heme systems, we extend the utility of the solvent-less media and low-temperature technique to investigate H_2S reactivity with iron porphyrins. Metal tetraaryl-porphyrins, sublimed onto a low temperature substrate form amorphous microporous layers. Subsequent addition of the ligand vapors allows one to construct different 5 and 6 coordinate complexes, which can be easily characterized by UV-visible and infrared spectroscopy without solvent interference [35]. In addition, FTIR spectroscopy is a powerful tool for investigation the active sites of hemoproteins and model systems, due to high

sensitivity of coordinated CO (O_2) stretches to the *trans*-influence of axial ligands. Both, dioxygen and carbon monoxide have been widely used previously, as a sensitive probe of the heme active site structure in proteins and model complexes, because of the strong metal-ligand back-bonding interactions, which allow to obtain important information about the presence and nature of the *trans* ligands [36-39]. Here we report the reactivity of H₂S with 5-coordinate complexes of Fe(II)(TPP)(O_2) and Fe(II)(TPP)(CO) at very low-temperatures and give direct spectroscopic evidences of formation respective 6-coordinate adducts, that is otherwise not possible in solutions or at ambient conditions.

2. Experimental section

Material and Measurements: $Fe(TPP)(Pip)_2$ or $Fe(TPP)(Py)_2$ complex, synthesized according to published methods [40], were used as a source of Fe(TPP). The Fe(TPP) sublimates on KBr or CaF₂ substrates of optical cryostats were obtained under continuous vacuum conditions, according to the procedure described elsewhere [35]. The hydrogen sulfide was prepared by heating the mixture of elementary sulfur and paraffin wax [41] in vacuum system and purified by multiple vacuum distillation before use. The IR spectra of the H₂S condensed on the low temperature substrate of cryostat and in the gas phase showed no impurities presence [42].

The dioxygen or carbonyl complexes were obtained by addition of a known quantity of O_2 or CO gas, measured with mercury manometer, to the low temperature (77 K) Fe(TPP) layers. After the formation of the corresponding five-coordinate complexes monitored by FTIR (the samples were allowed to warm up to ~100 K in the case of the dioxygen complex and up to ~220 K for the mono-carbonyl complex), the excess gas was pumped out, the samples were cooled down to 77 K and small quantities of H₂S, controlled by a mercury manometer, were introduced

into the cryostat. Formation of the adducts prepared for UV–Vis measurements in the 450-700 nm range were first confirmed by FTIR spectroscopy and the visible spectra were then recorded. The ¹⁸O₂ (Cambridge Isotope Laboratories, Inc., 95%) and ¹³CO (Institute of Isotopes, Republic of Georgia, with isotopic enrichment 98,5%) were used to obtain the corresponding isotopically substituted complexes. The infrared spectra were measured on Nicolet "Nexus" FTIR spectrometer and the UV–Vis spectra were measured on a "Specord M-40" and Nicolet "Helios Gamma" spectrophotometers. All density functional theory (DFT) calculations were performed at unrestricted TPSSTPSS/DGDZTVP and/or B3LYP/6-31G* levels of theory in vacuum using Gaussian'16 and/or Spartan'14 software packages.

3. Results and discussions

3.1. Reaction of dioxygen and monocarbonyl complexes of Fe(TPP) with hydrogen sulfide.

An earlier work has demonstrated that Fe(II)(TPP) is capable of O₂ binding in the Ar matrix at 15 K with $v(O_2)$ of the bent form at 1195 cm⁻¹ [43]. The reaction of Fe(II)(TPP) sublimed layers with dioxygen at 80-100 K results in the formation of a new IR band at 1185 cm⁻¹ assigned to $v(O_2)$ of coordinated dioxygen [44]. This band is specific to the iron tetraaryl-porphyrins dioxygen complexes and disappears when the O₂ ligand dissociates under vacuum at elevated temperatures. When ¹⁸O₂ is used to obtain the dioxygen complex this band occurs at 1114 cm⁻¹, which is in good agreement with the 68 cm⁻¹ shift, calculated in the diatomic harmonic oscillator approximation. The IR spectral changes obtained before and after the addition of H₂S into the cryostat containing dioxygen adduct of Fe(TPP) are shown in Fig.1.



Fig.1. FTIR spectra of sublimed Fe(II)(TPP) layers in the range of coordinated O_2 (a) and ${}^{18}O_2$ (b) at 130 K. Solid line – Fe(TPP), dashed line – Fe(TPP)(O_2), dotted line – spectra obtained after suppling 15 torr of H₂S to the cryostat containing Fe(TPP)(O_2) at 80 K and slow warming to 130 K.

It is seen from Fig.1, that upon warming from 80 K to 130 K the $v(O_2)$ of the coordinated dioxygen completely shifts down from 1185 to 1170 cm⁻¹ (from 1114 to 1100 cm⁻¹ when ¹⁸O₂ was used). These observations led us to conclude that the (O₂)Fe(TPP)(SH₂) has been formed.

This is also in agreement with previous spectroscopic results, showing that the coordination of the *trans* donor ligand upon formation of six-coordinate iron porphyrin adducts results in the $v(O_2)$ shift to the lower frequencies [37, 38, 45]. This six-coordinate complex is very unstable. Warming of the H₂S ligated oxyferrous adduct above 130 K leads to a slow disappearance of the $v(O_2)$ band at 1170 cm⁻¹, indicating nearly concomitant loss of both ligands, the coordinated H₂S and O₂.



Figure 2. Visible spectrum of Fe(TPP) (solid line), Fe(TPP)(O_2) (dashed line) and spectra obtained after suppling 10 torr of H₂S to the cryostat containing Fe(TPP)(O_2) at 80 K and slow warming to 130 K (dotted line).

Formation of the six-coordinate adduct is also supported by visible spectral changes observed upon ligation of $Fe(II)(TPP)(O_2)$ by hydrogen sulfide (Fig.2). Upon formation of the dioxygen adduct the prominent peak of Fe(TPP) at 544 nm shows a shift to 532 nm, similar to previously reported oxyferrous porphyrin complexes [37, 44]. The subsequent treatment of the $Fe(TPP)(O_2)$ with H₂S at 110-130 K leads to the spectral changes, which are consistent with the formation of $(O_2)Fe(TPP)(SH_2)$ and represented by the batochromic shift from 532 nm to 547 nm, and the growth of a new absorbance band at 585 nm. These bands resemble those observed

in the reaction of $Fe(II)(TPP)(O_2)$ with S- and N-donors [38, 44] further supporting the assignment of the species in Figure 1 as the six-coordinate iron(II) complex.

When discussing the formation of the $(H_2S)Fe(TPP)(O_2)$ complex, one should address a possible oxidation of H_2S by hemoglobin and myoglobin in the presence of oxygen, as was reported earlier. For example, interaction of H_2S with the oxygenated form of human hemoglobin and myoglobin produces a sulfheme protein complex, that has been implicated in H_2S degradation. The final sulfheme product is a modified chlorin-type heme with a sulfur atom incorporated into one of the pyrrole rings [46, 47]. More recently, several papers have described a new chemical interaction between ferric neuroglobin, myoglobin, hemoglobin and H_2S that leads to catalytic turnover of sulfide. The products of this heme-promoted sulfide oxidation are thiosulfate and iron-bound hydropolysulfides [48-51]. We can however, rule out the further H_2S reactivity for the following reasons.

In the natural hemes proximal and distal histidine (His) residues are present, which trigger the formation of ferryl intermediate and final products as has been proposed for the mechanism of catalytic H₂S degradation reaction [48,49,51]. These hemes catalyzes sulfide conversion to a mixture of thiosulfate and polysulfides only at aerobic conditions. Under anaerobic conditions, the decrease in free H₂S concentration is proportional to the heme concentration and consistent with H₂S binding to the iron but not being oxidized further [48, 51]. It follows that excess of O_2 is required for the further conversion of initially bound sulfide to the products. In our experiments with model iron porphyrins only stoichiometric amount of coordinated O_2 is present under excess H₂S. We assume therefore, that if even porphyrin modification or iron bound polysulfides were formed at the stoichiometric level, they should be readily detected. Indeed, as has been shown by X-ray crystallography, metallochlorin and

metalloporphyrin molecules have profoundly different structural properties. For example, whereas Ni tetramethylporphyrin with essentially planar macrocycle has a center of inversion with D_{4h} symmetry, the Ni tetramethylchlorin is S₄-ruffled and extremely nonplanar, thus losing an inversion center [52]. Consequently it may be suggested, that metalloporphyrin and metallochlorin molecules should have also substantially different vibrational properties. Formation of metallochlorin (or heteroatom insertion into the one of pyrrole rings of the metalloporphyrin) results in the loss of inversion center and decrease in effective molecular symmetry. Thus, the several modes are no longer IR forbidden and should become active increasing complexity of the metallochlorin IR spectrum [53]. Earlier analysis of the FTIR and Resonance Raman spectroscopic properties of Cu(II) tetraphenylporphyrin with respective chlorin analogue revealed more complex IR spectrum of Cu(II)TPC with appearance of the set of new bands [54]. The most notable new feature is a strong IR band near 1621 cm⁻¹, which is completely absent in porphyrin derivative. On the best of our knowledge, vibrational spectra of iron bound polysulfides of the heme or model compounds are not reported. However it is known, that metal bounded di- and polysulfides show intensive v(S-S) bands in the 480-600 cm⁻¹ of IR spectra [55]. For example, the IR spectrum of molybdenum disulfide showed intensive Mo-S band in the 499 cm⁻¹ and a broad peak at 520 cm⁻¹ attributed to S–S stretching vibrations [56]. Similarly v(S-S) of Fe₂(S₂)(CO)₆ was found at 555 cm⁻¹ [53]. Electronic absorption spectra of metalloporphyrin and metallochlorin are also different. The lowest energy Q transition in metallochlorins is significantly more pronounced relative to metalporphyrins and produces the very intense "chlorin" transition observed near 600 nm concomitant with the other relatively weak new Q transition. [57]. For example, whereas Soret band in Cu(II)TPP with respective chlorin analogue remain almost unchanged, while substantially changes with the formation of a

new very intense absorption at 616 nm were observed in the Q region [54]. We also preclude formation of reactive oxoferryl (O=Fe(TPP) compound in our simple system, because generation of this species using heme models requires strong chemical oxidant, or can be achieved by electrooxidation or photolysis [58]. Comparison of the IR spectra freshly sublimated Fe(TPP) with that obtained after ligands dissociation and pumping from $(H_2S)Fe(TPP)(O_2)$ (not shown) did not revealed any difference suggesting that H_2S oxidation (or porphyrin moiety modification) do not take place under our experimental conditions. The absence of intense band near 600 nm in our visible spectra during and after reaction also supports this conclusion.

Exposure of the Fe(TPP) sublimed layers to excess CO gas at 80 K results in the formation of a very strong IR band at 2028 cm⁻¹ and a smaller one at 1960 cm⁻¹ assigned earlier to the bis- and mono-coordinated linear carbonyl species respectively [59]. Upon pumping out of the excess CO gas and slowly warming, a six-coordinated species converts into a five-coordinated, that reflected by disappearance of the band at 2028 cm⁻¹ and rise in intensity of the band at 1960 cm⁻¹, which reaches its maximum at 200 K.





Fig. 3. FTIR spectra of sublimed Fe(TPP) layers in the range of coordinated CO: (a) solid line - Fe(TPP)(CO), dashed line - spectra obtained after suppling the H_2S (12 torr equiv.) to the cryostat containing Fe(TPP)(CO) at 77 K and slow warming to 130 K, (b) spectral changes during the same reaction of Fe(TPP)(¹³CO) and H_2S .

Figure 3 shows the infrared spectra of the monocarbonyl complex Fe(TPP)(CO) (a small amount of $Fe(TPP)(CO)_2$ is formed again upon cooling the sample back to 77 K) before and after treatment with hydrogen sulfide. The shift of v(CO) from 1960 cm⁻¹ (1915 cm⁻¹ for ¹³CO) to 1974 cm⁻¹ (1930 cm⁻¹ for ¹³CO) confirms the conversion to the six-coordinate complex. Similar IR spectral pattern was observed, when six-coordinate ethanthiol (EtSH) and dimethylsulfide (Me₂S) ligated ferrous porphyrin carbonyl adducts were formed at low temperatures [44]. The (CO)Fe(TPP)(SH₂) releases hydrogen sulfide at temperatures above 140 K. At the room temperature, only a small band of partially decomposed Fe(TPP)(CO) is seen in the IR spectra.

The visible spectra of the Fe(TPP)(CO) and (CO)Fe(TPP)(SH₂) are displayed in Fig. 4. The spectrum of the carbonyl complex is similar to those reported earlier in toluene solution [57]. Coordination of the sixth ligand is accompanied with the appearance of the absorbance bands at 547 and 580 nm. The spectral changes upon formation (CO)Fe(TPP)(SH₂) are almost

identical to those we have earlier reported for the low-temperature six-coordinate adducts with Me_2S and EtSH instead of H_2S [44].





Fig. 4. Visible spectra of Fe(TPP) (solid line), Fe(TPP)(CO) (dashed line) and spectrum obtained after suppling 10 torr of H_2S to the cryostat containing Fe(TPP)(CO) at 80 K and slow warming to 130 K (dotted line).

DFT computational analysis confirms the viability of six-coordinate model compounds Fe(II) Porphine (P) with an axial H₂S *trans* to CO or O₂ ligands. Both Fe(P)(CO)(H₂S) and Fe(P)(O₂)(H₂S) converged with a distance Fe-S of 2.46 and 2.50 Å, strongly suggesting H₂S coordination to iron. The Fe–S distances are comparable with the recently reported for hydrogen-sulfido iron(II) derivative [33]. Comparison of the calculated vibrational frequencies of CO in Fe(P)(CO) and Fe(P)(CO)(H₂S) reveals the modest increase in v(CO) by 6 cm⁻¹, which is close to the experimental value. In addition, The Fe-CO bond has increased by 0.02 Å, and C-O bond has very slightly shortened upon H₂S coordination. These changes are consistent with a decreased population of π^* orbitals of the carbonyl ligand due to sigma *trans* interaction between CO and H₂S ligand mediated by *d*-orbitals of Fe, as seen on a HOMO-1 orbital, Fig.5. This orbital is obviously nonbonding with respect to H₂S showing a nodal plane between Fe and S

atoms. This helps to understand the low stability of $Fe(P)(CO)(H_2S)$ and easy loss of hydrogen sulfide with increase in temperature. Similar arguments can be made with regards to $Fe(P)(O_2)(H_2S)$ as well.



Fig. 5. Calculated HOMO-1 orbitals for $Fe(P)(CO)(H_2S)$ (a) and $Fe(P)(O_2)(H_2S)$ (b)

It may be suggested, that other interactions, such as hydrogen bonding of the H₂S with the O atoms (either the coordinated dioxygen or the carbon monoxide) can be responsible for the shifts of their stretching frequencies. Indeed, it has been reported that H₂S may form weak Hbonds of type H₂S – HSH and H₂O – HSH [60]. A small shift (~3 cm⁻¹) of v(CO), as a result of the H-bonding between H₂S and adsorbed CO molecules has also been reported [61]. Formation

of the H-bond by H_2S would be expected to lead to the decrease in the value of S-H stretching in comparison to its free value, and weak perturbation of the H-bond acceptor frequency. However, the significant shifts of the coordinated v(CO) and v(O₂) bands (Table1) in the IR spectra when reacting with hydrogen sulfide, comparable positions of these bands for H_2S and Me_2S (which is not an H-bond donor) ligands and the unchanged frequencies of these peaks upon evacuation of the excess ligand cannot be caused by hydrogen bonding. Moreover, distinct changes in visible spectra rule this possibility out.

Additional IR evidence of the H₂S coordination to the iron center might be detection of the S-H stretch of the coordinated hydrogen sulfide. This (usually weak) band has been detected for several Ru(II) complexes. The v(SH) between 2340 and 2400 cm⁻¹ in $[Ru(H_2S)(PPh_3)('S_4')]$ was reported by Sellman [27]. James and co-workers have detected the v_3 and v_1 vibrations of the coordinated H₂S in the few ruthenium complexes at 2506–2495 and 2476–2449 cm⁻¹ regions respectively [30]. Collman and co-workers have reported that ferrous Fe-only and Fe-Cu of binuclear site cytochrome c oxidase model complexes exhibit weak S-H stretch at 2250 cm⁻¹, which shifts to 1600 cm⁻¹ using D_2S [34]. We detected the v_3 , v_1 , and v_2 vibration modes of the adsorbed H₂S at 2549, 2528 and 1168 cm⁻¹ respectively at 77 - 100 K (Fig. S1). However, in the IR spectra of both complexes, where the sulfide coordination are confirmed by the shift in the frequency of the diatomic ligand, we were failed to detect and certainly assign the S-H stretch, possibly because the v(SH) is masked by the broad band of the H₂S excess (Fig. S1). It should be noted, that the formation of the six-coordinate dioxygen and carbonyl complexes required large excess of hydrogen sulfide. Removal of H₂S excess under high vacuum at the temperature near 130K did not help to detect coordinated v(SH). Evacuation at elevated temperatures results in almost simultaneously losing of both ligands in dioxygen complex, while mostly H₂S detachment takes place for carbonyl adduct.

Complex	$\nu(O_2)$	$v(^{18}O_2)$	v(CO)	v(¹³ CO)
Fe(TPP)	1185	1114	1960	1915

Fe(TPP)(H ₂ S)	1170	1100	1974	1930
Fe(TPP)(EtSH)*	1166	1099	1978	1935
Fe(TPP)(Me ₂ S)*	1164	1097	1980	1937

Table 1. The stretching frequencies of coordinated diatomic ligands in the mixed complexes of Fe-porphyrins with sulfur donor ligands (L)Fe(TPP)(S-donor) (L = O_2 , CO). *- Ref. 44

Table 1 presents the infrared stretching frequencies of O_2 and CO in the series of Fe(TPP) adducts containing S-donors and illustrates the relative influence of the *trans* ligands.

It is known, that in the model iron porphyrin complexes O_2 and CO adopt bent and linear coordination geometry respectively. The dioxygen and carbonyl binding to porphyrin iron is well explained in terms of both σ -donation from CO (O_2) to iron d_{z^2} orbital and π -back-bonding of iron d_{π} to CO (O_2) π^* orbitals. The degree of back-bonding is correlated to the relative energies of the ligands π orbitals and is significant for Fe(II)(TPP)O₂ complex, while much less charge transfer from the metal take place in case of Fe(II)(TPP)CO [62]. Indeed, the v(O₂) and v(CO) values in the gas phase at 1540 cm⁻¹ (in Raman) and 2143 cm⁻¹ are decreased to 1185 cm⁻¹ and 1960 cm⁻¹ respectively when coordinated to Fe(TPP) in our experiments. However, as evidenced by experimental results and theoretical calculations the responses of the O₂ and CO adducts to *trans* ligand binding are different [63].

Coordination of the donor ligand *trans* to dioxygen increase the back-bonding and lead to the lower $v(O_2)$ frequencies. As it can be seen from the Table 1, the coordination of the H₂S

results in 15 cm⁻¹ downshift of $v(O_2)$, while binding of ethanethiol and dimethylsulfide caused 19 and 21 cm⁻¹ shift respectively. This is in agreement with a weak σ -donor properties of this ligands and greater electron donor ability of the alkyl group in comparison to hydrogen [64]. The $v(O_2)$ at 1157 cm⁻¹ was reported for a strong σ -donor piperidine ligand in Fe(TPP)(O₂)(pip) complex [38].

Comparison of v(CO) values in Table I show that binding of H₂S, EtSH and Me₂S shifts the v(CO) to the higher frequencies by 14 cm⁻¹, 18 cm⁻¹ and 20 cm⁻¹ respectively. It might be expected that this trend reflects the competition between the CO and the *trans*- ligands for the d_{π} electrons of Fe(II). Thioethers and thiols are also weak π -acceptors [65] and are able to compete for iron d_{π} electrons thereby decreasing the electron density on the CO π *-orbital, that leads to the increase of v(CO). Indeed, if the sixth ligand is also CO (bis-carbonyl complex) the v(CO) increases from 1960 to 2028 cm⁻¹ (in sublimated layers). The v(CO) of mono and biscarbonyl complexes of Fe(TPP) were reported at 1973 and 2042 cm⁻¹ in nujol mull [60]. Iron octaethylporphyrin complexes Fe(OEP)(CO), Fe(OEP)(CO)(1-MeIm) and FeOEP(CO)₂ revealed v(CO) at 1944 , 1980 and 2021 cm⁻¹ respectively [66]. The solid state complex Fe(TPP)(CO)(Py) showed v(CO) at 1983 cm⁻¹ [67].

The lowest shifts of both $v(O_2)$ and v(CO) caused by H₂S coordination among ligands listed in the Table1 are in correlation with a weak binding and low stability of these adducts. The complexes of Me₂S and EtSH with Fe(TPP)(O₂) were still stable at slightly higher temperatures (at 150 K instead 130K in H₂S case), before decomposition at elevated temperatures. At the same time, the carbonyl complexes of Fe(TPP)(CO) with Me₂S and EtSH were significantly more

stable than with H_2S and retained six-coordination at room temperature in the presence of a few torr of S-donors in the cryostat [44].

It is widely accepted that a low-spin state is diagnostic of six-coordination in both ferrous and ferric states [68]. Early studies has established relationship between positions of some marker bands in the IR and RR spectra of axial complexes Fe(TPP) and spin states of the iron center. The bands in the range 1350–1330 cm⁻¹, and 469–432 cm⁻¹ have been detected at higher wavelengths in low spin complexes [69]. In sublimated Fe(II)(TPP) which has an intermediate (triplet) spin state [70], this bands are displaced at 1346 cm⁻¹ and 466 cm⁻¹. Formation of the Fe(TPP)(O₂) and Fe(TPP)(CO) is accompanied with small shifts of the marker bands in both adducts and their peak positions are still in the range, suggesting low spin state of these complexes (Fig. S2). Upon subsequent generation of six-coordinate sulfide adducts, no further shifts were observed. The low spin state was established for six coordinate iron porphyrin carbonyl and dioxygen complexes with N-donors [37, 71], however intermediate spin state of (H₂S)Fe(TPP)(O₂) adduct cannot be excluded.

4. Conclusion.

FTIR and UV-vis experiments, as well as DFT computations provide evidences that H_2S coordinates at the metal center of the ferrous tetraphenylporphyrin monocarbonyl and dioxygen adducts at very low temperatures. By using infrared spectroscopy we have measured the v(O₂) and v(CO) of the six-coordinate complexes, containing neutral H_2S as a *trans* ligand, suggesting a weak bonding of H_2S in both adducts. These findings show that neutral hydrogen sulfide can act as a ligand in the ferrous centers of biologically relevant targets.

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Appendix A. Supplementary data.

Fig.S1. IR spectroscopic data for $(H_2S)Fe(TPP)(O_2)$ formation in the range 400-3000 cm⁻¹, Fig.S2. IR spectroscopic data of spin sensitive bands, DFT calculation results, atomic coordinates, additional orbital pictures.

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- The interaction of hydrogen sulfide (H₂S) with ferrous porphyrin monocarbonyl and dioxygen complexes was investigated.
- (H₂S)Fe(II)(TPP)(CO) and (H₂S)Fe(II)(TPP)(O₂) adducts were stabilized at low temperatures and studied by spectoscopic methods.
- Density functional theory (DFT) computations supports formation of the six-coordinate adducts.
- Influence of H₂S coordination on the stretching frequencies of diatomic ligands are compared with those, known for the other S- and N- donor ligands.

TOC



FTIR, Uv-Vis and DFT data support formation of the weak six -coordinate ferrous porphyrin adducts (H₂S)Fe(Por)(O₂) and (H₂S)Fe(Por)(CO) in solid state at low temperatures.