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Статья

Low Temperature Spectroscopic Study of the Sulfides Binding by Dioxygen Adduct of Cobalt Porphyrin

Garik G. Martirosyan,[a@] Astghik A. Hovhannisyan,[a] Arsen S. Azizyan,[a]
Gohar S. Hovhannisyan,[a] and Alexei V. Iretskii[b]

[a]*The Scientific Technological Centre of Organic and Pharmaceutical Chemistry NAS RA, Molecule Structure Research Centre, 0014 Yerevan, Armenia*
[b]*Lake Superior State University, Department of Chemistry, Sault Ste. Marie, MI 49783, USA*
[@]*Corresponding author E-mail: ggmartirosyan@gmail.com*

Dedicated to the blessed memory of our beloved leader,
colleague and friend Tigran Kutikyan

The interaction of dimethyl sulfide ($(CH_3)_2S$) and hydrogen sulfide (H_2S) with cobalt porphyrin and its five-coordinate dioxygen complex was studied at low temperatures in sublimated porphyrin layers using electronic and infrared absorption spectroscopy. Upon addition of sulfides to a cryostat containing $Co(TTP)O_2$ (TTP is meso-tetratolyl-porphyrinato dianion) at low temperatures, the FTIR and Vis electronic spectral changes were observed which are consistent with sulfide binding in axial trans-position to dioxygen. Density functional theory (DFT) computational analysis also supports formation of the six-coordinate adducts. These complexes are stable only at low temperatures and dissociate upon heating.

Keywords: Cobalt porphyrins, dioxygen complex, coordinated sulfides, infrared spectroscopy.

Низкотемпературное спектральное исследование присоединения сульфидов кислородным комплексом порфирината кобальта

Г. Мартиросян,[a] А. Оганесян,[a] А. Азизян,[a] Г. Оганесян,[a] А. Ирецкий[b]

[a]*Научно-технологический центр органической и фармацевтической химии НАН, Центр исследования строения молекул, 0014 Ереван, Республика Армения*
[b]*Государственный университет Лейк-Супериор (озера Верхнее), Солт Сент. Мари, Мичиган 49783, США*
[@]*E-mail: ggmartirosyan@gmail.com*

Посвящается светлой памяти нашего любимого руководителя, коллеги и друга
Тиграна Степановича Куртикяна

Методами электронной и инфракрасной абсорбционной спектроскопии изучено взаимодействие диметилсульфида ($(CH_3)_2S$) и сероводорода (H_2S) с порфирином кобальта и его пяти-координированным кислородным комплексом при низких температурах в сублимированных слоях порфирина. При добавлении паров сульфидов в криостат, содержащий $Co(TTP)O_2$ (TTP – мезо-тетратолил-порфиринат дианион) при низких температурах, наблюдались изменения в Фурье ИК и видимом спектрах, которые согласуются со связыванием сульфида атомом кобальта в аксиальном к кислороду положении. Теоретические расчеты также подтверждают образование шести-координированных аддуктов. Эти комплексы стабильны только при низких температурах и диссоциируют при нагревании.

Ключевые слова: Порфиринат кобальта, кислородный комплекс, координированный сульфид, ИК спектро-скопия.

Introduction

Dioxygen is one of the most important molecules for aerobic life. In biological reactions, metalloenzymes bind and activate O_2, generating metal–oxygen intermediates, such as metal-superoxo, -peroxo, -hydroperoxo, and -oxo species. Biomimetic coordination and activation of dioxygen by metalloporphyrins has been intensively investigated over the past several decades.[1,2] The interaction of molecular oxygen with model Fe porphyrins has received considerable attention because its relevance to the physiological problems of dioxygen storage, transport, as well as generation of highly reactive metal-oxygen intermediates that undergo a wide range of subsequent reactions.[3] In the studies of O_2 binding, beside the model iron porphyrins, a number of other transition metal porphyrins were also investigated to better understand the metal-O_2 bonding nature and effects of the proximal ligands on the O-O bond in native hemoproteins.[4,5] The cobalt porphyrins are among the most common models for the active sites of heme-proteins, which have a biological task of carrying dioxygen. However, at the ambient temperature unprotected porphyrins of the bivalent metals are rapidly oxidized by dioxygen, demanding low-temperature conditions for stabilization of oxy-complexes.[6]

While six-coordinate cobalt porphyrin dioxygen complexes with axial N-donor have been a subject of many investigations,[7–10] a little is known on the complexes bearing S-donor ligands. On the best of our knowledge, the only six-coordinate cobalt porphyrin dioxygen complexes with trans S-donors were studded by Kazuo Nakamoto group, who made an invaluable contribution to the field of coordination chemistry of porphyrins and other organometallic compounds. By means of resonance Raman spectroscopy it has been shown, that at low temperatures cobalt porphyrins are able to form mixed dioxygen complexes with both, thiophenol and its deprotonated form – thiophenolate.[11]

At the same time, reactions of sulfides, especially H_2S with model bioinorganic transition metal complexes is of interest, due to in the light of recent research the hydrogen sulfide has been considered as a third signaling molecule after carbon monoxide (CO) and nitric oxide (NO) and exhibits a variety of important biological functions.[12] H_2S is produced in the mammalian cardiovascular and central nervous system and functions through interaction with heme proteins.[13,14] Under the physiological conditions hydrogen sulfide exists in different protonation states (H_2S or $HS^- \sim 1/3$), thus both species, neutral and deprotonated, could potentially interact with active centers of biological targets. Based on the importance of heme iron in biological systems, the majority of investigations on H_2S reactivity have focused on iron-based systems which usually form HS^- bound complexes.[15,16]

The H_2S ligated transition-metal compounds are quite rare. The only air stable ruthenium complex and several, which are able to reversibly coordinate H_2S under anaerobic conditions, have been reported.[17–20] The [(L)Fe]·BPh_4, (L – five nitrogen donors) reacted with hydrogen sulfide in solution to give the H_2S ligated derivative. X-Ray analysis revealed hydrogen(sulfido) iron(II) complex, where H_2S was stabilized by an intramolecular hydrogen bond.[21]

The studies of 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 are able to coordinate the hydrogen sulfide.[22]

Metallo-porphyrins and phthalocyanines have been also used to study the chemistry of H_2S/SH^- interactions with metal centers as the possible H_2S gas sensors.[23] Moreover, the extra-complexes of porphyrinates with sulfur-containing organic compounds have been proven to be effective catalysts.[24,25] Investigation of H_2S and HS^- interaction with zinc(II) and cobalt(II) phthalocyanine complexes revealed that both complexes react with HS^-, but not H_2S.[26] Similar studies with series of ferrous and ferric FeTPP, and protected iron porphyrin complexes showed ligation by HS^-, while H_2S binding was not detected.[27] The same group has later reported the studies of chemical reactivity of hydrogen sulfide with a series of Mg(II), Cu(II), Co(II), Zn(II), Cr(II), Sn(IV), and Mn(II/III) protoporphyrin complexes by UV-Vis, NMR and EPR spectroscopy. [28] These studies did not reveal the ability to coordinate H_2S in none of the studied compounds, although some of them formed complexes with HS^-. An interaction of the hydrosulfide ion HS^- with iron porphyrinates shows the formation of $[Fe(Por)(SH)]^-$, $[Fe(Por)(SH)_2]^{2-}$, and the mixed-ligand species $[Fe(Por)(Imidazole)(SH)]^-$.[29] These studies show that the model porphyrin complexes do not bind H_2S in ambient temperature solutions. Although there are many studies devoted to the interaction of H_2S with heme-containing proteins, there are many unresolved questions related to the interaction of H_2S with the heme metal center and the nature of the H_2S-heme binding, which requires more experimental efforts. For instance, ability of the heme iron to transport oxygen and hydrogen sulfide simultaneously has been suggested for extracellular hemoglobins of the marine beard worm *Oligobrachia mashikoi* (Pogonophora)[30] and deep sea animal *Riftia pachyptila* (Vestimentifera).[31]

Earlier we reported that neutral S-donors, dimethyl sulfide and ethanethiol can form six-coordinate complexes with Fe(TPP)(O_2) at 150 K.[32] Later we conducted similar experiments using H_2S as a ligand and reported IR and UV-vis evidences of the formation of weak bounded (H_2S)Fe(TPP)(O_2) adduct at low temperatures.[33] These studies show that coordinated dioxygen can act as a good marker of axial coordination of sulfides. Herein, we extend this work to the cobalt analog by examining the $(CH_3)_2S$ and H_2S binding by a five-coordinate dioxygen complex of cobalt porphyrin through infrared and visible electronic spectroscopy, as well as the DFT calculations. Specifically, we show that $(CH_3)_2S$ and H_2S bind to the coordinatively unsaturated Co porphyrin center to give a six-coordinate superoxo species.

Experimental

Co(TTP) complex was synthesized according to published methods.[34] The porphyrin sublimates on KBr substrates of optical cryostats were obtained under continuous vacuum conditions, according to the procedure described elsewhere.[35] The hydrogen sulfide was prepared and purified as described in [33]. The dioxygen complexes were obtained by addition of a known quantity of O_2

gas, measured with mercury manometer, to the low temperature (77 K) Co(TTP) layers. After the formation of the corresponding five-coordinate complexes monitored by FTIR (the samples were allowed to warm up to ~100 K), the excess O_2 was pumped out, the samples were cooled down to 77 K and small quantities of $(CH_3)_2S$ or H_2S, controlled by a mercury manometer, were introduced into the cryostat. In some cases, six-coordinate complexes were prepared as follows. The sulfides were introduced to the cryostat firstly at 77 K, the samples were allowed to warm up to ~130 K and again cooled to 77 K. Then dioxygen was added and reaction was monitored under the excess of O_2. Formation of the adducts prepared for electronic absorption measurements in the 450–700 nm range were first confirmed by FTIR spectroscopy and then visible spectra were recorded. The $^{18}O_2$ (Cambridge Isotope Laboratories, Inc., 95 %) 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 Nicolet "Helios Gamma" spectrophotometer. All density functional theory (DFT) calculations were performed at unrestricted TPSSTPSS/DGDZTVP level of theory in vacuum using Gaussian'16 software packages.

Results and Discussion

Five-coordinate base-free dioxygen adducts of iron(II) and cobalt(II) porphyrins are very unstable and can be prepared only at low temperature conditions. An earlier work has demonstrated that Co tetraphenylporphyrin was capable of binding O_2 in the bent form in Ar matrix at 15 K with $\nu(O_2)$ at 1278 cm^{-1}.[36] Addition of dioxygen to the cryostat containing sublimed Co(TTP) layers at 77 K results in formation of the new IR band at 1250 cm^{-1} previously assigned to the coordinated O_2.[37] When isotopic $^{18}O_2$ was used, this band appears near 1184 cm^{-1}. The isotopic shift of 66 cm^{-1} is in good agreement with 68 cm^{-1} value calculated in the approximation of a harmonic diatomic oscillator. Addition of $(CH_3)_2S$ vapors into the cryostat containing dioxygen adduct of Co(TTP) at 77 K and slow warming to ~130 K results in disappearance of the band at 1250 cm^{-1} and formation of the new band at 1161 cm^{-1}. In experiments with $^{18}O_2$ the latter band appears at 1095 cm^{-1}.

This transformation is inherent in the sixth ligand binding in *trans*-position to dioxygen and led us to conclude that the $((CH_3)_2S)Co(TPP)(O_2)$ adduct has been formed under our experimental conditions. This is also in agreement with previous spectroscopic results, showing that the $\nu(O_2)$ in the six-coordinate $Co(Porphyrin)(L)(O_2)$ adducts appears at the lower frequencies than in the five-coordinate.[4] For example, the $\nu(O_2)$ band of $(1\text{-MeIm})Co(TPP)(O_2)$ is shifted down to 1144 cm^{-1} [8] because electron donation from the base ligand leads to increase of the negative charge on coordinated O_2, weakening the O-O bond and strengthening the M-O_2. Indeed, the six-coordinate Co porphyrin dioxygen complexes are much more stable, then free bases. Heating of the adduct above 140 K leads to a slow disappearance of the $\nu(O_2)$ band at 1161 cm^{-1}, indicating decomposition of the complex. The $(CH_3)_2S$ adduct is also easy to obtain by adding sulfide firstly, heating to 130–140 K and cooling to 77 K after O_2 gas addition. Interestingly, using different N-, O-, P- and S-donor ligands we have noted that porphyrin band at 1000 cm^{-1} can serve as a good marker of the formation of ligand – Co(TPP) adducts. After supplying the ligand vapors to the cryostat with Co(Porphyrin)
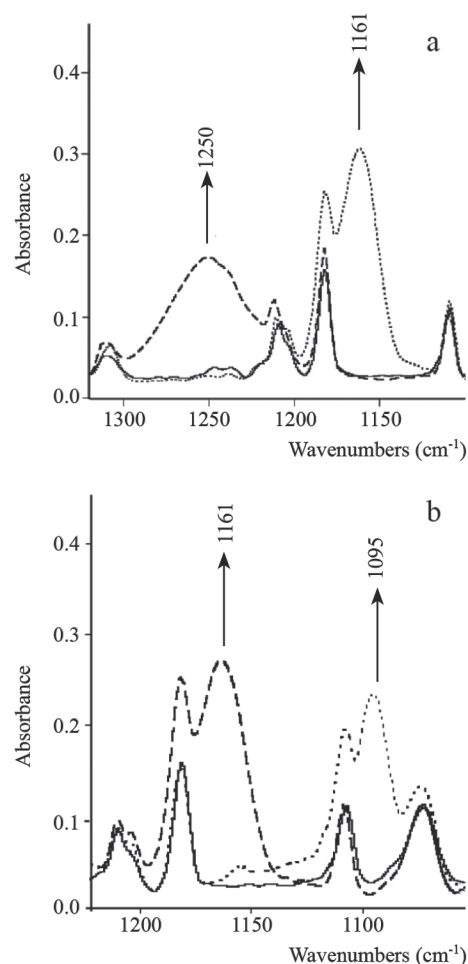

Figure 1. FTIR spectra at 77 K. **a** – Co(TTP) – solid line, Co(TTP)O_2 – dashed line, after reaction with 3 torr of $(CH_3)_2S$ – dotted line. **b** – Co(TTP) – solid line, $((CH_3)_2S)Co(TTP)O_2$ – dashed line, $((CH_3)_2S)Co(TTP)^{18}O_2$ dotted line.

at 77 K and heating to 130–140 K this band slow shifts down to 996 cm^{-1} and rises in the intensity. Upon formation of six-coordinate dioxygen complexes the band shifts back to the initial position.[38]

In contrast to $(CH_3)_2S$ adduct of cobalt porphyrin and earlier reported $(H_2S)Fe(TPP)O_2$, we had much more experimental difficulties in preparation of $(H_2S)Co(TTP)O_2$. Indeed, as noted above, the Co(TTP)O_2 is extremely unstable. Coordinated dioxygen of this adduct slow dissociates under continuous vacuum conditions even at 77 K. At elevated temperatures this process is accelerating. By this reason many attempts resulted in only partial formation of six-coordinated dioxygen complex that reflected in relatively low intensity of the new band at 1138 cm^{-1}, which we assigned to the $\nu(O_2)$ of $(H_2S)Co(TTP)O_2$. Upon reaction of hydrogen sulfide with Co(TTP)O_2 dioxygen dissociates parallel with penetration of the H_2S into the bulk of porphyrin layer. However, upon cooling cryostat to stabilize the temperature, the H_2S quickly comes out from porphyrin layers and settles on colder metal parts of the substrate. In addition, much more excess of H_2S is required in comparison with $(CH_3)_2S$ to obtain six-coordinated adduct. Nevertheless, we were successful in obtaining the $(H_2S)Co(TTP)O_2$ with good
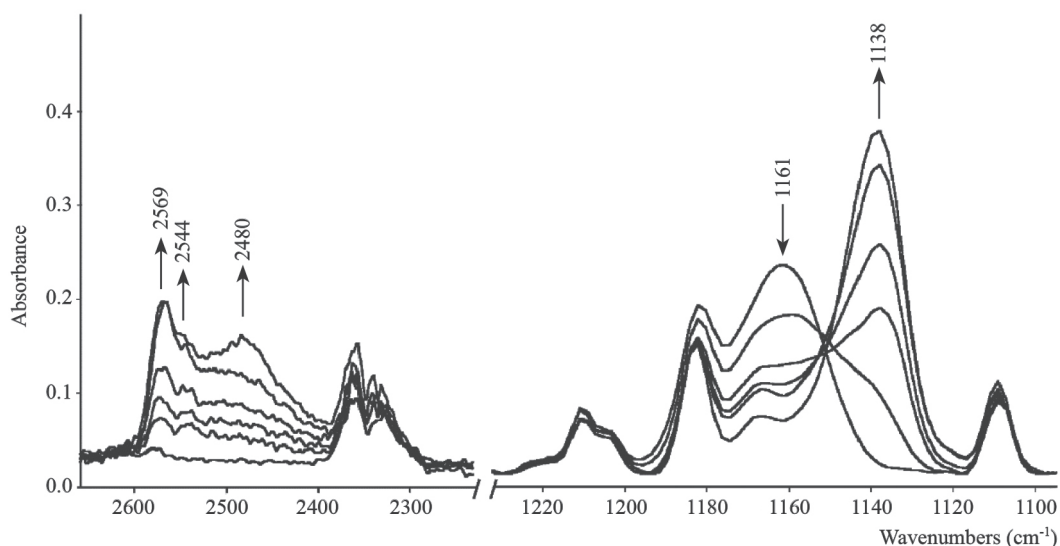
Figure 2. FTIR spectral changes upon addition of 15 torr of H$_2$S into the cryostat containing ((CH$_3$)$_2$S)Co(TTP)O$_2$.

yield using the ligand exchange reaction, which is well known for solutions. Addition of the large excess of hydrogen sulfide on the ((CH$_3$)$_2$S)Co(TTP)O$_2$ complex at 130 K leads to gradual disappearance of the band at 1161 cm^{-1} and generates formation of the above mentioned band at 1138 cm^{-1} with nearly isosbestic point at 1150 cm^{-1} suggesting clean transformation of the (CH$_3$)$_2$S ligated adduct to the hydrogen ligated one. Concomitant changes were observed in the range of the ν(SH) as shown in Figure 2.

In parallel with the appearance of the bands of adsorbed H$_2$S at 2569 and 2544 cm^{-1}, a wide absorption band centered near 2480 cm^{-1} is gaining growth. Rise in the intensity of this band correlates with one of 1138 cm^{-1}. Thus, it is obviously that this band is associated with coordinated H$_2$S. Although, two ν(SH) bands, asymmetric and symmetric, should be expected for coordinated H$_2$S, we believe that this broad absorption contains two closely spaced and unresolved bands. On the best of our knowledge, two ν(SH) bands of coordinated hydrogen sulfide have never been reported in H$_2$S gas excess absorption or coordination studies. In contrast, X-ray structural and spectroscopic characterization of the metal-organic Ru(II)-H$_2$S complexes revealed ν(SH) IR bands at 2506 and 2476 cm^{-1} or 2495 and 2449 cm^{-1}.[19] The IR spectra of (H$_2$S)Co(TTP)^{18}O$_2$ with ν(^{18}O$_2$) at 1074 cm^{-1} was also obtained by similar way and is shown in Figure 3.

It has been reported for the series of (L)Co(TTP)O$_2$ complexes that ν(O$_2$) of coordinated dioxygen depends on the ligand basicity and is shifted consistently down for the ligands with higher pK_a.[9] The 23 cm^{-1} ν(O$_2$) downshift by going from (CH$_3$)$_2$S to H$_2$S ligand is in agreement with this trend due to pK_a of former is negative, but it is 7.02 (at 298 K) for the latter.[39] Moreover, in the reported (HSC$_6$H$_5$)Co(TPP)O$_2$ the ν(O$_2$) band appears at 1137 cm^{-1} in Raman spectrum and pK_a of thiophenol is 6.62 (at 298 K).[11] Similarly to adduct with (CH$_3$)$_2$S, heating of the (H$_2$S)Co(TTP)O$_2$ above 140 K results in its slow decomposition. In addition, it is obvious that the both six-coordinate adducts are the superoxo complexes bearing
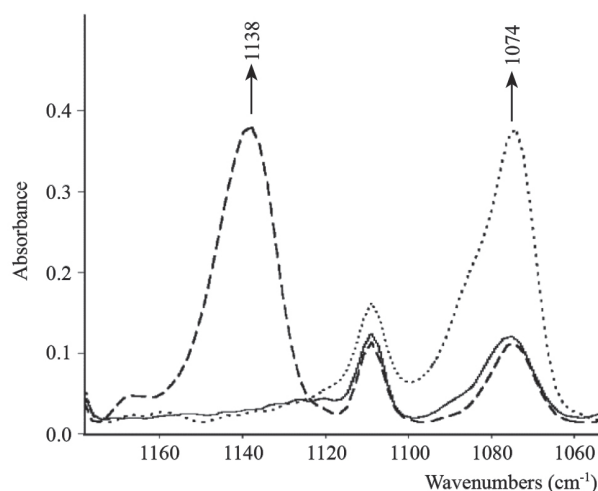

Figure 3. FTIR spectra of Co(TTP) – solid line, (H$_2$S)Co(TTP)O$_2$ – dashed line, and (H$_2$S)Co(TTP)^{18}O$_2$ – dotted line.

bent, end-on bound dioxygen. Indeed, the complexes with stretching frequencies in the range of 1070 – 1280 cm^{-1} typically represent the superoxo complexes with end-on bound dioxygen, while compounds with frequencies in the range between 740 and 930 cm^{-1} are considered as the side-on and fall into the peroxide category.[4] The ν(O$_2$) of the six-coordinate dioxygen adducts of cobalt(II) porphyrins with S-donor ligands are compared in Table 1. As it is seen, the ν(O$_2$) decreases as the negative charge on the π^* orbital of the dioxygen increases via electron donation from the axial base ligand. Our results are consistent with previous Co-O$_2$ bond formulation[4,40] and suggest that the O$_2$ in the cobalt porphyrin system is best described as a Co(III)-O$_2^-$ superoxide.

To support the sulfide coordination we have also promoted the electronic absorption spectral studies (Figure 4). As it was noted before, the visible spectra of Co(TTP) and Co(TTP)O$_2$ are almost similar showing prominent peak

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Table 1. The $\nu(O_2)$ values in cm^{-1} of cobalt porphyrin adducts.

Compound	$\nu(^{16}O_2)$	$\nu(^{18}O_2)$
Co(TTP)O$_2$	1250	1184
((CH$_3$)$_2$S)Co(TTP)O$_2$	1161	1095
(H$_2$S)Co(TTP)O$_2$	1138	1074
(HSC$_6$H$_5$)Co(TPP)O$_2$[11]	1137*	–

* data from Raman spectra

at 535 nm.[41,42] Formation of the six-coordinate dioxygen adduct generates significant changes in the Q-band region of visible spectra. Subsequent treatment of the Co(TTP)(O$_2$) with (CH$_3$)$_2$S leads to disappearance of the band at 535 nm and formation of two new absorption bands at 551 nm and 592 nm. Similar reaction with hydrogen sulfide produces the absorption bands at 555 nm and 593 nm. Notably, the both visible spectra, obtained by the direct reaction of Co(TTP)(O$_2$) with H$_2$S or via ligand exchange are similar. These spectral changes are characteristic and similar to those, observed upon N-bases binding to the Co(Porphyrin)O$_2$.[43]
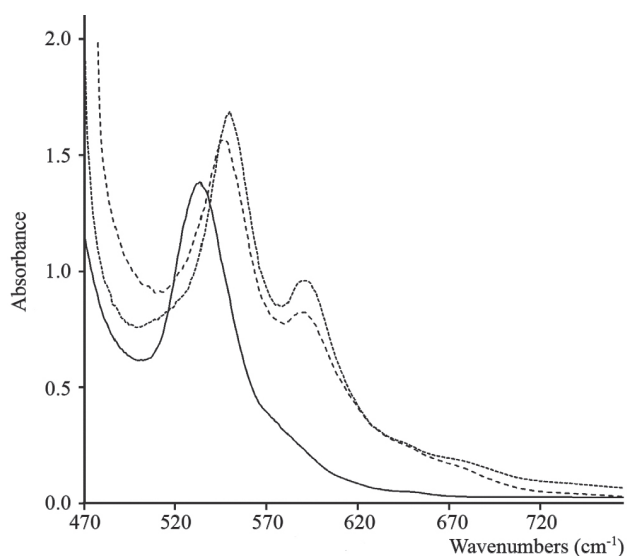
Figure 4. Visible spectra of Co(TTP)O$_2$ – solid line, ((CH$_3$)$_2$S)Co(TTP)O$_2$ – dashed line, and (H$_2$S)Co(TTP)O$_2$ – dotted line at 77 K.

The geometry optimizations by DFT computational analysis of the model system Co(TPP)O$_2$ confirms the viability of six-coordinate model compounds (Figure 5). Both ((CH$_3$)$_2$S)Co(TPP)O$_2$ and (H$_2$S)Co(TPP)O$_2$ converged in the doublet ground state with a distance Co-S of 2.43 and 2.48 Å, strongly supporting sulfide coordination to cobalt. Comparison of the computed O$_2$ bonds lengths show that O-O bond lengthening from 1.28 Å in Co(TPP)O$_2$ to 1.29 Å in the both six-coordinate sulfide complexes in consistence with the lowering of the $\nu(O_2)$ frequencies. The charge distribution also show increase of negative charge on oxygen from –0.181 at Co(TPP)O$_2$ to –0.226 and –0.243 at (H$_2$S)Co(TPP)O$_2$ and ((CH$_3$)$_2$S)Co(TPP)O$_2$ respectively, sup-
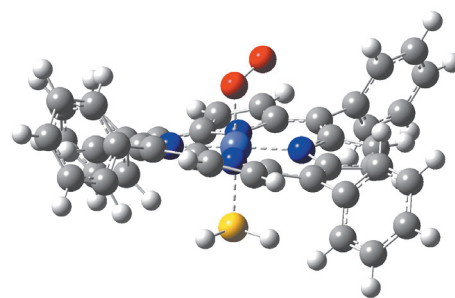
Figure 5. Optimized geometry of the (H$_2$S)Co(TPP)O$_2$.

porting the description for the Co-O$_2$ bond as a Co(III)-O$_2^-$. The weak bonding of H$_2$S to cobalt porphyrinate was also suggested in the previous theoretical calculations.[44]

Conclusions

Infrared and electronic absorption spectral data, as well as DFT computations provide evidences that (CH$_3$)$_2$S and H$_2$S can serve as the ligands at the metal center of the cobalt porphyrin dioxygen adducts at low temperatures. By using infrared spectroscopy we have measured for the first time the $\nu(O_2)$ of the coordinated dioxygen in the six-coordinate complexes, containing these sulfides as the *trans* ligands. Taken together, these results provide matter to further comprehending the coordination chemistry of H$_2$S with different bioinorganic targets.

References

1. Nam W. *Acc. Chem. Res.* **2007**, *40*(7), 465.
2. Que L. Jr. *J. Biol. Inorg. Chem.* **2017**, *22*, 171–173.
3. Yee G.M., Tolman W.B. Transition Metal Complexes and the Activation of Dioxygen. In: *Sustaining Life on Planet Earth: Metalloenzymes Mastering Dioxygen and Other Chewy Gases. Metal Ions in Life Sciences* (Kroneck P., Sosa Torres M., Eds.), Vol. 15, Springer, Cham., **2015**. 131–204.
4. Nakamoto K. *Coord. Chem. Rev.* **1990**, *100*, 363–402.
5. Momenteau M., Reed C. A. *Chem. Rev.* **1994**, *94*, 659–698.
6. Nakamoto K., Watanabe T., Ama T., Urban M.W. *J. Am. Chem. Soc.* **1982**, *104*. 3744–3745.
7. Nakamoto K., Paeng I.R., Kuroi T., Isobe T., Oshio H. *J. Mol. Struct.* **1988**, *189*, 293–300.
8. Bajdor K., Kincaid J.R., Nakamoto K. *J. Am. Chem. Soc.* **1984**, *106*, 7741–7747.
9. Kincaid J., Proniewicz L., Bajdor K., Bruha A., Nakamoto K. *J. Am. Chem. Soc.* **1985**, *107*, 6775–6781.

10. Bajdor K., Nakamoto K., Kincaid J. *J. Am. Chem. Soc.* **1983**, *105*, 678–679.
11. Nakamoto K., Oshio H. *J. Am. Chem. Soc.* **1985**, *107*, 6518–6521.
12. Abe K., Kimura H. *J. Neurosci.* **1996**, *16*(3), 1066–1071.
13. Yang G., Wu L., Jiang B., Yang W., Qi J., Cao K., Meng Q., Mu W., Zhang S., Snyder S., Wang R. *Science* **2008**, *322*, 587-590.
14. Eto K., Kimura H. *J. Neurochem.* **2002**, *83*, 80–86.
15. Mittra K., Singha A., Dey A. *Inorg. Chem.* **2017**, *56*, 3916–3925.
16. Bostelaar T., Vitvitsky V., Kumutima J., Lewis B., Yadav P., Brunold T., Filipovic M., Lehnert N., Stemmler T., Banerjee R. *J. Am. Chem. Soc.* **2016**, *138*, 8476−8488.
17. Chatwin S., Diggle R., Jazzar F., Macgregor S., Mahon M., Whittlesey M. *Inorg. Chem.* **2003,** *42*, 7695–7697.
18. Sellman D., Lechner P., Knoch F., Moll M. *J. Am. Chem. Soc.* **1992**, *114*, 922–930.
19. Mudalige D., Ma E., Rettig S., James B., Cullen W. *Inorg. Chem.* **1997**, *36*, 5426–5427.
20. Erin S., Ma S., Rettig B., James P. *Inorg. Chem.* **2012**, *51*, 5427−5434.
21. Galardon E., Roger T., Deschamps P., Roussel P., Tomas A., Artaud I. *Inorg. Chem.* **2012**, *51*, 10068–10070.
22. Collman J., Ghosh S., Dey A., Decreau R. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 22090–22095.
23. Koifman O.I., Ageeva T.A., Beletskaya I.P. *et al. Macroheterocycles* **2020**, *13*, 311–467.
24. Vashurin A.S., Pukhovskaya S.G., Semeikin A.S., Golubchikov O.A. *Macroheterocycles* **2012**, *5*, 72–75.
25. Klaine S., Bratcher F., Winchester C., Zhang R. *J. Inorg. Biochem.* **2020**, *204*, 110986.
26. Hartle M., Sommer S., Dietrich S., Pluth M. *Inorg. Chem.* **2014**, *53*, 7800−7802.
27. Hartle M., Prell J., Pluth M. *Dalton Trans.* **2016**, *45*, 4843–4853.
28. Hartle M., Tillotson M., Prell J., Pluth M. *J. Inorg. Biochem.* **2017**, *173*, 152–157.
29. Pavlik J., Noll B., Oliver A., Schulz C., Scheidt W. *Inorg. Chem.* **2010**, *49*, 1017–1026.
30. Yuasa H., Green B., Takagi T., Suzuki S., Vinogradov S., Suzuki T. *Biochim. Biophys. Acta* **1996**, *1296*, 235–244.
31. Nakagawa T., Onoda S., Kanemori M., Sasayama Y., Fukumori Y. *Zool. Sci.* **2005**, *22*, 283–291.
32. Martirosyan G., Chinaryan V., Dalaloyan A., Kurtikyan T. *Vibr. Spectroscopy* **2009**, *51*, 294–298.
33. Martirosyan G., Hovhannisyan A., Hovhannisyan G., Kurtikyan T., Iretskii A. *Inorg. Chim. Acta*, **2018**, *482*, 894–899.
34. Walker A. *J. Am. Chem. Soc.* **1970**, *92*, 14, 4235–4244.
35. Kurtikyan T., Ford P. *Coord. Chem. Rev.* **2008**, *252*, 1486–1496.
36. Kozuka M., Nakamoto K. *J. Am. Chem. Soc.* **1981**, *103*, 2162–2168.
37. Kurtikyan T., Martirosyan G., Gasparyan A., Zhamkochyan G. *J. Appl. Spectr.* **1993**, *59*, 815–819.
38. Kurtikyan T.S. *Nitrogen Oxides and Heme Models: a Mosaic of Interactions*, Antares, **2018**, 367 p. [Куртикян Т.С. *Оксиды азота и гем-модели: мозаика взаимодействий.* Изд-во «Антарес» **2018**, 367 с.].
39. Smith R., Martell A.E. *The Critical Stability Constant Database, NIST Standard Reference Database*, Washington, **1993**.
40. Newton J., Hall M. *Inorg. Chem.* **1984**, *23*, 4627–4632.
41. Collman J., Yan Y., Eberspacher T., Xie X., Solomon E. *Inorg. Chem.* **2005**, *44*, 9628−9630.
42. Kurtikyan T., Eksuzyan S., Hayrapetyan V., Martirosyan G., Hovhannisyan G., Goodwin J. *J. Am. Chem. Soc.* **2012**, *134*, 13861–13870.
43. Stynes D., Stynes H., James B., Ibers J. *J. Am. Chem. Soc.* **1973**, *95*, 1796–1801.
44. Gu H., Huang X., Yao L., Teyea E., Wen Y. *Anal. Methods* **2014**, *6*, 3360–3364.