

Six-Coordinate Nitrosyl and Nitro Complexes of *meso*-Tetratolylporphyrinatocobalt with Trans Sulfur-Donor Ligands

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By Fourier transform infrared and optical spectroscopy, it has been observed that interactions of dimethyl sulfide and tetrahydrothiophene with nitrosyl and nitro complexes of *meso*-tetra-*p*-tolylporphyrinatocobalt [Co(TTP)] lead to the formation of previously unknown six-coordinate species. Nitrosyl complexes of the general formula (S-donor)Co(TTP)(NO) are thermally unstable and can be seen only at low temperatures both in the solid state and in solution. The nitro complexes (S-donor)Co(TTP)(NO₂) are fairly stable at room temperature in the solid state but partly decompose upon dissolution. The binding constants for these complexation reactions were determined. In contrast to the solid-state iron nitritoporphyrin complexes, oxo-transfer reactions from the coordinated nitro group of Co(TTP)(NO₂) to the S donors, resulting in oxidation of these sulfides and the formation of Co(TTP)(NO), were not observed.

Introduction

Interest continues in the nitrosyl complexes of metalloporphyrins with transition metals of biological importance. The five- and six-coordinate nitrosyl complexes of especially important iron porphyrins have been characterized structurally^{1a} and investigated by a large number of available spectral methods including UV–vis, electron spin resonance, Mössbauer spectroscopy, magnetic circular dichroism, etc.² Despite the fact that the five-coordinate nitrosyl complex Co(TPP)(NO) (TPP = *meso*-tetraphenylporphyrinato dianion) was the first reported structure of a metalloporphyrin containing a coordinated nitrosyl group,^{1b} six-coordinate nitrosyl complexes with trans electron donor ligands were not known for a long time. Only recently were the six-coordinate complexes of cobalt porphyrins with trans nitrogen bases (B)Co(TTP)(NO) (B = pyridine and piperidine) stabilized at low temperatures in the solid state and a toluene solution and characterized by Fourier transform infrared (FTIR) and UV–vis spectroscopy.³ To date the only characterized six-coordinate complexes of cobalt

nitrosylporphyrins have involved trans nitrogen-donor ligands. At the same time, sulfur ligation of methionine was observed for cobalt hemoglobin, cobalt myoglobin,^{4a} and cobalt cytochrome *c*.^{4b} Taking into account the exceptional physiological importance of NO, the existence and stability of six-coordinate nitrosyl complexes with trans sulfur-donor ligands are also significant.

Nitro complexes of cobalt porphyrins are also the center of attention because of their ability to take part in stoichiometric and catalytic oxo-transfer reactions from the coordinated nitro group to various oxygen acceptors.⁵ It was shown that five-coordinate nitro complexes are active in the catalytic oxidation of alkenes, while six-coordinate complexes with nitrogen- or oxygen-bound ligands trans to the nitro group are not reactive because of unfavorable oxo-transfer thermodynamics. However, derivatives with weakly bound sixth ligands are capable of alkene oxidation perhaps because of the presence of five-coordinate nitro species that exist in equilibrium in solution. Hence, the nature of the trans ligand appears to be an important factor regulating the oxo-transfer reactivity of (cobalt) nitroporphyrins. The six-coordinate

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(1) (a) Wyllie, G. R.; Scheidt, R. W. *Chem. Rev.* **2002**, *102*, 1067–1089. (b) Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8281–8283.

(2) (a) Yoshimura, T. *Inorg. Chim. Acta* **1982**, *57*, 99–105. (b) Perera, R.; Sono, M.; Sigman, J. A.; Pfister, T. D.; Lu, Y.; Dawson, J. H. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3641–3646. (c) Praneeth, V. K. K.; Haupt, E.; Lehnert, N. *J. Inorg. Biochem.* **2005**, *99*, 940–948. (d) Praneeth, V. K. K.; Näther, C.; Peters, G.; Lehnert, N. *Inorg. Chem.* **2006**, *45*, 2795–2811. (e) Berto, T. C.; Praneeth, V. K. K.; Goodrich, L. E.; Lehnert, N. *J. Am. Chem. Soc.* **2009**, *131*, 17116–17126.

(3) Kurtikyan, T. S.; Markaryan, E. R.; Marduykov, A. N.; Goodwin, J. A. *Inorg. Chem.* **2007**, *46*, 1526–1528.

(4) (a) Dickinson, C. L.; Symons, M. C. R. *J. Phys. Chem.* **1982**, *86*, 917–921. (b) Dickinson, C. L.; Chen, J. C. W. *Biochemistry* **1975**, *14*, 3534–3542.

(5) (a) Goodwin, J. A.; Bailey, R.; Pennington, W.; Rasberry, R.; Green, T.; Shasho, S.; Echevarria, V.; Tiedeken, J.; Brown, C.; Fromm, G.; Lyerly, S.; Watson, N.; Long, A.; De Nitto, N. *Inorg. Chem.* **2001**, *40*, 4217–4225. (b) Goodwin, J. A.; Kurtikyan, T. S.; Bin Zheng, B.; Parmley, D.; Howard, J.; Green, S.; Walsh, R.; Standard, J.; Marduykov, A. N.; Przybyla, D. E. *Inorg. Chem.* **2005**, *44*, 2215–2223. (c) Kurtikyan, T. S.; Marduykov, A. N.; Goodwin, J. A. *Inorg. Chem.* **2003**, *42*, 8489–8493. (d) Seki, H.; Okada, K.; Iimura, Y.; Hoshino, M. *J. Phys. Chem. A* **1997**, *101*, 8174–8178.

nitro complexes of nitroporphyrins are known for trans nitrogen,⁶ oxygen,⁷ and phosphorus⁸ ligands. For sulfur donors, however, to the best of our knowledge, no literature reports are available to date.

In this paper, the six-coordinate nitrosyl and nitro complexes of Co(TTP) with trans sulfur-containing ligands were obtained and characterized by electronic and FTIR spectroscopy in both layered solids and solutions and the equilibrium constants of their complexation reactions are reported.

Experimental Section

Co(TTP) was synthesized using a literature method.⁹ Before the experiment, Co(TTP) was additionally purified by column chromatography with dry alumina using reagent-grade chloroform as the eluent. Co(TTP)(NO) for solution experiments was prepared by introducing a solid sample of Co(TTP) under a NO atmosphere (~100 Torr) for 2 h in an airtight flask connected with a high-vacuum line. This procedure led to the formation of an intense nitrosyl stretching band ($\nu = 1680 \text{ cm}^{-1}$, $\epsilon = 1100 \text{ M}^{-1} \text{ cm}^{-1}$ in toluene). NO (¹⁵NO) was purified by passing it through KOH pellets and a cold trap (dry ice/acetone) to remove the higher nitrogen oxides and trace quantities of water. The purity was checked by IR measurements of the layer obtained by the slow deposition of NO onto the cold substrate of the optical cryostat (77 K). The IR spectrum did not show the presence of N₂O, N₂O₃, or H₂O. ¹⁵NO with 98.5% enrichment was purchased from the Institute of Isotopes, Republic of Georgia, and was purified by the same procedures. Sulfur donors dimethyl sulfide (DMS; 99%, Aldrich) and tetrahydrothiophene (THT; 99+, Aldrich) were freshly distilled over sodium before use. Before their introduction into the cryostat, they were degassed by multiple cycles of the freeze–pump–thaw method. NO₂ (¹⁵NO₂) was obtained by oxidation of NO (¹⁵NO) with an excess of pure dioxygen. After preliminary drying under P₂O₅, it was purified by fractional distillation using a low-temperature vacuum technique until a pure white solid was obtained.

Sublimed layers of Co(TTP) were obtained on the cold (77 K) KBr support of an optical cryostat according to a published procedure.¹⁰ These layers were then heated to 250 K under a dynamic vacuum ($P \approx 2 \times 10^{-5}$ Torr), and NO (¹⁵NO) was applied to the cryostat from a vessel provided with a mercury manometer to measure the equilibrium pressure of the NO gas. This procedure rapidly led to the formation of the nitrosyl complex, which manifests itself by an intense NO stretching band. The excess NO was pumped out, the layer was cooled to 120 K, and a few torr of the sulfur donor (DMS or THT) was introduced into the cryostat. The layer was then slowly warmed to 170 K, and the FTIR or UV–vis spectra were run at various controlled temperatures measured by a thermocouple. This procedure was accompanied by the gradual disappearance of the $\nu(\text{NO})$ band at 1680 cm^{-1} and the appearance of the new NO stretching band of the six-coordinate nitrosyl at lower wavenumbers. After the complete disappearance of the five-coordinate nitrosyl complex, the layer was cooled (to temperatures of

160 K for DMS and 170 K for THT), at which it was possible to pump out the excess of the sulfur-donor ligands without destroying the six-coordinate species. The FTIR spectra were then measured at given temperatures to follow the decomposition of the six-coordinate species as it warmed to room temperature.

The interaction of sulfur donors with Co(TTP)(NO) in a toluene solution was carried out in an optical cryostat provided with a 0.05 cm CaF₂ cell. A measured quantity of Co(TTP)(NO) was fed into the airtight flask provided with a septum. Known quantities of previously degassed solutions of sulfur donors in toluene or the pure sulfur donor were transferred into this flask by vacuum techniques. The solutions thus prepared were transferred to an IR cell using an airtight Hamilton syringe. The cell was then tightly closed and placed in the cryostat. Over the course of the IR measurements, the 1280–1320 cm^{-1} range, in which $\nu_s(\text{NO}_2)$ values of Co(TTP)(NO₂)^{6d} or (B)Co(TTP)(NO₂)^{6c} are observed, was also thoroughly inspected. There were no indications of Co(TTP)(NO) oxidation during the study. The cell was then cooled using liquid nitrogen vapors, and the FTIR spectra were taken at temperatures controlled by a thermocouple that was in close contact with the cell. Through changes in the flow rate of liquid nitrogen, it was possible to maintain the temperature of solution at a given temperature ($\pm 1 \text{ }^\circ\text{C}$).

The sublimed layers of the nitro complexes Co(TTP)(NO₂) and Co(TTP)(¹⁵NO₂) were obtained by supplying a low pressure of NO₂ (¹⁵NO₂) on the amorphous layers of Co(TTP) as described elsewhere.^{6d} This procedure rapidly led to the formation of the nitro complex, which manifests itself by an intense $\nu_s(\text{NO}_2)$ band of coordinated NO₂ at 1283 cm^{-1} . The unreacted NO₂ was then pumped out, and a few torr of the sulfur donor (DMS or THT) was introduced into the cryostat. This procedure led to the fast formation of the six-coordinate nitro complexes (L)Co(TTP)(NO₂) (L = DMS, THT), which appear by the new set of NO₂ vibrations. After the complete disappearance of the five-coordinate nitro complex, the excess of the base ligand was quickly pumped out to provide spectra of the six-coordinated complexes uncomplicated by the presence of sulfur donors adsorbed in the layer.

The solution studies of the nitro complexes were carried out as follows. The weighed quantity of Co(TTP)(NO₂) scraped from the KBr substrate was dissolved in the measured quantity of solvent, as described for Co(TTP)(NO). In the titration experiments, the measured quantities of sulfur donors were added to the Co(TTP)(NO₂) solution with an airtight Hamilton syringe through the septum. The 1.00 cm quartz and 0.05 cm cells with KBr windows were used for UV–vis and FTIR measurements, respectively.

For study of the oxo-transfer reactivity of the six-coordinate nitro complexes, measured quantities of the sulfur bases were introduced into the cryostat with the layered Co(TTP)(NO₂) at room temperature. The layer was maintained under sulfur-donor vapors overnight, after which the gaseous contents of the cryostat was analyzed by FTIR spectroscopy and mass spectrometry. For the first purpose, the gaseous contents of the cryostat was deposited through the vacuum connection to the cold (77 K) KBr substrate of the second cryostat. Then the layer was heated under vacuum to the temperatures at which the sulfur donor was completely eliminated from the deposit and the FTIR spectra of the possible oxidation products could be measured. The mass spectrometric measurements were performed using a residual gas analyzer. In this case, also the bulk of the sulfur donor was pumped out at lowered temperatures, and then the remaining gas was introduced into the chamber of the gas analyzer through a needle valve.

The FTIR and UV–vis spectra were acquired on Nexus (Thermo Nicolet) and “Specord M-40” (Carl Zeiss, Jena) or Helios γ (Thermo Electron Corp.) spectrometers, respectively, and mass spectra by an RGA-200 residual gas analyzer

(6) (a) Kaduk, J. A.; Scheidt, W. R. *Inorg. Chem.* **1974**, *13*, 1875–1880. (b) Yamamoto, K.; Itaka, Y. *Chem. Lett.* **1989**, *18*, 697–698. (c) Jene, P. G.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 3823–3827. (d) Kurtikyan, T. S.; Stepanyan, T. G.; Gasparyan, A. V. *Russ. J. Coord. Chem.* **1997**, *23*, 563–567. (e) Stepanyan, T. G.; Akopyan, M. E.; Kurtikyan, T. S. *Russ. J. Coord. Chem.* **2000**, *26*, 425–428.

(7) Kurtikyan, T. S.; Marduykov, A. N.; Goodwin, J. A. *Russ. J. Coord. Chem.* **2008**, *34*, 606–611.

(8) Adachi, H.; Suzuki, H.; Miyazaki, Y.; Iimura, Y.; Hoshino, M. *Inorg. Chem.* **2002**, *41*, 2518–2524.

(9) (a) Bhatti, W.; Bhatti, M.; Imbler, P.; Lee, A.; Lorenzen, B. *J. Pharm. Sci.* **1972**, *61*, 307–309. (b) Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235–4244.

(10) Kurtikyan, T. S.; Gasparyan, A. V.; Martirosyan, G. G.; Zhamkochyan, G. H. *J. Appl. Spectrosc.* **1995**, *62*, 62–66 (Russian).

Table 1. Spectral Characteristics of Six-Coordinate Nitrosyl Complexes of Co(TTP) and Equilibrium Constants for the Reaction $\text{Co(TTP)(NO)} + \text{L} \leftrightarrow (\text{L})\text{Co(TTP)(NO)}$ in a Toluene Solution or in the Neat Coordinating Solvent (for Sulfur-Donor Ligands)^a

	UV-vis; λ_{max} (nm)	$\nu(\text{NO})$ (cm^{-1})	$\Delta\nu(\text{NO})$	K_{298} (M^{-1})	ref
Co(TTP)(NO)	416, 541	1679 (1649)			this work
(DMS)Co(TTP)(NO)	427, 546, 585	1661 (1633)	18 (16)	~0.012	this work
(THT)Co(TTP)(NO)	429, 545, 584	1658 (1629)	21 (20)	~0.007	this work
(Pip)Co(TTP)(NO)	545	1650 (1621)	29 (28)	0.45	3

^aData for the ^{15}NO isotopomer are given in parentheses.

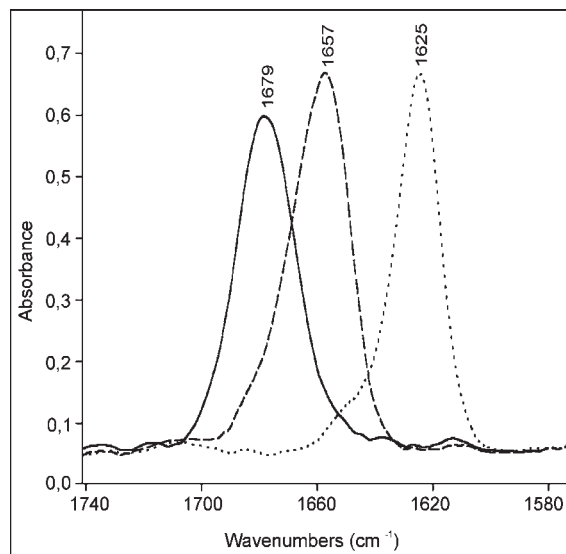


Figure 1. FTIR spectra of Co(TTP)(NO) (solid line) in the range of $\nu(\text{NO})$ stretching after the introduction of 2 Torr of THT into the cryostat ($T = 120$ K), slow warming until 170 K (dashed line), and pumping out of the THT excess. The same procedure was carried out with layered Co(TTP)(^{15}NO) (dotted line).

of Stanford Research Systems. The backgrounds for FTIR measurements were collected for pure sulfur donors or toluene–ligand solutions at each studied temperature.

Results and Discussion

Six-Coordinate Nitrosyl Complexes. Interaction of NO gas with low-temperature sublimed layers of Co(TTP) in the optical cryostat led to the facile formation of the nitrosyl complex Co(TTP)(NO), which manifests itself by the strong stretching band of the coordinated NO group with $\nu(\text{NO}) = 1679 \text{ cm}^{-1}$ (1651 cm^{-1} for ^{15}NO ; Figure 1, solid line). After the NO excess was pumped out, the KBr substrate was cooled to 120 K and the sulfur-donor ligands were introduced into the cryostat. The layered Co(TTP)(NO) was slowly warmed as FTIR measurements were made. Beginning from 130 K, the band at 1679 cm^{-1} began to decrease in intensity and a new band at 1657 cm^{-1} appeared and gained in intensity at the expense of the initial band. At about 170 K, the latter completely displaced the former (Figure 1, dashed line). This band certainly corresponds to the nitrosyl stretching of another species because the experiments with ^{15}NO result in isotopic shifts close to those predicted for the diatomic molecule in the harmonic oscillator approximation (Figure 1, dotted line). The same changes of the FTIR spectra with some minor deviations in the frequency (Table 1) were observed when DMS was used in the experiments. Warming these layers led to spectral changes that provide evidence for decomposition of the new adduct with a shifted $\nu(\text{NO})$ band.

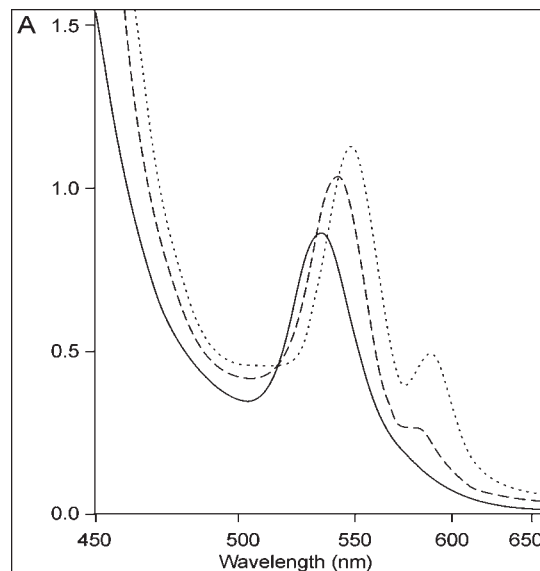


Figure 2. UV-vis spectra at 170 K of the Co(TTP) sublimed layer (solid line) after sequential interaction with NO and DMS (2 Torr), forming Co(TTP)(NO) (dashed line) and (DMS)Co(TTP)(NO) (dotted line). The FTIR spectra of the same samples were initially measured to confirm the formation of aforementioned species.

At room temperature, the initial spectrum of the five-coordinate nitrosyl complex, Co(TTP)(NO), is completely restored.

Decomposition of the new adduct occurs both in vacuum and in the presence of the sulfur-donor atmosphere.

For iron (nitrosyl)porphyrins, coordination of the electron-donor ligands in the trans position to the nitrosyl group led to the low-frequency shift of $\nu(\text{NO})$ by a few tens of reciprocal centimeters.^{2c} The value of the shift noticeably depends on the nature of the base ligand and the relative orientation of the axial ligand planes.^{11a–c} The same characteristic of $\nu(\text{NO})$ shifting was observed upon coordination of the nitrogen bases to cobalt (nitrosyl)porphyrins.³

The electronic absorption spectroscopy (EAS) spectrum of layered Co(TTP) also underwent noticeable changes in the course of sequential interaction with NO and sulfur-containing ligands. As seen in Figure 2, the single band of Co(TTP) in the visible range at 534 nm shifts to 542 nm and displays a shoulder at 578 nm upon formation of the nitrosyl complex Co(TTP)(NO). Upon low-temperature interaction with DMS, this band undergoes a further high-frequency shift to 548 nm (549 nm for THT) and a second less intense band grows at 587 nm (589 nm for THT). The spectra were recorded after the FTIR spectra of the same samples first

(11) (a) Piccolo, P. G.; Rupprecht, G.; Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 5293–5295. (b) Scheidt, W. R.; Piccolo, P. G. *J. Am. Chem. Soc.* **1976**, *98*, 1913–1919. (c) Scheidt, W. R.; Brinegar, A. C.; Ferro, E. B.; Kirner, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 7315–7322.

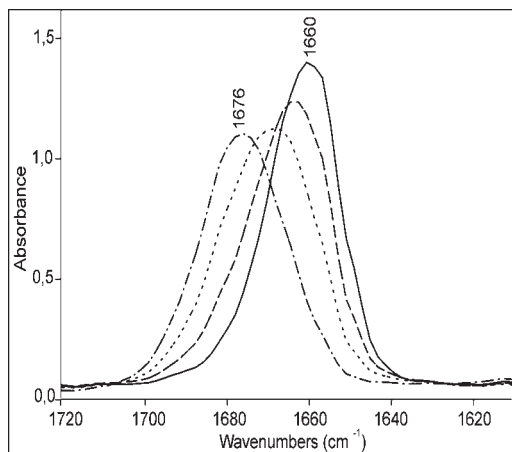
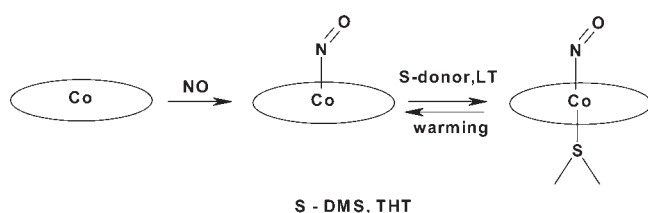


Figure 3. FTIR spectral changes in the range of $\nu(\text{NO})$ observed in a THT solution of $\text{Co}(\text{TTP})(\text{NO})$ upon decreases in the temperature: ---, +25 °C; ···, -20 °C; - · -, -60 °C; —, -95 °C.

Scheme 1



demonstrated the formation of $\text{Co}(\text{TTP})(\text{NO})$ (dashed line) and then a species with complete shifting of $\nu(\text{NO})$ to the lower frequency range (dotted line). The final spectrum is typical for six-coordinate complexes of cobalt *meso*-tetraarylporphyrins.¹² From FTIR and EAS data given above, it can be concluded that the reaction represented by Scheme 1 takes place and the species with lower $\nu(\text{NO})$ are the six-coordinate complexes of cobalt (nitrosyl)porphyrins with the trans sulfur-donor ligands (L) $\text{Co}(\text{TTP})(\text{NO})$ (L = DMS, THT).

The formation of the six-coordinate nitrosyl complexes of cobalt porphyrin with trans sulfur-donor ligands was also observed in solution. The binding constant of this reaction (Scheme 1) is very low (see below), and almost complete transformation to six-coordinate species has been obtained only when pure sulfur donors were used as the solvent. Principally, the same results were obtained for the concentrated toluene solutions of sulfur donors. In this case, however, some five-coordinate complexes were still left at temperatures close to the freezing point of the solvent. Figure 3 shows the temperature dependence of $\text{Co}(\text{TTP})(\text{NO})$ FTIR spectra in a THT solution. The $\nu(\text{NO})$ band of five-coordinate $\text{Co}(\text{TTP})(\text{NO})$ at 1676 cm^{-1} shifts to 1660 cm^{-1} with the lowering of the temperature from 25 to -95 °C, demonstrating the formation of the six-coordinate (THT) $\text{Co}(\text{TTP})(\text{NO})$ complex. The binding constants of the complexation reaction were calculated and summarized in Table 1 together with data obtained previously for the $\text{Co}(\text{TTP})(\text{NO})$ complex with a trans nitrogen base. As seen from Table 1, the values of $\nu(\text{NO})$ shifting and binding constants are noticeably less for the complexes with sulfur donors. This correlates

with the basicities of these ligands that are much higher for the nitrogen donors.¹³ Stronger σ -donor ligands form more stable complexes with cobalt nitrosylporphyrins, although their binding is still very weak. It should be added that the binding of thioethers with iron (nitrosyl)porphyrins is also very weak.² At the same time, according to our study, these adducts reveal bigger $\nu(\text{NO})$ shifts and higher equilibrium constants than those found for cobalt derivatives in this paper, showing extremely weak binding in this case.

The following mechanism was suggested by Berto et al. for an explanation of the decrease of $\nu(\text{NO})$ upon coordination of the sixth nitrogen-donor ligand to iron nitrosylporphyrins.^{2c} They showed that donation from the nitrogen ligand to the d_{z^2} orbital of iron weakens the Fe-NO σ bond, and, subsequently less spin density transfers from the singly occupied π^* orbital to iron. This leads to a weakening of the N-O bond and a lowering of its stretching frequency. The same effect should be realized in cobalt nitrosylporphyrins, although the additional electron density in the d_{z^2} orbital in this case should weaken the binding of the sixth ligand, and this is observed.

Six-Coordinate Nitro Complexes. There are several modes by which a nitrite ion as an ambidentate ligand may bind to metal centers to form nitro (N-coordinated, M-NO₂) and nitrito (O-coordinated, M-ONO) complexes as well as the bidentate-coordinated linkage isomer $\text{M}(\eta^2\text{-O}_2\text{N})$. For cobalt nitritoporphyrin complexes, however, only nitrogen-bound nitro complexes were observed,^{5a,b} although it was shown that the products of $\text{CoTPP}(\text{NO}_2)(\text{H}_2\text{O})$ laser photolysis, CoTPP and NO_2 , initially recombine to give nitrito intermediate $(\text{O}=\text{NO})\text{Co}(\text{TTP})$,^{5d} which eventually returns to $\text{CoTPP}(\text{NO}_2)(\text{H}_2\text{O})$. The vibrations of the coordinated nitro group lie in the ranges of 1470–1420 (ν_{as}), 1320–1280 (ν_{s}), and 820–800 (δ_{NO_2}).^{6d,e} In the analogous iron porphyrin complexes, the nitro form revealed vibrations in the closely related spectral ranges,^{14a,b} while for the nitrito (oxygen-bound) form observed in five-^{14c} and six-coordinate metastable complexes,^{14d-f} the $\nu(\text{ON})$ and $\nu(\text{N}=\text{O})$ modes are significantly more separated and give a reliable means for distinguishing between these forms.

It has been shown previously that sublimed layers of *meso*-tetraphenylporphyrinatocobalt(II) give the five-coordinate nitro complex upon interaction with NO_2 gas.^{6d} This layered complex was readily transformed to six-coordinate aminonitro complexes (B) $\text{Co}(\text{TTP})(\text{NO}_2)$ (B = pyridine, piperidine, and ammonia) when exposed to the vapors of corresponding amines.^{6c} Similarly, the introduction of a few torr of sulfur donor to the layered $\text{Co}(\text{TTP})(\text{NO}_2)$ led to a fast reaction, resulting in the species with the new set of FTIR bands in the ranges where normal vibrations of coordinated nitro groups are disposed. The $\nu_{\text{s}}(\text{NO}_2)$, $\nu_{\text{a}}(\text{NO}_2)$, and $\delta(\text{NO}_2)$ bands of parent $\text{Co}(\text{TTP})(\text{NO}_2)$ are observed at

(13) The $\text{p}K_{\text{a}}$ of Pip is equal to 11.12, while the values for THT and DMS are negative. *Heterocyclic Chemistry*; Joule, A., Smith, G. F., Eds.; Van Nostrand Reinhold Company: New York, 1972.

(14) (a) Kurtikyan, T. S.; Hovhannisyanyan, A. A.; Gulyan, G. M.; Ford, P. C. *Inorg. Chem.* **2007**, *46*, 7024–7031. (b) Kurtikyan, T. S.; Hovhannisyanyan, A. A.; Iretskii, A.; Ford, P. C. *Inorg. Chem.* **2009**, *48*, 11236–11241. (c) Kurtikyan, T. S.; Ford, P. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 492–496. (d) Kurtikyan, T. S.; Hovhannisyanyan, A. A.; Iretskii, A.; Ford, P. C. *Aust. J. Chem.* **2009**, *62*, 1226–1230. (e) Kurtikyan, T. S.; Hovhannisyanyan, A. A.; Hakobyan, M. E.; Patterson, J. C.; Iretskii, A.; Ford, P. C. *J. Am. Chem. Soc.* **2007**, *129*, 3576–3585. (f) Novozhilova, I. V.; Coppens, P.; Lee, J.; Richter-Addo, G. B.; Bagley, K. A. *J. Am. Chem. Soc.* **2006**, *128*, 2093–2104.

(12) (a) Wayland, B. B.; Minkiewitz, J. V.; Abd-Elmageed, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 2795–2801. (b) Wayland, B. B.; Minkiewitz, J. V. *J. Chem. Soc., Chem. Commun.* **1976**, 1015–1016.

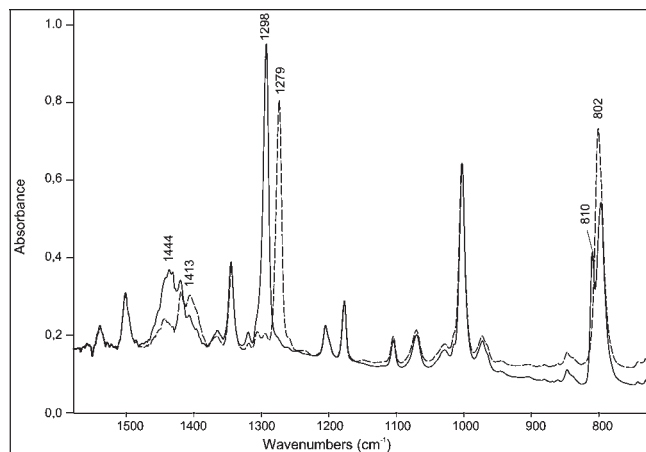


Figure 4. FTIR spectra of the Co(TTP)(NO₂) sublimed layer after a brief exposure under 3 Torr DMS and the pumping out of unreacted DMS (solid line). The same procedure was carried out with layered Co(TTP)(¹⁵NO₂) (dashed line).

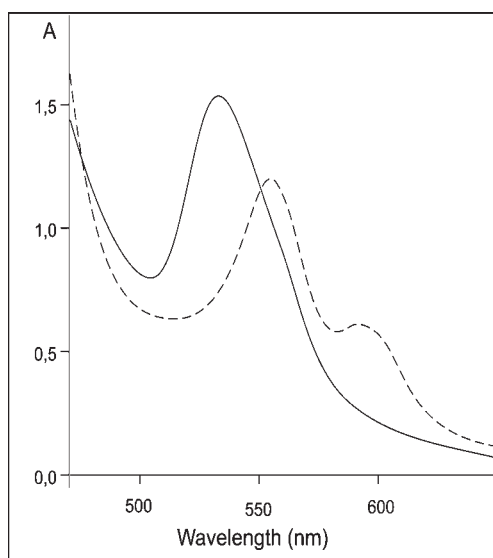


Figure 5. EAS spectra of layered Co(TTP)(NO₂) (solid line) after reaction with THT (dashed line).

1470, 1282, and 803 cm⁻¹, respectively. After reaction with DMS, these bands shift to 1444, 1298, and 809 cm⁻¹ (Figure 4, solid line). They have their isotopic analogues at 1413, 1279, and 802 cm⁻¹ when Co(TTP)(¹⁵NO₂) was used, indicating that they belong to a coordinated nitro group (Figure 4., dashed line).

The EAS spectra also underwent noticeable changes upon the introduction of layered Co(TTP)(NO₂) under vapors of sulfur donors. Figure 5 demonstrates this for the case of the THT ligand. The band of Co(TTP)(NO₂) at 530 nm shifts to higher wavelengths to give two bands at 554 and 592 nm. The characteristics of the spectral changes in FTIR and EAS upon sulfur-donor interaction with Co(TTP)(NO₂) are the same as those observed during the formation of six-coordinate nitro complexes of cobalt porphyrins with trans to the nitro group nitrogen-,^{6e} oxygen-,⁷ and phosphorus-donor⁸ ligands. From these data, it can be concluded that interaction of sulfur donors with Co(TTP)(NO₂) led to the formation of six-coordinate nitro complexes, as shown in Scheme 2.

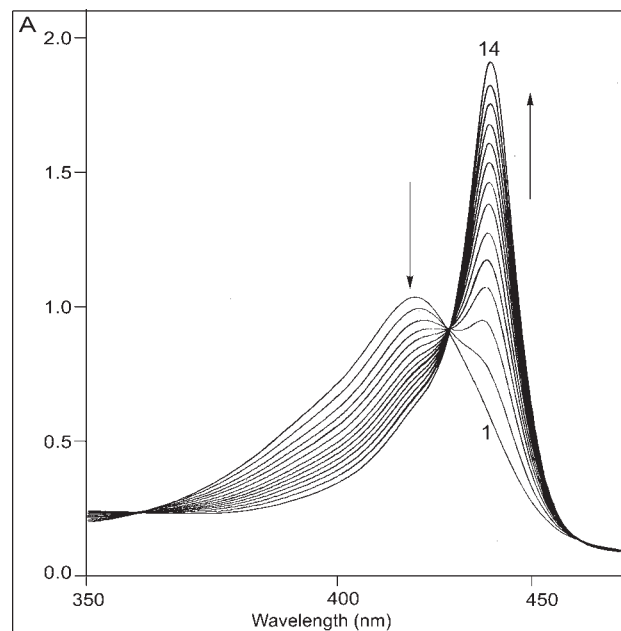
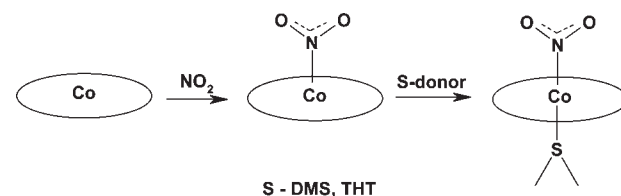


Figure 6. Changes in EAS (Soret band) of a CCl₄ solution of Co(TTP)(NO₂) ($C_0 = 8.3 \times 10^{-6}$ mol L⁻¹) upon sequential additions of DMS. The concentration of DMS is changed from 0 (first curve) to 1.6×10^{-3} mol L⁻¹ (14th curve).

Scheme 2



The complexes (L)Co(TTP)(NO₂) (L = DMS, THT) are stable at room temperature in the solid state (the complex with DMS very slowly eliminates DMS upon high-vacuum pumping, restoring a small quantity of the five-coordinate nitro complex) but upon dissolution partly decompose to give a mixture of the five- and six-coordinate species. A molar excess of sulfur donor is necessary to prevent the complex decomposition. The absorption spectral changes observed for a carbon tetrachloride solution of Co(TTP)(NO₂) at various concentrations of DMS are shown in Figure 6.

Upon the sequential addition of DMS portions, the Soret band of Co(TTP)(NO₂) at 419 nm gradually shifts to 439 nm with isosbestic points observed at 357, 430, and 477 nm, showing the presence of two species in solution. The equilibrium constants at 298 K are calculated from these data and given in Table 2.

It was found previously^{14a,b} for the iron nitroporphyrin complexes with different trans nitrogen- and sulfur-donor ligands (L)Fe(Por)(NO₂) (L = nitrogen and sulfur donors) that there is a negative correlation between the magnitude of the difference of coordinated nitro group asymmetric and symmetric modes $\Delta\nu = \nu_{as}(\text{NO}_2) - \nu_s(\text{NO}_2)$ and the σ -donor ability of the trans ligand. A higher magnitude of electron transfer from the trans ligands to the nitro group led to the closer disposition of ν_{as} and ν_s , i.e., lesser $\Delta\nu$ values. The same pattern is observed for six-coordinate cobalt nitroporphyrin complexes: stronger trans nitrogen-donor ligands

Table 2. Spectral characteristics of 6-coordinate nitro complexes of Co(TTP) and equilibrium constants for the reaction $\text{Co(TTP)(NO}_2\text{)} + \text{L} \leftrightarrow \text{(L)Co(TTP)(NO}_2\text{)}$ in CCl_4 solution^a

	UV-vis, λ_{max} (nm)	IR frequencies (cm^{-1})	$\Delta\nu = [\nu_{\text{as}}(\text{NO}_2) - \nu_{\text{s}}(\text{NO}_2)]$	K_{298} (M^{-1})	ref
Co(TTP)(NO ₂)	419, 530	1468 (~1440), 1282 (1264), 805 (796)	186		6d
(DMS)Co(TTP)(NO ₂)	439, 551, 588	1444 (1413), 1298 (1279), 810 (~802)	146	3990 ± 180	this work
(THT)Co(TTP)(NO ₂)	440, 552, 591	1443 (1413), 1300 (1282), 810 (~802)	143	1900 ± 90	this work
(Pip)Co(TTP)(NO ₂)	435, 550, 582sh	~1440 (1403), 1305 (1284), 815 (805)	135	$(5.1 \pm 0.55) \times 10^5$	6e, this work

^aData for ¹⁵NO₂-labeled compounds are given in parentheses.

result in a closer disposition of ν_{as} and ν_{s} than weak sulfur-donor ones (see Table 2).

It was found recently that maintaining layered five-coordinate iron nitritoporphyrin complexes under a vapor of a sulfur donor led to the appearance in the FTIR spectra of a nitrosyl band of Fe(Por)(NO) (Por = TPP, TTP). Additionally, sulfoxides (DMSO and THTO) were found in the gaseous phase of the cryostat in which sulfur-donor ligands were maintained over the Fe(Por)(ONO) layers overnight.^{14b} This was reasonably interpreted as evidence of the oxo-transfer reactivity of iron nitritoporphyrin complexes in the solid state, as was found for solutions.¹⁵ The same experiments with layered Co(TTP)(NO₂) did not reveal either the formation of cobalt nitrosylporphyrin complexes or evidence of sulfoxide formation. It seems that the cobalt nitroporphyrin complexes do not possess oxo-transfer reactivity in regards to sulfides under these conditions. One of the reasons for different oxo-transfer reactivity may be connected with the fact that the binding of sulfur-donor ligands with iron nitritoporphyrin complexes, resulting in the formation of six-coordinate nitro species (S-donor)Fe(Por)(NO₂), is much weaker and the excess of sulfur donors is necessary for stabilizing six-coordinate compounds. Therefore, five-coordinate nitrito and six-coordinate nitro complexes simultaneously exist for the iron system, as opposed to the cobalt case, in which the less reactive^{5a} six-coordinate complexes (S-donor)Co(TTP)(NO₂) are much more stable. We believe

that this higher stability of the cobalt nitroporphyrin complex with trans sulfur ligands in comparison with analogous iron species prevents the occurrence of oxo-transfer reactions, although even in the case of reactive iron porphyrins, it is not clear what kind of species (nitro or nitrito) is responsible for the promotion of sulfur-donor ligand oxidation.¹⁵

In summary, the six-coordinate nitrosyl and nitro complexes of cobalt porphyrin with trans sulfur-donor ligands (DMS and THT) have been obtained for the first time. The nitrosyl complexes are very unstable and can be observed only at low temperatures both in the solid state and in solution. This observation, however, implicates the potential ability of a sulfur-donor-ligated cobalt hemoglobin, cobalt myoglobin, and cobalt cytochrome *c* for the momentary binding of external NO. The nitro complexes of cobalt porphyrins form fairly stable six-coordinate complexes with sulfur-donor ligands in the solid state that partly decompose upon dissolution. The FTIR and EAS spectra are reported for these species, and the binding constants of complexation reactions are determined. In contrast to iron nitritoporphyrin complexes Fe(Por)(η^1 -ONO) in thin layers, which reveal oxo-transfer reactivity in oxidizing sulfides, the layered Co(TTP)(NO₂) complexes do not show such reactivity. Most likely, this is connected with the fast formation of fairly stable six-coordinate (S-donor)Co(TTP)(NO₂) complexes that are not active in oxo-transfer reactions from the coordinated nitro group.

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