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Low-Temperature Spectral Observation of the First Six-Coordinate Nitrosyl Complexes of Cobalt(II) *meso*-Tetratolylporphyrin with Trans Nitrogen Base Ligands

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Low-temperature interaction of nitrogen base ligands with layered Co(TTP)(NO) (TTP = *meso*-tetratolylporphyrinato dianion) as well as its toluene solution leads to the formation of the first six-coordinate species of the general formula (B)Co(TTP)(NO) (where B = piperidine and pyridine). The ν(NO) stretching bands of these species appear at lower frequencies compared with the five-coordinate nitrosyl derivative and depend on the nature of the trans axial ligand. The equilibrium constants and enthalpies of formation of these new species are determined. Fairly stable at low-temperature conditions in the solid state, they slowly dissociate the nitrogen base ligands upon warming to restore the five-coordinate nitrosyl complex Co(TTP)(NO).

Nitric oxide (NO) is an important bioregulatory molecule playing an active role in a variety of physiological processes.[1] One of the pathways of its activity involves its reaction with different metal centers of proteins.[2] For this reason, a great number of nitrosyl complexes of biologically important iron and cobalt porphyrins have been obtained and studied in detail.[3] The five-coordinate nitrosyl complex Co(TPP)(NO) (TPP = *meso*-tetraphenylporphyrinato dianion) studied in 1973 by Scheidt and Hoard[4] was the first reported structure of a metalloporphyrin containing a coordinated nitrosyl group. This square-pyramidal complex displays a bent M−N−O geometry with a bond angle of $\sim$135°. Five-coordinate nitrosyl complexes of the aforementioned metalloporphyrins are the most stable form. Less stable six-coordinate nitrosyls containing base ligands in the trans axial position were also characterized for iron and manganese porphyrins.[3−5] For cobalt porphyrins, however, to the best of our knowledge, the six-coordinate nitrosyl complexes have not yet been characterized and reported.

It was found that *meso*-tetraarylporphyrins (TAPs) can form microporous “porphyrin sponges”, which allows incorporation of guest molecules with different shapes and sizes.[6a,b] The structure of the sublimed layers of these species is also spongelike.[6c] The amorphous layers of M(TAP) obtained by sublimation on a low-temperature (77 K) surface have high microporosity. In these layers, potential reagents easily diffuse across the thickness, and the adducts thus formed can be studied by IR spectroscopy without solvent interference. This methodology also provides the opportunity to investigate various gas−solid interactions at low-temperature conditions for characterization of unstable and intermediate species.[7]

It has been shown previously that sublimed layers of *meso*-tetraphenylporphyrinatocobalt(II) give the five-coordinate nitro complex upon interaction with NO_2 gas.[8a] This layered complex was readily transformed to a six-coordinate amino−nitro complex (B)Co(TPP)(NO_2) (B = pyridine, piperidine, and ammonia) when exposed to the vapors of the corresponding amines.[8b] Taking into account the results of the aforementioned work in this paper, attempts were made to obtain six-coordinate nitrosyl complexes (B)Co(TTP)(NO) (TTP = *meso*-tetratolylporphyrinato dianion) by the interac-

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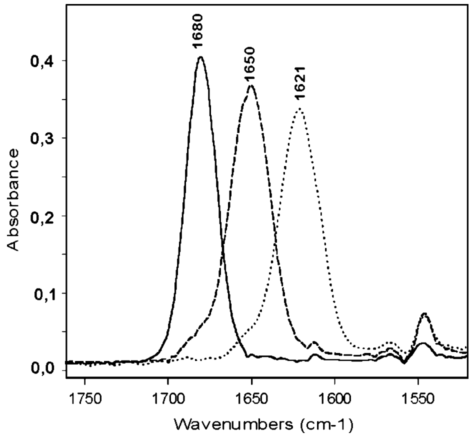


Figure 1. FTIR spectra of the Co(TTP) sublimed layer after interaction with NO (solid line) and the subsequent addition of 2 Torr of piperidine vapor at −50 °C (dashed line). The FTIR spectrum indicated by the dotted line was obtained by the addition of 2 Torr of piperidine to Co(TTP)-(^{15}NO) at −50 °C.

Table 1. FTIR and UV−Visible Data for Five- and Six-Coordinate Nitrosyl Complexes of Co(TTP) with Trans Lewis Base Ligands[a]

	Co(TTP)	Co(TTP) (NO)	(Pip)Co(TTP) (NO)	(Py)Co(TTP) (NO)
$\nu(^{14}NO)$, cm^{-1}		1680	1650 (30)	1643 (37)
$\nu(^{15}NO)$, cm^{-1}		1651	1621 (30)	1615 (36)
λ_{max}, nm	533	542	545	546
K_{298}, M^{-1}			0.45	0.2
$\Delta H°$, kcal/mol			−6 ± 0.4	−5 ± 0.4
$\Delta S°$, (cal/mol) K^{-1}			−22 ± 2	−20 ± 2

[a] In parentheses, the values of ν(NO) shifts upon Lewis base coordination are given.

tion of base ligands B (B = piperidine and pyridine) with layered mononitrosyl complex Co(TTP)(NO).

Interaction of NO gas with low-temperature sublimed layers of Co(TTP) in the optical cryostat leads to the easy formation of the nitrosyl complex Co(TPP)(NO), which manifests itself by the strong stretching band of the coordinated NO group with ν(NO) = 1680 cm^{-1} (1651 cm^{-1} for ^{15}NO) (Figure 1). When ~2 mmHg of the base ligand (piperidine or pyridine) was introduced into the cryostat containing the layered nitrosyl complex at room temperature, spectral changes were limited to the appearance of small bands resulting from the intensely absorbing base ligand's IR bands at very low concentration. They should reasonably be assigned to base molecules simply adsorbed onto the layer. No change of the nitrosyl stretching band is observed at this temperature. However, when the temperature of the layer was slowly lowered, the intensity of the ν(NO) band began to decrease and a shoulder appeared in the low-frequency range of this band. With further lowering of the temperature, this shoulder grew in intensity at the expense of the high-frequency band until it finally almost completely displaced the former ν(NO) band (Figure 1, dashed line). This new band appeared at 1650 cm^{-1} in the case of the piperidine ligand and somewhat lower for the pyridine base (see Table 1). This band certainly corresponds to the nitrosyl stretching of another species because substitution of ^{15}NO results in isotopic shifts close to those predicted for a diatomic molecule in the harmonic oscillator approximation. Intense evacuation of these systems by high-vacuum pumping at low temperatures (≤−60 °C) did not change the intensity of the nitrosyl stretching bands, demonstrating the stability of these new species under these conditions. However, warming these layers leads to spectral changes represented in Figure 2 and provides evidence for the decomposition of the new adduct with a shifted ν(NO) band. At room temperature, the initial spectrum of the five-coordinate nitrosyl complex, Co(TTP)-(NO), is completely restored.

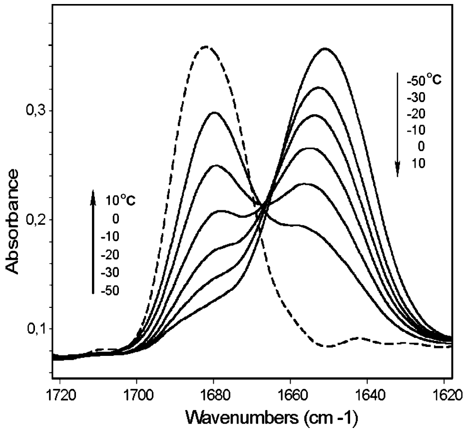
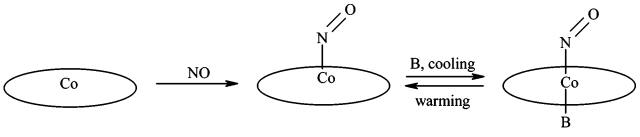


Figure 2. FTIR spectra of thin (Pip)Co(TTP)(NO) layers upon its warming (solid lines) and of the same layer maintained under vacuum overnight at room temperature (dashed line).

There are two possible explanations for the shifts of the NO stretching bands. The first one involves a direct and specific interaction of the base ligand with the coordinated nitrosyl group, leading to the lowering of ν(NO). At least for piperidine, this type of interaction could arise from hydrogen bonding between the Lewis base's NH hydrogen and the N or O atom of the nitrosyl group. However, with this interpretation, it would be very difficult to explain the greater extent of ν(NO) shifting in the case of the pyridine base and the significant changes observed in the electronic spectra (see below). The second explanation involves the coordination of the base ligands at the Co metal center in the open axial position and its trans influence on the frequency of NO stretching. Such six-coordinate complexes are known for iron(II) and manganese(II) nitrosylporphyrins. In the former, the nitrosyl ligand is coordinated in a bent fashion. Upon coordination of base ligands in the trans axial position, a low-frequency shift of the nitrosyl band, ν(NO), by a few tens of reciprocal centimeters is observed as those in our experiments. The value of the shift noticeably depends on the nature of the base ligand and the relative orientation of the axial ligand planes.[3b] The structurally characterized six-coordinate manganese nitrosylporphyrins have a linear Mn−N−O group. In these derivatives, the dependence of the changes in the nitrosyl stretching frequency, ν(NO), on the coordination of the sixth ligand is very minor and cannot provide direct information about the presence of the trans ligand.[5] The results of our study, with regard to the direction and values of the ν(NO) shifts, are close to those obtained for the six-coordinate iron porphyrin nitrosyls[3b] (B)Fe(Por)-(NO). As was mentioned above, these derivatives have a bent Fe−NO geometry, as is observed in the cobalt porphyrin nitrosyls. We believe, therefore, that the spectral changes

Scheme 1



B – pyridine, piperidine

described provide evidence for the formation of new six-coordinate nitrosyl complexes with trans axial base ligands, i.e., (B)Co^{II}(TTP)(NO).

The electronic absorption spectra also undergo changes both upon the addition of NO to the sublimed layers of Co(TTP) and with further interaction with base ligands at low-temperature conditions (Figure S1 in the Supporting Information). Upon the formation of the nitrosyl complex, the porphyrin Q band underwent a bathochromic shift from 533 to 542 nm and further red shifting upon interaction with the bases. These changes are typical for Co^{II}(TAPs) upon the formation of their axial complexes.[9] The latter spectral changes are reversible, and upon warming of the layer to room temperature, the spectrum of Co^{II}(TTP)(NO) is restored.

Hence, the reaction represented in Scheme 1 is realized in the amorphous layers of Co(TTP) upon sequential interaction with NO and Lewis bases.

Results closely related to those obtained in the solid state have been obtained for low-temperature toluene solutions (see Figure S2 in the Supporting Information). From the temperature dependence of the equilibrium constants, the thermodynamic parameters of the reaction represented in Scheme 1 were determined. The results obtained are summarized in Table 1.

In summary, the low-temperature interaction of Lewis bases with a five-coordinate cobalt nitrosyl complex, Co(TTP)(NO), leads to the formation of a six-coordinate adduct, (B)Co(TTP)(NO), which is stable at temperatures below −60 °C and slowly decomposes upon warming to room temperature, thus restoring the parent five-coordinate nitrosyl species Co(TTP)(NO). This is the first direct observation of the ability of cobalt porphyrin nitrosyls to form six-coordinate species. Although thermally unstable, these adducts obviously can figure as intermediates in the reactions of cobalt porphyrins in vivo.

Co(TTP) was synthesized using the literature method.[10] Before the experiment, Co(TTP) was additionally purified by column chromatography with dry alumina using reagent-grade chloroform as an eluent. Co(TTP)(NO) for solution experiments was prepared by introducing a solid sample of Co(TTP) under a NO atmosphere (~100 mmHg) for 2 h in an airtight flask connected with a high-vacuum line. This procedure leads to a sample with an intense band of nitrosyl stretching ($\upsilon = 1680$ cm^{-1}; $\epsilon = 1100$ M^{-1} cm^{-1}). NO (^{15}NO) was purified by passing it through KOH pellets and a cold trap (dry ice/acetone) to remove higher nitrogen oxides and trace quantities of water. The purity of the layer obtained was checked by IR measurements by slow deposition of NO onto the cold substrate of the optical cryostat (77 K). The IR spectra did not show the presence of N_2O, N_2O_3, or H_2O. ^{15}NO with 98.5% enrichment was purchased from the Institute of Isotopes, Republic of Georgia, and was purified by the same procedures. Freshly distilled Lewis bases (pyridine and piperidine) were stored over KOH. Before their introduction into the cryostat, they were degassed by the freeze−pump−thaw method.

Sublimed layers of Co(TTP) were obtained on the cold (77 K) KBr support of an optical cryostat according to a published procedure.[5b] These layers were then heated to 250 K under a dynamic vacuum ($P \approx 2 \times 10^{-5}$ mmHg), and NO (^{15}NO) 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 leads 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 heated to room temperature, and a few millimeters of mercury base (piperidine or pyridine) was introduced into the cryostat. The layer then slowly cooled, and FTIR or UV−visible spectra were measured at various controlled temperatures by a thermocouple. After the complete disappearance of the five-coordinate nitrosyl complex, the excess of the base ligand was pumped out, and 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 base ligands with Co(TTP)(NO) in a toluene solution was carried out in the optical cryostat having a 0.05 cm CaF_2 cell attached. A measured quantity of Co(TTP)(NO) was fed into the airtight flask through a septum. Known quantities of preliminary degassed solutions of base ligands in toluene were then transferred to this flask by vacuum techniques. The solutions thus prepared were transferred to the IR cell by an airtight Hamilton syringe. The cell was then tightly closed and placed into the cryostat. As IR measurements were made, the 1280−1320 cm^{-1} range in which the $\nu_s(NO_2)$ of Co(TTP)(NO_2) or (B)Co(TTP)(NO_2)[8] are disposed was also thoroughly inspected. There were no indications of Co(TTP)(NO) oxidation to (B)Co(TTP)(NO_2) during the study. The FTIR and UV−visible spectra were measured on Nexus and "Specord M-40" spectrometers, respectively. The background for FTIR measurements was collected for a toluene−ligand solution at each temperature studied.

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Supporting Information Available: Figure S1 demonstrating UV−visible spectra of sublimed layers containing Co(TTP), Co(TTP)(NO), and (Py)Co(TTP)(NO) and Figure S2 displaying the temperature dependence of FTIR spectra of the Co(TTP)(NO) plus base ligand in a toluene solution in the −10 to −90 °C temperature interval. This material is available free of charge via the Internet at http://pubs.acs.org.

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