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# ОБЩАЯ И ФИЗИЧЕСКАЯ ХИМИЯ

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### SPECTRAL STUDIES OF NITROGEN OXIDES INTERACTION WITH HEME MODELS

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Using FTIR and UV-vis spectroscopy comprehensive information was obtained regarding to interaction of nitrogen oxides with metalloporphyrin (MP) complexes of biologically important elements, such as, Fe, Co and Mn. Using differently labeled nitrogen oxides and DFT calculations the mode of coordination and electronic structure were reliably determined for the nitrosyl, nitrite and nitrate complexes of these MPs. Dependence of these parameters on the nature of metal has been clarified. Transformations of nitrogen oxides in the coordination sphere of MPs and their mechanisms were elucidated. The previously unknown 6-coordinate nitrosyl, nitrite and nitrate complexes of these MPs with *trans* electron donor ligands were obtained and spectrally characterized.

Fig. 9, tables 6, references 72.

# Introduction

The interaction of metalloporphyrins (MPs) with various nitrogen oxides is of enormous physiological importance. Nitrosyl, nitrite and nitrate MP complexes are involved in key processes in both the nitrogen cycle and mammalian physiology. Examples of the latter include neurotransmission, vasodilation and prevention of platelet aggregation. It is interesting that the ability of nitric oxide to induce vasodilation and prevent blood clotting is also utilized by several species of insects that feed upon the blood of the mammalian hosts.

Most of these processes proceed with the participation of heme-proteins. These are enzymes, the prosthetic group of which contains an iron-porphyrin ring. This

ring is usually immobilized by coordination with the electron donor atom of the protein's amino acid residue at the proximal site (see Figure 1 for myoglobin). The 6-th coordination distal site is usually occupied by a weak ligand, i.e. water, or remains free. Namely at this site the various transformations of interacting molecules occur.



Fig. 1. Myoglobin structure.

Iron porphyrinato complexes are often used as models for heme proteins. In order to elucidate the processes taking place in the coordination sphere of metal, it is important to have physical methods to characterize effectively the nature of the intermediates formed. Vibrational spectroscopy is one such tool, and Raman and especially resonance Raman spectroscopy have provided valuable information regarding the reactions of heme models and proteins. In contrast, the data obtained by infrared spectroscopy, which is complementary, are often limited by the interference with the solvent bands. This problem can be overcome by using sublimed layers methodology elaborated in our laboratories.

It was shown that sublimed layers of MPs obtained by deposition on to lowtemperature substrate are both amorphous and microporous [1]. They provide unimpeded diffusion of volatile reactants into the bulk of the layer and the species thus formed can be examined by FTIR and optical spectroscopy without the masking effects of the solvent. This methodology also provides an opportunity to investigate various gas-solid interactions at low-temperature conditions for characterization of unstable and intermediate species. By means of this methodology especially broad information has been obtained regarding to the interaction of various nitrogen oxides with the metallocomplexes of porphyrins containing biologically important metals, with Fe, Co and Mn among them.

In studies of heme proteins the technique of replacement of the neutral iron porphyrin prosthetic group with different MPs has been very useful [2] especially with Co-porphyrins that possess dioxygen binding ability, but contrary to EPR silent Fe<sup>II</sup>-porphyrins ( $d^6$ ) these can be studied by EPR due to single odd-electron configuration ( $d^7$ ). The EPR studies of Co heme proteins provided many important 456

insights for understanding the electronic and geometric structures which were not possible for the diamagnetic deoxy and oxy iron heme proteins [2, 3]. Mn-substituted heme proteins are also EPR-active ( $d^5$ ) and Mn prosthetic group were inserted into different apoproteins and EPR spectra and reactivity of the Mn components in the heme pocket were measured to evaluate the electronic structure of Mn-complexes [2, 4].

In this review we summarized the results obtained by our research group for the nitrogen oxides interaction with Fe-, Co- and Mn-porphyrins. Some of these results devoted to the reactions of nitrogen oxides with ferrous- and ferric-porphyrins were presented in the review published earlier [5]. For reactions with the nitrogen oxides, the use of isotopically labeled nitric oxide and nitrogen dioxide is very helpful for reliable assignments [5]. The earlier, detailed analysis of 5- and 6-coordinate Fe(TPP) (TPP - *meso*-tetraphenylporphyrinato dianion) complexes by Nakamoto and co-authors showed that the IR spectra display several bands indicative of the spin and oxidation states [6]. These additional data are very useful for the detailed information about the electronic structure of the species formed.

**Nitrosyl complexes of metalloporphyrins**. Nitric oxide (NO) has several wellestablished roles in mammalian biology closely tied to its interactions with metalloproteins, especially heme proteins [7]. A key example is the vasodilation triggered by the interaction of NO with the ferroheme center of soluble-guanylate cyclase leading to at least 200 fold increase in sGC activity [8]. This is due to NO binding with iron accompanied with the disruption of the Fe-Histidine bond (Fig. 1) and corresponding change of the enzyme conformation [9].

In the beginning of this century controversial data were published for the reaction of NO with simple ferrous heme models [10-13]. Some authors claimed that nitric oxide disproportionation reaction takes place leading to formation of the nitronitrosyl complex [10, 11] while the others [12, 13] have rejected this reaction pathway. This system was reexamined by using the sublimed layer technique and it was shown that in the similar experimental conditions Ru-porphyrins promote NO disproportionation while ferrous porphyrins do not [14]. It was shown later that in contrast to iron-analog manganese(II)-porphyrins promote NO disproportionation.

Low-temperature interaction of NO excess with sublimed layers of Mn(Por) resulted eventually in the formation of Mn(Por)( $\eta^1$ -ONO) and evolution of nitrous oxide N<sub>2</sub>O [15, 16]. Using different Mn-porphyrins and isotopically labeled NO the mechanism of this reaction was clarified in details [16].

In the case of Fe-porphyrins the only intermediate detected at low temperatures was dinitrosyl complex that loses one of the axial ligands upon warming to room temperature (RT) resulting in the formation of the well-known mononitrosyl complex (Scheme 1) [17]. According to the DFT calculations in the dinitrosyl complex the nitrosyls are tilted in the same side [18], making the NO synphase stretching IR active, as is seen in the FTIR spectrum (Fig. 2, dashed line, IR band at about 1775  $cm^{-1}$ ). Recent studies showed [19] that for the activation of the soluble guanylate cyclase two equivalents of nitric oxide is necessary. This led to the

speculation that a proximal NO is responsible for histidine displacement, giving an intermediate 6-coordinate NO-Fe-NO complex. Our observation of the di-nitrosyl complex supports this point of view. An alternative hypothesis states that a second, non-heme binding site accounts for the second NO dependent activation process to give the fully active enzyme [20].



Fig. 3. FTIR spectra of Mn(TPP)(solid), Mn(TPP)(NO) (dashed) and  $Mn(TPP)(^{15}NO)$  (dotted) in the range of v(NO) [21].

Fig. 4. Temperature dependence of the Mn(TPP)(NO) FTIR spectra [21].

Very interesting results were obtained in the course of the nitric oxide interaction with amorphous layers of Mn-porphyrins [21] leading to the formation of two isomeric nitrosyl complexes with the v(NO) disposed at 1739 and 1614  $cm^{-1}$ (Fig. 3) reversibly interconverting with changes in temperature. Cooling the layers containing the nitrosyl complex(es) from 290 K was accompanied with a decrease in intensity at 1614 cm<sup>-1</sup> and an increase at 1739 cm<sup>-1</sup> (Fig. 4). At 20 K, the spectrum is dominated by the latter band. This process is reversible; repeated cooling and warming of the sample gave identical results. From the temperature dependence of these FTIR band ratios, the enthalpy difference between the two species was calculated to be ~1 kcal/mol. DFT computations predict the existence of a linear nitrosyl Mn(TPP)(NO) complex with a singlet ground electronic state (Scheme 2a) and another state close in energy with a bent Mn-N-O geometry and a triplet electronic state (Scheme 2b). The isomers are in dynamic equilibrium and as the temperature is decreased, the second isomer almost completely passes to the linear species. Recently an unprecedented bent geometry of NO-binding with Mn(II) was detected in Mn-substituted horse heart myoglobin [22]. The authors attributed this to an H-bonding of  $N_{\epsilon}$  atom of the distal His64 residue with the N-and O-atoms of coordinated NO. It cannot be excluded that the ability of Mn-nitrosyl porphyrins to be bent in the intermediate spin state additionally contributes to the realization of the bent geometry. It would be of interest to know whether the distortion observed for the horse heart myoglobin is accompanied by a spin state change. It should be also stressed that this isomerism is inherent only to the amorphous samples. Crystallization, accompanying with the closer packing of the molecules in the layer, leads to the complete disappearance of the bent species.

Scheme 2 Ph Ph

Since most of the heme proteins contain an axial electron donor ligand in the proximal site, the 6-coordinate nitrosyl complexes are of particular interest. Such complexes containing N-donor ligands in the *trans* axial position were characterized for iron and manganese porphyrins [23, 24]. For Co-porphyrins, however, the first 6-coordinate nitrosyl complexes with *trans* amino ligands were obtained only by the application of low-temperatures due to the thermal instability of such species [25]. Low-temperature interaction of nitrogen base ligands with layered Co(TTP)(NO) (TTP = *meso*-tetra-*p*-tolylporphyrinato dianion) as well as its toluene solution leads

to the formation of the first 6-coordinate species of the general formula (B)Co(TTP)(NO) (where B - piperidine and pyridine). The v(NO) stretching bands of these species appear at lower frequencies in comparison with the 5-coordinate nitrosyl derivative and depend on the nature of the *trans* axial ligand (Table 1). Fairly stable at low-temperature conditions in the solid state, they slowly dissociate the nitrogen base ligands upon warming to restore the 5-coordinate nitrosyl complex Co(TTP)(NO).

Six-coordinate nitrosyl complexes with *trans* sulfur-containing ligand were also obtained and spectrally characterized [26]. The FTIR spectral changes observed for Co(TTP)(NO) sublimed layer in the range of v(NO) stretching after introducing tetrahydrothiophene (THT) into cryostat at T = 120 K and slow warming till 170 K are presented in Fig. 5.



Fig. 5. FTIR spectra at 170 K of sublimed layers containing Co(TTP)(NO) (solid line), Co(TTP)(THT)(NO) (dashed line) and  $Co(TTP)(THT)(^{15}NO)$  (dotted line) [27].

Fig. 6. UV-visible spectra at 170 K of sublimed layers containing Co(TTP) (solid line) Co(TTP)(NO) (dashed line) and (DMS)Co(TTP)(NO) (dotted line) [27].

The UV-visible spectrum of the layered Co(TTP) also undergo noticeable changes in the course of sequential interaction with NO and sulfur-containing ligands. As seen in Fig. 6 the single band of Co(TTP) in the visible range at 533 *nm* shifts to 542 *nm* and displays a shoulder at 578 *nm* upon the formation of the nitrosyl complex Co(TTP)(NO). Upon low-temperature interaction with DMS this band undergoes 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 demonstrated the formation of the Co(TTP)(NO) (dashed line) then a species with the complete shifting of v(NO) to the lower frequency range (dotted line).

The equilibrium constants and enthalpies of the formation of these new species are determined and presented in Table 1.

	Co(TTP)	(Pip)Co(TTP)	(Py)Co(TTP)	(DMS)Co(TTP)	(THT)Co(TTP)
	(NO)	(NO)	(NO)	(NO)	(NO)
$v(NO), cm^{-1}$	1680 (1650)	1650 (1621)	1643 (1615)	1661 (1633)	1658 (1629)
$\Delta v(NO)$		30 (29)	37 (35)	19 (17)	22 (21)
$\lambda_{\rm max}, nm$	542	545	546	427, 546, 585	429, 545, 584
$K_{298}$ , $M^{-1}$		0,45	0,2	~ 0.012	~ 0.007
$\Delta H^{o}$ , kcal/mol		$-6 \pm 0,4$	$-5 \pm 0,4$	-	$-4.72 \pm 0.4$
$\Delta S^{\circ}, cal mol^{-1} K^{-1}$		$-22 \pm 2$	$-20 \pm 2$	-	$-30, 23 \pm 4$
$\Delta G^{o}$ , kcal/mol		$+0,56\pm0,5$	+ 0,596±0,6	_	+ 4,28±0,5

FTIR, UV-Visible Data and Thermodynamic Parameters for 5- and 6-Coordinate Nitrosyl Complexes of Co(TTP) with Trans N- and S-donor Ligands [25, 26]. In parenthesis data for <sup>15</sup>NO isotopomer are given.

The data represented in Table 1 show that for 6-coordinate Co-porphyrin nitrosyls both the values of v(NO) shifts and equilibrium constants are larger for the N-donor *trans* ligands than for the S-donors. These complexes are very unstable and can be observed only at low-temperatures both in the solid state and solutions. This observation however implicates the potential ability of N- and S-donor-ligated cobalt hemoglobin, cobalt myoglobin and cobalt cytochrome *c* for momentary binding of external NO.

Many heme proteins contain amino acid residues with sulfur and oxygen electron donor atoms as a proximal ligand. Therefore it was of interest to investigate whether 6-coordinate nitrosyl complexes of ferrous porphyrins with this type of axial ligation can be formed. The interaction of the S- and O-donor ligands tetrahydrothiophen (THT) and tetrahydrofuran (THF) with ferrous nitrosyl complex Fe(TTP)(NO) was studied at various temperatures both in solid state and solution using electronic and infrared absorption spectroscopy. Upon addition of these ligands into a cryostat containing the sublimed layers of Fe(TTP)(NO), no complex formation was detected at RT. However, upon decreasing the temperature, spectral changes were observed that are consistent with ligand binding in axial position *trans* to the NO (the proximal site) and formation of the six-coordinate adducts [27]. Analogous behavior was observed in solution. In both media, the 6-coordinate adducts are stable only at low temperature and dissociate to the 5-coordinate nitrosyl complexes upon warming. The NO stretching frequencies of the 6-coordinate thioether and ether complexes were recorded and the binding constants for the weak bonding of proximal THF and THT ligands were determined from the spectral changes. These parameters are compared with those obtained for the N-donor ligand pyrrolidine. The spectral and thermodynamic data of such complexes are presented in Table 2.

	Fe(TTP)(NO)	Fe(TTP)(THF)(NO)	Fe(TTP)(THT)(NO)	Fe(TTP)(Pyrr)(NO)
$v(NO) (cm^{-1})$	1676 (1645)	1651(1626)	1648(1622)	1636(1605)
$\Delta v(NO) (cm^{-1})$	_	25(19)	28(23)	40(40)
$\lambda_{\max}(nm)$	409	425	427	427
$K_{298}, (M^{-1})$		$0.014 \pm 0.001$	$0.038\pm0.002$	$38 \pm 0.2$
$\Delta H^{O}$ (kcal mol <sup>-1</sup> )		$-2.2 \pm 0.2$	$-2.0 \pm 0.2$	$-9.3 \pm 0.7$
$\Delta S^{O}(cal mol^{-1} K^{-1})$		- 16 ± 2	- 13 ± 2	- 24 ± 3
$\Delta G^{O}$ (kcal mol <sup>-1</sup> )		$+2.5 \pm 0.2$	$+1.9 \pm 0.2$	$-2.2 \pm 0.2$

Spectral data and thermodynamic parameters for the ferrous nitrosyl complex Fe(TTP)(NO) and the corresponding 6-coordinate adducts [27]. In parenthesis data for <sup>15</sup>NO isotopomer are given.

Although nitrosyl complexes with trans S- and O-donor ligands are thermally unstable, the results of this study imply that such species may be formed in heme proteins with proximal S- and O-containing ligands as intermediates. The data presented in Table 2 show that both the values of the v(NO) shifts and the equilibrium constants are larger for the N-donor *trans* ligands when compared to those of the S-donors. The same pattern was observed for the 6-coordinate Coporphyrin nitrosyls (Table 1).

Nitrite complexes of metalloporphyrins. The roles of nitrogen dioxide (NO<sub>2</sub>) and of nitrite ion  $(NO_2)$  in mammalian biology are hard to overestimate [28-32]. NO<sub>2</sub> is a strong oxidant and nitrating species that initiates destructive pathways in living systems [28], and several disease states have been suggested to be connected with exogenously and endogenously formed NO<sub>2</sub> [29, 30]. Likely endogenous sources of NO<sub>2</sub> are the reactions of nitric oxide (NO) with oxyglobins and with superoxide ion  $(O_2)$  leading to coordinated and free peroxynitrite (ONOO), subsequent decay of which afford both nitrate ion and  $NO_2$  [32]. Furthermore, there is increasing evidence that  $NO_2$  may also be formed *via* enzymatic pathways with participation of heme peroxidases [28]. Nitrogen dioxide has also been shown to be a product of the reaction of NO and nitrate as mediated by a heme center [33]. With regard to nitrite, the  $NO_2^{-1}$  ion is ubiquitous in mammalian tissues and fluids and the largest reservoir of accessible NO equivalents in the cardiovascular system [31, 34]. Recent studies have suggested that  $NO_2^-$  itself is a vasodilator or forms the known vasodilator NO via reaction with hemes [35-38] and has been proposed as a therapeutic agent under hypoxic ischemia conditions [39, 40].

The ambidentate nitrite ion can coordinate to metals either at the oxygen to give nitrito or at the nitrogen to give nitro complexes [41]. A third potential coordination mode involving bidentate binding of both oxygens to the metal is unknown for MPs and related metalloproteins.

By interaction of small increments of nitrogen dioxide with Fe-porphyrins amorphous layers the first 5-coordinate nitrite complexes were obtained. The FTIR and optical spectral data indicate the coordination of nitrite through the oxygen atom and the high-spin state of the metal [42] (Scheme3).



R - phenyl, *p*-tolyl

Such 5-coordinate O-nitrito complexes have repeatedly been postulated as intermediates in iron-porphyrins reactions with  $NO_x$  species, but before the publication of Kurtikyan and Ford [42] the elusive O-nitrito complex had never been identified. In heme models and hemeproteins the nitrite group in 6-coordinate complexes is usually bound via the nitrogen atom [23]. However from these data and consequent DFT calculations [43] performed for the 5-coordinate complex in different spin states it is seen that the O-bound isomer has lower energy (Table 3).

Table 3

Complex	Total Energy, au	ΔE, au	ΔE, kJ/mole	HOMO eV	LUMO eV	Dipole Moment (Db)
$^{2}\text{Fe}^{\text{III}}(\text{P})(\text{NO}_{2})$	-1316.99793	0.00029	0.8	-5.44	-2.95	2.99
<sup>4</sup> Fe <sup>III</sup> (P)(NO <sub>2</sub> )	-1316.99466	0.00356	9.3	-5.34	-2.44	4.03
<sup>6</sup> Fe <sup>III</sup> (P)(NO <sub>2</sub> )	-1316.98632	0.01190	32.2	-5.44	-2.49	3.72
<sup>2</sup> Fe <sup>III</sup> (P)(ONO)	-1316.99236	0.00586	15.4	-5.49	-2.76	3.87
<sup>4</sup> Fe <sup>III</sup> (P)(ONO)	-1316.99822	0.00000	0.0	-5.45	-2.9	5.22
<sup>6</sup> Fe <sup>III</sup> (P)(ONO)	-1316.99584	0.00238	6.3	-5.48	-2.5	4.07

Computed total energies for all spin states of the N-nitro  $Fe(P)(\eta^1-NO_2)$ and O-nitrito  $Fe(P)(\eta^1-ONO)$  isomers of the NO<sub>2</sub> adduct of the iron(III) porphinato complex [43]

As it will be shown below the 5-coordinate nitrito complexes can serve as a convenient entry for synthesis of the 6-coordinate species. For example, addition of NO to nitrito complex at low temperatures leads to the formation of a nitrito-nitrosyl complex that isomerizes to the known nitro-nitrosyl complex upon warming thus demonstrating that NO binding to Fe(Por)( $\eta^1$ -ONO) leads to concomitant nitrito ( $\eta^1$ -ONO) to nitro ( $\eta^1$ -NO<sub>2</sub>) isomerization (Scheme 4).



R - phenyl, p-tolyl

Similarly the low temperature interaction of ammonia with the iron-porphyrin nitrito species leads to the formation of nitrito-ammonia complex [44]. Upon warming nitrito-nitro isomerization takes place as was in the case of the aforementioned NO ligand. At room temperature, the latter is stable only in the presence of excess NH<sub>3</sub> (> 20 *Torr*). When instead this system was warmed up to RT under intense high vacuum pumping, the Fe(TTP)(NH<sub>3</sub>)(NO<sub>2</sub>) underwent complete transformation to the initial nitrito complex Fe(TTP)( $\eta^1$ -ONO) (Fig. 7). Hence, the loss of the *trans* ammine results in reverse linkage isomerization.



**Fig. 7.** FTIR spectra of ammine-nitro complex  $Fe(TTP)(NH_3)(NO_2)$  (dashed line) after warming from 240 K to 293 K upon intense pumping. The bands of coordinated nitro group at 1401 and 1312  $cm^{-1}$  disappear with concomitant growth of the bands at 1528, 901 and 751  $cm^{-1}$  belonging to coordinated O-nitrito group in the 5-coordinate nitrito species  $Fe(TTP)(\eta^{-1}-ONO)$  [44].

The interaction of a weak electronodonor ligand tetrahydrofuran (THF) with the nitrito complex led to an unexpected result. The FTIR and UV-vis spectra demonstrate that tetrahydrofuran reacts with the 5-coordinate iron(III)-porphyrin nitrito complex Fe(Por)( $\eta^1$ -ONO) in low temperature layered solids to give two 6-coordinate THF complexes, O-nitrito and N-nitrito isomers Fe(Por)(THF)( $\eta^1$ -ONO) and Fe(Por)(THF)( $\eta^1$ -NO<sub>2</sub>), respectively (Scheme 5). These products also differ in their apparent spin states; the nitrito isomer being in high-spin while the nitro is in

low-spin. Both are thermally unstable, and when the layers are warmed up in vacuum the initial Fe(Por)( $\eta^1$ -ONO) is largely restored [45].

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R - phenyl, p-tolyl

The reaction of the stronger and less volatile electronodonor ligands (Py, 1-MeIm) with 5-coordinate nitrito complexes leads to formation of the 6-coordinate nitro complexes [44] that are stable at ambient conditions in solid state.

These data confirm that, for these ferriheme model complexes, the nitrite ligand is preferably bound via the O-coordination in the absence of an axial ligand but adopts the N-bonded configuration when the second axial site is occupied. Richter-Addo and co-workers have determined the crystal structures of nitrite ion complexes for human hemoglobin and horse heart myoglobin and found both to be nitrito species [46, 47]. The authors attributed this to the H-bonding of the N<sub> $\varepsilon$ </sub> atom of the distal His64 residue with the N-and O-atoms of the coordinated nitrite. Sustaining this suggestion the H64V mutant of metMb, which has the distal histidine replaced by a valine, binds NO<sub>2</sub><sup>-</sup> as a nitro complex [47]. These data confirm that the energy difference between nitrito and nitro species is small and subtle environment changes can give preference to one or the other coordination mode.

Low-temperature interaction of S-donor thioethers DMS and THT with 5coordinate iron porphyrin O-nitrito complexes  $Fe(Por)(\eta^1-ONO)$  (Por - TPP and TTP) leads to the formation of the 6-coordinate nitro species (R<sub>2</sub>S)Fe(Por)(NO<sub>2</sub>) [48]. Hence, the coordination of the proximal S-donor ligand leads to nitrito  $\rightarrow$  nitro isomerization of the nitrite ligand. In the presence of gas phase R<sub>2</sub>S donors these 6coordinate complexes can be observed even at RT. In contrast to high spin 5coordinate nitrito complexes, the 6-coordinate S-donor species are in the low spin state. DFT calculations for these 6-coordinate species give minimal energies for the low-spin doublet states for the nitro and nitrito isomers with the nitro isomer only 8 kJ/mol more stable than nitrito one. There are several indications of oxo-transfer reactivity of solid-state iron porphyrin nitrite system in the presence of gas phase R<sub>2</sub>S: appearance of the iron-nitrosyl band in the layered solid and formation of the corresponding sulfoxides demonstrating by the FTIR and mass spectrometric measurements together with <sup>18</sup>O isotope labeling experiments [48].

Via a room temperature reaction of small  $NO_2$  increments with the layered Coporphyrins the 5-coordinate nitro complexes  $Co(Por)(NO_2)$  were obtained and characterized by FTIR and optical spectroscopy [49]. These 5-coordinate nitro complexes reveal the oxygen atom transfer reaction from the coordinated nitrogroup to free nitric oxide leading to formation of Co-porphyrin nitrosyls [50]. Using  $Co(Por)(NO_2)$  species as a synthetic precursor to the 6-coordinate complexes,  $(L)Co(Por)(NO_2)$  species (where L is N-, S- and O-donor ligands) have been obtained [51, 26, 52]. Complexes with N-donors are stable compounds both in the solid state and solutions, while complexes with S- and O-donors are stable in the solid state but partly decompose in non-coordinating solvent. The spectral characteristics of these species are summarized in Table 4.

The FTIR data summarized in Table 4 for the 6-coordinate nitro Fe(III) complexes and for the Co(III) analogs provide the basis for assigning vibrational frequencies to the coordinated nitro group, and these assignments are sustained by data for <sup>15</sup>NO<sub>2</sub> labeled isotopomers. The Table 4 also suggests an interesting correlation between the nature of the ligand *trans* to the nitro group and the difference between the frequencies of asymmetric and symmetric stretches,  $\Delta v =$  $v_a(NO_2) - v_s(NO_2)$ . Within each series Fe(Por)(B)(NO<sub>2</sub>) (Por = TTP or TPP)  $\Delta v$ follows the order for the respective *trans* ligand: 1-MeIm < NH<sub>3</sub> < Py < S-donors  $\le$ THF << NO, while the cobalt(III) series Co(Por)(B)(NO<sub>2</sub>) follows an analogous order 1-MeIm < NH<sub>3</sub> < Py < S-donors < O-donors << empty coordination site (no ligand). Electronic communication between the axial ligands, B and NO<sub>2</sub>, occurs largely through the metal  $d_z^2$  and  $d_{xz}$ ,  $d_{yz}$  orbitals. In this context, we propose that  $\Delta v$ is reflective of the net charge transfer to or from the nitro group with the smaller  $\Delta v$ representing more charge transfer. Actually in nitrite anion NO2<sup>-</sup> representing the case with complete electron transfer the  $v_a(NO_2)$  and  $v_s(NO_2)$  are close to each other with  $v_a(NO_2)$  even lower than  $v_s(NO_2)$  [54]. In all series, the order 1-MeIm < NH<sub>3</sub> < Py holds true for  $\Delta v$ . This does not correlate with the Broensted base strengths of these ligands, where 1-MeIm is intermediate between Py and  $NH_3$  (the pKa's of the conjugate acids for Py, 1-MeIm and  $NH_3$  are equal to 5.25, 6.95 and 9.25 correspondingly [55]), however, the observed order may be rationalized by taking into account the modest  $\pi$ -donor character of 1-MeIm, while NH<sub>3</sub> is a  $\sigma$ -donor only and Py is a  $\pi$ -acceptor [56]. In the Co(III) series, the empty coordination site clearly leads to a much larger value of  $\Delta v$  as would be expected from the premise that this reflects the relative electron donor strength (in this case, none) of the *trans* ligand. If so, however, the position of NO in the Fe(III) series (largest  $\Delta v$ ) is especially interesting, since it suggests that there is very little net electron transfer from NO to the nitro ligand in the complex Fe(Por)(NO)(NO<sub>2</sub>). Such a conclusion draws some confirmation in DFT calculations (both B3LYP/3-21g and B3LYP/6-31g) for  $Fe(P)(NO)(NO_2)$  (P = porphinato dianion) that found the coordinated NO to have a slightly negative charge, hence having a net electron withdrawing effect. The data of Table 4 reveal less charge transfer for Co-porphyrins in comparison with Feporphyrins.

FTIR frequencies of the coordinated nitro group in the 6-coordinate complexes of
metalloporphyrins (data for <sup>15</sup> NO <sub>2</sub> isotopomer are given in parenthesis)

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		$(\mathbf{NO})$	$(\mathbf{NO})$	S(ONO)			
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Compound	$v_{a}(NO_{2}),$	$v_{s}(NO_{2}),$	$\delta(ONO),$	$\Delta v = v_a(NO_2)$ -	Reference	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(NO)E_{-}(TTD)(NO)$	1455(1402)	1205(1275)	205 (200)	$V_{s}(1(0_{2}))$	42	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(NO)Fe(TTP)(NO_2)$	1455(1423)	1295(1275)	805 (800)	160 (148)	43	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(NO)Fe(TPP)(NO_2)$	1456(1424)	1295(1274)	803(797)	161 (150)	43	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	(NH <sub>3</sub> )Fe(TTP)(NO <sub>2</sub> )	(1367)	(1291)	810 (~804)	89 (76)	44	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(NH_a)Fe(TPP)(NO_a)$	1399(1373)	1312(1291)	812(~805)	87 (82)	44	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\frac{(1(113))E(111)(1(02))}{(D_{11})E_{0}(TTD)(NO_{1})}$	1377(1373) 1405(1272)	1312(12)1) 1206(1297)	812(-803)	00 (86)	44	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(Fy)Fe(TTF)(NO_2)$	1403(1373)	1207	010(~004)	99 (80)	44	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(Py)Fe(TPP)(NO <sub>2</sub> )	(1270)	(1287)	810	99 (92)	44	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		(1379)	(1287)	(~804)			
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(1-MeIm)Fe(TTP)(NO <sub>2</sub> )	1396	1312	813	84 (72)	44	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		(1363)	(1291)	(~805)			
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(1-MeIm)Fe(TPP)(NO <sub>2</sub> )	1395	1312	812	83 (81)	44	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		(13/1)	(1290)	(~805)	(- )		
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(THF)Fe(TPP)(NO_2)$	1409	1310	812 (802)	99(96)	45	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	()()(2)	(1384)	(1288)				
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(THF)Fe(TTP)(NO_2)$	1411	1307	811(803)	104(100)	45	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		(1386)	(1286)	011(005)	104(100)	-15	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(DMS)E_{0}(TDD)(NO)$	1399	1302	810 (802)	97(90)	18	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(DWS)Te(TTT)(TO_2)$	(1373)	(1283)	810 (802)	97(90)	40	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	(DMS)Fe(TTP)(NO <sub>2</sub> )	1401(1374)	1300(1281)	809(~805)	101(93)	48	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(THT)Fe(TPP)(NO <sub>2</sub> )	1407(1377)	1303(1284)	807(~802)	104(93)	48	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(THT)Fe(TTP)(NO_2)$	1405(1376)	1302(1283)	808(~802)	103(93)	48	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1468	1282	~805	186(176)	49	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$Co(TPP)(NO_2)$	(~1440)	(1264)	(796)			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1431	1309	(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,			
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(NH_3)Co(TPP)(NO_2)$	(1400)	(1289)	814 (805)	122(111)	51	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		~1439	1310				
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(Py)Co(TPP)(NO_2)$	(1404)	(1288)	816 (806)	129(116)	51	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		~1/137	1308		129(117) 107(102)	51 52	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(Pip)Co(TPP)(NO <sub>2</sub> )	(1402)	(1285)	808 (-)			
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		(1402)	(1203)				
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(1-MeIm)Co(TPP)(NO <sub>2</sub> )	(1204)	(1202)	816 (809)			
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		(1394)	(1292)	910( 900)	14((124)	26	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(DMS)Co(TTP)(NO_2)$	1444(1413)	1298(1279)	810(~802)	146(134)	26	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$(THT)Co(TTP)(NO_2)$	1443(1413)	1300(1282)	810(~802)	143(131)	26	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(Acetone)Co(TPP)(NO_2)$	1459	1300	810 (802)	159(147)	53	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	(	(1429)	(1281)				
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(2-butanone)(Co(TPP)(NO_2))$	1458	1302	811 (803)	156(147)	53	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		(1428)	(1281)	011 (005)	156(117)		
$\begin{array}{c ccccc} (\operatorname{AcctophenoleCo(TTT)})(\operatorname{NO}_2) & (\sim 1441) & (1276) & 007(002) & 174(103) & 53 \\ \hline (\operatorname{Benzaldehyde})\operatorname{Co(TPP)}(\operatorname{NO}_2) & 1465 & 1303 \\ (1433) & (1282) & 811(803) & 162(151) & 53 \\ \hline (\operatorname{Epichlorohydrin})\operatorname{Co(TPP)}(\operatorname{NO}_2) & 1458 & 1301 \\ (1432) & (1281) & 806(802) & 157(151) & 53 \\ \hline (\operatorname{THF})\operatorname{Co(TPP)}(\operatorname{NO}_2) & 1462 & 1300 \\ (1430) & (1279) & 808(800) & 162(151) & 53 \\ \hline (\operatorname{Methanol})\operatorname{Co(TPP)}(\operatorname{NO}_2) & 1463 & 1301 \\ (1433) & (1282) & 809(803) & 162(151) & 53 \\ \hline (\operatorname{Ethanol})\operatorname{Co(TPP)}(\operatorname{NO}_2) & 1463 & 1298 \\ (\operatorname{Itat}) & (1278) & 804(798) & 165(153) & 53 \\ \hline (\operatorname{iso-propanol})\operatorname{Co(TPP)}(\operatorname{NO}_2) & 1462 & 1301 \\ (\operatorname{iso-propanol})\operatorname{Co(TPP)}(\operatorname{NO}_2) & 1462 & 1301 \\ (1428) & (1281) & 804(798) & 161(147) & 53 \\ \hline \end{array}$	$(Acetophenone)Co(TPP)(NO_{a})$	1471	1297	807 (802)	174(165)	53	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	(7 detophenone) Co(111)(1(0 <sub>2</sub> )	(~1441)	(1276)	007 (002)	174(105)	55	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(Panzaldahyda)Co(TDD)(NO)	1465	1303	911 (902)	162(151)	52	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$(\text{Belizal delive}) CO(111)(100_2)$	(1433)	(1282)	811 (803)	102(131)	55	
$\begin{array}{c c} (Epichlofolydrin)Co(TPP)(NO_2) & (1432) & (1281) & 806(802) & 157(151) & 53 \\ \hline (THF)Co(TPP)(NO_2) & 1462 & 1300 \\ (1430) & (1279) & 808(800) & 162(151) & 53 \\ \hline (Methanol)Co(TPP)(NO_2) & 1463 & 1301 \\ (1433) & (1282) & 809(803) & 162(151) & 53 \\ \hline (Ethanol)Co(TPP)(NO_2) & 1463 & 1298 \\ (1431) & (1278) & 804(798) & 165(153) & 53 \\ \hline (iso-propanol) Co(TPP)(NO_2) & 1462 & 1301 \\ \hline (iso-propanol) Co(TPP)(NO_2) & 1462 & 1301 \\ (1428) & (1281) & 804(798) & 161(147) & 53 \\ \hline \end{array}$	(Enichlouchudzin)Co(TDD)(NO)	1458	1301	Q06 (Q02)	157(151)	52	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(Epichioronydrin)Co(TPP)(NO <sub>2</sub> )	(1432)	(1281)	806 (802)	157(151)	55	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1462	1300		1 (0(151)	50	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$(THF)Co(TPP)(NO_2)$	(1430)	(1279)	808 (800)	162(151)	53	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1463	1301				
$\begin{array}{c ccccc} (1202) & (1202) & (1202) \\ \hline (Ethanol)Co(TPP)(NO_2) & 1463 & 1298 \\ (1431) & (1278) & 804 (798) & 165(153) & 53 \\ \hline (iso-propanol)Co(TPP)(NO_2) & 1462 & 1301 \\ (1428) & (1281) & 804 (798) & 161(147) & 53 \\ \hline \end{array}$	$(Methanol)Co(TPP)(NO_2)$	(1433)	(1282)	809 (803)	162(151)	53	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1463	1298				
$\begin{array}{c ccccc} (121) & (1210) \\ \hline (130-\text{propanol}) \text{ Co}(\text{TPP})(\text{NO}_2) & 1462 & 1301 \\ \hline (1428) & (1281) & 804 (798) & 161(147) & 53 \end{array}$	(Ethanol)Co(TPP)(NO <sub>2</sub> )	(1431)	(1278)	804 (798)	165(153)	53	
$(\text{iso-propanol}) \operatorname{Co}(\operatorname{TPP})(\operatorname{NO}_2)$ $(1428)$ $(1281)$ $804 (798)$ $161(147)$ 53		1462	1301				
	(iso-propanol) Co(TPP)(NO <sub>2</sub> )	(1428)	(1281)	804 (798)	161(147)	53	

A higher value of  $\Delta v$  corresponds a larger ONO angle. Actually in NO<sub>2</sub> molecule ONO angle is equal to 134°, while in nitrite anion it is 115°, and intermediate values were obtained for the structurally characterized nitro-complexes of the Co- and Fe-porphyrins. The  $\Delta v$  values are systematically higher for the Co(III) complexes Co(TPP)(B)(NO<sub>2</sub>) than for the Fe(III) analogs suggesting less charge transfer in the former case. This is also consistent with the ONO angles which are in the 120-124° range [57] for the Co(III) complexes compared to the more acute angles (116-120°) seen for similar nitro complexes of Fe(III) porphyrins [58].

Similar to ferrous-porphyrins [42], the interaction of small NO<sub>2</sub> increments with layered Mn(TPP) leads to the formation of the 5-coordinate nitrito complex Mn(TPP)( $\eta^1$ -ONO) [59] that was previously chemically synthesized and structurally characterized by Suslick and Watson [60]. In analogy to the Fe(Por)( $\eta^1$ -ONO) species, nitrito coordination is characteristic of the 5-coordinate Mn<sup>III</sup>(TPP)( $\eta^1$ -ONO) complex [60]. Although crystal structure of the 6-coordinate manganese substituted met-myoglobin Mn(III)Mb(ONO) has been determined and also reveals the O-bound nitrito coordination [61], the 6-coordinate nitrite complexes of other Mn-porphyrin models have not been obtained and characterized. In this context, we used sublimed porous layers of Mn(TPP)( $\eta^1$ -ONO) as a synthetic precursor to the 6-coordinate complexes with various proximal ligands and used *in situ* spectroscopy to determine effect on the coordination mode of the nitrite ligand [59].

Low-temperature interaction of  $Mn(TPP)(\eta^1-ONO)$  with vapors of various ligands L leads to the formation of 6-coordinate nitrito  $Mn^{III}(TPP)(L)(\eta^1-ONO)$  (L = O-, S- and N-donors) complexes (Scheme 6). Formation of the 6-coordinate nitrito complexes is accompanied



R - phenyl; L - THF, DMS, Py

by the shifts of the v(N=O) band to lower frequencies and of the v(N-O) band to higher frequencies. The frequency difference between these bands  $\Delta v = v(N=O) - v(N-O)$  is a function of L and is smaller for the stronger bases (see Table 5). In this Table data for not numerous examples of the 6-coordinate O-nitrito complexes of Fe-porphyrins are also included.

### Table 5

Frequencies of stretching vibrations in cm <sup>-1</sup> for coordinated O-nitrito group in the
6-coordinated complexes of Mn- and Fe-porphyrins with the various electron donor
ligands. In parenthesis the data for <sup>15</sup> N-labeled nitrito group are given.

Complex	v(N=O), <i>cm</i>	v(N-O), <i>cm</i> <sup>-1</sup>	$\Delta v = v(N=O) - v(N-O),$ $cm^{-1}$	Q-bands, nm	Ref.
$Mn(TPP)(\eta^1-ONO)$	1445(1421)	1040(~1020)	405(401)	587, 625	59
$Mn(TPP)(DMS)(\eta^1-ONO)$	1416(1394)	~1072(1052)	344(342)	581, 622	59
$Mn(TPP)(THF)(\eta^1-ONO)$	1415(1391)	1084(1055)	331(336)	577, 616	59
$Mn(TPP)(Py)(\eta^1-ONO)$	1398(1375)	1105(1084)	293(291)	576, 616	59
$Mn(TPP)(NH_3)(\eta^1-ONO)$	1384(1357)	1115(1094)	269(263)	-	59
$Mn(TPP)(1-MeIm)(\eta^1-ONO)$	1382(1356)	1121(~1100)	261(256)	581, 619	59
Fe(TPP)(η <sup>1</sup> -ONO)	1526(1499)	904(885)	622(614)	508,577sh, 659, 689	42
Fe(TPP)(THF)(η <sup>1</sup> -ONO)	1481(1448)	963(946)	518(502)		45
Fe(TPP)(NH <sub>3</sub> )(η <sup>1</sup> -ONO)	1475(1445)	971(952)	504(493)	552, 595sh, 650sh, 695sh	44
Fe(TPP)(NO)(η <sup>1</sup> -ONO)	1496(1471)	938(920)	558(551)	548, 574	43

The reaction of excess NH<sub>3</sub> with Mn(TPP)( $\eta^1$ -ONO) leads to the formation of Mn(TPP)(NH<sub>3</sub>)( $\eta^1$ -ONO) and cation [Mn(TPP)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> plus ionic nitrite NO<sub>2</sub><sup>-</sup> [59] (Scheme 7). When the layer is warmed up to higher temperature, the intensity of the v<sub>a</sub>(NO<sub>2</sub><sup>-</sup>) band begins to decrease with the concomitant increase in the intensity of the bands of 6-coordinate Mn(TPP)(NH<sub>3</sub>)( $\eta^1$ -ONO) complex demonstrating reverse binding of NO<sub>2</sub><sup>-</sup> after the release of one ammine ligand from the thermally unstable diammine complex. However not all of the diammine complex is converted back to the mixed 6-coordinate species, since under these experimental conditions, some of the latter decomposes to restore the parent O-nitrito complex Mn(TPP)( $\eta^1$ -ONO). These data indicate that complex equilibrium exists between three species represented on the Scheme 7 depending on the pressure of NH<sub>3</sub> and temperature.



None of the 6-coordinate nitrito complexes of Mn-porphyrins were thermally stable at higher temperature, and each slowly decomposes by losing the L upon warming to RT. More stable are the adducts with less volatile Py and 1-MeIm ligands. Pumping overnight leads to complete decomposition of the Py complex

while about half of the 1-MeIm complex still is present in the layer after this procedure.

Comparison of the results obtained for the 6-coordinate nitrite complexes of Feand Mn-porphyrins show that in the former the coordination of the electron donor ligands *trans* to nitrite leads to the nitrito  $\rightarrow$  nitro isomerization while in the latter the nitrito mode of the coordinaton remains unchanged.

Nitrate complexes of metalloporphyrins. Nitrate complexes of MPs are involved in key processes in nitrogen cycle and are transients formed as the result of heme mediated nitric oxide dioxygenation (NOD) [62]. For the mononuclear metallocomplexes two modes of coordination are known for nitrate ligand: the bidentate form through 2 oxygen atoms that is realized in the complex with Fe(TPP) and monodentate form realized for the iron-octaethylporphyrin complex Fe(OEP). While the 5-coordinate nitrato complexes are synthesized and characterized by Xray analysis [23] the 6-coordinate nitrato complexes of MPs were not known and became possible to characterize only by the use of the sublimed layers methodology. It is worth noting that nitrato complexes of MPs cannot be sublimed without partial decomposition. The following reaction observed in our studies helps to have nitrato complexes of Fe- and Mn-porphyrins in sublimed layers. It was found that the nitrogen dioxide reaction with amorphous layers of Fe- and Mn-porphyrins eventually leads to the formation of the nitrato complexes [63, 64]. This reaction proceeds through the two distinct steps. The nitrito complexes are initially formed that transfers to the nitrato species upon supplying into the cryostat of new  $NO_2$ portions [43, 59]. These processes taking place for the Mn-derivative are demonstrated on the Scheme 8.

Scheme 8



R - phenyl

In contrast, Co-porphyrins reveal different reactivity; after the formation of 5coordinate nitro-complexes Co(TPP)(NO<sub>2</sub>) at low NO<sub>2</sub> pressures [65], introduction of the new NO<sub>2</sub> increments results in oxidation of the porphyrin ring with the formation of a  $\pi$ -cation radical [66].

Supplying small portions of electronodonor ligands into the cryostat containing thin layers of 5-coordinate Fe-porphyrin nitrato-complex it was possible to spectrally detect the formation of the 6-coordinate complexes. The coordination of the 6th ligand is accompanied with monodentate-bidentate isomerization of the coordinated nitrato ligand. Depending on the nature of the 6th ligand the corresponding species can be low or high spin. In case of strong nitric oxide ligand the nitrato-nitrosyl complex (NO)Fe(Por)( $\eta^1$ -ONO<sub>2</sub>) is low-spin [67] whereas for the weak THF ligand remains high-spin as the parent nitrato complex [68].

It was found that the interaction of nitric oxide with the nitrato complexes of iron-porphyrins is not limited by the formation of nitrato-nitrosyl complex. In the presence of excess NO the nitrato-complex  $Fe(TPP)(\eta^2-O_2NO)$  undergoes a series of transformations both in solid state and in non-coordinating solvent that results in the formation of iron-porphyrin complexes ligated by the various nitrogen oxides [33, 5]. The final products of solid state reactions are the nitrosyl complex Fe(TPP)(NO), the nitro-nitrosyl complex  $Fe(TPP)(NO_2)(NO)$  and the nitrato complex  $Fe(TPP)(\eta^2-O_2NO)$ , the relative quantities of which are the function of NO partial pressure. The formation of the nitro-nitrosyl complex (NO)Fe(Por)(NO<sub>2</sub>) is accompanied with a concomitant formation of nitrogen dioxide NO<sub>2</sub>. Hence the nitrate can be activated by heme-models to produce other highly reactive species that is strong oxidizing and nitrating agent. By using differently labeled by nitrogen nitrate complex and nitric oxide it was possible to suggest the mechanisms of these transformations [33].

6-coordinate nitrato complexes of Mn-porphyrins can also be obtained by the low temperature interaction of electron donor ligands with the layered  $Mn(Por)(\eta^1 - ONO_2)$  [59].



R - phenyl; L - THF, DMS

Introduction of small increments of relatively weak O- and S-electronodonor ligands (THF and DMS) vapors into the cryostat containing thin layers of  $Mn(Por)(\eta^1-ONO_2)$  at liquid nitrogen temperature followed by slow warming process leads to shifts of the IR bands of the coordinated nitrato group as it is shown in Figure 8 for the (THF)Mn(TPP)( $\eta^{1-18}ON^{18}O_2$ ) derivative.



Fig. 8. FTIR spectra of  $Mn(TPP)(\eta^{1}-{}^{18}ON^{18}O_2)$  (solid line) and of  $Mn(TPP)(THF)(\eta^{1}-{}^{18}ON^{18}O_2)$  (dashed line).

By analogy with other monodentate nitrato complexes [53] the two highfrequency stretching bands of the nitrato group can be assigned to the  $v_a(NO_2)$  and  $v_s(NO_2)$  vibrations of the uncoordinated  $NO_2$  fragment. The third band which belongs to the v(O-N) stretching of the coordinated oxygen is usually disposed in the range of 1000  $cm^{-1}$  and in the spectra of natural abundance atoms in nitrato group is masked by the intense porphyrin band in this range. This band is apparent at 959 cm<sup>-</sup> <sup>1</sup> in the spectrum of species containing the <sup>18</sup>O labeled nitrato group (Table 6, Fig. 8, solid line). From Figure 8 it is also clear that this band has low intensity and can readily be obscured by the intense porphyrin band in this range. As can be seen in Figure 8 upon coordination with a *trans* THF ligand the high-frequency  $v_a(NO_2)$ band noticeably shifts to a lower frequency, while the low frequency  $v_s(NO_2)$  band undergoes a minor higher frequency shift. The low-intensity v(O-N) band also undergoes a shift to higher frequency as can be seen in Fig. 8. The abovementioned bands show the appropriate isotopic shifts when the <sup>15</sup>N- or <sup>18</sup>O-labeled nitrato complexes were used, confirming that they belong to the coordinated nitrato group (Table 6). The data of Table 6 show that for the 6-coordinate nitrato complexes of Mn-porphyrins the values of  $\Delta v = v_a(NO_2) - v_s(NO_2)$  correlate well with the electron donor strengths of the sixth ligand being smaller for the stronger base ligands.

Adduct	$v_a(NO_2)$	$v_{s}(NO_{2})$	v(O-N)	Q bands, nm	Ref.
$Mn(TPP)(\eta^1-ONO_2)$	1470	1284	998	580, 615	59
$Mn(TPP)(DMS)(\eta^1-ONO_2)$	1451(1407)	1289(1263)		583, 618	59
$Mn(TPP)(THF)(\eta^1-ONO_2)$	1446(1410)	1290(1262)		575, 610	59
Mn(TPP)(THF)( $\eta^{1}$ - <sup>18</sup> ON <sup>18</sup> O <sub>2</sub> )	1419	1269	969		59
$Mn(TPP)(Py)(\eta^1-ONO_2)$	1427(1393)	1393(1269)		578, 614	59
$Mn(TPP)(1-MeIm)(\eta^1-ONO_2)$	1418(1390)	1293(1264)			59
$Mn(TPP)(NH_3)(\eta^1-ONO_2)$	1426(1403)	1290(1260)			59
$Fe(TPP)(NO)(\eta^1-ONO_2)$	1505(1472)	1265(1246)	969(954)	547, 582	67
$Fe(TPP)(THF)(\eta^1-ONO_2)$	1491(1457)	1280(1258)	~997(986)		68
$Fe(TPP)(NH_3)(\eta^1-ONO_2)$	1499(1472)	1268(1249)	938(925)		68
$Fe(TPP)(1-MeIm)(\eta^1-ONO_2)$	1475(1434)	1278(1257)			69
$Co(TPP)(NH_3)(\eta^1-ONO_2)$	1484(1459)	1270(1248)	983(970)	558, 597	70
$Co(TPP)(Py)(\eta^1-ONO_2)$	1477(1449)	1270(1247)	985(979)	549	71

IR frequencies in *cm*<sup>-1</sup> of differently labeled nitrato group in 6-coordinate complexes of metalloporphyrins with various *trans* electron donor ligands. In parenthesis the data for <sup>15</sup>N labeled nitrato group are given.

The THF adduct Mn(TPP)(THF)( $\eta^1$ -ONO<sub>2</sub>) can also be obtained at RT by the exposure of Mn(TPP)( $\eta^1$ -ONO<sub>2</sub>) to THF vapor (a few tens of torr). It is stable at RT when a few torr of THF are present in the cryostat, but it slowly loses the THF ligand in the course of pumping to restore the spectrum of the initial nitrato complex Mn(TPP)( $\eta^1$ -ONO<sub>2</sub>). The THF complex readily decays when it is dissolved in non-coordinating solvent. Interaction of the S-donor ligand DMS with Mn(TPP)( $\eta^1$ -ONO<sub>2</sub>) leads to the same spectral changes as in the case of THF manifesting the formation of the 6-coordinate complex Mn(TPP)(DMS)( $\eta^1$ -ONO<sub>2</sub>). In this case, however, the complex is less stable and begins to decompose at temperatures higher than  $-30^{0}$ C.

The reactions of  $Mn(Por)(\eta^1-ONO_2)$  with N-donor ligands NH<sub>3</sub>, pyridine or 1methylimidazole are more complex. With these ligands, nitrato complexes  $Mn^{III}(TPP)(L)(\eta^1 - ONO_2)$  and cationic complexes  $[Mn(TPP)(L)_2]^+$  coexist in the layer, the latter formed as a result of  $NO_3^-$  displacement when L is in excess. The same pattern was observed earlier upon interaction of the iron-porphyrin nitrato complexes with strong ammonia ligand demonstrating lability of the coordinated nitrate [68]. Warming of the Mn(TPP)( $\eta^1$ -ONO<sub>2</sub>) + NH<sub>3</sub> system to room temperature led to partial loss of [Mn(TPP)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation accompanied by the reformations of the 6-coordinate nitrato-complex Mn(TPP)(NH<sub>3</sub>)( $\eta^1$ -ONO<sub>2</sub>) and Mn(TPP)( $\eta^1$ -ONO<sub>2</sub>). Thus, it appears that there is equilibrium between three different species represented in Scheme 10. The relative quantities of these complexes depend on the temperature and NH<sub>3</sub> pressure. Our attempts to find conditions where only the 6coordinate nitrato-complex was present in layered medium were unsuccessful. With the less volatile Py ligand, however, it was possible to convert all the species present in the layer to 6-coordinate  $(Pv)Mn(TPP)(n^1-ONO_2)$  by vacuum pumping at RT (Fig. 9).



Fig. 9. FTIR spectra of layered  $Mn(TPP)(\eta^1-ONO_2)$  (dashed line) after exposure under vapors of Py (5 Torr) and short pumping (solid line) [59].

A ligand of special interest is 1-methyl-imidazole (1-MeIm), which is a mimic of histidine imidazole in hemeproteins. When layers of  $Mn(TPP)(\eta^1-ONO_2)$  in the cryostat were treated with saturated vapors of 1-MeIm, the IR bands of  $Mn(TPP)(\eta^1-ONO_2)$  disappeared with concomitant growth of bands characteristic to a 6-coodinate species. However, a significant quantity of  $[Mn(TPP)(1-MeIm)_2]^+ \cdot NO_3^-$  was also formed. The latter did not transform back to the 6-coordinate nitrato complex  $Mn(TPP)(1-MeIm)(\eta^1-ONO_2)$  upon high-vacuum pumping. Thus the binding of two axial 1-MeIm ligands in bis-ligated cationic complex is stronger than for Py. The  $[Mn(TPP)(1-MeIm)_2]^+$  complex has really been isolated and structurally characterized [72].

The following strategy was implemented to obtain the 6-coordinate nitrato complex with an axial 1-MeIm ligand. The 5-coordinate nitrito-complex Mn(TPP)( $\eta^1$ -ONO) was first prepared as amorphous layers on the cryostat substrate. The reaction of this species with 1-MeIm vapors led to the formation of the 6-coordinate nitrito species (1-MeIm)Mn(TPP)( $\eta^1$ -ONO) without displacement of the nitrite ion by excess of 1-MeIm. Since Mn(TPP)(1-MeIm)( $\eta^1$ -ONO) was relatively stable to intense pumping, some of the 1-MeIm excess could thus be removed. Then the small portions of NO<sub>2</sub> gas were introduced to react with Mn(TPP)(1-MeIm)( $\eta^1$ -

ONO) upon which intense bands at 1418 and 1293 cm<sup>-1</sup> (1390 and 1264  $cm^{-1}$  for <sup>15</sup>N labeled isotopomer) (Table 5) appeared manifesting the formation of the Mn(TPP)(1-MeIm)( $\eta^1$ -ONO<sub>2</sub>) complex according to Scheme 11 [59].

# Scheme 11



The same reaction sequence was earlier observed for iron-porphyrin nitrito complex Fe(TPP)( $\eta^1$ -ONO) [69]. The 6-coordinate nitrato complexes of Mn-porphyrins with trans Py and 1-MeIm ligands are stable in the solid state at RT, but dissolution in non-coordinating solvent leads to their decomposition.

Although nitrato complexes of Mn- and Fe-porphyrins reveal significant similarity in their reactions with electronodonor ligands, they substantially differ in their reactivity regarding to nitric oxide NO. Neither formation of the nitrato-nitrosyl complexes nor further transformations of the nitrato ligand were observed in the course of low-temperature interaction of Mn-porphyrins nitrato complexes with NO.

It was mentioned above that the nitrato complexes of Co-porphyrins, in contrast to Fe- and Mn- analogs, cannot be obtained via interaction of gaseous  $NO_2$  with their sublimed layers [66]. However, it was recently shown, that they can be achieved as a result of nitric oxide dioxygenation (NOD) reaction, in which NO interact with specially constructed 6-coordinate dioxygen complexes of Co-porphyrins (L)Co(Por)(O<sub>2</sub>) at low-temperatures [70, 71]. The 6-coordinate nitrato complexes of Co-porphyrins with *trans* ammonia and pyridine ligand have been obtained and spectrally characterized at low-temperatures through this reaction. The IR frequencies of nitrato group in these species are given in Table 6.

The fate of the 6-coordinate nitrato complexes  $(Py)Co(Por)(\eta^1-ONO_2)$  upon warming to room temperatures depends on the experimental conditions. When nitric oxide was pumped out from the cryostat at 200 K and the layers were allowed to be warmed to RT the spectral changes clearly indicated that the 6-coordinate nitratocomplexes of Co-porphyrins decompose to nitrate-anion and amino-complexes of Co(III)-porphyrins. On the other hand if after the formation of the nitrato complexes some excess of the electronodonor ligand was pumped out and a new higher portion of NO was added into the cryostat the spectral changes indicate the formation of 6coordinate nitro complexes. These data indicate that the oxo-transfer reaction from the coordinated nitrato group to nitric oxide takes place as is represented on Scheme 12. Using differently labeled NO in the stages of nitrato complex formation and its reduction to nitro complex the mechanism of this transformation was determined.



In summary the data presented in this review show that the sublimed layers methodology together with *in-situ* FTIR and electron absorption spectroscopy measurements and DFT computations give comprehensive information about the interactions of nitrogen oxides with heme models that otherwise could not be obtained.

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### ՆԵՄ-ՄՈԴԵԼ ՆԵՐԻ ՆԵՏ ԱԶՈՏԻ ՕՔՍԻԴ ՆԵՐԻ ՓՈԽԱԶԴԵՑՈԻԹՅԱՆ ՍՊԵԿՏՐԱԼ ՈԻՍՈԻՄ ՆԱՍԻՐՈԻԹՅՈԻՆԸ

### Տ. Ս. ԿՈԻՐՏԻԿՅԱՆ

Աղոտի օքսիդները (NO, NO2, NO2, NO3 և այլն) կարևոր դերակատարումներ ունեն կաԹնասունների օրգանիզմներում ընԹացող ֆիզիոլոգիական պրոցեսներում` պայմանավորված Հիմնականում Հեմ-սպիտակուցների Հետ դրանց փոխազդեցություններով։ Սին-Թետիկ մետաղապորֆիրինները մոդելավորում են Հեմ-սպիտակուցների ակտիվ կենտրոնը և ագոտի օքսիդների ներկայուԹյամբ դրանց կոորդինացիոն ոլորտում ընԹացող քիմիական պրոցեսների ուսումնասիրուԹյունը Հույժ կարևոր է Հասկանալու Համար բազմաԹիվ ֆերմենտների գործելաձևը։ Ակնարկում ներկայացված են Հեղինակի փորձարաններում կատարված Հետագոտությունները` նվիրված ազոտի օքսիդների փոխազդեզություններին կենսաբանական կարևորություն ունեցող Fe-, Co- և Mn-պորֆիրինների Հետ: Օդտվելով էլեկտրոնային կյանման և Ֆուրյե ձևափոխությամբ ինֆրակարմիր սպեկտրաչափական եղանակներից, Հարուստ ինֆորմացիա է քաղվել այդ փոխազդեցուԹյունների վերաբերյալ։ Ազոտի օջսիդները ամբիդենդատ լիդանդներ են Հանդիսանում։ Օգտագործելով տատանողական սպեկտրալ չափումներում իզոտոպային ազոտ և/կամ ԹԹվածին պարունակող օքսիդներ և օգտվելով իստուԹյունների ֆունկցիոնալի տեսուԹյան Հաչվարկներից ստացված լրացուցիչ ինֆորմացիայից, Հնարավոր է դարձել միանչանակորեն պարզել աղոտի օքսիդների կապման ձևերը և էլեկտրոնային կառուդվածքը նչված մետաղապորֆիրինների 5- և 6-կոորդինացված նիտրոդիլային, նիտրիտային և նիտրատային կոմպլեջոներում։ Որոչվել է այդ պարամետրերի կախվածուԹյունը մետաղի բնուլԹից։ Հետագոտվել են ագոտի օջսիդների փոխակերպումները մետաղների կոորդինացիոն ոլորտում և բացաՀայտվել են դրանց մեխանիզմները: Ստացվել են նչված մետաղապորֆիրինների Նախկինում անՀայտ 6-կոորդինացված նիտրոզիլային, նիտրիտային և նիտրատային կոմպլեջոները տրանա-N-, S- և 0-էլեկտրոնոդոնոր լիգանդների Հետ և տատանողական սպեկտրերում կոորդինացված ազոտի օքսիդների կլանման չերտերի միանչանակ վերագրումներ են կատարվել:

## СПЕКТРАЛЬНЫЕ ИССЛЕДОВАНИЯ ВЗАИМОДЕЙСТВИЯ ОКСИДОВ АЗОТА С ГЕМ-МОДЕЛЯМИ

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Оксиды азота (NO, NO<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> и др.) играют важную роль в физиологических процессах, протекающих в организмах млекопитающих, что обусловлено, в первую очередь, их взаимодействием с гемопротеинами. Синтетические металлопорфирины моделируют активный центр гемопротеинов, и выявление химических процессов, имеющих место в их координационной сфере в присутствии оксидов азота, чрезвычайно важно для понимания механизмов функционирования многочисленных ферментов. В обзоре представлены работы, осуществленные в лабораториях автора и посвященные исследованиям взаимодействия оксидов азота с порфиринатами биологически значимых Fe, Co и Mn. C помощью электронной абсорбционной и Фурье ИК-спектроскопии извлечена богатая информация относительно характера таких взаимодействий. Оксиды азота являются амбидентатными лигандами. Измерением колебательных спектров изотопозамещенных по азоту и/или кислороду оксидов и привлечением рассчитанных по теории функционала плотности данных однозначно определены способы координации и электронное строение 5- и 6-координационных нитрозильных, нитритных и нитратных комплексов исследованных металлопорфиринов. Выявлена зависимость этих параметров от природы металла. Исследованы превращения оксидов азота в координационной сфере металлов и выявлен их механизм. Получены ранее не известные 6-координационные нитрозильные, нитритные и нитратные комплексы отмеченных металлопорфиринов с *транс*-N-, S- и О-электронодонорными лигандами, и сделаны однозначные отнесения полос поглощения координированных оксидов азота в их колебательных спектрах.

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