

ОБЩАЯ И ФИЗИЧЕСКАЯ ХИМИЯ

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SPECTRAL STUDY OF DMSO INTERACTION WITH MANGANESE PORPHYRIN NITROSYL

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Five coordinate manganese(II) porphyrin nitrosyls, in its sublimed layers, show two $\nu(\text{NO})$ bands in room temperature IR spectra, assigned earlier to the linear and bent Mn-NO isomers. The interaction of the dimethylsulfoxide (DMSO) donor ligand with the sublimed layers of manganese(II) porphyrin nitrosyl complex Mn(TPP)(NO) (TPP is meso-tetraphenyl-porphyrinato dianion) was studied using electronic and infrared absorption spectroscopy. Upon DMSO interaction with Mn(TPP)(NO), the bent isomer is disappeared while the $\nu(\text{NO})$ band of linear one shifted and increased in intensity. This IR spectral changes, as well as the changes observed by UV-Vis spectroscopy are consistent with the ligand binding at the axial position trans to the NO and formation of the six-coordinate adduct. This six-coordinate adduct in the solid state is quite stable at room temperature.

Figs. 3, references 23.

Introduction

Nitric oxide (NO) is widely accepted bioregulatory molecule playing an important role in a variety of physiological processes [1]. The main targets of NO in vivo are heme-iron containing enzymes. For example, the binding of NO to the heme iron in soluble guanylyl cyclase (sGC) led to the activation of this enzyme, resulting eventually in vasodilation [2, 3]. NO binds to both ferrous Fe(II) and ferric Fe(III) hemes, although NO binding to ferric hemes is weaker than that for ferrous hemes. In addition six-coordinate ferric nitrosyl porphyrins are difficult to obtain, and there are only few examples for which spectroscopic and crystallographic

studies are reported [4]. Ferric nitrosyl porphyrins belong to the $\{\text{FeNO}\}^6$ class, as defined by Enemark and Feltham [5]. At the same time manganese(II) nitrosyl porphyrins are isoelectronic with the ferric nitrosyls and also are belonging to the $\{\text{MnNO}\}^6$ classification. This gives the possibility to study five- and six-coordinate Mn nitrosyl porphyrins to mimic the labile Fe-NO bond in ferric nitrosyl porphyrins. A number of manganese substituted derivatives of the heme-containing biomolecules have been reported in literature including hemoglobin, myoglobin, cytochrome P450, cytochrome c and sGC [6-10]. In contrast, the coordination chemistry of Mn nitrosyl porphyrins remain less investigated by comparison to the Fe(II)- and Co(II)-nitrosyl porphyrins [11]. To date, there are only few structurally and spectroscopically studied six-coordinate manganese(II) nitrosyl porphyrins, namely those of (TPP)Mn(NO)(4-Mepip) [12], (TTP)Mn(NO)(CH₃OH), (TTP)Mn(NO)(1-MeIm) and (TTP)Mn(NO)(pip) (TTP is meso-tetra-p-tolylporphyrinatodianion) [13] that were obtained and revealed the linearity of Mn-NO units in these complexes. Recently we have reported an unusual spectroscopic observation. Reaction of NO with amorphous Mn(TPP) layers shows two Mn(TPP)(NO) isomers in IR spectra with linear ($\nu(\text{NO})$ at 1739 cm^{-1}) and bent ($\nu(\text{NO})$ at 1614 cm^{-1}) Mn-N-O geometries which reversibly interconvert with changes in temperature [14].

As a continuation of that work it was of interest to study behavior of the isomers in presence of sixth ligand. DMSO is of interest, because can coordinate to metal ions via sulfur or oxygen atoms [15]. In order to better understand the binding of NO to manganese porphyrin and to determine the influence of the trans ligand on the bound NO in these complex, we have prepared a six-coordinate complex containing DMSO and studied it by IR and UV-Vis spectroscopy. The six-coordinate manganese porphyrin nitrosyl having DMSO ligand is reported for the first time.

Experimental Section

The Mn(TPP)(Pip) (piperidine) or Mn(TPP)(Py) (pyridine), synthesized according to published methods [16], were the precursors of the manganese(II) porphyrinato complexes used to prepare the sublimed layers. The Mn(TPP) sublimates on the KBr or CaF₂ substrates of the optical cryostats were prepared under continuous vacuum conditions, according to a procedure described elsewhere [17]. Earlier, it has been reported that *meso*-tetraarylporphyrins can form microporous “porphyrin sponges”, which allows incorporation of guest molecules with different shapes and sizes [18]. Thin layers of metallo-tetraarylporphyrins, sublimed onto a low-temperature (77 K) surface are also sponge-like and have high microporosity that allows potential ligands to diffuse easily across the bulk. The species thus formed are convenient for spectroscopic studies due to absence of solvent interference. To avoid NO disproportionation [19] the substrate was allowed to warm to 273 K and the nitric oxide gas, measured by a mercury manometer was

slowly admitted and then pumped out from the cryostat. IR spectra show instant formation of the 5-coordinate Mn(TPP)(NO) complex. Vapors of DMSO ligand were added at room temperature into the cryostat by the same procedure as NO. The nitric oxide was purified by passing multiple times through a column containing KOH pellets. Anhydrous DMSO was purchased from "Aldrich" and purified by vacuum distillation. Infrared spectra were measured on Thermo Nicolet "Nexus" FTIR spectrometer and UV-Vis spectra were measured on a Thermo Helios γ spectrophotometer.

Results and Discussion

Fig.1 shows IR spectra of amorphous layers of Mn(TPP)(NO) before and after addition of DMSO vapors into the cryostat at room temperature. Two strong IR bands at 1739 and 1614 cm^{-1} have been assigned to the $\nu(\text{NO})$ of five-coordinate Mn(TPP)(NO) isomers, the band at 1739 cm^{-1} to the linear Mn–N–O species, while that at 1614 cm^{-1} to the isomer with bent NO binding mode [14]. When vapors of the DMSO were introduced into the cryostat containing the layered nitrosyl complex, distinct spectral changes were observed.

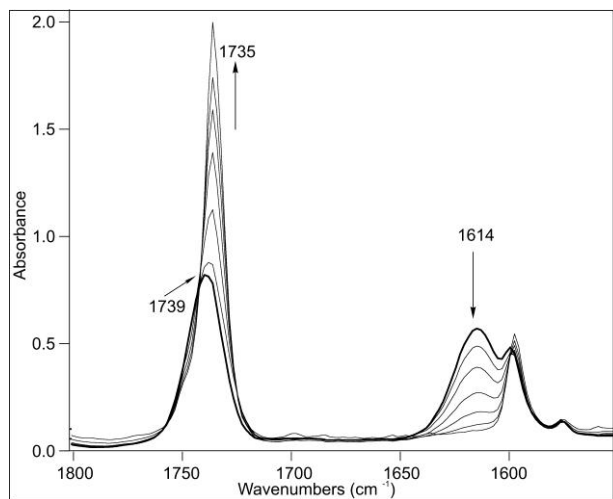
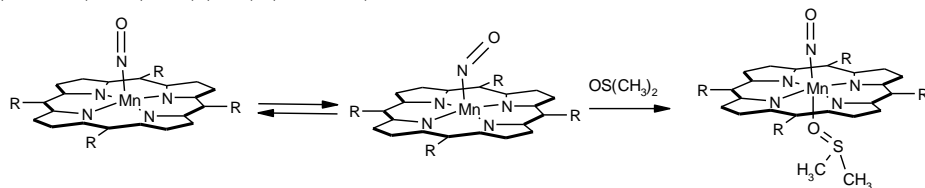


Fig. 1. FTIR spectral changes in the range of $\nu(\text{NO})$ upon addition to the cryostat containing Mn(TPP)(NO) vapors of DMSO.

It is clearly seen, that the band of the bent isomer decrease in intensity and eventually completely disappears, while the band of linear isomer at 1739 cm^{-1} concomitantly increase in intensity and shifts down to 1735 cm^{-1} . The sum of integral intensity of the bands remain the same, suggesting an absence of dissociation of coordinated NO upon Mn(TPP)NO interaction with ligand. This spectral changes takes several hours and are irreversible: pumping out of the ligand vapors does not affect the intensity of $\nu(\text{NO})$ band at 1735 cm^{-1} . Lowering of $\nu(\text{NO})$ may be explained by the coordination of the ligand at the Mn center and formation of the six-coordinate complex. Such six-coordinate complexes are known for the iron(II) and cobalt(II) nitrosyl porphyrins [11, 20]. In both, coordination of the sixth donor ligand results in lowering of $\nu(\text{NO})$. The value of the shift noticeably depends

on the nature of the base ligand and the relative orientation of the axial ligand planes. We believe, therefore, that the spectral changes presented at Fig.1 provide evidence for the formation of new six-coordinate nitrosyl complex i.e., (DMSO)Mn(TPP)(NO) (Scheme).



Scheme

As noted above as an ambidentate ligand the DMSO can coordinate to the metal ions via sulfur or oxygen atoms [15]. For example, ligation mode of the sulfoxide ligands was reported to be O-bound in iron(III) and S-bound in iron(II) porphyrinate systems [21]. Moreover, it is also known that S-coordinated DMSO ligands exhibit S=O stretching frequencies that range from 1080 to 1154 cm^{-1} , while O-bound DMSO ligands exhibit lower vibrational frequencies, ranging from 862 to 997 cm^{-1} [22]. As seen from Fig. 2, concomitant with the spectral changes in the range of $\nu(NO)$, the new bands are seen at 1120 and 960 cm^{-1} . However, only latter band remain in the IR spectra after high vacuum pumping, supporting O-coordination of DMSO. Hence, in this case Mn(II) porphyrins indeed mimics the properties of isoelectronic Fe(III) porphyrins.

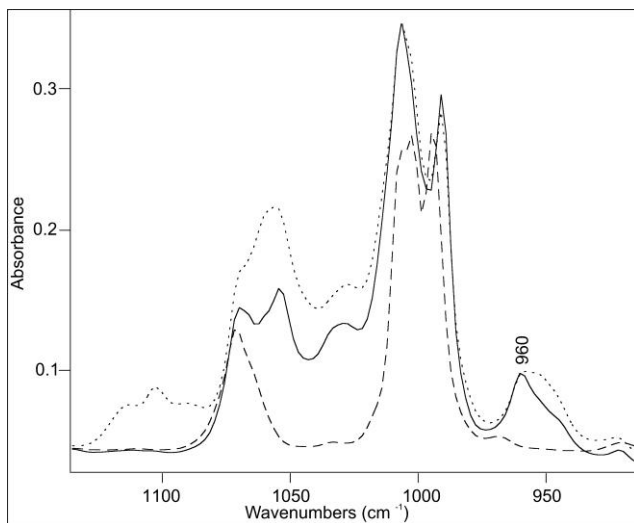


Fig. 2. Dashed line – Mn(TPP)(NO), dotted line – (DMSO)Mn(TPP)(NO), formed after addition of ligand vapors to Mn(TPP)(NO), solid line – (DMSO)Mn(TPP)(NO) after pumping out of ligand vapors.

Formation of the six-coordinate complex is also supported by UV-vis spectroscopy (Fig. 3). The electronic absorption spectrum undergoes distinct changes, both upon the addition of NO to the sublimed layers of Mn(TPP) and with further interaction with donor ligand (formation of all species shown in the visible spectra was first controlled by FTIR). Upon the formation of the nitrosyl complex, the porphyrin Q bands at 570 and 608 nm disappear, while new prominent

absorbance appears at 530 nm with shoulders at 543 and 577 nm. Treatment of Mn(TPP)(NO) with DMSO, induce farther spectral changes which are consistent with formation of six-coordinate (DMSO)Mn(TPP)(NO). The absorbance at 533 nm undergoes bathochromic shift to 549 nm with the concomitant formation of new absorbancies at 582 nm and 613 nm.

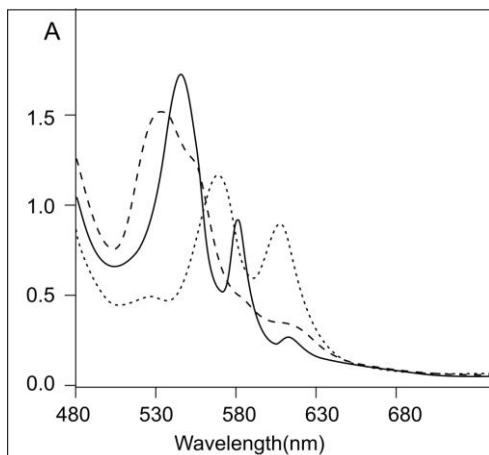


Fig.3. Mn(TPP) – dotted line, Mn(TPP)(NO) – dashed line, (DMSO)Mn(TPP)(NO) – solid line.

The nitrosyl stretching frequencies of the six-coordinate iron(II) and iron(II) nitrosyl porphyrins are very sensitive to the type and donor-acceptor properties of trans ligands [4, 11]. The same effect may be also expected for manganese porphyrin nitrosyls. However, the nitrosyl stretching frequency obtained for (NO)Mn(TPP)(DMSO) is displayed the $\nu(\text{NO})$ at 1735 cm^{-1} , showing only 4 cm^{-1} lowering relative to the $\nu(\text{NO})$ of linear Mn(TPP)(NO) isomer. In part, relatively low shift may be due to low basicity of ligand. The DMSO is known to be the poor ligand, having negative pK_a (-2.16) [23]. Apparently, the changes in the nitrosyl stretching frequency on the coordination of the sixth ligand alone (without UV-vis data), cannot provide reliable information about the presence and nature of the trans ligand in manganese nitrosyl porphyrins.

In summary, interaction of DMSO with a five-coordinate manganese nitrosyl complex Mn(TPP)(NO), leads to the formation of a six-coordinate adduct, which is stable at room temperatures. In the field even such a weak ligand, the (DMSO)Mn(TPP)(NO) does not retain bent isomer existing in the five-coordinate complex, which transforms to the linear one concomitantly with the formation of six-coordinate complex. The spectroscopic data demonstrate that coordination of DMSO to Mn(TPP)(NO) occurs via O-atom and has a minor impact on $\nu(\text{NO})$, which shows small shift consistent with low basicity of the ligand.

Acknowledgment. The financial support of SCS (Project 15T-1D172) is gratefully acknowledged.

**ՄԱՆԳԱՆ(II) ՊՈՐՓԻՐԻՆԻ ՆԻՏՐՈԶԻԼԱՅԻՆ ԿՈՄՊԼԵՔՍԻ ՆՏՏ
ԴԻՄԵԹԻԼՍՈՒԼՖՕՔՍԻԴԻ ՓՈԽԱԶԳԻԵՑՈՒԹՅԱՆ ՍՊԵԿՏՐԱԿ
ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ**

Գ. Գ. ՄԱՐՏԻՐՈՍՅԱՆ և Տ. Ս. ԿՈՒՐՏԻԿՅԱՆ

Մանգան(II) պորֆիրինի սուբլիմված թաղանթների 5-կոորդինացված նիտրոզիլային կոմպլեքսները սենյակային ջերմաստիճաններում ինֆրակարմիր սպեկտրերում ցուցաբերում են կոորդինացված NO-ի երկու կլանման շերտեր, որոնք ապելի վաղ վերագրվել են Mn-NO ֆրագմենտի գծային և թեք կառուցվածքներին: Դիմեթիլսուլֆօքսիդի (DMSO) փոխազդեցությունը մանգան պորֆիրինի նիտրոզիլային կոմպլեքսների Mn(II)(TPP)(NO) (TPP – մեզո-տետրաֆենիլպորֆիրինատո դիանիոն) սուբլիմված թաղանթների հետ ուսումնասիրվել է էլեկտրոնային և ինֆրակարմիր սպեկտրալ եղանակներով: Mn(TPP)(NO)-ի հետ լիգանդի գոլորշիների փոխազդեցության արդյունքում ԻԿ սպեկտրերում դիտվում են հետևյալ փոփոխությունները. թեք կառուցվածքին վերագրվող կլանման շերտը վերանում է, իսկ գծային իզոմերին վերագրվող կլանման շերտը շեղվում է և նրա ինտենսիվությունը աճում է: ԻԿ սպեկտրալ տվյալները, ինչպես նաև էլեկտրոնային կլանման սպեկտրերի տեսանկյնի մարզում դիտվող փոփոխությունները համապատասխանում են NO-ի նկատմամբ տրանս-դիրքում լիգանդի կոորդինացիային, ինչի արդյունքում գոյանում է սենյակային ջերմաստիճաններում կայուն 6-կոորդինացված կոմպլեքս: Սպեկտրալ տվյալները վկայում են այն մասին, որ DMSO-ի կոորդինացիան մանգանի իոնի հետ իրականացվում է թթվածնի ատոմի միջոցով:

**СПЕКТРАЛЬНОЕ ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ
ДИМЕТИЛСУЛЬФОКСИДА С НИТРОЗИЛЬНЫМ КОМПЛЕКСОМ
ПОРФИРИНА МАРГАНЦА**

Г. Г. МАРТИРОСЯН и Т. С. КУРТИКЯН

Пятикоординированные нитрозильные комплексы сублимированных слоев порфиринов Mn(II) проявляют в ИК-спектрах при комнатной температуре две полосы координированного NO. Эти полосы были отнесены ранее к линейной и изогнутой структуре фрагмента Mn-NO. Взаимодействие DMSO с сублимированными слоями нитрозильного комплекса порфирина Mn(II)(TPP)(NO) (TPP – мезо-тетрафенилпорфирино дианион) исследовано с использованием электронной и инфракрасной спектроскопии. При взаимодействии паров лиганда с Mn(TPP)(NO) в ИК-спектре наблюдаются изменения: полоса изомера с изогнутой структурой исчезает, а полоса линейного изомера сдвигается и увеличивает свою интенсивность. Эти ИК-спектральные изменения, а также изменения, наблюдаемые в видимой области электронного спектра поглощения, согласуются с координацией лиганда в транс-положении к NO и образованием шестикоординированного аддукта, в твердом состоянии стабильного при комнатной температуре. ИК-спектральные данные свидетельствуют о том, что координация DMSO с ионом марганца происходит посредством атома кислорода. Ввиду низкой основности транс-влияние DMSO на частоту координированного NO невелико.

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