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SPECTRAL STUDY OF TRIMETHYLPHOSPHINE INTERACTION WITH NITRO COMPLEX OF CO-MESO-TETRAPHENYLPORPHYRIN

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Low-temperature reaction of trimethylphosphine (PMe_3) with sublimed layer of Co(TPP) (TPP - *meso*-tetraphenyl-porphyrinato dianion) nitro complex (Co(TPP)(NO_2)) leads initially to formation of the 6-coordinate nitro complex Co(TPP)(NO_2)(PMe_3) that at higher temperature under PMe_3 excess converts to the $\{Co^{III}(TPP)(PMe_3)_2\}\cdot NO_2^-$ as is shown by FTIR spectroscopy reinforced by the data with isotopic $^{15}NO_2^-$ group. Neither Co(TPP)(NO_2)(PMe_3) nor $\{Co^{III}(TPP)(PMe_3)_2\}\cdot NO_2^-$ take part in the oxygen atom transfer reaction from 6-coordinate nitro group or outer sphere NO_2^- anion.

Figs. 4, table 1, references 19.

Nitro complexes of cobalt porphyrins have ability to take part in stoichiometric and catalytic oxo-transfer reactions from the coordinated nitro group to various oxygen acceptors. It was shown by Goodwin and co-workers [1] 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 due to the presence of five-coordinate nitro species that exist in equilibrium in a 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 nitro complexes of Co-porphyrins are known for trans nitrogen [2-4], sulfur [5], oxygen [6] and phosphorus [7] ligands. Triphenylphosphine was used as a phosphorus ligand and it was found that Ph_3P thermally abstracted an oxygen atom from the NO_2

moiety of $(NO_2)(H_2O)$CoIII(TPP) resulting in the formation of nitrosyl cobalt porphyrin (NO)Co(TPP) and oxidation of Ph_3P to triphenylphosphine oxide Ph_3P=O.

In this paper the interaction of trimethylphosphine (PMe_3) with nitro complex Co(TPP)(NO_2) was studied and it is shown that this reaction leads eventually to the formation of a cationic complex $\{Co(TPP)(PMe_3)_2\}^+$ and outer sphere NO_2^- anion. It is also shown that neither initially formed 6-coordinate nitro complex Co(TPP)$(NO_2)(PMe_3)$ nor eventually formed ion pair $\{Co(TPP)(PMe_3)_2\}^+ \cdot NO_2^-$ promote oxygen atom transfer reaction with formation of trimethylphosphine oxide ($O=PMe_3$) and nitrosylcobalt porphyrin (NO)Co(TPP).

Experimental Section

Co(TPP) was synthesized using a literature method [8]. NO_2 ($^{15}NO_2$) was obtained by oxidation of NO (^{15}NO) with an excess of pure dioxygen. NO was synthesized according to the procedure given in [9] and 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 (77K). The IR spectrum 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. After preliminary drying under P_2O_5, the NO_2 ($^{15}NO_2$) was purified by fractional distillation using a low-temperature vacuum technique until a pure white solid was obtained. Sublimed layers of Co(TPP) were obtained on the cold (77K) KBr support of an optical cryostat according to a published procedure [10]. The sublimed layers of the nitro complexes Co(TPP)(NO_2) and Co(TPP)$(^{15}NO_2)$ were obtained by supplying a low pressure of NO_2 ($^{15}NO_2$) vapors on the amorphous layers of Co(TPP) as described elsewhere [11]. This procedure rapidly led to the formation of the nitro complex, which manifests itself by an intense $\nu_s(NO_2)/\nu_s(^{15}NO_2)$ band of coordinated NO_2 ($^{15}NO_2$) at 1283 cm^{-1} and 1265 cm^{-1} correspondingly. The unreacted NO_2 ($^{15}NO_2$) was then pumped out, the samples were cooled to 130 K, and small increments of PMe_3 ligand were introduced into the cryostat. Since PMe_3 may be oxidized to the phosphine oxide with an oxygen, as a source of PMe_3 air-stable silver iodide complex AgI(PMe_3) (Aldrich) that releases PMe_3 upon heating was used in the experiments. This complex was placed into glass tube provided with the vacuum valve and was preliminary vacuum-dried at RT. The tube was attached to the cryostat and the vapors of PMe_3 could be obtained in tube by mild heating. Small portions of PMe_3 were then introduced into the cryostat with layered Co(TPP)(NO_2) {Co(TPP)$(^{15}NO_2)$} and FTIR spectra were measured at

different temperatures of the substrates controlled by thermocouple. The FTIR spectra were acquired on a Nexus (Thermo Nicolet, USA) spectrometer.

Results and discussion

It has been shown previously that sublimed layers of *meso*-tetraphenyl porphyrinato cobalt(II) give the five-coordinate nitro complex upon interaction with NO_2 gas [11]. This layered complex was readily transformed to six-coordinate nitro complexes (B)Co(TPP)(NO_2) (B - N-, S- and O-donors) when exposed to the vapors of corresponding compounds [4-6]. Similarly, the introduction of trimethylphosphine (PMe_3) to the layered Co(TPP)(NO_2) led to the species with the new set of FTIR bands in the ranges where normal vibrations of coordinated nitro groups are disposed. The $\nu_{as}(NO_2)$, $\nu_s(NO_2)$, and $\delta(NO_2)$ bands of parent Co(TPP)(NO_2) are observed at 1470, 1283 and 806 cm^{-1} and shift to 1388, 1314 and 808 cm^{-1} (Fig. 1) after stepwise addition of PMe_3 vapors to the layers of Co(TPP)(NO_2) and its warming from 130K to 170K. They have their isotopic counterparts when Co(TPP)($^{15}NO_2$) was used. For this system the bands located at 1444, 1265 and ~800 cm^{-1} shift to 1368, 1288 and 802 cm^{-1} (Fig. 2) and in the spectral range free of the bands of 5-coordinate nitro complexes a new band at 950 cm^{-1} grows in intensity that belongs to the most intense band of coordinated PMe_3. From these data it can be concluded that interaction of trimethylphosphine with Co(TPP)(NO_2) led to the formation of six-coordinate nitro complexes, as shown in Scheme 1 (first reaction). Additionally in this temperature interval a small band in the range of 1230 cm^{-1} begins to grow (dashed arrow in the Fig.1) that has its isotopic analogue at ~1200 cm^{-1} in the experiments with $^{15}NO_2$ (Fig. 2).

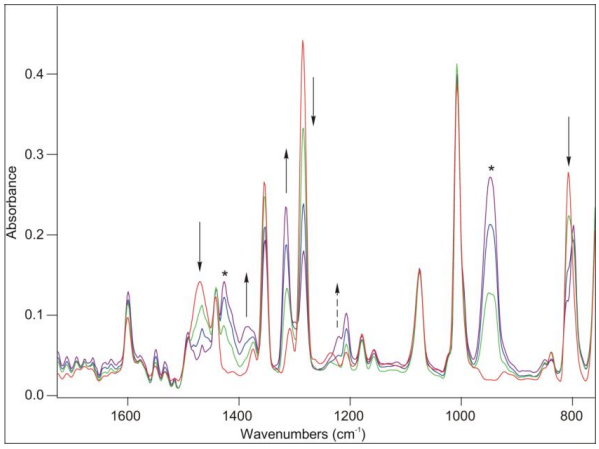

Fig.1. FTIR spectral changes upon stepwise addition of PMe_3 vapors to the layer of Co(TPP)(NO_2) and its warming from 130K to 170K. The bands of coordinated PMe_3 are denoted with asterisks.

Scheme

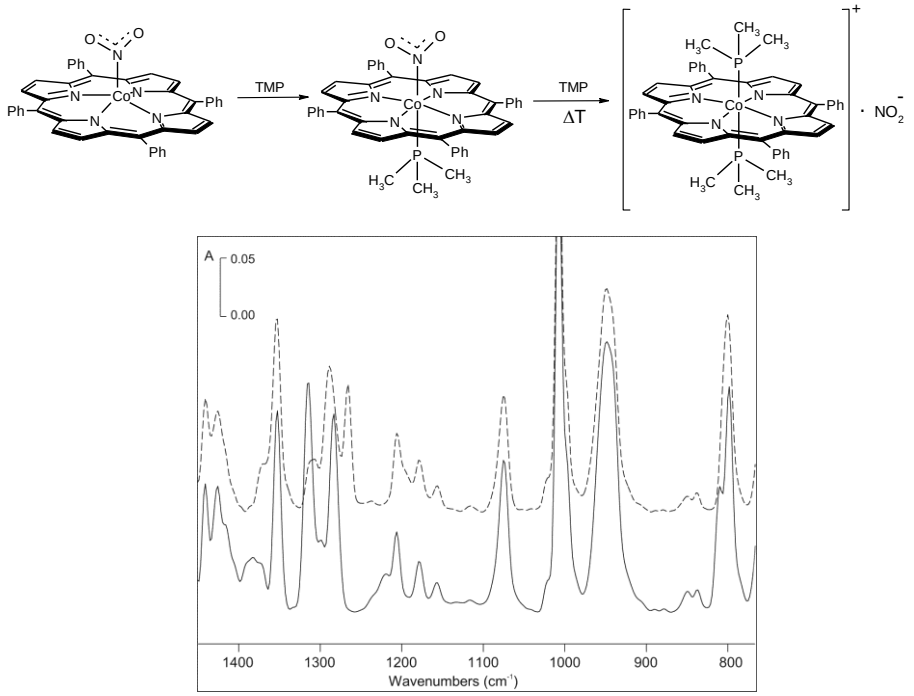

Fig. 2. FTIR spectra at 170K of mostly $Co^{III}(TPP)(PMe_3)(NO_2)$ (solid line) and $Co^{III}(TPP)(PMe_3)(^{15}NO_2)$ (dashed line).

It was found previously for the cobalt nitroporphyrin complexes with different *trans* ligands (L)Co(Por)(NO_2) (L=nitrogen-, sulfur- and oxygen-donors) that there was a negative correlation between the magnitude of the difference of coordinated nitro group asymmetric and symmetric modes $\Delta\nu=\nu_{as}(NO_2)-\nu_s(NO_2)$ and the σ-donor ability of the *trans* ligand [4-6]. A higher extent of the electron density 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 was reported for six-coordinate iron nitroporphyrin complexes [12]. In the case of PMe_3 as a *trans* ligand the values of $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ are closer to each other than for nitrogen, sulfur and oxygen σ-donor ligands (Table) indicating greater electron density transfer from phosphine to coordinated nitro-group.

Addition of new portions of PMe_3 into the cryostat and further increase in temperature leads to the growth in intensity of a previously noted weak band disposed at 1227 cm^{-1} (Fig. 3). This process is accompanied by complete disappearance of the bands of the six-coordinate nitrocomplexes with *trans* PMe_3 ligand (the weak remaining band at 1315 cm^{-1} belongs to the coordinated PMe_3). In the experiments with $^{15}NO_2$ an isotopic analogue of the 1227 cm^{-1} band appears at 1205 cm^{-1} (Fig. 4).

Table

Spectral characteristics of 6-coordinate nitro complexes (B)Co(TPP)(NO_2)[a]

Donor ligand (B)	ν_{as}	ν_s	δ	$\Delta\nu = \nu_{as} - \nu_s$	Ref.
-	1468(1440)	1282(1264)	805(796)	186(176)	[11]
Tetrahydrofuran	1462(1430)	1300(1279)	808(800)	162(151)	[6]
Acetone	1459(1429)	1300(1281)	810(802)	159(138)	[6]
Dimethylsulfide	1444(1413)	1298(1279)	810(802)	146(134)	[5]
Tetrahydrothiophene	1443(1413)	1300(1282)	810(802)	143(131)	[5]
Piperidine	1436(1403)	1305(1284)	815(805)	131(119)	[4]
Ammonia	1431(1400)	1309(1289)	814(805)	122(111)	[4]
Trimethylphosphine	1388(1368)	1314(1288)	808(802)	74(80)	[this work]

[a]Data for $^{15}NO_2$-labeled compounds are given in parenthesis

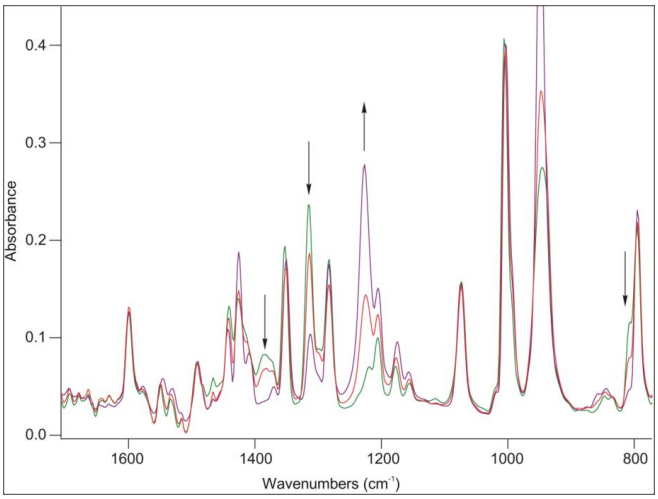

Fig. 3. FTIR spectral changes upon warming the layer, containing mostly $Co^{III}(TPP)(PMe_3)(NO_2)$ from 170K to room temperature.

These data testify for the detachment of the nitro group in the form of a nitrite anion and the occupation of its place by an additional phosphine molecule (the second reaction in the Scheme 1) as evidenced by a sharp increase in the intensity of the coordinated phosphine band with a maximum at 950 cm^{-1} (Fig. 3). A free anion NO_2^- (in the ground electronic state $^1A_1$) is characterized by the point symmetry C_{2v} and has full-symmetric valence vibration ν_1, deformational vibration ν_2, antisymmetric valence vibration ν_3. Indeed, in the nitrite anion NO_2^- that represents the limiting case with greatest extent of the electron density transfer, the $\nu_{as}(NO_2^-)$ and $\nu_s(NO_2^-)$ denoted in the case of anion as ν_3 and ν_1 correspondingly are close to each other, with ν_3 even lower than ν_1 [13]. The

band representing ν_3 is much more intense than that of ν_1 and usually overlaps it. The deformation mode ν_2 is weak and is located near 800 cm^{-1} where the intense porphyrin band is disposed. The fundamentals of NO_2^- are strongly dependent on the measurements conditions. Notably, the ν_3 frequency of $NaNO_2$ measured in Nujol mull is found at 1261 cm^{-1} [14], in aqueous solution it is disposed at 1236 cm^{-1} [14] and in a doped KBr crystal at 8K is reported to be at 1275(1250) cm^{-1} [15]. In the argon matrix, this band is located at 1244(1218) cm^{-1} [16] (data for $^{15}NO_2^-$ are given in parenthesis). These literature data show that both the range where band ν_3 is located and the value of isotopic shift are close to that observed in our system and support our conclusion. As can be seen from these data the ν_3 band shifts to the lower frequency when ionic interactions in the sample weaken.

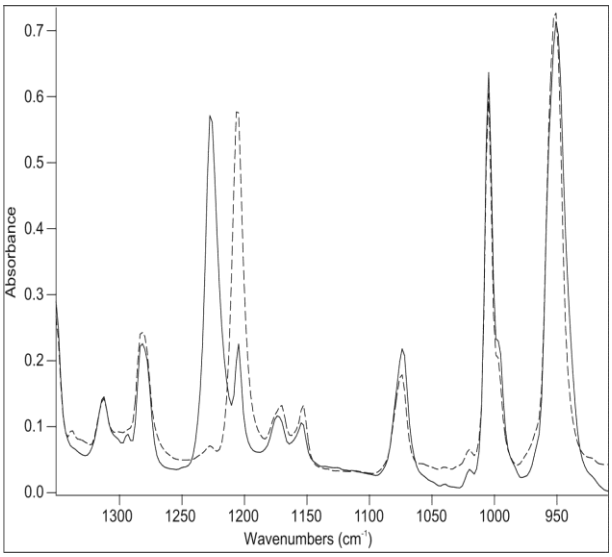

Fig. 4. FTIR spectra of $Co^{III}(TPP)(NO_2)+PMe_3$ (solid line) and $Co^{III}(TPP)(^{15}NO_2)+PMe_3$ (dashed line) after warming these systems to room temperature.

It should be noted that in the experiments with layered $Co(TPP)(NO_2)$, neither the formation of cobalt nitrosylporphyrin, nor the signs of trimethylphosphine oxidation were detected as seen in Figures 1 and 3. There are no new bands in the range 1600 -1700 cm^{-1} where ν(NO) of the five- or six-coordinated nitrosyl complexes of Co-porphyrins are located [5], nor in the range 1050-1200 cm^{-1} where the ν(PO) of free or coordinated trimethylphosphine oxide are disposed [18]. As noted above, when triphenylphosphine was used as a phosphorus ligand it was found that Ph_3P thermally abstracted an oxygen atom from the NO_2 moiety of $(NO_2)(H_2O)Co^{III}TPP$ resulting in the formation of nitrosylcobalt porphyrin (NO)Co(TPP) and oxidation of Ph_3P to triphenylphosphine oxide $Ph_3P{=}O$ [7]. Thus, the cobalt nitroporphyrin complexes with *trans* PMe_3 do not promote the oxo-transfer reaction in contrast to the triphenylphosphine under our

experimental conditions. The reasons for different oxo-transfer reactivity may be connected with the fact that the binding of trimethylphosphine ligand with cobalt nitroporphyrin complexes in $(PMe_3)Co(TPP)(NO_2)$ is much stronger. It is most likely that such a different behavior of the two phosphines is due to their significantly different electron-donating strength. The pK_a values of trimethylphosphine and triphenylphosphine are 8.65 and 2.73, correspondingly. Finally, we assume that the higher stability of the nitro complex with a trimethylphosphine ligand prevents an oxygen atom transfer in our system.

Co-ՄԵԶՈ-ՏԵՏՐԱՖԵՆԻԼՊՈՐՖԻՐԻՆԻ ՆԻՏՐՈ ԿՈՄՊԼԵՔՍԻ ՀԵՏ ԵՌՄԵԹԻԼՖՈՍՖԻՆԻ ՓՈԽԱԶԴԵՑՈՒԹՅԱՆ ՍՊԵԿՏՐԱԼ ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ

Ա. Ա. ՀՈՎՀԱՆՆԻՍՅԱՆ, Գ. Գ. ՄԱՐՏԻՐՈՍՅԱՆ, Գ. Շ. ՀՈՎՀԱՆՆԻՍՅԱՆ և Տ. Ս. ԿՈՒՐՏԻԿՅԱՆ

Ֆուրիե սպեկտրաչափական եղանակով ուսումնասիրվել է եռմեթիլֆոսֆինի (PMe_3) փոխազդեցությունը Co-մեզո-տետրաֆենիլպորֆիրինի նիտրոկոմպլեքսի ($Co(TPP)NO_2$) հետ: Ռեակցիան ընթանում է երկու փուլերով: Առաջին փուլում ցածր ջերմաստիճաններում (120-170 K) դիտվում է Co-պորֆիրինի տրանս-եռմեթիլֆոսֆին պարունակող նիտրոկոմպլեքսի՝ $(PMe_3)Co(TPP)(NO_2)$ գոյացումը: Ֆոսֆինի նոր չափաբաժինները և տաքացումը մինչև սենյակային ջերմաստիճան հանգեցնում է իոնային զույգի առաջացման՝ բաղկացած երկեռմեթիլֆոսֆին պարունակող կատիոնից $[Co(TPP)(PMe_3)_2]^+$ և նիտրիտ-անիոնից՝ NO_2^-: Այդպիսով PMe_3 դուրս է մղում նիտրոլիգանդը նիտրիտ-անիոնի տեսքով: Ստացված արդյունքները լրացուցիչ հիմնավորում են ստացել $^{15}NO_2$ իզոտոպոմերի կիրառմամբ:

Co-պորֆիրինների նիտրոկոմպլեքսները ընդունակ են մասնակցելու թթվածնի ատոմի տեղափոխման ռեակցիաներում կոորդինացված նիտրոխմբից համապատասխան թթվածնի ակցեպտոր հանդիսացող մոլեկուլի վրա: Ուսումնասիրված համակարգը միկրոծակոտկեն թաղանթներում չի դրսևորում այդպիսի ունակություն, թեև 6-կոորդինացված նիտրոխմբից, թեև նիտրիտ-անիոնից, ի տարբերություն եռֆենիլֆոսֆինի: Դա, ամենայն հավանականությամբ, պայմանավորված է այդ երկու լիգանդների էլեկտրոնատոր հատկությունների զգալի տարբերությամբ:

СПЕКТРАЛЬНОЕ ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ ТРИМЕТИЛФОСФИНА С НИТРОКОМПЛЕКСОМ Co-*МЕЗО*-ТЕТРАФЕНИЛПОРФИРИНА

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Методом Фурье ИК спектроскопии исследовано взаимодействие триметилфосфина (PMe_3) с нитрокомплексом Co-*мезо*-тетрафенилпорфирина. Реакция протекает в две стадии. На первой, при низких температурах (120-170 K), наблюдает-

ся образование 6-координированного нитрокомплекса Co-порфирина, содержащего *транс*-триметилфосфинный лиганд (PMe_3)Co(TPP)(NO_2). Подача новых порций PMe_3 и нагрев системы до комнатной температуры ведет к образованию ионной пары, состоящей из катионного ди-триметилфосфинного комплекса Co-порфирина и нитрит-аниона. Таким образом координированная нитрогруппа вытесняется триметилфосфином в виде нитрит-аниона.

Нитрокомплексы Co-порфиринов способны участвовать в реакции переноса атома кислорода с координированной нитрогруппы на соответствующий акцептор кислорода. Исследованная система, в отличие от трифенилфосфина, не проявляет такой способности ни от 6-координированной нитрогруппы, ни от нитрит-аниона, что, по-видимому, связано со значительным различием в электронодонорной силе этих лигандов.

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