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Comparative FTIR study of the cobalt and iron porphyrin reactions with CO. Does cobalt

porphyrin form a bis-carbonyl complex in the Ar matrix?

G. G. Martirosyan^{1*}, H. V. Adonts¹, G. S. Hovhannisyan¹ and T. S. Kurtikyan^{1*}.

The Scientific Technological Centre of Organic and Pharmaceutical Chemistry NAS RA, Molecule Structure Research Centre, 26 Azatutyan Av., Yerevan, 0014, Armenia

Corresponding author.

E-mail address: ggmartirosyan@gmail.com

Abstract.

The adducts of Co(II)(TPP) and Fe(II)TPP (TPP is *meso*-tetraphenyl-porphyrinato dianion) with carbon monoxide in Ar matrix at 10 K have been studied by FTIR spectroscopy using CO, C¹⁸O and their equimolar mixture. It is shown that both metals may form mono-carbonyl adducts with CO, however formation of bis-carbonyl adduct was confirmed only for iron porphyrin. These results refute an earlier assumption regarding existence of Co(TPP)(CO)₂ in Ar matrix.

Keywords.

FTIR spectroscopy; Iron(II) and Cobalt(II) porpyrin; carbonyl complexes; Ar matrix;

Introduction.

The coordination chemistry of carbon monoxide binding with metalloporphyrins and related model complexes has a long history and has been of particular interest in elucidation of the nature of the heme binding site. [1-3]. Numerous studies has focused on probing the

interaction of CO with Fe(II) and Ru(II) metalloporphyrin model complexes, to better understand the factors that govern CO binding in heme centers of the proteins. The investigations have also been extended to the six-coordinate CO- adduct of Fe(II) and Ru(II) porphyrins with donor or acceptor ligands trans to carbon monoxide, revealing high sensitivity of CO to the bonding changes [4-9]. While spectroscopic data on the reactions of iron(II) and ruthenium(II) porphyrins with CO are well documented, significantly less information is available on Co(II) porphyrin complexes containing bond CO. Both, mono- and bis-coordinated carbonyls have been reported for iron and ruthenium porphyrin complexes at room temperature and low temperature noble gas matrix [10-14]. In contrast, only low temperature binding of CO to the Co porphyrins have been achieved. The reaction of cobalt(II) porphyrins with CO has been initially studied by electron paramagnetic resonance (EPR) in frozen solution. It has been shown that Co(TPP) forms a 1:1 adduct with CO at 90 K [15, 16]. We have also reported that only mono-carbonyl complex was detected by infrared spectroscopy upon reaction of CO gas with low temperature sublimed layers of Co(II)(TPP) at 77K [17]. The only bis-carbonyl Co(TPP)(CO)₂ adduct was reported to form at 15 K in Ar matrix and studied by IR and Raman spectroscopy [18]. However, comparison and analysis of the currently available vibrational data for iron, ruthenium and cobalt porphyrins revealed some discrepancies in interpretation of the IR spectra and assignment of the biscarbonyl adduct Co(TPP)(CO)₂ in Ar matrix.

It is well established, that due to competition for metal d_p electrons the frequency of CO vibration in bis-carbonyl of iron and ruthenium porphyrins is noticeably higher (~ 60 cm⁻¹) than in the monocarbonyl complex. For example, CO frequencies of mono and bis-carbonyl complexes Fe(TPP) in Ar matrix are reported at 1974 and 2036 cm⁻¹ respectively [13]. Similarly, the stretching frequency modes for Ru(TPP)(CO) and Ru(TPP)(CO)₂ are observed at 1951 and

2015 cm⁻¹ in the same matrix [14]. At the same time the v(CO) of mono and bis-carbonyl complexes of Co(TPP) were reported at 2073 and 2077 cm⁻¹ in Kr matrix, while the same adduct in the Ar matrix revealed only a single band at 2078 cm⁻¹ [18]. The authors suggested that v(CO) of the 1:1 and 1:2 adducts are probably overlapped in Ar matrix.

An infrared spectroscopy is a powerful tool for studying the structure and bonding of carbonyl adducts of heme proteins and model compounds. The spectral features associated with CO binding to the metallo-complexes can be easily identified in the IR spectra and assigned by using isotopically labeled CO. At the same time FTIR spectroscopy is a unique tool to differentiate between coordination numbers for simple diatomic molecules applying the mixtures of isotopes [19]. Indeed, mixed isotopic spectra are extremely important for determination of the number of CO subunits in the metal carbonyls. With the equal mixture of $C^{x}O + C^{y}O$ (if oxygen atom is isotope labeled) the mono-carbonyl metal porphyrin complex should display a doublet containing only the bands of the pure isotopic molecules Me(Por)(C^xO) and Me(Por)(C^yO) with 1:1 intensities ratio. In contrast, the bis-carbonyl is spectroscopically manifested by a formation of an additional band between the bands of doublet, due to the mixed isotopic molecule $Me(Por)(C^{x}O)(C^{y}O)$. For the strong antisymmetric C-O vibrations of the $Me(TPP)(C^{x}O)_{2}$, $Me(TPP)(C^{x}O)(C^{y}O)$ and $Me(TPP)(C^{y}O)_{2}$ the intensities of the IR bands should follow the 1:2:1 (statistical weights) distribution [19]. In this paper we report comparative FTIR spectral study of the Co(TPP) and Fe(II)(TPP) reactions with CO, C¹⁸O and their equimolar mixture in Ar matrix at 10 K.

2. Experimental section

Material and Measurements: H_2TPP was purchased from PorphyChem. Co(TPP) and Fe(TPP)(Py)₂ were synthesized and purified according to the published methods [20,21]. The

metalloporphyrin was placed in Knudsen cell and heated at 420-450 K for 3-4 h to remove solvates or/and protective pyridine ligands (in case of iron porphyrin). Then metalloporphyrin was vaporized under continuous vacuum conditions at 500-550 K and co-deposited with previously prepared CO/Ar mixture on a CsI window cooled to 10 K by a closed cycle helium cryostat DE-202. The temperature of the substrate was controlled with LakeShore 331 temperature controller. The gases, Ar (99.9995%, Linde), CO (99.9%) and C¹⁸O (99.5%, with 81.4% isotopic enrichment, Institute of Isotopes, Republic of Georgia) were used without further purification. CO^x/Ar mixtures were prepared in a glassy bulb using a vacuum system equipped with mercury manometer. Equimolar mixtures of CO + C¹⁸O were prepared taking into the account C¹⁸O isotope enrichment. The infrared spectra were measured using Nicolet "Nexus" FTIR spectrometer at 2 cm⁻¹ resolution.

Results and Discussion.

Fe(II)(TPP) + CO.

Figure 1 represents the IR spectra of the adducts of Fe(TPP) co-condensed with CO/Ar, C¹⁸O/Ar and mixture (CO+ C¹⁸O)/Ar at 10 K. The CO stretching bands at 2138 cm⁻¹ (2086 cm⁻¹ for C¹⁸O) and 2149 cm⁻¹ (2097 for C¹⁸O cm⁻¹) are due to well-known matrix isolated monomeric carbon monoxide and CO bound H₂O traces respectively [22-25].



Fig. 1. FTIR spectra of the co-condensation adducts of Fe(TPP) with CO (a), $C^{18}O$ (b) and CO+C¹⁸O mixture (c) in Ar matrix at 10 K, (Ar/CO=200).

The bands in the spectrum (a) at 1974 cm⁻¹ and 2036 cm⁻¹ are the v(CO) of mono- and biscarbonyl complex of Fe(TPP) and have been assigned previously in Ar matrix using ¹²CO -¹³CO substitution [13]. Similarly, the bands at 1926 cm⁻¹ and 1987 cm⁻¹ in the spectrum (b) should be assigned to the respective v(C¹⁸O) of the mono- and bis-carbonyl complex Fe(TPP), in excellent agreement with the 1926.4 cm⁻¹ and 1986.9 cm⁻¹ values, calculated by the diatomic harmonic oscillator approximation. It is clearly seen in the spectrum (c), that a new band at 2003 cm⁻¹ has appeared between the bands of Fe(TPP)(CO)₂ and Fe(TPP)(C¹⁸O)₂ at 2036 cm⁻¹ and 1987 cm⁻¹. Thus, the band at 2003 cm⁻¹ should be undoubtedly assigned to the mixed bis-carbonyl complex Fe(TPP)(CO)(C¹⁸O). A weak sign of this isotope mixed bis-carbonyl complex (due to not fully enriched C¹⁸O) is also seen in the spectrum (b).

Co(II)(TPP) + CO.

The IR spectra of the adducts of Co(II)(TPP) co-condensed with CO/Ar , $C^{18}O/Ar$ and mixture (CO+ $C^{18}O$)/Ar are shown in Figure 2.



Fig. 2. FTIR spectra of the co-condensation adducts of Co(TPP) with CO (a), $C^{18}O$ (b) and CO+ $C^{18}O$ mixture (c) in Ar matrix at 10 K, (Ar/CO=200).

Similar to Fig. 1, the bands of monomeric CO and CO-H₂O are also present in the spectra. However, in contrast to the Fe(TPP) showing two widely spaced bands of mono- and bis-coordinated adducts, only a single band persists in the spectrum at 2078 cm⁻¹ (a). This spectrum completely reproduces the earlier reported data, where the band at 2078 cm⁻¹ has been assigned to the bis-carbonyl complex Co(TPP)(CO)₂ [18]. The band at 2078 cm⁻¹ shifts to 2028 cm⁻¹ upon C¹⁸O substitution (calculated value is 2027 cm⁻¹). It is clearly seen that spectrum (c), obtained by co-condensation of Co(TPP) and (CO+ C¹⁸O)/Ar shows only doublet of the pure isotopic CO adducts at 2078 cm⁻¹ and 2028 cm⁻¹. However, if Co(TPP)(CO)₂ exists under given experimental conditions, three bands should be expected similarly to Fe(TPP). Experiments with higher concentration of CO/Ar resulted in the same spectral picture. Thus, this result makes the previous assignment of the band at 2078 cm⁻¹ to the v(CO) of Co(TPP)(CO)₂ questionable.

As it can be seen from Fig. 1, predominantly mono-carbonyls of Fe(TPP) were formed in low-temperature rigid Ar matrix at 10 K. Similar spectral pictures have also been observed for iron and ruthenium porphyrins. However, upon stepwise elevation of the temperatures to 20-30

K the free monomeric CO diffused and reacted with the five-coordinate complexes to form a sixcoordinate adduct [13, 14].

Figures 3 and 4 show changes in the IR spectra of the Fe- and Co(TPP) co-condensation adducts with CO isotopic mixture in the Ar matrix as a function of temperature. Annealing of the Ar matrix leads to an increase of the bis-carbonyl adducts in case of Fe(TPP), while only a small rise in intensities of the bands at 2078 cm⁻¹ and 2028 cm⁻¹ are seen in the spectra of Co(TPP) adducts upon the same procedure.



Fig.3. FTIR spectra of co-condensation adducts of Fe(TPP) with CO+C¹⁸O in Ar at 10 K-

(a), spectra taken after a stepwise 10K-30K-10K procedure - (b). Ar/CO=200.



Fig.4. FTIR spectra of co-condensation adducts of Fe(TPP) with CO+C¹⁸O in Ar at 10 K-

(a), spectra taken after a stepwise 10K-30K-10K procedure - (b). Ar/CO=200.

As a possible reason for the existence of a single band in the suspected Co(TPP)(CO)₂ (2078 cm⁻¹) in Ar matrix, bending of the Co-C-O bonds has been suggested [18]. Generally, since the σ -bonding interaction involves an electron pair in the sp hybridized carbon on CO, the preferred geometry for CO binding to a metal is linear [26]. The X-ray crystal structures of the molecular Co(II) porphyrin carbonyl complexes are yet not known, however X-ray data of Fe(OEP)CO and Fe(OEP)(CO)₂ (OEP- octaethyl porphyrin) show, that the Fe-C-O angles are essentially linear to be 177° and 174° respectively [12]. On the other hand, the X-ray structural analysis of the bis-carbonyl Ru(TPP)(CO)₂ revealed markedly bent Ru-C-O bonds (154°) [27]. Nevertheless, even in this case the v(CO) of Ru(TPP)(CO)₂ and Ru(TPP)(CO) were quiet largely spaced and measured at 2005 and 1945 cm⁻¹ [10, 28]. We also have detected the v(CO) of monoand bis-carbonyls of Ru(TPP) at 1944 and 2009 cm⁻¹ in the solid sublimed films [29]. Thus, even the bent coordinated CO ligands can still quite effectively compete for metal d_p electrons.

A new approach has recently been applied for investigation of the coordinatively unsaturated metal porphyrins with the gaseous ligands. It is based on incorporation of the metal porphyrins into a metal organic frameworks (MOF), which exhibit remarkable stabile organic–inorganic hybrid porous solids that enable facile diffusion of gas-phase substrates to interact with immobilized metal porphyrin centers [31-32]. In the very recent work an interaction of CO gas with Zr-based porphyrinic MOF PCN-224Co(II) (PCN - porous coordination network) has been reported [33]. In particular, under 1 atm of dry CO single-crystal X-ray diffraction analysis at 8 K revealed formation of the cobalt porphyrin bis-carbonyl adduct of PCN-224Co(CO)₂, with Co–C–O angles of 180°. This bis-carbonyl complex was also observed by low temperature by EPR spectroscopy, and warming of the sample showed the conversion of this species to a monocarbonyl analogue. In addition, the CO binding at the Co(II) center of PCN-

224Co was detected by diffuse-reflectance infrared Fourier transform spectroscopy. Upon cooling the sample to 238 K, a strong v(CO) stretching vibration appeared at 2086 cm⁻¹. Based on the temperature at which the spectra were collected, this species was postulated to be a monocarbonyl adduct. However, the v(CO) of bis-carbonyl adduct was not reported. The interaction of CO with the cobalt porphyrin center in this MOF is distinct from molecular cobalt(II) porphyrin complexes. The slightly higher (relative to the matrix isolated analogue) v(CO) stretching vibration and exact of 180° angles Co–C–O measured in MOF are possibly reflective for the absence of intra- and/or intermolecular interactions between well spatially separated in the MOF porphyrin molecules. It is well known, that energies of CO stretches are very sensitive to the structural constraint of model complexes or bulky amino acid residues of hemes, which can affect geometry and frequencies of Fe–CO group [34].

It should be also noted, that Co(H)(TPP) (compared to Ru- and Fe(II)(TPP)) has an additional electron in the metal dz² orbital that may decrease π back-bonding. Indeed, recent detailed computations of Fe(II) and Co(II) porphyrin mono-carbonyls predict much less pronounced back-donation from cobalt d orbitals than from iron [35]. At the same time, similarly to their isoelectronic iron(II) analogues, mono and bis-carbonyls of cobalt(III) porphyrins are also known. The v(CO) of [Co(III)(OEP)(CO)]ClO₄ and [Co(III)(OEP)(CO)₂]ClO₄ were observed at 2110 and 2137 cm⁻¹ respectively [36]. Finally, taking the abovementioned experimental results together with the literature data, the band at 2078 cm⁻¹ should be re-assigned to the v(CO) of monocarbonyl adduct of Co(TPP)(CO) in Ar matrix. Splitting of this band into two closely spaced bands at 2073 and 2077 cm⁻¹, observed in Kr matrix is probably due to Co(TPP)(CO) and it's six coordinate complex with H₂O, which is a typical impurity in low-temperature matrix isolation experiments.

Conclusions.

The FTIR spectra of co-condensation products of Fe(II)(TPP) and Co(II)(TPP) with CO/Ar, $C^{18}O/Ar$ and equimolar (CO+ $C^{18}O)/Ar$ at 10 K, are all consistent in supporting formation of the bis-carbonyl complex of iron porphyrin, but testifies against the existence of the earlier suggested similar adduct of cobalt porphyrin.

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R



CO+Ar

10 K



0 ||| C

R = Phenyl

Highlights:

- Adducts of Co(II)(TPP) and Fe(II)TPP with CO have been isolated in Ar matrix at 10K.
- The CO, C¹⁸O and their equimolar mixture were used.
- FTIR spectra of the adducts were measured.