SPECTRAL INVESTIGATION OF A MIXED ISONITRILE-CARBONYL EXTRACOMPLEX OF MESO-TETRAPHENYLPORPHYRINATOIRON(II) AT LOW TEMPERATURES

T. S. Kurtikyan, G. G. Martirosyan, A. V. Gasparyan, M. E. Akopyan, and G. A. Zhamkochyan UDC 543.4:547.979.733

The study of the coordination of additional ligands of varied nature by ferroporphyrins is of fundamental importance for understanding the biological processes in which they take part. Particular attention was directed by the research workers to donor nitrogen-containing ligands [2] in addition to molecular oxygen [1]. The coordinational properties of ferroporphyrins with donor ligands also having π -acceptor properties, such as carbon monoxide and isonitriles have been investigated to a lesser extent. The attention paid to the coordination of CO has been limited mainly to pentacoordinated complexes with a nitrogeneous base as the additional ligand [3]. The coordination of CO was studied in [4] (which article deserves attention) without additional ligand, where the complexation of CO with meso-tetraphenylporphyrinatoiron(II) (FeTPP) in solution was studied by electron-spectroscopy and NMR methods. Diamagnetism of a monocarbonyl complex - FETPP·CO was discovered, which indicates a low-spin state of Fe(II) in the pentacoordinated complex.

In continuation of our studies on the spectral examination of the ability of various metalloporphyrins to coordinate the isonitrile ligand [5], we prepared isonitrile complexes $FeTPP(CNCH_3)_n$ (n = 1, 2) of various stoichiometric composition [6]. The combination of the data on the IR spectroscopy and the resonance Raman spectra of the monoisonitrile complex indicated an intermediate spin state (S = 1) of Fe(II) in the complex.

An attempt was made in the present work to obtain a mixed isonitrile-carbonyl complex, and to investigate the relative σ -donor and π -acceptor properties of two isoelectronic ligands, taking advantage of the specificity of the results of the vibrational spectroscopy for the coordination of ligands containing triple bonds. It should be noted that for the interpretation of the kinetic data on the substitution of the isonitrile ligand in a complex of ferroporphyrin with additionally coordinated imidazole residue by a carbonyl ligand, the authors of [7] were required to postulate the formation of a mixed isonitrile-carbonyl complex of ferroporphyrin in the solution.

The gas mixtures of CH_3NC with CO were prepared directly before the experiment by charging the components in the required ratio into a closed chamber, fitted with a manometer. The gas mixture was then condensed simultaneously with sublimed FeTPP on a liquid nitrogen cooled support. The FeTPP was obtained from FeTPP(piperidine)₂ according to a procedure described in [6]. A KBr plate served as a support for the IR investigations, and an indium plate was used in running the resonance Raman spectra. The method of preparation of samples for the spectral investigations has been described in detail in [8].

Although the condensation of carbon monoxide on the support at T = 80 K is not possible under high vacuum conditions, it was noted that during cocondensation with FeTPP, the CO molecules are captured by ferroporphyrin with the formation of a mono- and dicarbonyl complex of FeTPP. This is indicated by the appearance of two intense absorption bands at 1960 and 2030 cm⁻¹ in the IR spectrum of the cocondensate (Fig. 1a). The ratio of their intensities is dependent on the experimental conditions and increases with decrease in the inflow rate of CO (decrease in the CO:FeTPPP ratio). This indicates that the band at 1960 cm⁻¹ belongs to the monocarbonyl and the band at 2030 cm⁻¹ to a dicarbonyl complex of FeTPP.

According to conclusions summarized in [9, 10], in the coordination of the carbonyl and isonitrile ligands with a metal, the unshared pairs of electrons occupying the higher filled molecular orbitals and distributed mainly on carbon atoms [10, 11] form a donoracceptor bond with the metal of the σ -type. If the metal has d-orbitals, capable of

Armenian Branch of Scientific-Research Institute of Chemical Reagents and Specially Pure Substances, Erevan. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 53, No. 3, pp. 421-426, September, 1990. Original article submitted October 2, 1989.



Fig. 1. IR spectra of cocondensates in the $v_{CO(NC)}$ region at 80 K: FeTPP with CO (a), FeTPP with a CH₃NC:CO \approx 1:10 mixture (b), and after its heating to 200 K with a short term evacuation (c).

Fig. 2. IR sepctra of cocondensates in $v_{CO(NC)}$ region at 80 K: FeTPP with a CH₃NC:CO \approx 1:4 mixture (b), and after heating to 200 K (b), after a prolonged evacuation at 200°C (c) and at 300 K (d).

overlapping with the lower-lying anti-bonding orbitals of these ligands, then a dative π -type bond is also formed. The formation of the latter is accompanied by a decrease in the order of the C = O and C = N bonds, and hence a decrease in their force coefficients and correspondingly of the ν_{CO} and ν_{NC} stretching vibration frequencies. On this basis, the higher ν_{CO} absorption frequencies of the dicarbonyl complexes of metalloporphyrins [12] can be readily explained, since as a result of the competition of two ligands in trans positions, the reversed supply of d-electrons onto the carbonyl ligand will be lower than in the case of the monocarbonyl complex.

The simultaneous condensation of FeTPP with a $CH_3NC:CO = 1:10^*$ mixture gave a product, whose IR spectrum in the 1800-2300 cm⁻¹ region is shown in Fig. 1b. Heating of the cocondensate to 200 K results in notable changes in the spectrum. The previously very weak band at 2216 cm⁻¹ increases, and in the region between the absorption bands of FeTPP·CO and FeTPP(CO)₂, an increase in the intensity of the band with a maximum at 2009 cm⁻¹ is observed. The intensities of the bands at 2030 and 1960 cm⁻¹ decrease in such a way that the first of these appears in the form of a weak shoulder on the 2009 cm⁻¹ band, and the second is also noticeably weakened (Fig. 1c). At the site of the v_{NC} band of the free isonitrile at 2169 cm⁻¹ (Fig. 1b), a new band forms at 2171 cm⁻¹, which, as has previously been shown [6], represents a v_{NC} of the diisonitrile complex - Fe(TPP)·(CNCH₃)₂. Its formation is due to the presence on the support of a free isonitrile and FeTPP, formed as a result of the decomposition of FeTPP·CO. The apparent lack of correspondence between the intensities of the bands at 2169 and 2171 cm⁻¹ (Fig. 1b and c) is due to the fact that the coordination of the isonitrile ligand is accompanied by a considerable increase in the intensity of the v_{NC} band [13].

Increase in the CH_3NC content in the condensed gaseous mixture to $CH_3NC:CO = 1:4$ results in the appearance of bands at 2009 and 2216 cm⁻¹ even immediately after the condensation (Fig. 2a). With increase in the temperature to 200 K, the intensity of these bands increases, while the intensity of the bands of mono- and dicarbonyl complexes decreases (Fig. 2b).

*The determination of the real $CO:CH_3NC$ content on the support is impossible because of the volatility of CO. Therefore the $CO:CH_3NC$ ratio that was used was not stoichiometric, but with a considerable excess of CO.



Fig. 3. Resonance Raman spectra of FeTPP at 80 K with a $CH_3NC:CO$ mixture (a) and with CO (b); $\lambda_{exc} = 441.6$ nm.

Prolonged evacuation under high vacuum at 200 K completely decomposes the mono- and dicarbonyl comlexes and removes a free isonitrile from the support (a $v_{\rm NC}$ band at 2169 cm⁻¹ and a $v_{\rm N^{13}C}$ band at 2132 cm⁻¹). Thus, in the region of 1800-2300 cm⁻¹, bands at 2009 and 2216 cm⁻¹, correlated with respect to the intensity, remain in the spectrum, as well as a band at 2171 cm⁻¹ of the FeTPP•(CHCH₃)₂ complex. Evacuation at room temperature leads to a decomposition of the complex characterized by bands at 2009 and 2216 cm⁻¹ and further increase in the amount of FeTPP(CNCH₃)₂.

Analysis of the above results totally substantiates the assignment of the bands at 2009 and 2216 cm⁻¹ to the v_{CO} and v_{NC} of the coordinated carbonyl and isonitrile ligands in the mixed carbonyl-isonitrile complex of FeTPP (see scheme below).



An additional coordination of the carbonyl and isonitrile ligands also influences the vibrational spectrum of the porphyrin macroring, which is strongly manifested in the resonance Raman spectra (Fig. 3). This is seen, in particular, in the shift of the structure-sensitive bands in the 390, 1370, and 1560 cm⁻¹ regions discovered in [2]. An analysis of the behavior of these bands, depending on the π -acceptor strength of the axial ligands is given below. Comparison of the frequency shifts: Δv_{CO} and Δv_{NC} during the coordination of the carbonyl and isonitrile ligands with FeTPP indicates that the π -acceptor properties of the former are TABLE 1. Frequencies of Structure-Sensitive Bands in the Resonance Raman Spectra of FeTPP Extracomplexes with π -Acceptor Ligands (T = 80 K)

Assignment	Extracomplexes			
	FeTPP-CO	FeTPP(CNCH ₃) ₂	CO.FeTPP.CNCH ₃	FeTPP(CO) ₂
Deformation of perphyrin	380	387	389	does not split
v_{C_aN} $v_{C_bC_b}$	1352 1546	1362 1561	1368 1563	1370 1570

stronger. Thus, the coordination of CO is accompanied by a low-frequency shift of v_{CO} by 184 cm⁻¹ (in the free CO, $v_{CO} = 2144$ cm⁻¹) in the case of FeTPP·CO and 114 cm⁻¹ in the case of FeTPP(CO)₂. In the monocomplex of monoisonitrile, which we have obtained previously in [6], the Δv_{NC} is 15 cm⁻¹, while in the dicomplex, the v_{NC} is even higher by 2 cm⁻¹ than the v_{NC} of the free ligand.

A further confirmation of the stronger π -acceptor properties of the carbonyl ligand is to be found in the vibrational spectrum of the mixed carbonyl-isonitrile complex. Addition in the trans position to the monocarbonyl complex FeTPP·CO ($\nu_{CO} = 1960 \text{ cm}^{-1}$) of the second ligand (see the scheme above) having π -acceptor properties, should clearly lead to a decrease in the reversed supply of the d_{xZ}-, d_{yZ}-electrons to the π *-orbitals of CO and increase in the ν_{CO} frequency. When the second ligand is also CO [in FeTPP(CO)₂] the increase in the frequency is 70 cm⁻¹. In the case of a mixed complex, this increase is lower and amounts to 49 cm⁻¹, i.e., the isonitrile group competes for the capture of the d_{xZ}-, d_{yZ}-electrons to a smaller extent than the carbonyl group.

When CH_3NC is the only axial ligand, as happens in the case of the monoisonitrile complex FeTPP·CNCH₃, it participates in the π -acceptor component of the bond and the ν_{NC} decreases by 15 cm⁻¹. Introduction of a strong acceptor, such as is the CO group, sharply decreases the reversed supply of electrons to the π^* -orbitals of isonitrile, and the binding of the isonitrile ligand is realized mainly due to the σ -donor component of the bond, which leads to an increase in the ν_{NC} frequency to 2216 cm⁻¹. In the previously obtained mixed isonitrile-oxygen complex $O_2 \cdot FeTPP \cdot CNCH_3$, the ν_{NC} was located still higher at 2233 cm⁻¹ [6], which indicates stronger π -acceptor properties of the molecular oxygen with respect to CO. The authors of [14] came to the same conclusion on the basis of the examination of the resonance Raman spectra of the carbonyl and oxygen complexes of ferroporphyrins with additional coordinated nitrogen-containing ligands.

We shall now deal with the question of the influence of the π -acceptor strength of additional ligands on the frequencies of structure-sensitive bands in the resonance Raman spectra. From the data obtained it could be assumed that in the series of the extra complexes I-IV, the overall transfer of electron density from the totally filled d_{XZ} - and d_{YZ} -orbitals of Fe(II) (according to the literature [4] and our [6] data, in complexes I-IV Fe(II) exists in a low-spin state and the d_{XZ} - and d_{YZ} -orbitals are filled with 4 electrons) to the π^{*} orbitals of the ligands should increase in the series FeTPP·CO < FeTPP·(CNCH₃)₂ < CO·FeTPP· CNCH₃ < FeTPP(CO)₂. In the above-noted series, we can question only the disposition of the members I and II of the series, since we cannot exclude the possibility that one strong π acceptor ligand (CO) could draw off to itself a higher electron density than two weak (CH₃NC) groups. The validity of the above series is confirmed by the resonance Raman spectral data (Table 1).

According to quantum-chemical calculations [15], the d_{XZ} - and d_{YZ} -orbitals of Fe(II) interact with a lower vacant π -orbital of porphyrin, which belongs to the eg symmetry type and has an anti-bonding character in the region of the C_aN and C_bC_b bonds. In [16], the bands in the 1370 and 1560 cm⁻¹ region were assigned to the vC_aN and v_{Cb}C_b vibrations, respectively. Since in the extra complex, both the degenerated eg-orbitals of porphyrin and the π^* -orbitals of the axial ligands compete for possession of d_{XZ}- and d_{YZ}-electrons, the increase in the π -acceptor bonding with the porphyrin should lead to a decrease in the population of eg-orbitals of the porphyrin, and correspondingly to an increase in the frequencies of the stretching vibrations of the above bonds. The data in Table 1 show that the expected regularity in fact does take place, and, in particular, in the same sequence according to which the series of compounds I-IV have been placed.

Thus, in the present work a mixed isonitrile-carbonyl complex III was obtained for the first time and spectrally characterized. The changes in the vibration frequencies of the

axial ligands during the coordination, and also of the frequencies of structure-sensitive bands of porphyrin in the resonance Raman spectra are in good agreement with those predicted by theory.

LITERATURE CITED

- 1. R. P. Evstigneeva, Porphyrins: Structure, Properties, Synthesis [in Russian], Moscow (1985), pp. 147-174.
- 2. J. M. Burke, J. R. Kincaid, S. Peters, et al., J. Am. Chem. Soc., <u>100</u>, No. 19, 6083-6088 (1978).
- 3. T. G. Spiro and J. M. Burke, J. Am. Chem. Soc., <u>98</u>, No. 18, 5482-5489 (1976).
- 4. B. B. Wayland, L. F. Mehne, and J. Swartz, J. Am. Chem. Soc., <u>100</u>, No. 8, 2379-2383 (1978).
- 5. T. S. Kurtikyan, A. V. Gasparyan, M. E. Akopyan, G. A. Zhamkochyan, et al., 5th All-Union Conference on Coordination and Physical Chemistry of Porphyrins. Summaries of Lectures [in Russian], Ivanovo (1988), p. 62.
- T. S. Kurtikyan, G. G. Martirosyan, A. V. Gasparyan, et al., Zh. Prikl. Spektrosk., <u>53</u>, No. 1, 67-75 (1990).
- 7. T. G. Traylor and D. V. Stynes, J. Am. Chem. Soc., <u>102</u>, No. 18, 5938-5939 (1980).
- 8. T. S. Kurtikyan, A. V. Gasparyan, G. G. Martirosyan, and G. A. Zhamkochyan, Zh. Prikl. Spektrosk., <u>52</u>, No. 1, 106-112 (1990).
- 9. L. P. Yur'eva, Methods of Heteroorganic Chemistry [in Russian], Moscow (1975), p. 162.
- 10. K. S. Krasnov, Molecules and Chemical Bond [in Russian], Moscow (1977), p. 245.
- 11. A. C. Saparu and A. F. Fenske, Inorg. Chem., <u>11</u>, No. 12, 3021-3025 (1972).
- 12. M. Kozuka and K. Nakamoto, J. Am. Chem. Soc., <u>103</u>, No. 9, 2162-2168 (1981).
- 13. T. S. Kurtikyan, Candidate of Chemical Sciences Dissertation, Moscow (1978).
- 14. L. Rimai, I. T. Salmeen, and D. H. Petering, Biochemistry, <u>14</u>, No. 2, 378-379 (1975).
- 15. T. Kitagawa, Y. Kyogoku, and T. Suzuki, J. Am. Chem. Soc., <u>98</u>, No. 17, 5169-5173 (1976).
- 16. J. M. Burke, J. R. Kincaid, and T. G. Spiro, J. Am. Chem. Soc., <u>100</u>, No. 19, 6077-6083 (1978).

COLLISION INDUCED SPECTRA OF MIXTURES OF CADMIUM VAPOR WITH INERT GASES NEAR THE $Cd(5^{3}P_{2} \rightarrow 4^{1}S_{0})$ FORBIDDEN LINE AND QUENCHING OF THE $Cd(5^{3}P_{2})$ METASTABLE STATE

A. L. Zagrebin and M. G. Lednev

UDC 539.185.3

In recent years interest has grown in the study of collision induced radiation and absorption near forbidden lines of second group metal vapors in inert gases in connection with the construction of high pressure gas lasers. By now, experimental emission and absorption spectra near the forbidden lines of the atomic transitions

$$Ca(4^{1}S_{0} - 3^{1}D_{2})[1, 2], Ca(4^{1}S_{0} - 5^{1}S_{0})[3], Mg(3^{1}S_{0} - 4^{1}S_{0})[4]$$

 $Hg(6^{1}S_{0} \rightarrow 6^{3}P_{2})$ [5] have been obtained. A theoretical analysis has been carried out for the $Mg(3^{1}S_{0} \rightarrow 4^{1}S_{0})$ [6] and $Hg(6^{1}S_{0} \rightarrow 6^{3}P_{2})$ [7, 8] transitions. Along with fluorescence of plasmas near forbidden atomic lines, collision induced radiative decay processes are also one of the possible reasons for the destruction of metastable states for thermal (T ≤ 1000 K) atomic collisions in a plasma [9-13]. Such processes are characterized by small cross sections ($\sigma \leq 10^{-20}$ cm²), nonetheless it is namely radiative transitions which determine the destruction of metastable states for the case when inelastic processes are adiabatically improbable, and the energy of the colliding particles is insufficient to ionize them (see, for example, [9-13]).

In this paper, the temperature dependence of the cross section $\langle \sigma_{rad}(T) \rangle$ for radiative quenching of the metastable state averaged over a Maxwellian distribution,

Leningrad Institute of Precision Mechanics and Optics, Leningrad. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 53, No. 3, pp. 426-432, September, 1990. Original article submitted October 18, 1989.

954