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Note

High-pressure infrared spectroscopic study of the nitric oxide complex of iron(II)-*meso*-tetraphenyl porphyrinate

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Dedicated to Brian James on the occasion of his 70th birthday.

Abstract

The infrared spectrum of iron(II)-*meso*-tetraphenylporphyrinate (FeTPP(NO)) has been measured as a function of pressure up to 3.1 GPa. The N–O stretching frequency decreases with increasing pressure, as expected for the bonding model for nitric oxide bound to iron in porphyrin complexes. Other peaks in the spectrum show positive pressure dependence.

Keywords: Iron porphyrinate; High-pressure; Infrared; N–O stretch

1. Introduction

There are many surprising relationships between iron proteins and nitric oxide. For example, heme proteins are involved in the biosynthesis (the NOS isoforms) and the biosensing (soluble Guanylate Cyclase) of physiological levels of nitric oxide. Although many metalloprophyrins bind NO, few have either the affinity or redox ambiguity that the iron porphyrins have. In the highest affinity redox combination, often described as a ferrous form [1], $\{FeNO\}^7$ [2], the NO binds in a bent fashion with the NO adopting an unusual tilted off axis geometry [3,4]. In the one electron oxidized ensemble, a ferric or $\{FeNO\}^6$ form, the NO is linear and much more labile [5]. Although many model systems have been structurally [6] and spectroscopically characterized [7], the fundamental problem of how sGC is able to reversibly bind NO remains unanswered. How is sGC able to distinguish between NO and O_2? How does it lose NO to regenerate the NO responsive enzyme? With regard to these problems, it is notable that the recent structure of the heme binding domain of sGC contains a highly distorted heme [8], and this has attendant affects on NO selectivity and affinity. In prior model system studies, we found, NO substitution kinetics can vary over six orders of magnitude with porphyrin ring distortion being an important factor leading to NO lability and facile substitution kinetics [9]. Porphyrin ring distortion has both steric and electronic consequences and these remain the key aspects of our research program.

Bonding models proposed to explain nitrosyl bending and tilting [10,11] involve a rotation of the iron d_{z^2} orbital with respect to the porphyrin plane in order to increase the overlap between this orbital and the NO π^* orbital. The N–O stretching frequency has a well-defined infrared absorption that is sensitive to the local environment and the stretching frequency decreases as the Fe–N–O angle increases [12,13]. This is consistent with a weakening of the N–O bond with the donation of electron density into the anti-bonding orbital. The application of high external pressure can induce changes in bond lengths and angles and it is anticipated that an increase in applied pressure will lead to a shortening of the Fe–N(O) bond and/or changes in the tilt angle and Fe–N–O bond angle, leading to increased donation into the NO antibonding orbital thus

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weakening the N–O bond and leading to a negative dependence of the vibrational frequency with pressure. Normally, vibrational frequencies increase with an increase in applied pressure but in some unusual bonding situations, such as the dπ–pπ backbonding in Zeise's salt [14] and the "dihydrogen bond" in the ammonia–borane complex [15], the frequencies decrease.

We have examined the effect of high applied pressure on the infrared spectrum of the nitrosyl complex of iron(II)-*meso*-tetraphenylporphyrinate (FeTPP(NO)), which has been a well-studied model compound, to provide spectroscopic evidence of the bonding model to complement the structural arguments. The crystal structure of FeTPP(NO) consists of statistically disordered chains of molecules arranged along a crystallographic fourfold axis, with the NO groups disordered over eight positions [16]. Vibrations below 600 cm^{-1}, i.e., those involving motions of the iron atom, have been reported by Sage and co-workers [17] and several modes at 56 cm^{-1} and below have been assigned to torsional motions involving the nitrosyl group. Thus the barrier to reorientation is low and the disorder may be dynamic, as is the case for the cobalt complex [18].

2. Experimental

The *meso*-porphyrin was prepared according to the method developed by Adler [19] and used without further purification in the metallation reaction [20]. The nitrosyl iron porphyrin was synthesized by literature methods [9], which briefly involves dissolving 0.2 g of the Fe(TPP)Cl compound in 30 mL of dichloromethane in a Fisher-Porter bottle with 10 drops each of 2,6-lutidine and methanol to catalyze the oxidation and the reaction vessel was pressurized with 30 psi of nitric oxide gas overnight. After purging the reaction vessel with nitrogen, the product was precipitated from the solution by the addition of methanol and dissolved in chloroform and recrystallized from hexanes. The purity of the product was verified by TLC, IR, and UV–Vis spectroscopy.

High-pressure studies were performed with the use of a diamond anvil cell purchased from High Pressure Diamond Optics Inc., Tucson, Arizona, with type IIA diamonds. Samples were contained in 200 μm thick stainless-steel gaskets. IR spectra were recorded on a Bruker IFS48 FT spectrometer equipped with a Bruker A-590 infrared microscope (objective 15×) and a liquid nitrogen cooled MCT detector. The spectra were collected at 4 cm^{-1} resolution and 100 scans. The pressures were measured using the shift of the anti-symmetric N–O stretching mode of sodium nitrite in a sodium bromide matrix [21] included with the sample.

3. Results and discussion

The pressure dependence of the N–O stretching frequency is shown in Fig. 1. At about 1.5 GPa, a shoulder appeared on the low wavenumber side and the separation increased with increasing pressure, Fig. 2. The pressure dependence for both peaks is negative, in agreement with the proposed the bonding model. The low barrier to torsional motion of the nitroxyl group should be increased as the interatomic distances are decreased with increasing pressure, which could explain the appearance of a second N–O stretching vibration if a different local environment occurs. The appearance of a second N–O stretching vibration is also consistent with the results of a Mössbauer study [22] of Fe(TPP)NO, which showed a quadrupole doublet with significant broadening of the lower-velocity line. This was attributed to the disorder.

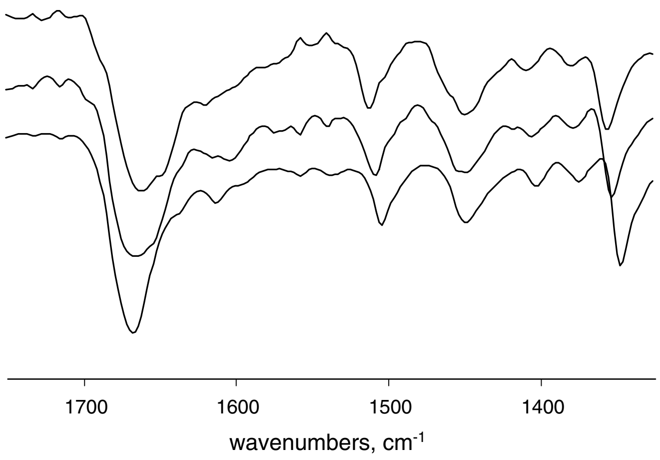

Fig. 1. FT-IR spectra at different pressures. Upper 0.33 GPa, middle 1.53 Gpa, lower 2.96 GPa.

Fig. 2 and Table 1 show the pressure dependences of other strong peaks in the spectrum. Certain peaks in the vibrational spectra of metal–porphyrin compounds have been identified as indicators of spin state and oxidation state [23,24]. These structure-sensitive peaks include the

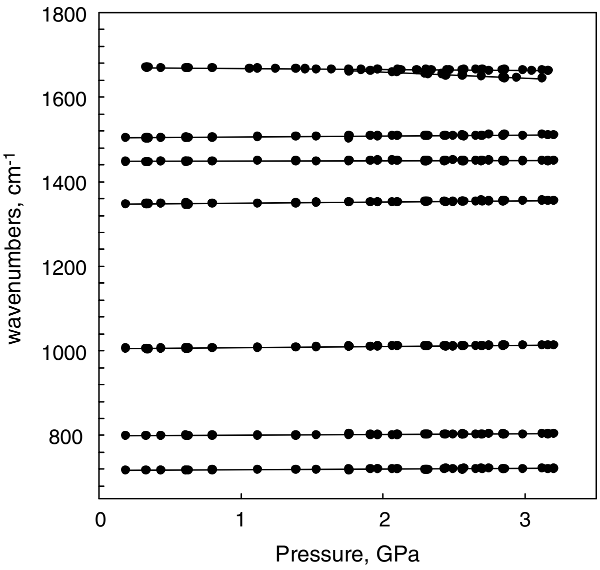

Fig. 2. Pressure dependence of vibrations of FeTPP(NO).

Table 1
Pressure dependence of vibrational frequencies

Frequency (cm^{-1})	dv/dP (cm^{-1} GPa^{-1})
717	1.50
799	1.56
1004	2.98
1346	2.82
1447	0.88
1508	2.49
1670	−2.36
1687[a]	−13.9[b]

[a] Extrapolated to 0 GPa.

[b] Above 1.5 Gpa.

porphyrin core mode at 1351 cm^{-1}, a ring deformation mode mixed with C_β-H in-plane bending at 800 cm^{-1} and a pyrrole ring breathing mode at 1004 cm^{-1}. These peaks showed no breaks or changes in slope over the same pressure range and, therefore, the splitting of the NO stretching vibration is not the result of any change in structure or a solid state phase transition. The peak at 1447 cm^{-1}, assigned as the C_α–C_m stretching vibration, has a much lower pressure dependence than the other vibrations. A high pressure X-ray crystallographic study of cobalt(II)tetraphenylporphyrinate revealed a phase transition from a tetragonal to triclinic structure at 0.49 GPa [25]. This study also included infrared spectroscopic results, which showed pressure dependences similar to those reported here.

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