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Low temperature NO disproportionation by Mn porphyrin. Spectroscopic characterization of the unstable nitrosyl nitrito complex Mn^{III}(TPP)(NO)(ONO)

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Reaction of NO gas with sublimed layers of the Mn^{II}TPP (TPP = *meso*-tetraphenylporphyrinato^{2-}) at low temperature leads to nitric oxide disproportionation. UV-Vis and FTIR spectroscopy with isotopically substituted nitrogen oxides revealed formation of the unstable species identified as *trans*-Mn^{III}(TPP)(NO)(ONO).

The discovery that nitric oxide plays key roles in mammalian biology has stimulated renewed interest in chemistry of the reactions of NO with transition metal ions, especially with models of metalloproteins.[1] The ability of certain transition metal complexes to promote NO disproportionation to form N_2O and metal-nitrite have long been known.[2] However among the various metalloporphyrin nitrosyls studied, only ruthenium and osmium porphyrins revealed further reactivity with excess NO. These complexes disproportionate NO to form nitrous oxide and relatively stable at room temperature nitrosyl-nitrito species M(P)(NO)(ONO) (P = various porphyrinato dianions).[3] On the other hand, to our knowledge only one manganese compound has been reported to facilitate NO disproportionation.[4] Here we give evidence for nitric oxide disproportionation mediated by sublimed layers of Mn(TPP) at low temperature. We also report the first IR and UV-vis characterization of the unstable manganese nitrosyl nitrito complex Mn(TPP)(NO)(ONO).

Low temperature sublimed layers of Mn^{II}(TPP) on the KBr or CaF_2 plates were obtained from the parent compound Mn^{II} (TPP)(B) (B = piperidine or pyridine) as described previously.[5a] Thin layers of the metallo-tetraarylporphyrins sublimed onto a low-temperature (77 K) surface are sponge-like[6a] and have high microporosity that allows potential ligands to diffuse easily across the bulk.[6b] The species thus formed are convenient for spectroscopic studies due to absence of solvent interference.

Exposure of sublimed layers of Mn^{II} (TPP) at 77 K to an excess of clean[7] NO displays formation of the NO dimer with strong IR bands at 1853 and 1754 cm^{-1} and known mononitrosyl complex Mn(TPP)(NO)[8a] with ν(NO) at ~1740 cm^{-1}, overlapping with the asymmetric NO dimer stretch.[9] Gradually warming the sample and keeping the temperature constant at 130 K leads to dramatic changes in the IR spectra. Concomitant with decreased intensity of the bands for the NO dimer and Mn(TPP)(NO), new bands correlated in intensities grew in at 2221 (not shown), 1818, 1480, 971 and 822 cm^{-1} (Fig. 1). The band centered at 2221 cm^{-1} undoubtedly represents the ν_3 vibration of N_2O,[10] while the band at 1818 cm^{-1}, which shifts to 1812 cm^{-1} as it reaches maximum intensity was assigned to the ν(NO) of a Mn^{III}(TPP)(NO)(X) complex (**1**), where X is an anion. This assignment is consistent with the literature data on the spectroscopic manifestation of the 6-coordinate manganese nitrosyl complexes with anionic ligands.[8a] When Mn^{II}(TPP) was exposed to excess of ^{15}NO the analogous bands appeared at lower frequencies: 2152, 1778, 1455, 950 and 818 cm^{-1}. These shifts indicate that all new bands are due to nitrogen oxides and suggest that X is coordinated NO_2 anion.

Infrared spectroscopy is very diagnostic in differentiating between N-bound nitro or O-bound nitrito NO_2^- coordination.[11a] Indeed, for the nitrosyl nitro complex FeTPP(NO)(NO_2) the asymmetric and symmetric modes of coordinated NO_2 are located[12,5a] in vicinity of 1440 and 1300 cm^{-1}, much closer to each other than in Mn(TPP)(NO)(X). On the other hand Ru(TPP)(NO)(ONO), for which X-ray structure revealed nitrito coordination,[5b] shows IR bands at 1522 and 930 cm^{-1}. The Ru(TPP)(NO)(ONO) complex obtained in sublimed layers[13] demonstrates IR bands at 1844, 1516 and 928 cm^{-1}, which were shifted to 1810, 1492 and 908 cm^{-1} respectively upon ^{15}NO substitution.[5a] Notably, the latter isotopic shifts are exactly the same as for complex (**1**). Thus, the literature data and spectroscopic results lead to the conclusion that NO has dispropotionated to give N_2O[14] and a compound we have formulated as *trans*-coordinated Mn(TPP)(NO)(ONO) (Scheme 1). In this interpretation the band at 1812 cm^{-1} corresponds to the $\nu(N\equiv O)$ stretch of the linear nitrosyl and three latter bands belongs to the O-bonded nitrite group. Indeed, the $\nu(N\equiv O)$ band lies within the conventional region reported for linear metal-NO porphyrin complexes with axially coordinated anions.[11b] The bands at 1480, 971 and 822 cm^{-1} are also consistent with ranges reported[3,11] for nitrito coordinated ONO^- and should be assigned to ν(N=O), ν(N–O) and δ(ONO) modes.

The evidence of the formation of (**1**) upon reaction the low-temperature layers of MnTPP(NO) with excess NO was also

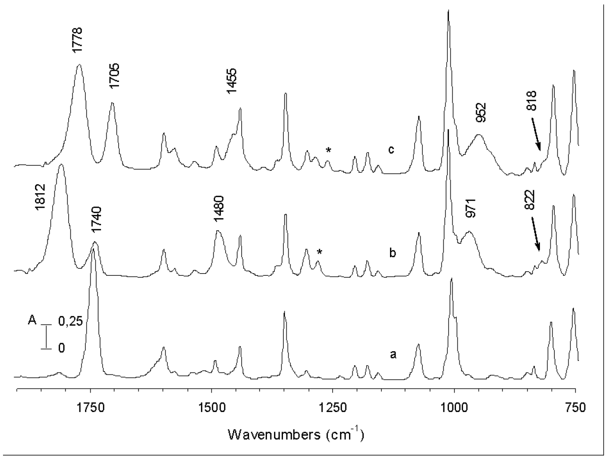
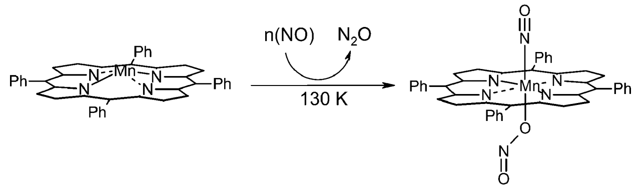


Fig. 1 IR spectra at 77 K: (a) Mn(TPP)(NO) formed by exposure of Mn(TPP) to NO (P = 5 Torr) for 10 min at 100 K followed by exhaustive high vacuum pumping, (b) Mn(TPP)(NO)(ONO) formed by exposure of Mn(TPP) to NO (*ca. P* = 15 Torr) at 77 K followed by annealing 130 K, (c) the same with ^{15}NO. ν_1 vibration of N_2O denoted by asterisk.[10]



Scheme 1

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supported by changes in the UV-Vis spectra (Fig. 2). Formation of the nitrosyl and nitrosyl-nitrito complexes was first monitored by FTIR spectroscopy (using CaF_2 plates), and then absorption spectra of the same samples cooled to 77 K were recorded. The spectrum of Mn(TPP)(NO) displays absorption bands at 539, 573 and 612 nm while that of (**1**) shows strong absorbance at 546 nm and shoulders at 578 and 618 nm. Although the absorption in this region cannot be measured with precision due to contribution of Mn(TPP)(NO) (seen in IR spectra), the strong band at 476 nm is characteristic for all Mn^{III}(TPP) nitrosyl complexes.[8a,c] The same oxidation state may be suggested for manganese ion in (**1**). The low-temperature spectra of Mn^{II}(TPP) and Mn(TPP)(NO) are in good agreement with those observed earlier in frozen solutions.[8a,b] However, NO disproportionation was not detected in those studies, possibly because excess NO was expelled before solution cooling. In the present case maintaining the Mn(TPP)(NO) under excess NO at 77 K for a lengthy period does not lead to any changes in optical or FTIR spectra. Only when the sample was warmed above 100 K were reactions leading to Mn(TPP)(NO)(ONO) observed.

It has been established that positions of the some porphyrin vibrations in the axial complexes of Fe(TPP) can serve as a markers of the spin and oxidation states of iron center.[15] The bands in the range 1350–1330 cm^{-1}, which belong to $\nu(C_a–C_m)$ mixed with $\nu(C_m$–phenyl), and porphyrin core deformation mode at 469–432 cm^{-1} lies at higher wavelengths in low-spin complexes. We have reported similar behavior of these bands in our studies of dioxygen and nitrate complexes of Mn(TPP).[16] Indeed, in Mn^{II}(TPP) these bands lie at 1343 and 428 cm^{-1}. Formation of Mn(TPP)(NO) complex leads to a high to low spin state transition[8a] as indicated by shifts of these bands to 1349 and 454 cm^{-1}, respectively. Upon generation of (**1**) there is no further shift of these bands, indicating that the Mn center remains in the low spin state. This suggestion is in agreement with literature data on the spin states of the 6-coordinated manganese nitrosyl porphyrins complexes with anionic ligands.[8a]

In summary, exposure of the low temperature sublimed layers of Mn^{II}(TPP) to excess nitric oxide leads to disproportionation of NO yielding a new Mn^{III}(TPP)(NO)(ONO) species and releasing nitrous oxide gas. Formation of the six-coordinate complex (**1**) is supported by FTIR and UV-Vis spectroscopy and low-spin state of the manganese ion is suggested. The characterized nitrosyl-nitrito complex is stable at low temperature conditions. Exhaustive evacuation of nitric oxide at 130 K does not affect the relative intensities and positions of the NO and NO_2 bands, but warming to room temperature leads to decomposition of (**1**). Under the same experimental conditions we have measured FTIR spectra of the Fe, Co, Cu, Ni and Zn TPP complexes upon exposure to excess NO. Except for formation of the known mononitrosyls of Fe and Co TPP, none of these compounds revealed further reactivity toward nitric oxide disproportionation.

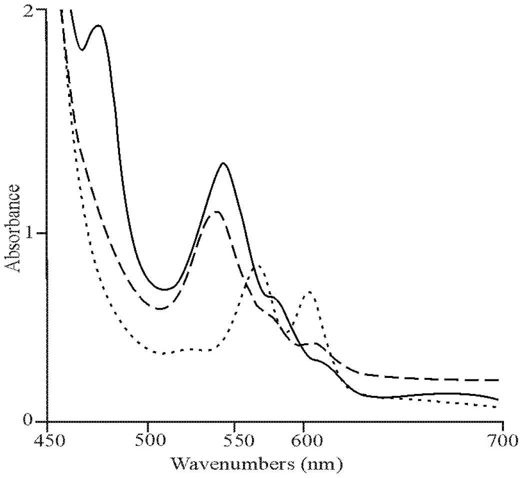

Fig. 2 Optical absorption spectra at 77 K: dotted line – Mn^{II}(TPP), dashed line – MnTPP(NO) formed by exposure of Mn^{II}TPP to the excess of nitric oxide (P = 10 Torr) at 100 K, solid line – subsequent slow warming of the MnTPP(NO) to 130 K.

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