Photo-induced metastable linkage isomers of ruthenium nitrosyl porphyrins

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IR spectroscopic results, combined with earlier crystallographic and spectroscopic evidence on Fe and Ru nitrosyl complexes, indicate that metastable η^1-O and η^2-NO linkage isomers are formed on low-temperature irradiation of the nitrosyl metalloporphyrins (OEP)Ru(NO)L (L = O-i-C_5H_{11}, SCH_2CF_3); the new compounds are stable at low temperature, but revert to the ground state on warming.

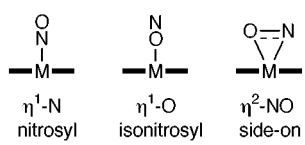
Nitric oxide (NO) plays a crucial role in several biologically important processes such as intercellular signal transduction, blood pressure regulation, and cytotoxic activity of immune systems.[1] NO is synthesized *in vivo* by the enzyme NO synthase, which contains a (por)Fe(SR) heme active site.[2] NO is now known to be produced by several heme-containing denitrifying enzymes.[3] One of the major biological functions of NO is to bind to the metal center of heme-containing soluble guanylyl cyclase, resulting in activation of the enzyme.[4] NO is also known to bind to other heme-containing biomolecules such as cytochrome P450, Hb, Mb, cytochrome *c* oxidase, and heme-containing nitrite reductases.[5]

The photochemistry of nitrosyl metalloporphyrins and -hemes reveal photodenitrosylation (A) and recombination (B) processes [eqn. (1)][6–8] that are probably governed by factors

$$\text{(por)M(NO)} \underset{\text{B}}{\overset{\text{A}}{\rightleftharpoons}} \text{(por)M} + \text{NO} \qquad (1)$$

that include metal oxidation state and the identity and orientation of the *trans* (proximal) ligand. Distal pocket residues also play a role in the geminate recombination of NO in heme proteins.[10] The results of kinetic studies of photochemically induced loss and recombination of NO with hemoproteins[9,10] and metalloporphyrins[11,12] suggest that recombination is a fast and multistage process at room temperature. Clearly, the mechanisms of NO approach, release and subsequent binding to heme and heme models require further investigation.

Until recently, established or proposed descriptions of NO binding to the metal center in heme or heme models have been restricted to N-binding of the NO group to the metal in either linear or bent forms. We have reported novel X-ray crystal structures of coordination and organometallic compounds with photoinduced O-bound (η^1-O) and side-on (η^2-NO) bound nitrosyl groups.[13–15]



These compounds were of the {MNO}^{6} and {MNO}^{10} formulations.[16] We were thus interested in determining if such linkage isomers could exist for group 8 {MNO}^{6} nitrosyl metalloporphyrins of the form (por)M(NO)X with X *trans* to NO. Here, we report the first spectroscopic detection of η^1-O and η^2-NO linkage isomers of nitrosyl metalloporphyrins.

Irradiation of (OEP)Ru(NO)L [L=O-i-C_5H_{11} **1**,† SCH_2CF_3 **2**;†[17] KBr pellets; 330 < λ < 460 nm; Xe lamp][18] at 20 K for 15 min results in IR spectral changes that are attributed to the formation of metastable states possessing η^1-O and η^2-NO linkage isomers (Table 1). For example, irradiation of the alkoxide compound **1** (υ_{NO} 1791 cm^{-1}) results in a reduction of intensity of the original υ_{NO} band, and the appearance of new bands at 1645 and 1497 cm^{-1}. Difference spectra from the samples before and after 15 min of photolysis are shown in Fig. 1(a). Upon ^{15}N labeling, these 1791 and 1645 cm^{-1} bands are downshifted by 36 cm^{-1} (expected shift of 34 cm^{-1} based on simple two-body model), whereas the 1497 cm^{-1} band is downshifted by 17 cm^{-1}. Similar results are observed during photolysis of the thiolate compound **2** [Fig. 1(b) and Table 1].

The following observations support the assignment of the new bands as being due to photoinduced η^1-O and η^2-NO linkage isomers at 20 K, respectively.

(i) Photolysis does not produce free NO which has an absorption band at 1880 cm^{-1}.[19]

(ii) The intensities of the parent nitrosyl bands were restored after the photolysis had ceased and the samples were warmed to room temperature and cooled back to 20 K. Thus, the light-induced reaction is thermally reversible, indicating the formation of a metastable species. For compound **1**, the new band at 1645 cm^{-1} can be seen only below 160 K, while the second new band at 1497 cm^{-1} can be generated only below 80 K. For compound **2**, the new bands are generated simultaneously upon irradiation at temperatures below 60 K. In all cases the photo-induced bands persist for at least several hours if the initial temperature is maintained.

(iii) Both new bands are subject to the ^{15}N-isotope shift, and thus associated with υ_{NO} (Table 1). Thus, the isotope shifts of the η^1-O υ_{NO} bands are 36 and 27 cm^{-1} for photoexcited **1** and **2**, respectively. The isotope shifts of the η^2-NO υ_{NO} bands are 17 and 19 cm^{-1}. Similar υ_{NO} downshifts of 19 and 14 cm^{-1} upon ^{15}N labeling were recently reported for Cr(η^2-NO)[20] and V(η^2-NO),[21] respectively, generated in an Ar matrix .

Table 1 Wavenumbers (cm^{-1}) and shifts of IR absorption bands of nitrosyl and light-induced isomers with iso- and side-on bound nitrosyl of complexes **1** and **2**

	υ(RuN–O)	υ(RuO–N)	υ[Ru(η^2-NO)]
(OEP)Ru(NO)(O-i-C_5H_{11})			
^{14}N	1791	1645 (−146)	1497 (−294)
^{15}N	1755	1609 (−146)	1480 (−275)
$\upsilon(^{14}N) - \upsilon(^{15}N)$	36	36	17
(OEP)Ru(NO)(SCH_2CF_3)			
^{14}N	1788	1660 (−128)	1546 (−242)
^{15}N	1753	1633 (−120)	1527 (−226)
$\upsilon(^{14}N) - \upsilon(^{15}N)$	35	27	19

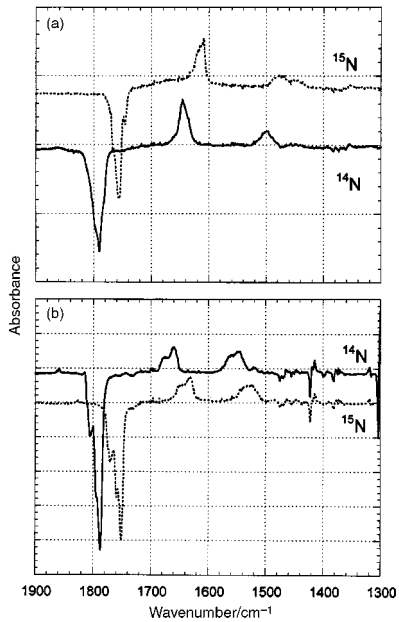


Fig. 1 Difference spectra (spectrum after irradiation minus spectrum prior to irradiation for 15 min) for the ^{14}N and ^{15}N labeled compounds (a) (OEP)Ru(NO)(O-i-C_5H_{11}) and (b) (OEP)Ru(NO)(SCH_2CF_3). The bimodal structure of some of the shifted bands is attributed to crystalline disorder and two possible orientations of the NO group. Conversion percentages are estimated as 1 and 1.5% for (a) and (b), respectively.

(iv) The observed decreases in υ_{NO} upon conversion from nitrosyl to isonitrosyl (η^1-O) and to side-on (η^2-NO) bound nitrosyl (Table 1) are very similar to those recorded for other excited Fe, Ru, Os and Ni nitrosyl complexes.[14,15,22–27] DFT calculations on the nitrosyl linkage isomers in $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$[28] predict related downshifts of υ_{NO} by 108 and 320 cm^{-1} for the η^1-O and η^2-NO isomers, respectively.

(v) Downshifts in a number of porphyrin skeletal modes (in the region 1600–900 cm^{-1})[31,32] by 3–5 cm^{-1} upon photolysis are also consistent with the data available for six-coordinate Fe(II) porphyrins which indicate that the reduction of π-acid character of the axial ligand causes downshifts of the skeletal absorption bands.[33]

Finally, we report that we have observed similar linkage isomers in two other complexes (OEP)Ru(NO)(Cl) **3** and [(OEP)Ru(NO)(py)]$^+$ **4**, thus expanding the range of compounds to include those having O-, S-, halide- and N-donors *trans* to NO.

In summary, we conclude that the low-temperature IR spectroscopic evidence presented here indicates that η^1-O and η^2-NO linkage isomers are achievable metastable states in nitrosyl metalloporphyrins.

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Notes and references

† OEP = octaethylporphyrinato dianion. (OEP)Ru(NO)(O-i-C_5H_{11}) was obtained from the reaction of (OEP)Ru(CO) with isoamyl nitrite. The ^{15}NO labeled analog was prepared using ^{15}N−labeled isoamyl nitrite. *Crystallographic data* for **1**: dark−red monoclinic crystals, space group *Pn*, a = 8.329(2), b = 10.627(2), c = 22.533(5) Å, β = 91.90(2)°, V = 1993.4 Å^3, Z = 2, T = 298 K, μ = 0.568 mm^{-1}, R_1 = 0.070, wR_2 = 0.187, GOF = 1.0.

(OEP)Ru(NO)(SCH_2CF_3) was prepared as previously described, and its purity checked by IR and ^{1}H NMR spectroscopy.[17] The ^{15}NO labeled analogue was prepared in 79% yield by reacting (OEP)Ru(CO) with $^{15}NOBF_4$ and then $KSCH_2CF_3$. *Crystallographic data* for **2**: dark-violet monoclinic crystals, space group *Pn*, a = 8.418(2), b = 10.485(2), c = 22.236(4), β = 91.80(3)°, V = 1961.6 Å^3, Z = 2, T = 298 K, μ = 0.641 mm, R_1 = 0.062, wR_2 = 0.138, GOF = 1.1. CCDC 182/1396.

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