NO₂-induced synthesis of nitrato-iron(III) porphyrin with diverse coordination mode and the formation of isoporphyrin[‡]

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Abstract. Two nitrato-iron(III) porphyrinates [Fe(4-Me-TPP)(NO₃)] **1** and [Fe(4-OMe-TPP)(NO₃)] **2** are reported. Interestingly, [Fe(4-Me-TPP)(NO₃)] **1** has nitrate ion coordinated as monodentate (by single oxygen atom), while [Fe(4-OMe-TPP)(NO₃)] **2** has nitrate coordination through bidentate mode. Compound **1** was found serendipitously in the reaction of [Fe(4-Me-TPP)Cl] with nitrous acid, which was performed for the synthesis of nitro-iron(III) porphyrin, [Fe(4-Me-TPP)NO₂]. The compound **2** was synthesized by passing NO₂ gas through a solution of [Fe(4-OMe-TPP)]₂O. Upon passing NO₂ gas through a solution of a μ-oxo-dimer, [Fe(4-Me-TPP)]₂O also produces **1**. It is interesting that in more electron-rich porphyrin **2**, binding of the nitrate in a symmetrical bidentate way while in less electron-rich porphyrin **1**, binding of the anion is unidentate by a terminal oxygen atom. However, it is expected that the energy difference between the monodentate and bidentate coordination mode is very small and the interchange between these coordination is possible. Upon passing NO₂ gas through a solution of μ-oxo-dimeric iron(III) porphyrin, the nitrato-iron(III) porphyrin forms first, that later gets oxidized to π-cation radical to yield hydroxy-isoporphyrin in the presence of trace amount of water. These nitrato-iron(III) porphyrinates in moist air slowly converted back to their respective μ-oxo-dimeric iron(III) porphyrins.

Keywords. Porphyrin; nitrate; iron; nitric oxide; X-ray crystallography.

1. Introduction

Nitric oxide and its derivatives nitrite and nitrate ion play important roles in a large number of biological reactions.[1] Most importantly, nitric oxide and its derivatives interact with heme proteins. Oxygen binding globins also react with nitrosyl hydride(HNO), one electron reduced and the protonated form of nitric oxide.[2] Nitrate is produced in heme proteins from oxidation of coordinated nitric oxide of heme and from the interaction of nitric oxide with coordinated dioxygen.[3] In addition, synergistic regulation of bicarbonate and nitrate transport occurs through their binding with proteins, which is necessary for the conservation of energy during the process of carbon fixation and nitrogen assimilation.[4] Iron nitrate(III) porphyrins and corrole-iron(IV) nitrate can be photochemically cleaved into highly reactive iron(IV)-oxo porphyrin radical cation and corrole-iron(V)-oxo species which are effective catalysts for both the hydroxylation of hydrocarbons and the epoxidation of olefins.[5] Nitrate ion can bind to the metal in diverse way. Variable coordination modes of the nitrate are known in several series of compounds,[6] but only a limited number of metallo-porphyrins containing a bound nitrate ligand are known.[7] Here, we report the synthesis of two nitrato-iron(III) porphyrins, one of which is coordinated to the iron in monodentate fashion and the other with a symmetrical bidentate mode. In addition, isoporphyrin the tautomer of porphyrin, where one of the *meso*-carbons is sp³ hybridized have distinct properties from porphyrins. These are known as intermediate products in several biochemical reactions of heme proteins.[8] Isoporphyrins have attracted much interest also because of its higher absorption at lower energy region. There is also a report of iron(III) *meso*chloro-isoporphyrin as an excellent reactive agent for chlorinating aromatic compounds and olefins.[9] Woodward[10] initially postulated the existence of isoporphyrin and later Dolphin and co-workers[11] showed the generation of zinc-isoporphyrin by nucleophilic attack of methanol on electrochemically generated zinc *meso*-tetraphenylporphyrin dication, [ZnTPP]²⁺. Since then different metallo-isoporphyrins have been synthesized by photo-oxidation and chemical oxidation but they are

unstable and reverted back to their porphyrin derivatives.[12] Recently, we have reported the isolation and structurally characterization of the iron and zinc iso-porphyrins as the oxidative product of iron and zinc porphyrin using NO_2 (NO and O_2).[13] To understand more about the interaction of NO_2 (NO and O_2) with heme group and to synthesize highly oxidized iron porphyrins, we wanted to explore the reaction between NO_2 and μ-oxo-dimeric iron(III) porphyrins. Here, we have used μ-oxo-dimeric iron(III) porphyrins made from the hydrolysis of the corresponding chloro complexes, [Fe(4-Me-TPP)Cl] and [Fe(4-OMe-TPP)Cl] for such reaction because of their electron-rich properties. Upon passing NO_2 gas through a solution of μ-oxo iron(III) porphyrin dimer, first nitrato-iron(III) porphyrin is formed. On prolonged passage of NO_2, the so formed nitrato-iron(III) porphyrin gets oxidized to π-cation radical and finally converted to hydroxy-isoporphyrin similar to its chloro analogue.[13] These nitrato-isoporphyrins may be used as reactive catalyst toward hydroxylation of alkenes and aromatic hydrocarbons. The nitrato-iron(III) porphyrinates in solution, in air slowly converted back to μ-oxo-dimeric iron(III) porphyrins which can be again used to form nitrato-iron(III) porphyrins using NO_2. In addition, nitration by nitrogen dioxide on metalloporphyrins depend on the co-ordinated metal.[14]

2. Experimental

2.1 *Material and methods*

All reactions were performed under dry N_2 with standard Schlenk techniques unless otherwise noted. Solvents like acetone, dichloromethane, hexane, petroleum ether, toluene and pyrrole were obtained from S D Fine-Chem Ltd. India, purified and dried before use by standard methods. 4-Methylbenzaldehyde and 4-methoxybenzaldehyde were procured from Sigma-Aldrich and dimethylformamide (DMF) from Thomas Baker. Electronic absorption spectral measurements were carried out by Perkin Elmer (Lamda 35) spectrophotometer. Infrared spectra were recorded on a Bruker Vertex 70, FT-IR spectrophotometer as pressed KBr disks in the IR region. Elemental analysis for carbon, hydrogen and nitrogen were analysed with Perkin-Elmer 2400 microanalyser. The ESI mass spectra (positive mode) were recorded on a Waters Micromass Q TOF Premier Mass Spectrometer. The sample (dissolved in acetonitrile) was introduced into the ESI source through a syringe pump at the rate of 5 μl/min. The ESI capillary was set at 2.3 kV and voltage was 36 V. *Meso*-tetrakis(4-methylphenyl)porphyriniron(III)chloride, [Fe(4-Me-TPP)Cl] and *meso*-tetrakis(4-methoxyphenyl)porphyriniron (III)chloride, [Fe(4-Me-TPP)Cl] were prepared by an one-pot method.[15]

2.2 *Synthesis of meso-tetrakis(4-methylphenyl)-porphyriniron(III) nitrate [Fe(4-Me-TPP)(NO$_3$)] (1)*

To a solution of 100 mg (0.131 mmol) *meso*-tetrakis (4-methylphenyl)porphyriniron(III) chloride in benzene 15 mg (0.216 mmol) $NaNO_2$ and 0.1 mL glacial acetic acid was added in argon atmosphere with constant stirring. Stirring was continued for another 30 min in argon atmosphere. The mixture was layered with three times petroleum ether (60–80°C) and allowed to stay for 14 days to yield dark purple block shaped diffraction quality crystals. Yield 57 mg (50%) Molecular Formula: $C_{54}H_{42}FeN_5O_3$; molecular weight: 864.78; UV/Vis (CH_2Cl_2) $\lambda_{max}(\varepsilon/ mol^{-1}dm^3cm^{-1})$: 415 (94 234), 523 (10 069), 584 (3 509), 690 (3755); FTIR (cm^{-1}); 1523 [ν NO_3], 1384 [ν NO_3], 1270 [ν NO_3], Elemental analysis calculated (found) in % for $C_{54}H_{42}FeN_5O_3$; C, 74.99 (75.06); H, 4.89 (5.01); N, 8.09 (8.15).

2.3 *Synthesis of meso-tetrakis(4-methoxyphenyl)-porphyriniron(III) nitrate [Fe(4-OMe-TPP)(NO$_3$)] (2)*

NO_2 (NO + O_2) gas was passed to a solution 100 mg (0.062 mmol) of μ-oxo dimer, [Fe(4-OMe-TPP)]$_2$O in dichloromethane for about 30 s. The colour of the solution changed from green to dark red, hexane was added and the reaction mixture was allowed to stay for 5 days to yield dark purple block shaped diffraction quality crystals. Yield 49 mg (90%) molecular formula: $C_{48}H_{36}FeN_5O_9$; molecular weight: 882.67; UV/Vis $(CH_2Cl_2)\lambda_{max}(\varepsilon/mol^{-1}dm^3cm^{-1})$: 417 (100 334), 520 (12 465), 583 (3 009), 692 (3345); FTIR (cm^{-1}); 1528 [ν NO_3], 1260 [ν NO_3]; Elemental analysis calculated (found) in % for $C_{48}H_{36}FeN_5O_9$; C, 65.31 (65.61); H, 4.11 (4.26); N, 7.93 (7.79).

2.4 *X-ray crystallography*

The crystals used were glued to a glass fibre and mounted on BRUKER SMART APEX diffractometer. Cell constant was obtained from the least-squares refinement of three-dimensional centroids through the use of CCD recording of narrow ω rotation frames, completing almost all-reciprocal space in the stated θ range. The instrument was equipped with CCD

area detector and data were collected using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at low temperature (100 K). All empirical absorption correction was applied using the SADABS program. All data were collected with SMART 5.628 (BRUKER, 2003), and were integrated with the BRUKER SAINT program. The structure was solved using SIR97[16] and refined using SHELXL-97.[17] The space group of the compound was determined based on the lack of systematic absence and intensity statistics. Full matrix least squares/difference Fourier cycles were performed which located the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters.

3. Results and discussion

3.1 *Synthesis and characterization*

Generally, nitrato-iron(III) porphyrins are synthesized by the metathesis reaction of chloro-iron(III) porphyrin using AgNO₃. The synthesis of **2** is presented in the scheme 1. The μ-oxo dimeric iron(III) porphyrins were synthesized by passing CH₂Cl₂ solution of chloro-iron(III) porphyrins [Fe(4-Me-TPP)Cl] and [Fe(4-OMe-TPP)Cl] through a long aqueous basic alumina column[18] and their purity were checked using FTIR and electronic spectroscopy.

We have recently reported the synthesis of iron-hydroxy isoporphyrin by passing NO₂ (a mixture of NO and O₂) through a solution of an iron porphyrin. But, on passing NO₂ (a mixture of NO and O₂) through a dichloromethane solution of [Fe(4-OMeTPP)]₂O and on standing the complex crystallizes out as nitrato-iron(III) porphyrin where nitrate coordinates in a symmetric bidentate fashion. The green solution of μ-oxo-

dimeric iron(III) porphyrin converts to dark red upon passing NO₂ and its uv-visible spectrum confirmed the formation of nitrato iron(III) porphyrin. The nitrato iron(III) porphyrin can be easily precipitated out using hexane. FTIR of **2** shows the presence of $\nu(NO_3)$ at 1528 and 1260 cm^{-1} due to the coordination of nitrate in bidentate way (supplementary information figure S1).[19] The [Fe(4-MeTPP)]₂O also produces its nitrato-complex on passing with NO₂ (a mixture of NO and O₂) through a dichloromethane solution.

Compound **1** was found serendipitously in the reaction of [Fe(4-Me-TPP)Cl] with nitrous acid, which was performed for the synthesis of nitro-iron(III) porphyrin, {Fe(4-Me-TPP)NO₂}. Isolation of a pure nitro-iron(III) porphyrin has been a challenge to inorganic chemists.[20] But it is interesting that chloro-iron porphyrin reacts with nitrous acid in argon atmosphere to form an intermediate nitro-complex, which in the presence of triphenylposphine transfers one oxygen atom forming triphenylposphine oxide and yielding iron nitrosyl porphyrin Fe(4-Me-TPP)NO.[21] A varied number of nitrosyl porphyrin synthesis are known using oxygen atom transfer reaction.[22] And this reaction shows that in the absence of oxygen abstracting agent nitrite ion abstracts one oxygen atom from bound nitro-complex forming nitrosyl porphyrin and nitrate ion. Thus, the so-formed nitrosyl porphyrin reacts further with NO₂$^-$ and forms iron-nitrosyl-nitro porphyrin [Fe(4-Me-TPP)(NO)(NO₂)]$^-$, which is very unstable and the nitrate ion immediately replaces the axial ligand to form the nitrato-iron(III) complex.[20] FTIR of **1** shows the presence of $\nu(NO_3)$ at 1523, 1384 and 1270 cm^{-1} due to the coordination of nitrate in monodentate fashion (supplementary information figure S2). It is interesting that in more electron-rich porphyrin **2**, binding of the nitrate occurs in a symmetrical bidentate way while in less electron rich porphyrin **1**, binding of the anion takes place by a terminal oxygen atom.
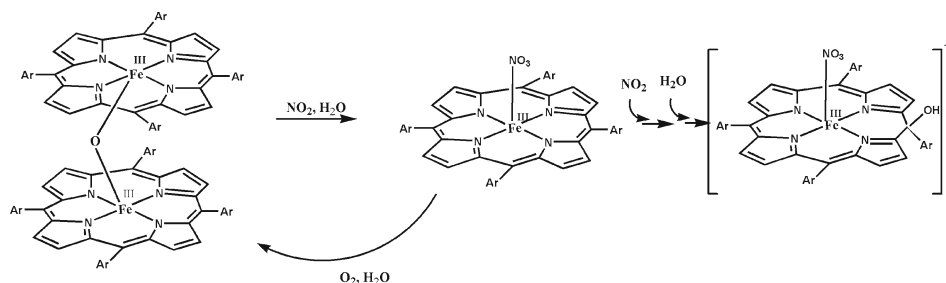

Scheme 1. Synthesis of nitrato-iron(III) porphyrin from μ-oxo-dimeric iron(III) porphyrin and the re-generation of the oxo-dimer in aerobic atmosphere in the presence of trace amount of water. If the passage of the NO₂ gas is prolonged, finally isoporphyrin is formed similar to its chloro analogue.[13a]

3.2 *Crystal structure description*

The perspective view of complexes **1** and **2** are shown in figure 1 and their crystallographic data are given in table 1. The complex **2** crystallized in the space group *C*2/*c* with half a molecule per asymmetric unit. The molecular structure (figure 1) shows that in compound **1** the nitrate coordinates through single oxygen atom. The monodentate coordination of the nitrate may be stable due to its involvement in C–H hydrogen bonding with solvent benzene molecule (figure 2a). The two C–H hydrogen of the solvent benzene are at a distance of 2.56 and 3.08 Å with weak H-bonding with two oxygen atoms of the coordinated nitrate. Such C–H...O hydrogen bonds are known.[23] The atom Fe1, N3 and O4 are located on a two-fold axis. The iron atom is shifted out of the porphyrin plane in the direction of

the nitrate ligand with a distance 0.18 Å and the distance between iron and bonded oxygen is 1.971(3) Å, while the other oxygen is at a distance of 2.81 Å. The Fe-N(py) bonds of **1** are almost equal length ranging from 2.049 to 2.078 Å which are typical for high spin iron(III) porphyrins.

An ORTEP diagram for [Fe(4-OMe-TPP)(NO$_3$)] **2** is shown in figure 1b. The symmetric bidentate coordination of the nitrate in **2** is clearly seen from figures 1b and 2b. The metal iron in [Fe(4-OMeTPP)(NO$_3$)] is above the porphyrin mean plane with a distance of 0.19 Å and the bond distance between the iron and two oxygen atoms are identical which are bonded with 2.169 (5) Å. This distance is longer than that of monodenate nitrato-iron(III) porphyrin **1**, but the distance is within the iron–oxygen distances of the known iron–nitrate porphyrins.[7]

(a)

(b)
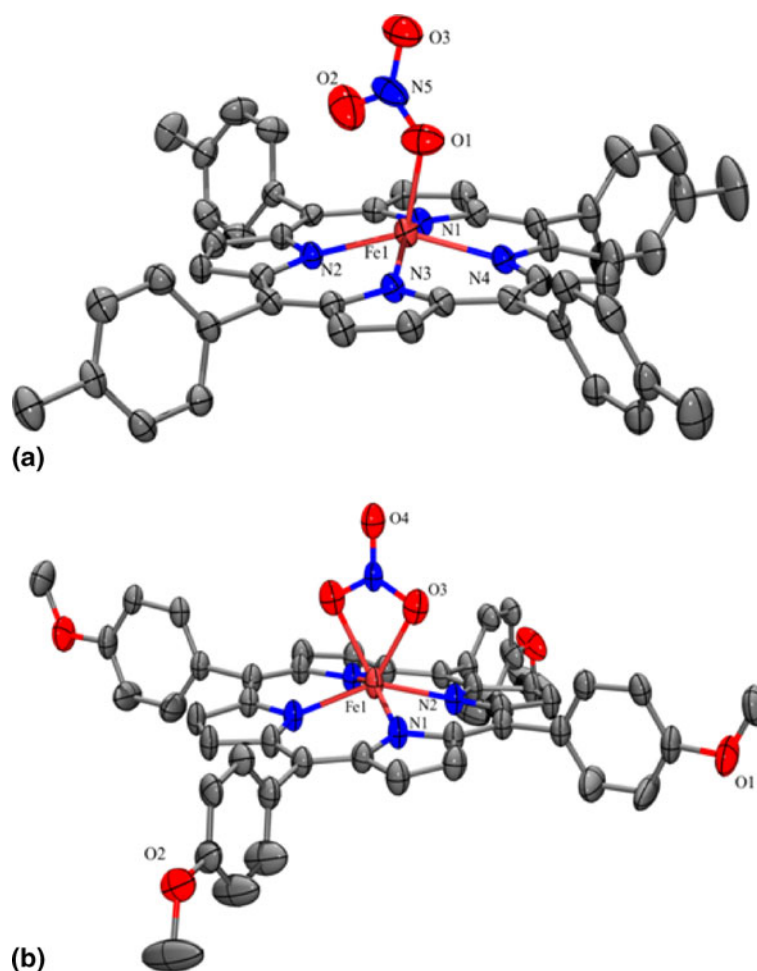
Figure 1. Perspective view of compound **1** (**a**, top) and **2** (**b**, bottom) with partial atom labelling scheme (50% thermal probability ellipsoid, showing nitrate ion coordinated as monodentate in **1** and as bidentate in **2**. Hydrogen atoms are omitted for clarity. Selected bond distances: Fe1-O1 = 1.971(3) Å in **1** and Fe1-O3 = 2.169(5) Å in **2**.

**Table 1.** Crystallographic data[a] for complexes **1** and **2**.

Complex	1	2
Formula	$C_{54}H_{42}FeN_5O_3$	$C_{48}H_{36}FeN_5O_9$
Formula weight	864.78	882.67
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$C2/c$
T, K	100	100
Z	4	4
a, Å	10.161(5)	18.779(5)
b, Å	48.906(5)	21.129(5)
c, Å	8.684(5)	14.839(5)
α, deg	90	90
β, deg	90	125.406(5)
γ, deg	90	90
V, Å^3	4315(3)	4799(2)
d_{calcd}, g/cm^3	1.331	1.222
μ, mm^{-1}	0.402	0.371
θ range, deg	2.05 to 28.42	2.56 to 26.00
GOF (F^2)	1.087	1.061
R_1^b (wR$_2^c$)	0.0610(0.159)	0.1032(0.3261.)

[a]Mo Kα radiation. [b]$R_1 = \sum ||F_0| - |F_c||/\sum |F_0|$. [c]$wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$

In **2** the Fe-N(py) bond lengths consists of two sets of identical length, 2.081(4) and 2.071(4) Å in diagonal Fe-N(py) position. These Fe-N(py) bond lengths are typical for a high spin iron(III) porphyrin. The thermal ellipsoids of both the monodentate and bidentate coordinated nitrates are good but the solvent water molecules present in the lattice of **2** are found to be vibrant. Interestingly, both the monodentate and bidentate nitrato-iron(III) porphyrin structures are fixed symmetrical structures and not an average or dynamic structure unlike to the reported bidentate nitrato-iron porphyrins.[7] The porphyrin core of the bidenate nitrato-iron(III) porphyrin **2** is slightly ruffled. The most interesting feature is that the nitrate ligand lies midway between the two Fe and Np vectors in both monodentate and bi-dentate mode of coordination in contrast to the reported bidentate nitrato-iron(III) porphyrins. The metal iron in complex **2** is in the plane of nitrate anion.

3.3 *Solution properties*

It is difficult to determine the exact coordination mode of the nitrato-iron(III) porphyrins in solution. The
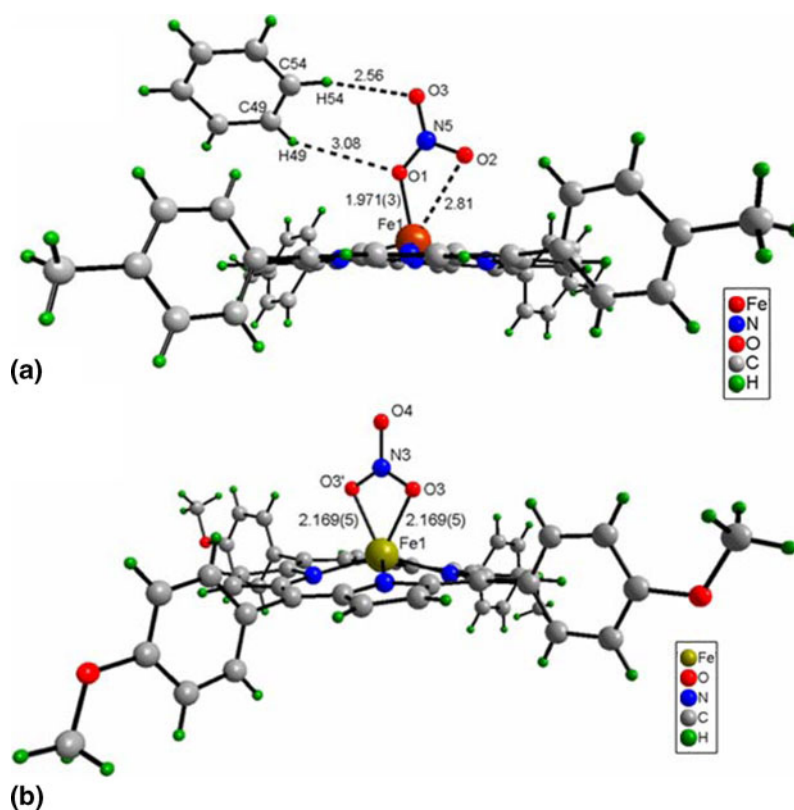
Figure 2. (**a**) Diamond view of compound **1** showing the C–H hydrogen bonding with solvent benzene molecule (nitrate ion coordinated as monodentate in **1**). (**b**) Diamond view of compound **2** showing the coordination of nitrate as symmetric bidentate mode.
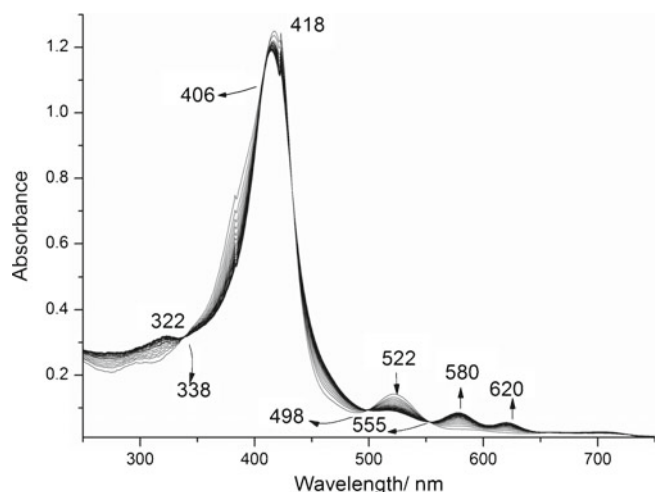
Figure 3. Spectral changes of **1** in aerobic atmosphere (solvent CH_2Cl_2). Time interval of each scans 10 min (total time 2 h). Clean isobestic points indicate the smooth conversion of **1** to μ-oxo-dimeric iron(III) porphyrin.

three possible coordination modes of nitrate anion are mono-dentate, symmetric bi-dentate and asymmetric bi-dentate. It is expected that the energy difference between the mono-dentate and bi-dentate coordination mode is small and the interchange between these two coordination modes is readily possible. The detail theoretical calculations to check the energy difference between mono-dentate and bi-dentate coordination mode of nitrate are under process. Compounds **1** and **2**, are stable in the solid state; however in solution in moist aerobic atmosphere these are slowly converted back to their respective μ-oxo-dimeric iron(III) porphyrins. Figure 3 shows the smooth conversion of nitrato-iron(III) porphyrin **1** to its oxo-dimer in moist air. Interestingly, under NO_2 atmosphere the oxidation of μ-oxo-dimeric iron(III) porphyrins do not occur instead they form nitrato-derivatives and, which, in aerobic atmosphere slowly converted back to their oxo-dimeric porphyrin (scheme 1).

This hydrolysis in aerobic atmosphere may be due to the unprotected iron(III) porphyrins containing weakly bound axial ligand nitrate. In addition, iron(III) nitrate porphyrins are known to photochemically cleaved into highly reactive iron(IV)-oxo porphyrin radical cation. In argon atmosphere the synthesized nitrato-iron(III) porphyrins are relatively stable even in solutions.

3.4 *Formation of isoporphyrin*

Relatively high intensity absorption band at the lower energy region around 900 nm coupled with the decrease in intensity of the Soret band is characteristic for

the formation of isoporphyrin.[12,13] This high intensity absorption near infrared region is due to the narrow HOMO–LUMO gap of isoporphyrin.[13b] On passing NO_2 gas through a DCM solution of μ-oxo-iron porphyrin dimer, the colour of the solution first changes from green to dark red which indicates the formation of the nitrato complex. If the passage of the NO_2 gas is prolonged, the colour finally changes from dark red to yellowish green indicating the formation of isoporphyrin. Figure 4 (blue colour) shows the formation of nitrato-iron(III) porphyrin upon passing NO_2 at the initial phase. The spectral changes of nitrato-iron(III) porphyrin (figure 4) supports the subsequent conversion of nitrato-iron(III) porphyrin into an isoporphyrin derivative. The isolated nitrato complex also forms isoporphyrin on passing NO_2 gas. Electronic spectra of [Fe(4-Me-TPP)Cl], [Fe(4-Me-TPP)(NO_3)] and the corresponding iron-hydroxy isoporphyrin are shown in figure S3 of the supplementary information. Excess NO_2 oxidizes the nitrato-iron(III) porphyrin to π-cation radical which responds to isoporphyrin formation in the presence of trace amount of water similar to its chloro-analogue.[13] We checked the formation of iron-hydroxy isoporphyrin through electronic spectroscopy of authentic iron hydroxy isoporphyrin of [Fe(4-OMe-TPP)Cl].

The spectral changes are similar to what we observed with chloro-analogue. The ESI mass spectrum, establishes the presence of the nitrato(hydroxy-iso-*p*-methoxy-tetraphenylporphyrin)iron(III) cation (m/z 867, supplementary information figure S4). The mass
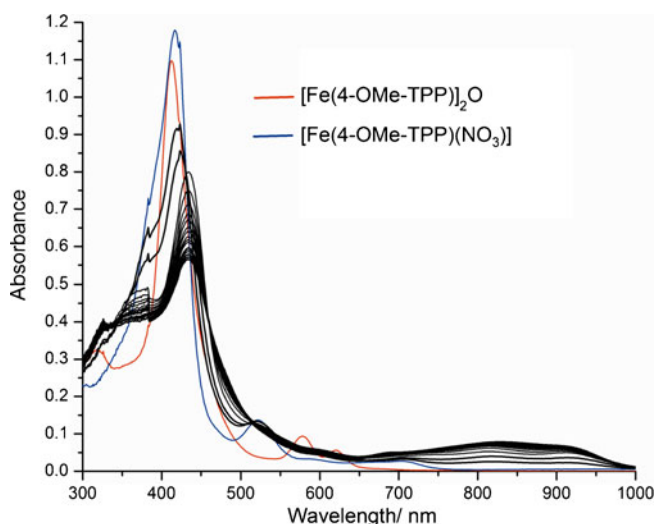
Figure 4. Spectral changes of [Fe(4-OMe-TPP)]_2O on passing NO_2 gas. [Fe(4-OMe-TPP)(NO_3)] is formed initially (blue line), then it get oxidized to cation radical and finally converted to hydroxy isoporphyrin. Time interval of each scans 2 min (solvent CH_2Cl_2) with a total time 1 h.

of the major fragment at m/z 805 correspond to 5-hydroxy-isoporphyrin fragment without coordinated nitrate. The FTIR also corroborates (supplementary information figure S5) the presence of hydroxy and nitrate groups with the peaks ν(OH) at 3428, and ν (NO$_3$) at 1512, 1383 cm^{-1}. These hydroxy-isoporphyrins may be reactive toward hydroxylation of alkenes and aromatic hydrocarbons and such studies are in progress.

4. Conclusions

In summary, two nitrato-iron(III) porphyrinates have been structurally characterized. Among these, one has nitrate ion coordinated as monodentate (by single oxygen atom), while the other has nitrate coordination through bidentate mode. It is presumed that the nitrate can interchange between these two coordination modes readily. Under the passage of NO$_2$ gas through the solution of a μ-oxo-dimeric iron(III) porphyrin, a nitrato-iron(III) porphyrin complex is formed at the initial stage and on further passing of NO$_2$ this gets oxidized to a π-cation radical that finally converted to hydroxy-isoporphyrin in the presence of trace amount of water. These nitrato-iron(III) porphyrinates in aerobic atmosphere in solution slowly converted back to μ-oxo-dimeric iron(III) porphyrins irrespective of their different nitrate coordination modes.

Supplementary material

CCDC 890195 and 890196 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For supplementary figures S1–S5, see the journal website (www.ias.ac.in/chemsci).

Acknowledgements

References

1. (a) Wyllie G R A and Scheidt W R 2002 *Chem. Rev.* **102** 1067; (b) Scheidt W R and Ellison M K 1999 *Acc. Chem. Res.* **32** 350; (c) Ford P C 2010 *Inorg. Chem.* **49** 6226; (d) Lehnert N, Berto T C, Galinato M G I and Goodrich L E 2011 *The handbook of porphyrin*, K M Kadish, K M Smith and R Guilard (eds) World Scientific Vol. 14, 1–247

2. (a) Kumar M R, Zapata A, Ramirez A J, Bowen S K, Francisco W A and Farmer P J 2011 *Proc. Natl. Acad. Sci. USA* **108** 18926; (b) Paolocci N, Saavedra W F, Miranda K M, Martignani C, Isoda T, Hare J M, Espey M G, Fukuto J M, Feelisch M, Wink D A and Kass D A 2001 *Proc. Natl. Acad. Sci. USA* **98** 10463

3. (a) Cheng L and Richter-Addo G B 2000 *The porphyrin handbook*, K M Kadish, K M Smith and R Guilard (eds) Academic Press, San Diego, Vol. 4, pp 2590–260; (b) Doyle M P and Hoekstra J W 1981 *J. Inorg. Biochem.* **14** 351; (c) Eich R F, Li T, Lemon D D, Doherty D H, Curry S R, Aitken J F, Mathews A J, Johnson K A, Smith R D, Phillips G N and Oleson J S 1996 *Biochemistry* **35** 6976

4. (a) Koropatkin N M, Pakras H B and Smith T J 2006 *PNAS* **103** 9820; (b) Bhuyan J, Sarkar R and Sarkar S 2011 *Angew. Chem. Int. Ed.* **50** 10604

5. (a) Harischandra D N, Zhang R and Newcomb M J 2005 *J. Am. Chem. Soc.* **127** 13776; (b) Pan Z, Zhang R, Fung L W M and Newcomb M 2007 *Inorg. Chem.* **46** 1517

6. Van Driel G J, Driessen W L and Reedjik J 1985 *Inorg. Chem.* **24** 2919

7. (a) Wyllie G R A, Munro O Q, Schulz C E and Scheidt W R 2007 *Polyhedron* **26** 4664; (b) Phillippi M A, Baenziger N and Goff H M 1981 *Inorg. Chem.* **20** 3904; (c) Ellison M K, Shang M, Kim J and Scheidt W R 1996 *Acta Crystallogr. Sect. C* **52** 3040

8. (a) Guzinski J A and Felton R H 1973 *J. Chem. Soc., Chem. Commun.* 715; (b) Barkigia K M, Renner M W, Xie H, Smith K M and Fajer J 1993 *J. Am. Chem. Soc.* **115** 7894

9. Cong Z, Kurahashi T and Fujii H 2012 *J. Am. Chem. Soc.* **134** 4469

10. (a) Woodward R B 1960 *Angew. Chem.* **72** 651; (b) Woodward R B 1961 *Pure Appl. Chem.* **2** 383; (c) Woodward R B 1967 *Ind. Chim. Belge* **27** 1293

11. Dolphin D, Felton R H, Borg D C and Fajar J 1970 *J. Am. Chem. Soc.* **92** 743

12. (a) Gold A, Ivey W, Toney G E, Sangaiah R 1984 *Inorg. Chem.* **23** 2932; (b) Takeda Y, Tskshara S, Kobyashi Y, Miswa H, Sauragi H and Tokumaru K 1990 *Chem. Lett.* **11** 2103; (c) Felton R H, Owen G S, Dolphin D, Forman A, Borg D C and Fajer J 1973 *Ann. N.Y. Acad. Sci.* **206** 504; (d) Harriman A, Porter G and Walters P 1983 *J. Chem. Soc., Faraday Trans. 1* **79** 1335; (e) Kadish K M and Rhodes R K 1981 *Inorg. Chem.* **20** 2961; (f) Shine H J, Padilla A G and Wu S M 1979 *J. Org. Chem.* **44** 4069; (g) Fawcett W R, Fedurco M, Smith K M and Xie H 1993 *J. Electroanal. Chem.* **354** 281

13. (a) Abhilash G J, Bhuyan J, Singh P, Maji S, Pal K and Sarkar S 2009 *Inorg. Chem.* **48** 1790; (b) Bhuyan J and Sarkar S 2010 *Chem. Eur. J.* **16** 10649

14. Catalano M M, Crossley M J, Harding M M 1984 *J. Chem. Soc. Chem. Commun.* 1535

15. Kumar A, Maji S, Dubey P, Abhilash G J, Pandey S and Sarkar S 2007 *Tetrahedron Lett.* **48** 7287

16. Altomare A, Burla M C, Camalli M, Cascarano G L, Giacovazzo C, Guagliardi A, Moliterni A G G, Polidori G and Spagna R 1999 *J. Appl. Crystallogr.* **32** 115

17. Sheldrick G M *SHELX97 Programs for crystal structure analysis (Release 97-2)*; University of Göttingen: Göttingen, Germany 1997

18. Bag N, Chern S, Peng S and Chang C K 1995 *Tetrahedron Lett.* **36** 6409
19. Nakamoto K 1986 *Infrared and Raman spectra of inorganic and coordination compounds*, John Wiley & Sons, New York, 4th Ed. pp 254–257
20. Finnegan M G, Lappin A G and Scheidt W R 1990 *Inorg. Chem.* **29** 181
21. Bhuyan J and Sarkar S 2012 *Chem. Asia. J.* **7** 2690
22. (a) Khin C, Heinecke J and Ford P C 2008 *J. Am. Chem, Soc.* **130** 13830; (b) Castro C E 1996 *J. Am. Chem. Soc.* **118** 3984; (c) O'shea S K, Wang W, Wade R S and Castro C E 1996 *J. Org. Chem.* **61** 6388; (d) Singh P, Saltsmana I, Mahammeda A, Goldbergb I, Tumanskiia B and Gross Z 2012 *J. Porphyrins Phthalocyanines* **16** 663
23. (a) Desiraju G 1991 *Acc. Chem. Res.* **24** 290; (b) Bernstein J 2013 *Cryst. Growth Des.* **13** 961; (c) Jin Y Z, Zhang R, Fu D and Lv Y 2011 *Acta Crystallogr.* **E67** o1594; (d) Mazika M, Bläserb D and Boeseb R 2001 *Tetrahedron* **57** 5791