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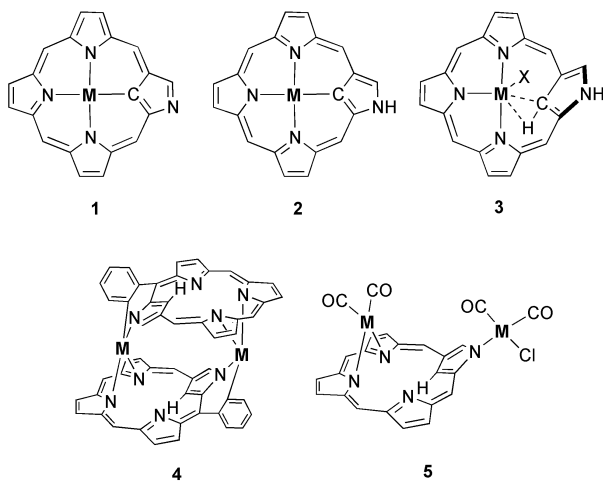
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A dimeric iron *N*-confused porphyrin, [Fe(NCTPP)]<sub>2</sub> was obtained from the anaerobic reaction of Fe(NCTPP)Br with NaSePh while under aerobic conditions a hydroxo bridged iron dimer with Na bridging the outer-*N* atoms was obtained and oxygenation occurred on the inner core pyrrolic carbon to form a novel ONCTPP porphyrinic ring.

*N*-Confused porphyrin (NCP), an isomeric porphyrin, has an inverted pyrrole ring joined to the porphyrinic conjugated system through a β-carbon, and exhibits a peripheral pyrrolic nitrogen and an inner core carbon. Recent studies on the *N*-confused porphyrin demonstrated that this molecule displays distinct physical properties and coordination chemistry.<sup>1</sup> *N*-Confused porphyrins were reported to stabilize metal centres with unusual oxidation states through a planar 3- or 2-charged porphyrin ring (1, 2).<sup>2,3</sup> We and others also showed that NCP can coordinate to divalent metals through a tridentate coordination mode to form a tilted inverted pyrrole ring (3).<sup>4,5</sup> In addition to mononuclear complexes, a binuclear Pd(II) double-decker complex (4)<sup>6</sup> with metals bridging two NCP rings, or a bis-Rh(I) NCP complex (5)<sup>7</sup> with metals simply coordinated to one NCP ring are observed.



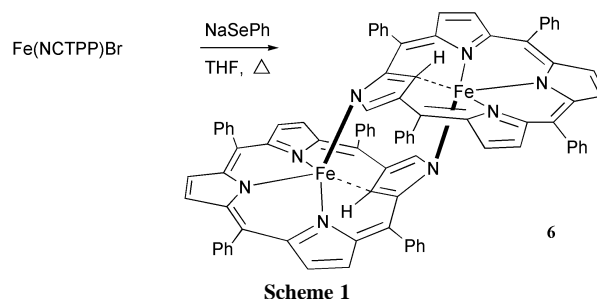
Based on our recent progress on iron NCP complexes,<sup>4</sup> herein we report that the reaction of Fe(NCTPP)Br with NaSePh gave a dimeric NCP complex with the metals retained in the NCP rings. Interestingly, when the dimeric iron complex was exposed to air, a hydroxo bridged dimeric iron porphyrin was isolated. Surprisingly, the NCP rings underwent oxygenations to form oxoporphyrin type NCP rings and a sodium ion was coordinated to both peripheral nitrogens.

Treatment of Fe(NCTPP)Br<sup>4</sup> with an excess (1.25 equiv.) of sodium benzeneselenate, NaSePh, in THF under anaerobic condition yields 85% of dark green crystalline [Fe(NCTPP)]<sub>2</sub> (6) after recrystallization (Scheme 1). The relatively weak

coordinating ability of selenate is essential to the formation of the dimeric complex. The UV-vis spectrum of the dimeric iron NCP complex 6 has a Soret band at 459 nm, a broad Q band at 755 nm and a shoulder around 660 nm. The energy of the Soret band in 6 is comparable to that for Fe(NCTPP)Br but the Q bands are slightly red-shifted. The similar absorption spectra suggest identical tautomeric forms for 6 and Fe(NCTPP)Br (3, M = Fe) with a dianionic NCP ring from the deprotonation of the inner core amino nitrogen and a peripheral amino nitrogen. SQUID measurement of dimer 6 gives a magnetic moment of 4.31 μ<sub>B</sub> at 300 K for each Fe. The magnetic moment decreases with a decrease in temperature to 1.64 μ<sub>B</sub> at 6 K. Preliminary fitting of the SQUID data suggested weak antiferromagnetic coupling between the two iron centers. However, fitting the data using magnetic susceptibility equations for binuclear complexes employing Heisenberg intercluster magnetic exchange with a combination of different spin quantum numbers<sup>8</sup> has not yet given a reliable result due to either partial oxidation of the extremely air sensitive 6 during data collection or because of a complicated electronic structure.

The geometry of the dimeric compound was determined by single crystal structure analysis.<sup>‡</sup> Compound 6 crystallized in an orthorhombic *Pbca* cell leading to an independent Fe(NCTPP) and a unit of Fe(NCTPP) generated from symmetry (Fig. 1). The dimeric structure assembles by a direct coordination of iron to the neighboring peripheral nitrogen on the other NCP ring. The inverted pyrrole rings cant significantly from the mean porphyrin plane with an angle of 137° between the Fe–C bond and the inverted pyrrole ring. The distance of iron to the inner carbon in the inverted pyrrole ring is 2.341(5) Å which is close to the distance of 2.361(10) Å in Fe(NCTPP)Br. The bond distances and bond angles around the porphyrin core resemble those in Fe(NCTPP)Br and suggest that the tautomer form remains unchanged from the monomeric compound to the dimer. The average Fe–N<sub>p</sub> distance of 2.075(5) Å is within the range 2.072–2.096 Å for the corresponding distance in five-coordinate high spin iron(II) complexes.<sup>9</sup> Interestingly, in order to release steric constraint between two NCP rings, one of the phenyl rings rotates significantly resulting in a dihedral angle of 44.6° between this phenyl ring and a neighboring pyrrole plane.

The dimeric iron complex 6 oxidizes readily in aerobic conditions. In the solution state in an anaerobic dry box, compound 6 still picks up oxygen from the environment to give a product with a UV-vis spectrum identical to compound 7 after several weeks. The mass spectrum of the oxidation product



† Electronic supplementary information (ESI) available: general information; preparation and crystal data for 6 and 7; Fig. S1: absorption spectra for 6 and 7; Figs. S2 and S3: magnetic susceptibility data for 6 and 7. See <http://www.rsc.org/suppdata/cc/b2/b202679a/>

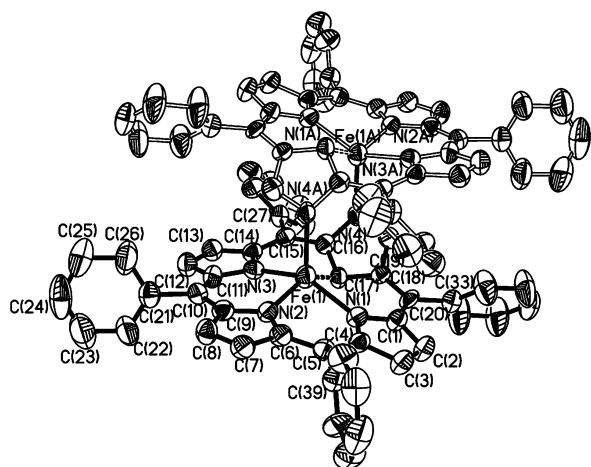
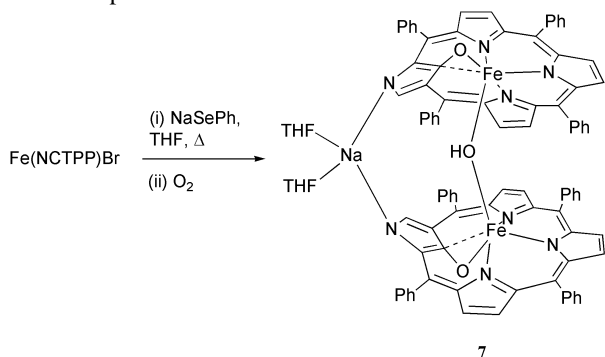


Fig. 1 The ORTEP diagram (35% ellipsoids) of  $[\text{Fe}(\text{NCTPP})]_2$  **6**.

suggested the insertion of an oxygen atom into the NCP core. The absorption spectrum of **7** isolated from the reaction shown in Scheme 2 gives an unusually broad Soret band at 389 nm without a clearly identified Q band and suggests perturbation of the N-confused porphyrin  $\pi$ -conjugated system. SQUID magnetic susceptibility measurement gives a magnetic moment of  $3.40 \mu_B$  at room temperature for each metal center and suggests a stronger antiferromagnetic coupling between the two iron centers compared to **6**.



Scheme 2

The crystal structure of **7** (Fig. 2)<sup>‡</sup> reveals unexpected chemistry and is important in understanding the NCP oxidation. Instability to oxidation of iron NCTPP complexes was observed in our previous report.<sup>4</sup> Recently, Furuta and Osuka<sup>10</sup> isolated a tripyrrinone complex from the aerobic preparation of Cu(NCTPP) complex and suggested mechanisms for NCP ring opening reactions. However, the structure of **7** suggests that the oxidation reaction of the iron NCP complex proceeds via a different pathway. According to the crystal structure, in addition to a normal  $\mu$ -hydroxo iron dimer, a novel oxo N-confused porphyrin (ONCP) is clearly observed. The oxygenation of porphyrin to oxophlorin or dioxoporphodimethene is well-known in the literature.<sup>11</sup> However, the oxygenation sites are

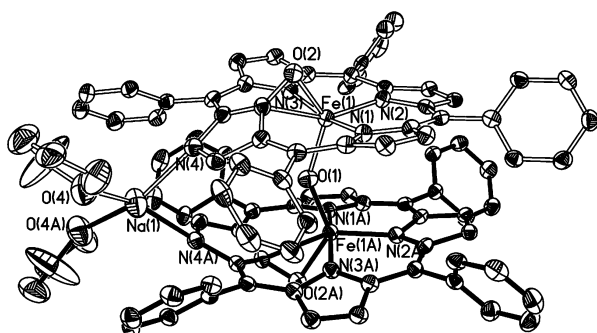


Fig. 2 The ORTEP diagram (35% ellipsoids) of  $[\text{Fe}(\text{ONCTPP})]_2(\text{OH})\text{Na}(\text{THF})_2$  **7**.

mainly on *meso* carbons. Compound **7** represents a new porphyrin analogue with a hydroxy group on the inner core pyrrolic carbon. The separation of 1.336(6) Å between oxygen (O(2)) and the inner core carbon is much longer than the average bond distance of 1.227(9) Å for C=O found in thallium dioxoporphodimethene,<sup>12</sup> but is close to that of 1.356(22) Å in the oxophlorin complex  $\text{Ni}^{\text{II}}(\text{OEPOH})$ .<sup>13</sup> Although the hydroxy form is observed in **7**, a tautomerization, as in oxophlorin, between the hydroxy and keto form for the free base of ONCTPP is expected. The short distance of 1.957(4) Å between iron and the oxo group on the ONCTPP ring suggests a coordination of oxygen to the iron center. Furthermore, the distance of 2.296(5) Å between iron and the inner core carbon is much closer in comparison with the corresponding distance for iron or manganese NCTPP complexes<sup>4</sup> and indicates a much stronger  $\text{Fe}\cdots\text{C}$  interaction. The distance of 1.945(2) Å between iron and oxygen on the  $\mu$ -hydroxo group is comparable to that of 1.924(2) Å in  $\{[\text{Fe}(\text{OEP})]_2(\text{OH})\}^+$ .<sup>14</sup> In contrast with mostly linear Fe–O–Fe bond in iron(III) porphyrin  $\mu$ -oxo dimers, the angle of 142.9(3) for Fe–OH–Fe further confirms the hydroxo bridging in **7**.<sup>15</sup> Finally, the distances of 2.414(6) and 2.315(6) Å for Na–N and Na–O are similar to literature values.<sup>16</sup> Overall, neglecting the potential electron delocalization, the ONCTPP cores are trianionic charged from the deprotonation of the peripheral nitrogen, the inner core amino nitrogen and the inner core hydroxy group. Both irons are in 3+ oxidation state and the negative charge of bridging hydroxy group is balanced by the sodium cation. The demetallation and purification of ONCTPP is under active study.

## Notes and references

<sup>‡</sup> Crystallographic data: for  $[\text{Fe}(\text{NCTPP})]_2$  **6**:  $\text{C}_{96}\text{H}_{72}\text{Fe}_2\text{N}_8\text{O}_2$ ,  $T = 293$  K,  $M = 1481.32$ , orthorhombic, space group *Pbca*,  $a = 15.867(5)$ ,  $b = 20.697(6)$ ,  $c = 22.397(7)$  Å,  $V = 7355(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.338$  Mg m<sup>-3</sup>,  $\lambda = 0.71073$  Å,  $\mu = 0.454$  mm<sup>-1</sup>,  $F(000) = 3088$ . The structure was solved by direct methods and refined by least squares against  $F^2$  to  $R1 = 0.0756$  ( $wR2 = 0.1546$ ) and  $S_{\text{gof}} = 0.983$ .

For  $[\text{Fe}(\text{ONCTPP})]_2(\text{OH})\text{Na}(\text{THF})_2$  **7**:  $\text{C}_{108}\text{H}_{95}\text{Fe}_2\text{N}_8\text{NaO}_8$ ,  $T = 293$  K,  $M = 1767.61$ , monoclinic, space group *C2/c*,  $a = 28.473(3)$ ,  $b = 18.7702(18)$ ,  $c = 16.8963(16)$  Å,  $\beta = 104.922(2)^\circ$ ,  $V = 8725.6(14)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.346$  Mg m<sup>-3</sup>,  $\lambda = 0.71073$  Å,  $\mu = 0.404$  mm<sup>-1</sup>,  $F(000) = 3704$ . The structure was solved by direct methods and refined by least squares against  $F^2$  to  $R1 = 0.0702$  ( $wR2 = 0.1815$ ) and  $S_{\text{gof}} = 0.924$ .

CCDC reference numbers 184398 and 184399. See <http://www.rsc.org/suppdata/cc/b2/202679a/> for crystallographic data in CIF or other electronic format.

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