Isolation and Crystal Structure of a Peroxo-Bridged Heme–Copper Complex**

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The reaction of dioxygen with transition metal complexes is important from the standpoint of O_2 binding and activation in biological systems.[1] Cytochrome c oxidase (CcO), which a catalyzes four electron reduction of O_2 to water, has a unique heme/nonheme copper dinuclear core in its active site.[2] A number of heme-based iron–copper dinuclear complexes have been synthesized to elucidate the mechanism of O_2 reduction in CcO.[3–6] We reported the reaction of O_2 with tetraphenylporphyrin (TPP)-Fe^{II}-linked tris(2-pyridylmethyl)amine (TPA)–Cu^{I} dinuclear complexes and the formation of peroxo-bridged dinuclear species Fe–O_2–Cu with a moderate stability in CH_3CN at room temperature.[4] Karlin et al. also reported a similar dioxygen reaction with both the analogous dinuclear complexes[5d] and the 1:1 mixture of the heme and the Cu complex.[5e,6] Although these peroxo-bridged dinuclear species were characterized by various spectroscopic methods, the detailed structure of Fe^{III}–O_2–Cu^{II} moiety has not been clarified. Moreover, to the best of our knowlege, the isolation and structure of such a heterodimetallic peroxo-bridged complex has never been reported. Herein, we describe the first report of the isolation and crystal structure of a peroxo-bridged heme–copper dinuclear complex.

We prepared a dinuclear complex, [(TMP)Fe^{II}-(5MeTPA)Cu^{I}]BPh_4 (**1**, TMP-5MeTPA = 10,15,20-tris(2,4,6-trimethylphenyl)-5-(2′-bis((5″-methyl-2″-pyridylmethyl)aminomethyl)pyridine-5′-carboxyamidophenyl)-porphyrin). The UV/Vis spectrum of **1** in CH_3CN showed absorption maxima at 428 and 534 nm. When **1** was exposed to O_2 in CH_3CN at −30 °C (Scheme 1), the 428 and 534 nm bands disappeared

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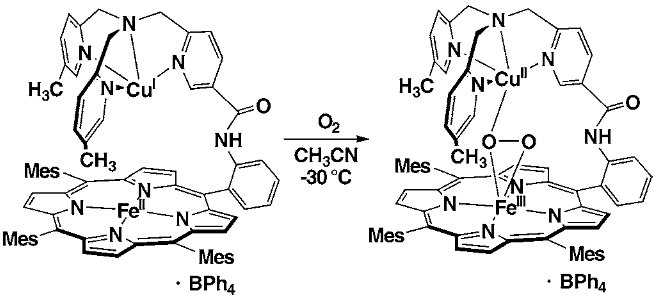

1 **2**

Scheme 1. Formation of $[(TMP)Fe^{III}\text{-}(O_2)\text{-}(5MeTPA)Cu^{II})]BPh_4$ (**2**) from $[(TMP)Fe^{II}\text{-}(5MeTPA)Cu^{I}]BPh_4$ (**1**) and dioxygen.

and bands at 420, 557 and 612 nm appeared (Figure 1), thus indicating the formation of a peroxo-bridged Fe–O_2–Cu species, as we described previously.[4] This peroxo species exhibited much higher stability in the CH_3CN solution than the previously reported analogues,[7] on account of the steric hindrance by the multiple methyl groups. The solution of the peroxo complex could be kept at −30 °C for several days without decomposition finally yielding dark-purple crystals. The formula of the crystals was determined as $[(TMP)Fe^{III}\text{-}(O_2)\text{-}(5MeTPA)Cu^{II}]BPh_4$ (**2**) from the elemental analysis and ESI-mass spectrum. The UV/Vis spectrum of the redissolved solution of **2** in CH_3CN (λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 420 (126000), 557 (8500), 612 (3500) nm) was in good agreement with that of the peroxo complex before the isolation. The resonance Raman spectrum of **2** in CH_3CN exhibited an isotope sensitive band at 790 ($^{16}O_2$)/746 ($^{18}O_2$) cm^{-1} (Figure 1, inset), which was assigned to peroxy ν(O–O) as were the analogues reported previously.[4] These results clearly indicate the successful isolation of the peroxo complex **2**. The decomposition of **2** was not observed for a sample that was left for several months in the solid state, even at room temperature.

The crystal structure of **2** was determined by single-crystal X-ray analysis (Figure 2).[8] The Fe–O_2–Cu moiety has a μ-η^2:η^1 coordination mode; both oxygen atoms (O(2) and O(3)) of the peroxo ligand bind to Fe(1) while only O(2) binds to Cu(1). The observed O–O bond length (1.460(6) Å) is reasonable for a peroxo ligand,[9] although this value is larger than those of other side-on peroxo-metalloporphyrins.[10–12] The Fe(1)–O(2)–Cu(1) unit is almost linear with the angle 166.0(3)°, being similar to that of the heme–copper μ-oxo species (Fe-O-Cu = 171.1(3)°).[5c] The μ-η^2:η^1 coordination mode in metal-peroxo species has been reported for the rhodium(III), vanadium(V) and palladium(II) homodinuclear complexes.[13] However, in those cases, the M-O-M units are bent with an angle 103 ≤ M-O-M ≤ 133°.

The iron ion is coordinated by the four pyrrole nitrogen atoms and the two oxygen atoms of the peroxo ligand. The peroxo ligand is bound to Fe(1) in a side-on mode eclipsing the two Fe–N bonds (Fe(1)–N(5) and Fe(1)–N(7)). The two Fe–O bond lengths are 2.031(4) (Fe(1)-O(2)) and 1.890(6) (Fe(1)-O(3)) Å. In mononuclear side-on peroxo–M–porphyrin complexes (M = Ti^{III},[10] Mo^{VI},[11] or Mn^{III}[12]) the M–O bond lengths are almost identical. On the other hand, the Fe(1)–O(2) bond length in complex **2** is considerably longer than that of Fe(1)–O(3), probably as a result of the coordination of Cu(1) to O(2). The iron ion lies 0.595(10) Å above the least-square plane based on the pyrrole nitrogen atoms towards the peroxo ligand. This displacement is also found in peroxo–M–por-

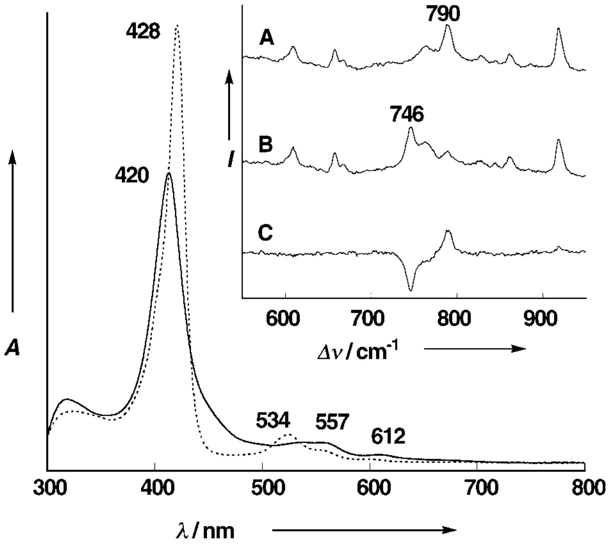

Figure 1. UV/Vis absorption spectra of **1** (-----) and **2** (——) in CH_3CN at −30 °C; inset. resonance Raman spectra of **2** (in CH_3CN, room temperature, λ_{ex} = 413.1 nm), A: $^{16}O_2$, B: $^{18}O_2$, C: A-B.

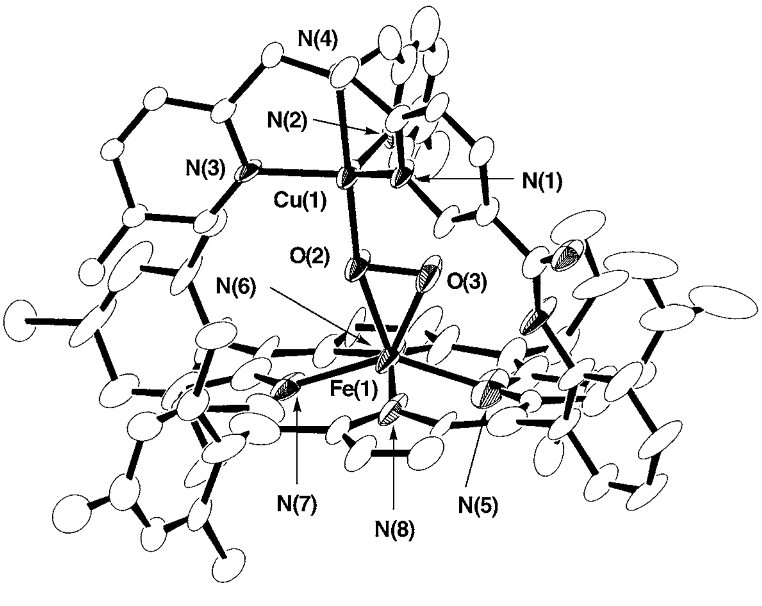

Figure 2. ORTEP view of $[(TMP)Fe^{III}\text{-}(O_2)\text{-}(5MeTPA)Cu^{II})]^+$ in crystals of **2** drawn with the thermal elliposids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°]: Cu(1)-O(2) 1.915(5), Cu(1)···O(3) 2.657(7), Fe(1)-O(2) 2.031(4), Fe(1)-O(3) 1.890(6), O(2)-O(3) 1.460(6), Cu(1)-N(1) 2.054(8), Cu(1)-N(2) 2.15(1), Cu(1)-N(3) 2.035(6), Cu(1)-N(4) 2.061(6), Fe(1)-N(5) 2.15(1), Fe(1)-N(6) 2.08(1), Fe(1)-N(7) 2.18(1), Fe(1)-N(8) 2.03(2), Cu(1)-O(2)-Fe(1) 166.0(3), Cu(1)-O(2)-O(3) 103.0(4).

phyrin complexes (M = Ti^{III},[10] or Mn^{III}[12]) and is consistent with the EXAFS structure of peroxo–iron(III) porphyrin.[14b]

The structure of the TPA-Cu-O-O unit is similar with that of the *trans*-(μ-1,2-peroxo)dicopper(II) complex derived from [(TMPA)Cu^{I}(CH$_3$CN)]$^+$ (TMPA = tris(2-pyridylmethyl)-amine) and dioxygen.[15] The copper ion is pentacoordinated with a distorted trigonal-bipyramidal geometry by the three pyridine nitrogen atoms, the one tertiary nitrogen atom and the one oxygen atom of the peroxo ligand. Cu(1) is displaced 0.319(2) Å out of the N(1), N(2), N(3) trigonal plane away from the tertiary nitrogen N(4) toward O(2) of the peroxo ligand. The Cu(1)-O(2) bond length (1.915(5) Å) and the Cu(1)-O(2)-O(3) angle (103.0(4)°) are close to those of the *trans*-(μ-1,2-peroxo)dicopper(II) complex.[15]

Evidence that the peroxo ligand bridges the iron and the copper ions is also obvious from magnetic studies. The peroxo complex **2** is ESR inactive at 4 K. The magnetic susceptibility of **2** was measured from 10 to 300 K. The determined effective magnetic moment is 4.65 μ_B and temperature independent within this temperature range. This magnetic moment is consistent with a spin-only value of $S = 2$ ($\mu_{eff} = 4.90\ \mu_B$), therefore, **2** is assigned as a paramagnetic species with an overall $S = 2$ spin state. The Mössbauer spectrum of **2** (77 K, zero field) showed a sharp quadrupole doublet with parameters ($\Delta E_q = 1.17\ \text{mm s}^{-1}$, $\delta = 0.56\ \text{mm s}^{-1}$) typical for high-spin Fe^{III} compound (see Supporting Information), and is in good agreement with those of peroxo-bound iron(III)-porphyrin complexes.[5e,14c] Based on these results, the iron ion has a high-spin d^5 configuration ($S = 5/2$), and is strongly coupled with the copper(II) ion ($S = 1/2$) in an antiferromagnetic fashion. This strong interaction between the metal ions is mediated by the bridging peroxo ligand.

In conclusion, we synthesized and characterized a peroxo-bridged iron-copper complex **2**. The successful isolation of **2** was confirmed by the elemental analysis and various spectroscopic methods. The X-ray structure analysis of **2** revealed that the Fe–O$_2$–Cu moiety has a μ-η^2:η^1 coordination mode. To the best our knowlege, this is the first example of the structure determination of a peroxo-bridged heterodinuclear complex. Further, this is the first X-ray structure of an “iron”-porphyrin complex with a side-on peroxo ligand.[14] Complex **2** is a paramagnetic species with a spin state of $S = 2$, as the bridging peroxo ligand mediates the strong antiferromagnetic coupling between the high-spin iron(III) and the copper(II) ions. Further studies of **2** are in progress in our laboratory.

Experimental Section

[(TMP)Fe^{II}-(5MeTPA)] was prepared by the similar procedure reported in reference [4].

Synthesis of complex **2**: [(TMP)Fe^{II}-(5MeTPA)] (48 mg, 42 mmol), [Cu(CH$_3$CN)$_4$]OTf (18 mg, 42 mmol) and NaBPh$_4$ (16 mg, 42 mmol) were dissolved in CH$_3$CN (20 mL) and cooled to −30 °C. The resulting solution was exposed to dry O$_2$ gas for 30 min, and then stored at −30 °C for 5 days, to give **2** (32 mg, 25 mmol, 60 %) as dark purple crystals. Elemental analysis (%) calcd for C$_{98}$H$_{87}$N$_9$O$_3$-Cu$_1$Fe$_1$B$_1$: C 75.02, H 5.59, N 8.03; found: C 74.64, H 5.59, N 7.87, ESI-MS: *m*/*z*: [(TMP)Fe^{III}-(^{16}O$_2$)-(5MeTPA)Cu^{II}]$^+$, 1248.

The ^{18}O-labeled peroxo complex for Raman experiment was synthesized and isolated by the same procedure. ESI-MS: *m*/*z*: [(TMP)Fe^{III}-(^{18}O$_2$)-(5MeTPA)Cu^{II}]$^+$, 1252.

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[7] The peroxo complex **2** in CH$_3$CN solution is stable for several days at room temperature. It gradually decomposes, to give the mixture of corresponding μ-oxo and μ-hydroxo complexes, as reported in ref. [4] and [5]. Detailed studies of the decomposition mechanism are in progress.

[8] The X-ray experiments for complexes **2** were carried out on a Rigaku RAXIS imaging plate area detector with graphite monochromated Cu$_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). The crystal was mounted on a glass fiber. The data were collected ($3.5 \leq 2\theta \leq 136.5°$) at −150 °C. To determine the cell constant and

orientation matrix, three oscillation photographs were taken with an oscillation angle of 5.0° and exposure time of 60 s per degree for each frame. Intensity data were collected by taking 180 oscillation photographs with an oscillation angle of 5.0° and exposure time of 90 s per degree for each frame. Refraction data were corrected for both Lorentz and polarization effects. **2**: $C_{98}H_{87}N_9O_3Cu_1Fe_1B_1$, dark purple crystals, monoclinic, $P2_1/n$, $a = 14.2898(4)$, $b = 13.0041(3)$, $c = 50.368(1)$ Å, $\beta = 91.4898(7)°$, $V = 9356.6(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.114\ \mathrm{g\,cm^{-3}}$, 91575 reflections collected, 15999 reflections used and 1126 parameters. $R = 0.095$ ($I > 3.0\sigma(I)$), $R_W = 0.223$. CCDC-205246 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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