A Dinuclear Iron(III) Porphyrin–Copper(II) Complex with a Sulphur Bridge: A Model for the Active Site of Cytochrome c Oxidase

Barbara R. Serr, Christine E. L. Headford, C. Michael Elliott,* and Oren P. Anderson*
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, U.S.A.

A dinuclear complex anion containing an iron(III) porphyrin and a copper(II) complex in which the metal atoms are bridged by a sulphur atom has been prepared and structurally characterized; the anion does not exhibit an e.s.r. spectrum at 4.7 K.

The nature of the active site of the resting oxidized form of the enzyme cytochrome c oxidase is of great interest, partly because of its unusual magnetic properties.[1] Two mechanisms have been proposed to explain the e.s.r. silence characteristic of this site: (i), very strong ligand-mediated antiferromagnetic coupling between the copper(II) and the iron(III) heme unit;[2] and (ii), spin-relaxation broadening mediated by small exchange coupling between these metal centres.[3] Model compounds[4] have thus far not reproduced the magnetic properties of the enzyme's active site.

An EXAFS study of the enzyme suggested that the iron and copper atoms of the active site may be bridged by a thiolate sulphur atom.[5] We have previously characterized a trinuclear complex (**1**)[3] involving two $[\mathrm{Fe^{III}(tpp)}]^+$ (tpp = 5,10,15,20-tetraphenylporphyrinato) moieties coupled to $[\mathrm{Cu^{II}(mnt)_2}]^{2-}$ (mnt = *cis*-1,2-dicyanoethylene-1,2-dithiolato) and a compound containing a tetranuclear species $\{[\mathrm{TBA}]\{[\mathrm{Fe}(p\text{-}\mathrm{Cl_4tpp})]_2[\mathrm{Cu(mnt)_2}]_2\}\cdot 3\mathrm{C_6H_6}$ (**2**) (TBA = tetra-n-butylammonium, *p*-$\mathrm{Cl_4}$tpp = 5,10,15,20-tetra(*p*-chlorophenyl)porphyrinato)}.[6] EXAFS studies indicated that a sulphur atom bridged the $\mathrm{Fe^{III}}$ and $\mathrm{Cu^{II}}$ centres in (**1**).[7] A single-crystal *X*-ray diffraction study established that (**2**) contained two

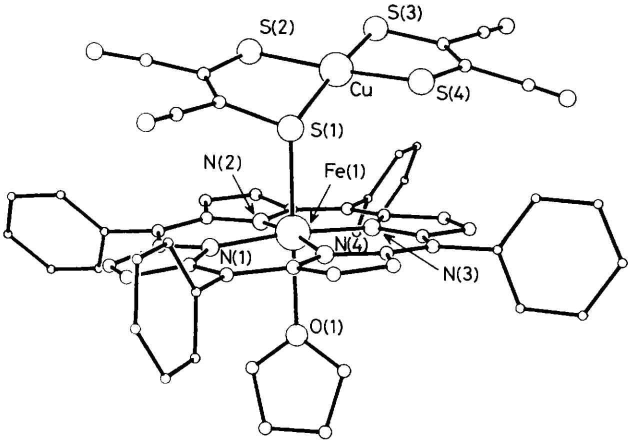

Figure 1. A view of the dinuclear $\{[\mathrm{Fe(tpp)(thf)}][\mathrm{Cu(mnt)_2}]\}^-$ anion of (**3**). All atoms have been drawn as spheres with arbitrary radii. Selected distances and angles: Fe(1) · · · Cu 4.039(1), Cu–S(1) 2.383(2), Cu–S(2) 2.289(5), Cu–S(3) 2.226(4), Cu–S(4) 2.229(5), Fe(1)–N(1) 2.02(1), Fe(1)–N(2) 2.02(1), Fe(1)–N(3) 2.00(1), Fe(1)–N(4) 1.99(1), Fe(1)–S(1) 2.450(1), Fe(1)–O(1) 2.38(1) Å; Cu–S(1)–Fe(1) 113.4(1)°.

$[\mathrm{Fe^{III}}(p\text{-}\mathrm{Cl_4tpp})]^+$ units linked by a $[\mathrm{Cu^{II}(mnt)_2}]^{2-}$ anion; sulphur atoms of the mnt^{2-} ligands connected the $\mathrm{Cu^{II}}$ and $\mathrm{Fe^{III}}$ atoms.[6]

Reaction of equimolar amounts of $\mathrm{Fe^{II}(tpp)}$ and $[\mathrm{TBA}][\mathrm{Cu^{III}(mnt)_2}]$ in tetrahydrofuran (thf) under N_2 allows isolation of a crystalline compound, $[\mathrm{Fe^{III}(tpp)(thf)_2}]\{[\mathrm{Fe^{III}(tpp)(thf)}][\mathrm{Cu^{II}(mnt)_2}]\}\cdot 2\mathrm{thf}$ (**3**).† Compound (**3**) contains a dinuclear anion,‡ in which the iron(III) atom of an $[\mathrm{Fe(tpp)(thf)}]^+$ unit is connected to the copper(II) atom of a $[\mathrm{Cu(mnt)_2}]^{2-}$ complex through a sulphur atom of one of the mnt^{2-} ligands; an $[\mathrm{Fe(tpp)(thf)_2}]^+$ cation serves as the counterion.

In the dinuclear anion (Figure 1), the $\mathrm{Cu^{II}}$ atom is four-co-ordinate, while the $\mathrm{Fe^{III}}$ atom is six-co-ordinate. The bridging interaction produces a tetrahedral distortion of the $[\mathrm{Cu(mnt)_2}]^{2-}$ anion, as well as inequivalencies in the Cu–S bond lengths. The longest Cu–S bond is to the bridging sulphur atom, S(1). The Fe(1)–$\mathrm{N_{porph.}}$ bond lengths are equivalent [Fe(1)–N, av. 2.01(2) Å] within experimental error. The Fe(1)–O(1) bond length of 2.38(1) Å is unusually long, as is the Fe(1)–S(1) bond length of 2.450(1) Å. The iron atom is displaced from the centre of the porphyrin toward S(1) [Fe(1)–$\mathrm{Ct_N}$ 0.12 Å ($\mathrm{Ct_N}$ is the centroid of the porphyrin ring as defined by the four nitrogen atoms)].

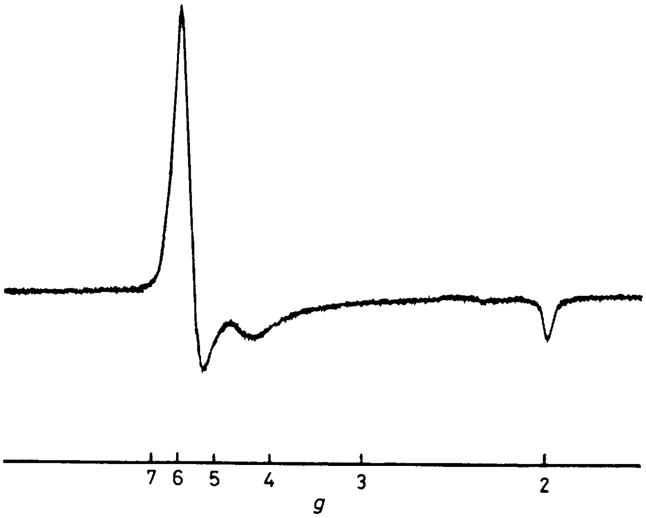

Figure 2. E.s.r. spectrum of a solution of (**3**) in 1,2-dichlorobenzene at 4.7 K.

The $\mathrm{Fe^{III}}$ atom in the $[\mathrm{Fe(tpp)(thf)_2}]^+$ cation is also six-co-ordinate. The Fe(2)–$\mathrm{N_{porph}}$ bond lengths are equivalent within experimental error [Fe(2)–N, av. 2.03(1) Å] and the Fe(2)–O bond lengths [2.29(1) and 2.20(1) Å] are unusually long. The Fe(2) atom is displaced slightly from the centre of the porphyrin toward the more strongly bound thf oxygen atom [Fe(2)–$\mathrm{Ct_N}$ 0.04 Å].

The metric parameters characteristic of the co-ordination about Fe(1) and Fe(2) do not allow unambiguous conclusions regarding the spin states of the $\mathrm{Fe^{III}}$ atoms in (**3**). Scheidt and Reed[8] have summarized the structural parameters expected for intermediate spin (S = 3/2) and quantum mechanically admixed (S = 3/2, 5/2) iron(III) porphyrin systems. In both cases, Fe–$\mathrm{N_{porph.}}$ bond lengths should be short (Fe–$\mathrm{N_{porph}}$ ≈ 1.98—2.00 Å for six-co-ordinate S = 3/2[8,9] and 1.99—2.01 Å for six-co-ordinate S = 3/2,5/2[8,10,11]) relative to the six-co-ordinate high spin case (Fe–$\mathrm{N_{porph.}}$ ≈ 2.04—2.06 Å[8,12]), and six-co-ordinate examples should exhibit long axial bonds. The Fe atom should be roughly centred in the porphyrin plane for the S = 3/2 case, and should probably be similarly centred for a six-co-ordinate S = 3/2,5/2 admixed spin system.

In the dinuclear anion of (**3**), the average Fe(1)–$\mathrm{N_{porph.}}$ bond length is short, suggesting considerable S = 3/2 character for this iron atom. The slightly longer Fe(2)–$\mathrm{N_{porph.}}$ bond lengths are still less than the values characteristic of high spin systems. Axial bonds in both cases are relatively long. $\mathrm{Fe^{III}_{porph.}}$–S bonds are generally[13] in the range 2.30—2.36 Å [*cf.* Fe(1)–S(1) 2.450(1) Å above], although in (**2**) $\mathrm{Fe^{III}}$–S bond lengths of 2.444(2) and 2.549(2) Å were observed.[6] In the $[\mathrm{Fe^{III}(oep)(thf)_2}]^+$ cation (oep = octaethylporphyrinato),[9] the Fe–O bond length was 2.19(1) Å [*cf.* Fe(1)–O(1) 2.38(1), Fe(2)–O av. 2.25 Å, above]. The Fe–$\mathrm{Ct_N}$ distances [Fe(1)–$\mathrm{Ct_N}$ 0.12, Fe(2)–$\mathrm{Ct_N}$ 0.04 Å] are low. On the basis of the metric results, the $\mathrm{Fe^{III}}$ atoms in (**3**) are most likely to be intermediate spin or admixed spin (S = 3/2,5/2) in character. We plan to use low temperature X-ray diffraction data for (**3**) to improve the rather high R values that characterize the room temperature structure and to strengthen the spin state inferences that can be drawn from the metric parameters.

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† (a) $\mathrm{Fe^{II}(tpp)}$ (0.075 mmol) was dissolved in thf (60 ml) under an N_2 atmosphere. A solution of $[\mathrm{TBA}][\mathrm{Cu^{III}(mnt)_2}]$ (0.075 mmol) in thf (20 ml) was added, and the reaction mixture was stirred for 2.5 h. Vapour diffusion of n-hexane into the reaction solution over a period of one week yielded dark crystals of (**3**) (72% yield). (b) Compound (**3**) can also be prepared by recrystallization of the trinuclear compound (**1**) from thf under an N_2 atmosphere. In a typical case, (**1**) (0.006 mmol) was dissolved in thf (100 ml); vapour diffusion with a n-hexane–thf mixture (4 : 1) over a period of one week yielded dark crystals of (**3**) (74% yield).

Products obtained by methods (a) and (b) above exhibited identical visible spectra and unit cell parameters.

‡ *Crystal data* for (**3**): $\mathrm{C_{116}H_{96}CuFe_2N_{12}O_5S_4}$; triclinic; T = 20(1) °C, a = 11.622(2), b = 13.582(2), c = 16.696(2) Å, α = 83.60(1), β = 74.91(1), γ = 88.60(1)°, U = 2528.7(5) Å^3; space group $P1$, Z = 1; Mo-K_α radiation (λ = 0.7107 Å); 9274 reflections were measured of which 7670 with $F \geqslant 2.5\,\sigma(F)$ were used in the solution and refinement (data/parameters = 9.25) to give R = 0.114 and R_w = 0.151, g.o.f. = 1.23. The structure was solved by using the direct methods routine RANT, written by G. M. Sheldrick. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The value of μ_{eff} for (**3**) in the solid state levels off above 220 K to a value of 7.26 μ_B.[14] This value is close to the spin only value of 7.28 μ_B that may be calculated for a non-interacting (or very weakly interacting) assemblage of the following spin states: Fe^{III} (S = 5/2), Fe^{III} (S = 3/2), Cu^{II} (S = 1/2). At low temperatures, the magnetic susceptibility data suggest weak spin interactions, but an unambiguous spin assignment for the two iron atoms cannot yet be made. E.s.r. spectra of a frozen solution of (**3**) (Figure 2) or of powdered solid (**3**) exhibit signals typical of intermediate or high spin Fe^{III}; no Cu^{II} signal is present (g = 2.0). Double integration of the frozen solution spectrum, using $[Fe(tpp)(OSO_2CF_3)]$ as a standard, indicates that only 50% of the iron in the sample is observed. We attribute the observed signal to the Fe^{III} atom of the $[Fe(tpp)(thf)_2]^+$ counterion; the sulphur-bridged Fe^{III} and Cu^{II} atoms of the dinuclear anion are therefore not seen in the e.s.r. spectrum. Based on our previous work with (**1**) and (**2**), it seems unlikely that the e.s.r. silence of the Fe^{III}–Cu^{II} anion in (**3**) is due to strong antiferromagnetic coupling. The second mechanism above seems more likely, *i.e.* relaxation broadening mediated by a small degree of exchange coupling through the bridging sulphur atom.

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