Formation of a novel tetranuclear iron(III) complex with a μ_4-PO_4 bridge from 4-nitrophenyl phosphate

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A novel tetranuclear iron(III) complex, $[\{Fe_2(tren)_2(\mu\text{-}O)\}_2(\mu_4\text{-}PO_4)][ClO_4]_5\cdot 2.5H_2O$ 1 [tren = tris(2-aminoethyl)amine], is synthesized; X-ray crystal structure analysis reveals that 1 contains a tetranuclear cation in which the iron atoms are linked by a μ_4-PO_4^{3-} bridge, which is a hydrolytic product from 4-nitrophenyl phosphate.

The important and diversified roles of iron in biology have long been recognized and intensively studied. Non-heme iron proteins, besides iron–heme and iron–sulfur proteins, have attracted intensive attention in recent years.[1] This class of iron proteins contain either mono- or oxo-bridged binuclear or polynuclear iron cores, such as those found in hemerythrin, ribonucleotide reductase, purple acid phosphatase and ferritin.[1] Therefore, tremendous efforts have been devoted to the synthesis and characterization of binuclear and polynuclear iron model complexes to facilitate the understanding of structure and function of nonheme iron proteins. Hitherto, at least two tetranuclear iron(III) complexes were found to occur in nature.[2] Almost all of the synthetic tetranuclear iron(III) compounds can be envisaged as dimers of dimers, at least in terms of their molecular architecture.[3–9] These complexes can be further classified into three structure types: the first is termed 'butterfly' with a $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ core[3] or $[Fe_4(\mu_3\text{-}OR)_2]^{10+}$ (R = H, Me) cores;[4,5] the second contains a distorted adamantane-like $[Fe_4(\mu\text{-}X)_2(\mu\text{-}OH)_2(\mu\text{-}O)_2]^{4+}$ (X = hydroxo, alkoxo or phenoxo) cores;[6] and the third can be viewed as consisting of two well separated $Fe_2(\mu\text{-}X)(\mu\text{-carboxylato})_n$ (X = O, OH, alkoxo; n = 1, 2) cores,[7–9] which are linked through two non-interacting hydrocarbon tethers,[7] two oxo[8] or two alkoxy[9] bridges. Another interesting tetranuclear iron(III) system contains a 'metallocrown' core which consists of an $(Fe\text{–}N\text{–}O)_3$ ring capped by another iron(III).[10]

In our effort to synthesize model complexes for purple acid phosphatase which catalyzes the hydrolysis of certain phosphate esters under acidic conditions,[1] a novel tetranuclear iron(III) complex, $[\{Fe_2(tren)_2(\mu\text{-}O)\}_2(\mu_4\text{-}PO_4)][ClO_4]_5\cdot 2.5H_2O$ **1** was produced. The most interesting aspect of **1** is that the bridging PO_4^{3-} group was a hydrolytic product of a phosphate monoester which was used as a precursor together with an iron(III) polyamine complex in our synthetic reaction. This suggests that the iron(III) polyamine actually expedites the hydrolytic cleavage of the ester bond in the phosphate monoester, a process likely involving a two- or poly-metal mechanism. To the best of our knowledge, this is the first example of a tetranuclear iron(III) complex in which the four iron(III) are linked with a μ_4-PO_4^{3-} bridge. Here we report the synthesis and structural characterization of the novel compound **1**.

When 4-nitrophenyl phosphate was treated with a methanol solution of Fe^{III} and tren, a green solid was readily formed. The tetranuclear iron(III) complex **1** was isolated by filtration.† Its structure was determined by single crystal X-ray analysis.‡ Two other products were also obtained when the filtrate was evaporated in air. One is yellow and spectral analysis shows that it is 4-nitrophenol which is another hydrolytic product from 4-nitrophenyl phosphate. The second product is red and is insoluble in common organic solvents. Its IR and Raman spectra show that it may be a mononuclear iron(III) complex containing tren and 4-nitrophenyl phosphate ligands, but no ClO_4^- anion.

The cation structure in complex **1** is shown in Fig. 1. Four iron centers, each chelated by a tetradentate tren ligand, are connected pairwise by two μ-oxo and further consolidated by a tetradentate phosphate. The complex can thus be viewed as consisting of two (tren)Fe–O–Fe(tren) units with a central tetradentate PO_4^{3-} group bridging all four irons. The two 'dimers' are structurally similar but crystallographically independent. The Fe–O(oxo) distances and Fe–O–Fe angles fall in the normal range.[1a] However, the bond lengths of Fe(3)–O(6) [1.813(6) Å] and Fe(4)–O(6) [1.822(6) Å] are slightly longer than those of Fe(1)–O(5) [1.805(6) Å] and Fe(2)–O(5) [1.785(6) Å], the angle Fe(3)–O(6)–Fe(4) [129.4(3)°] is smaller than that of Fe(1)–O(5)–Fe(2) [134.2(3)°], and the distance of Fe(3)···Fe(4) (3.286 Å) is slightly shorter than that of Fe(1)···Fe(2) (3.307 Å). This can be elucidated by the formation of a hydrogen bond between the bridging O(6) and a neighboring water molecule [O(6)···O(1w) 2.743 Å]. The presence of this hydrogen bond confers a partial hydroxo character to O(6) and results in elongation of the Fe–O(6) bond

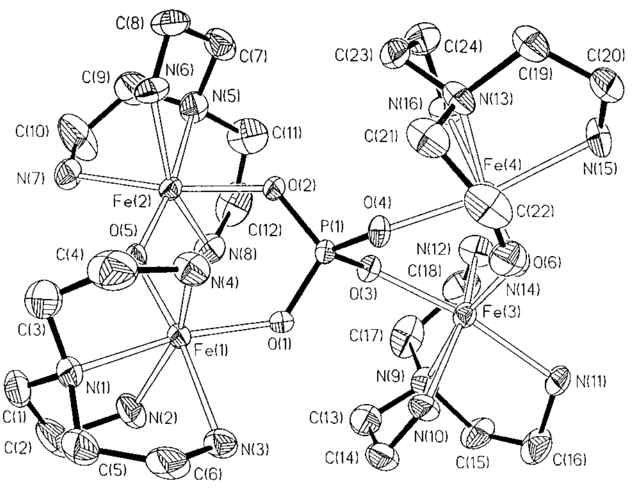

Fig. 1 Structure of the tetranuclear iron cation in **1**. Selected interatomic distances (Å) and angles (°): Fe(1)···Fe(2) 3.307, Fe(3)···Fe(4) 3.286, Fe(1)···Fe(3) 5.768, Fe(1)···Fe(4) 5.942, Fe(2)···Fe(3) 6.014, Fe(2)···Fe(4) 6.013, Fe(1)–O(1) 1.955(6), Fe(1)–O(5) 1.805(6), Fe(1)–N(1) 2.204(8), Fe(1)–N(2) 2.180(9), Fe(1)–N(3) 2.223(8), Fe(1)–N(4) 2.195(8), Fe(2)–O(2) 2.008(6), Fe(2)–O(5) 1.785(6), Fe(2)–N(5) 2.237(8), Fe(2)–N(6) 2.163(8), Fe(2)–N(7) 2.177(8), Fe(2)–N(8) 2.216(8), Fe(3)–O(3) 2.005(6), Fe(3)–O(6) 1.813(6), Fe(3)–N(9) 2.225(8), Fe(3)–N(10) 2.185(8), Fe(3)–N(11) 2.196(8), Fe(3)–N(12) 2.182(9), Fe(4)–O(4) 1.984(6), Fe(4)–O(6) 1.822(6), Fe(4)–N(13) 2.231(8), Fe(4)–N(14) 2.172(8), Fe(4)–N(15) 2.197(8), Fe(4)–N(16) 2.186(8); Fe(1)–O(5)–Fe(2) 134.2(3), Fe(3)–O(6)–Fe(4) 129.4(3), Fe(1)–O(1)–P(1) 131.5(3), Fe(2)–O(2)–P(1) 129.9(4), Fe(3)–O(3)–P(1) 126.1(3), Fe(4)–O(4)–O(4) 130.7(3).

distances, narrowing of the Fe(3)–O(6)–Fe(4) angle, and shortening of the Fe(3)···Fe(4) distance. Furthermore, there is a small but significant structural *trans* influence exerted by the oxo-bridges on each of the four iron atoms in complex **1**. The four P–O lengths (av. 1.533 Å) and P–O–P angles (av. 109.8°) are almost equivalent within experimental error, indicating the trianionic charge of the PO_4^{3-} is equally distributed over the four oxygen atoms of the phosphate. The phosphate can therefore be viewed as an ideal tetrahedron. All of the lattice water molecules are found to be involved in hydrogen bonds either to perchlorate [O(2w)···O(18) 2.841, O(2w)···O(21) 2.930, O(3w)···O(25) 2.426 Å] or toμ-oxo [O(6)···O(1w) 2.743 Å].

The UV–VIS spectrum of **1** in acetonitrile exhibits rich features in the 400–500 nm region similar to those of other tetranuclear iron(III) compounds.[7] It displays three strong absorption bands at *ca*. 213, 237 and 320 nm, which are readily assigned to the intraligand transitions. The weak band at *ca*. 693 nm is due to a ligand field transition. The IR spectrum of **1** shows two strong peaks at *ca*. 1145 and 978 cm^{-1} which are characteristic of PO_4^{3-} stretch vibrations. The peak at 778 cm^{-1} can be assigned to the asymmetric Fe–O–Fe stretch vibration, comparable with that found in other oxo-bridged iron(III) compounds.[3b,6a,b,7a,b,8] The symmetric stretch vibration of the Fe–O–Fe unit is Raman active and was found at 464 cm^{-1} in the Raman spectrum of **1**.

Although quite a few tetranuclear iron(III) complexes have been synthesized, almost all of them are bridged by carboxylate ligands. Hence **1** provides the first example of a tetranuclear iron(III) complex linked by a tetradentate phosphate. The most interesting observation in this reaction is that the phosphate monoester undergoes hydrolysis in the presence of the iron(III) polyamine complex, and the intermediate PO_4^{3-} anion functions in the μ_4-mode to generate tetranuclear iron complex **1**. This may involve either a two- or poly-metal mechanism in the hydrolysis reaction. Complex **1** also provides a good model for the hydrolysis of phosphate ester *in vivo* by purple acid phosphatase. Study of the detailed mechanism of the hydrolysis of phosphate mono-, di- and tri-esters by iron polyamine complexes is in progress.

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Footnotes and References

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† *Preparation of* **1**: to a red solution of methanol (10 ml) containing $Fe(ClO_4)_3·9H_2O$ (0.492 g, 1 mmol) was added tren (0.15 g, 1.03 mmol) dissolved in methanol (10 ml) with stirring at room temp. After stirring for 20 min, to the brown solution was added $Na_2(O_2NC_6H_4OPO_3)·6H_2O$ (0.19 g, 0.51 mmol), the solution turned graminaceous in a few minutes, followed by precipitation of the complex as a green powder. The mixture was further stirred for 4 h and filtered. The green solid was dissolved in MeCN (5 ml) and filtered, and dark-green crystals were obtained by diffusing ethyl acetate into the acetonitrile solution. Anal. Found: C, 19.21; H, 5.40; N, 14.95. Calc. for $C_{24}H_{77}Cl_5Fe_4N_{16}O_{28.5}P$: C, 19.49; H, 5.21; N, 15.16%. UV–VIS spectrum (MeCN): λ_{max} = 213 nm (ε = 4.5 × 10^4 dm^3 mol^{-1} cm^{-1}), 237 (4.7 × 10^4), 320 (3.4 × 10^4), 362 (sh), 415 (sh), 448 (712), 490 (540), 693 (br, 120). IR data (ν/cm^{-1}, KBr pellet): 1145s ($\nu_{P–O}$), 1113–1088s ($\nu_{Cl–O}$ + $\nu_{P–O}$), 978s ($\nu_{P–O}$), 778m ($\nu_{Fe–O–Fe}$) 627s ($\nu_{Cl–O}$). Raman shift (cm^{-1}): 1026 ($\nu_{P–O}$), 941 ($\nu_{Cl–O}$), 627 ($\nu_{Cl–O}$), 464 ($\nu_{Fe–O–Fe}$).

‡ *Crystal data* for **1**: $C_{24}H_{77}Cl_5Fe_4N_{16}O_{28.5}P$, M = 1477.64, monoclinic, space group $P2_1/c$ (no. 14), a = 11.749(3), b = 17.357(2), c = 28.271(4) Å, β = 97.41(1)°, U = 5721.9(4) Å^3, Z = 4, D_c = 1.715 g cm^{-3}, μ = 1.351 mm^{-1}; 7873 independent reflections were collected, of which 7870 were used in the F^2 refinement; R = 0.071 [5347 observed reflections with $I > 2\sigma(I)$]. The intensities were collected at 293 K on a Siemens P4 diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The crystal structure was solved by direct methods. Two of the five independent perchlorate groups exhibit two-fold orientational disorder. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were placed in calculated positions with C–H 0.96 Å, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. All computations were carried out on a PC-486 using the SHELXTL-PC program package. CCDC 182/659.

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