The First Binuclear Iron(III) Complex with a Terminally Coordinated Phosphato Ligand—A Model Compound for the Oxidized Form of Purple Acid Phosphatase from Beef Spleen

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Reaction of *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane dihydrochloride (Htbpo·2HCl) with $Fe(ClO_4)_3·9H_2O$ and diphenylphosphate yields red crystals of $[Fe_2Cl_2\{O_2P(OPh)_2\}(tbpo)(MeOH)](ClO_4)_2·3MeOH$; the X-ray structure shows a phosphate ligand terminally coordinated to Fe(2) and a methanol ligand coordinated to Fe(1).

Purple acid phosphatases (PAP) catalyse the hydrolysis of activated phosphoric acid esters under acidic conditions.[1] The purple, inactive forms of uteroferrin[1b] and of the photosphatase isolated from bovine spleen contain Fe^{III}–Fe^{III} units in their active sites, and are characterized by typical absorption maxima at λ_{max} = 550–570 nm.[1a] The centre of the catalytical active, pink species consists of a Fe^{II}–Fe^{III} core, the absorption maximum of which is shifted to higher frequencies (505–515 nm).[1a] The proposed structure of the inactive form of PAP from bovine spleen exhibits a terminally coordinated phos-

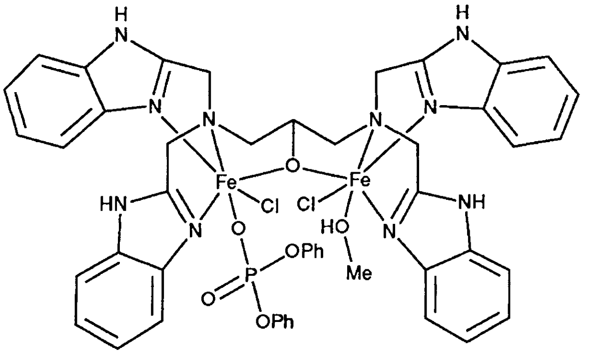

Fig. 1 Schematic structure of **1**

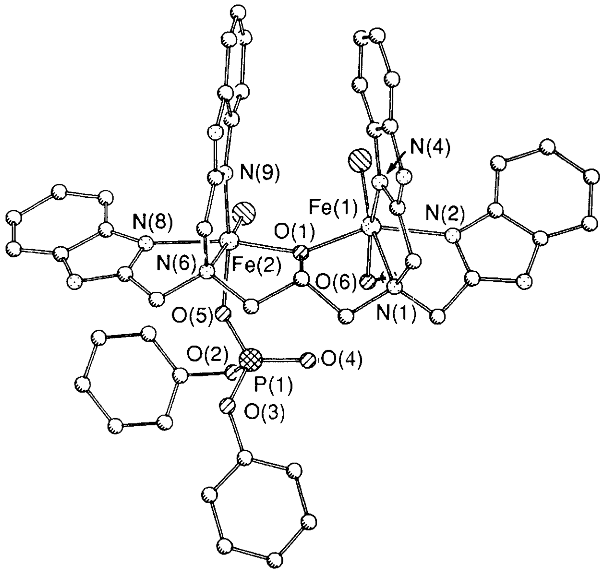

Fig. 2 Structure of the cation $[Fe_2Cl_2\{O_2P(OPh)_2\}(tbpo)(MeOH)]^{2+}$ in crystals of **1**. Selected bond lengths (Å) and angles (°): Fe(1)···Fe(2); 3.700(2), Fe(2)···P(1) 3.346(2), Fe(1)–O(1) 2.011(4), Fe(2)–O(1) 2.056(4), Fe(1)–O(6) 2.053(3), Fe(2)–O(5) 1.996(4), Fe(1)–N(1) 2.295(4), Fe(1)–N(2) 2.120(5), Fe(1)–N(4) 2.106(4), Fe(2)–N(6) 2.276(4), Fe(2)–N(8) 2.138(5), Fe(2)–N(9) 2.073(4), P(1)–O(2) 1.587(4), P(1)–O(3) 1.589(4), P(1)–O(4) 1.486(5), P(1)–O(5) 1.494(4), Fe(1)–O(1)–Fe(2) 130.9(2).

phato ligand which is bound to the non-reduceable Fe^{III} ion—according to spectroscopic, magnetic and EXAFS investigations.[1d,g]

In terms of the synthesis of model complexes for the inactive form of PAP, a coordination—especially a terminal—of phosphate or phosphate esters to binuclear Fe^{III} cores is of extraordinary importance.

Recently, diiron(II,III) and diiron(III,III) model compounds containing a bridging coordination of phosphate and phosphate esters have been synthesized and characterized in some cases.[2,3] Nevertheless, all attempts to produce a diiron complex with a terminal coordination of a phosphato ligand have been unsuccessful so far.

We report here the first binuclear iron(III) complex with a terminally coordinated phosphato ligand, the novel mode of coordination of which may be a model for the proposed structure of the Fe^{III}–Fe^{III} form of PAP.

N,N,N',N'-Tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane (Htbpo), which has proven to be suitable for the synthesis of binuclear metal complexes,[4] was used as a ligand. Reaction of a double molar amount of $Fe(ClO_4)_3 \cdot 9H_2O$ in methanol with equimolar amounts of Htbpo dihydrochloride and diphenylphosphate leads, after addition of small amounts of triethylamine, to red crystals of $[Fe_2Cl_2\{O_2P(OPh)_2\}(tbpo)(MeOH)](ClO_4)_2 \cdot 3MeOH$ **1**. A schematic structure of **1** is shown in Fig. 1. The structure of **1** (Fig. 2)† reveals that the Fe^{III} ions in the binuclear complex are coordinated by the heptadentate ligand $tbpo^-$; each metal atom is bound to two benzimidazole moieties, to one tertiary nitrogen atom as well as to the bridging alkoxo oxygen atom. The distorted octahedral environment of Fe(1) is completed by the chloro ligand Cl(1) and a methanol ligand, whereas Fe(2) is bound to the chloro ligand Cl(2) and the terminal diphenylphosphate ligand. According to recent studies on PAP from bovine spleen,[1e] the Fe···Fe distance in **1** [3.700(2) Å] is very similar to that postulated for the enzyme. However, because of the missing bridging ligands, it is larger than that found in the tetranuclear compounds $[Fe_4O_2(tbpo)_2(OBz)_2](ClO_4)_2(OTs)_2$ and $[Fe_4O_2(tbpo\text{-}Et)_2(OAc)](BF_4)_4$, which exhibit Fe···Fe distances between 3.49 and 3.59 Å in their carboxylato bridged Fe_2 units.[4e]

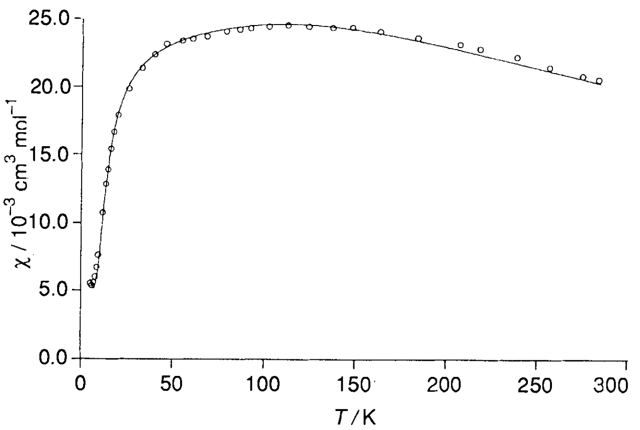

Fig. 3 Magnetic susceptibility of **1** (χ *vs.* T)

The magnetic susceptibility in the range of 4.2 to 284.0 K (Fig. 3) indicates antiferromagnetic behaviour. The values could be fitted based on an isotropic Heisenberg model, $H' = -2\,J \cdot S_1 \cdot S_2$ ($S_1 = S_2 = 5/2$) and $g = 2.0$ (fixed). The coupling constant found for **1** [J −13.7(5) cm^{-1}] represents the typical range for μ-alkoxo or μ-hydroxo bridged binuclear Fe^{III} systems. The magnetic moment decreases from 6.77 μ_B at 284 K to 0.43 μ_B at 4.2 K, which is consistent with antiferromagnetic coupling.

Mössbauer spectroscopic investigations confirm the existence of octahedral Fe^{III} ions. The values for isomeric shifts (δ) (referred to metallic iron at 298 K) and quadrupole splittings (ΔE_Q) are: $\delta = 0.46$ mms^{-1} and $\Delta E_Q = 0.59$ mms^{-1} at 295 K and $\delta = 0.59$ mms^{-1} and $\Delta E_Q = 0.55$ mms^{-1} at 4.2 K.[5]

The electronic spectrum of **1** in methanol shows absorption maxima at $\lambda_{max} = 247$ nm (ε *ca.* 26100 cm^{-1} mol^{-1}), $\lambda_{max} = 273$ nm (ε *ca.* 32000 cm^{-1} mol^{-1}), $\lambda_{max} = 279$ nm (ε *ca.* 29900 cm^{-1} mol^{-1}) and $\lambda_{max} = 330$ nm (sh, ε *ca.* 6410 cm^{-1} mol^{-1}). An absorption maximum in the region of the charge transfer transition in PAP (500–600 nm) could not be observed in **1** owing to the absence of phenolate oxygen donors.

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† *Crystal data* for **1**: $C_{51}H_{59}N_{10}Cl_4Fe_2O_{17}P$, $M = 1368.56$, triclinic, space group $P\bar{1}$, $a = 13.194(5)$, $b = 13.252(6)$, $c = 17.748(5)$ Å, $\alpha = 87.51(3)$, $\beta = 84.69(3)$, $\gamma = 72.56(3)°$, $Z = 2$, $V = 2947.2$ Å^3, $D_c = 1.54$ g cm^{-3}, $D_m = 1.52$ g cm^{-3}. With the use of 8400 unique reflections [$I > 1.96\,\sigma(I)$] collected at 140 K with Mo-$K\alpha$ (λ 0.71069 Å) radiation out to $2\theta = 54°$ on a single crystal X-ray diffractometer (Siemens), the structure was solved by standard direct and difference Fourier methods (program SHELXTL PLUS) and refined by using 761 parameters to a current value of discrepancy index $R = 0.0632$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue no. 1, 1991.

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References

1 (*a*) B. C. Antanaitis and P. Aisen, *Adv. Inorg. Biochem.*, 1983, **5**, 111; (*b*) R. B. Lauffer, B. C. Antanaitis, P. Aisen and L. Que, Jr., *J. Biol. Chem.*, 1983, **258**, 14212; (*c*) J. T. Sage, Y.-M. Xia, P. G. Debrunner, D. T. Keough, J. de Jersey and B. Zerner, *J. Am. Chem. Soc.*, 1989, **111**, 7239 and references cited therein; (*d*) B. A. Averill, J. C. Davis, S. Burman, T. Zirino, J. Sanders-Loehr, T. M. Loehr, J. T. Sage and P. G. Debrunner, *J. Am. Chem. Soc.*, 1987, **109**, 3760; (*e*) D. Münstermann, M. Dietrich, H. Suerbaum and H. Witzel, *Eur. J. Biochem.*, in the press; (*f*) K. Cichutek, H. Witzel and F. Parak, *Hyperfine Interactions*, 1988, **42**, 885; (*g*) S. M. Kauzlarich, B. K. Teo, T. Zirino, S. Burman, J. C. Davis and B. A. Averill, *Inorg. Chem.*, 1986, **25**, 2781.

2 K. Schepers, B. Bremer, B. Krebs, G. Henkel, E. Althaus, B. Mosel and W. Müller-Warmuth, *Angew. Chem.*, 1990, **102**, 582; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 531.

3 (*a*) S. Drüeke, K. Wieghardt, B. Nuber, J. Weiss, H. P. Fleischhauer, S. Gehring and W. Haase, *J. Am. Chem. Soc.*, 1989, **111**, 8622; (*b*) W. H. Armstrong and S. J. Lippard, *J. Am. Chem. Soc.*, 1985, **107**, 3730; (*c*) P. N. Turowski, W. H. Armstrong, M. E. Roth and S. J. Lippard, *J. Am. Chem. Soc.*, 1990, **112**, 681; (*d*) S. Yan, D. D. Cox, L. L. Pearce, C. Juarez-García, L. Que, Jr., J. H. Zhang and C. J. O'Connor, *Inorg. Chem.*, 1989, **28**, 2507; (*e*) R. E. Norman, S. Yan, L. Que, Jr., G. Backes, J. Ling, J. Sanders-Loehr, J. H. Zhang and C. J. O'Connor, *J. Am. Chem. Soc.*, 1990, **112**, 1554.

4 (*a*) T. Sakurai, H. Kaji and A. Nakahara, *Inorg. Chim. Acta*, 1982, **67**, 1; (*b*) V. McKee, M. Zvagulis, J. V. Dagdigian, M. G. Patch and C. A. Reed, *J. Am. Chem. Soc.*, 1984, **106**, 4765; (*c*) Y. Nishida, M. Takeuchi, H. Shimo and S. Kida, *Inorg. Chim. Acta*, 1984, **96**, 115; (*d*) P. Mathur, M. Crowder and G. C. Dismukes, *J. Am. Chem. Soc.*, 1987, **109**, 5227; (*e*) Q. Chen, J. B. Lynch, P. Gomez-Romero, A. Ben-Hussein, G. B. Jameson, C. J. O'Connor and L. Que, Jr., *Inorg. Chem.*, 1988, **27**, 2673.

5 B. Bremer, K. Schepers and B. Krebs, unpublished results.