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Title:	Bio-mimetic of catecholase and phosphatase activity by a tetra-iron(III) cluster
Authors:	Yadav, H.R. (/jspui/browse?type=author&value=Yadav%2C+H.R.) Choudhury, A.R. (/jspui/browse?type=author&value=Choudhury%2C+A.R.)
Keywords:	Iron X-ray structure Electrochemistry Catecholase activity Phosphatase study
Issue Date:	2019
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Citation:	Polyhedron
Abstract:	<p>An oxido- and acetato-bridged tetranuclear iron(III) cluster, $[\text{Fe}_4\text{III}(\mu\text{-O})_2(\mu\text{-OAc})_6(\text{phen})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_3$ (1), [OAc = acetate; phen = 1,10-phenanthroline] has been prepared in the crystalline phase. X-ray structural analysis of the compound reveals that all the Fe(III) centres in 1 adopt an octahedral coordination geometry and the tetra-iron(III) core exists in an unusual asymmetric conformation. Bond valence sum (BVS) calculations recommend the existence of all iron ions in the +3 oxidation state in the crystalline phase. The tetra-iron(III) cluster elegantly catalyzes the oxidation of 3,5-di-tert-butylcatechol (DTBC), viz. catecholase-like activity, with a good turnover number, $k_{\text{cat}} = 9.28 \times 10^2 \text{ h}^{-1}$ in acetonitrile medium. Spectrophotometric titration shows the existence of two distinct isosbestic points, which unanimously proves the rarely observed enzyme-substrate binding phenomenon in solution. Electrochemical analysis recommends the production of Fe(II)-semiquinone species in the course of the catalytic oxidation of DTBC. Furthermore, the same iron(III) cluster displays phosphoester cleavage activity towards the disodium salt of p-nitrophenylphosphate (PNPP) in aqueous-methanol medium with rate of $7.20 \times 10^{-4} \text{ m}^{-1}$. ESI-MS measurements of the tetra-iron(III) complex in the presence of PNPP indicate the formation of an organophosphorus intermediate in solution and solvent aqua molecules probably make a nucleophilic attack on the phosphorus centre, favouring the generation of the organophosphorus intermediate.</p>
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