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Bio-relevant manganese(II) compartmental ligand complexes: Syntheses, crystal structures and studies of catalytic activities

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ABSTRACT

Three new mono-manganese(II) complexes of a compartmental ligand, namely $[Mn(HL)(H_2O)_3](NO_3)_2\cdot H_2O$ (**1**), $[Mn(HL)(SCN)_2(H_2O)]\cdot H_2O$ (**2**), and $[Mn(HL)\{N(CN)_2\}(H_2O)_2](NO_3)\cdot H_2O$ (**3**), where L = 2,6-bis{2-(N-ethyl)pyridineiminomethyl}-4-methylphenolato, have been synthesized and characterised by routine physicochemical techniques and complexes **1**, **2** also by X-ray single crystal structure analysis. All the mono nuclear complexes contain Mn^{II} high spin species at octahedral core as evidenced by magnetic moment (measured at 300 K) and EPR study at 77 K. As revealed by crystal structure analyses, the protonation of one imine nitrogen atom of the potential dinucleating ligand L hampers to form the expected dinuclear Mn^{II} complex. However, complexes **1**–**3** show excellent catecholase-like activity with both 3,5-di-*tert*-butylcatechol and tetrachlorocatechol as substrates. In addition complexes **1** and **2** also exhibit phosphatase activity, while **3** forms an adduct with *p*-nitrophenyl phosphate as substrate. To the best of our knowledge this is the first report of Mn^{II} complexes being able to catalyze the oxidation of TCC to TCQ. Catecholase and phosphatase activities have been monitored by UV–vis spectrophotometer and Michaelis–Menten equation has been applied to rationalize all the kinetic parameters where complex **1** shows maximum k_{cat} value followed by **2** and **3** (where for phosphatase activity **3** only forms an adduct).

1. Introduction

Phenol based compartmental ligands are of current interest to the bio-inorganic chemists as the most desirable target to synthesize dinuclear complexes as corroborative models of some metallobiosites namely catechol oxidase, urease, catalase etc. [1–12]. Recently our group have got excellent results while working with phenol based compartmental ligand complexes of Ni^{II}, Cu^{II} and Zn^{II} [13]. Manganese is one of the most important trace transition element in biological systems, being present in several metalloenzymes of varied nuclearity. Literature survey reveals that although manganese is one of the most important trace transition element in biological systems (being present in several metalloenzymes with varying nuclearity, e.g. mononuclear manganese species exist in superoxide dismutase [14] and manganese dioxygenase [15], as dinuclear species in catalase [16,17], ribonucleotide reductase [18], and arginase [19] and as the tetra nuclear cluster found in the oxygen evolving complex (OEC) of photo system II (PS II) [20–24]) the reports on bio-relevant catalytic activities of manganese(II) compartmental ligand complexes are surprisingly scanty.

We started this work with the goal to generate manganese mimics of catecholase [dicopper(II) containing type-III copper protein] and of phosphatase [dizinc(II) containing hydrolase enzyme] since such reports are rare in literature. In order to stabilize manganese in its +2 oxidation state, we have accordingly designed a phenol based compartmental ligand, 2,6-bis{2-(N-ethyl)pyridineiminomethyl}-4-methylphenolato (L) as depicted in Scheme 1, a system having vacant π^* orbitals, necessary condition to stabilize metals in low oxidation states. Interestingly, instead of getting dinuclear manganese(II) complexes we have obtained mono-manganese(II) species, $[Mn(HL)(H_2O)_3](NO_3)_2\cdot(H_2O)$ (**1**), $[Mn(HL)(SCN)_2(H_2O)]\cdot 0.5H_2O$ (**2**) and $[Mn(HL)\{N(CN)_2\}(H_2O)_2](NO_3)\cdot H_2O$ (**3**) most likely due to the protonation of one of the imine nitrogen atoms of the dinucleating ligand, L. As a result of such peculiarities of the structures these three complexes show excellent catalytic activities. Here

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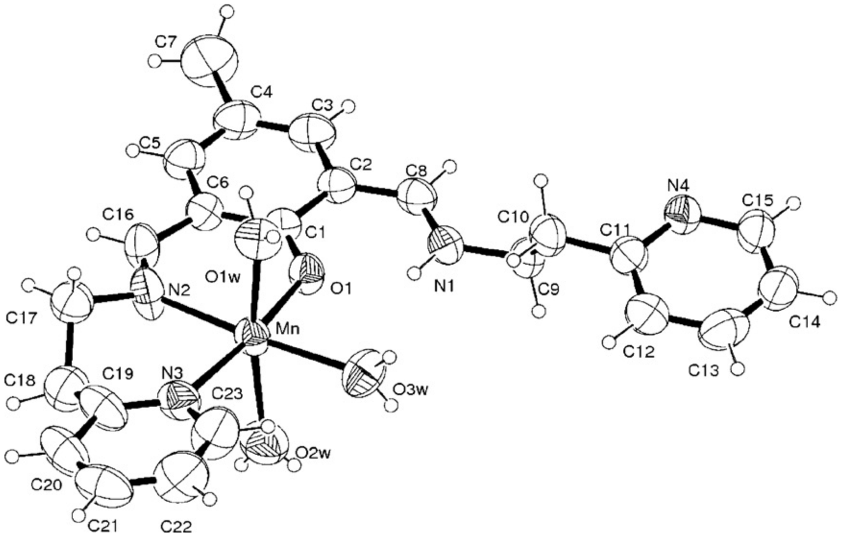

Fig. 1. ORTEP drawing (30% probability ellipsoid) of the complex cation of **1**. Of the disordered ethylene bridge only the C17/C18 atoms at higher occupancy are shown.

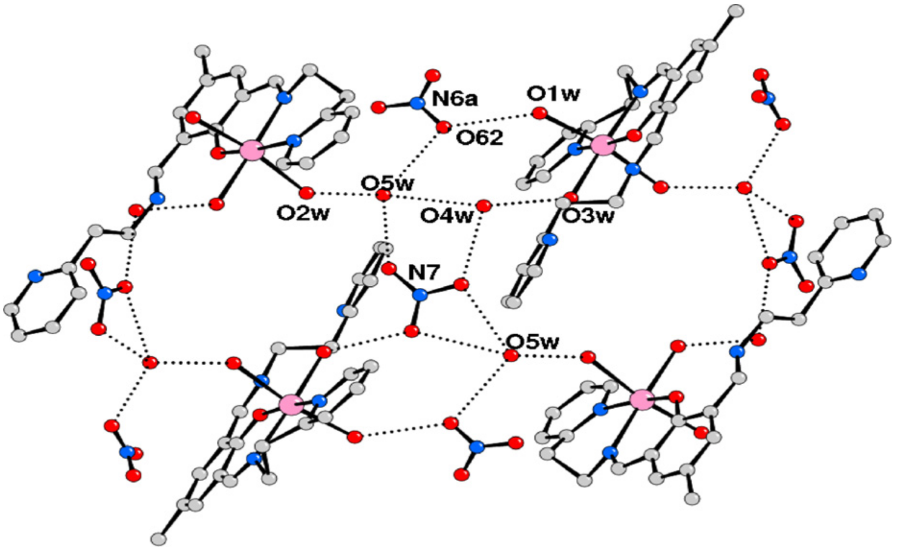

Fig. 2. Detail of the H-bonding pattern in the crystal packing of **1**. Ow4 and nitrate N7 are close to a centre of symmetry and their positions can be interchanged.

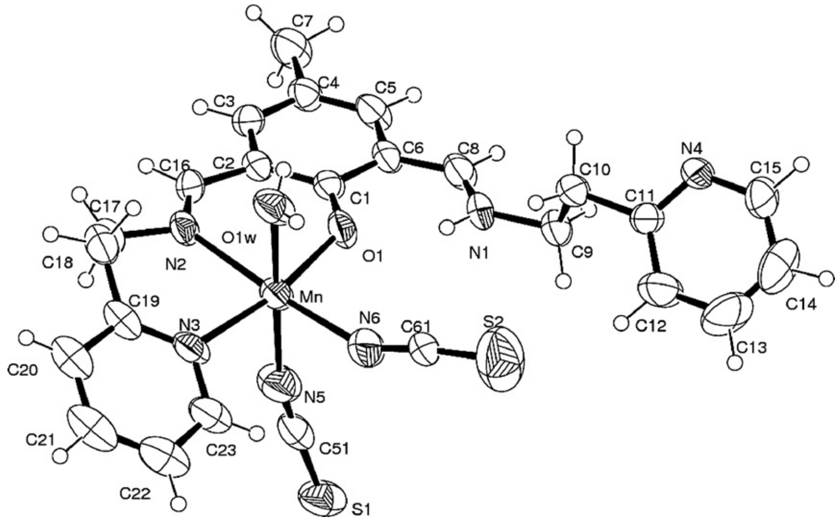

Fig. 3. ORTEP drawing (40% probability ellipsoid) of complex **2**.