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Manganese complexes with acyclic compartmental Schiff bases

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ABSTRACT

The end-off acyclic compartmental ligands H_5-L_A and H_6-L_B have been prepared by [2 + 1] or [3 + 1] condensation of the appropriate amounts of pyridoxal hydrochloride with 1,3-diamine-2-propanol and 3-formylsalicylic acid with tris-2-(aminoethyl)amine, respectively. The ligand H_5-L_A, which contains two adjacent N_2O chambers, bears an endogenous hydroxo potentially bridging group and H_6-L_B, which contains an inner N_4O_3 and an outer O_3O_3 compartment, bears three potentially bridging phenolic groups. The complexes $[Mn_2(H_2\text{-}L_A)(CH_3COO)_2](Cl)\cdot 5H_2O$ and $[Mn(H_3\text{-}L_B)]\cdot 0.25H_2O\cdot CH_3OH$ have been obtained by the template condensation of the appropriate amine and formyl precursors in the presence of $Mn(CH_3COO)_2\cdot 4H_2O$ in methanol. When recrystallized $[Mn_2(H_2\text{-}L_A)(CH_3COO)_2](Cl)\cdot 5H_2O$ undergoes demetalation reaction giving rise to $[Mn(H_3\text{-}L_A)(H_2O)_2](Cl)(H_2O)$ where the octahedral manganese(III) ion is surrounded by two axial water molecules trans with respect to the equatorial plane formed by the two imine nitrogen atoms and the two phenolate oxygen atoms of the Schiff base $[H_3\text{-}L_A]^{2-}$. The central –OH group of $[H_3\text{-}L_A]^{2-}$ does not participate in the coordination. In $[Mn(H_3\text{-}L_B)]\cdot 0.25H_2O\cdot CH_3OH$ the octahedral environment about the manganese(III) ion is reached by the coordination of three carboxylate and three phenolate oxygen atoms of the external O_3O_3 site and the three imine nitrogen atoms are protonated.

Variously shaped acyclic ligands have been prepared in the recent past and successfully used in selective coordination of metal ions. The properties arising from this metalation process were studied in detail by different physico-chemical measurements. Compartmental acyclic ligands, i.e. compounds with two (or more) coordination chambers in close proximity, represented a relevant evolution, owing to their capability to give rise to different, well selective recognition of charged and/or neutral species in their adjacent chambers. These systems quite often are Schiff bases obtained by condensation of suitable formyl- and primary amine precursors [1,2]. The Schiff bases, derived from salicylaldehyde with di- or polyamine are the most widely studied ligands and the related complexes with a variety of metal ions have been used as synthetic oxygen carriers, catalysts for asymmetric epoxidation [3–7], for the synthesis of optical and magnetic materials [8,9], as bio-mimetic catalysts [10–13]. The chain length of the Schiff base manganese complexes, derived from alkoxy-substituted salicylaldehyde, strongly influences the spin crossover, very attractive for device fabrication. Due to their amphiphilic character these complexes can give rise to Langmuir films [13]. Furthermore, Schiff bases of pyridoxal, an analogue of pyridoxine (vitamin B6), and their metal complexes are attractive candidates for screening biological activities. Though Schiff bases derived from pyridoxal and salicylaldehyde are likely to have very similar coordination chemistry, the former ligands are expected to prove superior as supramolecular synthons, because of additional sites for H-bond acceptance and donation [14].

The acyclic compartmental ligands bear endogenous bridging groups (quite often phenolic or alcoholic –OH groups) capable of linking two metal ions, generating complexes with specific chemical and/or physical properties. These ligands can be progressively metalated producing, according to the experimental conditions employed, mononuclear, dinuclear or polynuclear complexes [1,2].

Furthermore, demetalation, site migration and transmetalation processes can occur, generating molecular metal ion movements inside and/or outside the compartmental ligand, which depends on the pH of the solution. These metal ion encapsulation/release processes under specific conditions are quite important for the use of manganese complexes in MR imaging as convincing alternative to the gadolinium(III)-DOTA based complexes. The two typologies of complexes act in different ways: the gadolinium(III) complexes must maintain their integrity, while the manganese complexes, approved for clinical practice, generate relaxation after release of the metal ion, thus originating high relaxivity values [15].

Thanks to the above mentioned ability to give rise to metalation/demetalation processes, the compartmental ligands can offer the basis for the design of highly efficient molecular devices for MRI. Noticeably, the acyclic ligands can be functionalized by inserting appropriate groups in the aliphatic and/or aromatic chains of the formyl- or keto- and amine precursors in order to maintain the metalation/demetalation capability, while changing their properties (i.e. solubility in water) [16]. Following this strategy, reactive groups can be introduced at the periphery of the coordinating moiety,

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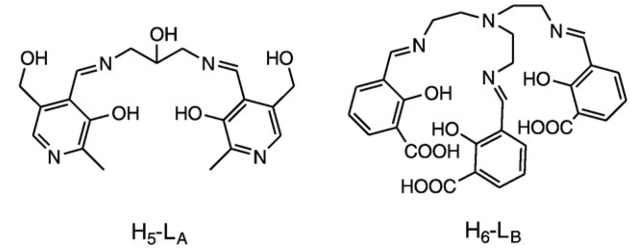

H_5-L_A H_6-L_B

Scheme 1. The [2+1] end-off (H_5-L_A) and the [3+1] polypodal [H_6-L_B) ligands.

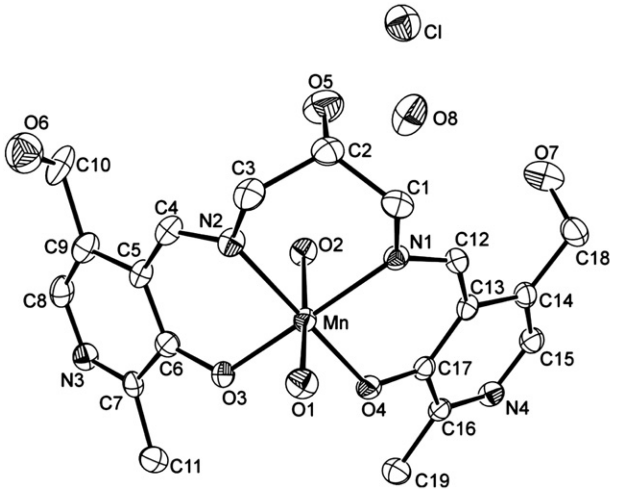

Fig. 1. ORTEP view of [Mn(H_3-L_A)(H_2O)$_2$](Cl)(H_2O) with thermal ellipsoid of 30% probability. Selected bond lengths (Å) and angles (°): Mn-N(1) 2.030(5), Mn-N(2) 2.027(5), Mn-O(1) 2.222(4), Mn-O(2) 2.268(4), Mn-O(3) 1.883(4), Mn-O(4) 1.878(4), N(1)-Mn-N(2) 92.2(2), N(1)-Mn-O(4) 88.7(2), N(2)-Mn-O(3) 88.2(2), O(3)-Mn-O(4) 90.7(2), O(1)-Mn-O(2) 174.1(2), N(1)-Mn-O(3) 177.3(2), N(2)-Mn-O(4) 176.8(2).

making their link to these supports quite feasible. Schiff bases complexes have a potential application in biologic systems as low molecular weight SOD mimics as scavenger of the superoxide anion [16].

In the present paper we report the synthesis and the X-ray structures of manganese(III) complexes with the [2+1] end-off (H_5-L_A) and the [3+1] polypodal (H_6-L_B) systems reported in Scheme 1.

The [2+1] end-off ligand H_5-$L_{A,}$ originated from the reaction of two equivalents of pyridoxal hydrochloride with one equivalent of 1,3-diamine-2-propanol and bearing an OH bridging group between the two primary iminic function, contains two adjacent N_2O donor sets while the [3+1] tripodal ligand H_6-L_B, derived from the condensation of 3-formyl salicylic acid and tris-2-(aminoethyl)amine in a 3:1 molar ratio, contains an inner N_4O_3 and an outer O_3O_3 chamber. Both chambers can act as manganese ion receptors, giving rise, under appropriate experimental conditions, to mono- or dinuclear species. Similar tripodal ligands and the related homo- and heterodinuclear complexes have been prepared and exhaustively characterised [16].

[Mn_2(H_2-L_A)(CH_3COO)$_2$](Cl)·5H_2O, whose occurrence is corroborated by elemental analysis, ESI-MS [17] and the presence of two ν C=O IR bands at 1553 and 1421 cm^{-1} due to the asymmetric and symmetric stretchings of the bidentate acetate groups in addition to the ν C=N bands at 1614 cm^{-1}, derives from the template reaction of pyridoxal hydrochloride (2 eq.) with 1,3-diamine-2-propanol (1 eq.) in the presence of $Mn(CH_3COO)_2·4H_2O$ (2 eq.) in refluxing methanol. From the mother liquor a solid is collected by addition of $CHCl_3$. Crystals of [Mn(H_3-L_A)(H_2O)$_2$](Cl)(H_2O) suitable for an X-ray determination [18], are obtained by ether diffusion into an ethanolic solution. This demetalation process has been detected by IR and HPLC-MS measurements. The strong IR bands due to the stretching modes of the acetate groups disappear while HPLC-MS shows the presence of only one species with a peak at m/z 441.08, clearly indicating the loss of $Mn(CH_3COO)_2$ and the consequent formation of the mononuclear complex.

Interestingly, as already found in other similar systems [19], the potentially bridging –OH group does not deprotonate, preventing from further complexation. Noticeably, this complex bears two additional –OH groups at the periphery of the coordinating moiety which can be engaged in further functionalization.

The molecular structure of [Mn(H_3-L_A)(H_2O)$_2$](Cl)(H_2O) (Fig. 1) consists of discrete [Mn(H-L_A)(H_2O)$_2$]$^+$ cations and one chloride anion. The coordination geometry around the metal ion is a distorted octahedron with two coordinated water molecules trans with respect to the equatorial square plane formed by two imino nitrogens and two phenolate oxygens of the Schiff base [H_3-L_A]$^{2-}$ ligand. The Mn–$O_{phenolic}$ bonds of 1.878(3) and 1.883(3)Å and Mn–N_{imine} bonds of 2.027(3) and 2030(3) Å are as usual for manganese(III) Schiff base complexes, whilst a significant elongation of the *trans* Mn-$O1_{water}$ and Mn-$O2_{water}$ bonds of 2.222(2) and 2.268(3) Å respectively is observed, consistent with a Jahn–Teller distortion [20], typical of d^4 system. Selected bond distances and angle fall in the common range of other Mn(III) Schiff base complexes [21–24].

The mononuclear [Mn(H_3-L_B)]·0.25H_2O·CH_3OH, deriving from the template reaction in methanol of 3-formyl-salicylic acid, tris-2-(aminoethyl)amine and $Mn(CH_3COO)_2·4H_2O$ in a 3:1:1 molar ratio, is recovered by reducing the volume of the reaction solution. Under the same experimental conditions but in a 3:1:2 molar ratio, the dinuclear complex [Mn_2(L_B)]·2.5H_2O is collected from mixture as confirmed by ESI-MS spectra where a peak at m/z 644.11 and m/z 697.04, in the mono- and dinuclear complexes, respectively, is clearly detectable [25]. The main IR difference between the two complexes is the shift of the C=N band from 1645 cm^{-1} in the mononuclear complex to 1627 cm^{-1} in the dinuclear one, owing to the coordination involvement of both the internal and external chambers in the latter complex.

It is well known that Schiff bases, derived from substituted salycilaldehydes and primary amines, because of the close connection of the deprotonable phenolic group and the protonable amine group, can give rise, at least, to two tautomeric forms A and B (Scheme 2). Excellent studies in the solid state and in solution demonstrate that quite often the Schiff base exists in the B form. Furthermore the protonation of the imine groups was recognised also in mononuclear

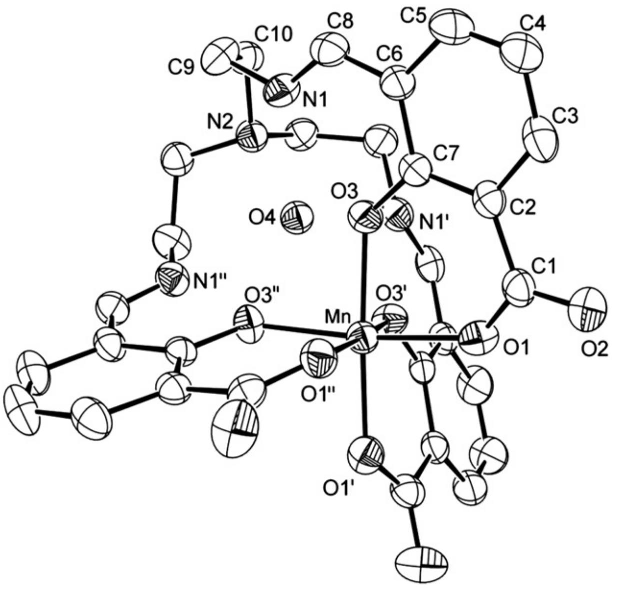

Fig. 2. ORTEP view of [Mn(H_3-L_B)] with thermal ellipsoids at 30% probability. Selected bond lengths ( ) and angles (°): Mn-O(1) 1.975(4), Mn-O(3) 1.980(3), O(1)-Mn-O(3) 87.2(1), O(1)-Mn-O(1)′ 91.7(2), O(3)-Mn-O(1)′ 173.4(2), O(3)-Mn-O(3)″ 86.4(1) (′ at 1−y, x−y, z; ″ 1−x+y, 1−x, z).