Versatile pentadentate 1,5-bis(salicylideneamino)pentan-3-ol type ligands yield novel tri- and tetra-manganese(II) complexes: structure and properties

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Novel manganese–oxygen cores observed in trinuclear $[Mn^{II}_3(L^3)_2(\mu_2\text{-}OAc)]Na$ and tetranuclear $[Mn^{II}_2L^3(\mu_3\text{-}OMe)(MeOH)]_2$ complexes [H_3L^3 = 1,5-bis(3-Cl,5-NO_2-salicylideneamino)pentan-3-ol] illustrate the coordination versatility of the 1,5-bis(salicylideneamino)pentan-3-ol type of trianionic pentadentate Schiff bases.

The coordination versatility of 1,3-bis(salicylideneamino)propan-2-ol type ligands towards transition metal ions, particularly manganese,[1] has prompted us to further explore the possible coordination modes of the related 1,5-bis(salicylideneamino)pentan-3-ol Schiff bases. The ligands in both series are potentially dinucleating pentadentate with two imine nitrogen, two phenolate and one alcoholate oxygen donors. Owing to the difference in aliphatic chain-length between their imine nitrogens, their dinucleating coordination mode results in five- and six-membered central chelate rings in the first and second series, respectively. As illustrated by work of Mikuryia *et al.*[2] with 1,5-bis(salicylideneamino)pentan-3-ol, H_3L^1, and manganese(III), the resulting increased flexibility allows formation of approximately planar dinuclear M_2L species which may be stabilized either with two additional bridges (one in-plane monoatomic and one out-of-plane triatomic), or through dimerization when two monoatomic μ_3-oxo and two triatomic bridges are provided. From the 3,5-NO_2-salicylidene substituted ligand H_3L^2, we have recently obtained a bis-dinuclear manganese(II) structure where two approximately planar dinuclear M_2L units are bridged by two μ_3-hydroxy anions.[3] Our efforts are directed towards exploration of the different types of manganese polynuclear structures obtainable from these flexible dinucleating pentadentate ligands, depending upon the electronic influence of the salicylaldimine-ring substituents, manganese oxidation state, and nature of the ancillary ligands.

As part of this project, we report here the first data concerning the novel bis-dinuclear $[Mn^{II}_2L^3(\mu_3\text{-}OMe)(MeOH)]_2$ **1** and trinuclear Na $[Mn^{II}_3(L^3)_2(\mu_2\text{-}OAc)]\cdot H_2O\cdot 0.25thf$ **2** complexes based on the same 1,5-bis(3-Cl,5-NO_2-salicylideneamino)pentan-3-ol pentadentate ligand, H_3L^3. Reaction of $Mn(OAc)_2\cdot 2H_2O$ with H_3L^3 and NaOH (2 : 1 : 3 molar ratio) in methanol yields a very air-sensitive orange precipitate within hours. Isolation and subsequent crystallisation from dmf–MeOH yields **1** as well shaped orange–red crystals. Treatment of the initial mother-liquor with water induces precipitation of a second compound. Crystallisation of this complex from thf–pentane gives red crystals of **2**.

The X-ray crystallographic study of **1**‡ revealed a bis-dinuclear structure related to that of $[Mn^{II}_2L^2(\mu_3\text{-}OH)(thf)]_2\cdot 2thf$ **3**:[3] two layered M_2L^3 dinuclear units bridged by two μ_3-methoxo anions and two L^3-phenolato oxygen atoms are related by a crystallographic inversion centre (Fig. 1). The significant differences between **1** and **3** are the presence of μ_3-methoxo (**1**) instead of μ_3-hydroxo (**3**) bridges, and of a Mn(2)-bonded methanol molecule (**1**) instead of thf (**3**). The two manganese atoms within the M_2L^3 unit have different coordination spheres: Mn(1) is in a square pyramidal NO_4 ligand environment while the NO_5 environment of Mn(2) is distorted octahedral. The Mn–L bond lengths and angles, and the intra- and inter-dinuclear Mn···Mn separations (Fig. 1) differ significantly from those in related Mn^{III}_4 and $Mn^{II}_2Mn^{III}_2$ species,[2,4] but are similar to those reported for **3** and characteristic of the +2 oxidation state of the Mn ions.[3] Two strong hydrogen bonds (Fig. 1) involving the coordinated Me*OH* molecules and *NO_2* substituents of L^3 link each dinuclear unit to its nearest neighbour, thus generating infinite 1D chains of bis-dinuclear molecules.

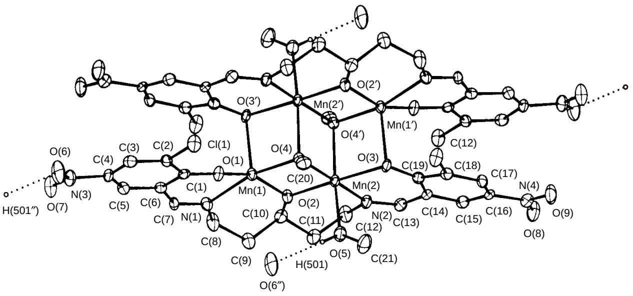

Fig. 1 Molecular structure of $[Mn^{II}_2(L^3)(\mu_3\text{-}OMe)(MeOH)]_2$ **1**. Selected distances (Å): Mn(1)–O(1) 2.080(3), Mn(1)–O(2) 2.032(3), Mn(1)–O(3′) 2.200(3), Mn(1)–O(4) 2.131(3), Mn(1)–N(1) 2.206(3), Mn(2)–O(2) 2.077(3), Mn(2)–O(3) 2.157(3), Mn(2)–O(4) 2.162(3), Mn(2)–O(4′) 2.237(3), Mn(2)–O(5) 2.271(3), Mn(2)–N(2) 2.216(4), Mn(1)···Mn(2) 3.154(1), Mn(1)···Mn(2′) 3.240(1), Mn(2)···Mn(2′) 3.372(1), Mn(1)···Mn(1′) 5.432(1) (′ = −*x*, −*y*, −*z*).

The X-ray crystallographic study of **2**‡ reveals an unprecedented surpamolecular array of trinuclear $[Mn^{II}_3(L^3)_2(\mu_2\text{-}OAc)]^-$ anions bonded to Na^+ cations (Fig. 2 and 3). The core of the complex anion, a triangle of Mn^{II} cations bridged by the alkoxo μ_3-O atoms of both L^3 ligands, is reminiscent of a [1.1.1]-

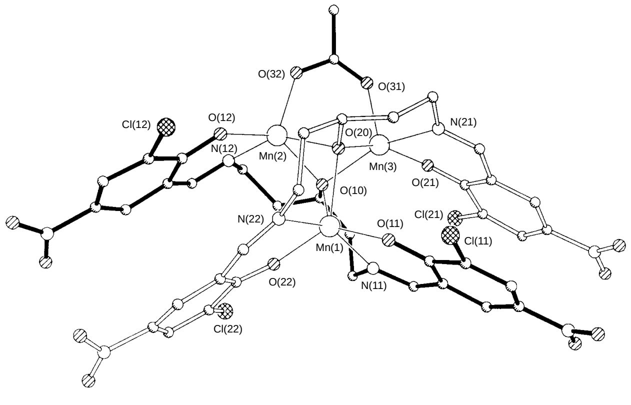

Fig. 2 Molecular structure of the trinuclear $[Mn^{II}_3(L^3)_2(\mu_2\text{-}OAc)]^-$ complex anion of **2**. Selected distances (Å): Mn(1)–O(10) 2.285(8), Mn(1)–O(11) 2.064(10), Mn(1)–O(20) 2.254(9), Mn(1)–O(22) 2.166(19), Mn(1)–N(11) 2.287(11), Mn(1)–N(22) 2.17(2), Mn(2)–O(10) 2.164(8), Mn(2)–O(12) 2.030(8), Mn(2)–O(20) 2.181(8), Mn(2)–O(32) 2.094(10), Mn(2)–N(12) 2.181(11), Mn(3)–O(10) 2.112(8), Mn(3)–O(20) 2.129(7), Mn(3)–O(21) 2.083(8), Mn(3)–O(31) 2.084(9), Mn(3)–N(21) 2.172(11), Mn(1)···Mn(2) 3.174(3), Mn(1)···Mn(3) 3.121(2), Mn(2)···Mn(3) 3.067(3).

propellane. The +2 oxidation state of the Mn ions is deduced from stoichiometric and structural considerations, further confirmed by the EPR and magnetic studies. In addition to the two alkoxo μ_3-oxygens, the trigonal prismatic Mn(1) coordination sphere includes one imine-N and one phenolate-O from each L^3 ligand. The basal plane of the square pyramidal ligand environment of Mn(2) and Mn(3) includes one imine-N, one phenolate-O and the alkoxo μ_3-O atoms from one L^3 ligand, in addition to the alkoxo μ_3-O atom from the second L^3 ligand. The apical position of each square pyramid is occupied by one oxygen atom of the bridging acetate. As a result, Mn(1) is doubly bridged to Mn(2) and Mn(3) while Mn(2) and Mn(3) are triply bridged, which is reflected in the 3.067(3) Å Mn(2)$\cdots$Mn(3) distance compared to the 3.174(3) [Mn(1)$\cdots$Mn(2)] and 3.121(2) Å [Mn(1)$\cdots$Mn(3)] separations. Both L^3 ligands are helically arranged around the trinuclear metal core, and show π-stacking interactions between their aromatic rings (Fig. 2). Interestingly, additional aromatic-ring interactions operate between adjacent trinuclear units throughout the crystal lattice, resulting in a 1D supramolecular array of alternating pairs of $[Mn^{II}_3(L^3)_2(\mu_2\text{-OAc})]^-$ anions and Na^+ cations (Fig. 3). Sodium cations interact with terminal 5-nitro and central alkoxo functions of L^3 and bridging acetate anions of the anionic trinuclear units. In addition each Na cation also interacts with one water molecule.

The structure of **2** is unique among the trinuclear manganese complexes reported: those including three Mn^{II} ions are linear[5] or triangular,[6] $Mn^{II}Mn^{III}_2$ complexes include the extensively studied oxo-centred carboxylato compounds,[7] and linear species;[8] Mn^{III}_3 complexes include oxo-centred carboxylato compounds,[9] and a triangular species including a double methoxo μ-oxygen bridge and two single alkoxo μ-oxygen bridges;[10] Mn^{IV}_3 complexes include the $[Mn_3O_4]^{4+}$ core with a double μ-oxo and two single μ-oxo bridges.[11]

The 300–80 K X-band powder spectra of complex **1** exhibit an extremely broad (*ca.* 3500 G) and featureless $g \approx 2$ centred resonance. At variance with the reasonably broad absorption typical of tetranuclear Mn^{II} complexes,[3] the broadness of this EPR absorption indicates the presence of weak extended interactions in the solid state.[12] This agrees with the crystallographic observation of 1D chains of tetramanganese(II) units. The 100 K dmf–toluene X-band glass spectrum of **1** exhibits a reasonably broad (*ca.* 700 G) $g \approx 2$ centred isotropic resonance devoid of any fine or hyperfine structure. This indicates that, (*i*) the tetranuclear structure is retained in solution, and (*ii*) the weak extended interactions are not operating in solution, *i.e.* the 1D chains of hydrogen-bonded tetranuclear molecules are broken. The 300–80 K X-band powder spectra of **2** are similar to those reported for **3**,[3] and typical of magnetically interacting Mn^{II} ions. On the other hand, the 100 K dmf–toluene glass X-band EPR spectrum of **2** indicates dissociation, not only of its supramolecular architecture, but also of the trinuclear Mn^{II} complex anions. Two resulting Mn^{II} species are clearly identified: (*i*) a mononuclear one showing the usual ^{55}Mn six-line hyperfine pattern at $g \approx 2$, and (*ii*) a dinuclear one showing the typical 11-line hyperfine pattern superimposed on several fine structure absorptions (0–5000 G).[13] The magnetic susceptibilities of complexes **1** and **2** have been measured in the 300–2 K temperature range. For both complexes, μ_{eff} mol^{-1} at 300 K is lower than the spin-only value for non-interacting spin systems (11.83 μ_B for four $S = 5/2$ spins and 10.25 μ_B for three $S = 5/2$ spins) and decreases from 10.50 to 4.89 μ_B (**1**) and 9.00 to 4.91 μ_B (**2**) at 2 K, indicating overall antiferromagnetic coupling of the $S = 5/2$ spins of the Mn^{II} ions in both complexes.

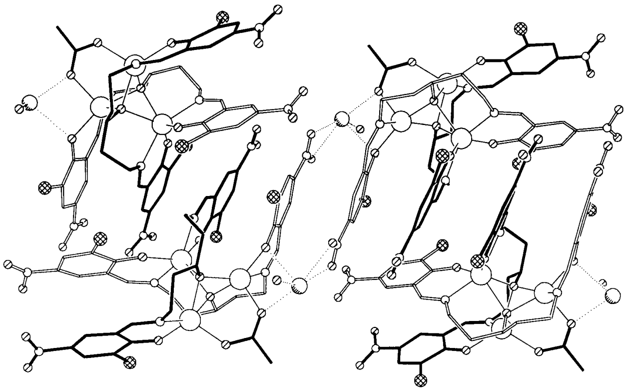

Fig. 3 View of four $[Mn^{II}_3(L^3)_2(\mu_2\text{-OAc})]^-$, $Na^+\cdot H_2O$ ion pairs **2** emphasizing the infinite π-stackings perpendicular to [001]. The intramolecular π-stacking distances are 3.4 and 3.5 Å. The two crystallographically independent intermolecular π-stacking distances are 3.3 and 3.4 Å.

Owing to the possible role of the vacant coordination sites at the Mn^{II} centres of both novel complexes, their redox behaviour and reactivity are currently under study.

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Notes and References

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‡ *Crystal data*: for **1**: $C_{21}H_{22}Cl_2Mn_2N_4O_9$, crystal size: 0.5 × 0.3 × 0.05 mm, triclinic, space group, $P\bar{1}$, $a = 9.203(1)$, $b = 11.071(1)$, $c = 13.50(1)$ Å, $U = 1270.3(2)$ Å^3, $Z = 2$, $D_c = 1.71$ g cm^{-3}, μ(Mo-Kα) = 12.23 cm^{-1}, 8646 reflections collected at 180 K (STOE-IPDS diffractometer) in the 2.8–48.4° 2θ range, 3373 unique, 2576 used with $I > 1.0\sigma(I)$, 348 parameters refined on F to final R indices: $R = 0.042$, and $R_w = 0.042$. For **2**: $C_{40}H_{35}Cl_4Mn_3NaN_8O_{17}\cdot 0.25$thf, crystal size: 0.45 × 0.25 × 0.13 mm, tetragonal, space group, $P4/ncc$, $a = 30.296(3)$, $c = 28.362(3)$ Å, $U = 26032(5)$ Å^3, $Z = 16$, $D_c = 1.273$ g cm^{-3}, μ(Mo-Kα) = 8.05 cm^{-1}, 17511 reflections collected at 180 K (STOE-IPDS diffractometer) in the 3.2–36.8° 2θ range, 4709 unique, 825 parameters refined on F^2 to final R indices: R_1 [$I > 2\sigma(I)$] = 0.0921, $wR2$ (all data) = 0.2789. Crystals of **2** were poorly shaped and weakly diffracting, giving low resolution data and relatively high R-values. One reason for this might be the high amount of disorder in the crystal structure. One half of one L^3 ligand is disordered and could be refined onto two positions using distance and ADP-restraints. The lattice bound thf molecule is disordered on a four-fold axis. CCDC 182/788.

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