



Crystal packing effects within $[\text{Mn}^{\text{III}}_3\text{O}]^{7+}$ single-molecule magnets: Controlling intermolecular antiferromagnetic interactions

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ABSTRACT

The reactions of 2-hydroxyphenylethanone oxime (Me-H₂salox) and (2-hydroxy-phenyl)-phenyl-methanone oxime (Ph-H₂salox) with $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in MeOH afford trinuclear manganese complexes of $[\text{Mn}_3\text{O}(\text{Me-salox})_3(\text{MeOH})_3(\text{ClO}_4)] \cdot \text{MeOH}$ (**1**·MeOH) and $[\text{Mn}_3\text{O}(\text{Ph-salox})_3(\text{MeOH})_3(\text{ClO}_4)] \cdot 2\text{MeOH}$ (**2**·2MeOH), respectively. X-ray analysis shows that both complexes contain a manganese triangle core, $[\text{Mn}^{\text{III}}_3\text{O}]^{7+}$. The structural distortion from the twisting of the oxime ligands dominates the ferromagnetic interactions within the three Mn ions in both compounds and results in an $S = 6$ ground state. The frequency dependence of out-of-phase signals in the alternating current (AC) magnetic susceptibility measurements and the temperature-dependent and sweep-rate-dependent hysteresis loops are indicative of single-molecule magnet behavior. Moreover, both complexes show step-wise magnetization, indicating the occurrence of quantum tunneling of magnetization (QTM). Interestingly, a tail to tail arrangement in the crystal packing of complex **1**·MeOH results in strong intermolecular H-bonding interactions and leads to the exchange-bias effect from the antiferromagnetic interaction between the adjacent Mn_3 molecules. In contrast, QTM steps of complex **2**·2MeOH show an absence of the exchange-bias effect due to a weak intermolecular interaction from a head to tail arrangement.

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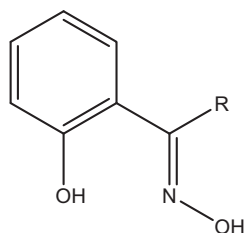
Single-molecule magnets (SMMs) have attracted extensive attention because they are nanoscale magnetic particles of a well-defined size [1,2]. They display sluggish magnetization relaxation phenomena such as magnetization hysteresis loops, frequency-dependent out-of-phase AC magnetic susceptibility and quantum tunneling of magnetization (QTM) [3–5]. In particular, the QTM was first observed in SMMs below the blocking temperature whenever a magnetic field applied parallel to the anisotropy axis brought into alignment a pair of energy levels on opposite sides of the anisotropy energy barrier (U) corresponding to different spin projections. These remarkable magnetic properties of an SMM arise from its high-spin ground state (S) split by a large negative axial zero-field splitting (ZFS, D), which results in an anisotropy energy barrier of $U = |D|S^2$ [5]. The first SMM reported was $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O}$ with $S = 10$ ground state and a negative ZFS of -0.5 cm^{-1} [3]. Since then, a lot of effort has been directed to the synthesis of new examples of Mn containing SMM, which have been reported with S values ranging from 3 to 83/2 and a maximum value of U_{eff} of 86 K [6]. Among the possible spin carriers that exhibit easy axis magnetic anisotropy, Mn^{III} ions are the most commonly employed given their large spin, $S = 2$, and

the Jahn–Teller (JT) elongation of the coordination octahedron. Thus, many current routes for synthesizing SMMs involve manganese(III) containing complexes to exploit the associated large single-ion anisotropy [7]. Employing salicylaldoxime ligands in manganese chemistry has proved to be extremely successful in the synthesis of new polynuclear complexes, including some SMMs [8] and single-chain magnets (SCMs) [9], suggesting that such ligands are excellent candidates for the preparation of polynuclear Mn complexes with interesting magnetic properties. Indeed, it has been found that weak intermolecular antiferromagnetic interactions between SMMs manifested as an exchange bias of all tunneling transitions, and the resulting hysteresis loop consequently displays unique features, such as the absence for the first time in a SMM of a QTM step at zero field [10].

Herein, we report the synthesis and characterization of two $[\text{Mn}^{\text{III}}_3\text{O}]^{7+}$ complexes (**1**·MeOH and **2**·2MeOH) using salicylaldoxime derivatives (Me-H₂salox, Ph-H₂salox), in which the methyl and phenyl groups twist Mn–N–O–Mn. This structural distortion results in ferromagnetic interactions between manganese ions. Their SMM properties are characterized by AC magnetic susceptibility and magnetic hysteresis loops. Interestingly, QTM steps of complex **1**·MeOH occur before ZFS, which is expected for an exchange-bias effect due to strong intermolecular H-bonding interactions from a tail to tail arrangement in the crystal. In contrast, complex **2**·2MeOH

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Scheme 1. R = Me; Me-H₂salox, R = Ph; Ph-H₂salox.

shows a head to tail arrangement, which results in a weak intermolecular interaction, with QTM steps obtained after ZFS.

Complexes **1**·MeOH and **2**·2MeOH were prepared by simple reactions of oxime ligands (Me-H₂salox and Ph-H₂salox) (Scheme 1) with Mn(ClO₄)₂·6H₂O and triethylamine. The reaction of Mn(ClO₄)₂·6H₂O with equiv of Me-H₂salox and NEt₃ in MeOH led to a reaction mixture comprising a dark green solution. Filtration and slow diffusion with Et₂O afforded dark green-brown crystals [Mn₃O(Me-salox)₃(MeOH)₃(ClO₄)₃·MeOH (**1**·MeOH) in a yield of 20% (based on Mn) after one week. [Mn₃O(Ph-salox)₃(MeOH)₃(ClO₄)₃·2MeOH (**2**·2MeOH) was obtained in the reaction of the same equiv of Mn(ClO₄)₂·6H₂O, Ph-H₂salox, and NEt₃ in MeOH, in which dark green crystals were formed after diffusion by Et₂O in a yield of 50%. Both complexes gave satisfactory analytical results.¹

The structures of the two complexes are very similar²; complex **1**·MeOH crystallizes in rhombohedral space group *R* $\bar{3}$, and complex **2**·2MeOH crystallizes in triclinic space group *P* $\bar{1}$. The ORTEP representations of **1**·MeOH and **2**·MeOH are shown in Figs. 1 and 2, respectively. The structure of **1** consists of a near-equilateral Mn^{III}₃ triangle core which is connected by a μ_3 -oxide (O1) on the central planar, and capped by one ClO₄[−] ion on the upper part of the planar in a rare $\eta^1:\eta^1:\eta^1:\mu_3$ mode. This capped ClO₄[−] elongates the JT axis in almost parallel orientation with the distance between Mn1–O4 and Mn1–O6 being 2.5786(11) and 2.1920(11) Å, respectively. Of note, the orientation and distance of the JT axis affords the *D* value of a molecule, which is an important factor in SMM properties. The C₃ axis is perpendicular to the Mn^{III}₃ plane and passes through the O5 and Cl1 of ClO₄[−] and the central oxygen. The core of the complex consists of a [Mn₃(μ_3 -O)]⁷⁺ moiety, in which the central oxo bridge lies 0.15 Å below the plane defined by the three manganese ions. Each edge of the triangle is bridged by a dianionic oximate group of a Me-salox^{2−} ligand in the $\eta^1:\eta^1:\eta^1:\mu_2$ mode, whose deprotonated hydroxyl group is bound terminally to a Mn^{III} ion. The methyl-group twists the Mn–N–O–Mn arrangement at a torsion angle of $\alpha_v = 39.25(12)^\circ$. One MeOH completes six-coordination at Mn1 and adopts a distorted octahedral geometry. The Mn^{III} oxidation states and O^{2−} protonation level were obtained using bond valence sum (BVS) calculations [11], charge considerations, and the presence of the Mn^{III} JT elongation axis (O4–Mn1–O6). In addition, the JT axes of Mn^{III} ions are almost parallel to each other as well as to the crystallographic C₃ axis. In the crystal packing, **1**·MeOH shows obvious hydrogen bonding interaction which involves the O atom of the Me-salox^{2−} and the O atom of a terminal

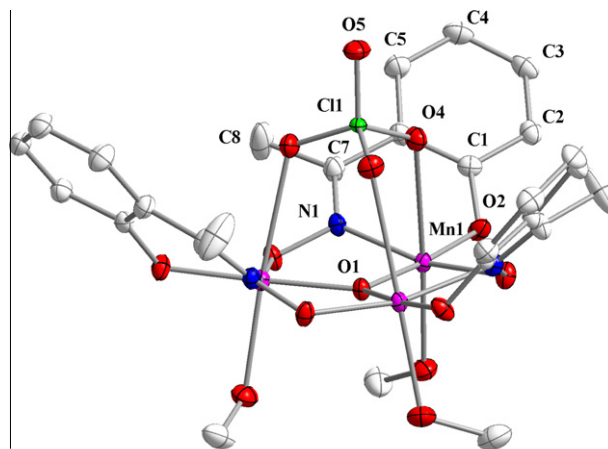


Fig. 1. ORTEP drawings (top) of the structure of **1**·MeOH with thermal ellipsoids set at 30% probability and (bottom) side view of Jahn–Teller axes. The solid black lines indicate the three Jahn–Teller axes. The solvent molecules and H atoms have been omitted for clarity.

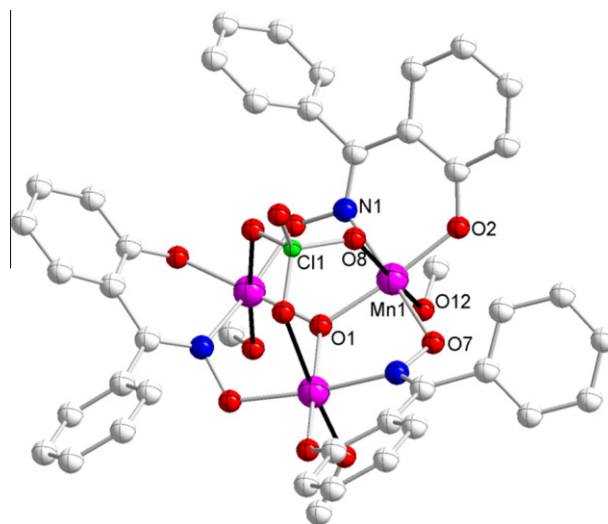


Fig. 2. ORTEP drawing of the structure of **2**·2MeOH with thermal ellipsoids set at 30% probability. The solvent molecules and H atoms have been omitted for clarity.

¹ Satisfactory elemental analytical data: *Anal. Calc.* for **1**·MeOH (C₂₈H₃₇ClMn₃N₃O₁₅): C, 38.98; H, 4.40; N, 4.93. Found: C, 39.29; H, 4.36; N, 4.91%. *Anal. Calc.* for **2**·2MeOH (C₄₄H₄₇ClMn₃N₃O₁₆): C, 48.98; H, 4.37; N, 3.95. Found: C, 49.20; H, 4.41; N, 3.91%.

² Crystallographic data in brief: For complex **1**·MeOH: C₂₈H₃₇ClMn₃N₃O₁₅, *M* = 855.88, rhombohedral, *R* $\bar{3}$, *a* = 13.0164(5) Å, *c* = 35.091(3) Å, *V* = 5148.8(5) Å³, *T* = 150(2) K, *Z* = 6, *D*_{calc} = 1.656 mg/m³, independent reflections 2872 [*R*_{int} = 0.0370], data 2872, parameters conventional 173, *R* [*F* > 2σ(*F*)] = 0.0277 (0.0756). For complex **2**·2MeOH: C₄₄H₄₇ClMn₃N₃O₁₆, *M* = 1074.09, triclinic, *P* $\bar{1}$, *a* = 8.3521(9) Å, *b* = 12.2772(13) Å, *c* = 23.854(3) Å, α = 98.833(2)°, β = 94.667(2)°, γ = 106.664(2)°, *V* = 2295(4) Å³, *T* = 100(2) K, *Z* = 2, *D*_{calc} = 1.550 mg/m³, independent reflections 11355 [*R*_{int} = 0.0257], data 11355, parameters conventional 628, *R* [*F* > 2σ(*F*)] = 0.0402 (0.0959).

MeOH from neighboring Mn₃ molecules [O2...O6' 2.7157(18) Å] in a tail to tail arrangement. These interactions effectively mediate a 2-D supramolecular network (Fig. 3) with an intermolecular Mn...Mn distance of 5.2439(4) Å. Complex **2**·2MeOH is isostructural to **1**·MeOH except for the chelating ligands of Me-salox^{2−} in **1** are substituted by Ph-salox^{2−} in **2**·2MeOH. The torsion angles in **2**·2MeOH are

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