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Spin Coupling and Magnetic Anisotropy in 1D Complexes with Manganese(III) Units and Carboxylate Bridges. Synthesis and Analysis, Calculations and Models.

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Abstract: We report the synthesis, structure and magnetic properties of a series of Mn(III) complexes based on 5MeO-salen, N,N'-ethylenebis(5-methoxysalicylideneiminate), and acetate ligands, namely $[Mn_2(5MeO-salen)_2(CH_3COO)]X$, X=CIO₄⁻ (1), PF₆⁻(2), CF₃SO₃⁻(3). The [Mn(5MeO-salen)]⁺ form oxo-bridged dimers whose further assembling by acetate groups, leads to zigzag chains. There are two alternating types of dimeric {Mn₂O₂} units, each of them intrinsically ferromagnetic and anisotropic, but mutually coupled antiferromagnetically along the chain. Magneto-structural analyses were carried out with the help of ab initio calculations, understanding the subtle factors of local magnetic anisotropy combined with the exchange effects. A qualitative mechanism of the exchange coupling was advanced, in the continuation of ab initio calculations, explaining the ferromagnetism inside the phenoxo-bridged dimer units and the antiferro behaviour of the acetate bridge.

Introduction

The molecular magnetism,^[1] as distinct branch of coordination chemistry, contributes with academic insight to the interests in developing new functional materials. In this respect, the design of supramolecular coordination networks on the basis of molecular building blocks concept, afforded a large number of compounds with different structural patterns, enabling case studies for various structure-property correlations.^[2] One may say that the main focus of the nowadays magneto-chemistry stays in producing and understanding the so-called Single Molecule Magnets (SMMs)^[3] and related systems. Extended 1D analogues of the SMMs are the Single Chain Magnets (SCM)^[4].

The manganese(III) ion is one of the best suited d-type ions to acquire SMM systems, being a good carrier of magnetic anisotropy, its complexes showing a large structural variety.^[5, 6] The tetradentate Schiff-base salen type ligands, where salen

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denotes the N,N'-Bis(salicylidene) ethylenediamine molecule, represent one of the most accessible class of Mn(III) building units, the axial positions, perpendicularly to the mean plane of the ligand, being at the same time easy magnetization axes and assembling points, binding the bridging agents.

The use of Mn(III) salen-type dimeric complexes as anisotropic building blocks in SCM-type systems was pioneered by Miyasaka.^[7] A particular achievement is the building of 1D coordination polymers,^[8,9] behaving as Single Chain Magnets (SCM). А particular SCM design^[10] bridged the $[Mn_2(naphtmen)_2(H_2O)_2](ClO_4)_2$ binuclear units (where H₂naphtmen is N,N'-(1, 1, 2, 2- tetra-methyl-ethylene) bis naphthylidene-imine) through a ligand having a nucleobase pattern: 6-amino-9-β-carboxyethylpurine. Aside assembling the 1D complexes, this ligand links the chains, by hydrogen bond. The coupling is ferromagnetic inside the Mn(III) dimeric units and antiferromagnetic along the nucleobase-alike ligand. The spin canting determined by the anisotropy of Mn(III) ions leads to a non-cancelled magnetic moment, whose dynamics is interpreted as a SCM feature.

Although not possessing special SCM or SMM properties, a system interesting for the molecular structure and supramolecular assembling is obtained with a bicompartmental Schiff base H₂3MeO-salen: N,N'-ethylene bis(3-methoxy salicylaldiimine), where the methoxy groups provide a potential second coordination site.^[11] The dimeric [Mn₂(3MeOsalen)₂(H₂O)₂]²⁺ units are assembled by hydrogen bonds. E.g. in the $[Mn_2(3MeO-salen)_2(H_2O)_2]$ (NO₃)₂ material, the aqua ligands, placed in the outer apical positions of the Mn(III) coordination spheres are linked to the nitrate counter-ions, forming chains of dimers. In a crystal isomeric form, the chains are realized with hydrogen bonds from the aqua ligand of one monomeric Mn(III) complex approaching the MeO groups of the other unit. Other supramolecular architectures of this complex unit are found, including a case where the open coordination compartment is occupied by potassium ions.

Complicate architectures are realized combining Mn(III) salen-type complexes with large polyoxometalate clusters.^[12] An interesting result is the successful attempt to produce multiproperty systems, like conducting magnets, in hybrid materials using dimers of the manganese(III) complex with the 5MeOsaltmen ligand (where 5MeOsaltmen is N,N'-(1,1,2,2-tetramethylethylene)bis(5-methoxysalicylideneiminate)) for the magnetic ingredient, while the conducting function is given by stacks of [Ni(dmit)₂]^{0,-1} complexes in mixed valence regime, with neutral and negative charges (where dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate).^[13]

In a large number of examples the Mn(III) dimers are identified with individual SMM behaviour,^[14] a property from where the SCM features are emerging. One of us contributed to one of the first SCM systems, cooperating with Miyasaka's group, synthesizing and analysing a coordination chain based on the [Mn(5MeO-salen)]⁺ unit,^[15] where 5MeO-salen is N,N'ethylenebis(5-methoxysalicylideneiminate). This was assembled with Fe(III) hexa-cyanide complex anions, generating a Mn-Mn-Fe-Mn-Mn-Fe- chain alternation. In the subsequent analyses on this system, we realized that the SMM qualities of the manganese dimers are the important actors. This issue, debated collaboratively, was reflected in a work produced in the same group and in the same interval with our above cited work. Thus, in the discussion of the [Mn₂(saltmen)₂(ReO₄)₂] compound, realized with the H₂saltmen Schiff base, N,N'-(1,1,2,2-tetramethyl-ethylene) bis (salicylidene-imine), the intrinsic SMM features of the on Mn(III) dimeric units were firstly acknowledged.[16]

A chemical proof that the Mn(III) dimeric units are the key carriers is the fact that polymeric chains incorporating single Mn(salen)-type nodes do not show SMM or SCM features, as is the case of a system^[17] assembling [Mn(5MeO-salen)]⁺ and [Fe(tp)CN₃]⁻ (where Tp⁻ is = hydro-tris-pyrazolyl- borate), yielding alternating -Mn-Fe-Mn-Fe- heterometallic complexes. A very interesting result is the incorporation of a Mn(III) dimeric SMM in a 3D hetero-bimetallic oxalate lattice with a [Mn(II)Cr(III)(ox)₃] skeleton.^[18]

Reportedly, the Mn(III)····Mn(III) magnetic interaction within the manganese dimeric units can be both ferromagnetic and antiferromagnetic, depending on the Mn...Mn distance and Mn-O(phenoxo)-Mn angles, parameters controlled by the apical ligands, but also by subtle packing effects.^[19] Experimental structural studies were combined with Density Functional Theory (DFT)^[20] calculations, revealing -in part- the parameters tuning the nature of the exchange coupling.^[21]

Using paramagnetic complexes as bridges, their magnetic behaviour is interplayed with those of the manganese units. Aiming to focus on the anisotropy due to manganese units, we oriented ourselves toward simpler ligands as bridges, considering, in the work presented herein, the acetate ligand. The carboxylate group is one of the most widely used bridging unit, its versatility determining multiple coordination modes.^[22, 23] Besides, the carboxylates are convenient for a preliminary control of coordination pattern, existing clear correlations between v(COO) frequencies and the carboxylate bringing geometries.^[24] Previous articles of 1D structures based on acetate-bridged manganese(III) dimers remained at the level of bare structure reports, without focusing in details of magnetic properties, magnetic anisotropy or assembling features.^[25] Onedimensional systems assembled with bridging deprotonated adipic and E,E-1,3- butadiene- 1,4-dicarboxylic acids where characterized with slow relaxation of magnetization and SCM behaviour.^[26]

Syntheses and magnetic properties of [Mn(III)salen]⁺ chain complexes with other carboxylate groups such as formate,^[27] chloro-acetate^[28] or a series^[29] consisting in cinnamate, phenylacetate and benzoate, have been reported. The chains were characterized as having a spin-canted pattern. However,

this discussion remained at elementary level.^[29] The spin-canting, either interpreted as determined by the so-called Dzyaloshinskii-Moriya coupling,^[30] or as anisotropy manifestation,^[31] is due to the imbrication of exchange and spin-orbit coupling, being one of the effects that help to achieve long-range magnetic ordering.^[32] However, such aspects are rarely discussed in concrete details, being often limited at the qualitative invocation. Our attention devoted to the magnetic anisotropy will attempt bringing new contributions in this respect also.

Results and Discussion

Structure Description.

Here we report chain coordination polymers with a (Mn-Mn-RCOO)_n skeleton, made of dimeric sequences bridged in *syn-anti* fashion by acetate moieties, bringing relevant on the magneto-structural considerations. The three new single-crystal structures are [Mn₂(5MeO-salen)₂(CH₃COO)]X, where 5MeO-salen is N,N'-ethylenebis(5-methoxysalicylideneiminate) and X=ClO₄⁻ (1), PF₆⁻ (2), CF₃SO₃⁻ (3).

The cationic binuclear units are formed by the link between one manganese centre and the phenoxo oxygen atom from the neighbouring Schiff base ligand. The cationic chains are surrounded by perchlorate anions in **1**, hexafluoro-phosphate and one methanol molecule in **2**, and triflate anions in **3**. The system **1** is illustrated in the Figure **1**, the other two being presented in the Supporting Information. In each compound, the manganese centres are crystallographically different, labelled Mn(1) and Mn(2). Each manganese centre is hexa-coordinated by two nitrogen and four oxygen atoms, having an elongated octahedron structure. Four equatorial positions are occupied by the two nitrogen and two oxygen atoms from the deprotonated tetradentate 5MeO-salen ligand.



Figure 1. The structure of the compound 1. The hydrogen atoms are omitted for clarity.

The bond lengths Mn-N and Mn-O vary within the ranges 1.968(2)- 1.998(2)Å and 1.881(2)-1.940(1) Å, respectively. General crystallographic data are given in Table 1, selected bonds and angles being summarized in Table S1 from Supporting Information.

In all three compounds, can be observed longer Mn-N and Mn-O equatorial bond lengths longer for Mn(2) centres, compared with Mn(1) sites. The longer bond lengths are correlated with the strain and the ligand conformation. For the Mn(2) centre, all the Schiff base present a more relaxed planar conformation, while for the Mn(1), the ligands have a rather strained conformation, with stepped pattern, for compounds 1-2 and umbrella-like for 3 (Figure 2). Each manganese centre is deviated out of the ligand plane, towards the axial oxygen atom belonging to the bridging carboxylate group. The acetate-type axial positions of the Mn(1) and Mn(2) sites are established with the O9 and O10 oxygen atoms, respectively, having the corresponding bond lengths: 2.119 Å and 2.113 Å for 1, 2.149 Å and 2.114 Å for 2 and 2.149 Å and 2.114 Å for 3.



Figure 2. Different salen-type Schiff base ligand conformation in compounds 1-3 and the details for the both out-of-plane Mn dimer units type (A and B).

In line with Jahn-Teller alike distortions expected for the Mn(III) complexes, the axial Mn-O bonds are significantly longer than the equatorial bonds. The *syn-anti* coordination mode for the bridging carboxylate group imposes a zig-zag feature for the chains and a distance of 5.233 Å (for 1), 5.226 (for 2) and 5.433 Å (for 3) respectively, between the Mn(1) and Mn(2) centres. Each second axial position is occupied by a phenoxo oxygen atom of the neighbouring ligand from the next Mn centre with the same symmetry. In this way, two types of centrosymmetric cationic binuclear units are formed, named in the following: A unit, including the Mn(1) centres and B unit, including the Mn(2) ones.

The Mn-O-phenoxo-Mn angles are, in the A and B units: 103.26° (A unit in 1), 98.55° (B unit in 1); 101.94° (A unit in 2), 87.79° (B unit in 2), 98.43° (A unit in 3) and 102.16° (B unit in 3). The Mn...Mn distances within each unit A and B are: 3.391 Å (A unit in 1), 3.436 Å (B unit in 1); 3.394 Å (A unit in 2), 3.729 Å (B unit in 2) and 3.303 Å (A unit in 3), 3.443 Å (B unit in 3).

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Table 1. Summary of the crystallographic data for 1, 2 and 3								
	1	2	3					
formula	$C_{38}H_{39}CIMn_2N_4O_{14}$	C ₃₉ H ₄₂ F ₆ Mn ₂ N ₄ O ₁₁ P	$C_{39}H_{39}F_{3}Mn_{2}N_{4}O_{13}S$					
formula weight	921.07	997.61	970.68					
crystal system	triclinic	triclinic	Triclinic					
space group	P1 (No. 2)	$P\overline{1}$ (No. 2)	$P\overline{1}$ (No. 2)					
a (Å)	11.0684(5)	11.771(6)	11.3151(6)					
b (Å)	11.7949(9)	11.824(5)	11.8514(7)					
c (Å)	16.0906(3	15.966(7)	16.1846(9)					
α (°)	81.973(13)	72.038(10)	79.249(2)					
β (°)	67.281(9)	78.804(11)	70.659(2)					
$\gamma(^{\circ})$	85.00(1)	80.694(12)	86.081(2)					
$V(Å^3)$	1917.4(2)	2061.0(16)	2011.87(19)					
Z	2	2	2					
$ ho_{calcd}$, g/cm ³	1.595	1.609	1.602					
F ₀₀₀	948	1024	996					
no. of	17435	10526	14573					
reflections								
no. of observations	6573	7074	4684					
no. of variables	528	610	564					
μ (Mo K _{α}), cm ⁻¹	8.04	7.44	7.65					
T. K	93	93	100					
$R1^{a}$	0.040	0.040	0.0376					
$(1>2.00\sigma(1))$								
R1 ^a (all data)	0.045	0.044	0.0311					
wR2 ^b (all	0.112	0.110	0.0802					
data)								
GOF	1.064	1.045	1.062					

[a] $R = \sum ||F_0| - |F_0|| / \sum |F_0|$ [b] $R = \left| \sum (|F_0| - |F_0|)^2 / \sum w |F_0|^2 \right|^2$

The packing diagrams of the **1-3** crystal structures show, for each compound, the zig-zag chain arrangement of the two different out-of-plane manganese dimers alternating units (A and B) (see Figure 3). The supramolecular interactions are mainly hydrogen-bonds established between the anions and the Schiff base ligand. The slipped stacking π - π interactions appear inside each dimer unit, but are not important for the inter-chain architecture.



Figure 3. Packing diagram of the crystal structure of compound 1, showing for each compound the zig-zag chain pattern of the two different out-of-plane Mn(III) dimeric units. The hydrogen atoms are omitted for clarity.

Voltammetry measurements

The obtained oxidation peaks, at almost the same positive potential for all three compounds, indicated that the processes take place on the metal centre of the complex. As is shown in the Figure 4, the voltammetry measurements upon anodic scanning suggest the progressive oxidation of the complexes, all the systems showing peaks at approximately the same abscissa points. The relatively small variation in the intensity profiles is due to kinetic specifics induced by the different anions. The

observed curves are most probably the superposed processes of the multiple species resulted from the dissociation equilibria of the complexes in the solution. Since the ligand itself shows an oxidation peak at about 0.8 eV, must presume that the same peak, visible for all the complexes, is due to the dissociated free ligand. The peaks at 1.2 V can be tentatively assigned to the $Mn(III) \rightarrow Mn(IV)$ oxidation of the monomeric $[Mn(5MeO-Salen)]^+$ units, whose axial coordination is probably completed with solvent, as ligand. We can speculate that the shoulders visible around 1.1 V are due to the oxidation of the free manganese ions (or better said, solvated), appeared altogether with the free ligand, by the dissolution of the complexes. The ligand itself is showing no peak in the 1.0-1.4 V range. The processes are not reversible because, once dissociated, the complexes cannot return to previous stages. Varying the parameters of the process the situation remains approximately the same. For instance, starting the scan from -0.8 V negative domain, the pattern and positions of the peaks in the positive side of potential are conserved (See Supporting Information), varying only the current intensity, because of a different conditioning of underlying kinetics.



Figure 4. The voltammograms for 1-3 recorded at a concentration of $5x \ 10^{-4}$ M, within the potential range 0 to 1.5V.

Magnetic properties

We recorded the magnetic susceptibility (χ) as function of temperature (*T*) as well as the magnetization (*M*) as function of field (*B*) and temperature, for all the three compounds, but for sake of conciseness we will present only the data of the system **2** (see Figure 5). The other ones, relatively similar, are shown in the Supporting Information.

The χT vs. *T* curves show antiferromagnetic-like pattern, but the picture of the active interactions is, in fact, more complex. There are multiple parameters, implied by the non-equivalence of the manganese units, aside the interplay between exchange coupling and the anisotropy effects. The topology of species and the related exchange coupling contacts are schematized in the Figure 6, including also the representation of the relative orientations of magnetization axes, perpendicularly to the salen ligand averaged planes.

Having two different dimeric building blocks, we must assign, in principle, three coupling parameters, J_A and J_B inside each binuclear unit and J_C for their bridging trough acetate. The description of magnetic anisotropy with the general Zero Field Splitting (ZFS) Hamiltonian demands, in general, two parameters per manganese mononuclear species, namely D_A and E_A for the constituents of one dimeric unit, while D_B and E_B for the other one. The interpretation of magnetic properties is complicated also by the extended nature of the system. The infinite chain (A₁A₂-B₁B₂)_n can be conceived as a closed ring with a sufficiently large number of elements, *n*, enforcing a connection between the first A₁ node and the *n*-th B₂ one, in order to achieve the complete equivalence of each *i*-th tetrameric sequence along the extended structure.

We must consider formally a tetranuclear repeating unit, since, otherwise, we cannot express, in topological sense, the inversion operation determined by the crystallographic symmetry (inversion inside the A_1A_2 and B_1B_2 dimers).



Figure 5. Magnetic data for compound **2**. Left side: χT vs, *T* curve with an inset showing the qualitative pattern of the magnetization swept at up and down field. Right side: Magnetization (*M*, in Bohr magneton units) represented as function of field and temperature dependence (*B*/*T*).

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Figure 6. The topology of magnetic chains, showing the different units and exhange couplings and local orientations of easy magnetization axes.

The general expression for a closed chain is:

$$\hat{H}_{HDVV} = -2\sum_{i=1}^{n} \left(J_{A} \ \hat{S}_{A_{1}(i)} \cdot \hat{S}_{A_{2}(i)} + J_{B} \ \hat{S}_{B_{1}(i)} \cdot \hat{S}_{B_{2}(i)} + J_{C} \ \hat{S}_{A_{2}(i)} + J_{C} \ \hat{S}_{A_{2}(i)} \cdot \hat{S}_{B_{2}(i)} \right) - 2J_{C} \ \hat{S}_{A_{2}(i)} \cdot \hat{S}_{B_{2}(i)}$$
(1)

$$\hat{H}_{ZFS} = -2\sum_{i=1}^{n} \sum_{K}^{\{A_{i}, A_{2}, B_{1}, B_{2}, \}} D_{K} \left(\left(\hat{S}_{K(i)}^{z} \right)^{2} - \frac{1}{3} S(S+1) \right)$$
(2)

Each Mn(III) unit carries a magnetic anisotropy with easy magnetization axis perpendicular to the average plane of the 5MeO-salen ligand. Because the symmetry is quasi-tetragonal, the *E* parameter is negligible, in comparison to the magnitude of *D*, as proven also by the following *ab initio* calculations. For a given centre, the ZFS Hamiltonian can be transformed to a diagonal form, with respect of the *D* parameter, if the local *z* axis is aligned to the easy magnetization axis. The local ZFS Hamiltonian for a species having a tilt by the α angle, with respect of the *z* axis, and *D*-only ZFS (i.e. *E*=0), is described by the following matrix:



This matrix is written in the basis of $S_z = \{-2, -1, 0, 1, 2\}$ spin projections. For an isolated single-site this matrix has the same eigenvalues as the α =0 alignment, but the trigonometric factors become non-trivial when inserted in the whole Hamiltonian of an extended system, with different orientations of the local anisotropy axes. If choose the z axis along the translation vector of the chain, then the normal to the {MnN₂} planes of A- and Btype units are inclined with +38.1 and -34.4 degrees with respect of this line, if take compound 1 as example, the other cases being similar. The magnetic anisotropy can be simplified if choose an averaged absolute value of the tilt, α =36.25 degrees, with $+\alpha$ for the units A and $-\alpha$ for the units B. Another idealization is the assumption of equal coupling parameters inside the dimer units. For a system with *n* sites of spin S, the Hamiltonian matrix has the dimension $(2S+1)^n$. Aiming to consider a $(A_1A_2-B_1B_2)_n$ oligomer as surrogate for the infinite chain, the Hamiltonian scales as 625ⁿ, being prohibitive, with customary procedures, already at the n=2 stage (when matrix dimension reaches almost 400000). The discussed alternation of anisotropy axes precludes the block factorization that occurs in the case of ZFS with coaxial D-only local Hamiltonians.

The non-diagonal elements in the above $H_{ZFS}(\alpha)$ one-site Hamiltonian lead to cross-elements in the matrix of the extended system. In such circumstances, the *n*=1 case is the sole tractable object. In spite of inherent limitations, even this smallest system can retain the basic elements of the interaction, being taken in the following as basis for the semi-quantitative interpretation of the magnetic data in this class of systems. With the presumed $J=J_A=J_B$ equivalence of the intra-dimer couplings, re-labelling by $J'=J_C$ the coupling over the acetate bridge, and enforcing a formal contact between A₁ and B₂ ends, in order to simulate the continuity, the Hamiltonian of the minimal tetranuclear is ascribed as follows:

$$\hat{H} = -2J \left(\hat{S}_{A_1} \cdot \hat{S}_{A_2} + \hat{S}_{B_1} \cdot \hat{S}_{B_2} \right) - 2J' \left(\hat{S}_{A_2} \cdot \hat{S}_{B_1} + \hat{S}_{A_1} \cdot \hat{S}_{B_2} \right) .$$
(4)

The succession of sites with the {+ α ,+ α ,- α ,- α } pattern in the tilting of anisotropy axes, with respect of the mean line of the chain, is formally ascribed by the following notation:

$$\hat{H}_{ZFS} = \hat{H}_{ZFS}^{A_{\rm I}}(\alpha) + \hat{H}_{ZFS}^{A_{\rm 2}}(\alpha) + \hat{H}_{ZFS}^{B_{\rm 1}}(-\alpha) + \hat{H}_{ZFS}^{B_{\rm 2}}(-\alpha)$$
(5)

Considering that the system under a *B* magnetic field, the Hamiltonian is completed with the Zeeman Hamiltonian, each site contributing with a $g\mu_BS \cdot B$ term, assuming a common *g* factor for all the sites. In the given circumstances, namely anisotropic system with different local axes, the S_z ceases to be an overall good quantum number and the popular van Vleck formula cannot be used. In turn, must use the general expressions based on the sum of state function *Z* (see the final section dedicated to methodological details). Besides, accounting the anisotropy, dependence is made explicit with respect of the directions from which the probe field is applied.

We proceeded to a rather advanced algorithm, fitting simultaneously the magnetization and susceptibility data. From experimental source, we have multiple experimental curves for magnetization, dependence on field and temperature (M vs. B and T), aside the standard susceptibility data (χT vs. T). Then, we handle a rather rich information, in a non-trivial treatment, that enables the several parameters of the model.

The results of the fit are outlined in the Table 2. Using the coupled fit procedures, we avoided the problem of parametric uncertainty that arises when monotonous χT vs. *T* patterns are to be considered in over-parameterization circumstances. The fit is good for χT vs. *T* curves and moderate for the *M* vs. *B*/*T* series, this limitation being the price paid to the limited tetranuclear sequence that stayed at the basis of the modelling. However, the dimension is a bottleneck issue and cannot be encompassed, the difficulty of the problem increasing exponentially, being intractable at higher levels.

Table 2. The results of simultaneous fit to the χT vs. T and M vs. B/T curves for compounds **1-3**.

Parameters			Compound		
	1	2	3		
g	2.020	1.998	2.010		
$D = D_A = D_B$	-5.13	-2.73	-5.87		
$J = J_{A} = J_{B}$	+0.26	+0.50	+0.33		
$J' = J_{\rm C}$	-1.08	-0.65	-1.16		
	g $D = D_{A} = D_{B}$ $J = J_{A} = J_{B}$ $J' = J_{C}$	Compound 1 g 2.020 $D = D_A = D_B$ -5.13 $J = J_A = J_B$ +0.26 $J' = J_C$ -1.08	Compound 1 2 g 2.020 1.998 $D = D_A = D_B$ -5.13 -2.73 $J = J_A = J_B$ +0.26 +0.50 $J' = J_C$ -1.08 -0.65		

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All the systems were evidenced with ferromagnetic, J > 0, coupling inside the oxo-bridged dimeric units and antiferromagnetic, J' < 0, over the carboxylate linkage. The ZFS parameter is negative, as expected for the axially elongated d^4 ions. In spite of the introduced simplifications, the advance is sensibly higher in comparison to existing interpretations on similar systems, considering the works cited in introduction.

The ab initio approach of the magnetic properties.

Ab initio multi-configuration calculations using Complete Active Space Self Consistent Field (CASSCF)^[33] procedures were performed on the system 2. The computed values are J_A =+0.165 cm⁻¹, J_B =+0.154 cm⁻¹ and J_C =-0.035 cm⁻¹, supporting qualitatively the fit results, i.e. yielding ferromagnetic coupling inside the oxo-bridged units and antiferromagnetism for the carboxylate bridge sequence, in spite of the fact that the absolute values from the fit to the experiment do not match very well. The ZFS parameters were extracted from spin-orbit (SO) calculations, subsequent to the CASSCF orbital optimization.

In order to describe the situation at one of A or B types of centres, we considered oxo-bridged dimers where one site is replaced by Co(III), working CASSCF-SO calculations on {Mn-Co}_A and {Mn-Co}_B systems. The lowest five states from such calculations can be fitted well to a ZFS model, obtaining $D_{A=}$ - 3.706 cm⁻¹, $E_{A=}$ 0.067 cm⁻¹ for the A-type site and $D_{B=}$ -3.246 cm⁻¹, $E_{B=}$ 0.121 cm⁻¹ for the B-type one. Note that the sign of *E*-parameter is not important, the ZFS spectrum being the same for both ±|*E*| values. At the same time, on may conclude that as compared with *D*, the *E* magnitude is small and can be neglected, in order to simplify the parameter list (as we actually did in the fit model).

The Figure 7 shows a comprehensive account of the various results of calculations characterizing one complex unit belonging the species A from system 2. The ZFS spectrum resulted from the CASSCF-SO calculation on the ground state is illustrated in the left panel (a). The energy levels depicted in the right side of panel (b) correspond to the computed CASSCF states, labelled according to the tetragonal idealization. The reversed CASSCF energy diagram, shifted with the barycentre in zero, can be assimilated to the ligand field orbital scheme.



Figure 7. Synopsis of orbital scheme determining the (a) ZFS groundstate scheme, (b) spectral terms and ligand field effects and (c) the magnetic orbitals involved in the exchange coupling from the corresponding dimer unit. The calculations are illustrated on a unit belonging to the species A from compound 2.

The groundstate is similar to a configuration $|(xz)(yz)(xy)(z^2)|$ which, in quasi-tetragonal effective symmetry, can be assigned to a ${}^5B_{1g}$ term. This configuration can be interpreted as a hole in the x^2-y^2 function, which correspondingly takes the higher position in the effective orbital scheme. Conversely, the energies of the highest spectral terms are related with the lowest effective *d* orbital, assignable to the quasi-degenerate doublet $e_g \equiv (xz, yz)$. The effective tetragonal symmetry can be approximated, if neglect the spacing between xz and yz components (about 715 cm⁻¹), small in comparison with the total gap of the scheme, about 23500 cm⁻¹.

Using the standard ligand field parameters for a tetragonal case, *Dq*, *Ds* and *Dt*, (see formulas written aside the levels from Figure 7b), the quantities computed for the A-type Mn(III) site of compound **2** are: $10Dq_A=19732.2$ cm⁻¹, *Ds*_A=2676.3 cm⁻¹, *Dt*_A=918.5 cm⁻¹. For the species B, the scheme is qualitatively similar, showing a slightly higher ligand field strength, with the following parameters: $10Dq_B=22014.5$ cm⁻¹, *Ds*_B=2849.8 cm⁻¹, *Dt*_B=1296.8 cm⁻¹

The orbitals depicted in section (c) are the functions obtained by the symmetry localization of the canonical orbitals resulted from the CASSCF calculation of the $\{Mn_2\}_A$ oxo-bridged dimer. Considering that the canonical molecular orbitals (MOs) were implied in the determination of exchange coupling parameter, the localized functions have also the meaning of magnetic orbitals. Observing details of the depicted orbitals and underlining the key features in Figure 8, one may advance a qualitative explanation for the ferromagnetic coupling along the oxo-bridges and antiferromagnetic over the carboxylate ligand.



Figure 8. Different interaction patterns explaining the nature of exchange coupling in the dimeric sequences of the discussed chains: (a) the σ -type and (b) the π -type interaction channels in oxo-bridged {Mn₂} dimeric units suggesting ferromagnetism determined by the orthogonality of magnetic orbitals; (c) the σ -type and (d) the π -type interaction in carboxylate bridged moiety showing mutual overlap of magnetic orbitals and antiferromagnetism.

Thus, a p_z -type atomic orbital (AO) from a bridging oxygen atom is involved in π -type bonding with the central metal ion of its unit and in σ -type overlapping with the metal ion of the other unit. The interacting couples figured in panels (a) $z^2 - p_z - z^2$ and (b) $yz - p_z - yz$ from Figure 8, contribute to ferromagnetic channels, containing orthogonality relationships, since the bridging p_z component cannot interact simultaneously with both *d* partners.

One may imagine other couples leading to delocalized overlapping, such as $z^2 - p_z - yz$, but one may assume the dominance of the frontier orbital couple, $z^2 - p_z - z^2$, determining the overall ferromagnetism over the oxo-bridges. Such a regularity is supported by the almost rectangular shape of the Mn₂O₂ frame, holding the relative purity of σ and π interaction labels. A more advanced distortion leads to the σ - π mixing and to the mutual overlapping that favours the antiferromagnetism. Such a situation occurs for the interaction along the carboxylate bridge. The panels (c) and (d) from Figure 8 suggest nonbonding and weakly bonding MOs on the acetate that interact simultaneously with both metal ions, leading to effective overlap and antiferromagnetism. Note that, in (a) and (b), the lobes located on the bridge show overlap only towards one Mn centre, while the overlap against the other is forbidden. Conversely, in (c) and (d) cases there are elements of bridge orbitals that are simultaneously overlapping with both metal ions.

Conclusions

We developed an extended and systematic analysis dedicated to experimental, computational and conceptual aspects of the molecular magnetism based on dimeric building blocks of Mn(III)-salen type complexes, which turn to be a rather large class of systems, with promising further chemistry. Particularly, we used the [Mn(III)(5MeO-salen)]⁺ unit, which in previous instances^[15] led to a SCM system with overall ferromagnetic coupling. The SCM features are induced by the intrinsic SMM characteristics of the [Mn₂(5MeO-salen)₂]²⁺ binuclear units, formed in the sequence of extended assemblies. We present a new series of coordination chains, resulted from the bridging of {Mn₂} with carboxylate groups. Because of the antiferromagnetic coupling over the Mn-OCO-Mn bridge, the systems cannot be claimed as SCM, but their magnetic behaviour is naturally interesting, because of the embodied dimeric SMMs.

The interpretation of magnetic properties of an infinite system is non-trivial, having a complex interaction scheme (two or three types of exchange coupling constants, *J*, anisotropy described by local *D* parameters, plus a spin canting due to the tilted local easy axes along the chain). We proceeded with care, performing a salient modelling of these features on finite systems, obtaining reasonable effective parameters.

The data were complemented with state of the art ab initio calculations, CASSCF followed by spin-orbit (SO) treatments, accounting the exchange coupling and ZFS parameters in semiquantitative way. The ferromagnetism inside the dimeric

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sequences is explained by orbital interactions^[34-37] Namely, the bridge functions that establish an overlap with one of the metal ions is orthogonal towards the other one. In turn, the acetate contact, having a lower local symmetry, realizes overlapping with both metal ions, leading to antiferromagnetism. The ferromagnetism inside the Mn(III) binuclears, combined with the anisotropy given by the negative D parameter of the ZFS Hamiltonian, makes these moieties intrinsic SMMs.^[38-39] However, because of the inter-dimer antifferomagnetic coupling, the systems are not SCMs, having yet interesting magneto-structural features.

Experimental Section

Materials. All reagents were of analytical grade and were used without further purification.

Caution! Perchlorate salts are potentially explosive and should only be handled in small quantities.

Preparation of Complexes. The Schiff base ligand, N, N"-bis(5-Methoxy-salicylidene)-1,2-diaminoethane (H₂5MeOsalen) was prepared by the stoichiometric condensation reaction of 5- methoxy-salicylaldehyde and 1,2-ethanediamine, in methanol.

[Mn₂(5Meosalen)₂(μ-CH₃COO)]_n(CIO₄)_n (1): A methanol solution (20 mL) of Mn(CH₃COO)₃•2H₂O (0.268 g, 1 mmol) was added to a methanol solution (40 mL) of the Schiff base ligand H₂5MeOSalen (0.324g, 1 mmol). After stirring for 30 min, NaClO₄ (0.07g, 0.5 mmol) was added. After 30 min heating at 50°C, the brown solution was filtered hot. The filtrate was left to stand for one week at room temperature to form brown-black crystals. Yield: 74%. Crystals were used for X-ray and magnetic measurements. Analysis: Calc. for C₃₈H₃₉ClMn₂N₄O₁₄ (M=921.07) C, 49.55; H, 4.27; N, 6.08 %. Found C, 49.63; H, 4.17; N, 6.12 %. IR (KBr) (σ/cm⁻¹): 1652(C=N), 1626(C=N), (C=0), 1107, 625 (CIO₄⁻).

[Mn₂(5Meosalen)₂(μ-CH₃COO)]_n(CF₃SO₃)_n (3): An analogous method as described for **1** was used, by replacing NaClO₄ with NaCF₃SO₃ (0.086g, 0.5 mmol). Yield: 54.2%. Crystals were used for X-ray and magnetic measurements. Analysis: Calc. for $C_{39}H_{39}F_3Mn_2N_4O_{13}S$ (M=970.68) C, 48.26; H, 4.05; N, 5.77% Found C, 48.22; H, 3.99; N, 5.83 %. IR (KBr) (σ / cm⁻¹): 1636(C=N), 1158, 1030, 845, 638 (CF₃SO₃⁻).

Physical Measurements. Infrared spectra were measured on a KBr disk with a Jasco FT-IR 4200 spectrometer.

X-ray Crystal Structure Analysis. Single crystals of 1 - 3 were prepared according to the described method in the synthesis section. Data collections for 1-2 were made on a Rigaku Saturn CCD diffractometer with graphite monochromated Mo-K α radiation (λ =0.71069 Å). The structure was solved by heavy-atom Patterson methods^[40] and expanded

using Fourier techniques.^[41] All calculations were performed using the CrystalStructure^[42] crystallographic software package, except for refinement, which was performed using SHELXL-97.^[43] The diffraction data for **3** were collected on SMART-1000/CCDD (Bruker AXS) area detector using the standard procedure (Mo-K α radiation). The data integration and reduction were undertaken with SAINT and XPREP.^[44] The structure was solved by direct methods and refined using least-squares methods on F² with SHELXL-97.^[43] The non-hydrogen atoms were modelled with anisotropic displacement parameters, and hydrogen atoms were placed by difference Fourier syntheses and refined isotropically. CCDC- 848820 (for **1**), 848821 (for **2**), 848822 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

Cyclic Voltammetry. The voltammetry measurements were carried out using a conventional three electrode glass cell, coupled to an PAR 273 A scanning potentiostat, while the system was controlled by a PC unit. The working electrode was a small platinum disk with about 0.07 cm² area; the counter electrode was a platinum coiled wire and the reference electrode an Ag/AgCl electrode immersed in a lithium perchlorate (0.1 M) in acetonitrile. All solutions were prepared using acetonitrile. The voltammograms were recorded at a concentration of the investigated compounds of 5x 10^{-4} M, within the potential range 0 to 1.5 V, or -0.8V to 1.5 V. As the supporting electrolyte, lithium perchlorate (Aldrich), were used, at a concentration of 0.1 M.

Magnetic measurements. Magnetic measurements for **1-3** were carried out on a Quantum Design SQUID MPMS 5S magnetometer on polycrystalline samples. The dc measurements were made using an external magnetic field of 1000 Oe over a temperature range of 1.8-300K and ac measurements using a 3Oe magnetic field oscillating at 100-1000 Hz. Diamagnetic corrections were estimated from Pascal constants.

Simulation of the magnetic properties. Expressing the magnitude of external field by *B* and its orientation by the of the θ and φ polar angles, we worked a general $Z(B, \theta, \varphi)$ for anisotropic sum of the states function. The explicit field dependence is introduced by the Zeeman components. Finally, because the experimental data are statistic averages, due to random orientation of the microcrystals in the sample, we shall consider the space integration, when simulate the magnetization,

$$\overline{M} = N_A k_B T \int_{\theta=0}^{\theta=\pi} \int_{\varphi=0}^{\varphi=2\pi} \left(\frac{d}{dB} \ln(Z(B,\theta,\varphi)) \right) \frac{1}{4\pi} \sin(\theta) d\theta d\varphi$$

or magnetic susceptibility,

$$\overline{\chi} = N_A k_B T \int_{\theta=0}^{\theta=\pi} \int_{\varphi=0}^{\varphi=2\pi} \left(\frac{d^2}{dB^2} \ln(Z(B,\theta,\varphi)) \right) \frac{1}{4\pi} \sin(\theta) d\theta d\varphi$$

Here N_A and k_B are the Avogadro and Boltzmann universal constants. The basic part of the procedure consists in solving the eigenvalues $\varepsilon_i(B, \theta, \varphi)$, (i=1 to 625) of a Hamiltonian matrix constructed in the above discussed manner, with the *J*, *J'*, *D* and *g* parameters. The sum of the state is expressed then:

$$Z(B,\theta,\phi) = \sum_{i} \exp\left(-\frac{\varepsilon_{i}(B,\theta,\phi)}{k_{B}T}\right)$$

The Hamiltonian and consequently the Z function are including an outer magnetic field *B*, applied from a direction expressed with polar angled θ and ϕ , i.e. having Cartesian components $B_x=Bsin(\theta)cos(\phi)$, $B_y=Bsin(\theta)sin(\phi)$, $B_z =Bcos(\theta)$. The derivatives from the Z function are solved numerically, taking finite differences after solving the Hamiltonian

at the *B*, *B*+*dB*, *B*-*dB*, where *dB*=0.001 T. The *dB* small perturbation has the same polar orientation as the external field. If the outer field is null, then the θ and φ dependence concerns the orientation of the applied *dB* perturbation. The integration contained in the orientation averaging is also considered numerically, taking a summation (corresponding weighted with the spherical sin(θ) factors) over a grid of 12 points for the θ coordinate and 24 points in the φ scan. As a whole, with the repeated solving of the large Hamiltonian matrix, as required by the numerical differentiation and integration procedures, the computation is rather demanding.

Ab initio calculations. Complete Active Space Self Consistent (CASSCF) calculations were performed with the GAMESS program^[45] using the 6-311G* basis set for the Mn, N, or O atoms, and 6-31G for the C or H atoms. The molecular models are cut from the experimental structure of system 2. For the building blocks of A or B type we considered the $\{Mn_2\}_A$ or $_B \equiv [Mn_2(5-MeOSalen)_2(CH_3COOLi)_2]^{2+1}$ molecular models, where Li atoms were imposed as prosthetic elements mimicking the next Mn(III) ions in the chain. In this way, the carboxylate moiety from a terminating Mn-carboxylate-Li sequence contains a part of the electrostatic polarization encountered in the chain, having a better description of corresponding contribution of this group to the axial ligand field. In order to estimate the exchange coupling over the carboxylate, bridge an asymmetric molecular unit $\{Mn_AMn_B\}$ = [(LiOH)Mn(MeOSalen)(CH₃COO)(MeOSalen)Mn(LiOH)]²⁺ was computed, with artificial terminating groups, namely Li⁺, instead of the following Mn^{III} ion, and HO instead of phenoxo group from next salen-type ligand that completes the axial coordination of the studied centre. The active spaces of the CASSCF(n,m) calculations (n electrons in m orbitals) were selected in accordance the considered problem. Thus, for estimating exchange coupling on selected dimer sequences, $\{Mn_2\}_A,\;\{Mn_2\}_B,$ and {Mn_A,Mn_B}, we performed CASSCF(8,10) calculations corresponding to the d^4-d^4 case. Focusing on local ligand field on a given d^4 site, the CASSCF(4,5) calculations were performed on {CoMn}_{A or B} = [(CH₃COOLi)Co^{III}(5-MeOSalen)Mn^{III}(5-MeOSalen)(CH₃COOLi)] idealized models, where a site was replaced with diamagnetic Co(III) and

excluded from the active space. Applying ab initio spin-orbit (SO) procedures, subsequently to the CASSCF(4,5) calculations, we accounted for the magnetic anisotropy resulted from the Zero Field Splitting (ZFS) effects.

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Keywords: Manganese complexes • Magnetic anisotropy • Spin Hamiltonian• Ab Initio calculations• Exchange mechanisms

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

A new series of compounds incorporating а Mn(III) dimeric building block behaving as molecular magnet, due to intrinsic magnetic anisotropy, is reported. Advanced analyses are performed, complemented with transparent qualitative mechanisms.



Ferromagnetic coupling in [Mn₂(5MeO-salen)₂]²⁺ dime



Chain with alternating magnetic anisotropy axe

Fanica Cimpoesu, Tanta Spataru, Cristina Maria Buta, Horst Borrmann, Olivia Georgeta Moga, and Marilena Ferbinteanu*

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Spin Coupling and Magnetic Anisotropy in 1D Complexes with Manganese(III) Units and Carboxylate Bridges. Synthesis and Analysis, Calculations and Models.