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Article

SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF NEW HOMOPOLYNUCLEAR MANGANESE(II) CHAIN COMPLEX

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ABSTRACT

A 1D-manganese chain complex was synthesized by self-assembling strategy using a paramagnetic building block, [Mn(bpca)$_2$], based on the ditopic ligand, Hbpca=bis-(2-pyridilcarbonyl)-amine. The chain consists in the alternation of {MnN$_6$} chromophores, with axial compression oriented parallel to the chain direction, and {MnO$_6$}units, with axial elongation perpendicular to the 1-D line. The {MnO$_6$} species are containing aqua-Mn(II)-perchlorate polar axes imposing a dipole of the chain, perpendicular to its extending direction. Dipole-dipole, dipole-charge and hydrogen bonding are contributing to the supramolecular cohesion. A weak antiferromagnetism, due to superexchange via π-system of bpca bridges is fitted to the J=-0.293 cm^{-1} value of coupling strength.

Keywords: ditopic ligand, self-assembling synthesis, manganese chain complexes, magnetic coupling.

1. INTRODUCTION

Coordination chemistry [1] is a central realm in the nowadays world of sciences oriented toward the achievement of new materials and technologies. The bonding mechanism in complex compounds [2] and the relation structure-properties are quite similar to those existing in solid state systems with recognized applicability such as magnetic or superconductor oxides. However, since at the molecular scale the recognition of causal

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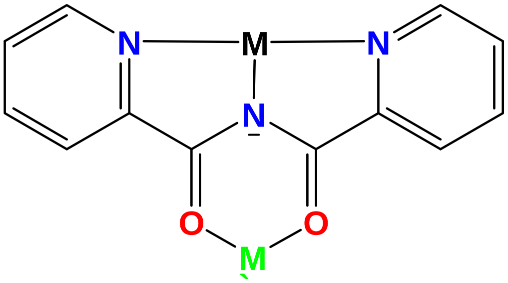
♣ Correspondent author: E-mail: marilena.cimpoesu@g.unibuc.ro factors producing a desired property is clearer than in the infinity of solid state, the coordination compounds offer various particularized case studies to get academic insight with possible ultimate relevance in property design. Besides, the size of coordination edifices can be tuned to progressive larger scale, e.g. from distinct molecules (0-D) to the 1-D, 2-D or bulk 3-D connection patterns of metal ions with the ligands [3]. Large molecular complexes, constituted by tens of metal ion centers, bridged by ligands (medium sized organic molecules, in the range of few tens of atoms) are approaching the nano-scale [4-5]. Extended coordination systems such as metal-organic frameworks are in the full focus possible applications in various areas, for instance in catalysis [6].

A central idea in the modern coordination sciences, in connection with the paradigms of supra-molecular chemistry [7-8], is that the specifics of each ligand, the topology of donors and propensity for non-covalent interactions, in conjuncture with the affinity or stereochemical match of the metal ions to the ligand active sites, can be handled to the purpose of rationally controlled complex structures. Although countless examples in the line of such desiderata are reported in the literature, the complete control of structure and properties is still at the learning curve. This makes the coordination paradigm a quite active and yet dynamic one. Particularly, the molecular magnetism [9-11] is a prominent domain of the coordination chemistry, with its speculative end in the yet elusive spintronics, but with a lot of significant solid conquests on academic ground, in the area of magneto-structural correlations, as pieces of knowledge paving the road to new high-tech devices and useful effects [12]. The vogue of the last years was devoted to special issue of magnetic anisotropy [13-16], a very essential ingredient for achieving a magnet at molecular scale, the so-called Single Molecule Magnets (SMMs) [17-18]. In this context, the coordination polymeric structures, designed - in principle- with specific properties as function of composition and topologies are interesting for achieving 1-D anisotropic systems with Single Chain Magnet (SCMs) behaviour [19].

We contributed with illuminating case studies to such issues, with one of the first small sized SMMs (d-f dinuclear) [22], one of the firsts SCMs [20], as well as several related advances [16, 22-26]. A part of these previously discussed magnetic systems were based on $[M^{q}(bpca)_2]^{q-2}$ coordinative donor building blocks, with the ditopic ligand Hbpca=bis-(2-pyridilcarbonyl)-amine, its ionized form ($bpca^{-}$) represented in Scheme 1. The ligand is planar, potentially pentadentate, acting as a divergent connector with three nitrogen donor atoms oriented in one direction and a two-oxygen chelate on opposite side.

The ligand is known since long time, but we pioneered its use in the d-f assembling strategies [22]. The Hbpca is obtained by reacting 1,3,5-tris(2-pyridyl)triazine with copper sulfate, the free organic ligand being isolated from the formed copper (II) complex by EDTA extraction [21]. The two coordination sites can select metal ions with different chemical affinities, for instance the nitrogen side for approaching d-transition metal ions, while the diketonato-type chelate moiety is suitable for oxofile lanthanide ions. Therefore, the anionic bpca− is particularly suited for assembling d−f systems and we exploited [22-26] its propensity to build oligomeric or chain d−f systems [27]. Aside to the new synthetic aspects, we complemented our magneto-structural insight with ab initio original approaches, designed for particularities of f systems, including Spin Orbit (SO), Ligand Field (LF) and exchange coupling terms [22]. Other synthesized d-f systems became study cases for another breakthrough of our group, the analysis of the magnetic anisotropy by polar map representations which allow to identify the easy magnetization axes respect with the molecular frame [24, 26].

Scheme 1: Coordination modes of the bpca ligand illustrating divergent tridentate function through nitrogen atoms and bidentate function through the oxygen ones.



Mononuclear complex $[M^q(bpca)_2]^{q-2}$ (q=2, 3) units are known for several transition metal ions like Mn(II) [28], Fe(II, III) [29-33], Co(III) [34-36], Rh(II, III) [37-39], Ni(II) [30], Cu(II) [21], Zn(II) [21]. The $[M^q(bpca)_2]^{q-2}$ units are building blocks, acting as complex ligand, in producing d-d discrete structures [35, 40-42], homo- or heteropolynuclear systems with 1-D [31,35,43-46], 2-D [41,45] or extended structures with the same or different transition metal ions. Among these compounds an unique d-d SCM was reported to have a twisted arrangement of ions with alternate orientation easy-plane magnetic anisotropy [43] accompanied by valuable studies concerning the magnetic properties [46, 47].

A $[M^q(bpca)_2]^{q-2}$ buiding block not exploited until now in the polynuclear chain structures design is based on Mn(II). We report here the case of $[Mn(bpca)_2]$ acting as a complex ligand to form a homonuclear 1-D complex with the {Mn(μ-bpca)Mn(μ-bpca)Mn} sequence. We describe syntheses, structures, and magnetic properties of the new chain.

Implying only Mn(II) ions it has very weak anisotropy, being not directly relevant, in itself for SCM systems, but it is interesting as matter of synthesis and structure. Besides, the manganese ion from at least one of the two coordination spheres can, in principle, be oxidized to Mn(III) state which has strong anisotropic features. Then, the manganese chain complexe could be a possible precursor of a SCM system, if further electrochemical controlled oxidation will be applied, preliminaries in this sense being attempted. Therefore, the present study is a prerequisite for further advances, consolidating structure-property correlation knowledge in the conjuncture of its relatively simple scheme of bonding and spin coupling.

2. METHODS

2.1. Experimental

Synthesis. All chemicals were reagent grade and used as received. The Hbpca and [Mn(bpca)$_2$] were prepared by the literature methods [28,30]. (*Caution!* Although no problems have been encountered in the present work, perchlorates are potentially explosive and should be treated in small quantities with care).

To a solution of [Mn(bpca)$_2$]·H_2O (31.75 mg, 0.06 mmol) in CH_3NO_2 (2 mL) was added $Mn(ClO_4)_2·6H_2O$ (21.71 mg, 0.06 mmol) in CH_3OH (3 mL). The orange reaction mixture was stirred for one hour at room temperature. Orange crystals of (**1**) were obtained in several days by slow evaporation at room temperature and then filtered and dried in the air. Yield: 42 mg (83%).

Elemental Analysis: Calculated for $C_{25}H_{25}Cl_2Mn_2N_7O_{15}$: C, 35.56; H, 2.98; N, 11.61. Found: C, 35.60; H, 3.10; N, 11.50. IR (KBr, cm^{-1}): ν(C=O) 1720, ν(ClO_4^-) 1087, 624.

X-ray Crystallography. The diffraction data were collected on Bruker AXS SMART-1000/CCDD area detector using the standard procedure (Mo Ka radiation). The data integration and reduction were undertaken with SAINT and XPREP [48]. The intensity data were empirically corrected for absorption using the program SADABS [49]. The structures were solved by direct methods and refined using least-squares methods on F^2 with SHELXL-97 [50]. Non-hydrogen atoms were modeled with anisotropic displacement parameters, and hydrogen atoms were placed by difference Fourier syntheses and refined isotropically.

λ(Mo Kα) = 0.71073Å, T = 200 K, orange blocks, formula $C_{25}H_{25}Cl_2Mn_2N_7O_{15}$, MW = 905.33, 0.80 x 0.65 x 0.60 mm, tetragonal, I-4, a = 15.3606(18) Å, b = 15.3606(18) Å, c = 30.433(6) Å, a = 90^o, b =90^o, c = 90^o, Z = 8, V = 7180.7(19) Å^3,

R_1 = 0.0828, wR_2 = 0.2142, GOF = 1.036. Selected bond lengths and angles are presented in Table 1 and 2.

Spectral Measurements. Fourier transform infrared spectroscopy on KBr pellets was performed on a JASCO FT/IR-620 instrument.

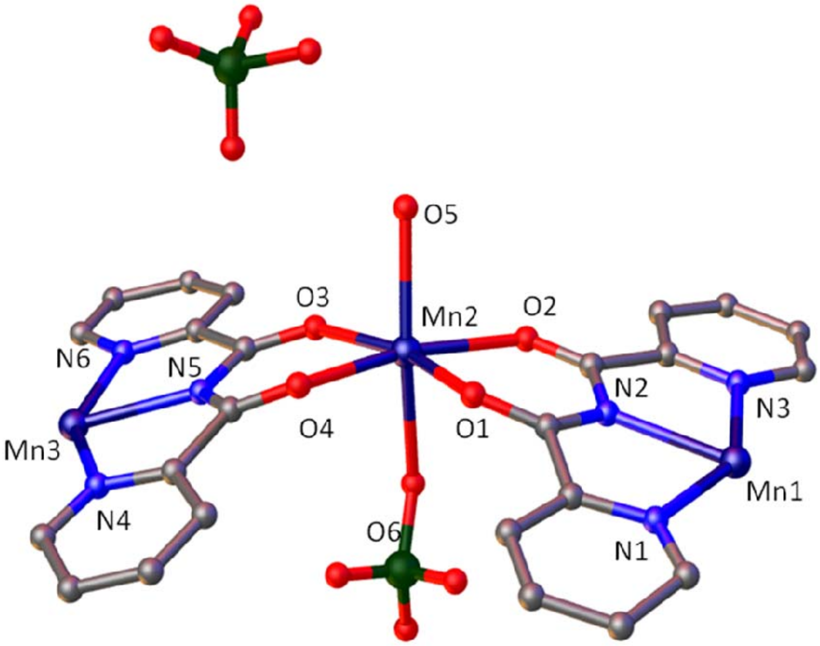
Magnetic Measurements. Variable-temperature magnetic susceptibility measurements were made by using a SQUID magnetometer MPMS 5S (Quantum Design) at 1 T field. Diamagnetic correction for each sample was determined from Pascal's constants.

3. RESULTS AND DISCUSSIONS

By the reaction of *in situ* formed [Mn(bpca)$_2$] with excess of Mn(II) ions (added from $Mn(ClO_4)_2·6H_2O$) a 1-D homopolynuclear [Mn(μ-bpca)$_2$Mn(H_2O)(ClO_4)]ClO_4 ·CH_3NO_2 (**1**) compound is collected, as orange crystals. The neutral [Mn(bpca)$_2$] act as buiding block, through the four outer oxygen atoms of the nitrogen – coordinated bpca- ligands. The formed chain is almost linear with a slight zig-zag tendency. It contains two Mn(II) species, one coordinated by six nitrogen atoms, pre-existent in [Mn(bpca)$_2$] and a center entirely based on oxygen donors.

The Figure 1 shows the asymmetric unit while the Figure 2 a sequence of two parallel chains in the crystal structure of [Mn(μ-bpca)$_2$Mn(H_2O)(ClO_4)]ClO_4 ·CH_3NO_2 (**1**).

Figure 1: Asymmetric units from molecule of Scheme (**1**) including the numbered atoms scheme. The solvent molecules and hydrogen atoms were omitted, for clarity.



The Figure 2 shows the alternating profile of chain, where Mn2 sites are bridged by the bpca ligands with the Mn1 and Mn3 neighbours. The Mn1-Mn2-Mn3 sequences are slightly angular (with the 150.40^{o} central angle) imposing a zig-zag arrangement with separations of 5.616 Å for Mn1-Mn2 and 5.618 Å for Mn2-Mn3, respectively. The Mn-Mn remote distances are lower than in the linear trinuclear compound previously reported [42]. The Mn2-Mn1-Mn2' and Mn2-Mn3-Mn2' sequences are almost linear.

The nitrogen-based coordination spheres of Mn1 and Mn3 sites are closely similar, but yet slightly different, probably because of the dynamic disordering induced by the perchlorate (coordinated and free) ions. These [Mn(bpca)$_2$] units are possessing C$_2$ symmetry operations, with axes placed between the two ligands of each coordination fragment, perpendicularly to the main direction of the chain. The tridentate nitrogen side of the bpca ligands contains two pyridine functions and a central amide, imposing a meridial arrangement of the donors in octahedron. The geometries of Mn1 and Mn3 coordination units are compressed octahedra with the short bonds on the N$_{amide}$-Mn-N$_{amide}$ direction. This is a characteristic of all the [M(bpca)$_2$] units, but in general rare for the manganese complexes. The four pyridine nitrogens can be taken as equatorial planes of the Mn1 and Mn3 units. For Mn1, the equatorial Mn1–N distances are 2.230(10) and 2.258(11) Å the short axial contacts with the two amide nitrogens (N2) with distances of 2.169(8) Å (see Table 2), each value repeated twice due to the two-fold axis.

Table 1: Selected bond distances (Å) and angles (°) for molecule of Scheme (**1**)

Mn-N		Mn-O		E-Mn-E	
Mn1-N1:	2.230(10)	Mn2-O1:	2.119(7)	N2-Mn1-N1:	74.4(3)
Mn1- N2:	2.169(8)	Mn2-O2:	2.130(7)	N2-Mn1-N3:	73.8(4)
Mn1- N3:	2.258(11)	Mn2-O3:	2.145(7)	N5-Mn3-N4:	74.1(3)
Mn3-N4:	2.227(10)	Mn2-O4:	2.122(7)	N5-Mn3-N6:	73.2(4)
Mn3- N5:	2.185(8)	Mn2-O5:	2.204(7)	O1-Mn2-O2:	81.7(3)
Mn3- N6:	2.261(11)	Mn2-O6:	2.245(9)	O1-Mn2-O5:	96.0(3)

The equivalent bonds, under the C_2 symmetry, are mutually placed in *cis* for the pyridine members of the mean equatorial plane and in *trans* in the case of the axial imides. The formal equatorial plane looks, in fact, like a flattened tetrahedron, the *trans* points making a 147.2 degrees with respect of the central metal ion. The octahedron frame is quite distorted, due to specific constrains of the bpca skeleton, having angles about the 74 degrees in the *cis* sequences between pyridine and amide donors of the same ligand. Similarly, Mn3 is surrounded by four pyridyl nitrogens (N4, N6) with 2.227(10)-2.261(11) Å bond lengths and two amide nitrogens (N5) with distances of 2.185(8) Å, the showing the same qualitative features described for the Mn1 unit. The pattern of Mn1 and Mn3 fragments is comparable with those in the parent monomeric [Mn(bpca)$_2$] [28].

The ionized beta-diketonate moieties from two [Mn(bpca)$_2$] units of Mn1 and Mn3 sites are forming the equatorial plane of the Mn(II) octahedral center labeled Mn2, while its axial positions are occupied by an aqua (H_2O) and one perchlorate (ClO_4^-) ligand. The FT-IR spectrum shows for the perchlorate group an intense and split band around 1087 cm^{-1}, accompanied by a weak band at 624 cm^{-1}, suggesting different perchlorate species, coordinated and free. Slightly higher frequency shift of C=O stretching (an intense band at 1720 cm^{-1} compared with 1700 cm^{-1} for the parent monomer [28]) suggest that the negative charge of the ligand is more localized on the central amide nitrogen atom, while the carbon-oxygen links tend to more double bond character. The oxygen-based coordination unit has the {O1-O2-Mn2-O3-O4 }equatorial plane with a slight pyramidal distortion, the planes of diketonate chelates having the appearance of a hinge opened at a dihedral plane of about 170 degrees. This feature determines the open angular placement of the Mn1-Mn2-Mn3 centers and the zig-zag aspect of the chain. Comparing the bond distances presented in Table 1, the geometry of the central atom appears as an octahedron elongated on the aqua-perchlorate O5-Mn1-O6 direction, with corresponding d(Mn2-O5)=2.204(7) Å and d(Mn2-O6)= 2.245(9) Å distances. This site has no symmetry. The carbon-oxygen bonds are slightly different, in the same ligand or comparing the two ligand species. Thus, for the ligand connecting the Mn2 and Mn1 ions the bond lengths are 1.210(11) and 1.247(12) Å, while 1.217(11) and 1.232(11)

Å for the bpca placed between Mn2 and Mn3 species. Aside the FT-IR data, the C-O distances are suggesting again that the negative charge of the bpca ligand is localized on the central N_{amide} atoms.

The *trans* O5-Mn2-O6 axis, made of aqua and perchlorate ligands, imposes a definite dipole moment to the $\{MnO_6\}$ oxygen based coordination sphere of the Mn2. In Figure 2 the sequence of the chain structure is represented, showing the coordination polyhedra. The chain is positively charged, being counter-balanced by a row of perchlorate anions placed in the neighborhood of the mentioned aqua ligands. Considering the above details, we observe the alternation of $\{MnN_6\}$ octahedra with axial compression parallel to the chain with $\{MnO_6\}$ units with axial elongation perpendicular to the 1-D line. Because of mutual rotation, by about 90 degrees, of the alternating bpca ligands, the H_2O-Mn-ClO_4 vectors from immediately repeated Mn2 units are also rotated in the same way. The next neighbouring units, at the count of Mn2 sites, show parallel orientation of the polar H_2O-Mn-ClO_4 moieties. Thus, if take the mean direction of the chain as z, and placing one aqua-Mn2-perchlorate axis on the positive direction of x, the vicinal Mn2 site will point its dipole towards y, the following one again on x, while the further one on y, and so on. Then, the whole chain carries a resultant dipole along the axis bisecting the xy plane, perpendicular to the z one-dimensional extension. The neighbor chain has the mirror image, with alternating H_2O-Mn-ClO_4 dipoles pointing reversely, with the $-x$ and $-y$ alternation. This relationship is visible comparing the parallel chains shown in Figure 2. One may infer the dipole-dipole interaction of the chain as an important mechanism of the supramolecular ordering. There is also a dipole-charge interaction, as well a hydrogen bonding, between the aqua edge of the H_2O-Mn-ClO_4 moiety and the non-coordinated perchlorate (shown in Figure 1, omitted in Figure 2, for a full clarity of the chain image).

Figure 2: Sequence of the zig-zag chain structure of compound of Scheme (**1**) with polyhedral representation for manganese ions coordination sites. Chains with opposite dipole resultants, due to ordered H_2O-Mn-ClO_4 polarized axes, are running parallel.

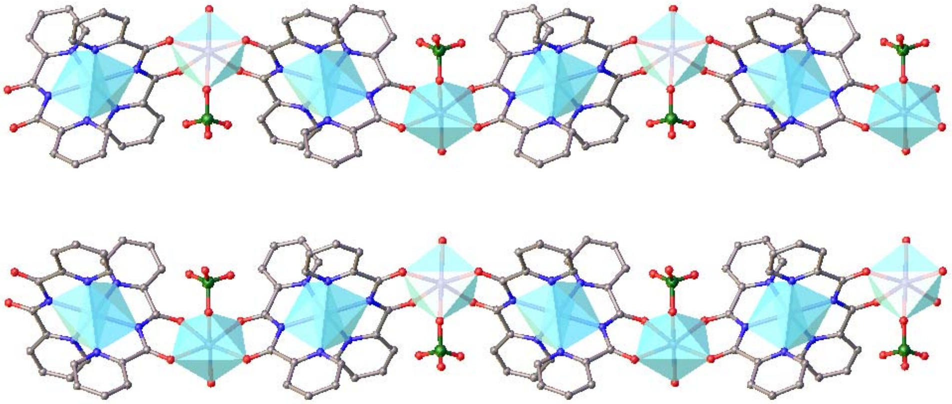


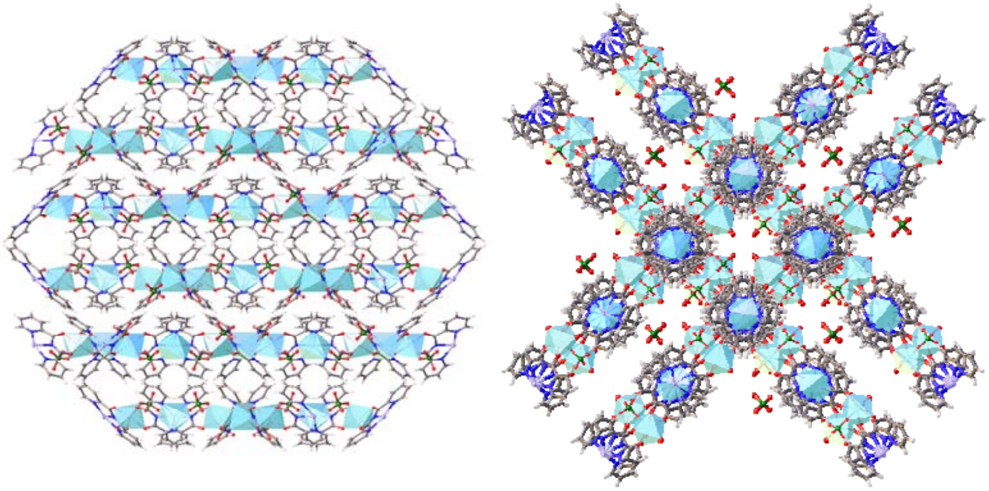
Table 2: Bond distances (Å) around manganese ion in the bridging buiding block in complex of Scheme (**1**) and other literature complex vs. mononuclear complexes [Mn(bpca)$_2$]

Mn-N$_{amide}$	Mn-N$_{py}$	Mn-N$_{amide}$^{a}	Mn-N$_{py}$^{a}	Mn-N$_{amide}$^{b}	Mn-N$_{py}$^{b}
2.185(8)	2.258(11)	2.196(2)	2.246(2)	2.179(7)	2.255(7)
2.169(8)	2.230(10)	2.203(2)	2.221(2)	2.169(7)	2.216(7)
	2.261(11)		2.262(2)		2.285(8)
	2.227(10)		2.242(2)		2.236(8)

^{a}Reference [42]. ^{b}Reference [28].

Looking at larger scale, one observes that, in the crystal, the chains are grouped in layers. Each layer contains a parallel arrangement of different enantiomeric chains, as presented in the packing diagrams from Figure 3.

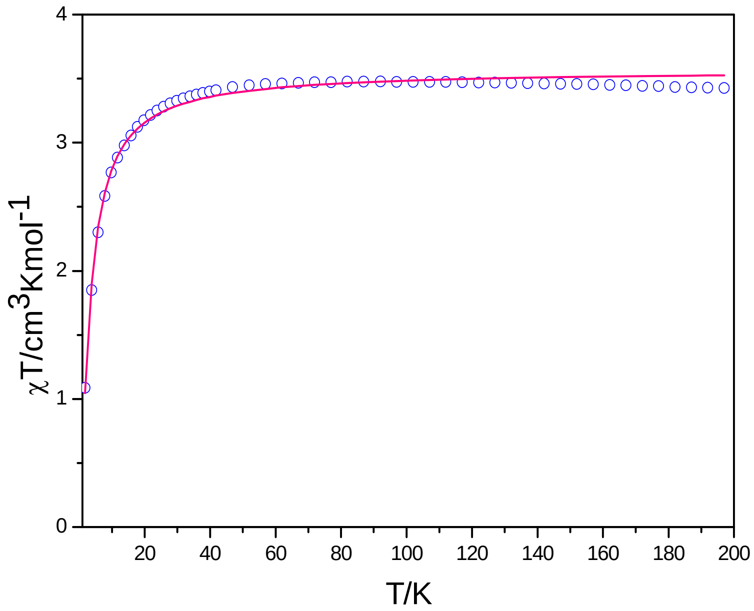
Figure 3: Packing diagram for the compound of Scheme (**1**) along *a* (a) and *c* (b) axis showing the parallel arrangement of the chains.



(a) (b)

The Figure 4 shows the temperature dependence of the magnetic susceptibility for (**1**) measured down to 2.0 K. The $\chi_M T$ value at room temperature, 3.5 cm^3 K mol^{-1}, is lower than the spin-only value of 4.4 cm^3 K $mol^{-1}$for a *S*=2 spin paramagnet with taking the gyromagnetic factor g =2.00, the level of the plateau estimating then g=1.8.

Figure 4: Plot of χT vs. T for molecule of Scheme (**1**). The circles correspond to the experimental points and the solid line corresponds to the theoretical curve for which parameters are given in the text.



On lowering the temperature, the $\chi_M T$ vs. T curve value decreases suggesting antiferromagnetic interaction between adjoining Mn(II) ions through the delocalized π-system of the bridging bpca ligands. In principle, there are two exchange coupling constants, alternating along the chain, between the Mn1-Mn2 and Mn2-Mn3 centers, but given the close structural similarity of the Mn1 and Mn3 species, one may a unique coupling parameter, *J*. The susceptibility was modeled with the Fisher equation [51-52] for an infinite uniform chain:

$$\chi_M = \frac{N\beta^2 g^2 S(S+1)}{3kT} \cdot \frac{1+u}{1-u} \tag{1}$$

Where $u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$ (2)

The least squares calculation yielded the best fit parameters of g = 1.807 and J = -0.293 cm^{-1}. The gyromagnetic factor is practically the same with the above estimation from the level of high temperature $\chi_M T$ plateau. The small absolute value of the coupling parameter is reasonable, conceivable as resultant of compensating different positive and negative orbital exchange channels at the d^5-d^5 exchange interaction, with a slight predominance of antiferromagnetic paths, probably due to the bridge-delocalized π-type interactions.

4. CONCLUSION

In this work we treated the synthesis, molecular structure and supramolecular assembling details of the $[Mn(\mu\text{-bpca})_2Mn(H_2O)(ClO_4)]ClO_4 \cdot CH_3NO_2$ compound. The 1-D pattern is due to the bridging capabilities of the bpca ligand. The tridentate nitrogen moiety is a strong coordinating agent, capturing the metal ions (Mn(II) in our case) in the center of an axially compressed octahedron. At the same time, the ligand possesses outer oxygen donors, suited to coordinated hard Lewis acids, such as lanthanide ions, the Mn(II) ion being also fitted to interact with this function. In other words, the $[Mn(bpca)_2]$ units with nitrogen-based coordination sphere act as complex ligands toward another metal ion, the symmetric divergent topology favoring the formation of the chain. The Mn(II) ions connecting the preformed $[Mn(bpca)_2]$ moieties have coordination spheres entirely based on oxygen donors, with two pairs from diketonate functions of the bpca placed equatorially, while one aqua and one perchoarate ligand, placed axially, confer a net dipole to the unit. The coordination polar axes are ordered in such a way that the whole chain has a dipole moment, perpendicular to its growth direction. In the crystal, each chain has an enatiomeric companion (mirror image) with opposed polar structure. The supramolecular dipolar interactions between chains are part of the mechanism of the crystal packing. Besides, dipole-charge interactions are established between polymeric coordination structures (with net positive charge) and rows of interstitial perchlorate anions. The perchlorates are forming also supramolecular hydrogen bond networks with the coordinated aqua axial ligands. Both the nitrogen-based and oxygen-type coordination spheres are visibly distorted from regular octahedron. In the former, there is an axial compression imposed by the structure of the bpca ligand, with pyridine functions forming an equatorial mean plane, which looks like a flattened tetrahedron, while amide donors are forming the short axial bonds. In the other coordination species, the diketonate planes of from different $[Mn(bpca)_2]$ complex ligands are forming a hinge distortion, shaping the zig-zag pattern of the chain. The magnetic susceptibility shows a weak antiferromagnetic coupling along the chain, fitted with Fisher equation to the J = -0.293 cm^{-1} value. This interaction is mediated by the π-type delocalization along the bridge. Consisting in Mn(II) homo-metallic composition, the system has no magnetic anisotropy, but the nitrogen based sites can supposedly be oxidized to Mn(III) with potential single-chain-magnet features, further attempts being invested in this direction.

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