



## The first member of a second generation family of ligands derived from metal-ion assisted reactivity of di-2,6-(2-pyridylcarbonyl)pyridine: Synthesis and characterization of a $\text{Mn}^{\text{II/III}}_4$ rhombus

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### ABSTRACT

Nucleophilic attack by the carbanion  $^-\text{CH}_2\text{COCH}_3$  at the carbonyl carbon atoms of 2,6-di-(2-pyridylcarbonyl)pyridine, pyCOpyCOpy, in the presence of  $\text{Mn}^{\text{n+}}$  ions under basic conditions has yielded the cationic cluster  $[\text{Mn}_4(\text{OH})_2(\text{L})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4$  (**1**), where  $\text{L}^{2-}$  is the  $(\text{py})\text{C}(\text{CH}_2\text{COCH}_3)(\text{O}^-)(\text{py})\text{C}(\text{CH}_2\text{COCH}_3)(\text{O}^-)(\text{py})$  dianion. The cluster cation possesses a planar  $\{\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2(\mu_3\text{-OH})_2(\mu\text{-OR})_4\}^{4+}$  rhombus core, resulting from two  $\mu_3\text{-OH}^-$  ions and two  $\eta^1:\eta^2:\eta^1:\eta^1:\eta^1:\eta^2:\eta^1:\mu_3$  bridging  $\text{L}^{2-}$  groups from the *in situ* formed ligand. Complex **1** is antiferromagnetically coupled with an unusual  $S = 2$  ground state resulting from spin frustration effects within the triangular  $\text{Mn}_3$  subunits of the cluster.

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There continues to be a growing interest in the synthesis and study of polynuclear 3d transition metal complexes (clusters) due to their relevance to various aspects of structural chemistry [1], bioinorganic chemistry [2] and molecular magnetism [3]. Manganese at intermediate oxidation states (III, IV) plays a special role in all of these fields.

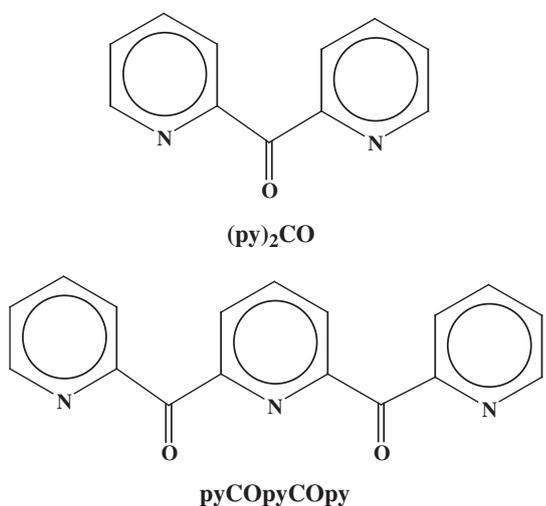
In the development of new synthetic routes to 3d-metal clusters, the choice of the bridging ligands is always a key issue. An example of a thoroughly studied such ligand is di-2-pyridyl ketone,  $(\text{py})_2\text{CO}$  (Scheme 1), which has led to a multitude number of clusters with a variety of metal ions [4] and nuclearities reaching 26 [5], some of which exhibiting large  $S$  values and single-molecule magnetism behavior [5,6]. The particular interest in this ligand stems from the reactivity of its carbonyl group, which can undergo metal-assisted hydrolysis or alcoholysis ( $\text{ROH}$ ;  $\text{R} = \text{Me}, \text{Et}$ ) forming the ligands  $(\text{py})_2\text{C}(\text{OH})_2$  [the *gem*-diol form of  $(\text{py})_2\text{CO}$ ] and  $(\text{py})_2\text{C}(\text{OR})(\text{OH})$  [the hemiketal form of  $(\text{py})_2\text{CO}$ ], respectively, which are considered as the first generation of ligands derived from  $(\text{py})_2\text{CO}$ . The impressive structural chemistry of the  $(\text{py})_2\text{CO}$ -based metal clusters arises from the ability of the anionic

ligands  $(\text{py})_2\text{CO}_2^-$ ,  $(\text{py})_2\text{C}(\text{OH})\text{O}^-$  and  $(\text{py})_2\text{C}(\text{OR})\text{O}^-$  to adopt no less than 16 distinct bridging coordination modes ranging from  $\mu_2$  to  $\mu_5$  [4]. A recent progress in the reactivity chemistry of the  $(\text{py})_2\text{CO}$  ligand involves the attack by nucleophiles other than  $\text{H}_2\text{O}$  and alcohols on its carbonyl C atom in the presence of metal ions, introducing the second generation of ligands derived from  $(\text{py})_2\text{CO}$  (Scheme 2) [4b,7]. These new derivatives of  $(\text{py})_2\text{CO}$  have led to new metal cluster topologies, different nuclearities, and interesting magnetic properties upon deprotonation of their hydroxyl groups [4b,7,8].

Inspired by the rich chemistry of  $(\text{py})_2\text{CO}$  and its related ligands, we have started a program aiming at the exploration of the coordination and reactivity chemistry of 2,6-di-(2-pyridylcarbonyl)pyridine (pyCOpyCOpy, Scheme 1), which contains two carbonyl groups directly bonded to two 2-pyridyl groups, each in a way similar to that found in  $(\text{py})_2\text{CO}$ . We thus considered that pyCOpyCOpy should be an excellent candidate to afford similar solvolysis, deprotonation and coordination chemistry, but, due to the increased number of coordination sites ( $N, N, N, O, O$ ), it might lead to 3d-metal clusters with different nuclearities, structural motifs and physical properties compared to the ones reported with  $(\text{py})_2\text{CO}$ -based ligands. Indeed, our synthetic endeavors have verified the above hypotheses [9]. In all of our studies the nucleophiles were restricted to  $\text{H}_2\text{O}$  and alcohols [9], producing a variety of ketone/diol, ketone/hemiketal, bis(diol), bis(hemiketal) and diol/hemiketal coordinated ligands.

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**Scheme 1.** Structural formulae and abbreviations of the ligands di-2-pyridyl ketone [(py)<sub>2</sub>CO] and 2,6-di-(2-pyridylcarbonyl)pyridine (pyCOPyCOPy).

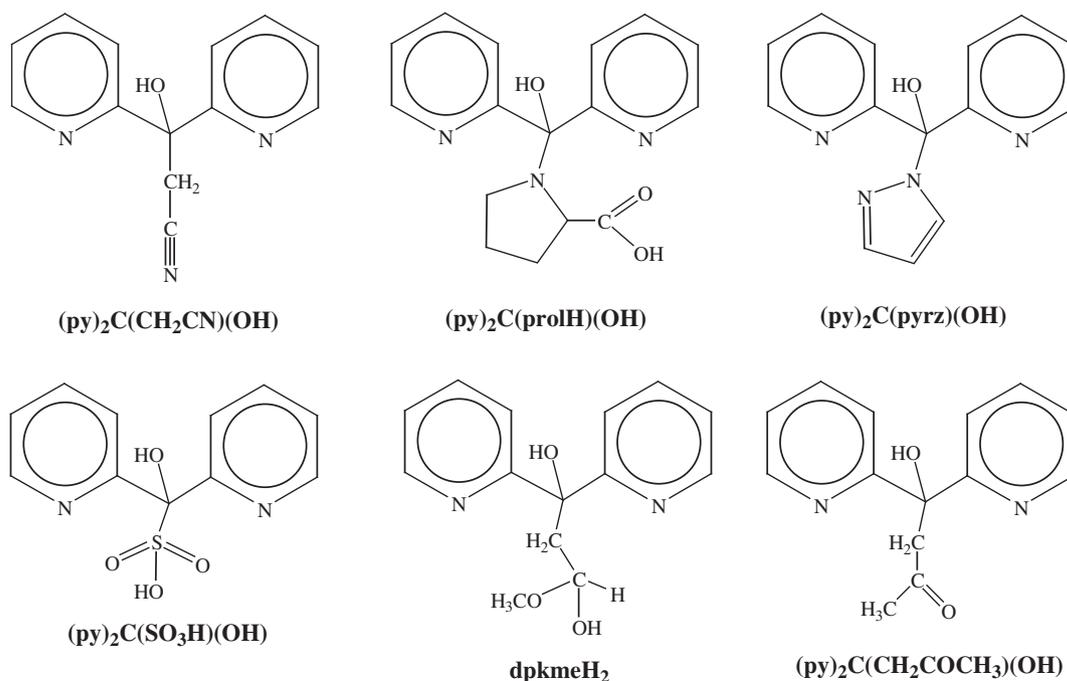
We have recently started to explore the 3d-metal chemistry of this ligand in the presence of nucleophiles other than H<sub>2</sub>O and alcohols. Since the α-hydrogens of acetone are weakly acidic (pK<sub>a</sub> ~ 20) [10], we have been interested in investigating whether pyCOPyCOPy would be capable of undergoing reactivity toward CH<sub>3</sub>COCH<sub>2</sub><sup>-</sup> in the presence of metal ions. The present work describes the realization of this goal by reporting a new Mn<sup>II/III</sup><sub>4</sub> cluster which incorporates the first member of a second generation family of pyCOPyCOPy-based ligands derived from a novel metal-ion assisted, crossed-aldol reaction of acetone with the bis(ketone) molecule.

The reaction of Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, pyCOPyCOPy [11], and NEt<sub>3</sub> in an 2:1:3 molar ratio in Me<sub>2</sub>CO gave an orange solution. The latter was stirred for a further 1 h, during which time the color turned to dark red. The resulting solution was filtered, and the filtrate left undisturbed to concentrate slowly by evaporation at room temperature. After 10 days, red plate-like crystals of [Mn<sub>4</sub>(OH)<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>

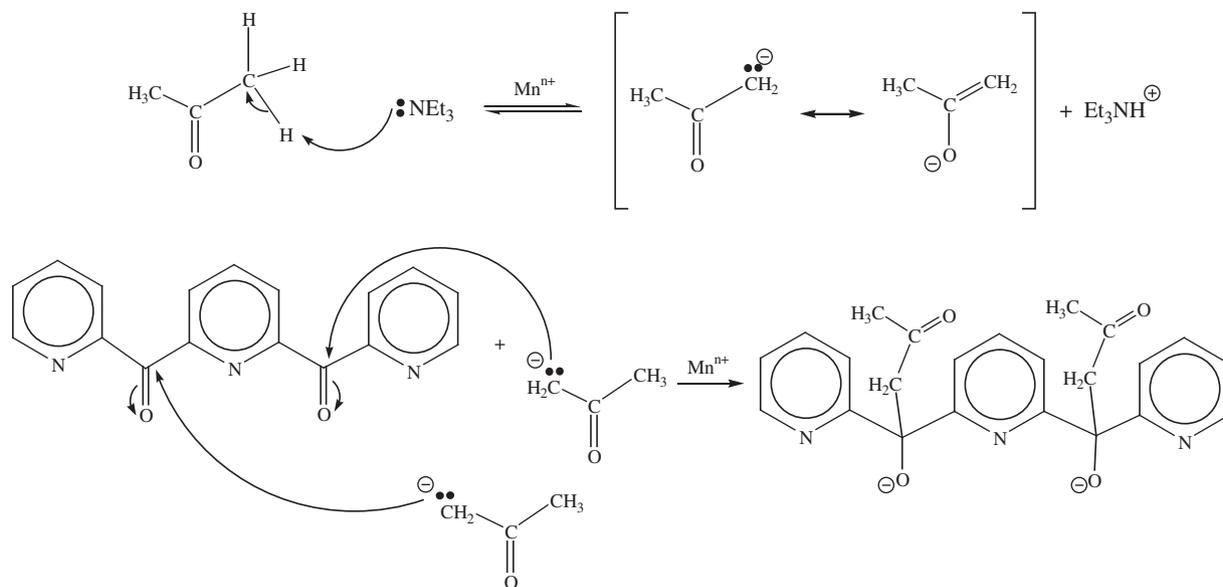
(ClO<sub>4</sub>)<sub>4</sub>·2Me<sub>2</sub>CO (**1**·2Me<sub>2</sub>CO) were collected by filtration, washed with cold Me<sub>2</sub>CO (2 × 3 mL), and dried under vacuum over silica gel; the yield was 35% (based on the total available Mn [12]). The new, *in situ* generated, ligand L<sup>2-</sup> is the dianion (py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py) (vide infra).

A simplified mechanism for the formation of (py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py) is proposed in Scheme 3. The relatively strong base NEt<sub>3</sub> abstracts an α-hydrogen from acetone which is in equilibrium with the corresponding, resonance-stabilized carbanion [8,10,13]. Once the carbanion CH<sub>3</sub>COCH<sub>2</sub><sup>-</sup> is formed, it attacks the positively charged carbonyl carbons of pyCOPyCOPy. As the carbanions form the C–C bonds, the π electrons of the two carbonyl groups of pyCOPyCOPy are transferred completely to the corresponding oxygen atoms, forming two alkoxide ions. The reaction that leads to (py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py) is not an aldol condensation, because the product is not further dehydrated to form a double carbon–carbon bond [8,10,13]. Possible reasons for the non-condensation of (py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py) are the strongly basic medium which does not permit the existence of neutral alcohol functions and/or its stabilization by the Mn<sup>n+</sup> centers. The formation of (py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>-</sup>)(py) is likely metal-ion promoted (or assisted). We have failed to date to synthesize the free neutral ligand (this compound is not known in organic chemistry) by the reaction of pyCOPyCOPy and acetone in the presence of NEt<sub>3</sub> or any other strong base under several reaction conditions.

Complex **1**·2Me<sub>2</sub>CO crystallizes in the triclinic space group *P* $\bar{1}$ . The structure [14] consists of tetranuclear [Mn<sub>4</sub>(OH)<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>4+</sup> cations, ClO<sub>4</sub><sup>-</sup> counterions and solvate Me<sub>2</sub>CO molecules. The tetranuclear cluster cation (Fig. 1) lies on an inversion center and contains a planar Mn<sub>4</sub> rhombus. Each Mn<sub>3</sub> triangular unit is bridged by an oxygen atom (O1X, O1X') from a μ<sub>3</sub>-OH<sup>-</sup> group, while each of the pairs Mn1/Mn2, Mn2/Mn1', Mn1'/Mn2' and Mn2'/Mn1 is further bridged by one deprotonated alkoxide arm (O1, O4, O1', O4') of a L<sup>2-</sup> group. Each of the Mn2, Mn2' centers is coordinated to one pyridine N atom (N2/N2') and two ketone O atoms (O2, O3/O2', O3') from one L<sup>2-</sup> ligand, as well as a terminal H<sub>2</sub>O molecule (O1W/O1W'), to complete a MnNO<sub>6</sub> chromophore. The coordination sphere of Mn1, Mn1' is each completed by



**Scheme 2.** The second generation family of ligands derived from (py)<sub>2</sub>CO. Note that none of them exist as free species but are found only in their respective metal complexes.

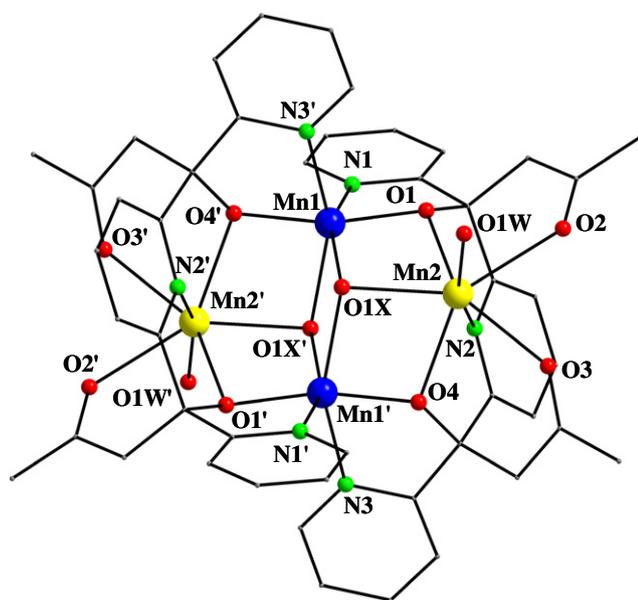


**Scheme 3.** The proposed simplified mechanism that leads to (py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>−</sup>)(py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>−</sup>)(py) which is present as ligand in complex **1**; the Mn<sup>n+</sup> ions stabilize the resonance-stabilized enolate intermediate and the final ketone/alkoxido product.

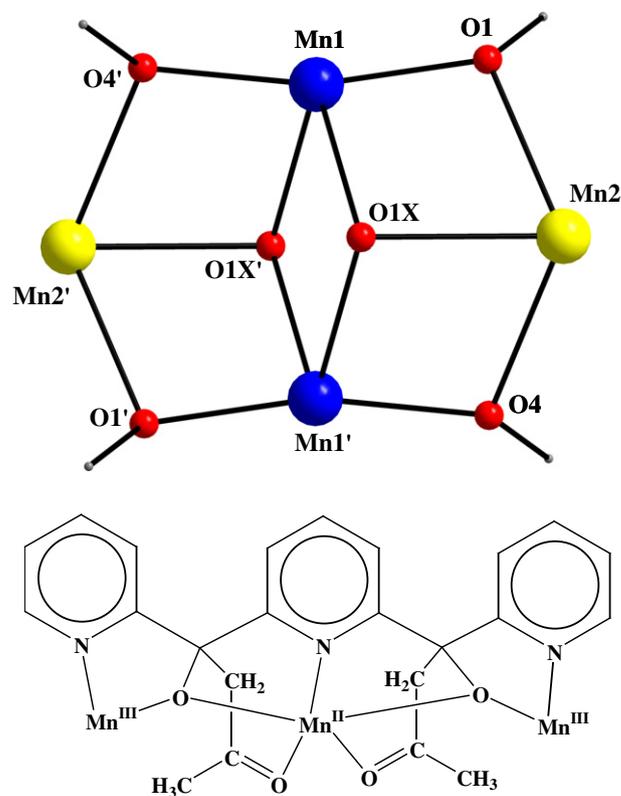
two pyridine N atoms (N1, N3/N1', N3') belonging to two different L<sup>2−</sup> ligands, thus giving a Mn<sub>2</sub>O<sub>4</sub> chromophore. Consequently, atoms Mn1 and Mn1' are six-coordinate with a distorted octahedral geometry, while atoms Mn2 and Mn2' are seven-coordinate with a distorted pentagonal bipyramidal geometry. The complex therefore contains the {Mn<sub>4</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(μ-OR')<sub>4</sub>}<sup>4+</sup> core (Fig. 2, top), with each of the L<sup>2−</sup> ions acting as a η<sup>1</sup>:η<sup>2</sup>:η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup>:η<sup>1</sup>:η<sup>1</sup>:μ<sub>3</sub> ligand (Fig. 2, bottom).

Charge considerations and inspection of the metric parameters indicate a Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub> mixed-valence situation, as additionally confirmed by BVS calculations [15] that gave values of 2.99 for Mn1/Mn1' (Mn<sup>III</sup>) and 2.00 for Mn2/Mn2' (Mn<sup>II</sup>). Mn1 also displays a Jahn–Teller (JT) distortion as expected for a high-spin d<sup>4</sup> ion in near-octahedral geometry, taking the form of an elongation of the N3'–Mn1–O1X' and symmetry-related N3–Mn1'–O1X axes. The protonation level of OH<sup>−</sup>,

OR<sup>−</sup> and H<sub>2</sub>O groups was also determined by BVS calculations. These gave values of 0.92 (O1X), 1.83 (O1)/1.79 (O4) and 0.22 (O1W), in excellent agreement with the theoretical values of 1.0–1.2, 1.7–2.0 and 0.2–0.5 expected for coordinated OH<sup>−</sup>, OR<sup>−</sup> and H<sub>2</sub>O groups, respectively [16]. The Mn···Mn distances within **1** are in the 3.202(2)–5.527(2) Å range. Distinguishable C–O single [C6–O1/C15–O4 = 1.426(6) Å] and



**Fig. 1.** Partially labeled plot of the cation present in **1**·2Me<sub>2</sub>CO. H atoms have been omitted for clarity. Color scheme: Mn<sup>III</sup>, blue; Mn<sup>II</sup>, yellow; O, red; N, green; C, gray. Primes are used for symmetry-related atoms.



**Fig. 2.** (top) PovRay representation of the complete (Mn<sub>4</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(μ-OR')<sub>4</sub>)<sup>4+</sup> core of **1**. (bottom) The coordination mode of the dianion (py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>−</sup>)(py)C(CH<sub>2</sub>COCH<sub>3</sub>)(O<sup>−</sup>)(py) in complex **1**. Color scheme: Mn<sup>II</sup> yellow; Mn<sup>III</sup> blue; O red; N green.

C=O double bonds [C8-O2 = 1.244(1) Å and C17-O3 = 1.217(1) Å] are evident, confirming two single and two double carbon–oxygen bonds (Fig. 2, bottom).

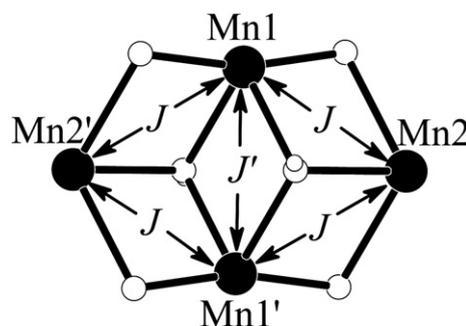
The crystal structure of **1**·2Me<sub>2</sub>CO is stabilized by OH···O hydrogen-bonds between the OH<sup>−</sup> and H<sub>2</sub>O groups, which act as donors, and ClO<sub>4</sub><sup>−</sup> counterions and Me<sub>2</sub>CO solvate molecules, which function as acceptors (Fig. S1).

The {Mn<sub>4</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(μ-OR')<sub>4</sub>}<sup>4+</sup> core of **1** has been reported only once before [17]. This is likely due to the preference of the Mn<sup>III</sup> ions (hard acids) to be bound to O<sup>2−</sup> groups rather than OH<sup>−</sup> ions. Complex **1** is also the first molecular species stabilized by the organic ligand L<sup>2−</sup> and the first homometallic Mn cluster bearing any form of the pyCOPyCOPy ligand.

Solid-state direct-current (dc) magnetic susceptibility ( $\chi_M$ ) data were collected on a powdered sample of dried **1** in the 2.0–300 K range in a 0.5 T field using a Quantum Design MPMS SQUID magnetometer. The magnetic susceptibilities were computed by exact calculation of the energy levels associated with the spin Hamiltonian through diagonalization of the full matrix with the enhanced version of a general program for axial symmetry [18]. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT [19]. Simulations of the magnetization ( $M$ ) versus field ( $H$ ) were carried out with the MAGPACK program package [20].

The  $\chi_M T$  product steadily decreases from 13.19 cm<sup>3</sup> K mol<sup>−1</sup> at 300 K to 2.43 cm<sup>3</sup> K mol<sup>−1</sup> at 2.0 K (Fig. 3). The room temperature  $\chi_M T$  value is lower than the spin-only ( $g=2$ ) value of 14.75 cm<sup>3</sup> K mol<sup>−1</sup> for two Mn<sup>II</sup> and two Mn<sup>III</sup> non-interacting ions, indicating the presence of dominant antiferromagnetic exchange interactions and suggesting a small ground-state spin ( $S$ ) value. The 2.0 K  $\chi_M T$  value suggests an  $S=2$  or 1 ground state, albeit closer to the former case; the spin-only ( $g=2$ ) values for  $S=2$  or 1 are 3 and 1 cm<sup>3</sup> K mol<sup>−1</sup>, respectively.

Given the symmetry of the complex, two isotropic-exchange interactions would be necessary to account for its magnetic behavior, one along the peripheral Mn<sup>II</sup>···Mn<sup>III</sup> ions of the Mn<sub>4</sub> rhombus ( $J$  coupling constant) and one between the central Mn<sup>III</sup>···Mn<sup>III</sup> ions ( $J'$  coupling constant), Scheme 4. No Mn<sup>II</sup>···Mn<sup>II</sup> diagonal interaction has been included, as this is expected to be very weak due to the long Mn2···Mn2' distance (5.527(2) Å) and the absence of any direct bridging ligand [17]. Moreover, due to the propensity of Mn<sup>III</sup> ions to exhibit large axial anisotropies, a single-ion zero-field splitting



**Scheme 4.** Magnetic exchange interactions in complex **1**. The Mn numbering scheme is the same with the one employed in the real structure, see Fig. 1.

parameter,  $D_{\text{Mn(III)}}$ , was taken into account for Mn1 and Mn1'. Thus, the Hamiltonian considered was:

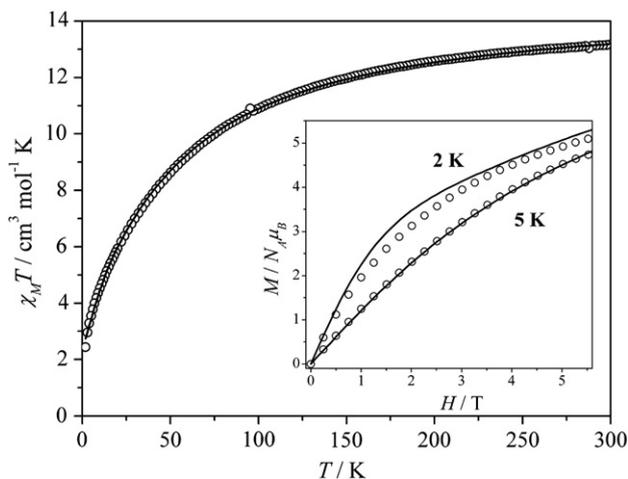
$$\hat{H} = -2 \left[ J (\hat{S}_1 \hat{S}_2 + \hat{S}_2 \hat{S}_{1'} + \hat{S}_{1'} \hat{S}_2 + \hat{S}_2 \hat{S}_1) + J' \hat{S}_1 \hat{S}_{1'} \right] + D_{\text{Mn(III)}} (\hat{S}_{z1}^2 + \hat{S}_{z1'}^2) + \beta g H \sum_i \hat{S}_i$$

Initial fitting attempts were carried out by fixing  $D_{\text{Mn(III)}}=0$ . These yielded a very satisfactory solution with best-fit parameters:  $J = -1.9$  cm<sup>−1</sup>,  $J' = -3.0$  cm<sup>−1</sup>,  $g = 1.99$  ( $R = 1.7 \times 10^{-4}$ , solution **A**, Fig. 3). This entails an  $S=2$  ground state with a low-lying  $S=1$  excited state at only 1.8 cm<sup>−1</sup> higher in energy. Subsequent fitting attempts liberating this parameter yielded solutions **B** ( $D_{\text{Mn(III)}} < 0$ ) and **C** ( $D_{\text{Mn(III)}} > 0$ ):  $J = -2.0$  cm<sup>−1</sup>,  $J' = -3.3$  cm<sup>−1</sup>,  $D_{\text{Mn(III)}} = -2.3$  cm<sup>−1</sup>,  $g = 2.01$  ( $R = 3.5 \times 10^{-5}$ , solution **B**) and  $J = -2.0$  cm<sup>−1</sup>,  $J' = -3.2$  cm<sup>−1</sup>,  $D_{\text{Mn(III)}} = 3.0$  cm<sup>−1</sup>,  $g = 2.00$  ( $R = 3.4 \times 10^{-5}$ , solution **C**). These solutions yielded significantly improved fits, which however were already of very high quality.

To verify that this improvement bears true physical meaning and is not due to overparametrization, we conducted simulations of isothermal magnetization measurements at 2 and 5 K (Fig. 3, inset). The simulations using the parameters from solution **A** provided a very good agreement with the experimental data. Simulations based on solution **B** yielded poorer results, while simulations based on solution **C** yielded results comparable to those based on solution **A**. Therefore, our conclusion was that although the improvement to the fits points to single-ion zero-field splitting effects of the Mn<sup>III</sup> ions, their precise magnitude cannot be safely derived from fits to the magnetic susceptibility data, possibly due to correlations with the other structural and electronic parameters of the system. However, the magnitude  $|D_{\text{Mn(III)}}|$  of such an effect is not expected to be greater than 2–3 cm<sup>−1</sup> [17].

The exchange interactions within the Mn<sup>II</sup><sub>2</sub>Mn<sup>III</sup><sub>2</sub> rhombus core of **1** are thus both antiferromagnetic and weak, in agreement with magnetic results from compounds with a similar {Mn<sub>4</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(μ-OR')<sub>4</sub>}<sup>4+</sup> core [17]. The weakest is  $J$  between the peripheral Mn<sup>II</sup>···Mn<sup>III</sup> ions, and this is expected since the bridging pathway is provided by an alkoxide O atom and a hydroxido O atoms at Mn<sup>II</sup>-OR'(H)-Mn<sup>III</sup> angles spanning the range 102.7(2)–105.2(2)° and 95.8(2)–96.0(2)°, respectively [21,22]. In contrast, the central Mn<sup>III</sup>···Mn<sup>III</sup> ions ( $J'$ ) are solely bridged by two hydroxido O atoms at an angle of 106.2(2)°, which are known (as well as bridging oxido groups) to promote stronger coupling [21,22], at an angle of 106.2(2)°. Given the fact that the Mn<sup>II</sup>···Mn<sup>III</sup> interactions are always weak [22], it is qualitatively reasonable for  $J$  to be the weakest interaction in the molecule, although the precise values of all the  $J_{ij}$  parameters are the net sum of contributions from ferro- and antiferromagnetic pathways and thus it is difficult to rationalize their differences accurately.

The fact that  $J \approx J'$  in **1** was expected to have a clear impact on the ground state because the rhombus {Mn<sup>II</sup><sub>2</sub>Mn<sup>III</sup><sub>2</sub>(μ<sub>3</sub>-OR)<sub>2</sub>(μ-OR')<sub>4</sub>}<sup>4+</sup> core has been well established from previous work to experience spin frustration effects as a result of the presence of triangular Mn<sub>3</sub>



**Fig. 3.**  $\chi_M T$  versus  $T$  plot for **1** in a 0.5 T dc field. The solid line is the best-fit of the data according to the model described in the text (solution **A**); see the text for the fit parameters. The inset shows isothermal magnetization data at 2 and 5 K, along with simulations considering the best-fit parameters of solution **A**.

subunits within its structure [21–23]. Since the interactions in **1** are all antiferromagnetic, they are competing and the precise ground state spin alignment is thus very sensitive to the  $J/J'$  ratio. This is indeed the case for the unusual  $S = 2$  ground state of **1**.

In summary, it has been shown that coordinated pyCOPyCOPy is capable of undergoing a unique reactivity in acetone under basic conditions which is due to the presence of a weakly acidic  $\alpha$ -hydrogen in the solvent and to the  $\delta^+$  character of the carbonyl carbon atoms of the ligand. The resulting dianion of the bis( $\beta$ -hydroxy)ketone that is formed comprises the first member of a second generation family of ligands derived from pyCOPyCOPy and bridges three Mn ions through its alkoxido groups facilitating the formation of a planar  $\{\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2(\mu_3\text{-OH})_2(\mu\text{-OR}')_4\}^{4+}$  rhombus core. The magnetic studies of the  $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}_4$  cluster revealed the presence of dominant antiferromagnetic exchange interactions and a small ground state spin value of  $S = 2$  with low-lying excited states very close in energy with the ground state. We are currently investigating (i) the incorporation of additional bridging groups, such as carboxylates, in the general  $\text{Mn}^{n+}/\text{pyCOPyCOPy}/\text{base/acetone}$  reaction system, (ii) the replacement of the  $\mu_3\text{-OH}^-$  ions by  $\eta^1\text{:}\mu_3\text{-N}_3^-$  (end-on) groups as a means of switching the coupling from antiferro- to ferromagnetic between the four Mn atoms within **1**, and (iii) the isolation of other 3d- and/or 4f-metal clusters that will contain the  $\text{L}^{2-}$  ligand.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.042.

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