Structure and Properties of Dinuclear Manganese(III) Complexes with Pentaanionic Pentadentate Ligands Including Alkoxo, Amido, and Phenoxy Donors

Liliana Stoicescu,†‡ Aurélie Jeanson,‡ Carine Duhyon,† Ana Tesouro-Vallina,† Athanassios K. Boudalis,§ Jean-Pierre Costes,* and Jean-Pierre Tuchagues*†

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 route de Narbonne, 31077 Toulouse Cedex 04, France, and Institute of Materials Science, NCSR “Demokritos”, 153 10 Aghia Paraskevi Attikis, Greece

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Doubly bridged \(\mu\)-alkoxo-\(\mu\)-X (\(X = \) pyrazolato or acetato) dinuclear Mn\(^{III}\) complexes of 2-hydroxy-N-{2-hydroxy-3-[\{2-hydroxybenzoyl\}amino\}propyl} benzamide (H\(_5\)L\(_1\)) and 2-hydroxy-N-{2-hydroxy-4-[\{2-hydroxybenzoyl\}amino\}butyl} benzamide (H\(_5\)L\(_2\)), \([\text{Mn}_2\text{(L}_2\text{)}](\text{py})\text{(MeOH)}_4\]) \(_1\), \([\text{Mn}_2\text{(L}_2\text{)}](\text{MeOH})_2\text{MeOH}\] \(_1\), \([\text{Mn}_2\text{(L}_2\text{)}](\text{Ac})_2\text{MeOH}\)] \(_3\), have been prepared, and their structure and magnetic properties have been studied. The X-ray diffraction analysis of \(_1\) \((\text{C}_{24.5}\text{H}_{34}\text{Mn}_2\text{N}_4\text{O}_{9.5}\), triclinic, \(P\_1\), \(a = 12.2050(7)\) \(\AA\), \(b = 12.7360(8)\) \(\AA\), \(c = 19.2780(10)\) \(\AA\), \(\alpha = 99.735(5)\), \(\beta = 96.003(4)\), \(\gamma = 101.221(5)\); \(V = 2867.6(3)\) \(\text{Å}^3\), \(Z = 4\)) and \(_2\) \((\text{C}_{25.5}\text{H}_{35}\text{Mn}_2\text{N}_4\text{O}_9\), triclinic, \(P\_1\), \(a = 9.4560(5)\) \(\AA\), \(b = 11.0112(5)\) \(\AA\), \(c = 13.8831(6)\) \(\AA\), \(\alpha = 90.821(4)\), \(\beta = 92.597(4)\), \(\gamma = 93.403(4)\); \(V = 1441.29(12)\) \(\text{Å}^3\), \(Z = 2\)) revealed that all complexes consist of dinuclear units which are further extended into 1D (1 and 3) and 2D (2) supramolecular networks via hydrogen-bonding interactions. Magnetic susceptibility data evidence antiferromagnetic interactions for all three complexes: \(J = -3.6\) \(\text{cm}^{-1}\), \(D \approx 0\) \(\text{cm}^{-1}\), \(g = 1.93\) (1); \(J = -2.7\) \(\text{cm}^{-1}\), \(D = 0.8\) \(\text{cm}^{-1}\), \(g = 1.93\) (2); \(J = -4.9\) \(\text{cm}^{-1}\), \(D = 3.8\) \(\text{cm}^{-1}\), \(g = 1.95\) (3).

Introduction

In the past decades, considerable attention has been dedicated to the synthesis of hetero-bridged \(\mu\)-alkoxo-\(\mu\)-X and \(\mu\)-alkoxo-\(\mu\)-X-\(\mu\)-Y (\(X, Y = \) carboxylato, pyrazolato, azido, cyanato, nitrito, hydroxo, methoxy) dinuclear transition metal complexes.\(^1\)\(^\text{a}\)-\(^8\) This ensues from their various interesting biomimetic and magnetic properties. The pentadentate dinucleating Schiff base ligands and the \(N,N',N''\)-tetrasubstituted-1,\(n\)-diamino-\(n'\)-hydroxyalkanes (\(n, n' = \) 3, 2; 4, 2, and 5, 3) having an endogenous alkoxo bridge have been used extensively to obtain doubly or triply bridged dinuclear complexes of copper,\(^1\) manganese,\(^2\) iron,\(^3\) nickel,\(^4\) cobalt,\(^5\) vanadium,\(^6\) and zinc.\(^7\) So far, very few structurally characterized doubly bridged \(\mu\)-alkoxo-\(\mu\)-acetato\(^2\) and \(\mu\)-alkoxo-\(\mu\)-pyrazolato\(^2\) manganese(II) and \(\mu\)-alkoxo-\(\mu\)-methoxy manganese(III)\(^2\)-\(^b\) dinuclear complexes based on these types of ligands have been reported. The structurally characterized Mn\(^{II}\) complex \([\text{Mn}_2\text{(L}_1\text{)}](\text{OAc})(\text{py})\text{(butanol)}]\text{(ClO}_4\text{)}_2\text{H}_2\text{O}\) \(^2\) includes a \(\mu\)-alkoxo bridge from the ligand HL \((\text{N},\text{N},\text{N}',\text{N}''\)-tetrakis(2-methylenecyanamidazoyl)-1,3-diaminopropan-2-ol). However, there are no structural informations on \(\mu\)-alkoxo-\(\mu\)-pyrazolato dinuclear manganese complexes. The unique report concerning a manganese(II) complex of this type\(^2\) was based only on analytical and spectroscopic data. From a dinucleating ligand incorporating (2-hydroxybenzamide) moiety, Bertoncello et al.\(^8\) have obtained doubly bridged (\(\mu\)-alkoxo)(\(\mu\)-acetato)dinuclear manganese(III) complexes of general formula \([\text{Mn}_2\text{(L}_1\text{)}](\text{OAc})(\text{B}_2)\]. Where \(B = \) pyridine, \(\gamma\)-picoline, and methanol. Only the molecular structure of the pyridine derivative \([\text{Mn}_2\text{(L}_1\text{)}](\text{OAc})(\text{py})\text{py}H_2O\] \((\text{H}_5\text{L}_1\) \(= \) 2-hydroxy-N-{2-hydroxy-3-[\{2-hydroxybenzoyl\}amino]-}

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propyl]benzamide) was described revealing that this complex exists as discrete molecules.

In this study, we describe the synthesis, crystal structure, and magnetic properties of three doubly bridged μ-alkoxy-μ-X (X = pyrazolato or acetato) dinuclear manganese(III) complexes: [Mn₃L₂(pz)(MeOH)₄]₂xMeOH (1, L = L¹, x = 0.5; 2, L = L², x = 0; H₂L₂ = 2-hydroxy-N-(2-hydroxy-4-

Supramolecular MnIII₂ Complexes with Amido Ligands


was stirred for 30 min at room temperature. The color of the solution turned immediately to dark brown. The solution was filtered and kept in a refrigerator for crystallization. After 3 days, brown crystals of \( \text{I} \) formed; they were filtered out and washed with cold methanol. Yield: 0.018 g (27.8%). Upon standing in the air for a few hours, the crystals lose \( \text{MeOH} \), pick up water, and lose crystallinity. The resulting samples analyze as \([\text{Mn}_2 (\text{L}_1 ) (\text{pz})(\text{MeOH})_2 (\text{H}_2 \text{O})_2]\) (Anal. Calcd for \( \text{C}_{43} \text{H}_{37} \text{Mn}_2 \text{N}_2 \text{O}_{11}: \text{C}, 42.44; \text{H}, 4.75; \text{N}, 4.71. \) Found: C, 43.3; H, 4.0; N, 9.5. IR (KBr pellet, cm\(^{-1}\)): 3385 (\( \nu_{\text{OH}} \)), 1598 (\( \nu_{\text{C=O}} \)), 1237 (\( \nu_{\text{COC}(\text{phenoxo})} \)), 1043 (\( \nu_{\text{COC(alkkoxo)}} \)). \( \nu_{\text{vis}} \) (\( \lambda_{\text{max}} \), nm): 355, 588, 638, 666, 688.

\[ \text{Mn}_2(\text{L}_1 ) (\text{pz})(\text{MeOH})_2(\text{H}_2 \text{O})_2 \] (2). This complex was prepared as described above for \( \text{I} \). Using 0.034 g of \( \text{H}_2 \text{L}_2 \) (0.1 mmol), 0.072 g (0.2 mmol) of \( \text{Mn(CIO}_4)_2 \cdot 6\text{H}_2 \text{O} \), and 0.049 mL (0.5 mmol) of piperidine, and 0.014 g (0.2 mmol) of pyrazole. After 3 days green crystals of \( \text{I} \) formed; they were filtered out and washed with cold methanol. Yield: 0.048 g (74.4%). Upon standing in the air for a few hours, the crystals lose \( \text{MeOH} \), pick up water, and lose crystallinity. The resulting samples analyze as \([\text{Mn}_2 (\text{L}_1 ) (\text{pz})(\text{H}_2 \text{O})_4]\) (Anal. Calcd for \( \text{C}_{32} \text{H}_{28} \text{Mn}_2 \text{N}_2 \text{O}_{11}: \text{C}, 42.44; \text{H}, 4.75; \text{N}, 4.71. \) Found: C, 43.0; H, 4.0; N, 9.4. IR (KBr pellet, cm\(^{-1}\)): 3383 (\( \nu_{\text{OH}} \)), 1598 (\( \nu_{\text{C=O}} \)), 1239, 1243 (\( \nu_{\text{COC(phenoxo)}} \)), 1051 (\( \nu_{\text{COC(alkkoxo)}} \)). \( \nu_{\text{vis}} \) (\( \lambda_{\text{max}} \), nm): 348, 588, 696.

\[ \text{Mn}_2(\text{L}_1 ) (\text{OAc})(\text{MeOH})_4 \] (3). \( \text{Mn(OAc)}_2 \cdot 2\text{H}_2 \text{O} \) was prepared as described above.\(^{10}\) To a stirred solution of \( \text{Mn(OAc)}_2 \cdot 2\text{H}_2 \text{O} \) (0.054 g, 0.2 mmol) in \( \text{MeOH} \) (10 mL) was added a solution of ligand (0.033 g, 0.1 mmol) in \( \text{MeOH} \) (30 mL) and piperidine (0.049 mL, 0.5 mmol). The reaction mixture was stirred for 15 min at room temperature. The color of the solution turned immediately to dark greenish-brown. The solution was filtered and left to stand undisturbed for crystallization. After 3 days crystals of \( \text{I} \) formed; they were filtered out and washed with cold methanol. Yield: 0.02 g (32.1%). Upon standing in the air for a few hours, the crystals lose \( \text{MeOH} \), pick up water, and lose crystallinity. The resulting samples analyze as \([\text{Mn}_2 (\text{L}_1 ) (\text{OAc})(\text{MeOH})_2 (\text{H}_2 \text{O})_2]\) (Anal. Calcd for \( \text{C}_{43} \text{H}_{37} \text{Mn}_2 \text{N}_2 \text{O}_{11}: \text{C}, 42.44; \text{H}, 4.75; \text{N}, 4.71. \) Found: C, 43.0; H, 4.0; N, 9.4. IR (KBr pellet, cm\(^{-1}\)): 3383 (\( \nu_{\text{OH}} \)), 1598 (\( \nu_{\text{C=O}} \)), 1239, 1243 (\( \nu_{\text{COC(phenoxo)}} \)), 1051 (\( \nu_{\text{COC(alkkoxo)}} \)). \( \nu_{\text{vis}} \) (\( \lambda_{\text{max}} \), nm): 351, 488, 528, 580, 630, 658.)

**Physical Measurements.** Microanalyses for C, H, and N were performed by the Microanalytical Laboratory of the Laboratoire de Chimie de Coordination at Toulouse, France. Infrared spectra for \( \text{C}_21 \text{H}_{28} \text{Mn}_2 \text{N}_2 \text{O}_{11} \) (\( \lambda_{\text{max}} \), nm): 348, 588, 696. Absorption corrections were applied using Multi-scan \( (\text{I} \) and \( \text{II} \)) or DELABS \(3. \) The figures were drawn with Cameran.\(^{20}\) Crystal data collection and refinement parameters are collated in Table 1.

**Results and Discussion**

**Synthesis.** The ligands were synthesized by condensation of phenyl salicylate with the corresponding \( n \)-diamino-\( n' \)-hydroxyalkanes \( (n, n' = 3, 2 \) and 4, 2) in the presence of triethylamine, in propan-2-ol. The reactions were carried out in the presence of \( \text{NE}_3 \) to avoid possible protonation of the primary amine functions before their reaction to form the amide bonds and also to avoid monocondensation of the diamine with formation of "half-unit" ligands.\(^{21}\) The synthesis of complexes \( \text{I} \) and \( \text{II} \) was accomplished by reaction of diluted methanolic solutions of \( \text{Mn(CIO}_4)_2 \cdot 6\text{H}_2 \text{O} \) and \( \text{C}_2 \text{H}_4 \text{L}_1 \) (\( \text{I} \)) or \( \text{C}_2 \text{H}_4 \text{L}_2 \) (\( \text{II} \)) and pyrazole, in the presence of piperidine. Formation of these complexes involves aerial oxidation of \( \text{Mn}^\text{II} \) to \( \text{Mn}^\text{III} \) and full deprotonation of \( \text{H}_2 \text{L}_1 \) and \( \text{H}_2 \text{L}_2 \) to \( [\text{L}_1 ]^{3-} \) and \( [\text{L}_2 ]^{5-} \), respectively. Complexes \( \text{I} \) and \( \text{II} \) are the first ever described doubly bridged \( \mu\)-alkkoxo-\( \mu \)-pyrazolato dinuclear \( \text{Mn}^\text{III} \) complexes of pentaanionic pentadentate

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ligands including amido donors. Complex 3 was synthesized by reaction of diluted methanolic solutions of Mn(OAc)$_3$·2H$_2$O and H$_2$L in the presence of piperidine. Attempts to obtain the μ-alkoxy-μ-acetato dinuclear complex incorporating [L]$^{3-}$ were unsuccessful. Complexes 1–3 are not soluble in common solvents, which precluded carrying out solution studies to gain some insight into their reactivity and electrochemical properties.

**Description of the Structures. Structure of [Mn$_2$(L)$^1$(pz)(MeOH)$_4$·0.5MeOH (1).** The crystals of 1 contain two crystallographically independent molecules having similar structural features. An ORTEP view of one molecule is shown in Figure 1. Selected bond distances and angles are collated in Table 2. The molecular structure of the dinuclear complex 1 shows that the two manganese ions are bridged by an alkoxo oxygen of the pentaanionic ligand and a pyrazolato nitrogen atom bound to O13 (alkoxo oxygen atom) is disordered over two locations, C19A (62%) and C19B (38%). The coordination polyhedra of the Mn$^{III}$ centers may be described as elongated octahedra. The equatorial plane of each Mn is occupied by the oxygen atom of methanol molecules with bond distances and angles involving polyhedra of the Mn$^{III}$ centers may be described as elongated octahedra.

![](image.png)

**Figure 1.** Plot of one of the two independent molecules of [Mn$_2$(L)$^1$(pz)(MeOH)$_4$·0.5MeOH (1) at the 30% probability level with atom numbering. Hydrogen atoms are omitted for clarity.
showing 1D chains of hydrogen-bonded molecules. Hydrogen atoms not involved in H-bonds are omitted for clarity.

Similarly to 1, the coordination polyhedra of the MnIII centers may be described as elongated octahedra. The equatorial plane of each Mn is formed by phenoxo-oxygen, amido-nitrogen, and alkoxo-oxygen donor atoms of [L2]− and by a pyrazolato nitrogen atom (1.839–2.028 Å range), while the axial positions are occupied by the oxygen atom of methanol molecules with significantly longer bond distances (2.190–2.417 Å range). The Mn–Oalkoxo bond distances are slightly longer than in complex 1. The bonding geometry around the alkoxo oxygen atom O3 is planar, the sum of the three bond angles around O3 being ≈359°.

However, the coordination mode of [L2]− is not planar, the angle between the phenyl rings being 52° vs 7 and 12° for the two independent molecules in 1. It is also worth noting that while the equatorial coordination planes and the pyrazolato mean-plane are roughly coplanar in 1 (7 and 3°), they significantly depart from coplanarity in 2 (13°). The distance Mn1–O3–Mn2 angle (123.15(8)°) is smaller than that in complex 1 (126.33(9)° and 126.69(10)°).

The crystal packing of 2 consists in 2D sheets (Figure 4) which result from hydrogen-bonding interactions similar to those found in complex 1. The distances between hydrogen-bonded oxygen atoms are O6⋯O2 = 2.630(3), O8⋯O4 = 2.664(2), O7⋯O4 = 2.616(2), and O9⋯O7 = 2.741(2) Å.

Structure of [Mn2(L2)(OAc)(MeOH)4] (3). A complex similar to 3 has been described in the literature: 8 [Mn2(L1)- (OAc)(py)3]py•H2O (3'). The molecular structure of 3 is shown in Figure 5, and selected bond distances and angles are listed in Table 4. The two manganese ions are bridged by the alkoxo oxygen atom of the fully deprotonated ligand and the acetato anion.

The bonding geometry around the alkoxo oxygen atom O3 is almost planar, the sum of the three bond angles around O3 (≈356°) being very close to those in 1 (≈355°) and 2 (≈359°). The Mn–Oalkoxo distances in the acetato-bridged complexes 3 and 3' are nearly equal to each other, 1.938–1.955 Å range, but longer than those in the pyrazolato-bridged complex 1 (1.894–1.907 Å range). In spite of this small difference, the coordination polyhedra of the MnIII centers in 3 may be described, similarly to 1 and 2, as elongated octahedra. The equatorial plane of each Mn is formed by phenoxy-oxygen, amido-nitrogen, and alkoxo-oxygen donor atoms of [L2]− and by an acetato oxygen atom (1.837–1.985 Å range), and the axial positions are occupied by the oxygen atom of methanol molecules with significantly longer bond distances (2.246–2.405 Å range). The apical donor atoms in complex 3, which are roughly perpendicular to the NO3 equatorial planes, deviate by more than 10° from linearity: O9–Mn1–O8 = 169.5(2)° and O10–Mn2–O11 = 168.5(3)°, while the corresponding angles range from 168.36(8) to 176.53(8)° in the pyrazolato-bridged complex 1. The Mn1⋯Mn2 distance in 3 (3.541(3) Å) is similar to
that found in 3' (3.552(2) Å) but is longer than that of the pyrazolato-bridged complex 1, as a consequence of the longer three-atom bridge in 3 and 3'. The Mn1−O3−Mn angle in 3, 130.9(3)°, is slightly smaller than the corresponding angle reported for 3', 132.5(2)°, but larger than those found in complex 1 (126.33(9) and 126.69(10)°).

The crystal packing of 3 consists in 1D infinite zigzag chains (Figure 6) resulting from intermolecular hydrogen-bonding interactions involving the axially coordinated methanol molecules and the amido-oxygen atoms. All apically coordinated methanol molecules participate in intramolecular hydrogen bonds. The diffraction data are not good enough to allow determining the location of the OH hydrogen atoms of the methanol molecules (d, Å: O8−O2 = 2.593(8), O9−O4 = 2.801(10), O10−O4 = 2.697(9), O11−O8 = 2.811−(9)).

**UV−Vis Spectroscopy.** The dinuclear MnIII complexes 1−3 exhibit solid-state electronic spectra typical of a high-spin d^4 electron configuration. The spectra are characterized by several absorption bands in the region ranging from 348 to 696 nm. The strong absorption around 350 nm (also present in the spectra of H3L1 and H3L2) is ligand related. Probably due to the very broad solid state absorptions, LMCT bands from phenoxo oxygens are not clearly visible. The weaker low-energy absorptions (488−696 nm) are assigned to d−d transitions. These spectral features are consistent with the elongated octahedral environment of manganese(III) ions.

**Magnetic Properties.** The magnetic susceptibility of complexes 1−3 has been measured in the 1.8−300 K range. The magnetic susceptibility of complex 1 shows a small ferromagnetic interaction, while complexes 2 and 3 show antiferromagnetic interactions.

![Figure 5](image5.png) **Figure 5.** Plot of [Mn2L1(OAc)(MeOH)] (3) at the 30% probability level with atom numbering. Hydrogen atoms are omitted for clarity.

![Figure 6](image6.png) **Figure 6.** Crystal packing diagram of [Mn2L1(OAc)(MeOH)] (3) showing 1D zigzag chains formed by hydrogen bonds in a plane perpendicular to α. Hydrogen atoms not involved in H-bonds are omitted for clarity.
temperature range, under an applied magnetic field of 0.1 T. The $\chi M T$ product of all three dinuclear compounds decreases upon cooling (Figure 7), suggesting operation of antiferromagnetic interactions between MnIII ions.

The magnetic susceptibility, $\chi M$, increases from values of 0.018 (1, 3) and 0.019 (2) $\text{cm}^3 \text{mol}^{-1}$ at 300 K to broad maxima of 0.123 and 0.064 $\text{cm}^3 \text{mol}^{-1}$ at $\sim$13 and $\sim$28 K for 2 and 3, respectively, typical of antiferromagnetic interactions. Characteristic paramagnetic tails appear below $\sim$5 K. The corresponding maximum of 1 is masked by the paramagnetic tail and appears as a shoulder around 15 K. The values of $\chi M T$ are 5.4 (1, 3) and 5.7 (2) $\text{cm}^3 \text{mol}^{-1}$ K at 300 K, which is lower than the spin-only value for two noninteracting $S = 2$ metal centers (6.00 $\text{cm}^3 \text{mol}^{-1}$ K). These values and the presence of maxima in the $\chi M$ vs $T$ data are both indications of antiferromagnetic interactions. The same conclusion may be drawn from the constant drop of $\chi M T$ upon decreasing temperature. The slight increase of $\chi M$ below 7 K is attributed to the presence of a small fraction of paramagnetic impurity ($p\%$). To fit these experimental data, a simple system of two exchange-coupled manganese(III) ions was considered.21 Initial attempts to fit the data with this simple model yielded satisfactory results only for 1, with discrepancies at lower temperatures for 2 and 3. Considering the lattice structures of the complexes, we may assume the interplay of H-bond-mediated intermolecular magnetic interactions. On the other hand, the axially elongated octahedral coordination spheres of the MnIII led us to assume that zero-field splitting effects might be operative. Introduction of an intermolecular interaction according to the mean-field $\hat{H} = -2 J S_1 S_2$ Hamiltonian afforded a slight improvement to the fits of 2 and 3, while the improvement to the fit of 1 was marginal. Introducing, however, a zero-field splitting term $D$, common for both manganese sites ($D_1 = D_2 = D$), brought about significant improvements to the fits of 2 and 3. On the other hand, the improvement to the fit of 1 was also marginal. It was thus decided that this was the most appropriate model for the interpretation of our data. The implemented Hamiltonian was

$$\hat{H} = -2J S_{\text{Mn1}} S_{\text{Mn2}} + D(S^2_{\text{Mn1}} + S^2_{\text{Mn2}})$$

This model reproduced the experimental curve very well, except for small disagreements at low temperature, which may be due to simultaneous operation of intermolecular interactions between adjacent dinuclear molecules through the weak $\text{O}\text{amido} \cdots \text{O} \text{methanol}$ contacts yielding 1D chains (1, 3) or 2D sheets (2) (see Description of Structures). However, since intermolecular interactions brought marginal improvements to the fits of 2 and 3, and to avoid overparametrization, only zero-field splittings were considered. The parameter values for the best fits, shown as solid lines in Figure 7, were as the following: $J = -3.6(3)$ cm$^{-1}$, $D = 0.0 \text{ cm}^{-1}$, $g = 1.93(6)$, $p = 3.3\%$ (1); $J = -2.7(3)$ cm$^{-1}$, $D = 0.8(2)$ cm$^{-1}$, $g = 1.93(6)$, $p = 1.5\%$ (2); $J = -4.9(4)$ cm$^{-1}$, $D = 3.8(3)$ cm$^{-1}$, $g = 1.95(5)$, $p = 0.5\%$ (3).

The $J$, $D$, $g$, and structural parameter values significant for magneto-structural correlations (Mn$\cdots$Mn distance and Mn$\cdots$Oalkoxo$\cdots$Mn angle) of compounds 1–3 are collated in Table 5, together with those of other $\mu$-alkoxo-bridged dinuclear manganese(III) complexes including one auxiliary bridge.

Compounds 1–3 including one alkoxo bridge associated with one pyrazolato (acetato) bridge are characterized by large Mn$\cdots$Mn distances (3.40–3.54 Å) and Mn$\cdots$Oalkoxo$\cdots$Mn angles in the 123–131° range. The $-2.7$ to $-4.9$ cm$^{-1}$ range of $J$ values for this first series is not very broad in agreement with the small $\Delta$(Mn$\cdots$Mn) and $\Delta$(Mn$\cdots$Oalkoxo$\cdots$Mn) ranges. The small absolute values of $J$ agree with overlap through the 2p oxygen orbitals, and the small prevalence of antiferromagnetic vs ferromagnetic interactions is in keeping with the quite large values of the Mn$\cdots$Oalkoxo$\cdots$Mn angle.

The compounds in lines 4–6 including one alkoxo bridge associated with one N–C–C–O bridge from the second pentadentate ligand are characterized by slightly larger Mn$\cdots$Mn distances (3.76–3.82 Å) and Mn$\cdots$Oalkoxo$\cdots$Mn angles in the 125–129° range. Similarly to the previous series, the $-3.6$ to $-5.8$ cm$^{-1}$ range of $J$ values for this second series is not very broad in agreement with the small $\Delta$(Mn$\cdots$Mn) and $\Delta$(Mn$\cdots$Oalkoxo$\cdots$Mn) ranges. Again, the small absolute values of $J$ agree with overlap through the 2p oxygen orbitals and the small prevalence of antiferromagnetic vs ferromagnetic interactions is in keeping with the quite large values of the Mn$\cdots$Oalkoxo$\cdots$Mn angle. However, due to (i) the four-atom auxiliary bridge vs the two- or three-atom auxiliary bridge in 1–3, (ii) the slightly larger Mn$\cdots$Mn distances, and (iii) the overlapping ranges of Mn$\cdots$Oalkoxo$\cdots$Mn angles, we would not expect slightly larger $J$ values than for 1–3. On the other hand, we note that the $J$

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Figure 7. $\chi M T$ vs $T$ data for [Mn2(L1)(pz)(MeOH)4]·0.5MeOH (1), [Mn2(L2)(pz)(MeOH)4] (2), and [Mn2(L3)(OAc)(MeOH)4] (3). The circles are measured data, and the lines are the best fits based on the Hamiltonian of eq 1 (see text).
ranges overlap (−3.6 to −5.8 cm⁻¹ vs −2.7 to −4.9 cm⁻¹) and the difference between these two ranges may not be significant because the two series of compounds do not pertain to the same structural type and also while the interpretation of the experimental data take both J and D for the first series, it only takes J into account for the second one.

Concerning 1–3, the Mn−Oalkoxo−Mn bridging angle seems to be the essential factor determining the magnitude of the antiferromagnetic exchange interaction. As previously discussed, this angle decreases in the order 3 (130.9°) > 1 (126.5°(average)) > 2 (123.2°), and the J value (Table 5) decreases in the same order. More precisely, the J magnitude shows a linear correlation (J = −3.49θ + 113.8, R = 0.99975) with the Mn−O−Mn angle θ for complexes 1–3, which exhibit similar coordination spheres and bridging modes.

Although the common characteristic of compounds in lines 7–10 is that, in addition to the alkoxo bridge common to all compounds of Table 5, they include one additional alkoxo modes.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [MnIII(L)3(OAc)(MeOH)] (3)

<table>
<thead>
<tr>
<th>complex</th>
<th>J (cm⁻¹)</th>
<th>D (cm⁻¹)</th>
<th>g</th>
<th>Mn−Mn (Å)</th>
<th>Mn−O−Mn (deg)</th>
<th>ref</th>
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<tr>
<td>Mn1−N1</td>
<td>1.962(7)</td>
<td>1.987(7)</td>
<td>1.93</td>
<td>3.906</td>
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<tr>
<td>Mn1−O3</td>
<td>1.939(7)</td>
<td>1.985(6)</td>
<td>1.93</td>
<td>3.428</td>
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<tr>
<td>Mn1−O8</td>
<td>2.940(7)</td>
<td>2.261(7)</td>
<td>1.95</td>
<td>3.541</td>
<td>130.9</td>
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</tr>
<tr>
<td>N1−Mn1−O8</td>
<td>93.2(3)</td>
<td>92.6(3)</td>
<td>92.6(3)</td>
<td>93.6(3)</td>
<td>95.7(3)</td>
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<tr>
<td>O1−Mn1−N1</td>
<td>93.5(3)</td>
<td>95.4(3)</td>
<td>95.4(3)</td>
<td>97.3(3)</td>
<td>95.4(3)</td>
<td></td>
</tr>
<tr>
<td>O3−Mn1−N1</td>
<td>83.1(3)</td>
<td>96.3(2)</td>
<td>96.3(2)</td>
<td>91.7(3)</td>
<td>89.13</td>
<td></td>
</tr>
<tr>
<td>O3−Mn1−O8</td>
<td>84.9(3)</td>
<td>87.2(3)</td>
<td>87.2(3)</td>
<td>97.3(3)</td>
<td>90.83</td>
<td></td>
</tr>
<tr>
<td>O6−Mn1−O8</td>
<td>86.3(2)</td>
<td>87.8(3)</td>
<td>87.8(3)</td>
<td>85.5(3)</td>
<td>85.23</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Magnetic Parameters for Complexes 1–3 and Related Dinuclear MnIII Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>J (cm⁻¹)</th>
<th>D (cm⁻¹)</th>
<th>g</th>
<th>Mn−Mn (Å)</th>
<th>Mn−O−Mn (deg)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−3.6</td>
<td>0.0</td>
<td>1.93</td>
<td>3.906</td>
<td>126.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>−2.7</td>
<td>0.8</td>
<td>1.93</td>
<td>3.428</td>
<td>125.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>−4.9</td>
<td>3.8</td>
<td>1.95</td>
<td>3.541</td>
<td>130.9</td>
<td></td>
</tr>
<tr>
<td>[MnIII(5Cl-salpro)(MeOH)]⁺</td>
<td>−3.6</td>
<td>1.95</td>
<td>3.808</td>
<td>128.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnIII(salpro)(H2O)]⁺</td>
<td>−5.5</td>
<td>2.00</td>
<td>3.756</td>
<td>124.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnIII(salpro)(H2O)]²⁺</td>
<td>−5.8</td>
<td>2.00</td>
<td>3.818</td>
<td>126.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnIII(5O2-salpro)(2dmf)²⁺</td>
<td>−1.6</td>
<td>2.06</td>
<td>3.223</td>
<td>100.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnIII(H2O)]²⁺</td>
<td>−4.5</td>
<td>2.00</td>
<td>3.243</td>
<td>100.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnIII(L)(OMe(CH3)(MeOH))]²⁻</td>
<td>−15.6</td>
<td>2.01</td>
<td>3.006</td>
<td>101.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnIII(L)(OMe(NCO)(H2O))²⁻</td>
<td>−16.5</td>
<td>2.00</td>
<td>2.980</td>
<td>100.3</td>
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</tr>
</tbody>
</table>


The obtained $D$ values are in the range of those previously reported.\textsuperscript{29} Positive $D$ parameters are usually associated with either tetragonal compression or trigonal bipyramidal five-coordination.\textsuperscript{29,30} However, by considering the interaction between the ground state and LMCT states with the valence bond configuration interaction (VBCI) model, it has been recently shown that $D$ can be positive for tetragonally elongated Mn\textsuperscript{III} complexes.\textsuperscript{31} Nevertheless, we recall that the sign of $D$ cannot be safely determined from magnetic susceptibility data alone; therefore, sign attribution is only tentative.

Conclusions

In this paper we report on the first examples of doubly bridged $\mu$-alkoxo-$\mu$-pyrazolato dinuclear manganese(III) complexes. The X-ray diffraction analysis revealed that complexes 1–3 consist of dinuclear units which are further extended into 1D (1 and 3) or 2D (2) supramolecular networks via hydrogen-bonding interactions involving the noncoordinated amido-oxygen atoms of the pentadentate ligands and coordinated methanol-oxygen atoms. These interactions are likely to play an important role in the stabilization of the crystal molecular structures. The magnetic behavior of these doubly bridged $\mu$-alkoxo-$\mu$-pyrazolato (or acetato) species is dominated by intradinuclear antiferromagnetic superexchange interactions suggesting that the intermolecular interactions operating through the extended network of $\text{OH}\text{methanol} \cdots \text{O amido}$ contacts are too weak to play a significant role in the magnetic properties of these manganese(III) complexes.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds 1–3. This material is available free of charge via the Internet at http://pubs.acs.org.

