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An Oxide-Centered Trinuclear Manganese(III) Compound with a Bulky Phenol-Pyrazolate Ligand

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A new oxide-centered trinuclear manganese(III) compound with the formula $[Mn_3(\mu_3\text{-}O)(naphpz)_3(O_2CMe)(MeOH)_2]_n$ (**1**) {H_2naphpz = 2-[1*H*-pyrazol-5(3)-yl]naphthalen-1-ol} has been synthesized and characterized. Three bulky doubly deprotonated phenol-pyrazole ligands are coordinated to the three manganese(III) ions with a μ_3-oxide bridge in the same plane. Methanol and acetate ligands are at the apical positions of the manganese(III) ions. The trinuclear units are bridged by acetate ligands in the *anti-anti* mode, leading to the formation of 1-D chains. Temperature-dependent magnetic susceptibility studies indicate the presence of overall antiferromagnetic interactions with magnetic exchange constants of $J_1 \approx -1.9$ and $J_2 \approx -5.5\ \text{cm}^{-1}$ and $g = 1.91$. Weak antiferromagnetic interactions ($zJ' = -0.37\ \text{cm}^{-1}$) between the trinuclear units in the 1-D chain (and between the chains) in compound **1** are present.

Introduction

Oxide-centered trinuclear manganese(III) compounds have been well known for several years in the literature.[1–22] All these compounds show predominant antiferromagnetic interactions between the three manganese(III) ions, with the only exception of those containing oximato-based ligands[4,12–14,20,22,23] and the compound $[NEt_3(CH_2Cl)]_2[Mn_3(\mu_3\text{-}O)(hmcH)_3(hmcH_2)_3]$ [$hmcH_3$ = 2,6-bis(hydroxymethyl)-*p*-cresol][6] in which ferromagnetic interactions are operative. Due to the complexity of the magnetic exchange paths, several factors have been proposed as the origin of the observed ferromagnetic interactions. In the family of compounds with oximato-based ligands, the ligand distortion which is mainly caused by the Mn–N–O–Mn angle favors ferromagnetic interactions.[4,12–14,20,22–24] In other trinuclear manganese(III) compounds, apparently, the sign of the magnetic exchange interactions between the manganese(III) ions in the trinuclear unit is governed by the distortion of the $[Mn_3(\mu_3\text{-}O)]^{7+}$ core.[6,16,17,25] When the Mn–O–Mn angle is smaller than 120° (value for an equilateral triangle), a switch from antiferromagnetic to ferromagnetic exchange is observed.[16,17] Another relevant factor is the displacement of the μ_3-oxide ligand from the plane of the three manganese(III) ions.[6,25] In order to establish magneto-structural correlations it is useful to compare a series of compounds. Therefore the synthesis of families of related compounds can help in the design of compounds with the desired structural features and magnetic properties.

Among the large amount of oxide-centered trinuclear manganese(III) compounds, in the last years there is an increase of such compounds containing phenol-pyrazole ligands.[3,8,9,15–17] They have the general formula of $[Mn_3(\mu_3\text{-}O)(Rphpz)_3(L)_x(S)_y]^{0/-}$ (L = azide, carboxylate ligand, S = methanol, ethanol, x = 1, 2 and y = 0–4).[3,8,9,15–17] In all the cases, the compounds are formed by three doubly deprotonated phenol-pyrazole ligands that are in the same plane of the $[Mn_3(\mu_3\text{-}O)]^{7+}$ core, whereas bridging ligands such as azide or carboxylates and alcoholic solvents are present at the axial positions of the manganese(III) ions. In most cases, these trinuclear manganese(III) units are linked by a bridging ligand, or just by hydrogen bonding to form 1-D chains.[3,8,9,15–17] In all trinuclear manganese(III) compounds containing phenol-pyrazole ligands, overall antiferromagnetic interactions are present in the trinuclear

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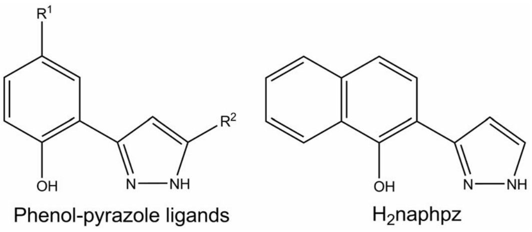
unit,[3,8,9,15–17] whereas ferromagnetic properties are operative between the trinuclear units of the 1-D chains in most of the cases.[3,8,9,15–17] The substituents in the phenol-pyrazole ligands (Scheme 1) have been crucial in determining the topology and dimensionality of these trinuclear compounds.[3,8,9,15–17] These substituents are found at the 4-position (R^1) of the phenol ring and also at the 5(3)-position (R^2) of the pyrazole ring.



Scheme 1. Phenol-pyrazole ligands and the H_2naphpz ligand.

In previous work,[16,17] we reported that certain substituents at the pyrazole ring, e.g. methyl, phenyl can distort the $[Mn_3(\mu_3\text{-}O)]^{7+}$ core and can preclude the formation of 1-D chains. Herein, we extend our studies to the effects of the substituents at the phenol ring on the structural topology and as consequence on the magnetic properties of oxide-centered trinuclear manganese(III) compounds. With this purpose, we have designed a phenol-pyrazole ligand with a bulky substituent in the phenol ring, i.e. 2-[1*H*-pyrazol-5(3)-yl]naphthalen-1-ol (H_2naphpz) (Scheme 1). Therefore, we report the synthesis and the structural and magnetic characterization of a new trinuclear manganese(III) compound, $[Mn_3(\mu_3\text{-}O)(naphpz)_3(O_2CMe)(MeOH)_2]_n$ (**1**).

Results and Discussion

The compound $[Mn_3(\mu_3\text{-}O)(naphpz)_3(O_2CMe)(MeOH)_2]_n$ (**1**) was synthesized from hydrated manganese(II) acetate and the H_2naphpz ligand in a ratio 1:1 in a solution of methanol/acetonitrile, 1:1 in reflux. Slow evaporation of the solution affords brown single crystals suitable for X-ray crystallographic analyses.

Compound **1** crystallizes in the monoclinic space group $P2_1/c$. Crystallographic data are summarized in Table S1 (Supporting Information). The crystal structure reveals a trinuclear manganese(III) compound in which the three manganese(III) ions are bridged by a central oxide. The deprotonated naphpz^{2-} ligands are in a plane with the three manganese(III) ions. Selected bond lengths and angles are listed in Table S2. Intracluster Mn···Mn distances are 3.310 Å, 3.293 Å and 3.302 Å for Mn(1)···Mn(2), Mn(1)···Mn(3) and Mn(2)···Mn(3), respectively. The μ_3-O^{2-} (O1) is located 0.024 Å above the Mn_3 plane. The Mn–O(1)–Mn angles are 121.50(7)°, 119.03(7)° and 119.43(7)° for Mn(1)–O(1)–Mn(2), Mn(1)–O(1)–Mn(3) and Mn(2)–O(1)–Mn(3), respectively. The dihedral angles between the naphthalene and the pyrazole rings are 3.54, 5.37 and 14.21°. One manganese(III) ion, Mn(3), is hexacoordinate, containing methanol molecules at the axial positions, whereas two manganese(III) ions, Mn(1) and Mn(2), are pentacoordinate, with an acetate ligand at the axial positions. The acetate molecule is bridging in *anti-anti* mode Mn(1) and Mn(2) ions from two different trinuclear units, thus forming a 1-D chain (Figure 1) with a Mn(1)···Mn(2) distance of 6.263 Å. Hydrogen bonding interactions involve the coordinated methanol and the acetate ligand [2.754(2) and 2.705(2) Å]. π-π stacking is present between several six-membered aromatic rings of the H_2naphpz ligand (Table S3). The separation between the centroids of the aromatic rings involved in the π–π stacking is in the range of 3.7396(15)–3.8417(15) Å. The shortest interchain Mn···Mn distance is 7.400 Å.

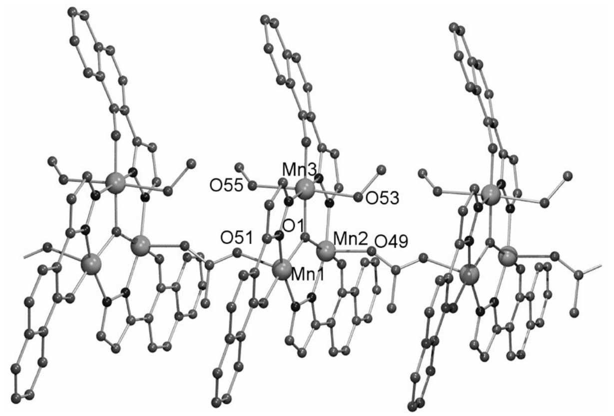


Figure 1. Pluton projection of the molecular structure of $[Mn_3(\mu_3\text{-}O)(naphpz)_3(O_2CMe)(MeOH)_2]_n$ (**1**). Hydrogen atoms are omitted for clarity.

As observed for other trinuclear manganese(III) compounds containing phenol-pyrazole ligands previously reported,[3,8,9,15–17] the introduction of a substituent in the 5-position (R^2) of the pyrazole ring as methyl or phenyl forces the carboxylate ligand to bind two manganese(III) ions from the same trinuclear unit.[16,17] If the carboxylate ligand is acetate,[16,17] these trinuclear units form 1-D chains because of the strong hydrogen interactions between the carboxylate and the solvent molecules (coordinated and noncoordinated solvents). If the carboxylate is bulkier, i.e. benzoate, two carboxylate ligands are present in the trinuclear unit and they become isolated.[17] Furthermore the introduction of these substituents in the 5-position of the pyrazole ring induces a distortion of the $[Mn_3(\mu_3\text{-}O)]^{7+}$ core, in which the Mn–O–Mn angles vary between ca. 113–126°.[16,17] The introduction of a substituent in the fourth position (R^1) of the phenol ring,[3,8,9,15–17] i.e. bromo, methyl, (hydrogen) or a bulky substituent as naphthalen-1-ol (compound **1**) does not preclude the formation of the 1-D chain, in which the trinuclear units are bridged by azide or acetate ligands. These substituents do not create a distortion of the $[Mn_3(\mu_3\text{-}O)]^{7+}$ core [Mn–O(1)–Mn angles are in the range of 118.75–121.50°]. In such cases, the Mn···Mn separations through the bridging ligands (in the 1-D chain) are in the range of 6.262–6.713 Å, being the shortest found in compound **1**. Apparently the presence of substituents in the fourth position (R^1) of the phenol ring is important in controlling the distance between the 1-D chains,[3,8,9,15–17] since supramolecular interactions or steric effects determine the packing of the chains. The shortest interchain Mn···Mn distance is in the range of 7.341–8.435 Å. Also, the number of coordinated solvent molecules, i.e. methanol and ethanol also depends on the type of phenol-pyrazole ligand and the bridging ligand (acetate or azide ligand). The number of coordinated solvent molecules varies between zero and four in all the trinuclear compounds.[3,8,9,15–17] In the case of pure 1-D chains,[3,8,9,15,16] the number is three or four, except for compound **1**, in which only two molecules of methanol are present.

Magnetic susceptibility was measured under 0.1 T field in the 1.8–300 K temperature range and is shown in Figure 2. The $\chi_M T$ value of **1** is 7.21 cm^3 K mol^{-1} at 300 K, which is lower than the calculated value (9 cm^3 K mol^{-1}) for three-non interacting manganese(III) ions with $g = 2$. By lowering the temperature, the $\chi_M T$ value decreases to 1.16 cm^3 K mol^{-1} at 1.8 K. The initial decrease is attributed to the presence of predominant antiferromagnetic interactions between the three manganese(III) ions of the trinuclear unit. The decrease of the magnetic susceptibility at low temperatures is due to intermolecular antiferromagnetic interactions (in the 1-D chain and between the chains) and might also be due in part to the zero-field splitting of the manganese(III) ions.

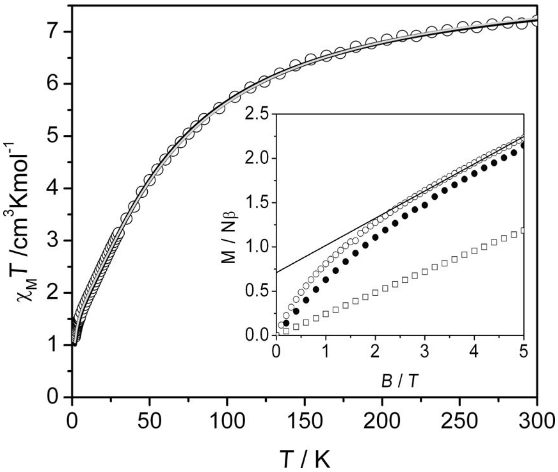


Figure 2. Plot of $\chi_M T$ vs. T for **1** in the range 1.8 to 300 K in 0.1 T applied field with the experimental fit (black solid line for isosceles triangle and grey line considering intermolecular interactions). Inset, field dependence of the magnetization measured at 2 (○), 4 (●) and 20 (□) K and the linear extrapolation of the high-field parts at 2 K.

Field dependence of the magnetization was carried out at 2, 4 and 20 K (see inset Figure 2). At 5 T, the value of molar magnetization measured at 2 K is 2.23 $N\beta$, which is far from the saturation limit of 12 $N\beta$ for three non-interacting manganese(III) ions. This indicates the presence of strong antiferromagnetic interactions, suggesting a low-spin magnetic ground state. At low fields, the small net moments per cluster become aligned by the applied field. By extrapolating the quasi-linear high field parts of the magnetization curve to zero field, the net moment δM per cluster can be estimated, giving about 0.7 $N\beta$. With the mean-field formula $zJ' \approx g^2\beta^2 B_{sat}/\delta M$, in which the field B_{sat} indicates where this initial process "saturates" (ca. 1 T), the intercluster coupling is estimated to be $zJ' \approx 0.6$ cm^{-1}.

The susceptibility data were fitted with the Hamiltonian for an isosceles triangle:

$$\hat{H} = -2[J_1(\hat{S}_1\hat{S}_3) + J_1(\hat{S}_2\hat{S}_3) + J_2(\hat{S}_1\hat{S}_2)] \quad (1)$$

where J_1 represents the Mn^{III}–Mn^{III} exchange interaction parameter of the two exchange paths with similar distances and Mn–O–Mn angles, and J_2 refers to the path characterized by a unique Mn–O–Mn angle [Mn(1)–O–Mn(2) 121.50(7)°]. The best fit of the experimental data for **1** above 50 K gave $J_1 = -2.0 \pm 0.2$ cm^{-1}, $J_2 = -5.7 \pm 0.3$ cm^{-1} and $g = 1.91 \pm 0.01$.

At low temperatures and low fields, intermolecular interactions become important. In view of the structure of compound **1**, which has the shortest intrachain Mn···Mn separation (6.262 Å) and presents strong π–π stacking interactions (Table S3), as compared with similar trinuclear compounds containing phenol-pyrazole ligands, the experimental susceptibility data of **1** were also fitted in the whole range of temperature. Therefore, a molecular field, $B_m = 2zJ'S/g\beta$ is added with zJ' as intermolecular interactions. The corrected susceptibility χ' has the formula $\chi' = \chi/(1 + \lambda\chi)$ in which the molecular field constant is given by $\lambda = 2zJ'/g^2\beta^2$. The best fit of the experimental data for **1** in the whole range of temperature gave $J_1 = -1.8 \pm 0.1$ cm^{-1}, $J_2 = -5.2 \pm 0.2$ cm^{-1}, $zJ' = -0.37 \pm 0.03$ cm^{-1} and $g = 1.92 \pm 0.01$. With the obtained magnetic exchange parameters and the magnetic energetic level for an isosceles triangle,[16,26] the ratio $r = J_2/J_1$ is found to equal about 3 for compound **1**, revealing a $S_T = 1$ magnetic ground state for the triangular units on basis of the previously published magnetic energetic level for an isosceles triangle,[16,17,26] i.e. of the same order as the value for δM found above.

Compound **1** contains overall antiferromagnetic interactions between the three manganese(III) ions in the trinuclear unit, as observed for all trinuclear μ$_3$-oxide-centered manganese(III) compounds containing phenol-pyrazole ligands.[3,8,9,15–17] The presence of overall antiferromagnetic interactions is expected, according to the structural features, since the distortion of the [Mn$_3$(μ$_3$-O)]$^{7+}$ core is very small.[16,17] When azide bridges the trinuclear units, antiferromagnetic or ferromagnetic interactions are present in the 1-D chain.[8,16] However, when the trinuclear units are bridged by carboxylate ligands, ferromagnetic interactions become operative between the trinuclear units between the 1-D chain,[3,9,15,16] except for compound **1** and compound [Mn$_3$(μ$_3$-O)(phpzMe)$_3$(MeOH)$_3$(O$_2$CMe)]·1.5MeOH,[16,17] that have the shortest (6.26 Å) and the largest (8.04 Å) separation between the Mn···Mn of neighboring trinuclear units in the 1-D chain, respectively. The presence of antiferromagnetic interactions between the trinuclear units and between the chains in compound **1** is not surprising. Although the separation between the 1-D chains is slightly larger than found for [Mn$_3$(μ$_3$-O)(phpzMe)$_3$(EtOH)(O$_2$CMe)][16,17] (6.4 Å as compared to 7.4 Å for **1**), strong π–π stacking interactions still remain present.

Conclusions

A new trinuclear manganese compound with the formula [Mn$_3$(μ$_3$-O)(naphpz)$_3$(O$_2$CMe)(MeOH)$_2$]$_n$ (**1**) has been synthesized and characterized. The use of a bulky phenol-pyrazole ligand does not induce any distortion in the trinuclear [Mn$_3$(μ$_3$-O)(naphpz)$_3$]$^+$ core, since the three naphpz$^{2–}$ ligands can be in the [Mn$_3$(μ$_3$-O)]$^{7+}$ plane without any steric constrains imposed by them. Thus, the acetate ligand can bridge the trinuclear manganese(III) units, forming 1-D chains. Strong π–π interactions are present between the phenol-pyrazole ligands stabilizing the packing of the 1-D chains in the crystal lattice. Antiferromagnetic interactions are present in the trinuclear unit and also between the 1-D chains, with magnetic exchange constants of $J_1 = –1.9$ cm$^{–1}$, $J_2 = –5.5$ cm$^{–1}$ (and $zJ' = –0.37$ cm$^{–1}$). These antiferromagnetic interactions (intra- and interchain) can be explained by the small distortion of the [Mn$_3$(μ$_3$-O)]$^{7+}$ core and the strong π–π interactions.

Experimental Section

General: Starting materials were purchased from Aldrich. All manipulations were performed using materials as received. The ligand 2-(1*H*-pyrazol-5(3)-yl)naphthalen-1-ol (H$_2$naphpz) has been synthesized according to a reported procedure.[27]

[Mn$_3$(μ$_3$-O)(naphpz)$_3$(O$_2$CMe)(MeOH)$_2$]$_n$ (1): A solution of Mn(OAc)$_2$·2H$_2$O (98 mg, 0.40 mmol) was added to a hot solution of the ligand H$_2$naphpz (84 mg, 0.40 mmol) in a 1:1 mixture of MeOH/CH$_3$N. After a reflux of 15 min, the solution was filtered. The filtrate was allowed to evaporate slowly, affording brown crystals; yield 59 % (73 mg). **1**: C$_{43}$H$_{35}$Mn$_3$N$_6$O$_8$ (928.60): calcd. C 55.62, H 3.80, N 9.05; found C 54.24, H 2.23, N 8.65. The discrepancy between calculated and obtained elemental percentages arises from analytical variations because of the incomplete combustion of the sample. IR: $\tilde{\nu}_{max.}$ = 3070 (w), 1597 (m), 1560 (m), 1550 (m), 1530 (s), 1496 (m), 1458 (s), 1322 (m), 1296 (vs), 1268 (vs), 1249 (vs), 1144 (w), 1127 (s), 1090 (m), 1062 (m), 1036 (s), 982 (w), 864 (s), 792 (s), 784 (m), 752 (s), 742 (s), 725 (s), 668 (vs), 647 (vs), 601 (vs), 484 (m), 418 (s), 381 (s), 312 (s) cm$^{–1}$.

Physical Measurements: Elemental analyses for C, H and N were performed with a Perkin–Elmer 2400 series II analyzer. Infrared spectra (4000–300 cm$^{–1}$) were recorded with a Perkin–Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. DC magnetic data were recorded using a Quantum Design MPMS-5 SQUID susceptometer. The magnetic susceptibilities were measured from 1.8 to 300 K on polycrystalline samples in a gelatin capsule with an applied field of 0.1 T. The magnetization was measured at 2, 4 and 20 K in the 0–5 T range. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.[28]

X-ray Crystallography: Intensity data for single crystals of **1** was collected using a Bruker APEX II CCD diffractometer on station 9.8 of the Synchrotron Radiation Source at CCLRC Daresbury Laboratory, at 0.6911 Å, from a silicon 111 monochromator. The data were corrected for absorption, the structure was solved by direct methods and the refinement and all further calculations were carried out using SHELX-TL suite.[29,30] Crystal and refinement data for **1** is collected in Table S1 (see Supporting Information). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in difference Fourier maps, including those of the methanol molecules, and placed geometrically on their riding atom.

CCDC-750381 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information (see also the footnote on the first page of this article): Crystallographic details, selected bond and angles and π–π interactions for compound **1**.

Acknowledgments

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