Manganese(III) compounds with phenol–pyrazole based-ligands: impact of the co-ligand and the carboxylate ligand on the trinuclear core $[Mn_3(\mu_3-O)(phpzR)_3(O_2CR')_n]^{1-n}$

Marta Viciano-Chumillas,^{*a,b*} Stefania Tanase,^{*a*} Ilpo Mutikainen,^{*c*} Urho Turpeinen,^{*c*} L. Jos de Jongh^{**b*} and Jan Reedijk^{**a*}

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The reaction of H₂phpzR (R = Me, Ph; H₂phpzMe = 3(5)-(2-hydroxyphenyl)-5(3)-methylpyrazole and $H_2phpzPh = 3(5)-(2-hydroxyphenyl)-5(3)-phenylpyrazole)$ with $Mn(O_2CR') \cdot nH_2O(R' = Me \text{ and } Ph)$ and ("Bu₄N)MnO₄ in ethanol (EtOH) affords three new manganese(III) compounds, [Mn₃(μ_3 -O)-(phpzMe)₃(O₂CMe)(EtOH)]·EtOH (1), (ⁿBu₄N)[Mn₃(µ₃-O)(phpzMe)₃(O₂CPh)₂] (2) and $(^{n}Bu_{4}N)[Mn_{3}(\mu_{3}-O)(phpzPh)_{3}(O_{2}CPh)_{2}]$ (3). Their synthesis, crystal structure and magnetic properties are reported. Compounds 1-3 are μ_3 -oxido-centered trinuclear manganese(III) compounds whose edges are bridged by phpzR²⁻ with average intracluster separations of 3.25 Å. The three Mn–O–Mn angles are distorted from the equilateral triangle with values in the range of 113° to 124°; 117° to 125°; and 117° to 126° for complexes 1-3, respectively. Hydrogen bonding interactions between the trinuclear units of 1 result in a one-dimensional chain structure. Compounds 2 and 3 have isolated trinuclear units, perhaps as a result of the presence of the bulky "Bu₄N⁺ cation. Temperature-dependent magnetic susceptibility studies indicate the presence of both antiferromagnetic and ferromagnetic interactions in compound 1 ($J_1 = -10.3 \text{ cm}^{-1}$, $J_2 = +10.9 \text{ cm}^{-1}$), while only antiferromagnetic interactions are present in compounds 2 and 3 ($J_1 = -4.2 \text{ cm}^{-1}$, $J_2 = -10.3 \text{ cm}^{-1}$ for 2; and $J_1 = -4.8 \text{ cm}^{-1}$, $J_2 = -10.2 \text{ cm}^{-1}$ for 3), with J_1 representing the similar Mn–O–Mn angles and J_2 representing the unique Mn–O–Mn angle (Mn(1)-O(1)-Mn(2)).

Introduction

Oxide-centered trinuclear manganese(III) compounds have been well known for several years in the literature.¹ The first reported compounds were commonly named basic carboxylates and they have the general formula $[Mn_3O(O_2CR)_6L_3]^+$ (R = Me, Et, Pr, Piv, Ph, and L = py, 3-Mepy, Im, H₂O).¹⁻⁶ Lately, the carboxylate ligands and solvent molecules have been replaced by other types of ligands, such as salicylaldoxime⁷⁻¹¹ or pyrazole derivatives,¹²⁻¹⁵thereby extending the group of trinuclear manganese(III) compounds. All these compounds show predominant antiferromagnetic interactions between the manganese(III) ions, with the exception of those containing oximato-based ligands where ferromagnetic interactions are operative.^{9-11,16-18} Due to the complexity of the magnetic exchange paths, several factors have been proposed as the origins of the observed ferromagnetic behavior.^{15,16,19} An important cause appears to be the distortion of the $[Mn_3(\mu_3-O)]^{7+}$ core, where the Mn–O–Mn angle is smaller than 120° (the value for an equilateral triangle);^{15,16,19} a switch from antiferromagnetic to ferromagnetic exchange is observed at angles below approximately 120°.²⁰ Recently, it has been shown that the ligand distortion, *i.e.* the Mn–N–O–Mn torsion angle in oximate ligands, plays an important role as well; a larger torsion angle gives rise to a stronger ferromagnetic coupling.^{9,10,16,19}

In our previous work,15 some trinuclear manganese(III) compounds were obtained by using phenol-pyrazole based ligands. Temperature-dependent magnetic susceptibility studies have revealed that the antiferromagnetic intramolecular interactions are dominant in most of the cases, with the exception of one compound that displays both antiferromagnetic and ferromagnetic interactions between the manganese(III) ions.15 In the later case, the ferromagnetic exchange interaction was found to correspond to the major distortion of the Mn–O–Mn angle of the $[Mn_3(\mu_3 - \mu_3)]$ O)]⁷⁺ core. In the present work, we report a new approach within the strategy of modifying known complexes, i.e. the controlled distortion of the $[Mn_3(\mu_3-O)]^{7+}$ core to elucidate the crucial magnetic exchange paths. In this respect, we report herein the effect of different carboxylate ligands and co-ligands on the geometry of the $[Mn_3(\mu_3-O)]^{7+}$ core. Three new trinuclear manganese(III) compounds, $[Mn_3(\mu_3-O)(phpzMe)_3(O_2CMe)(EtOH)]$ ·EtOH (1), $(^{n}Bu_{4}N)[Mn_{3}(\mu_{3}-O)(phpzMe)_{3}(O_{2}CPh)_{2}]$ (2) and $(^{n}Bu_{4}N)[Mn_{3}(\mu_{3}-O)(phpzMe)_{3}(O_{2}CPh)_{3}]$ (2) and ($O(phpzPh)_3(O_2CPh)_2$ (3) are presented and their synthesis, X-ray crystal structures and magnetic properties are described in detail.

^aGorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands. E-mail: reedijk@ chem.leidenuniv.nl; Fax: +31 71 527 4671; Tel: +31 71 527 4459 ^bKamerlingh Onnes Laboratory, Leiden Institute of Physics, Leiden University, PO Box 9504, 2300 RA Leiden, The Netherlands. E-mail: jongh@physics.leidenuniv.nl; Fax: +31 71 527 5404; Tel: +31 71 527 5466 ^cLaboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, PO Box 55 (A.I. Virtasen aukio 1), 00014 Helsinki, Finland † CCDC reference numbers 713048–713050. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b905396d

Experimental

General remarks

Starting materials were purchased from Aldrich. All manipulations were performed using materials as received. $Mn(O_2CPh)_2 \cdot 2H_2O$,²¹ ("Bu₄N)MnO₄⁵ and the ligands²² 3(5)-(2-hydroxyphenyl)-5(3)-methylpyrazole (H₂phpzMe) and 3(5)-(2-hydroxyphenyl)-5(3)-phenylpyrazole (H₂phpzPh) have been synthesized according to reported procedures.

General synthesis

Solid ("Bu₄N)MnO₄ (0.07 mmol) was added to a solution of $Mn(O_2CR')_2 \cdot nH_2O$ (R' = Me, Ph) (0.28 mmol) in ethanol. The resulting solution was stirred for a few minutes, followed by the addition of H₂phpzR (R = Me, Ph) (0.21 mmol) in ethanol. The solution mixture resulted in the formation of a brown precipitate, which was filtered off and discarded. The filtrate was allowed to evaporate slowly, affording brown crystals within a few days in all cases. The crystals were collected by filtration, washed with Et₂O and dried in vacuum.

[Mn₃(\mu_3-O)(phpzMe)₃(O₂CMe)(EtOH)]-EtOH (1). Yield: 17% (30 mg). Anal. Calcd for 1 ($C_{36}H_{39}Mn_3N_6O_8$): C, 50.96; H, 4.63; N, 9.90. Found: C, 50.53; H, 5.05; N, 9.90. IR (ν_{max}/cm^{-1}): 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).

("Bu₄N)[Mn₃(μ_3 -O)(phpzMe)₃(O₂CPh)₂] (2). Yield: 11% (28 mg). Anal. Calcd for 2 (C₆₀H₇₀Mn₃N₇O₈): C, 60.97; H, 5.97; N, 8.29. Found: C, 60.47; H, 6.78; N, 8.36. IR (v_{max} /cm⁻¹): 2964 (m), 2875 (w), 1594 (s), 1563 (s), 1558 (vs), 1540 (m), 1531 (m), 1494 (s), 1456 (vs), 1374 (vs), 1330 (m), 1296 (vs), 1268 (vs), 1254 (vs), 1152 (m), 1127 (s), 1088 (m), 1064 (s), 1056 (s), 1034 (s), 988 (m), 938 (m), 866 (s), 834 (m), 782 (m), 766 (s), 760 (s), 752 (vs), 720 (vs), 680 (vs), 668 (vs), 642 (vs), 612 (s), 580 (s), 542 (m), 442 (s), 422 (s), 417 (s), 379 (vs), 350 (s), 334 (s).

(*Bu₄N)[Mn₃(μ_3 -O)(phpzPh)₃(O₂CPh)₂] (3). Yield: 13% (37 mg). Anal. Calcd for 3 (C₇₅H₇₆Mn₃N₇O₈): C, 65.84; H, 5.60; N, 7.17. Found: C, 65.21; H, 6.37; N, 7.21. IR (ν_{max}/cm^{-1}): 2962 (m), 2880 (w), 1595 (s), 1564 (m), 1558 (vs), 1539 (m), 1532 (m), 1506 (m), 1476 (vs), 1456 (s), 1448 (s), 1428 (m), 1378 (vs), 1297 (s), 1266 (s), 1249 (s), 1175 (w), 1122 (s), 1098 (s), 1026 (m), 995 (m), 935 (w), 864 (s), 836 (w), 797 (m), 752 (s), 719 (vs), 710 (s), 696 (vs), 686 (s), 668 (vs), 662 (s), 646 (s), 610 (m), 588 (m), 534 (m), 492 (w), 456 (m), 448 (m), 435 (m), 421 (s), 378 (m), 374 (m), 333 (s).

Physical Measurements

Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 series II analyzer. Infrared spectra (4000– 300 cm⁻¹) were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using reflectance technique. DC and AC magnetic data were recorded using a Quantum Design MPMS-5 SQUID susceptometer. The magnetic susceptibilities were measured from 1.8 to 300 K on powdered single-crystal samples in a gelatin capsule with an applied field of 0.1 T. The magnetization was measured from 2 up to 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 constants.²³

X-Ray crystallography[†]

Intensity data for single crystals of 1, 2 and 3 were collected using Mo K α radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer. Crystal and refinement data for 1, 2 and 3 are collected in Table 1. The intensity data were corrected for Lorentz and polarization effects, and for absorption (multiscan absorption correction²⁴). The structures were solved by Patterson methods.²⁵ The programs EvalCCD,^{26,27} DIRDIF96,²⁸ SHELXS-97²⁹ and SHELXL-97³⁰ were used for data reduction, structure solution and refinement, respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at calculated positions and were refined riding on the parent atoms. CCDC-713048 (1), CCDC-713050 (2) and CCDC-713049 (3) contain the supplementary crystallographic data for this paper.† Geometric calculations and molecular graphics were performed with the PLATON package.³¹

Results and discussion

Synthesis

µ₃-Oxide bridged trinuclear manganese(III) compounds were previously obtained by reacting mononuclear manganese(III) building blocks containing phenol-pyrazole based ligands with manganese(II) acetate or with sodium azide.15 These compounds contain the same core with the general formula $[Mn_3(\mu_3 -$ O)(phpzR)₃]⁺; methanol molecules, and acetate or azide bridging ligands have been found at the terminal positions. In the present paper the influence of a different carboxylate ligand, namely benzoate and a different starting solvent, namely ethanol, in these type of trinuclear manganese(III) compounds is presented. In addition, we have explored new synthetic routes by starting from manganese(II) carboxylate salts, ("Bu₄N)MnO₄ and phenol-pyrazole ligands in the same reaction. Manganese(II) salts together with ("Bu₄N)MnO₄ are an excellent and well known starting source to generate manganese(III) and/or manganese(IV) ions; depending on the used ratio, complexes of different nuclearities can be obtained.5,21 In our case, the manganese(II): manganese(VII) ratio employed can be either 4:1 or 3:1. The use of other $({}^{n}Bu_{4}N)^{+}$ salts, *i.e.* $({}^{n}Bu_{4}N)Br$ instead of (ⁿBu₄N)MnO₄, resulted in a decrease of the reaction yields. The presence of ⁿBu₄N⁺ in the final product is necessary to balance the charges in compounds (ⁿBu₄N)[Mn₃(µ₃-O)(phpzMe)₃(O₂CPh)₂] (2) and $({}^{n}Bu_{4}N)[Mn_{3}(\mu_{3}-O)(phpzPh)_{3}(O_{2}CPh)_{2}]$ (3), because there are two benzoate groups present. Compound $[Mn_3(\mu_3 -$ O)(phpzMe)₃(O₂CMe)(EtOH)]·EtOH (1) contains one acetate group only, therefore the ⁿBu₄N⁺ is absent. The infrared spectra of complexes 1-3 are very similar. The main difference is that compounds 2 and 3 exhibit the bands expected for the ${}^{n}Bu_{4}N^{+}$ at 2964, 2875 and 1374 cm⁻¹ that are absent in compound 1, which is in agreement with the X-ray crystallographic studies.

	1	2	3
Formula	$C_{34}H_{33}Mn_3N_6O_7, C_2H_6O_7$	$C_{44}H_{34}Mn_3N_6O_8, C_{16}H_{36}N_6N_6N_6N_6N_6N_6N_6N_6N_6N_6N_6N_6N_6N$	$C_{59}H_{40}Mn_3N_6O_8, C_{16}H_{36}N_6N_8$
FW/g mol ⁻¹	848.55	1182.05	1368.24
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\overline{1}$	P21/c	$P\bar{1}$
a/Å	8.4040(13)	12.4030(10)	13.805(2)
b/Å	11.5702(15)	21.1640(10)	16.257(2)
c/Å	18.427(2)	24.603(2)	16.495(2)
$\alpha/^{\circ}$	98.205(10)	90	101.53(2)
$\beta/^{\circ}$	91.345(7)	120.27(1)	100.39(2)
$\gamma/^{\circ}$	93.355(11)	90	109.06(2)
$V/Å^3$	1769.5(4)	5577.7(9)	3305.6(10)
Ζ	2	4	2
$D_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.593	1.408	1.374
Crystal size	$0.15 \times 0.20 \times 0.20$	$0.10 \times 0.20 \times 0.20$	$0.12 \times 0.25 \times 0.28$
Number of collected reflections (unique)	28 899(7338)	52922(12736)	58 112(12 942)
Number of observed reflections $(I_0 > 2\sigma(I_0))$	6261	8686	10168
Internal R factor	0.0280	0.048	0.055
Number of parameters	488	710	889
Goodness-of-fit S on F^2	1.05	1.05	1.08
μ/mm^{-1}	1.118	0.731	0.627
$R_1^a \left[I > 2\sigma(I) \right]$	0.0280	0.0383	0.0408
wR_2^{b} [all data]	0.0696	0.0887	0.0979
T/K	173	173	173
^{<i>a</i>} $R_1 = \sum F_o - F_c $. ^{<i>b</i>} $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2]$	$[2]/\sum w(F_o^2)^2\}^{1/2}.$		

 $\label{eq:construction} \begin{array}{l} \textbf{Table 1} \quad Crystal \mbox{ data and structure refinements for } [Mn_3(\mu_3-O)(phpzMe)_3(O_2CMe)(EtOH)] \cdot EtOH \mbox{ (1), (}^nBu_4N)[Mn_3(\mu_3-O)(phpzMe)_3(O_2CPh)_2] \mbox{ (2) and } (nBu_4N)[Mn_3(\mu_3-O)(phpzPh)_3(O_2CPh)_2] \mbox{ (2) and } (nBu_4N)[Mn_3(\mu_3-O)(phpzPh)_3(O_3CPh)_2] \mbox{ (2) and } (nBu_4N)[Mn_3(\mu_3-O)(phpzPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3CPh)_3(O_3$

Description of the molecular structures

Compound 1 crystallizes in the triclinic space group $P\overline{1}$. As shown in Fig. 1, the crystal structure reveals a trinuclear manganese(III) compound in which the three manganese(III) ions are bridged by a central oxide. The oxidation states for the three manganese(III) ions were established by charge-valence considerations, by bond length distances and by bond valence sum (BVS) calculations with the obtained values of 3.23, 3.29 and 3.20 for Mn(1), Mn(2) and Mn(3), respectively.³² Selected bond lengths and angles are listed in Table 2. Intracluster Mn \cdots Mn distances are 3.153 Å, 3.330 Å and 3.300 Å for Mn(1) \cdots Mn(2), Mn(1) \cdots Mn(3) and Mn(2) \cdots Mn(3), respectively. The μ_3 -O²⁻(O1) is located 0.064 Å above the Mn₃ plane. The Mn–O(1)–Mn angles are 112.65(6)°, 124.28(6)° and 122.73(7)° for Mn(1)–O(1)–Mn(2),

Fig. 1 Pluton projection of the molecular structure of $[Mn_3(\mu_3-O)-(phpzMe)_3(O_2CMe)(EtOH)]$ -EtOH (1). Hydrogen atoms and non-coordinated ethanol molecules are omitted for clarity. Color code: green, manganese; blue, nitrogen; red, oxygen; grey, carbon.

Mn(1)–O(1)–Mn(3) and Mn(2)–O(1)–Mn(3), respectively. All the manganese(III) ions are penta-coordinated square-pyramidal based. An acetate molecule is bridging the Mn(1) and the Mn(2) ions, whereas Mn(3) contains an ethanol molecule at the axial position. In the lattice, another ethanol molecule is present, forming intermolecular hydrogen bonds with the coordinated ethanol of one trinuclear unit and also with the acetate group of a neighboring trinuclear unit (O(5)–H(5)…O(7) = 2.591(2) Å and O(7)–H(7)…O(3) = 2.783(2) Å), thus forming a chain structure along the *a* direction (Fig. 2). The shortest distance between the manganese(III) ions from the trinuclear units bridged by hydrogen bonding is Mn(1)…Mn(3), equal to 7.404 Å. The shortest interchain Mn…Mn distance is 6.386 Å, along the *c* direction and it belongs to a Mn(2)…Mn(2) distance.



Fig. 2 Crystal packing of $[Mn_3(\mu_3-O)(phpzMe)_3(O_2CMe)(EtOH)]$ ·EtOH (1) showing the intermolecular hydrogen bonds. Hydrogen atoms that are not involved in hydrogen bonding are omitted for clarity. Color code: green, manganese; blue, nitrogen; red, oxygen; grey, carbon.

Compounds 2 and 3 crystallize in the monoclinic space group P21/c and in the triclinic space group $P\overline{1}$, respectively. Their molecular structures are shown in Fig. 3 and Fig. 4, respectively.

Table 2	Selected bonds	lengths [Å] and	angles [°] for th	e compound [Mn ₃	$(\mu_3-O)(phpzMe)$	(O ₂ CMe)(EtOH)]·EtOH (1)
				· · · · · · · · · · · · · · · · · · ·	VE 1 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 -	

Bond lengths			
Mn(1)–O(1)	1.8979(13)	Mn(1)–O(3)	2.1026(13)
Mn(1)–O(112)	1.8377(14)	Mn(1) - N(11)	1.9375(15)
Mn(1) - N(32)	2.0175(15)	Mn(2)-O(1)	1.8911(12)
Mn(2)-O(2)	2.0794(13)	Mn(2)–O(212)	1.8257(14)
Mn(2)-N(12)	2.0195(16)	Mn(2)-N(21)	1.9518(15)
Mn(3)–O(1)	1.8689(12)	Mn(3)–O(5)	2.1458(15)
Mn(3)–O(312)	1.8247(14)	Mn(3)–N(22)	2.0385(16)
Mn(3) - N(31)	1.9679(16)	$Mn(1)\cdots Mn(2)$	3.153
$Mn(1)\cdots Mn(3)$	3.330	$Mn(2)\cdots Mn(3)$	3.300
Bond angles			
O(1)–Mn(1)–O(3)	94.17(5)	O(1)-Mn(1)-O(112)	174.50(6)
O(1)-Mn(1)-N(11)	87.87(6)	O(1)–Mn(1)–N(32)	88.27(6)
O(3)–Mn(1)–O(112)	90.60(6)	O(3)–Mn(1)–N(11)	102.02(6)
O(3)-Mn(1)-N(32)	102.87(6)	O(112)–Mn(1)–N(11)	88.45(6)
O(112)-Mn(1)-N(32)	93.35(6)	N(11)–Mn(1)–N(32)	155.02(7)
O(1)–Mn(2)–O(2)	90.97(5)	O(1)-Mn(2)-O(212)	178.90(6)
O(1)-Mn(2)-N(12)	87.07(6)	O(1)-Mn(2)-N(21)	89.51(6)
O(2)–Mn(2)–O(212)	89.19(6)	O(2)-Mn(2)-N(12)	106.01(6)
O(2)-Mn(2)-N(21)	117.60(6)	O(212)–Mn(2)–N(12)	93.92(6)
O(212)–Mn(2)–N(21)	89.46(6)	N(12)–Mn(2)–N(21)	136.30(6)
O(1)–Mn(3)–O(5)	93.65(6)	O(1)-Mn(3)-O(312)	173.12(6)
O(1)–Mn(3)–N(22)	89.61(6)	O(1)-Mn(3)-N(31)	87.84(6)
O(5)–Mn(3)–O(312)	92.98(6)	O(5)-Mn(3)-N(22)	94.27(6)
O(5)–Mn(3)–N(31)	96.77(6)	O(312)–Mn(3)–N(22)	91.76(6)
O(312)–Mn(3)–N(31)	89.53(6)	N(22)-Mn(3)-N(31)	168.80(6)
Mn(1)-O(1)-Mn(2)	112.65(6)	Mn(1)–O(1)–Mn(3)	124.28(6)
Mn(2)-O(1)-Mn(3)	122.73(7)		



Fig. 3 Pluton projection of the molecular structure of ("Bu₄N)- $[Mn_3(\mu_3-O)(phpzMe)_3(O_2CPh)_2]$ (2). Hydrogen atoms are omitted for clarity. Color code: green, manganese; blue, nitrogen; red, oxygen; grey, carbon.

For both compounds, the crystallographic analyses reveal a trinuclear manganese(III) unit containing a μ_3 -oxide bridge. The oxidation states for the three manganese(III) ions were established by charge-valence considerations, by bond length distances and by bond valence sum (BVS) calculations.³² The obtained values for **2** are 3.28, 3.30 and 3.26 for Mn(1), Mn(2) and Mn(3), respectively; and 3.23 for all the manganese(III) ions in compound **3**. Each edge of the Mn₃ triangle is bridged by a η^1, η^1, μ -pyrazolato ligand with the phenolic oxygen and one pyrazole



Fig. 4 Pluton projection of the molecular structure of ("Bu₄N)- $[Mn_3(\mu_3-O)(phpzPh)_3(O_2CPh)_2]$ (3). Hydrogen atoms are omitted for clarity. Color code: green, manganese; blue, nitrogen; red, oxygen; grey, carbon.

nitrogen atom chelating a manganese(III) ion. Selected bond lengths and angles are listed in Table 3 for both compounds **2** and **3**. For compound **2**, intracluster Mn \cdots Mn distances are 3.299 Å, 3.214 Å and 3.224 Å for Mn(1) \cdots Mn(2), Mn(1) \cdots Mn(3) and Mn(2) \cdots Mn(3), respectively. For compound **3**, intracluster Mn \cdots Mn distances are 3.350 Å, 3.209 Å and 3.250 Å for Mn(1) \cdots Mn(2), Mn(1) \cdots Mn(3) and Mn(2) \cdots Mn(3), respectively. The μ_3 -O²⁻(O1) ion lies 0.029 Å above the Mn₃ plane for compound **2** and 0.001 Å for compound **3**, respectively. In

88.65(8)

91.60(8)

125.59(9)

Table 3	Selected	bonds	lengths	[Å]	and	angles	[°]	for	the	compound	$(^{n}Bu_{4}N)[Mn_{3}(\mu_{3}-O)(phpzMe)_{3}(O_{2}CPh)_{2}]$	(2)	and	$(^{n}Bu_{4}N)[Mn_{3}(\mu_{2})]$
O)(phpz	$Ph)_3(O_2CF)$	h_{2} (3)												

Compound 2							
Bond lengths							
Mn(1) - O(1)	1.8615(18)	Mn(1)–O(58)	2.0648(16)	Mn(1)–O(112)	1.835(2)	Mn(1)–N(11)	1.9704(19)
Mn(1)–N(22)	2.0354(19)	Mn(2)-O(1)	1.8629(17)	Mn(2)–O(48)	2.0035(17)	Mn(2)–O(212)	1.8515(18)
Mn(2)–N(21)	1.953(2)	Mn(2)–N(32)	2.0740(18)	Mn(3)-O(1)	1.9006(16)	Mn(3)–O(49)	2.2987(18)
Mn(3)-O(59)	2.274(2)	Mn(3)–O(312)	1.8627(16)	Mn(3)–N(12)	2.011(2)	Mn(3)–N(31)	1.9515(19)
$Mn(1) \cdots Mn(2)$	3.299	$Mn(1) \cdots Mn(3)$	3.214	$Mn(2) \cdots Mn(3)$	3.224		
Bond angles							
O(1)-Mn(1)-O(58)	96.47(7)	O(1)–Mn(1)–O(112)	164.51(8)	O(1)–Mn(1)–N(11)	88.07(8)	O(1)-Mn(1)-N(22)	87.09(8)
O(58)–Mn(1)–O(112)	98.89(8)	O(58)–Mn(1)–N(11)	95.66(7)	O(58)–Mn(1)–N(22)	101.22(7)	O(112)-Mn(1)-N(11)	88.43(8)
O(112)-Mn(1)-N(22)	91.87(8)	N(11)-Mn(1)-N(22)	162.85(8)	O(1)–Mn(2)–O(48)	91.18(7)	O(1)–Mn(2)–O(212)	175.57(8)
O(1)-Mn(2)-N(21)	87.31(8)	O(1)-Mn(2)-N(32)	87.64(7)	O(48)–Mn(2)–O(212)	89.82(7)	O(48)-Mn(2)-N(21)	124.13(8)
O(48)-Mn(2)-N(32)	105.91(8)	O(212)-Mn(2)-N(21)	88.55(8)	O(212)-Mn(2)-N(32)	96.23(8)	N(21)-Mn(2)-N(32)	129.77(8)
O(1)–Mn(3)–O(49)	85.75(7)	O(1)–Mn(3)–O(59)	89.42(7)	O(1)–Mn(3)–O(312)	177.29(7)	O(1)-Mn(3)-N(12)	87.83(8)
O(1)-Mn(3)-N(31)	88.43(7)	O(49)-Mn(3)-O(59)	168.38(7)	O(49)-Mn(3)-O(312)	94.61(7)	O(49) - Mn(3) - N(12)	81.22(8)
O(49)-Mn(3)-N(31)	94.51(7)	O(59)-Mn(3)-O(312)	90.70(7)	O(59)-Mn(3)-N(12)	88.05(8)	O(59)-Mn(3)-O(31)	95.91(7)
O(312)-Mn(3)-N(12)	94.88(8)	O(312)-Mn(3)-N(31)	88.87(8)	N(12)-Mn(3)-N(31)	174.52(8)	Mn(1)-O(1)-Mn(2)	124.67(9)
Mn(1)–O(1)–Mn(3)	117.35(8)	Mn(2) - O(1) - Mn(3)	117.91(10)				
Compound 3							
Bond lengths							
Mn(1) - O(1)	1.8700(17)	Mn(1)-O(59)	2.0404(18)	Mn(1)-O(318)	1.8402(18)	Mn(1) - N(12)	2.051(2)
Mn(1) - N(31)	1.988(2)	Mn(2)-O(1)	1.8970(16)	Mn(2)–O(48)	2.036(2)	Mn(2)–O(218)	1.8402(18)
Mn(2)-N(21)	1.957(2)	Mn(2)-N(32)	2.053(2)	Mn(3)-O(1)	1.8999(17)	Mn(3)–O(49)	2.296(2)
Mn(3)-O(58)	2.2245(19)	Mn(3)-O(118)	1.8576(19)	Mn(3)-N(11)	1.972(2)	Mn(3)-N(22)	2.041(2)
$Mn(1) \cdots Mn(2)$	3.350	$Mn(1) \cdots Mn(3)$	3.209	$Mn(2) \cdots Mn(3)$	3.250		
Bond angles							
O(1)-Mn(1)-O(59)	95.25(7)	O(1)-Mn(1)-O(318)	169.72(8)	O(1)-Mn(1)-N(12)	90.00(8)	O(1)-Mn(1)-N(31)	85.93(8)
O(59)–Mn(1)–O(318)	94.47(8)	O(59)–Mn(1)–N(12)	94.81(8)	O(59)–Mn(1)–N(31)	107.59(8)	O(318)-Mn(1)-N(12)	92.55(9)
O(318)-Mn(1)-N(31)	87.93(9)	N(12)-Mn(1)-N(31)	157.50(9)	O(1)-Mn(2)-O(48)	90.01(8)	O(1)-Mn(2)-O(218)	174.03(9)
O(1)-Mn(2)-N(21)	88.46(8)	O(1)-Mn(2)-N(32)	88.18(8)	O(48)–Mn(2)–O(218)	95.91(9)	O(48)-Mn(2)-N(21)	105.74(9)
O(48)-Mn(2)-N(32)	102.85(8)	O(218)–Mn(2)–N(21)	89.20(8)	O(218)–Mn(2)–N(32)	91.24(8)	N(21)-Mn(2)-N(32)	151.21(9)
O(1)-Mn(3)-O(49)	81.99(7)	O(1)-Mn(3)-O(58)	89.54(7)	O(1)-Mn(3)-O(118)	174.95(8)	O(1)-Mn(3)-N(11)	89.96(8)

168.40(7)

95.41(8)

92.22(8)

117.75(9)

O(49)-Mn(3)-O(58)

O(58)-Mn(3)-O(118)

O(118)-Mn(3)-N(22)

Mn(2)-O(1)-Mn(3)

compound 2, the Mn–O(1)–Mn angles are Mn(1)–O(1)–Mn(2) = $124.67(9)^{\circ}$, Mn(1)–O(1)–Mn(3) = 117.35(8)^{\circ} and Mn(2)–O(1)– $Mn(3) = 117.91(10)^{\circ}$; whereas in compound 3, the Mn–O(1)– Mn angles are Mn(1)–O(1)–Mn(2) = $125.59(9)^{\circ}$, Mn(1)–O(1)– $Mn(3) = 116.66(8)^{\circ}$ and $Mn(2)-O(1)-Mn(3) = 117.75(9)^{\circ}$. For both compounds, one manganese(III) ion is hexa-coordinated and the other two manganese(III) ions are penta-coordinated. The shortest intermolecular Mn · · · Mn distance is 8.816 Å and 7.228 Å for compounds 2 and 3, respectively. Therefore in the case of 3, π - π stacking interactions (3.717 Å) are present between the pyrazole ring of one trinuclear unit and the phenol ring of the closest trinuclear unit, with a dihedral angle between the rings of 6.92°. The main difference with compound 1 is the presence of two bridging benzoate ligands in 2 and 3, and the ${}^{n}Bu_{4}N^{+}$ as a counter ion, whereas in compound 1 only one bridging acetate is present. As a consequence, the coordination sphere of the manganese(III) ions in 1 is completed with solvent molecules. In 1, the solvent present in the lattice is involved in hydrogen bonding that links the trinuclear units, thus forming a chain. On the other hand, compounds 2 and 3 are isolated trinuclear units.

88.65(8)

96.10(8)

89.60(9)

116.66(8)

Some structural differences are observed between the trinuclear manganese(III) compounds reported here and those de-

scribed previously,12-15 all containing phenol-pyrazole ligands. The introduction of a substituent on the fifth position of the pyrazole ring as methyl or phenyl drives the carboxylate to bind to two manganese(III) ions from the same trinuclear unit, instead of bridging the trinuclear manganese(III) units, as was observed previously.12,14,15 If the carboxylate ligand is small, *i.e.* acetate, these trinuclear units can form chains because of the hydrogen bonds established between the carboxylate and the solvent molecules (e.g. compound 1 and $[Mn_3(\mu_3 - \mu_3)]$ O)(phpzMe)₃(O₂CMe)(MeOH)₃]·1.5MeOH¹⁵). However, if the carboxylate is bulkier, such as benzoate, the trinuclear units become isolated and no intermolecular hydrogen bonding interactions are observed. It appears that the size of the co-ligand or the solvent molecule is also an important driving force in stabilizing the type of structure as the replacement of methanol¹⁵ by ethanol (e.g. compounds 2 and 3) induces the coordination of two bridging carboxylate ligands in the same $[Mn_3(\mu_3-O)]^{7+}$ core.

O(49)-Mn(3)-N(11)

O(58)-Mn(3)-N(22)

Mn(1)-O(1)-Mn(2)

92.97(8)

83.51(8)

174.92(9)

O(49)-Mn(3)-O(118)

O(58) - Mn(3) - N(11)

N(11)-Mn(3)-N(22)

Magnetic properties

Magnetic susceptibilities were measured as a function of temperature under a 0.1 T applied field in the range 1.8–300 K. In Fig. 5,

O(1)-Mn(3)-N(22)

O(49)-Mn(3)-N(22)

Mn(1)-O(1)-Mn(3)

O(118)-Mn(3)-N(11)



Fig. 5 Plot of $\chi_M T$ vs. T for 1 (black), 2 (blue) and 3 (red) in the range 1.8 to 300 K in 0.1 T applied field with the experimental fit from 50–300 K (-).

300

the results as a plot of $\chi_{\rm M}T$ vs. T are shown for compounds 1-3. Similar to that observed for other trinuclear manganese(III) compounds,^{2-5,12-15,33} the $\chi_{\rm M}T$ product is still increasing with temperature near room temperature and the measured $\chi_{\rm M}T$ values at 300 K are therefore below the high-temperature limit of 9.00 cm³ K mol⁻¹ expected for three non-interacting manganese(III) ions. For compounds 1, 2 and 3, the $\chi_M T$ values measured at room temperature are 6.68 cm3 K mol-1, 6.18 cm3 K mol-1 and 6.52 cm³ K mol⁻¹, respectively. With decreasing temperatures the $\chi_{\rm M}T$ value is seen to decrease drastically in all cases. This behavior can be attributed to the presence of predominant intramolecular antiferromagnetic interactions (J) between the three manganese(III) ions composing the trinuclear units. As a result, the magnetic energy level spectrum of the triangular units spans a wide energy range of the order of 40–70 times the exchange interaction constants (also see Fig. 6), i.e. amounting to a few hundreds Kelvin in thermal energy, even for $J/k_{\rm B}$ values of a few Kelvin only. As compared to the other two compounds, 1 is exceptional in that the product $\chi_{\rm M}T$ passes through a minimum of 2.87 cm³ K mol⁻¹ at 30 K, increases up to about 5.26 cm³ K



Fig. 6 Energy levels for an isosceles triangle with $S_1 = S_2 = S_3 = 2$ calculated for $J_1 < 0$. States are labeled as (S_T, S^*) .

mol⁻¹ at 2.6 K and finally decreases again to 5.05 cm³ K mol⁻¹ at 1.8 K (Fig. 5). For compound **2** the $\chi_{\rm M}T$ product shows a continuous gradual decrease with temperature, reaching a value of 0.67 cm³ K mol⁻¹ at 1.8 K (Fig. 5). For compound **3** upon cooling the $\chi_{\rm M}T$ value likewise decreases continuously down to a value of 1.53 cm³ K mol⁻¹ at 15 K, and then more steeply to 0.41 cm³ K mol⁻¹ at 1.8 K (Fig. 5).

As will become clear from the theoretical analysis presented below, the upturn of the $\chi_M T$ product in 1 below 30 K is due to a partial ferromagnetic coupling between the manganese(III) moments within the triangular cluster, in combination with a ferromagnetic intermolecular interaction between the trinuclear units along the chains. The latter interaction will be propagated through the hydrogen bonds present between the acetate and the ethanol molecules within the one-dimensional chain (see Fig. 2). For compounds 2 and 3 all intracluster interactions turn out to be antiferromagnetic.

Field-dependent magnetization studies were carried out at low temperatures for all three materials and are shown in Fig. 7. As can be noted, even at the maximum field of 5 T the values measured for the molar magnetization fall far below the saturation limit of 12 N β appropriate for three non-interacting manganese(III) ions. This confirms that the just mentioned large extent in energy of the magnetic energy level spectrum for the trinuclear cluster, compared to which the Zeeman-energy of the applied field is verv small. Compound 1 is again exceptional in that its M(B)measured at lowest temperatures shows a fast initial increase, reaching a value of ≈ 3 NB at about 1 T already, not far below the 4 NB corresponding to one manganese(III) ion or one third of the saturated moment of the trinuclear unit. This feature again strongly suggests a partial ferromagnetic coupling within the triangle, which should result in a ground state of $S_{\rm T} = 2$ for the triangular unit, as found previously for [Mn₃(μ_3 -O)(phpzMe)₃(MeOH)₃(O₂CMe)]·1.5MeOH.¹⁵ Indeed, the experimental M(B) curve for 1 at 2 K is very close to the Brillouin function for a single spin S = 2 calculated for that temperature, included in Fig. 7. At 2 K, the experimental data at lower fields (<1 T) are slightly above this Brillouin function, indicating the presence of additional ferromagnetic intermolecular interactions,



Fig. 7 Field dependence of the magnetization for $1(\bigcirc)$, $2(\square)$ and $3(\bigcirc)$ measured at 2 K. The Brillouin function is included for one S = 2 and g = 2 at 2 K.

as also mentioned above in connection with the observed upturn in the magnetic susceptibility below 30 K. The behaviors of the magnetization for compounds 2 and 3, on the other hand, indicate a low-spin magnetic ground state for the triangular units, *i.e.* all intramolecular interactions are apparently antiferromagnetic in these materials.

For a more quantitative analysis of the exchange interactions, the susceptibility data were fitted with the Hamiltonian for an isosceles triangle:

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

where J_1 represents the Mn(III)–Mn(III) exchange interaction parameter of the two exchange paths with similar Mn···Mn distances and Mn–O_{oxide}–Mn angles, and J_2 refers to the path characterized by the unique Mn–O_{oxide}–Mn angle (Mn(1)–O(1)– Mn(2)). This model and its predictions has been explained in more detail in our previous paper.¹⁵

Briefly, the energy levels for the isosceles triangle of spins S are given by

$$E(S_{\rm T}, S^*) = -J_1[S_{\rm T}(S_{\rm T}+1) - S^*(S^*+1) - S(S+1)] -J_2[S^*(S^*+1) - 2S(S+1)]$$
(2)

Here $S^* = S_2 + S_3$ and can take the values $S^* = 2S, 2S - 1, ..., 0$, whereas the total spin $S_T = (S^* + S), (S^* + S - 1), ..., |S^* - S|$. In Fig. 6 the so-obtained energy spectrum is plotted as $E(S_T, S^*)/|J_1|$ vs. the ratio $r = J_2/J_1$. For some levels the corresponding values for the total spin S_T of the trinuclear compound have been indicated. Note that the diagram shown is for antiferromagnetic (negative) values for J_1 , for ferromagnetic J_1 the diagram has to be inverted.

When fitting the experimental data to these predictions one should restrict preferably to the temperature range above 50 K, to avoid the complications of intercluster interactions and zero-field Mn(III) splittings (crystal field anisotropy) which may influence the data at lower temperatures and are obviously not taken into account in the model of eqn (1).

On the basis of the data above 50 K then, the best fitting parameters for compound **1** gave $g = 1.87 \pm 0.03$, $J_1 = -10.3 \pm 0.3 \text{ cm}^{-1}$ and $J_2 = +10.9 \pm 2.4 \text{ cm}^{-1}$. Furthermore, the best fits of the experimental data above 50 K were $g = 1.88 \pm 0.02$, $J_1 = -4.2 \pm 0.1 \text{ cm}^{-1}$ and $J_2 = -10.3 \pm 1.2 \text{ cm}^{-1}$ for compound **2**, and $g = 1.93 \pm 0.02$, $J_1 = -4.8 \pm 0.1 \text{ cm}^{-1}$ and $J_2 = -10.2 \pm 1.2 \text{ cm}^{-1}$ for compound **3**. Referring to the magnetic energy level diagram calculated for the isosceles triangle as presented in Fig. 6, one may note that the ratio $r = J_2/J_1$ equals to about -1.0 for compound **1**. This ratio corresponds indeed with an $S_T = 2$ ground state for the triangle, the nearest excited magnetic level being at a distance of $\approx 6 \text{ cm}^{-1}$ in this case.

For compounds **2** and **3** we find r = +2.5 and +2.1, respectively, corresponding to an antiferromagnetic ($S_T = 1$) ground state, as already anticipated in the above. The solid curves drawn in Fig. 5 represent the predictions based on the above mentioned intramolecular interaction constants. For the purely antiferromagnetic compounds **2** and **3** the downward trend with lowering *T* of the predicted $\chi_M T$ curve is closely followed by the experiments over the whole range; the somewhat more rapid decrease of the experimental data at the lowest temperatures (≤ 15 K) can be attributed to the effects of antiferromagnetic intercluster couplings and zero-field splitting of the Mn(III) levels not considered in

the Hamiltonian of eqn (1). For compound 1, on the other hand, the upturn of the experimental data below 30 K from the calculated solid curve (representing purely paramagnetic behavior for the net spins $S_T = 2$ per cluster), should be ascribed to ferromagnetic intercluster couplings between these spins along the crystallographic chains. AC-susceptibility measurements were carried out on compound 1 in the range 1.8–10 K in a zero DC field and in frequencies up to 997 Hz. Although no maximum in the susceptibility is yet in sight, the data do show slight frequency dependence with the appearance of an out-of-phase signal at highest frequencies. This could be interpreted either as signalling the advent of single-chain magnet behavior or as the approach of a transition to long-range 3D magnetic order induced by weak interchain interactions, *e.g.* of dipolar origin. Further studies at lower temperatures (<2 K) would be needed to clarify this behavior.

To summarize, it has been shown that compound 1 presents both ferromagnetic and antiferromagnetic intracluster interactions whilst only antiferromagnetic intracluster interactions are present in compounds 2 and 3. As described in our previous work,¹⁵ the occurrence of the ferromagnetic interaction in 1 can be attributed to the major distortion of the Mn–O–Mn angle of the [Mn₃O]⁷⁺ triangle, *i.e.* $Mn(1)-O(1)-Mn(2) = 112.65^{\circ}$. Previous theoretical and experimental studies have shown that the superexchange interaction can change from antiferromagnetic to ferromagnetic when the metal ion-ligand-metal ion angle decreases, with a the critical angle value of around 120°.^{20,34} In compound 1, the ferromagnetic interaction is stronger than observed previously¹⁵ for $[Mn_3(\mu_3 - \mu_3)]$ O)(phpzMe)₃(MeOH)₃(O₂CMe)]-1.5MeOH; we attribute this to the appreciably shorter Mn-O distances observed in 1 as compared to those in $[Mn_3(\mu_3-O)(phpzMe)_3(MeOH)_3(O_2CMe)]$ ·1.5MeOH.¹⁵ For compounds 2 and 3, the deviation of the Mn–O–Mn angle from the value of 120° (corresponding to an equilateral triangle) towards lower values is less pronounced. As a consequence, all intracluster magnetic interactions are antiferromagnetic. Similar behavior has also been reported previously in related compounds.12-15 However, in the compounds with phenol-pyrazole ligands, the magnetic exchange interaction could be expected to also depend on the geometry of the pyrazolato bridge, as it has been shown that the dihedral angle ($\delta_{pz-bend}$) of the least-squares plane of the pyrazole ring relative to the M-N(pz)-N(pz)-M plane is also an important factor affecting the magnetic interaction.³⁵ Therefore Table 4 contains the structural and magnetic data of the [Mn₃O]⁷⁺ compounds containing phenol-pyrazole derivatives. From this compilation it can be concluded that it is difficult to correlate the magnetic exchange parameters with this structural parameter.

As discussed above, the overall intracluster magnetic interactions are antiferromagnetic in μ_3 -oxide trinuclear manganese(III) compounds with phenol–pyrazole ligands.¹²⁻¹⁵ When the trinuclear units are linked by carboxylate bridges, ferromagnetic interactions emerge between the trinuclear units within the chain,^{14,15} whilst antiferromagnetic or ferromagnetic interactions are observed when the trinuclear units are linked by end-toend azido bridges.^{13,15} However for the compound [Mn₃(μ_3 -O)(Meppz)₃(EtOH)₄(O₂CMe)]¹² in which the trinuclear units are bridged by acetate ligands, antiferromagnetic interactions are present. For the one-dimensional chains formed through hydrogen bonds established between the trinuclear units, ferromagnetic intrachain interactions are operative if the separation between the manganese(III) ions that bridge the clusters is smaller than *ca*.

 Table 4
 Selected magnetic and structural data for trinuclear oxide-bridged manganese(III) compounds containing phenol-pyrazole ligands

	J_1/cm^{-1}	J_2/cm^{-1}	zJ'/cm	$g^{-1}g$	r ^b	Mn–O–Mn ^c	$\delta_{\text{pz-bend}}{}^{d}$	$\delta_{(\text{MnNNMn})-(\text{MnOMn})}{}^{e}$	Reference
$[Mn_3(\mu_3-O)(ppz)_3(MeOH)_3(O_2CMe)],$ $[Mn_3(\mu_3-O)(phpzH)_2(MeOH)_3(O_3CMe)]$	-3.01	-3.01	+0.32	1.88	1.0	119.88; 119.15: 119.98	2.87; 2.50; 6.98	14.87; 2.07; 13.47	14,15
$[Mn_3(\mu_3-O)(Meppz)_3(MeOH)_4(O_2CMe)]$	-3.21	-3.21	+0.68	1.93	1.0	120.42; 119.41: 120.14	3; 3.37; 7.63	2.63; 7.91,9.96	14
$[Mn_{3}(\mu_{3}-O)(Meppz)_{3}(EtOH)_{4}(O_{2}CMe)]$	-1.87	-5.61	-0.014	1.99	3.0	120.43; 118.44: 121.13	1.47; 3.60; 3.69	0.86; 6.84; 7.46	12
$[Mn_3(\mu_3\text{-}O)(Brppz)_3(MeOH)_3(N_3)]\text{-}2MeOH$	-3.87	-8.20	-0.07	2.12	2.1	119.91; 119.17: 119.35	5.89; 2.30; 4.91	6.82; 18.43; 2.35	13
$[Mn_{3}(\mu_{3}\text{-}O)(Brppz)_{3}(MeOH)_{3}(N_{3})]$	-4.66	-7.35	-0.30	2.12	1.6	120.33; 118.75; 120.61	4.93; 1.47; 4.71	13.02; 14.57; 8.48	13
$[Mn_3(\mu_3-O)(phpzMe)_3(O_2CMe)(MeOH)_3] \cdot 1.5 MeOH$	-7.2	+7	_	2.13	-1.0	120.61; 116.10; 120.85	11.97; 2.44; 24.86	12.57; 40.11; 26.02	15
$[Mn_3(\mu_3\text{-}O)(phpzH)_3(MeOH)_4(N_3)]\cdot MeOH$	-5.7	-3.9	—	2.17	0.7	120.79; 118.96; 120.11	4.69; 3.59; 7.12	4.51; 4.22; 1.29	15
$[Mn_3(\mu_3\text{-}O)(phpzMe)_3(O_2CMe)(EtOH)]\cdot EtOH$	-10.3	+10.9	_	1.87	-1.0	112.65; 122.73; 124.28	6.21; 2.89; 3.90	48.09; 7.31; 10.38	This work
$(^{n}Bu_{4}N)[Mn_{3}(\mu_{3}-O)(phpzMe)_{3}(O_{2}CPh)_{2}]$	-4.2	-10.3	_	1.88	2.5	124.67; 117.91; 117.35	2.04; 4.12; 4.57	21.41; 38.51; 37.96	This work
$(^{n}Bu_{4}N)[Mn_{3}(\mu_{3}\text{-}O)(phpzPh)_{3}(O_{2}CPh)_{2}]$	-4.8	-10.2	_	1.93	2.1	117.75; 125.58; 116.66	3.82; 3.36; 17.00	34.66; 5.13; 33.17	This work

^{*a*} H₂phpzH, H₂ppz = 5(3)-(2-hydroxyphenyl)-pyrazole, H₂Meppz = 3-(5-methyl-2-phenolate)-pyrazole, H₂Brppz = 4-bromo-2-(1*H*-pyrazol-3-yl)phenol, H₂phpzMe = 3(5)-methyl-5(3)-(2-hydroxyphenyl)pyrazole. ^{*b*} $r = J_2/J_1$. ^{*c*} Mn- μ_3 -O-Mn angle, Mn(1)-O-Mn(2); Mn(2)-O-Mn(3); Mn(1)-O-Mn(3) respectively. ^{*d*} Dihedral angle between the pz ring plane and Mn-N(pz)-N(pz)-Mn plane. ^{*e*} Dihedral angle between the Mn-N(pz)-N(pz)-Mn plane and Mn-O-Mn plane.

7.4 Å, as it is the case for compound **1**. The intrachain interactions become antiferromagnetic for larger separation between the trinuclear units of *ca.* 8.04 Å, as observed¹⁵ for the compound $[Mn_3(\mu_3-O)(phpzMe)_3(MeOH)_3(O_2CMe)]\cdot 1.5MeOH.$

Conclusions

The synthesis, crystal structure and magnetic studies of three new manganese(III) compounds are reported. Compounds 1-3 are trinuclear µ3-oxide-bridged manganese(III) compounds containing phenol-pyrazole ligands. Following previous results,¹⁵ the effect of the solvent or co-ligand and the type of carboxylate ligand were studied in the present work. Compound 1 forms 1-D chains due to the intermolecular hydrogen bonding between an ethanol molecule and an acetate group, whereas 2 and 3 are isolated trinuclear manganese(III) compounds with two benzoate ligands and ${}^{n}Bu_{4}N^{+}$ as a counter ion. Compounds 1–3 present overall intramolecular antiferromagnetic interactions between the three manganese(III) ions composing the trinuclear unit. In addition, compound 1 shows a ferromagnetic interaction between two manganese(III) ions in the trinuclear unit that can be ascribed to the most distorted structural path, resulting in a $S_{\rm T} = 2$. Moreover, ferromagnetic intermolecular interaction along the chain are propagated through the hydrogen bonds present between the acetate and the ethanol molecules.

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