

Preparation and properties of $[\text{NH}_2\text{Et}_2][\text{Mn}_{10}(\text{OH})_3(\text{phth})_9(\text{bpy})_6]$, a new decanuclear Mn(II) compound with a variety of phthalate binding modes

Cristina Cañada-Vilalta,^a Maren Pink^a and George Christou^{*a,b}

^a Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, IN 47405-7102, USA

^b Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA.
E-mail: christou@chem.ufl.edu

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The synthesis and characterisation are reported of the new decanuclear manganese compound $[\text{NH}_2\text{Et}_2][\text{Mn}_{10}(\text{OH})_3(\text{phth})_9(\text{bpy})_6]$ (**2**; phthH_2 = phthalic acid, bpy = 2,2'-bipyridine), obtained from the reaction of phthH_2 , bpy and NET_3 with either $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (**1**) or manganese(II) acetate; the latter is by far the superior method. Complex **2** is the highest nuclearity Mn^{II} cluster yet prepared, and it crystallizes in the triclinic space group $P\bar{1}$. The structure of the anion consists of a pinwheel-like arrangement of ten Mn^{II} ions bridged by three $\mu_3\text{-OH}^-$ ions and nine bridging phth^{2-} groups. Six chelating bpy groups complete octahedral coordination at each Mn^{II} ion. There are three different bridging modes for the phth^{2-} groups, some of them unprecedented. Solid-state, variable-temperature dc and ac magnetic susceptibility measurements reveal weak, antiferromagnetic exchange interactions between the Mn^{II} ions resulting in a low-spin ground state of $S \approx 2$ and low-lying excited states. The non-zero ground state is rationalized as due to the presence of competing exchange interactions (spin frustration) within the Mn_{10} topology.

Introduction

There are several reasons why manganese carboxylate chemistry is the focus of such great interest at the present time. Small Mn carboxylate clusters are found at the active sites of a variety of metalloproteins such as the water oxidizing complex of photosystem II, which contains a Mn_4 cluster whose exact structure and mechanism of function have yet to be fully elucidated.¹ In the last ten years, the synthesis and study of polynuclear Mn compounds have also been stimulated by the discovery that some of them can function as single-domain nanomagnets (superparamagnets) at very low temperatures. They have since been called "single-molecule magnets" to reflect the fact that their properties are not due to intermolecular exchange interactions and long-range ordering, but instead to a combination of two intramolecular properties, namely a large ground-state spin (S) and a large magnetoanisotropy, the latter reflected in a large and negative value of the zero-field splitting parameter, D .²

There is thus a continuing need to develop new synthetic methods for the preparation of new polynuclear Mn carboxylate compounds. A particularly successful approach on several previous occasions has been the aggregation of smaller nuclearity starting materials, usually Mn_3 or Mn_4 species, into higher nuclearity products. Examples of large clusters obtained in this way include $[\text{Mn}_8\text{O}_6\text{Cl}_6(\text{O}_2\text{CPh})_7(\text{H}_2\text{O})_2]^-$,³ $[\text{Mn}_9\text{Na}_2\text{O}_7(\text{O}_2\text{CPh})_{15}(\text{MeCN})]_4$,⁴ and $[\text{Mn}_{18}\text{O}_{16}(\text{O}_2\text{CPh})_{22}(\text{phth})_2(\text{H}_2\text{O})_4]^{4-}$ (phth^{2-} = phthalate),⁵ all derived from the treatment of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]^-$ with particular reagents. In a similar fashion, $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_4\text{L}_2]^{2+}$ ⁶ and $[\text{Mn}_6\text{O}_7(\text{mpdp})_3(\text{bpy})_3]^{3+}$ (mpdp^{2-} = the dianion of *m*-phenylenedipropionic acid)⁷ were obtained from related trinuclear species. More recently, the reverse reaction has also proven useful, namely the fragmentation of a high nuclearity cluster. This method has, for example, been used to synthesize compounds with the new $[\text{Mn}_3\text{O}_4]^{4+}$ core by treatment of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (**1**) with bpy (2,2'-bipyridine) in $\text{MeCN-MeCO}_2\text{H}$.⁸ The present work resulted from a modification of the latter reaction by the addition of a dicarboxylic acid, phthalic acid, as well as bpy . Phthalic acid has been used only sparingly in manganese chemistry to date. Known compounds comprise: Two polymeric

chains with Mn(II) and either Schiff base⁹ or bpy ancillary ligands;¹⁰ a mononuclear Mn(II) complex;⁹ the tetranuclear Mn(II) compound $[\text{Mn}_4(\text{phth})_2(\text{bpy})_8](\text{ClO}_4)_4$,¹¹ and the above mentioned $\text{Mn}^{\text{III}}_{18}$ cluster $[\text{Mn}_{18}\text{O}_{16}(\text{O}_2\text{CPh})_{22}(\text{phth})_2(\text{H}_2\text{O})_4]^{4-}$.⁵ We now report a new high nuclearity Mn(II) product, $[\text{NH}_2\text{Et}_2][\text{Mn}_{10}(\text{OH})_3(\text{phth})_9(\text{bpy})_6]$ (**2**), and describe its unusual structure and selected properties. It was originally prepared in small yield from **1**, but we have also developed a more convenient, high yield method.

Experimental

Syntheses

All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (**1**) was prepared as described elsewhere;^{2e} phthH_2 = phthalic acid, bpy = 2,2'-bipyridine.

$[\text{NH}_2\text{Et}_2][\text{Mn}_{10}(\text{OH})_3(\text{phth})_9(\text{bpy})_6]$ (2**). Method A.** A solution containing $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (0.30 g, 0.16 mmol) in MeCN (15 mL) was allowed to slowly diffuse over several weeks through a glass frit into a solution of bpy (0.23 g, 1.5 mmol), phthalic acid (0.21 g, 1.3 mmol) and NET_3 (0.36 mL, 2.6 mmol) in MeCN (15 mL). This gave crystals of **2** suitable for crystallography, as well as an uncharacterized brown powder. The yield of **2** was 8%.

Method B. A solution of bpy (0.15 g, 0.98 mmol), phthalic acid (0.55 g, 3.3 mmol) and NET_3 (0.90 mL, 6.5 mmol) in CH_2Cl_2 (10 mL) was treated with manganese(II) acetate tetrahydrate (0.40 g, 1.6 mmol) in MeCN (10 mL). The resulting yellow solution was filtered and allowed to slowly evaporate. Yellow crystals formed after several days in 74% yield. Their identity was established by IR spectroscopic comparison with crystallographically characterized material from Method A, and elemental analysis. Anal. Found: C, 52.61; H, 4.09; N, 6.76. $2 \cdot 2.5\text{MeCN} \cdot 2\text{H}_2\text{O}$ requires C, 52.43; H, 3.54; N, 6.72%.

Method C. The previous method was followed employing NET_3H (0.48 g, 6.5 mmol) in place of NET_3 . The light yellow

mixture was filtered and allowed to evaporate over several days, producing a light yellow precipitate that was collected by filtration and dried under vacuum. Its identity was established by IR spectroscopic comparison with crystallographically characterized material from Method A, and elemental analysis. Anal. Found: C, 51.39; H, 3.69; N, 5.41. **2** requires C, 50.99; H, 3.12; N, 5.68%. Yield, 65%.

X-Ray crystallography and solution of structure

Data were collected using a Bruker SMART 6000 system. A suitable crystal of of $2 \cdot 9\text{MeCN} \cdot \frac{1}{2}\text{H}_2\text{O}$ was attached to the tip of a 0.1 mm diameter glass capillary, mounted on the goniostat, and cooled to 120 K. The intensity data were corrected for absorption (SADABS).¹² The space group $P\bar{1}$ was determined from the intensity statistics and the lack of systematic absences. The structure was solved by direct methods using SIR-92¹³ and refined with SHELXL-97.¹⁴ The non-hydrogen atoms of the Mn_{10} anion were refined with anisotropic displacement parameters. The non-hydrogen atoms of the solvent molecules and cation were refined with isotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The exception were the hydrogen atoms of the OH^- groups, which were refined with individual isotropic displacement parameters, and the hydrogen atoms of the water molecule, which were placed in reasonable positions based on geometrical considerations and not refined. The final full matrix least squares refinement converged to $R1 = 0.0669$ and $wR2 = 0.1847$ (F^2 , all data). The remaining electron density is located in the vicinity of the metals, solvent molecules and cations. The structure also contains at least nine MeCN molecules and half a water molecule per formula unit. Additional solvent may be present in the structure.

CCDC reference number 194176.

See <http://www.rsc.org/suppdata/dt/b2/b209237a/> for crystallographic data in CIF or other electronic format.

Other studies

Infrared spectra were recorded in the solid state (KBr pellets) on a Nicolet Model 510P FTIR spectrophotometer in the 4000–400 cm^{-1} range. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 Series II Analyzer. Magnetic measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet at Indiana University. Pascal's constants were used to estimate the diamagnetic correction, which was subtracted from the experimental susceptibility to give the molar magnetic susceptibility (χ_M).

Results and discussion

Syntheses

The reaction that we initially investigated was that between $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (**1**) and a combination of bpy, phthalic acid and NEt_3 in MeCN. In the absence of the phthalic acid and NEt_3 , the product is $[\text{Mn}_3\text{O}_4(\text{O}_2\text{CMe})_4(\text{bpy})_2]$, as mentioned in the Introduction, and we had hoped that the presence of the dicarboxylate might lead to higher nuclearity analogues. Instead, the reaction yields a mixture of insoluble materials. Slow diffusion of the reactant solutions allowed brownish-yellow crystals of one of the products to be obtained in a form suitable for crystallography, and it was identified as the interesting new decanuclear cluster $[\text{NH}_2\text{Et}_2][\text{Mn}_{10}(\text{OH})_3(\text{phth})_9(\text{bpy})_6]$ (**2**). This Mn(II) complex, obtained in a very low yield (8%), was clearly only one of several products of what is obviously a complicated reaction system. A large amount of insoluble brown powder was also obtained, and its insolubility in all solvents we explored suggests that it might be

a polymeric material, or mixture of materials, facilitated by the presence of the dicarboxylate ligand. We did not study this brown material further. With the identity of **2** established, an alternative and convenient synthesis was developed involving the reaction of bpy, phthH_2 , NEt_3 and $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ in CH_2Cl_2 and MeCN. Concentration of the resulting solution by evaporation gave complex **2** in a much higher yield of 74%.

It is noteworthy that the cation of **2** is NH_2Et_2^+ , which arose from a reaction employing NEt_3 . It may be simply due to NHET_2 impurities in the NEt_3 (although we saw no clear evidence for this in the NMR spectrum of our NEt_3) and to the fact that the voids left by the packing of the Mn_{10} anion may accommodate the NH_2Et_2^+ cation better than NHET_3^+ . Alternatively it may have been produced *in situ* from the NEt_3 . A possible pathway might be the binding of NEt_3 to Lewis acidic Mn^{2+} (or traces of Mn^{3+} formed from aerial oxidation) facilitating nucleophilic attack by another NEt_3 or a carboxylate group leading to removal of an ethyl group, or an acid-catalyzed loss of ethylene. Although unusual, such transformations are not unprecedented: there are several examples in the organic chemistry literature of the conversion of tertiary amines into secondary ones under different conditions, such as with ammonia and a catalyst at moderate to high temperatures,¹⁵ photocatalysis employing visible light,¹⁶ or reaction with a hydroxyl radical.¹⁷ In the present case, this putative conversion would be taking place under quite mild conditions. In any event, an alternative synthesis employing NHET_2 instead of NEt_3 afforded the same product in a comparable yield.

Structural description of $[\text{NH}_2\text{Et}_2][\text{Mn}_{10}(\text{OH})_3(\text{phth})_9(\text{bpy})_6] \cdot 9\text{MeCN} \cdot \frac{1}{2}\text{H}_2\text{O}$

Crystallographic details for complex **2** are provided in Table 1. A labelled ORTEP¹⁸ plot of the anion of complex **2** is shown in Fig. 1 and a stereoview is shown in Fig. 2. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with the asymmetric unit containing a complete anion and a NH_2Et_2^+ cation disordered over two positions with equal occupancies. The structure also contains at least nine MeCN molecules and half a water molecule per formula unit. Selected bond distances and angles are presented in Table 2.

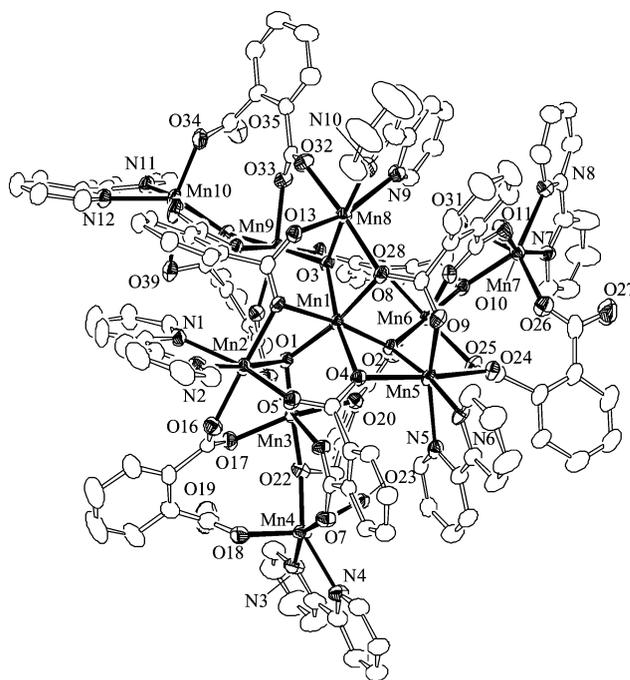
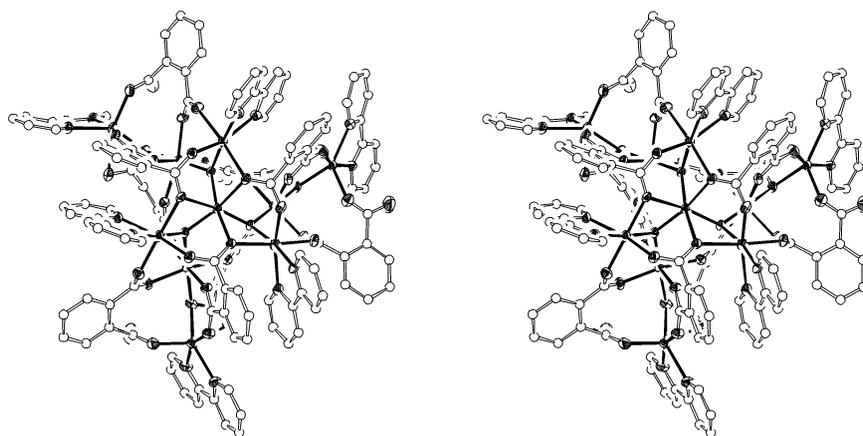


Fig. 1 ORTEP representation of $[\text{NH}_2\text{Et}_2][\text{Mn}_{10}(\text{OH})_3(\text{phth})_9(\text{bpy})_6]$ (**2**) with the atoms drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1 Crystallographic data for $[\text{NH}_2\text{Et}_2][\text{Mn}_{10}(\text{OH})_3(\text{phth})_9(\text{bpy})_6]\cdot 9\text{MeCN}\cdot \frac{1}{2}\text{H}_2\text{O}$

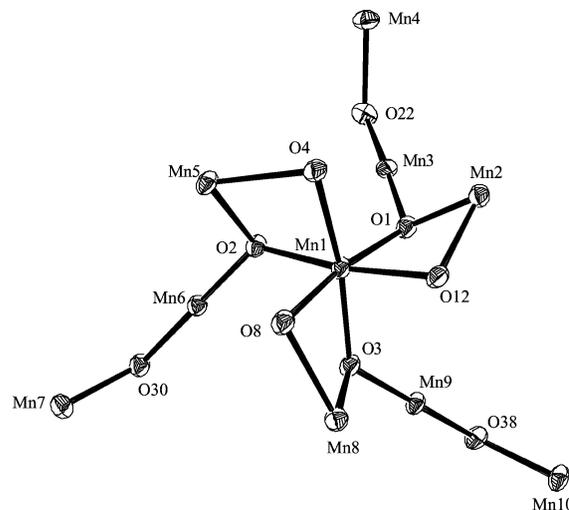
Empirical formula	$\text{C}_{154}\text{H}_{127}\text{Mn}_{10}\text{N}_{22}\text{O}_{39.50}$
Formula weight	3467.18
Crystal color, shape, size/mm	Light brown block, $0.15 \times 0.13 \times 0.10$
Temperature/K	120(2)
Wavelength/Å	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 15.002(4)$ Å, $\alpha = 74.952(1)^\circ$ $b = 17.407(2)$ Å, $\beta = 80.348(1)^\circ$ $c = 33.082(3)$ Å, $\gamma = 69.182(1)^\circ$
Volume/Å ³	7774(1)
Z	2
$D_c/\text{Mg m}^{-3}$	1.481
Absorption coefficient/mm ⁻¹	0.869
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	26487/24/1913
Goodness-of-fit on F^2	1.029 ^a
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0669$, $wR2 = 0.1684^{b,c}$
R indices (all data)	$R1 = 0.0938$, $wR2 = 0.1840^{b,c}$
Largest diff. peak and hole/e Å ⁻³	1.408 and -0.713

^a Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)]/(N_{\text{observns}} - N_{\text{params}})]^{1/2}$, all data. ^b $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^c $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

**Fig. 2** Stereoview representation of complex **2**. All atoms are drawn at a 50% probability level except hydrogen atoms, which have been omitted for clarity.

The structure of the anion of **2** consists of ten Mn(II) ions bridged by a combination of three $\mu_3\text{-OH}^-$ ions and nine phth^{2-} groups. Six chelating bpy groups complete octahedral coordination at each metal. Although the anion has no imposed crystallographic symmetry, it possesses virtual C_3 symmetry, with the approximate C_3 rotation axis passing through the central Mn1, and perpendicular to the O1–O2–O3 plane. A $\mu_3\text{-OH}^-$ ion and a $\mu_2\text{-oxo}$ atom from a carboxylate group form two mono-atomic bridges between the central Mn1 and each of the Mn ions Mn2, Mn5 and Mn8 (Fig. 3). Three more Mn ions, Mn3, Mn6 and Mn9, are bridged to these Mn ions, and to the central Mn1, by the $\mu_3\text{-OH}^-$ ions. The final three Mn ions, Mn4, Mn7 and Mn10, on the periphery of the anion are mono-atomically bridged to Mn3, Mn6 and Mn9, respectively, by a $\mu_2\text{-oxo}$ atom from each of three phth^{2-} groups. The resulting pinwheel-shape of the $[\text{Mn}_{10}\text{O}_9]$ core is emphasized in Fig. 3. The presence of triply bridging OH^- ions is unusual in Mn(II) chemistry, with only three previous examples of such a bridging mode.^{19–21} The protonation of the bridging O atoms O1, O2 and O3 was confirmed by bond valence sum (BVS) calculations, which yielded values of *ca.* 1.1, consistent with a hydroxide group.²² In addition, there are hydrogen-bonding contacts between these O atoms and those from nearby phth^{2-} groups ($\text{O} \cdots \text{O} = 2.74\text{--}2.77$ Å), supporting the presence of hydrogen atoms and thus $\mu_3\text{-OH}^-$ ions.

The rest of the bridging system comprises nine phth^{2-} groups bound in a variety of bridging modes. There are three types of phth^{2-} groups. The first (Type A) consists of three that use one of their carboxylate groups to bridge two Mn ions in the common *syn,syn*- $\eta^1\text{-}\eta^1\text{-}\mu_2$ fashion (bridging Mn3/Mn4, Mn6/Mn7

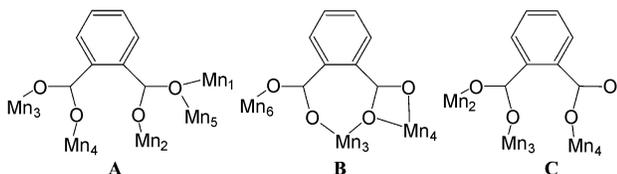
**Fig. 3** ORTEP representation of the pinwheel-shaped $[\text{Mn}_{10}\text{O}_9]$ core of complex **2**.

and Mn9/Mn10), and their other carboxylate group to bridge three Mn ions in a rarer $\eta^1\text{-}\eta^1\text{-}\mu_3$ mode (bridging Mn2/Mn1/Mn5, Mn5/Mn1/Mn8 and Mn8/Mn1/Mn2). Overall, each of these type A phth^{2-} groups is μ_3 , and this is an unprecedented binding mode for the phth^{2-} ligand. The second type (Type B) consists of three phth^{2-} groups that use one of their carboxylate groups to bridge two Mn ions in a *syn,anti*- $\eta^1\text{-}\eta^1\text{-}\mu_2$ fashion (bridging Mn3/Mn6, Mn6/Mn9 and Mn9/Mn3), and their other carboxylate group to bridge two Mn ions in a $\eta^2\text{-}\eta^1\text{-}\mu_2$

Table 2 Selected bond distances (Å) and angles (°) for [NH₂Et₂][Mn₁₀(OH)₃(phth)₉(bpy)₆]·9MeCN·½H₂O

Mn(1)–O(1)	2.160(3)	Mn(6)–O(30)	2.228(3)
Mn(1)–O(2)	2.160(3)	Mn(7)–O(30)	2.224(4)
Mn(1)–O(3)	2.176(3)	Mn(8)–O(3)	2.120(3)
Mn(1)–O(4)	2.251(3)	Mn(8)–O(8)	2.291(3)
Mn(1)–O(8)	2.269(4)	Mn(9)–O(3)	2.153(3)
Mn(1)–O(12)	2.306(3)	Mn(9)–O(38)	2.273(3)
Mn(2)–O(1)	2.129(3)	Mn(10)–O(38)	2.187(3)
Mn(2)–O(12)	2.242(4)	O(18)–C(32)	1.262(7)
Mn(3)–O(1)	2.165(3)	O(19)–C(32)	1.230(8)
Mn(3)–O(22)	2.282(4)	O(26)–C(48)	1.244(7)
Mn(4)–O(22)	2.202(4)	O(27)–C(48)	1.253(8)
Mn(5)–O(2)	2.115(3)	O(34)–C(64)	1.280(7)
Mn(5)–O(4)	2.356(3)	O(35)–C(64)	1.242(7)
Mn(6)–O(2)	2.162(3)		
O(1)–Mn(1)–O(2)	99.7(1)	O(2)–Mn(6)–O(30)	178.7(1)
O(1)–Mn(1)–O(3)	99.1(1)	O(3)–Mn(8)–O(8)	78.20(1)
O(2)–Mn(1)–O(3)	98.7(1)	O(3)–Mn(9)–O(38)	175.77(1)
O(1)–Mn(1)–O(4)	91.7(1)	Mn(2)–O(1)–Mn(1)	100.19(1)
O(2)–Mn(1)–O(4)	77.8(1)	Mn(2)–O(1)–Mn(3)	115.70(2)
O(3)–Mn(1)–O(4)	169.1(1)	Mn(1)–O(1)–Mn(3)	128.03(2)
O(1)–Mn(1)–O(8)	169.8(1)	Mn(5)–O(2)–Mn(1)	102.71(1)
O(2)–Mn(1)–O(8)	90.3(1)	Mn(5)–O(2)–Mn(6)	113.38(1)
O(3)–Mn(1)–O(8)	77.6(1)	Mn(1)–O(2)–Mn(6)	129.37(2)
O(4)–Mn(1)–O(8)	92.0(1)	Mn(8)–O(3)–Mn(9)	114.78(2)
O(1)–Mn(1)–O(12)	77.3(1)	Mn(8)–O(3)–Mn(1)	101.10(1)
O(2)–Mn(1)–O(12)	171.3(1)	Mn(9)–O(3)–Mn(1)	129.07(2)
O(3)–Mn(1)–O(12)	89.9(1)	Mn(1)–O(4)–Mn(5)	92.90(1)
O(4)–Mn(1)–O(12)	94.1(1)	Mn(1)–O(8)–Mn(8)	93.34(1)
O(8)–Mn(1)–O(12)	93.0(1)	Mn(2)–O(12)–Mn(1)	92.65(1)
O(1)–Mn(2)–O(12)	79.3(1)	Mn(4)–O(22)–Mn(3)	113.91(2)
O(1)–Mn(3)–O(22)	177.4(1)	Mn(7)–O(30)–Mn(6)	113.5(2)
O(2)–Mn(5)–O(4)	76.4(1)	Mn(10)–O(38)–Mn(9)	111.6(2)

manner (bridging the Mn3/Mn4, Mn6/Mn7 and Mn9/Mn10 pairs). One of the Mn ions (Mn4, Mn7, Mn10) is thus chelated by a single carboxylate group, forming a four-membered ring, while another Mn ion (Mn3, Mn6, Mn9) is chelated using both carboxylates to give a seven-membered ring. The four-membered chelate rings contain two distinctly different Mn–O bond distances, with averages of 2.2 Å vs. 2.5 Å, respectively. The Type B bridging mode is also very unusual for phth²⁻, with only one previous example, a cadmium(II) phthalate polymer.²³ The third type (Type C) consists of three phth²⁻ groups that have one carboxylate group coordinated in a *syn,syn*- $\eta^1:\eta^1:\mu_2$ mode (bridging Mn2/Mn3, Mn5/Mn6 and Mn8/Mn9), and the other carboxylate group bound in a monodentate fashion (terminally ligated to Mn4, Mn7 and Mn10). Finally, the remaining coordinating positions are occupied by six bipyridine ligands, which chelate the ions Mn2, Mn4, Mn5, Mn7, Mn8 and Mn10.



Magnetochemistry

Dc magnetic susceptibility measurements were performed on a crystalline sample of compound **2**, powdered and restrained in eicosane to prevent torquing. Samples obtained by both Methods A and B were studied, and they gave the same results. The data were recorded at 5000 G in the 2.00–300 K temperature range. The results are plotted as effective magnetic moment (μ_{eff}) vs. temperature in Fig. 4. The μ_{eff} value of 16.8 μ_{B} at 300 K is slightly below that (18.7 μ_{B} for $g = 2$) expected for ten non-interacting Mn(II) ions. This is consistent with the presence of weak exchange interactions, as commonly observed between Mn(II) ions. The pairwise exchange parameter (J) in such systems is typically in the range 1 to -3 cm^{-1} .^{24–28} As the

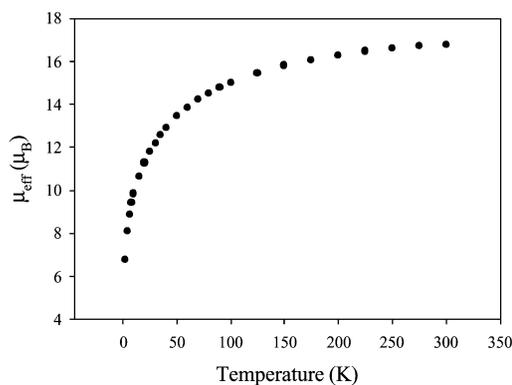


Fig. 4 Plot of the effective magnetic moment ($\mu_{\text{eff}}/\text{Mn}_{10}$) vs. temperature for complex **2**.

temperature decreases, μ_{eff} gradually decreases, reaching a minimum of 6.8 μ_{B} at 2.00 K. The data do not appear to be heading for zero, suggesting a non-zero ground state spin (S) value for **2**. To avoid the Zeeman effects of the applied dc field and allow a better estimate of the S value of the ground state, ac magnetic susceptibility data were collected. The ac susceptibility is often useful in these situations: in the absence of an out-of-phase (χ''_{M}) signal, the in-phase (χ'_{M}) signal is equal to the dc susceptibility, and its value at low temperature can give an often safer indication of the ground state than the dc measurement. For complex **2**, however, this was not the case. The ac susceptibility data were collected in the 2.00–10.0 K range in a zero dc magnetic field and a 3.5 G ac magnetic field oscillating at 1500 Hz. The in-phase signal, plotted as ($\chi'_{\text{M}}T$), is nearly superimposable on the dc data (Fig. 5), and there is no out-of-phase ac susceptibility (χ''_{M}) observed in this temperature range. The $\chi'_{\text{M}}T$ vs. T plot does not reach a plateau at very low temperatures, and this is indicative of population of low-lying excited states, and thus the ground state is not well isolated relative to the thermal energy available at these temperatures. This is not surprising given the weak exchange interactions typical of

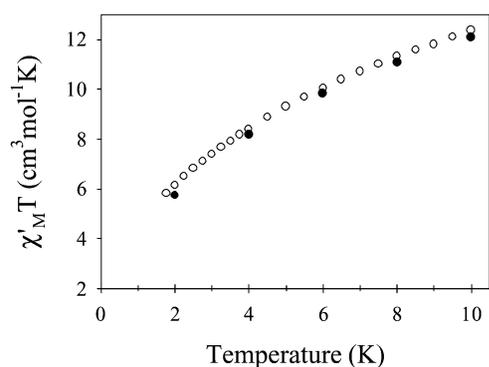


Fig. 5 Plot of the ac magnetic susceptibility data for compound **2** at an oscillation frequency of 1488 Hz (empty circles). The full circles are the dc susceptibility data in this temperature range for comparison.

Mn(II) and the high nuclearity of the complex, giving a high density of spin states and low-lying excited states near the ground state. Extrapolation of the plot to 0 K gives a $\chi'_M T$ value of $\sim 3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which corresponds to a ground state with a spin $S = 2$ and $g = 2$.

A non-zero S value for the ground state can be rationalized by the complicated topology of the Mn_{10} core. With the various pairwise exchange interactions all expected to be weakly antiferromagnetic and thus comparable in magnitude, there will be a spin frustration situation within the triangular Mn_3 units bridged by the $\mu_3\text{-OH}^-$ ions, *i.e.*, the spins of the three Mn(II) ions cannot all be antiparallel to each other. Thus, the spins will not all be compensated (paired) and the ground state will not be $S = 0$. Such spin frustration effects have been commonly observed in Mn(III)²⁹ and mixed-valent Mn(II)/Mn(III)³⁰ clusters, and are the primary cause of the often large values of S observed for these compounds.

Conclusions

The synthesis, structure and magnetic properties of a new decanuclear Mn(II) complex have been described. The complex is the highest nuclearity Mn(II) molecular species discovered to date, and this can be attributed to the presence of three triply-bridging OH^- ions. The resulting Mn_{10} topology possesses a novel structural architecture, and the phthalate ligands display rare and unprecedented bridging modes. The magnetic properties are indicative of a spin frustration situation consistent with the Mn_{10} topology, and the presence of low-lying excited states is as expected for Mn(II) complexes. In this regard, it would be of interest to oxidize some of the Mn(II) ions to Mn(III) with approximate retention of the structure, because this would strengthen the exchange interactions and give a more isolated ground state, and probably even increase the spin of the latter.

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