CrystEngComm

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c5ce02215k

Structural, electrochemical and magnetic analyses of a new octanuclear $Mn^{III}_2Mn^{II}_6$ cluster with linked-defect cubane topology†

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Received 12th November 2015,
Accepted 22nd January 2016

DOI: 10.1039/c5ce02215k

www.rsc.org/crystengcomm

The employment of the 3,5-dimethyl-1-(hydroxymethyl)-pyrazole (Hdmhmp) ligand in a manganese carboxylate cluster afforded the new mixed-valent octanuclear manganese cluster $[Mn^{III}_2Mn^{II}_6O_2(PhCOO)_{10}(dmhmp)_4(H_2O)_2]\cdot 4CH_3CN$ (**1**). Complex **1** was isolated by the reaction of $Mn(ClO_4)_2\cdot 6H_2O$, Hdmhmp and benzoic acid in a mixed solvent of acetonitrile and methanol. The structure of **1** can be described as a μ_4-O^{2-}-linked pair of $[Mn_4O_3]$ defect cubanes protected by ten $PhCO_2^-$ and four μ_3-$dmhmp^-$ ligands. Complex **1** is slightly soluble in acetonitrile, and high-resolution electrospray mass spectrometry (HRESI-MS) indicated that it could keep the $[Mn^{III}_2Mn^{II}_6O_2]$ core integrity in solution but with detectable ligand exchange between $PhCOO^-$ and $dmhmp^-$. The electrochemical studies show that **1** possesses a characteristic $Mn^{II} \rightarrow Mn^{III}$ oxidation peak at +0.82 V and $Mn^{III} \rightarrow Mn^{II}$ reduction peaks at −0.79 and −1.51 V (*versus* Fc/Fc^+), respectively. A detailed magnetic properties investigation has revealed only a weak intramolecular antiferromagnetic interaction between the Mn^{II} and Mn^{III} ions and no characteristic single-molecule magnetic properties.

Introduction

Polynuclear manganese clusters have attracted great interest given their relevance to various applications, mainly including molecular magnetic materials and as model compounds of oxygen-evolving centers (OECs) in bioinorganic chemistry, and given their structural aesthetics.[1] As molecular magnets, manganese clusters often possess large numbers of unpaired electrons from 3d orbitals, offering large ground state spin values from ferromagnetic exchange interactions,[2] and if coupled with significant magnetoanisotropy of the Ising (easy-axis) type, then such clusters become single-molecule magnets (SMMs).[3] In green plants, the pentanuclear $CaMn_4$ cluster (cubane $[Mn_3Ca]$ + a fourth Mn) was confirmed to be the active sites of OECs in Photosystem II, as revealed by its crystal structure at 1.9 Å resolution.[4] From then on, many synthetic chemists started to mimic manganese-based clusters as artificial catalysts for the visible-light splitting of water to molecular dioxygen through a 4e process.[5] The preparation and detailed study of such closely-related manganese clusters, similar to the $CaMn_4$ cluster, would greatly deepen our understanding of the spectroscopic, physical and catalytic mechanism of the water oxidation catalyst. The groups of Christou, Powell, Winpenny and Tong have developed versatile bridging and/or chelating ligands including aliphatic or aromatic alcohols,[6] alcohol amines,[7] di-2-pyridyl ketone,[8] pyridyl alcohols[9] and pyridyl ketone oximes[10] to construct polynuclear manganese clusters, and many fascinating products have been isolated; however, a hydroxymethyl-pyrazole ligand-based manganese cluster has never been seen in the literature.

As we know, the hydroxymethyl-pyrazole ligand[11a] contains both aromatic pyrazole and a flexible hydroxymethyl arm; the latter, upon deprotonation, usually acts as a bridging group and thus favors the formation of polynuclear products. However, the rarity of its polynuclear metal clusters may be due to its instability related to the decomposition reverse reaction, especially in the presence of Cu^{II} atoms.[11b,11c] For

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† Electronic supplementary information (ESI) available: Tables, TGA, powder X-ray diffractogram, IR and crystal data in CIF files, for 1. CCDC 1423562. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ce02215k

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the above reasons and more, there is a continuing necessity to achieve new polynuclear Mn clusters. One important exploration in our group is to design and synthesise new alcohol-containing chelating/bridging ligands involving controllable bulk near the alkoxide group, and then to check their desirability for developing new clusters and functionalities. Initial work has concentrated on 3,5-dimethyl-1-(hydroxymethyl)-pyrazole (Hdmhmp), which is the first alcohol-containing ligand used in the construction of polynuclear Mn cluster chemistry. In the present work, we present (i) the usage of mixed Hdmhmp and benzoic acid in a reaction with a Mn salt (Scheme 1), (ii) the structure and solution behavior of this octanuclear mixed-valent Mn cluster and (iii) its electrochemical and magnetic properties. This work not only provides a hydroxymethyl-pyrazole-based Mn cluster, but also deepens our understanding of Mn cluster assembly and related properties in solution and in the solid state.

Results and discussion

Crystal structural description

X-ray crystallographic analysis indicated that **1** is a neutral cluster comprised of eight Mn atoms, which crystallizes in the triclinic space group $P\bar{1}$. The cluster **1** is located on a crystallographic inversion center and has C_i point symmetry. The asymmetric unit of **1** contains one half of the octanuclear cluster with eight Mn atoms, four dmhmp$^-$, ten PhCOO$^-$, two oxo anions and two coordinated aqua ligands. As shown in Fig. 1a, all Mn atoms have six-coordinated octahedral geometry. Mn1 and Mn4 are in the $MnNO_5$ octahedral geometry, whereas Mn2 and Mn3 are in MnO_6 octahedral geometry. The Mn–O bond lengths range from 1.878(3) to 2.462(4) Å and the Mn–N bond length is 2.187(5) Å, which is similar to those observed in many mixed-valent Mn clusters.[12] Notably, the longest Mn–O bonding distance (Mn2–O1 = 2.462(4) Å) indicates the presence of a Mn^{III} Jahn–Teller (JT) distortion (axial elongations) for Mn2.[13] Bond valence sum (BVS) calculations were performed for the atoms Mn1–Mn4. As expected, Mn2 is in a +3 oxidation state and the remaining Mn atoms are +2 (Table 1). Considering the charge neutrality, the core of **1** should be assigned to $[Mn^{III}_2Mn^{II}_6]$, which is linked by μ_4-O^{2-} and μ_3-O_{dmhmp} bridges to form an opened bicubane motif (Fig. 1b). The origination of the Mn^{III} should be the *in situ* oxidation of Mn^{II} by oxygen in air. The junction of two opened cubanes contains two Mn2–O11^i and Mn2^i–O11 edges as well as two μ_2-O_{PhCOO} bridges. Within the core, the Mn⋯Mn separations are in the range of 2.8011(17)–3.5086(13) Å with an average value of 3.223 Å. The overall core is protected by ten $PhCO_2^-$, four μ_3-dmhmp$^-$ ligands and two terminal aqua ligands. It should also be noted that the PhCOO$^-$ ligands show three coordination modes: four as μ_3-O^1:O'^2 bridges, four as μ_2-O^1:O'^1 bridges and the last two as terminal monodentate ligands bound to Mn1. The aqua ligand binds to Mn3 and forms intramolecular H-bonding with unbound O8 of the monodentate PhCOO$^-$ ligand (O1W⋯O8 = 2.76 Å). In addition, the aqua ligand also forms intermolecular H-bonding with another centrosymmetric O8 atom

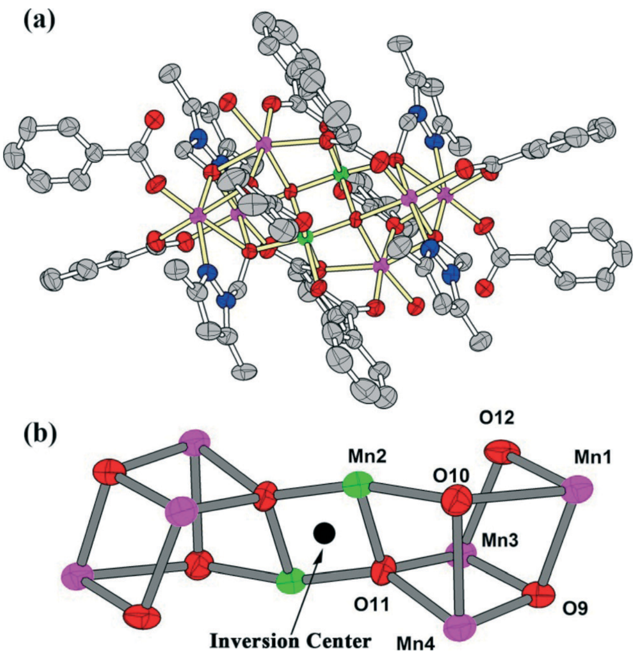
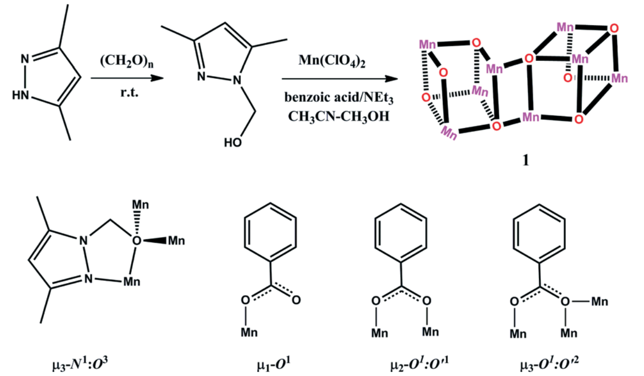


Fig. 1 Molecular structures of the $[Mn^{III}_2Mn^{II}_6O_2(PhCOO)_{10}(dmhmp)_4(H_2O)_2]$ (a) and the opened bicubane motif in **1** (b). H atoms are omitted for clarity. Colour code: Mn^{II} = purple; Mn^{III} = green; O = red; N = blue; C = gray.



Scheme 1 The synthesis of the ligand and the assembly route of cluster **1**.

Table 1 BVS calculations for the Mn atoms of **1**

Atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	*2.133*	2.000	1.971
Mn2	3.290	*3.034*	2.977
Mn3	*1.714*	1.580	1.551
Mn4	*2.145*	2.011	1.981

The italicised value is the one closest to the charge for which it was calculated.

The oxidation state can be taken as the integer nearest to the italicised value.

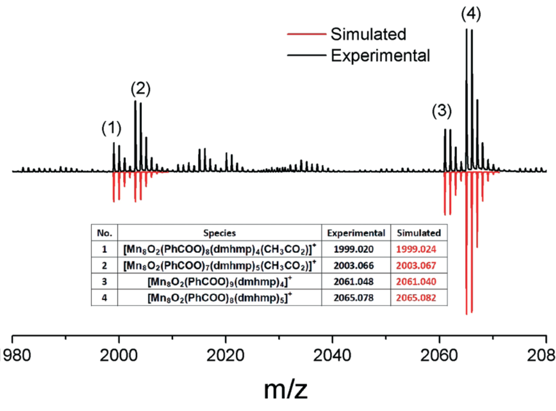
with a O1W⋯O8 distance of 2.74 Å. The intra- and intermolecular hydrogen bonds construct a $R_4^2(8)$ motif based on the graph set analysis nomenclature.[14a] As we know and as the summarized examples in a comprehensive review by Powell demonstrate,[14b] octanuclear Mn clusters have very rich geometries.[15–22] However, the linked defect-dicubane core in **1** is not common, having been seen only two times before in Mn cluster chemistry.[23]

Stability in solution of the Mn_8 cluster

Mass spectrometry has been justified as a miscellaneous tool to i) check the solid structure integrity once dissolved in solvents,[24] ii) examine the composition of the possible molecular species under the complex coordination-dissociation equilibria and the abundance of corresponding species,[25] and even iii) establish the catalytic mechanism in solution and track the formation mechanism of polynuclear metal clusters.[26] In order to check the integrity of the Mn_8 cluster in solution and its coordination-dissociation behavior, crystals of **1** were dissolved in CH_3CN and probed by high-resolution electrospray mass spectrometry (HRESI-MS) at a dry gas temperature of 40 °C. The HRESI-MS shows four main signals at m/z = 1999.020, 2003.066, 2061.048 and 2065.078 in the positive-ion mode, and the last peak is the most abundant in the m/z range of 1000–2500. These four signals can be attributed to Mn_8 intact cluster species, which are assigned to $[Mn_8O_2(PhCOO)_8(dmhmp)_4(CH_3CO_2)]^+$ (m/z = 1999.020), $[Mn_8O_2(PhCOO)_7(dmhmp)_5(CH_3CO_2)]^+$ (m/z = 2003.066), $[Mn_8O_2(PhCOO)_9(dmhmp)_4]^+$ (m/z = 2061.048) and $[Mn_8O_2(PhCOO)_8(dmhmp)_5]^+$ (m/z = 2065.078) by comparing the experimental isotopic envelopes with those simulated (Fig. 2). Comparing the parent formula of **1**, $[Mn_8O_2(PhCOO)_{10}(dmhmp)_4(H_2O)_2]$, we found that the solution species presents different degrees of dissociation and substitution between $dmhmp^-$, $PhCOO^-$, aqua and CH_3COO^-; however, the Mn_8O_2 core is kept intact in solution. In the competitive and complex coordination-dissociation equilibria, we found that the coordinated $dmhmp^-$ was difficult to be replaced by other ligands, and that it even more actively binds on the empty metal center left by other dissociated ligands, indicating that the $dmhmp^-$ is a strong multidentate ligand. Compared to the numbers of $PhCOO^-$ and aqua ligands in the solid state structure of **1**, some of them dissociated from the Mn_8O_2 core in the solution, suggesting that the monodentate $PhCOO^-$ and terminal aqua are the most labile ligands once dissolved in solution.

Electrochemistry

As we know, Mn atoms in coordination cluster compounds can exhibit II, III and IV valences, and thus mixed-valent clusters such as the famous Mn_{12} molecular magnet usually show rich redox behavior, involving multistep quasi-reversible oxidation and reduction processes.[27] In addition, the electronic effect of ligands, as expected, also influences the redox potentials.[28] Thus, for the new mixed-valent Mn cluster, the electrochemical behavior deserved to be tested. To this purpose, the electrochemical properties of **1** were studied in a MeCN solution, in the presence of $^nBu_4NPF_6$ (TBFP; 0.1 M) as a supporting electrolyte, using cyclic and differential pulse voltammetry (CV and DPV) at room temperature. As shown in Fig. 3, there are two quasi-reversible reduction peaks at −0.79 and −1.51 V (*versus* Fc/Fc$^+$), respectively, which should be assigned to the two-step consecutive reduction of two Mn^{III} to two Mn^{II}. The oxidation of Mn^{II} to Mn^{III} occurred at +0.82 V, which is similar to the $Mn^{II} \rightarrow Mn^{III}$ oxidation potential observed in another octanuclear cluster $[Mn_8O_6Cl_6(PhCOO)_7(H_2O)_2]^-$.[29]



No.	Species	Experimental	Simulated
1	$[Mn_8O_2(PhCOO)_8(dmhmp)_4(CH_3CO_2)]^+$	1999.020	1999.024
2	$[Mn_8O_2(PhCOO)_7(dmhmp)_5(CH_3CO_2)]^+$	2003.066	2003.067
3	$[Mn_8O_2(PhCOO)_9(dmhmp)_4]^+$	2061.048	2061.040
4	$[Mn_8O_2(PhCOO)_8(dmhmp)_5]^+$	2065.078	2065.082

Fig. 2 The positive-ion mode HR-ESI mass spectrum of **1** dissolved in CH_3CN.

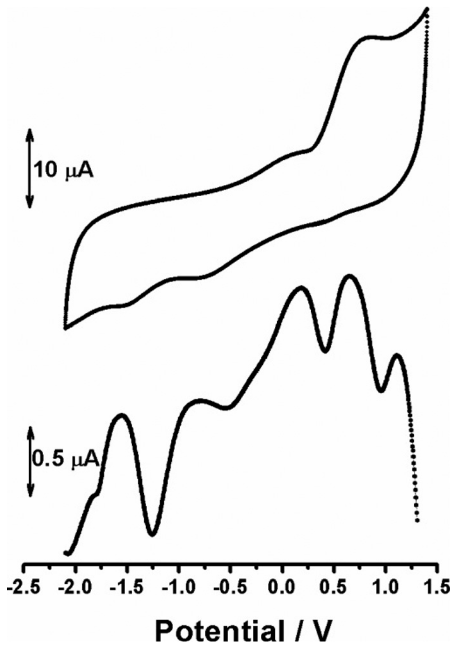


Fig. 3 Cyclic voltammogram at 100 mV s^{-1} (top) and differential pulse voltammogram (bottom) for **1** in CH_3CN containing 0.1 M $^nBu_4NPF_6$ as supporting electrolyte. The indicated potentials are *vs.* Fc/Fc$^+$.

Magnetic properties

Temperature-dependent magnetic susceptibility and the effective magnetic moment on the crystalline sample were measured in a magnetic field of 1000 Oe (Fig. 4). All presented data have been corrected for a temperature-independent diamagnetic contribution of inner shell electrons as obtained from Pascal's tables.[30]

The susceptibility decreases with increasing temperature while the effective magnetic moment linearly increases between 50 K and room temperature. The expected average effective magnetic moment per manganese ion for a molecule with six Mn(II) and two Mn(III) ions is $\mu_{\text{eff}} = \sqrt{\frac{1}{8}\left(6\cdot\mu_{\text{eff(II)}}{}^{2} + 2\cdot\mu_{\text{eff(III)}}{}^{2}\right)} = 5.7\mu_{\text{B}}$. We used $\mu_{\text{eff(II)}} = 5.9\ \mu_{\text{B}}$ for Mn(II) ($S = J = 5/2$) ions and $\mu_{\text{eff(III)}} = 5.0\ \mu_{\text{B}}$ for Mn(III) ($S = J = 2$) ions.[31] The measured average magnetic moment per Mn ion at 300 K is 5.2 μ_{B}, appreciably less than the expected value of 5.7 μ_{B}. With decreasing temperature, the average effective magnetic moment became even smaller (3.7 μ_{B} at 2 K), indicating a weak antiferromagnetic interaction between Mn ions in the molecule. The strength of this interaction can be estimated by applying a Curie–Weiss fit for the high-temperature susceptibility data: $\chi = C/(T - \theta)$. The result for $T > 100$ K is shown as a full line in Fig. 4, with parameters $C = 27.8$ emu K mol^{-1} and $\theta = -13.6$ K. The rather small and negative value of the Curie–Weiss temperature θ is in agreement with the proposed weak antiferromagnetic interaction.

The most dominant exchange interactions in the molecule are those of oxygen-bridged Mn(II)–Mn(II) and Mn(II)–Mn(III) ions. Typically these exchange interactions are weak and antiferromagnetic,[23a,31] as obtained for our system, too. A similar temperature-dependent susceptibility and a weak antiferromagnetic interaction was detected also in two structurally very similar compounds with six Mn(II) and two Mn(II) ions per molecule and the same bridges.[23] Finally, we measured isothermal magnetization at low temperatures and ac susceptibility, in search for typical single-molecule magnet properties such as step-like hysteresis[32] or a frequency-dependent out-of-phase ac susceptibility signal.[23b]

In Fig. 5, isothermal magnetization curves at temperatures 7 K, 5 K and 2 K are shown. The curves were analysed by applying a fit with a Brillouin function for $S = J = 5/2$ isolated magnetic moments. At the temperature of 7 K, where the weak antiferromagnetic interaction is not yet very effective, the fit is good. With decreasing temperature, the fit with the Brillouin function becomes unsatisfactory. Due to the antiferromagnetic interaction, the measured magnetization curves below 7 K are somehow suppressed and linearly increase in magnetic fields above 20 kOe instead of saturating. No steps in the measured magnetization curves up to the magnetic field of 70 kOe in the hysteresis loops were detected at temperature of 2 K and higher.

The real, χ', and imaginary (out-of-phase), χ'', parts of the ac susceptibility were measured between 2 K and 30 K in an alternating magnetic field with an amplitude of 3 Oe and eleven different frequencies ranging from 11 Hz up to 2311 Hz. For clarity we show in Fig. 6 susceptibility for 11 Hz, 1111 Hz and 2111 Hz only. The χ' for all frequencies practically superimpose and the susceptibility is the same as that measured in a static magnetic field. The absence of any distinguishable signal in the imaginary part χ'' that would usually accompany slow magnetization relaxation processes can be understand as a confirmation of no single-molecule magnetism. This is different from results shown in the literature,[23b] where, in addition to antiferromagnetic, a weak ferromagnetic interaction between oxygen-bridged six Mn^{ii} and ten Mn^{iii} ions has been detected. Wide hysteresis loops have been measured below 1 K.[23] The absence of such a hysteresis loop in our sample may be because of the following factors: a) the $M(H)$ curves being collected at too high temperatures (due to the experimental limitations, we were not able to reach temperatures below 1.8 K), and (or) b) the influence of ligands on the magnetic interaction, that does not provide a weak ferromagnetic component. It has been demonstrated that ligands in structurally-similar structures of oxygen-

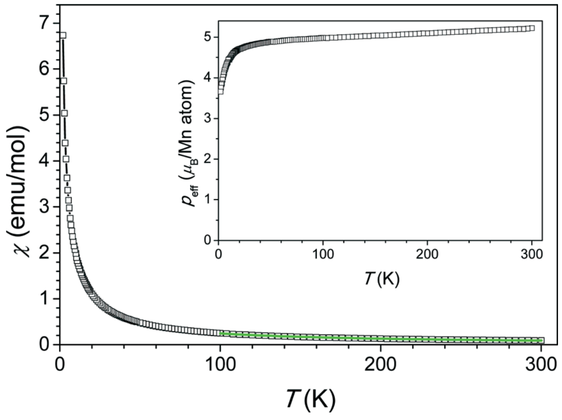


Fig. 4 Magnetic susceptibility and effective magnetic moment (inset) between 2 K and 300 K measured in a magnetic field of 1000 Oe. The full green line is a Curie–Weiss fit.

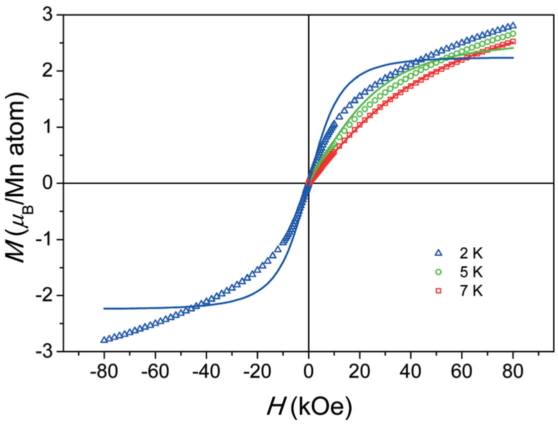


Fig. 5 Isothermal magnetization curves. Full lines are fits with a Brillouin function for $S = J = 5/2$.

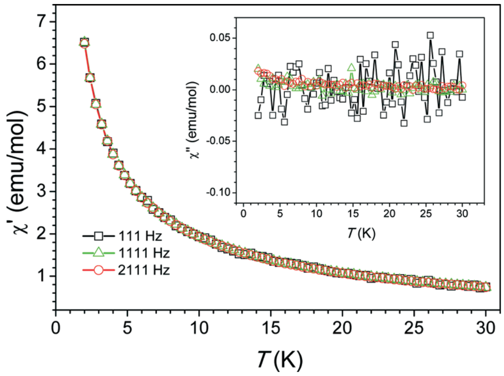


Fig. 6 Real part and imaginary part (inset) of the ac susceptibility.

bridged manganese ions have an enormous impact on the magnetic interaction between Mn ions.[33]

Solid-state UV-vis-NIR diffuse reflectance spectroscopy

The UV-vis-NIR spectrum for **1** was measured in the solid state using the diffuse reflectance mode and is shown in Fig. 7. The absorption at 272 nm has its origin in the $\pi \rightarrow \pi^*$ transition of the $PhCO_2^-$ or dmhmp$^-$ ligands, and the shoulder at around 490 nm may originate from metal-to-ligand charge transfer.[34] The fine structure for the d–d band is not observed, although both d^4 Mn^{III} and d^5 Mn^{II} exist in **1**.

Experimental

Methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were recorded on a PerkinElmer Spectrum Two in the frequency range of 4000–400 cm^{-1}. The elemental analyses (C, H, N contents) were determined on a Vario EL III analyzer. The variable-temperature magnetic susceptibilities were collected on a Magnetic Property Measurement System (MPMS), SQUID-VSM (superconducting quantum interference device-vibrating sample magnetometer) (Quantum Design, USA). Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with MoK$_\alpha$ radiation equipped with an X'Celerator detector. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer from room temperature to 800 °C under a nitrogen atmosphere, at a heating rate of 10 °C min^{-1}. The diffuse reflectance spectrum was collected using a UV-vis spectrophotometer (Evolution 220, ISA-220 accessory, Thermo Scientific) using a built-in 10 mm silicon photodiode with a 60 mm Spectralon sphere.

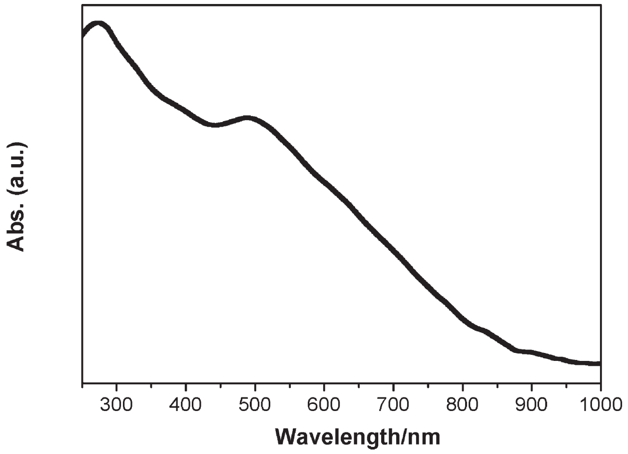


Fig. 7 Diffuse reflectance UV-visible-NIR spectrum of **1**.

Synthesis of $[Mn^{III}_2Mn^{II}_6O_2(PhCOO)_{10}(dmhmp)_4(H_2O)_2]\cdot 4CH_3CN$ (1)

$Mn(ClO_4)_2\cdot 6H_2O$ (181 mg, 0.5 mmol), benzoic acid (61 mg, 0.5 mmol) and Hdmhmp (63 mg, 0.5 mmol) were dissolved in a mixture of 5 mL CH_3CN–CH_3OH (1 : 1) with 100 μL NEt_3 to get a pale-yellow solution. This solution was filtered and the filtrate was allowed to evaporate slowly in air at room temperature. Complex **1** crystallized as brown crystals after two days in a yield of 85% based on Hdmhmp. Anal. calc. (found) for ($C_{102}H_{102}Mn_8N_{12}O_{28}$): C, 51.40 (51.38); H, 4.31 (4.36); N, 7.05 (6.99)%. Selected IR bands (cm^{-1}): 1603(m), 1562(m), 1540(m), 1491(w), 1463(w), 1394(s), 1265(w), 1103(m), 1078(m), 1046(m), 1025(m), 835(w), 790(w), 712(s), 675(m), 623(m), 603(m).

X-ray crystallography

Crystals of **1** quickly lost the solvents from the lattice once they left the mother liquor. Therefore, a crystal was quickly picked out from the mother liquor then transferred to a cryogenic environment for the collection of intensity data on a Bruker APEX II CCD diffractometer (200(2) K) with a graphite-monochromated Cu Kα radiation source (λ = 1.54178 Å). Cell refinement, data reduction and absorption correction were carried out using the Bruker SAINT software package.[35] The intensities were extracted by the program XPREP. The structures were solved with direct methods using SHELXS, and least-squares refinement was done against F^2_{obs} using routines from the SHELXTL software.[36] In **1**, the unit cell contains a large region of disordered solvent water molecules, which could not be modeled as discrete atomic sites, and thus we employed PLATON/SQUEEZE to produce a set of solvent-free diffraction intensities,[37] which was used for further refinement. Crystal data for **1** are given in Table 2. Selected bond lengths and angles are listed in Table S1.†

Conclusions

In summary, a new mixed-valent Mn$_8$ cluster constructed from 3,5-dimethyl-1-(hydroxymethyl)-pyrazole and benzoic acid has been successfully isolated, which shows a paired [Mn_4O_3] defect cubanes core protected by ten $PhCO_2^-$ and four μ$_3$-dmhmp$^-$ ligands. The HRESI-MS indicates that its [$Mn^{III}_2Mn^{II}_6O_2$] core structure is not decomposed in solution, and interesting ligand exchange between PhCOO$^-$ and

Table 2 Crystal data for complex **1**

Empirical formula	$C_{94}H_{90}Mn_8N_8O_{28}$
Formula weight	2219.26
Temperature/K	200(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	14.0134(7)
b/Å	14.8016(7)
c/Å	15.2457(6)
α/°	105.689(5)
β/°	113.922(4)
γ/°	103.178(5)
Volume/Å^3	2570.0(2)
Z	1
ρ_{calc} mg mm^{-3}	1.434
μ/mm^1	8.374
$F(000)$	1134.0
2θ range for data collection	6.72 to 120°
Index ranges	$-15 \le h \le 15$, $-16 \le k \le 16$, $-17 \le l \le 17$
Reflections collected	18731
Independent reflections	7272[R(int) = 0.0873]
Data/parameters	7272/626
Final R indexes [$I \leqq 2\sigma(I)$]	$R_1 = 0.0534$, w$R_2 = 0.1121$
Final R indexes [all data]	$R_1 = 0.0935$, w$R_2 = 0.1249$
Largest diff. peak/hole/e Å^{-3}	0.57/−0.37

dmhmp$^-$ was evidenced. Both the characteristic oxidation process of $Mn^{II} \rightarrow Mn^{III}$ and reduction process of $Mn^{III} \rightarrow Mn^{II}$ were identified in cyclic voltammetry measurement. Weak intramolecular antiferromagnetic interactions between the Mn^{II} and Mn^{III} ions were found in the Mn_8 cluster.

Acknowledgements

This work was supported by the NSFC (Grant No. 21201110, 21227001 and 21571115), Young Scholars Program of Shandong University (2015WLJH24), The Fundamental Research Funds of Shandong University (2015JC045), and Slovenian Research Agency (ARRS), Program Number P2-0348.

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