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ARTICLE

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

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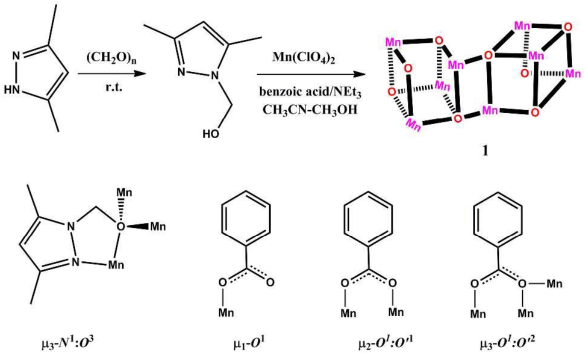
The employment of the 3,5-dimethyl-1-(hydroxymethyl)-pyrazole (Hdmhmp) ligand in manganese carboxylate cluster afforded the new mixed-valent octanuclear manganese cluster $[Mn^{III}_2Mn^{II}_6O_2(PhCOO)_{10}(dmhmp)_4(H_2O)_2]\cdot 4CH_3CN$ (**1**). Complex **1** was isolated by the reaction of $Mn(ClO_4)_2\cdot 6H_2O$, Hdmhmp, and benzoic acid in mixed solvent of acetonitrile and methanol. The structure of **1** can be described as μ_4-O^{2-} linked a pair of $[Mn_4O_3]$ defected cubanes protected by ten $PhCO_2^-$ and four μ_3-dmhmp$^-$ ligands. Complex **1** is slightly soluble in acetonitrile and the High-Resolution Electrospray Mass Spectrometry (HRESI-MS) indicates 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 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. Detail magnetic properties investigation reveals only a weak intramolecular antiferromagnetic interaction between Mn^{II} and Mn^{III} ions and no characteristic single molecule magnetic properties.

Introduction

Polynuclear manganese cluster have attracted great interest in the relevance to various perspectives, mainly including structural aesthetics, molecular magnetic materials and model compound of oxygen-evolving center (OEC) in bioinorganic chemistry.[1] As molecular magnets, manganese clusters often possess large numbers of unpaired electrons from 3d orbital, offering large ground state spin values from ferromagnetic exchange interactions,[2] and if coupling with significant magnetoanisotropy of the Ising (easy-axis) type, then such clusters become single-molecule magnets (SMMs).[3] In the green plant, pentanuclear $CaMn_4$ cluster (cubane $[Mn_3Ca]$ + fourth Mn) was confirmed to be the active sites of OEC in the 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 visible-light splitting water to molecular dioxygen through a 4e process.[5] The preparation and detailed study of such closely related manganese clusters similar to $CaMn_4$ cluster would greatly deepen our understanding of the spectroscopic, physical and catalytic mechanism of the water oxidization catalyst. Christou, Powell, Winpenny, and Tong groups have developed versatile bridging and/or chelating ligands including aliphatic or aromatic alcohols,[6] alcohol amines,[7] di-2-pyridylketone,[8] pyridyl-alcohols,[9] and pyridyl ketone oximes,[10] to construct polynuclear manganese clusters products, and many fascinating products have been isolated, however, hydroxymethyl-pyrazole ligand based manganese cluster has never been seen in literatures.

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



As we know, the hydroxymethyl-pyrazole ligand[11a] contains both aromatic pyrazole and flexible hydroxymethyl arm, the latter upon deprotonation usually act as bridging groups and thus favor the formation of polynuclearity product. 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} atom.[11b, 11c] For 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 synthesis of

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†Electronic Supplementary Information (ESI) available. Tables, TGA and powder X-ray diffractogram, diffuse-reflectance spectrum, 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/b000000x.

new alcohol-containing chelating/bridging ligand involving the controllable bulk near the alkoxide group and then to check its desirability function 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 present work, we present (i) the usage of mixed Hdmhmp and benzoic acid in the reaction with Mn salt (Scheme 1); (ii) the structure and solution behavior of this octanuclear mixed-valent Mn cluster; and (iii) electrochemical and magnetic properties. This work not only provides a hydroxymethyl-pyrazole based Mn cluster but also deepen our understanding on Mn cluster assembly and related properties in solution and solid state.

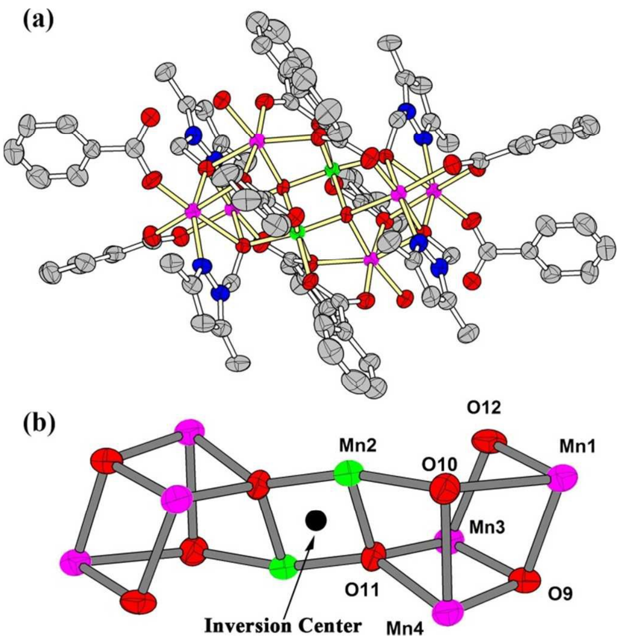


Fig 1. Molecular structures of the $[Mn^{III}_2Mn^{II}_6O_2(PhCOO)_{10}(dmhmp)_4(H_2O)_2]$ (a) and the opened bicubane motif in **1** (b). H atoms omitted for clarity. Colour code: Mn^{II} purple; Mn^{III} green; O red; N blue; C gray.

Results and discussion

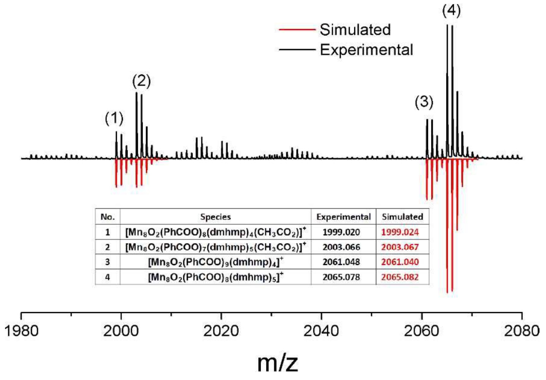
Crystal Structural description. X-ray crystallographic analysis indicated that **1** is a neutral cluster comprised of eight Mn atoms and crystallizes in the triclinic space group *P*-1. The **1** locates on an crystallographic inversion center and belongs to C_i point symmetry. The asymmetric unit of **1** contains one half of the octanuclear cluster with eight Mn atoms, four $dmhmp^-$, ten $PhCOO^-$, two oxo anions and two coordinated aqua ligand. As shown in Figure 1a, all Mn atoms are six-coordinated octahedral geometry. Mn1 and Mn4 are in the $MnNO_5$ octahedral geometry, whereas Mn2 and Mn3 in MnO_6 octahedral geometry. The Mn-O bond lengths range from 1.878(3) to 2.462(4) Å and 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 Mn^{III} Jahn-Teller (JT) distortion (axial elongations) for Mn2.[13] The bond valence sum (BVS) calculations are performed for Mn1-Mn4 atoms. As expected, Mn2 is in +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 (Figure 1b). The origination of 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 also should be noted that $PhCOO^-$ ligands show three coordination modes: four as μ_3-O^{1}:O'^{2} bridge, four as μ_2-O^{1}:O'^{1} bridge and the last two as terminal monodentate ligand bound to Mn1. The aqua ligand binds to Mn3 and forms intramolecular H-bonding with unbound O8 of monodentate $PhCOO^-$ ligand (O1W···O8 = 2.76 Å). In addition, the aqua ligand also forms intermolecular H-bonding with another centrosymmetric O8 atom 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,[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]

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 underlined 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 underlined value.

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) exam 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 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 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 *m*/*z* range of 1000-2500. These four signals can be attributed to Mn_8 intact cluster species, which 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 (Figure 2). Compared the parent formula of **1**, $[Mn_8O_2(PhCOO)_{10}(dmhmp)_4(H_2O)_2]$, we found the solution species presents different degrees of dissociation and substitute 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 find the coordinated $dmhmp^-$ was difficult to be replaced by other ligands, even more actively binds on the empty metal center left by other dissociated ligand, indicating the dmhmp$^-$ is a strong multidentate ligand. Compared to the numbers of PhCOO$^-$ and aqua ligands in solid state structure of **1**, some of them dissociated from Mn_8O_2 core in the solution, suggesting the monodentate PhCOO$^-$ and terminal aqua are most labile ligands once dissolved in solution.



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.

Electrochemistry. As we know, Mn atom in coordination cluster compounds can exhibit II, III and IV valences, thus mixed-valent clusters such as famous Mn_{12} molecular magnetism usually showed rich redox behaviors involving multistep quasi-reversible oxidation and reduction processes.[27] In addition, the electronic effect of ligands, as expected, also influence the redox potentials.[28] Thus, for new mixed-valent Mn cluster, the electrochemical behavior is 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 Figure 3, there are two quasi-reversible reduction peaks at -0.79 and -1.51 V (versus Fc/Fc$^+$), respectively, which should be assigned to two-step consecutive reduction of two Mn^{III} to two Mn^{II}. The oxidation of Mn^{II} to Mn^{III} was occurred at +0.82 V, which is similar to the Mn^{II}→Mn^{III} oxidation potential observed in another octanuclear $[Mn_8O_6Cl_6(PhCOO)_7(H_2O)_2]^-$.[29]

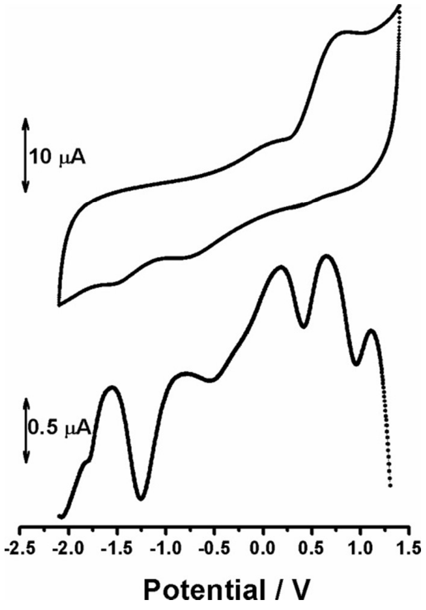


Fig 3. Cyclic voltammogram at 100 mV s^{-1} (top) and differential pulse voltammogram (bottom) for **1** in CH_3CN containing 0.1 M $^nBu_4NPF_6$ as supporting electrolyte. The indicated potentials are vs Fc/Fc$^+$.

Magnetic properties. Temperature dependent magnetic susceptibility and effective magnetic moment on crystalline sample were measured in magnetic field of 1000 Oe (Figure 4). All presented data are corrected for a temperature independent diamagnetic contribution of inner shell electrons as obtained from Pascall's tables.[30]

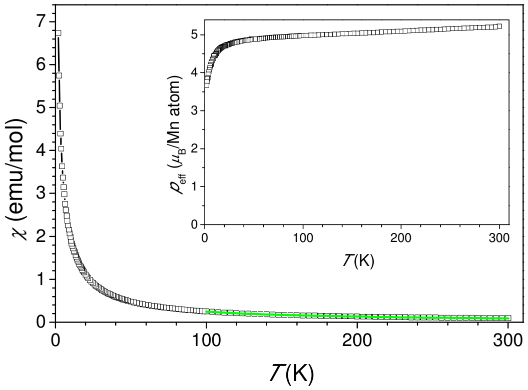


Fig. 4 Magnetic susceptibility and effective magnetic moment (inset) between 2 K and 300 K measured in a magnetic field of 1000 Oe. Full green line is a Curie-Weiss fit.

Susceptibility decreases with increasing temperature while 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 $\mu_{\rm eff} = \sqrt{\frac{1}{8}(6\cdot\mu^2_{\rm eff(II)} + 2\cdot\mu^2_{\rm eff(III)})} = 5.7\ \mu_{\rm B}$. We used $\mu_{eff(\rm II)} = 5.9\ \mu_B$ for Mn(II) (S = J = 5/2) ion and $\mu_{\rm eff(III)} = 5.0\ \mu_{\rm B}$ for Mn(III) (S = J = 2) ion.[31] The measured average magnetic moment per Mn ion at 300 K is 5.2 μ_B, appreciable less than the expected value of 5.7 μ_B. With decreasing temperature the average effective magnetic moment becomes even smaller (3.7 μ_B at 2 K) indicating a weak antiferromagnetic interaction between Mn ions in the molecule. A strength of this interaction can be estimated by applying 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 Figure 4 with parameters C = 27.8 emu K/mol and θ = -13.6 K. The rather small and negative value of Curie-Weiss temperature θ is in agreement with the proposed weak antiferromagnetic interaction.

The most dominant exchange interactions in the molecule are oxygen bridged Mn(II)-Mn(II) and Mn(II)-Mn(III) ions. Typically these exchange interactions are weak and antifferomagnetic[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(III) ions per molecule and the same bridges.[23] Finally we measured isothermal magnetization at low temperatures and ac susceptibility in search for a typical single molecule magnet properties as steps like hysteresis[32] or frequency dependent out-of-phase ac susceptibility signal.[23b]

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

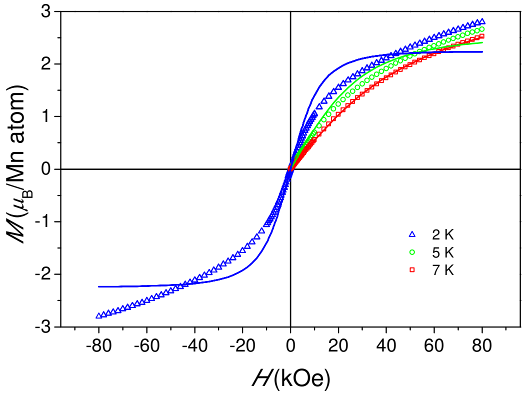


Fig. 5 Isothermal magnetization curves. Full lines are fits with Brillouin function for $S = J = 5/2$.

The real χ' and imaginary (out-of-phase) part χ'' of ac susceptibility were measured between 2 K and 30 K in an alternating magnetic field with amplitude of 3 Oe and eleven different frequencies ranging from 11 Hz up to 2311 Hz. For clarity we show in Figure 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 measured in a static magnetic field. The absence of any distinguish signal in imaginary part χ'' that is usually accompanied with a slow magnetization relaxation processes can be understand as a confirmation of no single molecule magnetism. This is different from the results shown in 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. A wide hysteresis loops have been measured below 1 K.[23] The absence of such hysteresis loop in our sample may be because of, a) too high temperature where $M(H)$ curves were taken (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 [V.S. Zagaynova, T.L. Makarova, N.G. Spitsina, D.W. Boukhvalov, J Supercond Nov Magn (2011) 24: 855–859 DOI 10.1007/s10948-010-1030-3] that ligands in structurally similar structures of oxygen bridged manganese ions have an enormous impact on the magnetic interaction between Mn ions.

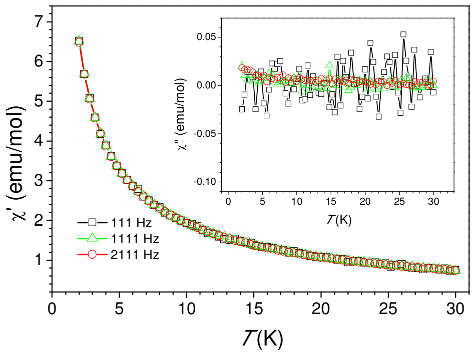


Fig. 6 Real part and imaginary part (inset) of ac susceptibility.

Solid-state UV-Vis-NIR diffuse reflectance spectroscopy. The UV-Vis-NIR spectrum for **1** was measured in solid state using the diffuse reflectance mode and shown in Figure 7. The absorption at 272 nm has origin in the $\pi \rightarrow \pi^*$ transition of the $PhCO_2^-$ or dmhmp$^-$ ligand, and the shoulder around 490 nm may be originated from metal-to-ligand charge transfer.[33] The fine structure for *d-d* band is not observed, although both d^4 Mn^{III} and d^5 Mn^{II} exist in **1**.

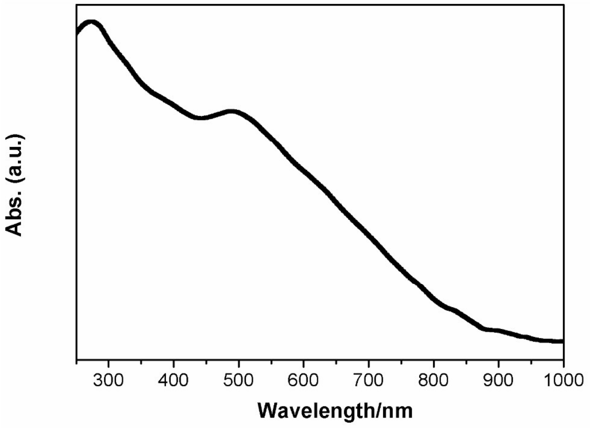


Fig. 7 Diffuse reflectance UV-visible-NIR spectrum of **1**.

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_α 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 nitrogen atmosphere at a heating rate of 10° C/min. The diffuse-reflectance spectrum were performed on UV–Vis spectrophotometer (Evolution 220, ISA-220 accessory, Thermo Scientific) using a built-in 10 mm silicon photodiode with a 60 mm Spectralon sphere.

Synthesis of $[Mn^{III}_2Mn^{II}_6O_2(PhCOO)_{10}(dmhmp)_4(H_2O)_2]\cdot4CH_3CN$ (1) $Mn(ClO_4)_2\cdot6H_2O$ (181 mg, 0.5 mmol), benzoic acid (61 mg, 0.5 mmol) and Hdmhmp (63 mg, 0.5 mmol) were dissolved in the 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).

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*-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 ≤ h ≤ 15, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	18731
Independent reflections	7272[R(int) = 0.0873]
Data/parameters	7272/626
Final R indexes [I>=2σ (I)]	R_1 = 0.0534, wR_2 = 0.1121
Final R indexes [all data]	R_1 = 0.0935, wR_2 = 0.1249
Largest diff. peak/hole / e Å^{-3}	0.57/-0.37

X-ray Crystallography. The crystal of **1** quickly lost the solvents from the lattice once leaving from mother liquor. So the crystal should be quickly pick out from mother liquor then transferred to the 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 Bruker SAINT software package.[34] 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_{obs}^2 using routines from the SHELXTL software.[35] In **1**, the unit cell contains a large region of disordered solvent water molecules, which could not be modeled as discrete atomic sites, thus we employed PLATON/SQUEEZE to produce a set of solvent-free diffraction intensities,[36] which was used for further refinement. Crystal data for **1** are given in Table 2. The selected bond length 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 $[Mn_4O_3]$ defected cubanes core protected by ten $PhCO_2^-$ and four μ_3-dmhmp$^-$ ligands. The HRESI-MS indicates its $[Mn^{III}_2Mn^{II}_6O_2]$ core structure is not decomposed in solution and interesting ligand exchange between PhCOO$^-$ and dmhmp$^-$ was evidenced. Both characteristic oxidation process of $Mn^{II}\rightarrow Mn^{III}$ and reduction process of $Mn^{III}\rightarrow Mn^{II}$ were identified in cyclic voltammetry measurement. The weak intramolecular antiferromagnetic interaction between Mn^{II} and Mn^{III} ions were found in Mn_8 cluster.

Acknowledgements

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New $Mn^{III}_2Mn^{II}_6$ coordination cluster from hydroxymethyl-pyrazole ligand was isolated and electrochemical and magnetic properties were studied in detail.