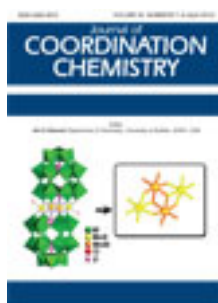


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Mixed-valence manganese cluster containing a sandwich-type polyoxometalate

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Mixed-valence manganese cluster containing a sandwich-type polyoxometalate

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Reaction of $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in the presence of $\text{K}_2\text{S}_2\text{O}_8$ in acidic aqueous solution leads to isolation of a $\{\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}\}$ cluster-containing sandwich-type compound: $\alpha\beta\beta\alpha\text{-K}_3\text{Na}_{11}\{\text{Mn}_2^{\text{III}}\text{Mn}_2^{\text{II}}(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2\} \cdot 40\text{H}_2\text{O}$ (**1**). Single-crystal X-ray diffraction analysis revealed that **1** shows the well-known Weakley-type sandwich-type structure consisting of two trivacant $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ Dawson moieties linked by a central symmetric rhomb-like mixed-valence manganese cluster *via* W–O–Mn and P–O–Mn connections. Mixed-valence Mn-cluster-substituted sandwich-type complexes based on trivacant Dawson units are rarely observed in polyoxometalate chemistry. Further, the sandwich-type polyoxoanions were connected by $[\text{K}_3\text{Na}_2]$ clusters into a 4⁴-layer. Magnetic study indicates that antiferromagnetic interactions exist in this compound.

Keywords: Magnetism; Mixed-valence; Polyoxometalate; Sandwich

1. Introduction

Polyoxometalates (POMs), as a rich class of inorganic metal-oxide clusters, have enormous structural diversity and various applications in catalysis, optics, magnetism, and medicine [1, 2]. Sandwich-type POMs, incorporating various paramagnetic transition-metal (TM) centers, have attracted much attention as their interesting properties have possible applications in catalysis, magnetism, and materials science [3–5]. Sandwich-type compounds, containing paramagnetic TM centers, such as $[\text{M}_y(\text{XW}_9\text{O}_{34 \text{ or } 33})_2]^{n-}$ or $[\text{M}_y(\text{X}_2\text{W}_{15}\text{O}_{56})_2]^{m-}$ ($\text{X} = \text{P}, \text{As}, \text{Si}, \text{Ge}, \text{Sb}, \text{Bi}, \text{Se}, y = 2, 3, 4$ etc.), are known with various TM ions [3–7]. Among the sandwich-type species, incorporation of manganese cations in intermediate oxidation states within the sandwich has received attention owing to two properties: (1) Mn^{III} ions possess active redox catalytic activities, which can be used to prepare a series of POM-based catalysts; (2) they have been extensively employed to construct interesting magnetic aggregates, especially single-molecule magnets (SMMs), attributed to their relatively high-spin values (S) and

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negative single-axis magnetic anisotropy (D). However, the synthesis of Mn^{III} -substituted POMs is usually difficult owing to instability in aqueous solution compared with other TM ions [8, 9] and few Mn^{III} -substituted polyoxoanions are reported. Pope's group reported several Mn^{III} -substituted polyoxoanions, $[\text{Mn}_2^{\text{III}}\text{SiW}_{10}\text{O}_{40}\text{H}_6]^{4-}$, $[\{\text{Mn}^{\text{III}}(\text{OH}_2)\}_3\text{SiW}_9\text{O}_{37}]^{7-}$, $[\text{Mn}_3^{\text{II}}\text{Mn}^{\text{III}}(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{9-}$, and $[\text{Mn}^{\text{II}}\text{Mn}_3^{\text{III}}(\text{OH})_2(\text{PW}_9\text{O}_{34})_2]^{9-}$ [8a–c]. Krebs *et al.* [8d] reported two Mn^{III} -containing sandwich-type polyoxoanions $[(\text{Mn}^{\text{III}}(\text{H}_2\text{O}))_3(\text{SbW}_9\text{O}_{33})_2]^{9-}$ and $[(\text{Mn}^{\text{III}}(\text{H}_2\text{O}))_{2.25}(\text{WO}(\text{H}_2\text{O}))_{0.75}(\text{AsW}_9\text{O}_{33})_2]^{8.25+}$. Mialane *et al.* [9a] reported an interesting Mn^{III} -azido-containing dimer $\{[(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Mn}_2^{\text{III}}(\text{OH})_2(\text{N}_3)_{0.5}(\text{H}_2\text{O})_{0.5}]_2(\mu_{-1,3}\text{-N}_3)\}^{10-}$. Cronin and co-workers [9b] reported two sandwich-type aggregates $[\text{Mn}_2^{\text{III}}\text{Mn}_4^{\text{II}}\text{O}_4(\text{H}_2\text{O})_4(\text{XW}_9\text{O}_{34})_2]^{12-}$ ($\text{X} = \text{Ge}, \text{Si}$), exhibiting SMM behavior. Recently, Fang *et al.* [9c, d] synthesized several $\{\text{Mn}_x^{\text{III}}\text{Mn}_y^{\text{IV}}\}$ -containing POMs, which exhibit slow relaxation and quantum tunneling of the magnetization, and also SMM behavior. We have focused on POM/ $\text{Mn}^{2+/3+/4+}$ systems for a long time and obtained three mixed-valence Mn-cluster containing compounds: $\{[\text{Mn}^{\text{II}}(\text{H}_2\text{O})\}_2\text{Mn}_4^{\text{III}}(\text{SiW}_6\text{O}_{26})(\text{SiW}_9\text{O}_{34})_2\}^{16-}$ [10a], $[\text{Mn}_{13}^{\text{III}}\text{Mn}^{\text{II}}\text{O}_{12}(\text{PO}_4)_4(\text{PW}_9\text{O}_{34})_4]^{31-}$ [10b], $[\text{Ce}_3^{\text{IV}}\text{Mn}_2^{\text{IV}}\text{O}_6(\text{OAc})_6(\text{H}_2\text{O})_9]_2[\text{Mn}_2^{\text{III}}\text{P}_2\text{W}_{16}\text{O}_{60}]_3^{20-}$ [10c]. Here, a $\{\text{Mn}_2^{\text{III}}\text{Mn}_2^{\text{II}}\}$ cluster sandwich-type compound, $\alpha\beta\beta\alpha\text{-K}_3\text{Na}_{11}\{\text{Mn}_2^{\text{III}}\text{Mn}_2^{\text{II}}(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2\} \cdot 40\text{H}_2\text{O}$ (**1**), was synthesized by the reaction of $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with $\text{K}_2\text{S}_2\text{O}_8$ in acidic aqueous solution. The sandwich-type polyoxoanions were connected by $[\text{K}_3\text{Na}_2]$ clusters into a 4⁴-layer.

2. Experimental

2.1. Materials and methods

All reagents were purchased commercially and used without purification. Elemental analyses (H and P) were performed on a Perkin-Elmer 2400 CHN elemental analyzer and a PLASMA – SPEC (I) ICP atomic emission spectrometer (W, Mn, K, and Na). IR spectra were obtained on an Alpha Centaur FTIR spectrometer from 400 to 4000 cm^{-1} with KBr pellets. Thermogravimetric (TG) was performed on a Perkin-Elmer TGA7 instrument with a heating rate of 10 $^\circ\text{C min}^{-1}$. Magnetic susceptibility data were collected from 2 to 300 K at a magnetic field of 1000 Oe on a Quantum Design MPMS-5 SQUID magnetometer. A CHI 660 electrochemical work station was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used. The working electrode was glassy carbon. Ag/AgCl was used as a reference electrode and Pt gauze as a counter electrode.

2.2. Synthesis of compound

A mixture of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.24 g, 0.98 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (0.16 g, 0.59 mmol), and $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ (1.0 g, 0.23 mmol) was dissolved in 15 mL distilled water with vigorous stirring. Then 5 mL CH_3COOH was added to the mixture. The solution was boiled for 30 min, and subsequently cooled to ambient temperature, filtered, and left to evaporate at room temperature. Brown block crystals of **1** were isolated after 1 week (yield 53% based on W). Anal. Found (%): H, 1.05; Na, 3.01; K, 1.19; Mn, 2.39; P, 1.27; W, 62.61; Calcd: H, 0.96; Na, 2.88; K, 1.34; Mn, 2.51; P, 1.41; W, 62.80.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	H ₈₄ K ₃ Na ₁₁ Mn ₄ P ₄ O ₁₅₄ W ₃₀
Formula weight	8778.00
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> 1
Unit cell dimension (Å, °)	
<i>a</i>	13.787(3)
<i>b</i>	13.980(3)
<i>c</i>	23.002(5)
α	90.10(3)
β	102.70(3)
γ	118.85(3)
Volume (Å ³), <i>Z</i>	3758.2(13), 1
Calculated density (Mg m ⁻³)	3.879
Absorption coefficient (mm ⁻¹)	23.448
<i>F</i> (000)	3874
Crystal size (mm ³)	0.31 × 0.13 × 0.09
θ range for data collection (°)	3.03–25.00
Data/restraints/parameters	13,091/168/938
<i>R</i> _{int}	0.0611
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0520
<i>R</i> indices (all data) ^b	0.1470
Goodness-of-fit on <i>F</i> ²	1.075

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; \quad ^b wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}.$$

2.3. X-ray crystallography

Crystallographic data collection was performed on a Rigaku R-AXIS RAPID IP diffractometer and collected at 150 K with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares on *F*² using the SHELXL-97 software [11]. During the refinement, all hydrogen atoms on water molecules and protonated oxygen atoms were directly included in the molecular formulae. Further details of the X-ray structural analysis are given in table 1.

3. Results and discussion

3.1. Structure

Polyoxoanion **1** shows the well-known Weakley-type sandwich-type structure consisting of two trivacant [α -P₂W₁₅O₅₆]¹²⁻ Dawson moieties sandwiching a central symmetric rhomb-like [Mn₂^{III}Mn₂^{II}(H₂O)₂] segment (figure 1). Each [α -P₂W₁₅O₅₆]¹²⁻ unit provides seven oxygen donors (one from the central PO₄ group and one each from the six W atoms) that are capable of coordinating to the central [Mn₂^{III}Mn₂^{II}(H₂O)₂] cluster to form the Weakley-type sandwich structure. This structure displays the conventional inter-POM connectivity known as β in Baker–Figgis notation (β -junctions), which is similar to that in [(Mn^{II}OH₂)₂(Mn^{II})₂(P₂W₁₅O₅₆)₂]¹⁶⁻ [12]. All the W and Mn centers exhibit octahedral coordination. The bond lengths of W–O are in the range

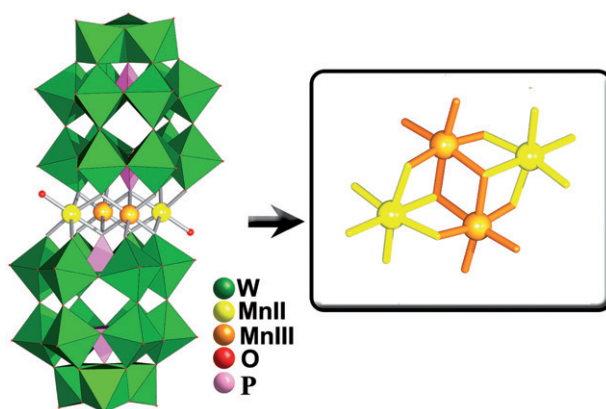


Figure 1. Mixed ball-and-stick and polyhedral representation of **1**.

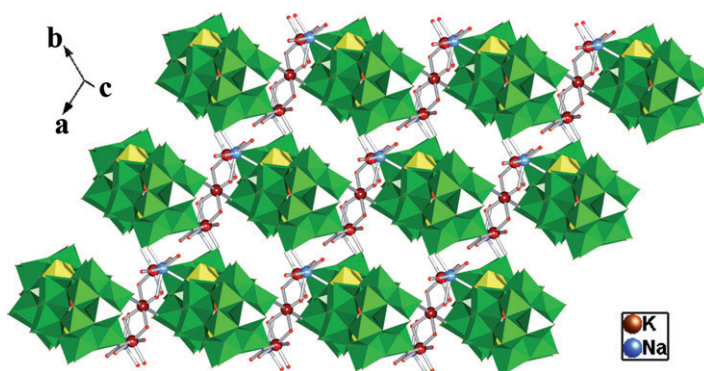
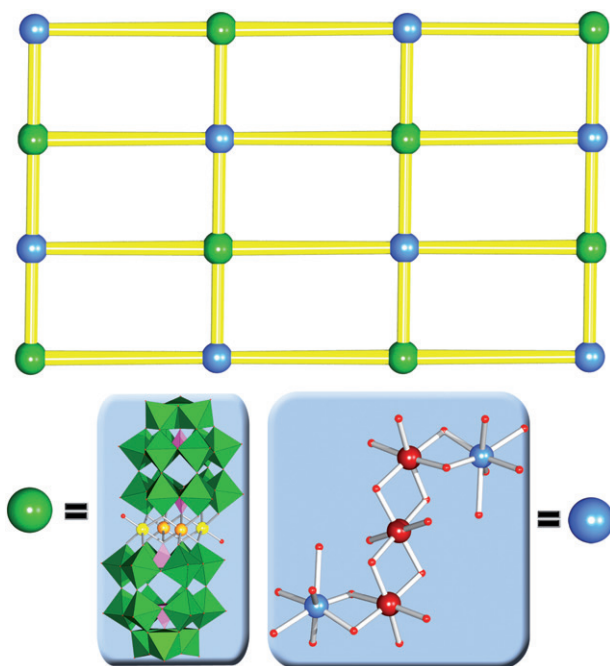
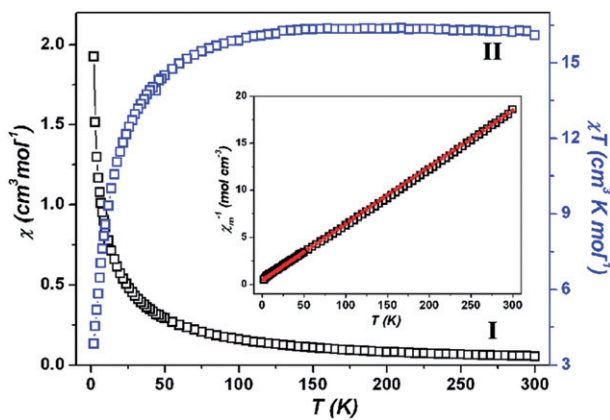


Figure 2. Mixed ball-and-stick and polyhedral representation of the 2-D layer in **1**.

1.665(14)–2.412(13) Å, while the bond lengths of Mn–O are 1.991(13)–2.277(11) Å. BVS indicates that there are two Mn³⁺ and two Mn²⁺ centers in the sandwich set of **1** (figure 1). Thus, **1** represents the first example of [Mn^{III}₂Mn^{II}₂(H₂O)₂]-containing sandwich-type complexes based on trivalent Dawson units. Interestingly, the sandwich-type polyoxoanions in **1** are further connected by [K₃Na₂] clusters into a 2-D layer (figure 2). In this 2-D layer, each sandwich-type polyoxoanion coordinates with four [K₃Na₂] clusters *via* six terminal oxygen atoms and each [K₃Na₂] cluster in turn coordinates to four sandwich-type polyoxoanions, giving a 2-D 4⁴-layer (figure 3). In the 2-D layer, all K⁺ exhibit octahedral coordination and Na⁺ in the linking units are all seven coordinate. K–O and the Na–O distances fall into the range of 2.353(15)–2.512(15) Å and 2.374(19)–2.87(2) Å, respectively.

3.2. Magnetic properties

The magnetism of **1** was studied at 1000 Oe between 2 and 300 K on single-crystal samples (figure 4). At room temperature, the $\chi_m T$ of **1** is 16.1 cm³ K mol⁻¹ and continuously decreases to 3.85 cm³ K mol⁻¹ at 2 K revealing the presence of dominant

Figure 3. Schematic view of the (4,4)-layer in **1**.Figure 4. Temperature dependence of χ_m (I) and $\chi_m T$ (II) values for **1** and (inset) temperature dependence of reciprocal magnetic susceptibility χ_m^{-1} for **1**.

antiferromagnetic interactions between Mn^{II} ($S=5/2$) and Mn^{III} ($S=2$) magnetic centers. The data obey a Curie–Weiss law leading to a Curie constant of $16.8 \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant of -11.2 K . The $\chi_m T$ value is $16.1 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K, a little higher than the calculated value for two Mn^{2+} and two Mn^{3+} centers ($C = 14.75 \text{ cm}^3 \text{ K mol}^{-1}$ assuming $g = 2.0$). The Weiss constants confirm the presence of antiferromagnetic interactions between the Mn sites in the sandwich set.

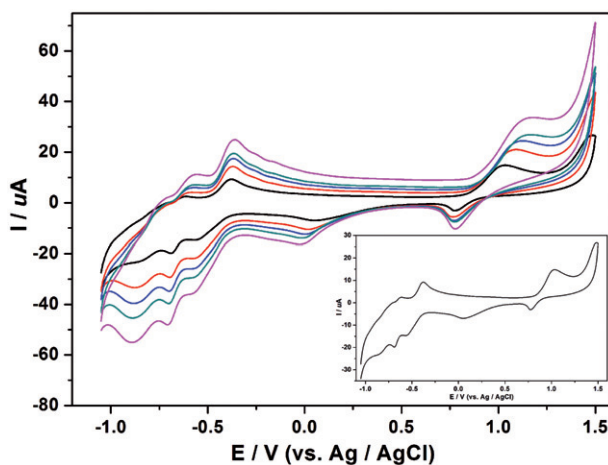


Figure 5. Cyclic voltammograms of **1** ($1 \times 10^{-3} \text{ mol L}^{-1}$) in a pH = 4 ($0.4 \text{ mol L}^{-1} \text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$) buffer solution at different scan rates (inner to outer: 20, 50, 75, 100, and 150 mVs^{-1}). The working electrode was carbon paste and the reference electrode was Ag/AgCl; inset: cyclic voltammogram of **1** ($1 \times 10^{-3} \text{ mol L}^{-1}$) in a pH = 4 buffer solution at a scan rate of 20 mVs^{-1} .

3.3. Electrochemistry

The electrochemical behavior of **1** was investigated by cyclic voltammetry. Figure 5 shows the typical cyclic voltammetric behavior of **1** in a pH = 4 ($0.4 \text{ mol L}^{-1} \text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$) buffer solution. In the potential range +1.5 to -1.0 V , five reduction peaks were observed with mean peak potentials at 0.775 V , 0.055 V , -0.557 V , -0.688 V , and -0.842 V (vs. the Ag/AgCl electrode). The first two reduction peaks and their reduction counterpart, a single-oxidation process located at $+1.030 \text{ V}$, are attributed to redox of the manganese centers [8e]. The reduction peaks at -0.557 V , -0.688 V , and -0.842 V are ascribed to reduction of W^{VI} centers. The effect of the scan rates (ν) on the peak currents (i_{pa} and i_{pc}) has been investigated from 20 to 150 mVs^{-1} . The W-centered and Mn-centered peak currents were proportional to the square root of the scan rate, indicating that the electrode process is diffusion-controlled. The stability of **1** is studied in pH = 4 ($0.4 \text{ mol L}^{-1} \text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$) buffer using cyclic voltammetric behavior every hour for five times. These curves were unchanged with time (figure S1), indicating that **1** is stable in the pH = 4 buffer solution.

3.4. Thermal analysis and IR spectrum

To examine the thermal stability of **1**, TG analysis was carried out. The weight loss is about 9.82% from 50°C to 330°C , which corresponds to loss of all non-coordinated and coordinated water molecules (calcd 8.61%; figure S2). In the IR spectrum of **1** (figure S3), the features at $1090(\text{m})$, $1047(\text{w})$, $933(\text{m})$, $824(\text{w})$, $771(\text{s})$, $720(\text{s}) \text{ cm}^{-1}$ can be attributed to $\nu(\text{P-Oa})$, $\nu(\text{W-Od})$, $\nu(\text{W-Ob-W})$, and $\nu(\text{W-Oc-W})$ in $[\text{Mn}_2^{\text{III}}\text{Mn}_2^{\text{II}}(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{14-}$ [13]. The peak at 517 cm^{-1} can be attributed to $\nu(\text{Mn-O})$. The broad band at 3450 cm^{-1} and medium peak at 1620 cm^{-1} can be regarded as features of the lattice and coordinated water molecules.

4. Conclusion

A new heteropolytungstate constructed from trivacant Dawson-type polyoxoanion fragments and mixed-valence manganese cluster has been obtained from conventional aqueous solution and is rarely observed in POM chemistry. Magnetic study reveals that antiferromagnetic interactions exist in this compound. Further exploration of their interesting physicochemical properties is in progress.

Supplementary material

TG curve and IR spectrum and X-ray crystallographic information file are available for **1**. Further details of the crystal structure investigations for **1** can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; E-mail: crystdata@fiz-karlsruhe.de) on quoting the depository number CSD-421038. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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