

A cationic 24-MC-8 manganese cluster with ring metals possessing three oxidation states $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_6\text{Mn}^{\text{IV}}_2(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu_3\text{-OCH}_3)_2(\text{pko})_{12}](\text{OH})(\text{ClO}_4)_3 \dagger \ddagger$

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Received (in Cambridge, UK) 8th August 2003, Accepted 10th September 2003

First published as an Advance Article on the web 30th September 2003

Reaction of $\text{Mn}(\text{ClO}_4)_2$ with di-pyridyl ketone oxime, $(2\text{-py})_2\text{C}=\text{NOH}$, gives the novel cluster $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_6\text{Mn}^{\text{IV}}_2(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu_3\text{-OCH}_3)_2(\text{pko})_{12}](\text{OH})(\text{ClO}_4)_3$ **1**. It is the only example of a 24-MC-8, and the first metallacrown with ring metal ions in three different oxidation states. Magnetic measurements show antiferromagnetic behavior.

Metallacrowns (MC) exhibit a cyclic structure generally analogous to crown ethers with transition metal ions and a nitrogen atom replacing the methylene carbons. The cavity size of metallacrowns is similar to organic crown ethers. $[9\text{-MC}_{\text{M}(\text{ox})\text{N}(\text{ligand})\text{-}3}]$, $[12\text{-MC}_{\text{M}(\text{ox})\text{N}(\text{ligand})\text{-}4}]$ and $[15\text{-MC}_{\text{M}(\text{ox})\text{N}(\text{ligand})\text{-}5}]$ metallacrowns^{1–3} with metal ions Mn^{III} , Fe^{III} , Ni^{II} , Cu^{II} , and VVO , inverse- $[12\text{-MC-}4]$, $[12\text{-MC-}6]$, $[16\text{-MC-}8]$, $[18\text{-MC-}6]$, $[18\text{-MC-}8]$, and $[30\text{-MC-}10]$ ^{4–8} as well as a variety of dimers and fused metallacrowns^{1,9} have been reported to date. The most metallacrowns have been prepared using hydroxamic acids and/or ketonoximic acids as constructing ligands, while a series of suitable organic molecules *i.e.* 3-hydroxy-2-pyridone,¹⁰ 3-thione-1,2-dithione-4,5-dithiolato,¹¹ and dipyridylketonediolate¹² have also been used as ligands. Though multi-nuclear, mixed valence manganese complexes are widely known, there are only rare examples^{13–17} in which Mn^{II} coexists in the presence of Mn^{IV} . In most cases, the Mn^{II} and Mn^{IV} oxidation states are unstable with respect to comproportionation reactions that yield Mn^{III} . Chan and Armstrong reported¹⁴ a tetranuclear cluster of composition $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$. In the class of dodecanuclear manganese clusters Christou *et al.* reported^{16,17} two examples of dodecanuclear manganese clusters with three oxidation states, $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_7\text{Mn}^{\text{IV}}_4$ and $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_6\text{Mn}^{\text{IV}}_4$. Very recently, we have demonstrated that Mn^{II} and Mn^{IV} could exist in a trinuclear¹⁸ or tetranuclear¹⁹ cluster in the absence of Mn^{III} .

In this report, we present the first dodecanuclear manganese cluster showing a metallacrown pattern of the formula 24-MC-8 and ring metal ions in three different oxidation states: Mn^{II} , Mn^{III} , Mn^{IV} . The reaction of $\text{Mn}(\text{ClO}_4)_2$ with di-pyridyl ketone oxime (Hpko), in 1:1 ratio in methanol in the presence of NaOH gives brown-black crystals of the mixed-valent $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_6\text{Mn}^{\text{IV}}_2(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\mu\text{-OCH}_3)_2(\text{pko})_{12}](\text{OH})(\text{ClO}_4)_3$ **1** cluster, by slow evaporation of the mother liquid. The synthesis of the 24-membered metallacrown **1** was achieved *via* the reaction in Scheme 1.

Compound **1** (Fig. 1) crystallizes in the space group $P4(2)/n$. The structure consists of a (Mn_{12}) mer located on an inversion center in the lattice. There are two types of perchlorate anions, one on a general position in the lattice and a second on a two-fold axis, with a OH^- ligand neutralizing the $\{\text{Mn}_{12}\}^{4+}$ cluster. The dodecanuclear manganese cluster contains a 24-membered

metallacrown core constructed by eight metal ions, 2Mn(1), 2Mn(2), 2Mn(3), and 2Mn(4), and eight pko[−] ligands. Therefore, a part of the cluster can be described as having the formally cationic $[24\text{-MC}_{\text{Mn}(\text{II/III/IV})\text{N}(\text{pko})\text{-}8}]^{4+}$ core (Fig. 2). The specific connectivity of the atoms forming the metallacrown ring is $[\text{Mn}^{\text{III}}(1)\text{-O}(1)\text{-N}(1)\text{-Mn}^{\text{II}}(2)\text{-N}(10)\text{-O}(8)\text{-Mn}^{\text{III}}(3)\text{-N}(5)\text{-O}(3)\text{-Mn}^{\text{IV}}(4)\text{-O}(12)\text{-N}(13)]_2$. The 24-membered metallacrown ring wraps a 16-membered ring of the formula $[\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_4\text{Mn}^{\text{IV}}_2(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]$ with the connectivity pattern $[\text{Mn}^{\text{III}}(1)\text{-O}(9)\text{-Mn}^{\text{II}}(2)\text{-OH}(2)\text{-Mn}^{\text{III}}(3)\text{-O}(6)\text{-Mn}^{\text{IV}}(4)\text{-OH}(7)]_2$. The metallacrown core is severely distorted from planarity, showing an S shaped arrangement. It is noticeable that the two rings, metallacrown and star-shaped, the manganese ions are common, while the heteroatoms forming the

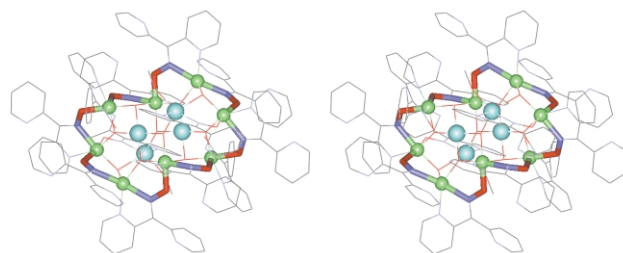
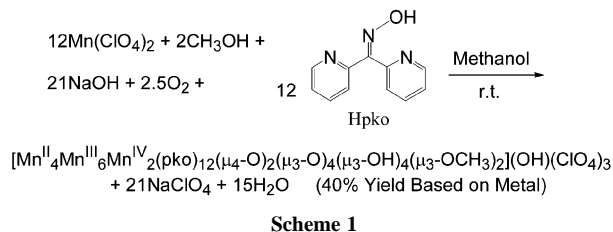


Fig. 1 Stereoview of **1** highlighting MC ring with core metals. Color scheme: Red-Oxygen, Blue-Nitrogen, Green-Ring Mn, Cyan-Core Mn.

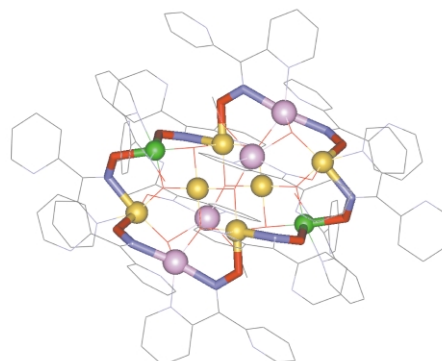


Fig. 2 Mn ions of **1** colored by oxidation state – Pink- Mn^{II} , Gold- Mn^{III} , Green- Mn^{IV} .

† Electronic Supplementary Information (ESI) available: Variable-temperature dc susceptibility of **1** at 2500 G and Magnetization (M) variable-field data of **1** at 4.5 K. See <http://www.rsc.org/suppdata/cc/b3/b309439a/>

two rings are coming from non-related ligands. Those of the metallacrown ring are coming from eight pko N–O moieties while those of the star-shaped ring from μ_3 -O or μ_3 -OH groups. Four of the manganese ions, Mn(1) and Mn(3), are in oxidation state 3+ (The average bond distance is 2.037 Å and the Jahn–Teller elongation along the $N_{\text{pko}}\text{--Mn}(1)$ or (3) axis is ~ 2.28 Å support a 3+ oxidation state) and an octahedral coordination environment, two manganese ions, Mn(2), are in the oxidation state 2+ (average Mn bond distance equals 2.214 Å) and an octahedral coordination environment while the remaining two, Mn(4), manganese ions are in oxidation state 4+ (average Mn bond distance equals 1.864 Å) with geometry that is best described as distorted octahedral. The metallacrown core accommodates a tetranuclear mixed valent manganese cluster of the formula $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{pko})_4]$. The two μ_4 -oxygen atoms are bridged the two Mn^{II} ions, Mn(5), and two Mn^{III} ions of the metallacrown ring, Mn(1), while the Mn^{II} ions are bridged to two Mn^{III} ions, Mn(3), of the metallacrown ring through N–O pko group. The μ_3 -O, O(6) and O(9), and μ_3 -OH, O(2) and O(7), atoms which bridge the tetranuclear cluster to the star-shaped ring are easily distinguished by their coordination environment. The μ_3 -O shows a trigonal-planar geometry (sum of the angles around O(6) and O(9) equals 360°), while the sum of the angles around the μ_3 -OH groups support a tetrahedral geometry (sum of the angles around O(2) equals 327.8° and O(7) equals 306.4°).

The original manganese dodecanuclear, $[\text{Mn}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4\text{O}_{12}] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ **2**, by T. Lis²⁰ has a vastly different conformation than **1** (Fig. 3). The oxidation states of the manganese in **2** are $\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4$. In addition, all eight Mn^{III} form a nonplanar ring, and the Mn^{IV} forms a cubane in the center of this planar ring. The Mn^{IV} core is connected to the Mn^{III} ring via eight μ_3 -oxide bridges. This molecule is the first recognized single-molecule magnet, and its properties are derived from its large ground state spin and large molecular zero-field splitting value.

Variable-temperature DC magnetic susceptibility data were collected on a powder/icosane matrix over a range of 2 K to 300 K at 2500 G under zero-field cooled conditions using a SQUID magnetometer. The μ_{eff} steadily decreased as the temperature was lowered from 300 K ($\mu_{\text{eff}} = 13.00$) to 2 K ($\mu_{\text{eff}} = 11.2$) indicating an overall antiferromagnetic interaction (Figure S1).[†] Plots of magnetization curves at 4.5 K over the range of 100 G to 55 000 G in an icosane matrix (Figure S2)[†] show no evidence for saturation precluding the determination of the ground spin state.

We collected AC susceptibility data to analyze the magnetization relaxation of the spins. AC SQUID experiments performed over the temperature range of 2.0 K to 10 K with zero-applied field and a 3.5 G oscillating AC magnetic field at 1000 Hz. Unfortunately, the cluster does not display an out-of-phase susceptibility signal and a blocking temperature for the compound could not be observed.

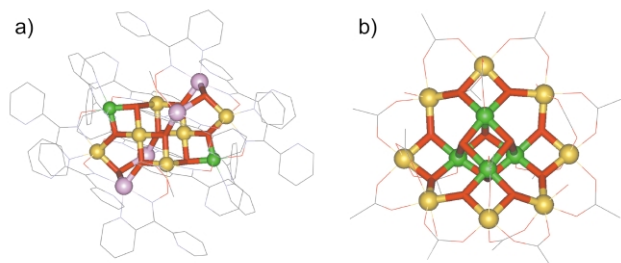


Fig. 3 Oxide connectivity between Mn ions in (a) **1** and (b) **2**. See Fig. 2 for color scheme.

In conclusion, we have synthesized a new member of the metallacrown family, and it is the only example of a metallacrown with the ring metal ions in three different oxidation states: Mn^{II} , Mn^{III} , and Mn^{IV} .

This work was supported by NSF CHE-0111428 to VLP. The authors wish to thank the Physics and Astronomy Department at Michigan State University for the use of their Quantum Design AC SQUID magnetometer. DK wishes to thank WG010 of COST action D21.

Notes and references

[†] Crystals of **1** have been structurally characterized with the formula $\text{C}_{138}\text{H}_{116}\text{N}_{37}\text{O}_{40}\text{Cl}_3\text{Mn}_{12}$. Analytical data for **1**: (Found C, 44.20; H, 3.00; N, 14.10 ($F_w = 3699.31$) requires C, 44.76; H, 3.16; N, 14.00); Crystal data for **1**: $M_r = 3699.31$, orthorhombic, space group $P4(2)/n$, $a = 29.6517(12)$ Å, $b = 29.6517(12)$ Å, $c = 17.6036(13)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 15477.5(14)$ Å³, $Z = 4$; $d_{\text{calc}} = 1.587$ mg m⁻³; $2.78^\circ < \theta < 21.93^\circ$; crystal dimensions (mm), $0.12 \times 0.16 \times 0.44$; $\mu = 1.084$ mm⁻¹; $T = 118(2)$ K; 6319 used of 85779 reflections collected. 9499 reflections and 997 parameters were used for the full-matrix, least-squares refinement of F^2 , $R1 = 0.0640$ [$I > 2\sigma(I)$], $R1 = 0.0995$ (all data); $wR2 = 0.1548$ [$I > 2\sigma(I)$], $wR2 = 0.1686$ (all data). Difference electron density maps revealed the presence of disordered lattice solvate molecules which were ultimately modelled by use of the SQUEEZE subroutine of the PLATON program suite. CCDC-216891. See <http://www.rsc.org/suppdata/cc/b3/b309439a/> for crystallographic data in CIF or other electronic format.

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