Research Article

Synthesis and Structural Characterization of a Metal Cluster and a Coordination Polymer Based on the $[\text{Mn}_6(\mu_4-O)_2]^{10+}$ Unit

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1. Introduction

The synthesis of Mn clusters has attracted significant interest due to their relevance to many areas including molecular magnetism, catalysis, and bioinorganic chemistry [1, 2]. In the bioinorganic area, extensive work has been carried out to model the structure and catalytic activity of a tetranuclear Mn cluster, which is present in the water oxidizing centre (WOC) of Photosystem II [3–7]. As a result, a number of oligonuclear high oxidation state Mn-carboxylate clusters have been prepared [3, 5], some of which have been studied for their ability to oxidize H$_2$O to molecular O$_2$ [3, 6, 7]. Furthermore, considerable effort has been expended in order to prepare structural and reactivity models of other Mn-containing enzymes, such as Mn catalases. These studies have resulted in a number of oligonuclear Mn complexes with oxo/alkoxo/hydroxo or carboxylate bridges, some of which have proven to be very efficient catalytic scavengers of H$_2$O$_2$ [8]. The synthesis of oligonuclear Mn model compounds often involves preformed Mn carboxylate clusters and coordination polymers as starting materials, with the most popular ones being complexes based on the $[\text{Mn}_3O]^{6+/7+}$ and the $[\text{Mn}_8O_2]^{10+}$ units [3, 9–11]. Since the various characteristics of the starting materials including their structural core, carboxylate bridges, and terminal ligation have a significant influence on the identity of the reaction product, there is always a need for new additions in the list of known metal precursor compounds.

Herein, we report the syntheses and the crystal structures of the 1D coordination polymer $\{[\text{Mn}_6O_2(O_2CMe)_10(H_2O)_4]·2.5H_2O\}_\infty$ and the cluster $[\text{Mn}_6O_2(O_2CPh)_10(py)_2(MeCN)(H_2O)]·2MeCN$ in the presence of 3-hydroxymethylpyridine (3hmpH) in acetonitrile. The structures of these complexes are based on hexanuclear mixed-valent manganese carboxylate clusters containing the $[\text{Mn}_4^{II}\text{Mn}_2^{III}(\mu_4-O)_2]^{10+}$ structural core. $\{[\text{Mn}_6O_2(O_2CMe)_10(H_2O)_4]·2.5H_2O\}_\infty$ consists of zigzag chain polymers constructed from $[\text{Mn}_6O_2(O_2CMe)_10(H_2O)_4]$ repeating units linked through acetate ligands, whereas $2\cdot2\text{MeCN}$ comprises a discrete Mn$_6$-benzoate cluster.

2. Experimental

2.1. Materials. All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received; water was distilled in-house. $[\text{Mn}_3O(O_2CMe)_6(py)_3]\cdot\text{py}$ and $[\text{Mn}_3O(O_2CPh)_6(py)_2(H_2O)]·0.5\text{CH}_3\text{CN}$ were prepared as described elsewhere [18].
2.2. *Compound Preparation.* [(Mn₂O₂(O₂CMe)₁₀·(H₂O)₄)·2.5H₂O]·2.5H₂O]∞ (1-2.5H₂O)∞: [Mn₂O₂(O₂CMe)₁₀(py)₃]·py (0.2 g, 0.24 mmol) was dissolved in MeCN (10 mL), and then 3 hmpH (0.05 g, 0.46 mmol) was added to the dark brown solution. The resulting red-brown solution was left under magnetic stirring for ~50 minutes, filtered off, and the filtrate was left undisturbed at room temperature. After a few weeks, brown crystals of (1·2.5H₂O)∞ suitable for X-ray crystallography were formed. The crystals were collected by filtration, washed with MeCN (10 mL), and Et₂O (2 × 10 mL) and dried in vacuo.

Data were collected on an Oxford-Di ffraction Xcalibur diffractometer, equipped with a CCD area detector and a graphite monochromator utilizing Mo-Kα radiation (λ = 0.71073 Å). Suitable crystals were attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Unit cell dimensions were determined and refined by using 4714 (3 ≤ θ ≤ 30.42°) and 23078 (3.07 ≤ θ ≤ 31.25°) reflections for (1·2.5H₂O)∞ and 2·2MeCN, respectively. Empirical absorption corrections (multiscan based on symmetry-related measurements) were applied using CrysAlis RED software [19]. The structures were solved by direct methods using SIR92 [20] and refined on F² using full-matrix least squares with SHELXL97 [21].

| Table 1: Crystallographic data for complexes (1·2.5H₂O)∞ and (2·2MeCN). |
|---|
| **Formula** | C₆₅H₇₆Mn₁₂O₇₉ | C₆₅H₇₆Mn₆N₅O₂₃ |
| **M_r** | 2138.33 | 1872.13 |
| **Crystal System** | Orthorhombic | Triclinic |
| **Space Group** | P b c a | P |
| a/Å | 13.615(2) | 14.4690(8) |
| b/Å | 21.274(3) | 15.8172(7) |
| c/Å | 30.459(4) | 18.6362(6) |
| α/° | 90 | 83.861(4) |
| β/° | 90 | 86.750(4) |
| γ/° | 90 | 83.463(4) |
| **V/Å³** | 8822(2) | 4208.4(8) |
| **Z** | 4 | 2 |
| **T/K** | 100(2) | 100(2) |
| **D_r, g/cm³** | 1.610 | 1.477 |
| **μ(Mo-Kα)/mm⁻¹** | 1.750 | 0.950 |
| **Goodness of fit on F²** | 0.807 | 0.974 |
| **Δρ max/min/e Å⁻³** | 0.891/−0.409 | 1.434/−1.333 |

*Including solvent molecules and all hydrogen atoms (even the H atoms of H₂O).*

2.3. *X-Ray Crystallography.* Data were collected on an Oxford-Diffraction Xcalibur diffractometer, equipped with a CCD area detector and a graphite monochromator utilizing Mo-Kα radiation (λ = 0.71073 Å). Suitable crystals were attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Unit cell dimensions were determined and refined by using 4714 (3.14 ≤ θ ≤ 30.42°) and 23078 (3.07 ≤ θ ≤ 31.25°) reflections for (1·2.5H₂O)∞ and 2·2MeCN, respectively. Empirical absorption corrections (multiscan based on symmetry-related measurements) were applied using CrysAlis RED software [19]. The structures were solved by direct methods using SIR92 [20] and refined on F² using full-matrix least squares with SHELXL97 [21].

2.4. *Physical Measurements.* Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Cyprus, Chemistry Department. IR spectra were recorded on KBr pellets in the 4000–400 cm⁻¹ range using a Shimadzu Prestige-21 spectrometer.

3. *Results and Discussion.*

3.1. *Syntheses.* The goal of the described research is the synthesis of multidimensional coordination polymers composed of polynuclear Mn carboxylate clusters with the use of hydroxymethyl-pyridine derivatives [e.g., 4-hydroxymethyl-pyridine (4hmpH), 3-hydroxymethyl-pyridine (3hmpH)] as bridging ligands. The initial result from these investigations was a new hexanuclear Mn complex [Mn₂O₂(O₂CPh)₁₀(4hmpH)(MeCN)], which contains the [Mn₂O₂]¹⁺ structural core and terminal 4hmpH ligands [12]. This compound was prepared from a reaction of [Mn₂O₂(CPh)₃]·2H₂O with 4hmpH in MeCN. Various modifications of this reaction system that were performed involved the use of preformed Mn clusters as precursor compounds together with 3hmpH. Thus, the reaction of [Mn₃(μ₃-O)(O₂CPh)₆(L)₂(L')₂] (R = Me, L = L' = py, (1-2.5H₂O)∞; R = Ph, L = py, L' = H₂O, 2·2MeCN) with 3hmpH in acetonitrile resulted in the isolation of compounds (1·2.5H₂O)∞ and 2·2MeCN, which however
did not contain the 3hmpH ligands. The formation of \((1)_{\infty}\) and 2 is summarized in equations 1 and 2, respectively:

$$2n\left[\text{Mn}_6\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3\right] + 4n\text{H}_2\text{O} + 2n\text{e}^- \rightarrow \left[\text{Mn}_6\text{O}_2(\text{O}_2\text{CMe})_{10}(\text{H}_2\text{O})_4\right]_n + 2n\text{MeCO}_2^- + 6n\text{py}$$

$$2\left[\text{Mn}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_2(\text{H}_2\text{O})_2\right] + \text{MeCN} + 2\text{e}^- \rightarrow \left[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{py})_2(\text{MeCN})(\text{H}_2\text{O})_2\right] \quad (2)$$

As it will be discussed in detail below, the structures of \((1-2.5\text{H}_2\text{O})_{\infty}\) and 2-2MeCN are very similar with one major difference between them being the fact that \((1-2.5\text{H}_2\text{O})_{\infty}\) is a coordination polymer, whereas 2-2MeCN is a discrete metal cluster. A possible explanation for this is that the bulky PhCO$_2$ groups that are present in 2-2MeCN prevent the polymerization of the Mn$_6$ clusters, whereas in \((1-2.5\text{H}_2\text{O})_{\infty}\) there are only acetate ligands that are more flexible and thus can easily bridge Mn$_6$ units leading to a polymeric species. We also note that the average oxidation state of the final products \((1-2.5\text{H}_2\text{O})_{\infty}\) is very similar to that of compound 1-2MeCN.

3.2. Crystal Structures. The structure of the repeating unit of \((1-2.5\text{H}_2\text{O})_{\infty}\) is very similar to that of compound 2-2MeCN (with the main differences between the two compounds being the terminal ligation and the type of carboxylate ligands) and thus, only the first one will be discussed in detail. Selected interatomic distances for \((1-2.5\text{H}_2\text{O})_{\infty}\) and 2-2MeCN are given in Tables 2 and 3, respectively.

### Table 2: Selected interatomic distances (Å) for complex \((1-2.5\text{H}_2\text{O})_{\infty}\)

| Bond Distances (Å) |
|---------------------|
| Mn1 ·· Mn2 | 3.138(2) | Mn3 ·· O26 | 2.186(4) |
| Mn2 ·· Mn6 | 2.798(2) | Mn3 ·· O24 | 2.195(4) |
| Mn2 ·· Mn5 | 3.164(2) | Mn3 ·· O12 | 2.201(4) |
| Mn3 ·· Mn6 | 3.131(2) | Mn4 ·· O19 | 2.138(5) |
| Mn4 ·· Mn6 | 3.187(2) | Mn4 ·· O22 | 2.160(5) |
| Mn1 ·· O7 | 2.130(5) | Mn4 ·· O6 | 2.173(5) |
| Mn1 ·· O24 | 2.162(4) | Mn4 ·· O9 | 2.191(5) |
| Mn1 ·· O3 | 2.164(5) | Mn4 ·· O25 | 2.240(4) |
| Mn1 ·· O21 | 2.172(4) | Mn4 ·· O8 | 2.313(5) |
| Mn1 ·· O1 | 2.176(4) | Mn5 ·· O20 | 2.125(5) |
| Mn1 ·· O5 | 2.293(5) | Mn5 ·· O11 | 2.142(5) |
| Mn2 ·· O25 | 1.883(4) | Mn5 ·· O18 | 2.193(5) |
| Mn2 ·· O24 | 1.891(4) | Mn5 ·· O14 | 2.193(4) |
| Mn2 ·· O4 | 1.943(4) | Mn5 ·· O23 | 2.207(4) |
| Mn2 ·· O17 | 1.962(5) | Mn5 ·· O25 | 2.265(4) |
| Mn2 ·· O5 | 2.229(4) | Mn6 ·· O24 | 1.892(4) |
| Mn2 ·· O14 | 2.257(4) | Mn6 ·· O25 | 1.894(5) |
| Mn3 ·· O2 | 2.143(4) | Mn6 ·· O10 | 1.931(4) |
| Mn3 ·· O15 | 2.155(5) | Mn6 ·· O16 | 1.973(5) |
| Mn3 ·· O13 | 2.163(5) | Mn6 ·· O8 | 2.202(4) |
| Mn6 ·· O2 | 2.224(3) | Mn6 ·· O12 | 2.232(4) |

### Table 3: Selected interatomic distances (Å) for complex 2-2MeCN.

| Bond Distances (Å) |
|---------------------|
| Mn1 ·· Mn2 | 3.133(2) | Mn3 ·· O22 | 2.206(3) |
| Mn2 ·· Mn6 | 2.8134(9) | Mn3 ·· N1 | 2.263(4) |
| Mn2 ·· Mn5 | 3.130(2) | Mn3 ·· O12 | 2.317(3) |
| Mn3 ·· Mn6 | 3.162(2) | Mn4 ·· O6 | 2.124(3) |
| Mn4 ·· Mn6 | 3.167(2) | Mn4 ·· O20 | 2.131(3) |
| Mn1 ·· O1 | 2.121(3) | Mn4 ·· O9 | 2.154(3) |
| Mn1 ·· O7 | 2.121(3) | Mn4 ·· O23 | 2.186(3) |
| Mn1 ·· O3 | 2.145(3) | Mn4 ·· N2 | 2.287(4) |
| Mn1 ·· O22 | 2.190(3) | Mn4 ·· O8 | 2.302(3) |
| Mn1 ·· N3 | 2.250(5) | Mn5 ·· O19 | 2.155(3) |
| Mn1 ·· O5 | 2.281(3) | Mn5 ·· O18 | 2.158(3) |
| Mn2 ·· O22 | 1.872(3) | Mn5 ·· O23 | 2.176(3) |
| Mn2 ·· O23 | 1.894(3) | Mn5 ·· O11 | 2.197(3) |
| Mn2 ·· O17 | 1.936(3) | Mn5 ·· O21 | 2.226(3) |
| Mn2 ·· O4 | 1.972(4) | Mn5 ·· O14 | 2.237(4) |
| Mn2 ·· O5 | 2.239(3) | Mn6 ·· O22 | 1.889(3) |
| Mn2 ·· O14 | 2.241(3) | Mn6 ·· O23 | 1.893(3) |
| Mn3 ·· O2 | 2.127(4) | Mn6 ·· O10 | 1.951(4) |
| Mn3 ·· O13 | 2.146(3) | Mn6 ·· O16 | 1.954(3) |
| Mn3 ·· O15 | 2.151(3) | Mn6 ·· O12 | 2.202(3) |
| Mn6 ·· O8 | 2.232(3) |

hexanuclear cluster \([\text{Mn}_6\text{O}_2(\text{O}_2\text{CMe})_{10}(\text{H}_2\text{O})_4]\) (Figure 1) and totally 2.5H$_2$O molecules of crystallization. Charge
The yellow lines emphasize the code: Mn II, green; MnIII, dark green; O, red; C, grey. H atoms are omitted for clarity.

Table 4: Bond valence sum (BVS)\(^a^b\) calculations for complexes (1-2.5H\(_2\)O)\(_n\) and (2-2MeCN)

|        | Complex 1 | Complex 2 |
|--------|-----------|-----------|
|        | Mn\(^{II}\) | Mn\(^{III}\) | Mn\(^{IV}\) | Mn\(^{II}\) | Mn\(^{III}\) | Mn\(^{IV}\) |
| Mn1    | 1.96      | 1.79      | 1.88      | 2.03      | 1.87      | 1.94      |
| Mn2    | 3.20      | 2.92      | 3.07      | 3.21      | 2.94      | 3.08      |
| Mn3    | 1.99      | 1.82      | 1.91      | 1.94      | 1.79      | 1.85      |
| Mn4    | 1.86      | 1.70      | 1.79      | 1.96      | 1.81      | 1.87      |
| Mn5    | 1.93      | 1.76      | 1.85      | 1.90      | 1.74      | 1.83      |
| Mn6    | 3.21      | 2.94      | 3.09      | 3.22      | 2.94      | 3.09      |

\(^a^b\)The bold value is the one closest to the charge for which it was calculated.

The oxidation state is the nearest whole number to the bold value.

Figure 1: A partially labeled plot of the repeating unit of (1)\(_n\). The yellow lines emphasize the [Mn\(^{II}\)Mn\(^{II}\)(\(\mu_4\)-O)]\(^{10+}\) core. Color code: Mn\(^{II}\), green; Mn\(^{III}\), dark green; O, red; C, grey. H atoms are omitted for clarity.

Considerations, bond valence sum calculations (Table 4) and inspection of metric parameters indicate that the cluster is mixed-valent containing four Mn\(^{II}\) and two Mn\(^{III}\) ions. The [Mn\(^{IV}\)Mn\(^{III}\)(\(\mu_4\)-O)]\(^{10+}\) core of I has appeared several times in the literature as will be discussed in detail below and can be described as consisting of two edge-sharing (\(\mu_4\)-O)Mn\(_4\) tetrahedra. Such units are defined as anti-T1 tetrahedra (T1 is a structural unit having a cation at the center and four anions at the apices of the tetrahedron) [26]. The common edge of the two anti-T1 tetrahedra is formed by the two Mn\(^{III}\) ions, whereas the four Mn\(^{II}\) ions occupy the corners of the [Mn\(^{IV}\)Mn\(^{III}\)(\(\mu_4\)-O)]\(^{10+}\) core. The peripheral ligation of the Mn atoms is completed by 4 terminal H\(_2\)O molecules (ligated to the four Mn\(^{II}\) atoms) and 10 acetate ligands.

All Mn atoms are in distorted octahedral geometries. Five of the intra-cluster acetate groups are \(\mu_2\) with each of their carboxylate oxygen atoms acting as terminal ligand for a Mn center. Four acetate ligands are coordinated in \(\eta^1: \eta^2: \mu_3\) fashion. The remaining carboxylate ligand bridges two Mn\(^{II}\) atoms (Mn···Mn distance = 4.7914(2) Å) of adjacent Mn\(_6\) clusters, thus resulting in the formation of a zigzag chain structure (Figure 2). The chains are interacting through hydrogen bonds (O···O distances 2.7–2.9 Å) involving the coordinated water molecules and carboxylate O atoms. Thus, a two-dimensional hydrogen-bonded polymer with a 4-connected topology is formed (Figure 3). The hydrogen bonds involving the lattice water molecules cannot be identified with accuracy due to the positional disorder of these molecules and thus, are not discussed here.

A representation of the structure of 2-2MeCN is given in Figure 4. The structure of 2-2MeCN is very similar to that of (1-2.5H\(_2\)O)\(_n\) with the main differences between them being (i) the type of terminal ligands [4H\(_2\)O for (1-2.5H\(_2\)O)\(_n\); 2 py, one MeCN and one H\(_2\)O for 2-2MeCN] (ii) the type of carboxylate groups (acetate for (1-2.5H\(_2\)O)\(_n\); benzoate for 2-2MeCN) and (iii) their dimensionality [(1-2.5H\(_2\)O)\(_n\) is a coordination polymer, whereas 2-2MeCN is a discrete metal cluster]. Regarding point (iii) we note that examination of the packing of 2-2MeCN revealed the existence of intermolecular hydrogen bonding interactions (O···O distances 2.792(4) and 2.809(4) Å) involving the terminal H\(_2\)O molecule and two \(\text{O}_{\text{benzate}}\) atoms of two neighboring Mn\(_6\) molecules resulting in the formation of a dimeric (2-2MeCN)\(_2\) aggregate.

The Mn\(_6\) unit that appears in (1-2.5H\(_2\)O)\(_n\) and 2-2MeCN, that is, the cluster [Mn\(_6\)O\(_2\)(O\(_2\)CR)\(_{10}\)(L)\(_2\)](L) (L) \(\text{L}_2\)' (L) \(\text{L}_2\)′) (R = Me, L = L′ = L′′ = H\(_2\)O, 1; R = Ph, L = py, L′′ = H\(_2\)O, L′′′ = MeCN, 2), has a structural motif found in several hexanuclear Mn clusters and coordination polymers [9, 12–16]. For example, we have recently reported the discrete cluster [Mn\(_6\)O\(_2\)(O\(_2\)CR)\(_{10}\)(4hmpH)\(_3\)](MeCN) containing the [Mn\(^{II}\)Mn\(^{III}\)(\(\mu_4\)-O)]\(^{10+}\) core and also three terminal 4hmpH groups linked through their N\(_{\text{pyridine}}\) atom and a MeCN molecule [12]. In addition, compound (1-2.5H\(_2\)O)\(_n\) is closely related to compound {[Mn\(_6\)O\(_2\)(O\(_2\)CEt)\(_{10}\)(H\(_2\)O)\(_4\)]2EtCO\(_2\)H\(_n\) (3-2EtCO\(_2\)H)\(_n\), recently published [14]. The main structural differences between them lie in the type of carboxylate ligands in these compounds, being acetate groups in (1-2.5H\(_2\)O)\(_n\) and propionate ligands in (3-2EtCO\(_2\)H)\(_n\) and also in the type of the crystallization solvent molecules. Other related examples to (1-2.5H\(_2\)O)\(_n\) comprise the chain polymers [Mn\(_6\)O\(_2\)(O\(_2\)CCMe\(_3\))\(_{10}\)(thf)\(_2\)](NIT-Me) [Mn\(_6\)O\(_2\)(O\(_2\)CCMe\(_3\))\(_{10}\)(thf)(CH\(_2\)Cl\(_2\))(NIT-Me))] (thf = tetrahydrofuran, NIT-Me = 4,5-dihydro-1H-imidazol-3-oxide-1-oxyl) [15] and [Mn\(_6\)O\(_2\)(O\(_2\)CCMe\(_3\))\(_{10}\)(HO\(_2\)CCMe\(_3\))\(_2\)](py) (py = 4′,4′-bipyridine) [16].

4 Conclusions

We reported the syntheses and the crystal structures of compounds (1-2.5H\(_2\)O)\(_n\) and 2-2MeCN, which are based on the well-known [Mn\(_6\)(\(\mu_4\)-O)]\(^{10+}\) structural core. Both compounds were prepared serendipitously in our
Figure 2: Wireframe representation of the zigzag chain of $(1)_\infty$ viewed along $a$-axis. Mn, green; O, red; C, grey. H atoms are omitted for clarity.

Figure 3: Wireframe representation of the layer formed by interchain hydrogen bonds in $(1)_\infty$. The hydrogen bonds are shown as dotted blue lines. Mn, green; O, red; C, grey. H atoms are omitted for clarity.
attempt to prepare polymeric species consisting of polynuclear Mn clusters linked through 3hmpH. Compound \((1 \cdot 2.5\text{H}_2\text{O})_\infty\) features a zigzag chain structure formed by \([\text{Mn}_6(\mu_4-\text{O})_2(\text{O}_2\text{CMe})_{10}(\text{H}_2\text{O})_4]\) clusters linked via bridging acetate ligands. This compound joins a family of coordination polymers based on the \([\text{Mn}_6(\mu_4-\text{O})_2]^{10+}\) unit, which numbers only a few members. Furthermore, compound \(2 \cdot 2\text{MeCN}\) represents a new addition in the growing family of Mn-benzoate clusters. Further work may involve replacement of the terminal solvent molecules in \((1 \cdot 2.5\text{H}_2\text{O})_\infty\) or \(2 \cdot 2\text{MeCN}\) by various bridging polytopic ligands, in order to isolate higher dimensionality (2D, 3D) polymers. Multidimensional coordination polymers consisting of oligonuclear Mn clusters would be potential candidates for various applications including gas storage and catalysis.

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