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Structural variation in cation-assisted assembly of high-nuclearity Mn arsonate and phosphonate wheels

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Comproportionation reactions between $MnCl_2$ and $KMnO_4$ in the presence of arsonate or phosphonate ligands promote the cation-assisted assembly of high-nuclearity, wheel-shaped or toroidal {Mn_8} (1) and {Mn_{24}} (2) complexes; the closely corresponding reaction systems provide insights into the complexation behaviour of homologous phosophonate/arsonate ligand species.

Organophosphonate-stabilised transition metal complexes have received significant attention mainly due to their interesting structures, their hydrolytic stabilities and potential applications in different areas such as catalysis, ion exchange technologies, corrosion inhibitor materials, proton conductors, photochemistry, molecular magnetism and etc.[1] Their strong coordination ability towards transition metal ions enabled the synthesis of extended networks and oxo-clusters incorporating various transition metal systems.[2] Of particular interest in the area of molecular magnetism are 0-D Mn phosphonate species in which competing ferromagnetic and antiferromagnetic interactions in combination with magnetic anisotropy can give rise to slow relaxation of the magnetisation and quantum effects, i.e. Single-Molecule Magnets (SMMs).[3] Applied synthetic approaches to nanoscopic molecular species include self-assembly approaches, hydrolysis or condensation reactions in the presence of suitable ligands, redox-mediated aggregate formations or reactions of phosphonate ligands with preformed Mn complexes in the presence of different bases.[2c,4] Although the structural chemistry of organoarsonates and phosphonates is generally expected to be similar, the coordination chemistry of the former is less investigated and their capacity as complexing agents has not yet been fully explored.[5] To date, Mn/organoarsonate-based SMMs or larger complexes[6] have not yet been reported, thus, studies are required to understand the chemistry of this ligand system.

We previously developed supramolecular approaches to mixed-valent Mn/phosphonate oxo-clusters whereby halide ions allowed

us to direct the assembly of distinct building units that form upon comproportionation between $MnCl_2$ and $KMnO_4$.[7] These assembly processes using Cl^- ions as structure-influencing agents are comparable to template effects observed in polyoxometalate chemistry, i.e. processes that result in nanoscopic polyoxovanadate Keplerates in which Archimedean $V^{IV/V}$ polyhedra incorporate Platonic halide templates.[8] This interest in template syntheses, prompted us to explore the possibility of developing cation-assisted syntheses of large polynuclear species. The motivation was provided by studies, which demonstrate that cation-induced wheel structures can be used for the synthesis of rotaxanes that allow the investigation of tunnelling effects or point towards applications as qubits for quantum information processing devices (QIP).[9]

To pursue these objectives we modified previously developed synthetic approaches and increased in comproportionation reactions between $KMnO_4$ and $MnCl_2$ the oxidant/Cl^- ratio. Furthermore, we introduced dipicolinic acid as a potential co-ligand. The latter is a good chelating ligand whose donor atoms preferentially occupy meridional binding sites in octahedral complexes; this binding behaviour was expected to limit 3D hydrolytic growth reactions or the formation of extended 2D/3D phosphonate/arsonate precipitates thus increasing the propensity to obtain 0D oxo/hydroxo species.[10] The approach resulted in two toroidal, high-nuclearity coordination complexes: the {Mn_8} complex in $[K(H_2O)_2 \subset Mn^{III}_8(\mu\text{-OH})_2(CH_3OH)_2(PhAsO_3)_4(PhAsO_3H)_6$ $(dipic)_4]Cl \cdot 18H_2O \cdot 4CH_3OH$ (1) and the {Mn_{24}} species in $(H_3O)_4[K_2(H_2O)_2 \subset Mn_{24}(\mu_3\text{-O})_4(\mu\text{-OH})_4(\mu\text{-CH}_3O)_4(H_2O)_8(PhPO_3)_{20}$ $(dipic)_{12}][Mn(H_2O)_6] \cdot solv$ (2) which both assemble around stabilising K^+ ions. The latter represents one of the largest wheel-shaped Mn-oxo complexes; {Mn_8} is a rare example of a polynuclear arsonate-stabilised Mn species. The closely related reaction conditions of both systems provide comparative insights into the coordination behaviour of homologous organoarsonate and phosphonates.

1 crystallises in the monoclinic space group $C2/c$ and represents an octanuclear Mn^{III} complex that assembles around a central, hydrated K^+ ion (Fig. 1). **1** is stabilised by ten partially deprotonated organoarsonate ligands, four dipicolinate ligands, two μ-OH$^-$ ligands and two coordinating methanol molecules. The core consists of two symmetry-related bent tetranuclear units with a C_2 symmetry axis coinciding with the atom positions of the central K^+ ion. Each symmetry-independent tetranuclear unit consists of four Mn ions

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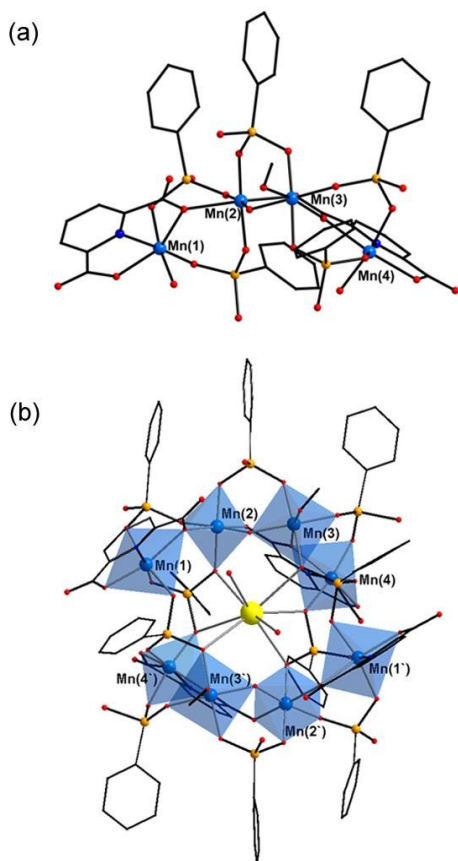
(a)

(b)

Fig. 1 Structure of the octanuclear Mn complex **1**; (a) symmetry-independent unit; (b) polyhedral representation of the complex; Colour code: Mn blue, As orange, K yellow, N blue, C black. All H atoms have been omitted for clarity.

connected through five organoarsonate and two dipicolinate ligands (ESI). All the Mn ions in **1** adopt distorted octahedral coordination geometries and each ion resides in the oxidation state +III as confirmed by bond valence sum (BVS) analyses and consistent with their Jahn-Teller distorted geometries.[11] The distorted nature of the coordination geometries of the Mn ions mainly arises from the geometrical restrictions of the binding dipicolinate ligands. Within the bent, tetranuclear subunits, the Mn coordination polyhedra share common vertices whereby the common O donors are provided by a μ-OH$^{⬚}$ and two dipicolinate ligands. Each tetranuclear unit consists of three outer bridging PhAsO$_3$H$^{⬚}$ and two inner bridging PhAsO$_3$$^{⬚}$ ligands which adopt bidentate μ-η^1:η^1:η^0 bridging modes. In the solid state, the {Mn$_8$} complexes are linked by weak H-bonds involving the constitutional solvent molecules and the O atoms of the arsonate and dipicolinate ligands. In the direction of the crystallographic *b*-axis, the ring structures stack on top of each other to form 1D tubular channels (ESI). It should be noted that in **1**, a K$^+$ ion stabilises the ring structure whereas in the previously reported {Mn$_{13}$} derivatives, Cl$^-$ ions act as structure directing agents.[7] The reason for this modified reaction behaviour can be attributed to the increased relative quantities of the KMnO$_4$. Contrarily, in the absence of the oxidant, no isolable product was obtained. **1** joins the small class of molecular Mn arsonates and is to the best of our knowledge the highest nuclearity Mn-arsonate complex reported to date.

2 forms when phenyl arsonic acid, that afforded the formation of **1**, is substituted by the corresponding phenyl phosphonic acid in the reaction mixture. **2** crystallises in the space group *Pnn*2. The tetraicosanuclear complex in **2** (Fig. 2) consists of two bent symmetry-equivalent {Mn$_{12}$} units which are linked to each other through donor atoms of four phosphonate functionalities. The {Mn$_{12}$} units can formally be sub-divided into two {Mn$_6$} units that are linked through O atoms of two phosphonate functionalities, which double-bridge the two subunits to form the {Mn$_{12}$} moiety (ESI). Within each {Mn$_6$} subunit, the six Mn ions are connected through five fully deprotonated PhPO$_3$$^{2-}$, three dipicolinate ligands, one μ-OH$^{⬚}$, one μ_3-O$^{2⬚}$ and one μ-CH$_3$O$^{⬚}$ ligands. The PhPO$_3$$^{2⬚}$ ligands adopt either μ_3-η^1:η^1:η^1 or μ-η^1:η^1:η^0 bridging modes. The coordination cluster in **2** can be considered as a wheel/cage with two crystallographically independent K$^+$ ions located at the centre. One K$^+$ ion is coordinated to six phosphonate O atoms and two H$_2$O molecules, whilst the second K$^+$ ion, is exclusively coordinated to phosphonate O donor atoms. It is noteworthy that with the exception of two phosphonate ligands, all the O-donor atoms of the remaining 18 phosphonate ligands are involved in bonding to Mn or K$^+$ centres (Fig. 2). The oxidation states of the Mn centres in **2** were assessed by BVS analysis (ESI) and structural analysis considering the degree of protonation of the O-donor ligands and the coordination geometries of the Mn centres. Whilst the BVS values are slightly high, the magnetic susceptibility data suggests that all 24 Mn centres in the cluster core of **2** adopt the oxidation state +III (see below).

The packing arrangement in **2** is stabilised by H-bonding interactions involving the O atoms of the ligands and constitutional solvent molecules. This arrangement creates cavities occupied by large quantities of lattice solvent molecules, and isolated [Mn^{II}(H$_2$O)$_6$]$^{2+}$ complexes. The large cavities may contain further charge-balancing hydronium ions, which have previously been observed to form in similar protic reaction systems.[12] In the direction of the crystallographic *c*-axis, the {Mn$_{24}$} complexes pack to form an assembly in which the {Mn$_{24}$} cores are separated by the organic ligands and constitutional water molecules, Fig. 2. To account for the diffuse electron density due to the large quantity of solvent molecules, we applied the Platon routine SQUEEZE during the crystallographic refinement (accounted for 1441 electrons/unit cell; void volume 4941.5 e/Å^3). The significant solvent content is further reflected in the thermogravimetric analysis (ESI).

The {Mn$_{24}$} complex in **2** joins the family of molecular Mn phosphonate species,[2c,4,13] and may also be discussed in the context of other larger wheel-shaped complexes.[14] It further relates to the largest previously reported Mn phosphonate species, {Mn$_{18}$},[15] {Mn$_{19}$},[16] {Mn$_{20}$},[17] {Mn$_{22}$}[18] or other recently or previously phosphonate species.[2c,4] The distinctive differences of the here reported {Mn$_{24}$} complex arise from the influencing role of the *mer*-coordinating dipicolinates and the K$^+$ ions. The latter direct the subunits into a wheel structure. This cation-effect further distinguishes the present reaction system from previously investigated Mn/phosphonate systems in which lower relative KMnO$_4$:MnCl$_2$ mole ratios give rise to Cl$^-$ influenced assembly processes. In these systems, the halide ions act as {Mn$_4$} capping ligands located in Jahn-Teller sites at the periphery of the final complex.[7] It is noteworthy that related polyoxovanadate/
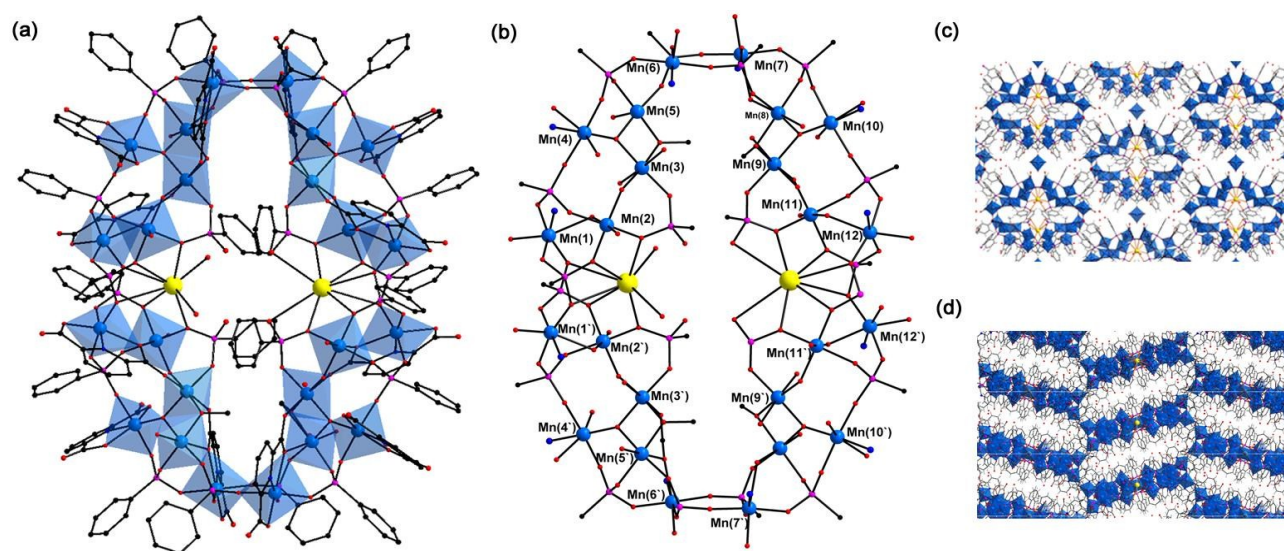
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Fig. 2 (a) and (b) Polyhedral and ball-stick representation of the {Mn$_{24}$} complex in **2**. (c) and (d) Packing arrangement of **2** viewed in the direction of the crystallographic *b*- and *c*-axes, respectively. Colour code: Mn blue, N dark blue. C black, P pink, K yellow, O red (All H-atoms have been omitted for clarity).

phosphonate systems incorporate {V$_4$}-stabilising halide templates in their cavities (see schematic in ESI).[8]

To our knowledge, there has not been any report that describes the reactivity of organoarsonates and -phosphonates in identical Mn-based systems. Thus, the comparable conditions that led to the formation of **1** and **2** provide some insights into the reactivity of the homologous ligands. Although their binding behaviour is generally expected to be closely comparable, the larger ionic radius of As^V compared to P^V can lead to structural differences.[5] Moreover, their reactivities in protic solvents are significantly influenced by their varying acid strengths, whereby the *p*K$_a$ values of PhAsO$_3$H$_2$ (3.39 and 8.25) are significantly higher than those of PhPO$_3$H$_2$ (1.86 and 7.51).[19] Indeed the structural differences observed in **1** and **2** can be attributed to the degree of protonation of the arsonate and phosphonate ligands. The 20 fully deprotonated phosphonates in **2** increase the connectivities between the Mn centres and facilitate μ_3-η^1:η^1:η^1 bridging modes. A larger relative number of arsonate moieties in **1** remain partially protonated and their coordination mode is restricted to bidentate μ-η^1:η^1:η^0 binding. Similar structural effects can also be observed in other transition metal arsonate systems where the lower *p*K$_a$ values of the phosphonic acids result in 3D MOFs[20] whilst protonated arsonates give rise to lower-dimensional 1D polymers or 2D structures.[5]

Magnetic properties of **1** and **2** were studied at 1000 Oe between 1.8 and 300 K (Fig. 3). At room temperature, the χT product of **1** reaches *ca.* 24.3 cm^3 K mol^{-1}, which is in good agreement with the presence of 8 high-spin Mn^{III} magnetic sites (*S* = 2, *C* = 3 cm^3 K mol^{-1}, *g* = 2). On decreasing the temperature, the χT product decreases slowly to 22.6 cm^3 K mol^{-1} at 100 K and then sharply to 5.9 cm^3 K mol^{-1} at 1.85 K. This thermal dependence reveals the presence of dominating antiferromagnetic interactions, between the Mn centres in **1** (Curie-Weiss fit of the data shown in Fig. 3 leads to *C* = 25.3 cm^3 K mol^{-1} and θ = -12 K). Moreover, the field dependences of the magnetisation below 8 K (Fig. S3) show that the magnetisation of **1** does not saturate even at 1.9 K and 7 T reaching a low value of 14.5 μ_B. In agreement with

the χT vs. *T* data, this behaviour is the direct consequence of the weak antiferromagnetic interactions, which induces low lying excited states that may be populated under an applied dc field. Moreover, it is likely that the observed *M* vs. *H* behaviour is also influenced by a substantial intrinsic magnetic anisotropy of the Mn^{III} ions.

Preliminary studies of the magnetic properties of **2** shown in Fig. 3 reveal a room temperature χT product of *ca.* 77.3 cm^3 K mol^{-1} in agreement with the calculated value of 76.4 cm^3 K mol^{-1} for 24 *S* = 2 Mn^{III} and one *S* = 5/2 Mn^{II} magnetic centers. With decreasing the temperature, the χT product decreases to 70.2 cm^3 K mol^{-1} at 30 K and then to 36.5 cm^3 K mol^{-1} at 1.9 K indicating the presence of dominating antiferromagnetic interactions in **2** (Curie-Weiss fit leads to *C* = 77.6 cm^3 K mol^{-1} and θ = -2.8 K). As for **1**, the magnetisation of **2** does not saturate in the investigated regime (reaching 75.6 μ_B at 1.9 K and 7 T) as expected in presence of weak antiferromagnetic interactions/low lying excited states and significant magnetic anisotropy (ESI).

In summary, we have conducted a comparative study using phenylarsonate and -phosphonate ligands to stabilize high-nuclearity {Mn$_8$} (**1**) and {Mn$_{24}$} (**2**) complexes. Their assembly is influenced by the binding mode of dipicolinate co-ligands and
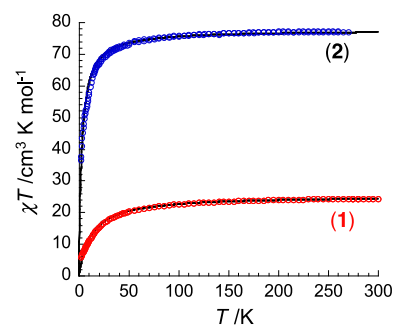

Fig. 3 Temperature-dependence of the χT product for the coordination compound cotaining the polynuclear complexes **1** (red symbols) and **2** (blue symbols) at 1000 Oe (χ is defined as molar magnetic susceptibility equal to *M*/*H*). The black lines are the fits discussed in the text.

central K^+ ions to produce toroidal structures. The structural differences between **1** and **2** reflect the different pK_a values of the organoarsonate and -phosphonate ligands, whereby fully deprotonated phosphonates have a high propensity to bridge between Mn centres and resulting in a higher nuclearity species. The results can be viewed in the context of other Mn and V phosphonate systems and provide insights into the underlying assembly-processes. The reported synthesis may provide a new approach to the cation-assisted synthesis of polynuclear Mn-based complexes which may assemble around various different inorganic or organic cations.

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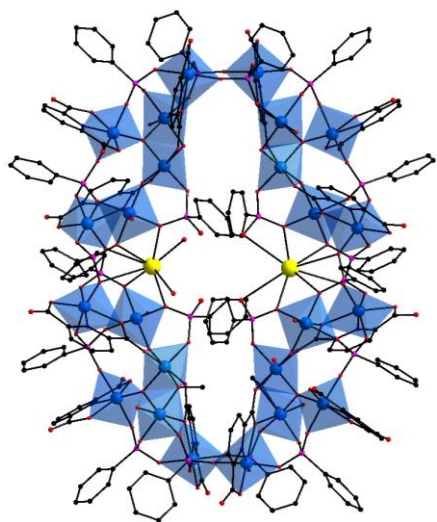
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The use of arsonate or phosphonate ligands in related reaction systems afforded the K^+-assisted assembly of high nuclearity {Mn_8} arsonate and {Mn_{24}} phosphonate complexes.