

## Structure, Magnetism, and Ionic Conductivity of the Gigantic $\{\text{Mo}_{176}\}$ -Wheel Assembly: $\text{Na}_{15}\text{Fe}_3\text{Co}_{16}[\text{Mo}_{176}\text{O}_{528}\text{H}_3(\text{H}_2\text{O})_{80}]\text{Cl}_{27} \cdot 450\text{H}_2\text{O}$

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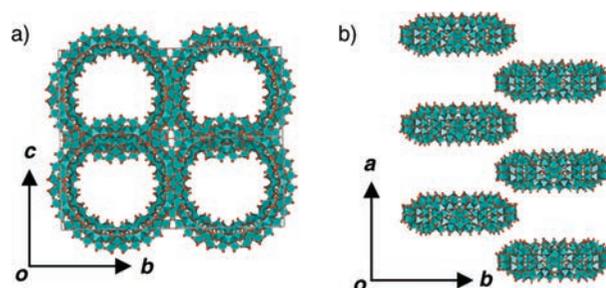
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Ever since the synthesis and structure of the gigantic polyoxomolybdate (POM) wheel of  $(\text{NH}_4)_{25} \pm 5[\text{Mo}_{154}\text{O}_{420}(\text{NO})_{14}(\text{OH})_{28}(\text{H}_2\text{O})_{70}] \cdot 350\text{H}_2\text{O}$  was unveiled by Müller et al.<sup>1</sup> in 1995, the race has been on to structurally characterize and exploit these gigantic molecular oxide systems to develop new types of nanostructured functional materials. Herein we outline a new approach to build upon the  $\{\text{Mo}_{176}\}$ -based wheel structure type:  $\text{Li}_{20}[\text{Mo}_{176}\text{O}_{528}\text{H}_{32}(\text{H}_2\text{O})_{80}]\text{Cl}_{20} \cdot 400\text{H}_2\text{O}$  (**1a**) and  $\text{Na}_{16}[\text{Mo}_{176}\text{O}_{528}\text{H}_{16}(\text{CH}_3\text{OH})_{17}(\text{H}_2\text{O})_{63}] \cdot 600\text{H}_2\text{O} \cdot 30\text{CH}_3\text{OH}$  (**1b**) to explore the ionic conductivity of these systems.<sup>2</sup> Among the structurally identified wheels to date, the  $[\text{Mo}_{176}\text{O}_{528}\text{H}_{16}(\text{H}_2\text{O})_{80}]^{16-}$  ( $\{\text{Mo}_{176}\}$ ) archetype is the largest<sup>3,4</sup> with an outer/inner diameter of 4.1/2.3 nm and is 1.3 nm thick.<sup>2</sup> The discovery of these clusters was paradigm shifting not only due to their nanostructure, associated cations, and extensive solvation but also due to their interesting electronic properties.<sup>3,4</sup>

Herein we report the crystal structure and physical properties (magnetic and ionic conductivity) of a new gigantic  $\{\text{Mo}_{176}\}$ -wheel containing  $\text{Co}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  ions as the external charge balancing counter cations in addition to Na cations. This nanostructured cluster-based material was simply prepared by the acidification of a suspension of  $\text{Na}_{0.4}\text{Co}_{0.8}(\text{MoO}_4) \cdot 1.5\text{H}_2\text{O}$  (**2**) with aqueous 0.5 M HCl utilizing iron powder as the reducing agent. The chemical composition of the new nanostructured material was investigated using inductively coupled plasma mass spectroscopy (ICP-MS), which revealed the presence of the Na, Cl, Fe, Co, and Mo. Using the elemental analysis, TGA, and X-ray structural analysis as a basis (including BVS analysis), a preliminary formula for the compound can be suggested as follows:  $\text{Na}_{15}\text{Fe}_3\text{Co}_{16}[\text{Mo}_{176}\text{O}_{528}\text{H}_3(\text{H}_2\text{O})_{80}]\text{Cl}_{27} \cdot 450\text{H}_2\text{O}$  (**3**). Although this is tentative with respect to the degree of protonation, the only assumption we had to make was the number of reduced  $\text{Mo}^{\text{V}}$  centers, which was possible by comparison to the seminal work of Müller.<sup>3</sup> This is because accurate REDOX titrations were not possible in this case due to interference from the  $\text{Co}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$ -based counter cations present in **3**.

Crystal data were collected using synchrotron X-ray radiation (KEK) at 150 K (703 242 reflections measured)<sup>5</sup> for **3** which is monoclinic  $P2_1/m$  with a unit cell volume of 55 785(4) Å<sup>3</sup>. Although the structural refinements of the  $\{\text{Mo}_{176}\}$ -wheel were possible with anisotropic thermal factors assigned to the framework atom positions, the direct assignment of the  $\text{Co}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}$  molecules was difficult to achieve from the differential Fourier analysis of the residual electron densities. Specifically, structural



**Figure 1.** Packing structures of  $\{\text{Mo}_{176}\}$ -wheels (a) viewed along the  $a$ -axis and (b) viewed along the  $c$ -axis of **3**.

analysis reveals that a half unit of  $\{\text{Mo}_{176}\}$ -wheel is found to be the asymmetric unit of **3** and the positional disorder associated with the  $\{\text{Mo}\}_2$ -dimer sites is confirmed; eight  $\{\text{Mo}_8\}$  units comprised of two  $(\text{MoO}_6)$  and a central pentagon of  $\{\text{Mo}(\text{Mo})_5\}$  were connected by the disordered inner  $\{\text{Mo}_2\}$ -dimer units via edge-sharing  $\text{Mo}-\text{O}-\text{Mo}$  bonds. Overall, the main structure of the  $\{\text{Mo}_{176}\}$ -wheel in **3** is consistent with previously determined data sets.<sup>3,4</sup> Since the synthetic process for the assembly of **3** involves the partial reduction of **2** in HCl, with iron powder as a reducing agent, the heterometal counterions are introduced in one step without need for cation exchange reactions. As such, the assembly condensation process appears preferentially to yield the  $\{\text{Mo}_{176}\}$ -wheels.

Figure 1a shows the packing structure of  $\{\text{Mo}_{176}\}$ -wheels viewed along the  $a$ -axis where the  $\{\text{Mo}_{176}\}$ -wheels were overlapped with respect to each other, forming an interdigitated molecular arrangement within the  $bc$ -plane. Since the presence of  $\text{Mo}-\text{O}-\text{Mo}$  bonded interactions between the wheels is not observed, the discrete nature of the gigantic  $\{\text{Mo}_{176}\}$ -wheel arrangements is a possibility. Further, the channels are elongated along the  $a$ -axis, being filled with  $\text{Na}^+$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}$  molecules. However, it could be postulated that the disordered structures surrounding the rigid  $\{\text{Mo}_{176}\}$ -wheel framework could provide liquid-like environments for ionic conduction, and certainly the high level of hydration for these clusters is comparable to that of proteins.

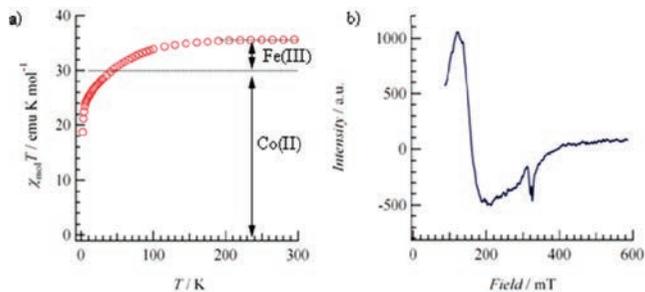
The electronic spectrum of **3**, obtained from a pressed in KBr pellet, shows two broad absorption maxima at  $9.0 \times 10^3$  and  $13.2 \times 10^3 \text{ cm}^{-1}$ , which are consistent with those of mixed-valence **1a** and **1b**.<sup>1-3</sup> Although the diamagnetic properties of **1a** and **1b** have been confirmed by temperature dependent magnetic susceptibility studies, conversely paramagnetic behavior with weak antiferromagnetic interactions was observed in **3** (Figure 2a). The  $\chi_{\text{mol}}T$  of **3** at higher temperatures ( $T > 100 \text{ K}$ ) gave a value of 35.7 emu K  $\text{mol}^{-1}$ , which is consistent with the incorporation of the  $\text{Co}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  into the compound. Further, the magnetic exchange interaction

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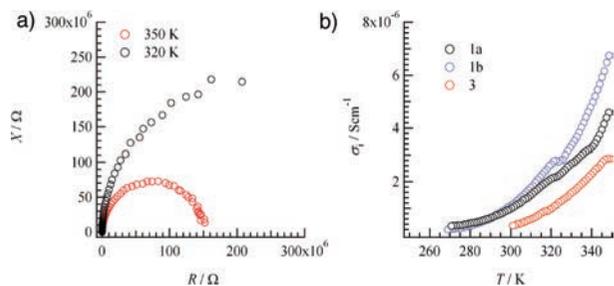
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**Figure 2.** Magnetic properties of **3**. (a) Temperature dependent magnetic susceptibilities of **3** ( $\chi_{\text{mol}}T$ – $T$  plots). (b) X-band ESR spectrum of **3** at 3.8 K.



**Figure 3.** Ionic conductivities of **1a**, **1b**, and **3**. (a) Resistance ( $R$ )–reactance ( $X$ ) plots of **3** at 350 and 320 K. (b) Temperature dependent  $\sigma_i$  of **1a**, **1b**, and **3**. The plots were obtained in the cooling process from 350 K. The conductivities were measured along the stacking direction of  $\{\text{Mo}_{176}\}$ -wheels using a single crystal with gold paste and wires.

between the  $\text{Co}^{\text{II}}$  and/or  $\text{Fe}^{\text{III}}$  ions is significantly weak from the small Weiss temperature  $-0.11$  K ( $T < 100$  K). The paramagnetic behavior of **3**, therefore, is dominated by the  $\text{Co}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  ions due to the diamagnetic properties of the  $\{\text{Mo}_{176}\}$ -wheel.

Although both high- ( $S = 3/2$ ) and low-spin ( $S = 1/2$ ) states are naturally possible for  $\text{Co}^{\text{II}}$ ,<sup>6,7</sup> electron spin resonance (ESR) studies of **3** at 3.8 K (Figure 2b) indicated that the ions are present exclusively in the high-spin configuration.<sup>8</sup> Further, the magnetic data are consistent for tetrahedral or octahedral geometries. As such, the 16 high-spin  $\text{Co}^{\text{II}}$  ions correspond to a  $\chi_{\text{mol}}T$  value of *ca.* 30  $\text{emu K mol}^{-1}$ , whereas free  $\text{Fe}^{\text{III}}$  ions in an acidic coordination environment usually form tetrahedral  $\text{FeCl}_4$  complexes. Also, high-spin  $\text{Co}^{\text{II}}$  complexes such as  $\text{CoCl}_4$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Co}(\text{H}_2\text{O})_6$  could also coexist with  $\text{FeCl}_4$ . Since the  $\chi_{\text{mol}}T$  of the  $\text{FeCl}_4$  ion was close to that of the free ion ( $1.26$   $\text{emu K mol}^{-1}$ ), the sum of the 16  $\text{Co}^{\text{II}}$  with the  $S = 3/2$  and three  $\text{Fe}^{\text{III}}$  with the  $S = 5/2$  corresponds to the  $\chi_{\text{mol}}T$  value of **3** of  $35.7$   $\text{emu K mol}^{-1}$  and this value is consistent with the assignment of 16 Co and 3 Fe ions in the formula of **3**.

The ionic conductivity ( $\sigma_i$ ) of a single crystal of compounds **1a**, **2b**, and **3** was evaluated by impedance measurements (Figure 3) along the  $a$ -axis. The resistance ( $R$ )–reactance ( $X$ ) plots of **3** revealed the temperature dependent semicircle traces (Figure 3a), which were consistent with the typical ionic conductors.<sup>9,10</sup> Also, a large hysteresis for the temperature interval was observed due to the changes of the water contents in the single crystal under study and the  $\sigma_i$  was measured in the cooling processes from 350 to 270 K. The weight loss at 350 K was  $\sim 20\%$  from the TG data, which corresponds to the desorption of *ca.* 300  $\text{H}_2\text{O}$  molecules, and the

$\sigma_i$  of **1a**, **1b**, and **3** at 300 K were  $1.0 \times 10^{-6}$ ,  $1.1 \times 10^{-6}$ , and  $0.3 \times 10^{-6}$   $\text{S cm}^{-1}$ , respectively. The  $\sigma_i$  value of **3** was lower than those of **1a** and **1b**, and the activation energy ( $E_a$ ) of **1a**, **1b**, and **3** were 0.33, 0.40, and 0.43 eV, respectively, suggesting that the ionic conductivity of **3** was lower than those of **1a** and **1b**. Since the possible conduction carriers present in **1a** and **1b** are  $\text{H}^+$ ,  $\text{Li}^+$ , and/or  $\text{Na}^+$ , while in **3** they  $\text{H}^+$  or  $\text{Na}^+$  ions, it could be postulated therefore that the liquid-like disordered environments surrounded by the rigid  $\{\text{Mo}_{176}\}$ -wheels are essential to achieve solid state ionic conduction. As such, the presence of  $\text{Co}^{\text{II}}$ - and  $\text{Fe}^{\text{III}}$ -based coordination compounds in the void space decreases the carrier mobility in **3** relative to compounds **1a** and **1b**.

In conclusion, the dehydration condensation of  $\text{Na}_{0.4}\text{Co}_{0.8}(\text{MoO}_4) \cdot 1.5\text{H}_2\text{O}$  using iron powder as a reducing agent yielded single crystals of  $\text{Na}_{15}\text{Fe}_3\text{Co}_{16}[\text{Mo}_{176}\text{O}_{528}\text{H}_3(\text{H}_2\text{O})_{80}]\text{Cl}_{27} \cdot 450\text{H}_2\text{O}$ . The  $\text{Co}^{\text{II}}$  ion with a spin state of high-spin  $S = 3/2$  was introduced into the single crystals of  $\{\text{Mo}_{176}\}$ -wheel assembly spectator counter cations. The ionic conductivity of a single crystal at 300 K was  $3 \times 10^{-7}$   $\text{S cm}^{-1}$  with an activation energy of 0.43 eV; the ionic conduction pathway was constructed from the rigid framework of the  $\{\text{Mo}_{176}\}$ -wheels filled with disordered  $\text{Na}^+$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}$  species. In further work we will aim to exploit this new found conductivity phenomenon and attempt to engineer polyoxometalate-based structures with tunable conductivities, e.g., by the design of intrinsically magnetic gigantic POM.

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**Supporting Information Available:** The atomic numbering scheme of  $\{\text{Mo}_{176}\}$ -wheel, UV–vis–NIR–IR spectra, TG diagram, and  $M$ – $H$  curve at 2 K. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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