

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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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.¹ 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.² 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^{3,4} with an outer/inner diameter of 4.1/2.3 nm and is 1.3 nm thick.² 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.^{3,4}

Herein we report the crystal structure and physical properties (magnetic and ionic conductivity) of a new gigantic $\{\text{Mo}_{176}\}$ -wheel containing Co^{II} and Fe^{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 Mo^{V} centers, which was possible by comparison to the seminal work of Müller.³ This is because accurate REDOX titrations were not possible in this case due to interference from the Co^{II} and Fe^{III} -based counter cations present in **3**.

Crystal data were collected using synchrotron X-ray radiation (KEK) at 150 K (703 242 reflections measured)⁵ for **3** which is monoclinic $P2_1/m$ with a unit cell volume of 55 785(4) Å³. 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 Co^{II} , Fe^{III} , Na^+ , Cl^- , and H_2O molecules was difficult to achieve from the differential Fourier analysis of the residual electron densities. Specifically, structural

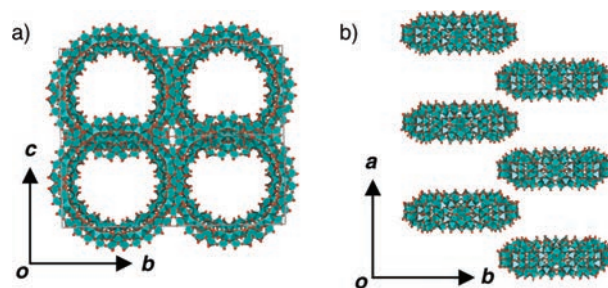


Figure 1. Packing structures of $\{\text{Mo}_{176}\}$ -wheels (a) viewed along the a -axis and (b) viewed along the c -axis of **3**.

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 (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.^{3,4} 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 Na^+ , Fe^{III} , Co^{II} , Cl^- , and H_2O 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 9.0×10^3 and $13.2 \times 10^3 \text{ cm}^{-1}$, which are consistent with those of mixed-valence **1a** and **1b**.¹⁻³ 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 mol^{-1} , which is consistent with the incorporation of the Co^{II} and Fe^{III} into the compound. Further, the magnetic exchange interaction

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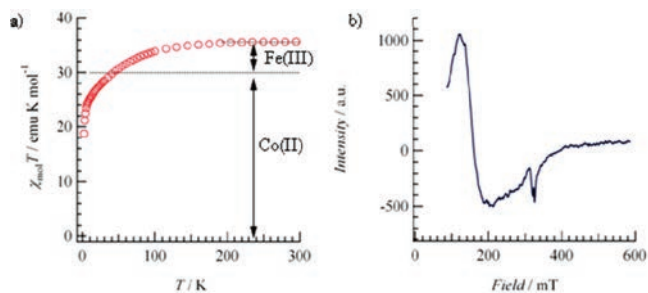


Figure 2. Magnetic properties of **3**. (a) Temperature dependent magnetic susceptibilities of **3** ($\chi_{\text{mol}}T$ – T plots). (b) X-band ESR spectrum of **3** at 3.8 K.

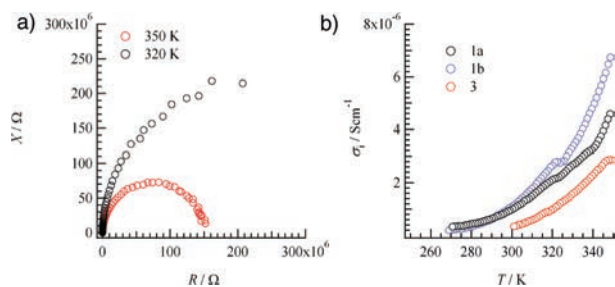


Figure 3. Ionic conductivities of **1a**, **1b**, and **3**. (a) Resistance (R)–reactance (X) plots of **3** at 350 and 320 K. (b) Temperature dependent σ_i of **1a**, **1b**, and **3**. The plots were obtained in the cooling process from 350 K. The conductivities were measured along the stacking direction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

between the Co^{II} and/or Fe^{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 Co^{II} and Fe^{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 Co^{II} ,^{6,7} 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.⁸ Further, the magnetic data are consistent for tetrahedral or octahedral geometries. As such, the 16 high-spin Co^{II} ions correspond to a $\chi_{\text{mol}}T$ value of *ca.* 30 emu K mol^{-1} , whereas free Fe^{III} ions in an acidic coordination environment usually form tetrahedral FeCl_4 complexes. Also, high-spin Co^{II} complexes such as 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 FeCl_4 . Since the $\chi_{\text{mol}}T$ of the FeCl_4 ion was close to that of the free ion (1.26 emu K mol^{-1}), the sum of the 16 Co^{II} with the $S = 3/2$ and three Fe^{III} with the $S = 5/2$ corresponds to the $\chi_{\text{mol}}T$ value of **3** of 35.7 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 (σ_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.^{9,10} 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 σ_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 H_2O molecules, and the

σ_i of **1a**, **1b**, and **3** at 300 K were 1.0×10^{-6} , 1.1×10^{-6} , and 0.3×10^{-6} S cm^{-1} , respectively. The σ_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 H^+ , Li^+ , and/or Na^+ , while in **3** they H^+ or 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 Co^{II} - and Fe^{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 Co^{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 3×10^{-7} 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 Na^+ , Fe^{III} , Co^{II} , Cl^- , and H_2O 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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