Ever since the synthesis and structure of the gigantic polyoxomolybdate (POM) wheel of $\left(\text{NH}_4\right)_{25}\text{Mo}_{176}\text{O}_{528}\text{H}_{16}\left(\text{H}_2\text{O}\right)_{80}$ was unveiled by Müller et al.\textsuperscript{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 with aqueous 0.5 M HCl utilizing iron powder as the reducing agent. The chemical composition of the new nanosctructured material was simply prepared by condensation process appears preferentially to yield the $\text{Mo}_{176}$-wheel in which is comparable to that of proteins. 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 introduce 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 Mo–O–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\textsuperscript{+}, Fe\textsuperscript{III}, Cl\textsuperscript{-}, 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 × 10$^3$ and 13.2 × 10$^3$ cm\textsuperscript{-1}, which are consistent with those of mixed-valence 1a and 1b.\textsuperscript{3,4} Although the diatomic 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 $\chi_{\text{iso}}T$ of 3 at higher temperatures ($T > 100$ K) gave a value of 35.7 emu K mol\textsuperscript{-1}, which is consistent with the incorporation of the Co\textsuperscript{II} and Fe\textsuperscript{III} into the compound. Further, the magnetic exchange interaction

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emu K mol$^{-1}$ corresponds to the desorption of $K$. The weight loss at 350 K was $\sim 20\%$ from the TG data, which corresponds to the desorption of $ca. 300$ H$_2$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 $0.3 \times 10^{-6}$ 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 $H^+$, $Li^+$, 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 {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 Na$_{0.6}$Co$_{0.4}$Mo$_6O$_{18}$·$1.5$H$_2$O using iron powder as a reducing agent yielded single crystals of Na$_{15}$Fe$_3$Co$_{16}$[Mo$_{176}$O$_{528}$H$_3$(H$_2$O)$_{80}$]Cl$_{27}$$\cdot$45OH$_2$O. The Co$^i$ ion with a spin state of high-spin $S = \frac{3}{2}$ was introduced into the single crystals of [Mo$_{176}$]-wheel assembly spectator counter cations. The ionic conductivity of a single crystal at 300 K was $3 \times 10^{-6}$ S cm$^{-1}$ with an activation energy of 0.43 eV; the ionic conduction pathway was constructed from the rigid framework of the [Mo$_{176}$]-wheels filled with disordered Na$^+$, Fe$^{III}$, Co$^{III}$, and H$_2$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 [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.

References


5. Crystal data: Monoclinic, P2$_1$/n, $a = 31.1199(1)$ Å, $b = 66.5281(6)$ Å, $c = 31.0020(1)$ Å, $\beta = 120.280(1)^\circ$, $\gamma$ = 118.085(5), $V$ = 55784.5(6) Å$^3$, $Z$ = 2. The structure was solved with the program SHELX-97 and refined using SHELX97 to $R = 0.0858$ for 108 942 reflections with $I > 2$os/$I$.


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