Structure, Magnetism, and Ionic Conductivity of the Gigantic \{Mo\textsubscript{176}\}-Wheel Assembly: Na\textsubscript{15}Fe\textsubscript{3}Co\textsubscript{16}[Mo\textsubscript{176}O\textsubscript{528}H\textsubscript{2}(H\textsubscript{2}O)\textsubscript{80}][Cl\textsubscript{127}•450H\textsubscript{2}O]

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Published on Web 09/04/2009

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Ever since the synthesis and structure of the gigantic polyoxomolybdate (POM) wheel of \((NH\textsubscript{4})\textsubscript{25}[(NO)\textsubscript{14}(OH)\textsubscript{28}(H\textsubscript{2}O)\textsubscript{70}]\cdot350H\textsubscript{2}O\) 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 \{Mo\textsubscript{176}\}-based wheel structure type: \(Li\textsubscript{20}[M\textsubscript{0}1\textsubscript{76}O\textsubscript{528}H\textsubscript{3}(H\textsubscript{2}O)\textsubscript{80}]Cl\textsubscript{127}•400H\textsubscript{2}O\) (a) and \(Na\textsubscript{16}[M\textsubscript{0}1\textsubscript{76}O\textsubscript{228}H\textsubscript{16}(CH\textsubscript{3}OH)\textsubscript{17}(H\textsubscript{2}O)\textsubscript{63}]•600H\textsubscript{2}O\cdot30CH\textsubscript{3}OH (b) to explore the ionic conductivity of these systems.\textsuperscript{2} Among the structurally identified wheels to date, the \(Na\textsubscript{16}[Mo\textsubscript{0}1\textsubscript{76}O\textsubscript{228}H\textsubscript{16}(CH\textsubscript{3}OH)\textsubscript{17}(H\textsubscript{2}O)\textsubscript{63}]•600H\textsubscript{2}O\cdot30CH\textsubscript{3}OH\) archetype is the largest\textsuperscript{3,4} with an outer/inner diameter of 4.1/2.3 nm and is 1.3 nm thick.\textsuperscript{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.\textsuperscript{3,4}

Herein we report the crystal structure and physical properties (magnetic and ionic conductivity) of a new gigantic \(\{Mo\textsubscript{0}1\textsubscript{76}\}\)-wheel containing \(Co\textsuperscript{II}\) and \(Fe\textsuperscript{III}\) ions as the external charges balancing counter cations in addition to Na cations. This nanostructured cluster-based material was simply prepared by the acidification of a suspension of \(Na\textsubscript{0.4}Co\textsubscript{0.8}(Mo\textsubscript{O}4)\) 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 spectrometry (ICP-M.S), 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: \(Na\textsubscript{15}Fe\textsubscript{3}Co\textsubscript{16}[Mo\textsubscript{176}O\textsubscript{528}H\textsubscript{2}(H\textsubscript{2}O)\textsubscript{80}][Cl\textsubscript{127}•450H\textsubscript{2}O (3)\). Although this is tentative with respect to the degree of protonation, the only assumption we had to make was the number of reduced \(Mo^{VI}\) centers, which was possible by comparison to the seminal work of Müller.\textsuperscript{3} This is because accurate REDOX titrations were not possible in this case due to interference from the \(Co\textsuperscript{II}\) and \(Fe\textsuperscript{III}\)-based counter cations present in 3.

Crystal data were collected using synchrotron X-ray radiation (KEK) at 150 K (703 242 reflections measured)\textsuperscript{5} for 3 which is monoclinic \(P2\textsubscript{1}/m\) with a unit cell volume of 55 785(4) Å\(^3\). Although the structural refinements of the \(\{Mo\textsubscript{0}1\textsubscript{76}\}\)-wheel were possible with anisotropic thermal factors assigned to the framework atom positions, the direct assignment of the \(Co\textsuperscript{II}\), \(Fe\textsuperscript{III}\), \(Na\textsuperscript{+}\), \(Cl\textsuperscript{-}\), and \(H\textsubscript{2}O\) molecules was difficult to achieve from the differential Fourier analysis of the residual electron densities. Specifically, structural

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Figure 1. Packing structures of \(\{Mo\textsubscript{0}1\textsubscript{76}\}\)-wheels (a) viewed along the a-axis and (b) viewed along the c-axis of 3.
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 {Mo$_{176}$}-wheel.

Although both high- ($S = \frac{3}{2}$) and low-spin ($S = \frac{1}{2}$) states are naturally possible for Co$^{II}$, the 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. Further, the magnetic data are consistent for tetrahedral or octahedral geometries. As such, the 16 high-spin Co$^{II}$ ions correspond to a $\chi_{MRT}$ 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$_4$, CoCl$_2$H$_2$O, and Co(H$_2$O)$_6$ could also coexist with FeCl$_4$. Since the $\chi_{MRT}$ of the Co$^{II}$ ion was close to that of the free ion (1.26 emu K mol$^{-1}$), the sum of the 16 Co$^{II}$ with the $S = \frac{3}{2}$ and three Fe$^{III}$ with the $S = \frac{1}{2}$ corresponds to the $\chi_{MRT}$ 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 ($\sigma_i$) 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. 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 ~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 $1.0 \times 10^{-8}$, $1.1 \times 10^{-6}$, and $0.3 \times 10^{-8}$ 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$_9$Co$_{28}$O$_{66}$(MoO$_4$)$_2$.1.5H$_2$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$_{27}$.45H$_2$O. The Co$^{II}$ ion with a spin state of high-spin $S = \frac{3}{2}$ was introduced into the single crystals of {Mo$_{176}$}-wheel as a counter cation. The ionic conductivity of a single crystal at 300 K was $3 \times 10^{-8}$ 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$^{II}$, Cl$^-$, 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 giant POM.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting Information Available: The atomic numbering scheme of {Mo$_{176}$}–wheel, UV–vis, NMR, 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$_1$/m, a = 31.1999(1), b = 66.5281(6), c = 31.0020(1), $\beta = 120.280(1)$, V = 55784.5(6), $\lambda$ = 12.32 Å, $\mu$ = 2. Z = 2. The structure was solved with the program SHELXL-97 and refined using SHELXLH-97 to R = 0.0858 for 108 942 reflections with $I > 2.0(I)$, R = 0.120 for all reflections.

J. AM. CHEM. SOC. • VOL. 131, NO. 38, 2009 13579