J|A|C|S
COMMUNICATIONS

Structure, Magnetism, and Ionic Conductivity of the Gigantic $\{Mo_{176}\}$-Wheel Assembly: $Na_{15}Fe_3Co_{16}[Mo_{176}O_{528}H_3(H_2O)_{80}]Cl_{27}\cdot 450H_2O$

Hiroyuki Imai,[†] Tomoyuki Akutagawa,*[,†,‡] Fumito Kudo,[‡] Mitsuhiro Ito,[§] Kazuhiro Toyoda,[‡]
Shin-ichiro Noro,[†,‡] Leroy Cronin,*[,||] and Takayoshi Nakamura*[,†,‡]

*Research Institute for Electronic Science, Hokkaido University, N20W10 kita-ku, Sapporo 001-0020, Japan,
Graduate School of Environmental Science, Hokkaido University, Japan, Venture Business Laboratory, Nagoya
Institute of Technology, Japan, WestCHEM, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.*

Received June 12, 2009; E-mail: takuta@es.hokudai.ac.jp; tnaka@es.hokudai.ac.jp; L.Cronin@chem.gla.ac.uk

Ever since the synthesis and structure of the gigantic polyoxomolybdate (POM) wheel of $(NH_4)_{25 \pm 5}[Mo_{154}O_{420}(NO)_{14}(OH)_{28}(H_2O)_{70}]\cdot 350H_2O$ 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 $\{Mo_{176}\}$-based wheel structure type: $Li_{20}[Mo_{176}O_{528}H_{32}(H_2O)_{80}]Cl_{20}\cdot 400H_2O$ (**1a**) and $Na_{16}[Mo_{176}O_{528}\ H_{16}(CH_3OH)_{17}(H_2O)_{63}]\cdot 600H_2O\cdot 30CH_3OH$ (**1b**) to explore the ionic conductivity of these systems.[2] Among the structurally identified wheels to date, the $[Mo_{176}O_{528}H_{16}(H_2O)_{80}]^{16-}$ ($\{Mo_{176}\}$) 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 $\{Mo_{176}\}$-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 $Na_{0.4}Co_{0.8}(MoO_4)\cdot 1.5H_2O$ (**2**) with aqueous 0.5 M HCl utilizing iron powder as the reducing agent. The chemical composition of the new nanosctructured 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: $Na_{15}Fe_3Co_{16}[Mo_{176}O_{528}H_3(H_2O)_{80}]Cl_{27}\cdot 450H_2O$ (**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) $Å^3$. Although the structural refinements of the $\{Mo_{176}\}$-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 analysis reveals that a half unit of $\{Mo_{176}\}$-wheel is found to be the asymmetric unit of **3** and the positional disorder associated with the $\{Mo\}_2$-dimer sites is confirmed; eight $\{Mo_8\}$ units comprised of two (MoO_6) and a central pentagon of $\{Mo(Mo)_5\}$ were connected by the disordered inner $\{Mo_2\}$-dimer units via edge-sharing Mo−O−Mo bonds. Overall, the main structure of the $\{Mo_{176}\}$-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 introduce in one step without need for cation exchange reactions. As such, the assembly condensation process appears preferentially to yield the $\{Mo_{176}\}$-wheels.

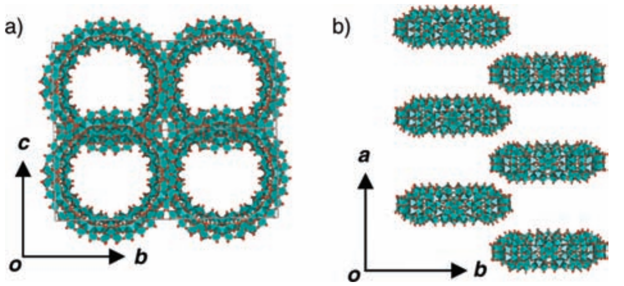

Figure 1. Packing structures of $\{Mo_{176}\}$-wheels (a) viewed along the *a*-axis and (b) viewed along the *c*-axis of **3**.

Figure 1a shows the packing structure of $\{Mo_{176}\}$-wheels viewed along the *a*-axis where the $\{Mo_{176}\}$-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 $\{Mo_{176}\}$-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 $\{Mo_{176}\}$-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 $13.2 \times 10^3\ cm^{-1}$, 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 $\chi_{mol}T$ of **3** at higher temperatures ($T > 100$ 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

---

[†] Research Institute for Electronic Science, Hokkaido University.
[‡] Graduate School of Environmental Science, Hokkaido University.
[§] Nagoya Institute of Technology.
[||] University of Glasgow.

10.1021/ja9048042 CCC: $40.75

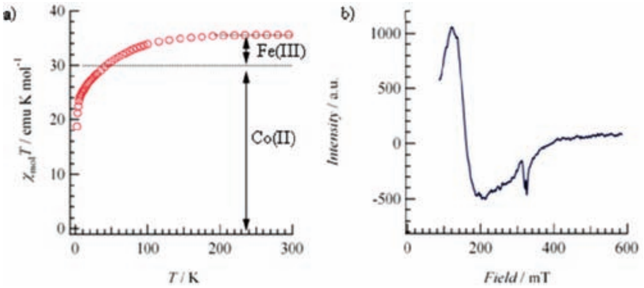

Figure 2. Magnetic properties of **3**. (a) Temperature dependent magnetic susceptibilities of **3** ($\chi_{mol}T-T$ plots). (b) X-band ESR spectrum of **3** at 3.8 K.

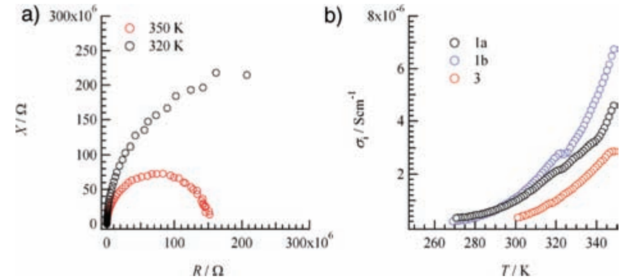

Figure 3. Ionic conductivities of **1a**, **1b**, and **3**. (a) Resistance (R)−reactance (X) plots of **3** at 350 and 320K. (b) Temperature dependent σ_i of **1a**, **1b**, and **3**. The plots were obtained in the cooling process from 350 K. The conductivities were measured along the stacking direction of $\{Mo_{176}\}$-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 $\{Mo_{176}\}$-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 $\chi_{mol}T$ 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 $CoCl_4$, $CoCl_2 \cdot 6H_2O$, and $Co(H_2O)_6$ could also coexist with $FeCl_4$. Since the $\chi_{mol}T$ 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 $\chi_{mol}T$ 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 ∼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 $\{Mo_{176}\}$-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 $Na_{0.4}Co_{0.8}(MoO_4) \cdot 1.5H_2O$ using iron powder as a reducing agent yielded single crystals of $Na_{15}Fe_3Co_{16}[Mo_{176}O_{528}H_3(H_2O)_{80}]Cl_{27} \cdot 450H_2O$. The Co^{II} ion with a spin state of high-spin $S = {}^3/_2$ 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 3×10^{-7} S cm^{-1} with an activation energy of 0.43 eV; the ionic conduction pathway was constructed from the rigid framework of the $\{Mo_{176}\}$-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.

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−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

(1) (a) Müller, A.; Krickemeyer, E.; Meyer, J.; Bögge, H.; Peters, F.; Plass, W.; Diemann, E.; Dillinger, S.; Nonnenbruch, F.; Randerath, M.; Menke, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2122. (b) Müller, A.; Das, S. K.; Fedin, V. P.; Krickemeyer, E.; Beugholt, C.; Bögge, H.; Schmidtmann, M.; Hauptfleisch, B. *Z. Anorg. Chem.* **1999**, *625*, 1187.

(2) (a) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Beugholt, C.; Kögerler, P.; Lu, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 1220. (b) Müller, A.; Koop, M.; Bögge, H.; Schmidtmann, M.; Beugholt, C. *Chem. Commun.* **1998**, 1501.

(3) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Beugholt, C.; Kögerler, P.; Lu, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 1220.

(4) Müller, A.; Koop, M.; Bögge, H.; Schmidtmann, M.; Beugholt, C. *Chem. Commun.* **1998**, 1501.

(5) Crystal data: Monoclinic, $P2_1/m$, $a = 31.3199(1)$ Å, $b = 66.5281(6)$ Å, $c = 31.0020(1)$ Å, $\beta = 120.280(1)°$, $V = 55784.5(6)$ Å^3, $T = 123 \pm 2$ K, $Z = 2$. The structure was solved with the program SHELXS-97 and refined using SHELXH-97 to $R = 0.0858$ for 108 942 reflections with $I > 2\sigma(I)$, $R = 0.120$ for all reflections.

(6) Van Uitert, L. G.; Sherwood, R. C.; Williams, H. J.; Rubin, J. J.; Bonner, W. A. *J. Phys. Chem. Solids* **1964**, *25*, 1447.

(7) Figgis, B. N.; Gerloch, M.; Mason, R. *Proc. R. Soc. London, Ser. A* **1964**, *279*, 210.

(8) (a) Drulis, H.; Dyrek, K.; Hoffmann, K. P.; Stanislaw, S.; Weselucha-Birczynska, A. *Inorg. Chem.* **1985**, *24*, 4009. (b) Makinen, M. W.; Kuo, L. C.; Yim, M. B.; Wells, G. W.; Fukuyama, J. M.; Kim, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 5245.

(9) *Proton Conductors, solids, membranes and gels materials and devices*; Ed. Colomban, P.; Cambridge University Press: Cambridge, 1992.

(10) Akutagawa, T.; Hasegawa, T.; Nakamura, T.; Inabe, T.; Saito, G. *Chem.—Eur. J.* **2002**, *8*, 4402.

JA9048042