New Synthetic Pathway to Novel Molybdenum Giant Cluster Compounds

Kazuo Eda,* Yuka Sato, and Yuichi Iriki
Faculty of Science, Kobe University, Rokkodai, Nada-ku, Kobe 657-8501

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We developed a new synthetic pathway to novel molybdenum giant cluster compounds, in which pathway the giant cluster solution free from alkali metal or ammonium cations and from residuary species due to the usual preparation (reduction) procedures was used. Through the pathway, we prepared a novel crystalline compound with Ni^{2+}. The crystals exhibited a monoclinic cell with $a = 2.9616(5)$ nm, $b = 4.5965(7)$ nm, $c = 2.9641(5)$ nm, $\beta = 103.342(15)^\circ$, and $V = 39.263(12)$ nm^3.

Several years ago Müller group revealed that the species "molybdenum blue" indefinitely known for a long time were very large species (with a diameter of about three nanometers) having some interesting structural features such as "wheel-like shape" and "nanosized cavity," as shown in Figure 1.[1,2] (We denote them " molybdenum giant cluster.") Owing to the features the clusters have attracted the attentions of materials scientists and are expected to provide very attractive properties and technological applications. For example, the clusters having magnetic or photoactive cations in their cavities are expected to become novel functionalized magnets or photonic materials. However, only a few compounds consisting of such clusters have been obtained so far,[3,4] because of synthetic limitations. (That is, all giant molybdenum cluster compounds have been prepared by reducing aqueous solutions of alkali metal or ammonium molybdate. Thus they have not been free from alkali or ammonium cations, which may compete with other metal cations desired for the target compounds for lattice sites of the compounds. Furthermore, residuary species due to the reduction or additives for the reduction may prevent the preparation of the compounds.)

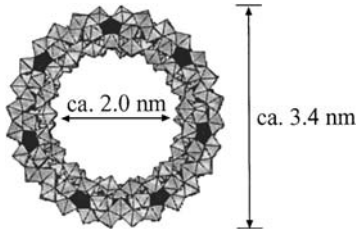

Figure 1. Polyhedral representation of the molybdenum giant cluster $\{Mo_{154}\}$ (after Müller et al., reference 2 in the text).

In order to open a new prospect of the molybdenum giant cluster compounds, we tried to prepare the cluster compounds by using molybdenum giant cluster solution that was free from alkali metal or ammonium cations and from residuary species resulting from the reduction procedure. The solution could be obtained by reducing aqueous molybdic acid with H_2/Pd treatments. The aqueous acid was prepared by ion-exchanging aqueous Na_2MoO_4 with an ion-exchange resin. [The content of Na was lower than 0.01 Na/Mo (molar ratio) in the ion-exchanged solution.] In order to control the concentration of the acid solution, the solution was once spray-dried into soluble amorphous powder. A desired concentration of the acid solution was prepared by dissolving the powder in water, and was reduced to obtain giant cluster solution.[5] Figures 2a and 3a show Raman and UV-vis spectra of the giant cluster solution obtained, respectively. The Raman bands at 531, 460, 326, 215 cm^{-1} and the UV-vis band at ca. 750 nm agreed well with the literature data of $\{Mo_{154}\}$(with and without defects),[6–8] and proved the presence of the clusters. (The Raman band at ca. 800 cm^{-1} was ascribed to highly reduced

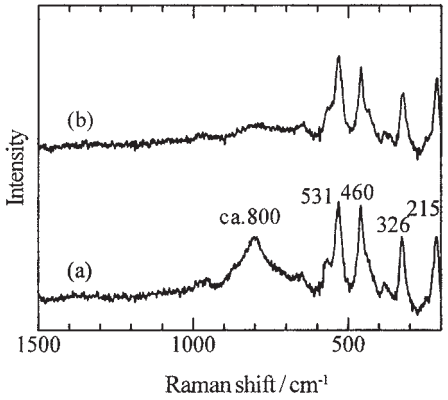

Figure 2. Raman spectra of the giant molybdenum cluster solution (with M.V.$Mo_{sol} = +5.85$ and [Mo] = 0.165 M) perpared by reducing the aqueous molybdic acid with the H_2/Pd treatment (a) and an aqueous solution ([Mo] = about 0.165 M) of the crystal.

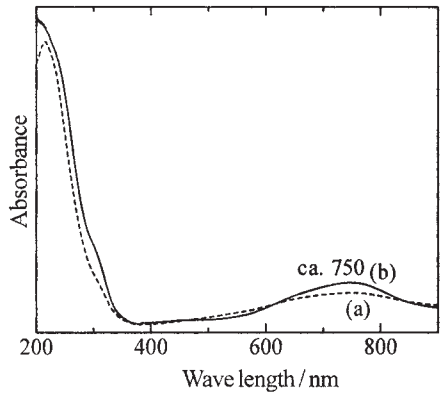

Figure 3. UV-vis spectra of the giant molybdenum cluster solution (M.V.$Mo_{sol} = +5.85$) prepared by reucing the aqueous molybdic acid with the H_2/Pd treatment (a) and an aqueous solution of the crystal. (The molar absorption coefficienct was 1.9×10^5 L mol^{-1} cm^{-1} at 750 nm in the spectrum (b), assuming the presence of molybdate species in the $\{Mo_{154}\}$ form.)

species of the molybdenum giant clusters,[9,10] and was predominantly observed for the solution with mean valence of Mo (M.V.Mo) lower than +5.75.) Aiming to prepare the target compounds desired metal cations and hydrochloric acid (as a precipitation promoter) were added to the solution. Then, we confirmed that the giant clusters could form crystalline compounds with various kinds of cations (Ni^{2+}, Co^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, and so on). In the present work the compound with Ni^{2+} is described as the first.

The systematic investigation was carried out to determine proper preparation conditions of the compound with Ni^{2+} by varying various parameters such as concentrations [Mo], [Ni], [HCl], and M.V.Mo of solution ($M.V.Mo_{sol}$).[11] (The $M.V.Mo_{sol}$ was varied by changing treatment time for the reduction of the molybdic acid solution with H_2/Pd.) Single crystals ranging in size from $0.1 \times 0.1 \times 0.05$ to $2 \times 2 \times 1\,mm^3$ were obtained under the conditions [Mo] = 0.15 M (1M = 1 mol^{-1} L), [Ni] = 0.5 M, $0.1\,M \leqq [HCl] \leqq 0.15\,M$, and $+5.82 \leqq M.V.Mo_{sol} \leqq +5.88$. Several crystals were investigated by means of a single crystal X-ray diffractometer.[12] Figure 4 shows a diffraction pattern of the crystal. Lots of spots, lined up at very short intervals, were observed, indicating a very large cell. A single monoclinic cell indexed all these spots. The lattice constants were $a = 2.9616(5)$ nm, $b = 4.5965(7)$ nm, $c = 2.9641(5)$ nm, $\beta = 103.342(15)^\circ$, $V = 39.263(12)\,nm^3$. All the crystals investigated gave the same unit cell. The Raman and UV-vis spectra of the aqueous solution of the crystal (obtained from the solution with $M.V.Mo_{sol} = +5.85$, [Mo] = 0.15 M, [Ni] = 0.5 M, [HCl] = 0.1 M, pH = 0.93) also showed the above mentioned bands due to the giant cluster, indicating that the crystal consisted of the giant clusters (Figures 2b and 3b). According to atomic absorption analysis and TG-DTA, the contents of Mo, Ni, H_2O in the crystal were 47.0 wt%, 1.0 wt%, and ca. 30 wt%, respectively. The M.V.Mo of the crystal was +5.80. On the basis of the results of Raman, UV-vis and so on, it was suggested that the giant cluster in the crystals was $\{Mo_{154}\}$ or its lacunary types.[6–8] The density of the crystal was $2.2\,g/cm^3$, indicating Z(number of formulaunits in unit cell) = 2. Detailed structural study is now in progress. The results will be presented in future.

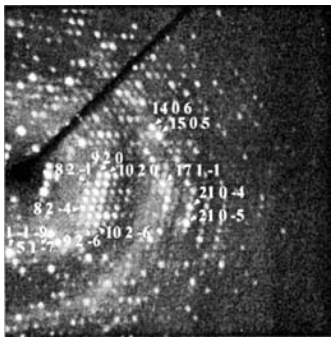

Figure 4. Diffraction pattern of the crystal obtained from the solution with $M.V.Mo_{sol} = +5.85$, [Mo] = 0.15 M, [Ni] = 0.5 M, [HCl] = 0.1 M. For several spots indices are shown in the figure.

In the present pathway very simple (solution) system is used. That is, no undesirable counter cation such as alkali metal or ammonium cation and no residuary species resulting from the reduction procedure is contained in the solution. Thus, it is easy to meet the composition of the solution suitable for the preparation of target compounds, and a wide range of applications are expected for the preparations of novel molybdenum giant cluster compounds.

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References and Notes

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5 In a typical preparation 100 ml of the molybdic acid solution with a concentration of [Mo] = 0.165 M was reduced with the H_2/Pd treatment (0.5 mm $\phi \times$ 10 m of Pd wire and a hydrogen flow of 2 ml/min). In order to promote the reduction Pd surface was subjected to ultrasonic irradiation during the H_2/Pd treatment of the solution. It took about three hours to get the giant cluster solution with $M.V.Mo_{sol} = +5.85$.
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11 To 10 ml of the giant cluster solution a desired amount of nickel chloride hexahydrate and 1 ml of hydrochloric acid solution adjusted to a desired concentration were added under continuous stirring. The solution was transferred into a glass tube closed with a plastic cap and kept at 293 K in an incubator. After about one week crystals began to precipitate.
12 The crystals picked up from the mother liquid spontaneously lost water of crystallization, leading to reduction of crystalinity. (Diffraction spots, thus, disappeared soon.) The crystals were coated with epox resin just after picked up from the mother liquid and cooled to 193 K for the X-ray diffraction measurement.