Chemistry

NW2/2003G186

Synthesis and structure of acetate free Mo_{138} giant cluster $[Mo_{138}O_{468}H_x]^{n-}$

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Introduction

The ring shaped giant cluster anion $[Mo_{138}O_{416}H_6(H_2O)_{58}(CH_3CO_2)_6]^{32-}$ (**1**) reported by Müller *et. al* [1] contains acetate ligands in its interior, which implies the possibility of a design of novel giant clusters by substituting functionalized carboxlate ligands for the acetates. However, the large excess amount of acetic acid used in the synthetic procedure of **1** exclude the possibility of the intake of newly added carboxylates. A different approach using an acetate free Mo_{138} ring as a precursor may avoid this difficulty. Here we report the synthesis and structure of acetate free Mo_{138} anion, $[Mo_{138}O_{468}H_x]^{n-}$ (**2**).

Results and Discussions

By using hydrochloric acid instead of acetic acid in the synthetic procedure of **1**, anion **2** was obtained as an ammonium salt. A dark blue single crystal of **2** with the dimension of 0.04×0.03×0.02 mm was mounted on a Rigaku MERCURY CCD diffractometer at the PF-AR NW2 beamline [2]. Compound **2** crystallized in monoclinic, space group *C*2/*m* with a = 26.9098(6) Å, b = 42.9546(14) Å, c = 29.4850(9) Å and β = 94.283(1)° at 123K. In spite of the relatively small size and poor diffraction ability of the sample crystal, high-flux X-rays from NW2 provided satisfactory quality of data. A total of 137166 reflections were measured, of which 31749 were unique with R_{int} = 0.1090. The structure was solved by the direct method using *SHELXS*-97 and refined with the full-matrix least-squares using *SHELXL*-97. The current agreement factor is: $R1$ = 0.0743 for 18740 reflections with $I>2\sigma(I)$ and $wR2$ = 0.2548 for all reflections.

Single crystal synchrotron X-ray structure analysis showed that **2** is a lacunary species of Mo_{154} anion like **1**. However, the aspects of defects in these two anions are different. Anion **1** has two kinds of defects. One is the missing of a $\{Mo_1\}$ unit that link a 7-coodinate Mo and two 6-coordinate Mo in the $\{Mo(Mo_5)\}$ pentagonal unit. The other is the missing of a $\{Mo_2\}$ unit that links two pentagonal units. In the anion **1**, 4 Mo atoms of 14 potential lacunary sites of the former type are missing and 6 pairs out of 14 $\{Mo_2\}$ linkers are lacking. In the anion **2**, there are no defects of the former type and 8 defects of the latter, as shown in Fig. 1. As was expected from its synthetic procedure, **2** contains no acetate ligands. At the current stage, bond valence sum calculations suggested that at least 46 O atoms are aqua ligands and at least 16 O atoms are hydroxy ligands. As shown in Fig. 2, the anion **2** is linked to its four neighboring anions to form two-dimensional network by sharing four oxo ligands at each junction. Addition of functionalized carboxylate groups during the synthesis of **2** may lead to novel giant clusters with tunable physicochemical properties.

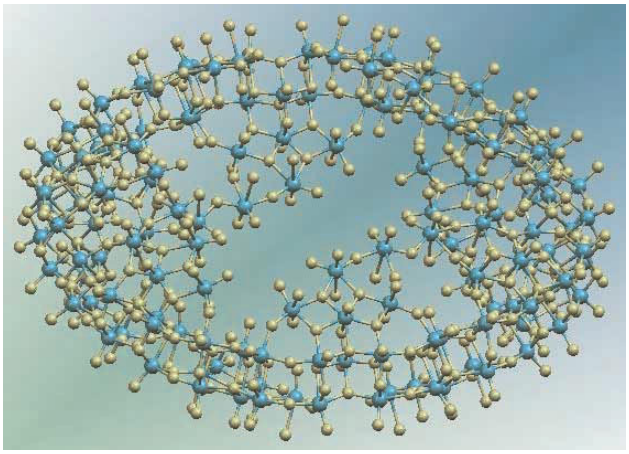

Figure 1. Structure of the $[Mo_{138}O_{468}H_x]^{n-}$ anion. Blue and yellow balls represent Mo and O atoms, respectively.

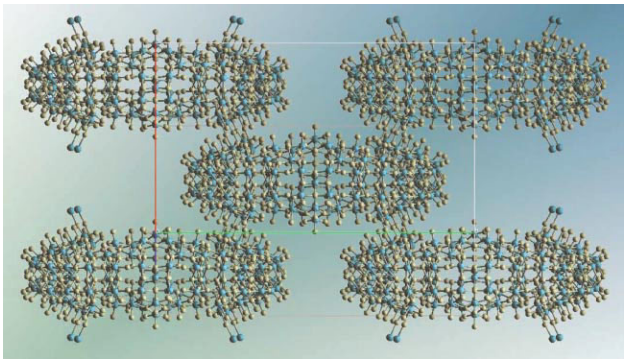

Figure 2. Packing diagram of **2** showing the two-dimensional network structure.

References

[1] A. Müller, R. Maiti, M. Schmidtmann, H. Bögge, S. K. Das and W. Zhang, *Chem. Commun.*, 2126-2127 (2001).
[2] T. Ozeki, T. Saeki, S. Adachi, T. Yamase, Photon Factory Activity Report, PART B, (2003) 272.

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