

Molecular weight tuning of the mixed-valence Mo spherical clusters

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Introduction

Polyoxometalate chemistry finds much similarity between the molybdates and tungstates [1]. However, the chemistry of the mixed-valence giant clusters is limited only to those of the molybdates [2]. Aiming at exploring the corresponding tungstate chemistry, introduction of tungsten atoms into molybdenum giant clusters was attempted as the first step. The Mo atoms in the $[\text{Mo}_{72}^{\text{VI}}\text{Mo}_{60}^{\text{V}}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ anion (abbreviated as $\{\text{Mo}_{132}\}$) [3] was proved to be partially replaceable with W atoms. The degree of the substitution simply depends on the ratio of the starting materials. Crystal structures of partially substituted clusters, as well as the pure molybdate precursor, have been determined by single crystal X-ray diffraction experiments using the PF-AR NW2 beamline [4].

Results and Discussions

Attempts to introduce the W atoms into $\{\text{Mo}_{132}\}$ were carried out with the conditions listed in Table 1. Brown octahedral crystals were obtained from each experiment. Single crystal X-ray diffraction experiments were performed at 123K using a CCD diffractometer at the PF-AR NW2 beamline. In spite of the relatively small sizes and poor diffraction abilities of the sample crystals, high-flux X-rays from NW2 provided satisfactory quality of data. Each sample crystallized in cubic, space group $Fm\bar{3}m$ with the unit cell dimensions listed below.

Table 1: Experimental conditions

Starting W/M ratio	$a / \text{\AA}$	Crystal Size / mm	R1	Refined W/M ratio
0.0	46.2070	0.06×0.05×0.05	0.0752	0.0
0.1	46.1165	0.04×0.04×0.04	0.0755	0.091
0.3	45.6687	0.12×0.12×0.12	0.0735	0.232
0.5	45.8315	0.04×0.04×0.04	0.0844	0.398

Crystals obtained from the syntheses using W sources turned out to contain partially W-substituted spherical clusters, the $[(\text{W}_x\text{Mo}_{1-x})_{72}^{\text{VI}}\text{Mo}_{60}^{\text{V}}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ anion (abbreviated as $\{\text{M}_{132}\}$), whose framework is identical with that of $\{\text{Mo}_{132}\}$. A distinct tendency of the substitution was unrevealed. The W atoms favor the pentagonal-bipyramidal seven-coordinate sites. To a less extent, they also occupy the octahedral six-coordinate

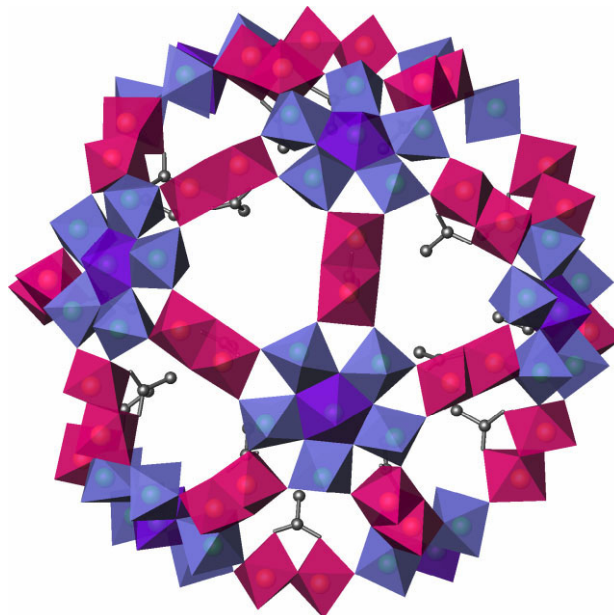


Figure 1. Structure of the $[(\text{W}_x\text{Mo}_{1-x})_{72}^{\text{VI}}\text{Mo}_{60}^{\text{V}}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ anion. Purple and blue polyhedra accommodate the hexavalent W or Mo atoms. They form the $\{\text{M}(\text{M}_5)\}$ pentagonal building units. Thirty pairs of red octahedra centred by Mo^{V} are linking twelve $\{\text{M}(\text{M}_5)\}$ units into a spherical shape.

sites adjacent to the seven-coordinate sites. Mo^{VI} occupied these sites in the pure-molybdate precursor, $\{\text{Mo}_{132}\}$. On the other hand, the M_2 units linking the $\{\text{M}(\text{M}_5)\}$ pentagonal building blocks, which were occupied by Mo^{V} in the precursor, never accommodate the W atoms. Except for the distribution of the Mo/W atoms, structures of the spherical clusters are essentially identical. Thus the $\{\text{M}_{132}\}$ anions can be interpreted as a series of anions that are identical in size and charge yet tunable in molecular weight.

References

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