Crystal Structure Determination and Small Angle X-Ray Scattering of A Novel Very Large Polyoxometalate

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1 Introduction
Many novel polyoxometalates have been synthesized by connecting lacunary polyoxometalates (prepared by partial hydrolysis of complete ones) with s, d and f block metal ions. However, the very large Keplerate-type polyoxometalates with the formula of [MoVI$_{72}$MoV$_{60}$O$_{372}$](CH$_3$COO)$_{30}$(H$_2$O)$_{72}$]$_{42}^-$ [1, 2] has not been used as a precursor for the larger structures, although its lacunary anion, [MoVI$_{66}$MoV$_{50}$O$_{331}$(CH$_3$COO)$_{30}$(H$_2$O)$_{56}$]$_{46}^-$ has been known since as early as 1999 [3,4]. By employing Ba$^{2+}$ as the linker elements, we have been successful in preparing a new very large polyoxometalate, [Ba$_{10}$(H$_2$O)$_{30}$(MoVI$_{71}$MoV$_{50}$O$_{351}$(CH$_3$COO)$_{20}$(H$_2$O)$_{61}$)]$_{72}^-$.  

2 Experiment
Single crystal X-ray diffraction data were collected by using the MERCURY CCD area detector system in the AR-NW2A beamline. The crystal is triclinic, space group P-1 with a = 35.372(1), b = 49.110(1), c = 51.642(1) Å, α = 83.174(1), β = 71.854(1) and γ = 89.787(2)°. Small angle X-ray scattering data were collected at PF-BL10C beamline using a quartz cell.

3 Results and Discussion
Single crystal X-ray structure determination revealed that the compound contains a novel polyoxometalate anion with 10 Ba$^{2+}$ and 242 Mo atoms, [Ba$_{10}$(H$_2$O)$_{30}$(MoVI$_{71}$MoV$_{50}$O$_{351}$(CH$_3$COO)$_{20}$(H$_2$O)$_{61}$)]$_{72}^-$. All atoms of which are crystallographically independent. The structure analysis involves refinements of more than 1500 independent atoms, which was successfully analyzed by using the high quality data obtained by using synchrotron radiation. Two lacunary [MoVI$_{71}$MoV$_{50}$O$_{351}$(CH$_3$COO)$_{20}$(H$_2$O)$_{61}$]$_{46}^-$ anions with the C$_s$ symmetry are connected by 10 Ba$^{2+}$ atoms to achieve [Ba$_{10}$(H$_2$O)$_{30}$(MoVI$_{71}$MoV$_{50}$O$_{351}$(CH$_3$COO)$_{20}$(H$_2$O)$_{61}$)]$_{72}^-$. To each Ba$^{2+}$ cations at the junction, 5 water molecules are ligated.

The integrity of the [Ba$_{10}$(H$_2$O)$_{30}$(MoVI$_{71}$MoV$_{50}$O$_{351}$(CH$_3$COO)$_{20}$(H$_2$O)$_{61}$)]$_{72}^-$ anion in the aqueous solution was confirmed by the small angle X-ray scattering (SAXS) experiments, showing significantly larger radius of gyration for [Ba$_{10}$(H$_2$O)$_{30}$(MoVI$_{71}$MoV$_{50}$O$_{351}$(CH$_3$COO)$_{20}$(H$_2$O)$_{61}$)]$_{72}^-$ than that for [MoVI$_{72}$MoV$_{60}$O$_{372}$](CH$_3$COO)$_{30}$(H$_2$O)$_{72}$]$_{42}^-$. Combined in-situ SAXS and UV-vis measurements allowed us to follow the formation reaction of the [Ba$_{10}$(H$_2$O)$_{30}$(MoVI$_{71}$MoV$_{50}$O$_{351}$(CH$_3$COO)$_{20}$(H$_2$O)$_{61}$)]$_{72}^-$.  

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References

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