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Single crystal diffraction experiments at AR-NW2 and its application to precise structure analyses of inorganic giant molecules

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Introduction

Although it seems to be a widely accepted preconception that inorganic materials generally assume either very small molecules or extended structures consisting of small building units, recent advances in synthetic inorganic chemistry (exploiting the recent advances in crystallography both in instrumentation and in data processing) have demonstrated that many inorganic (both purely inorganic and inorganic-organic hybrid) compounds assume molecules or ions with the dimensions of several nanometers or even larger. The demand for analyzing the structures of such inorganic giant molecules using single crystal X-ray diffraction is rapidly growing. When investigating the structures of these compounds, it is desirable to collect atomic resolution data with high redundancy. Atomic resolution data is critically important in order to obtain unambiguous structural information since these molecules tend to exhibit unprecedented geometry and thus rigid body approximations based on the known geometries of commonly appearing fragments are not applicable. Highly redundant data is also necessary in order to analyze the structure at high precision to certify such unprecedented geometries.

Results

To collect diffraction data of inorganic giant molecules with the quality satisfying above-mentioned demands, X-ray diffraction studies have been carried out using a tailored CCD diffractometer system on the NW2 beamline of PF-AR [1] where X-rays with the photon energy as high as 23 keV are available. The diffractometer is equipped with a three-circle goniometer with a quarter χ cradle to allow highly redundant data collection and a 2θ arm carrying a CCD detector that can travel up to 110°, ensuring the ability to observe high-resolution data that can also be utilized for the charge density analyses. The diffractometer is settled on a bench that can be controlled by a PC using the LabView software to facilitate its precise alignment to the SR beam.

To check the performance of this instrument, diffraction data of an identical crystal of $[Mo^{VI}_{110}Mo^{V}_{28}O_{416}H_6(H_2O)_{58}(CH_3CO_2)_6]^{32-}$ [2] have been measured using this instrument and another diffractometer with a CCD detector of the same model on a rotating-anode X-ray generator both using the 0.71073 Å X-rays. Exposure time for each frame was 8 seconds at AR-NW2 and 60 seconds at the laboratory. Ammonium salt of $[Mo^{VI}_{110}Mo^{V}_{28}O_{416}H_6(H_2O)_{58}(CH_3CO_2)_6]^{32-}$ crystallizes in monoclinic, space group $C2/m$ with a = 42.278, b = 40.206, c = 26.067 Å and β = 111.925°. Figure 1 illustrates the distributions of the completeness of the reflections with certain I/σ criteria. It clearly shows that measurement at AR-NW2 provided with much larger number of diffraction data observed with satisfactory quality than those obtained by the instrument on a rotating-anode generator. R_{merge} values support this conclusion: 0.046 for the AR-NW2 data and 0.090 for the laboratory data. Structure analyses using these data to evaluate the data quality are under progress.

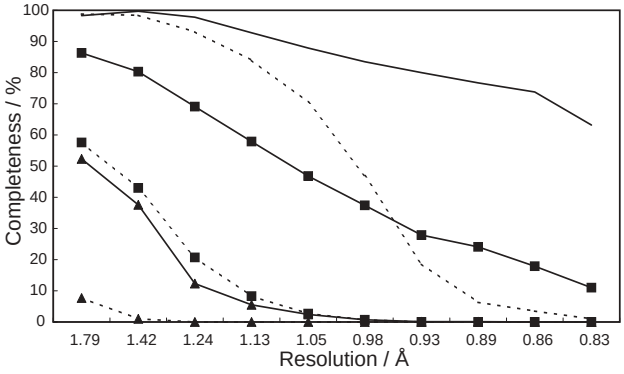

Figure 1. Completeness versus resolution for the data obtained using the AR-NW2 beamline and a rotating-anode X-ray generator. Solid lines: AR-NW2 data; dotted lins: rotating-anode data. Triangle markers: completeness with respect to data with I/σ greater than 20; square markers: completeness with respect to data with I/σ greater than 3; lines without markers: completeness with respect to all reflections.

References

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