Small Crystal Diffraction Experiments on Bicapped C_{60}/ γ-cyclodextrins Complex

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Based on the superatom concept for C_{60}, proposed by Z.Yoshida, the water soluble bicapped C_{60}/ γ-cyclodextrins complex is designed as an artificial nitrogenase. The bicapped C_{60} operates well under mild condition in the presence of $Na_2S_2O_4$ and ATP or inorganic triphosphate , and converts molecular nitrogen into ammonia with extremely high efficiency. This is a revolutionary discovery that alters the current scientific knowledge of nitrogen fixation. The results provide important implications for biological nitrogen fixation, and significant advancement in catalytic nitrogen fixation process. The bicapped C_{60}/γ-cyclodextrins complex forms purple plate crystal together with $15H_2O$, and is soluble in water . Although its X-ray crystal structure has not yet been determined because of the difficulty in growing single crystals, its symmetric structure was suggested from no splitting of ^1H and ^{13}C NMR signals for the two γ-cyclodextrins units.

The water soluble bicapped C_{60} / γ-cyclodextrins complex was prepared by the following procedure: To a solution of γ-cyclodextrins in water was added, a solution of C_{60} / C_{70} mixture in toluene. The mixture of two liquid phases was refluxed at 100°C, 48h under vigorous magnetic stirring. After cooling to room temperature, the aqueous layer containing precipitated C_{60} / γ-cyclodextrins complex was centrifuged at 15 Krpm for 5min. The crude purple solid was washed with cold water and dried well in vacuo. The obtained solid was dissolved in warm water and then the aqueous solution was filtered to remove the insoluble materials (free C_{60} and C_{70}).The filtrate was freeze-dried to give stable C_{60}/ γ-cyclodextrins complex. It was recrystalized from water to give a small purple plate .

In order to elucidate essentials of this compound, the crystal structure determination was carried out. A single crystal with the size of 10x30x30μm^3 was irradiated by 30.75 Kev X-rays. Diffraction pattern was collected using the vacuum camera at BL02B1. The crystal was oscillated six times by 6°, and the scan speed was 2° /min. The overlapped rotation angle were 1° for the scaling of intensities recorded on separate IP plates. It required 15 hours for 29 photographs. The ring current was 18.0mA during the measurements. Unfortunately, the specimen was deteriorated in the course of exposures and the whole diffraction data could not be collected. An indexing of the image data were carried out, but the integrated intensities were not accurately determined by the existing computer programs because the peaks are too close to be distinguished.

We can demonstrate as preliminary experiment , however , that the intensity collection using the vacuum camera system can be utilized for such a small crystal from which diffraction pattern could not be recorded using a convensional laboratory system.