Crystal Structure Analysis of a Cobaloxime Complex

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The vacuum chamber Imaging Plate camera in BL02 was designed and made for the wide range of crystal structure analyses using synchrotron radiation. Although several single crystal structure analyses were performed using this camera, the standard procedure of the data collection and crystal structure analysis for a small molecule crystal is not established yet. So, in order to examine the ability of this camera and the quality of the diffraction data, the single crystal diffraction measurement of *R*-1-cyanoethyl-*R-sec*-butylamine cobaloxime ($CoC_{15}H_{29}N_6O_4$) crystal was performed. This crystal structure was also analyzed using a four circle diffractometer (MoKα). As this cobaloxime complex is known to make a photo isomerization reaction in crystalline state, the crystal structure is highly interested.

The wave length of the SR was set to 0.4 Å. In such a short wave length, an absorption by the crystal becomes about a quarter of that of Mo Kα radiation (0.21 v.s. 0.91mm^{-1}) and the higher diffraction angle reflections were expected to be recorded. A specimen crystal, 0.2 x 0.2 x 0.1 mm, was mounted in the IP camera of BL02. The chamber is evacuated to avoid the diffraction by the air. 19 oscillation photograph, an oscillation angle 10° with 1° overlap, 20 min. exposure, were taken within 9 hours. Thus total oscillation angle was 172 degree and the total exposure time was 6.3 hours. The decrease of the SR intensity was 7.6%. The IP reader made by MAC Science, and the indexing and integration program, DENZO were used.

The cell dimensions, a=8.506, b=9.729, c=6.807Å, α=108.46, β=102.21, γ=102.35°, V=491.14Å^3, were determined by the post refinement procedure. The absorption effect was not corrected because of the negligible μx value of 0.04mm^{-1}. The decay correction was made in the post refinement. 7301 reflections up to 2θ value of 48° were obtained (completeness is 83.1%). The space group is P1, Z=1. No equivalent reflections and Rσ value is 0.1027. The crystal structure was determined using SHELXS97 Patterson analysis and refined using SHELXL97. Final R1 value is 0.0451 for 4593 reflections ($I > 2\sigma(I)$), wR2 0.1202, S 0.950. As this refinement involved many high angle reflections, R1 value is larger than MoKα measurement(R1 0.029 for 2321 reflections). The reflection / parameter ratio of 7301 / 241 is three times larger than MoKα measurement. This is because very high resolution ($\sin\theta/\lambda$=1.01) was achieved by using 0.4Å SR. The sigma values of Co-N, N-C, C-C bonds are 0.003, 0.005, 0.005Å respectively, smaller by 0.001 than MoKα measurement These results are indicating that by using shorter wavelength (0.4Å) SR, many number of high resolution diffraction data are obtained and the quality of the molecular structure is improved significantly.