Micro-Crystal Structure Analysis and Its Application to the Study of Photo-Induced Structural Change of the Metal Complex

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Introduction. Molecular structure analysis in a photo-excited state by single crystal X-ray diffractometry should be interesting from many points of view such as the chemical reaction of molecules and solid state physics of a crystal. However, the excited state crystallography has not been carried out except for some frontier works since there are many difficulties such as low concentration of excited state molecules. It should be necessary to use an extremely small crystal with dimension of μm and cool the crystal as low as possible in the experiment.

Experimental and Results. Several single crystal diffraction experiments were carried out by using 20 keV X-ray beam monochromatized by a Si(111) and focused by a mirror. The vacuum IP camera, which is mounted on a ϕ axis of the 7-circle goniometer were used for the intensity measurements. The flat IP cassette, which was attached to the long 2θ arm of the diffractometer, was applied to the intensity measurement at variable temperatures. The Rigaku cold N_2 gas stream type low-temperature apparatus was installed.

Intensity data were collected for a single crystal of the platinum dimer complex of $Pt_2(EtCS_2)_4$ with dimensions of 40x50x100 μm by using the vacuum IP camera. The crystallographic data and integrated intensities were obtained by applying the DENZO program. Structural analysis was successfully made by the teXsan to give an R value of 0.043 for 836 independent reflections (see Figure 1).

X-ray diffuse scattering was also measured for some halogen-bridged metal complexes having linear-chain structures, $Pt_2(dta)_4I$, $Pt_2(dtp)_4I$, $Pt(chxn)_2I{\bullet}I_2$, $Ni(chxn)_2Br{\bullet}Br_2$, and $Ni(en)_2Br{\bullet}(ClO_4)_2$ (β-form). X-ray rotation photographs around the chain axes were taken by the vacuum IP camera at room temperature and by the flat IP cassette at variable temperatures. For the mixed-valence compounds, diffuse streaks corresponding to twice the original cell dimensions along the linear chain structures could be observed, indicating ordering of the Pt atoms with different valence states on one-dimensional structures. For the $Ni(chxn)_2Br{\bullet}Br_2$, however, no diffuse scattering was observed, proving the Ni(III)-Br-Ni(III) structure which has been suggested by some physical and X-ray diffraction experiments.

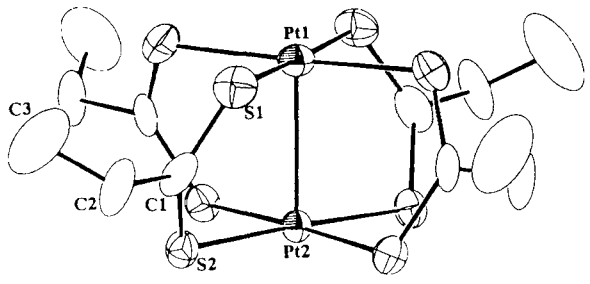

Fig. 1. ORTEP drawing of $Pt_2(EtCS_2)_4$.