

Photoexcited Crystallography of Diplatinum Complex by Multiple-exposure IP Method

Yoshiki Ozawa,* Madoka Terashima, Minoru Mitsumi, Koshiro Toriumi,* Nobuhiro Yasuda,† Hidehiro Uekusa,† and Yuji Ohashi†

Department of Material Science, Himeji Institute of Technology, Kamigori-cho, Hyogo 678-1297

† Graduate School of Science and Engineering, Tokyo Institute of Technology, Ookayama, Tokyo 152-8551

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Molecular distortion of a photoexcited diplatinum(II) complex in a single crystal has been directly observed by accurate synchrotron radiation diffraction studies. Photoexcited crystallographic analysis has revealed that a small portion of $[\text{Pt}_2(\text{pop})_4]^{4-}$ ($\text{pop} = \text{H}_2\text{O}_5\text{P}_2^{2-}$) complex shows the Pt–Pt bond shrinkage of 0.23 Å under blue laser irradiation.

Direct observation of geometrical changes accompanied by photoexcitation of molecules provides essential information for transient species such as metastable states in chemical reactions and excited states, which are sometimes hardly described by molecular orbital calculations. Although single crystal X-ray crystallography is a powerful tool to obtain accurate molecular geometries and their packing in crystals, there are some difficulties to be overcome to determine the structure of photoexcited molecules using ordinary diffractometer: extremely small populations and small geometrical changes of excited-state molecules in crystals. So photoexcited crystallography requires more accurate measurements of diffraction intensities. To achieve the photoexcited crystallography, we have developed a new low-temperature vacuum (LTV) X-ray camera which was installed at the SPring-8 BL02B1 beamline.¹ A special data collection technique, the multiple-exposure IP method has also been developed for diffraction measurements of reversible photoexcited single crystals. We have reported here the instrumentation for the photoexcited crystallography and results of its application for a luminescent diplatinum(II) complex $\{(\text{C}_4\text{H}_9)_4\text{N}\}_2\text{H}_2[\text{Pt}_2(\text{pop})_4]$.

The $[\text{Pt}_2(\text{pop})_4]^{4-}$ complex ion consists of two Pt(II) atoms bridged by four pyrophosphate ligands. Two PtP_4 moieties of square planar geometries are stacked with an eclipsed configuration and the Pt–Pt distance is 2.925 Å.² Formally, there is no direct metal–metal bonds. The complex shows strong green luminescence which has been assigned to $^3\text{A}_{2u} \rightarrow ^1\text{A}_{1g}$ phosphorescence by spectroscopic investigations.³ Emission spectra of the Ba^{2+} salts at 5 K exhibit fine structures with spacing of 150 cm^{-1} , which are assigned to Pt–Pt stretching vibration in the $^3\text{A}_{2u}$ excited state.⁴ The frequency of the vibrational structure in the excited states is higher than that in the ground state (116 cm^{-1}) suggesting an effective Pt–Pt bond formed in the excited states. The $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2u}$ absorption corresponds to $5d\sigma^* \rightarrow 6p\sigma$ electron transitions. We have tried to observe this Pt–Pt bond distortion directly by measuring X-ray diffraction intensity changes under light illumination.

The LTV camera is specially designed for diffractometer to obtain accurate intensities with high S/N ratio at low temperature ($<80\text{ K}$) using synchrotron radiation. In order to obtain diffraction images with extremely low background, an image plate (IP) detector attached on a half piped holder is placed in a vacuum chamber preventing X-ray scattering from air and vacuum windows. A crystal specimen is mounted on a cold head of He refrigerator and can be cooled down to 20 K under high vacuum.

Crystal rotation, IP positioning, and IP readout system are fully computer controlled for phi-oscillation and screenless Weissenberg modes. An additional feature of this camera is the multiple-exposure mode, by which both diffraction patterns measured for light irradiated (light-on) and nonirradiated (light-off) conditions are recorded on the same IP frame. The first exposure by phi-oscillation mode under the light-off condition is followed by the second one under the light-on after a slight shift (1 to 2 mm) of the IP holder, and these processes are repeated several times in order to minimize systematic errors in the intensity measurements: the fading effect of IP detector, long-term fluctuation of laser power and PMT sensitivity of the readout system,⁵ and decrease in intensity of SR beam. The doubly recorded diffraction image can be read at the same time under the same conditions, giving accurate measurement of intensity change for each reflection. A laser light for photoexcitation can be introduced through fiber optics into the vacuum chamber and focused on a crystal (Figure 1). Since these instrumentation and techniques are under development,⁶ the details on the multiple-exposure method will be reported elsewhere.

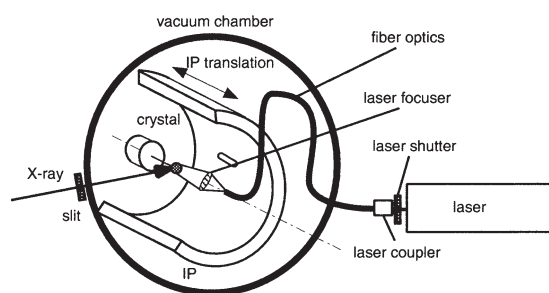


Figure 1. Schematic layout of the low-temperature vacuum X-ray camera (LTV camera) with laser irradiation optics.

$(n\text{-Bu}_4\text{N})_2\text{H}_2[\text{Pt}_2(\text{pop})_4]$ were prepared by the literature method² with minor modifications.⁷ A single crystal of $250 \times 200 \times 50\ \mu\text{m}$ attached on the top of carbon fibers was mounted on the camera and was kept at 54 K. A CW He–Cd blue laser (442 nm, 100 mW) was used for continuous photoexcitation during the light-on period so that the crystal is considered to be a pseudosteady states. In the intensity measurement by multiple-exposure mode, a phi-oscillation exposure ($\Delta\phi = 4^\circ$) at the light-off and -on periods for 24 s each was repeated ten times to record one IP frame.⁸ Total 52 frames which covered the whole data collection area were subjected to intensity integration and data reduction. Usual crystal structure analyses are performed for each light-on and -off intensity data set independently.⁹ Lattice constants for the light-on data set are slightly larger than that of the light-off data set (Table 1). There are no differences in atomic parameters except increase of temperature factors of all atoms for the light-on data set. These results indicate that the heating effect by laser irradiation have caused a small temperature rise with expansion of the unit-cell

Table 1. Lattice constants at the light-on and -off data sets

	Light-on	Light-off	Δ (on-off) ^b
Space group	triclinic, $P\bar{1}$		
$a/\text{\AA}$	9.578(1)	9.576(1)	0.002
$b/\text{\AA}$	12.932(1)	12.926(1)	0.006
$c/\text{\AA}$	20.987(1)	20.976(1)	0.011
α°	89.617(3)	89.611(3)	0.006
β°	87.412(3)	87.431(3)	-0.019
γ°	82.908(19)	82.880(20)	0.028
$V/\text{\AA}^3$	2577.0(3)	2573.8(3)	3.2
Z	2		
No of refin.	9039	9100	
$R/R_w(I > 2\sigma(I))^c$	0.040/0.072	0.041/0.076	
GOF	1.061	1.034	

^aRefinements were performed by the *ScaLpack* program. ^bDifferences of the light-on parameters from the light-off ones. ^cFull-matrix least-squares calculations were performed by the *Xtal 3.7* program package.

volume in the light-on period.

To reveal small changes of crystal structure between these two data sets, difference Fourier syntheses were performed for $|F_{\text{on}}| - |F_{\text{off}}|$ using the phase factors calculated by the atomic parameters of the light-off data set.¹⁰ The observed electron density map (Figure 2) shows positive and negative peaks with heights of 1–2 $e/\text{\AA}^3$ near the Pt atoms.¹¹ This indicates that a small portion of the metal atoms moves toward the positive peaks in the light-on crystal. The Pt(1) atom shifts toward the Pt(2) position, while the Pt(2) atom shifts within the plane perpendicular to the Pt–Pt vector. These obviously reflect shrinkage in the Pt–Pt distance. Changes in the geometrical parameters of the Pt atoms were analyzed quantitatively by least-squares calculations based on the response ratio (defined as $\eta = (I_{\text{on}} - I_{\text{off}})/I_{\text{off}}$).¹² The positional and occupancy parameters of the Pt atoms in the excited states (Table 2) reveal that the Pt(1*)–Pt(2*) distance in the excited state is 2.70(4) \AA which is 0.23 \AA shorter than that of the ground state (Pt(1)–Pt(2) 2.9289(2) \AA). The occupancy parameter in the excited state Pt atoms converged at 0.014(2), which will be discussed in the following paper along with the analysis of the excited-state lifetime in the crystal.

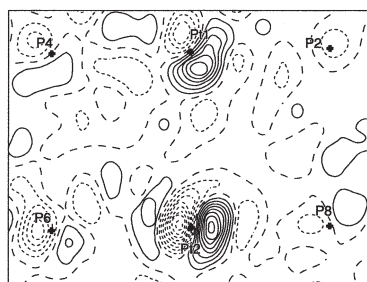


Figure 2. Difference Fourier map of $|F_{\text{on}}| - |F_{\text{off}}|$ in a plane containing the Pt(1)–Pt(2) bond and four coordinated P atoms of the ligands. Continuous lines and dashed lines indicate positive and negative densities drawn at every 0.2 $e/\text{\AA}^3$, respectively. Cross symbols represent atom positions in the ground state.

Recently, Kim et al.¹³ reported on the photoexcited state crystallographic analysis of a tetraethylammonium salt of the same diplatinum complex by time-resolved X-ray diffraction technique using a pulse laser and a CCD detector system.¹⁴ They also reported

Table 2. Positional and occupancy parameters of Pt atoms in the ground state and the excited state

Atom	x	y	z	Occupancy
Pt(1) ^a	0.59606(3)	0.14880(2)	0.24623(1)	0.986(2)
Pt(2) ^a	0.41677(2)	0.34964(2)	0.24902(1)	0.986(2)
Pt(1*) ^b	0.571(3)	0.171(2)	0.253(1)	0.014(2)
Pt(2*) ^b	0.390(3)	0.349(2)	0.258(1)	0.014(2)

^aPositional parameters are taken from the light-off refinements.

^bParameters are obtained by least-squares refinement of the response ratios.¹²

a similar result of 0.28 \AA shortening of the Pt–Pt bond, although the measured intensity data covered only a limited rotation range of the whole data collection area.

Although the residual factor in the refinements is still high (~50%), characteristics of the molecular distortion due to the photoexcitation are well detected and consistent with the spectroscopic results. The multiple-exposure IP technique should be a powerful tool in crystal structure analyses of short-lived species such as electronic excited molecules and transition states of photochemical reactions.

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References and Notes

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- 7 0.5 g (1.9 mmol) of PtCl_2 was suspended in 10% HCl and the solution was heated at 80 $^\circ\text{C}$ with stirring. To the resulting deep red solution was added 0.925 g (11.3 mmol) of phosphonic acid and refluxed until the solution became colorless. $(\text{Bu}_4\text{N})\text{Cl}$ was added to the solution followed by evaporation under nitrogen atmosphere to give fluorescent pale yellow precipitate. Anal. Calcd for $\text{C}_{32}\text{H}_{82}\text{N}_2\text{O}_{20}\text{P}_8\text{Pt}_2$: C 26.45, H 5.69, N 1.93%. Found: C 26.32, H 5.43, N 1.90%.
- 8 Synchrotron radiation from BL02B1 bending magnet was monochromatized at 23 keV (0.5364 \AA) by Si (311) double crystals and focused by double mirror optics.
- 9 Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-197085 and 197086. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- 10 The temperature rising effect for the light-on data set was corrected, and observed structure factors of the light-off and -on were scaled before calculations of Fourier syntheses.
- 11 We made a blank test for the multiple-exposure method in which intensity measurements for both two data sets were performed without photoirradiation. The difference Fourier syntheses gave no significant positive or negative electron densities.
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