Distortion of the Unit Cell of Platinum(II) Complexes under Light Irradiation

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The shift of X-ray powder pattern of Platinum(II) complexes was observed under light irradiation by using X-ray powder diffractometer. The peaks were returned to the original one when the irradiation of light was cut off. The observed X-ray powder patterns show that the unit cell of $[Pt(acac)_2]$ is expanded under light irradiation, however, that of $[Bu_4N]_4[Pt_2(pop)_4]$ ($pop^{2-}=P_2O_5H_2^{2-}$) is contracted.

A group of dimeric complexes that have received considerable attention because of their photochemical and photophysical properties are those of platinum derived from the dianion of diphosphorous acid $(OH)(O)POP(O)(OH)^{2-}$. The most widely studied complex with this ligand is the diplatinum(II) complex $[Pt_2(pop)_4]^{4-}$ which contains bridging diphosphito ligands. The anion complex has a Pt-Pt separation of 2.925 Å with no axial ligands. Photophysical studies confirm that the properties of the photo active excited state are a manifestation of d^8-d^8 metal-metal interactions. Transition metal complexes containing acetylacetonato ligands have been widely studied. The crystal structure of bis(acetylacetonato) platinum(II) ($[Pt(acac)_2]$) has been also determined.[1] $[Pt(acac)_2]$ is monomeric and the coordination geometry is squareplanar. In this letter, we report that the distortion of the unit cell of Platinum(II) complexes is brought about under light irradiation.

$[Pt(acac)_2]$ was synthesized by the method of the literature.[2] $[Bu_4N]_4[Pt_2(pop)_4]$ was prepared by using a Gray's procedure.[3] The measurement was performed by a Rigaku X-ray powder diffractometer, RINT-2400 and intensity data of powder X-ray were collected with 2θ (5°<2θ<70°) at room temperature. Light irradiation was performed by Xe-lamp through water cell and UV-cut filter.

$[Pt(acac)_2]$ has electronic absorption bands at 346 nm ($\varepsilon = 3.5\times10^3$ $M^{-1}cm^{-1}$) and 287 nm ($\varepsilon = 7.0\times10^3$ $M^{-1}cm^{-1}$). The crystal structure is monoclinic, space group $P\bar{1}$, a=7.13 Å, b=5.75 Å, c=7.957 Å, α=70.0°, β=98.9°, γ=113.2°.[1]

$[Bu_4N]_4[Pt_2(pop)_4]$ has electronic absorption bands at 369 nm ($\varepsilon = 3.4\times10^4$ $M^{-1}cm^{-1}$) and 435 nm ($\varepsilon = 120$ $M^{-1}cm^{-1}$) that are attributable to the singlet and triplet $1a_{2u}\rightarrow2a_{1g}$ transitions.[4] The complex salt emits an intense phosphorescence at 514 nm. The phosphorescence in crystal has a lifetime of 7.7 μs and 800 μs at room temperature and 77K, respectively. This phosphorescence from a triplet excited state is accompanied by a shorter lived fluorescence from a singlet excited state which has a lifetime of <ns at 407 nm.

Figure 1 and Figure 2 show the powder X-ray pattern of $[Pt(acac)_2]$ and $[Bu_4N]_4[Pt_2(pop)_4]$ before and under light irradiation, respectively. The X-ray pattern of $[Pt(acac)_2]$ under light irradiation shifted to low angle. On the other hand, that of $[Bu_4N]_4[Pt_2(pop)_4]$ shifted to high angle. The magnitude of the shifts was different at each diffraction peak. The peaks were returned to the original one when the irradiation of light was cut off, that is, only under the irradiation of light, the shift of powder X-ray pattern was observed. By the results of powder X-ray structure analysis and the crystal data, the distortion of the unit cell of $[Pt(acac)_2]$ occurs in the direction of a and b axes (Figure 3). The unit cell of $[Pt(acac)_2]$ is expanded under light irradiation. It is considered that the molecule of $[Pt(acac)_2]$ expands in plane by photo irradiation because the shift of c axis refraction pattern were small.

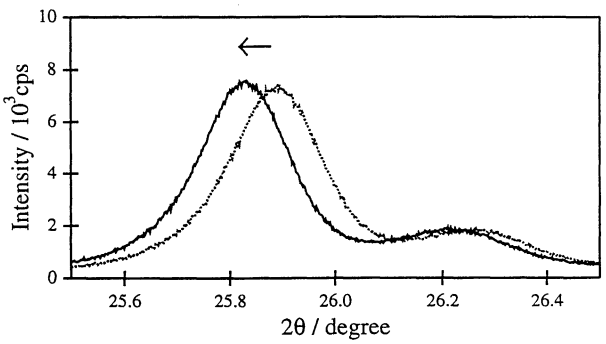

Figure 1. Powder X-ray diffraction of $Pt(acac)_2$ (under non light irradiation (dotted line) and irradiation (solid line)).

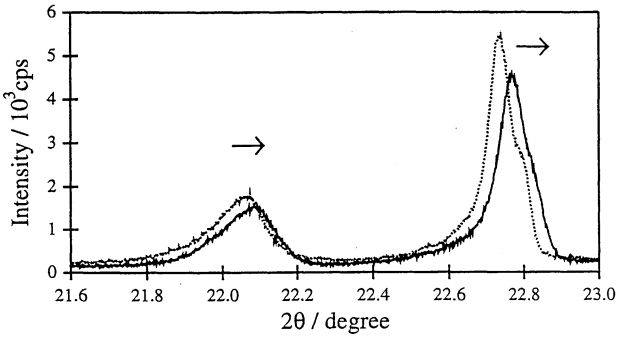

Figure 2. Powder X-ray diffraction of $[Bu_4N]_4[Pt_2(pop)_4]$ (under non light irradiation (dotted line) and irradiation (solid line)).

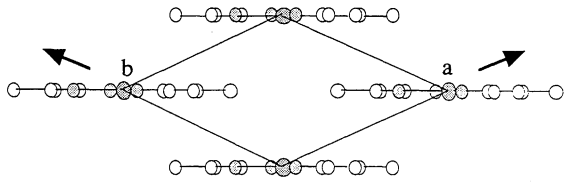

Figure 3. Distortion of $Pt(acac)_2$

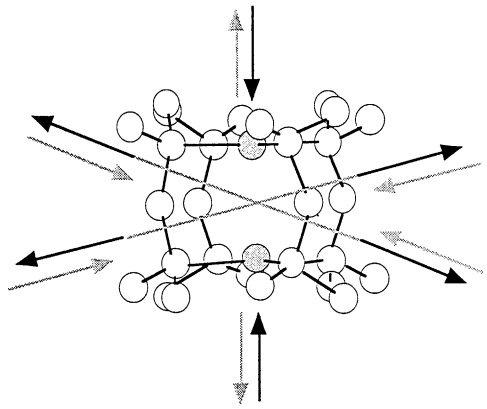

Figure 4. Distortion of $[Bu_4N]_4[Pt_2(pop)_4]$

On the other hand, the results of powder X-ray structure analysis of $[Bu_4N]_4[Pt_2(pop)_4]$ mean the contraction of the unit cell under light irradiation. The structure of $[Bu_4N]_4[Pt_2(pop)_4]$ is determined as tetragonal. However there are many possibilities of the definition of the unit cell. Most plausible crystal structure is space group $P4_2/nmc$, with a=16.54 Å, c=16.64 Å, and V=4554 Å^3. From simulations of the shifts of observed powder X-ray pattern, there are two possibilities. One is that the crystal cell constant is changed into a=16.50 Å, c=16.67 Å, and V=4540 Å^3. This result shows that the distance between Pt-Pt atom is expanded and the equatorial direction is contracted(Figure 4(gray arrows)). The other is that the crystal cell constant is changed into a=16.56 Å, c=16.50 Å, and V=4525 Å^3. In this case, the distance of Pt-Pt is contracted and the equatorial direction is expanded as shown in Figure 4(solid arrows). As the transfer of an electron from an antibonding orbital, constructed two $5d_{z^2}$ orbitals, to a bonding orbital, constructed two $6p_z$ orbitals, causes the enhancement of Pt-Pt bonding interactions in the excited state from MO's theory, it is expected that the distance between Pt metals is shortened. Though we cannot determine the direction of the distortion from the results of X-ray pattern shift, it is clear that the volume of the unit cell reduced by the change of the geometry of molecules. Although the excited molecules are very few, the change of unit cell is caused by the distortion of the excited molecules concertedly.

The analysis of the structure by three-dimensional X-ray diffraction is now in progress and the distortion will be determined.

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References

1 S. Onuma, H. Inoue, and S. Shibata, *Bull. Chem. Soc. Jpn.*, **53**,2679 (1980).
2 A. A. Grinberg and I. N. Chapurskii, *Russ. J. Inorg. Chem.*, **4**, 137 (1959); "Inorg. Synth.", vol.XX (1980), p65.
3 C. M. Che, L. G. Butler, P. J. Grunthaner, and H. B. Gray, *Inorg. Chem.*, **24**, 4664 (1985).
4 R. E. Marsh and F. H. Herbstein, *Acta Cryst.*, **B39**, 280 (1983).