Excited-state Structure of a Platinum Complex by X-ray Analysis

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Irradiating a crystal of $[N(C_5H_{11})_4]_2[Pt_2(H)_2(pop)_4]$, (pop = pyrophosphate), with a xenon lamp on a diffractometer, the intensity data were collected and the structure was analyzed by X-rays at low temperatures. The unit-cell volume and the Pt–Pt distance of the Pt anion became significantly smaller than the corresponding ones without irradiation. The Pt–Pt bond shortening is due to the formation of the excited molecules in the crystal, although the amount of the excited molecules may be about 5%.

It has long been believed that X-ray analysis is only applicable to the ground-state structure of molecules and solids. However, several excited-state structures have been analyzed using synchrotron radiation. A combination of excitation by laser light and Laue diffraction method by polychromatic synchrotron radiation made it possible to obtain the excited-state structure. A picosecond diffraction study of *N*,*N*-dimethylaminobenzonitrile has shown the torsional distortion at the excited state.[1] The reaction processes in macromolecules have been reported.[2] Recently the excited-state structure of a Pt complex anion, $[Pt_2(H)(pop)_4]^{3-}$ (pop = pyrophosphate, $(H_2P_2O_5)^{2-}$), has been analyzed by Coppens et al.[3] They called a stroboscopic technique, in which the molecule is repeatedly excited and the structural change probed for a period of microseconds immediately after the excitation. Although these methods are effective to analyze the unstable structures, the structural change is assumed to be reversible in infinite times of the light on and off process. However, the reversible structural change, how quickly it occurs, should be also observed by usual X-ray structure analysis, considering from the observation of the thermal vibration of atoms and molecules in a crystal. But the equilibrium between ground- and excited-state molecules should be satisfied during the photoirradiation and the concentration of the excited molecules should exceed the threshold values (≈5%).

Recently Kaizu et al. reported that the powder pattern of the Pt complex, $[Pt_2(pop)_4]^{4-}[N(C_4H_9)_4]^{+}{}_4$, shifted reversibly to its higher diffraction angle when the powdered sample was irradiated with a xenon lamp.[4] This indicates that the structure of the Pt complex at the excited state is significantly changed and the concentration of the excited molecules is significantly large. This brought about an idea that the excited structure can be analyzed if the three-dimensional intensity data are collected during the irradiation with a xenon lamp. This paper reports the first example of the excited-state structure observed by usual X-ray analysis.

The $[Pt_2(pop)_4]^{4-}$ complex with tetrapentylammonium cation was synthesized in the method reported previously.[5] The crystals were obtained from an aqueous solution. The preliminary structure analysis, however, revealed that the Pt anion should be written as $[Pt_2(H)_2(pop)_4]^{2-}$ since there are only two cations for one of the Pt anion complexes. This means that two protons are attached to the oxygen atoms of the eight P=O groups of $[Pt_2(pop)_4]^{4-}$. The two oxygen atoms are not disordered as shown in Figure 1, since the P–OH bond distances are clearly different from the remaining P=O bond distances. By virtue of the proton attachment, only two tetrapentylammonium cations are necessary for each Pt anion.

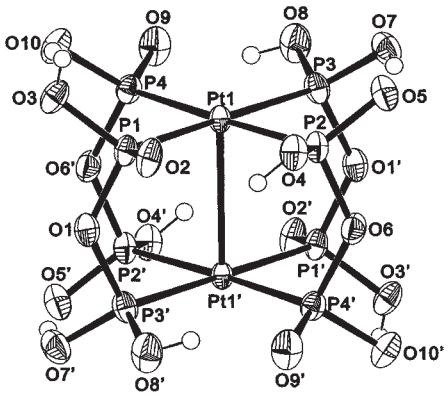

Figure 1. Structure of one of $[Pt_2(H)_2(pop)_4]^{2-}$ anions in the $[N(C_5H_{11})_4]$ complex at 173 K (without irradiation), showing atoms with 50% thermal ellipsoids.

A crystal of $0.2 \times 0.1 \times 0.1\,mm^3$ was mounted on a RIGAKU R-AXIS RAPID diffractometer, irradiated with visible light (>400 nm), which was brought by a glass-fiber tube through a cut-filter from a xenon lamp. The three dimensional intensity data were collected without (light-off) and with (light-on) photoirradiation at three temperatures, 123, 173, and 223 K. Since the crystal temperature would increase when the crystal was irradiated, the comparison of the structure with those at different temperatures is indispensable. Table 1 shows the crystal data at six stages, under light-off and light-on conditions at three temperatures.[6] At each temperature, the unit-cell volume decreased significantly when the light was on and the Pt anion was excited. The structures were solved by the direct method and refined by the full-matrix least-squares method.[7]

The two crystallographically independent Pt anions occupy the origin and the body-centered inversion. Figure 1 shows one of the light-off molecular structures at 173 K. The bond distances and angles of the light-on structure are compared with the corresponding ones of light-off at each temperature. Table 1 lists the differences of the unit-cell volume and Pt–Pt distances at three temperatures. The significant differences in unit-cell volume and Pt–Pt distances, 11 $Å^3$ and 0.01 Å, respectively, are observed at 173 K, although the differences are not so significant at the other two temperatures. The amount of excited molecules becomes smaller at the higher temperatures than 173 K, whereas the structure would be hardly changed at lower temperatures than 173 K. This is a reason why the largest differences were observed

Table 1. Crystallographic data of $[N(C_5H_{11})_4]_2[Pt_2(H)_2(pop)_4]$

	223 K-off	223 K-on	173 K-off	173 K-on	123 K-off	123 K-on
T/K	223(2)	223(2)	173(2)	173(2)	123(2)	123(2)
a/Å	17.2741(3)	17.2632(3)	17.2143(6)	17.2358(8)	17.1554(9)	17.1355(4)
b/Å	18.7632(3)	18.7520(3)	18.6847(5)	18.6567(8)	18.6380(10)	18.6112(2)
c/Å	9.67670(10)	9.67930(10)	9.6750(3)	9.6453(3)	9.6787(4)	9.6681(2)
α/°	90.5033(4)	90.4710(10)	90.8190(10)	90.6840(10)	90.7990(10)	90.6753(4)
β/°	102.4806(5)	102.4360(10)	102.7130(10)	102.8150(10)	102.9900(10)	102.7223(5)
γ/°	93.6503(4)	93.6340(10)	93.594(2)	93.6090(10)	93.5100(10)	93.7434(5)
$R1[I > 2\sigma(I)]$	0.0221	0.0225	0.0415	0.0558	0.026	0.0305
$Rw[I > 2\sigma(I)]$	0.0395	0.0392	0.1251	0.1363	0.0428	0.0515
No. of $I > 2\sigma(I)$	11830	11830	10911	10547	11721	11329
Goodness of fit	0.982	0.971	1.072	0.973	0.915	0.897
$\Delta\rho_{max}$/e.Å^{-3}	0.636	0.749	1.672	1.827	1.806	2.067
$\Delta\rho_{min}$/e.Å^{-3}	−1.278	−1.282	−2.044	−2.028	−0.931	−1.069
V/Å^3	3055.24(8)	3052.94(8)	3028.39(16)	3017.3(2)	3008.6(3)	3000.08(11)
Pt1–Pt1/Å	2.93684(18)	2.93584(18)	2.9381(4)	2.9278(5)	2.9379(2)	2.9314(2)
Pt2–Pt2/Å	2.94846(17)	2.94729(17)	2.9527(4)	2.9420(5)	2.9441(2)	2.9452(2)

at 173 K. As shown in Figure 2, there are no unusually short contact between the anions and cations. One-dimensional hydrogen bond network between the anions is extended along the c axis. Two Pt–Pt bonds are oriented along the [111] and [1$\bar{1}$1] axes, respectively. This is a reason why all the a, b and c axis lengths contracted under the light-on condition.

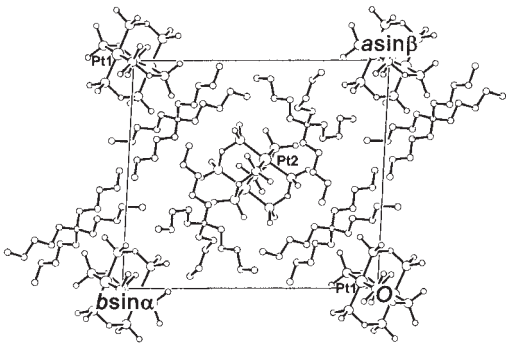

Figure 2. Crystal structure of $[N(C_5H_{11})_4]_2[Pt_2(H)_2(pop)_4]$.

From Frank-Condon analysis of the vibrational fine structure of the absorption and emission spectra, a shortening of 0.21 Å was proposed.[8] In the crystal of $[Pt_2(H)(pop)_4]^{3-}[N(C_2H_5)_4]^+_3$, the excited structure by stroboscopic X-ray analysis at 17 K showed that the Pt–Pt distances decreased by 0.28(9) Å.[3] Considering from the preliminary estimation by spectroscopic experiments, the concentration of the excited molecules may be about 5% for the present crystal. It is clear that we can observe the structure of the excited state of the $[Pt_2(H)_2(pop)_4]$ anion using the usual X-ray technique.

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References and Notes

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6 Formula $C_{40}H_{98}N_2O_{20}P_8Pt_2$; fw = 1565.14; triclinic; space group $P\bar{1}$ (No. 2); $Z = 2$; D_{calcd} and μ(Mo Kα) at 173 K before irradiation, 1.716 gcm^{-3} and 48.93 cm^{-1}, respectively; two crystallographically independent Pt anions occupy the positions at (0,0,0) and (1/2,1/2,1/2); the crystal was cooled with the nitrogen-gas-flow-method using the RIGAKU low-temperature equipment; the cell dimensions were refined using all the reflections.
7 Each structure was refined with the full-matrix least-squares method using SHELXL-97. The Pt anion has a center of symmetry. The two protons attach to the oxygen atoms, O7 and O8, since P3–O7 has nearly the same distance as P3–O8. This means P3 is bonded by two hydroxyl groups. Although the four alkyl chains of one of the cations are all trans, only two alkyl chains of the other cation are all trans and the central C–C bonds of the other two alkyl chains are gauche. There is one-dimensional hydrogen bond network along the c axis through O3–H$\cdots$O2′ and O2$\cdots$H′–O3′. Since the structural difference between the light-on and off conditions at 173 K is essential, the data collections and the structure analyses were performed using another crystal and CCD diffractometer under the same conditions. The differences in unit-cell volume, Pt1–Pt1′ and Pt2–Pt2′ distances between the light-off and light-on structures are 20.3(2) Å^3, 0.0083(3) and 0.0080(3) Å, respectively, which are comparable with the corresponding ones in Table 1, 11.1(2) Å^3, 0.0103(5) and 0.0107(5) Å, respectively.
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