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X-ray Analysis of Excited-State Molecular Structure of $[AuCl(PPh_3)_2]$

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When a chloroform solvate crystal of the three-coordinated Au(I) complex $[AuCl(PPh_3)_2]\cdot CHCl_3$ was irradiated with a mercury lamp at low temperatures, the crystal showed bright green emission from the excited molecules. From X-ray analysis, the unit-cell volume significantly decreased under photoirradiation. The three-dimensional intensity data were collected in the dark (light-off) and under photoirradiation (light-on) at 175, 156, 136, and 84 K. As the temperature decreased, the difference in unit-cell volume between the light-off and -on experiments increased. The molecular structures in the light-off and -on experiments revealed that the Au–P and Au–Cl bonds are significantly contracted by photoirradiation at every temperature. The changes in the other bond lengths were within the experimental errors. The shortening becomes greater as the temperature is lowered. The bond shortening, which causes the decrease in unit-cell volume, is in good agreement with the theoretical assumption that excitation from an anti-bonding orbital to a bonding orbital occurs in the Au(I) complex by photoirradiation.

Although a variety of studies on the energy of the excited states of the molecules have been reported, the molecular structures of the excited states have only been estimated from theoretical calculations or spectroscopic methods. But recently, several long-lived excited-state structures were analyzed by X-ray diffraction. Coppens et al. reported the excited-state structures of the complexes $[Pt_2(pop)_3(popH)]^{3-}$ (pop is diphosphonate, $(H_2P_2O_5)^{2-}$),[1] $[Rh_2(dimen)_4]^{2+}$ (dimen is 1,8-diisocyano-*p*-menthane),[2] and $[Cu_3\{3,5\text{-}(CF_3)_2Pz\}_3]$ (Pz is pyrazolate),[3] using time-resolved crystal structure analysis. Although this method is very attractive, it remains uncertain whether or not enough excited molecules exist in a single crystal for X-ray analysis after exposure to a laser pulse for a very short time. Moreover, the molecular structure determined by X-ray analysis is not a real structure but an averaged one. This is different from the structure in the gas state or in a dilute solution, in which there are no strong intermolecular interactions. If the stable excited-state structure is significantly different from the stable structure of the ground state, the excited molecules should appear in the unit-cell at random and that the periodic structure should rearrange to accommodate the produced excited-state molecules. The unit-cell dimensions should also be different between the light-on and -off analysis.

If there are only two structures, i.e., the ground- and excited-state molecules, when the crystal was irradiated with UV or visible light, the diffraction occurs due to the periodic structure of the equilibrium state between the ground and excited states regardless of lifetime of the excited molecule. However, longer lifetimes result in a higher concentration of the excited molecules at the equilibrium state. If the concentration of the excited molecules exceeds the threshold value (more than 5%),[1,2,6] the structure can be determined using the diffraction data during the photoirradiation (at light-on stage). Yasuda et al.[4,5] and Ozawa et al.[6] reported the excited structures of the complex anion $[Pt_2(pop)_2(popH)_2]^{2-}$. The unit-cell volumes decreased in light-on stage at low temperatures, and the Pt–Pt and Pt–P bonds were significantly shortened in the unit-cell. Such structural changes are in good agreement with those estimated from theoretical calculations.

In a previous study,[7] we reported the excited structure of the $[VO(acac)_2]$ (acac = acetylacetonato) complex at 168, 160, 150, and 140 K. At every temperature, the unit-cell volume were larger, and the V=O and V–O distances were elongated. The elongation of the V=O and V–O bonds is in good agreement with theoretical calculations assuming a transition from the weak bonding orbital of V–O to anti-bonding orbital of V=O.

In this paper, we present the excited-state structure of a three-coordinated mononuclear Au(I) complex, which has a long-lived excited-state ($t = 4$–$10\,\mu s$) and shows phosphorescence with Stokes' shift.[8] Because of their characteristic photophysical properties, which have been extensively studied,[9–11] Au(I) complexes are potentially useful as light-emitting devices (LED) or diodes. In the case of dinuclear Au complexes, the Stokes' shift is related to the Au⋯Au interaction if the Au⋯Au distance is less than the sum of the van der Waals radii of Au atoms (ca. 3.6 Å).[12,13] However, in the mononuclear Au complexes, the structural differences relating to the shift has not been structurally characterized yet. In previous studies, it was proposed that a significant distortion in the excited state may be responsible for the shift.[8,14] Recently, Omary et al. reported theoretical calculations on the excited-state molecular structure of the mononuclear Au(I) complex $[Au(PH_3)_3]^{3+}$ and its derivatives, which have a trigonal planar (D_{3h}) ground-state geometry.[15] The three-coordinated Au(I) complex $[AuCl(PPh_3)_2]$ (Scheme 1) was selected because its excited

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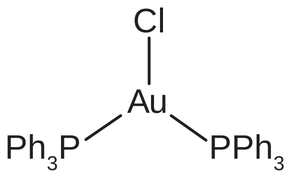

Scheme 1. The structure of $[AuCl(PPh_3)_2]$.

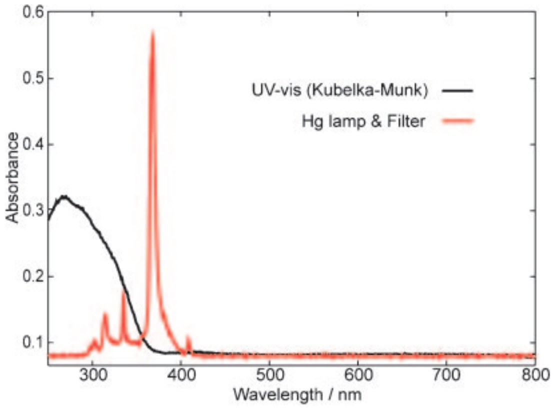

Fig. 1. Kubelka–Munk spectrum and wavelength distribution of the light source.

state has a fairly long lifetime ($t = 3.7\,\mu s$) at room temperature and phosphoresces ($\lambda_{max} = 511$ nm) after excitation ($\lambda = 330$ nm).[8] Although the crystal structure of $[AuCl(PPh_3)_2]$ was already reported,[16] we prepared the chloroform solvate crystal, which showed similar intense phosphorescence. In this paper, the structure of the excited molecule of $[AuCl(PPh_3)_2]$ in an equilibrium state in the chloroform solvate crystal was determined by X-ray diffraction analysis.

Experimental

Preparation of the Intensity Data Collection. $[AuCl(PPh_3)]$ was synthesized by the published procedure.[17] $[AuCl(PPh_3)]$ and an equimolar amount of triphenylphosphine were dissolved in warm acetonitrile and stirred. By evaporating the solvent, $[AuCl(PPh_3)_2]$ was obtained. Colorless single crystals were obtained by vapor diffusion of diethyl ether into a chloroform solution. Diffuse reflectance spectra were measured on a JASCO V-560 spectrometer equipped with an integrating sphere accessory. A powder mixture of the crystal (7 mg) and $BaSO_4$ (350 mg) was packed into the sample holder, and the reflectance data were collected and converted into absorbance by the Kubelka–Munk equation, as shown in Fig. 1 (black line). An absorption band was observed in the UV region (λ_{max} = ca. 290 nm), which was assigned to $^3E'' \leftarrow {}^1A_1'$ derived from p_z (bonding) $\leftarrow$ d_{xy}, $d_{x^2-y^2}$ (antibonding).[8,14,15] Light from a mercury lamp with an optical filter (TOSHIBA UV-D33S) was used for the excitation source, and the wavelength distribution is shown in Fig. 1 (red line). For deep penetration of the light, the wavelength distribution does not correspond to the maximum peak of the complex but roughly to the threshold of the absorption band. This method is not effective for quick generation of excited molecules as compared to excitation by a pulsed laser with the wavelength at maximum absorption. However, the concentration of the excited molecules at the equilibrium state is expected to be enough for X-ray diffraction. Upon irradiation, green emission was observed, Fig. 2.

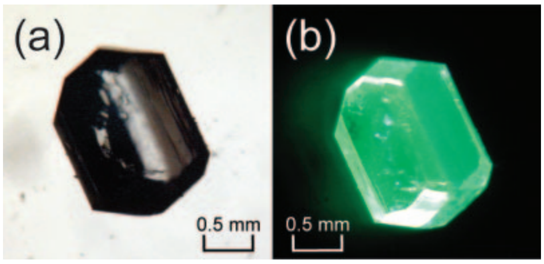

Fig. 2. Photos of the single crystals: (a) light-off, (b) light-on.

Crystal Structure Analysis. Intensity data were collected using a crystal with the dimensions of $0.30 \times 0.25 \times 0.15\,mm^3$ on a Bruker SMART CCD diffractometer equipped with a Rigaku nitrogen-gas cooling system. Intensity data were collected at four temperatures (175, 156, 136, and 84 K) in the dark (light-off) and under photoirradiation (light-on). The crystal, mounted on the diffractometer, was directly irradiated via glass fiber. Data collection occurred as follows: four sets of 606 frames, 0.3° increment of ω and 5 s exposure of X-rays per frame, θ and ϕ arm were $\theta = 32°$, $\phi = 0$, 90, 180, and 270°. The intensity data were integrated with the program *SAINT*,[18] and an absorption correction was applied via the program *SADABS*.[19]

Each structure was solved by direct methods (*SHELXS-97*)[20] and refined by the full-matrix least-squares method (*SHELXL-97*).[21] The diffraction data with $2\theta < 65°$ were used for structure refinement. All of the hydrogen atoms were found in the difference Fourier map. The non-hydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC 270432–270439. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Crystal Structure of $[AuCl(PPh_3)_2]\cdot CHCl_3$. In the crystal structure, there are two $[AuCl(PPh_3)_2]$ and two solvent $CHCl_3$ molecules per $P\bar{1}$ unit-cell, and the molecular structure of $[AuCl(PPh_3)_2]$ is somewhat different from the reported one,[16] which has metal–ligand bonds that are shorter by ca. 0.01 Å. The crystal structure viewed along the *b* axis and the molecular structure are shown in Figs. 3 and 4, respectively. The shortest Au···Au distance is ca. 7.2 Å in the crystal structure, which means that the Au···Au interaction should be neglected. The green emission could be caused by an excited-state distortion.

The geometry around the central Au atom is approximately trigonal planar, and the Au complex has approximately two-fold symmetry through the Au–Cl bond. The Au–Cl bond is slightly bent from the triangle plane due to an intermolecular Cl···H–C hydrogen bond with the solvent $CHCl_3$ molecule (at 84 K, C···Cl distance is 3.585(2) Å and C–H···Cl angle is 168(2)°), as shown in Fig. 3 by red dotted lines.

Change of the Unit-Cell Dimensions Due to Photoirradiation. The continuous emission of the crystal induced by photoirradiation indicates that each molecule in the crystal continuously cycles between the excited state and the ground

Table 1. Crystallographic Data of $[AuCl(PPh_3)_2]\cdot CHCl_3$ for the Light-Off and Light-On Experiments

	175 K-off	175 K-on	156 K-off	156 K-on	136 K-off	136 K-on	84 K-off	84 K-on
Formula	$C_{37}H_{31}P_2Cl_4Au$							
Formula weight	876.32							
Temperature/K	175(2)	175(2)	156(2)	156(2)	136(2)	136(2)	84(2)	84(2)
Wavelength/Å	0.71073							
Crystal system	Triclinic							
Space group	$P\bar{1}$ (No. 2)							
Z	2							
a/Å	10.8276(3)	10.8186(2)	10.8208(1)	10.8089(4)	10.8264(3)	10.8064(1)	10.8015(2)	10.7812(1)
b/Å	13.1320(4)	13.1268(1)	13.1123(2)	13.1031(5)	13.1125(2)	13.0876(1)	13.0618(3)	13.0338(2)
c/Å	14.1539(3)	14.1525(3)	14.1479(3)	14.1350(5)	14.1517(3)	14.1251(2)	14.1168(3)	14.0858(2)
α/°	99.276(1)	99.331(1)	99.175(1)	99.238(1)	99.095(1)	99.139(1)	98.946(1)	98.939(1)
β/°	108.982(1)	108.937(1)	108.985(1)	108.975(1)	109.017(1)	109.013(1)	109.117(1)	109.104(1)
γ/°	107.071(1)	107.045(1)	107.164(1)	107.120(1)	107.218(1)	107.182(1)	107.309(1)	107.292(1)
V/Å^3	1744.35(8)	1742.46(5)	1739.65(5)	1735.02(11)	1740.67(7)	1730.99(3)	1724.56(6)	1714.33(4)
μ/mm^{-1}	4.641	4.646	4.653	4.666	4.651	4.677	4.694	4.722
R_{int}	0.0273	0.0277	0.0274	0.0274	0.0275	0.0274	0.0264	0.0287
$R[I > 2\sigma(I)]$	0.0210	0.0210	0.0205	0.0207	0.0202	0.0203	0.0192	0.0200
$Rw[I > 2\sigma(I)]$	0.0514	0.0512	0.0497	0.0504	0.0493	0.0495	0.0472	0.0487
GOF	1.001	0.992	0.993	0.982	0.990	0.989	1.008	1.002
Au···Au/Å$^{a)}$	7.23960(20)	7.24071(19)	7.23331(18)	7.22720(30)	7.23103(18)	7.21772(18)	7.19954(19)	7.18679(17)

a) The shortest Au···Au contacts, between Au and Au $(-x+1, -y+1, -z+1)$.

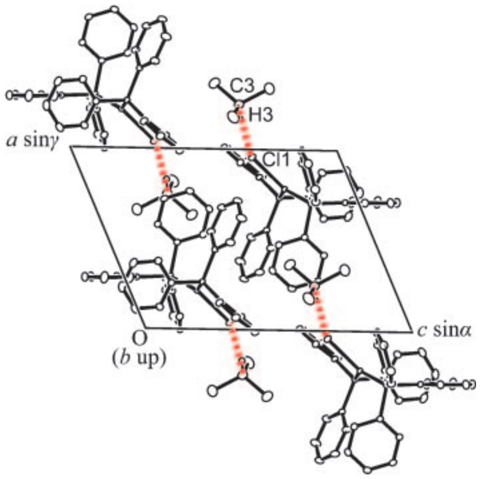

Fig. 3. Crystal structure of $[AuCl(PPh_3)_2]\cdot CHCl_3$ viewed along the b axis.

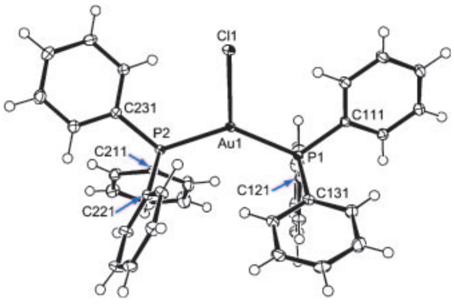

Fig. 4. ORTEP diagram of $[AuCl(PPh_3)_2]$ at 84 K (light-off), showing atoms with 50% thermal ellipsoids.

Table 2. Lattice Volumes at Four Temperatures

	Light-off stage/Å^3	Light-on stage/Å^3	$\Delta_{on-off}{}^{a)}$/Å^3
175 K	1744.35(8)	1742.46(5)	−1.89(8)
156 K	1739.65(5)	1735.02(11)	−4.63(11)
136 K	1740.67(7)	1730.99(3)	−9.68(7)
84 K	1724.56(6)	1714.33(4)	−10.23(6)

a) Difference between light-on and light-off stages for lattice volume.

state and that the populations of the excited-state and ground-state molecules reach equilibrium at the ambient temperature in the crystal. This causes the rearrangement of the crystal lattice corresponding to the equilibrium state.[4] The crystallographic data in the light-off and -on experiments at 175, 156, 136, and 84 K are summarized in Table 1. The unit-cell dimensions significantly decreased at every temperature with the light on (equilibrium state). Since the lattice volume increased with increasing temperature in the dark, the decrease in the lattice volume must be caused by photoirradiation. The differences in lattice volume between the light-off and -on stages at the four temperatures are summarized in Table 2. As the temperature decreased, the unit-cell contraction increased. This trend is the same for each crystal. This suggests that the concentration of the excited molecules in the crystalline lattice increases at lower temperatures. However, it must be noted that for the Pt complex, the unit-cell did not contract as the temperature decreased below 173 K.[4] This indicates that the concentration of the excited molecules decreases below 173 K because the structural change in the excited state becomes harder due to strong intermolecular interactions. For the present crystal, the decrease in lattice volume may be smaller below 80 K.

Change of the Molecular Structure Due to Photoexcitation. The difference in bond distances and angles between the light-off and light-on experiments at 84 K are given in Table 3. Upon photoirradiation, the Au–P and Au–Cl bond distances are significantly shorter with a difference in the

Table 3. Selected Bond Lengths (Å) and Angles (°) at 84 K

	Light-off stage	Light-on stage	$\Delta_{\text{on-off}}$[a)]
Au1–P1	2.3278(4)	2.3222(4)	−0.0056(4)
Au1–P2	2.3457(4)	2.3403(4)	−0.0054(4)
Au1–Cl1	2.5821(4)	2.5764(4)	−0.0057(4)
P1–C111	1.8253(17)	1.8208(17)	−0.0045(17)
P1–C121	1.8285(17)	1.8245(18)	−0.0040(18)
P1–C131	1.8335(17)	1.8291(18)	−0.0044(18)
P2–C211	1.8342(17)	1.8287(18)	−0.0055(18)
P2–C221	1.8257(17)	1.8221(17)	−0.0036(17)
P2–C231	1.8251(17)	1.8212(18)	−0.0039(18)
P1–Au1–P2	136.446(15)	136.441(15)	−0.005(15)
P1–Au1–Cl1	115.184(14)	115.179(15)	−0.005(15)
P2–Au1–Cl1	108.276(14)	108.286(15)	+0.010(15)
Au1–P1–C111	120.45(6)	120.47(6)	+0.02(6)
Au1–P1–C121	110.10(5)	110.05(6)	−0.05(6)
Au1–P1–C131	109.63(6)	109.69(6)	+0.06(6)
Au1–P2–C211	112.21(6)	112.17(6)	−0.04(6)
Au1–P2–C221	109.25(5)	109.30(6)	+0.05(6)
Au1–P2–C231	119.75(6)	119.79(6)	+0.04(6)

a) Difference between light-on and light-off stages for each bond length and angle.

Table 4. Change in Averaged Bond Lengths by Photoexcitation[a)]

	175 K	156 K	136 K	84 K
Au–P/Å	−0.0017(5)	−0.0028(5)	−0.0049(4)	−0.0055(4)
Au–Cl/Å	−0.0014(5)	−0.0024(5)	−0.0040(4)	−0.0057(4)
P–C/Å	−0.0001(19)	−0.0017(19)	−0.0033(18)	−0.0043(18)
C–C/Å	−0.001(4)	−0.002(3)	−0.003(4)	−0.003(3)

a) Difference between light-on and light-off stages.

Au–P and the Au–Cl bonds of 0.0055(4) and 0.0057(4) Å, respectively. However, the other bond lengths remained within the experimental error. The bond angles also remained within experimental error. The averaged changes in bond lengths at different temperatures are given in Table 4. As the temperature increased, the bond shortening decreased which is in agreement with the changes in the lattice volume, Table 2. As the temperature increased, molecular motion becomes larger. Therefore, the apparent structural changes of the molecule are smaller, and the change of the lattice volume is also smaller. Recently, the non-solvate crystal was prepared, and preliminary photoirradiation experiments were performed. The changes in the unit-cell dimensions below 135 K are smaller than those of the present crystal. The crystal packing of the molecules, or the intermolecular interactions, may have an effect on the photoexcitation in the crystal.

It is clear that, in the excited state, the Au–P and Au–Cl bonds of the[AuCl(PPh$_3$)$_2$] molecule are shortened. These shortenings correspond to the excitation of ^{3}E″ ← ^{1}A$_1$′ derived from the electronic transition from d_{xy}, $d_{x^2-y^2}$ (anti-bonding) orbitals to p_z (bonding) orbitals.[8,14,15] From the theoretical calculations involving [Au(PH$_3$)]$^{3+}$, the Au–P bonds are shortened in the excited state if the excited-state structure is constrained to D_{3h} geometry, and the shortening in a free molecule was estimated to be 0.05 Å.[15] Since the molecules in the crystal are involved in strong intermolecular interactions, the shortening of the bond in the crystal should be much smaller than the estimated value for a free molecule. As well, the shortening in the crystalline state depends on the concentration of the excited molecules in the equilibrium state (light-on).

Structural Change of the Excited Molecules at the Equilibrium State. Recently, we reported bond elongation occurred in a bis(acetylacetonato)oxovanadium(IV), [VO(acac)$_2$], complex by photoirradiation,[7] and the unit-cell dimensions increase upon irradiation. The anisotropic expansion was completely different from the thermal expansion. The expansion during irradiation increased as the temperature decreased. The crystal data and intensity data were measured at 141 K, since the crystal decomposed due to a phase transition below 140 K. The volume of the $P\bar{1}$ unit-cell changed from 577.45(3) to 581.52(3) Å^3 at 140 K. In the light-on experiment, the change was 4.07(3) Å^3. Structure analysis showed that the V=O bond was elongated by 0.0043(8) Å and that the average elongation of the four equatorial V–O bonds was 0.0045(7) Å. The changes in the other bonds were within the experimental error. The structural changes suggest that, in the excited state, a d–d electronic transition occurs from the weak bonding orbital of the equatorial V–O bonds to the anti-bonding orbital of the axial V=O bond as derived from orbital theory.[22,23]

In a previous paper,[4] we reported the photo-excited structures of [Pt$_2$(popH)$_2$]$^{2-}$ and [Pt$_2$(pop)$_4$]$^{4-}$ in the five different kinds of crystals which had tetrabutylammonium, tetrapentylammonium, benzyltriethylammonium, benzyltributylammonium, and benzyldimethylphenylammonium as cations. When each crystal was irradiated with a xenon lamp at low temperatures, the unit-cell dimensions decreased significantly. In the molecular structure of each crystal in the light-on experiments (equilibrium state), the Pt–Pt and Pt–P bonds were significantly shortened. For example, the Pt–Pt and Pt–P bonds are shortened by 0.0127(5) and 0.0085(14) Å in the crystal with the benzyltriethylammonium cation. The change was explained by orbital theory arising from an electronic transition from ^{1}A$_{1g}$ state to ^{1}A$_{2u}$ state. From theoretical calculations the Pt–Pt bond length was predicted to decrease by 0.18–0.51 Å and the Pt–P bond length should increase by 0.01–0.05 Å.[24]

In the vanadium complex, the platinum complexes, and the Au complex, the structural changes in the excited state were determined if the crystal structures were, in fact, analyzed accurately in the light-on experiments (equilibrium state). However, the extent of the bond elongation or shrinkage is somewhat smaller than those predicted by theoretical calculations. It must be emphasized that the theoretical calculation was performed assuming a vacuum and no intermolecular interactions. In the crystal, however, the molecule is closely packed with the other molecules, and therefore, it is impossible to change the structure as if the molecule were in vacuum. Since the lifetime of the excited molecule may be several µs, the molecule should cycle between the excited state and the ground state rapidly in the equilibrium state. Thus, the energy diagrams of the ground and excited states are different in a vacuum and in a crystal. As shown in Fig. 5 by solid curves, the structure at the energy minimum in the excited state is significantly different from the corresponding one in

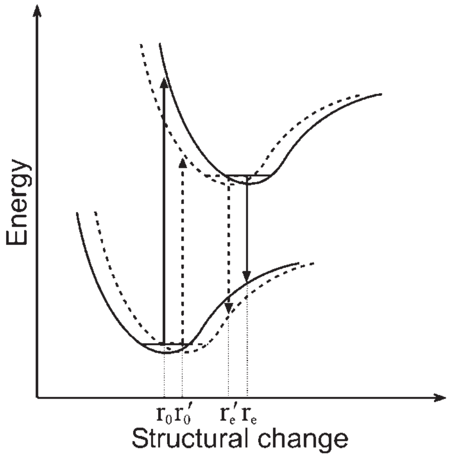

Fig. 5. Proposed energy diagram under vacuum (solid curves) and in the crystal (dotted curves).

the ground state under vacuum. On the other hand, the structures at the energy minimum in the ground and excited states should be similar to each other in the crystal, Fig. 5 (dotted curves), due to large steric hindrance in the crystal lattice. Thus, the amount of bond elongation and shrinkage is smaller than predicted by theoretical calculations. From preliminary emission spectroscopy in the solid state and in solution, $\lambda_{\max}$ in the solid state was significantly blue shifted as compared to that in solution, supporting the energy diagram in Fig. 5.

The concentration of excited molecules in the equilibrium state may also have an effect. We carefully determined the excitation wavelengths that generate the maximum concentration of excited molecules. Assuming that the largest volume change of the unit-cell should occur with the maximum concentration, a combination of the lamp and filters were selected for each experiment. Although we have no clear information about the concentration of the excited molecules, it is probably larger than 10%. In our report involving the excited-state structures of Pt complexes, we assumed that the concentration was 4–5% based on a comparison of the results from X-ray diffraction analysis and theoretical calculations. However, the estimation was incorrect and 4–5% is the minimum concentration obtained if there is no intermolecular interaction in the crystal. We are currently trying to determine an accurate estimate of the concentration.

Finally, it must be emphasized that the structure determined by X-ray diffraction analysis is a periodic structure. Non-periodic substances, no matter the concentration, cannot be observed by X-ray diffraction. This is different than spectroscopy, in which very small numbers of substances are detectable with a sensitive detector. Although excitation by a pulsed laser light is very effective in generating excited molecules, it is very difficult to confirm that the excited molecules exist not only on the surface but also in the bulk at random and that the periodic structure occurs in the whole crystal. In preliminary experiments using a new time-resolved detector, MSGC, at SPring-8, it was found that more than one second is necessary after photoirradiation to reach an equilibrium state.[25] Since there is no vacant space in the crystal lattice, the unit-cell dimensions will only change if enough of the excited molecules that have a different structure are produced periodically in the crystal lattice. Since the bond distances and angles depend on the unit-cell dimensions, a change in the cell dimensions must occur. Moreover, an increase in the temperature of the crystal due to the laser light irradiation should be taken into account. Therefore, diffraction analysis at equilibrium is required if we wish to quantitatively determine the structural changes in the excited state.

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