Single-Crystalline Photochromism of Bis[2-(aminomethyl)pyridine]platinum(II) Chloride Monohydrate

Hajime Nishimura and Nobuyuki Matsushita*
Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902

(Received May 17, 2002; CL-020424)

Bis[2-(aminomethyl)pyridine]platinum(II) chloride monohydrate [Pt(amp)$_2$]Cl$_2$·H$_2$O has been found to exhibit photochromism in single-crystalline phase. Single crystals of the chloride were changed from almost colorless to pale-blue by the irradiation of the light. Its aqueous solution, however, shows no photochromic behavior. Absorption bands induced by the irradiation of the light show dichroism in the single crystals. The photochromic behavior of the present platinum complex chloride is very interesting, because it occurs in single-crystalline phase but not in solution.

Photochromic compounds have attracted much attention because they can be applied to opt-electronic device such as optical memory, optical switch and so on. So far many photochromic compounds have been already reported. Most of them were organic compounds, and most of their photochromic behavior occurred in solution phase. Recently it has reported that *N*-salicylidenaniline[1] and diarylethenes,[2–7] which are organic compounds, show photochromism in the single-crystalline phase. Metal complexes exhibiting photochromic behavior in the single-crystalline phase have, however, not yet known in our best knowledge. Very recently, we have found that bis[2-(aminomethyl)pyridine]platinum(II) chloride monohydrate, [Pt(amp)$_2$]Cl$_2$·H$_2$O (amp=2-(aminomethyl)pyridine), exhibits photochromism in the single-crystalline phase. Here we report the photochromic behavior and the crystal structure.

[Pt(amp)$_2$]Cl$_2$·H$_2$O was prepared by adding an aqueous solution of 2-(aminomethyl)pyridine to an aqueous solution containing [PtCl$_4$]$^{2-}$. A considerable yellow precipitate produced was filtered out, and then the concentration of the filtrate under reduced pressure gave crystals (Yield 28%). Elongated plate-like single crystals suitable for X-ray and optical measurements were recrystallized from the aqueous solution of the crystals by evaporation. Elemental analysis of the present platinum complex reproduced the formula. Single-crystal X-ray diffraction intensity data were collected on a RIGAKU RAXIS-RAPID Imaging Plate diffractometer equipped with graphite-monochromated Mo Kα under room light. Spectroscopic data for the single crystals were measured with a microspectroscopic system composed of an OLYMPUS BX60 microscope and a JASCO CT-25 monochromator combined with an optical fiber, using a tungsten lamp for the light source and a polarizer for polarizing light. A lock-in system working with a HTV R316 photomultiplier was used for detection.

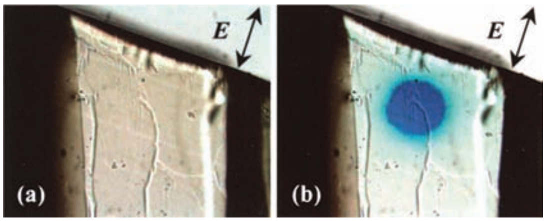

Figure 1. Photographs of the single crystal (a) before the irradiation of the light and (b) after the irradiation of the light (390–500 nm, ca. 5 mW/cm^2) with a small spot to a part of the single crystal for one hour.

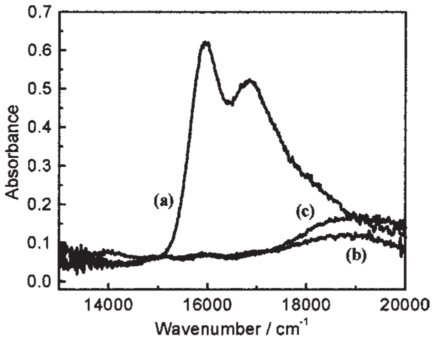

Figure 2. Single-crystal polarized absorption spectra of [Pt(amp)$_2$]Cl$_2$·H$_2$O (a) after the irradiation of the light for one hour, (b) after three days under dark, (c) after one month under dark.

The fresh crystals of [Pt(amp)$_2$]Cl$_2$·H$_2$O just after separating from the solution exhibit colorless or almost colorless which is slightly pale-blue. Then, the color of the crystals was immediately changed to pale-blue under room light for several minutes. The pale-blue crystals were changed back to colorless under dark for one night at room temperature. The pale-blue state of the crystal was stable under dark for at least 5 days at 77 K. On the other hand, at 323 K, the color of the pale-blue bleached for only 2 h under dark. This color-changed behavior is reproducible. Two photographs of the single crystal are shown in Figure 1, one being before the irradiation of the light, and the other being after the irradiation of the light (390–500 nm, ca. 5 mW/cm^2) with a small spot to a part of the single crystal for one hour. Figure 2 shows single-crystal polarized absorption spectra of the complex in the visible region. Spectra (a) and (b) show ones after the irradiation of the light using a tungsten lamp for one hour and after three days under dark, respectively. Absorption bands are observed at 628 and 595 nm in the pale-blue state shown by the spectrum (a). The two absorption bands disappear under dark as shown by the spectrum (b), and develop again by irradiating light. This result shows that the two absorption bands at 628 nm and 595 nm are reproducible photo-induced absorption bands. The photo-induced absorption bands are the origin of the photochromism.

The crystals under dark for one month exhibit pale-red. Spectrum (c) in Figure 2 shows one after one month under dark. The two photo-induced absorption bands disappear and another absorption band at 520 nm appears. The pale-red crystals also again change to pale-blue by the irradiation of the light. For its 7–8 repeats, the pale-blue was reproduced well. The repeat did not intensify the red color.

$[Pt(amp)_2]Cl_2 \cdot H_2O$ is only reported in a literature[8] with respect to the crystal structure. The literature has not, however, mentioned the photochromism. The single-crystal X-ray structure analysis[9] has been performed in order to confirm whether our crystal of exhibiting the photochromism is the same as the crystal reported in the literature or not. The result shows that the both crystals have the identical crystal structure as shown in Figure 3.

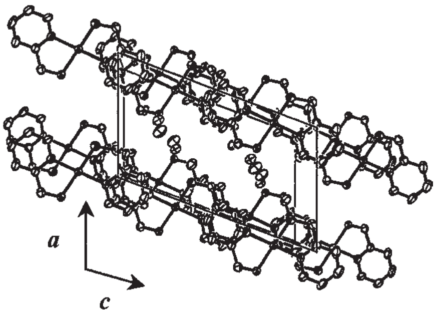

Figure 3. Perspective view of crystal packing of $[Pt(amp)_2]Cl_2 \cdot H_2O$ viewed along *b* axis. Thermal ellipsoids are drawn at 50% probability level, and H atoms are omitted for clarity.

The absorption spectra in Figure 2 were measured on a (0 1 0) plane of the single crystal, and an angle between the electric field vector of the polarized light and the elongated direction of the single crystal was about 20°. The pale-blue color, which is the photo-induced color, changes to colorless by rotating the crystal to 90°. That is, the single crystal in the photo-irradiated pale-blue state has the dichroism. The angle dependence of the intensity of the photo-induced absorption band at 628 nm is shown in Figure 4. This remarkable angle dependence indicates that the photochromic species are regularly arranged in the crystal. That is, the photochromism of $[Pt(amp)_2]Cl_2 \cdot H_2O$ is not one at crystal surface or boundary of crystallite but the same single-crystalline photochromism as that of diarylethenes reported by Irie's group.[2–7]

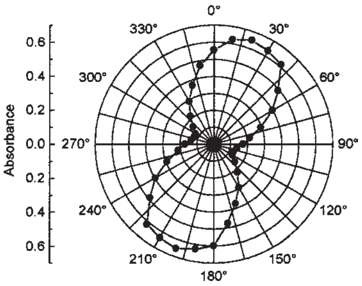

Figure 4. Polar plots of absorbance of photo-induced absorption band at 628 nm for the single crystal of $[Pt(amp)_2]Cl_2 \cdot H_2O$ after the irradiation of the light for one hour.

Interestingly, the irradiation of the light for a saturated aqueous solution of $[Pt(amp)_2]Cl_2 \cdot H_2O$, from which the crystals were separated, did not induce the change in color. These crystals, however, often have colored slightly to the pale-blue in the same condition of the irradiation of the light as the solution. From this result, it is possible that the present platinum complex moiety $[Pt(amp)_2]^{2+}$ is not a photochromic species in the solution. Almost of all photochromic molecules exhibit photochromic behaviors in the solution phase but not in the crystal phase because of a restriction of photochromic changes of the molecules by crystal packing. Only some molecules like the diarylethenes[2–7] show the photochromism in the single crystal phase as well as in the solution. By contrast, $[Pt(amp)_2]Cl_2 \cdot H_2O$ is unusual because of exhibiting the photochromic behavior in the single crystal phase but not in the solution phase.

Although mechanism of the single-crystalline photochromism for $[Pt(amp)_2]Cl_2 \cdot H_2O$ has not yet been clarified, we can consider that the structure of the coordination polyhedron around the platinum atom in the crystal phase suggests its source. In general, $[PtN_4]$ coordination structure is square and compounds having its structure such as $[Pt(NH_3)_4]Cl_2$ and $[Pt(en)_2]Cl_2$ are colorless. The $[PtN_4]$ structure of the pale-blue crystal of $[Pt(amp)_2]Cl_2 \cdot H_2O$ under the room light is, however, slightly distorted to tetrahedron as shown in Figure 5. The dihedral angle between one PtN_2 plane and another PtN_2 plane, composed of Pt and amp, is 3.29(4)°. This fact lets us speculate that a metastable state, produced from a photoexcited state by the irradiation of the light, and having a tetrahedrally distorted square $[PtN_4]$ structure and a pale-blue color, is stabilized by a crystal packing and have a significant lifetime at room temperature.

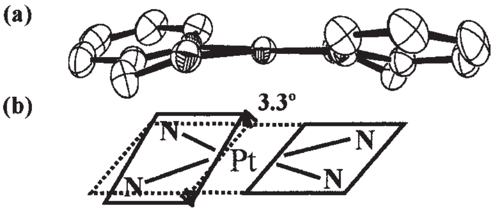

Figure 5. (a) ORTEP drawing of $[Pt(amp)_2]^{2+}$ with thermal ellipsoids at 50% probability level. (b) Schematic drawing of the distorted tetrahedron of $[PtN_4]$.

Various bis[2-(aminomethyl)pyridine]platinum(II) salts have been prepared to clarify the relation between the crystal packing and the photochromism. The single-crystalline photochromisum has been observed for the bromide and the iodide, but not for the tetrafluoroborate, the perchlorate and the hexafluorophosphate. Studies of their single-crystalline photochromism in detail and the crystal structures are in progress. Theoretical study for the electronic state of $[Pt(amp)_2]^{2+}$ moiety is also in progress.

References and Notes

1 J. Harada, H. Uekusa, and Y. Ohashi, *J. Am. Chem. Soc.*, **121**, 5809 (1999).

2 M. Irie, K. Uchida, T. Eriguchi, and H. Tsuzuki, *Chem. Lett.*, **1995**, 899.

3 M. Irie, *Chem. Rev.*, **100**, 1685 (2000).

4 S. Kobatake, M. Yamada, T. Yamada, and M. Irie, *J. Am. Chem. Soc.*, **121**, 8450 (1999).

5 S. Kobatake, T. Yamada, K. Uchida, N. Kato, and M. Irie, *J. Am. Chem. Soc.*, **121**, 2380 (1999).

6 T. Yamada, S. Kobatake, K. Muto, and M. Irie, *J. Am. Chem. Soc.*, **122**, 1589 (2000).

7 T. Yamada, S. Kobatake, and M. Irie, *Bull. Chem. Soc. Jpn.*, **73**, 2179 (2000).

8 F. D. Rochon and R. Melanson, *Acta Crystallogr.*, **B35**, 2313 (1979).

9 Crystal data for $[Pt(amp)_2]Cl_2 \cdot H_2O$: $C_{12}H_{18}Cl_2N_4OPt$, $M_r = 500.29$, monoclinic, $P2_1/c$, $a = 8.1732(3)$, $b = 14.6930(7)$, $c = 13.9588(4)$ Å, $\beta = 110.696(1)°$, $V = 1568.1(1)$ Å^3, $Z = 4$, $Dx = 2.119$ g/cm^3, $T = 296$ K, $R[F_o^2 \geq 2\sigma(F_o^2)] = 0.0357$, $wR = 0.0974$, $GOF = 1.058$ for 4473 observed reflections $[F_o^2 \geq 2\sigma(F_o^2)]$, 5593 independent reflections and 187 parameters. Programs used were *SHELXS97* for solution and *SHELXL97* for refinement.