Cell-expansion of Tris(2,4-pentanedionato)chromium and -aluminum under Light Irradiation

Toshihiko Okumura, Takashi Ikagawa,[†] Takuhiro Otsuka, and Youkoh Kaizu*
Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152
[†]CREST, Japan Science and Technology (JST)

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In the previous letter,[1] we have reported on the cell-expansion and contraction of platinum(II) complexes under light irradiation and discussed the results in the term of the molecular structures in the excited states. For tris(2,4-pentanedionato)chromium and -aluminum (abbreviated as $Cr(acac)_3$ and $Al(acac)_3$, respectively), we also found the cell-expansion under light irradiation. The X-ray powder patterns of these complexes were shifted to low reflect-angle than original one by light absorption of the complexes. The shift of X-ray powder pattern of $Al(acac)_3$ is due to thermal cell-expansion caused by internal conversion of the molecule under light irradiation. In case of $Cr(acac)_3$, however, the shifts are due to not only the thermal cell-expansion but also another reason concerned with the structures in the excited states.

It was found that the X-ray powder patterns of some platinum(II) complexes were shifted by light irradiation.[1] However it has not been cleared what brings about these shifts. In the previous letter, we interpreted the cell-expansion and -contraction under light irradiation of the samples as a reflection of excited molecular structures. On the other hand, the heat caused by internal conversion after light absorption of the complexes should be considered. Then we carried out measurements of X-ray powder patterns of $Cr(acac)_3$ and $Al(acac)_3$ under light irradiation with and without temperature control of these samples.

$Cr(acac)_3$ and $Al(acac)_3$ are mostly same molecular and crystal structures.[2,3] The space group of both complexes is $P2_1/c$, and the unit cell dimensions of $Cr(acac)_3$ and $Al(acac)_3$ (shown in parenthesis) are a=14.031(14.07) Å, b=7.551(7.57) Å, c=16.379(16.38) Å, and β=99.06(99.0)°. Both complexes have UV absorption bands. In addition, $Cr(acac)_3$ has absorption bands at visible region,[4] while $Al(acac)_3$ has no absorption band at that region (Figure 1). Emission of both complexes cannot be observed at room temperature. In this letter, we report that the shift of X-ray powder pattern of $Al(acac)_3$ are due to the heat caused by internal conversion of molecule under light irradiation, whereas that of $Cr(acac)_3$ are due to not only the thermal cell-expansion but also another reason concerned with the structures of the excited states.

$Cr(acac)_3$ and $Al(acac)_3$ were purchased from DOJINDO Laboratories and recrystallized from EtOH twice and toluene. The X-ray powder patterns ($5° < 2\theta < 40°$) were obtained with a Rigaku X-ray powder diffractometer RINT-2400 at room temperature or under temperature control of the samples. Water was flowed at the back of the sample-plate in order to keep sample temperature constant. Light used by Xe-lamp (Usio 150W) was focused through a convex lens to irradiate to the samples. A wavelength region of irradiation light was adjusted by a water cell which was through about 200 nm - 1350 nm light and by Toshiba Glass color filter C-50S about 300 nm - 700 nm as shown in Figure 1.

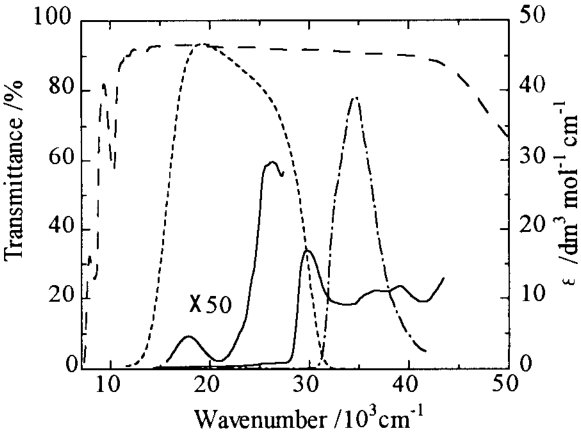

Figure 1. Absorption spectra of the complexes and transmittances of filters (absorption spectra of $Cr(acac)_3$ (———) and $Al(acac)_3$ (—·—·—), transmittances of water cell (— —) and C-50S filter (------)).

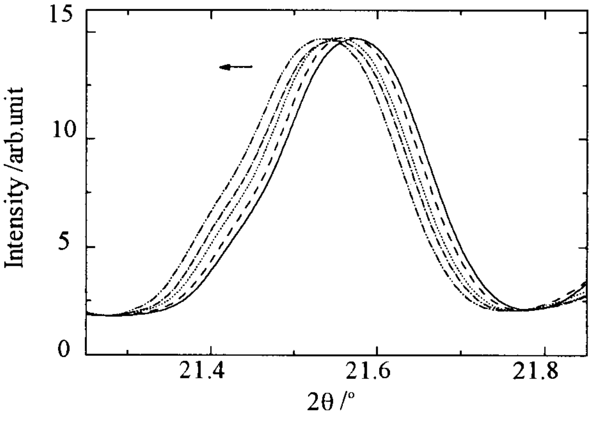

Figure 2. X-ray powder patterns of $Al(acac)_3$ at 30 °C (———), 35 °C (— —), 40 °C (------), 45 °C (—·—·—) and 50 °C (—··—).

The shifts of X-ray powder patterns of $Al(acac)_3$ and $Cr(acac)_3$ were observed at constant sample temperatures from 30 °C to 50 °C by 5 °C without light irradiation. Figure 2 shows typical shifts in X-ray powder pattern of $Al(acac)_3$. The peak corresponds to the reflection from (212) plane. Since all peaks in X-ray powder patterns of $Al(acac)_3$ and $Cr(acac)_3$ were shifted to low-reflect angle, the cells of these complexes were expanded by heating.

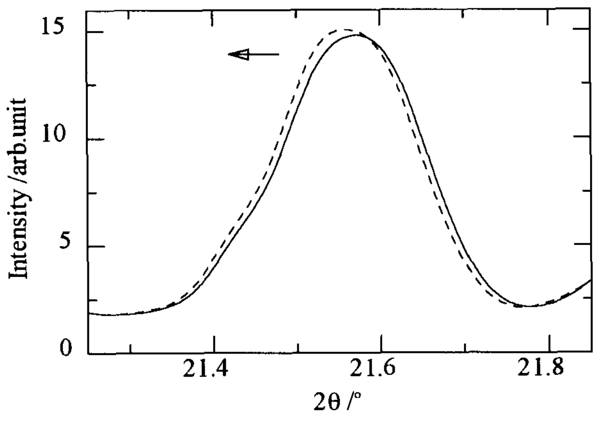

Figure 3. X-ray powder patterns of Al(acac)$_3$ without temperature control of the sample (under non irradiation (———), and under irradiation through water cell (— —)).

Figure 3 shows the shift of X-ray powder pattern of Al(acac)$_3$ under light irradiation without control of sample temperature. The solid line shows the pattern under no irradiation, and the broken line shows the pattern under light irradiation from 200 nm to 1350 nm (using the water cell). All peaks of X-ray powder pattern were shifted to low-reflect angle. However, no shift of X-ray powder pattern was observed under light irradiation cut off the UV region by C-50S filter. From these results it is cleared that light absorption is necessary for the shifts. When similar measurements were carried out with control of sample temperature at 30 ℃, no shift was observed in both cases. These results suggest that the shift observed above was due to increase in the temperature of the sample by the light absorption, e.g., the optical energy absorbed by Al(acac)$_3$ molecule was converted to the heat by internal conversion.

Figures 4a and 4b show X-ray powder patterns of Cr(acac)$_3$ measured without and with temperature control, respectively. All peaks of X-ray powder patterns were also shifted to low-reflect angle. By contrast with Al(acac)$_3$, X-ray powder patterns were shifted by light irradiation under both temperature conditions. The extents of the shifts were different between the results using two filters at uncontrolled temperature (Figure 4a). On the other hand, under controlled temperature at 30 ℃, the extents of the shifts were independent of the filters (Figure 4b). These results suggest that the shifts of X-ray powder patterns of Cr(acac)$_3$ at controlled temperature are due to not the heat but another mechanism, although the heat caused by the internal conversion of Cr(acac)$_3$ shifts the X-ray powder pattern. The mechanism can be considered to reflect the structures of the excited states of Cr(acac)$_3$.

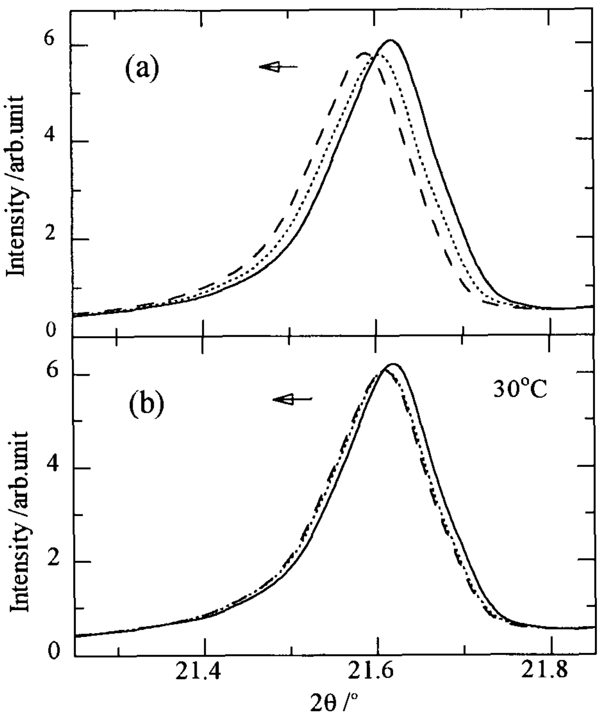

Figure 4. X-ray powder patterns of Cr(acac)$_3$ with (b) and without (a) temperature control of the sample. (under non irradiation(———), under irradiation through water cell (— —) and under irradiation through C-50S filter(·········)).

The appearances of X-ray powder patterns of two complexes were not changed by light irradiation and heating, while all peaks of X-ray powder patterns were shifted. All peaks shifted by light irradiation in this letter returned to original peaks when the light irradiation was cut off.

In case of [Bu$_4$N]$_4$[Pt$_2$(pop)$_4$] (pop^{2-}=P$_2$O$_5$H$_2$$^{2-}$), X-ray powder pattern was shifted to high-reflect angle by visible light irradiation under the both condition with and without temperature control of the sample.

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