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Unusually long-lived light-induced metastable state in a thermochromic copper(II) complex

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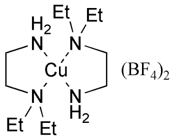
We report the first observation of a color change from red to purple for a thermochromic complex, $[Cu(dieten)_2](BF_4)_2$ (dieten = *N*,*N*-diethylethylenediamine), which is induced by illuminating with UV light.

There has been a great interest in developing novel molecular-based inorganic solids whose physical properties can be controlled by external perturbation.[1–5] One class of compounds that have been extensively studied are thermochromic materials.[1,2] Thermochromic phenomena have evoked a lot of interest because of their wide potential for different applications, ranging from temperature sensors to coatings. However, the change in the electronic structure *via* the thermal procedure is quite slow, limiting the utility of those systems. Hence, in order to access the materials with high speed and superior resolution, it is desirable that the electronic structure can be controlled by illumination. Until now, several photo-responsive inorganic solids such as Fe spin-crossover complexes, one-dimensional Pt complexes, sodium nitroprusside, and Prussian blue analogues have been reported.[6–9] However, unfortunately, the number of such phototunable inorganic molecular solids is quite small. Hence, it is important to search for new compounds whose physical properties can be controlled by light. Through the exploration of many different inorganic solids, we have discovered that a thermochromic complex $[Cu(II)(dieten)_2](BF_4)_2$,[10–19] where dieten represents *N*,*N*-diethylethylenediamine, can be trapped in an extremely long-lived metastable state, leading to a colour change from red to purple. To our knowledge, this is the first mononuclear Cu(II) complex exhibiting a photoswitchable phenomenon.



$[Cu(dieten)_2](BF_4)_2$

The Cu(II) complex, $[Cu(dieten)_2](BF_4)_2$, was prepared by the method reported earlier[10,11] and a sample annealed to 60 °C was used for all of the measurements.[12] Fig. 1 shows the absorption spectra measured by using a thin film of the complex on a CaF_2 plate. At room temperature, absorption peaks are observed at 515, 305 and 255 nm. The absorption peak at 515 nm is ascribable to the d–d transition of the Cu(II) ion.[13] On the other hand, the absorption bands in the UV region are ascribable to the ligand-to-metal charge transfer (LMCT) band.[13] On cooling, the absorption peak in the visible region shifted to shorter wavelength, resulting in the colour change from purple to red. At 35 K the absorption peak was observed at 455 nm. Furthermore, the absorption at 255 nm increased in intensity. According to previous papers, this colour change is caused by an increase in the in-plane field strength. That is, the copper atom lies in a square-planar configuration in the low-temperature (red) phase and in a dynamically disordered, slightly tetrahedral-distorted configuration in the high-temperature (purple) phase. Magnetic properties measured from 320 to 5 K show that the μ_{eff} value is constant, *i.e.* 1.8 μ_B, where μ_{eff} is the effective magnetic moment.

In order to excite the LMCT band, UV-light (Hg Lamp; 250–400 nm) which had passed through a band-pass filter was used as a pump light. After illumination at 35 K for 2 min (light intensity = *ca.* 10 mW cm^{-2}), it was clearly demonstrated that the absorption peak around 500 nm increased in intensity in the UV spectra shown in Fig. 1. This suggests that the unusually long-lived metastable state was induced by light. On the other hand, illumination with visible light (Hg–Xe lamp; 400–650 nm and YAG laser; 532 nm) instead of the UV light has no effect on the absorption spectra. The wavelength dependence shows that the observed phenomena proceeds *via* the photon mode and not the photo-thermal mode. It should be noted that this light-induced metastable state was quite stable and could be maintained for at least several hours after the illumination was stopped, even at 77 K. Furthermore, the change could be detected in the IR spectra after the sample was illuminated for 10 min at 16 K. However, the change is not a drastic one, but merely a slight change in intensity. The magnetic properties measured at 5 K showed that no change was observed in the μ_{eff} value (1.8 μ_B) after UV light illumination. These two observations mean that the change in the absorption spectra is not due to a change in the oxidation state, but to a change in the coordination geometry. By analogy to previous work relating to

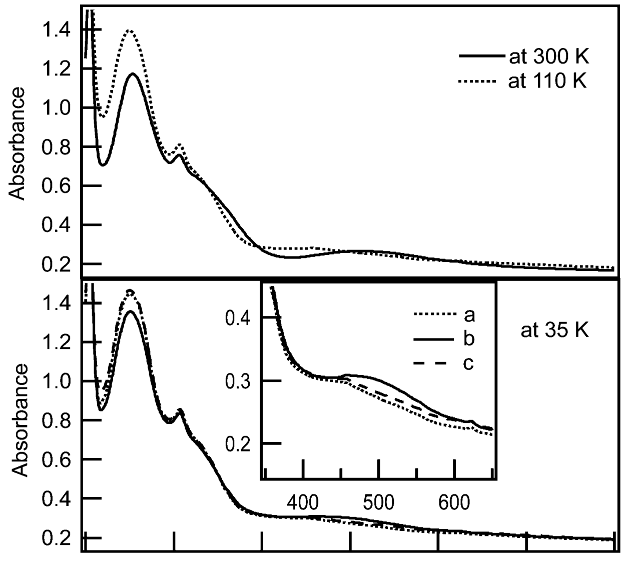


Fig. 1 UV–vis absorption spectra. Top: temperature-dependent spectra. Bottom: spectra (a) before and (b) after illumination, and (c) after thermal treatment to 150 K. Inset: expanded spectra from 350 to 650 nm.

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thermal colour change, the change in the UV spectra suggests that the UV-light illumination induces the transformation from a square-planar configuration to a slightly tetrahedral-distorted one around the copper atom.[11,12,20–22] This idea is consistent with the fact that Cu(I) ions, which are generated transiently by exciting the LMCT band, favour tetrahedral conformation rather than a planar structure.

The metastable state was found to have relaxed back to the original ground state after the temperature was raised to 150 K for a few minutes and then lowered again to 35 K. The reversible phenomenon, *i.e.* a recovery of the original ground state from the photo-induced one with thermal treatment, could be repeated several times. Furthermore, the reverse conversion from the light-induced state could be carried out by visible light illumination with a YAG laser (532 nm). Thus the colour of the complex can also be controlled by light as well as temperature.

In order to further investigate the structural change in the light-induced metastable state, powder X-ray diffraction (XRD) measurements were made before and after illumination at 20 K. Fig. 2 shows that after the UV light illumination for 10 min, a remarkable change in the diffraction pattern was observed between 20 and 30° (2θ). The characteristic difference was that the peak at 21.3° disappeared and the peak at 22.8° both shifted to lower angle and broadened. The photo-induced metastable state is stable for at least several hours at 20 K. After annealing, the original patterns were reproduced, indicating that this structural change was completely reversible. This observation is consistent with the result from the UV–vis spectra. It should be noted that the photo-induced metastable states in several molecular compounds such as FeCo Prussian blue have been reported to resemble that of their high-temperature phase. However, this is not the case for the present light-induced metastable state of the Cu complex. That is, the XRD pattern after illumination is not consistent with the pattern of the high-temperature phase.[20] This result, however, is not an unexpected one. As is described above, the Cu(II) compound has a dynamically disordered slightly tetrahedral-distorted conformation in the high-temperature phase. However, at low temperature, the puckering of the ethylene group must be substantially prevented. Hence, the structure of the metastable state should be a ‘static’ slightly tetrahedral-distorted one, not a dynamic structure. This indicates that the photo-induced transformation can realize a new state that is distinct from the thermally induced high-temperature phase.

An analogous compound, [Cu(dieten)$_2$](ClO$_4$)$_2$, isolated in 1938,[10] has been reported to be thermochromic. In this work we have also investigated the illumination effects for this compound. When it was illuminated with UV-light at 20 K, a change in the UV–vis spectra was clearly observed. That is, the absorbance at around 515 nm increases after illumination, and the resultant metastable state could be maintained for at least several hours at 20 K. It is thought that, as in the case of the BF$_4$ salt, a transformation from square-planar to the tetrahedral configuration was induced by UV-light. Thus the observation of an unusually long-lived metastable state in these discontinuous thermochromic Cu(II) complexes suggests that the materials showing bistability and strong cooperative interactions are expected to potentially realize a photo-induced transition of their physical properties.

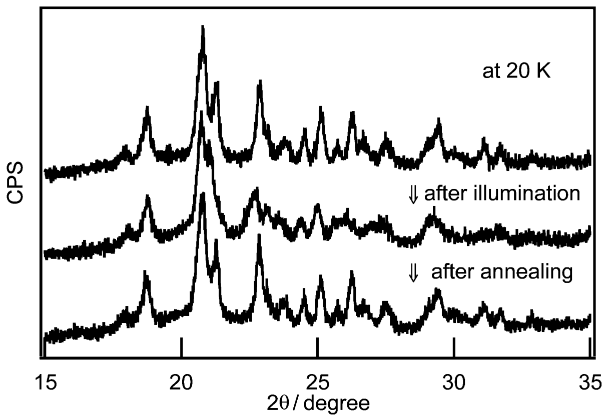

Fig. 2 X-Ray powder diffraction patterns before and after illumination.

In summary, we have investigated the illumination effects for a thermochromic Cu(II) compound. When the complex, [Cu(dieten)$_2$](BF$_4$)$_2$, was illuminated by UV-light, a structural change involving a color change was induced. The lifetime of the metastable state at 77 K was more than several hours. The structural change could be restored to the original state by either thermal treatment above 150 K or by illumination with visible light.

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