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Photo-induced valence tautomerism in a Co compound

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Abstract

Photo-illumination effects have been measured for $[\mathrm{Co^{III\text{-}LS}(tmeda)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)}]\cdot 0.5\mathrm{C_6H_5CH_3}$, where LS, tmeda, 3,5-DBSQ and 3,5-DBCat denote low-spin, *N,N,N′,N′*-tetramethylethylenediamine, 3,5-di-*tert*-butyl-1,2-semiquinonate and 3,5-di-*tert*-butyl-1,2-catecholate, respectively. When the title compound was illuminated at 5 K, the magnetization value increased from $\mu_{\mathrm{eff}} = 1.7$ to $2.3\mu_{\mathrm{B}}$. The absorption spectra after illumination show that the absorption band at around 800 nm, characteristic of the $[\mathrm{Co^{II\text{-}HS}(tmeda)(3,5\text{-}DBSQ)_2}]$ state (HS denotes high-spin), increased and the charge transfer band from 3,5-DBCat to 3,5-DBSQ at 2500 nm was reduced. IR spectra show that the C–O stretching peak at $1280\,\mathrm{cm^{-1}}$ is significantly decreased. These results confirm that a photo-induced intra-molecular electron transfer, $[\mathrm{Co^{III\text{-}LS}(tmeda)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)}] \rightarrow [\mathrm{Co^{II\text{-}HS}(tmeda)(3,5\text{-}DBSQ)_2}]$, was induced. The lifetime of the metastable state at 5 K was 175 min.

Keywords: Valence tautomerism; Photo-induced electron transfer; Long lifetime

1. Introduction

There has been a great interest in the study of the magnetic and optical properties of valence tautomeric compounds [1–16]. The valence tautomers are characterized by their having different distributions of electron density, where metal-to-ligand and metal-to-metal electron transfer accomplishes interconversion between tautomers. Buchanan and Pierpont reported that a Co complex, $[\mathrm{Co^{II\text{-}HS}(bpy)(3,5\text{-}DBSQ)_2}]$, shows Co-quinone electron transfer in toluene solution, where HS denotes high-spin [3]. We have reported that CoFe Prussian blue shows a photo-induced magnetization effect [9–11]. Furthermore, it has been reported that Co complexes exhibit photo-mechanical crystal vibration and photo-induced long-lived electron transfer [7,8,13–16]. Recently, Yokoyama et al. clarified the electronic state of the photo-induced metastable state by X-ray absorption spectroscopy [16]. Here, we describe that a novel Co compound, $[\mathrm{Co^{III\text{-}LS}(tmeda)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)}]\cdot 0.5\mathrm{C_6H_5CH_3}$, shows an intra-molecular electron transfer with extremely long lifetime in response to visible light. The lifetime of the metastable state at 5 K was 175 min. The photo-induced valence tautomerism is of interest in connection with the photo-induced magnetization and photo-induced spin transition [9–12,17,18].

2. Experimental details

The Co complex, $[\mathrm{Co^{II\text{-}HS}(tmeda)(3,5\text{-}DBSQ)_2}]\cdot 0.5\mathrm{C_6H_5CH_3}$, was prepared by adding 15 ml toluene solution of tmeda (0.046 g) to 50 ml toluene solution suspended $[\mathrm{Co(3,5\text{-}DBSQ)_2}]_4$ (0.20 g), followed by slow evaporation under a flow of Ar gas. Anal. Calcd. (found) for $[\mathrm{CoC_{34}H_{56}N_2O_4}]\cdot 0.5\mathrm{C_6H_5CH_3}$: C, 68.60 (67.93); H, 9.30 (9.09); N, 4.10 (4.18); Co, 8.63 (8.73). The magnetic susceptibilities were measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) in an external field of 0.5 T. Light was guided into the SQUID magnetometer via an optical fiber in order to study the photo-effects. A powder sample (100–300 μg) was supported on a commercial transparent adhesive tape and placed on the edge of the optical fiber. The infra-red (IR) and UV–VIS spectra were measured with an FTS-40A (Bio-Rad) and UV-3100 (Shimazu) spectrophotometer, respectively. The IR measurements were performed by the KBr method. UV–VIS spectra were measured for

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the polystyrene film in which the Co complex was embedded. The film was prepared by dissolving the Co complex and polystyrene in a toluene solution and solution-casting on glass slides. Note that the Co complexes are dispersed randomly in the polystyrene film and hence no cooperative interaction operates. This means that the sample condition for the UV–VIS measurement is different from that for IR and magnetization measurements. Temperature control for the IR and UV–VIS measurements were performed by using a helium-flow type refrigerator (Helitran LT-3-110) with a model 331 temperature controller (LakeShore). An Hg–Xe lamp (Yamashita Denso XFL-300L) and a laser-diode pumped Nd:YAG laser (Crystal Laser GCL-150-M) with a wavelength of 532 nm were used as light sources. Band-pass filters with 50 nm band-width (Melles Griot Visible 40 Filter Set) were used to choose an appropriate wavelength in the visible light spectrum of the Hg–Xe lamp.

3. Results and discussion

Fig. 1 shows the μ_{eff} versus *T* curve measured for [$\mathrm{Co^{II\text{-}HS}}$(tmeda)(3,5-DBSQ)$_2$], where μ_{eff} is the molar effective magnetic moment and *T* is the temperature. The μ_{eff} value at 300 K is equal to 5.2μ_B. On cooling, it abruptly decreases at around 195 K. The μ_{eff} value at 5 K is equal to 1.7μ_B. The valence tautomeric behavior, [$\mathrm{Co^{II\text{-}HS}}$(tmeda)(3,5-DBSQ)$_2$] $\leftrightarrows$ [$\mathrm{Co^{III\text{-}LS}}$(tmeda)(3,5-DBSQ)(3,5-DBCat)], is consistent with that reported previously [1–8]. Fig. 2 shows the change in the absorption spectra. The characteristic absorption in the high-temperature phase is the $\mathrm{Co^{II\text{-}HS}}$ to 3,5-DBSQ charge transfer (CT) band observed at around 800 nm. On the other hand, the low temperature phase has a characteristic absorption band at around 2500 nm, which is ascribable to a CT band from 3,5-DBCat to 3,5-DBSQ. Additionally, in analogy with the UV–VIS spectrum of [$\mathrm{Co^{II\text{-}HS}}$(1,10-phenanthrolin)(3,5-DBSQ)$_2$]·$C_6H_5CH_3$, it can be concluded that the absorption at around 650 nm is constituted from the transition from the filled molecular π-orbital to the unoccupied π*-orbital of 3,5-DBSQ and the transition from 3,5-DBCat to $\mathrm{Co^{III\text{-}LS}}$ [6].

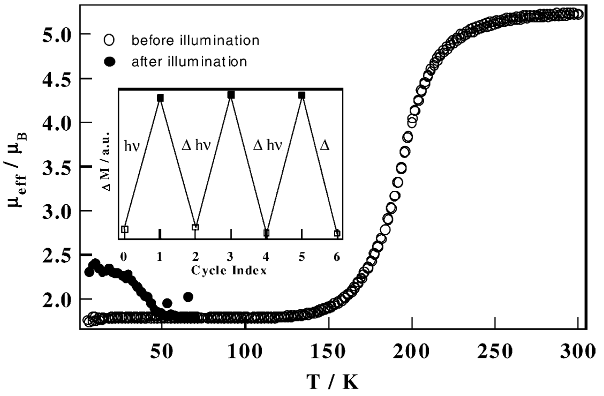

Fig. 1. The μ_{eff} vs. *T* plots before and after illumination. The sweep rate is 2 K min^{-1}. Inset: changes in the magnetization at 5 K. The notations, *hν* and *Δ*, represent illumination at 5 K and thermal treatment at 60 K, respectively.

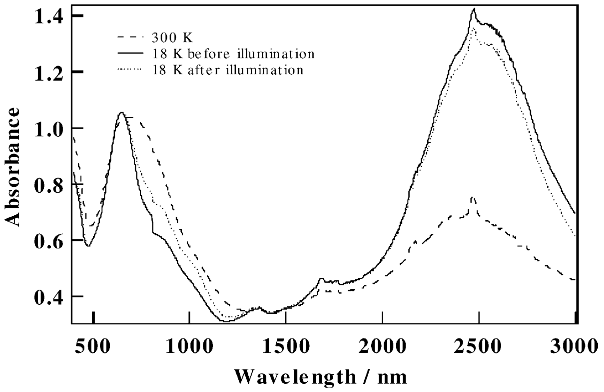

Fig. 2. UV–VIS spectra at 300 K, 18 K before illumination and 18 K after illumination. In contrast to the discontinuous transition in the polycrystalline sample, the transition from [$\mathrm{Co^{II\text{-}HS}}$(tmeda)(3,5-DBSQ)$_2$] to [$\mathrm{Co^{III\text{-}LS}}$(tmeda)(3,5-DBSQ)(3,5-DBCat)] in polystyrene film is a continuous one. This is because the Co complexes are dispersed in the film and hence no cooperativity operates. Hence, the [$\mathrm{Co^{III\text{-}LS}}$(tmeda)(3,5-DBSQ)(3,5-DBCat)] moieties with a characteristic ligand to ligand CT band at 2500 nm are present even at 300 K.

When the complex, [$\mathrm{Co^{III\text{-}LS}}$(tmeda)(3,5-DBSQ)(3,5-DBCat)], was illuminated at 5 K in the SQUID cavity with the 532 nm light (diode pumped Nd:YAG laser) in order to excite the 3,5-DBCat to $\mathrm{Co^{III\text{-}LS}}$ CT band, an increase in the magnetization value was observed. The time dependence of the change in magnetization under light illumination with an intensity of ca. 10 mW/cm^2 at 5 K shows that the magnetization value started to increase upon illumination, and then saturated. This indicates that an intra-molecular charge transfer, [$\mathrm{Co^{III\text{-}LS}}$(tmeda)(3,5-DBSQ)(3,5-DBCat)] → [$\mathrm{Co^{II\text{-}HS}}$(tmeda)(3,5-DBSQ)$_2$], is induced by the illumination. Similar behavior could be observed at 15, 25 and 35 K. However, when the illumination was carried out at 55 K, no change could be observed. Furthermore, it was found that the change at 5 K could be observed when the compound was illuminated by the visible light, i.e. light at 450, 550 and 650 nm with a band-width of 50 nm.

Fig. 3 shows the relaxation curves measured after the light was turned off. Although the decrease in the magnetization value is clearly observed, the decay rate is quite slow. The lifetimes at 5 and 15 K are 175 and 70 min, respectively. The μ_{eff} versus *T* curve measured after illumination at a rate of 2 K min^{-1} shows that the magnetization value at 5 K is ca. 2.3μ_B (Fig. 1). The change in magnetization induced by the light can be maintained at low temperature. However, at 50 K, the metastable state recovered to the original one. This means that the lifetime at 50 K becomes less than several seconds, during which time interval the dc magnetization value can be measured in our SQUID system. This is consistent with the fact that the change in the magnetization by light cannot be observed above 50 K. This phenomenon, i.e.

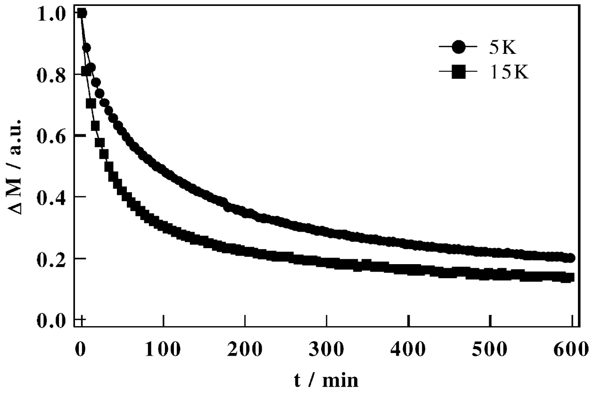

Fig. 3. Relaxation curves after illumination at 5 and 15 K. The change in magnetization, ΔM, induced by light is normalized at $t = 0$ min.

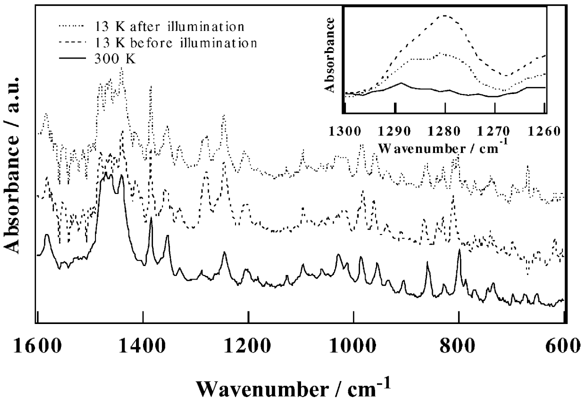

Fig. 4. IR spectra at 300 K, before illumination at 13 K and after illumination at 13 K. Inset: expanded spectra from 1300 to 1260 cm^{-1}. The peak at 1280 cm^{-1} is ascribable to the C–O stretch vibration of 3,5-DBCat.

an increase in magnetization induced by light that could be recovered to the original state by thermal treatment above 50 K, could be repeated several times (Fig. 1).

The absorption spectra after illumination show that the $Co^{II\text{-}HS}$ to 3,5-DBSQ CT band at around 800 nm, characteristic of the $[Co^{II\text{-}HS}(tmeda)(3,5\text{-}DBSQ)_2]$ state, is increased. Furthermore, it was found the absorption band at 2500 nm, which is ascribable to the charge transfer from 3,5-DBCat to 3,5-DBSQ of the $[Co^{III\text{-}LS}(tmeda)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]$ state, is reduced after illumination. These spectra show that intra-molecular charge transfer is induced by light. Furthermore, by heating the sample at 100 K we could restore the change in the absorption spectra. This means that the relaxation involving the electron transfer from $Co^{II\text{-}HS}$ to 3,5-DBSQ is thermally induced. The absorption spectra show that less than 10% of the moieties were changed to $[Co^{II\text{-}HS}(tmeda)(3,5\text{-}DBSQ)_2]$ state by illumination.

The C–O stretching modes are sensitive to the charge of the ligand moieties. The C=O stretching for free quinone occurs at around 1675 cm^{-1}, while the peak shifts to lower energy by ca. 60 cm^{-1} when the quinone is coordinated to a metal ion [19]. Furthermore, when the quinone is reduced to catechole, the stretching mode shifts further to lower frequency. Fig. 4 shows the IR spectra before and after illumination. The C–O stretch vibration of 3,5-DBCat in $[Co^{III\text{-}LS}(tmeda)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]$ is observed at 1280 cm^{-1} [20]. On warming, the peak significantly decreased due to thermally induced valence tautomerism. When the complex, $[Co^{III\text{-}LS}(tmeda)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]$, is illuminated at 13 K (ca. 30 mW/cm^2), the peak of the C–O stretch vibration is significantly decreased. This clearly shows that the visible light induces the charge transfer from 3,5-DBCat to $Co^{III\text{-}LS}$. When the fraction of the metastable state was estimated from the peak at 1280 cm^{-1}, about 50 ± 10% of the moieties were changed to $[Co^{II\text{-}HS}(tmeda)(3,5\text{-}DBSQ)_2]$ state by illumination. Note that this value is different from that estimated from UV–VIS spectra. This is because, as is described above, the sample condition is different from each other, i.e. the polystyrene film for UV–VIS measurements and polycrystalline sample for IR measurements. In our opinion, this suggests that the cooperativity due to the intermolecular interaction play a key role in achieving the long-lived metastable state.

An important characteristic of the present phenomena is that the magnetization value after illumination does not reach the level observed for $[Co^{II\text{-}HS}(tmeda)(3,5\text{-}DBSQ)_2]$ at 300 K, i.e. $5.2\mu_B$. Because the magnetization was measured for the polycrystalline sample, it is thought that about 50 ± 10% of the moieties were changed to $[Co^{II\text{-}HS}(tmeda)(3,5\text{-}DBSQ)_2]$ state by illumination. Assuming that 50% of the moieties change to the metastable state, the magnetization value should be $3.5\mu_B$. However, the experimental value at 5 K is $2.3\mu_B$. Such a small magnetization value can be explained by the presence of intramolecular magnetic exchange interactions between the 3,5-DBSQ ligands and the $Co^{II\text{-}HS}$ ion. The exchange interactions in the present compounds can be divided into two types. The interaction between the π-orbital of 3,5-DBSQ and the e_g orbital of the $Co^{II\text{-}HS}$, which are orthogonal to each other, is ferromagnetic. The other interaction between the π-orbital of 3,5-DBSQ and t_{2g} orbital of the $Co^{II\text{-}HS}$, which overlap with each other, gives rise to anti-ferromagnetic character. When the ferromagnetic and anti-ferromagnetic interactions are superimposed, the anti-ferromagnetic term, in general, dominates the interactions. Therefore, anti-ferromagnetic interactions are expected between 3,5-DBSQ ligands and the $Co^{II\text{-}HS}$ ion. In fact, the magnetic interaction of $[Co_4{}^{II\text{-}HS}(3,5\text{-}DBSQ)_8]$ is anti-ferromagnetic with an exchange parameter of $J = -30\ cm^{-1}$ [21]. Furthermore, it has been reported that the interaction in $[Co^{II\text{-}HS}(1,10\text{-}phenanthrolin)(3,5\text{-}DBSQ)_2]\cdot C_6H_5CH_3$ can be calculated to be anti-ferromagnetic in nature with $J = -594\ cm^{-1}$ [6]. The presence of the exchange interactions gives rise to four different electronic states: one $S = \frac{1}{2}$ spin state, two $S = \frac{3}{2}$ states and one $S = \frac{5}{2}$ state. When the anti-ferromagnetic interaction operates in the compounds, the lowest energy in the four states is the $S = \frac{1}{2}$ state and

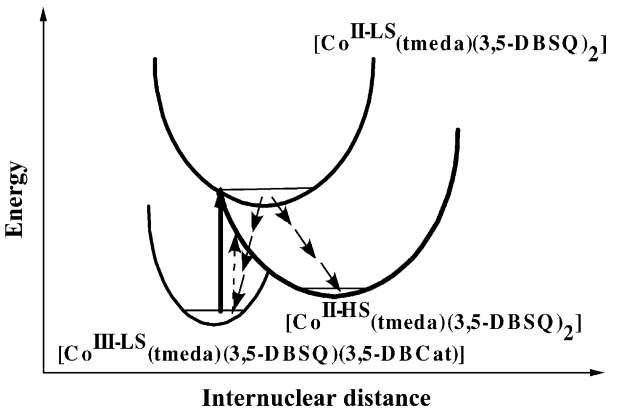

Fig. 5. Potential energy diagram of electronic charge transfer states of the Co complex.

the highest is the $S = \frac{5}{2}$ state. Hence, the $S = \frac{1}{2}$ state is mainly populated at sufficiently low temperature. As a result, the magnetization value after illumination is small compared with $\mu_{\mathrm{eff}} = 3.5\mu_{\mathrm{B}}$, which is estimated from the magnetization at 300 K. It is important to note that, in order to further clarify the origin of the small magnetization value, the measurement of the crystal structure after illumination is needed.

The charge transfer process is schematically illustrated in Fig. 5. Two possible optical CT transition routes can be considered. One is the direct transition to [Co$^{\mathrm{II\text{-}HS}}$(tmeda)(3,5-DBSQ)$_2$], but the spin-forbidden process may not be seen in the spectrum. Another transition to [Co$^{\mathrm{II\text{-}LS}}$(tmeda)(3,5-DBSQ)$_2$] is spin-allowed and could be induced by exciting the CT band. After excitation, some fractions of the excited state relax back to the initial state. However, an alternative spin forbidden decay path, [Co$^{\mathrm{II\text{-}LS}}$(tmeda)(3,5-DBSQ)2] → [Co$^{\mathrm{II\text{-}HS}}$(tmeda)(3,5-DBSQ)$_2$], could be possible due to spin–orbit coupling. Consequently, the metastable [Co$^{\mathrm{II\text{-}HS}}$(tmeda)(3,5-DBSQ)$_2$] state can be populated by using visible light.

In summary, we have shown that a Co complex, [Co$^{\mathrm{III\text{-}LS}}$(tmeda)(3,5-DBSQ)(3,5-DBCat)]·0.5$C_6H_5CH_3$, exhibits a photo-induced valence tautomerism. Upon illumination, one electron in 3,5-DBCat is transferred to Co$^{\mathrm{III\text{-}LS}}$, yielding Co$^{\mathrm{II\text{-}HS}}$ and 3,5-DBSQ. The process is expressed as [Co$^{\mathrm{III\text{-}LS}}$(tmeda)(3,5-DBSQ)(3,5-DBCat)] → [Co$^{\mathrm{II\text{-}HS}}$(tmeda)(3,5-DBSQ)$_2$]. The photo-induced metastable state could be trapped for 175 min at 5 K.

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