

Mechanism and relaxation kinetics of photo-induced valence tautomerism of $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$

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Abstract

Photo-illumination effects have been measured for $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl}$, where LS, phen, 3,5-DBSQ and 3,5-DBCat denote low-spin, 1,10-phenanthroline, 3,5-di-*tert*-butyl-1,2-semiquinone and 3,5-di-*tert*-butyl-1,2-catechol, respectively. When the Co compound was illuminated at 5 K, the magnetization value, μ_{eff} increased from 1.7 to 2.7 μ_{B} . The UV-Vis absorption spectra after illumination show that the absorption band at around 800 nm, characteristic of the $[\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2]$ 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 cm^{-1} is significantly decreased. These results confirm that a photo-induced intra-molecular electron transfer, $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl} \leftrightarrow [\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$, was induced by 532 or 830 nm light. The relaxation kinetics of valence tautomerism was studied. For $T \geq 25$ K, $k_{\text{T}}^0 = 0.205 \text{ s}^{-1}$ and $E_{\text{a}} = 110.38 \text{ cm}^{-1}$. Below 25 K, the rate constant for the valence tautomeric relaxation as T approaches the 0 K, which suggests that tunneling is the predominant mechanism for the relaxation.

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1. Introduction

There has been a great interest in the study of the magnetic and optical properties of valence tautomeric compounds [1–11]. These compounds are excellent model systems for elucidating factors that control intra-molecular electron transfer and can serve as fast optical switching devices. 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. Adams et al. [7] reported results of the first picosecond time-resolved optical experiments on valence tautomeric cobalt complexes. Buchanan and Pierpont [8] reported that a Co complex, $[\text{Co}^{\text{II-HS}}(\text{bpy})(3,5\text{-DBSQ})_2]$, shows Co-quinone electron transfer in toluene solution, where HS denotes high-spin. Yokoyama et al. [9] clarified the electronic state of the

photo-induced metastable state by X-ray absorption spectroscopy. Sato et al. [10] have reported that a Co compound, $[\text{Co}^{\text{III-LS}}(\text{tmeda})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$, shows an intra-molecular electron transfer with extremely long lifetime in response to visible light, where LS denotes low-spin.

In this paper, we study the photo-induced valence tautomerism and the relaxation kinetics of a novel Co compounds, $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$.

2. Experimental procedures

The Co complex, $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$, was synthesized according to the methods reported by Adams et al. [11]. 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 com-

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mercial transparent adhesive tape and placed on the edge of the optical fiber. The infrared (IR) and UV-Vis spectra were measured with an FTS-40A (Bio-Rad) and UV-3100 (Shimadzu) spectrophotometer, respectively. The IR measurements were performed by the KBr method. UV-Vis spectra were measured for the polystyrene film in which the Co complex was embedded. The film was prepared by dissolving the Co complex 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). A laser-diode with a wavelength of 830 nm, a laser-diode pumped Nd:YAG laser (Crystal Laser GCL-150-M) with a wavelength of 532 nm were used as the light sources.

3. Results and discussion

When the complex was illuminated at 5 K with the 532 nm light, an increase in the magnetization value was observed. Fig. 1 shows the curve of μ_{eff} versus illumination time of 532 nm light, where μ_{eff} is the molar effective magnetic moment. The μ_{eff} of $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ increased from 1.7 to $2.7\mu_{\text{B}}$ in 1 min, and then saturated during the illumination. The rapid response to light irradiation of this complex could be used for optical switching devices.

Fig. 2 shows the μ_{eff} versus T curve measured for $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$, where T is the temperature. The μ_{eff} value at 300 K is equal to $4.75\mu_{\text{B}}$. On cooling, it abruptly decreases at around 250 K. The μ_{eff} value at 5 K is equal to $1.7\mu_{\text{B}}$. $T_{1/2}$ is about 225 K. The valence tautomeric behavior, $[\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})]\cdot\text{C}_6\text{H}_5\text{Cl} \leftrightarrow [\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl}$, is consistent with that reported previously [1–8]. When the complex, $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl}$ was

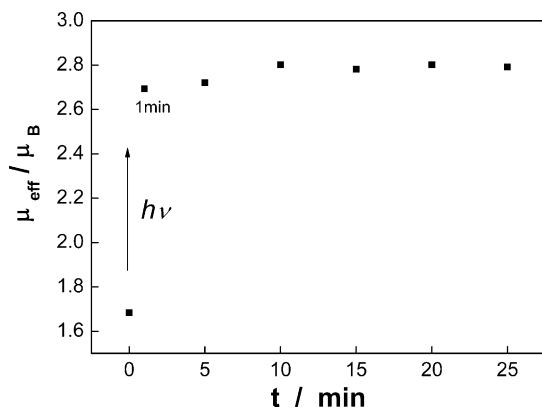


Fig. 1. Rapid photo-response of $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ illuminated with 532 nm at 5 K.

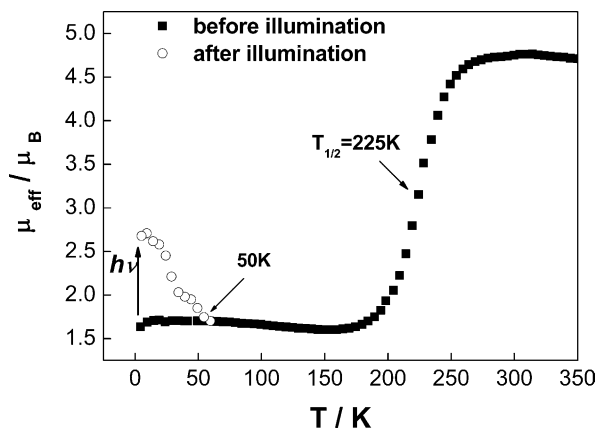


Fig. 2. The μ_{eff} vs. T plots of $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ before and after illumination. The sweep rate is 5 K min^{-1} .

illuminated at 5 K in the SQUID cavity with the 532 nm light (diode pumped Nd:YAG laser) of an intensity of ca. 70 mW cm^{-2} in order to excite the 3,5-DBCat to $\text{Co}^{\text{III-LS}}$ CT band, an increase in the magnetization value was observed convenient with Fig. 1. When temperature increased from 5 K, the magnetization value began to decrease till 50 K.

Fig. 3 shows the change in the UV-Vis absorption spectra of $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ at 300 K, 11 K before and after illumination. The characteristic absorption in the high-temperature phase is the $\text{Co}^{\text{II-HS}}$ 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 $[\text{Co}^{\text{II-HS}}(1,10\text{-phenanthroline})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{CH}_3$, it can be concluded that the absorption at around 650 nm

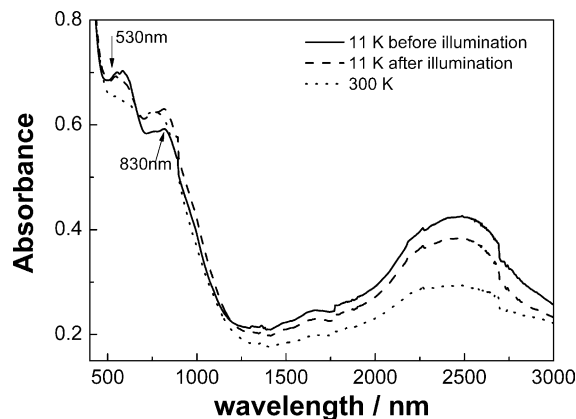


Fig. 3. UV-Vis spectra of $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ at 300, 11 K before and after illumination. In contrast to the discontinuous transition in the polycrystalline sample, the transition from $[\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ to $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl}$ 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 $[\text{Co}^{\text{III-LS}}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{phen})]\cdot\text{C}_6\text{H}_5\text{Cl}$ moieties with a characteristic ligand to ligand CT band at 2500 nm are present even at 300 K.

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 $\text{Co}^{\text{III-LS}}$ [5]. This indicates that an intra-molecular charge transfer, $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})] \cdot \text{C}_6\text{H}_5\text{Cl} \rightarrow [\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2] \cdot \text{C}_6\text{H}_5\text{Cl}$, is induced by the illumination. Similar behavior could be observed at 16, 25 and 35 K. However, when the illumination was carried out at 55 K, no change could be observed.

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 [12]. Furthermore, when the quinone is reduced to catecholate, 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 $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})] \cdot \text{C}_6\text{H}_5\text{Cl}$ is observed at 1280 cm^{-1} [13]. On warming, the peak significantly decreased due to thermally induced valence tautomerism. When the complex, $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})] \cdot \text{C}_6\text{H}_5\text{Cl}$, is illuminated at 16 K, the peak of the C–O stretch vibration between 1280 and 1290 cm^{-1} is significantly decreased. This clearly shows that the 532 nm light induces the charge transfer from 3,5-DBCat to $\text{Co}^{\text{III-LS}}$.

Fig. 5 shows the change in magnetization after heating treatment and illumination with two type of lights for $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2] \cdot \text{C}_6\text{H}_5\text{Cl}$. Before illumination, the magnetization value is ca. $1.7\mu_{\text{B}}$ at cycle 1. After the LMCT

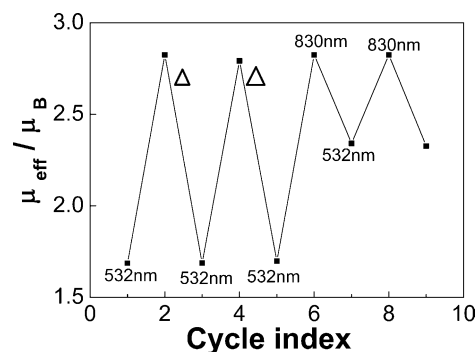


Fig. 5. Magnetization variations of $\text{Co}(\text{phen})(3,5\text{-DBSQ})_2 \cdot \text{C}_6\text{H}_5\text{Cl}$ by thermal treatment at 100 K and alternate illumination with 532 and 830 nm light.

band in the ground state was excited with 532 nm light (ca. 70 mW cm^{-2}), the magnetization value was increased to $2.7\mu_{\text{B}}$. Upon heating, the μ_{eff} value decreases and reaches the original value of $1.7\mu_{\text{B}}$ for the low-spin state. By the thermal treatment, the excited state can be reduced to ground state due to the thermal valence tautomerism. This can be repeated several times as shown in Fig. 5. Moreover, when the metastable complex, $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2] \cdot \text{C}_6\text{H}_5\text{Cl}$ was illuminated at 5 K with 830 nm light (ca. 30 mW cm^{-2}), the magnetization value decreases to $2.3\mu_{\text{B}}$. This means that the back electron transfer from the $\text{Co}^{\text{II-HS}}$ to 3,5-DBSQ was induced in the metastable state by light, which is consistent with the result of the absorption spectra described above. The reversible change in magnetization induced by alternate

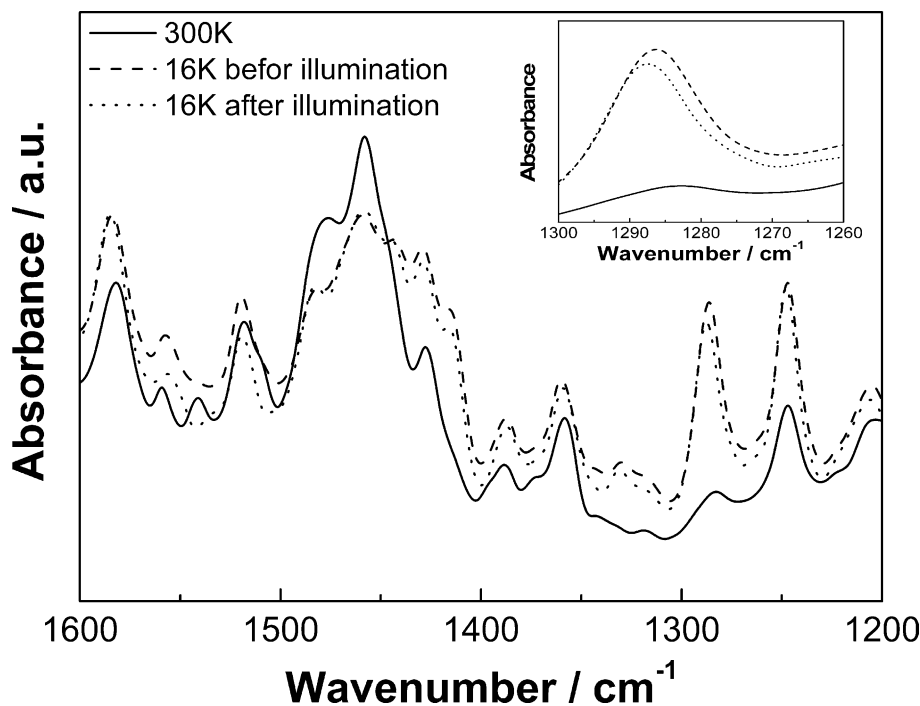


Fig. 4. IR spectra at 300 K, at 16 K before illumination and 16 K after illumination. Inset: expanded spectra from 1300 to 1260 cm^{-1} . The peak between 1280 and 1290 cm^{-1} is ascribable to the C–O stretch vibration of 3,5-DBCat.

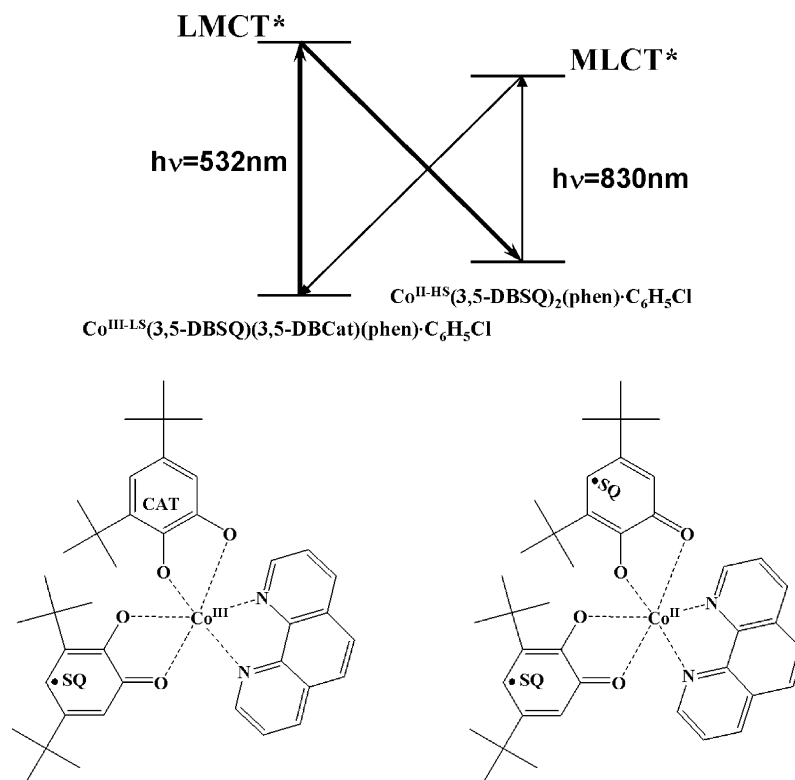


Fig. 6. Simplified Jablonski-type energy-level diagram of $[\text{Co}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$.

illumination with 532 and 830 nm light could be repeated several times.

The photo-induced valence tautomerism of the Co complex can be explained by the charge transformation between ligand and metal ion. When the ligand-to-metal charge transfer (LMCT) in the Co complex was excited with 532 nm light below 50 K, the ground state, $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl}$ was transformed into the metastable state, $[\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$. The electronic structure of this metastable state is identical with the high temperature phase. Hence, after illumination, the MLCT band from $\text{Co}^{\text{II-HS}}$ to 3,5-DBSQ at around 830 nm in the metastable state increased and the LMCT band from 3,5-DBCat to 3,5-DBSQ at 2500 nm in the ground state, $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl}$, decreased as shown in UV-Vis spectra [5]. On the other hand, when the metastable state was illuminated with 830 nm light, the metal-to-metal charge transfer (MLCT) from $\text{Co}^{\text{II-HS}}$ to 3,5-DBSQ was excited. The metastable state, $[\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ was transformed back into the ground state, $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl}$. As a result, the magnetization value decreased. The charge transfer process is schematically illustrated in Fig. 6.

The relaxation kinetics of HS to LS state transitions for the Co complex were studied following the photo-induced valence tautomerism effect at different temperatures. Fig. 7(a) shows the relaxation of the excited state,

$[\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ at four temperatures. For each run, the crystalline sample was cooled to the set temperature, irradiated for 10 min with 532 nm light until the magnetization value saturated. The decays of the valence tautomeric molar fraction, γ_{VT} , versus time at various temperatures are represented; γ_{VT} is deduced from the magnetization value in Eq. (1) and normalized to unity at time 0. An analysis of these data indicates that the relaxation curves can be satisfactorily fitted with an Arrhenius law up to 40 K shown in Eq. (2) [14].

$$\gamma_{\text{VT}}(t) = \frac{M(t) - M^0}{M(0) - M^0} \times 100\% \quad (1)$$

where $M(t)$ is the magnetization value at time t after illumination, $M(0)$ the saturated magnetization value at time 0 after illumination and M^0 is the magnetization value before illumination.

$$\gamma_{\text{VT}}(t) = \exp(-k_{\text{VT}}(T)t) \quad (2)$$

where $k_{\text{VT}}(T)$ is the rate constant of valence tautomeric relaxation at temperature T . The $k_{\text{VT}}(T)$ values were obtained from a least-squares fitting of the experimental data. Fig. 7(b) presents the $\ln[k_{\text{VT}}(T)]$ versus $1/T$ plot. A thermally activated relaxation behavior at elevated temperatures and a nearly temperature independent relaxation behavior at low temperatures can be observed. For $T \geq 25$ K, the $\ln[k_{\text{VT}}(T)]$ versus $1/T$ plot gives a straight line, with $k_{\text{VT}}^0 = 0.205 \text{ s}^{-1}$ and $E_a = 110.38 \text{ cm}^{-1}$. For $5 \text{ K} \leq T < 25 \text{ K}$,

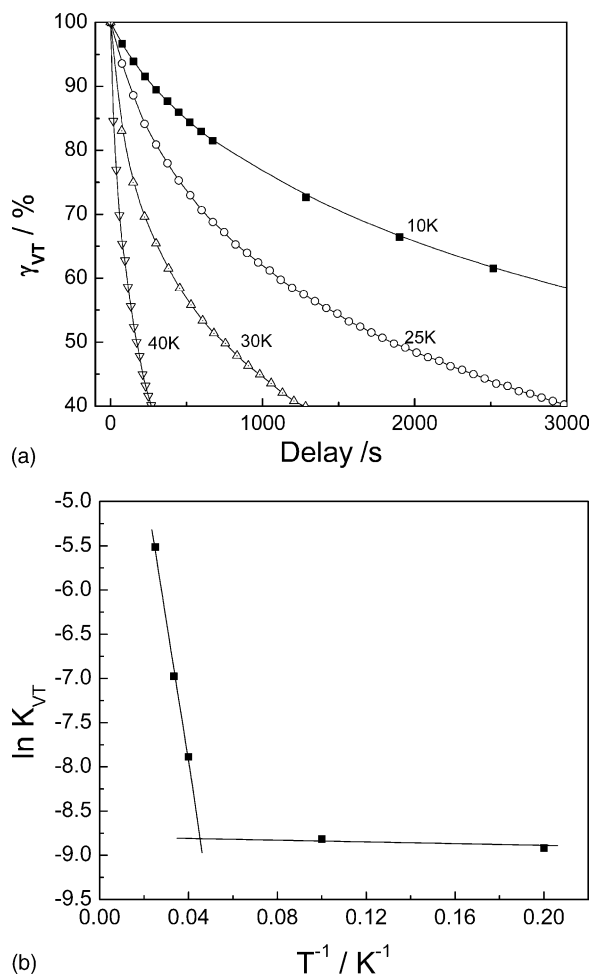


Fig. 7. Photo-induced valence tautomerism relaxation of $[\text{Co}^{\text{III-LS}}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{phen})]\cdot\text{C}_6\text{H}_5\text{Cl}$: (a) photo-induced valence tautomerism relaxation curves of $[\text{Co}^{\text{III-LS}}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{phen})]\cdot\text{C}_6\text{H}_5\text{Cl}$ at different temperatures: 10, 25, 30 and 40 K; (b) rate constants for the photo-induced valence tautomerism relaxation plotted as $\ln k_{VT}$ vs. $1/T$.

the $\ln[k_{VT}(T)]$ versus $1/T$ plot gives a straight line with a near-zero slope and a pre-exponential factor k_{VT}^0 of $1.48 \times 10^{-4} \text{ s}^{-1}$. The rate constant for the valence tautomeric re-

laxation as T approaches the absolute 0, which suggests that tunneling is the predominant mechanism for the relaxation below 25 K [14].

4. Conclusion

In summary, we have shown that a Co complex, $[\text{Co}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{phen})]\cdot\text{C}_6\text{H}_5\text{Cl}$, exhibits a photo-induced valence tautomerism. Upon illumination with 532 nm light, one electron in 3,5-DBCat is transferred to $\text{Co}^{\text{III-LS}}$, yielding $\text{Co}^{\text{II-HS}}$ and 3,5-DBSQ. The metastable state, $[\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$ returns back to the ground state by illuminating with 830 nm light, or relaxation during enough time. The processes can be expressed as $[\text{Co}^{\text{III-LS}}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})]\cdot\text{C}_6\text{H}_5\text{Cl} \leftrightarrow [\text{Co}^{\text{II-HS}}(\text{phen})(3,5\text{-DBSQ})_2]\cdot\text{C}_6\text{H}_5\text{Cl}$.

References

- [1] C.G. Pierpont, R.M. Buchanan, *Coord. Chem. Rev.* 38 (1981) 45.
- [2] P. Gütllich, A. Dei, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2734.
- [3] O.-S. Jung, C.G. Pierpont, *Inorg. Chem.* 33 (1994) 2227.
- [4] D.M. Adams, D.N. Hendrickson, *J. Am. Chem. Soc.* 118 (1996) 11515.
- [5] D.M. Adams, L. Noodleman, D.N. Hendrickson, *Inorg. Chem.* 36 (1997) 3966.
- [6] O. Sato, Y. Einaga, A. Fujishima, K. Hashimoto, *Inorg. Chem.* 38 (1999) 4405.
- [7] D.M. Adams, B. Li, J.D. Simon, D.N. Hendrickson, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1481.
- [8] R.M. Buchanan, C.G. Pierpont, *J. Am. Chem. Soc.* 102 (1980) 4951.
- [9] T. Yokoyama, K. Okamoto, K. Nagai, T. Ohta, S. Hayami, Z.-Z. Gu, R. Nakajima, O. Sato, *Chem. Phys. Lett.* 345 (2001) 272.
- [10] O. Sato, S. Hayami, Z. Gu, K. Takahashi, R. Nakajima, K. Seki, A. Fujishima, *J. Photochem. Photobiol. A* 149 (2002) 111.
- [11] D.M. Adams, A. Dei, A.L. Rheingold, D.N. Hendrickson, *J. Am. Chem. Soc.* 115 (1993) 8221.
- [12] P.J. Crowley, H.M. Haendler, *Inorg. Chem.* 1 (1962) 904.
- [13] M.W. Lynch, M. Valentine, D.N. Hendrickson, *J. Am. Chem. Soc.* 104 (1982) 6982.
- [14] J.-F. Létard, P. Guionneau, L. Rabardel, J.A.K. Howard, A.E. Goeta, D. Chasseau, O. Kahn, *Inorg. Chem.* 37 (1998) 4432.