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Journal of Photochemistry and Photobiology A: Chemistry 161 (2004) 243–246

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Novel Co complex with high transformation temperature of valence tautomerism

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Received 11 July 2003; received in revised form 22 July 2003; accepted 2 August 2003

Abstract

The preparation and characterization of [$Co^{II\text{-}HS}$(dpa)(3,5-DBSQ)$_2$] are presented first time. From the magnetic curve, the phase transition temperatures, T_c is 380 K. To our knowledge, the T_c value is the highest among the species exhibiting thermal valence tautomerism. After illumination with 532 nm light at 5 K, the magnetization values increase from $\mu_{eff} = 1.73$ to $2.0\mu_B$, showing valence tautomerism. The metastable state will recover to the original state with the increase of temperature. The alternate illumination with 532 and 830 nm light at 5 K can induce a reversible change in magnetization. The quick response to light means that this compound can be used for the development of optical–magnetic switch.

Keywords: Co compound; Valence tautomerism; Photo-induced electron transfer

1. Introduction

The magnetic and optical properties of valence tautomeric compounds and spin crossover complexes have recently attracted great attention [1–6]. The valence tautomers are characterized by different distributions of electron density, where metal-to-ligand and metal-to-metal electron transfer accomplishes interconversion between tautomers. Transition metal complexes containing semiquinone (SQ) and catecholate lgands have shown a unique facility for electron transfer between the metal and chelated quinone ligands [1]. This has been most dramatically illustrated for the complexes of cobalt where temperature-dependent equilibria between Co^{III}-Cat and Co^{II}-SQ tautomers have been observed to occur in solution and in the solid state shown as follows, [2,3]

$$Co^{III}(N–N)(SQ)(Cat) \leftrightarrow Co^{II}(N–N)(SQ)_2$$

Shifts in charge distribution induced either thermally or optically change the chemical reactivity of both the metal and quinone, and result in a physical response such as the variation of magnetic properties [3–5]. The transformation temperatures, T_c, of valence tautomerism of different compounds were reported. Attia and Pierpont synthesized many quinone complexes of Co, Mn [6]. They mainly studied the temperature-dependent magnetic properties of these compounds, but the optical–magnetic responses of these compounds were not discussed. Sato et al. reported the photo-illumination effects for valence tautomeric complexes [7,8]. These compounds show a photo-induced ligand-tometal electron transfer at low temperature and reverse valence tautomerism can be induced by exciting the metal-toligand charge transfer band.

In this paper, we study the thermally-induced intramolecular electron transfer and photo-induced valence tauitomerism of a novel Co compound, [$Co^{III\text{-}LS}$(dpa)(3,5-DBSQ)(3,5-DBCat)] (Fig. 1).

2. Experimental details

The Co complex, [$Co^{II\text{-}HS}$(dpa)(3,5-DBSQ)$_2$], was prepared by adding 15 ml toluene solution of dpa (4 mmol) to 50 ml toluene solution suspended [Co(3,5-DBSQ)$_2$]$_4$ (1 mmol), followed by slow evaporation under a flow of Ar gas. After 1 day, dark blue microcrystalline solid were obtained. Anal. Calcd. (found) for Co(dpa)(3,5-DBSQ)$_2$: C 68.42 (68.05); H 7.81 (7.36); N 5.99 (6.26).

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doi:10.1016/j.nainr.2003.08.001

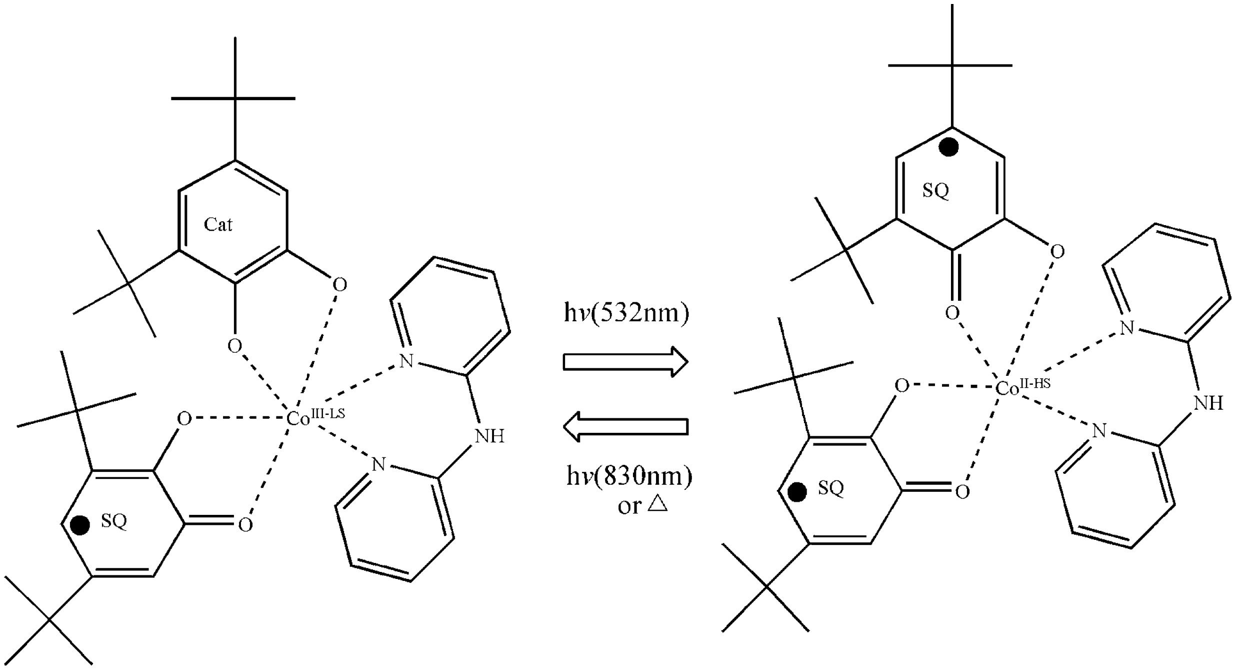

Fig. 1. Photo-induced valence tautomerism of [Co^{III-LS}(dpa)(3,5-DBSQ)(3,5-DBCat)].

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. Lights of 532 and 830 nm were guided into the SQUID magnetometer via an optical fiber in order to study the photo-effects.

3. Results and discussion

The temperature dependence of the magnetic susceptibility for [Co^{II-HS}(dpa)(3,5-DBSQ)$_2$] was measured at a rate of 5 K/min. Fig. 2 shows the relationship between the molar effective magnetic moment, μ_{eff} and temperature. The μ_{eff} value at 5 K is equal to 1.73μ_B. Above 300 K, the value of μ_{eff} for this complex increases with temperature to a value of 4.6μ_B (Bohr Magneton) at the available highest temperature, 400 K. To clarify the relationship between magnetization property and temperature, transition temperature of valence tautomerism, T_c, defined as the temperature at which Co^{III} and Co^{II} redox isomers are present at equal concentration, [9] was obtained from solid state magnetic measurements shown in Eq. (1),

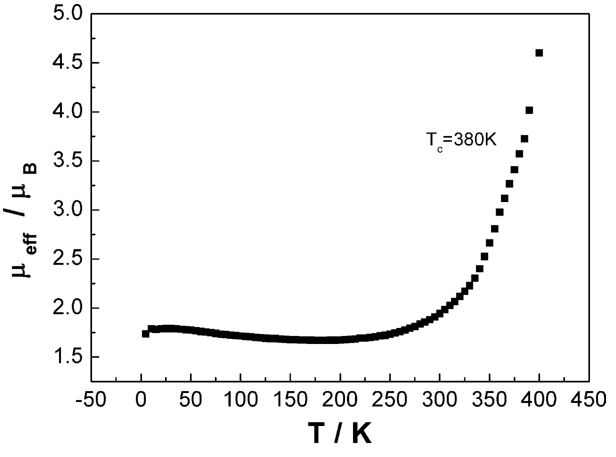

Fig. 2. Plot of the effective magnetic moment (μ_{eff}) vs. temperature for Co^{II-HS}(dpa)(3,5-DBSQ)$_2$.

$$T_c = T\left(\frac{M_L + M_H}{2}\right) \tag{1}$$

M_L, M_H means the magnetic moment of before and after valence tautomerism.

The abrupt increase in μ_{eff} indicates the occurrence of phase transition at about 380 K. To the best of our knowledge, the T_c value of complex *d* is the highest among the species exhibiting thermal valence tautomerism. The change in the magnetization behavior is consistent with the valence tautomeric behavior, which has been reported by Jung et al. [10,11].

Although there were many reports on Co series compounds with valence tautomerism, the N–N ligand of the Co compounds in this paper is not used in Co series compounds before. This Co compound shows higher transition temperature than other compounds listed in Table 1. The transition temperature valence tautomerism varied with different N–N ligands. It is suggested that the transition temperature were controlled by the splitting energy of octahedral coordination compounds that are related with the coordinating fields of

Table 1
Comparison of the transition temperatures of different compounds

Compounds	T_c (K)	Reference
Co(tmeda)(3,5-DBSQ)$_2$·0.5C$_6$H$_5$CH$_3$	195	[12][a]
Co(Phen)(3,5-DBSQ)$_2$	None	[13][a]
[Co(Phen)(3,5-DBSQ)$_2$]·C$_6$H$_5$Cl	225	[13][a]
[Co(Phen)(3,5-DBSQ)$_2$]·C$_6$H$_5$CH$_3$	250	[13][a]
Co(py$_2$O)(3,6-DBSQ)$_2$	330	[14]
Co(py$_2$S)(3,6-DBSQ)$_2$	370	[14]
Co(py$_2$Se)(3,6-DBSQ)$_2$	290	[14]
Co(py$_2$Te)(3,6-DBSQ)$_2$	210	[14]
Co(Ph$_2$bpy)(3,6-DBSQ)$_2$	350	[15]
Co(Me$_2$bpy)(3,6-DBSQ)$_2$	287	[15]
Co(tmeda)(3,6-DBSQ)$_2$	310	[16]
Co(tmmda)(3,6-DBSQ)$_2$	280	[16]
Co(tmpda)(3,6-DBSQ)$_2$	<180	[16]
Co(bpy)(3,6-DBSQ)$_2$	275	[2]
Co(phen)(3,6-DBSQ)$_2$	265	[2]
Co(NO$_2$-phen)(3,6-DBSQ)$_2$	<180	[2]
Co (HN(C$_5$H$_4$N)$_2$)(3,5-DBSQ)$_2$	380	–

[a] The transition temperature, T_c, of the compounds was calculated according to the reported data in the literatures [12,13] by above method.

N–N ligands. Because the transition temperature of Co compound with dpa ligand is higher than other ligands, it can be concluded that the dpa ligand has stronger coordinating field.

When the Co compound was illuminated at 5 K with 532 nm light, the magnetization value increased from $\mu_{\text{eff}} = 1.73$ to $2.0\mu_B$ as shown in Fig. 3. It is revealed from the X-ray absorption near-edge structure (XANES) spectra that the electronic structure of the state is essentially identical to that of the high temperature (HT) phase. Upon irradiation, one electron in DBCAT is transferred to low-spin (LS) Co^{III}, yielding high-spin (HS) Co^{II} and DBSQ [17].

In order to induce the reverse valence tautomerism, the metastable Co complex with the [Co$^{II\text{-}HS}$(dpa)(3,5-DBSQ)$_2$] state was illuminated with 830 nm light. Fig. 2 shows the change in the magnetization. As shown in the figure, the magnetization value decreased after the excitation of Co$^{II\text{-}HS}$ to the 3,5-DBSQ CT band. This means that an electron transfer from the Co$^{II\text{-}HS}$ to 3,5-DBSQ was induced. The photo-induced process due to the 830 nm light can be expressed as:

$$[\text{Co}^{\text{II-HS}}(\text{dpa})(3,5\text{-DBSQ})_2](\text{metastable state}) \xrightarrow{830\,\text{nm light}} [\text{Co}^{\text{III-LS}}(\text{dpa})(3,5\text{-DBSQ})(3,5\text{-DBCat})] \times (\text{ground state})$$

A reversible change in the magnetization, induced by alternate illumination with 532 and 830 nm light, could be repeated several times as shown in Fig. 3.

Important characteristics of the photo-induced valence tautomerism are that only several percent of moieties change to the metastable state and that, even if the Co$^{II\text{-}HS}$ to 3,5-DBSQ CT band is excited for the induction of the reverse valence tautomerism, the magnetization value does not reach its original level, i.e. $1.73\mu_B$, of the pure [Co$^{III\text{-}LS}$(dpa)(3,5-DBSQ)(3,5-DBCat)] state at 5 K. This is because excitation at the wavelengths of 532 and 830 nm induces CT from 3,5-DBCat to Co$^{III\text{-}LS}$ in the [Co$^{III\text{-}LS}$(dpa)(3,5-DBSQ)(3,5-DBCat)] (ground state) as well as reverse CT from Co$^{II\text{-}HS}$ to 3,5-DBSQ in the [Co$^{II\text{-}HS}$(dpa)(3,5-DBSQ)$_2$] (metastable state). As a result, a photo-stationary state is achieved under the illumination with both 532 and 830 nm lights.

The effective magnetic moment of Co$^{II\text{-}HS}$(dpa)(3,5-DBSQ)$_2$ reaches saturation in 1–2 min after illumination with 532 nm light as shown in Fig. 4. This means that this compound responds with light very quickly and can be used for the development of optical–magnetic switch.

In summary, the Co compound [Co$^{II\text{-}HS}$(dpa)(3,5-DBSQ)$_2$] was synthesized first time in this paper. This

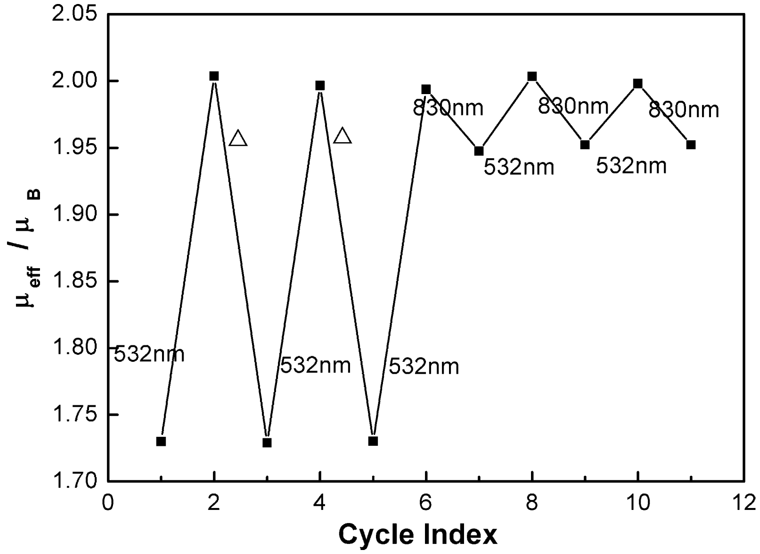

Fig. 3. Reversible changes of the magnetization at 5 K. The notations, $h\nu$ and Δ represent illumination at 5 K and thermal treatment at 100 K, respectively.

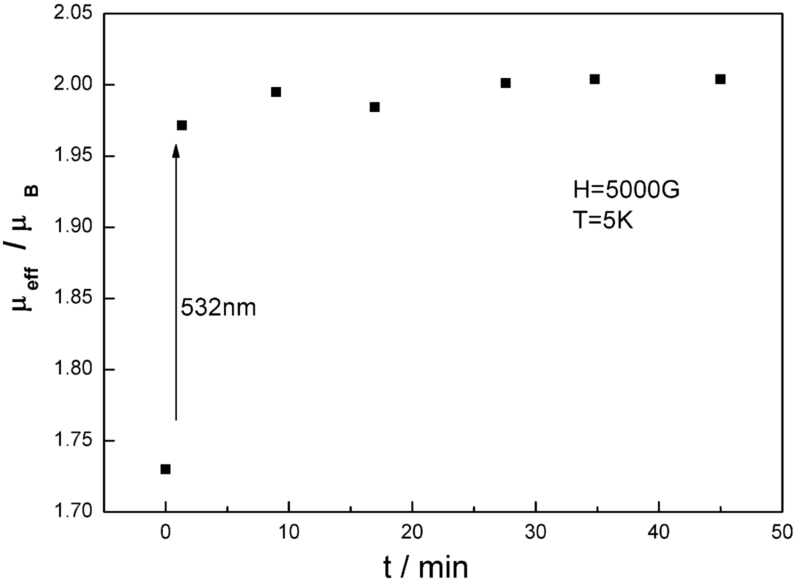

Fig. 4. Effective magnetic moment vs. time after illumination with 532 nm light.

compound exhibits high T_c of valence tautomerism about 380 K. The alternate illumination with 532 and 830 nm light at 5 K can induce a reversible change in magnetization, showing photo-reversible valence tautomerism. The quick response to light means that this compound can be used for the development of optical–magnetic switch.

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