



Magnetic and photo-magnetic properties of Co dinuclear complexes

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ABSTRACT

The magnetic and photo-magnetic properties of Co dinuclear compounds were studied. The Co compounds, $[\{Co(tpa)_2(dhbq)\}(BF_4)_3 \cdot 2H_2O]$ and $[\{Co(tpa)_2(dhbq)\}(ClO_4)_3 \cdot 2H_2O]$, have the structure $[(tpa)Co^{III-Ls}-(\mu-dhbq)^{3-}-Co^{III-Ls}(tpa)]^{3-}$ (where LS, H₂dhbq, tpa denote low-spin, 2,5-di-hydroxy-1,4-benzoquinone and tris(2-pyridylmethyl)amine, respectively) at room temperature. On heating, these compounds exhibit valence-tautomeric inter-conversion; $[(tpa)Co^{III-Ls}-(\mu-dhbq)^{3-}-Co^{III-Ls}(tpa)]^{3-} \rightleftharpoons [(tpa)Co^{II-Hs}-(\mu-dhbq)^{2-}-Co^{III-Ls}(tpa)]^{3-}$ (where HS denotes high-spin). Furthermore, both of these compounds exhibit photo-induced valence tautomerism at low temperature (<60 K). These results show that the electronic structures of these complexes can be controlled by modifying the counter anions.

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1. Introduction

There has been great interest in the study of the magnetic properties of molecular compounds [1]. One of the current popular topics in this field is the development of molecular nano-magnets. In particular, Gatteschi and co-workers have reported the development of single molecule magnets and single chain magnets, which have attracted great attention recently [2,3]. Since their discovery, a large number of molecular nano-magnets have been studied [4].

Another important field is the preparation of magnetic compounds that respond to light [5–8]. Examples of this phenomenon are spin crossover complexes that exhibit light-induced excited spin state trapping (LIESST) effects [9]. Iron(II) and Iron(III) LIESST complexes have already been reported [9,10]. Another group of interesting compounds are molecular photo-magnets [11]. Prussian blue analogues, octa-cyanide-based magnets, Mn-TCNE, etc. have been reported to produce photo-responsive magnets [11–13]. More recently, photo-induced valence tautomerism has been observed in Co valence-tautomeric compounds [14–16]. So far, mono-nuclear, di-nuclear and poly-nuclear Co complexes that show photo-induced valence tautomerism have been reported [14,17–20].

Following these principles, we have been carrying out studies of molecular magnetic compounds, and we have recently succeeded

in developing a novel single molecule magnet and a single chain magnet [21,22]. Furthermore, we have reported an Fe(III) LIESST complex [10,23], an Fe(II) LIESST complex with a high relaxation temperature (130 K) [24], and a molecular photo-magnet, based on an Fe–Co Prussian blue compound [11,25–28]. More recently, we reported a Co complex that shows photo-induced valence tautomerism [14,16,17,19,29–32]. That is, when the Co valence-tautomeric complex was excited, a metastable state with an extremely long life-time was generated. As a result, an appreciable increase in magnetization was observed.

However, the number of such photo-responsive valence-tautomeric compounds that have been identified is very small, and relatively few examples have been reported. Hence, we decided to study the magnetic properties of several Co dinuclear complexes, and we found that $[\{Co(tpa)_2(dhbq)\}(BF_4)_3 \cdot 2H_2O]$ and $[\{Co(tpa)_2(dhbq)\}(ClO_4)_3 \cdot 2H_2O]$ exhibit thermally- and photo-induced valence tautomerism.

2. Experimental

$[\{Co(tpa)_2(dhbq)\}(BF_4)_3 \cdot 2H_2O]$ (**1**) (Fig. 1): A solution of $CoCl_2 \cdot 6H_2O$ (2.0 mmol) and tpa (2.0 mmol) in MeOH (60 mL) was added to a solution of H₂dhbq (1.0 mmol) and Et₃N (0.28 mL, 2.0 mmol) in MeOH (10 mL). The resulting suspension was stirred at room temperature for 5 min, after which the solution was refluxed for 30 min and an aqueous solution (10 mL) of KBF₄ (4.0 mmol) was added. Small, block-like red crystals were obtained

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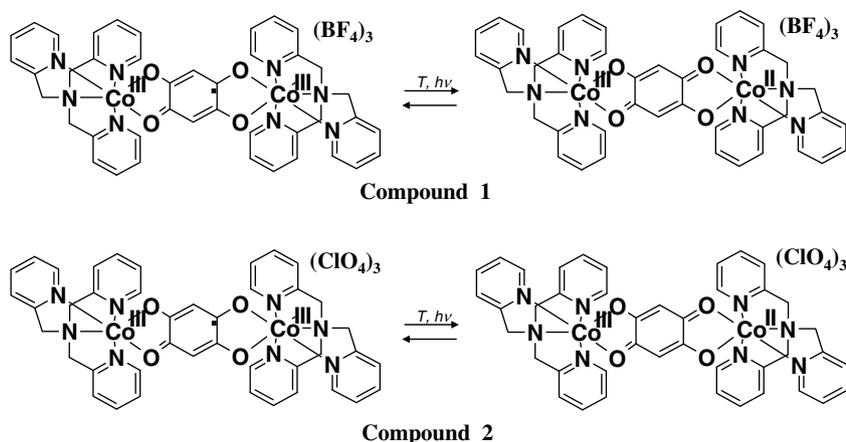


Fig. 1. Chemical structure of compounds **1** and **2**. They exhibit thermally- and photo-induced valence tautomerism.

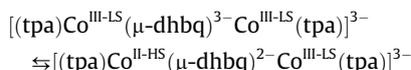
by slow evaporation of the resulting solution, which was washed several times with water and methanol. Yield: ~16%. *Anal. Calc.* for $C_{42}H_{42}B_3Co_2F_{12}N_8O_6$: C, 44.52; H, 3.74; N, 9.89. Found: C, 44.32; H, 3.76; N, 9.85%.

$[[Co(tpa)]_2(dhbq)](ClO_4)_3 \cdot 2H_2O$ (**2**) (Fig. 1): a solution of $CoCl_2 \cdot 6H_2O$ (2.0 mmol) and tpa (2.0 mmol) in MeOH (60 mL) was added to a solution of H_2dhbq (1.0 mmol) and Et_3N (0.28 mL, 2.0 mmol) in MeOH (10 mL). The resulting suspension was stirred at room temperature for 5 min. The solution was then refluxed for 30 min and an aqueous solution (10 mL) of $NaClO_4$ (4.0 mmol) was added. Small, needle-like red crystals were obtained by slow evaporation of the resulting solution, which was washed several times with water and methanol. Yield: ~4.0%. *Anal. Calc.* for $C_{42}H_{42}Cl_3Co_2N_8O_{18}$: C, 43.08; H, 3.62; N, 9.57. Found: C, 43.14; H, 3.67; N, 9.49%.

The magnetic susceptibilities of these complexes were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). Their infrared (IR) spectra were measured by the KBr method using a JASCO FT/IR-600. UV–Vis absorption spectra were measured using a UV-3100 (Shimadzu) spectrophotometer. A laser-diode pumped Nd:YAG laser (Crystal Laser GCL-150-M) with a wavelength of 532 nm was used as the light source.

3. Results and discussion

The magnetic properties of **1** were measured in an external field of 0.5 T. The $\chi_m T$ versus T curve is shown in Fig. 2, where χ_m is the magnetic susceptibility and T is the temperature. The $\chi_m T$ value at 5 K is equal to $0.32 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, meaning that the redox state of **1** can be expressed as $[(tpa)Co^{III-LS}(\mu-dhbq)^3-Co^{III-LS}(tpa)](BF_4)_3 \cdot 2H_2O$. On warming, the value of $\chi_m T$ increases above 350 K. The $\chi_m T$ value at 400 K was $1.24 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. This means that valence-tautomeric conversion was induced in the complex. The valence-tautomeric behavior can be expressed as follows:



This behaviour is consistent with the (PF_6) salt of the Co complex [19]. Gravimetric analysis showed that the water molecules are removed at around 370 K in the initial warming process. Hence, the temperatures at which valence-tautomeric transitions occur are different between the first cycle and the second cycle. The phase transition temperature of **1** during the second cycle is ca. 370 K. On the other hand, the phase transition temperature of $[(tpa)Co^{III-LS}(\mu-dhbq)^3-Co^{III-LS}(tpa)](PF_6)_3$ was ca. 300 K [19]. A shift in the phase transition temperature of 70 K was induced by replacing (PF_6) with (BF_4) .

The magnetic properties of **2** are shown in Fig. 3. The $\chi_m T$ value at 300 K is ca. $0.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, meaning that the redox state of **2** is

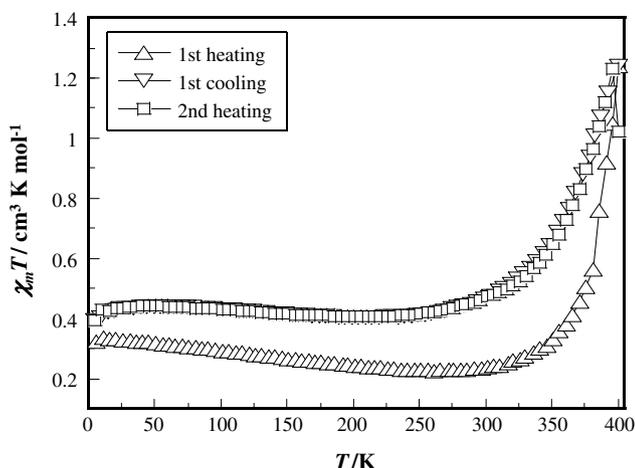


Fig. 2. $\chi_m T$ vs. T curve of **1**.

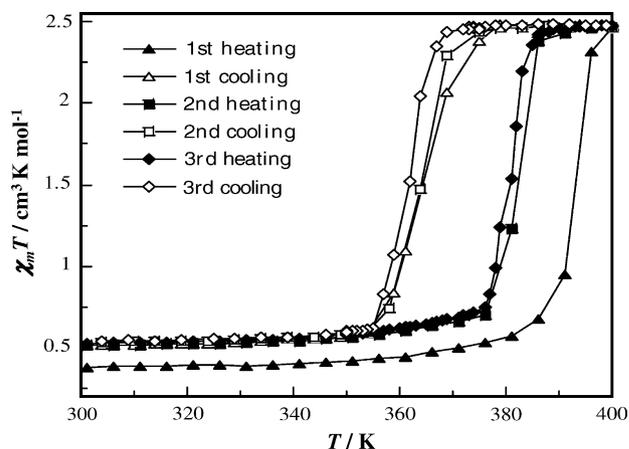
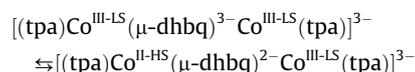


Fig. 3. $\chi_m T$ vs. T curve of **2**.

$[(\text{tpa})\text{Co}^{\text{III-L5}}(\mu\text{-d}(\text{hbq}))^3\text{-Co}^{\text{III-L5}}(\text{tpa})] (\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. The $\chi_m T$ value abruptly increases at 390 K. The $\chi_m T$ value at 400 K is ca. $2.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is consistent with the expected value for the $[(\text{tpa})\text{Co}^{\text{III-L5}}(\mu\text{-d}(\text{hbq}))^2\text{-Co}^{\text{II-HS}}(\text{tpa})]^{3-}$ state. This means that the valence-tautomeric inter-conversion, $[(\text{tpa})\text{Co}^{\text{III-L5}}(\mu\text{-d}(\text{hbq}))^3\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-} \rightleftharpoons [(\text{tpa})\text{Co}^{\text{II-HS}}(\mu\text{-d}(\text{hbq}))^2\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-}$, was induced in this complex too. On cooling, the magnetization value abruptly decreased at around 360 K, reaching a value of ca. $0.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. When the temperature was increased again up to 400 K, the abrupt increase was observed at ca. 380 K. When the temperature was decreased, the abrupt decrease occurred at 360 K. Therefore, an important characteristic to note is that hysteresis was observed in complex **2**: The hysteresis width is ca 20 K. The reason why the first cycle is different from the second and third cycles is that water molecules are removed from the crystal during the first cycle, as confirmed by gravimetric analysis. We have reported that $[(\text{tpa})\text{Co}^{\text{III-L5}}(\mu\text{-d}(\text{hbq}))^3\text{-Co}^{\text{III-L5}}(\text{tpa})](\text{PF}_6)_3$ shows hysteresis at around room temperature [19]. However, this is a two-step transition. Only 50% of the moieties show transitions at around room temperature. On the other hand, almost 100% of the moieties undergo valence-tautomeric transition in **2** with (ClO_4) , which is distinguishable from the (PF_6) salt.

It has been reported that the Co valence-tautomeric compounds show photo-induced valence tautomerism [15,16,18,19]. Hence, we have studied the photo-magnetic behavior of compounds **1** and **2**. The absorption spectrum for **2** is shown in Fig. 4. A strong absorption peak was observed at around 550 nm, which is ascribable to the ligand-to-metal charge transfer (LMCT) band of these complexes. In order to excite the LMCT band, a diode-pumped Nd:YAG laser with a wavelength of 532 nm was used as a light source, and we measured the photo-magnetic properties. Light was guided into the SQUID magnetometer via an optical fiber in order to study the photo-effects, and the powder sample was supported on a commercial transparent adhesive tape.

When complex **1** was irradiated at 5 K, an increase in the magnetization value was clearly observed. Fig. 5 shows the photo-magnetic properties of **1**. As shown in the figure, the magnetization value increased after irradiation. This shows that, as in the case of other Co valence-tautomeric compounds [16], complex **1** exhibited photo-induced valence tautomerism. The photo-induced process can be expressed as follows:



It is believed that the spin-allowed $[(\text{tpa})\text{Co}^{\text{II-HS}}(\mu\text{-d}(\text{hbq}))^2\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-}$ state is induced by exciting the LMCT band. After the excitation, it relaxes to the $[(\text{tpa})\text{Co}^{\text{II-HS}}(\mu\text{-d}(\text{hbq}))^2\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-}$ state due to spin-orbit coupling. The resulting metastable state, $[(\text{tpa})\text{-}$

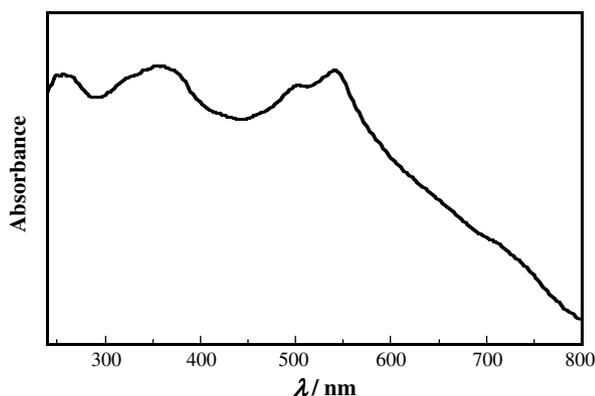


Fig. 4. Absorption spectra for **2**.

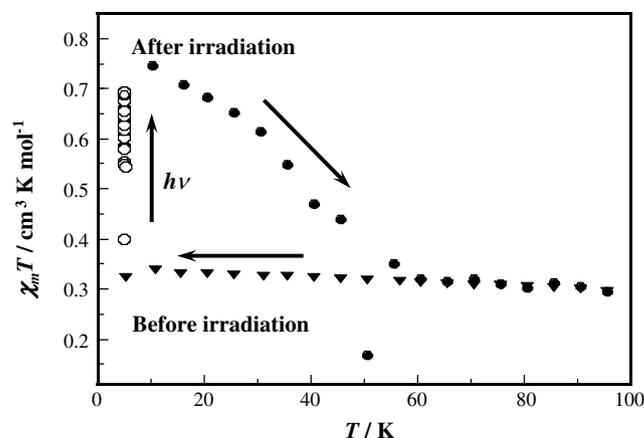


Fig. 5. Magnetic properties of **1** before and after photo-irradiation.

$\text{Co}^{\text{II-HS}}(\mu\text{-d}(\text{hbq}))^2\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-}$, was trapped at 5 K. Note that the spin-allowed transition described above is symmetry forbidden. Hence, the photo-process should be further studied.

When the temperature was increased after photo-irradiation, the magnetization value decreased and recovered to the original level at around 60 K. This means that back electron-transfer from $\text{Co}^{\text{II-HS}}$ to $(\text{d}(\text{hbq}))^{2-}$ was induced via a thermal activation process. That is, the metastable state recovered to the original ground state, $[(\text{tpa})\text{Co}^{\text{III-L5}}(\mu\text{-d}(\text{hbq}))^3\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-}$.

Similar photo-magnetic effects were observed for **2**. Fig. 6 shows the photo-magnetic properties of **2**. The photo-induced valence-tautomeric behavior is $[(\text{tpa})\text{Co}^{\text{III-L5}}(\mu\text{-d}(\text{hbq}))^3\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-} \rightleftharpoons [(\text{tpa})\text{Co}^{\text{II-HS}}(\mu\text{-d}(\text{hbq}))^2\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-}$. When the temperature was increased after photo-irradiation, the metastable state completely recovered to the $[(\text{tpa})\text{Co}^{\text{III-L5}}(\mu\text{-d}(\text{hbq}))^3\text{-Co}^{\text{III-L5}}(\text{tpa})]^{3-}$ state at around 60 K, meaning that reverse valence tautomerism was induced.

These measurements show that both **1** and **2** are photo-responsive compounds. That is, they exhibit photo-induced magnetization effects due to valence-tautomeric inter-conversion. The resulting meta-stable state can be reversed to the ground state by heating the sample. A general feature of photo-induced valence tautomerism in Co complexes is that the magnetization value after photo-irradiation is much lower than the value expected for 100% conversion [16]. It has been reported that only the surface layer responds to light irradiation [18]. As shown in Figs. 5 and 6, the magnetization value after irradiation does not come close to reaching

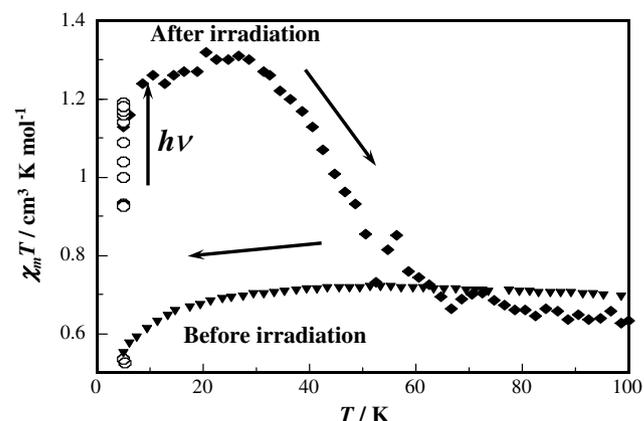


Fig. 6. Magnetic properties of **2** before and after photo-irradiation.

the expected value for 100% conversion. This means that photo-induced valence tautomerism occurs only at the surface layer for compounds **1** and **2**.

In summary, we have reported the magnetic properties of Co dinuclear complexes. The Co complexes **1** and **2** exhibited valence tautomerism. In contrast to the case of $[(\text{tpa})\text{Co}^{\text{III-LS}}(\mu\text{-dnhbq})^2\text{-Co}^{\text{II-HS}}(\text{tpa})](\text{PF}_6)_3$, both **1** and **2** showed a one-step transition. Compound **1** does not undergo hysteresis, while compound **2** exhibited a hysteresis loop with a width of 20 K. Furthermore, we found that both **1** and **2** undergo photo-induced valence tautomerism when the LMCT band is excited by light. This effect can be expressed as $[(\text{tpa})\text{Co}^{\text{III-LS}}(\mu\text{-dnhbq})^3\text{-Co}^{\text{III-LS}}(\text{tpa})]^{3-} \rightleftharpoons [(\text{tpa})\text{Co}^{\text{II-HS}}(\mu\text{-dnhbq})^2\text{-Co}^{\text{III-LS}}(\text{tpa})]^{3-}$. This means that **1** and **2** are photo-responsive complexes.

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