

# Photo-induced Valence Tautomerism in Co Complexes

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## ABSTRACT

A number of photofunctional molecular compounds have been developed recently. Typical examples of these are phototunable valence tautomeric compounds, which are now attracting great attention. When the charge-transfer bands of some Co valence tautomeric compounds are excited at low temperature, metastable redox isomers can be created after irradiation. The lifetimes of the metastable states can be more than several hours. These transformations can involve changes in the magnetic properties of the compounds, as well as their color. Hence, these compounds can be regarded as novel photomagnetic materials. The photoresponsive behaviors of these valence tautomeric compounds are similar to those of spin-crossover complexes (light-induced excited spin-state trapping effects).

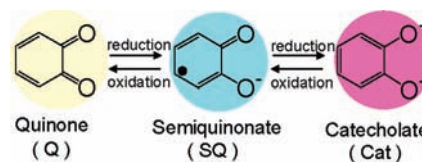
## 1. Introduction

There has recently been great interest in the study of functional molecular compounds, with the aim of developing future high-density molecular devices. In particular, the design of phototunable compounds has attracted great attention because of their possible application to photo-recording and photoswitching devices.<sup>1</sup> When molecular-scale media are used for recording data, it is anticipated that the size of the recording unit could be reduced to the nanometer scale (i.e., the size of a single molecule or a single cluster). Furthermore, it is believed that light (or

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**FIGURE 1.** Quinone molecules undergo two-step redox reactions. They can be used as redox-active ligands.

photons) will be used more and more instead of electrons in future devices. Hence, the development of novel photofunctional molecules is quite an important challenge. Indeed, many photofunctional molecules have already been developed, ranging from photochromic molecules and phototunable liquid crystals to phototunable molecular magnets.<sup>2–5</sup>

Among the many photoresponsive compounds that are available, we are currently interested in developing novel photofunctional metal complexes that exhibit valence tautomeric behavior. One characteristic of valence tautomers is that they can exhibit different distributions of electron density, usually caused by metal–metal or metal–ligand electron transfer.<sup>6–21</sup> Typical examples that exhibit valence tautomerism are those molecules that contain redox-active quinone ligands.<sup>6–13,16–21</sup> As shown in Figure 1, the quinone molecules undergo two-step redox reactions. The one-electron reduced molecule is named “semiquinone”, while the two-electron reduced state is known as “catecholate”. When this molecule is used as a ligand for metal complexes, some compounds exhibit thermally induced charge transfer (CT) between the metal and ligand. The molecule with the original electronic structure and the one with the altered redox state can be regarded as redox isomers (or valence isomers). Among the various valence tautomeric systems that have been identified, Co compounds have been most extensively studied. It has been reported that many Co complexes with redox-active quinone ligands exhibit thermally induced interconversion between two valence tautomers because of intramolecular CT. These compounds are

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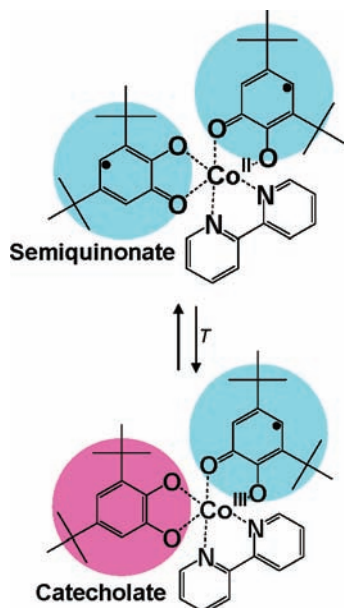
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**FIGURE 2.** Valence tautomeric interconversion of a Co complex, which was first reported by Buchanan et al.<sup>26</sup>

expected to be used for future memory and switching devices. Furthermore, the development of such CT systems is important from the viewpoint of basic science, as well as for practical applications. This is because CT is the key process in various biological systems. Indeed, it has been reported that some metalloporphyrins undergo valence tautomerism.<sup>22,23</sup> Hence, many research groups have been investigating the electrical, optical, and magnetic properties of valence tautomeric compounds. Here, we describe the photoresponsive behavior that has been observed in mono- and dinuclear Co complexes, which is the field that has been studied by our group.

It should be noted that the term “valence tautomerism” is used not only for metal complexes but also for organic compounds. “Valence tautomerism” in organic terminology means systems that undergo reorganization of the bonding electrons. Bullvalene and heterocyclic compounds are typical examples that exhibit such valence tautomerism.<sup>24,25</sup> Among the various known valence tautomeric systems, in this paper, we focus only on “valence tautomerism” involving Co complexes in which the CT between Co and a ligand can be induced by light and variations in temperature and not on “valence tautomerism” in purely organic compounds, such as bullvalene and heterocyclic compounds.

## 2. Challenges in the Development of Valence Tautomeric Compounds

Thermally induced valence tautomerism in Co compounds was first reported in 1980 by Buchanan et al.<sup>26</sup> Since then, many valence tautomeric compounds have been developed.<sup>6–11</sup> The valence tautomeric behavior of the first compound is shown in Figure 2.<sup>26</sup> The change in the oxidation state involves a distinct color change, as well as a change in magnetization.

To apply these materials to future molecular devices, it is desirable that the valence tautomeric conversion can be induced by photo-irradiation. This is because the compounds could then be switched between their two different states by the application of light in a given temperature range. If this were to be realized, these compounds could then be used in future photorecording devices. It should be noted that spin-crossover compounds can exhibit light-induced excited spin-state trapping (LIESST) effects.<sup>27–30</sup> However, trapping the light-induced metastable state has never been reported in the case of valence tautomeric compounds, although transient photo-induced valence tautomerism has been observed.<sup>31,32</sup>

Furthermore, it is desirable for the valence tautomeric conversion to exhibit a room-temperature hysteresis loop. This would allow the compounds to take two different states at room temperature. Then, one of the two states could be used as the “on” state, and the other could be used as the “off” state, in memory and switching devices.

Hence, we have been studying the development of valence tautomeric compounds that exhibit photo-induced valence tautomerism and a hysteresis loop, and we have recently succeeded in preparing just such Co complexes that are bistable in nature.<sup>13,33–39</sup>

## 3. Photo-induced Valence Tautomerism in Mononuclear Compounds

### 3.1. Valence Tautomerism Induced by Visible Light.

We recently found that some Co complexes can exhibit photo-induced valence tautomerism. The phototunable Co compounds reported by our group and several other groups are listed in Table 1.<sup>13,33–42</sup>

An example of thermally and photo-induced valence tautomeric behavior is shown in Figure 3.<sup>37</sup> The value of  $\mu_{\text{eff}}$  at 300 K is equal to  $5.2 \mu_{\text{B}}$ . Upon cooling, the magnetization value suddenly decreases at about 195 K and reaches  $1.7 \mu_{\text{B}}$ . This means that, at room temperature, the Co complex takes the form of  $\text{Co}^{\text{II-HS}}$  with two semiquinone ligands. Upon cooling, an electron is transferred from the  $\text{Co}^{\text{II-HS}}$  to the semiquinone, generating the  $\text{Co}^{\text{III-LS}}$  species with catecholate and semiquinone ligands. This demonstrates that this Co complex is a valence tautomeric compound. The transition temperature of the valence tautomerism is 195 K. The valence tautomeric behavior can be expressed as  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcate})(3,5\text{-dbsq})(\text{tmeda})] \rightleftharpoons [\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{tmeda})]$ , where 3,5-dbcate, 3,5-dbsq, and tmeda are 3,5-di-*tert*-butyl-1,2-catecholate, 3,5-di-*tert*-butyl-1,2-semiquinonate, and *N,N,N,N*-tetramethylethylenediamine, respectively.

The photo-irradiation effects of the valence tautomeric compounds were studied using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). This was effective because valence tautomerism involves a distinct change in the magnetization value, which can easily be detected by a SQUID magnetometer, in which the light is guided via an optical fiber. Note that a powder sample was supported on

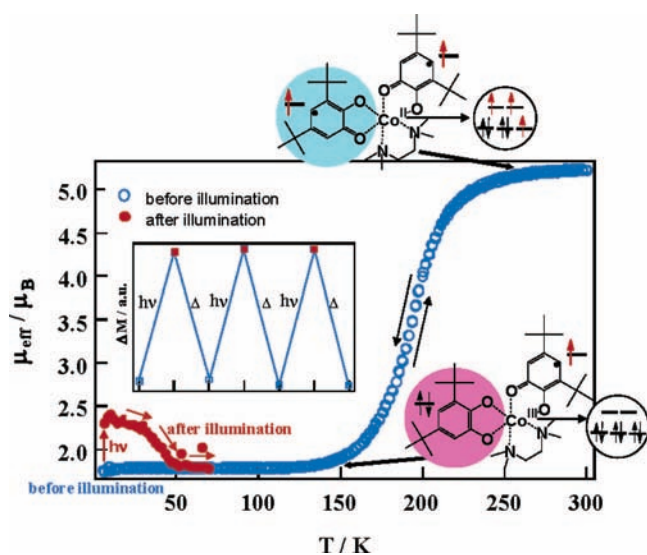
**Table 1. Co Valence Tautomeric Compounds That Exhibit Photo-induced Valence Tautomerism**

compound	$T_c$ (K)	lifetime	excitation wavelength (nm)	reference
$[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$ $\rightleftharpoons [\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$	240	$> 3.6 \times 10^3$ s at 5 K	532	38, 39, 40
$[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$ $\rightleftharpoons [\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$	225	$6.8 \times 10^3$ s at 10 K	532 830 <sup>a</sup>	33
$[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{tmeda})]$ $\rightleftharpoons [\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{tmeda})]$	195	$1.05 \times 10^4$ s at 5 K $4.2 \times 10^3$ s at 15 K	532 830 <sup>a</sup>	36, 37
$[\text{Co}^{\text{III-LS}}(3,6\text{-dbcat})(3,6\text{-dbsq})(\text{tmpda})]$ $\rightleftharpoons [\text{Co}^{\text{II-HS}}(3,6\text{-dbsq})_2(\text{tmpda})]$	165	$9.0 \times 10^2$ s at 5 K	532	35
$[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{dpa})]$ $\rightleftharpoons [\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{dpa})]$	380	not reported	532 830 <sup>a</sup>	34
$[\text{Co}^{\text{III-LS}}(\text{cth})(\text{dhbq})\{\text{Co}^{\text{III-LS}}(\text{cth})\}](\text{PF}_6)_3$ $\rightleftharpoons [\text{Co}^{\text{II-HS}}(\text{cth})(\text{dhbq})\{\text{Co}^{\text{II-HS}}(\text{cth})\}](\text{PF}_6)_3$	175	not reported	647.1–676.4	41
$[\text{Co}^{\text{III-LS}}(\text{tpa})(\text{dhbq})\{\text{Co}^{\text{III-LS}}(\text{tpa})\}](\text{PF}_6)_3$ $\rightleftharpoons [\text{Co}^{\text{II-HS}}(\text{tpa})(\text{dhbq})\{\text{Co}^{\text{II-HS}}(\text{tpa})\}](\text{PF}_6)_3$	$T_c^\uparrow = 310$ $T_c^\downarrow = 297$	not reported	532	13
$[(\text{phen})\text{Co}^{\text{III-LS}}-\mu-(\text{Cat-Ph-SQ})]_n$ $\rightleftharpoons [(\text{phen})\text{Co}^{\text{II-HS}}-\mu-(\text{SQ-Ph-SQ})]_n$	305	$3.1 \times 10^5$ s at 9 K $1.5 \times 10^5$ s at 20 K	658	42

<sup>a</sup> Excitation wavelength for reverse valence tautomerism.  $T_c$ , transition temperature;  $T_c^\uparrow$ , transition temperature on the warming mode;  $T_c^\downarrow$ , transition temperature on the cooling mode.

commercial transparent adhesive tape and placed on the edge of the optical fiber.

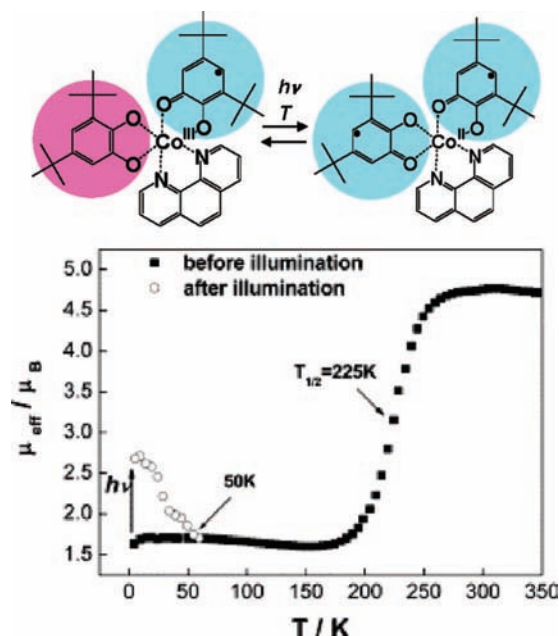
The Co valence tautomeric compounds have a ligand–metal charge-transfer (LMCT) band around the visible region.<sup>31,32,43</sup> Hence, to excite the LMCT band, a laser-diode pumped Nd:YAG laser with a wavelength of 532 nm was used as the light source. As shown in Figure 3, the magnetization values increase after light illumination. The magnetization value at 5 K is ca.  $1.7 \mu_B$  before irradiation, while it is ca.  $2.3 \mu_B$  after irradiation. The photo-induced valence tautomeric behavior can be expressed as  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{tmeda})] \rightarrow [\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{tmeda})]$ . Measurements of the UV–vis and the IR spectra support the idea that the metastable  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{tmeda})]$  state was created. That is, the absorption spectra after illumination show that the  $\text{Co}^{\text{II-HS}}$  to 3,5-dbsq CT band at around 800 nm has



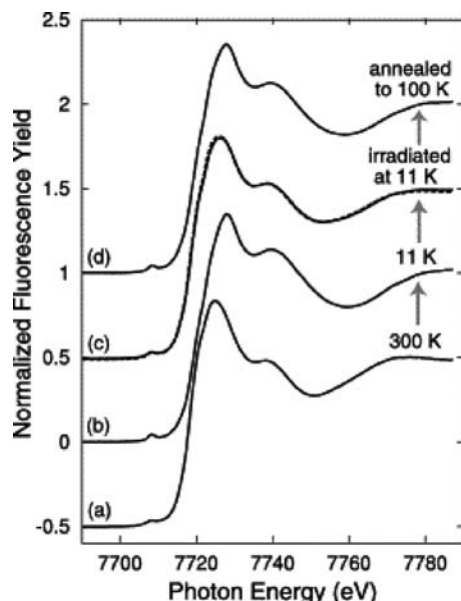
**FIGURE 3.** Magnetic properties of  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{tmeda})]$  before (○) and after (●) irradiation. (Inset) Reversible changes in the magnetization at 5 K. The notations,  $h\nu$  and  $\Delta$ , represent illumination at 5 K and thermal treatment at 60 K, respectively. Reprinted from ref 37, Copyright 2002, with permission from Elsevier.

increased and that the absorption band at 2500 nm, which is ascribable to the ligand–ligand CT band, has reduced in intensity. Furthermore, when the complex  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{tmeda})]$  is illuminated, the peak intensity of the C–O stretch vibration for 3,5-dbcat is decreased. These changes are consistent with the induction of valence tautomerism by light.

Another example is shown in Figure 4. The valence tautomeric transition occurs at 225 K.<sup>33</sup> The high-temperature phase is composed of  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$ , while the low-temperature phase is  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$ , where phen is phenanthroline. When  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$  was excited by 532 nm light at 5 K, an increase in the magnetization was observed. The values of  $\mu_{\text{eff}}$  before and after irradiation were  $1.7$  and  $2.7 \mu_B$ ,



**FIGURE 4.**  $\mu_{\text{eff}}$  versus  $T$  plots of  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$  before (●) and after (○) illumination. Reprinted from ref 33, Copyright 2004, with permission from Elsevier.



**FIGURE 5.** Co K-edge XANES spectra taken in fluorescence-yield mode. They are measured at (a) 300 K, (b) 11 K, (c) during visible-light irradiation at 11 K, (d) and after annealing of the irradiated sample to 100 K. A simulated spectrum obtained by the superposition of the 300 and 11 K spectra with a ratio of 0.65:0.35 is represented by the dashed line in c. Reprinted from ref 39, Copyright 2001, with permission from Elsevier.

respectively. This means that the  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$  state was created by light. The photo-process can be expressed as  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcac})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{Cl}) \rightarrow [\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$ .

Similarly,  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcac})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$ ,<sup>38,40</sup>  $[\text{Co}^{\text{III-LS}}(3,6\text{-dbcac})(3,6\text{-dbsq})(\text{tmpda})]$ ,<sup>35</sup> and  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcac})(3,5\text{-dbsq})(\text{dpa})]$ <sup>34</sup> exhibited photo-induced valence tautomerism, where 3,6-dbcac, 3,6-dbsq, tmpda, and dpa are 3,6-di-*tert*-butyl-1,2-catechol, 3,6-di-*tert*-butyl-1,2-semiquinone, *N,N,N',N'*-tetramethylpropylenediamine, and 2,2'-dipyridylamine, respectively.

### 3.2. Structure of the Photo-induced Metastable State.

As described above, some Co complexes can exhibit photo-induced valence tautomerism. An important characteristic of this phenomenon is that the conversion fraction of the metastable state is quite small (Figures 3 and 4). One possible explanation is that the photo-induced metastable state is a new electronic state that is different from the high-temperature phase. Indeed, Roux et al. have discussed the possibility that the thermally induced valence tautomeric conversion of  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcac})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3) \rightleftharpoons [\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$  occurs in two steps, in which the intermediate state is  $[\text{Co}^{\text{II-LS}}(3,5\text{-dbsq})_2(\text{phen})]$ ,<sup>44</sup> although they finally concluded that their extended X-ray absorption fine structure (EXAFS) data are more in accordance with a one-step mechanism for the thermally induced conversion. Hence, to investigate the structure of the photo-induced metastable state more carefully, we studied the X-ray absorption spectra of the Co compounds.<sup>39</sup>

The Co K-edge X-ray absorption near-edge structure (XANES) spectra are shown in Figure 5. The XANES spectra were measured using the fluorescence-yield mode.<sup>39</sup> As

shown in the figure, the spectrum after irradiation at 11 K is different from those measured at 300 and 11 K. However, assuming that the metastable state is composed of 35% of the high-temperature phase and 65% of the low-temperature phase, the spectra could be simulated very well by using the spectra at 300 and 11 K. The simulated data are shown by the dashed line in Figure 5. As shown in the figure, the simulated line fits almost perfectly with the data that was obtained experimentally. This means that the photo-induced metastable state is essentially identical to the high-temperature phase,  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$ . This is consistent with the results obtained from IR and UV-vis absorption spectra.

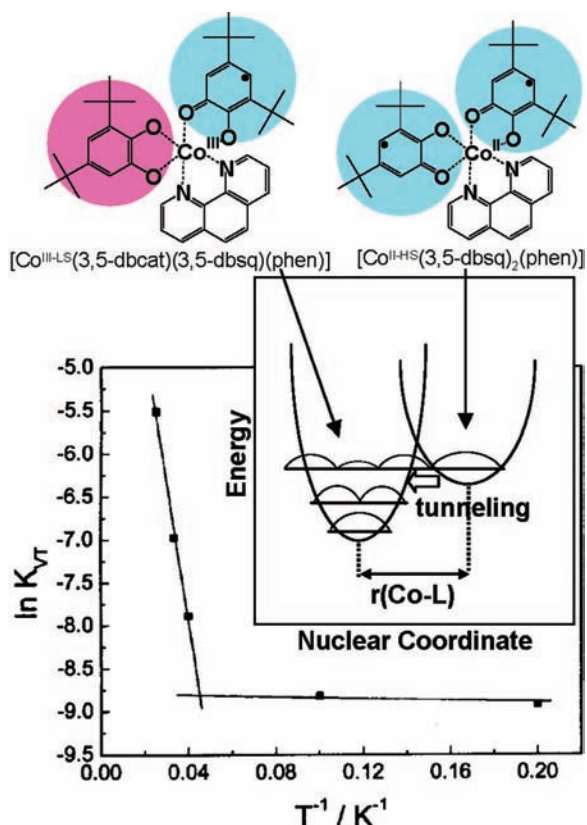
Hence, it is believed that the strong opacity of the sample might prevent the penetration of light in the bulk phase, which results in the small change of the magnetization after irradiation. Indeed, Carbonera et al. studied reflection spectra in a SQUID magnetometer, and they clearly showed that an almost quantitative photo-induced interconversion occurs at low temperature at the surface.<sup>41</sup> Furthermore, the LMCT band of the ground state overlaps with the MLCT band of the metastable state. Hence, as a result of the realization of the photostationary state, the value of the magnetization cannot increase to match that of the high-temperature phase. Because of these two factors, the changes observed in the magnetization are smaller than expected.

### 3.3. Relaxation from the Photo-induced Metastable State to the Ground State via a Tunneling Process.

As described above, the electronic structure of the photo-induced metastable state is almost identical to that of the high-temperature phase. This means that the ligand-metal bond length between the Co and ligand (O or N) is elongated by an average of ca. 0.18 Å after irradiation. This is explained by the work of Adams et al., who reported that the change in the ligand-metal bond length between  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcac})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$  and  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$  is ca. 0.18 Å.<sup>32</sup> Note that the ligand-metal bond length of the  $\text{Co}^{\text{II-HS}}$  state is generally longer than that of  $\text{Co}^{\text{III-LS}}$  by 0.18–0.22 Å.<sup>32</sup>

It has been reported that large changes in the ligand-metal bond length play a key role in trapping the photo-induced metastable state of spin-crossover complexes.<sup>29,30</sup> Hence, the change in the ligand-metal bond length between the metastable and ground states might be key to the observation of the long-lived metastable state in Co valence tautomeric compounds. That is, a large change in the ligand-metal bond length prevents the fast relaxation from  $\text{Co}^{\text{II-HS}}$  to  $\text{Co}^{\text{III-LS}}$  via tunneling effects, allowing for the observation of the long-lived photo-induced metastable state.

Figure 6 shows the temperature dependence of the relaxation rate of  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$  as measured by Cui et al.<sup>33</sup> As shown in the figure, the  $\ln[k_{\text{VT}}(T)]$  versus  $1/T$  plot follows a straight line at temperatures higher than 25 K, indicating that the relaxation process is a typical, thermally activated one. Note that  $k_{\text{VT}}(T)$  is the rate constant for valence tautomeric relaxation at a given temperature  $T$ . However, when the



**FIGURE 6.** Relaxation rate from  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$  to  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$  plotted as  $\ln[k_T(T)]$  versus  $1/T$ . The  $\ln[k_T(T)]$  versus  $1/T$  plot shows that the relaxation at low temperature proceeds via a tunneling process. (Inset) Potential energy diagram for the above Co valence tautomeric compound. Reprinted from ref 33, Copyright 2004, with permission from Elsevier.

temperature is decreased further, the line deviates from the original straight line and finally gives a line with a nearly 0 slope. This means that slow back electron transfer is induced via a tunneling process.

As described above, transient photo-induced valence tautomerism was first reported more than 10 years ago.<sup>31,32</sup> However, those measurements were performed above 110 K.<sup>32</sup> Hence, the tunneling region has not been detected, although the deviation from the straight line in the  $\ln[k_T(T)]$  versus  $1/T$  plot has been observed. In contrast, because we measured photo-effects at low temperature and because a large change in the ligand-metal bond length is induced in the case of Co valence tautomeric compounds, we could successfully observe temperature-independent relaxation because of tunneling effects for the first time. The trapping of the metastable state and the relaxation via tunneling are very similar to those attributed to LIESST effects.<sup>27,29,30</sup>

#### 3.4. Photo-induced Valence Tautomerism from the Metastable State to the Ground State by Near-IR Light.

Back electron transfer of the metastable state is not only induced by thermal treatment (heating samples up to the relaxation temperature) but also by photo-irradiation.<sup>36</sup> To induce this reverse valence tautomerism by light, the metastable compound,  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{tmeda})]$ , was excited by a diode laser that emitted 830 nm light. This is

because the metastable state has a CT band from  $\text{Co}^{\text{II-HS}}$  to semiquinone at around 800 nm.<sup>32</sup> If reverse valence tautomerism can be induced, the magnetization value after illumination should decrease, and indeed, the magnetization value decreased from ca. 2.3 to 2.2  $\mu_B$ . This means that back electron transfer from  $\text{Co}^{\text{II-HS}}$  to semiquinone was induced in the metastable Co compound. This reversible change in magnetization could be observed repeatedly and was confirmed by the UV-vis and IR spectra. However, it was noted that the magnetization did not completely recover its original value. This is because the CT bands from ligand-metal and metal-ligand overlap, leading to the realization of a photostationary state when excited by visible and near-IR light. This is consistent with the description in the last part of section 3.2; i.e., the magnetization value never reaches that of the high-temperature phase because of the formation of the photostationary state. Note that, when the metastable Co compound,  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$ , is excited by 1100 nm light, the observed decrease in the magnetization value is larger than it is when it is excited by 830 nm light. This is because the 1100 nm light overlaps less with the LMCT band of  $[\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{CH}_3)$  when compared with 830 nm light.

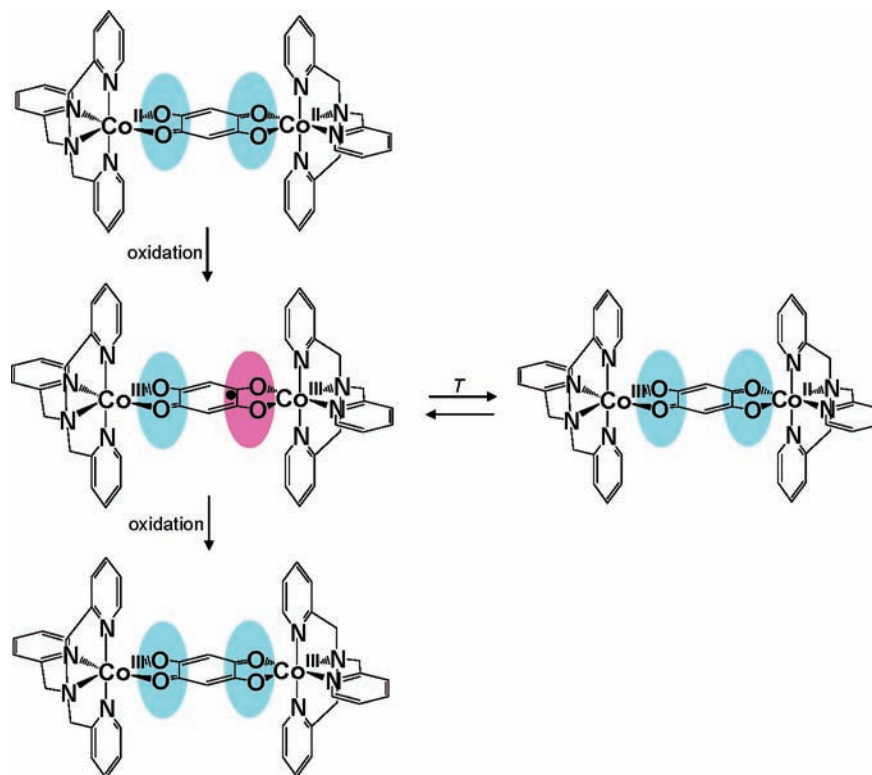
Photo-irradiation effects were also studied for metastable  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$ .<sup>33</sup> As described above, the value of the magnetization could be increased from 1.7 to 2.7  $\mu_B$  by irradiation with 532 nm light. On the other hand, when the metastable compound was excited by 830 nm light, a decrease in the magnetization from 2.7 to 2.3  $\mu_B$  was induced. This means that the transformation from the metastable state to the ground state,  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl}) \rightarrow [\text{Co}^{\text{III-LS}}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$ , could be induced by 832 nm light. Hence, it can be concluded that this compound is a photoreversible one.

Furthermore, we have reported that a similar reverse valence tautomerism can be induced for the metastable Co compound,  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{dpa})]$ .<sup>34</sup>

## 4. Photo-induced Valence Tautomerism in Dinuclear Compounds

Recently, several di- and polynuclear Co valence tautomeric compounds have been reported.<sup>13,41,42,45,46</sup> The di- and polynuclear valence tautomeric compounds have the potential to show multistable character, which is essential for applications involving memory and switching devices. Furthermore, it is expected that the interactions between Co ions in a molecule may lead to the production of novel properties because of synergistic effects. Hence, studies of the magnetic and optical properties of di- and polynuclear Co valence tautomeric systems have attracted great attention recently.

Carbonera et al. have succeeded in preparing a dinuclear Co compound that exhibits both thermally and photo-induced valence tautomerism.<sup>41</sup> Their compound is known as  $\{[\text{Co}^{\text{III-LS}}(\text{cth})](\text{dhbq})^{3-}\{\text{Co}^{\text{III-LS}}(\text{cth})\}(\text{PF}_6)_3$ ,

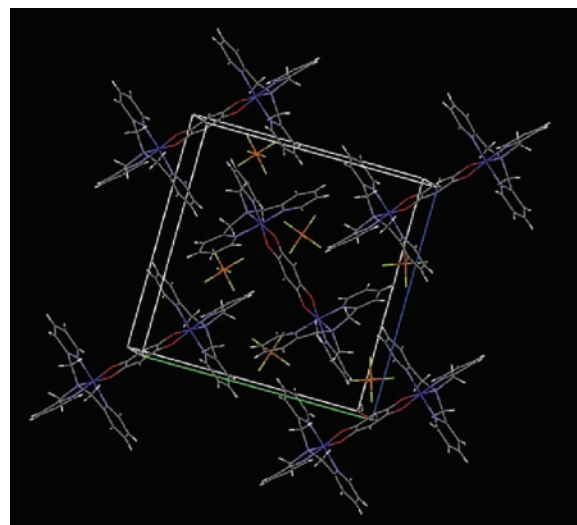


**FIGURE 7.** Chemical structures of dinuclear Co compounds synthesized by our group (Tao et al.).<sup>13</sup> The synthesized Co compounds have different oxidation states, i.e.,  $\{[Co^{II-HS}(tpa)](dhbq)^{2-}\{Co^{II-HS}(tpa)\}\cdot(PF_6)_2$  (**1**),  $\{[Co^{III-LS}(tpa)](dhbq)^{3-}\{Co^{III-LS}(tpa)\}\cdot(PF_6)_3$  (**2**), and  $\{[Co^{III-LS}(tpa)](dhbq)^{2-}\{Co^{III-LS}(tpa)\}\cdot(PF_6)_4$  (**3**). Compound **2** exhibits thermally and photo-induced valence tautomerism, forming  $\{[Co^{III-LS}(tpa)](dhbq)^{2-}\{Co^{II-HS}(tpa)\}\cdot(PF_6)_3$ .

where cth and dhbq are D,L-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and 2,5-dihydroxy-1,4-benzoquinone, respectively. The transition temperature is ca. 175 K. When this compound was excited with 647.1–676.4 nm light, the following valence tautomerism could be induced:  $\{[Co^{III-LS}(cth)](dhbq)^{3-}\{Co^{III-LS}(cth)\}\cdot(PF_6)_3 \rightarrow \{[Co^{III-LS}(cth)](dhbq)^{2-}\{Co^{II-HS}(cth)\}\cdot(PF_6)_3$ .

On the other hand, we synthesized a family of novel dinuclear Co compounds by using tpa [tpa = tris(2-pyridylmethyl)amine] ligands instead of cth.<sup>13</sup> The complexes that we produced can take three different oxidation states. These are  $\{[Co^{II-HS}(tpa)](dhbq)^{2-}\{Co^{II-HS}(tpa)\}\cdot(PF_6)_2$  (**1**),  $\{[Co^{III-LS}(tpa)](dhbq)^{3-}\{Co^{III-LS}(tpa)\}\cdot(PF_6)_3$  (**2**), and  $\{[Co^{III-LS}(tpa)](dhbq)^{2-}\{Co^{III-LS}(tpa)\}\cdot(PF_6)_4$  (**3**). Their chemical structures are shown in Figure 7. The presence of the  $(dhbq)^{3-}$  radical in **2** was confirmed by electron spin resonance (ESR) signals. Furthermore, we have succeeded in determining the crystal structures of all of these compounds. The crystal structure of  $\{[Co^{III-LS}(tpa)](dhbq)^{3-}\{Co^{III-LS}(tpa)\}\cdot(PF_6)_3$  is shown in Figure 8.

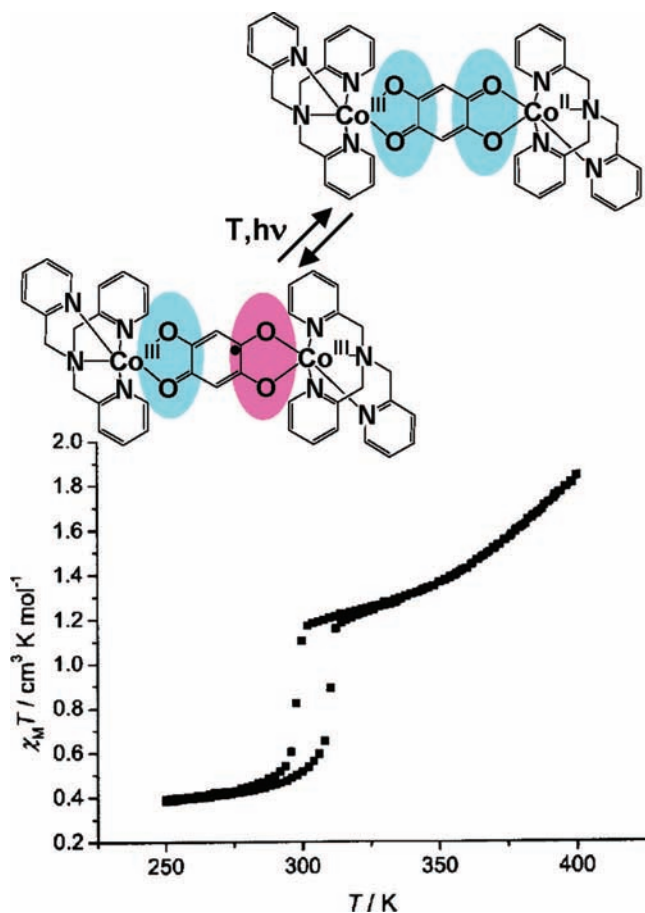
The magnetic properties of the Co complex show that **1** is a paramagnetic compound with  $\chi_M T = 4.81 \text{ cm}^3 \text{ K mol}^{-1}$ , while **3** is a diamagnetic compound. Furthermore, **2** exhibited thermally induced valence tautomerism (Figure 9). An important characteristic of this system is that hysteresis was observed at around room temperature. As shown in the figure, an abrupt increase was observed at around 310 K upon warming. The high-temperature phase was  $\{[Co^{III-LS}(tpa)](dhbq)^{2-}\{Co^{II-HS}(tpa)\}\cdot(PF_6)_3$ . On the



**FIGURE 8.** Structure of the dinuclear Co compound,  $\{[Co^{III-LS}(tpa)](dhbq)^{3-}\{Co^{III-LS}(tpa)\}\cdot(PF_6)_3$ .<sup>13</sup>

other hand, the  $\chi_M T$  value decreased sharply at 297 K. The width of the thermal hysteresis loop was 13 K. As shown in Figure 7, the entropy-driven valence tautomerism can be expressed as  $\{[Co^{III-LS}(tpa)](dhbq)^{3-}\{Co^{III-LS}(tpa)\}\cdot(PF_6)_3 \rightleftharpoons \{[Co^{III-LS}(tpa)](dhbq)^{2-}\{Co^{II-HS}(tpa)\}\cdot(PF_6)_3$

The presence of such a hysteresis loop suggests that strong intermolecular interactions operate in the crystals.<sup>29,47</sup> Indeed, careful investigation of the crystal structure shows that the cationic **2** species are assembled by an off-set  $\pi \cdots \pi$  interaction of the pyridine rings of the



**FIGURE 9.** Magnetic properties of the dinuclear Co compound,  $[\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{dmbq})_3]^{3-}\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{PF}_6)_3$ . The valence tautomeric transition observed at around 300 K exhibits a hysteresis loop.<sup>13</sup>

terminal tpa's and an edge-to-face interaction between the terminal tpa pyridine rings and the dmbq benzene rings. We believe that these interactions play an important role in creating molecular compounds that exhibit a hysteresis loop.

Another important point is that the transition occurs in two steps. The  $\chi_M T$  value at around 305 K is ca.  $1.2 \text{ cm}^3 \text{ K mol}^{-1}$ , which is close to half of the  $\chi_M T$  value for 100%  $[\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{dmbq})_3]^{2-}\{\text{Co}^{\text{II-HS}}(\text{tpa})\}(\text{PF}_6)_3$ . This is an intriguing phenomenon, but the mechanism has not been clarified as of yet. Note that some of the Fe spin-crossover complexes also show a two-step transition. In some cases, this can be explained by the presence of antiferromagnetic-type short-range interactions.<sup>48</sup> Hence, to explain the two-step behavior described above, we may have to consider the competition between antiferromagnetic-type short-range interactions and ferromagnetic-type interactions.

Furthermore, we have also investigated the effect of light on this compound. There are CT absorption bands around the visible region, and hence the photo-effects were investigated using 532 nm light. When it was irradiated at 5 K for 30 min, the magnetic moment increased abruptly. This suggests that CT from dmbq to  $\text{Co}^{\text{III-LS}}$  was induced by light. The induction of the CT was confirmed by the IR spectra. After photo-irradiation, a mixed valence state was created via the following photo-

process:  $[\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{dmbq})_3]^{3-}\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{PF}_6)_3 \rightarrow [\{\text{Co}^{\text{III-LS}}(\text{tpa})\}(\text{dmbq})_2]^{2-}\{\text{Co}^{\text{II-HS}}(\text{tpa})\}(\text{PF}_6)_3$ .

As already mentioned, the challenging issues in this field are the preparation of valence tautomeric compounds that exhibit photo-induced valence tautomerism and feature large hysteresis. We have therefore succeeded in preparing such a Co complex for the first time, although its magnetic properties are still a long way from being suitable for practical applications.

Furthermore, just recently, a photoresponsive polynuclear Co valence tautomeric compound with dioxolene ligand 3,5-bis(3',4'-dihydroxy-5'-*tert*-butylphenyl)-1-*tert*-butylbenzene was reported by Beni et al.<sup>42</sup> Although it is not our work, their findings will now be introduced briefly. Their compound is  $[(\text{phen})\text{Co}^{\text{III-LS}}-\mu-(\text{Cat-Ph-SQ})-]_n$ . The transition temperature of the valence tautomerism,  $[(\text{phen})\text{Co}^{\text{III-LS}}-\mu-(\text{Cat-Ph-SQ})-]_n \rightleftharpoons [(\text{phen})\text{Co}^{\text{II-HS}}-\mu-(\text{SQ-Ph-SQ})-]_n$ , is ca. 305 K. When this compound is excited by 658 nm light, the following photoreaction is induced:  $[(\text{phen})\text{Co}^{\text{III-LS}}-\mu-(\text{Cat-Ph-SQ})-]_n \rightarrow [(\text{phen})\text{Co}^{\text{II-HS}}-\mu-(\text{SQ-Ph-SQ})-]_n$ .

The relaxation behavior is similar to the mononuclear Co compound  $[\text{Co}^{\text{II-HS}}(3,5\text{-dbsq})_2(\text{phen})](\text{C}_6\text{H}_5\text{Cl})$  described above. That is, the temperature dependence of the relaxation rate suggests a typical, thermally activated process at temperatures higher than 30 K. On the other hand, relaxation that was basically temperature-independent was observed at temperatures lower than 20 K. This means that relaxation at low temperatures (9–20 K) occurs via a tunneling process.

These results show that the dynamic behavior, i.e., photo-induced valence tautomerism and relaxation via tunneling at low temperatures, of polynuclear Co valence tautomeric compounds is basically consistent with that of the mononuclear Co compounds.

## 5. Concluding Remarks

We have reported that some valence tautomeric compounds can exhibit photo-induced valence tautomerism. That is, when a Co valence tautomeric compound is excited by 532 nm light, LMCT is induced and the metastable  $\text{Co}^{\text{II-HS}}$  state can be trapped at low temperatures. The metastable state is essentially equivalent to the high-temperature phase. The relaxation of the photo-induced  $\text{Co}^{\text{II-HS}}$  state is thermally activated at high temperatures. However, it relaxes back to its original state via a temperature-independent tunneling process at low temperatures. Furthermore, it was found that back electron transfer can be induced by exciting the metal–ligand CT band. These observations show that this Co valence tautomeric compound exhibits intriguing photomagnetic properties, in common with  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  LIESST complexes and Prussian blue analogues.<sup>15,27,28</sup>

Note that almost all of the compounds we studied exhibited photo-induced valence tautomerism. This suggests that the observed photo-induced magnetization is not an anomalous phenomenon but rather is a general property of Co valence tautomeric com-

pounds. Hence, we believe that there is a strong possibility that photomagnetization effects will be observed in other valence tautomeric compounds. Furthermore, the lifetime of the photo-induced metastable state in this case seems to be a little bit short compared with that of Fe<sup>II</sup> and Fe<sup>III</sup> LIESST complexes. However, this is not a general feature of valence tautomeric compounds, because Beni et al. have recently reported that [(phen)Co<sup>II-HS</sup>-μ-(SQ-Ph-SQ)]<sub>n</sub> exhibits quite a long lifetime, as in the case of the LIESST compounds.<sup>42</sup> Hence, we believe that Co valence tautomeric compounds have the potential for use in future photoswitching and memory devices. Furthermore, we believe that the Co compounds are ideal materials to study photo-induced electron-transfer processes, which are key processes in many biological systems.

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