Inorg. Chem. **2007**, *46*, 1039–1041

Inorganic Chemistry

Communication

Reverse Photochromic Behavior of an Iron–Magnesium Complex

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Received September 8, 2006

We have obtained a novel heterobimetallic iron–magnesium complex, $(THF)_4Mg(\mu\text{-}Br)_2FeBr_2$ (THF = tetrahydrofuran), which showed reverse photochromism in THF. The response exhibited in this system is associated with d-orbital splitting of the Fe atom and a change in the molecular aggregation state (dimerization).

Materials with reversible photoresponse are potentially useful[1] and occur in nature. For example, photoisomerization of rhodopsin to give the trans isomer in the retina of the eye provides an electrical signal to the nervous system, and the trans isomer thermally reverts to the cis isomer, affording a reversible photoresponse.[2] Artificial π-conjugated organics, such as azobenzenes, diarylethenes, and fulgides, have stimulated interest in the construction of photoresponsive molecular devices.[3] Some metal complexes, such as metal clusters containing lattice vacancies (or dopants) in their crystals[4] and spin-crossover complexes with light-induced excited spin state trapping,[5] have already been reported. However, in general, metal complexes are difficult to use as reversible photoresponsive devices, in spite of their high quantum efficiency to induce electron transfer, because the reverse reaction, releasing the excited energy without molecular motion, is too rapid. In this work, we report a novel iron–magnesium complex with reverse photochromism.

While studying the reactivity of ferrous chloride with a methyl Grignard reagent,[6] we isolated the hitherto unknown complex $(THF)_4Mg(\mu\text{-}Br)_2FeBr_2$ (**1**; THF = tetrahydrofuran) as pale-green, almost colorless crystals. The ORTEP drawing of **1** is illustrated in Figure 1. The geometry at the Fe center is best described as a distorted tetrahedron. The Fe–Mg distance of 3.656 Å, which is much larger than the sum of the covalent radii, excludes the formation of a direct bond. These observations are similar to those reported for several metal pairs of chloro-bridged heterobimetallic complexes.[7]

Unexpectedly, we found that **1** exhibits reverse-photochromic behavior. With time after dissolution of **1** in THF, the colorless solution gradually turned yellow (Figure 2a).[8] We were surprised to observe that the yellow color quickly disappeared under UV irradiation (Figure 2b).[9] The photoresponsive decoloration could be observed even upon exposure to sunlight. Interestingly, the decolorized solution began to turn yellow again when stored in the dark after irradiation. The photoresponsive color change could be observed repeatedly and reproducibly. It is noteworthy that the recovery of the intensity of UV–vis absorbance was almost complete, as evaluated by monitoring the absorbance profile after repeated UV irradiation at intervals of 3 h

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(8) The time response of UV–vis spectra, measured at intervals of 30 min after dissolution, is shown in the Supporting Information.

(9) The UV irradiations were carried out using the light of a 150 W tungsten–xenon source equipped with cutoff filters to pass the 365 nm wavelength.

10.1021/ic0616986 CCC: $37.00

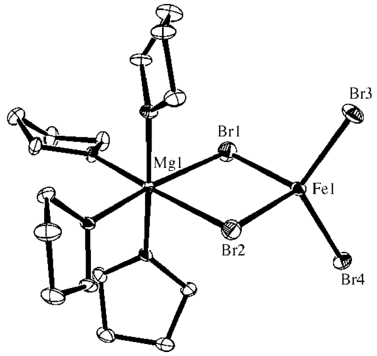

Figure 1. ORTEP drawing of **1**. H atoms and disorder of THF are omitted for clarity.

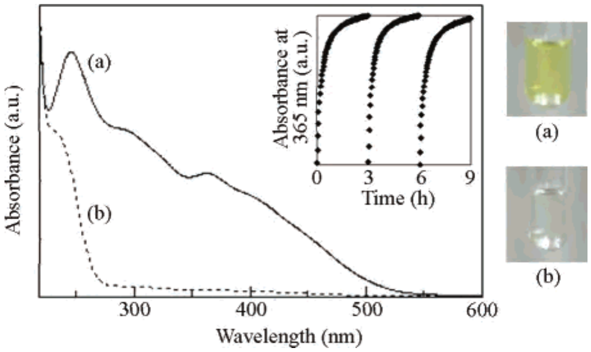

Figure 2. UV−vis spectra of **1** in a THF solution before (a, solid line) and after irradiation (b, dash). Inset: Time dependence plot of **1**, obtained from the absorption change at 365 nm. UV irradiation at time zero and thereafter at intervals of 3 h.

(Figure 2, inset). Such reversible decoloration by irradiation is called reverse photochromism. This is the first example of reverse-photochromic behavior of a complex in the solution state.

To examine the photoresponsive behavior more precisely, the changes caused by UV irradiation were examined in detail. Although the redox behavior on cyclic voltammetry was hardly altered,[10] the electron spin resonance (ESR) signal showed a remarkable change. The yellowed complex, before the irradiation, gave a strong ESR signal at large *g* values with anisotropy, while the signal almost disappeared after irradiation (Figure 3). These results would be explained by considering the degeneracy of d orbitals, which affects to the absorbance wavelength of a d−d transition. Before irradiation, lower symmetry around the Fe atom results in removal of the degeneracy, as shown by a strong ESR signal with a high zero-field splitting of the d orbitals (Figure 3a). UV irradiation changes the d-orbital splitting of the iron chromophore to restore the degeneracy, with loss of the ESR signal (Figure 3b). Degenerate iron(II) complexes are usually ESR-silent because the spin−orbit coupling of degenerate d orbitals makes the spin−lattice relaxation time too short for ESR measurements.[11]

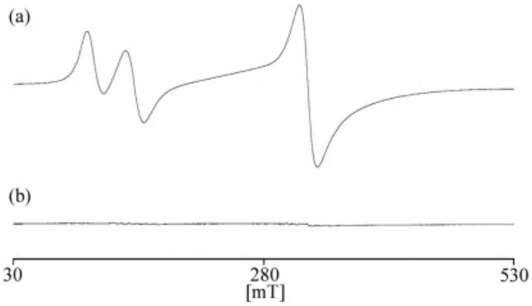

Figure 3. ESR spectrum measured in THF at 77 K: (a) before irradiation (yellow); $g_1 = 7.630$, $g_2 = 4.764$, $g_3 = 2.010$; (b) after irradiation (colorless). Referred to the Mn^{2+}/MnO marker. Measured under the same conditions.

Next, the coloring process was examined. The UV−vis behavior (Figure 2) indicates that **1** is converted to a yellow complex in a THF solution. Our preliminary theoretical calculations suggest that the yellow color, and the strong UV absorbance, is not generated by the original structure of **1**.[12] By kinetic analysis of the UV−vis absorbance profile, the coloring process was found to show a good fit to a second-order reaction (Figure S2 in the Supporting Information), which suggests dimerization of the colorless complex **1** to form a thermodynamically stable chromophore.

On the basis of these results, we propose the formation of an assembled structure, such as the open dicubane complex $Fe_2Mg_2(\mu_3\text{-}Br)_2(\mu\text{-}Br)_4Br_2(THF)_6$. Similar structures have been reported for divalent *homo*metallic chloride complexes (M = Mg, Ti, Mn, Fe, Co), which exist as centrosymmetric tetranuclear species with two different types of metal centers, octahedral ML_6 and trigonal-bipyramidal ML_5.[13a,14] While the crystal structures of *homo*metallic chlorides are reported as tetranuclear structures (dimer), that of *hetero*metallic chlorides are reported as dinuclear structures (monomer).[7] Although the crystal structure of *hetero*metallic bromide (**1**) is monomeric (Figure 1), the larger Br atom could reduce the energy gap between monomer and dimer to form the dimer in solution. The dimeric structure would also be supported by the magnetic moment (μ_{eff}), determined by the Evans method.[15] The observed μ_{eff} of the yellow complex was equal to 6.14 μ_B, which is considerably higher than the

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[10] In a cyclic voltammogram of the complex in THF (0.1 mM), platinum counter and working electrodes and a Ag/AgCl reference electrode with $[^{n}Bu_4P][PF_6]$ (0.1 M) as an electrolyte were used. The same sample before and after the UV irradiation showed a Fe^{III}/Fe^{II} redox wave at −0.37 and −0.35 V (vs ferrocenium/ferrocene), respectively. (See the Supporting Information for details.)

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[12] The low-lying 30 excited states of **1a** (theoretical model for **1**) were computed using TDDFT (TD-B3LYP//UB3LYP/TZVP for iron and bromine; 6-31+G* for others). No significant oscillator strength was detected (wavelengths from 3454 to 267 nm). (See the Supporting Information for details.)

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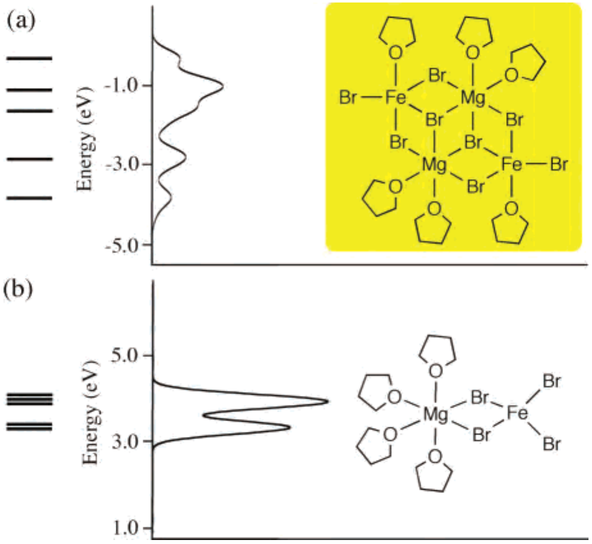

Figure 4. pDOS of Fe 3d orbitals calculated with DV-Xα: (a) dimer cluster model (undegenerated); (b) monomer (degenerated).

characteristic values for mononuclear iron(II) complexes.[13] This indicates the presence of ferromagnetic interactions, caused by the clustering of Fe atoms.

To discuss the electronic structures between monomer and dimer, nonrelativistic DV-Xα calculations were performed.[16] The partial density of states (pDOS) diagrams of the Fe 3d orbitals are shown in Figure 4. The degeneracy was completely lost in the dimer model (a), while degeneracy existed in the monomer (b). This information of the d-orbital splitting pattern would be useful in explaining the differences in both the solution color and the ESR signals.

Concerning the photoresponse mechanism, the key molecular unit of the assembled structure would be the trigonal-bipyramidal iron chromophore, which converts the light energy to restore the degeneracy of the d orbitals, along with molecular separation of the dimer to the monomer. In other words, the molecular separation prevents a rapid energy release from the excited state, achieving stabilization of the metastable state after excitation. Thus, control of the molecular separation could be a novel strategy for achieving a reversible photoresponse, as well as conventional cis−trans isomerization. This idea may open the door for metal-assembled supramolecular materials to generate function as photoresponsive molecular devices.

In summary, we have obtained a novel heterobimetallic iron−magnesium complex (**1**), which exhibits reverse photochromism. The response exhibited in this system is associated with d-orbital splitting of the Fe atom and a change in the molecular aggregation state. Given the wide variety of available metals and ligands with different stabilities and functional properties, there is potential scope for a wide variety of photoresponsive metallo-supramolecular materials based on the present findings. We are currently extending this chemistry to other metal bromides in order to determine the photoresponse mechanism. A detailed description of the photochromic process along with the magnetic behavior will be reported in full elsewhere.

Acknowledgment. We thank Prof. Hiroharu Suzuki and Ryuichi Tenjinbayashi of Tokyo Institute of Technology for help with the ESR experiments.

Supporting Information Available: Crystallographic data, in CIF format, for structure **1** and detailed experimental information and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The nonrelativistic DV-Xα calculations were performed with a Slater exchange parameter, α, of 0.7 for all atoms and with 29000 and 9000 DV sampling points, respectively. (See the Supporting Information for details.)