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Spin Crossover by Encapsulation

Kosuke Ono,[†] Michito Yoshizawa,*[,‡] Munetaka Akita,[‡] Tatsuhisa Kato,*[,§] Yoshihide Tsunobuchi,[⊥]
Shin-ichi Ohkoshi,[⊥] and Makoto Fujita*[,†]

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, PRESTO, Japan Science and Technology Agency (JST), and Department of Chemistry, Faculty of Science, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, Japan, and Department of Chemistry, School of Science, The University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received November 17, 2008; E-mail: mfujita@appchem.t.u-tokyo.ac.jp; yoshizawa.m.ac@m.titech.ac.jp; rik@josai.ac.jp

Spin crossover is a phenomenon in which the electronic configuration of transition metal centers (high and low spin states) changes in response to external stimuli[1] such as thermal,[2] pressure,[3] light,[4] and magnetic ones.[5] Because of potential applications to sensors and digital memory, spin crossover materials have attracted considerable interests in chemistry and materials fields for many years. Typically, spin crossover is observed for octahedral Fe(II), Fe(III), and Co(II) complexes, but rarely for other metal complexes.[6] Here, we report that square planar Ni(II) and Co(II) complexes show spin crossover upon *encapsulation* by coordination cages of the general structure **1** (Figure 1).[7] The confined cavity of the hosts inhibits changes in the metal coordination number or geometry and promotes configuration change presumably via electronic interactions between the metal d_{z^2} orbital and the π orbitals of the aromatic cage panels.

Given that cage **1a** is a suitable host for planar aromatics,[7] the planar, low-spin Ni(II)(acen) (acen = *N*,*N'*-ethylenebis(acetylacetoneiminato)) **2** is an appropriate guest for cage **1a**. Ni(acen) **2** is a red solid, indicative of a low-spin configuration,[8] but when powdered **2** (2 molar equiv) was suspended in a colorless, aqueous solution of **1a** at room temperature the solution color dramatically changed to dark green. After stirring for 30 min, excess solid **2** was removed and ^{1}H NMR analysis revealed an apparent diamagnetic **1a**$\supset$**2** complex with the expected 1:1 stoichiometry. The methyl signals of **2** were shifted highly upfield, being typical upon encapsulation but not conclusive of a high-spin state (Figure 2a). The formation and stoichiometry of **1a**$\supset$**2** were further confirmed by CSI-MS measurements. The UV−vis spectrum of **1a**$\supset$**2** in aqueous solution shows a new broad band around 570 nm. The color change is reversible and extraction of the Ni(acen) with chloroform returns to the original red color.

SQUID measurements demonstrated that the dark green **1a**$\supset$**2** shows paramagnetic behavior. A $\chi_M T$ value of 0.16 cm^3·K·mol^{-1} was estimated from $\chi_M T$ versus T plots and corresponds to 16% of the value expected from the pure high-spin configuration of the encapsulated Ni(II) ions ($S = 1$; Figure 2c). The ground spin state should be rather described as the state of the low spin configuration ($S = 0$) coupled with the pure high-spin one ($S = 1$) via a spin−orbit interaction. The apparent diamagnetic NMR indicates that the spin density of the molecule well localizes at the metal center Ni(II) and penetrates into neither the acen ring nor the coordination cage. The UV−vis spectrum of solid-state **1a**$\supset$**2** shows an extended, broad absorption band centered at 690 nm (Figure 2b). High-spin Ni(II)(acen) was also observed in the larger pillared cage **1b**. The 1:2 H/G stoichiometry, **1b**$\supset$(**2**)$_2$, was confirmed by NMR and CSI-MS. The

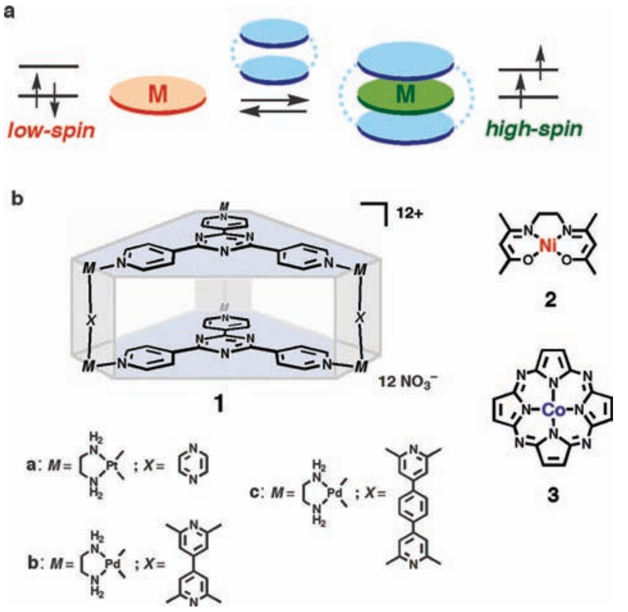

Figure 1. (a) Schematic drawing for the concept of encapsulation-driven spin crossover. (b) Chemical structures of **1**−**3**.

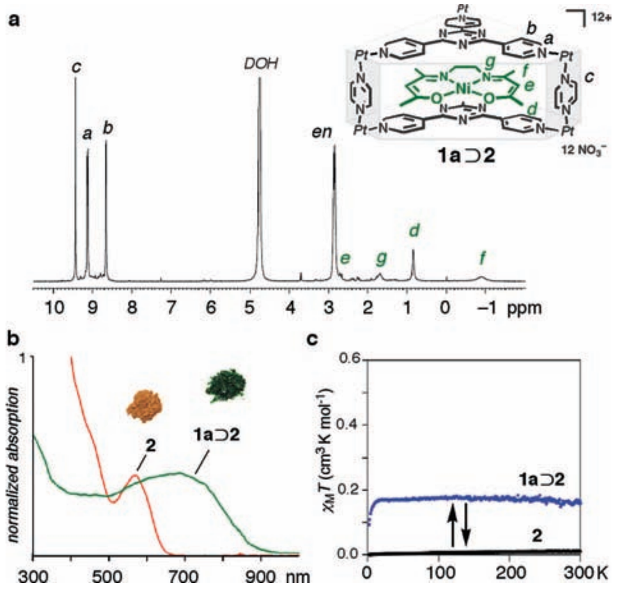

Figure 2. (a) NMR spectrum (500 MHz, D$_2$O, rt) of **1a**$\supset$**2**. (b) UV−vis spectra of **1a**$\supset$**2** and **2** in solid state. (c) $\chi_M T$ vs T plots for **1a**$\supset$**2** and **2**.

[†] School of Engineering, The University of Tokyo.
[‡] Tokyo Institute of Technology.
[§] Josai University.
[⊥] School of Science, The University of Tokyo.

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drastic color change from red to dark green was again observed and the $\chi_M T$ value of 0.46 cm^3·K·mol^{-1} (Figure 3) corresponds to 23% of that expected from two encapsulated Ni(II) centers in the high-spin configuration. X-ray crystallographic analysis of the dark green-colored single crystals of **1b**⊃(**2**)$_2$ obtained from slow evaporation gave the final structural proof (Figure 4). Within the cage, the square planar geometry of the two Ni(acen) molecules is perfectly preserved. The short (3.33 Å) distance between the cage panels and the guests implies increased interactions and efficient π-stacking between the guest and the host. The two guest molecules are also in close proximity but are twisted by 150° and separated by 3.59 Å, presumably due to steric repulsion of the methyl groups. Thus, contrary to typical spin state transitions for Ni(II), the observed spin crossover is not accompanied by changes in the coordination geometry and/or coordination number.

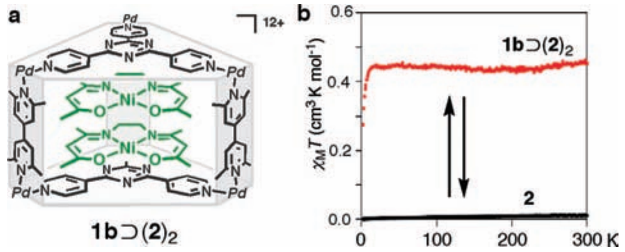

Figure 3. (a) Chemical structure of **1b**⊃(**2**)$_2$. (b) $\chi_M T$ vs T plots for **1b**⊃(**2**)$_2$.

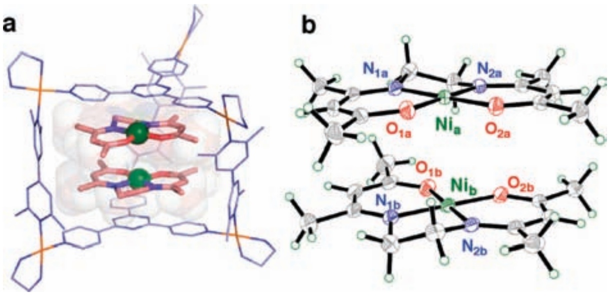

Figure 4. (a) X-ray structure of **1b**⊃(**2**)$_2$. (b) ORTEP view of the guest molecules (30% probability).

Co(II) has one less electron than Ni(II) and can also undergo spin-crossover, so Co(II)(tap) (tap = tetraazaporphinato) complex **3** was examined to establish a general effect of cage encapsulation on spin transitions. Inclusion within cage **1a** alone did not suffice to form the Co(II) spin crossover complex (see Supporting Information), but inclusion within the sandwich complex **1c**⊃(**4**·**3**·**4**) (where compound **4** is coronene) did alter the Co(II) spin state. Sandwich complex **1c**⊃(**4**·**3**·**4**) self-assembled after heating in water at 100 °C for 2 h (Figure 5). The stoichiometry and alternating structure were confirmed by ^{1}H NMR and CSI-MS. UV−vis spectrum showed changes and a strong red-shift but was inconclusive of the spin state.

The 1D-ESR spectrum was anisotropic implying the participation of high spin states. The intensity of the ESR signal of **1c**⊃(**4**·**3**·**4**) is temperature dependent and significantly deviates from the Curie−Weiss law above 170 K (Figure 5c). This is also indicative of an increased involvement of a high spin state, resultant ease in thermal promotion from the low spin ($S = 1/2$) to high spin ($S = 3/2$) state, and opening the additional relaxation path of the ESR process. The 2D-ESTN (electron spin transient nutation) spectrum at low temperature (6 K) showed a nutation frequency of 20.8 MHz for **1c**⊃(**4**·**3**·**4**), which is slightly larger than the value of 17.5 MHz for the low spin ($S = 1/2$) reference complex **1a**⊃Cu(II)(tap). The higher nutation frequency is due to the involvement of a higher spin state with a larger magnetic moment. Therefore, the high spin state of Co(II) complex **3** in **1c**⊃(**4**·**3**·**4**) is best described as a mixture of the $S = 1/2$ and $S = 3/2$ state.[9]

The spin crossover of Ni(II) and Co(II) complexes after encapsulation in cages **1a**−**c** is ascribed to interactions between the metal d_{z^2} orbital and the π orbitals of aromatic cage panels or coguests. Inside the confined cavity space, the panel ligands perturb the Ni(II) orbitals, forming a "pseudo octahedral" ligand field, and stabilize the paramagnetic, high spin $^3B_{1g}$ state with an apparent square-planar geometry.[10] In the case of Co(II) complex **1c**⊃(**4**·**3**·**4**), the electron-rich coronenes perturb the Co(II) ligand field and permit spin−orbit coupling between the quartet state $^4A_2$ and the doublet state $^2A_1$.[11]

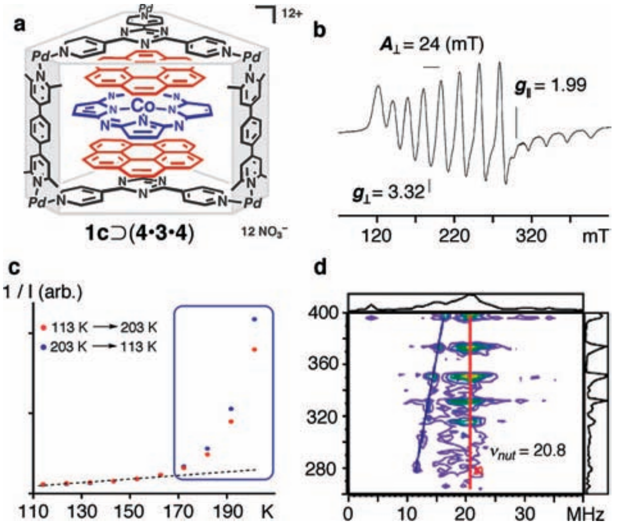

Figure 5. Chemical structure (a) and property of **1c**⊃(**4**·**3**·**4**). (b) 1D-CW ESR spectrum at 113 K. (c) 1/I vs T plot (I: intensity of ESR signal; temperature range: 113−203 K). (d) 2D-ESTN spectrum at 6 K.

In summary, encapsulation within synthetic hosts can induce spin-crossover of square planar Ni(II) and Co(II) complexes. To our knowledge, this is the first example where Ni(II) or Co(II) complexes show spin crossover behavior without changing the coordination geometry or number. The constrictive environment within the hydrophobic host cavity enables one to establish new intermolecular interactions and control the resultant properties of the enclathrated metal complexes.

Supporting Information Available: Experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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