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Takahashi, Kazuyuki

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Editorial

Spin-Crossover Complexes

Kazuyuki Takahashi

Department of Chemistry, Graduate School of Science, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan; ktaka@crystal.kobe-u.ac.jp; Tel.: +81-78-803-5691

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Spin-crossover (SCO) is a spin-state switching phenomenon between a high-spin (HS) and low-spin (LS) electronic configurations in a transition metal center. The SCO phenomenon is widely recognized as an example of molecular bistability. The SCO compounds most widely studied are six-coordinate first-row transition metal complexes with d^4–d^7 configurations. A relative small enthalpy variation between LS and HS states can be realized by coopetition between ligand field stabilization (LFS) and spin pairing energies, which is illustrated by the Tanabe–Sugano diagrams in common coordination chemistry textbooks. Since an entropy variation in spin multiplicity from LS to HS is always positive, an increase in temperature can induce the transformation in Gibbs free energy from a positive to a negative sign, at which point SCO conversion occurs from the LS to HS state.

Cambi and co-workers' pioneering work on the anomalous magnetic behaviors of mononuclear Fe(III) dithiocarbamate complexes [1] was first recognized as SCO phenomena in the early 1930s. However, progress on SCO complexes awaited the dissemination of ligand field theory into coordination chemistry. The concept of controlling LFS energies by substitution with different field strength ligands resulted in the corroboration of SCO phenomena in some Co(II) and Fe(II) complexes in the early 1960s. Moreover, subsequent findings that pressure [2] and light [3] can induce an SCO phenomenon may attract attention to SCO complexes. In the 1990s the demonstration of device applications using the SCO complex [4] illuminated the potential of SCO complexes in future practical applications in memory, display, and sensing devices. Figure 1 shows the number of published articles per year whose titles or topics contain the words "spin-crossover," "spin equilibrium," or their derivatives. Studies concerning SCO complexes have apparently increased since the 1980s; moreover, the number has more rapidly developed after the 2000s. The fundamentals and applications of SCO complexes have attracted growing interest not only in inorganic coordination chemistry but also in a wide range of relevant research fields.

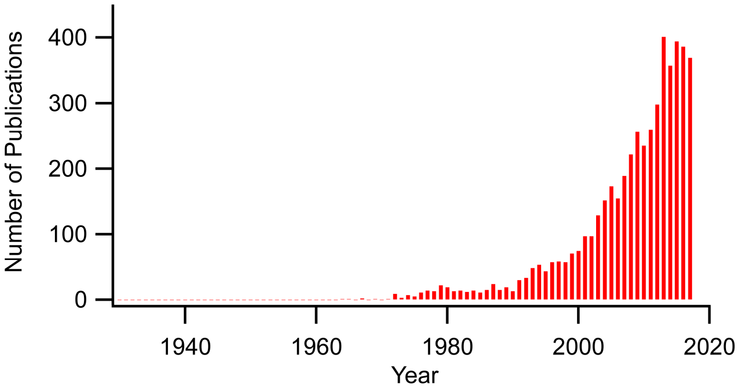

Figure 1. The number of publications per year whose titles or keywords contain "spin-crossover," "spin equilibrium," or their derived words, retrieved from Web of Science.

In the history of SCO complexes, three volumes of earlier research on SCO complexes were edited by Gütlich and Goodwin [5] in 2003. Later, a book edited by Halcrow [6] and a review by Gütlich and co-workers [7] concerning recent advances in SCO complexes were published in 2013. Moreover, a large number of reviews on specific subjects relating to SCO complexes have been published to date. Although considerable knowledge concerning SCO complexes has been accumulated, it is still challenging to design and synthesize an SCO complex that exhibits the target SCO behavior.

The impact on the occurrence of SCO can be considered to be divided into the inner and outer effects on a coordination sphere. The former effect is the prerequisite requirement of the LFS energy of a transition metal complex near the SCO region, as described above, which is strongly dependent on a transition metal center, coordinating ligands, and the coordination geometry. The latter effect arises from various interactions between SCO complexes, counter ions, and solvate molecules, if any. These interactions may affect the coordination structure of an SCO complex and/or SCO cooperativity, which represents the correlation of a spin state between SCO active metal centers. Therefore, further investigation has been undertaken to clarify the impact on SCO complexes.

This Special Issue is devoted to various aspects of recent research on SCO complexes by means of open-access way. Excellent, well-organized, and impressive reviews are contributed by three groups. Kuroiwa [8] reviews the recent advances in supramolecular approaches to SCO complexes, indicating that the successful control of molecular assemblies of SCO complexes provides an opportunity to contribute toward nanoscience for transition metal complexes including SCO complexes. Sugahara and co-workers [9] disclose the outer effects of functional counterions on SCO behaviors for the well-known one-dimensional triazole-coordinated Fe(II) complex. Moreover, they demonstrate that extended X-ray absorption fine structure (EXAFS) is a very useful technique to analyze the coordination structures for non-crystalline SCO complex solids. Banerjee and co-workers [10] give an overview of recent progress in theoretical treatments on SCO complexes and review the applications of the state-of-the-art density functional theory-based calculation technique to microscopic understanding of SCO cooperativity.

This Special Issue also contains 11 original research articles that are devoted to the synthesis and characterization of various molecular systems of SCO complexes. For the investigation of isolated mononuclear SCO complexes, Stock and co-workers [11] report structural dynamics in isolated LS Fe(II) complexes from extended-tripod ligands by means of laser flash photolysis and find that the slowing-down of dynamic exchange from the metastable HS state may arise from the trigonal torsion of a coordination octahedron. With respect to mononuclear SCO complex solids, Kimura and Ishida [12] describe the substitution effect on the pybox ligand in an Fe(II) SCO complex and reveal that the decrease in LFS energy originates from the electron-donating ability of substituents; moreover, the comparison between the solid and solution states may shed light on the possibility of separating the inner and outer effects from a substitution effect. Phonsri and co-workers [13] describe the ethoxy substitution effect on homoleptic and heteroleptic Fe(III) SCO systems and find that the steric effect leads to less cooperative SCO conversions. Nakanishi and co-workers [14] investigate the halogen substitution effect on both the ligand and counter-anion for an Fe(III) SCO complex. They were successful at isolating and characterizing four isostructural SCO complexes and found that the substitution of the ligand may result in an inner electronic effect, whereas substitution of the counter-anion may create an outer chemical pressure effect. As for dinuclear SCO complex solids, Craze and co-workers [15] report the steric effect of bridging groups between two SCO active centers in dinuclear Fe(II) triple helicate complexes and observed slight changes in SCO transition behavior. Hora and Hagiwara [16] also disclose the bridging alkyl length effect in the dinuclear Fe(II) helicate system and discover the widest thermal hysteresis loop among the related dinuclear Fe(II) helicate complexes. For polynuclear SCO complex assemblies, Kosone and co-workers [17] investigate the substitution effect on the axial pyridine ligands in the 2D bilayer Hofmann-type Fe(II) coordination polymer and reveal steric and chemical pressure effects on SCO cooperativity and transition temperature. Iwai and co-workers [18] report a series of Fe(II) assembled complexes from a bidentate bridging ligand with different co-ligands. They indicate that the parallel configuration of coordinated pyridine rings in an FeN_6 coordination core favors the HS state. Imoto and co-workers [19] demonstrate the metal dilution effect on SCO cooperativity for the cyano-bridged Fe(II) SCO network and reveal that the decrease in cooperativity by increasing Co(II) concentration may lead to more gradual SCO transitions and lower transition temperatures. For the development of novel multifunctional SCO hybrid compounds, Kuramochi and co-workers [20] develop Fe(II) SCO hybrid molecular systems with a polyoxometalate (POM) anion, which is known as a multi-functional unit. They clarify the crystal structures and magnetic properties of the SCO–POM hybrids and find that the hydrogen bonding interactions between the Fe(II) cation and POM anion strongly influenced the spin state of the Fe(II) cation. Similarly, Takahashi and co-workers [21] report the crystal structures and physical properties of a new hybrid compound from a well-known Fe(III) SCO complex cation with a π-radical anion. They reveal that the coordination distortion induced by strong π-stacking interactions between an Fe(III) cation and a π-radical anion may suppress the occurrence of SCO. As summarized above, this Special Issue covers a wide range of molecular systems of SCO complexes, and various experimental and theoretical techniques. I am grateful to all the authors for their diverse contributions.

I hope readers will increase their knowledge by engaging with this Special Issue and will go on to contribute to further progress in the research field of SCO complexes. Finally, I am particularly grateful to all the reviewers for their rigorous evaluations and valuable suggestions, which will help to enhance the quality of this Special Issue. In addition, I sincerely thank the editorial staff for their dedicated support in the planning, reviewing, and publishing of this Special Issue.

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