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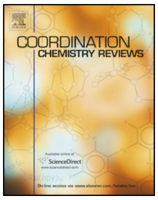

Review

Symmetry-breaking structural phase transitions in spin crossover complexes

Michael Shatruk[a,*], Hoa Phan[a], Bruno A. Chrisostomo[a], Akmaral Suleimenova[b]

[a] *Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA*
[b] *Department of Chemistry, L.N. Gumilyov Eurasian National University, 5 Munaitpasov Str, 010008 Astana, Kazakhstan*

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[*] Corresponding author. Tel.: +1 850 417 8417.
E-mail address: shatruk@chem.fsu.edu (M. Shatruk).

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ABSTRACT

We review spin-crossover (SCO) complexes of 3*d* transition metal ions that exhibit structural phase transitions (SPTs) associated with changes in the space group symmetry. An analysis of the existing cases extracted by data-mining the Cambridge Structural Database reveals that they can be classified according to the particular cause of symmetry breaking. One class of complexes exhibits the SPT caused by concerted displacive atomic motions due to the change in the metal-ligand bond lengths during the SCO. Such transitions are usually abrupt, with strong coupling between the SCO and SPT. The second class is characterized by symmetry lowering due to the stabilization of an intermediate mixed high-spin/low-spin state. The abruptness of the SCO is not a necessity in such case. Finally, in the third class, the SPT takes place due to the crystallographic ordering of peripheral groups, counter ions, or solvent molecules that are remote from the SCO centers. Such SPTs exhibit only weak coupling (if any) to the SCO. This analysis is expected to assist in the design of multifunctional SCO materials that rely on the symmetry-breaking SPTs.

1. Introduction

The ability of certain complexes of d^4–d^7 transition metal ions to exist in two different electronic spin configurations has been stimulating consistent research efforts directed at uncovering the fundamental and practical aspects of this phenomenon [1,2]. The spin state conversion, commonly referred to as spin crossover (SCO), can be controlled by temperature, pressure, or photoexcitation, thus causing great interest in applications that would leverage the associated magnetic, structural, and optical bistability [3]. From the practical viewpoint, one would like to exploit such bistability in the form of hysteresis curves, where the memory effect makes it possible to use an external field to switch between the spin states while keeping another external parameter constant. For example, the existence of a thermal hysteresis allows the use of pressure or photoexcitation for the spin state control at constant temperature within the hysteresis loop (Fig. 1).

Obviously, the emergence of the hysteretic behavior requires an abrupt spin transition, which is known to be dependent on the strength of interactions between the SCO centers, so-called cooperativity [4]. Strongly cooperative transitions result in the abrupt change not only in the magnetic, but also in the structural and optical properties, due to the change in the population of the antibonding e_g orbitals. The abrupt shrinkage or expansion of the metal-ligand bonds can cause dramatic changes in the crystal packing, often inducing cracking or even pulverization of crystals [5]. Arguably, the most dramatic crystallographic effect under such circumstances is the change in the space group that describes the symmetry of the corresponding crystal structure. Upon review of existing literature, we have noted the lack of a systematic assessment of such symmetry-breaking structural changes that would be of great interest for the researchers who attempt to design SCO materials with potentially intriguing properties, for example, such as switchable non-linear optical behavior or ferroelectric response. The only brief attempt to summarize the structural phase transitions (SPTs) coupled to SCO was made by Rao nearly 30 years ago [6]. Herein, we provide a systematic account of the known cases of spin transitions accompanied by space-group changes and discuss the structure–property relationships in the associated compounds. Our coverage might not be exhaustive, but we attempted, to the best of our ability, to consider as many relevant examples as we could find.

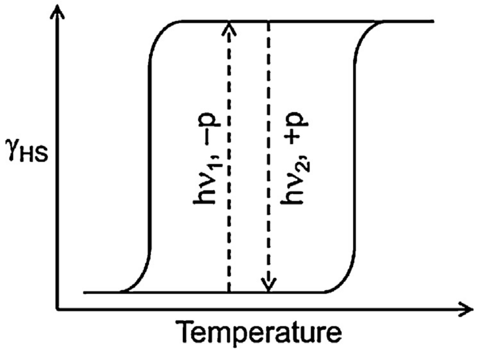

Fig. 1. The conversion between the high-spin (HS) and low-spin (LS) states of an SCO complex is quantified by monitoring the fraction of the HS state, γ_{HS}, as a function of an external parameter (in this case temperature). The hysteretic nature of the transition allows reversible switching between the HS and LS states by means of other external stimuli.

2. Methodology

To explore the known cases of SCO accompanied by the change in the crystallographic space group, we performed the search of crystal structures of all iron and cobalt complexes in the Cambridge Structural Database (CSD). The large number of data obtained was analyzed for the presence of identical compounds structurally characterized at different temperatures and then, within the new data set, for the cases where the structures determined at different temperatures crystallized in different space groups, and where the space group change was also accompanied by the change in the Fe-ligand bond lengths, characteristic of the HS ↔ LS interconversion. The analysis resulted in a relatively limited range of compounds. For each particular compound, the possibility to reduce the space group notation to the same symmetry was carefully examined, and if such possibility was confirmed the compound was discarded from the list. (We imply here the use of different space group settings for structures with equivalent symmetry elements. For example, the space group $P2_1/n$ is just an alternative setting of $P2_1/c$, and thus we found that the same structure was reported in these two different space group notations by different authors.) Likewise discarded were those that did not exhibit SCO. The remaining compounds considered in this review are summarized in Table 1, where we indicate the CSD reference codes, define the SCO transition temperatures ($T_{1/2}$), and give some other relevant information. The list is dominated by Fe(II) complexes, but we also mention a few other relevant examples of Fe(III) and Co(II) complexes found in the literature. The ligand structures and abbreviations are explained in Scheme 1.

In the following, we primarily describe and analyze the structure–property relationships in compounds where the change in the space group is truly coupled to the SCO or occurs (nearly) simultaneously with the SCO. In the end of this account, we also will mention briefly several cases where the existence of a material in different space groups is due to polymorphism rather than to a

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