Unlocking hidden phases in Fe(II) spin crossover complexes under pressure

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Abstract

Spin crossover (SCO) is typically described, in its simplest form, as a two-state electronic equilibrium between high-spin (HS) and low-spin (LS) configurations. Within this framework, temperature and pressure are often treated as equivalent thermodynamic variables capable of shifting the same underlying equilibrium. However, in the solid state, the spin transition is intrinsically coupled to a deformable and cooperative lattice, whose collective response can significantly influence not only the transition conditions but also the transformation pathway. In particular, phase transitions may lead to a substantial shift of the SCO regime towards significantly higher pressures than anticipated, [1] or even to the stabilisation of the HS state under conditions where a LS state would normally be expected. [2]

Among the most widely studied SCO compounds are Fe(II)-based systems (d^6) in octahedral coordination environments, which typically undergo switching between S = 2 and S = 0 spin states. These materials have attracted considerable attention for solid-state refrigeration applications, as some exhibit large to colossal barocaloric effects. [3,4] Consequently, there is growing interest in mapping their pressure–temperature (p,T) phase diagrams and understanding their behaviour under pressure.

In this contribution, we investigate a series of Fe(II) complexes exhibiting contrasting (p,T) responses. By comparing different structural motifs, we demonstrate that lattice topology plays a decisive role in governing how the electronic transition evolves under pressure. Depending on the system, the lattice may reorganise prior to spin switching, evolve cooperatively with the SCO, or become unstable upon compression, enabling structural rearrangements not observed along the thermal pathway.

A combination of high-pressure Raman spectroscopy, together with synchrotron single-crystal and powder X-ray diffraction and X-ray absorption spectroscopy, allows us to unravel the interplay between spin state and structure under different thermodynamic stimuli. Our results highlight how pressure can reveal hidden lattice instabilities and alternative transformation routes, and further emphasise that SCO in molecular solids arises from a delicate balance between electronic configuration and collective structural response.

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