Spin Cross-over Complexes: Structures and Photomagnetism of High spin, Low Spin and Metastable States and the LIESST effect, Judith A. K. Howard,[a*] Victoria A. Money,[a] Jerome Elhaïk,[b] Malcolm A. Halcrow,[b] José Sánchez Costa,[c] Sylvia Marcén[c] and Jean-François Létard[c], [a]*Department of Chemistry, Durham University, South Road, Durham. DH1 3LE, UK,* [b]*School of Chemistry, University of Leeds, Leeds, LS2 9IT, UK, and* [c]*Groupe des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS No. 9048, 87 Av. Doc. A. Schweitzer, F-33608 Pessac, France.* E-mail: j.a.k.howard@durham.ac.uk

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Materials which undergo transitions between the high and low spin states are of interest for their potential in applications such as molecular switches, display devices and information storage as well as their importance in geological and biological systems. One of the most fascinating areas of spin crossover research is the so called LIESST effect (Light Induced Excited Spin State Trapping). Irradiation of a sample in the low spin ground state can result in the formation of a metastable high spin state with a long lifetime at low temperatures (usually <50 K). Crystallographic information about the metastable state is unusual and can give valuable insights into the effect of the spin transition on structure divorced from the temperature effects associated with the thermal spin transition. Derivatives of the 2,6-di(pyrazol-1-yl)pyridine ligand exhibit a wide range of spin crossover behaviour varying. LIESST transitions have been reported in a number of cases. The results of detailed variable temperature crystallographic studies of these materials are presented which show the effect of the thermal spin transition on the crystal structure and *vice versa*. These studies demonstrate the critical importance of the role played by the counter anions in determining the course of the spin transition. For example the unusual shape of the two stage spin transition seen in $[Fe(\mathbf{L1})_2](BF_4)_2$ and $[Fe(\mathbf{L1})_2](ClO_4)_2$, **L1** = 2,6-di(3-methylpyrazol-1-yl)pyrazine can be shown to be caused by an order - disorder transition in the counter anions which increases the distance between the iron centres, reducing the strength of intermolecular interactions and thus the cooperativity and the rate of the transition. Full structural analyses of the metastable state of two of $[Fe(\mathbf{L2})_2](BF_4)_2$ and $[Fe(\mathbf{L3})_2](BF_4)_2$ (**L2** = 2,6-di(pyrazol-1-yl)pyridine and **L3** = 2,6-dipyrazol-1-yl-4-hydroxymethylpyridine) have been performed and show that the structure of the metastable high spin state of these materials is very similar to that of the high spin state at room temperature. This behaviour differs from that reported for $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ in which significant differences were observed between the two high spin states but is supported by photomagnetic studies which suggest that the degree of intermolecular interactions in the two states is similar.