Application of the multivariety statistical methods in analysing the spin crossover behaviour

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In a series of hexacoordinate Fe(III) complexes of the $[Fe^{III}L^5X]$ type, where L^5 stands for a pentadentate Schiff-base ligand and X^- is an unidentate (pseudo)halide coligand, the structural and thermodynamic characteristics of the spin crossover have been analyzed. Multivariety statistical methods have been applied such as Cluster Analysis, Principal Component Analysis, and pair Correlation Analysis.

The structural characteristics in the first group of complexes show a grouping into two clusters according to the spin state of the complexes (low-spin and/or high-spin) at the temperature of the X-ray experiment. Within the $FeN_2N'O_2X$ chromophore, the bond lengths Fe-Nim, Fe-Nam and Fe-O display a tight mutual correlation along with the angle Σ (overall deviation for the octahedral pattern).

In the second group of the spin crossover complexes the thermodynamic characteristics, such as enthalpy and entropy of the spin transition, transition temperature, and the solid state cooperativeness have been assessed. The tight correlation shows $T_{1/2}$ and ΔH and this proceeds according to a straight line: $T_{1/2}$ [K] = 76 [K] + 38[K kJ^{-1} mol]* ΔH[kJ mol^{-1}]. On the other side, the theory of the spin transition predicts $T_{1/2} = \Delta H/\Delta S$ because this is an entropy driven unimolecular reaction.

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