Structural Studies of Manganese(III) Complex with Spin-Crossover and Thermochromic Properties

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The phenomenon of spin-crossover (SCO) has been of great interest due to the bistability of the materials and the search for new technologies and applications. The transition implies a reversible change from high to low spin or vice versa[1]. This magnetic behavior can be induced by external disturbances, such as, temperature, pressure and/or light (LIESST) in 3d4 to 3d7 configurations. More rare and exceptional are the cases in Cr(II) and Mn(III)[2,3].

A new SCO manganese(III) complex with the formula [MnIII(5-MeO-sal-N-1-5-8-12)]Cl has been studied by X-ray diffraction, using the octahedral deviation parameters[4] Σ/° (12 angles of 90°) and trigonal distortion θ/° (24 angles of 60°), that allow the classification of spin states. The crystallographic study was carried out at four different temperatures (100 K, 290 K, 350 K and 400 K) and the unit cell was analyzed at twelve different temperatures in a range of 90 K to 400 K, finding large changes in the coordination sphere. At 400 K octahedral deviations parameters were obtained according to high spin (HS) with 59.2(4)° and 149.5(7)°, and at 100 K the values are typical of low spin (LS) with 34.0(4)° and 79.8(6)°, for Σ/° and θ/°, respectively. The magnetic susceptibility confirms a gradual transition with a T1/2 of 281K, according to the large changes of the unit cell between 250 K and 310 K (figure 1). The definitive evidence of the electronic transition corresponds to the thermochromism in solid state. On cooling to below 250 K, the color begins to visually change and by 90 K the single crystal has turned red (figure 2) with all the electronic population in LS state (3T1g ground state). Finally, a comparison with the MnIII analogous complexes was made using the octahedral distortion parameters obtaining a trend and dispersion diagram of the reported values.

References

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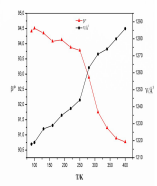

Figure 1: . β angle (red triangles) and volume (black dots)

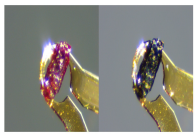

Figure 2: Thermochromism at 100 K and variation by temperature