“Towards "better" molecular magnets. Correlation of structure and magnetic anisotropy.”

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The theoretical and experimental study carried out in recent years allowed to determine the properties that guarantee SMM or SIM type behavior, which are: high spin state S, large magnetic anisotropy with both a negative ZFS parameter D (easy-axis anisotropy) and an easy-plane anisotropy (D > 0), as well as the formation of a significant energy barrier (increasing with S and D). These properties lead to bistable systems, showing the longer the relaxation times, the higher the energy barrier. However, since the specific conditions for the occurrence of SMM and SIM are not easy to achieve in practice, and the blocking temperatures of the molecular magnets obtained so far oscillate in a low range, our activities focused on finding a path of "tuning" the values of magnetic parameters. The correlation of the magnetic study with the crystal and molecular structure is the basis for the control of the synthesis and properties of the obtained magnetic materials, and ensures a change in magnetic anisotropy as a result of rational changes in structural anisotropy. However, achieving a high D value requires understanding how to adjust the geometry of the compound to obtain a significant contribution of spin-orbital coupling to magnetic anisotropy. The results of our research work conducted for a series of Co(II) complexes with the different N- donor ligands, its derivatives and halide or pseudohalide linkers show that the modulation of the geometry of the system is possible by modifying structural factors: substituent replacement in the ligand, disturbance of the ligand field strength, introduction of anionic ligands (Scheme 1). The presence of high magnetic anisotropy affecting a significant increase in the energy barrier in the obtained materials was additionally confirmed by high-field EPR (HFEPR) studies in the frequency range of 100-650 GHz supported, due to the large splitting of energy levels, by the innovative FIRMS (Far–Infrared Magnetic Spectroscopy) method consisting in on terahertz frequency sweeps and measurement of radiation absorption as a function of frequency. Our research shows also that not only the negative sign of the D parameter is not a necessary condition to observe relaxation processes, but also no or almost negligible zfs effect or high ground state spin. An example we reported the field induced slow magnetic relaxation in Cu(II), Mn(II) and Cr(III) complexes.