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Opponent's Review of the Habilitation Thesis:
"From Crystallography to Quantum Crystallography of Magnetically Bistable Materials"
by Dr. Ivan Nemec

The research summarized in Dr. Nemec's habilitation thesis focuses on magnetically bistable materials, in particular on their crystal structure and magnetic properties assessed experimentally and by theoretical calculations.

The thesis consists of four chapters, occupying a total of 53 pages, and series of attachments containing reprints of 10 published scientific articles. The chapters constitute a very well written introduction to the subject and a detailed summary of the most important results and conclusions of Dr. Nemec's research work. Dr. Nemec is the corresponding author of 8 attached articles and the first author of 6 articles. All articles are published in peer-reviewed good or very good international journals.

Dr. Ivan Nemec conducted research on two types of magnetically bistable materials: single-ion magnets (SIMs) based on Co(II) or Cu(II) ions, which exhibit magnetic field hysteresis below the blocking temperature, and mononuclear iron (III) complexes with spin crossover (SCO) behavior, showing thermal hysteresis. Dr. Nemec aimed to understand how to control intermolecular interactions and intramolecular semi-coordination in SIMs. By redesigning ligands, he sought to induce or stabilize molecular and magnetic anisotropy and increase the blocking temperature. He also explored ways to enhance the ability of SIM to create stable thin films that retain the magnetic properties of the bulk material. In the case of SCO compounds, Dr. Nemec investigated intermolecular cooperativity through intermolecular interactions. These interactions play a crucial role in controlling spin transitions and thermal hysteresis. Analyses of intermolecular interactions, such as hydrogen binding, halogen bonding, pi…pi stacking, etc., played crucial role in his research. Initially, Dr. Nemec applied simple structural analysis based on geometry obtained from standard single-crystal X-ray diffraction (XRD). Later, he adopted more modern quantum crystallographic (QCr) approaches, such as Hirshfeld atom refinement (HAR), which improved the interpretation of experimental XRD data and provided more accurate atomic structures, especially for hydrogen atom positions. He supplemented the atomic structure with theoretical analyses of electronic structure, using topological analyses of electron density (QTAIM), electron localization function (ELF), and non-covalent interaction (NCI) methods. Dr. Nemec deeply investigated the magnetic properties of the studied materials, employing both experimental and theoretical approaches, and correlated his findings with analyses of intermolecular interactions.

The most interesting finding in his research, in my opinion, is observation that the temperature at which spin-crossover occur for a given crystalline material depends on the way how crystals were obtained, i.e. the quality of crystals. This points towards importance of taking this factor into account in the studies aiming at understanding magnetic behavior of matter.

Dr. Nemec's work contributes significantly to the field of molecular magnetism and materials science. His investigations provide valuable knowledge for advancing such areas as spintronics, quantum computing, molecular electronics, memory storage and sensing devices.

QCr is a field of Natural Sciences experiencing recently a revival. Although the exact definition of QCr is currently under debate, the field undoubtedly is built upon a combination of quantum theory and scattering experiments, both applied to crystalline materials. The basic goal of QCr is to provide methodologies allowing to extract maximum information from the experiment and to obtain theoretical quantum models as close to the reality as possible. I wonder what additional QCr approaches Dr. Nemec would apply in studying his magnetic materials, assuming he could obtain exceptionally high-quality, high-resolution XRD data and what more he could learn from them?

The research outlined in the thesis is unquestionably original, as it involves the development of novel magnetic materials using Quantum Crystallography (QCr) methodologies. Dr. Nemec's work convincingly demonstrates his ability to conduct independent, high-quality research. The thesis fulfils more than the standard requirements for a habilitation thesis in the field of inorganic chemistry. Therefore I recommend the thesis for further advancement in the habilitation procedure.

Sincerely yours,

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