Opponent's review of Habilitation Thesis entitled

From Crystallography to Quantum Crystallography of Magnetically Bistable Materials'

submitted by

Ing. Ivan Nemec, PhD.

The evaluated Habilitation Thesis, authored by Ing. Ivan Nemec, PhD. and submitted to the Palacký University Olomouc for defence is devoted to studying various types of magnetically bistable materials, based typically on coordination complexes of several transition metals. As outlined by the Author at the very beginning of this Thesis, the phenomenon of magnetic bistability is considerably complicated in its nature, which owes its existence to various physical measures like molecular/solid-state geometry, bonding relations, spin states and consequently magnetic properties. To provide an exhaustive and state-of-art studies of such phenomena, a broad research methodology has to be employed, calling for the application of several physical and chemical methods (including a broad range of advanced spectral techniques), which presupposes mastering several physical and chemical methods from the researchers' side.

The present work incorporates a comprehensive selection of the Author's scientific efforts in the particular field of quantum crystallography and the majority of the included articles deal with correlating molecular (solid-state) geometries with possible different electronic spin states and magnetic properties. Detailed bonding modes within selected coordination compounds were also described and various intra- and intermolecular interaction mechanisms were classified using geometry parameters; these studies were augmented sometimes by topology analyses of electron densities. The effects of structural and bonding characteristics were then discussed in relation to magnetic properties.

It can be safely concluded, that Ing. Ivan Nemec, PhD. has mastered completely all the methods required to conduct research within the field of quantum crystallography (denoting effectively advanced crystallography supplemented by quantum chemical studies) on a very advanced level. This statement is proven both by the introductory part of his Thesis and by the fact, that a compilation of ten articles published in renowned international scientific journals has been included in its Appendix. The evaluation of the current Thesis was thus highly facilitated by the fact that the texts in the Appendix have already undergone rigorous evaluation by various international referees, so the introductory part of the Thesis needed only to be evaluated in more detail by the current opponent.

This introductory part serves as roadmap to all the articles included in the Appendix — it outlines the research aims, describes the methods employed during these studies and most importantly summarizes the results published within each reprint. The introductory part of the Thesis was written with meticulous care and it was really a joy for the current opponent to read it through. The Author used a scientifically rigorous wording, yet he expressed all his ideas very clearly and with all the goals clearly outlined. He summarized all the results summarized in a completely understandable, yet rigorous way and even kept paying attention to the possible practical future applications. The were no major points that could be raised against the introduction; only the following unimportant points can be mentioned in this respect and these points should be regarded more as a proof for the opponent going through the Thesis indeed:

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- Fig. 3 (page 10), left. It's unclear whether this figure depict the contours of the electron density or of some specific orbital.
- Page 18 and onwards. The chapter numbering is non-contiguous.
- Page 27. The introductory text states a unique Co−π interaction to exert influence on both static and dynamic magnetic properties. The reader is then referred in this respect to Chapter 2.1., which is however absent from the work.
- Most of the graphical Figures are too small in size, which makes some of them nearly impossible to follow parallel with the text. This shortcoming can be demonstrated on Fig. 12c (page 27), in which neither the Laplacian contours, nor the atomic labels were well discernible at their current size and resolution.

The above points are of minor significance though and in cases of doubt, any required information could be looked up in the included reprints.

The article reprints selected for the current Thesis pose a quite coherent canon and I have no major questions to be raised in conjunction with this selection. The only topic that could be worthy for discussion during the defence is the very interesting observation reported on page 47 — here the Author provides description for the correlation between R_{int} values with the respective $T_{½↓}$ values. It goes without saying that some changes observed in the software parameters e_1, e_2 and e_3 were inherent along with the changes in R_{int} values. However, these software parameters are probably too general *per se* and are designed to cope with mosaicity in diffraction data at all symmetries, so they are inappropriate to neatly describe the specific problem discussed in the text. Did the Author(s) notice any particular trend in the indices of the most disagreeable reflections that contributed to the elevation of R_{int} values the most (in some specific crystallographic orientation(s))?

Concluding this review, it is my pleasure to acknowledge that the Habiliation Thesis of Ing. Ivan Nemec, PhD. is an important contribution to the field of magnetic materials, with emphasis on bistable systems. The applicant has proven his acquisition of all skills required to conduct a comprehensive research in this specific scientific field. I therefore strongly recommend the current Thesis to be accepted for defence by the committee. Following the successful defence of this Thesis and completion of the whole habilitation procedure, I recommend granting the title "Associate Professor" ("docent" in Czech) in the field of Inorganic Chemistry ("Anorganická chemie") to Ing. Ivan Nemec, PhD.

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