Review Report on PhD Thesis

Faculty: **Central European Institute of Technology**
Brno University of Technology

Academic year: **2022/2023**

Student: **Mgr. Lubomír Havlíček**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **doc. Dr. Ing. Petr Neugebauer**

Co-Supervisor: **Dr. Ing. Ivan Nemec, Ph.D.**

Reviewer**:** **prof. RNDr. Jiri Pinkas, Ph.D.**

PhD thesis title**: SINGLE-MOLECULE MAGNETS WITH TRIGONAL SYMMETRY OF THE COORDINATION POLYHEDRON: STRUCTURE, MAGNETIC PROPERTIES AND DEPOSITION ON SURFACES**

The topicality of the doctoral thesis:

The work of Mr. Havlicek, as summarized in his doctoral thesis, is focused on the preparation and structural and magnetic characterization of four series of Co(II) and Dy(III) complexes that may feature slow relaxation of magnetization and thus present behavior characteristic for single-molecule magnets (SMM). These complexes should then be anchored to the metal or graphene surfaces, and their magnetic properties examined with the aim of fabricating an addressable molecular array. Recent growth in interest in the area of SMM is due to their potential applications in high-density data storage, molecular spintronics, and quantum computing devices. This field is at the borderline of inorganic, physical, and materials chemistry and is currently a research area of tremendous activity and extreme importance.

Meeting the goals set:

The aims of the doctoral thesis are briefly stated in Chapter 2 on page 7. They are logically ordered as 1) synthesis of coordination compounds with Co(II) and Dy(III), 2) experimental measurements of magnetic susceptibility, HF-EPR spectroscopy, and theoretical calculations, all together providing complete information about magnetic properties, 3) deposition of selected SMM complexes on various

surfaces, chemical and morphological analysis of fabricated layers, and comparison of their magnetic properties with bulk materials. The thesis work followed the individual steps of the set research plan.

Problem solving and dissertation results:

The thesis is presented in English on 101 pages, including Appendices. The introduction defines SMMs and their properties, summarizes the history of development in this area, and presents the highlights of the currently attained SMM parameters, including the systems anchored on surfaces. The second chapter states the aims of the thesis. The third chapter discusses the basics of magnetism, types of magnetic behavior, superparamagnetism, and magnetic anisotropy. Specifically, properties of SMMs, methods used to identify SMMs, and characterize parameters of slow magnetization reversal are then treated. The major part of this chapter is devoted to examples of various coordination compounds featuring SMM properties highlighting the most important milestones with emphasis on coordination compounds of Dy(III) and Co(II) with trigonal coordination symmetry. This chapter also briefly discusses the methodology used for the characterization of these compounds. Finally, the previously reported results on depositions of SMMs on various surfaces (metal, graphene) are discussed. In chapter 4, the methodology and theoretical background of analytical, spectroscopic, and theoretical methods used in this thesis for SMM characterization and their deposition on surfaces are discussed, as well as the influence of the geometry of coordination compounds of Co(II) on magnetic properties.

Importance for practice or development of the discipline:

Chapter 5 devoted to results, starts with attempts to prepare Dy(III) coordination compounds with a series of Mannich type ligands, which were not successful. An alternative ligand, H_3tipa, provided only one characterized dimeric Dy(III) compound **1a**, which was shown to be field-induced SMM. In the second area, the effort was directed to the Co(II) complexes of the ligand, trenb. An extensive series of 13 coordination compounds were prepared and structurally, magnetically, EPR and XPS spectroscopically, and computationally characterized. The complexes possess small or medium axial magnetic anisotropy. However, these trenb complexes proved not to be suitable for wet or sublimation deposition due to their low solubility or decomposition. Subsequently, the H_3tipa ligand provided with Co(II) and various ancillary ligands, six coordination compounds. Three are mononuclear, one tri- and two tetranuclear. Interesting magnetic exchange pathways through the non-covalent interactions were identified. Magnetic susceptibility measurements revealed that the trinuclear $Co(III)_2Co(II)$ complex behaves as field-induced SMM. Finally, a series of alkali metal salts of the $[Co(acac)_3]^-$ anion were prepared, featuring supramolecular chain-like substructures. Their 1D arrangement and weak magnetic exchange interaction between the molecules resulted in large axial magnetic anisotropy.

Formal adjustment of the thesis and language level:

From the point of view of a formal setting, this thesis would deserve more time spent on careful proofreading. The author should have paid better attention to missing or extra spaces in the text, missing spaces between variables and equal/larger than/smaller than signs, missing letters in words, punctuation, proper punctuation for the et al. abbreviation, periods at the end of sentences, commas in front of and, use of articles, maintaining the English word order (SVOMPT), including one subject and one verb in a sentence, proper word selection (adj. polyhedral – noun polyhedron), not repeating the same word is one sentence, using the correct form of irregular past tense (not grinded but ground),

subject-verb agreement in number, correct selection and use of prepositions, completing sentences, proper spelling, placing a space between a number and its unit. A number of these errors were marked directly in the reviewer's pdf copy of the thesis, which will be sent back for the candidate's information and editing.

Questions and comments:

Comments listed below should be addressed in the preparation of the defense presentation but do not have to be explicitly discussed at the final defense:

P. 5: Figures 1 and 2 are not mentioned in the text.
P. 8: Equation 1 is incorrect.
P. 11: Starting at Fig. 5, the numbering of figures is shifted by 2.
P. 11, Fig. 5: The caption should read …Dependence of molar susceptibility (top right) and reciprocal (top left)…
P. 15: Reference to Eq. 10 is not correct, it should be Eq. 12.
P. 17: References to Figures should be mentioned in the regular order of increasing numbers – Fig. 26 should be moved forward in the text to its first appearance.
P. 18: Starting at Fig. 12, all figures adapted from the literature should be properly referenced.
P. 19: A missing formula in the caption of Fig. 14.
P. 23,24: The sentences….compound/molecule XXX possesses coordination number 4…should be reworded; a compound/molecule cannot possess a coordination number, but only the Co atom can.
P. 24: There is no labeling of the H axis in Fig. 21.
P. 25: The formula [Co(Me6tren)Cl](ClO4) does not correspond to Figure 26p, there are NHiPr groups.
P. 27: Deprotonated ligand should be written with a negative charge: H_2tea^-.
P. 28: Carbonate anions should have the charge of 2–.
P. 29: The caption of Fig. 24 – what does Cl3 derivate mean?
P. 33: Dipivaloylmethane is abbreviated as HDPM here, but on p. 36, dpm is used instead. Abbreviations should be unified in the whole text.
P. 35: The formula Tb2@C80(CH2Ph) is incomplete, there should be the pyrene groups – Fig. 29.
P. 47: TGA method has been used in the characterization of prepared complexes, however, there is no mention of it in the Experimental part.
P. 48: The formulae of complexes [Dy(LX)(HLX)] and [Dy(HLX)$(NO_3)_2$] do not add up with respect to charges of deprotonated forms of the H_3LX ligand.
P. 48: The name of the H_3tipa ligand is not triisopropylamine.
P. 50: This sentence does not make sense:…. magnetic moment…. decreasing from about 30.71 at 300 K down to 32.33…..
P. 51: The name of the ligand trenb is actually tris[2-(benzylamino)ethyl]amine.
P. 52: The complexes that are known from the literature should have been discussed in the Theoretical part.
P. 54: There are no alpha, beta angles in Table 1, in contrast what the caption says.
P. 59: The energy levels of the d-orbitals should be labelled in Fig. 47.
P. 64: A sentence should not start with a number.
P. 71: Drawings of complexes **3d**, **3e**, and **3f** in Fig. 57 and 58 do not correspond with the structures in Fig. 59.
P. 72: There are missing molecules of water in the formula of **3f**: [{Co_2(tipa)$_2$}{$CoCl_2$}$_2$].
P. 77: Missing units at the separation of the first LF terms.
P. 78: Acetylacetone should be abbreviated as Hacac.
P. 79: The sentence….powder was filtered through the paper filter…should be corrected.
P. 79: The main axis = the principal axis. It should be mentioned that the angle Li-Co-Li of 180° is crystallographically imposed.

P. 81: Where is the data for continuous measure indexes?
P. 87 – References: Do not use the et al. abbreviation, but list all authors. Ref. 3 is corrupted. Refs 122, 123, 124, and 126 contain html markings.

Questions to be addressed during the final defense presentation:

P. 32: There were several SCM species prepared in this thesis, however, there is no mention of this class of molecular magnets in the theoretical part. Could you point out their specific features?

P. 33: XMCD is mentioned in the theoretical part as an important characterization technique. Could you explain the principles of this method and the kind of information which is obtained from it?

P. 48: There are 3 chiral centers in the H3tipa ligand. Have you used a mixture of diastereomers or just one pure species?

P. 49: Clarify the charges of ligands and resulting formulae [Dy(H_2tipa)(Htipa)(NO_3)], [Dy(tipa)(NO_3)$_2$], and [Dy_2(Htipa)$_2$(NO_3)$_4$]·2Et_2O (**1a**). What is the protonation state the tipa ligand in **1a** in Fig. 39?

P. 50: How stable is the stoichiometry of **1a** during the magnetic measurements with respect to Et_2O release?

P. 52: What are the differences in crystal structures of **2c** (a MeOH solvate) and [Co(trenb)(NCS)]Cl by Y. Xie et al. ref. 95?

P. 53: Are the three equatorial Co-N distances the same or different (on the 3sigma criterion)?

P. 55: There should be a clear statement, about which complexes were measured before (references) and which were studied in this thesis for the first time.

P. 58: Why there are only two significant figure in values of g_x, g_y, and g_z for the complex **2a**?

P. 72: Have the Co oxidation states been checked by the Bond valence sum (BVS) calculations?

P. 80: Are the Co-O distance the same or different (on the 3sigma criterion)?

Conclusion:

This work is focused on a very topical area of magnetic materials, single-molecule magnets, and polynuclear triangular complexes with a large application potential. Synthetic experiments brought us a number of new compounds and magnetic characterization experiments revealed some previously unknown facts. The author demonstrated his ability to carry out both synthetic experiments and a wide array of characterization measurements by structural, magnetochemical, spectroscopic, and computational techniques. A number of compounds were meticulously characterized by single-crystal X-ray diffraction studies and their magnetic properties experimentally established. The author is also capable of analyzing obtained data and of drawing reasonable conclusion based on experimental facts. Figures and graphs presented throughout the work clearly convey information to a reader. The large number of references (128) and their temporal distribution show that the author possesses a good comprehension of the current status of the field and its recent development. The published paper in international journals, where the candidate is the first author, describes a part of his research results.

This peer-reviewed publication demonstrates Mr. Havlicek`s ability to obtain and communicate scientific results of a high standard.

In conclusion, I can declare that the overall amount and quality of this work is adequate for a doctoral thesis. In my opinion, the reviewed thesis **fulfills all requirements** posed on theses aimed for obtaining a Ph.D. degree and is ready to be defended orally in front of the respective committee. I recommend this work to **be accepted** in partial fulfillment of requirements for a Ph.D. degree.

In Brno, date November 28, 2022

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