Review Report on PhD Thesis

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

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, Ph.D.**

Reviewer**:** **doc. RNDr. Erik Čižmár, PhD.**

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

Topicality of doctoral thesis:

The thesis is focused on the preparation of novel coordination compounds based on Dy(III) and Co(II) ions, which are suitable for the observation of slow magnetic relaxation prominent to the class of single-molecule or single-ion magnets. Especially, the compounds with the trigonal symmetry of the central ion as presented in the submitted thesis may display a large energy barrier if carefully designed. The attempt to prepare a compound chemically suitable for deposition on a suitable substrate represents an important next step to produce a well-controlled distribution of molecules for individual control of their properties as required for high-density data recording and other quantum information applications.

Meeting the goals set:

The goals to prepare new Dy(III) and Co(II)-based complexes were successfully met, although, some difficulties in the preparation of Dy(III) complexes with Mannich type of ligands were addressed. The attempts to prepare deposited layers on the graphene substrate of functional molecules were discussed and the results were analyzed. A very high number of newly prepared Co(II)-based complexes was reported using trenb, H_3tipa, and acac ligands. Magnetic properties, ab initio, and DFT predictions were analyzed to estimate especially anisotropy parameters important for the presence of the slow magnetic relaxation and blocking temperature of SMM/SIMs.

Problem solving and dissertation results:

I appreciate that synthetic procedures were modified during the work, once the first attempts to synthesize Dy(III)-based complexes using Mannich type of ligands were not successful, a new strategy and more

suitable ligands were chosen for the following synthesis or the modification of the synthetic procedure to obtain new complexes of Co(II) with H_3tipa ligands. The work resulted in the preparation and characterization of 20 new complexes, some of which were characterized by magnetic and EPR measurements as the first step in their identification as possible SIMs. Although the deposition of prepared molecules on the graphene was not successful, a systematic study was performed to identify the pitfalls of the deposition. The author claims some of the prepared complexes as suitable SMM/SIMs due to the large axial anisotropy observed, one of them proven by dynamic susceptibility studies.

Importance for practice or development of the discipline:

The results of the complex deposition are important for further development in this field, which needs to overcome several obstacles, how to prepare suitable molecules that will remain stable during the deposition process, how to keep or modify the properties originating from bulk material, etc. New knowledge obtained during the synthesis with ligands in this work provides valuable hints on how to design new materials with local symmetry suitable to increase the relaxation barrier and blocking temperature.

Formal adjustment of the thesis and language level:

The thesis certainly contains original results, new materials were prepared and identified by structural analysis and their magnetic properties were studied.
From the formal point, the thesis is well written, first, the overview of the subject is presented, and then the original results are discussed. Still, some criticism is necessary for the way how the last checks of the text itself were made by the author. After Fig. 4, the numbering of figures went back again by two numbers, but the text remains to reference the intended numbering, which leads the reader into some confusion. In addition, Fig. 24 (intended to be 26) is referenced much earlier in the text on page 18 and some following pages. Also, the equations are not written in sentences when first defined, but are placed outside of the sentences. Sure it would require some rephrasing of the sentences, but the text would be more fluent in those paragraphs. At last, some additional spellchecking would remove some unwanted typos, e.g. "… in one directio. Such particle produce …" on page 13 and some others.

Questions and comments:

Comments:

1. Page 15 - "The SQUID allow to study …" – don't use jargon in scientific text, in fact, the author used mostly a VSM magnetometer to study the magnetic properties, which does not contain the SQUID-based detector (on page 39 again "… can be studied only by using SQUID magnetometer").
2. Page 38 – the author states PPMS and SQUID as magnetometry techniques, but they are not. PPMS is a general measurement instrument and SQUID is a detection circuit. VSM is later correctly identified as the magnetometry method. As I understood, the author worked with the PPMS instrument, perhaps with MPMS as well, for future work in the research field, this needs to be distinguished
3. Page 84-85 - compounds 4a-c, it seems from the temperature dependence of the effective magnetic moment that a more pronounced effect of exchange coupling is visible for 4a by a sharp drop at low temperatures and deviation from a simple spin Hamiltonian model (i.e. AFM exchange coupling), whereas the DFT predicts the opposite. For some higher values of J and large anisotropies an effective model based on Griffith-Figgis Hamiltonian as shown by Lloret et al., Inorg. Chim. Acta 361 (2008) 3432 (e.g., Eq. 21 therein) might be useful for the analysis of complexes 4a-c or 3e-f.

Questions:

1. Page 50 and 51 – please define the Hamiltonian for the exchange coupling, is the negative sign ferromagnetic or antiferromagnetic?
2. Page 56-57 – Regarding the discussion of the sign of the D-parameter obtained from HF-EPR, was there an attempt to simulate the EPR spectra with negative D as obtained from magnetic data or ab initio calculations? Could you present such a comparison?
3. Page 66 – the magnetic moment of sample 3a shows some variation around 150 K, is that some experimental effect or possibly some low-temperature structural changes that could affect the magnetic moment?
4. Page 75 – the magnetic data analysis certainly overestimates the antiferromagnetic exchange in 3f if D >0, since the drop of molar magnetization is not as significant as suggested by the simulation (as the curvature of the field dependence of magnetization). Perhaps, the D<0 with the stronger exchange as suggested by an initio calculations would yield a better agreement?
5. Please, elaborate on publication outcomes from the presented thesis, what is ready to publish or submitted?

In my opinion, the reviewed thesis **fulfill** all requirements posed on theses aimed for obtaining PhD degree. This thesis **is** ready to be defended orally, in front of respective committee.

In Košice, date 22.11.2022

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Erik Čižmár

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