



Ph.D. thesis of Szymon Chorazy

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“Multifunctional magnetic molecular materials based on 3d/4f metal ions and octacyanidometallates”

Review of the doctoral dissertation

Szymon Chorazy has completed his Ph.D. thesis, entitled “Multifunctional magnetic molecular materials based on 3d/4f metal ions and octacyanidometallates.” He has 8 publications in high-level international academic journals and has given 6 presentations at formal academic conferences. In his Ph.D. work, he has synthesized several new molecular materials using octacyanidometallates $[M^{IV/V}(\text{CN})_8]^{4-/3-}$ ($M = \text{W}, \text{Nb}$) and 3d/4f metal ions, exhibiting functionalities such as interesting magnetic and optical properties, among others. His work can be divided into four topics: (i) magnetic anisotropy of $\text{Co}^{\text{II}}-[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$ coordination systems, (ii) charge transfer and spin transition in trimetallic $\text{Co}_x\text{Fe}_{9-x}[\text{W}(\text{CN})_8]_6$ clusters, (iii) implementation of chirality into $[\text{M}(\text{CN})_8]$ -based magnetic molecular materials, and (iv) exploration of $\text{Ln}^{\text{III}}-[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$ coordination systems towards chiral-magneto-luminescent multifunctionality.

In topic (i), he has reported novel molecular magnetic materials, such as $\{\text{Co}^{\text{II}}(2,2'\text{-bpdo})_2\}[\text{Co}^{\text{II}}(2,2'\text{-bpdo})(\text{H}_2\text{O})_2][\text{W}^{\text{V}}(\text{CN})_8]_2 \cdot 8\text{H}_2\text{O}$ (1), $\{\text{Co}^{\text{II}}[\text{Co}^{\text{II}}(\text{MeOH})_3]_8[\text{W}^{\text{V}}(\text{CN})_8]_6\} \cdot 4,4'\text{-bpdo} \cdot \text{MeOH} \cdot 2\text{H}_2\text{O}$ (2), and $\{\text{Co}^{\text{II}}[\text{Co}^{\text{II}}(4,4'\text{-bpdo})_{1.5}(\text{MeOH})]_8[\text{W}^{\text{V}}(\text{CN})_8]_6\} \cdot 2\text{H}_2\text{O}$ (3).

Material 1 has a two-dimensional layered structure, with the layers parallel to the bc crystallographic plane. Magnetic and specific heat properties indicated that 1 exhibits ferromagnetic long-range ordering below T_C of 6 K. The strong magnetic anisotropy of the magnetic phase was indicated by single-crystal magnetic studies.



The theoretical calculation suggests two different types of local anisotropy of Co^{II} in **1** [S. Chorazy, et al., *CrystEngComm*, 15, 2378 (2013)].

Materials **2** and **3** are molecular chains that reveal $\text{Co}^{\text{II}}-\text{W}^{\text{V}}$ ferromagnetic couplings. Anisotropic Co^{II} centers lead to single-molecule magnet behavior of **2** and **3** [S. Chorazy, et al., *Cryst. Growth Des.*, 13, 3036 (2013)]. These works are meaningful in the field of molecular magnetic materials. This is because Co^{II} single-ion anisotropy has been applied in the design and synthesis of molecular magnets possessing strong magnetic anisotropy, which leads to interesting magnetic behavior.

My comments are as follows: I would like to know the values of magnetic coercive forces (H_c) along the hard axis of **1**, since the H_c values of both the easy and hard axes are important magnetic properties. For the specific heat of **1**, which is shown as figure 8 in the article, I would like to see specific heat data, including the lattice contribution (before subtracting), because evaluating the relationship between the lattice contribution and the magnetic contribution is important to studying magnetic heat capacity. Furthermore, it seems that the magnetic specific heat data can be divided into two peaks, i.e., two types of magnetic transitions may occur. It means that magnetic dimensional crossover may occur, e.g., from one- or two-dimensional Heisenberg magnetic model to three-dimensional Heisenberg magnetic model with decreasing temperature.

In topic (ii), novel molecular magnetic materials have been synthesized, consisting of $\{\text{Fe}[\text{Fe}(\text{MeOH})_3]_8[\text{W}(\text{CN})_8]_6\} \cdot x\text{MeOH}$ (**4**) and $\{\text{Fe}_6\text{Co}_3(\text{MeOH})_{24}[\text{W}^{\text{V}}(\text{CN})_8]_6\} \cdot x\text{MeOH}$ (**5**). Here **4** is a mixed-valence compound between $\text{Fe}^{\text{II}}-\text{W}^{\text{V}}$ and $\text{Fe}^{\text{III}}-\text{W}^{\text{IV}}$ valence states, exhibiting thermal-induced charge-transfer (CT) phase transition between the two valence states [S. Chorazy, et al., *Chem. Commun.*, 50, 3484 (2014)]. Material **5** is a trimetallic cluster, which exhibits a thermal-induced phase transition due the CT between $\text{Fe}^{\text{II}}-\text{W}^{\text{V}}$ and $\text{Fe}^{\text{III}}-\text{W}^{\text{IV}}$ valence states and charge-transfer induced spin transition (CTIST) between $\text{Co}^{\text{II}}_{\text{HS}}-\text{W}^{\text{V}}$ and $\text{Co}^{\text{III}}_{\text{LS}}-\text{W}^{\text{IV}}$ valence isomers [R. Podgajny, S. Chorazy, et al., *Angew. Chem. Int. Ed.*, 52, 896 (2013)]. For the first time the CT phase transition between



$\text{Fe}^{\text{II}}-\text{W}^{\text{V}}$ and $\text{Fe}^{\text{III}}-\text{W}^{\text{IV}}$ states is observed in cyano-bridged assemblies. Furthermore, the work in **5** is the first example of coexistence of the CT phase transition and CTIST in such molecular materials. These works open a new class of bistable molecule-based functional magnets. I would like to know which is the real origin of the phase transition in **5**. I.e., does CT induce CTIST or vice versa, or do CT and CTIST occur independently?

In topic (iii), novel molecular chiral magnets are synthesized, consisting of $\{[\text{Co}^{\text{II}}(\text{SS}/\text{RR}-i\text{Pr-Pybox})(\text{MeOH})]_3[\text{W}^{\text{V}}(\text{CN})_8]_2\} \cdot 5.5\text{MeOH} \cdot 0.5\text{H}_2\text{O}$ (**6**) and $\{[\text{Mn}^{\text{II}}(\text{S}/\text{R}-\text{mpm})_2]_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ (**7**). In **6**, these pairs of enantiomorphic cyano-bridged coordination chains show strong natural optical activity in the UV-vis range, and slow magnetic relaxation behavior of single-chain magnets that originates from single-ion anisotropy of Co^{II} centers [S. Chorazy, et al., *J. Am. Chem. Soc.*, 134, 16151 (2012)]. Material **7**, a two-dimensional enantiopure cyano-bridged assembly, exhibits ferromagnetic long-range ordering with $T_{\text{C}} = 23.5$ K. Natural optical activity and magnetic optical activity under an applied magnetic field, with the enhancement of the signal below T_{C} were observed [S. Chorazy, et al., *Chem. Commun.*, 49, 6731 (2013)]. This is the first report of enantiopure molecule-based magnets revealing T_{C} , which were precisely studied using natural optical activity and magnetic optical activity effects.

In topic (iv), novel molecular chiral magnets are reported, consisting of pairs of $\{[\text{Eu}^{\text{III}}(\text{SS}/\text{RR}-i\text{Pr-Pybox})(\text{dmf})_4]_3[\text{W}^{\text{V}}(\text{CN})_8]_3\} \cdot \text{dmf} \cdot 8\text{H}_2\text{O}$ helical chains (**8**), $\{[\text{Ln}^{\text{III}}(\text{SS}/\text{RR}-i\text{Pr-Pybox})(\text{dmf})_4]_3[\text{W}^{\text{V}}(\text{CN})_8]_3\} \cdot \text{dmf} \cdot 4\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}, \text{Gd}$) (**9**), and $\{[\text{Ln}^{\text{III}}(\text{SRSR}/\text{RSRS}-\text{Ind-Pybox})(\text{dmf})_4][\text{W}^{\text{V}}(\text{CN})_8]\} \cdot 5\text{MeCN} \cdot 4\text{MeOH}$ ($\text{Ln} = \text{Nd}, \text{Gd}$) (**10**) helical chains. For **8**, they show thermally switchable luminescence between blue ligand-based emission and red f -centered luminescence, dominating at room and low temperatures, respectively. They are paramagnets with negligible magnetic coupling due to the diamagnetic centers of Eu^{III} [S. Chorazy, et al., *RSC Advances*, 3, 1065 (2013)]. By the application of different lanthanide (III) ions (Nd^{III} or Gd^{III}) to the framework, the above-mentioned weak point, undetectable magnetic coupling effect in **8**, was overcome in **9** and **10**, and optical activity, luminescence, and magnetic



coupling have been revealed. Nd^{III} -compounds exhibit f -centered near-infrared luminescence and ferromagnetic coupling due to $\text{Nd}^{\text{III}}\text{-NC-W}^{\text{V}}$ linkages, while Gd^{III} -compounds indicate ligand-driven red phosphorescence and antiferromagnetic interactions leading to overall ferromagnetic character of spin chains [S. Chorazy, et al., *Chemistry – A European Journal*, in press (2014)].

In conclusion, during his doctoral course, Szymon Chorazy has succeeded in synthesizing more than 10 novel molecular magnetic materials and observing novel functionalities, such as magnetic properties, optical properties, and their coupling effects. His achievements are very significant in the field of material science, especially in molecular materials. These his outstanding findings highly exceeds the requirements for the Ph.D. thesis. I think that these works are perfectly suited to completing his doctoral degree requirements.

I consider that all conditions imposed on doctoral dissertations in accordance with Article 13 of the Act of March 14, 2003 Academic Degrees and Title and Degrees and Title in Art (Journal of Laws of 2003, nr.65 poz.595 as amended) are fulfilled. Therefore, I recommend to admit mgr Szymon Chorazy to further stages of doctoral procedure.

Moreover, I recommend his Ph.D. Dissertation for the award of the doctoral dissertation, because of the exceptionality high standard of his work, as I expressed above in concluding remarks. The excellent results achieved in the dissertation as well as during his Ph.D. study are reflected in 12 articles in high-level international academic journals ($\Sigma\text{IF}=74.522$) and 6 presentations at formal academic conferences.

Yours faithfully,

Hiroko Tokoro

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