

Synthesis and Molecular Magnetism in Cobalt(II) Complexes with Tridentate N-Donor Ligands

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The single molecule magnets (SMMs) are defined as molecules that show the slow relaxation of magnetisation based on purely molecular origin. This is the fundamental difference between the SMMs and molecular ferro- or ferrimagnets. They illustrate the smallest possible magnetic storage devices, which can possibly maintain information in a single molecule rather than in a magnetic particle consisted of domains. Hysteresis loop in magnetization vs. field dependency below the blocking temperature T_B of SMMs is observed. The T_B of the most molecule-based magnets is below 10 K, although the rare examples up to 80 K can be found [1], [2]. To be viewed as a good SMM, a compound should exhibit a large effective anisotropy barrier against magnetization switch U_{eff} , relatively high blocking temperature T_B and high value of relaxation time τ . Over the time, mononuclear and polynuclear complexes have been studied. Especially those, which contain Mn(III), Fe(I), Fe(II), Co(II) and lanthanides are the subjects of particular interest [3].

The aim of this contribution is to discuss about synthesis, structural and magnetic properties of new Co(II) coordination compounds with derivatives of 2,6-bis(1*H*-benzimidazolyl)pyridine (bzimpy). First, ligands **L1** (2,6-bis(1-octyl-1*H*-benzimidazol-2-yl)pyridine) and **L2** (2,6-bis(1-dodecyl-1*H*-benzimidazol-2-yl)pyridine) were prepared and characterized by elemental analysis (**L1**), IR and UV-VIS spectroscopy and NMR spectroscopy. The preparation of ligands **L1** and **L2** was based on N-alkylation of imidazole rings of bzimpy. The main purpose of alkylation in this case was to increase the solubility of ligands and corresponding complexes. Solubility of complexes in solvents such as CH_2Cl_2 or acetone, which can be considered as low boiling point solvents, is important for further deposition using lithography techniques. In addition, the change of magnetic properties with the alkyl chain lengths can be studied as well. Ligands were used for the synthesis of mononuclear complexes. Four new pentacoordinated complexes expressed by general formula $[\text{Co}(\text{L1})\text{X}_2]$ ($\text{X} = \text{Cl}^-$ for **1** and Br^- for **2**) and $[\text{Co}(\text{L2})\text{X}_2]$ ($\text{X} = \text{Cl}^-$ for **3**, Br^- for **4**) were prepared. Newly prepared complexes were analysed by elemental analysis, IR, UV-VIS spectroscopy, single crystal X-ray diffraction analysis and static magnetic measurements. The dynamic magnetic investigations of complexes revealed slow magnetic relaxation under small applied static magnetic field. Complexes **1** – **4** exhibit energy barrier U_{eff} in the range of 23 to 37 K and relaxation time τ of the order of 10^{-7} s, which are values typical for Co(II) mononuclear complexes. The value of relaxation time τ of **1** at the lowest temperatures is 0.02 s, which is considered as relatively high value among other similar compounds. In addition, hexacoordinated Co(II) compounds **5** and **6** expressed by formula $[\text{Co}(\text{L3})_2\text{Cl}](\text{C}_7\text{H}_7\text{O}_3\text{S})$ and $[\text{Co}(\text{L3})_3](\text{CF}_3\text{SO}_3)_2$, respectively, which employ ligand **L3** (2-(6-(phenyldiazenyl)pyridin-2-yl)-1*H*-benzimidazole) were synthesised and structurally characterised.

[1] F.S. GUO, et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 11445

[2] F.S. GUO, et al. *Science* **2018**, *362*, 1400

[3] SLAGEREN, *Introduction to Molecular Magnetism*. Available from: <http://obelix.physik.uni-bielefeld.de/~schnack/molmag/material/123.pdf>