

Semicoordination in Co(II) Single-Ion Magnets

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Single-Molecule Magnets (SMMs) are coordination compounds that exhibit slow relaxation of magnetization of molecular origin. In the case when SMMs contain only one paramagnetic metal center we distinguish the group of so-called Single-Ion Magnets (SIMs) [1]. In SIMs, the occurrence of slow relaxation of magnetization is closely related to the existence of non-negligible magnetic anisotropy on the magnetic center of the molecule. Since the magnetic anisotropy is strongly influenced by the topology and strength of the applied ligand field it could be expected that significant prolongation of coordination bonds or occurrence of non-covalent interactions involving the metal center may have a fundamental impact on resulting magnetic properties.

In 2016, we reported on static and dynamic magnetic properties of compound [Co(dpt)(NCS)₂], (dpt = 1,7-diamino-4-azaheptane). Two non-covalent interactions between the Co(II) atoms and π electrons of NCS⁻ ligands from the neighboring complex molecule ($d(\text{C}\cdots\text{NC}_{\text{centroid}}) = 3.55 \text{ \AA}$) caused a mediation of ferromagnetic exchange interaction within the centrosymmetric dimer and also the dynamic magnetic properties were affected markedly [2]. This inspired us to investigate in greater detail the magnetic properties of Co(II) compounds having some of their metal-ligand bonds at distances longer than typical coordination bonds.

Semicoordination bond can be considered as a non-covalent analogue of the coordination bond, which occurs when a weak attractive non-covalent interaction between an electrophilic region (associated with a metal center) and a nucleophilic region (associated with a nonmetal atom in another or in the same molecular entity) is formed [3,4]. In typical semicoordination bonds, the distances between the metal atoms and electron-donating groups are significantly longer than the sum of their covalent radii but shorter than the sum of van der Waals radii, the interactions are dominantly of electrostatic character and topology of electron density between the particular atoms exhibits bond path and critical point [4].

In line with the above-mentioned considerations, we chose to investigate three different series of mononuclear Co(II) compounds: (a) [Co(2NH₂-R₁-py)₂(R₂COO)₂], where R₁ = H, 3/4/5-CH₃, R₂ = CH₃, C₆H₅, t-Bu, the carboxylate ligand form Co-O bonds with lengths of 2.0 – 3.1 Å, (b) [Co(bq)(NO₃)₂(ROH)], where bq is 2,2'-biquinoline and ROH are various alcohol ligands, one of the nitrate ligands forms the Co-O bond with lengths of 2.5 – 3.3 Å, (c) [Co(R-pymep)₂], where H-R-pymep are various derivatives of 2-[(E)-(pyridin-2-yl)imino]methyl}phenol, two Co-N bonds with lengths between 2.5 and 2.7 Å. We studied these compounds by a combination of experimental (X-ray diffraction, magnetometry, HF-EPR) and theoretical (DFT, CASSCF, Electronic localization function, non-covalent interaction index, and QTAIM) methods. In this talk, we report on the character of semicoordination in these compounds and the relationship between the structure and observed magnetic properties.

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Keywords: Single-Ion Magnets, Semicoordination, Magnetic Anisotropy