Poster

Interplay of halogen bonding and semi-coordination in Co(II) single-ion magnets

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Recently, we reported findings on the properties of [Co(R-pymep)$_2$] compounds with the derivatives of 2-{(E)-[(pyridin-2-yl)imino]methyl}phenol (H-pymep), featuring two semi-coordination Co···N$_{py}$ bonds with lengths between 2.5 and 2.8 Å (N$_{py}$ stands for pyridine nitrogen atom). These complexes exhibit Single-Ion Magnets (SIMs) behaviour and, notably, display remarkable thermal stability, enabling their sublimation deposition in the form of 100nm-thick thin layers on selected surfaces [1].

In our attempt of achieving and controlling the surface deposition of SIMs through their self-assembly into organized supramolecular structures, we introduced halogen atoms to the ligands of [Co(R-pymep)$_2$]. We prepared two closely related series of complexes with the formulas [Co(4X-pymep)$_2$] and [Co(4X-pyp)$_2$], where X = F, Cl, Br and I, H-4X-pymep = 4-halogeno-2-{(E)-[(6- methylpyridin-2-yl)imino]methyl}phenol, and H-4X-pyp = 4-halogeno-2-{(E)-[(pyridin-2-yl)imino]methyl}phenol. The only distinction between ligands H-4X-pymep and H-4X-pyp lies in the presence of a methyl group on the pyridine moiety. Analysis of crystal structures unveiled significant differences in the structures of complexes within each series. The [Co(4X-pymep)$_2$] complexes showcase two Co···N$_{py}$ interactions, while the [Co(4X-pyp)$_2$] complexes exhibit only one. In the latter case, the other N$_{py}$ atom engages in non-covalent interaction with the halogen atom of the neighbouring molecule (**Figure 1**).

In this contribution we present the outcomes of comprehensive experimental and theoretical investigations conducted for both series. We explored crystal structures, thermal stability and static and dynamic magnetic properties of complexes in both series. The DFT, QT-AIM and CASSCF/NEVPT2 calculations support the experimental work, offering insights into the nature of observed non-covalent interactions. Furthermore, the calculations also shed light on the impact of the unique coordination environment induced by the N$_{py}$···X non-covalent interaction on the magnetic anisotropy of the [Co(4X-pyp)$_2$] complexes.

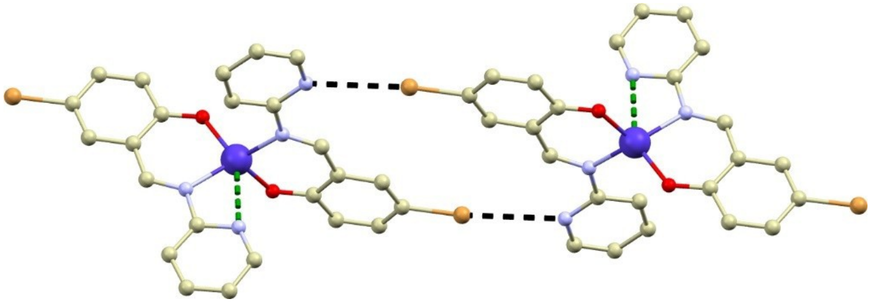

Figure 1. A perspective view of a fragment of non-covalent interactions in the crystal structure of [Co(4Br-pyp)$_2$]. The Co···N$_{py}$ interaction is depicted as a green dashed line while N$_{py}$···Br interaction as a black dashed line.

[1] Giraldo, J. N.; Hrubý, J.; Vavrečková, Š.; Fellner, O. F.; Havlíček, L.; Henry, D.; De Silva, S.; Herchel, R.; Bartoš, M.; Šalitroš, I.; Santana, V. T.; Barbara, P.; Nemec, I.; Neugebauer, P.. (2023). *Phys. Chem. Chem. Phys.*. **70**, 3554.

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