Electron density studies on a Cobalt Single-Molecule Magnet

Katharina Rachuy[1], Regine Herbst-Irmer[1], Dietmar Stalke[1]

[1]Institut für Anorganische Chemie, Universität Göttingen, Germany, k.rachuy@stud.uni-goettingen.de

In March 2021, Legendre et al published a new Cobalt Single-Molecule Magnet (SMM), $Co\{(N^tBu)_2SPh\}_2$, with very good magnetic anisotropy and hysteresis [1]. Up to now, CASSCF calculations and SQUID Magnetometer measurements were carried out by Legendre et al. However, this compound should be investigated in more detail, especially regarding the electronic properties to get a better insight in the origin of magnetical properties. It was shown for example by Damgaard-Møller et al. that electron density studies are a good way to determine d-orbital populations [2]. Therefore we have performed a multipolar refinement of the $Co\{(N^tBu)_2SPh\}_2$ compound with the program XD [3]. To confirm the experimental results, further theoretical calculations are planned as well.

In a multipolar refinement [4] against high-resolution X-ray diffraction data not only a spherical density is modelled as in the Independent Atom Model (IAM), but the distortion caused by the bonding can be taken into account. This density is described by spherical harmonics, which have a similar shape as orbitals [5]. The multipole parameters can then be used to calculate d-orbital populations.

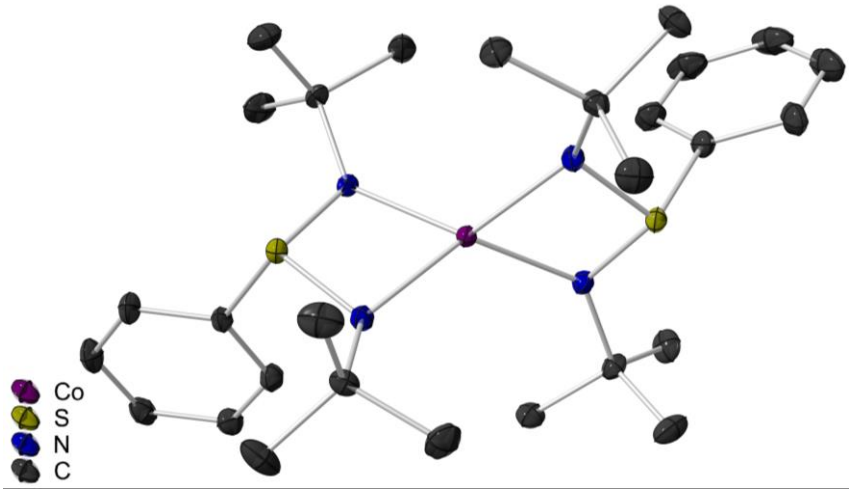

Fig. 1 The structure of $Co\{(N^tBu)_2SPh\}_2$. The anisotropic displacement parameters are displayed at the 50 % level. Hydrogen atoms are omitted for clarity.

[1] Legendre C, Damgaard-Møller E, Overgaard J, Stalke D. The Quest for Optimal 3d Orbital Splitting in Tetrahedral Cobalt Single-Molecule Magnets Featuring Colossal Anisotropy and Hysteresis. Eur. J. Inorg. Chem., 30, 1434-1948 (2021)

[2] Damgaard-Møller E, Krause L, Tolborg K, Macetti G, Genoni A, Overgaard J. Quantification of the Magnetic Anisotropy of a Single-Molecule Magnet from the Experimental Electron Density. Angew. Chem. Int. Ed., 59, 1433-7851 (2020)

[3] Volkov A, Macchi P, Farrugia L J, Gatti C, Mallinson, P, Richter, T, Koritsanszky T. XD2016 - A computer program for multipole refinement, topological analysis of charge densities and evaluation of intermolecular interaction energies from experimental or theoretical structure factors. (2016)

[4] Hansen N K, Coppens P. Testing Aspherical Atom Refinements on Small-Molecule Data Sets. Acta Cryst., A31, 909-921 (1978)

[5] Holladay A, Leung P, Coppens P. Generalized Relations Between d-Orbital Occupancies of Transition-Metal Atoms and Electron-Density Multipole Population Parameters from X-ray Diffraction Data. Acta Cryst., A39, 377-387 (1983)