

Further insights into controlling the anisotropy of pentacoordinate Co(II) field-supported single-molecule magnets

Autorzy

Katarzyna Choroba

Barbara Machura

Alina Bieńko

Jacek Sawka

Dariusz C. Bieńko

Cyril Rajnák

Jan Titiš

Roman Boča

Mykhaylo Ozerov

Andrew Ozarowski

Rok wydania

2025

Czasopismo

Dalton Transactions

Numer woluminu

54

Strony

16973-16985

DOI

10.1039/d5dt02098k

Kolekcja

Naukowa

Język

Angielski

Streszczenie

To gain a better insight into understanding the factors affecting the enhancement of magnetic anisotropy in single-molecule magnets, two pentacoordinate cobalt(II) complexes $[\text{CoCl}_2(\text{R}^1\text{-terpy})]$ (R^1 -furan-2-yl) (**1**) and $[\text{CoCl}_2(\text{R}^2\text{-terpy})]$ (R^2 -1-methyl-1*H*-pyrrol-2-yl) (**2**) based on the tridentate ligand 2,2':6',2''-terpyridine (terpy) functionalised with two different heterocyclic groups have been synthesised and fully characterized by X-ray crystallography and physicochemical methods. Complex **1** is an interesting example of a compound with two crystallographically independent molecules (**1A** and **1B**) differing by the structural parameters and magnitude of magnetic anisotropy, confirmed experimentally by HFEPR and FIRMS spectroscopy. The *ab initio* calculations (CASSCF + NEVPT2 + SOC) confirm that the spin-Hamiltonian formalism can be applied. The calculated energy gap (at the SOC level) between the lowest Kramers doublets is $\delta = 107$ and 58 cm^{-1} for **1A** and **1B** units, and 85 cm^{-1} for **2**. The axial zero-field splitting parameter is predicted as $D = -51$ and -26 cm^{-1} for **1A** and **1B**, and $+42 \text{ cm}^{-1}$ for **2**, accompanied by some rhombic component. The FIRMS spectra reveal the energy gaps of 89 and 60 cm^{-1} for **1**, and 89 cm^{-1} for **2**. The last value matches the *ab initio* data, as well as the analysis of susceptibility and magnetisation ($\delta = 2D = 80 \text{ cm}^{-1}$). In case of **1**, the agreement is worse. Both samples exhibit a field-supported slow magnetic relaxation with two relaxation modes. The high-frequency relaxation time at higher temperature follows a temperature dependence characteristic for the Raman process, $1/\tau(\text{HF}) = \text{CT}^n$ with $n \sim 6$; at low temperature the temperature coefficients are characteristic of the phonon-bottleneck or direct process, $n \sim 2.5$ and 1.5 , respectively.

Adres publiczny

<https://doi.org/10.1039/D5DT02098K>

Artykuł

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Plik został wygenerowany dnia 2026-10-08 09:39:24

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