Large Magnetic Anisotropy in Mono- and Binuclear cobalt(II) Complexes: The Role of the Distortion of the Coordination Sphere in Validity of the Spin-Hamiltonian Formalism

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Rok wydania

2024

Czasopismo

Inorganic Chemistry

Numer woluminu

63

Strony

1068-1082

DOI

10.1021/acs.inorgchem.3c03405

Kolekcja

Naukowa

Język

Angielski

Streszczenie

To get a better insight into understanding the factors affecting the enhancement of the magnetic anisotropy in single molecule (single ion) magnets, two cobalt(II) complexes based on a tridentate ligand 2,6-di(thiazol-2-yl)pyridine substituted at the 4-position with *N*-methyl-pyrrol-2-yl have been synthesized and studied by X-ray crystallography, AC and DC magnetic data, FIRMS and HFEPR spectra, and theoretical calculations. The change of the counteranion in starting Co(II) salts results in the formation of pentacoordinated mononuclear [Co(mpyr-dtpy)Cl_2]·2MeCN (**1**) complex and binuclear [Co(mpyr-dtpy)$_2$][Co(NCS)$_4$] (**2**) compound. The observed marked distortion of trigonal bipyramid geometry in **1** and cationic octahedral and anionic tetrahedral units in **2** brings up a question about the validity of the spin-Hamiltonian formalism and the possibility of determining the value and sign of the zero-field splitting *D* parameter. Both complexes exhibit field-induced slow magnetic relaxation with two or three relaxation channels a t B_{DC} = 0.3 T. The high-frequency relaxation time in the reciprocal form $\tau(HF)^{-1} = CT^n$ develops according to the Raman relaxation mechanism (for **2**, n = 8.8) and the phonon-bottleneck-like mechanism (for **1**, n = 2.3). The high-frequency relaxation time at T = 2.0 K and B_{DC} = 0.30 T is τ(HF) = 96 and 47 μs for **1** and **2**, respectively.

Słowa kluczowe

Energy, Ligands, Magnetic properties, Mathematical methods, Quantum mechanics

Adres publiczny

http://dx.doi.org/10.1021/acs.inorgchem.3c03405

Strona internetowa wydawcy

https://www.acs.org/content/acs/en.html

Typ publikacji

Artykuł