Easy-axis magnetic anisotropy in tetragonally elongated cobalt(II) complexes beyond the spin-Hamiltonian formalism

Autorzy

Romana Mičová

Cyril Rajnák

Jan Titiš

Alina Bieńko

Jan Moncol

Erika Samolová

Roman Boča

Rok wydania

2023

Czasopismo

Dalton Transactions

Numer woluminu

52

Strony

7885-7892

DOI

10.1039/d3dt00990d

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Two hexacoordinate Co(II) complexes $[Co(hfac)_2(etpy)_2]$ (**1**) and $[Co(hfac)_2(bzpyCl)_2]$ (**2**) were synthesized and spectrally and structurally characterized. The $\{CoO_4N_2\}$ chromophore adopts a geometry of the elongated tetragonal bipyramid with a small *o*-rhombic component. This less common arrangement causes the magnetic data to need be analysed using the Griffith-Figgis model, instead of the commonly used spin-Hamiltonian with zero-field splitting parameters *D* and *E*. In the case of the elongated bipyramid for d^7 complexes, the source of the magnetic anisotropy of an easy-axis type is the axial crystal field splitting Δ_{ax}. The *ab initio* CASSCF calculations followed by the NEVPT2 module confirm that the ground electronic term is quasi-degenerate owing to the splitting of the ^4E_g (D_{4h}) mother term. The lowest spin–orbit multiplets appear as four Kramers doublets belonging to the Γ_5 irreducible representation of the double point group D_2'. They exhibit a serious mixing of the $|\pm1/2\rangle$ and $|\pm3/2\rangle$ spins which reflects a sizable effect of the spin–orbit coupling. Both complexes exhibit field-supported slow magnetic relaxation governed by the Raman process.

Adres publiczny

http://dx.doi.org/10.1039/d3dt00990d

Strona internetowa wydawcy

https://www.rsc.org/