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Effect of the counter anion to slow magnetic relaxation of hexacoordinate Co(II) complexes

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Streszczenie

Three mononuclear Co(II) complexes have been synthesized and fully characterized using X-ray crystallography and physicochemical methods. They contain *trans*-{$Co^{II}N_2O_4$} for **1** and **2**, but *cis*-{$Co^{II}N_2O_4$} for **3**. *Ab initio* CASSCF followed by NEVPT2 calculations confirm that **1** has a quasi-degenerate electronic ground term derived from ^4E which, after inclusion of spin–orbit coupling, gave the zero-field energy gap δ = 209 cm^{-1}. This obstacle prevents a quantitative interpretation of high-field electron paramagnetic resonance (HFEPR) spectra for **1**. In **2** and **3**, the ground electronic state is orbitally non-degenerate ^4A and then the spin-Hamiltonian formalism applied to HFEPR spectra gave the zero-field splitting parameters D = 77.78 cm^{-1} and E = 23.72 cm^{-1} for **2**, and D = 70.58 cm^{-1} and E = 9.56 cm^{-1} for **3**. These data match the analysis of DC susceptibility and magnetization data. The AC susceptibility measurement confirms that all three complexes show slow magnetic relaxation upon an applied small external field. Three relaxation channels are visible: low-frequency (LF), high-frequency (HF), and intermediate-frequency (IF). The relaxation times at B_{DC} = 0.3 T and T = 2.0 K for **1** are τ_{LF} = 1.5 s, τ_{HF} = 1.9 ms, and the mole fraction of the LF fractionx_{LF} = 0.28, which alter at B_{DC} = 0.6 T and T = 2.0 K to τ_{LF} = 2.5 s, τ_{HF} = 1.3 ms, and x_{LF} = 0.48.

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