

Mixed-valence outer-sphere Ru^{II}/Ru^{III} ion-pair complexes. Synthesis, experimental, and theoretical studies.

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Streszczenie

Two new ion-pair complexes, consisting of a cationic polypyridyl Ru(II) complex ([Ru^{II}(terpy)(bipy)Cl]⁺ or [Ru^{II}(terpy)(phen)Cl]⁺) and the *cis*-[Ru^{III}Cl₂(pic)₂]⁻ anion (terpy = 2,2':6',2''-terpyridine, bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline and pic⁻ = picolinate) were synthesized. Magnetic and EPR studies were preceded by identifying the obtained species and checking the homogeneity and purity of the bulk material using various analytical techniques: single-crystal and powder X-ray diffraction, SEM, EDX, and FT-IR spectroscopies in the solid state, and ESI-MS in solution. The spectral characteristics in the UV-vis range and redox behavior of the ion-pair complexes were examined. The principal *g* components for [Ru^{II}(terpy)(bipy)Cl]⁺[*cis*-Ru^{III}Cl₂(pic)₂]⁻·(CH₃)₂CO·H₂O, **1**, and [Ru^{II}(terpy)(phen)Cl]⁺[*cis*-Ru^{III}Cl₂(pic)₂]⁻·2H₂O, **2**, and their Ru^{III} precursor [H(pic)₂]⁺[*cis*-Ru^{III}Cl₂(pic)₂]⁻·2H₂O were similar and typical for low-spin *d*⁵ species. The presence of one unpaired electron (in the *d*_{xy} orbital) was shown by DFT calculations. The EPR spectra of **1** and **2** were characteristic for species in a singlet state (*S* = ½ systems) in contrast to that of their analog, previously reported for the first Ru^{II}/Ru^{III} ion-pair complex, [Ru^{II}(bipy)₂(pic)]⁺[*cis*-Ru^{III}Cl₂(pic)₂]⁻, typical for a species in the triplet state (*S* = 1 system).

Słowa kluczowe

Mixed - valence Ru II / Ru III ion pair complexes, EPR, DFT calculation

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