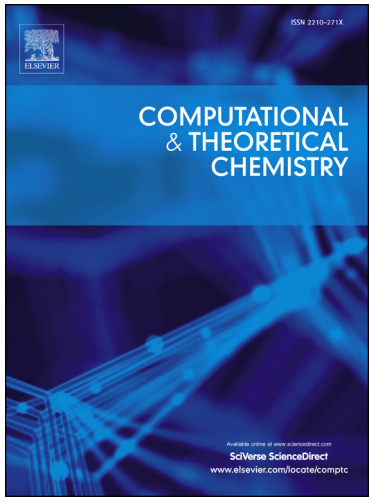

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Alyona A. Starikova, Andrey G. Starikov, Vladimir I. Minkin

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Adducts of manganese diketonates with redox-active ligands: computational modeling of valence tautomeric systems

Alyona A. Starikova[a*], Andrey G. Starikov[a, b], Vladimir I. Minkin[a, b]

[a] *Institute of Physical and Organic Chemistry at Southern Federal University, Stachka Avenue 194/2, Rostov-on-Don, Russian Federation, 344090, e-mail: alstar@ipoc.sfedu.ru*

[b] *Southern Scientific Center of the Russian Academy of Sciences, st. Chehova 41, Rostov-on-Don, Russian Federation, 344006*

The potential valence tautomeric (VT) properties of 1:1 adducts of Mn^{II} bis-malonates and Mn^{II} bis-hexafluoroacetylacetonates with bidentate redox-active ligands – *o*-benzoquinone, its imine and diimine derivatives (complexes **I**) and 1,4-diazabuta-1,3-diene (complexes **II**) were computationally studied. According to the DFT B3LYP*/6-311++G(d,p) calculations, the ground electronic states of the mixed-ligand complexes **I** are represented by the high-spin electromeric forms $_{HS}Mn^{III}–L^{\cdot-}$ exhibiting strong antiferromagnetic exchange coupling between unpaired electrons of the paramagnetic centers located at the metal ion and radical-anionic ligand. Same type magnetic ordering is characteristic also of the structures containing manganese center in its intermediate spin-state. Stabilization of the electromers $_{HS}Mn^{II}–L^{0}$ containing a redox-active ligand in the non-reduced form is achieved in the complexes formed by Mn^{II} hexafluoroacetylacetonate with benzoquinone imine and diimine and adducts on the basis of 1,4-diazabuta-1,3-diene (**II**) possessing stronger than carbonyl oxygens ligating centers (NH). The adducts **I** (X=Y=NH; R=CF_3), (X=O, Y=NH; R=CF_3) and **II** (R=H) characterized by the narrow energy gaps between the $_{HS}Mn^{III}–L^{\cdot-}$ and $_{HS}Mn^{II}–L^{0}$ electromeric forms and low energy barriers (estimated as minimum energy crossing points MECP at seams of intersection of the corresponding potential energy surfaces) for their interconversion may be considered as promising candidates for the observation of thermally driven valence tautomeric rearrangements.

Keywords: DFT calculations, manganese complexes, redox-active ligands, valence tautomerism, spin-forbidden reactions, minimum energy crossing points

1. Introduction

Last years have seen the rapidly growing interest in the synthesis and study of bistable metal coordination compounds capable of switching their physical properties under the action of various external stimuli [1]. This trend is dictated by the persistent widening of the areas of technical applications of the materials based on the use of these compounds as molecular switches and molecular memories in information processing and storage devices [2-5]. Of