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Magnetic Properties of Adducts of Trinuclear Heterometallic Complexes with Acetonitrile: Quantum Chemical Study

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Abstract—Computational modeling (DFT UTPSSh/6-311++G(d,p)) of heterometallic complexes comprising the transition metal bis(chelate) as a linker with coordinated acetonitrile molecules and 2,6-di(pyrazolyl)pyridine iron complexes in the terminal moieties is performed. The variation of the central metal atom (Co, Ni) and donor centers (NH, O) in the linker makes it possible to find compounds capable of undergoing one- and two-step spin-crossover of the iron ions. The character of exchange interactions is shown to be determined by the properties of the bis(chelate) linker. The calculated energy and magnetic characteristics of the studied compounds allow one to regard them as candidates for the design of molecular electronics and spintronics devices.

Keywords: iron complexes, magnetic properties, spin-crossover, bis(chelate) linker, quantum chemical modeling

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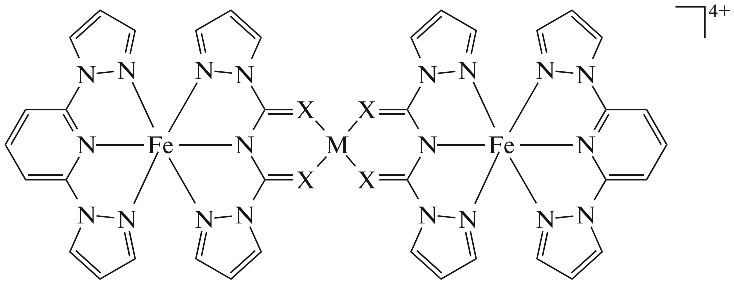
INTRODUCTION

The search for metal complexes suitable for the development of molecular electronics and spintronics devices is an urgent trend of coordination chemistry [1–3]. The cluster compounds [4] and heterometallic rings [5] containing weakly coupled (quantum-mechanically entangled) paramagnetic centers separated by linkers can find use for the development of spin qubits (logical units of quantum computers) [3]. The ability of the polynuclear carboxylate complexes with 3*d*- and 4*f*-metal ions to manifest the properties of molecular magnetics [6, 7] has recently been shown. This ability can be used for the production of novel functional materials. A considerable contribution to the investigation of molecular magnetism is made by the works on studying the magnetic behavior of the polymer systems based on the complexes of transition metal diketonates with nitroxyl radicals [1, 8–10].

Continuing these studies, we proposed another approach [11, 12] to the construction of magnetically active bi- and polynuclear compounds, whose metal-containing moieties are capable of undergoing spin-crossover [1] and/or valence tautomerism [13]. The magnetic properties of these complexes can be controlled by exchange interactions between the paramagnetic centers and using the mechanisms of magnetic bistability. Fine tuning of the structural parameters (reasonable choice of the complexing agent, variation of the linker, and functionalization of terminal ligands) makes it possible to reveal compounds with the properties of molecular switches and spin qubits [14]. The redox-active ligand [12], hydrocarbon bridges [11, 15], π-conjugated systems [16], cycloalkanes [17], and metal bis(chelates) [18, 19] can act as a linker group.

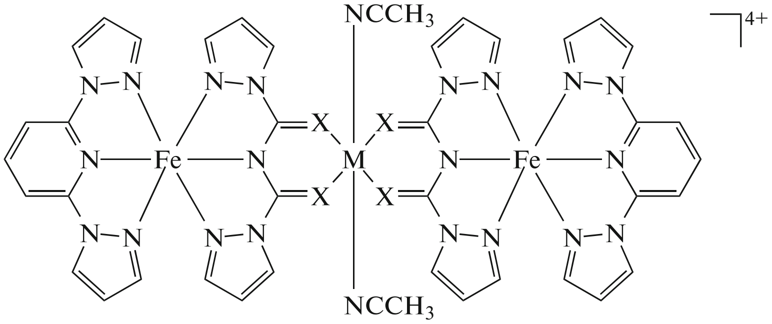
The earlier quantum chemical study of the trinuclear complexes with the bis(chelate) linker (**I**) based on the 1,3,5-triazapentadiene ligands [20] and their oxygen analogs (*N*-formylformamides) [21] showed the possibility of controlling the magnetic properties of these compounds by external effects [22]. The terminal moieties of complexes **I** (M = Co, Ni, Cu, Zn; X = NH, O) include iron ions and tridentate 2,6-di(pyrazolyl)pyridines [23] thus building the coordination site to FeN_6, which is characteristic of compounds of this metal manifesting spin-crossover [24].



I: M = Co, Ni, Cu, Zn; X = NH, O

The most promising complexes of this type are the compounds containing the paramagnetic bis(chelate) linker providing an exchange channel between the terminal metal-containing moieties. The building of the coordination site of the central metal ion of complexes **I** to an octahedron will favor the transition of Ni(II) and Co(II) to the octahedral environment and, as a consequence, the stabilization of the high-spin state [25, 26].

This work concerns the quantum chemical study of adducts **II** (M = Co, Ni; X = NH, O) based on heterometallic complexes **I** with two acetonitrile molecules. It is expected that the variation of the central metal ion and donor groups of the bis(chelate) linker would allow one to control the magnetic properties of the systems under study.



II: M = Co, Ni; X = NH, O

CALCULATION PROCEDURE

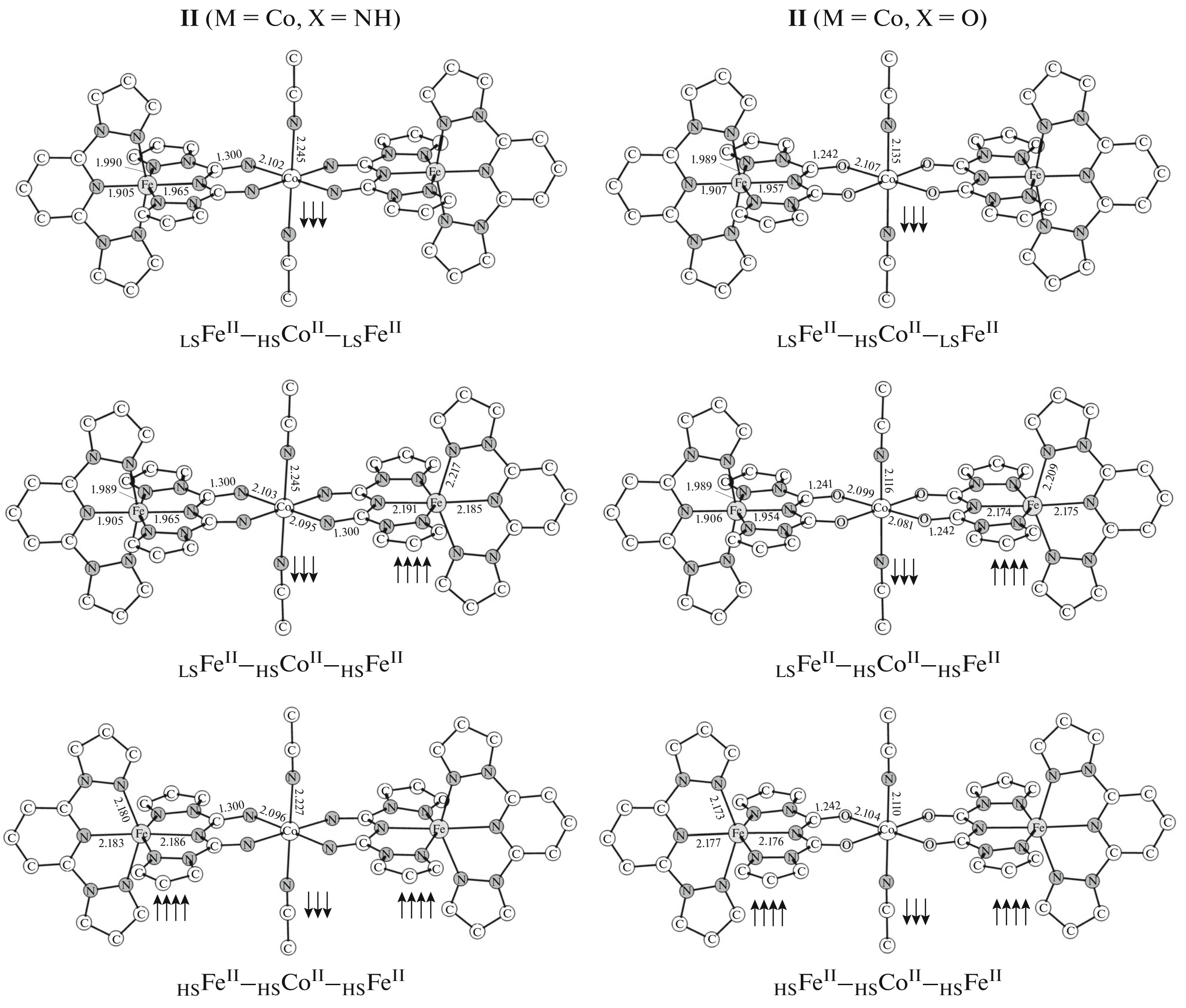
Calculations were performed using the Gaussian 09 program [27] in the framework of the density functional theory (DFT) using the UTPSSh functional [28, 29] and 6-311++G(d,p) extended basis set. The chosen approximation reproduces well the energy characteristics of spin-crossover in the cationic complexes [30–32]. Stationary points were localized on the potential energy surface by the full geometry optimization of the molecular structures checking the DFT stability of the wave function. The exchange interaction parameters (*J*) were determined by the calculation of all possible spin states in terms of the broken symmetry (BS) formalism [33] using the generalized spin projection (GSP) method proposed by Yamaguchi [34]. The graphical images of the molecular structures presented in Figs. 1 and 2 were obtained using the ChemCraft program [35].

RESULTS AND DISCUSSION

Adducts II (M = Co; X = NH, O). According to the calculations, the ground state of trinuclear adduct **II** (M = Co, X = NH) is the structure ${}_{LS}Fe^{II}–{}_{HS}Co^{II}–{}_{LS}Fe^{II}$ containing the low-spin (LS) iron(II) ions and the high-spin (HS) cobalt(II) ion (Fig. 1). The geometric characteristics and spin density distribution of the electromer on the octet potential energy surface indicate that the electromer contains iron(II) ions in different spin states (${}_{LS}Fe^{II}–{}_{HS}Co^{II}–{}_{HS}Fe^{II}$). The difference in energies between these isomers of complex **II** (M = Co, X = NH) is 7.4 kcal/mol (Table 1), which allows one to expect that spin-crossover would take place in one of the terminal moieties. A substantial destabilization of the high-spin ${}_{HS}Fe^{II}–{}_{HS}Co^{II}–{}_{HS}Fe^{II}$ species relative to the low-spin ground state (ΔE = 14.8 kcal/mol) prevents the complete two-step spin transition to occur in this compound.

The study of the magnetic properties of the complex showed weak antiferromagnetic exchange interactions ($J_{Fe–M}$ = –5.0 cm^{-1}) between the paramagnetic metal centers of the isomer ${}_{LS}Fe^{II}–{}_{HS}Co^{II}–{}_{HS}Fe^{II}$. Two channels of exchange coupling are possible in the high-spin ${}_{HS}Fe^{II}–{}_{HS}Co^{II}–{}_{HS}Fe^{II}$ isomer: Fe–Co and Fe–Fe (Table 1). In the first case, the exchange value correlates with that found in the electromer containing two paramagnetic centers, whereas a weak ferromagnetic exchange ($J_{Fe–Fe}$ = 6.6 cm^{-1}) is predicted between the terminal moieties of complex **II** (M = Co, X = NH). A comparison of the energy and magnetic characteristics of adduct **II** (M = Co, X = NH) with the previously studied trinuclear complex without coordinated solvent molecules [22] shows that the solvation of acetonitrile accompanied by the transition of the central metal ion to the high-spin state results in the destabilization of the electron-excited isomers ${}_{LS}Fe^{II}–{}_{HS}Co^{II}–{}_{HS}Fe^{II}$ and ${}_{HS}Fe^{II}–{}_{HS}Co^{II}–{}_{HS}Fe^{II}$ and the appearance of exchange interactions between the iron(II) ions.

The replacement of the imino groups by oxygen atoms in the bis(chelate) linker favors the narrowing of the difference in energies between the electromers to the values (Table 1) characteristic of the complete two-step spin-crossover. The expected transitions will be accompanied by a change in the spin of the molecule (*S*) from 3/2 to 11/2, which makes it possible to regard adduct **II** (M = Co, X = O) as a potential



$_{LS}Fe^{II}$—$_{HS}Co^{II}$—$_{LS}Fe^{II}$ $_{LS}Fe^{II}$—$_{HS}Co^{II}$—$_{LS}Fe^{II}$

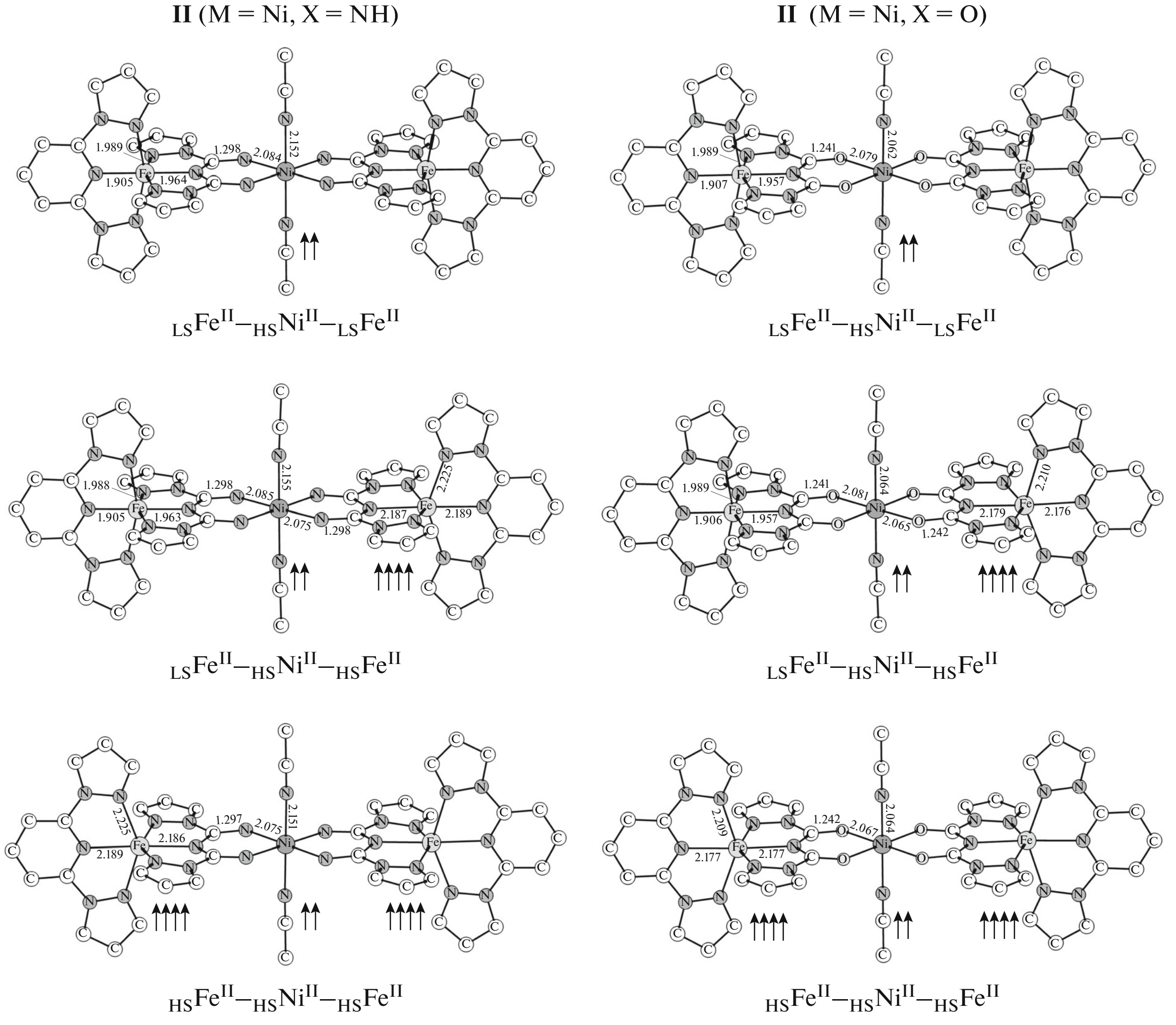
$_{LS}Fe^{II}$—$_{HS}Co^{II}$—$_{HS}Fe^{II}$ $_{LS}Fe^{II}$—$_{HS}Co^{II}$—$_{HS}Fe^{II}$

$_{HS}Fe^{II}$—$_{HS}Co^{II}$—$_{HS}Fe^{II}$ $_{HS}Fe^{II}$—$_{HS}Co^{II}$—$_{HS}Fe^{II}$

Fig. 1. Optimized geometries of the isomeric species of adducts **II** (M = Co; X = NH, O) calculated by the DFT UTPSSh/6-311++G(d,p) method. Here and in Fig. 2, all structures has the charge +4, hydrogen atoms are omitted, bond lengths are given in Å, and orientations of spins of unpaired electrons are shown by arrows.

molecular switch with the magnetic response function. As follows from the exchange parameters presented in Table 1, the variation of the donor group in the bis(chelate) linker exerts no substantial effect on the character of exchange interactions. In adducts **II** (M = Co, X = NH and M = Co, X = O), the spins of unpaired electrons localized on the cobalt and iron ions undergo the antiferromagnetic interaction, whereas the terminal moieties are coupled ferromagnetically.

Adducts II (M = Ni; X = NH, O). The results of calculations of the adducts containing nickel bis(chelate) as a linker are presented in Table 2 and in Fig. 2. As in the above considered complexes with the central cobalt ion, the ground state of compounds **II** (M = Ni; X = NH, O) are the low-spin structures $_{LS}Fe^{II}$—$_{HS}Ni^{II}$—$_{LS}Fe^{II}$ to which the minima on the triplet potential energy surface correspond. The differences in energies of the electromers of complex **II** (M = Ni, X = NH) suggest spin-crossover in this complex, the second step of which will occur incompletely because of a considerable destabilization of the high-spin species (ΔE = 13.9 kcal/mol). In the $_{LS}Fe^{II}$—$_{HS}Ni^{II}$—$_{HS}Fe^{II}$ and $_{HS}Fe^{II}$—$_{HS}Ni^{II}$—$_{HS}Fe^{II}$ isomers, weak ferromagnetic interactions (1.2 and 1.5 cm^{-1}) are predicted between the spins of unpaired electrons of the $_{HS}Ni^{II}$ and $_{HS}Fe^{II}$ ions regardless of the spin state of the second iron ion. A comparison of the exchange parameters J_{Fe-M} in the adducts with the central cobalt and nickel ions (Tables 1, 2) indicates that the variation of the metal atom of the bis(chelate) linker makes it pos-



II (M = Ni, X = NH) **II** (M = Ni, X = O)

$_{LS}Fe^{II}$—$_{HS}Ni^{II}$—$_{LS}Fe^{II}$ $_{LS}Fe^{II}$—$_{HS}Ni^{II}$—$_{LS}Fe^{II}$

$_{LS}Fe^{II}$—$_{HS}Ni^{II}$—$_{HS}Fe^{II}$ $_{LS}Fe^{II}$—$_{HS}Ni^{II}$—$_{HS}Fe^{II}$

$_{HS}Fe^{II}$—$_{HS}Ni^{II}$—$_{HS}Fe^{II}$ $_{HS}Fe^{II}$—$_{HS}Ni^{II}$—$_{HS}Fe^{II}$

Fig. 2. Optimized geometries of the isomeric species of adducts **II** (M = Ni; X = NH, O) calculated by the DFT UTPSSh/6-311++G(d,p) method.

sible to control the magnetic properties of the trinuclear complex based on this linker.

The study of the magnetic properties of the high-spin species of adduct **II** (M = Ni, X = NH) showed no exchange interactions between the terminal metal ions. The value of $J_{\text{Fe–Fe}}$ is –2 cm^{-1} in a similar complex without solvent molecules [22]. Therefore, the coordination of acetonitrile results in the weakening of exchange interactions, which is consistent with the results of calculations of the tetranuclear transition metal complexes with the 1,3,5-triketone ligands, demonstrating the variation of the magnetic properties for the coordination of nitrogen-containing molecules [36].

The replacement of the 1,3,5-triazapentadiene metalloligand by its oxygen analog (complex **II**: M = Ni, X = O) is accompanied by the shortening of the coordination bonds (Fig. 2). This leads to a decrease in the distance between the terminal moieties and the appearance of ferromagnetic coupling of the iron ions: $J_{\text{Fe–Fe}} = 9.5$ cm^{-1}. In the electromer with the intermediate spin state $_{LS}Fe^{II}$—$_{HS}Ni^{II}$—$_{HS}Fe^{II}$ and in the high-spin structure $_{HS}Fe^{II}$—$_{HS}Ni^{II}$—$_{HS}Fe^{II}$, as in the considered above adduct **II** (M = Ni, X = NH), the exchange interactions between the bis(chelate) linker and paramagnetic iron(II) ion are weakly ferromagnetic (Table 2). The differences in energies between the isomers of the compound discussed do not exceed 11 kcal/mol, indicating the possibility of the complete two-step spin-crossover to occur on iron(II) ions. The calculated magnetic and energy characteristic of the trinuclear complex with the nickel-containing linker (**II**: M = Ni, X = O) allow one to regard it as a building block for the design of molecular electronics devices.

Table 1. Spin (S), total energy (E_{tot}), relative energy (ΔE), spin-squared operator (S^2), and exchange interaction parameter (J) in the isomeric species of adducts **II** (M = Co; X = NH, O) calculated by the DFT UTPSSh/6-311++G(d,p) method

Structure	S	E_{tot}, au	ΔE, kcal/mol	S^2	J_{Fe-M}, cm^{-1}	J_{Fe-Fe}, cm^{-1}
X = NH						
${}_{LS}Fe^{II}{-}{}_{HS}Co^{II}{-}{}_{LS}Fe^{II}$	3/2	−6958.33589	0.0	3.76		
${}_{LS}Fe^{II}{-}{}_{HS}Co^{II}{-}{}_{HS}Fe^{II}$	7/2	−6958.32404	7.4	15.78	−5.0	
BS	1/2	−6958.32431		3.77		
${}_{HS}Fe^{II}{-}{}_{HS}Co^{II}{-}{}_{HS}Fe^{II}$	11/2	−6958.31228	14.8	35.79	−5.0	6.6
BS αβα*	5/2	−6958.31282		11.79		
BS βαα	3/2	−6958.30982		7.80		
X = O						
${}_{LS}Fe^{II}{-}{}_{HS}Co^{II}{-}{}_{LS}Fe^{II}$	3/2	−7037.87930	0.0	3.76		
${}_{LS}Fe^{II}{-}{}_{HS}Co^{II}{-}{}_{HS}Fe^{II}$	7/2	−7037.86916	6.4	15.78	−11.2	
BS	1/2	−7037.86977		3.77		
${}_{HS}Fe^{II}{-}{}_{HS}Co^{II}{-}{}_{HS}Fe^{II}$	11/2	−7037.86528	8.8	35.75	−5.2	3.6
BS αβα	5/2	−7037.86584		11.78		
BS βαα	3/2	−7037.86530		7.80		

* α and β correspond to the orientation of spins up and down, respectively.

Table 2. Spin (S), total energy (E_{tot}), relative energy (ΔE), spin-squared operator (S^2), and exchange interaction parameter (J) in the isomeric species of adducts **II** (M = Ni; X = NH, O) calculated by the DFT UTPSSh/6-311++G(d,p) method

Structure	S	E_{tot}, au	ΔE, kcal/mol	S^2	J_{Fe-M}, cm^{-1}	J_{Fe-Fe}, cm^{-1}
X = NH						
${}_{LS}Fe^{II}{-}{}_{HS}Ni^{II}{-}{}_{LS}Fe^{II}$	2/2	−7083.86632	0.0	2.01		
${}_{LS}Fe^{II}{-}{}_{HS}Ni^{II}{-}{}_{HS}Fe^{II}$	6/2	−7083.85539	6.9	12.02	1.2	
BS	2/2	−7083.85534		4.02		
${}_{HS}Fe^{II}{-}{}_{HS}Ni^{II}{-}{}_{HS}Fe^{II}$	10/2	−7083.84424	13.9	30.04	1.5	0.1
BS αβα	6/2	−7083.84413		14.03		
BS βαα	2/2	−7083.84418		6.04		
X = O						
${}_{LS}Fe^{II}{-}{}_{HS}Ni^{II}{-}{}_{LS}Fe^{II}$	2/2	−7163.41120	0.0	2.00		
${}_{LS}Fe^{II}{-}{}_{HS}Ni^{II}{-}{}_{HS}Fe^{II}$	6/2	−7163.40276	5.3	12.02	1.3	
BS	2/2	−7163.40271		4.02		
${}_{HS}Fe^{II}{-}{}_{HS}Ni^{II}{-}{}_{HS}Fe^{II}$	10/2	−7163.39422	10.7	30.04	1.3	9.5
BS αβα	6/2	−7163.39412		14.04		
BS βαα	2/2	−7163.39348		6.04		

Thus, the performed quantum chemical (DFT UTPSSh/6-311++G(d,p)) study of the adducts of trinuclear heterometallic complexes **II** (M = Co, Ni; X = NH, O) containing the bis(chelate) linker with acetonitrile molecules showed the possibility of controlling the magnetic properties of these compounds. Spin-crossover on the iron(II) ions in one of the terminal moieties was predicted in compounds **II** (M = Co, Ni; X = NH) based on the 1,3,5-triazapentadiene ligands, whereas two-step spin transitions are expected in oxygen-containing adducts **II** (M = Co, Ni; X = O). The complexes with the cobalt-containing linker are characterized by weak antiferromagnetic interactions between the iron and central metal ions. The paramagnetic centers are ferromagnetically coupled in the compounds based on the nickel(II) bis(chelate). The systems capable of exhibiting the properties of molecular switches and spin qubits were found by the reasonable choice of the structural parameters.

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