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Tetranuclear Cu(II) and Ni(II) Complexes with 1,3,5-Triketone Ligands: A Quantum-Chemical Simulation of Exchange Interactions

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Abstract—A series of tetranuclear copper and nickel coordination compounds based on 1,3,5-triketone ligands is calculated using the B3LYP/6-31G(d,p) method of the density functional theory. The antiferromagnetic exchange is predicted to be in all studied complexes, regardless of the type of the metal, the size of linker groups, and the presence of additional solvent (pyridine) molecules. The Ni(II) complexes are characterized by weak exchange interactions, which makes it possible to consider them as candidates for the development of spin qubits.

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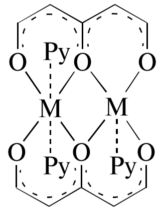
INTRODUCTION

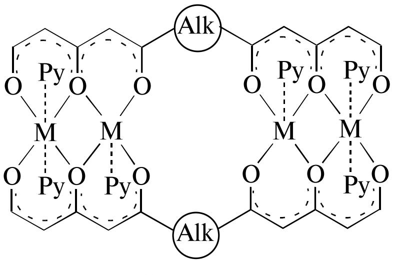
Practical processing of quantum information is one of the most significant tasks of chemistry and materials science. A promising trend in this area is a search for coordination metal compounds and their clusters containing weakly coupled (entangled) metal centers with an open shell. Electron spins of these complexes can act as quantum bits (qubits) due to their unique properties, primarily such as scalability warranted by the identity of the molecular structures and the possibility of precise tuning of the interaction of spins by attracting a series of suitable ligands [1, 2]. The main conditions to which a system of spin-based quantum gates known as DiVincenzo criteria [3] should satisfy contain the following requirements applied to coordination metal compounds: (1) the distinct determination of spin states of a molecule, (2) the fast initiation of qubits by irradiation or cooling in an external magnetic field to transit a molecule to the ground state, (3) the decoherence time is much longer than the time necessary for switching over the magnetic states, and the coherence time of the system should be much longer than that necessary for a logical operation to be performed, and (4) the readability of spin states of each magnetic fragment of a molecule.

The most part of these conditions can be fulfilled using molecular magnets based on transition metal clusters or heterometallic rings, whose fragments are linked by suitable organic or organometallic linkers [4–8]. This type of molecular associates contains a pair of rigidly certain paramagnetic centers capable of acting as promising two-qubit quantum systems under the conditions of a weak exchange interaction (a prerequisite for quantum entanglement) between them.

It has previously been shown that 1,3,5-triketones form an appropriate basis for assembling metal-containing (Co(II), Ni(II), Cu(II)) polyspin systems [9–12] that potentially can find use in quantum electronics [13, 14], in particular, for the development of quantum gates [15, 16]. The phenylene group was used as a linker [11, 12, 16]. In order to predict new coordination compounds with the properties necessary for spin qubits, we calculated the tetranuclear copper and nickel complexes based on 1,3,5-triketones containing two exchange fragments linked by methylene linker groups. The corresponding adducts **I** and **II** were considered to establish the influence of the coordination of the solvent (pyridine) molecules on the character and strength of exchange interactions in the studied compounds:



I: M = Cu, Ni; *x*Py



II: M = Cu, Ni; Alk = C_2H_4, C_3H_6, C_4H_8; *x*Py

CALCULATION PROCEDURE

All calculations were performed using the Gaussian 09 program [17] by the method of the density functional theory (DFT UB3LYP/6-31g(d,p)) [18] that well reproduces the characteristics of coordination compounds with an open shell [19, 20]. The full geometry optimization of the molecular structures was performed to determine stationary points on the potential energy surface. Exchange interactions between unpaired electrons of the paramagnetic centers were estimated using the broken symmetry (BS) approach [21]. The exchange interaction constant (J, cm^{-1}) was calculated by the Yamaguchi equation [22, 23]. The graphical images of the molecular structures shown in Figs. 1–4 were obtained using the ChemCraft program [24]. The corresponding Cartesian coordinates of atoms obtained in the quantum-chemical calculations were applied as input parameters for the program used.

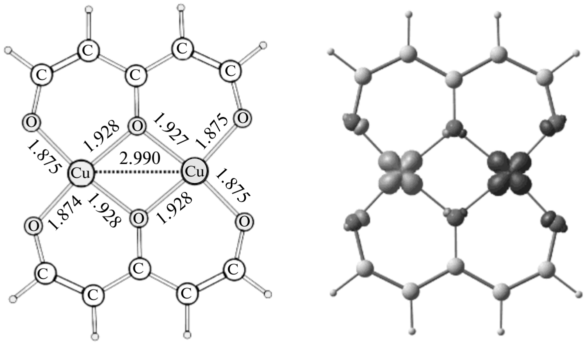
RESULTS AND DISCUSSION

Tetranuclear Cu(II) complexes with 1,3,5-triketone ligands. According to the calculation results, an isolated molecule of complex **I** (M = Cu) is characterized by the planar structure of the coordination site. The high-spin state is destabilized by 2.2 kcal/mol relatively to the BS state, indicating antiferromagnetic ordering. The unpaired electrons are predominantly localized on the copper atoms, but a significant fraction of the spin density is observed on the oxygen atoms (Fig. 1). The calculation of the exchange interaction parameter J gives a value of –716 cm^{-1} (Table 1), which makes it possible to predict diamagnetism of complex **I** (M = Cu) in a wide temperature range.

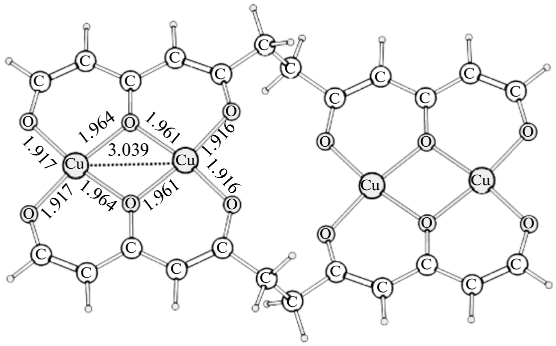
The binding of two such complexes by methylene linkers results in the formation of tetranuclear structures **II** (M = Cu; Alk = C_2H_4, C_3H_6, C_4H_8) accompanied by the elongation of the Cu–O bonds by 0.04 Å compared to similar parameters for an isolated molecule of complex **I** (M = Cu). As a consequence, the distance between the copper atoms increases and favors the weakening of the exchange interactions inside the dimer fragments (BS1) to values of –299...–309 cm^{-1}. The exchange interactions between two paramagnetic centers (BS2) are also antiferromagnetic: the J parameter is –455, –442, and –455 cm^{-1}, depending on the number of methylene groups (2–4), respectively. Similar values of J in complexes **II** (M = Cu; Alk = C_2H_4, C_3H_6, C_4H_8) indicate an insignificant influence of the number of methylene groups on the strength of exchange interactions of the considered compounds.

Adducts of complexes **I** (M = Cu) and **II** (M = Cu; Alk = C_2H_4, C_3H_6, C_4H_8) with pyridine were studied to elucidate the influence of solvate molecules on the magnetic properties of the compounds. The geometry optimization of the compound containing complex **I** (M = Cu) and two pyridine molecules gave structure **I** (M = Cu; 2Py) (Fig. 2) for which a strong distortion of the coordination site is predicted. The distortion is caused by the shift of the copper atoms from the ligand plane toward the donor nitrogen atoms and along with the elongation of the distance between the copper atoms favors the weakening of the overlap of the magnetic orbitals, which is observed as a decrease in the strength of the exchange interactions to –516 cm^{-1} (Table 1). The “cross-linking” of two complexes **I** (M = Cu; 2Py) through the methylene bridges results in the stabilization of tetranuclear adducts **II** (M = Cu; Alk = C_2H_4, C_3H_6, C_4H_8; 4Py) with the monotonically decreasing antiferromagnetic exchange interactions between the binuclear fragments (–280, –277, and –265 cm^{-1}). The calculated magnetic exchange constants are consistent with the experimental data for similar complexes [16]. Therefore, complexes **II** (M = Cu; Alk = C_2H_4, C_3H_6, C_4H_8; 4Py) are characterized by a medium-strength exchange and can potentially be considered as a basis for spin qubits.

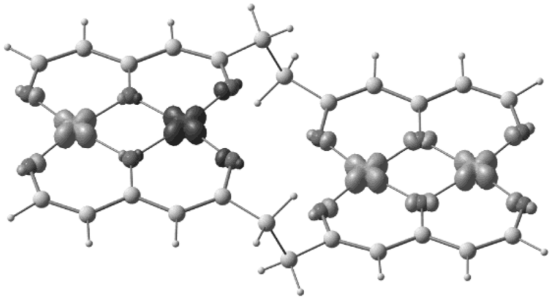
Tetranuclear Ni(II) complexes with 1,3,5-triketone ligands. The studies of the Ni(II) complexes with the triketone ligands were started from the adduct containing pyridine molecules, since the nickel atom is diamagnetic in the compounds with the planar coordination site. Complex **I** (M = Ni; 2Py) is characterized by the shortened M–N distance (2.005 Å) compared to a similar copper compound and has a different orientation of the pyridine molecules relatively to the ligand (Fig. 3). Unlike the copper complexes characterized by the presence of a spin density on the oxygen atoms (Fig. 1), in complex **I** (M = Ni; 2Py) and other considered nickel compounds the spin density is nearly completely concentrated on the metal atoms. The calculated value of parameter J (–51 cm^{-1}) indicates weak antiferromagnetic exchange interactions between unpaired electrons of the nickel atoms. The geometry optimization of the tetranuclear complexes containing adducts **I** (M = Ni; 2Py) bonded by the methylene linker groups gave structures **II** (M = Ni; Alk = (C_2H_4, C_3H_6, C_4H_8; 4Py). Complex formation is not accompanied by a change in the characteristics of the chelate sites of the binuclear fragments but favors the weakening of their exchange interactions to –18...–19 cm^{-1} (Table 2). The BS2 states in which the



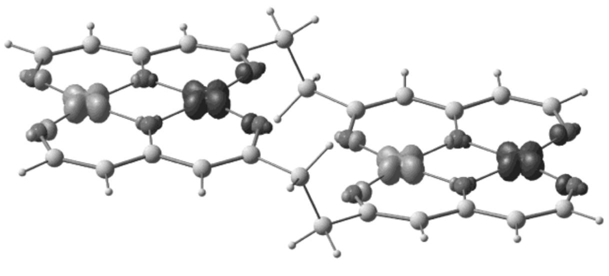
I (M = Cu)



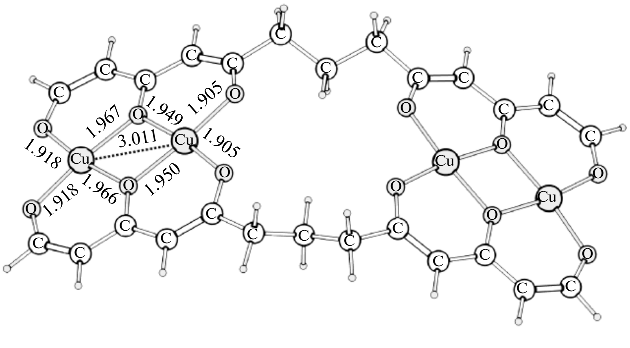
II (M = Cu; Alk = C_2H_4)



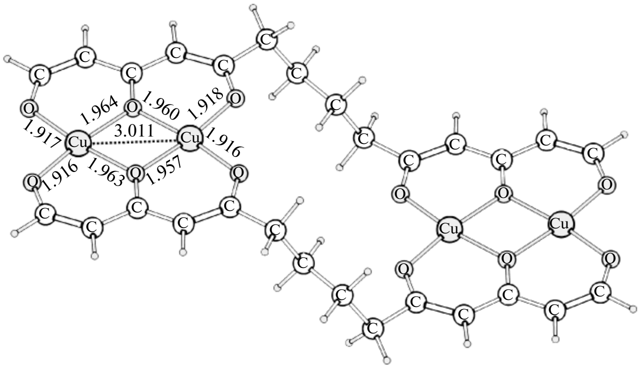
BS1



BS2

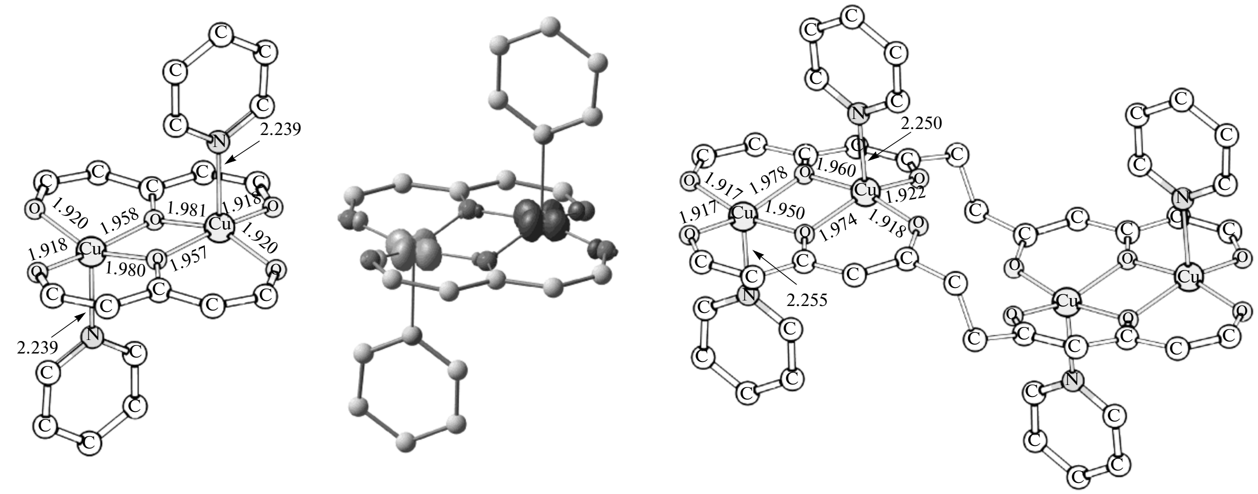


II (M = Cu; Alk = C_3H_6)



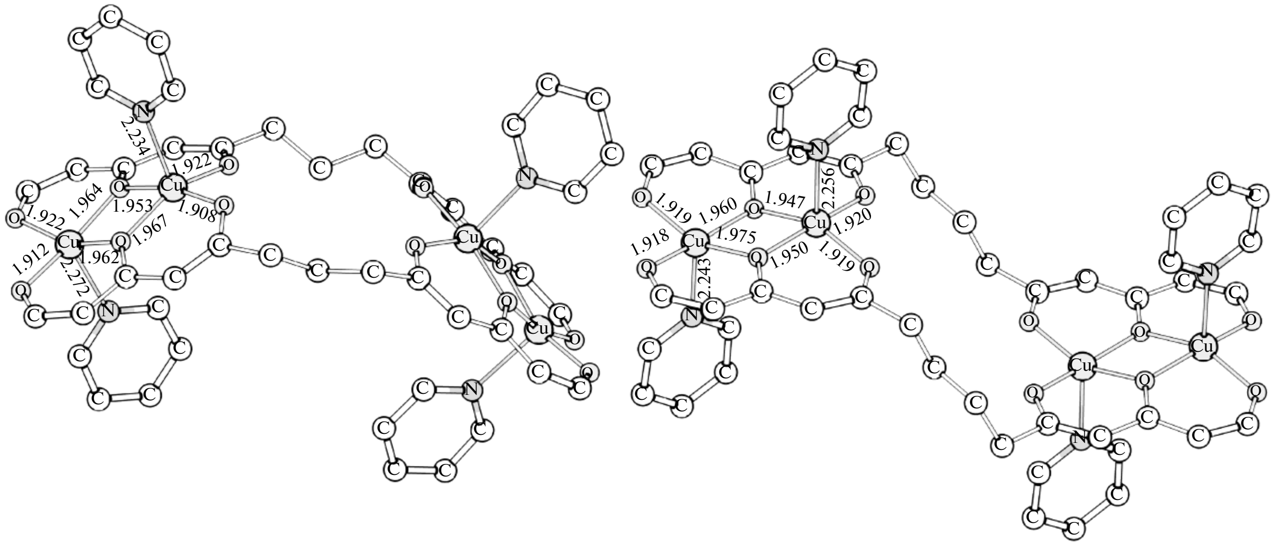
II (M = Cu; Alk = C_4H_8)

Fig. 1. Geometric characteristics of structures **I** (M = Cu) and **II** (M = Cu; Alk = C_2H_4, C_3H_6, C_4H_8) calculated by the DFT UB3LYP/6-31g(d,p) method. The spin density distribution in the BS state of structure **I** (M = Cu) is presented above. The spin density distribution in the BS1 and BS2 states is presented for structure **II** (M = Cu; Alk = C_2H_4).



I (M = Cu; 2Py)

II (M = Cu; Alk = C_2H_4; 4Py)



II (M = Cu; Alk = C_3H_6; 4Py)

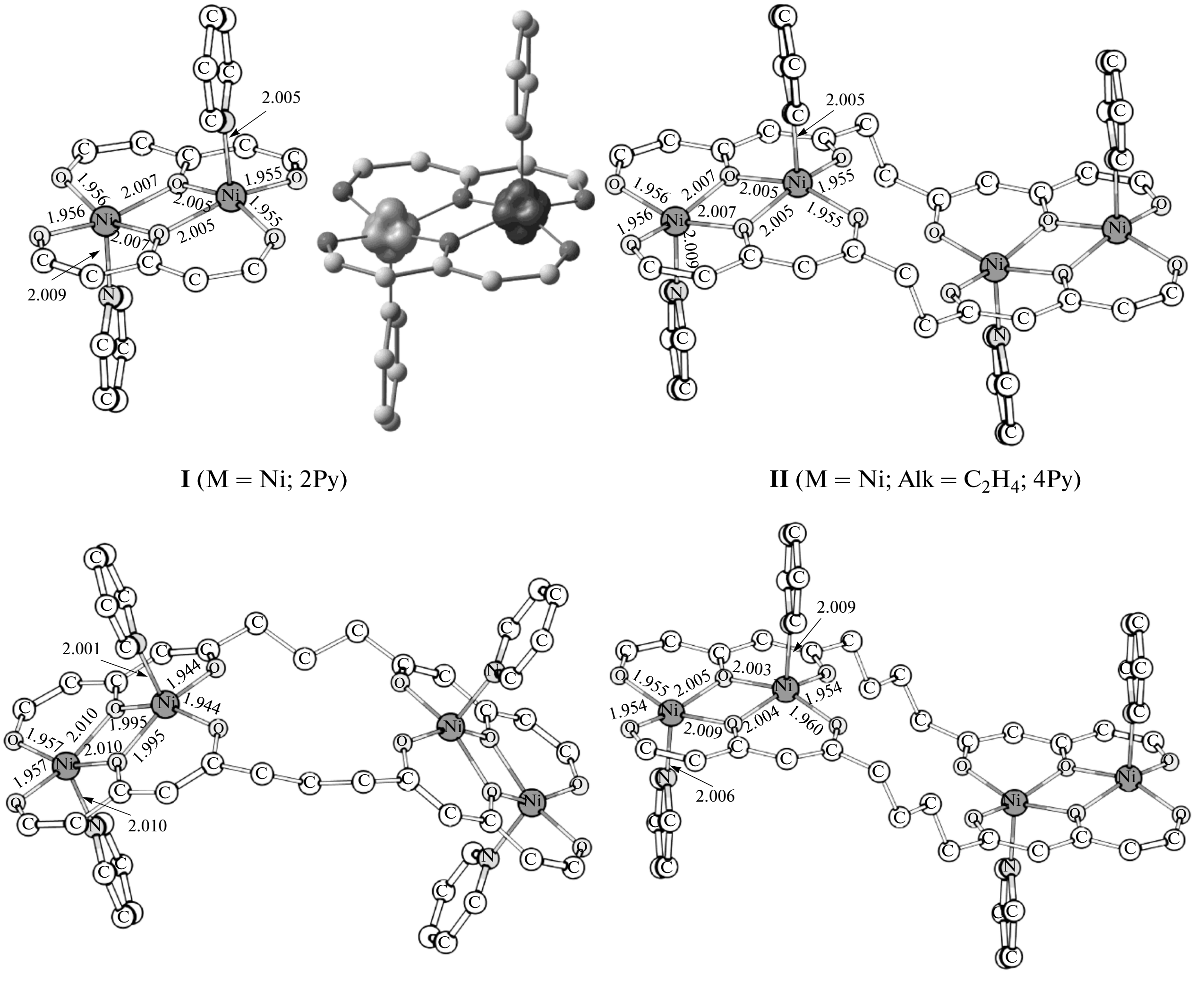
II (M = Cu; Alk = C_4H_8; 4Py)

Fig. 2. Geometric characteristics of structures **I** (M = Cu; 2Py) and **II** (M = Cu; Alk = C_2H_4, C_3H_6, C_4H_8; 4Py) calculated by the DFT UB3LYP/6-31g(d,p) method. The spin density distribution in the BS state is presented for structure **I** (M = Cu; 2Py). Hereafter hydrogen atoms are omitted for clarity.

antiferromagnetic exchange between adducts **I** (M = Ni; 2Py) is predicted are the most stable form of compounds **II** (M = Ni; Alk = C_2H_4, C_3H_6, C_4H_8; 4Py). As follows from the data presented in Table 2, the value of parameter J corresponding to these interactions is $-26...-29$ cm^{-1}. The weak exchange interactions between the antiferromagnetically coupled paramagnetic centers of complexes **II** (M = Ni; Alk = C_2H_4, C_3H_6, C_4H_8; 4Py) predicted by the calculations suggest that these compounds are good candidates for the development of spin qubits.

The interaction of the Ni(II) bis(chelates) with pyridine results, as a rule, in the complexes containing two donor molecules [25, 26]. However, steric hindrances created by the linker groups of the studied tetranuclear compounds block the formation of adducts containing two pyridine molecules per each metal atom. The structures containing three pyridine molecules per binuclear fragment are predominantly stabilized in similar complexes [27].

The nickel complex with three pyridine molecules **I** (M = Ni; 3Py) is characterized by different positions



I (M = Ni; 2Py)

II (M = Ni; Alk = C_2H_4; 4Py)

II (M = Ni; Alk = C_3H_6; 4Py)

II (M = Ni; Alk = C_4H_8; 4Py)

Fig. 3. Geometric characteristics of structures **I** (M = Ni; 2Py) and **II** (M = Ni; Alk = C_2H_4, C_3H_6, C_4H_8; 4Py) calculated by the DFT UB3LYP/6-31g(d,p) method. The spin density distribution in the BS state is presented above for structure **I** (M = Ni; 2Py).

of the metal atoms relatively to the ligand (Fig. 4). The nickel atom to which two donor molecules are coordinated lies in the ligand plane, whereas another atom shifts from this plane by 0.4 Å. The exchange interactions in complex **I** (M = Ni; 3Py) are weakly antiferromagnetic, $J = -46$ cm^{-1} (Table 2). The binding of two molecules **I** (M = Ni; 3Py) by the alkyl linker groups gives tetranuclear compounds **II** (M = Ni; Alk = C_2H_4, C_3H_6, C_4H_8; 6Py) with the geometric characteristics of the coordination sites close to those found for dimer **I** (M = Ni; 3Py), which suggests the absence of the electron density transfer during complex formation. This hypothesis is confirmed by the results of calculations of the exchange interactions between the antiferromagnetically coupled dimer fragments, according to which $J = -21...-24$ cm^{-1}. This value is consistent with the magnetochemical data for similar complexes [27].

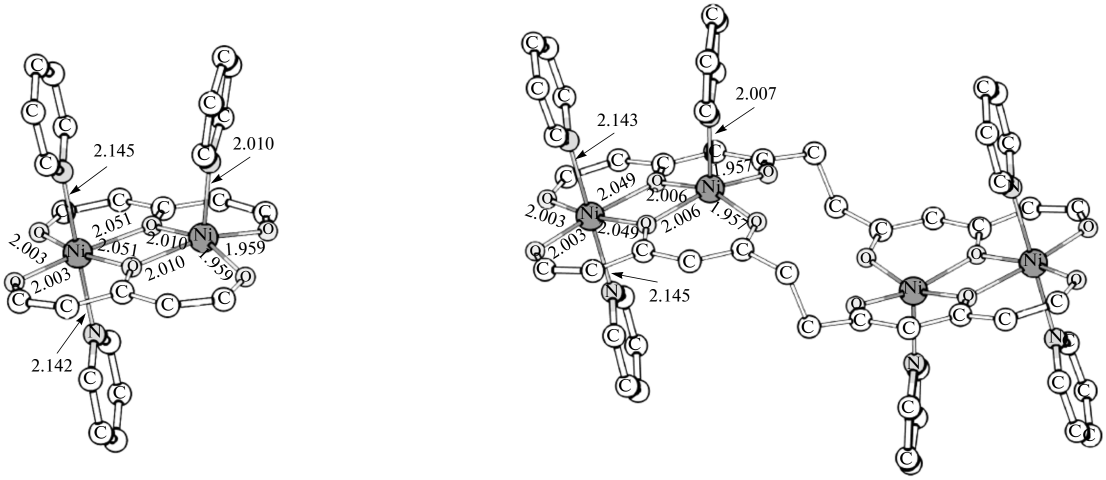
Thus, the simulation performed for a series of the tetranuclear copper and nickel complexes with the 1,3,5-triketone ligands bonded by the alkyl linker groups predicts the antiferromagnetic exchange in all studied compounds. The coordination of the pyridine molecules to the copper complexes is accompanied by a significant decrease in the strength of the exchange interactions. The adducts of the nickel complexes with

Table 1. Spin (S), total energies (E_{tot}), relative energies (ΔE), squared spin density (S^2), and exchange interaction constant (J) for complexes **I** (M = Cu; *x*Py) and **II** (M = Cu; Alk = C_2H_4, C_3H_6, C_4H_8; *x*Py) calculated by the DFT UB3LYP/6-31g(d,p) method

Structure	S	E_{tot}, au	ΔE, kcal/mol	S^2	J, cm^{-1}
I (M = Cu)	2/2	–4117.10049	0.0	2.0037	
BS	0	–4117.10399	–2.2	0.9339	–716
II (M = Cu; Alk = C_2H_4)	4/2	–8390.23625	0.0	6.0090	
BS1	2/2	–8390.24062	–2.7	2.9062	–309
BS2	0	–8390.24469	–5.2	1.8105	–455
II (M = Cu; Alk = C_3H_6)	4/2	–8468.83701	0.0	6.0000	
BS1	2/2	–8468.84123	–2.6	2.9093	–299
BS2	0	–8468.84545	–5.3	1.8095	–442
II (M = Cu; Alk = C_4H_8)	4/2	–8547.42805	0.0	6.0000	
BS1	2/2	–8547.43240	–2.7	2.9096	–309
BS2	0	–8547.43674	–5.5	1.8050	–455
I (M = Cu; 2Py)	2/2	–4613.39383	0.0	2.0038	
BS	0	–4613.39630	–1.5	0.9526	–516
II (M = Cu; Alk = C_2H_4; 4Py)	4/2	–9381.55297	0.0	6.0074	
BS1	2/2	–9381.55560	–1.7	2.9510	–189
BS2	0	–9381.55821	–3.3	1.8950	–280
II (M = Cu; Alk = C_3H_6; 4Py)	4/2	–9460.14015	0.0	6.0000	
BS1	2/2	–9460.14276	–1.6	2.9515	–187
BS2	0	–9460.14533	–3.2	1.8960	–277
II (M = Cu; Alk = C_4H_8; 4Py)	4/2	–9538.71170	0.0	6.0075	
BS1	2/2	–9538.71420	–1.6	2.9533	–179
BS2	0	–9538.71668	–3.1	1.8950	–265

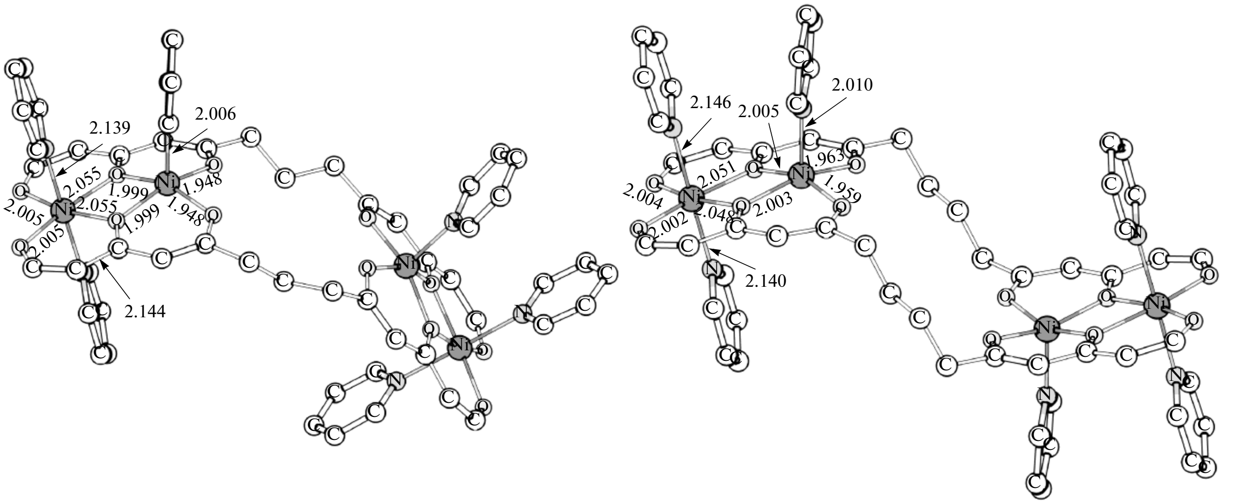
Table 2. Spin (S), total energies (E_{tot}), relative energies (ΔE), squared spin density (S_2), and exchange interaction constant (J) for complexes **I** (M = Ni; xPy) and **II** (M = Ni; Alk = C_2H_4, C_3H_6, C_4H_8; xPy) calculated by the DFT UB3LYP/6-31g(d,p) method

Structure	S	E_{tot}, au	ΔE, kcal/mol	S^2	J, cm^{-1}
I (M = Ni; 2Py)	4/2	–4349.17218	0.0	6.0105	
BS	0	–4349.17310	–0.6	1.9932	–51
II (M = Ni; Alk = C_2H_4; 4Py)	8/2	–8853.10855	0.0	20.0208	
BS1	4/2	–8853.10960	–0.7	8.0027	–19
BS2	0	–8853.11065	–1.3	3.9837	–29
II (M = Ni; Alk = C_3H_6; 4Py)	8/2	–8931.69476	0.0	20.0213	
BS1	4/2	–8931.69572	–0.6	8.0033	–18
BS2	0	–8931.69667	–1.2	3.9868	–26
II (M = Ni; Alk = C_4H_8; 4Py)	8/2	–9010.26815	0.0	20.0210	
BS1	4/2	–9010.26913	–0.6	8.0027	–18
BS2	0	–9010.27010	–1.2	3.9847	–27
I (M = Ni; 3Py)	4/2	–4597.31492	0.0	6.0101	
BS	0	–4597.31577	–0.5	1.9954	–46
II (M = Ni; Alk = C_2H_4; 6Py)	8/2	–9349.39247	0.0	20.0202	
BS1	4/2	–9349.39334	–0.6	8.0054	–16
BS2	0	–9349.39422	–1.1	3.9906	–24
II (M = Ni; Alk = C_3H_6; 6Py)	8/2	–9427.98010	0.0	20.0204	
BS1	4/2	–9427.98087	–0.5	8.0045	–14
BS2	0	–9427.98163	–1.0	3.9927	–21
II (M = Ni; Alk = C_4H_8; 6Py)	8/2	–9506.55246	0.0	20.0203	
BS1	4/2	–9506.55328	–0.5	8.0045	–15
BS2	0	–9506.55411	–1.0	3.992	–22



I (M = Ni; 3Py)

II (M = Ni; Alk = C_2H_4; 6Py)



II (M = Ni; Alk = C_3H_6; 6Py)

II (M = Ni; Alk = C_4H_8; 6Py)

Fig. 4. Geometric characteristics of structures **I** (M = Ni; 3Py) and **II** (M = Ni; Alk = C_2H_4, C_3H_6, C_4H_8; 6Py) calculated by the DFT UB3LYP/6-31g(d,p) method.

pyridine are characterized by weak (–21...–30 cm^{-1}) antiferromagnetic exchange interactions between the dimer fragments, which makes them appropriate candidates for the development of the element basis of quantum electronics devices.

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REFERENCES

1. Nielsen, M.A. and Chuang, I.L., *Quantum Computation and Quantum Information,* Cambridge: Cambridge Univ., 2000.
2. Timco, G.A., Carretta, S., Troiani, F., et al., *Nat. Nanotechnol.*, 2009, vol. 4, no. 3, p. 173.
3. Loss, D. and DiVincenzo, D.P., *Phys. Rev. A: At., Mol., Opt. Phys.*, 1998, vol. 57, no. 1, p. 120.
4. Stamp, P.C.E. and Gaita-Arino, A., *J. Mater. Chem.*, 2009, vol. 19, no. 12, p. 1718.
5. Troiani, F. and Affronte, M., *Chem. Soc. Rev.*, 2011, vol. 40, no. 6, p. 3119.

6. Aromí, G., Aguilà, D., Gamez, P., et al., *Chem. Soc. Rev.*, 2012, vol. 41, no. 2, p. 537.
7. Timco, G.A., Faust, T.B., Tuna, F., and Winpenny, R.E.P., *Chem. Soc. Rev.*, 2011, vol. 40, no. 6, p. 3067.
8. Faust, T.B., Tuna, F., Timco, G.A., et al., *Dalton Trans.*, 2012, vol. 41, no. 44, p. 13626.
9. Lintvedt, R.L., Borer, L.L., Murtha, D.P., et al., *Inorg. Chem.*, 1974, vol. 13, no. 1, p. 18.
10. Guthrie, J.W., Lintvedt, R.L., and Glick, M.D., *Inorg. Chem.*, 1980, vol. 19, no. 10, p. 2949.
11. Lintvedt, R.L. and Zehetmair, J.K., *Inorg. Chem.*, 1990, vol. 29, no. 12, p. 2204.
12. Aromí, G., Gamez, P., and Reedijk, J., *Coord. Chem. Rev.*, 2008, vol. 252, nos. 8–9, p. 964.
13. Lai, S.Y., Lin, T.W., Chen, Y.H., et al., *J. Am. Chem. Soc.*, 1999, vol. 121, no. 1, p. 250.
14. Liu, I.P.C., Benard, M., Hasanov, H., et al., *Chem.-Eur. J.*, 2007, vol. 13, no. 31, p. 8667.
15. Affronte, M., Casson, I., Evangelisti, M., et al., *Angew. Chem., Int. Ed. Engl.*, 2005, vol. 44, no. 40, p. 6496.
16. Barrios, L.A., Aguila, D., Roubeau, O., et al., *Chem.-Eur. J.*, 2009, vol. 15, no. 42, p. 11235.
17. Frisch, M.J., Trucks, G.W., Schlegel, H.B., et al., *GAUSSIAN 09. Revision D.01*, Wallingford: Gaussian Inc., 2013.
18. Kohn, W. and Sham, L.J., *Phys. Rev. A,* 1965, vol. 140, no. 4, p. A1133.
19. Starikov, A.G., *Russ. J. Gen. Chem.*, 2009, vol. 79, no. 12, p. 2792.
20. Starikov, A.G., Minyaev, R.M., and Minkin, V.I., *J. Mol. Struct.: THEOCHEM*, 2009, vol. 895, nos. 1–3, p. 138.
21. Noodleman, L., *J. Chem. Phys.*, 1981, vol. 74, no. 10, p. 5737.
22. Yamaguchi, K., Takahara, Y., Fueno, T., and Nasu, K., *Jpn. J. Appl. Phys.*, 1987, vol. 26, no. 8, p. L1362.
23. Yamaguchi, K., Okumura, M., Mori, W., et al., *Chem. Phys. Lett.,* 1993, vol. 210, nos. 1–3, p. 201.
24. Chemcraft: http://www.chemcraftprog.com
25. Boyd, P.D.W., Lee, K.S., and Zvagulis, M., *Aust. J. Chem.*, 1986, vol. 39, no. 8, p. 1249.
26. Starikov, A.G., Minyaev, R.M., Starikova, A.A., and Minkin, V.I., *Russ. J. Coord. Chem.*, 2010, vol. 36, no. 8, p. 597.
27. Barrios, L.A., Aguila, D., Mellat, S., et al., *C.R. Chim.*, 2008, vol. 11, no. 10, p. 1117.

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