

A computational study of structural and magnetic properties of bi- and trinuclear Cu(II) complexes with extremely long Cu---Cu distances

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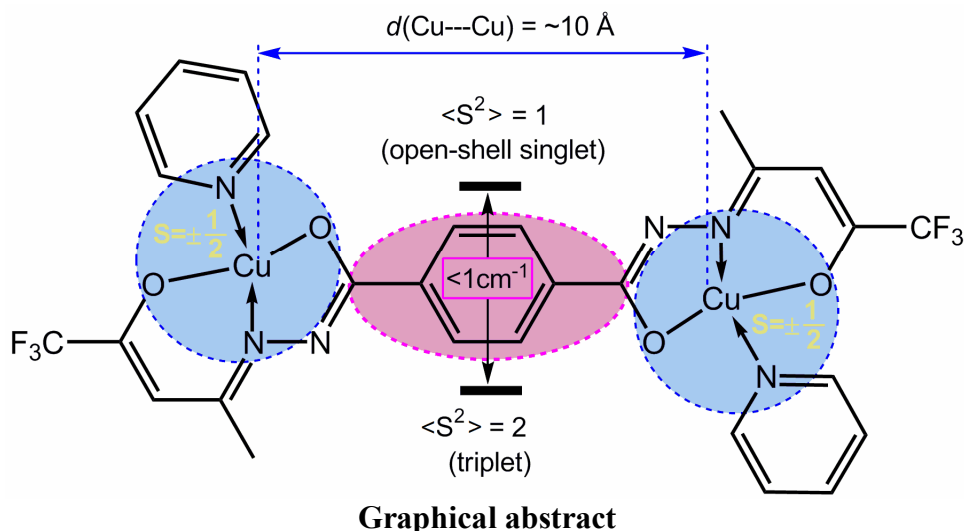
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Abstract

Three recently synthesized copper(II) complexes with aroylhydrazones of trifluoroacetic and benzenecarboxylic acids (*Dalton Trans.*, 2013, 42, 16878) have been computationally investigated by density functional theory within the broken symmetry approximation accounting for empirical dispersion corrections. A topological analysis of electron density distributions has been carried out using Bader's "quantum theory of atoms in molecules" formalism. The calculated values of spin-spin exchange for the studied dinuclear complexes indicate a very weak ferromagnetic coupling of the unpaired electrons in good agreement with experimental data. At the same time, the trinuclear copper(II) complex possesses a low-spin doublet ground state with one ferromagnetic and two antiferromagnetic spin projections between the triangular-positioned Cu²⁺ ions. The estimated values of the coupling constants for the spin-spin exchange in this trinuclear complex are in a qualitative agreement with experimental observations. The calculations support a mechanism of exchange coupling through the aromatic links in these strongly spin-separated systems.

Keywords: Cu(II) complexes, spin-spin exchange, ferromagnetic coupling, "broken symmetry" approximation, DFT calculations, Bader analysis, open-shell singlet.



1. Introduction

Polynuclear copper(II) complexes represent interesting objects for investigations of magnetic phenomena [1-5] due to the presence of one unpaired d-electron for each copper(II) center (electronic configuration of Cu^{2+} is $[\text{Ar}]3d^9$). Because of the strong localization of the unpaired d-electron around the copper(II) ion and the nearest surrounding one can formally separate these single-electron magnetic centers in space [1]. Spin-spin interaction between the magnetic electrons, i.e. between the corresponding singly-occupied molecular orbitals (so-called SOMOs), determines the type of coupling – ferromagnetic when the ground electronic state corresponds to the high-spin configuration with parallel orientation of electronic spins and antiferromagnetic when the ground electronic state is characterized by the low total spin with antiparallel orientation of the electronic spins [1, 2]. Nowadays, the most prevalent and well studied organometallic magnetic systems are dinuclear copper(II) complexes with different types of linkers between the ligand-coordinated magnetic centers (-Hal-, [6, 7], -OH-, [4, 6, 8, 9] -OR-, [10–13] CN-, [14] -N^N-, [8, 9, 15] -N^O- [16, 17] etc.). These complexes can demonstrate a variety of coupling types from strongly antiferromagnetic (exchange coupling constant J_{CuCu} is strongly negative up to -1000 cm^{-1}) [4-6] to moderately ferromagnetic (J_{CuCu} is positive, typically of order 100 cm^{-1}) [10, 18]. Herein the J_{CuCu} constant originates from the standard Heisenberg-Dirac-Van Vleck spin-Hamiltonian $\hat{H} = -J_{12}\hat{S}_1\hat{S}_2$, where \hat{S}_1 and \hat{S}_2 are local spin operators for each of the paramagnetic centers. At the same time, a lot of dinuclear copper complexes with strongly space-separated (6–10 Å) copper(II) ions [19-25] possess a very weak ferro-/antiferromagnetic character due to the very weak exchange between the magnetic SOMOs. These systems are interesting from a fundamental point of view since the nature of weak exchange interactions is a key topic of modern molecular spintronics [25]. Moreover, small values of J_{CuCu} are responsible for the general form of the detected EPR spectrum; when the absolute value of exchange coupling constant J is comparable with the hyper-fine structure (HFS) constant for the copper atom ($a_{\text{Cu}} \approx |J|$) the EPR result could not be correctly assigned without spectral simulation, while in the cases $a_{\text{Cu}} \gg |J|$ and $a_{\text{Cu}} \ll |J|$ the spectrum typically consist of four

and seven lines, respectively, with the distinctive intensity ratio of 1:1:1:1 and 1:2:3:4:3:2:1 and hyperfine splitting of \mathbf{a} and $\mathbf{a}/2$, respectively [19].

Trinuclear copper(II) magnetic complexes are not so widespread systems as the dinuclear complexes, but the theory of spin coupling between triangular-positioned paramagnetic centers is well developed [2, 26-31]. The spin Hamiltonian for a completely asymmetric trinuclear species can be written as $\hat{\mathbf{H}} = -(\mathbf{J}_{12}\hat{\mathbf{S}}_1\hat{\mathbf{S}}_2 + \mathbf{J}_{13}\hat{\mathbf{S}}_1\hat{\mathbf{S}}_3 + \mathbf{J}_{23}\hat{\mathbf{S}}_2\hat{\mathbf{S}}_3)$, where \mathbf{J}_{12} , \mathbf{J}_{13} and \mathbf{J}_{23} are exchange coupling constants for each pair of neighboring centers. Due to the multiconfigurational nature of the three-electron doublets, the individual spins ($S_1 = S_2 = S_3 = 1/2$) will result in two spin doublets (D1) $\left|\frac{1}{2}; 0\right\rangle$, (D2) $\left|\frac{1}{2}; 1\right\rangle$ and one spin quartet (Q) $\left|\frac{3}{2}; 1\right\rangle$ by the following energies [26, 28]:

$$E\left(\left|\frac{3}{2}; 1\right\rangle\right) = -\frac{(\mathbf{J}_{12} + \mathbf{J}_{13} + \mathbf{J}_{23})}{4}, \quad (1)$$

$$E\left(\left|\frac{1}{2}; 0\right\rangle\right) = \frac{(\mathbf{J}_{12} + \mathbf{J}_{13} + \mathbf{J}_{23})}{4} - \frac{(\mathbf{J}_{12}^2 + \mathbf{J}_{13}^2 + \mathbf{J}_{23}^2 - \mathbf{J}_{12}\mathbf{J}_{13} - \mathbf{J}_{12}\mathbf{J}_{23} - \mathbf{J}_{13}\mathbf{J}_{23})^{1/2}}{2}, \quad (2)$$

$$E\left(\left|\frac{1}{2}; 1\right\rangle\right) = \frac{(\mathbf{J}_{12} + \mathbf{J}_{13} + \mathbf{J}_{23})}{4} + \frac{(\mathbf{J}_{12}^2 + \mathbf{J}_{13}^2 + \mathbf{J}_{23}^2 - \mathbf{J}_{12}\mathbf{J}_{13} - \mathbf{J}_{12}\mathbf{J}_{23} - \mathbf{J}_{13}\mathbf{J}_{23})^{1/2}}{2}, \quad (3)$$

where each state is presented in the determinant form as eigenstates of two operators $|S_1 + S_2 + S_3; S_1 + S_3\rangle$. It is straightforward to show that for the asymmetric trinuclear case ($\mathbf{J}_{12} \neq \mathbf{J}_{13} \neq \mathbf{J}_{23}$) the D₁-D₂ and D₂-Q energy gaps are equal to:

$$\Delta_1(D_1-D_2) = -(\mathbf{J}_{12}^2 + \mathbf{J}_{13}^2 + \mathbf{J}_{23}^2 - \mathbf{J}_{12}\mathbf{J}_{13} - \mathbf{J}_{12}\mathbf{J}_{23} - \mathbf{J}_{13}\mathbf{J}_{23})^{1/2}, \quad (4)$$

$$\Delta_2(Q-D_2) = -\frac{(\mathbf{J}_{12} + \mathbf{J}_{13} + \mathbf{J}_{23} + \Delta_1)}{2}. \quad (5)$$

For the case of isosceles trinuclear species ($\mathbf{J}_{12} = \mathbf{J}_{13} \neq \mathbf{J}_{23}$) Eqns. (4)-(5) can be simplified as follows:

$$\Delta_1(D_1-D_2) = \mathbf{J}_{23} - \mathbf{J}_{12}, \quad (6)$$

$$\Delta_2(D_2-Q) = -\frac{(\mathbf{J}_{23} + 2\mathbf{J}_{12})}{2}. \quad (7)$$

As we can see from the above presented Eqns. (4)-(7) in both the cases $\mathbf{J}_{12} \neq \mathbf{J}_{13} \neq \mathbf{J}_{23}$ and $\mathbf{J}_{12} = \mathbf{J}_{13} \neq \mathbf{J}_{23}$, the D₁, D₂ and Q spin states are characterized by the non-zero energy splitting (Figure 1) which depends on three and two \mathbf{J}_{CuCu} coupling constants, respectively. The main problem in the case of the completely asymmetric trinuclear spin-orientation is that the \mathbf{J}_{12} , \mathbf{J}_{13} and \mathbf{J}_{23} coupling constants are strongly correlated and therefore the common least-square fitting procedure of the temperature (T) – magnetic susceptibility (χ) fails. It should be clarified that \mathbf{J}_{12} , \mathbf{J}_{13} and \mathbf{J}_{23} are not correlated in the statistical sense. Simply, there are only two independent energy differences between the ground state and two excited states, and they can be reproduced by infinite number of three-parameter sets

J_{12} , J_{13} and J_{23} . Due to this reason the experimentally observed $\chi(T)$ dependence is usually fitted through the Δ_1 and Δ_2 values by the modified Van Vleck expression [26]:

$$\chi = \frac{N\mu_B^2 g^2}{k(T+Q)} \times \frac{0.5 + 0.5 \exp(-\Delta_1/kT) + 5 \exp(-\Delta_2/kT)}{2 + 2 \exp(-\Delta_1/kT) + 4 \exp(-\Delta_2/kT)}, \quad (8)$$

where N is Avogadro's number, μ_B is the Bohr magneton, k is the Boltzmann constant and Q is a correction for possible intermolecular interaction defined by the own coupling constant J' (usually very small) and by the number of nearest neighbours.

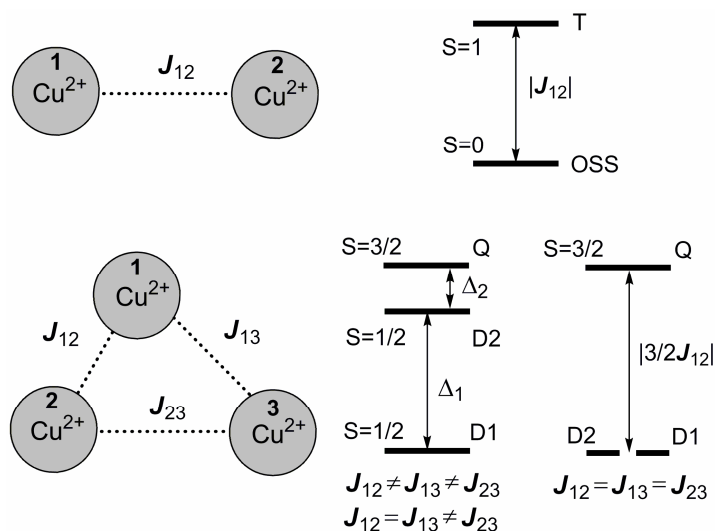


Figure 1. Schematic representation of magnetic exchange interactions for the dinuclear and triangular trinuclear Cu(II) complexes.

In the most simplified case of equilateral trinuclear complexes ($J_{12} = J_{13} = J_{23}$), Eqns. (4)-(5) can be reduced by the way that the doublet-doublet splitting Δ_1 disappears (i.e. D₁ and D₂ become strictly degenerate), while Δ_2 can be expressed *via* only one J_{CuCu} parameter (Figure 1) [29]:

$$\Delta(D_{1,2}-Q) = -\frac{3}{2} J_{12}, \quad (9)$$

that is quite similar for the singlet-triplet splitting in dinuclear complexes [32]:

$$\Delta(T - \text{OSS}) = -J_{12}, \quad (10)$$

where the OSS abbreviation corresponds to the open-shell singlet state configuration when each unpaired electron is localized on its own Cu-centered “magnetic” SOMO. Of course, such a state can not be correctly described within the common single-determinant DFT method. The usage of accurate *ab initio* MC SCF methods is also a very complicated task for real Cu(II) complexes due to limitations of the system size. An alternative is the so-called “Broken-Symmetry” (BS) approximation [32, 33] that has been widely used for investigations of magnetic properties of numerous organometallic systems at the DFT level of theory [4-6, 14, 24]. In the present work we have particularly focused on the magnetic properties of two dinuclear and one trinuclear Cu(II) complexes with aroylhydrazones of trifluoroacetic and benzenecarboxylic acids (Figure 2) with

extremely large space-separation of the paramagnetic centers (about 10 Å) [19]. Despite such a long Cu---Cu distance the studied complexes still demonstrate non-vanishing exchange coupling between space-separated unpaired electrons as has been detected by V. F. Shul'gin and coauthors by EPR spectroscopy and by $\chi(T)$ magnetic susceptibility measurements [19]. Unfortunately, an unambiguous explanation of the magnetic exchange mechanism for the studied and related systems is rather difficult and remains an open task for computational inorganic chemistry. In this work we have tried to solve this task within the BS-DFT approximation using Bader's "quantum theory of atoms in molecules" for comprehensively interpreting the electronic structure of the studied complexes.

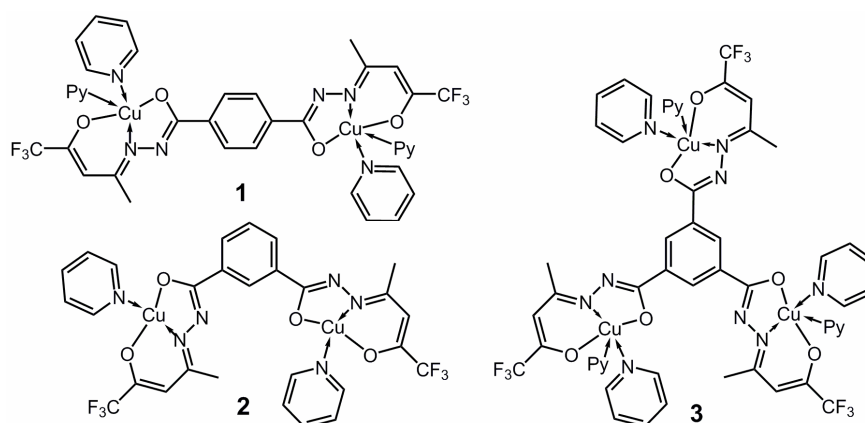


Figure 2. The structure of the Cu(II) complexes with aroylhydrazones of trifluoroacetic and isophthalic (**1**), terephthalic (**2**) and trimesic (**3**) acids.

2. Computational details

The BS-DFT calculations for the complexes **1-3** have been carried out for the non-stationary geometries extracted from the single-crystal X-ray data published in Ref. [19]. Checking the stability of the calculated high-spin (HS) and low-spin (BS) states indicates that all are internally stable. Such a simplification is very important for the direct comparison of the calculated and experimental J_{CuCu} values; even a small distortion of experimental geometry upon the optimization procedure could provide a dramatic impact on the exchange parameters (especially in the present case when J_{CuCu} values are less than 1 cm^{-1}).

We have used the common B3LYP [34, 35] hybrid exchange-correlation functional and the extended 6-311++G(3df,3pd) basis set [36–39] for the Cu(II) ions. For the rest of C, N, O and H atoms the 6-31G(d) basis set [40, 41] has been used. In order to take into account the long-range exchange interactions we have additionally used Grimme's D2 empirical dispersion correction [42] realized in the Gaussian09 package [43]. Such computational methodology has been successfully applied in our recent work for the related strongly space-separated Cu(II) complexes [24]. The plots of SOMOs and spin density isosurfaces has been simulated within the Chemissian software [44].

In order to estimate J_{CuCu} exchange parameter for the dinuclear complexes **1** and **2** the calculated energies of the HS and BS states have been subsequently implemented into the following expression of the spin-projected method proposed by Yamaguchi et. al. [45]:

$$J_{12} = \frac{2(E_{\text{BS}} - E_{\text{HS}})}{\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}}}, \quad (11)$$

where E_{HS} and E_{BS} are the total energies of HS and BS states, respectively, and $\langle S^2 \rangle_{\text{HS}}$ and $\langle S^2 \rangle_{\text{BS}}$ are the expectation values of the spin-squared operator for the corresponding triplet and OSS states. For estimation of the J_{CuCu} value in trinuclear complex **3** we have used the high-symmetry limit Eq. 8 taking into account that all Cu---Cu distances are almost equally long (about 9.5 Å). We also assume that the BS single determinant could be a correct solution for the doublet state of the trinuclear copper system [19].

The electronic peculiarities of the Cu(II) coordination polyhedra have been analyzed by means of an analysis of the electronic density distribution function within the above-mentioned Bader's "quantum theory of atoms in molecules" (QTAIM) method [46] using the AIMAll program package [47]. The energies of coordination and intramolecular hydrogen bonds (E_{bond}) have been estimated by the simple Espinosa-Molins-Lecomte relationship [48,49]:

$$E_{\text{bond}} = \frac{1}{2}v(\mathbf{r}), \quad (12)$$

where $v(\mathbf{r})$ is the potential energy density value in the corresponding bond critical point of the (3, -1) type [46].

3. Results and discussion

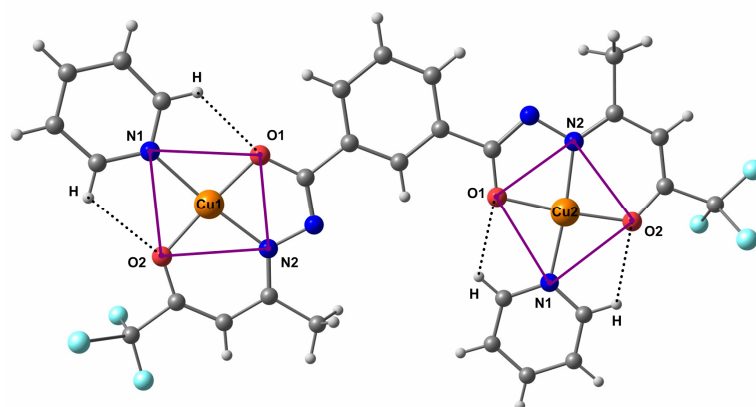
3.1. QTAIM analysis for complexes 1–3.

As one can be seen from Figure 3 all the studied complexes are characterized by different structures of the Cu(II) coordination polyhedra. In the case of the dinuclear complex **1** each of the Cu(II) centers is square coordinated by the [2O+2N] surrounding. The main ligand demonstrates a denticity equal to 6, while the other two positions are coordinated by the neutral pyridine (Py) ligand. The whole complex possesses an almost planar structure and even the σ -coupled Py ligands lie in the same plane due to the additional stabilization by the two CH---O_{1,2} hydrogen bonds with about 3.3 kcal mol⁻¹ per each hydrogen bond. As can be seen from Table 1, the structural and electronic parameters for the coordination polyhedra of complex **1** are not identical (there are clear differences in the Cu₁/Cu₂–O₁ and Cu₁/Cu₂–N₂ distances: 1.900Å vs. 1.917Å and 1.937Å vs. 1.919Å, respectively) that probably can be caused by the crystal packing effect due to the lopsided intercomplex stacking interactions [19].

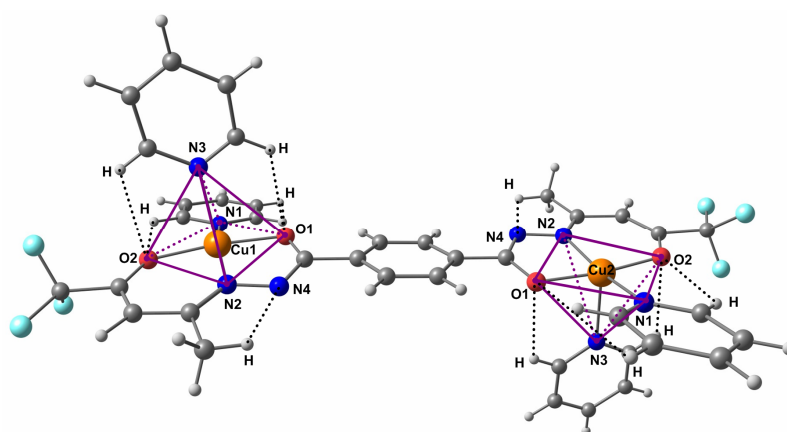
In contrast to complex **1**, both complexes **2** and **3** are characterized by square pyramidal pentacoordinated [2O+3N] Cu(II) polyhedra due to the positioning of the additional Py molecule in

the axial position relative to the [2O+2N] plane. Complex **2** possesses a strict centrosymmetric structure in accordance with the S_2 symmetry point group, so the structural and electronic features of the Cu₁/Cu₂ polyhedra are the same including also the stabilizing CH---O_{1,2} bonds (two bonds per one Py ligand analogously to complex **1**). The axial Py ligand is significantly more weakly coupled to the copper center comparing with the equatorial Py moiety: the Cu_{1,2}–N₃ distance is quite large (2.341 Å) comparing with the Cu_{1,2}–N₁ bond length (2.025 Å) that corresponds to a twice smaller covalence for the Cu_{1,2}–N₃ bonds (see DI values in Table 1). The energy of the axial Cu_{1,2}–N₃ bonds are also comparatively low with respect to the equatorial Cu_{1,2}–N₁ and Cu_{1,2}–N₂ bond energies.

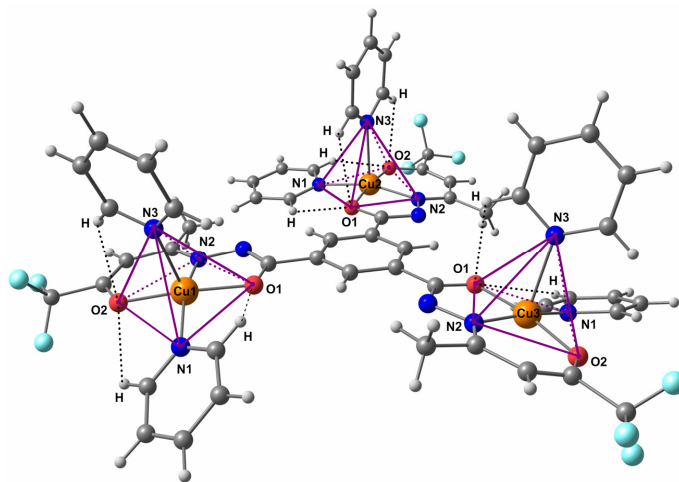
The trinuclear complex **3** demonstrates a similar square pyramidal coordination around the Cu(II) ions but now with the axial Cu_{1,2}–N₃ bonds being unequal for each Cu₁, Cu₂, and Cu₃ center (Table 3). As a result the axial Py ligand is less strongly coupled with Cu₃ center comparing with Cu₁ and Cu₂ ones, taking into account also the CH---O_{1,2} stabilizing contribution (Table S1, Figure 3).



1



2



3

Figure 3. Structure of the complexes **1–3** in accordance with X-ray data and QTAIM analysis.

In terms of the QTAIM formalism [46], all the coordination Cu–N and Cu–O bonds should be assigned to the intermediate type interactions that are characterized by positive values of the electron density Laplacian $\nabla^2\rho(\mathbf{r})$ and the negative electron energy density $h_e(\mathbf{r})$ values. From one aspect, the positive $\nabla^2\rho(\mathbf{r})$ values indicate outflow of electron density from interatomic space into the atomic basins, but from another aspect the negative $h_e(\mathbf{r})$ values denote the prevailing potential energy density $v(\mathbf{r})$ over the kinetic energy density $g(\mathbf{r})$ in the corresponding critical point. Both these aspects specify the coordination bonds as intermediate type interactions between the covalent (shared) and non-covalent (closed-shell) bonds. The moderate DI values additionally approve this statement. Another important characteristic of the coordination bonds in the studied complexes is the extremely small ellipticity (ε) of the order of 10^{-2} - 10^{-3} . It means that the curvature elements of the electronic density in the corresponding critical point are well balanced and that the coordination bonds only slightly deviate from the cylindrical symmetry that additionally indicates the dynamic stability of these bonds.

Table 1. Topological characteristics of the Cu–O and Cu–N coordination bonds calculated by the QTAIM method for the triplet state of complexes **1-3**.

Bond	d_{exp} , Å	$\rho(\mathbf{r})$, $e \cdot a_0^{-3}$ *	$v(\mathbf{r})$, a.u.	$g(\mathbf{r})$, a.u.	$h_e(\mathbf{r})$, a.u.	$\nabla^2\rho(\mathbf{r})$, $e \cdot a_0^{-5}$	E kcal/mol	ε	DI
Complex 1 (iso)									
Cu ₁ –O ₁	1.900	0.1021	-0.1828	0.1491	-0.0337	0.4617	-57.4	0.019	0.530
Cu ₂ –O ₁	1.917	0.0981	-0.1729	0.1405	-0.0325	0.4319	-54.3	0.017	0.515
Cu ₁ –O ₂	1.891	0.1010	-0.1857	0.1541	-0.0315	0.4905	-58.3	0.002	0.518
Cu ₂ –O ₂	1.898	0.0998	-0.1815	0.1501	-0.0315	0.4745	-57.0	0.001	0.520
Cu ₁ –N ₁	2.006	0.0875	-0.1447	0.1104	-0.0343	0.3043	-45.4	0.013	0.454
Cu ₂ –N ₁	2.008	0.0871	-0.1436	0.1096	-0.0340	0.3027	-45.1	0.012	0.454
Cu ₁ –N ₂	1.937	0.1059	-0.1796	0.1340	-0.0456	0.3535	-56.4	0.034	0.550
Cu ₂ –N ₂	1.919	0.1099	-0.1899	0.1423	-0.0476	0.3787	-59.6	0.034	0.563
Complex 2 (tere)									
Cu _{1,2} –O ₁	1.938	0.0925	-0.1606	0.1305	-0.0301	0.4017	-50.4	0.019	0.465
Cu _{1,2} –O ₂	1.919	0.0941	-0.1680	0.1388	-0.0292	0.4381	-52.7	0.011	0.473
Cu _{1,2} –N ₁	2.025	0.0832	-0.1364	0.1044	-0.0319	0.2901	-42.8	0.022	0.423

Cu _{1,2} -N ₂	1.950	0.1019	-0.1729	0.1299	-0.0430	0.3476	-54.2	0.039	0.516
Cu _{1,2} -N ₃	2.341	0.0422	-0.0501	0.0448	-0.0053	0.1578	-15.7	0.055	0.215
Complex 3 (tri)									
Cu ₁ -O ₁	1.951	0.0902	-0.1533	0.1237	-0.0297	0.3760	-48.1	0.022	0.470
Cu ₂ -O ₁	1.928	0.0946	-0.1659	0.1352	-0.0307	0.4179	-52.0	0.011	0.469
Cu ₃ -O ₁	1.932	0.0937	-0.1636	0.1331	-0.0305	0.4105	-51.3	0.015	0.466
Cu ₁ -O ₂	1.927	0.0925	-0.1638	0.1347	-0.0291	0.4225	-51.4	0.018	0.460
Cu ₂ -O ₂	1.915	0.0953	-0.1704	0.1407	-0.0297	0.4440	-53.5	0.013	0.483
Cu ₃ -O ₂	1.921	0.0939	-0.1670	0.1376	-0.0293	0.4332	-52.4	0.006	0.482
Cu ₁ -N ₁	2.019	0.0842	-0.1389	0.1064	-0.0325	0.2959	-43.6	0.039	0.421
Cu ₂ -N ₁	2.040	0.0806	-0.1299	0.0994	-0.0305	0.2755	-40.7	0.018	0.414
Cu ₃ -N ₁	2.054	0.0778	-0.1234	0.0946	-0.0288	0.2634	-38.7	0.043	0.404
Cu ₁ -N ₂	1.936	0.1048	-0.1809	0.1366	-0.0443	0.3692	-56.8	0.041	0.523
Cu ₂ -N ₂	1.943	0.1030	-0.1766	0.1332	-0.0434	0.3590	-55.4	0.035	0.513
Cu ₃ -N ₂	1.947	0.1025	-0.1742	0.1309	-0.0433	0.3500	-54.7	0.034	0.514
Cu ₁ -N ₃	2.282	0.0479	-0.0614	0.0527	-0.0087	0.1760	-19.3	0.047	0.240
Cu ₂ -N ₃	2.306	0.0455	-0.0562	0.0491	-0.0071	0.1681	-17.6	0.049	0.226
Cu ₃ -N ₃	2.349	0.0415	-0.0489	0.0440	-0.0049	0.1564	-15.3	0.041	0.211

The binding energy per one coordination center is almost equivalent for the complexes **1-3** and equals about 220 kcal mol⁻¹. This fact is in a qualitative agreement with the thermal analysis (TGA) data [19] that indicate high thermal stability of the complexes up to 250 °C. The Py-Cu bonds are comparatively weaker than the other Cu-O and Cu-N bonds (Table 1), and therefore an increase of temperature before 250 °C leads to the removal of the pyridine molecules. The next gradual rising of temperature up to 600 °C leads to an oxidative decomposition of the organic ligands and finally to a complete degradation of the complexes [19].

3.1. Magnetic properties of the dinuclear complexes **1** and **2**.

As can be seen from Figure 2 both complexes **1** and **2** formally are isomeric except the additional axially-coordinated pyridine ligand in complex **2**. The distance between the Cu(II) ions for complexes **1** and **2** equals 9.56 and 10.94 Å as determined by X-ray crystallography studies [19]. Thus, it is not surprising that both complexes demonstrate a similar ferromagnetic coupling behavior with almost the same experimental exchange coupling values (Table 2). Our calculations reproduce well the experimental values and also the tendency that J_{CuCu} for complex **1** is slightly smaller than for complex **2**. In order to explain the mechanism of exchange interactions for the studied dicuclear complexes we have constructed spin densities and magnetic SOMOs plots (Figure 4) with a subsequent analysis of SOMOs decomposition coefficients.

Table 2. Comparison between the calculated and experimentally estimated exchange coupling constants J_{CuCu} for the complexes **1-3**.

Complex	$\langle S^2 \rangle_{\text{HS}}$	$\langle S^2 \rangle_{\text{BS}}$	J, cm^{-1}	$J_{\text{exp}}, \text{cm}^{-1}$
1	2.005888	1.005876	0.11	0.33
2	2.005731	1.005716	0.26	0.37
3	3.758796	1.758780	-0.08	-0.33

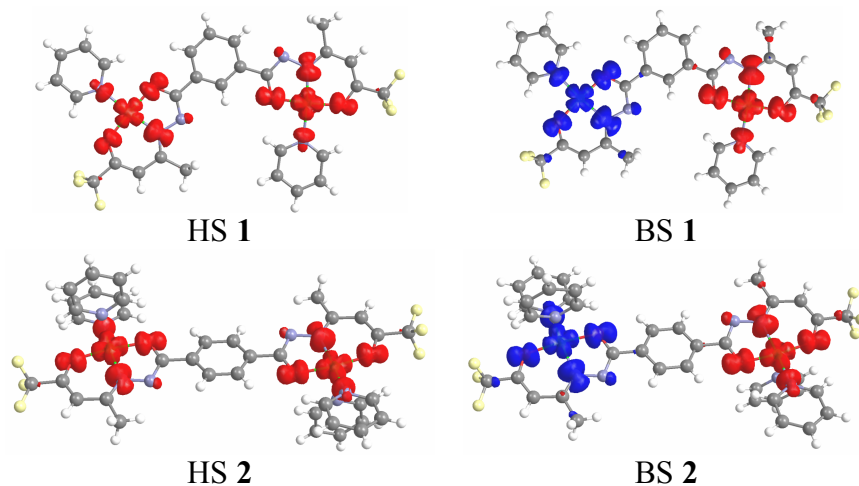


Figure 4. Spin density plots for the HS and BS states of the dinuclear complexes **1** and **2**.

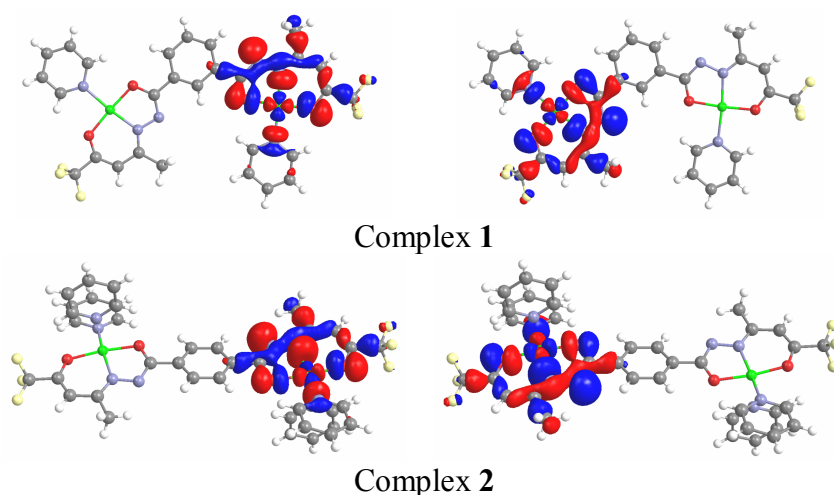


Figure 5. Magnetic SOMOs plots for the dinuclear complexes **1** and **2** that are occupied by two “parallel” α -spins for the HS state and “opposite” α/β -spins for the BS state.

Comparing Figures 4 and 5 one can stress that spin density plots for both complexes **1** and **2** could be understood as the squared SOMO wave functions which correspond to σ -type orbitals. The main contributions to the SOMOs (and spin density patterns, respectively) are provided by the $d_{x^2-y^2}$ orbital on the copper(II) center and the p_x, p_y orbitals on the neighboring N and O atoms (x and y axes oriented along $O_1\text{-Cu-O}_2$ and $N_1\text{-Cu-N}_2$ lines, respectively; z axis oriented in axial direction relative to Cu(II) center). It is important to note that the axially coordinated Py ligand in complex **2** does not provide any contribution to the magnetic SOMO wave functions and spin density plots. It proves the solely coordinative role of this Py ligand which is also the reason that the J_{CuCu} coupling constant is insensitive to the presence/absence of the axial Py ligand as established experimentally (Table 2). A detailed analysis of the decomposition coefficients clearly shows that both SOMOs for each complex have non-zero coefficients on the common atoms of the linker moiety. The absolute values of these coefficients (C) are of the order of 10^{-2} (and even 10^{-1} in some

cases) and correspond to the atomic ns ($n = 1-3$) and np ($n = 2, 3$) atomic orbital contributions. In the simple INDO approximation [50], the exchange integrals between the magnetic SOMOs could be proportional to the product of C^4 ($10^{-7}-10^{-6}$) and Coulomb integrals for the s and p electrons of carbon atom (10^5 cm^{-1} order). The resulting value of exchange integrals between σ -SOMOs orbitals could be of $10^{-2}-10^{-1} \text{ cm}^{-1}$ that is in qualitative agreement with calculated and experimental data (Table 1). Actually, magnetic SOMOs are sufficiently delocalized to provide a very small but non-zero overlapping area on the linker. In the case of complex **1** the magnetic orbitals are mutually rotated about 120° relative to the inner linker moiety, that means they are side-to-side overlapping in contrast to complex **2** for which head-to-head overlapping occurs. The latter case is more spatially preferable and therefore J_{CuCu} for complex **2** is two times higher than for complex **1** despite its longer Cu---Cu distance (10.94 Å vs. 9.56 for complex **1**).

3.2. Magnetic properties of the trinuclear complex **3**

In contrast to the dinuclear complexes **1** and **2**, the trinuclear complex **3** demonstrates a spin-frustrated low-spin doublet ground state ($J_{\text{CuCu}} < 0$) in accordance with experimental measurements [19] and BS-DFT simulations. In our calculations we accepted the simplification that the three Cu(II) ions are positioned in equilateral triangular form, which makes it irrelevant for which copper(II) center the spin is inverted in the simulation of the BS state. The HS quartet state corresponds to the ferromagnetically coupled configuration with the same spin projections for each unpaired electron. Of course, we have checked each possible configuration for the BS state ($\text{Cu}_1(\uparrow)\text{-Cu}_2(\downarrow)\text{-Cu}_3(\uparrow)$, $\text{Cu}_1(\uparrow)\text{-Cu}_2(\uparrow)\text{-Cu}_3(\downarrow)$ and $\text{Cu}_1(\downarrow)\text{-Cu}_2(\uparrow)\text{-Cu}_3(\uparrow)$) - their energies were found to be practically equivalent. Moreover, it is formally incorrect to describe the BS state by each of the above proposed configurations because the two possible doublet states (D_1 and D_2 , Figure 1) originate from the combination of these configurations in order to become eigenfunctions of the \hat{S}^2 operator [29]. The calculated spin density plots and the SOMO isosurfaces for the quartet (HS) and doublet (BS) states are presented in Figures 6 and 7. As can be seen from these figures, they are closely similar to the corresponding Figures 4 and 5 for the dinuclear species. In the ferromagnetic high-spin Q state each electron stills delocalizes over its own Cu center ($d_{x^2-y^2}$ orbital) and neighbouring N, O atoms (p_x and p_y orbitals, Figure 6). For the doublet BS state the spin distribution pattern is exactly the same except for the opposite sign for one of the unpaired spins.

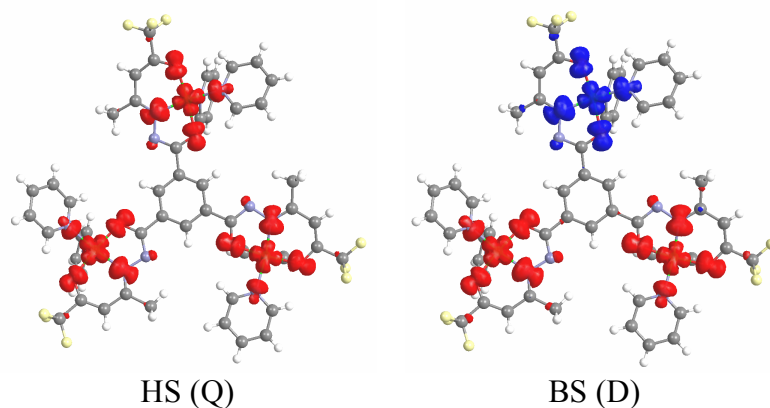


Figure 6. Spin density plots for the quartet (HS) and doublet (BS) states of trinuclear complex **3**.

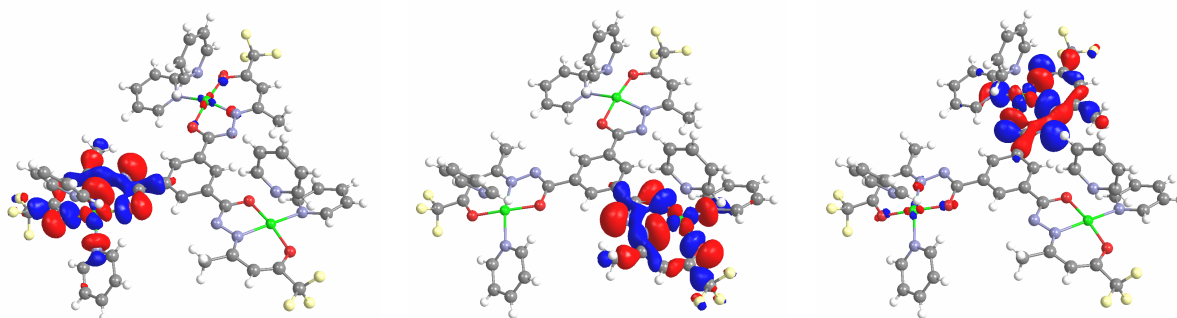


Figure 6. Magnetic SOMOs plots for the trinuclear complex **3** that is occupied by three “parallel” α -spins for the HS quartet state and by $2\alpha+\beta$ -spins for the BS doublet state.

Assuming that the HS quartet and BS doublet states can be expressed by a single determinant representation the J_{CuCu} value estimated by Eqn. 9 has found to be equal -0.08 cm^{-1} in good agreement with experimental data (-0.33 cm^{-1}) [19]. Similarly to complex **1**, the SOMO orbitals for complex **3** are mutually rotated (Figure 6) relative to the linker benzene core. Due to this circumstance the long-range exchange interaction in the xy plane should be rather small with inefficient side-to-side overlap. Finally, we should note that accounting for empirical dispersion in our computations is extremely important because of the diffuse nature of the exchange interactions. Actually, the more accurately we can account for the long-range exchange interactions the more reliable agreement with experiment is achieved. In our recent publication [24] we have shown that OSS and triplet states of weakly coupled dinuclear Cu(II) complexes become strictly degenerate if we exclude empirical dispersion corrections from our computational scheme.

4. Conclusion

In this work we have presented a quantum-chemical simulation of electronic and magnetic properties for the recently synthesized di- and trinuclear complexes of copper(II) with aroylhydrazones of trifluoroacetic and benzenecarboxylic acids [19]. These complexes are characterized by extremely long intramolecular Cu---Cu distances, of about $9.5 - 11 \text{ \AA}$, and very weak exchange coupling between the paramagnetic centers (ferromagnetic coupling for the studied dinuclear species and antiferromagnetic coupling for the trinuclear complex). The most likely

exchange mechanism between the space-separated magnetic orbitals refers to a non-zero, but very small and diffuse, overlap inside the aromatic spacer. Actually, the calculated singly-occupied molecular orbital (SOMO) wave functions are sufficiently delocalized to produce the observed weak exchange interactions through the aromatic linker.

A Bader analysis of the electronic density distribution function for the studied systems indicates that the square-planar coordination of Cu(II) ions are most preferable and stable while the the additional axially-coordinated Py ligand in complexes **2** and **3** is only weakly coupled to the Cu(II) ion and can be easily removed by heating. This ligand does not affect the magnetic behaviour of the studied systems. The conformational orientation of the axial and equatorial Py ligands is only slightly stabilized by the series of CH---O bonds.

The present study could be useful for the explanation of magnetic properties for structurally similar “spacer-armed” polynuclear Copper(II) complexes, like those presented in Refs. [20-23]. We also plan to extend our studies for more complicated systems of tetranuclear Cu(II) complexes, particularly for complexes with porphyrin and tetraoxa[8]circulene sheets as the macrocyclic polydentate ligands [51-53].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemphys.XXXX.XX.XXX>.

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