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Crystal structure and nontrivial magnetic properties of Cu^{II} binuclear complex based on 4-methyl-2,6-bis{[2-(4,6-dimethylpyrimidin-2-yl)hydrazono]methyl}phenol

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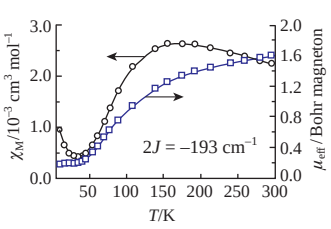
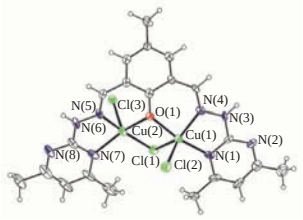
The new complex $[Cu_2(H_2L)Cl_3]$ with axial chloride ions coordination based on 4-methyl-2,6-bis{[2-(4,6-dimethylpyrimidin-2-yl)hydrazono]methyl}phenol was obtained and its crystal structure was determined. Magnetic studies revealed the presence of antiferromagnetic exchange interaction of –193 cm^{-1} that is extremely high for such type of complexes. The quantum chemical calculation of 2*J* value has perfectly matched an experiment.

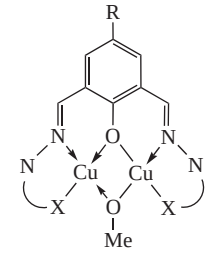




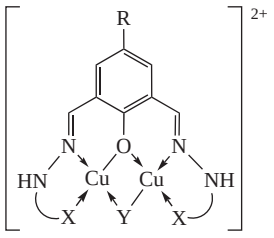
The studies of homo- and heteropolynuclear complexes are important areas in coordination chemistry[1] due to their wide applications for technology and pharmacology,[2] as well as for the development of new single molecule magnets.[3]

The design of ligand systems, which are capable of binding metal sites in well-defined arrays and placing them in a close proximity to facilitate effective magnetic communication, led to fundamental studies in the field of magnetochemistry.[4]

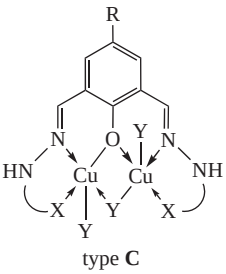
In this context, the polytopic hydrazone-based ligands are of importance owing to their design attributes and power of self-assembly, which account for their candidature in the synthesis of polymetallic systems and nanosized supramolecular objects.[5] Some data on transition metal complexes with the 2,6-diformyl-4-R-phenol bis-hetarylhydrazone ligands, including hydrazinopyridine, quinoline, benzimidazole derivatives, and their analogues, have been published.[6]



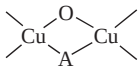
type **A**



type **B**



type **C**



exchange fragment

A = O, Cl

X = O, N, S

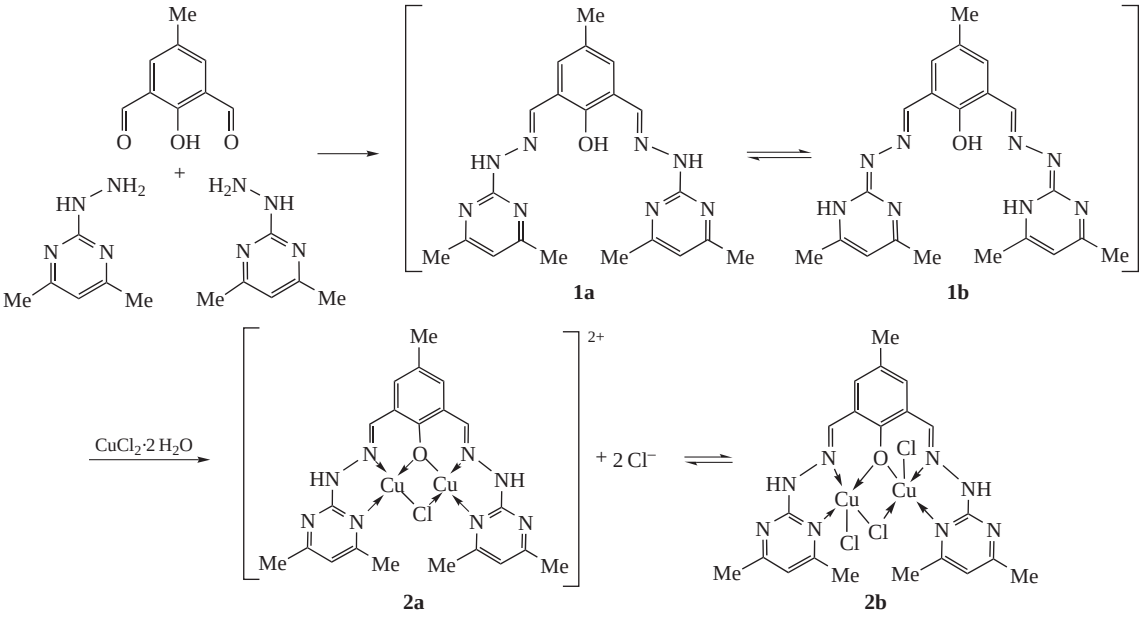
Y = Hal, OMe

The Cu^{II} ion possesses $S = 1/2$ spin and provides the simplest model for magneto-structural correlation. The complexes with 2,6-diformyl-4-R-phenol bis-hydrazone ligands can be related to three types owing to large differences in their magnetic properties. The first group includes binuclear complexes produced from copper(II) acetate (type **A**), while two others are formed by copper(II) halogenates, nitrate, and perchlorate (types **B** and **C**). Structure **A** implies essential overlap of copper(II) magnetic orbitals, which results in a fairly strong antiferromagnetic exchange interaction (the exchange parameter –2*J* varies from 300 to 1000 cm^{-1}). In the case of complexes **B**, there are medium values of exchange antiferromagnetic interaction (–2*J* = 200–500 cm^{-1}) and rather small ones in complexes **C** (–2*J* < 140 cm^{-1}) causing the distortion of exchange fragment.[7]

In this work, bis-hetarylhydrazone ligand (H_3L) was prepared in 49% yield *via* the reaction between 2,6-diformyl-4-methylphenol and 2-hydrazino-4,6-dimethylpyrimidine (Scheme 1).†

Such hydrazine derivatives are known as frequently revealing a tautomeric equilibrium.[8] In particular, the co-existence of two hydrazone **1a** and azine **1b** tautomeric forms is caused by the prototropic tautomerism, which often occurs in hetarylhydrazone compounds.[3(a)] According to the quantum chemical calculations of both spatial and electronic structures, hydrazone tautomeric form **1a** is the more preferred one. The stabilization energies relative to azine form **1b** are 16.63 and 25.18 kcal mol^{-1} for an isolated molecule and in ethanol solution, respectively. Two downfield signals in the ^1H NMR spectra at 11.2 ppm corre-

† See Online Supplementary Materials for the experimental details and characterization.



Scheme 1 Synthetic route to bis-hetarylhydrazone **1** including its tautomeric equilibrium and Cu^{II} complex **2** with possible types of chloride ions coordination, *viz.* out-of-sphere **2a** and intra-sphere **2b** ones.

sponding to amino N–H groups imply the existence of tautomer **1a**. The good match between calculated and experimental data in IR spectra was obtained for tautomeric form **1a** (Table S6, see Online Supplementary Materials).

Bis-hetarylhydrazone H_3L was crystallized from ethanol as hydrazone tautomeric alcoholate. The molecular structure of bis-hetarylhydrazone **1** is shown in Figure 1(*a*) (Table S7, Online Supplementary Materials).‡ Both experimental and theoretical data confirmed that hydrazone form **1a** exists in a crystalline phase as well as in solution.

The reaction of bis-hetarylhydrazone **1** with $CuCl_2 \cdot 2H_2O$ resulted in formation of binuclear Cu^{II} complex **2** (see Scheme 1). The behavior of monodeprotonated ligand and coordination of Cu^{II} ions *via* the phenoxide oxygen atom as well as azomethine and heterocyclic nitrogen atoms were proved by disappearance of ν(OH) (phenolic) stretching vibration and by a 5–10 cm^{-1} shift of ν(C=N) stretching vibration of azomethene and heterocyclic fragments in the IR spectrum.

Single crystals of complex **2** suitable for X-ray diffraction analysis were grown from a methanol solution. The compound crystallized in $P2_1/n$ space group in the monoclinic crystal system [Figure 1(*b*), Table S8]. According to the X-ray data, the complex possesses a composition of $[Cu_2(H_2L)Cl_3] \cdot 0.3H_2O$. The bis-hetarylhydrazone ligand is coordinated in the monodeprotonated hydrazone tautomeric form. The coordination polyhedra of copper atoms differ significantly. The Cu(1) atom exhibits a distorted trigonal bipyramidal geometry with a Cl_2N_2O ligand environment. The equatorial positions are occupied by bridging chloride ion Cl(1), azomethine atom N(4), and chloride ion Cl(2). The equatorial coordination positions are occupied by bridging phenoxide atom O(1) and pyrimidine nitrogen atom N(1). Cu(1) atom deviates from the Cl(1)Cl(2)N(4) plane by 0.075 Å towards the pyrimidine nitrogen atom N(1). The coordination polyhedron of Cu(2) atom with the same donor atoms set is a highly distorted square pyramid. The equatorial positions are occupied by bridging phenoxide atom O(1), bridging chloride ion Cl(1), azomethine N(5) and pyrimidine N(7) nitrogen atoms. The apical coordination place is occupied by chloride ion Cl(3). Furthermore, the bridging phenoxide atom O(1) is significantly deviated (by 0.714 Å) from the average plane going through the Cu(2) and others equatorial donor centers. The five-membered metal-chelate cycle Cu(1)N(1)

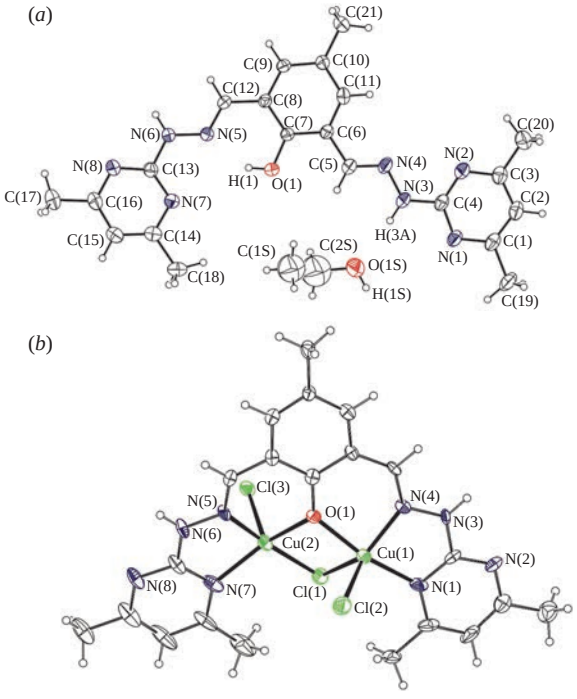


Figure 1 Molecular structure of (*a*) bis-hetarylhydrazone **1** and (*b*) complex **2** (thermal ellipsoids are shown at the 30% probability level).

‡ *Crystal data for* **1**: $C_{23}H_{30}N_8O_2$, M = 450.55, monoclinic, space group $P2_1/n$, a = 17.308(2), b = 8.2354(12) and c = 17.646(3) Å, β = 106.462(3)°, V = 2412.1(6) Å^3, Z = 4, d_{calc} = 1.241 g cm^{-3}, F(000) = 960, μ = = 0.084 mm^{-1}, T = 296 K, 1.45 ⩽ θ ⩽ 26.76, 14686 reflections measured, 4993 independent reflections (R_{int} = 0.0822), R_1 = 0.0719, wR_2 = 0.1747 [$I > 2\sigma(I)$]; R_1 = 0.1656, wR_2 = 0.2209 (for all data), GOF = 1.001, largest diff. peak/hole 0.594/–0.425 e Å^{-3}.

Crystal data for **2**: $C_{21}H_{23.6}Cl_3Cu_2N_8O_{1.3}$, M = 642.31, monoclinic, space group $P2_1/n$, a = 11.230(4), b = 20.912(7) and c = 11.507(4) Å, β = 98.372(5)°, V = 2673.5(15) Å^3, Z = 4, d_{calc} = 1.596 g cm^{-3}, F(000) = = 1300, μ = 1.922 mm^{-1}, T = 120 K, 1.948 ⩽ θ ⩽ 20.406, 13205 reflections measured, 2645 independent reflections (R_{int} = 0.1533), R_1 = 0.0507, wR_2 = 0.0996 [$I > 2\sigma(I)$]; R_1 = 0.1172, wR_2 = 0.1254 (all data), GOF = 0.998, largest diff. peak/hole 0.504/–0.376 eÅ^{-3}.

CCDC 1845761 and 1845762 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

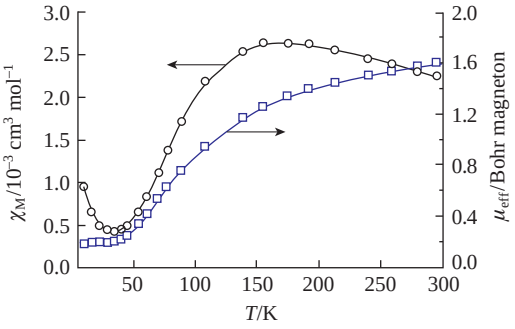


Figure 2 Temperature dependences of χ_m (○) and μ_{eff} (□) per Cu ion for complex **2** (the solid line represents the best fit of the experimental data).

C(4)N(3)N(4) is almost planar. Another five-membered metal-chelate cycle Cu(2)N(5)N(6)C(13)N(7) possesses 'envelope' conformation with the deviation of Cu(2) atom from the average plane of another four atoms by 0.754 Å.

Magnetic measurements for complex **2** revealed the antiferromagnetic exchange interaction with 2*J* value equals to –193 cm^{-1}. Plots of χ_m *vs.* *T* and μ_{eff} *vs.* *T* are shown in Figure 2. Magnetic susceptibility data were fitted by using a modified Bleaney–Bowers equation (see Online Supplementary Materials) with the isotropic spin Hamiltonian $\hat{H} = 2J\hat{S}_2\hat{S}_2$. The best-fit parameters are listed in Table S4.

The value μ_{eff} for complex **2** at room temperature is 1.59 BM (BM is a Bohr magneton). Upon cooling, it goes down to a value of 0.18 BM at 10 K (see Figure 2). The temperature dependence of χ_m *vs.* *T* revealed a steady increase in χ_m upon cooling to approximately 175 K followed by a broad maximum and a subsequent decrease upon cooling down to 35 K. A moderate increase in χ_m in the limiting low temperature region (below 35 K), suggests the presence of small amount of paramagnetic impurity (see Table S4).

The exchange parameter of complex **2** exhibited rather unusual character. The comparison of values 2*J* for complex **2** and similar copper(II) metallochelates[6] showed that the closest value can be attributed to $[Cu_2(H_2L\text{-}R^d)Cl]\cdot 2Cl$ complex based on bis(8-quinolylhydrazone) with out-of-sphere coordination of chlorine atom (see Table S5).

To understand the influence of halogen ions coordination on values 2*J*, DFT-BS calculations were performed for two types of complex **2** structures (**2a** and **2b**). Although the X-ray data for complex **2** revealed the tetragonal pyramidal surroundings of copper ions (structure **2b**), we decided to consider the square-planar structure of coordination polyhedron (structure **2a**). The spatial views, total energies of states, and calculated values 2*J* of complexes **2a** and **2b** are shown in Figure 3.

The exchange fragment can be approximated as a quadrangle or rhombus. The geometrical parameters obtained from DFT calculation for complex **2b** are consistent with the X-ray data (Table S8). The maximal deviation of bond lengths does not exceed 5%, and for the valence angles, exerting the important influence upon exchange interaction, the accuracy is about 90%. The BS state is the lowest energy state for complexes **2a** and **2b**. The triplet state is characterized by the larger energy corresponding to antiferromagnetic exchange interaction. There is no deviation of exchange fragment from the plane in both structures **2a** and **2b** (0.08° and 0.433°, respectively). The values of Cu(1)–O(1)–Cu(2) and Cu(1)–X(1)–Cu(2) angles being most significant for propagation of exchange interaction between copper ions are 106.58° and 88.842° (**2a**), 113.32° and 83.11° (**2b**), respectively.

To the best of our knowledge, it is the first example of atypically strong exchange coupling in binuclear copper(II) complexes with similar ligands. The adequacy of our quantum-

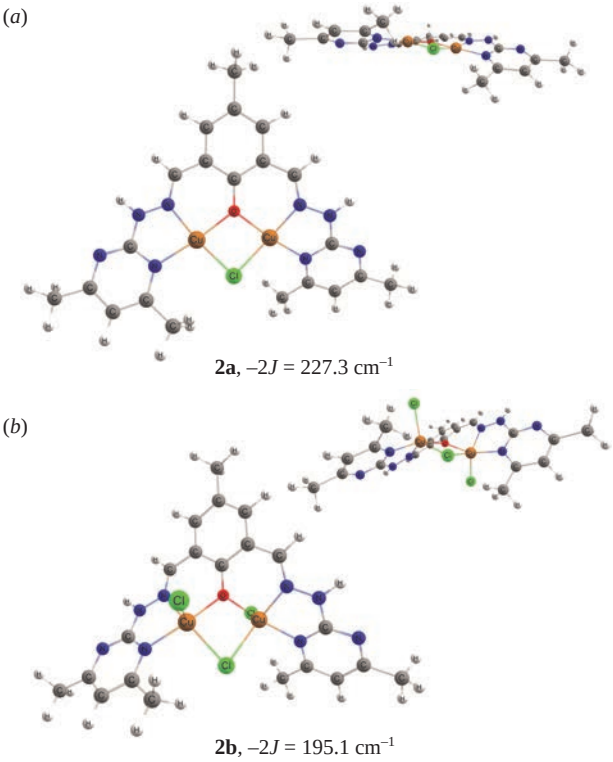


Figure 3 Optimized structures of complex **2** with different types of chloride ions coordination, *viz.* (*a*) out-of-sphere (**2a**) and (*b*) intra-sphere (**2b**) ones.

chemical approach to the interpretation of magnetic properties of such exchange coupled system is supported by the excellent agreement between the theoretical (–195.1 cm^{-1}) and experimental (–193 cm^{-1}) 2*J* values. This is a significant conclusion of our work, since these results demonstrate the successful theoretical treatment of strong antiferromagnetic exchange in copper(II) binuclear complexes with ligands of such a type and axially coordinated chlorine atoms.

Moreover, it is noteworthy that the main difference between complex **2** and known[6(c)] $[Cu_2(H_2L\text{-}R^d)Cl]\cdot 2Cl$ complex is the out-of-sphere halogen atom coordination. However, the bond between copper atoms and axially coordinated chloride ions is not strong enough. The conductivity measurements (molar concentration of complex $C_m = 10^{-3}$ M, $\lambda = 122\ \Omega^{-1}\ cm^2\ mol^{-1}$) revealed that complex **2** behaved as 1:2 electrolyte in DMF solution, indicating the dissociation (see Scheme 1).

In conclusion, we have successfully prepared binuclear Cu^{II} complex with unprecedented chlorine ion coordination and non-trivial magnetic behavior, *i.e.* unusually strong antiferromagnetic interactions between paramagnetic Cu^{II} centers. The DFT-BS calculations revealed the excellent agreement between theoretical and experimental 2*J* values, which validates the adequacy of suggested quantum-chemical approach to our interpretation of rather strong exchange coupling in binuclear Cu^{II} complexes with bis-hetarylhydrazone ligands. The established and successfully interpreted theoretically interrelation between both the electronic and geometrical structural features of copper(II) binuclear complex and character of exchange effects has especial importance for the development of directed design of one, two and three-dimensional magnetically ordered materials.

Quantum chemical calculations were performed on the clusters of the Joint Resource Center 'High Performance Calculation' at the Southern Federal University. The NMR spectra were recorded using the facilities of Resource Centers 'Molecular Spectroscopy' at the Southern Federal University.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.013.

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