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# Structure and Magnetic Properties of Binuclear Copper(II) Complexes with 2,6-Diformyl-4-*tert*-butylphenol Bis(imidazolinyl)hydrazone

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**Abstract**—Binuclear copper(II) complexes with bis(imidazolinyl)hydrazone of 2,6-diformyl-4-*tert*-butylphenol have been prepared and studied. In all complexes the antiferromagnetic exchange interaction between the copper(II) ions is observed.

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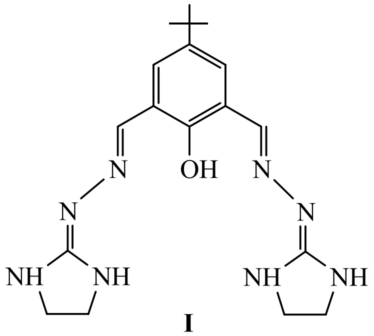
Hydrazinoimidazoline and its hydrazone derivatives are attractive due to their biological activity and strong complexing ability. The antifungal and anticancer activity as well as cytotoxicity of a series of hydrazinoimidazoline hydrazones has been studied in [1–3]. The complexes of Pt(II) and Pd(II) with hydrazinoimidazoline have been described [4–6]; the former has been considered a probable analog of cisplatin [6]. The dimeric complex of copper(II) with pyridine-2-carbaldehyde imidazolinylhydrazone is known [7], containing two mononuclear [Cu(L)Br] fragments connected via the sulfate bridge. However, we are not aware of any systematic study of the complexing ability of imidazolinylhydrazones.

Here we report on the preparation and physicochemical studies of bis(imidazolinyl)hydrazone of 2,6-diformyl-4-*tert*-butylphenol **I** and its binuclear complexes with copper(II). The complexes of transition metals with azomethines and 2,6-diformylphenol hydrazones, the so-called Robson's ligands [8, 9], are known as convenient models for the study of the factors influencing the magnetic exchange interaction of paramagnetic transition metal ions [10–12]. Such information is of high importance in view of development of new molecular magnetic materials [13–15].

Composition and structure of the isolated compounds were confirmed by elemental analysis, IR and NMR spectroscopy, magnetic properties, and X-ray diffraction data.

In the $^1$H NMR spectrum of **I**, the singlet signal of the methylene group as well as the broad singlet signal of NH (4H, $\delta = 7.45$ ppm) disappearing upon addition of $D_2O$ were observed; therefore, we concluded that the compound existed in the diazine form due to the hydrazine proton transfer to the imidazoline nitrogen. Noteworthily, the singlet of imidazoline $CH_2$ group was observed in the spectra of the other imidazolinylhydrazones [2, 3]; the diazine form of imidazolinylhydrazone of 3-hydroxy-5-pregnan-20-one was confirmed by X-ray diffraction study [3].

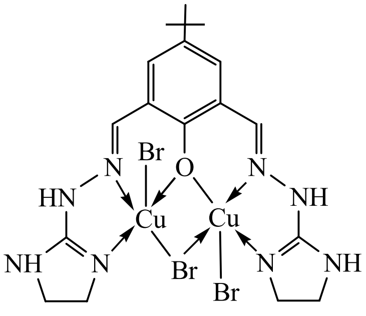


**I**

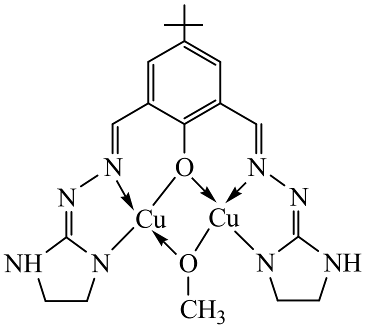
The interaction of **I** dihydrobromide with copper(II) perchlorate, of **I** with copper(II) bromide, and of **I** with copper(II) acetate gave the following complexes: $[Cu_2(H_2L)Br_2]\cdot ClO_4$ (**II**), $[Cu_2(H_2L)Br_3]$ (**III**), and $[Cu_2L(OCH_3)]$ (**IV**). The thermogravimetric analysis of the complexes revealed no endothermic effects below 180°C, thus proving the absence of the solvent molecules in the complexes structure [16, 17]. The thermal oxidative destruction of the organic ligand occurred at 290–310°C.

In the IR spectra of **II**–**IV** the ν(OH) band was absent, whereas the ν(C=N) band assigned to the azomethine fragment was shifted to lower wavenumbers (1610–1620 $cm^{-1}$), therefore, the coordination of copper(II) ions to azomethine nitrogen atoms was postulated. Based on the IR data, the deprotonation of bishydrazone in the complexes could not be evaluated unambiguously. In the spectra of all complexes the bands assigned to NH group vibrations were observed: at 3250 $cm^{-1}$ (broad) in the case of **II**, at 3322 and 3169 $cm^{-1}$ in the case of **III**, and at 3308 $cm^{-1}$ in the case of **IV**. From the elemental analysis data and the information from the referenced literature it was suggested that in the case of **II** and **III** the ligand was coordinated in the monodeprotonated form, whereas in the case of **IV**, triply deprotonated form of the ligand was more probable. Higher degree of deprotonation in the case of **I** interaction with copper(II) acetate was due to the deprotonating ability of the acetate ion in the methanol solution [18–22]. In all previously described cases of 2,6-diformylphenol bishydrazones interaction with copper(II) halides or perchlorate the complexes containing monodeprotonated bishydrazone were formed [21–23].

The effective magnetic moments of complexes **II**–**IV** significantly decreased upon cooling to –196°C, thus evidencing the exchange interaction of the antiferromagnetic type and proving the binuclear structure of the compounds. The exchange interaction parameters $^2J$ as calculated in the frame of the isotropic exchange model [24] using the Bleaney–Bowers equation [25] were –108 $cm^{-1}$ (**II**), –52 $cm^{-1}$ (**III**), and –408 $cm^{-1}$ (**IV**) (Table 1).



**III**



**IV**

From the collected data the above shown structures of **III** and **IV** were reliably assumed.

The significant difference in the strength of the antiferromagnetic exchange interaction in the cases of **III** and **IV** coincided with the known correlations between the structure and the magnetic properties. The bridged coordination of bromine led to a noticeable distortion of the exchange fragment, whereas in the complexes with the alkoxide bridge the exchange fragment was almost planar, as was the overall structure of the metal chelate macrocycle. The planar structure enhances the overlap of $d_{x^2-y^2}$ copper ions orbitals, thus improving the exchange interaction [10, 12, 19].

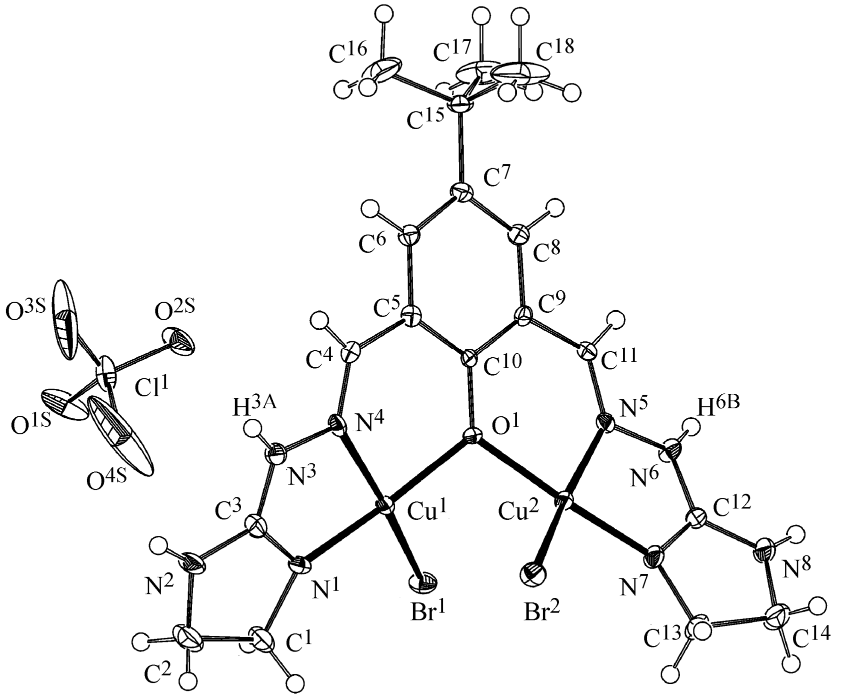
Structure of **II** could be hardly elucidated from the above presented data. The complex composition was rather unusual; to the very best of our knowledge, the complexes of 2,6-diformylphenol bishydrazone containing both perchlorate and halide ions were not mentioned either in the literature nor in the Cambridge

**Table 1.** Magnetic properties of **II**–**IV**

| Comp. no. | $T$, K | $\mu_{eff}$, $\mu_B$ [a] | $^2J$, $cm^{-1}$ | $g$ | $f$ |
|---|---|---|---|---|---|
| **II** | 297 | 1.81 | –108 | 2.24 | 0.068 |
| | 77.4 | 1.26 | | | |
| **III** | 297 | 1.75 | –52 | 2.08 | 0.006 |
| | 77.4 | 1.52 | | | |
| **IV** | 295 | 1.27 | –408 | 2.20 | 0.056 |
| | 77.4 | 0.47 | | | |

[a] $\mu_{eff}$ is calculated per one copper atom.

**Scheme 1.** General view of molecule of **II** (thermal vibration ellipsoids correspond to 50% probability)



Structural Database. All known examples of copper(II) perchlorate with the Robson's ligands were binuclear complexes with exogenous hydroxy or alkoxide bridge [23, 26].

Structure of **II** was found by the X-ray diffraction analysis. The single crystal suitable for the analysis was prepared by recrystallization from methanol. In **II**, the bishydrazone was coordinated to copper ions in its monodeprotonated hydrazone tautomeric form. The coordination polyhedra of both copper ions were found to be distorted squares formed by the phenoxide oxygen atom, azomethine and imidazoline nitrogen atoms, and bromine (see Shceme 1). The $Br^1$ and $Br^2$ atoms were off the $O^1N^4N^1$ and $O^1N^5N^7$ planes by 1.008 and 0.904 Å, respectively. Each of the bromine atoms was bound to the second copper ion via weak coordination bond [$Br^2$–$Cu^1$ 3.1840(7) Å long and $Br^1$–$Cu^2$ 3.1388(7) Å long], thus supplementing copper coordination polyhedron to the elongated square pyramid (4+1). The distance between copper atoms was 3.1222(7) Å; the $Cu^1O^1Cu^2$ bond angle at the bridging oxygen atom was 106.4(1)° (Table 2).

The five-membered chelate rings, $Cu^1N^4N^3C^3N^1$ and $Cu^2N^5N^6C^{12}N^7$, were almost planar, whereas the six-membered chelate rings were highly distorted due to bending along the $O^1$–$N^4$ and $O^1$–$N^5$ lines. The organic ligand fragment on the whole was not planar, the $N^1C^3N^2C^2C^1$ and $N^7C^{12}N^8C^{14}C^{13}$ imidazoline rings were turned with respect to the benzene ring by 28.15° and 29.62°, respectively.

The perchlorate ion was located in the outer sphere of the complex. In the crystal, each of the complex ions formed two hydrogen bonds with perchlorate ions (Table 3), thus giving the infinite zigzag one-dimensional chains stretched along *c* crystallographic axis.

The bromine atoms coordination in **II** was significantly different from that in the other known halogen-containing complexes of transition metals with 2,6-diformylphenol hydrazones. In the previously described complexes of that type, the bridging coordination of one of the halogen atoms was observed by X-ray diffraction analysis [26–31]. If other halogen atoms were present in the molecule, they were axially coordinated to one or both copper atoms, supplementing their coordination polyhedron to the distorted square pyramid.

Among the previously described copper(II) complexes with the Robson's ligands, the following ones exhibited the coordination of the exogenous acido ligands most similar to that observed in this work: bis-$\mu_2$-chlorine bridged copper(II) complex with bis(2-dimethylaminoethyl)pyridine-2,6-dicarboxamide-1-

**Table 2.** Selected interatomic distances and angles of the copper coordination polyhedron in complex **II**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Br$^{1}$–Cu$^{1}$ | 2.3661(7) | Br$^{2}$–Cu$^{2}$ | 2.3752(7) |
| Cu$^{1}$–N$^{4}$ | 1.969(4) | Cu$^{2}$–N$^{5}$ | 1.981(4) |
| Cu$^{1}$–N$^{1}$ | 1.923(4) | Cu$^{2}$–N$^{7}$ | 1.919(3) |
| Cu$^{1}$–O$^{1}$ | 1.950(3) | Cu$^{2}$–O$^{1}$ | 1.949(3) |
| Br$^{2}$–Cu$^{1}$ | 3.1840(7) | Br$^{1}$–Cu$^{2}$ | 3.1388(7) |
| Angle | ω, deg | Angle | ω, deg |
| N$^{1}$Cu$^{1}$O$^{1}$ | 166.08(15) | N$^{7}$Cu$^{2}$O$^{1}$ | 167.46(14) |
| N$^{1}$Cu$^{1}$N$^{4}$ | 81.29(15) | N$^{7}$Cu$^{2}$N$^{5}$ | 81.57(15) |
| O$^{1}$Cu$^{1}$N$^{4}$ | 87.98(13) | O$^{1}$Cu$^{2}$N$^{5}$ | 87.99(13) |
| N$^{1}$Cu$^{1}$Br$^{1}$ | 100.82(12) | N$^{7}$Cu$^{2}$Br$^{2}$ | 99.40(11) |
| O$^{1}$Cu$^{1}$Br$^{1}$ | 91.96(9) | O$^{1}$Cu$^{2}$Br$^{2}$ | 92.51(9) |
| O$^{1}$Cu$^{1}$Br$^{2}$ | 70.75(8) | O$^{1}$Cu$^{2}$Br$^{1}$ | 71.24(8) |
| N$^{4}$Cu$^{1}$Br$^{1}$ | 163.80(10) | N$^{5}$Cu$^{2}$Br$^{2}$ | 164.60(10) |
| Cu$^{1}$Br$^{1}$Cu$^{2}$ | 67.42(2) | Cu$^{1}$Br$^{2}$Cu$^{2}$ | 66.50(2) |

oxide [$Cu_2LCl_2$] [32] and the polymeric complex of copper(II) with 2,6-bis[N-(2-pyridylethyl)formidoyl]-4-ethylphenol [33]. It was suggested that in the [$Cu_2L(NCS)_2$] binuclear fragments of the latter, the copper atoms were only bound via the phenoxide bridge, and the coordination surrounding of copper atoms was as follows: $N_3OS$ and $N_4O$. In the former complex, the exchange interaction between copper(II) ions was not noticeable [32], whereas in the latter complex, strong antiferromagnetic exchange was observed ($^2J$ –210 cm$^{-1}$) [33].

The $^2J$ value in the case of **II** fell into a quite wide range of the exchange parameters reported in the cases of copper(II) complexes with various 2,6-diformylphenol hydrazones, containing copper atoms bridged by phenoxide or by bromide (from –10 to –160 cm$^{-1}$) [10, 12]. At the same time, the antiferromagnetic exchange in **II** was noticeably weaker than that described in [33]. Taking into account that in the case of **II** the exchange interactions could only be translated via the phenoxide oxygen bridge, it was suggested that the weakening of the exchange interaction was due to the decrease in the bond angle of the phenoxide bridge [106.4(1)° and 110.13(8)°, respectively]. Indeed, that bond angle was shown to affect the antiferromagnetic exchange in similar systems [10–12, 34, 35].

**Table 3.** Characteristics of the intermolecular hydrogen bonds in the crystal of complex **II**[a]

| D–H···A | D–H, Å | H···A, Å | D···A, Å | ∠DHA, deg |
|---|---|---|---|---|
| N$^{3}$–H$^{3A}$···O$^{2S}$ | 0.881(3) | 2.095(3) | 2.905(5) | 152.5(2) |
| N$^{6}$–H$^{6B}$···O$^{1Si}$ | 0.880(3) | 2.064(4) | 2.889(5) | 155.8(2) |

[a] Symmetry code: (i) –*x* + 1/2, –*y* + 1/2, *z* – 1/2.

## EXPERIMENTAL

Elemental analysis was performed on the Perkin-Elmer 240C analyzer in the Laboratory of Microanalysis, Southern Federal University. IR spectra of the suspensions in mineral oil were registered on a Varian Scimitar 1000 FT-IR spectrometer at 400–4000 cm$^{-1}$. $^1$H NMR spectra of the solutions in DMSO-$d_6$ were registered on a Varian Unity 300 (300 MHz) spectrometer in the pulse Fourier mode, with hexamethyldisiloxane as the internal reference. Magnetic susceptibility was determined by the relative Faraday method at 77.4–300 K; the calibration reference was Hg[Co(CNS)$_4$]. The thermogravimetric analysis preformed on a Diamond TG/DTA (Perkin-Elmer) instrument at the heating rate of 10 deg/min, ramp to 650°C.

Bishydrazone **I** was prepared from the commercially available hydrazinoimidazoline dihydrobromide. 2,6-Diformyl-4-*tert*-butylphenol was prepared as described in [36].

**Bishydrazone I.** The equimolar amount of sodium acetate was added to the hot solution of 10 mmol of hydrazinoimidazoline dihydrobromide in 20 mL of ethanol, and the mixture was refluxed during 10 min. Then, the hot solution of 5 mmol of 2,6-diformyl-4-*tert*-butylphenol in 10 mL of ethanol was added; the mixture was refluxed during 5 h and left overnight. The yellow precipitate was filtered off and recrystallized from acetonitrile–methanol, 1 : 1. Yield 75%, mp 256–258°C. IR spectrum, ν, cm$^{-1}$: 3308 (OH), 3170 (NH), 1660, 1625 (C=N). $^1$H NMR spectrum, δ, ppm: 12.188 s (1H, OH), 8.364 s (2H, CH$_{\mathrm{azometh}}$), 7.622 s (2H, CH$_{\mathrm{arom}}$), 7.45 br.s (4H, NH), 3.529 s (8H, CH$_2$), 1.293 s (9H, *t*-Bu). Found, %: C 58.90; H 6.79; N 30.54. $C_{18}H_{25}N_8O$. Calculated, %: C 58.52; H 6.82; N 30.33.

**Dihydrobromide of I** was prepared similarly, without addition of sodium acetate. Yield 80%, mp >260°C. Found, %: C 40.87; H 5.29; N 20.99.

$C_{18}H_{27}Br_2N_8O$. Calculated, %: C 40.69; H 5.12; N 21.09.

**Preparation of complex II.** The hot solution of 2 mmol of copper(II) perchlorate in 10 mL of methanol was added to the hot solution of 1 mmol of **I** dihydrobromide in 20 mL of methanol. The mixture was boiled during 1 h; the formed precipitate was filtered off, washed with methanol, and dried in a vacuum at room temperature. Yield 75%, mp >260°C (decomp.). IR spectrum, ν, $cm^{-1}$: 3250 (NH), 1619, 1598 (C=N), 1101 ($ClO_4$). Found, %: C 28.12; H 3.49; N 15.08; Cu 16.90. $C_{18}H_{25}Br_2ClCu_2N_8O_5$. Calculated, %: C 28.61; H 3.33; N 14.83; Cu 16.82.

**Preparation of complexes III and IV.** The hot solution of 2 mmol of either copper(II) bromide (**III**) or copper(II) acetate (**IV**) in 20 mL of methanol was added to the hot solution of 1 mmol of **I** in 20 mL of methanol. The mixture was boiled during 1 h; the precipitate was filtered off, washed with methanol, and dried in a vacuum at room temperature.

**Complex III.** Yield 85%, mp >260°C. IR spectrum, ν, $cm^{-1}$: 3322, 3166 (NH), 1615, 1585 (C=N). Found, %: C 29.54; H 3.50; N 15.39; Cu 17.11. $C_{18}H_{25}Br_3Cu_2N_8O$. Calculated, %: C 29.36; H 3.42; N 15.22; Cu 17.26.

**Complex IV.** Yield 60%, mp >260°C. IR spectrum, ν, $cm^{-1}$: 3308 (NH), 1609, 1590 (C=N). Found, %: C 43.15; H 5.12; N 21.17; Cu 24.40. $C_{19}H_{26}Cu_2N_8O_2$. Calculated, %: C 43.42; H 4.99; N 21.32; Cu 24.18.

**X-ray diffraction study.** The single crystal of **II** was prepared by slow cooling of the methanol solution. Green prismatic crystals ($M$ 755.81), orthorhombic, at 123 K: $a$ 24.9416(12), $b$ 11.4195(5), $c$ 17.8524(8) Å; $V$ 5084.7(4) $Å^3$, space group $P_{bcn}$, $Z$ 8, $d_{calc}$ 1.975 $g/cm^3$. Unit cell parameters and the intensities of 43143 reflections were measured on a Bruker Smart Apex II diffractometer [$\lambda$(Mo-$K_\alpha$) 0.71073 Å, graphite monochromator, ω scanning, $2\theta_{max}$ 59.8°] on a single crystal sample of $0.32\times0.13\times0.07$ $mm^3$. The array of the measured intensities was processed in the SAINT [37] and SADABS [38] software. The structure was solved by the direct method and refined for non-hydrogen atoms by the full-matrix least squares method in the anisotropic approximation with respect to $F^2_{hkl}$. Hydrogen atoms were placed in the geometrically calculated positions that were refined using the *rider* model [$U_{iso}(H) = nU_{eq}(C)$ with $n = 1.5$ in the case of methyl groups carbon and $n = 1.2$ in the case of other carbon atoms]. The final divergence factors were $R_1$ 0.0479 and $wR_2$ 0.1240 for 4933 independent reflections with $I > 2\sigma(I)$; and $R_1$ 0.0862 and $wR_2$ 0.1440 for the total 7524 independent reflections. With 325 of the refined parameters, GOOF equaled 1.000. All calculations were performed in the SHELXL-97 software package [39]. The structure was analyzed in the PLATON [40] software. The selected interatomic distances and bond angles are collected in Table 2, the hydrogen bonds parameters are given in Table 3. The atomic coordinates and the temperature factors were deposited to the Cambridge Structural Database under CCDC 908059.

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