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Crystal Structure and Magnetic Properties of the Binuclear Copper(II) Complex with 2,6-Diformyl-4-*tert*-Butylphenol Bis(imidazolinylhydrazone)

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Abstract—The binuclear copper(II) complex with 2,6-diformyl-4-*tert*-butylphenol bis(imidazolinylhydrazone) (H_3L), $[Cu_2(H_2L)Br_2]ClO_4$ (**I**), was synthesized. The structure of complex **I** was determined by X-ray diffraction analysis. The antiferromagnetic exchange interaction ($2J = -108$ cm^{-1}) translated through the phenoxide oxygen atom is observed between the copper(II) ions. The exchange parameter was calculated by the quantum-chemical “broken symmetry” method.

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INTRODUCTION

Interest of researchers in hydrazinoimidazoline and related hydrazones is due to both high complexation ability and biological activity. The Pt(II) and Pd(II) complexes with hydrazinoimidazoline were described [1–3], and the former is considered as a possible analog of cisplatin [3]. A series of hydrazinoimidazoline hydrazones, their binding with α_1- and α_2-adrenergic and imidazoline I_1 and I_2 receptors, and their cytotoxic and anticancer activity were studied [4, 5]. The dimeric copper(II) complex based on pyridine-2-carbaldehyde imidazolylhydrazone in which two mononuclear [Cu(L)Br] fragments are bonded by the sulfate bridge is described [6]. However, there are no systematic studies of the complexation ability of imidazolinylhydrazones to the moment.

Here we present the results of the synthesis, X-ray diffraction analysis, and magnetochemical study of the new binuclear copper(II) complex with 2,6-diformyl-4-*tert*-butylphenol bis(imidazolinylhydrazone) (H_3L) of the $[Cu_2(H_2L)Br_2]ClO_4$ composition (**I**).

EXPERIMENTAL

IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in the range from 400 to 4000 cm^{-1} (suspension in Nujol). ^{1}H NMR spectra were measured in DMSO-d_6 on a Varian Unity 300 spectrometer (300 MHz) in a pulse Fourier mode using HMDS as an internal standard. Elemental analysis was carried out on a PerkinElmer 240C instrument at the Microanalysis Laboratory of the Southern Federal University. The specific magnetic susceptibility was determined by the relative Faraday method in the temperature range 77.4–300 K using $Hg[Co(CNS)_4]$ as a standard for calibration.

2,6-Diformyl-4-*tert*-butylphenol was synthesized according to a described procedure [7]. Commercially available hydrazinoimidazoline dihydrobromide was used for the synthesis of H_3L.

Synthesis of $H_3L \cdot 2HBr$. An equimolar amount of sodium acetate was added to a hot solution of hydrazinoimidazoline dihydrobromide (10 mmol) in ethanol (20 mL), and the mixture was refluxed for 10 min. Then a hot solution of 2,6-diformyl-4-*tert*-butylphenol (5 mmol) in ethanol (10 mL) was added. The mixture was refluxed for 5 h and left overnight. A yellow precipitate was filtered off and recrystallized from an acetonitrile–methanol (1 : 1) mixture. The yield was 75%. Mp = 256–258°C.

For $C_{18}H_{27}N_8OBr_2$			
anal. calcd., %:	C, 40.69,	H, 5.12,	N, 21.09.
Found, %:	C, 40.87,	H, 5.29,	N, 20.99.

IR, ν, cm^{-1}: 3308 ν(OH), 3170 ν(NH), 1660, 1625 ν(C=N). ^{1}H NMR (DMSO-d_6, δ, ppm): 12.188 s (1H, OH), 8.364 s (2H, $CH_{azometh}$), 7.622 s (2H, CH_{arom}), 7.45 s (6H, NH), 3.529 s (8H, CH_2), 1.293 s (9H, *t*-Bu).

Table 1. Crystallographic data and experimental and refinement characteristics for compound **I**

Parameter	Value
Formula weight	755.81
Crystal size, mm	0.32 × 0.13 × 0.07
Crystal system	Orthorhombic
Space group	*Pbcn*
a, Å	24.9416(12)
b, Å	11.4195(5)
c, Å	17.8524(8)
α, deg	90.00
β, deg	90.00
γ, deg	90.00
V, Å^3	5084.7(4)
Z	8
ρ_{calcd}, g/cm^3	1.975
μ, mm^{-1}	4.97
$F(000)$	2992
$2\theta_{max}$, deg	59.8
Ranges of reflection indices	$-35 \le h \le 35$, $-16 \le k \le 13$, $-25 \le l \le 24$
Number of measured reflections	43143
Number of independent reflections	7524
Number of reflections with $I > 2\sigma(I)$	4933
Number of refined parameters	325
Goodness-of-fit (all reflections)	1.000
R_1 ($I > 2\sigma(I)$)	0.0479
wR_2 (all reflections)	0.1440
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.648/–2.276

Synthesis of complex I. A hot solution of copper(II) perchlorate (2 mmol) in methanol (20 mL) was added to a hot solution of $H_3L \cdot 2HBr$ (1 mmol) in methanol (20 mL). The mixture was refluxed for 1 h. The precipitate was filtered off, washed with hot methanol, and dried in vacuo. The yield was 70%. Mp > 260°C (with decomp.).

For $C_{18}H_{25}N_8O_5ClBr_2Cu_2$				
anal. calcd., %:	C, 28.61,	H, 3.33,	N, 14.83,	Cu, 16.82.
Found, %:	C, 28.12,	H ,3.49,	N, 15.08,	Cu, 16.90.

IR, ν, cm^{-1}: 3250 ν(NH), 1619, 1598 ν(C=N).

X-ray diffraction analysis of complex **I** was performed on a Bruker Smart Apex II diffractometer (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) at 123 K. The initial array of measured intensities was processed using the SAINT [8] and SADABS [9] programs. The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms for F^2. Hydrogen atoms were placed in geometrically calculated positions and refined using the riding model ($U_{iso}(H) = nU_{iso}(C)$, where $n = 1.5$ for the carbon atoms of the methyl groups and $n = 1.2$ for other C atoms). All calculations were performed using the SHELXTL program package [10]. The experimental characteristics and crystallographic data are given in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The coordinates of atoms and the temperature factors of structure **I** were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 908059; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/data_request/cif).

Quantum-chemical calculations were performed in the framework of the density functional theory using the B3LYP hybrid exchange correlation functional [11–13] and the 6-311G(d) extended split valence basis set. All quantum-chemical calculations were performed using the Gaussian 03 program [14]. The Chemcraft program was used for data preparation, presentation graphics, and visualization of the results [15].

The magnetic exchange parameter (2*J*) of complex **I** was calculated using an earlier approved procedure [16, 17] based on the broken symmetry approach [18, 19]. The 2*J* parameter was accepted proportional to the difference in energies of two one-determinant states calculated in the framework of the spin-unrestricted Kohn–Sham scheme: the triplet state (T, $S = 1$) and the broken symmetry state (BS, $S = 0$). It is assumed for the latter that the symmetry of molecular orbitals can be lower than that of the molecule [20, 21]. The geometry of the complex in the T and BS states was optimized with respect to all geometric parameters without symmetry restraints.

RESULTS AND DISCUSSION

The compositions and structures of the isolated compounds were determined from the data of elemental analysis, IR and ^{1}H NMR spectroscopy, magnetochemistry, and X-ray diffraction analysis (for complex **I**).

The reaction of bishydrazone dihydrobromide H_3L with copper(II) perchlorate affords complex $[Cu_2(H_2L)Br_2] \cdot ClO_4$ (**I**).

The data of IR spectroscopy indicate the coordination of the ligand in the monodeprotonated form H_2L^-: the spectrum of complex **I** contains no absorption band ν(OH) at 3300 cm^{-1} but has a broad band at 3250 cm^{-1} attributed to vibrations of the NH groups. The ν(C=N) band in the spectrum of the complex shifts to 1620 cm^{-1}, which confirms the coordination of the azomethine nitrogen atoms to the copper(II) ions.

Single crystals of complex **I** suitable for X-ray diffraction analysis were obtained by crystallization from methanol. Bishydrazone H_3L is coordinated in the monodeprotonated hydrazone tautomeric form. The coordination polyhedron of both copper atoms is a distorted square formed by the phenoxide oxygen atom, azomethine and imidazoline nitrogen atoms, and bromine atom (Fig. 1). The Br(1) and Br(2) atoms shift from the root-mean-square planes of other donor atoms O(1)N(4)N(1) and O(1)N(5)N(7) by 1.008 and 0.904 Å, respectively, due to the mutual repulsion. Each bromine atom is also bound by a very weak coordination bond with the second copper atom (Br(2)–Cu(1) 3.1840(7), Br(1)–Cu(2) 3.1388(7) Å), supplementing its coordination polyhedron to a strongly elongated square pyramid (4 + 1). The distance between the copper atoms is 3.1222(7) Å, and the bond angle Cu(1)O(1)Cu(2) at the bridging oxygen atom is 106.4(1)°.

The 5-membered chelates Cu(1)N(4)N(3)C(3)N(1) and Cu(2)N(5)N(6)C(12)N(7) are nearly planar. The six-membered metallocycles are strongly distorted because of the bending along the lines of the O(1)–N(4) and O(1)–N(5) atoms, and the Cu(1) and Cu(2) atoms deviate from the mean plane of other atoms of the cycles by 0.562 and 0.519 Å, respectively. On the whole, the monodeprotonated organic ligand is nonplanar: the imidazole rings N(1)C(3)N(2)C(2)C(1) and N(7)C(12)N(8)C(14)C(13) are unfolded relative to the benzene rings by angles of 28.15° and 29.62°, respectively. The first of these five-membered rings is nearly planar, and the second ring has an envelope conformation, C(14) in the apical position deviating from the mean plane of other four atoms by 0.184 Å.

The perchlorate ion is localized in the external sphere of the complex. In crystal each complex cation forms two intermolecular hydrogen bonds with the perchlorate ions (Table 3), which results in the formation of infinite zigzag one-dimensional chains extended along the crystallographic axis *z* (Fig. 2).

A substantial distinction of complex **I** from other halogen-containing transition metal complexes with 2,6-diformylphenol azomethines and hydrazones (so-called Robson-type ligands [22, 23]) is the coordination mode of the bromine atoms.

The bridging coordination mode of one of the bromine atoms is observed in all earlier described complexes of this type studied by X-ray diffraction analysis [24–28]. If a molecule of the complex includes other halogen atoms, they are axially coordinated to one or both copper atoms, supplementing their coordination polyhedron to a distorted square pyramid. Among the earlier described copper(II) complexes with the Robson-type ligands, the polymer copper(II) complex with 2,6-bis[N-(2-pyridylethyl)formydoyl]-4-ethylphenol demonstrates the closest coordination mode of the exogenic acido ligands. In authors' opinion, the copper atoms in the binuclear fragments $[Cu_2(L)(NCS)_2]$ of this complex are bonded by the phenoxide bridge only and have the coordination environment N_3OS and N_4O [29].

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of the copper atoms in structure **I**

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)

Table 3. Geometric characteristics of intermolecular hydrogen bonds in the crystal structure of complex **I***

Contact D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(3)–H(3*A*)···O(2S)	0.88	2.095	2.905(5)	152
N(6)–H(6*B*)···O(1S)^i	0.88	2.064	2.889(5)	156

* Symmetry codes: ^{i} $-x + 1/2, -y + 1/2, z - 1/2$.

The effective magnetic moment of complex **I** is 1.81 μ_B at ambient temperature and decreases to 1.26 μ_B on cooling to the boiling point of liquid nitrogen, indicating a fairly strong antiferromagnetic exchange interaction between the copper ions.

The exchange interaction parameter in complex **I** was calculated in the framework of the Heisenberg–Dirac–Van Vleck model of isotropic exchange [30] using the multiparametric optimization by the Bleaney–Bowers equation

$$\chi'_M = \frac{2N_A g^2 \beta^2}{3kT} \times \left[(1-f)\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + fS(S+1)\right] + N_\alpha, \qquad (1)$$

where χ'_M, N_A, g, β, k, J, f, and N_α are the molar magnetic susceptibility corrected to diamagnetism of the atoms, Avogadro's number, the Landé factor, Bohr magneton, Boltzmann constant, exchange parameter,

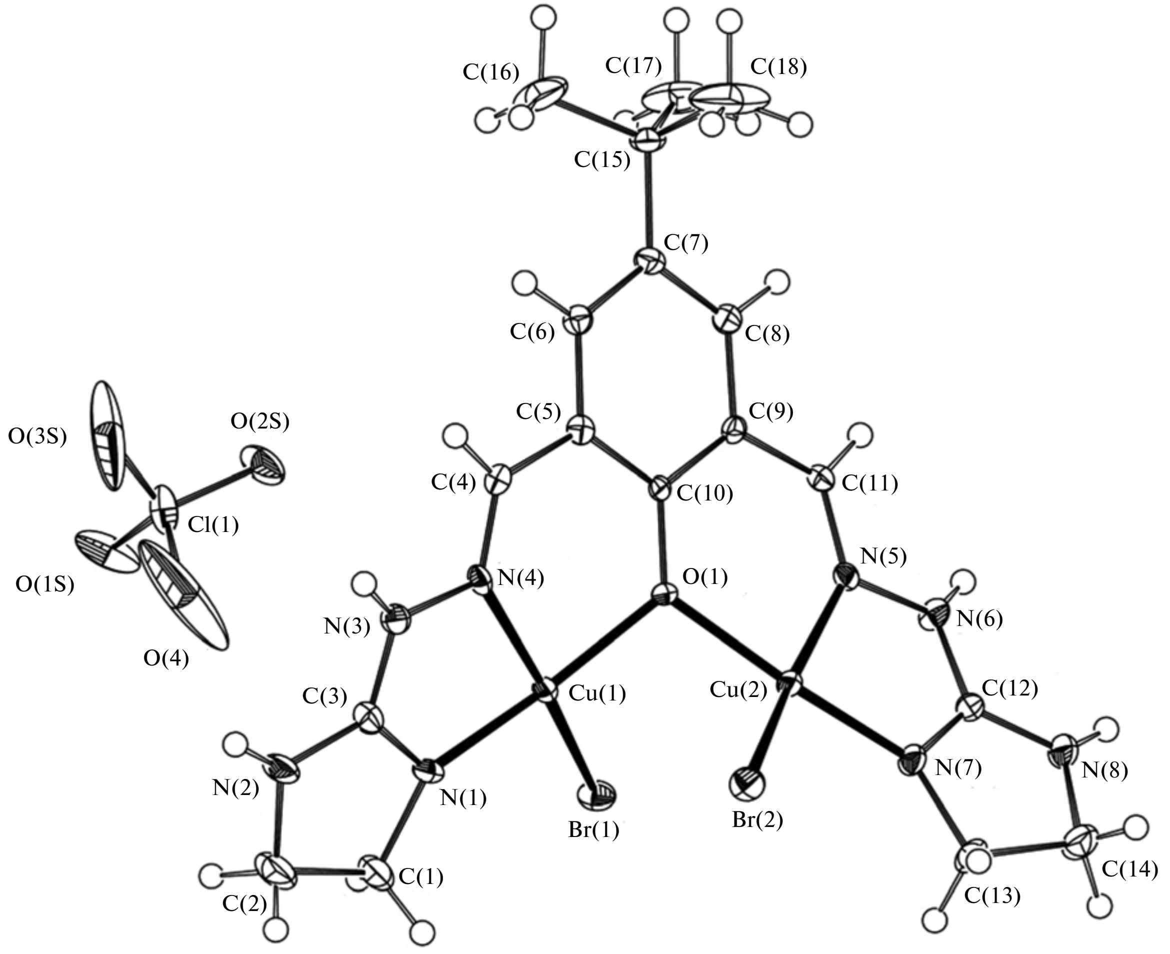

Fig. 1. Structure of complex **I** in the representation of atoms as thermal displacement ellipsoids with 50% probability.

molar fraction of a paramagnetic admixture, and temperature-independent paramagnetism.

The best agreement between the theory and experiment is attained at the following parameters of the model: $2J = -108$ cm^{-1}, $g = 2.24$, $f = 0.068$, $N_\alpha = 60 \times 10^{-6}$ cm^3/mol.

The exchange parameter in complex **I** is noticeably lower than that for the complex described [29] in which the copper ions are bound through the phenoxide bridge only ($2J = -210$ cm^{-1}, $g = 2.24$). At the same time, the value of $2J$ in complex **I** falls in the very wide range of exchange parameter values for the earlier described copper(II) complexes with various 2,6-diformylphenol hydrazones in which the copper ions are bound by both phenoxide and bromide bridges (from -10 to -160 cm^{-1}) [31, 32].

The quantum-chemical calculation of the exchange parameter was performed in the framework of the broken symmetry approach for both the fixed (from the X-ray diffraction data) and preliminarily optimized geometries of the complex in order to theoretically study the exchange interaction between the copper(II) ions in complex **I**. The magnetic exchange parameter was calculated using the Yamaguchi formula (2), which shows good results in combination with the hybrid exchange correlation functionals [33]

$$2J = \frac{2(E_{\rm BS} - E_{\rm T})}{\left\langle S_{\rm T}^2 \right\rangle - \left\langle S_{\rm BS}^2 \right\rangle}, \tag{2}$$

where $E_{\rm T}$ and $E_{\rm BS}$ are the total energies, and $\left\langle S_{\rm T}^2 \right\rangle$ and $\left\langle S_{\rm BS}^2 \right\rangle$ are the expected values of the operator of the squared full spin for the T and BS states, respectively.

The calculation results are presented in Table 4. The calculation of the exchange interaction parameter in the complex using the X-ray diffraction geometry gives $2J = -132$ cm^{-1}, which noticeably exceeds its experimental value. The separate geometry optimization of the complex for each state results in a substantial decrease in their energies and affects the value of singlet–triplet splitting. The value of $2J$ calculated for the optimized geometry of complex **I** is -91 cm^{-1}, which is much closer to the experimentally detected value.

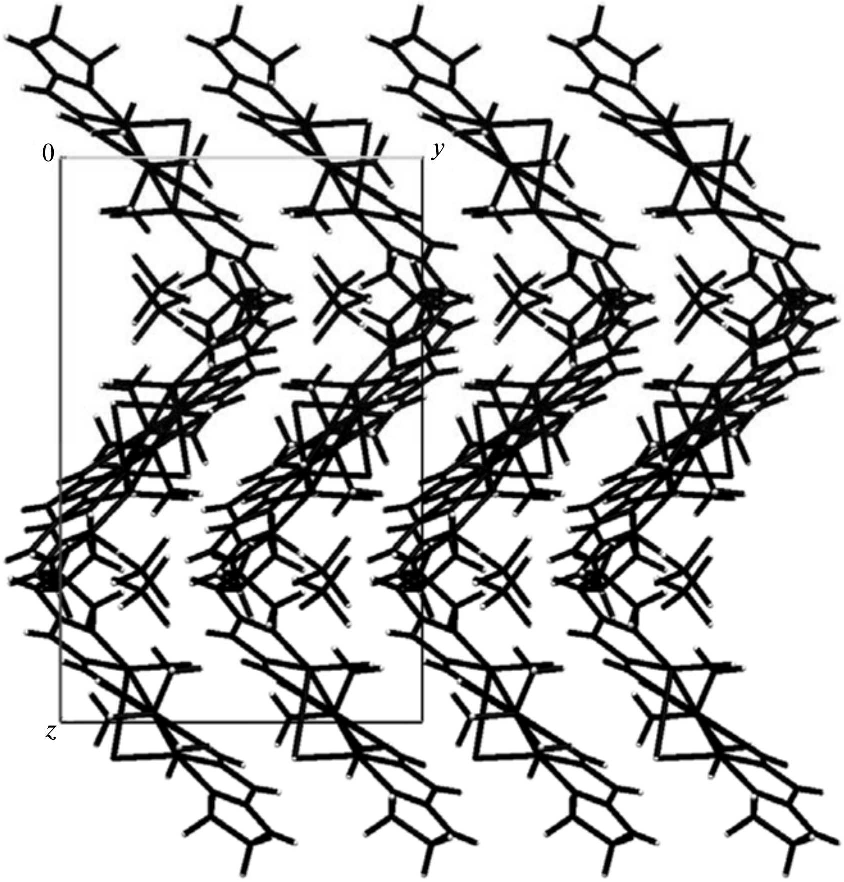

Fig. 2. Molecular packing of complex **I** in crystal (the view along the crystallographic axis *x*).

The spin density of the paramagnetic centers in the triplet state is significantly delocalized over atoms of the nearest coordination environment of the copper ions and is delocalized to the highest extent on the bromide ions and nitrogen atoms of the imidazoline fragments (Figs. 3, 4). The transition to the BS state results in the inversion of the spin density sign in one of the coordination nodes at an almost unchanged modulus.

The spin density distribution in the broken symmetry state (Fig. 3) indicates that the single exchange channel is the phenoxide oxygen atom on which the sign of the spin density changes. The spin density on the bromine atoms is significant but is completely concentrated on the p_σ orbitals oriented to the copper ion to which the bromide ion is coordinated.

A considerably lower value of the exchange parameter in complex **I** compared to that in the described complex [29] is explained by both the low value of the CuOCu bond angle (106.4(1)° and 110.13(8)°, respectively) and the withdrawal of the spin density from the bridging oxygen atom to the bromide ions and nitrogen atoms of the imidazoline fragment.

Table 4. Energies (a.c.), the expected value of the squared full spin moment $\langle S^2\rangle$, and the calculated value of $2J$ (cm^{-1}) for the T and BS states calculated for the X-ray diffraction and optimum geometries of complex **I** in the framework of B3LYP/6-311G(d)

Geometry	BS		T		$2J_{\text{calcd}}$, cm^{-1}
	E, a.c.	$\langle S^2\rangle$	*E*, a.c.	$\langle S^2\rangle$	
X-ray diffraction	–9643.359638	0.9952	–9643.357577	2.0061	–132
Optimum	–9643.663681	0.9964	–9643.663471	2.0058	–91

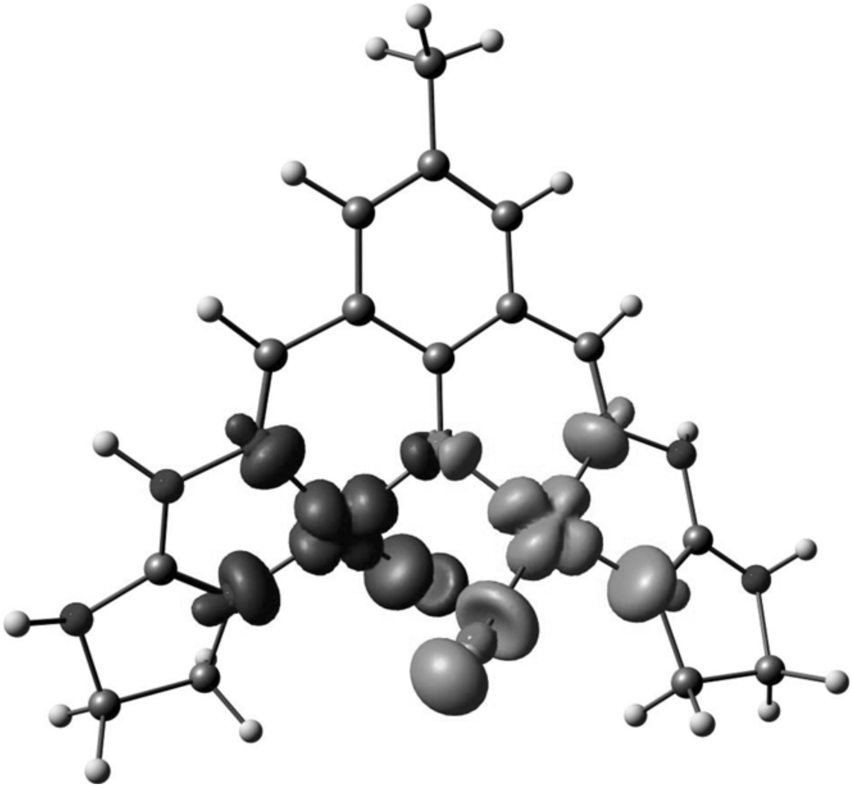

Fig. 3. Spin density distribution in the BS state of complex **I** (contour value 0.005 e/A^3, the *tert*-butyl group is omitted).

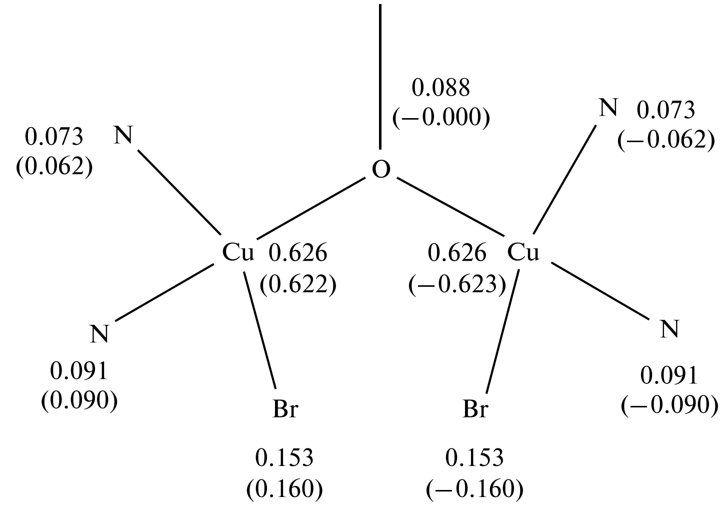

Fig. 4. Mulliken spin density on the atoms in the T and BS states (in parentheses) of complex **I**.

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