

Structure of Copper(II) *N*-Methylbenzoylhydroxamate in the Crystalline State and in Solution

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Abstract—The geometrical structure of CuL₂ (**I**), where L = R₁N(O)–(O)CR₂, R₁ = Me, R₂ = Ph, was studied by X-ray diffraction in the crystalline state and by stationary ESR spectroscopy in solution. In the crystalline state, **I** is a chain polynuclear complex. According to ESR data, in frozen solutions, complex **I** exists as three species, two being mononuclear and one being binuclear. The magnetic resonance parameters and concentrations of the species in frozen solutions were determined. The electronic structure of the complex with full geometry optimization of all systems was calculated in terms of the unrestricted density functional theory (DFT) method.

Keywords: copper(II) complexes, hydroxamic acids, X-ray diffraction, electron spin resonance, electronic structure of complexes

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INTRODUCTION

Both hydroxamic acids and their metal complexes can exist as various isomers and polymolecular structures [1]. Most *N*-substituted copper(II) hydroxamates in the crystalline state are mononuclear square planar complexes with *trans*-coordinated ligands [2–5]. The binuclear compound [CuL₂]₂ (L = R₁N(O)–(O)CR₂, R₁ = R₂ = Me) was prepared and structurally characterized [6]. In organic solvents at room temperature, crystalline copper hydroxamates exist as two species, the ESR spectra of which are characteristic of mononuclear complexes. The difference between the ESR parameters of the monomers are attributed to the coexistence of *cis*- and *trans*-isomers of the complexes in solutions. According to ESR data, both isomers are present in solutions both at room temperature and in low-temperature glass. As solutions of copper(II) hydroxamate complexes are cooled below the solvent freezing point, [CuL₂]₂ dimers can be manifested in the ESR spectrum, apart from the CuL₂ monomers [6, 7]. The stationary ESR spectra do not exhibit the hyperfine structure (HFS) caused by coupling of the unpaired electron with ligand atoms. However, there are published data on pulsed ESR, pointing to additional hyperfine coupling of the unpaired electron with the ligand nitrogen atoms in Cu(II) hydroxamates [8].

In this study, the structure of copper(II) hydroxamate CuL₂ (L = R₁N(O)–(O)CR₂, R₁ = Me, R₂ = Ph) (**I**) was determined by X-ray diffraction analysis. The structure of the complex in a toluene solution was found by ESR spectroscopy. The electronic structure of copper complexes was calculated by density functional theory (DFT) calculations with full geometry optimization for all systems. These results were used to determine the magnetic parameters of compound **I**, which were compared with experimental ESR data.

EXPERIMENTAL

Complex **I** was synthesized by a procedure reported in [9]. For more accurate interpretation of the ESR spectra, the samples were synthesized using the single ⁶⁵Cu isotope.

Single crystal X-ray diffraction study of compound **I** obtained by slow evaporation of a toluene solution was carried out at the Center for Collective Use of Physical Investigation Methods, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, on a Bruker D8 Venture Photon diffractometer in the φ - and ω -scan modes at a temperature of 150 K ($\lambda = 0.71073$ Å, Incoatec I μ S 3.0 microfocus X-ray source). Determination and refinement of unit cell parameters and integration of experimental set of reflection intensities for **I** were performed using the

Table 1. Crystallographic data and structure refinement details for complex **I**

Parameter	Value
Molecular formula	C ₁₆ H ₁₆ N ₂ O ₄ Cu
<i>M</i>	363.85
Color, habit	Green, prism
Crystal size, mm	0.045 × 0.030 × 0.025
Measurement temperature, K	150(2)
Wavelength, Å	0.71073
System	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> , Å	6.7643(3)
<i>b</i> , Å	14.3222(7)
<i>c</i> , Å	31.2441(15)
<i>V</i> , Å ³	3026.9(2)
<i>Z</i>	8
ρ(calcd.), g/cm ³	1.597
μ, mm ⁻¹	1.465
<i>F</i> (000)	1496
θ _{min} –θ _{max} , deg	2.608–30.605
Ranges of reflection indices	–9 ≤ <i>h</i> ≤ 9, –20 ≤ <i>k</i> ≤ 20, –44 ≤ <i>l</i> ≤ 44
Number of measured reflections	47 535
Number of unique reflections (<i>R</i> _{int})	4656 (0.0392)
Number of reflections with <i>I</i> > 2σ(<i>I</i>)	3793
Reflections/constraints/parameters	4656/0/210
GOOF	1.089
<i>R</i> -factors for <i>I</i> > 2σ(<i>I</i>)	<i>R</i> ₁ = 0.0372, <i>wR</i> ₂ = 0.0793
<i>R</i> - <i>R</i> -factors for all reflections	<i>R</i> ₁ = 0.0495, <i>wR</i> ₂ = 0.0839
Residual electron density (min/max), e Å ⁻³	–0.326/0.494

Bruker APEX3 program package [10]. The absorption corrections were applied using the SADABS program [10]. The structure was solved by direct methods [11] and refined by full-matrix least-squares method on F^2 [12] in the anisotropic approximation for all non-hydrogen atoms without geometric or thermal constraints for atoms in the model. The hydrogen atoms were placed in the geometrically calculated positions and refined in the riding model with $U_{\text{iso}}(\text{H})$ equal to $1.5U_{\text{eq}}(\text{C})$ for methyl group hydrogens and $1.2U_{\text{eq}}(\text{C})$ for phenyl group hydrogens. The calculations were carried out using the SHELXTL program package [12] in the OLEX2 data processing and visualization software [13].

The crystal data and structure refinement parameters for **I** are summarized in Table 1 and selected bond lengths and bond angles are given in Table 2.

The full set of X-ray crystallographic parameters of structure **I** was deposited with the Cambridge Crystal-

lographic Data Centre (CCDC no. 2128056; <https://www.ccdc.cam.ac.uk/structures/>).

The ESR spectra were run on an Elexsys-E680X BRUKER radiospectrometer at the Center for Collective Use of Physical Investigation Methods, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences (Moscow, Russian Federation). The spectrometer operation frequency was ~9.8 GHz (X-range). The solutions of the complexes were cooled down to $T = 100$ K with an Oxford Instruments block.

The spin Hamiltonian (SH) parameters of the complexes were determined by finding the best fit between the experimental and theoretical spectra via minimization of the error functional [14]:

$$F = \sum_i (Y_i^T - Y_i^E)^2 / N,$$

where Y_i^E is the array of experimental ESR signal intensities with a constant step in the magnetic field H ;

Y_i^T are the theoretical values at the same field H ; and N is the number of points. The sum of the Lorentz and Gauss functions was used as the line shape function [15]. According to the relaxation theory [16], the line width was specified by the expression:

$$\Delta H = \alpha + \beta m_I + \gamma m_I^2,$$

where m_I is the projection of the nuclear spin on the magnetic field direction, α , β , γ are parameters. Minimization was performed by varying the relative concentrations of complexes, g -factors, HFS constants, and line width and shape parameters for each complex. The other parameters that were varied for the dimer include the zero-field splitting parameter (D), orthorhombic distortion parameter (E), the distance between point dipoles (R), the angle between the radius-vector connecting the metal atoms and the z axis of the local environment of the metal (ξ), and the angle between the X axis and projection of the radius-vector connecting the metal atoms on the XY plane (η).

The electronic structure calculations with full geometry optimization of all systems were performed using unrestricted DFT method with the BP86 functional [17, 18] and split valence def2-TZVP basis set [18]; Grid4 was used for integration (in ORCA). The calculated vibrational frequencies characterize the optimized structures as energy minima. The magnetic parameters were calculated according to published recommendations [19] in the B3PW91/def2-TZVP approximation [20–22] in combination with the aug-cc-pVTZ-J auxiliary basis set [23] on the metal atom and Grid6. All calculations were carried out using the ORCA program, version 4.2.3 [24].

RESULTS AND DISCUSSION

According to X-ray diffraction data, complex **I** crystallizes without solvent molecules in the orthorhombic space group $Pbca$. All atoms of the independent part of the unit cell are located in general positions (Fig. 1), and the local coordination environment of copper(II) atoms, which are central atoms of the complex, consists of the ligand oxygen atoms with the uniform distribution of Cu(1)–O interatomic distances in the 1.9314(12)–1.9525(12) Å range, which does not differ much (although is somewhat greater) from the corresponding distances in the previously described structures [5]. The OCu(1)O angles are in the range from 83.72(5)° to 97.19(5)°. The Cu(1) atom virtually does not deviate from the O(1)–O(2)–O(3)–O(4) plane; the deviation is only 0.0113(6) Å, while the main planes of the opposing ligands that form the Cu(1)–O(1)–N(1)–C(2)–O(2) and Cu(1)–O(3)–N(2)–C(9)–O(4) five-membered rings are rotated by an angle of 3.32(11)° relative to each other.

It should be noted that these molecular groups form stacks extended along the crystallographic a axis;

Table 2. Selected distances (d) and bond angles (ω) in the structure of **I**

Bond	d , Å
Cu(1)–O(1)	1.9335(12)
Cu(1)–O(2)	1.9494(12)
Cu(1)–O(3)	1.9314(12)
Cu(1)–O(4)	1.9525(12)
Cu(1)–O(1) ^{#1}	2.5963(14)
Cu(1)–O(3) ^{#2}	2.6106(13)
Angle	ω , deg
O(1)Cu(1)O(2)	83.72(5)
O(3)Cu(1)O(4)	83.77(5)
O(2)Cu(1)O(3)	95.34(5)
O(1)Cu(1)O(4)	97.19(5)
O(2)Cu(1)O(4)	178.20(5)
O(1)Cu(1)O(3)	179.02(5)
O(3)Cu(1)O(1) ^{#1}	83.88(5)
O(1)Cu(1)O(1) ^{#1}	96.31(5)
O(2)Cu(1)O(1) ^{#1}	86.70(5)
O(4)Cu(1)O(1) ^{#1}	91.64(5)
O(3)Cu(1)O(3) ^{#2}	96.32(5)
O(1)Cu(1)O(3) ^{#2}	83.45(5)
O(2)Cu(1)O(3) ^{#2}	90.66(5)
O(4)Cu(1)O(3) ^{#2}	90.99(5)
O(1) ^{#1} Cu(1)O(3) ^{#2}	177.36(4)
Symmetry code ^{#1}	$x + 1/2, y, -z + 3/2$
Symmetry code ^{#2}	$x - 1/2, y, -z + 3/2$

the copper coordination environment is thus completed to a somewhat distorted square bipyramidal (SBP), with the O(1)–O(4) oxygen atoms of one molecule forming the bipyramid base and the O(1) and O(3) atoms of the neighboring moieties being at the vertices (Fig. 2). The Cu(1)–O(1)^{#1} and Cu(1)–O(3)^{#2} distances (^{#1} $x + 1/2, y, -z + 3/2$, ^{#2} $x + 1/2, y, -z + 3/2$) are fairly long, amounting to 2.5963(14) and 2.6106(13) Å, respectively, which markedly exceeds the sum of covalent radii for copper and oxygen ($r_{\text{cov}}(\text{Cu}) = 1.32$ Å, $r_{\text{cov}}(\text{O}) = 0.66$ Å, $\Sigma r_{\text{cov}}(\text{Cu}, \text{O}) = 1.98$ Å) [25], but is within the sum of their van der Waals radii ($r_{\text{vdW}}(\text{Cu}) = 2.38$ Å, $r_{\text{vdW}}(\text{O}) = 1.50$ Å, $\Sigma r_{\text{vdW}}(\text{Cu}, \text{O}) = 3.88$ Å) [26]. In combination with the molecular geometry, this generally ensures proximate positions of the metal centers and formation of the chain structure in which the distance between the metals in the Cu(1)–Cu(1) chain (3.38302(16) Å) is also shortened compared to those in the complexes with *N-tert*-butylbenzoylhydroxamic acid [5].

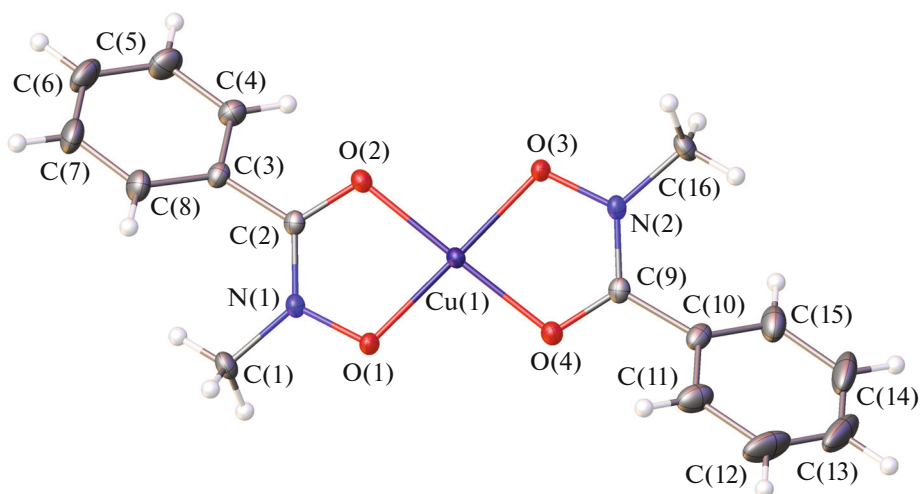


Fig. 1. Structure of the molecular fragment of complex I and scheme of atom numbering; the ellipsoids of root-mean-square deviations of the atoms are given at 50% probability level.

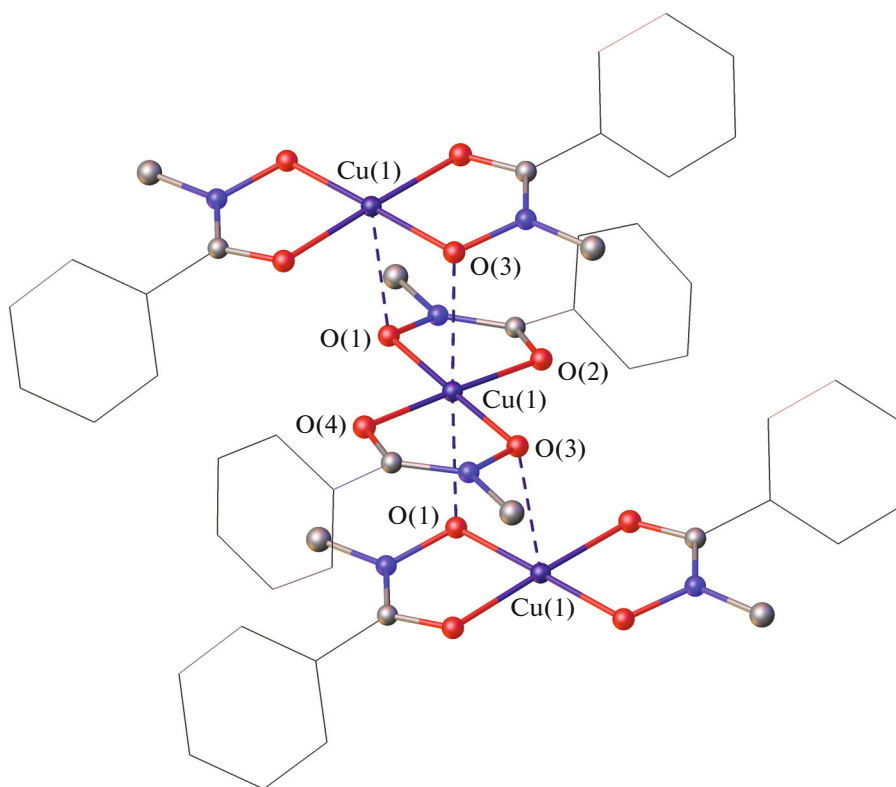


Fig. 2. Fragment of the stacked molecules of complex I. The phenyl groups are shown schematically for clarity.

At room temperature, the ESR spectrum of the complex in toluene is a superposition of the spectra of two mononuclear complexes, each of them being described by the isotropic SH of the form

$$H_i = g_i \beta H S_i + a_i I_i S_i,$$

where β is the Bohr magneton; $i = A, B$; S is the electron spin equal to $1/2$; I is the ^{65}Cu nuclear spin equal to $3/2$. In the simulated spectra, the SH parameters of the two compounds at room temperature are substantially different. The compound whose ESR spectrum is described by SH with greater HFS constant, will be

designated as form A. Form B will refer to the complex whose ESR spectrum is described by SH with smaller HFS constant. For compound A, $g_A = 2.119$, $a_A = 88.4 \times 10^{-4} \text{ cm}^{-1}$; for compound B, $g_B = 2.118$, $a_B = 76.4 \times 10^{-4} \text{ cm}^{-1}$; the concentration ratio of the complexes $c_A/c_B = 1.5$. According to the measurements of the molecular weight of copper hydroxamates in solution, the complexes are mononuclear [27]; therefore, the presence of two monomeric species can be attributed to the existence of *cis*- and *trans*-isomers. Previously, it was assumed that the ESR spectra of complexes with *cis*-coordinated ligands are described by SH with higher hyperfine structure (HFS) constants than the spectra of complexes with *trans*-coordination [4, 5]. On this basis, compound A was identified as the *cis*-isomer of the complex, and compound B was assigned to the *trans*-isomer.

The ESR spectrum of a frozen solution of **I** in toluene is a superposition of the spectra of two forms (A and B) of mononuclear copper(II) compound and the spectrum of the dimer (Fig. 3). The ESR spectrum of the dimer has the following parameters: $g_z = 2.233$, $g_x = 2.029$, $g_y = 2.060$; $A = 190.9 \times 10^{-4} \text{ cm}^{-1}$, $B = 13.9 \times 10^{-4} \text{ cm}^{-1}$, $C = 36.0 \times 10^{-4} \text{ cm}^{-1}$. The parameters corresponding to the interaction of the monomeric parts of the dimer: $R = 3.5 \text{ \AA}$, $\xi = 29.75^\circ$, $\eta = 2.8^\circ$, $D = 122 \times 10^{-4} \text{ cm}^{-1}$, $E = 19.3 \times 10^{-4} \text{ cm}^{-1}$. The concentration of the monomers that form the dimer is 69%. The geometric and electronic structure of the dimeric Cu(II) N-substituted hydroxamates in the crystalline state and in frozen solutions was described in detail previously [6, 7]. According to X-ray diffraction data, CuL_2 ($L = R_1\text{N(O)-(O)CR}_2$, $R_1 = R_2 = \text{Me}$) is a dimer in the crystalline state [6]. According to ESR data, complex dimers with spectral parameters close to the parameters of compound **I** were detected in the frozen solution of this compound.

The spectra of mononuclear complexes are described by the rhombic SH of the following form:

$$H_i = g_i \beta H_z S_{iz} + g_{ix} \beta H_x S_{ix} + g_{iy} \beta H_y S_{iy} + A_i I_{iz} S_{iz} + B_i I_{ix} S_{ix} + C_i I_{iy} S_{iy},$$

where β is the Bohr magneton; $i = A, B$; g_{iz}, g_{ix}, g_{iy} are the z -, x -, and y -components of the g -tensor; A_i, B_i, C_i are the z -, x -, and y -components of the HFS tensor; S_{iz}, S_{ix}, S_{iy} are the projections of the electron spin operator on the coordinate axes; $S = 1/2$; I_{iz}, I_{ix}, I_{iy} are the projections of the nuclear spin operator of the central atom of the complex on the coordinate axes ($I = 3/2$). Spin Hamiltonian parameters of the ESR spectra of copper compounds in frozen solutions obtained by best fitting of the experimental data are summarized in Table 3. The same table also gives the values $g_{iso} = (g_{iz} + g_{ix} + g_{iy})/3$ and $a_{iso} = (A_i + B_i + C_i)/3$ and SH parameters of the ESR spectra of mononuclear complexes that do not form dimers in the frozen solutions: CuL_2 ($L = R_1\text{N(O)-(O)CR}_2$, where $R_1 =$

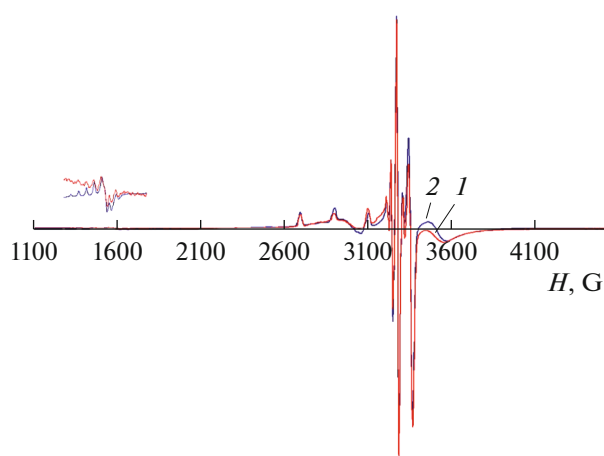


Fig. 3. ESR spectra of the frozen solution of compound **I**: (1) experimental, (2) simulated (concentration ratio $c_{IA}/c_{IB} = 2$).

tert-Bu, $R_2 = \text{Me}$ (compound **II**) [4] and $R_1 = \text{tert}$ -Bu, $R_2 = \text{Ph}$ (compound **III**)) [5]. Presumably, compounds whose ESR spectra are described by SH with lower g -factors and higher HFS constants (A) are the *cis*-isomers, while the compounds the spectra of which are described by SH with higher g -factors and lower HFS constants (B) are the *trans*-isomers.

Quantum chemical calculations of the electronic and geometrical structures of the complexes proved to be useful for interpreting experimental ESR data [28]. Table 4 summarizes the SH parameters describing the ESR spectra of *cis*- and *trans*-isomers of compound **I** in toluene. The g -factors for the two isomers are similar and weakly reflect the differences between the structures. The HFS constants proved to be more structure-sensitive. The constants g_{iso} and A_{cis} for the *cis*-isomer are greater than g_{iso} and A_{trans} for the *trans*-isomer. Note also that the differences in the planar parameters B and C are lower for the *cis*-isomer than for the *trans*-isomer. In the stationary ESR spectra of copper hydroxamates, it is impossible to detect HFS caused by the interaction of the unpaired electron with the ligand atoms. However, there are known pulsed ESR data indicating additional hyperfine coupling of the unpaired electron with the ligand nitrogen atom in Cu(II) hydroxamates. According to [8], the additional hyperfine coupling constant $a_{iso} = 0.43 \times 10^{-4} \text{ cm}^{-1}$. The results of our calculations are also given in Table 4.

Thus, according to X-ray diffraction data, compound **I** exists in the crystalline state as a chain polynuclear structure. According to ESR data, in solution at room temperature, the compound exists as two mononuclear species, presumably *cis*- and *trans*-isomers. The assignment of the isomers was substantiated by analysis of ESR data and results of quantum chemical calculations. It was shown that HFS constants are

Table 3. Spin Hamiltonian parameters of the ESR spectra of Cu(II) hydroxamates in the low-temperature toluene glass at 100 K*

Compound	g_z	g_x	g_y	A	B	C	g_{iso}	a_{iso}	Concentration, %
				$\times 10^{-4} \text{ cm}^{-1}$					
IA	2.229	2.049	2.039	210.2	22.9	20.4	2.106	84.4	67
IB	2.241	2.047	2.048	206.4	31.0	15.1	2.112	84.1	33
IIA	2.229	2.061	2.046	205.7	26.7	23.7	2.112	85.4	63
IIB	2.247	2.080	2.051	198.5	11.8	33.7	2.126	81.2	37
IIIA	2.235	2.055	2.053	204.9	24.2	23.8	2.114	84.2	65
IIIB	2.243	2.077	2.044	187.5	6.5	36.3	2.121	77.0	35

* The constant a_{iso} and tensor components A , B , C correspond to the ^{65}Cu .

Table 4. Hyperfine coupling constants (A , B , C) and z , x , y -components of the g -tensor calculated for toluene solutions (according to the B3PW91/def2-TZVP//BP86/def2-TZVP calculation)

Isomer	g_z	g_x	g_y	Cu			N		
				A	B	C	A	B	C
				$\times 10^{-4} \text{ cm}^{-1}$			$\times 10^{-4} \text{ cm}^{-1}$		
<i>cis</i>	2.172	2.050	2.053	218.8	10.0	13.1	0.75	0.33	0.53
<i>trans</i>	2.173	2.048	2.055	211.3	1.2	9.0	0.73	0.32	0.52

most structure-sensitive to the geometry of isomers. Apart from the mononuclear species, dimer of the complex is detected in the frozen solution.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

ADDITIONAL INFORMATION

This article is prepared for the memorial issue in tribute to the Corresponding Member of the Russian Academy of Sciences K.Yu. Zhizhin on his 50th birthday.

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