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Water-Soluble Chiral Y(III)–Cu(II) Metallamacrocyclic Phenylalaninehydroximate Complex

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Abstract—A chiral Y(III)–Cu(II) metallamacrocyclic complex with L-phenylalaninehydroximate ligands was synthesized. The chirality of initial L-aminohydroximate ligands dictates the one-side orientation of the R-substituent relative to the internal O–Cu–N–O moiety. The molecular and electronic structures of the synthesized complex were studied by X-ray diffraction (CIF file CCDC no. 1903232) and quantum chemical calculations.

Keywords: synthesis, polynuclear metallamacrocyclic complexes, copper(II), yttrium(III), phenylalaninehydroximate ligands, structure, DFT calculations

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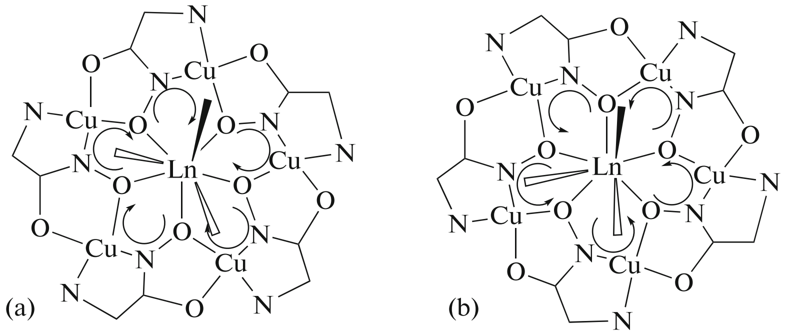
INTRODUCTION

The modern trends of the world pharmaceutical industry indicate increasing significance of the use of chiral compounds in an optically pure state, which is caused by various biological and pharmacological properties of single enantiomers [1, 2]. Currently, a promising line of research is the study of metal complexes with chiral ligands obtained by modifying organic natural products whose fragments are encountered as parts of proteins and nucleic acids. [3]. The metal ion in these compounds is usually coordinated to the donor nitrogen, oxygen, and sulfur atoms of amino acid protein moieties that model the metal environment in natural compounds.

α-Amino acids are N,O-type chelating ligands owing to the presence of donor carboxy and amino groups. The replacement of the carboxyl group by a hydroxamic group gives rise to a more efficient N,N- and O,O-type coordination without changing the chirality of the molecule. The prospects of aminohydroxamic acids for coordination chemistry are related to the possibility to prepare polynuclear heterometallic compounds containing simultaneously copper and lanthanide ions [4–8]. A very interesting class of these compounds are metallamacrocyclic complexes 15-MC-5, which are based on a virtually planar cyclic moiety composed of five Cu^{2+} ions with five aminohydroximate ligands with a lanthanide(III) central ion coordinated to five oxygen atoms of the metallamacrocycle [9]. Currently, the popularity of Ln(III)–Cu(II) 15-MC-5 complexes is largely due to their plentiful coordination chemistry, diverse properties, and easy synthesis [10–13].

Previously, we developed an original synthetic approach to Ln(III)–Cu(II) aqua complexes based on glycinehydroxamic acid, $Ln(H_2O)_3[15\text{-}MC_{Cu(II)Glyha}\text{-}5](Cl)_3$ [14–16]. Glycine, the simplest amino acid, has a hydrogen atom as the side chain. Correspondingly, X-ray diffraction study of the glycinehydroximate complex identified the presence of two types of molecule containing (+) and (–) chiral moieties, (a)—ONCuO– and (b)—OCuNO– (Scheme 1).



Scheme 1.

Concerning the chirality of Ln(III)–Cu(II) 15-MC-5 complexes, it is of interest to study, both theoretically and experimentally, compounds containing optically active ligands, e.g., L-phenylalaninehydroximate (Phalaha). L-Phenylalanine is a proteinogenic amino acid, which occurs in proteins of all known living organisms. Previously, it was shown that Phalaha can be utilized to prepare water-soluble metallacrowns 15-MC-5 containing lanthanide ions [17–20]. Meanwhile, the data on 15-MC-5 aqua complexes with an yttrium central ion are scarce. It is noteworthy that sophisticated composition and structure of these compounds and poor quality of single crystalline samples make X-ray diffraction experiment complicated and labor-consuming. It is difficult to solve the structures that contain a large number of heavy atoms and especially to refine positions of solvent molecules (water), which are abundant in these compounds. That is why resorting to quantum chemical modeling for studying the spatial structures of these compounds is relevant. From the standpoint of electronic structure, of considerable interest is the effect of benzyl substituents of the Phalaha ligands on the orbital structure and charge distribution of the metallamacrocyclic complex. The Y(III)–Cu(II) 15-MC-5 systems are convenient as model compounds for quantum chemical studies. Previously, we carried out a DFT study of formation of Cu(II)–Y(III) glycinehydroximate 15-MC-5 complexes [21]. The properties of yttrium(III), which belongs to rare earth metal group, make it the optimal analogue for quantum chemical modeling of lanthanide compounds, thus providing an acceptable resource intensity of calculations.

Here we set ourselves the task to prepare the Y(III)–Cu(II) 15-MC-5 aqua complex with L-phenylalaninehydroximate ligands (Phalaha) and to perform a comprehensive study of its structure and spectral properties by experimental methods and quantum chemical calculations.

EXPERIMENTAL

Commercially available copper acetate monohydrate and yttrium chloride hexahydrate (Aldrich) were used. L,α-Phenylalaninehydroxamic acid was synthesized in 92% yield from L,α-phenylalanine according to a reported procedure [20].

Synthesis of $Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5](Cl)_3 \cdot 11.5H_2O$ (I). L-α-Phenylalaninehydroxamic acid (0.18 g, 1 mmol) was added with intense stirring to a solution containing $YCl_3 \cdot 6H_2O$ (0.06 g, 0.2 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.2 g, 1 mmol) in doubly distilled water (30 mL). After 1.5 h, the solution turned deep blue-violet. The mixture was stirred for 48 h at 20°C and filtered. The dark blue needle crystals were produced by slow evaporation of the aqueous filtrate at 40°C and twice recrystallized from water. The yield was 0.28 (85%).

For $C_{45}H_{79}N_{10}O_{24.5}Cl_3Cu_5Y$

Anal. calcd., %	C, 32.46	H, 4.78	N, 8.41
Found, %	C, 32.49	H, 4.73	N, 8.39

IR (ν, cm^{-1}): 3321 w, 1598 s, 1579 s, 1496 m, 1405 m, 1344 m, 1302 m, 1211 w, 1181 w, 1156 w, 1120 w, 1081 w, 1073 m, 1026 s, 974 w, 935 m, 866 w, 847 w, 832 w, 756 w, 742 m, 703 s, 617 w, 573 w, 488 m. UV (293 K, H_2O): $\lambda = 575$ nm.

IR spectra were recorded on an FSM 1201 FT IR spectrometer. The samples were prepared by a standard procedure as mineral oil mulls. UV/Vis spectra were measured on a Perkin Elmer Lambda 25 spectrometer. Elemental analysis was performed using a Euro EA 3000 C,H,N-analyzer.

Single crystal X-ray diffraction of complex **I** was carried out at 100 K on a Bruker D8 Quest diffractometer (graphite monochromator, MoK_α radiation, λ = 0.71073 Å). The experimental reflection intensities were integrated using the SAINT software [22]. The absorption corrections were applied by means of the SADABS software [23]. The structure of **I** was solved by the SHELXT software [24] and refined by full-matrix least-squares method on F^2 in the anisotropic approximation for all non-hydrogen atoms using the SHELXTL software [25]. The hydrogen atoms were placed into geometrically calculated positions and refined in the riding model ($U_{iso}(H) = 1.2U_{equiv}(C, N)$). The crystal cell of **I** contains eight solvate water molecules per molecule of the complex. The water hydrogen atoms were not located.

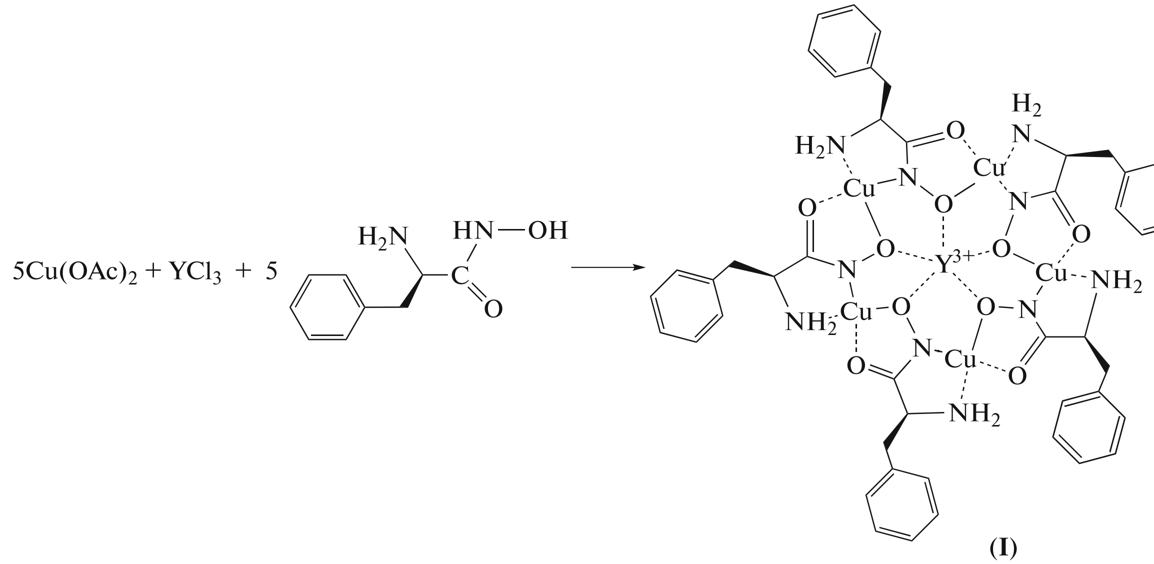
Altogether 72391 reflections were measured, of which 34223 reflections (R_{int} = 0.0558) wee unique with $I > 2\sigma(I)$. Single crystal unit cell parameters were as follows: a = 14.7137(7), b = 32.7696(15), c = 15.4541(7) Å, β = 117.800(2)°, V = 6591.3(5) Å^3. Space group $P2_1$, Z = 2, ρ(calcd.) = 1.678 g/cm^3, crystal size 0.24 × 0.17 × 0.12 mm, μ = 2.657 mm^{-1} , F(000) = 3400, 2.01° ≤ θ ≤ 29.00°, R_1 = 0.0803, wR_2 = 0.1979 ($I > 2\sigma(I)$), R_1 = 0.0904, wR_2 = 0.2021 (for all data), $S(F^2)$ = 1.072, ρ_{max}/ρ_{min} 1.635/–1.480 eÅ^{-3}, flack parameter 0.112(3).

The crystallographic data are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1903232; https://www.ccdc.cam.ac.uk/structures/).

DFT study of copper-containing ionic 15-MC-5 was implemented with a Gaussian09 [26] program package. Full structure optimization was performed for $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ and $\{Y(H_2O)_3\text{-}[15\text{-}MC_{Cu(II)Glyha}\text{-}5]\}^{3+}$ using the B3LYP functional [27–29] and split valence double basis set DGDZVP with polarization functions [30, 31]. The subsequent analysis of harmonic oscillations did not reveal imaginary frequencies, which attests to compliance of optimized structures to minima in the potential energy surface. For calculations of each complex, the total charge was specified to be +3. In order to avoid the problems caused by admixture of high-spin states to the low-spin state in DFT calculations, the complexes were modeled as high-spin systems with a multiplicity of 6. This approach to description of 15-MC-5 was substantiated in our previous study [21]. The maps of electron localization function (ELF) were obtained using the Multiwfn software, version 3.3.9 [32]. The quantum theory of atoms in molecules (QTAIM) calculations [33, 34] were performed using the AIMAll program [35].

RESULTS AND DISCUSSION

L-Phenylalaninehydroxamic acid was prepared from L-phenylalanine by a reported procedure [20]. The reaction of copper acetate, yttrium chloride, and L-phenylalaninehydroxamic acid results in the formation of water-soluble polynuclear Y(III)–Cu(II) metallamacrocyclic complex **I** (Scheme 2).



(I)

Scheme 2.

The molecular structure of complex **I** is shown in Fig. 1. The structure of **I** is in good agreement with the geometry of the Y(III) glycinehydroximate 15-MC-5 [16]. Selected bond lengths and angles of **I** and Y(OAc)$(H_2O)[15\text{-}MC_{Cu(II)Glyha}\text{-}5](NO_3)_2$ [16] (for comparison) are summarized in Table 1. Apart from the five oxime O atoms, the coordination sphere of Y(III) in complex **I** incorporates three oxygen atoms of water molecules in the axial positions. Unlike the glycinehydroximate complex [16], two molecules of complex **I** with similar structure are present in the independent part of the cell. The key difference between the structures of the independent molecules of **I** is in copper-coordinated water molecules. One of the molecules (A) coordinates additionally four H_2O molecules, whereas the other one (B) coordinates only one water molecule. The metallamacrocycles of independent molecules A and B are substantially nonplanar. The mean deviation from the plane is 0.286 and 0.291 Å (with maximum deviation of 0.799 and 0.772 Å) in A and B, respectively. As shown in Fig. 1, all $PhCH_2$ substituents are located on one side of the plane of the metallamacrocycle. The chirality of the initial L-aminohydroximate ligands is responsible for the one-side orientation of the R-substituent relative to the internal O–Cu–N–O moiety.

It is of interest that molecules of cerium aqua complex with phenylalaninehydroximate ligands that we synthesized previously form jaw-like sandwich structures owing to the bridging μ-Cl anion [36]. Unlike Ce(III) complex, the molecules of complex **I** do not form dimers. The distance between the yttrium atoms in the closest neighboring molecules A and B increases up to 9.133 Å versus 6.925 Å between cerium atoms [36] and the metallamacrocycles are markedly shifted relative to each other (Fig. 2).

The DFT-optimized geometry of the $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ ion is in good agreement with the X-ray diffraction structure of **I** (Table 1). The calculations reproduce a considerable increase in the Cu–N distances on going from N_{imine} to N_{amine}. The DFT calculations of normal vibrational frequencies and the corresponding intensities in the IR spectrum of $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ attest to the presence of strong CN stretching bands at 1580–1630 cm^{-1}; this is in good agreement with the experimental fre-

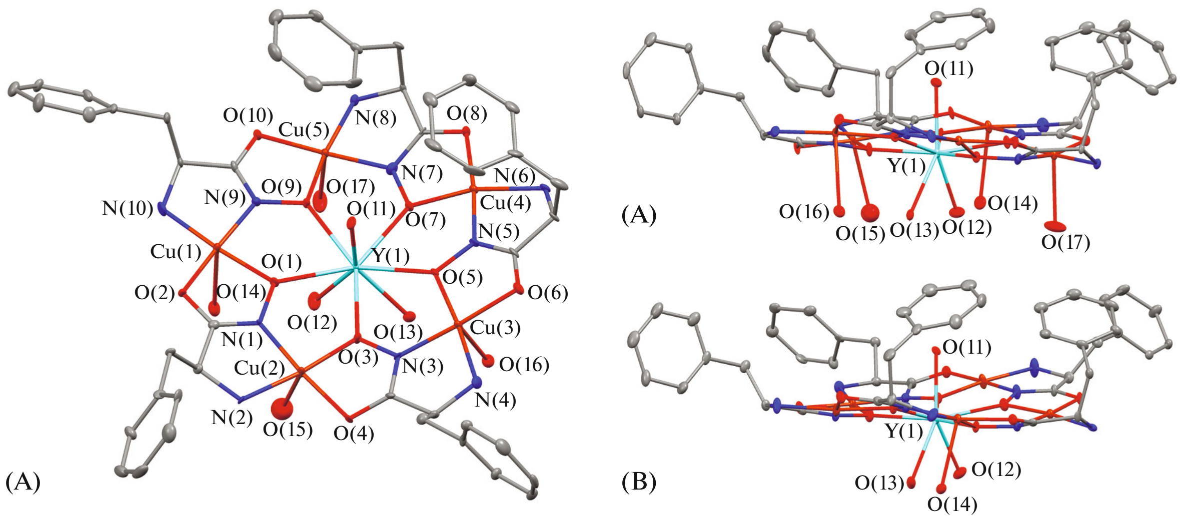


Fig. 1. Structure of complex **I**. The thermal ellipsoids are drawn at 30% probability level. The hydrogen atoms, Cl^- ions, and uncoordinated H_2O molecules are not shown.

quencies of 1579 and 1598 cm^{-1}. Orbital analysis (Fig. 3) predicts the energy gap of 2.38 eV between β-LUMO and the highest occupied MO containing contributions of copper 3*d* orbitals (β-HOMO-10). A similar value (2.34 eV) was found for the glycinehydroximate analogue, $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Glyha}\text{-}5]\}^{3+}$, where it corresponds to the β-LUMO and β-HOMO energy difference. This energy gap is in good agreement with the position of the *d*–*d* absorption band at 575 nm (2.16 eV) in the UV/Vis spectra of **I** and $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Glyha}\text{-}5]\}^{3+}$. The α- and β-orbitals of $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$, which are close in energy and are located between HOMO and HOMO-10, are concentrated on the benzyl substituents. The introduction of $PhCH_2$ group into the glycinehydroximate ligands increases the energies of occupied and unoccupied orbitals of the metallamacrocycle (Fig. 3), indicating the electron-donating effect of substituents. Correspondingly, QTAIM calculations attest to increasing negative and decreasing positive charges on Cu, N_{amine}, and $O_{carbonyl}$ atoms on going from $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Glyha}\text{-}5]\}^{3+}$ to $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ (Table 2). Meanwhile, the charges on the N_{imine} and O_{oxime} atoms

Table 1. Selected bond lengths (Å) and bond angles (deg) in complex **I** and $Y(OAc)(H_2O)[15\text{-}MC_{Cu(II)Glyha}\text{-}5](NO_3)_2$ according to X-ray diffraction data and calculated geometric parameters for the $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ ion

Bond	**I** (X-ray diffraction)	$\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ (DFT)	$Y(OAc)(H_2O)[15\text{-}MC_{Cu(II)Glyha}\text{-}5](NO_3)_2$ [16]
	d, Å		
$Y{-}O_{oxime}$	2.365(8)–2.434(8)	2.375–2.477	2.370(2)–2.410(2)
$Y{-}O_{aq}$	2.309(8)–2.422(9)	2.416–2.551	2.369(3)
$Cu{-}O_{oxime}$	1.905(9)–1.946(8)	1.975–1.984	1.936(2)–1.975(3)
$Cu{-}O_{carbonyl}$	1.895(9)–1.964(8)	1.944–1.951	1.928(3)–1.965(3)
$Cu{-}O_{aq}$	2.393(12)–2.642(11)		2.298(3)–2.479(3)
$Cu{-}N_{imine}$	1.859(10)–1.923(8)	1.906–1.926	1.898(3)–1.912(3)
$Cu{-}N_{amine}$	1.990(11)–2.017(12)	2.049–2.053	2.008(3)–2.042(3)
Angle	ω, deg		
$O_{oxime}CuN_{imine}$	89.0(4)–91.4(4)	90.2–92.3	88.45(11)–91.40(12)
$O_{oxime}YO_{oxime}$	70.2(3)–72.8(3)	72.1–73.6	70.59(9)–74.05(9)

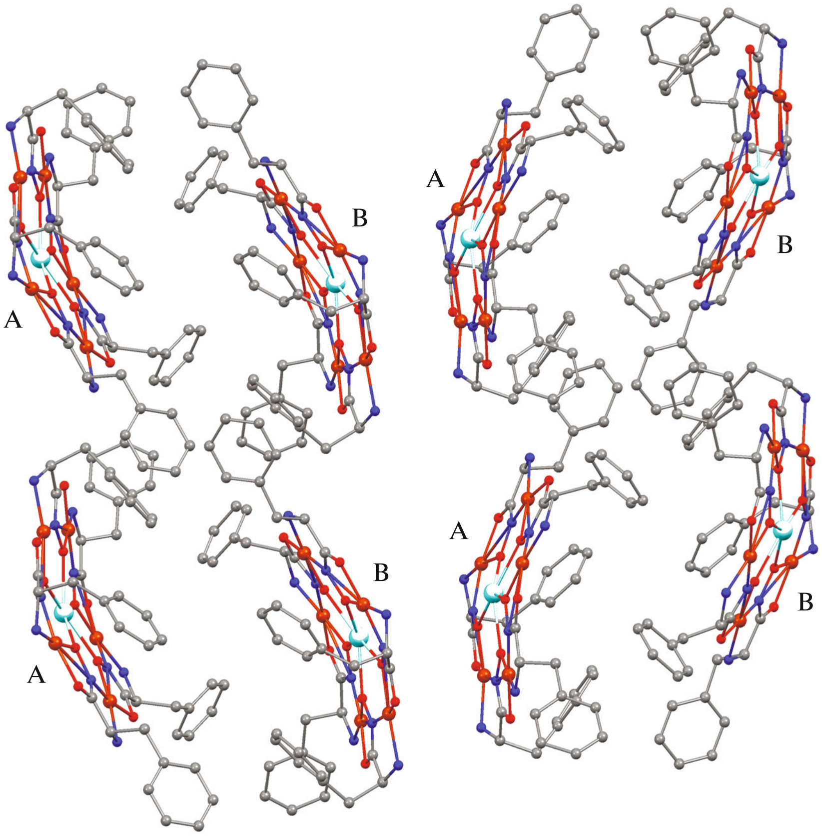


Fig. 2. Fragment of the crystal packing of complex **I**. The hydrogen atoms, Cl^- ions, and H_2O molecules are not shown.

located more closely to the Y(III) ion remain almost invariable.

The topology of the electron localization function (ELF) of the $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ ion (Fig. 4) has domains corresponding to lone pairs of nitrogen and oxygen atoms of the coordination bonds of the phenylalaninehydroximate ligand with the Cu^{2+} and Y^{3+} cations. In the $CuO_{oxime}Y$ plane, the ELF shows increased area of electron pair localization and increased value of the function for O_{oxime} in the direction towards the Y^{3+} ion compared with the direction towards Cu^{2+}. The ELF distribution pattern around the metallamacrocycle does not change on going to the glycinehydroximate analogue, which is in good agreement with the minor influence of the benzyl moieties on the charge and electron density distribution around the N_{imine} and O_{oxime} atoms.

Thus, the results indicated the possibility to prepare a chiral water-soluble Y(III)–Cu(II) aqua complex based the optically active L-phenylalaninehydroxamic acid. The molecular and electronic structures of the synthesized complex were studied by X-ray diffraction and quantum chemistry. The chirality of the initial ligands dictates the one-side orientation of the benzyl substituents relative to the metallamacrocycle. Benzyl substituents increase the energies of frontier orbitals and participate in the formation of the

Table 2. Average charges on the atoms of the metallamacrocycle in the ionic Y(III)–Cu(II) 15-MC-5 calculated by QTAIM

Atom	$\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$	$\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Glyha}\text{-}5]\}^{3+}$
Cu	1.0148	1.0200
O_{oxime}	–0.7808	–0.7768
$O_{carbonyl}$	–1.1132	–1.1046
N_{imine}	–0.6798	–0.6790
N_{amine}	–0.9792	–0.9698

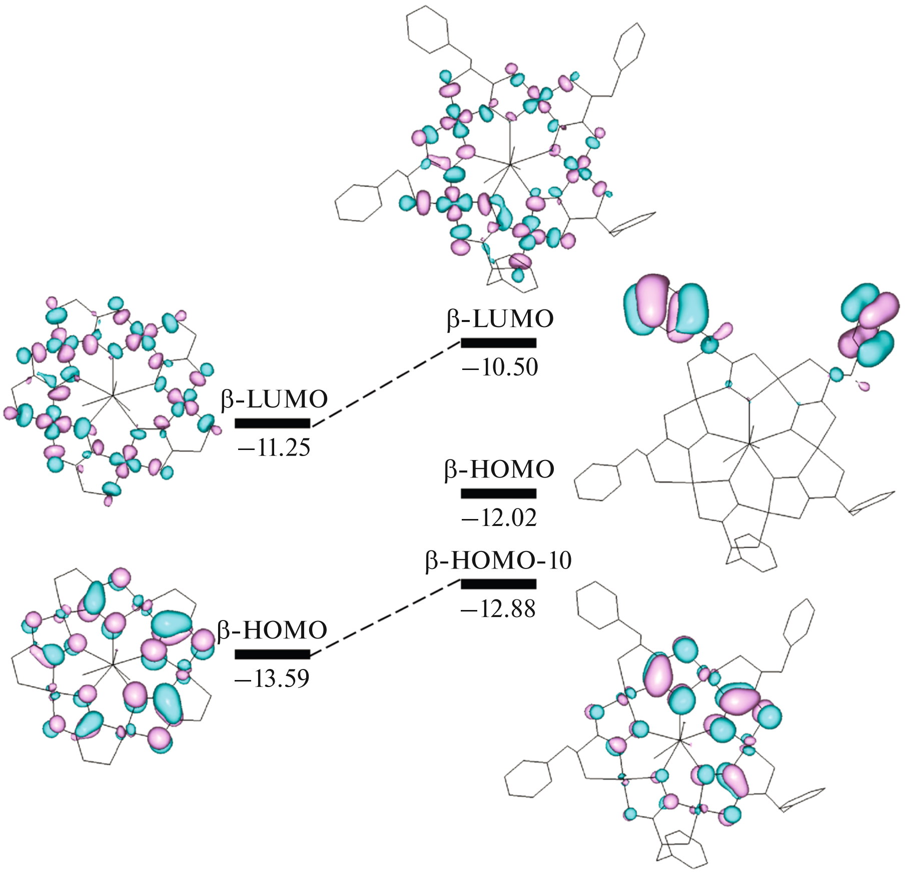


Fig. 3. Iso-surfaces at 0.03 value and MO energies (eV) of the complexes $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Glyha}\text{-}5]\}^{3+}$ and $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ calculated at the B3LYP/DGDZVP level.

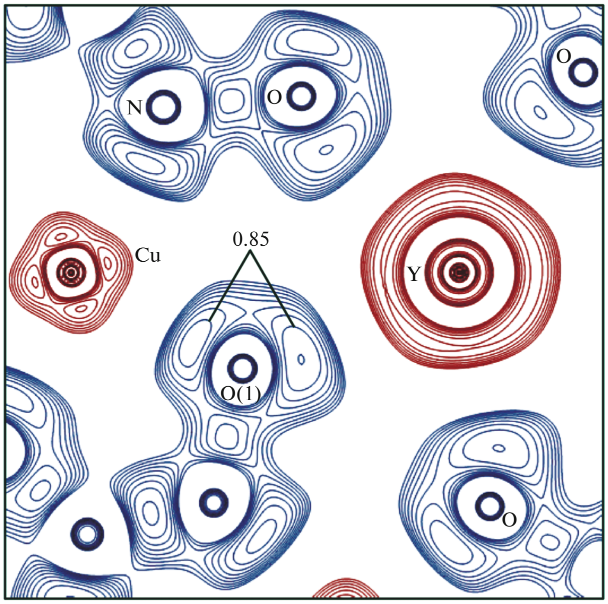


Fig. 4. Electron localization function (ELF) map in the plane of Cu, O(1), and Y atoms for $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$; the other indicated atoms deviate from the plane by not more than 0.05 Å. The iso-lines are drawn from 0.5 a.u. with a step of 0.05 a.u.

higher occupied MOs of the $\{Y(H_2O)_3[15\text{-}MC_{Cu(II)Phalaha}\text{-}5]\}^{3+}$ ion. The electron-donating properties of the $PhCH_2$ groups influence the charge distribution for outer atoms of the metallamacrocycle (Cu, N_{amine}, $O_{carbonyl}$), without affecting the inner atoms (N_{imine} and O_{oxime}), which is confirmed by ELF topology. Owing to the chirality, this compound is of considerable interest for the subsequent biological activity assays.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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