

ELECTRONIC STRUCTURE OF DIAQUABIS (P-CHLORO-PHENOXYACETATO) COPPER(II) COMPLEX BY DFT METHOD

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Abstract: *On the base of p-chlorophenoxyacetic acid and copper sulphate (II) has been obtained early described coordination compound $[Cu(4-D)_2(H_2O)_2]$. Its electronic structure were studied by DFT metod using ORCA program package. The electron-donor and electron-acceptor parts of the ligand and complex molecules were determined by analysis of Malliken atomic charges and ECP surface. It was found a low-lying LUMO in the case of a metal complex in which the proportion of the d-orbital of the metal is more than 60%.*

Key words: *Chlorophenoxy herbicides, p-chlorophenoxyacetic acid, copper (II) complex, X-Ray, DFT, electronic structure.*

Introduction. Chlorophenoxy herbicides are known to be one of the widely used pesticide families. In addition, they are synthetic auxins that are used to control weeds in fields where corn, rice and wheat are grown [1]. Despite the introduced form (free acids, alkali and amine salts and esters) into the environment, they retain pesticide activity. They remain in soil for about 1 month [2] and dissolve well in water. In soil, they can bind with metal ions such as Cu (II), Co (II), Ni (II) [3].

Flexible organic carboxylic acid ligands have great deformability, abundant configuration and conformation and have good potential in synthesizing coordination compounds with novel structures and functions [4-8].

p-chlorophenoxyacetic acid is one of these compounds and its biological activity has been broadly studied [9]. From a theoretical point of view, p-chlorophenyl acetate has not been studied. The vibrational and electronic spectra of some phenoxyacetic acid herbicides have been studied only by the DFT method [10]. In the reference, complexes of p-chlorophenoxyacetic acid with copper, cobalt, zinc and cadmium have been obtained and their structure has been established by X-ray diffraction analysis [11, 12]. Metal complexes can be more active than ligands. With this in mind, we studied interaction of 4-chlorophenoxyacetic acid with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and it has been theoretically studied electronic structure of the obtained complex.

Material and methods. The reagents used in the synthesis were purchased from Sigma-Aldrich and were used without any purification. Dissolved 373 mg (0.2 μmol) 4-chlorophenoxyacetic acid in absolute ethyl alcohol and 250 mg (0.1 μmol) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water. Both solutions were mixed, added to it 0.12 ml of MEA and vigorously stirred with a magnetic stirrer at 60 ° C for 30 minutes. The solution was allowed to slowly evaporate at room temperature, and after a week it was found that pale blue needle-shaped single crystals had formed. The single crystal was filtered off from the solution, washed with ethanol, air dried. Yield: 75%. Elemental analysis for $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{O}_8\text{Cu}$ (470.47) calcd: C 40.86, H 3.49%. Found: C 40.79, H 3.35%.

The structure was early studied by single crystal XRD method [11, 12] and they deposited to CCDC by following RefCodes: PHXCUA, PHXCUA01 and PHXCUA02. The unit cell of the crystal ($a= 5.1108(8)$ (Å), $b=7.0620(13)$ (Å), $c=13.253(3)$ (Å), $\alpha= 81.783(16)$ (°) $\beta= 86.401(14)$ (°) $\gamma=76.367(15)$ (°), $V=459.857(\text{Å}^3)$, and $Z=1$) contains two molecules of the complex(parallel located to each other).

The structure of diaquabis(p-chlorophenoxyacetato) copper(II) consists of centrosymmetric trans related bischelate phenoxyacetate ligands about the copper(II) ions [11].

In order to DFT calculations, the initial geometry of the complex was obtained from X-ray data (cif file). The initial geometry of the ligand molecule was built using the Avogadro [13] program package. Density functional theory (DFT) calculations by B3LYP/def2-TZVP method have been performed in ORCA 5.0 program package [14]. The results of DFT calculations visualized in Avogadro, MultiWFN [15] and VMD [16] program packages.

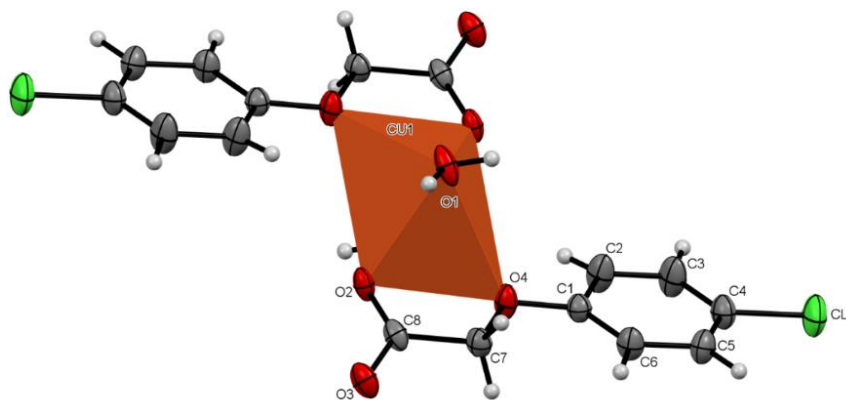


Fig.1. X-Ray determined structure of the complex (ellipsoid and numbering)

Results and discussion. After optimization of the geometry of the complex, the calculated geometric characteristics (bond lengths and angles) were compared with the X-ray diffraction data. The largest error is found when comparing the lengths of the Me-O bonds (oxygen atom of a water molecule) (Table 1.). The good correlation coefficient and low values of mean absolute error (MAE) and LE (largest error) shows suitability of chosen method for further studies (Table 2).

The distribution of total charge on atoms represents the electron density in the vicinity of the atom. There are several methods (Mulliken, Mulliken, Mulliken, Mulliken, Mulliken and etc.) for calculating the total charge on an atom [17]. The most widely used calculation is charge distribution by Mulliken. Most positively and negatively charged atoms play an essential role in chemistry to predict electrophile and nucleophile centers of any molecule. Based on this, the total charges on atoms of the ligand molecule and the complex were calculated (Fig.2). The calculation results show the localization of the largest negative charge on oxygen atoms of the ligand molecule. The largest positive charge is localized on the hydrogen atom of carboxylic group, which participate in forming of intramolecular H-bond with oxygen atom of phenoxy group (Fig.2, a). A higher negative charge in oxygen atoms is also found in the complex (Fig. 2, b). The largest negative charges are localized in the oxygen atoms of the water molecule included in the complex.

Table 1.

Bond	Experiment	DFT	$\Delta l, \text{\AA}$
Cu1-O1	1.956	2.149	0.19
Cu1-O2	1.957	1.891	0.066
Cu1-O4	2.398	2.411	0.012

Table 2. Statics for experimental and calculated bond lengths and angles

Parameter	MAE	LE	R ²
Bond lengths, Å	0.06	0.19	0.97
Bond angle, °	2.80	1.00	0.99

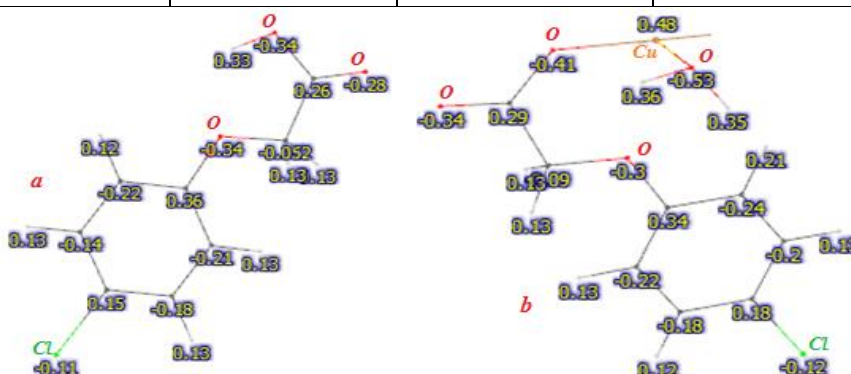
Fig.2. Atomic charge distribution on atoms of the ligand (*a*) and complex molecules (*b*, for the the asymmetric part).

Table 3. FMO characteristics of the ligand molecule and complex

Ligand			
HOMO(α), eV	-6.72	HOMO(β), eV	-6.72
LUMO(α), eV	-1.17	LUMO(β), eV	-1.17
Energy gap (α), ΔE (eV)	5.55	Energy gap (β), ΔE (eV)	5.55
HOMO(α) composition, %	p : 93.5	HOMO(β) composition, %	p : 93.5
LUMO(α) composition, %	p : 89.1	LUMO(β) composition, %	p : 89.1
Complex			
HOMO(α), eV	-6.56	HOMO(β), eV	-6.56
LUMO(α), eV	-1.02	LUMO(β), eV	-3.91
Energy gap (α), ΔE (eV)	5.54	Energy gap (β), ΔE (eV)	2.65
HOMO(α) composition, %	p : 93.4, d : 4.5	HOMO(β) composition, %	p : 93.4, d : 4.5
LUMO(α) composition, %	s : 32.9, p : 65.3	LUMO(β) composition, %	p : 22.4, d : 66.8

As is well known that the electron-donor and electron-withdrawing properties and, consequently, the electrophilic and nucleophilic reactivity of chemical compounds is closely related to the energies of the frontier molecular orbitals (FMO) and the electron densities in them (FED) [18]. In this regard, the energies of FMO and FED were analyzed for the ligand molecule and complex. A higher stability (large energy gap) is characteristic for the ligand molecule due to the presence of an intramolecular hydrogen bond between OH and O (Fig. 4). FMO energies of the ligand are the same for alpha and beta MOs. However, in the case of the complex, the energies of the alpha and beta MOs are different. The complex has a low-lying LUMO, in which the proportion of the d-orbital of the metal is more than 60% (Fig. 4 , Table 3).

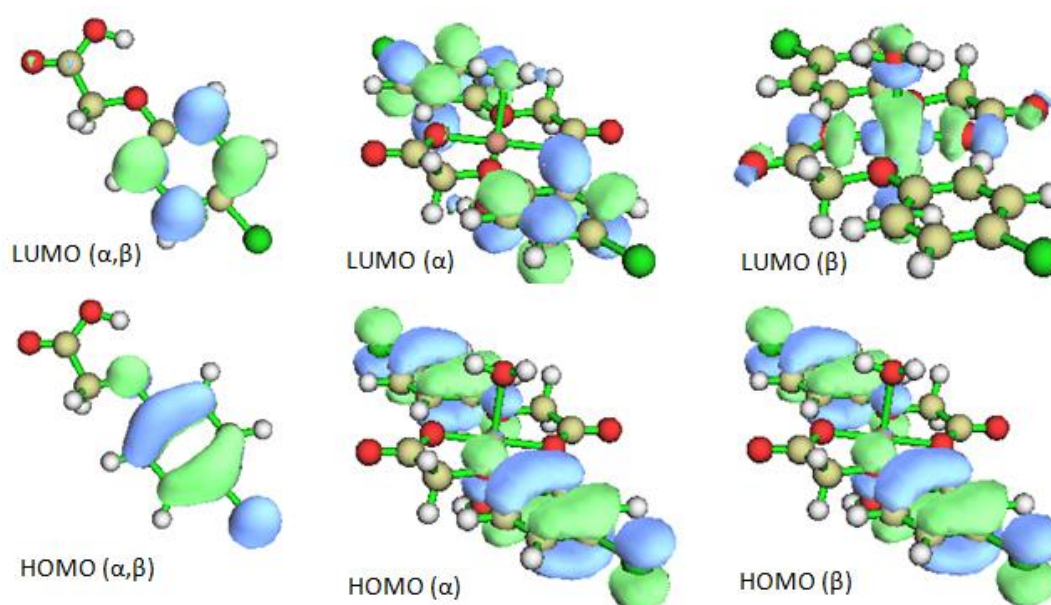


Fig. 4. Frontier electron densities for ligand molecule and complex.

It is known [19] that the electrostatic potential surface is an useful guide to the molecule's reactive behavior, especially in non-covalent interactions. Electrostatic potential map is used to locate the positive and negative charged electrostatic potential in the molecule. The color scale indicates the negative (blue) and positive (red) value. The blue color indicates the minimum electrostatic potential (place of excess electrons) and that atoms act as nucleophile. Red indicates electron deficiency in vicinity of an atom and it act as electrophile.

Analysis of the ECP surface of the ligand showed the presence of the minimum in the vicinity of oxygen atom of C=O group and the maximum at the H atom of OH group. In the case of a complex, the maxima are localized at the H atoms of the water molecule, and the minima are in the vicinity of the oxygen of the C = O groups (Fig.5).

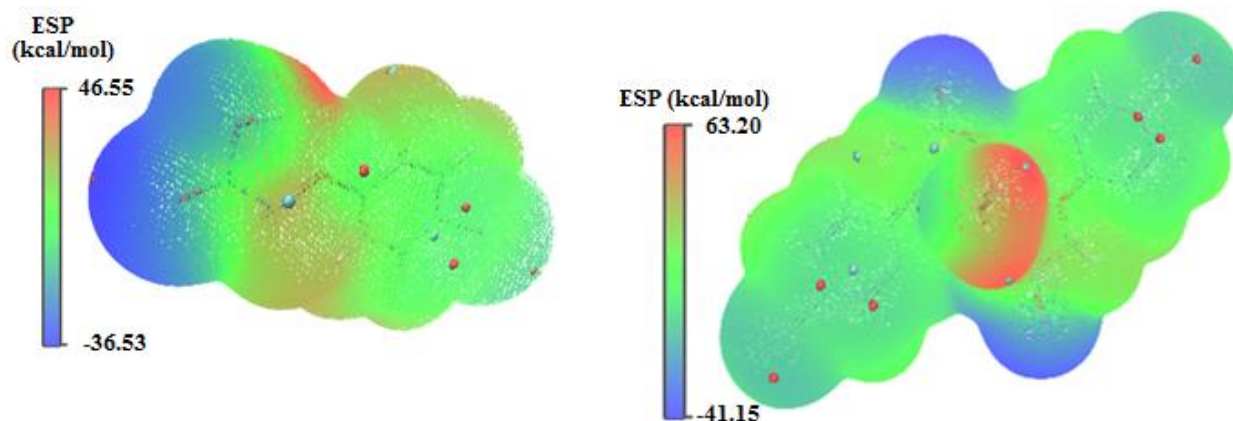


Fig. 5. The ESP surface maxima and minima for ligand molecule and complex. Red colored part (blue circle) is maxima, cyan colored (red circles) part is minima

Conclusion. Thus, by studying the interaction of p-chlorophenoxyacetic acid with a copper salt, a complex of metals was obtained, and their electronic structure was also investigated by the DFT method. The analysis of the total charge on atoms and frontier MOs is carried out. The electron-donor and electron-acceptor parts of the ligand and complex molecules were determined. Low-lying LUMO was determined in the case of a metal complex in which the portion of the d-orbital of the metal is more than 60%.

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