

Impact Factor:

ISRA (India) = 6.317
 ISI (Dubai, UAE) = 1.582
 GIF (Australia) = 0.564
 JIF = 1.500

SIS (USA) = 0.912
 ПИИИ (Russia) = 3.939
 ESJI (KZ) = 9.035
 SJIF (Morocco) = 7.184

ICV (Poland) = 6.630
 PIF (India) = 1.940
 IBI (India) = 4.260
 OAJI (USA) = 0.350

SOI: [1.1/TAS](#) DOI: [10.15863/TAS](#)

International Scientific Journal
Theoretical & Applied Science

p-ISSN: 2308-4944 (print) e-ISSN: 2409-0085 (online)

Year: 2021 Issue: 10 Volume: 102

Published: 28.10.2021 <http://T-Science.org>

QR – Issue



QR – Article



Bekmurod Khurramovich Alimnazarov

Termez State University

Senior teacher of the Department of Inorganic and Analytical Chemistry (TerSU),
 190111, Republic of Uzbekistan, Termez, Barkamol Avlod str., 43.
alimnazarov2016@mail.ru

Jamshid Mengnorovich Ashurov

Institute of Bioorganic Chemistry of the Uzbekistan Academy of Sciences
 Senior scientist of the laboratory of Complex compounds
 Republic of Uzbekistan, Tashkent, Mirzo Ulugbek str., 83
atom.uz@mail.ru

Alisher Gulumbaevich Eshimbetov

Institute of Bioorganic Chemistry of the Uzbekistan Academy of Sciences
 Senior scientist of the laboratory of Complex compounds
 Republic of Uzbekistan, Tashkent, Mirzo Ulugbek str., 83.
evalisberg@yahoo.com

Khayit Khudainazarovich Turaev

Termez State University

Doctor of Chemistry, Professor,

Dean of the Faculty of Chemistry, TerSU

190111, Republic of Uzbekistan, Termez, Barkamol Avlod str., 43.

Bakhtiyar Tulyaganovich Ibragimov

Institute of Bioorganic Chemistry of the Uzbekistan Academy of Sciences
 Leading scientist of the laboratory of Complex compounds
 Republic of Uzbekistan, Tashkent, Mirzo Ulugbek str., 83.
bakhtiyar.i@yahoo.com

**ELECTRONIC STRUCTURE OF DIAQUABIS(P-
 CHLOROPHOXYACETATO) COPPER(II) COMPLEX BY DFT
 METHOD**

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 method using ORCA program package. The electron-donor and electron-acceptor parts of the ligand and complex molecules were determined by analysis of Mulliken 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.

Language: English

Citation: Alimnazarov, B. Kh., Ashurov, J. M., Eshimbetov, A. G., Turaev, Kh. Kh., & Ibragimov, B. T. (2021). Electronic structure of diaquabis(*p*-chlorophenoxyacetato) copper(II) complex by DFT method. *ISJ Theoretical & Applied Science*, 10 (102), 964-968.

Soi: <http://s-o-i.org/1.1/TAS-10-102-109> **Doi:** <https://dx.doi.org/10.15863/TAS.2021.10.102.109>

Impact Factor:

ISRA (India) = 6.317	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 1.582	PIIHQ (Russia) = 3.939	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 9.035	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 7.184	OAJI (USA) = 0.350

Scopus ASCC: 1604.

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.

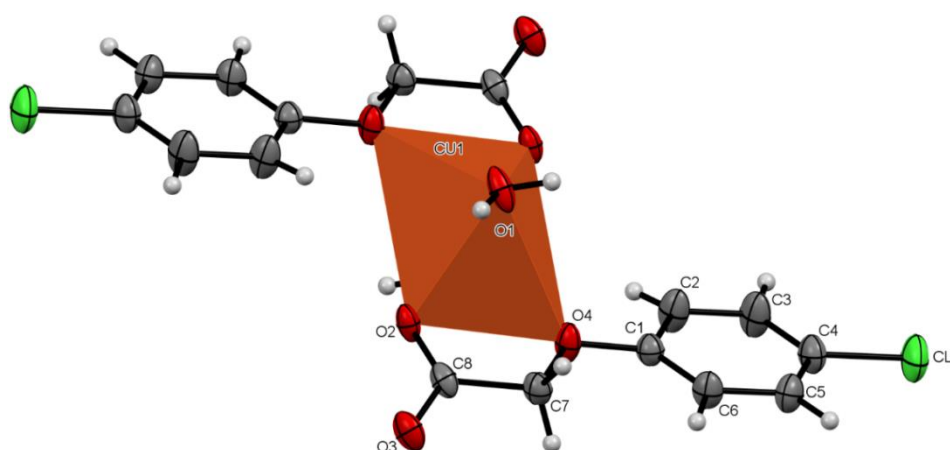


Fig.1. X-Ray determined structure of the complex (ellipsoid and numbering)

Impact Factor:

ISRA (India) = 6.317
 ISI (Dubai, UAE) = 1.582
 GIF (Australia) = 0.564
 JIF = 1.500

SIS (USA) = 0.912
 ПИИЦ (Russia) = 3.939
 ESJI (KZ) = 9.035
 SJIF (Morocco) = 7.184

ICV (Poland) = 6.630
 PIF (India) = 1.940
 IBI (India) = 4.260
 OAJI (USA) = 0.350

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).

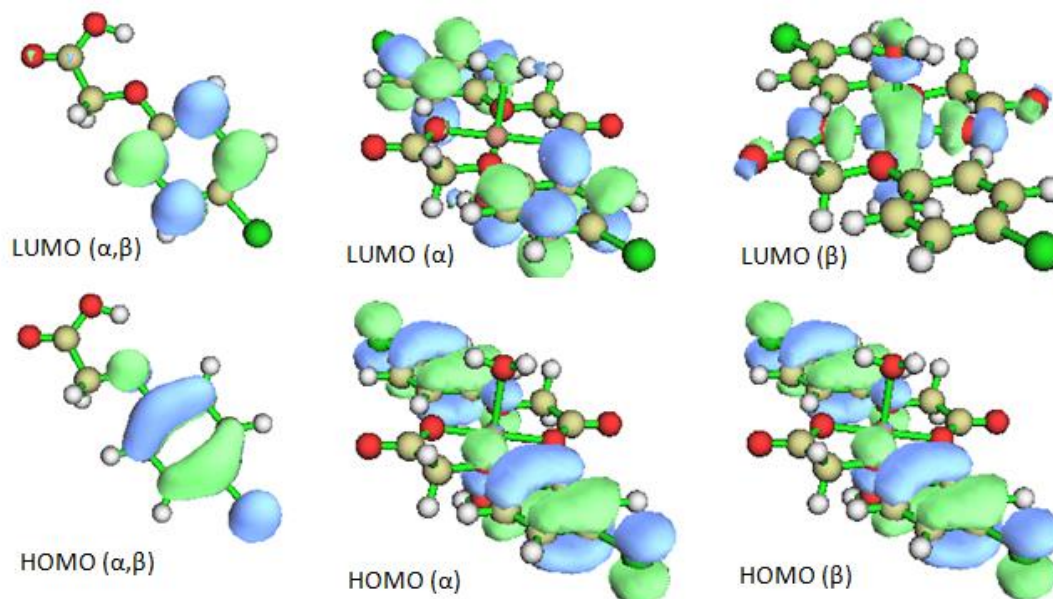


Fig. 4. Frontier electron densities for ligand molecule and complex.

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).

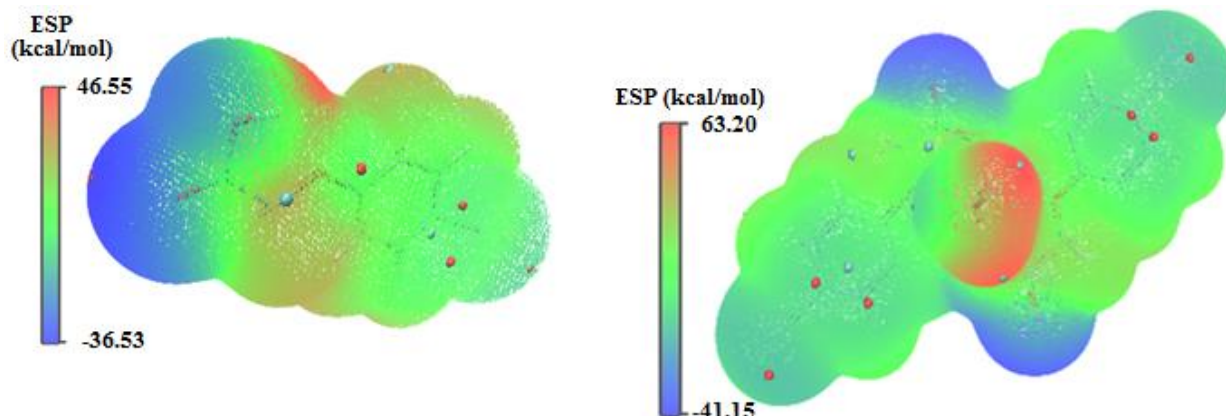


Fig. 5. The ESP surface maxima and minima for ligand molecule and complex. Red colored part (blue circle) is maxima, cyan colored (red circles) part is minima

Impact Factor:

ISRA (India) = 6.317
ISI (Dubai, UAE) = 1.582
GIF (Australia) = 0.564
JIF = 1.500

SIS (USA) = 0.912
ПИИИ (Russia) = 3.939
ESJI (KZ) = 9.035
SJIF (Morocco) = 7.184

ICV (Poland) = 6.630
PIF (India) = 1.940
IBI (India) = 4.260
OAJI (USA) = 0.350

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%.

References:

1. Krieger, R. (2010). *Hayes' Handbook of Pesticide Toxicology*, third ed., Academic Press.
2. (n.d.). – *PPDB Pesticide Properties Database; EXTOTOXNET – Extension Toxicology Network*. Retrieved from <http://sitem.herts.ac.uk/aeru/iupac/>
3. Skiba, E., et al. (2016). *Influence of 2,4-D and MCPA herbicides on uptake and translocation of heavy metals in wheat (Triticum aestivum L.)*. Environmental Pollution, <http://dx.doi.org/10.1016/j.envpol.2016.10.072>
4. Xu, X.X., Ma, Y., & Wang, E.B. (2007). Different aliphatic dicarboxylates affected assemble of new coordination polymers constructed from flexible-rigid mixed ligands. *J. Solid State Chem.*, 180 (11), 3136-3145.
5. Zhang, W.H., Wang, Y.Y., Lermontova, E.K., et al. (2010). Interaction of 1,3-adamantanediactic acid (H(2)ADA) and ditopic pyridyl subunits with cobalt nitrate under hydrothermal conditions: pH influence, crystal structures, and their properties. *Cryst. Growth Des.*, 10 (1), 76-84.
6. Sposato, L.K., Nettleman, J.H., Braverman, M.A., et al. (2010). Synthesis and magnetic properties of dual-ligand divalent copper coordination polymers with rhomboid layer, archimedean grid, and self-penetrated network topologies. *Cryst. Growth Des.*, 10 (1), 335e343.
7. Wu, A.Q., Li, Y., Zheng, F.K., et al. (2006). Different molecular frameworks of zinc(II) and cadmium(II) coordination polymers constructed by flexible double betaine ligands, *Cryst. Growth Des.*, 6 (2), 444-450.
8. Gao, G.G., Xu, L., Qu, X.S., et al. (2008). New approach to the synthesis of an organopolymolybdate polymer in aqueous media by linkage of multicarboxylic ligands. *Inorg. Chem.*, 47 (8), 3402-3407.
9. Xin-Xian, L., Fumiyuki, K., Hiromi, I., & Yasuyoshi, H. (n.d.). Chlorophenoxyacetic acid and chloropyridylphenylurea accelerate translocation of photoassimilates to parthenocarpic and seeded fruits of muskmelon (Cucumismelo). *J. Plant Physiol.*, Vol.168. No.9. 920-926.
10. D. Arul Dhas, et al. (2013). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 108, 89–99.
11. Smith, G., O'Reilly, E. J., et al. (1981). Crystal and Molecular Structures of Diaquabis(p-chlorophenoxyacetato) copper(II) and Diaquabis(phenoxyacetato)-zinc(II). *Inorganic Chimica Acta.*, 41, 111-120.
12. Long, L., Kaisheng, D., Yuqiu, D., & Xianhong, Y. (2014). Synthesis and Structure of Three Novel Complexes Based on 4-Chlorophenoxyacetic Acid. *Mol. Cryst. Liq. Cryst.*, Vol. 588: pp. 63–73.
13. Hanwell, M.D., Curtis, D.E., Lonie, D.C., Vandermeersch, T., Zurek, E., & Hutchison, G.R. (2012). *J Cheminform*, 4:17.
14. Neese, F. (2012) ORCA Program system. *Comput. Mol. Sci.*, 2, 73.
15. Lu, T., & Chen, F.W. (2012). Multiwfn: A multifunctional wavefunction analyzer. *J. Comp.Chem.*, 2, 15.
16. Humphrey, W. Dalke, A., & Schulten K. (1996). "VMD - Visual Molecular Dynamics", *J. Molec. Graphics*, vol. 14, pp. 33-38.
17. Storer, J.W., Giesen, D.J., Cramer, C.J., et al. (1995). Class IV charge models: A new semiempirical approach in quantum chemistry. *J Computer-Aided Mol Des*, 9, 87–110. <https://doi.org/10.1007/BF00117280>
18. Rauk, A. (2001). *Orbital interaction. Theory of Organic chemistry*. Wiley-Interscience, Hoboken, New Jersey
19. Murray, J.S., & Politzer, P. (2011). The electrostatic potential: an overview. © John Wiley & Sons, Ltd. *WIREs Comput Mol Sci*, 1, 153–163. DOI: 10.1002/wcms.19