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Preparation of Metal Complexes of 4,5-Dichlorphthalic Acid as Nanoscale and Electronic Properties

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ABSTRACT: Here phthalic acid metal complexes with acid function were synthesized. Fourie transform infrared spectroscopy (FT- IR), X-ray diffraction analysis (XRD), Scanning electron microscopy-Energy Dispersive Spectrometry (SEM+EDS) devices were used for structure analysis. The structural parameters of the copper and zinc complexes of 4,5-dichlorphthalic acid were determined by the LanL2DZ basis base set of B3LYP method. Electronic properties such as HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies and molecular electrostatic potential (MEP) were obtained. Stability, charge delocalization of molecules resulting from hyperconjugative interactions were analyzed using natural bond orbital (NBO) analysis. The comparison of the theoretical and experimental FT-IR spectra of Zn and Cu-4,5-dichlorphthalic acid (DCPA) were made and R = 0.97204 for Cu and R = 0.97929 for Zn complex were found in linear fit studies. Two characterization results were found to be consistent.

Key words: Phthalic acid derivative, synthesis, metal, electronic properties.

Nano-Ölçekli Olarak 4,5-Diklorftalik Asit Metal Komplekslerinin Hazırlanması ve Elektronik Özellikler

ÖZET: Burada asit fonksiyonlu ftalik asit metal kompleksleri sentezlendi. Yapı analizi için Fourie dönüşümü kızılötesi spektroskopisi (FT-IR), X-ışını kırınım analizi (XRD), Taramalı elektron mikroskopisi-Enerji Dağıtıcı Spektrometresi (SEM + EDS) cihazları kullanılmıştır. 4,5-diklorftalik asidin bakır ve çinko komplekslerinin yapısal parametreleri, B3LYP yönteminin LanL2DZ baz seti ile belirlenmiştir. HOMO (en yüksek işgal edilen moleküler orbital) ve LUMO (en düşük işgal edilmeyen moleküler orbital) enerjileri ve elektron yoğunluk dağılım potansiyeli (MEP) gibi elektronik özellikler elde edildi. Hiperkonjugatif etkileşimlerden kaynaklanan moleküllerin stabilitesi, yük delokalizasyonu, doğal bağ orbital (NBO) analizi kullanılarak analiz edildi. Zn ve Cu-4,5-diklorftalik asidin (DCPA) teorik ve deneysel FT-IR spektrumlarının karşılaştırılması yapıldı ve Cu için R = 0.97204 ve Zn kompleksi için R = 0.97929 doğrusal çalışmalar formunda bulundu. İki karakterizasyon sonucunun tutarlı olduğu bulunmuştur.

Anahtar Kelimeler: Ftalik asit türevi, sentez, metal, elektronik özellikler

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INTRODUCTION

Phthalic acid and its derivatives are industrially needed chemical compounds. This compound and its derivatives are used in many fields such as paint, detergent, photocatalytic, cosmetic (Liu L.-C. et al., 2014). Due to technological developments and increasing world population, the new chemical demand has also increased. The use of phthalic acid derivatives in the reduction of toxic pollutants such as Cr (VI) by modifying them on the TiO_2 surface is of interest for research (Liu H. et al., 2011). In this study, it is considered that especially prepared compounds can be used as support materials. There are studies based on phthalic acid supported synthesis of silver nanoparticles. It is used for sensor studies. However, similar copper and zinc nanoparticles are not found in the literature. Zinc and copper-containing phthalic acid derivatives may also be used as sensors or catalyst support (Detsri and Seeharaj, 2017). The theoretical chemical calculations of DFT B3LYP have been studied well and consistently (Cabir et al., 2020; Prabhaharan et al., 2015; Priya et al., 2019; Rocha et al., 2015). Theoretical studies have been used in many studies on organo metal compounds (El Bourakadi et al., 2019; Kumar et al., 2019; Pandey et al., 2017; Solğun et al., 2020). It is also important to understand the behavior of the more dense phases of the complexes (Cabir et al., 2019; Jayaprakash et al., 2011; Mıhçıokur and Özpozan, 2017). 4,5-dichlorphthalic acid and its complexes have been the most frequent subject of experimental research due to their importance in the industry. To the best of our knowledge, literature review has shown that there are no their DFT studies.

In this study, structural analyzes were calculated theoretically. Molecular geometry optimized structural parameters and HOMO - LUMO band gap, MEP and NBO analyzes were calculated by B3LYP method. Local and global chemical reactivity descriptors were calculated. The comparison of the theoretical and experimental FT-IR spectra of Zn and Cu-DCPA were made and the results of the two characterizations were found to be consistent.

EXPERIMENTAL AND THEORETICAL SECTION

Preparation of the copper complex (1)

0.227 g of 4,5-dichlorphthalic acid was dissolved in 10 ml of ethanol. Then 0.200 g of NaOH was added to the medium and stirred. To this mixture was added 0.190 g of $CuCl_2$ dissolved in 15 ml of ethanol. The green solution turned to light green and began to precipitate. Stirring was continued at room temperature for 2 hours. The reaction was then stopped and filtered. Washed with ethanol. It was dried at 40 ° C. Yield: 0.575 g. EN> 320 ˚C. IR spectrum (cm^{-1}): 1612, 1544, 1400, 1323, 1170, 1128, 1005, 920, 900, 844, 808, 617.

Preparation of the zinc complex (2)

0.227 g of 4,5-dichlorphthalic acid was dissolved in 10 ml of ethanol. Then 0.200 g of NaOH was added to the medium and stirred. To this mixture was added 0.190 g of $ZnCl_2$ dissolved in 15 ml of ethanol. The white solution began to precipitate. Stirring was continued at room temperature for 2 hours. The reaction was then stopped and filtered. It was washed with ethanol. It was dried at 40 ° C. Yield: 0.487 g. EN> 320 ˚C. IR spectrum (cm^{-1}): 1612, 1544, 1400, 1398, 1323, 1170, 1128, 1003, 920, 900, 844, 808, 617.

Computational Study

The potential energy profile of the compound was determined using the B3LYP / LanL2DZ method to find stable optimization. Theoretical calculations were made with the Gaussian-09 package program(M. J. Frisch, 2016), which promotes geometry optimization of B3LYP correlation

functionality. The resulting stable conformers were further optimized using LanL2DZ basis sets. Thermodynamic properties and energy of the compound were determined using optimized geometry.

RESULTS AND DISCUSSION

Phthalic acid derivatives are chemical compounds needed in the chemical industry. Especially these derivatives can be used in many fields such as detergent, paint, photocatalytic, cosmetics. Technological advances and increased comfort, new chemical demand has also increased. Bringing phthalic acid derivatives to nanoscale may also allow the application of new functional properties.Metal complexes modified with DCPA (4,5-dichlorphthalic acid) are synthesized in Figure 1. DCPA is an aromatic-carboxylic acid capable of resonating only a pair of electrons on carbonyl and oxygen. As is known, the carboxylate moiety (-COO) is a common and popular functional group for the stabilization of NPs (Henglein and Giersig, 1999; Rawat et al., 2017).

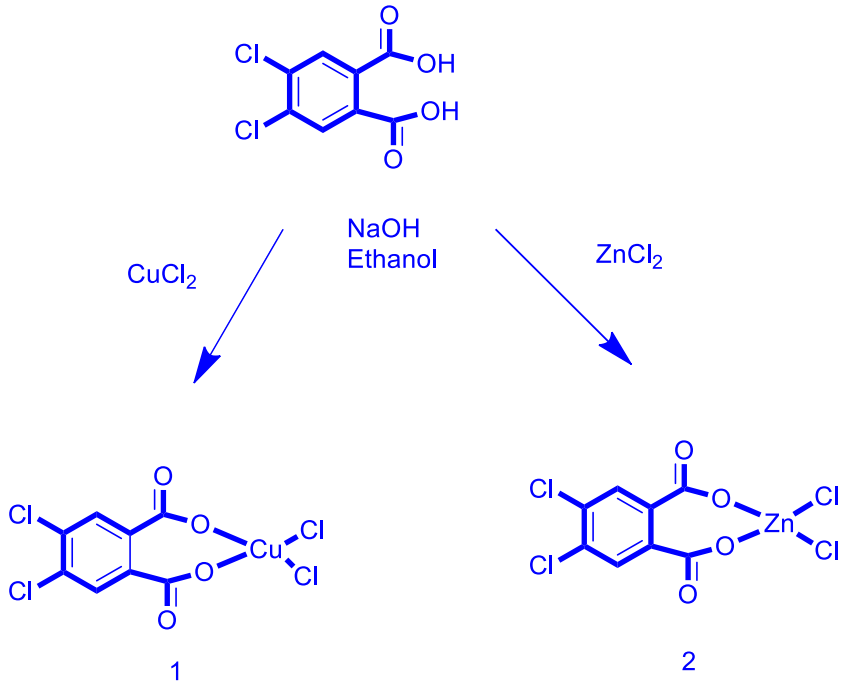

Figure 1. Synthesis of metal complexes

The size and particle morphology of Zn and Cu complexes of DCPA were examined using SEM + EDS analysis (Figure 2,3). These images show that the compounds have reached nano dimensions. These data show that the compounds can be used to form active catalysts on surfaces.

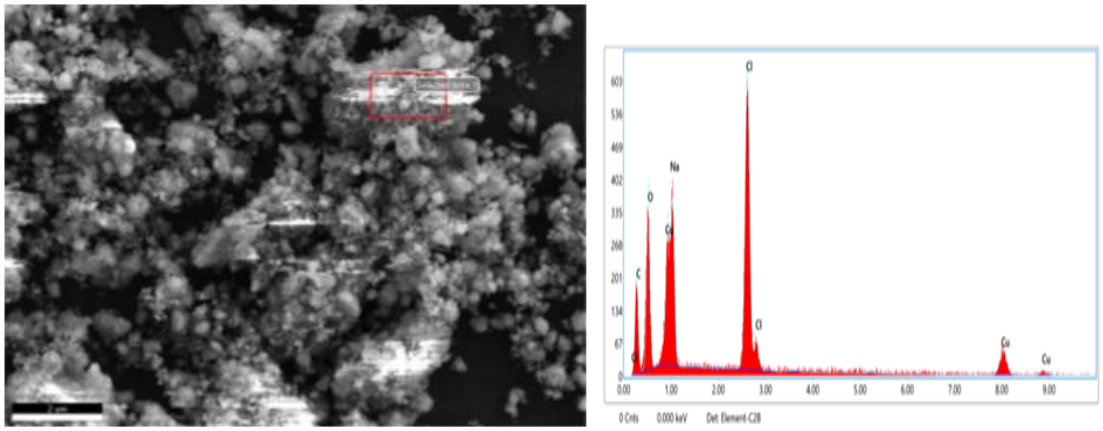

Figure 2. SEM image of the copper complex with EDS

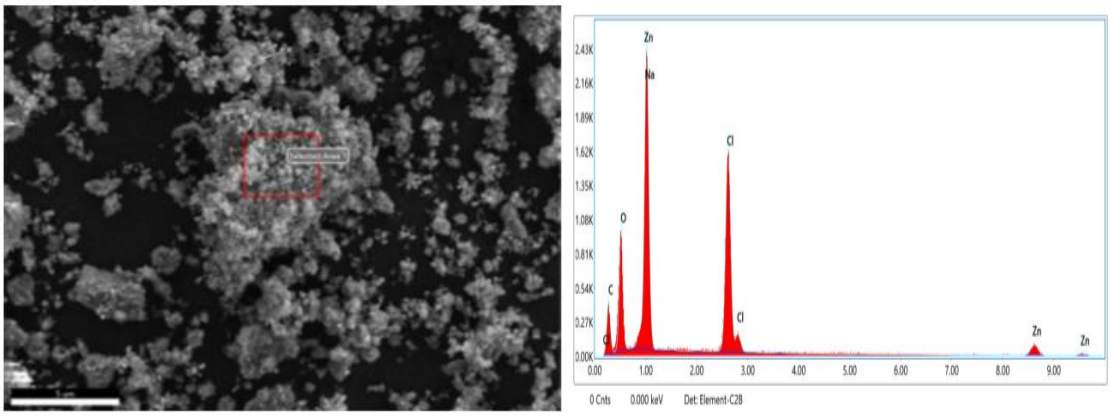

Figure 3. SEM image of the zinc complex with EDS

X-ray diffractometer (XRD) was used to analyze the crystallographic structure of the Zn and Cu complexes of DCPA. XRD diagrams of these compounds are given in Figure 4. XRD patterns also confirm the structure.

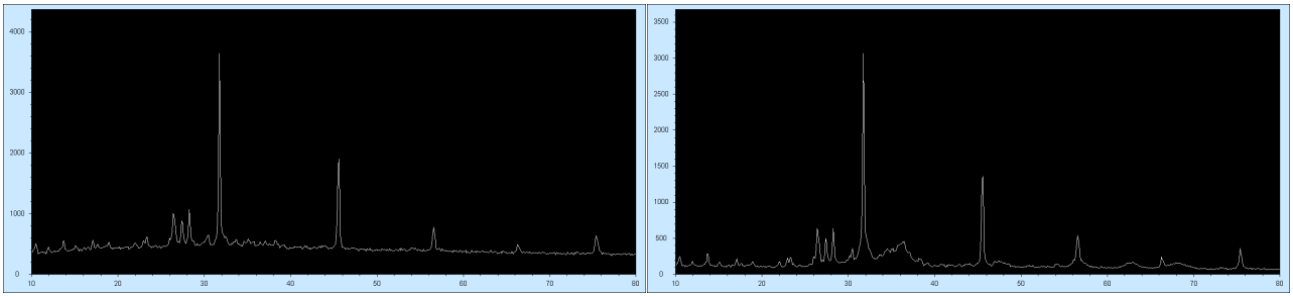

Figure 4. XRD patterns of the compound 2 (left)and 1(right)

Molecular Geometry

The most stable geometry of the compounds was optimized by the B3LYP method using higher level basis sets such as LanL2DZ The optimized geometry of the Cu and Zn compounds is shown in Figure 5. Cu-Cl groups in Cu-4,5-dichloro phthalic acid groups were in the range of Cu19-C17 2.334 Å for the DFT method, and Zn17-Cl18 2.450 Å for Zn-4,5-dichloro phthalic acid. In both complexes, bonding distance of O atom to metal atoms was found very close. When the bond angles O-Cu-Cl were examined, it was found 111.76 and O-Zn-Cl 131.16.

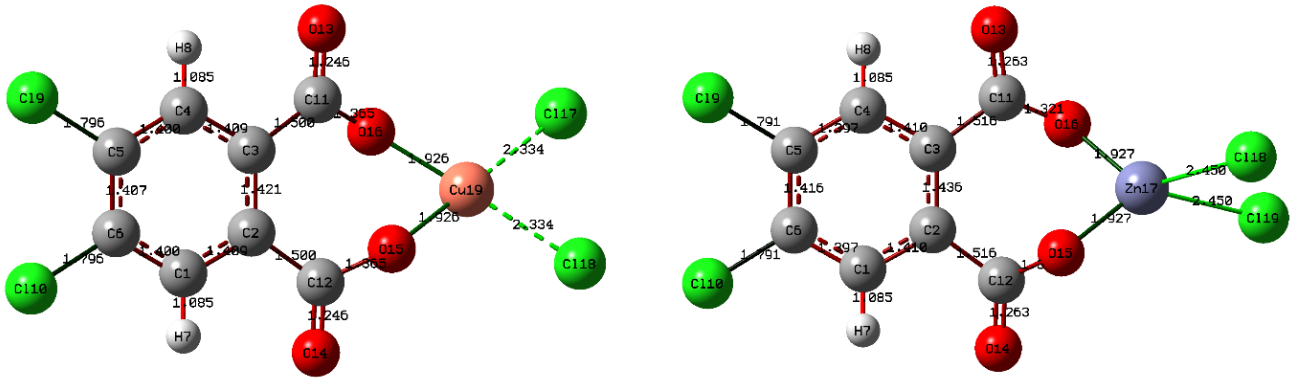

Figure 5. Optimized geometry of 4,5-dichlorphthalic acid complexes

Frontier Molecular Orbitals [HOMO-LUMO]

Both HOMO and LUMO are the main orbitals involved in chemical stability (Demir and Akman, 2017; Prabhaharan et al., 2015; Srivastava et al., 2015). HOMO represents the ability to give an electron and LUMO represents the ability to become an electron acceptor. The four important molecular orbitals (MOs) for complex molecules are HOMO, LUMO and, the highest and second highest filled orbital (HOMO -1) and the lowest and lowest second empty orbital(LUMO + 1), respectively (Demir and Akman, 2017; Khajehzadeh and Moghadam, 2017; Prabhaharan et al., 2015; Rocha et al., 2015; Srivastava et al., 2015). These orbital energies were calculated by the B3LYP / LanL2DZ method and the figures are shown in Figure 6.

Table 1. Comparison of HOMO, LUMO, energy gaps (HOMO - LUMO) and related Zn and Cu complex DCPA molecular properties

Molecules Energy	Cu- DCPA	Zn- DCPA
E_{LUMO}	-6.4753	-7.5679
E_{HOMO}	-8.2389	-8.0917
Energy Gap (Δ) E_{HOMO}- E_{LUMO}	1.7636	0.5238
Ionization Potential ($I = -E_{HOMO}$)	8.2389	8.0917
Electron Affinity ($A = -E_{LUMO}$)	6.4753	7.5679
Chemical hardness ($\eta = (I - A)/2$)	0.8818	0.2619
Chemical softness ($s = 1/2\ \eta$)	0.4409	0.1309
Chemical Potential ($\mu = (I + A)/2$)	-7.3571	-7.8298
Electronegativity ($\chi = (1+ A)/2$)	3.7376	-3.2839
Electrophilicity index ($\omega = \mu^2/2\ \eta$)	30.6911	117.0404

According to the calculated band gap, the large LUMO - HOMO value shows a hard molecule and the small LUMO - HOMO value shows a soft molecule structure. The chemical stability of the synthesized molecules also depends on the hardness, the decrease in bandwidth will make the molecule even more reactive. Frontier molecular orbitals calculations lead to show the reactivity and kinetic stability of the molecule. The LUMO - HOMO energy difference of DCPA was calculated in B3LYP / LanL2DZ. The HOMO energy of the Cu complex compound is -8.2389 eV and the LUMO energy is -6.4753 eV. The energy difference between LUMO and HOMO was 1.7636 eV. The HOMO energy of the Zn complex compound is -8.0917 eV and the LUMO energy is -7.5679 eV. The energy difference between LUMO and HOMO was 0.5238 eV. The Zn complex is more reactive than the Cu complex.

Vibration Analysis

FT-IR spectra of Zn and Cu complex DCPA were obtained by DFT method using LANDL2DZ basis set. The theoretical and experimental FT-IR spectra of Zn and Cu-DCPA were compared. R = 0.97204 for Cu and R = 0.97929 for Zn complex were found in linear fit studies. Two characterization results were found to be consistent. Comparison of the theoretical and experimental FT-IR frequencies are shown in Figure 7,8.

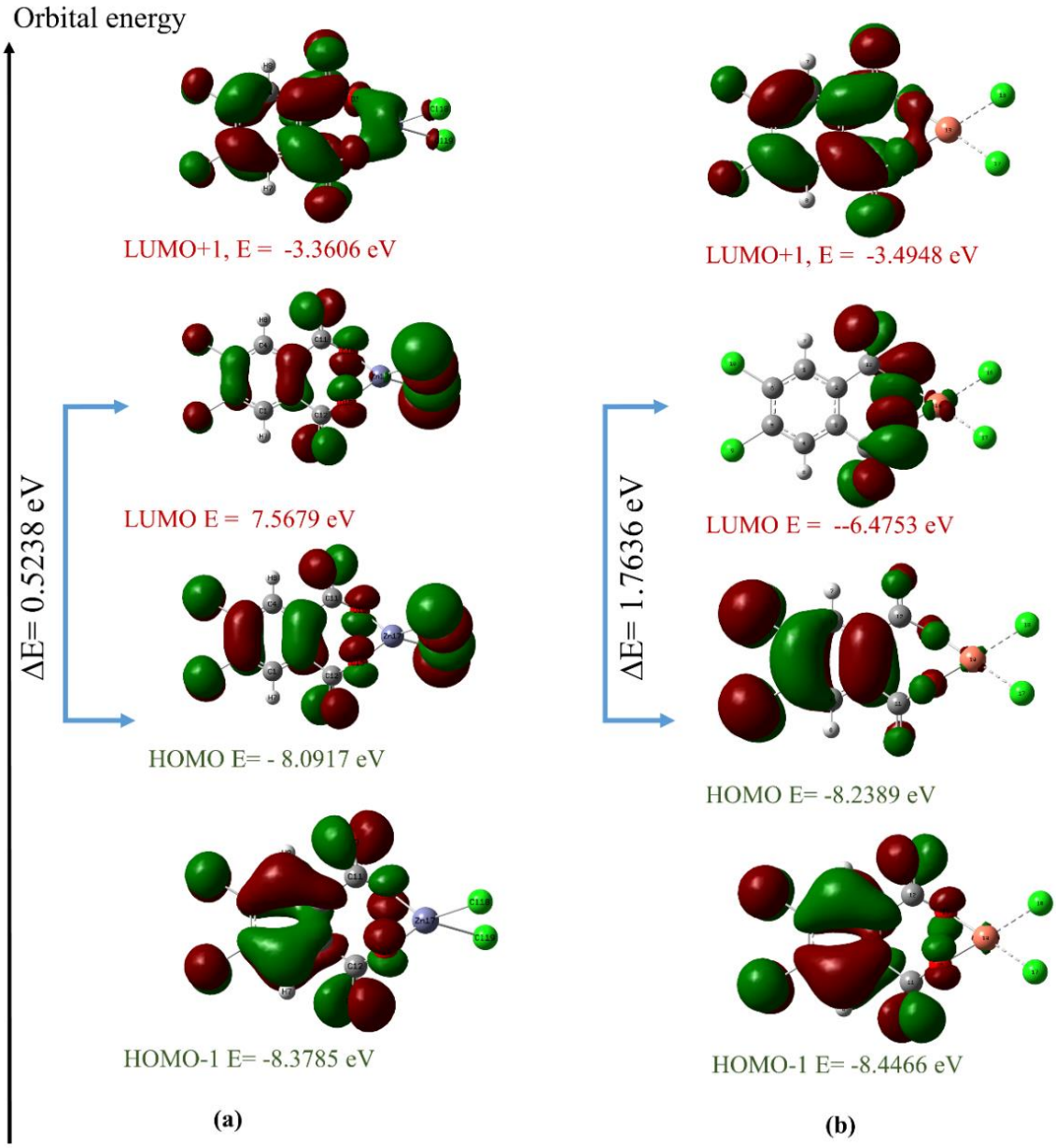

Figure 6. Frontier molecular orbitals of Zn (a) and Cu (b) complexes of 4,5-dichlorphthalic acid

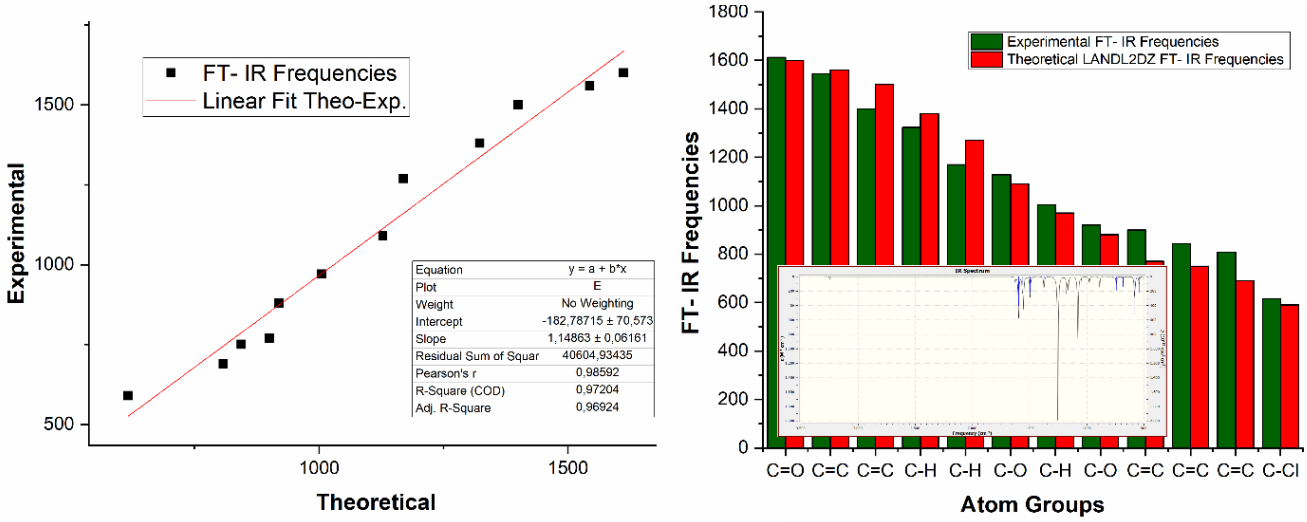

Figure 7. Comparison of theoretical and experimental FT-IR spectrum of Cu- DCPA

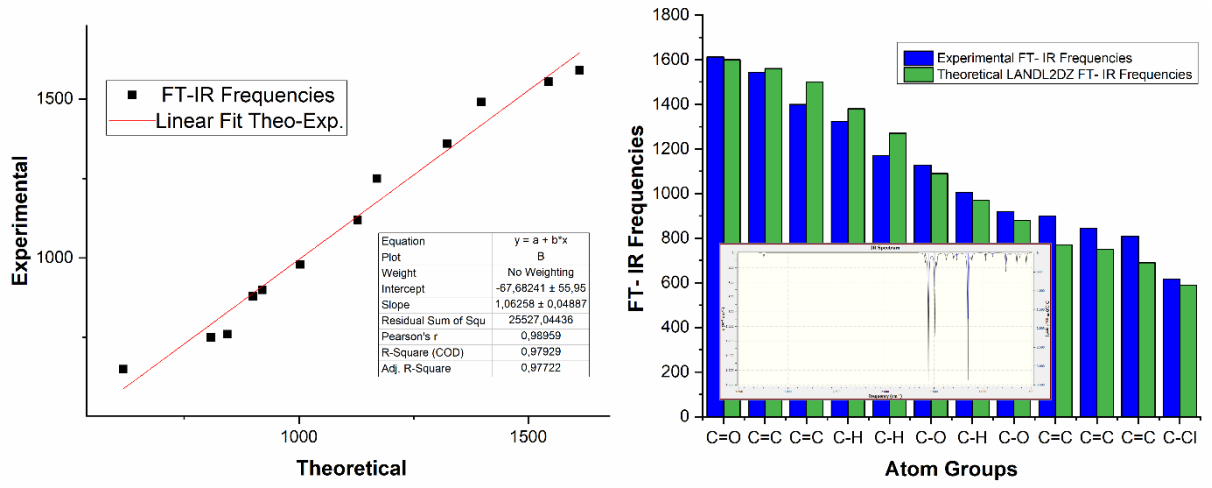

Figure 8. Comparison of theoretical and experimental FT-IR spectrum of Zn- DCPA

Molecular Electrostatic Potential (MEP)

In this study, molecular electrostatic potential (MEP) maps were obtained for both complexes. As shown in Figure 9, MEP maps of the Compound were mapped with the basis set LanL2DZ. It shows that the central atom has positive region regions characterized by the blue color around it. The contour map of the compounds verifies the negative and positive regions in accordance with the electrostatic surface potential (ESP) (Jayaprakash et al., 2011; Khajehzadeh and Moghadam, 2017; Saravanan et al., 2014; Srivastava et al., 2015; Vennila et al., 2016).

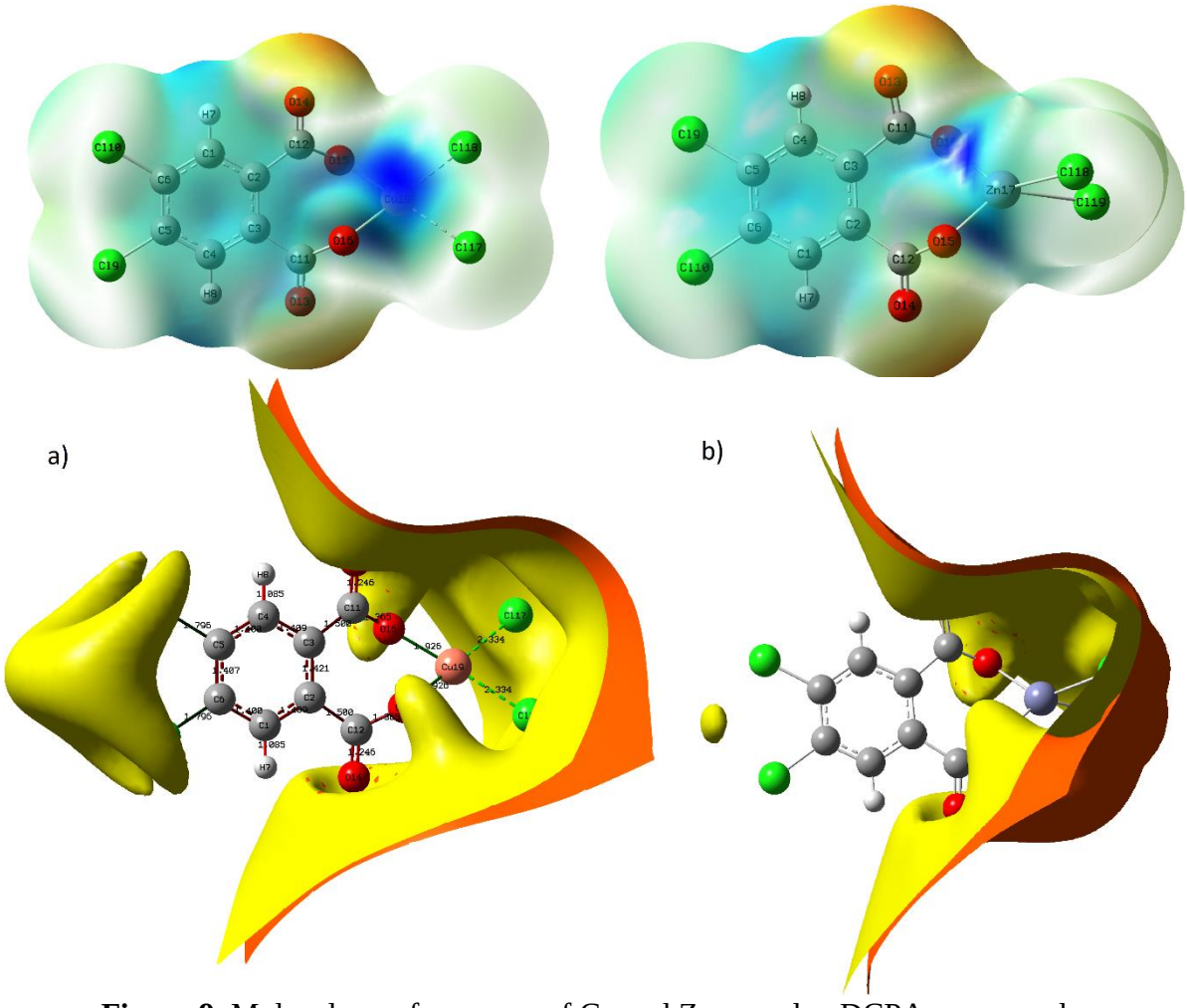

Figure 9. Molecular surface maps of Cu and Zn complex DCPA compounds

Natural Bond Orbital (NBO) Analysis

The total stabilization energies of C1-C2 (occ. 0.79811)- C3-C4 (occ. 0.16115) $\sigma \rightarrow \sigma^*$ is 9.83 kcal mol^{-1} and C12-O15 (occ. 1.98331) - Zn17-Cl18 (occ. 0.16881) $\sigma \rightarrow \sigma^*$ 0.23 kcal mol^{-1} were calculated. C5-C6 (occ. 0.77158) and C1-C2 (occ. 0.14989) between $\pi \rightarrow \pi^*$ 9.98 kcalmol^{-1}. CR1-Cu19 (occ. 0.99921) and C11-O16 (occ. 0.05184) were calculated as $\sigma \rightarrow \sigma^*$ 0.99 kcal mol^{-1}. Between C5-C6 (occ. 0.77158) and C1-C2 (occ. 0.14989) $\pi \rightarrow \pi^*$ 9.98 kcal mol^{-1}, CR1-Cu19 (occ. 0.99921) and C11-O16 (occ. 0.05184) $\sigma \rightarrow \sigma^*$ 0.99 kcal mol^{-1} were calculated. The high values of $E^{(2)}$ stabilization energies from the NBO analysis of the metalo complex compounds indicate the stability and π-electrons delocalization of the molecules (Eşme and Sağdınç, 2017; Khajehzadeh and Moghadam, 2017; Mathammal et al., 2015; Pandey et al., 2017). The natural electron configuration of Zn – Cu complex compounds DCPA was calculated as Cu 19 = [core] $4s^{(0.18)}3d^{(4.40)}4p^{(0.33)}$ and Zn 17= [core] $4s^{(0.35)}$ $3d^{(9.97)}$ $4p^{(0.56)}5p^{(0.01)}$. The results analyzed are given in Table 2,3.

Table 2. Selected NBO results of Cu - complex compounds DCPA

NBO(i)	Type	ED/e	NBO(j)	Type	ED//e	E(2)[a] (Kcal/mol)	E (j)-E(i)[b] (a.u.)	F (i, j)[c] (a.u)
C1-C2	σ	0.98195	C1-C6	σ*	0.01424	1.09	1.24	0.047
			C1-H7	σ*	0.00753	0.58	1.25	0.034
			C6-Cl10	σ*	0.01668	2.35	0.89	0.058
			C12-O15	σ*	0.04486	1.06	0.94	0.041
	π	0.79811	C3-C4	π*	0.16115	9.83	0.29	0.068
			C12-O14	π*	0.11460	7.59	0.24	0.056
C1-C6	σ	0.98670	C1-H7	σ*	0.00753	0.66	1.26	0.036
			C2-C12	σ*	0.03817	1.96	1.06	0.058
			C5-Cl9	σ*	0.01668	2.37	0.91	0.059
C1-H7	σ	0.98438	C1-C2	σ*	0.01080	0.40	1.05	0.026
			C2-C3	σ*	0.01439	2.98	1.05	0.024
			C6-Cl10	σ*	0.01661	0.33	0.70	0.019
C5-C6	σ	0.98670	C1-C6	σ*	0.01425	1.22	1.29	0.050
			C1-H7	σ*	0.00746	1.24	1.30	0.051
	π	0.77158	C1-C2	π*	0.14989	9.98	0.32	0.072
			C3-C4	π*	0.14989	9.98	0.32	0.072
C6-Cl10	σ	0.99052	C1-C2	σ*	0.01080	1.80	1.18	0.058
			C4-C5	σ*	0.01425	2.12	1.18	0.063
C11-O13	σ	0.99551	C2-C3	σ*	0.01439	0.90	1.53	0.047
	π	0.92270	C2-C3	π*	0.01439	0.31	0.90	0.021
			C3-C4	π*	0.14989	1.31	0.40	0.031
CR1-C1	σ	0.99946	C2-C3	σ*	0.01439	0.46	10.60	0.089
			C2-C12	σ*	0.04043	0.36	10.41	0.079
			C5-C6	σ*	0.02421	0.51	10.61	0..094
			C6-Cl10	σ*	0.01661	0.28	10.26	0.068
CR1-O14	σ	0.99994	C2-C12	σ*	0.04043	0.27	19.26	0.092
CR1-Cu19	σ	0.99921	C11-O16	σ*	0.05184	0.99	4.59	0.087
			C12-O15	σ*	0.05184	1.02	4.59	0.088
LP1-Cl10	σ	0.99445	C1-C6	σ*	0.01425	1.01	1.18	0.044
			C5-C6	σ*	0.02421	0.81	1.17	0.039
LP2-Cl10	σ	0.98544	C1-C2	σ*	0.01080	0.32	0.83	0.021
			C1-C6	σ*	0.01425	1.98	0.83	0.051
			C4-C5	σ*	0.01425	0.31	0.83	0.020
			C5-C6	σ*	0.02421	2.63	0.83	0.059
LP3-Cl10	σ	0.93030	C5-C6	σ*	0.02421	6.98	0.29	0.063
LP1-O16	σ	0.95134	C3-C11	σ*	0.04043	4.46	0.78	0.075
			C11-O13	σ*	0.01721	1.38	0.92	0.046

Table 3. Selected NBO results of Zn - complex compounds DCPA

NBO(i)	Type	ED/e	NBO(j)	Type	ED//e	E(2)[a] (Kcal/mol)	E (j)-E(i)[b] (a.u.)	F (i, j)[c] (a.u)
C1-C2	σ	1.96155	C1-C6	σ*	0.02745	1.98	1.24	0.044
			C1-H7	σ*	0.01354	1.07	1.24	0.033
			C6-Cl10	σ*	0.03231	4.69	0.89	0.058
			C12-O15	σ*	0.06665	1.68	0.97	0.036
C1-C6	σ	1.97280	C1-H7	σ*	0.01354	1.26	1.26	0.036
			C2-C12	σ*	0.06646	4.57	1.06	0.063
			C5-Cl9	σ*	0.03231	4.62	0.91	0.058
	π	1.63987	C1-C6	π*	0.34451	0.64	0.29	0.012
			C4-C5	π*	0.34451	20.94	0.29	0.070
C1-H7	σ	1.97038	C1-C2	σ*	0.02368	0.79	1.05	0.026
			C2-C3	σ*	0.03197	5.91	1.07	0.071
			C6-Cl10	σ*	0.03231	0.61	0.70	0.018
C5-C6	σ	1.98369	C1-C6	σ*	0.02745	2.31	1.28	0.049
			C1-H7	σ*	0.01354	2.49	1.29	0.051
C6-Cl10	σ	1.98102	C1-C2	σ*	0.02368	3.49	1.18	0.057
			C4-C5	σ*	0.02745	4.17	1.17	0.063
C11-O13	σ	1.96013	C2-C3	σ*	0.03197	1.19	1.33	0.036
	π	1.96013	C2-C3	π*	0.03197	1.40	0.87	0.031
			C3-C4	π*	0.02368	1.29	0.85	0.030
CR1-C1	σ	1.99891	C2-C3	σ*	0.03197	0.95	10.63	0.091
			C2-C12	σ*	0.06646	0.88	10.42	0.087
			C5-C6	σ*	0.04829	1.01	10.60	0.093
			C6-Cl10	σ*	0.03231	0.56	10.26	0.068
CR1-C12	σ	1.99917	C1-C2	σ*	0.02368	0.63	10.78	0.074
			C2-C3	σ*	0.03197	0.60	10.80	0.072
			C12-O14	σ*	0.05805	0.65	10.51	0.075
LP1-Cl10	σ	1.98882	C1-C6	σ*	0.02745	1.97	1.17	0.043
			C5-C6	σ*	0.04829	1.62	1.17	0.039
LP2-Cl10	σ	1.97091	C1-C2	σ*	0.02368	0.63	0.83	0.021
			C1-C6	σ*	0.02745	4.02	0.83	0.051
			C4-C5	σ*	0.02745	0.62	0.83	0.020
			C5-C6	σ*	0.04829	5.30	0.82	0.059
LP3-Cl10	σ	1.87827	C1-C6	σ*	0.02745	13.93	0.31	0.062
LP1-O16	σ	1.90400	C3-C11	σ*	0.06646	3.07	1.09	0.052
			C11-O13	σ*	0.05805	0.52	1.01	0.021
C2-C12	σ	1.97022	Zn17-Cl19	σ*	0.16881	0.24	0.96	0.014
C12-O15	σ	1.98331	Zn17-Cl18	σ*	0.16881	0.23	1.11	0.015
			Zn17-Cl19	σ*	0.16881	0.12	1.11	0.011
CR1-C12	σ	1.99917	Zn17-Cl18	σ*	0.16881	0.10	10.56	0.030
LP1-O13	σ	1.60745	Zn17-Cl18	σ*	0.16881	0.10	1.09	0.010
LP5-Zn17	σ	1.96913	Zn17-Cl18	σ*	0.16881	6.74	0.88	0.071
LP1-Cl19	σ	1.99182	Zn17-Cl19	σ*	0.16881	5.25	0.82	0.061

CONCLUSIONS

In this study, zinc and copper phthalic acid complexes with surface analysis and characterization were reported. These compounds may have the potential to be used as support materials to obtain effective catalysts or reducing agents. The structure of complex DCPAs was optimized by the B3LYP method using LanL2DZ basis sets. The energy gap between LUMO and HOMO was 1.7636 eV in the Cu complex and 0.5238 eV in the Zn complex. Global and local reactivity descriptors NBO values and MEP maps were defined using DFT method. R = 0.97204 for Cu and R = 0.97929 for Zn complex were found in linear fit studies. The theoretical and experimental FT-IR results were found to be consistent.

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