Comparative Studies of Some Novel Cu(II) Polymeric Complexes Derived from Cyanoacetylhydrazine (CAH; L). The Role of Solvents Used on the Structure and Geometry of the Isolated Cu²⁺ Complexes

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Abstract

Novel polymeric Cu²⁺ complexes derived from the reaction of cyanoacetylhydrazine (CAH; L) with CuCl₂·2H₂O in different solvents were synthesized and characterized. The isolated solid polymeric complexes were investigated using modern conventional physicochemical and spectral (IR, ¹H-NMR, UV-Vis. ESR, Raman), magnetic and thermal studies. The results revealed that CAH behaves in different ways towards the coordination of the Cu²⁺ ion. The promotion of solvents to the cyano group was discussed on the basis of the solvent and the Cu²⁺ ion used. Magnetic and spectral studies suggest octahedral geometry is proposed for the Cu²⁺ complexes. EPR studies indicate the existence of polymeric complexes depending on the results of g-values. The results suggest that the number of copper atoms ranges from three to twelve atoms. The molecular modeling is drawn and some chemical characteristics are calculated such as chemical reactivity and energy components are investigated between the different types of the ligands.

Keywords

Polymeric Cu(II) Complexes, ESR Studies, Cyanoacetylhydrazine, DFT Studies

1. Introduction

The class of organic compounds contains the functional active group (-CONHNH₂) is known as hydrazides. Great interest in the chemistry of hydrazides is explained...
by diversity and at times by the originality of their properties. Hydrazides have
acquired great importance due to their multifarious biological properties includ-
ing antibacterial, antifungal, anti-inflammatory and anti-tuberculosis activities [1]
[2] [3] [4] [5]. CAH is considered as an intermediate for the synthesis of a va-
the compound is a favorable unit for addition followed by cyclization or via
cyclo-addition with numerous reagents providing heterocyclic compounds hav-
ing different ring sizes with one or several heteroatoms that are interesting as
pharmaceuticals [10] [11], herbicides [12], antibacterial agents [13], and dyes
[14] [15]. Also, hydrazides find wide applications as drugs, chemical preservers
for plants, manufacturing polymers, glues and many other purposes [16]. Mosta-
tafa et al. [17] reported the reactions of cyanoacetylhydrazine (SCH, L) with
some metal ions (Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and UO²⁺) in EtOH. Three types
of complexes with the general formulae, [M(L)ₓXᵧ]S (M = Co²⁺, Ni²⁺ or Cd²⁺; x =
Cl⁻ or Ac⁻; S = EtOH or (H₂O), [M(L-H)]S (M = Co²⁺, Cu²⁺, Zn²⁺, UO²⁺; S
(H₂O) and [Hg(L-H)Cl·H₂O], were isolated and characterized. On the other
hand, the reaction of Fe³⁺ and Cu²⁺ chloride or bromide with L in aqueous etha-
nolic solution is accompanied by the reduction to Fe²⁺ and Cu⁺, respectively [17].
The synthesis and characterization of some metal complexes containing salicylal-
dehyde cyanoacetylhydrazone (SCH), 1-salicyl-hydrazo-3-imino-3-isoproxy prop-
ionic acid hydrazide (SIPPH) and 1-salicylhydrazo-3-imino-3-tertbutoxy propio-
nic acid hydrazide (SIBPH) were reported [18]. The complexes were characte-
ized using elemental analyses, spectral (¹H-NMR, IR, visible), conductance and
magnetic measurements. IR spectral data suggest that the ligands (SCH, SIPPH
and SIBPH) coordinated in tridentate and/or bidentate manners with different
modes of bonding toward the metal ions. Moreover, a polymeric structure via an
imido group for some Cu²⁺ complexes is discussed. Finally, the ¹H-NMR spectra
of the ligands and some diamagnetic complexes are discussed. The reactions of sa-
licylaldehyde with a suspension of cyanoacetylhydrazone and/or malonic acid
amido-hydrazide complexes in aqueous EtOH solutions afford novel complexes
[19]. The structures of the isolated complexes have been confirmed by conven-
tional physical and chemical measurements. The absence or the weakness of the
cyano group in the IR spectra of all complexes, except those of Co²⁺ and Ni²⁺
complexes, suggests the promotion of H₂O to the cyano group forming amido
group [19]. In this paper, the use of the Cu²⁺ salts which act as a catalyst in the
synthesis of the polymeric complexes helps to a great extent the promotion of the
solvents to the cyano group.

The goal of our study is to investigate the role of the solvents on the reaction
products of CAH in the presence of Cu²⁺ ions. The isolated polymeric complexes
were characterized using different physical, chemical, thermal, spectral and mag-
netic methods. The results of EPR were studied and the values of ε₀, γ₀, Κ₀,
K₁, α₂ and B² were calculated. Also, the structures of ligands were elucidated using
molecular modeling. Thermal analyses were carried to determine the number
of solvents inside or outside the coordination sphere.
2. Experimental

2.1. Instrumentation and Materials

All chemicals were of AR quality and used without further purification. Elemental analyses (C, H, N) were carried out by Perkin-Elmer CHN 2400 analyzer based on catharometric detection after combustion. Chloride and copper contents were determined by the micronalysis centre, CNRS service central of analysis at Vernaison (France). TGA analysis was performed using Dupont-950 thermogravimetric analyser in KBr discs were recorded on a Mattson 5000 FTIR (Mansoura University) and Perkin-Elmer in the range 20°C - 800°C and recorded on a TGA-50 Shimadzu TGA analyzer at a heating rate of 15°C/min and nitrogen flow rate of 20 ml/min. IR spectra (4000 - 200 cm⁻¹) in Perkin-Elmer 883 IF spectrophotometers (France). Electronic spectra were recorded on a Unicam UV-Vis, V-100 and Perkin-Elmer Lambda 9 spectrophotometers. The magnetic measurements were carried out at room temperature (25°C) on a Sherwood magnetic balance. Diamagnetic corrections were calculated using Pascal’s constants [20]. ¹H-NMR measurements in d₆-DMSO at room temperature were carried out on Jeol-90Q Fourier transform (400 MHz) and Bruker AM 250 spectrometers. The results of EPR measurements were obtained using Bruker EPR 200 provided with Hewlett-Packard frequency meter (modulation frequency, 100 KHz; microwave power; 20 mW; field modulation intensity; 3.2 Gpp and gain, 2.5 × 10⁵).

2.2. Synthesis of Cyanoacetylhydrazine (CAH; L)

CAH (L) was synthesized by adding equivalent amounts of hydrazine hydrate (3 ml; 0.1 mol) drop by drop with constant stirring to ethyl cyanoacetate (11 ml, 0.1 mol) in EtOH for 1.5 h at room temperature (25°C). The reaction mixture was cooled in ice bath till a white solid product was obtained. The precipitate was filtered off, recrystallized from absolute ethanol (yield: 89%) and finally dried in a desiccator over P₄O₁₀. The purity was checked by elemental analyses, TLC and spectra data (IR, ¹H-NMR, Vis-Uv, Raman and TGA). The uncorrected melting point of the product was found to be (108°C - 110°C).

2.3. Synthesis of Cu²⁺ Complexes

Twelve novel polymeric Cu²⁺ complexes were isolated and characterized with the aid of elemental analyses, physical and spectroscopic methods. The different complexes were synthesized by mixing in each reaction equivalent amounts of L (0.2 M) in different solvents (H₂O, MeOH, EtOH, n-propanol, n-butanol and n-pentanol) and CuCl₂·2H₂O (0.1 M) in EtOH. The reaction mixtures were refluxed on a hot plate for a time depending on the solvent used. The polymeric complexes formed in the flask were poured in a beaker followed by scratching the reaction mixture in each experiment by a glass rod till solid precipitates were formed as fine powders. The complexes were filtered off and washed several times with the solvent used in the preparation of the complexes followed by
washing with diethyl ether. The isolated products were preserved in a vacuum desiccator over P₂O₅. The analyses of the isolated solid complexes together with some physical data are depicted in Table 1. The complexes are stable in air and soluble in polar solvents. The numbers of the copper ions in the isolated complexes were estimated from the data of elemental analyses as well as results of EPR and found to be in the range from 3 - 12 atoms. The electronic spectra and the magnetic moments of the Cu(II) complexes are recorded in Table 2. The data of the polymeric complexes are summarized as follow:

**Complex (1)** (C₆H₁₂Cl₂N₉O₆Cu₃); yield: 70%; color: dark brown powder; MP > 270°C; M.Wt: 638.9; μₑffective (1.95 BM) and conductivity (DMSO): 6 Ω⁻¹·cm²·mol⁻¹.

**Complex (2)** (C₆H₁₂Cl₄N₇O₁₈Cu₁₂); yield: 83%; color: yellowish-green powder; MP > 270°C; M.Wt: 2400.0; μₑffective (0.91 BM); conductivity (DMSO): 9 Ω⁻¹·cm²·mol⁻¹.

**Complex (3)** (C₁₇H₃₅Cl₂N₃₅O₂₃Cu₈); yield: 76%; color: brown powder; MP > 270°C; M.Wt. 1908.6; μₑffective (1.24 BM); conductivity (DMSO): 13 Ω⁻¹·cm²·mol⁻¹.

**Complex (4)** (C₁₉H₃₈Cl₇N₁₅O₈Cu₄); yield: 90%; color: kaki-green powder; MP > 270°C; M.Wt: 1107; μₑffective (1.02 BM); conductivity (DMSO): 13 Ω⁻¹·cm²·mol⁻¹.

Table 1. Analys solvent used in synthesis

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical formula</th>
<th>(M. Wt)</th>
<th>C % Found</th>
<th>H % Found</th>
<th>Cu % Found</th>
<th>Cl % Found</th>
<th>N % Found</th>
<th>Solvent</th>
<th>Solvent used in synthesis</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>C₁₁H₂₃Cl₂N₉O₆Cu₃</td>
<td>638.9</td>
<td>20.7</td>
<td>3.6</td>
<td>29.8</td>
<td>11.1</td>
<td>19.7</td>
<td>5.7</td>
<td>H₂O</td>
</tr>
<tr>
<td>2</td>
<td>C₁₉H₃₈Cl₂N₇O₁₈Cu₁₂</td>
<td>2400.0</td>
<td>18.0</td>
<td>2.7 (3.0)</td>
<td>31.8</td>
<td>20.7</td>
<td>15.8</td>
<td>---</td>
<td>MeOH</td>
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<tr>
<td>3</td>
<td>C₁₇H₃₅Cl₂N₃₅O₂₃Cu₈</td>
<td>1908.6</td>
<td>19.5</td>
<td>4.0</td>
<td>26.6</td>
<td>12.9</td>
<td>17.2</td>
<td>7.7</td>
<td>H₂O + MeOH</td>
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<tr>
<td>4</td>
<td>C₁₇H₃₅Cl₂N₉O₆Cu₄</td>
<td>1107.0</td>
<td>19.8</td>
<td>3.4</td>
<td>24.0</td>
<td>23.0</td>
<td>20.4</td>
<td>6.0</td>
<td>H₂O + EtOH</td>
</tr>
<tr>
<td>5</td>
<td>C₁₆H₂₇Cl₂N₉O₆Cu₄</td>
<td>952.5</td>
<td>20.3</td>
<td>3.0</td>
<td>26.5</td>
<td>18.6</td>
<td>19.1</td>
<td>8.5</td>
<td>EtOH + H₂O</td>
</tr>
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<td>6</td>
<td>C₁₇H₃₅Cl₂N₉O₆Cu₄</td>
<td>611.3</td>
<td>18.6</td>
<td>3.0</td>
<td>31.9</td>
<td>15.5</td>
<td>14.2</td>
<td>12.4</td>
<td>EtOH + H₂O</td>
</tr>
<tr>
<td>7</td>
<td>C₁₆H₂₇Cl₂N₉O₆Cu₃</td>
<td>1719.2</td>
<td>19.5</td>
<td>3.1</td>
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<td>21.9</td>
<td>21.4</td>
<td>19.1</td>
<td>10.5</td>
<td>EtOH</td>
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<td>9</td>
<td>C₁₇H₃₅Cl₂N₉O₆Cu₃</td>
<td>673.8</td>
<td>18.6</td>
<td>2.8</td>
<td>27.9</td>
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<td>19.4</td>
<td>6.4</td>
<td>EtOH</td>
</tr>
<tr>
<td>10</td>
<td>C₁₆H₂₇Cl₂N₉O₆Cu₃</td>
<td>1934.5</td>
<td>23.2</td>
<td>3.3</td>
<td>22.7</td>
<td>18.3</td>
<td>21.9</td>
<td>7.4</td>
<td>Butanol</td>
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<tr>
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<td>1224.4</td>
<td>27.4</td>
<td>3.0</td>
<td>25.3</td>
<td>11.5</td>
<td>20.9</td>
<td>14.0</td>
<td>Pentanol</td>
</tr>
<tr>
<td>12</td>
<td>C₁₃H₃₅Cl₂N₉O₆Cu₃</td>
<td>1140.0</td>
<td>21.1</td>
<td>3.1</td>
<td>22.7</td>
<td>22.6</td>
<td>21.7</td>
<td>3.8</td>
<td>Pentanol</td>
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Table 2. The most important IR, electronic spectral bands and the values of $U_{\text{eff}}$.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>$\nu$(OH)</th>
<th>$\nu$(NH$_2$)</th>
<th>$\nu$(C≡N); Amide I band</th>
<th>$\nu$(H$\equiv$O); $\nu$(N=N)</th>
<th>$\lambda$(nm) in $\nu$ (cm$^{-1}$), Nujol</th>
<th>$U_{\text{eff}}$ (BM)</th>
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<tbody>
<tr>
<td>L$^1$</td>
<td>3280, 3199</td>
<td>2263</td>
<td>1710, 1680</td>
<td>1619</td>
<td>1530, 1492, 998</td>
<td>257.3, 38,865</td>
</tr>
<tr>
<td>1</td>
<td>3440</td>
<td>3182, 2997</td>
<td>2264</td>
<td>1660, 1634</td>
<td>1586</td>
<td>1519, 1435, 975</td>
</tr>
<tr>
<td>2</td>
<td>3400</td>
<td>3320, 3185</td>
<td>2260</td>
<td>1720, 1670</td>
<td>1589</td>
<td>1401, 940, 400</td>
</tr>
<tr>
<td>3</td>
<td>3445</td>
<td>2993</td>
<td>2264</td>
<td>1760, 1640</td>
<td>1585</td>
<td>1440, 1360, 980</td>
</tr>
<tr>
<td>4</td>
<td>3400</td>
<td>3180, 3100</td>
<td>2264</td>
<td>1710, 1640</td>
<td>1582</td>
<td>1440, 1400, 975</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>3180, 3210</td>
<td></td>
<td></td>
<td></td>
<td>1700, 1650, 976</td>
</tr>
<tr>
<td>6</td>
<td>3415</td>
<td>3346</td>
<td>2270</td>
<td>1740, 1600</td>
<td>1540</td>
<td>1406, 1300, 940</td>
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<td>7</td>
<td>3480</td>
<td>3220, 3170, 2980</td>
<td>1636</td>
<td>1618</td>
<td>1575, 1540</td>
<td>955, 400, 399</td>
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<td>8</td>
<td>3350</td>
<td>2968, 2930, 2800</td>
<td>2260</td>
<td>1720</td>
<td>1529, 1402</td>
<td>940, 440, 393</td>
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<td>9</td>
<td>3440</td>
<td>3280, 3231, 3180</td>
<td>1638</td>
<td>1620</td>
<td>1572, 1440</td>
<td>940, 433, 400</td>
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<tr>
<td>10</td>
<td>3426</td>
<td>3200, 2987</td>
<td>2263</td>
<td>1700, 1660</td>
<td>1590</td>
<td>1531, 1430, 980</td>
</tr>
<tr>
<td>11</td>
<td>3420</td>
<td>3260, 3200</td>
<td>2260</td>
<td>1700</td>
<td>1621</td>
<td>1540, 1416, 953</td>
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<td>12</td>
<td>3426</td>
<td>3200</td>
<td>2263, 2170</td>
<td>1700, 1660</td>
<td>1590</td>
<td>1537, 1430, 940</td>
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</table>

Complex (5) ($\text{C}_{16.5}\text{H}_{29.5}\text{Cl}_{5}\text{N}_{13.5}\text{O}_{6.5}\text{Cu}_4$); yield: 69%; color: brown powder; MP > 270°C; M.Wt: 952.5; $\mu_{\text{eff}}$ (1.14 BM); conductivity (DMSO): 13 Ω$^{-1}$·cm$^2$·mol$^{-1}$.

Complex (6) ($\text{C}_{10}\text{H}_{22}\text{Cl}_{3}\text{N}_{6}\text{O}_{5.5}\text{Cu}_3$); yield: 69%; color: brown powder; MP > 270°C; M.Wt: 611.3; $\mu_{\text{eff}}$ (0.78 BM); conductivity (DMSO): 8 Ω$^{-1}$·cm$^2$·mol$^{-1}$.

Complex (7) ($\text{C}_{16.5}\text{H}_{29.5}\text{Cl}_{5}\text{N}_{13.5}\text{O}_{6.5}\text{Cu}_4$); yield: 77%; color: yellowish-green powder; MP 155°C; M.Wt: 1719.2; $\mu_{\text{eff}}$ (0.75 BM); conductivity (DMSO): 7 Ω$^{-1}$·cm$^2$·mol$^{-1}$.

Complex (8) ($\text{C}_{16}\text{H}_{31}\text{Cl}_{5}\text{N}_{12}\text{O}_{6}\text{Cu}_3$); yield: 77%; color: dirty-green powder; MP > 270°C; M.Wt: 855.4; $\mu_{\text{eff}}$ (0.85 BM); conductivity (DMSO): 6 Ω$^{-1}$·cm$^2$·mol$^{-1}$.

Complex (9) ($\text{C}_{11}\text{H}_{19}\text{Cl}_{4}\text{N}_{9}\text{O}_{4}\text{Cu}_3$); yield: 90%; color: military-green powder; MP > 270°C; M.Wt: 673.8; $\mu_{\text{eff}}$ (0.85 BM); conductivity (DMSO): 4 Ω$^{-1}$·cm$^2$·mol$^{-1}$.

Complex (10) ($\text{C}_{38}\text{H}_{66}\text{Cl}_{10}\text{N}_{30}\text{O}_{12}\text{Cu}_7$); yield: 85%; color: kaki-green powder; MP > 270°C; M.Wt: 1934.5; $\mu_{\text{eff}}$ (0.75 BM); conductivity (DMSO): 9 Ω$^{-1}$·cm$^2$·mol$^{-1}$.

Complex (11) ($\text{C}_{28}\text{H}_{48}\text{Cl}_{4}\text{N}_{18}\text{O}_{8}\text{Cu}_5$); yield: 79%; color: brownish-green powder; MP: 200°C; M.Wt: 1224.4; $\mu_{\text{eff}}$ (0.84 BM); conductivity (DMSO): 10 Ω$^{-1}$·cm$^2$·mol$^{-1}$.

Complex (12) ($\text{C}_{20.5}\text{H}_{35}\text{Cl}_{7}\text{N}_{18}\text{O}_{6.5}\text{Cu}_4$); yield: 85%; color: grayish-green powder; MP: 103°C; M.Wt: 1140.0; $\mu_{\text{eff}}$ (0.85 BM); conductivity (DMSO): 10 Ω$^{-1}$·cm$^2$·mol$^{-1}$.

3. Results and Discussion

The data of some physical properties and elemental analysis of the isolated Cu$^{2+}$ complexes are summarized in Table 1. The structures of the compounds are established by elemental analyses, spectral, magnetic studies and confirmed by weight loss determination. The values of molar conductivity of all complexes lie in the 4 - 13 Ω$^{-1}$·cm$^2$·mol$^{-1}$ range indicating the non-electrolytic nature of the Cu$^{2+}$ complexes [21]. Also, it suggests the polymeric nature as well as the strong covalent bonding between the ligand and the copper(II) ion. Unfortunately, the
isolation of single crystal for any one of the isolated solid complexes to confirm the exact coordination sites and the geometry around the Cu$^{2+}$ ions is very difficult due to the polymeric nature of these complexes.

3.1. IR, $^1$H-NMR, Raman, Electronic and Mass Spectra of L (CAH)

The IR spectra of CAH (L) in KBr and/or Nujol mull are cognate and show three bands at 3280s, 3199s and 3056s cm$^{-1}$ assigned to $\nu$($\text{NH}_2$), $\nu$($\text{NH}_2$) and $\nu$($\text{NH}_2$) vibrations, respectively. Also, the bands located at 2263s, 1710sh and 1680sh cm$^{-1}$ are assigned to $\nu$(C$\equiv$N)s, $\nu$(C=O)sh (free) and $\nu$(C=O)s (hydrogen-bonded) vibrations, respectively. Moreover, the two bands at 1530m and 1492s are attributed to amide II vibrations. The observation of the carbonyl band as a shoulder together with the existence of the NH$_2$ at lower wavelength suggests that the carbonyl group is partially hydrogen-bonded to the amino group as shown in Figure 1. Also, the $^1$H-NMR spectrum of L in d$_6$-DMSO shows three signals at 10.06, 9.53 and 9.1 ppm assigned to NH$_2$ and NH groups which obscured on adding D$_2$O. Both the methyl and ethyl proton signals are observed as triplet signals in the ranges 1.76 - 1.96 and 3.66 - 3.76 ppm, respectively. The calculated value of the mass spectrum of L equals 141 which is quite agrees with the experimental value of M + 1 (142). The electronic spectrum of L in DMSO shows two bands at 220 nm (45,455 cm$^{-1}$) and 262 nm (38,170 cm$^{-1}$) attributed to $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the C=O and C=O groups, respectively. The Raman spectrum of CAH shows active bands at 3341m, 2926m, 2260s 1670w and 1010 cm$^{-1}$ assigned to $\nu$(NH$_2$), $\nu$(CH), $\nu$(C=O) and $\nu$(N-N) vibrations, respectively. These foundations are taken as strong evidences for our assumptions and the existence of the ligand (CAH) as shown in Figure 1.

A comparison of the IR spectra of CAH and its Cu$^{2+}$ complexes (Table 2) shows that the ligand behaves in a neutral bidentate fashion via the (C=O) and NH$_2$ groups.

The mode of chelation is confirmed by the following remarks:

1) The measurably shifts of both the (C=O) and (NH$_2$) groups to lower wave-numbers in all complexes indicating that these groups are participating in coordination of the Cu$^{2+}$ ion.

2) The vibrations of the amide II bands are also shifted to lower wavenumbers suggesting the participation of both groups in coordination.

3) New bands are observed in the range 400 - 440 and 350 - 400 cm$^{-1}$ are assigned to (M-O) and (M-N), respectively [13].

4) The spectra of the complexes show broad medium band in the region 3440 - 3426 cm$^{-1}$, attributable to the existence of solvent inside and/or outside the coordination sphere [14].

Figure 1. Hydrogen bond exists in CAH (L$^1$).
5) The observation of two bands at 1710s and 1680sh together with the presence of weak broad bands in the 2800 - 2920 cm$^{-1}$ suggests the existence of strong hydrogen bonding.

All these foundations suggest that the ligand is existed as a mixture of the keto (A) and enol (B) forms as shown in Figure 1.

The obscure and/or the weakness of the cyano group (C≡N) in some Cu$^{2+}$ complexes is taken as strong evidence for the promotion of the solvent as shown in Scheme 1. The mechanism of promotion was proposed and confirmed in our previous works [18] [19].

3.2. Molecular Modeling

**Global Reactivity Descriptors**

Quantum chemical calculations are concerned with the determination of energies of both HOMO (π-donor) and LUMO (π-acceptor) parameters. HOMO orbital acts as an electron donor while LUMO orbital acts as an electron acceptor. These molecular orbitals are also called the frontier molecular orbitals (FMOs).
1) The negative values of both $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ and their neighboring orbitals (Table 3) indicate that the molecules are stable [22].

2) The FMOs theory predicts the essential sites participate in coordination (electrophilic attack). An initial assumption proposes that the reaction occurred with maximum overlap between the HOMO on one molecule and the LUMO on the other. The overlap between HOMO and the LUMO is essential factor in any reactions. The goal obtained from the calculations is to get the largest values of molecular orbital coefficients. Accordingly the orbitals of the ligands under investigation have the largest value of molecular orbital.

3) Gutmann’s variation rules indicate that the strength of bonds increase as the adjacent bonds become weaker as found by Linert et al. [23].

4) The energy gap ($E_{\text{HOMO}} - E_{\text{LUMO}}$) expresses the stability index which helps to characterize the chemical reactivity and kinetic stability of the molecule [24]. The gap ($E_{\text{HOMO}} - E_{\text{LUMO}}$) is patented to develop a theoretical model to explain the structure and verify the barriers in different systems, which affect the biological activity of the molecule. Small gap within the molecule means that the molecule is polarized and acts as soft molecule. It is well known that the soft molecules are more reactive than hard ones since they easily donate electrons to an acceptor. The energy gap is small in the compound indicate that the charge-transfer easily occurs in it influencing the biological activity of the molecule. Energy gap with low values is also attributed to the groups that enter into conjugation [24].

5) Low energy values of HOMO indicate that the donating electron ability of the molecules is the weaker. Contrarily, the higher HOMO energy suggests that the molecule is a good electron donor. LUMO energy presents the ability of a molecule receiving electron [25]. The results are depicted in Figures 2-7.

DFT concept illustrates neatly the chemical reactivity and the site selectivity of the molecular systems. Both the energies of ($E_{\text{HOMO}} + E_{\text{LUMO}}$) and band gap ($E_{\text{HOMO}} - E_{\text{LUMO}}$) illustrate preemptory the charge-transfer interplay within the molecule, electronegativity ($\chi$), chemical potential ($\mu$), global hardness ($\eta$), global softness ($S$) and global electrophilicity index ($\omega$) [26] [27] [28] are listed in Table 4.

$$\chi = -\frac{1}{2}(E_{\text{LUMO}} + E_{\text{HOMO}})$$  \hspace{1cm} (1)

Table 3. Some of energetic properties of the ligands and calculated by DMOL3 using DFT-method.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)</th>
<th>Binding energy (Kcal/mol)</th>
<th>Total energy (Kcal/mol)</th>
<th>Kinetic energy (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L: CAH (C₃H₅N₃O)</td>
<td>−5.575</td>
<td>−0.449</td>
<td>−5.126</td>
<td>−1233.73</td>
<td>−2.24 × 10⁵</td>
<td>−2106.03</td>
</tr>
<tr>
<td>2</td>
<td>L₁: (C₃H₇N₃O₂)</td>
<td>−5.538</td>
<td>−0.321</td>
<td>−5.217</td>
<td>−1500.15</td>
<td>−2.72 × 10⁵</td>
<td>−2267.83</td>
</tr>
<tr>
<td>3</td>
<td>L₂: (C₄H₉N₃O₂)</td>
<td>−4.802</td>
<td>0.405</td>
<td>−4.397</td>
<td>−1748.98</td>
<td>2.96 × 10⁵</td>
<td>−1910.25</td>
</tr>
<tr>
<td>4</td>
<td>L₃: (C₅H₁₁N₃O₂)</td>
<td>−5.36</td>
<td>−0.242</td>
<td>−5.118</td>
<td>−2063.23</td>
<td>−3.21 × 10⁵</td>
<td>−3174.85</td>
</tr>
<tr>
<td>5</td>
<td>L₄: (C₆H₁₃N₃O₂)</td>
<td>−5.597</td>
<td>−0.243</td>
<td>−5.354</td>
<td>−2358.60</td>
<td>−3.46 × 10⁵</td>
<td>−3538.18</td>
</tr>
<tr>
<td>6</td>
<td>L₅: (C₇H₁₆N₃O₂)</td>
<td>−5.630</td>
<td>−0.293</td>
<td>−5.337</td>
<td>−2655.31</td>
<td>−3.70 × 10⁵</td>
<td>−3879.51</td>
</tr>
<tr>
<td>7</td>
<td>L₆: (C₈H₁₈N₃O₂)</td>
<td>−5.832</td>
<td>−0.529</td>
<td>−5.303</td>
<td>−2949.04</td>
<td>−3.95 × 10⁵</td>
<td>−4468.66</td>
</tr>
</tbody>
</table>
Figure 2. (a, b, c, d) Molecular modeling of (a) L₁, (b) electron density, (c) HOMO, and (d) LUMO.

Figure 3. (a, b, c, d) Molecular modeling of (a) L₂, (b) electron density, (c) HOMO, and (d) LUMO.
Figure 4. (a, b, c, d) Molecular modeling of (a) $\mathbf{L}_3$, (b) electron density, (c) HOMO, and (d) LUMO.

Figure 5. (a, b, c, d) Molecular modeling of (a) $\mathbf{L}_4$, (b) electron density, (c) HOMO, and (d) LUMO.

Figure 6. (a, b, c, d) Molecular modeling of (a) $\mathbf{L}_5$, (b) electron density, (c) HOMO, and (d) LUMO.
Figure 7. (a, b, c, d) Molecular modeling of (a) $L^6$, (b) electron density, (c) HOMO, and (d) LUMO.

Table 4. Calculated $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, energy band gap ($E_{\text{H}} - E_{\text{L}}$), chemical potential ($\mu$), electro-negativity ($\chi$), global hardness ($\eta$), global softness ($\sigma$) and global electrophilicity index ($\omega$) for ligands.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{H}}$ eV</th>
<th>$E_{\text{L}}$ eV</th>
<th>($E_{\text{H}} - E_{\text{L}}$) eV</th>
<th>$\chi$ eV</th>
<th>$\mu$ eV</th>
<th>$\eta$ eV</th>
<th>$\sigma$ eV</th>
<th>$\omega$ eV</th>
<th>$\Sigma$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>L: CAH ($C_3H_5N_3O$)</td>
<td>-5.575</td>
<td>-0.449</td>
<td>-5.126</td>
<td>3.01</td>
<td>-3.01</td>
<td>2.56</td>
<td>2.56</td>
<td>1.28</td>
<td>1.76</td>
</tr>
<tr>
<td>L$^1$: ($C_3H_7N_3O_2$)</td>
<td>-5.538</td>
<td>-0.321</td>
<td>-5.217</td>
<td>2.93</td>
<td>-2.93</td>
<td>2.61</td>
<td>2.61</td>
<td>1.31</td>
<td>1.64</td>
</tr>
<tr>
<td>L$^2$: ($C_4H_9N_3O_2$)</td>
<td>-4.802</td>
<td>0.405</td>
<td>-4.397</td>
<td>2.6</td>
<td>-2.6</td>
<td>2.2</td>
<td>2.2</td>
<td>1.1</td>
<td>1.53</td>
</tr>
<tr>
<td>L$^3$: ($C_5H_11N_3O_2$)</td>
<td>-5.36</td>
<td>-0.242</td>
<td>-5.118</td>
<td>2.8</td>
<td>-2.8</td>
<td>2.56</td>
<td>2.56</td>
<td>1.28</td>
<td>1.53</td>
</tr>
<tr>
<td>L$^4$: ($C_6H_14N_3O_2$)</td>
<td>-5.597</td>
<td>-0.243</td>
<td>-5.354</td>
<td>2.92</td>
<td>-2.92</td>
<td>2.67</td>
<td>2.67</td>
<td>1.34</td>
<td>1.59</td>
</tr>
<tr>
<td>L$^5$: ($C_7H_16N_3O_2$)</td>
<td>-5.630</td>
<td>-0.293</td>
<td>-5.337</td>
<td>2.96</td>
<td>-2.96</td>
<td>2.67</td>
<td>2.67</td>
<td>1.34</td>
<td>1.64</td>
</tr>
<tr>
<td>L$^6$: ($C_8H_18N_3O_2$)</td>
<td>-5.832</td>
<td>-0.529</td>
<td>-5.303</td>
<td>3.18</td>
<td>-3.18</td>
<td>2.65</td>
<td>2.65</td>
<td>1.9</td>
<td>1.9</td>
</tr>
</tbody>
</table>

$H = \text{HOMO, L = LUMO.}$

$$\mu = -\chi = 1/2\left( E_{\text{LUMO}} + E_{\text{HOMO}} \right)$$

$$\eta = 1/2\left( E_{\text{LUMO}} - E_{\text{HOMO}} \right)$$

$$S = 1/2 \eta$$

$$\omega = \mu^2 / 2\eta$$

The inverse value of the global hardness is designed as the softness ($\sigma$) as follow:

$$\sigma = 1/\eta$$

The electrophilicity index ($\omega$) is considered as important quantum chemical descriptors. Also, this value used to estimate the stabilization energy when the system acquires an additional electronic charge from the environment. The molecular stability and reactivity of the compounds depends mainly on the values of...
η and σ. The ligand acts as a Lewis base while the metal ion acts as a Lewis acid during complex formation.

The three-dimensional plots of frontier orbital energies using the DFT method for $L^2\cdot L'$ are shown in Figures S1-S6.

### 3.3. EPR Spectral Studies of the Isolated CuII Complexes

The results of the EPR spectra of the polymeric Cu$^{2+}$ complexes in DMSO at low temperature (127°C - 160°C) are depicted in Table 5. The trend $g_{\|} > g_{\perp} > g_e$ (2.0023) observed for the Cu$^{2+}$ complexes suggests that the unpaired electron is localized in the $d_{x^2-y^2}$ ($2B_1g$) orbital [29] [30]. It is well known that the axial symmetry parameter ($G$) is defined as:

$$G = (g_{\|} - 2.0023)/(g_{\perp} - 2.0023)$$

If $G > 4$ the exchange interaction is negligible between Cu(II) ions, whereas $G < 4$ means a significant Cu-Cu interaction and tone straightly with measured magnetic moment [31]. The $G$ values for all complexes are larger than 4 (4.0-6.0) suggesting the absence of any copper-copper interaction. Orbital reduction factors ($K_{\|}$ and $K_{\perp}$) which are a measure of covalence were determined using the following two expressions:

$$2K_{\|} = \frac{(g_{\|} - 2.0023)}{8\lambda_o} \times \Delta E$$

$$2K_{\perp} = \frac{(g_{\perp} - 2.0023)}{2\lambda_o} \times \Delta E$$

The value of $\lambda_o$ (spin-orbital coupling constant) for $d^9$-system equals $-828 \text{ cm}^{-1}$. Hathaway [31] pointed out that that in case of pure σ-bonding, $K_{\|} = K_{\perp} = \ldots$

#### Table 5. EPR X-band data of the CuII complexes in DMSO at low temperature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp. (K)</th>
<th>$g_{|}$</th>
<th>$g_{\perp}$</th>
<th>$g_e$</th>
<th>$G$</th>
<th>$A_b \times 10^{-4}$ cm$^{-1}$</th>
<th>$K_{|}$</th>
<th>$K_{\perp}$</th>
<th>$H$</th>
<th>$g_o/A_b$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{11}$H$</em>{12}$Cl$_3$N$_9$O$_4$Cu$_3$ (1)</td>
<td>149</td>
<td>2.07</td>
<td>2.33</td>
<td>2.16</td>
<td>4.71</td>
<td>195</td>
<td>0.59</td>
<td>0.81</td>
<td>2303</td>
<td>100</td>
<td>0.94</td>
<td>0.86</td>
<td>0.63</td>
</tr>
<tr>
<td>C$<em>{13}$H$</em>{21}$Cl$<em>4$N$</em>{12}$O$_{12}$Cu$_2$ (2)</td>
<td>132</td>
<td>2.07</td>
<td>2.32</td>
<td>2.15</td>
<td>4.57</td>
<td>200</td>
<td>0.55</td>
<td>0.65</td>
<td>3160</td>
<td>116</td>
<td>0.94</td>
<td>0.69</td>
<td>0.59</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (3)</td>
<td>127</td>
<td>2.08</td>
<td>2.44</td>
<td>2.20</td>
<td>5.50</td>
<td>190</td>
<td>0.59</td>
<td>0.83</td>
<td>3200</td>
<td>136</td>
<td>0.90</td>
<td>0.92</td>
<td>0.66</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (4)</td>
<td>160</td>
<td>2.06</td>
<td>2.29</td>
<td>2.14</td>
<td>4.83</td>
<td>190</td>
<td>0.45</td>
<td>0.56</td>
<td>3245</td>
<td>121</td>
<td>0.88</td>
<td>0.64</td>
<td>0.51</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (5)</td>
<td>155</td>
<td>2.07</td>
<td>2.33</td>
<td>2.16</td>
<td>4.71</td>
<td>185</td>
<td>0.52</td>
<td>0.64</td>
<td>3190</td>
<td>126</td>
<td>0.91</td>
<td>0.70</td>
<td>0.57</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (6)</td>
<td>155</td>
<td>2.08</td>
<td>2.44</td>
<td>2.20</td>
<td>5.50</td>
<td>170</td>
<td>0.57</td>
<td>0.63</td>
<td>3150</td>
<td>144</td>
<td>0.98</td>
<td>0.64</td>
<td>0.58</td>
</tr>
<tr>
<td>C$<em>{13}$H$</em>{21}$Cl$<em>4$N$</em>{12}$O$_{12}$Cu$_2$ (7)</td>
<td>135</td>
<td>2.06</td>
<td>2.36</td>
<td>2.16</td>
<td>6.00</td>
<td>180</td>
<td>0.46</td>
<td>0.67</td>
<td>3106</td>
<td>131</td>
<td>0.92</td>
<td>0.73</td>
<td>0.50</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (8)</td>
<td>127</td>
<td>2.07</td>
<td>2.31</td>
<td>2.15</td>
<td>4.43</td>
<td>195</td>
<td>0.55</td>
<td>0.61</td>
<td>3160</td>
<td>119</td>
<td>0.92</td>
<td>0.66</td>
<td>0.60</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (9)</td>
<td>127</td>
<td>2.07</td>
<td>2.31</td>
<td>2.15</td>
<td>4.43</td>
<td>160</td>
<td>0.54</td>
<td>0.61</td>
<td>3240</td>
<td>144</td>
<td>0.82</td>
<td>0.74</td>
<td>0.66</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (10)</td>
<td>139</td>
<td>2.11</td>
<td>2.43</td>
<td>2.22</td>
<td>4.00</td>
<td>170</td>
<td>0.83</td>
<td>0.83</td>
<td>3210</td>
<td>143</td>
<td>0.99</td>
<td>0.78</td>
<td>0.84</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (11)</td>
<td>137</td>
<td>2.06</td>
<td>2.30</td>
<td>2.14</td>
<td>5.00</td>
<td>180</td>
<td>0.47</td>
<td>0.61</td>
<td>3175</td>
<td>128</td>
<td>0.87</td>
<td>0.70</td>
<td>0.54</td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{13}$Cl$<em>4$N$</em>{14}$O$_{14}$Cu$_4$ (12)</td>
<td>140</td>
<td>2.07</td>
<td>2.39</td>
<td>2.18</td>
<td>5.57</td>
<td>190</td>
<td>0.56</td>
<td>0.80</td>
<td>3106</td>
<td>121</td>
<td>0.89</td>
<td>0.90</td>
<td>0.63</td>
</tr>
</tbody>
</table>
0.77 and for in-plane π-bonding $K_{\parallel} < K_{\perp}$, while for out-of-plane π-bonding $K_{\parallel} < K_{\perp}$ the following simplified expressions were used to calculate $K_{\parallel}$ and $K_{\perp}$. In all cases of Cu(II) complexes under investigation the observed $K_{\parallel} > K_{\perp}$ indicating that the presence of out-of-plane π-bonding as depicted in Table 5. The value of $K_{\parallel} = K_{\perp} = 0.83$ in case of the Cu$^{2+}$ complex (10) suggesting the existence of pure σ-bonding. For all the complexes the evaluated values of $\alpha^2$, $\beta^2$ and $\gamma^2$ are consistent with both in plane σ-bonding and in plane π-bonding as shown in Table 5. Moreover, all the above values ($\alpha^2$, $\beta^2$ and $\gamma^2$) are less than 1 suggesting 100% ionic nature of the bonds [32]. The bonding parameters for the Cu(II) complexes are found to be $\alpha^2$ in the 0.82 - 0.99, $\beta^2$ in the 0.64 - 0.92 and $\gamma^2$ in the 0.5 - 0.84 ranges. The extent of departing of these parameters from unity measures the range of delocalization of metal electrons due to M-L bonding and hence $\alpha^2$ measures σ-bonding within the complexes [33], $\beta^2$ measures out of (xy) plane π-bonding while $\gamma^2$ shows in plane π-bonding contribution. No doubt that the deviation from unity in $\beta^2$ and $\gamma^2$ values suggests the presence of considerable out of plane and in plane π-bonding contribution in M-L π-bonding. Accordingly, the EPR studies of the copper complexes have provided supportive evidence to the optical and magnetic results.

3.4. Electronic Spectra and Magnetic Behavior

The electronic spectra of the Cu(II) complexes were displayed in Nujol mull and/or DMSO. The electronic spectra show a broad band lie in the 13,551 - 17,860 cm$^{-1}$ range suggesting d-d transition ($^2E_{2g} \rightarrow ^2T_{2g}$) in octahedral geometry around the Cu$^{2+}$ ion [34] [35]. Also, the values of the corrected subnormal magnetic moment of the complexes (2-12) fall in the 0.75 - 1.24 BM are taken as strong evidence for the existence of polymeric nature [36] [37] and strong Cu-Cu interaction. The value of magnetic moment of complex (2, C$_{11}$H$_{23}$Cl$_{2}$N$_{9}$O$_{6}$Cu$_{3}$) was found to be 1.95 BM. The high value of magnetic moment of complex (2) in comparison to the previous complexes (3-12) in spite of the polymeric nature of this complex, which contains three copper atoms, is due to the absence of any Cu-Cu interaction within this complex either in the xy or directions. The data of electronic spectra and magnetic moments are shown in Table 2.

3.5. TGA Studies

The amounts of the coordinated solvents and/or the hydrated solvents have been determined in the range 25°C - 200°C. The experimental weight loss values are in good agreement with the calculated values. The TGA curves of the Cu$^{2+}$ complexes exhibit two different types of weight loss, in the above range, indicating the presence of two types of solvents. The Former in the 50°C - 120°C range suggesting the presence of hydrated solvents while the latter in the range 125°C - 200°C illustrating the presence of coordinated solvents.

4. Conclusion

The new polymeric Cu$^{2+}$ complexes derived from cyanoacetylhydrazine in dif-
ferron solvents were characterized by spectral, magnetic and thermal analyses. The different ligands obtained by the promotion of different solvents to the cyanogroups were suggested according to the spectral studies. The ligands obtained coordinate in a bidentate manner via the carbonylate and the NH2 groups forming five-membered rings around the copper(II) ion. The results of spectral together with the values of magnetic moments suggest distorted-octahedral geometry around the Cu2+ ion. The Spin-Hamiltonian parameters obtained from the EPR spectra of the complexes in DMSO at low temperature were used to calculate the bonding parameters. DFT calculations illustrate the chemical reactivity and the site selectivity of the molecular systems. Both the energies of \((E_{\text{HOMO}} + E_{\text{LUMO}})\) and band gap \((E_{\text{HOMO}} - E_{\text{LUMO}})\) illustrate preemptory the charge-transfer interplay within the molecule, electron negativity, chemical potential, global hardness, global softness and global electrophilicity index are listed.

**Conflicts of Interest**

The article is original and unpublished and is not being considered for publication elsewhere. The author declares that he has no conflict of interests that could influence this work.

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https://doi.org/10.1016/j.bmc.2009.10.064

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https://doi.org/10.1016/j.bmc.2009.01.037


[36] Kato, M., Jonassen, KB and Fanning, GC, (1964) Copper(II) Complexes with Sub-
Supplementary

Figure S1. Three-dimensional plots of frontier orbital energies using the DFT method for L₂.

Figure S2. Three-dimensional plots of frontier orbital energies using the DFT method for L₃.
Figure S3. Three-dimensional plots of frontier orbital energies using the DFT method for \( L^4 \).

\[
E_{\text{LUMO}} = -0.04067 \text{ ev}
\]

\[
E_{\text{HOMO}} = -0.23683 \text{ ev}
\]

\[
E_{\text{GAP}} = 0.19616 \text{ ev}
\]

Figure S4. Three-dimensional plots of frontier orbital energies using the DFT method for \( L^5 \).

\[
E_{\text{LUMO}} = -0.06395 \text{ ev}
\]

\[
E_{\text{HOMO}} = -0.25546 \text{ ev}
\]

\[
E_{\text{GAP}} = 0.19151 \text{ ev}
\]
Figure S5. Three-dimensional plots of frontier orbital energies using the DFT method for \( L^6 \).

\[ E_{\text{LUMO}} = -0.02074 \text{ ev} \]
\[ E_{\text{GAP}} = 0.18015 \text{ ev} \]
\[ E_{\text{HOMO}} = -0.20089 \text{ ev} \]

Figure S6. Three-dimensional plots of frontier orbital energies using the DFT method for \( L^7 \).

\[ E_{\text{LUMO}} = -0.04412 \text{ ev} \]
\[ E_{\text{GAP}} = 0.20208 \text{ ev} \]
\[ E_{\text{HOMO}} = -0.24620 \text{ ev} \]