

Study of Thermodynamic and Structure of Cu(II) 1,2,4 H-Triazole Complex using The ab Initio Method

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Abstract. The complex of Cu(II) 1,2,4 H-triazole is one complex compound having a polymeric structure. The objective of this study determines the difference in energy formation and structure data of Cu(II) 1,2,4 H-triazole complex. The computational study used the Hartree-Fock method and the basis set 3-21G and 6-31G(d). The complex was studied of $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ and $[\text{Cu}_2(\text{Htrz})_6]^{4+}$. The result of a computational study with function/ basis set UHF/ 6-31G(d) shows the distance between Cu(II) ions for complexes with deprotonated ligands of 3,433Å, while complexes with undepronated ligands are 3,551Å. Bond length of Cu-N in the complex with deprotonated ligands are 1,953Å - 2,167Å, whereas for the complex with undepronated ligands are 2,063Å - 2,123Å. The difference of energy from a computational study using the function/ basis set UHF/ 6-31G(d) for the $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ complex is -3693.43 KJ/ Mol and the $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ complex is -1666.01 KJ/ Mol.

Keywords: Cu(II) 1,2,4 H-triazole, the computational study, the structure data, and difference of energy

1 Introduction

The ion of Cu(II) has nine electrons in orbitals of d (d^9) formed the octahedral structure in the complex compounds. The Cu(II) 1,2,4 H-triazole complex was formed the covalent coordination bonds with the octahedral structure. The ligand of 1,2,4 H-triazole (Htrz) is an intermediate field ligand. The atom of H, which is bonded the N4 atom from the Htrz ligand can be released to form a trz^{-1} ion. The structure of the Htrz and trz^{-1} ligand rings are presented in Figure 1.

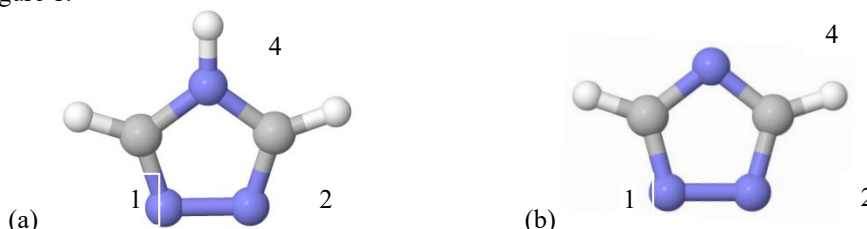


Fig 1. The structure of the ligand rings of (a) Htrz and (b) trz^{-1} .

The Cu(II) ions with Htrz ligand have a polymeric structure in which between the Cu(II) ions is connected with the Htrz ligand bridge. The structure of the Cu(II) 1,2,4 H-triazole

(Cu(II)-Htrz) complex is similar to Fe(II) 1,2,4 H-triazole. The structure of the Cu(II) 1,2,4 H-triazole complex is shown in Figure 2.

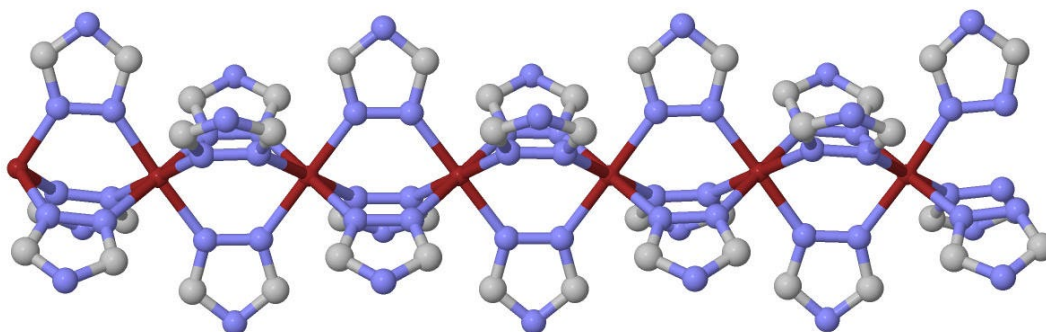


Fig. 2 Polymeric complex structure of Cu(II)-Htrz.

Experimental studies of Cu(II)-Htrz complexes or derivatives have been carried out by various methods. Analysis of the single crystal structure of the complex $[\text{Cu}(\text{hyetrz})_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (hyetrz) 4-(2-hydroxyethyl)-1,2,4-triazole was carried out using Enraf-Nonius CAD4 diffractometer and EXAFS13 spectrometer. The final coordinate data and isotropic thermal parameters are visualized by CRYSTAL MAKER to get the crystal structure of the complex. The crystal structure obtained shows between Cu(II) ions are connected by three bridges N_1 , N_2 -Htrz with a distance between Cu1-Cu2 of $3.8530(8)\text{\AA}$ and Cu2-Cu3 of $3.8293(2)\text{\AA}$. Complex forms a chain with an angle between pairs of Cu(II) ions between Cu1-Cu2 and Cu2-Cu3 at $175.18(2)^\circ$. The data show the complex forms a chain that only slightly deviates from the linearly shaped chain (Garcia et al, 1997). The structural characteristics of $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ (1) and $[\text{Cu}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (2) complexes have been observed using SEM and XRPD. A single crystal complex (2) has been observed using XRD, lead to the complex structural parameter data is obtained (Dirtu et al., 2010). Both complex crystal form shows similarities based on SEM images with greater magnification.

An experimental study of the Cu(II)-Htrz complex was carried out by several previous researchers. The computational chemistry methods could predict the crystal structure of Cu(II)-Htrz complex. The data are compared with structural data has been obtained experimentally. The study determined differences energy data of Cu(II)-Htrz complex too. This study was used in the ab initio method with UHF functions and basis sets of 3-21G and 6-31G(d).

Determination of energy with the completion of the Schrödinger equation is carried out using analytic and semi-empirical methods (Hückel method) for a set of molecular orbitals obtained in the form the variations of energy. This energy can be integrated as an orbital for each of these energies (one electron formalism). The wave functions for many electrons are a result of the Hartree (Hartree Product) wave function as stated in equation 1.

$$H = \sum_{i=1}^N h_i \quad (1)$$

where h_i is a wave function for each electron. An interaction between nuclei is considered zero because the core is considered motionless (Born Oppenheimer Approximation).

$$h_{i=-1/2} \nabla_i^2 - \sum_{i=1}^M \frac{Z_k}{r_{ik}} \quad (2)$$

where M represents the total number of cores

Fock proposed the addition of the Hartree SCF with Slater Determinant of the wave function. The Fock operator for one electron defined for each electron i is:

$$f_i = -\frac{1}{2}\nabla_i^2 - \sum_k^{inti} \frac{Z_k}{r_{ik}} + V_i^{HF}\{J\} \quad (3)$$

The Hartree-Fock assumption states that each electron is in a fixed field produced by the other electron densities (Cramer, 2004).

Determination of structure, vibration frequency, relative energy, and dipole moments are calculated using basis sets 3-21G almost the same compared to the results using a basis set 6-21G (Binkley et al., 1980). Comparison of geometry parameters, normal vibration frequency modes, and dipole moments from computational using basis sets 3-21G and 3-21G* according to the experimental data (Pietro et al., 1982). Determination of bond length using a basis set 6-21G is more in line with experimental results than using a basis set 3-21G (Gordon et al., 1982). The determination of energy using 6-31G* is closer to the experimental results than the determination of energy using 3-21G* (Schleyer et al., 1984). The calculated activation energy with MP4 (SDTQ)/ 6-31G*// MP2/ 6-31G* is in accordance with experimental data. One point calculation at MP2 / 6-31G* level with geometry optimization at 3-21G gives an energy value that is in accordance with the experimental data (Spellmeyer et al., 1987).

The geometry optimization at Hartree-Fock (RHF) level with basis set of 3-21G and 6-31+G* for the complex compounds with alkali metals. The results of this study obtained that the calculation results using a basis set 6-31+G* are more suitable with experimental data than basis set 3-21G (Glendening et al., 1994). Results of a study of various compounds using a Local density functional (LDF) theory with a basis set of STO-3G and 3-21G obtained suitability with experimental data with an average deviation of 0.026Å. Specifically for the compound Fe(CO)₅ basis set 3-21G more in line with the experimental results compared to the STO-3G basis set. Determination of frequency the LDF results are better than the results of Hartree-Fock (Sosa et al., 1992). The results of the geometry optimization show that the basis set 6-31G(d) is in accordance with the experiment compared to STO-3G, 6-31G, 6-31+G, and 6-31+G(d) (Foresman et al., 1991). Based on comparisons of computational results with experimental data show that the basis set 3-21G and 6-31G(d) is quite good to be used in the determination of structure and energy. Prediction of the structure and the difference of energy [Fe₄(Htrz)₈(trz)₄]⁴⁺ and [Fe₄(Htrz)₁₂]⁸⁺ complexes used the function/basis set TPSSh/ TZVP. The results showed that the energy difference in the formation of the [Fe₄(Htrz)₈(trz)₄]⁴⁺ was -9285.974 KJ/ Mol and [Fe₄(Htrz)₁₂]⁸⁺ of -3501.534 KJ/ Mol (Nugraha et al., 2015).

2 Computational Method

The computational calculations to determine the structure and the difference of energy using the UHF function and the basis set of 3-21G and 6-31G(d). The software used is NWChem 6.6 (Valiev et al., 2010) for computational chemistry calculations, Jmol (<http://www.jmol.org/>) and Avogadro (Hanwell et al., 2012) for visualization structure complexes. The data obtained from computational calculations are used to determine the difference in energy complexes (Ochterski, 2000).

2.1 Determination of complex structured data.

Based on the structured from the geometry optimization results obtained the bond length and bond angle data for the Cu(II)-Htrz complex.

2.2 Determination of complex energy difference.

The difference in energy complex is obtained energy data from computational chemistry calculations.

3 Results and Discussion

3.1 Determination of Complex Structure

The result of geometry optimization with function/ basis set UHF/ 6-31G(d) shows that the Cu(II)-Htrz complex has a polymeric structure and between Cu(II) ions connected by three Htrz ligand rings. Structural visualization of the results of geometry optimization of the complexes $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ and $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ are shown in Figure 3.

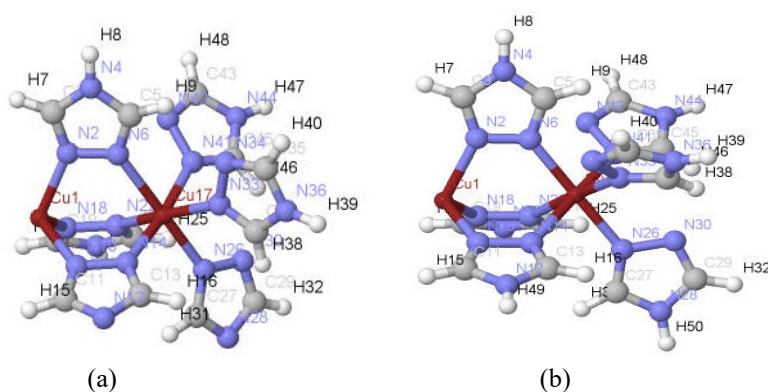


Fig. 3. Structure from geometry optimization results of the (a) $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ and (b) $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ complexes.

The parameter's structure of the Cu(II)-Htrz complex were studied data on the distance between Cu(II) ions and the bond length of Cu-N. The distance between Cu(II) ions as a result of geometry optimization with functions/basis set UHF/ 3-21G for the complex with deprotonated ligands is 3.635Å, while complex with undepronated ligands of 3.194Å. The distance between Cu(II) ions as a result of geometry optimization with function /basis set UHF/ 6-31G(d) for the complex with deprotonated ligands is 3.433Å, while complex with undepronated ligands is 3.551Å. The data of distance between Cu(II) ions of $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ and $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ complexes results of computational calculations with UHF functions and 3-21G and 6-31G(d) basis sets stated in Table 1.

Table 1 The distance between Cu(II) ions result in geometry optimization		
Functions/ basis sets	The distance between Cu(II) ions (Å)	
	$[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$	$[\text{Cu}_2(\text{Htrz})_6]^{4+}$
UHF/ 3-21G	3.635	3.194

The bond length of Cu-N on deprotonated complexes are shorter than undepronated complexes. For the deprotonated complexes, the bond length of Cu-N on the deprotonated ring is shorter than the undepronated ring. The computational study with the function/ basis set UHF/ 3-21G shows that the bond length of Cu-N in the complexes with the deprotonated ligand are 1.953Å - 2.087Å, while the undepronated ligand is 1.885Å - 2.109Å. The computational calculation of the function/ basis set UHF/ 6-31G(d) shows that the bond length of Cu-N in the complexes with a deprotonated ligand is 1.953Å - 2.167Å, while the undepronated ligand is 2.063Å - 2.123Å. Bond length of Cu-N in the $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ and $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ complexes result of the computational calculations with UHF functions and the basis sets 3-21G and 6-31G(d) presented in Table 2.

Table 2 The bond length of Cu-N as a result of geometry optimization

Functions/ basis sets	The bond length of Cu-N (Å)		
	$[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$		$[\text{Cu}_2(\text{Htrz})_6]^{4+}$
	The deprotonated ring	The undepronated ring	
UHF/ 3-21G	1.953 – 1.967	2.035 - 2.087	1.885 – 2.109
UHF/ 6-31G(d)	1.953 – 2.002	2.077 – 2.167	2.063 – 2.123

3.2 Determination of complex energy

Determination energy of Cu(II)-Htrz complex was carried out on complexes with one deprotonated ligand and undepronated ligands for the UHF functions and 3-21G and 6-31G (d) basis sets. The data on energy difference of $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ and $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ complexes result of computational calculations on UHF functions and 3-21G and 6-31G(d) basis sets are presented in Table 3.

Table 3 The difference energy of $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ and $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ complexes with the UHF function and 3-21G and 6-31G(d) basis sets.

The complexes	Functions / Basis Sets	The amount of Energy (Ht)				The Energy Difference	
		Cu	Htrz	trz	Complexes	(Ht)	(kJ/mol)
$[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$	UHF/ 3-21G	-1630.11	-239.36	-238.79	-4696.88	-1.65	-4338.32
	UHF/ 6-31G(d)	-1637.79	-240.73	-240.17	-4720.25	-1.41	-3692.43
$[\text{Cu}_2(\text{Htrz})_6]^{4+}$	UHF/ 3-21G	-1630.11	-239.36		-4697.18	-0.81	-2130.70
	UHF/ 6-31G(d)	-1637.79	-240.73		-4720.58	-0.63	-1666.01

4 Conclusion

The computational calculation to function/ basis set UHF/ 6-31G(d) shows the distance between Cu(II) ions for the complexes with deprotonated ligands of 3.433Å, while undepronated ligand is 3.551Å. The bond length of the Cu-N in the complexes with a deprotonated ligand is 1.953Å – 2.167 Å, whereas for the complexes with undepronated ligand are 2.063Å - 2.123Å. The difference energy from computational chemistry calculations for $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ and $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ complexes are -3693.43 KJ/ Mol; and -1666.01 KJ/ Mol. $[\text{Cu}_2(\text{Htrz})_4(\text{trz})_2]^{2+}$ complex is more stable than the $[\text{Cu}_2(\text{Htrz})_6]^{4+}$ complex.

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