The Ab Initio study of the structure of the $[Fe_2(Htrz)_6(trz)_3]BF_4$ and the $[Fe_4(Htrz)_{10}(trz)_5](BF_4)_3$ complexes at the low spin and the high spin states

Asep Wahyu Nugraha[1], Ani Sutiani[2], Djulia Onggo[3], Muhamad A. Martoprawiro[4]

{aw.nugraha@unimed.ac.id[1], anisutiani@unimed.ac.id[1], djulia@itb.ac.id[2]}

Chemistry Department, Universitas Negeri Medan, Medan 20222 Indonesia[1, 2],
Chemistry Department, Institut Teknologi Bandung, Bandung 40132 Indonesia[3, 4]

Abstract. The aim of this study was to determine structure of the $[Fe_{2.}(Htrz)_{6.}(trz)_3]BF_4$ and the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$ complexes in the low spin state and high spin state Determination of the complex structure using the visualization of the results of computational chemistry calculations. The computational chemistry calculations using the function UHF and basis set 6-31G(d). The results of this study showed the distance between Fe (II) ions in the [Fe(Htrz)2(trz)]BF4 complex at the low spin (LS) and the high spin (HS) states respectively, were 3.792Å-3.839Å and 3.995Å-4.043Å. The Fe-N bond lengths on the complex at LS was 2.047Å-2.228Å and HS states was 2.140Å-2.502Å.

Keywords: complex structure, the 1, 2, 4 H-triazole Iron (II), computational chemistry, and visualization.

1 Introduction

The 1,2,4 H-triazole Iron(II) (Fe(II) Htrz) complex is one of the complexes with the spin transition (ST) characteristics. The characteristics ST in the complex compound are because the 1,2,4 H-triazole ligand is a ligand has an intermediate ligand field strength. Complex have inter-mediate ligand field strengths will cause the magnitude of the difference in the splitting energies eg and t2g to be small, so that changes between these two spin states can take place reversibly the influence of the temperature, the pressure, and the light [1], [2]. Another factor causes this spin transition characteristic is the Fe(II) ion which has an outermost d6 orbital, resulting in the different changes of magnetic properties between the LS state and HS state. In the LS state, complex is diamagnetic characteristic because the all electron are paired in the t2g orbital. In the HS state only one is paired while the other four electrons are unpaired, so the complex is paramagnetic characteristic. In addition to different magnetic properties, these complexes have different colors, at low spin states, these complexes are lilac (purple) colour and when the temperature is raised, these complexes are colorless [3].

ICIESC 2022, October 11, Medan, Indonesia

DOI 10.4108/eai.11-10-2022.2325492

Sugiyarto, et al [4] have succeeded in synthesizing the $Fe(trzH)_2(trz)X$, with X = BF_4^-, ClO_4^-, and PF_6^- complex. The complex obtained that the characterized with magnetic measurements and Mössbauer spectra. Results showed the Iron(II) H-triazole complex with B F_4^- and ClO_4^- anion had a T½ above room temperature while the P F_6^- anion occurred below room temperature. Lavrenova, et. al. [5] have synthesized Fe(II) H-triazole complex compound with chloride anion. Faulmann et. al. [6] have synthesized a complex $[Fe(Htrz)_{2.}(trz)](BF_4)$ with nano size with silica matrix.

The EXAFS study discussed two model compounds $[Fe(p\text{-}MeOptrz)_{8.}(H_2O)_4(BF_4)_6$ and $[Fe(p\text{-}MeOptrz)_{6.}(H2O)_6(tos).4H_2O$ showed that in the process of changing from a LS state into a HS state resulted in the bond length of Fe-N increasing by 0.18Å and FeN_6 core was more distorted. Distance between Fe^{2+} ion for LS of 3.65Å and HS of 3.87Å [7]. Structure studies using WAXS on the compounds $[Fe(Htrz)_{2.}(trz)](BF_4)$ and $[Fe(NH_{2.}trz)_3](NO_3)_2$ gave $[Fe(Htrz)_{2.}(trz)](BF_4)$ for LS the distance of Fe - Fe of 3.63Å and Fe-N bond length is 1.99Å, while at HS the distance of Fe ... Fe is 3.83Å and the Fe - N bond length is 2.17Å [8]. Determination of the crystal structure of $[Fe(Htrz)_{2..}(trz)]BF_4$ have the distance between Fe…...Fe at LS state 3.671(1)Å and at HS state 3.891(1) Å, while Fe - N bond length at LS state is 1.827(5) Å – 1.981(6) Å and the HS state 2.04(2) Å – 2.042(5) Å [9].

The computational chemistry calculations have been carried out on Cu (II) 1,2,4 Htriazole to determine enthalpy data and structure data using function UHF and basis set 3 - 21G and 6 - 31G (d). Data obtained showed that the distance between Cu^{2+} ions complex with deprotonated ligand of 3.306 Ǻ - 3.541 Ǻ, while the complex with un-deprotonated ligand were 3.577Ǻ - 3.729Ǻ. The Cu-N bond length in complexes with deprotonated ligands is 1.923Ǻ - 2.036Ǻ, while for complexes with undeprotonated ligands it is 1.872Ǻ - 2.065Ǻ. The change in enthalpy resulting from the computational chemistry using functions UHF and basis sets 6-31G(d) for the formation of complex $(Cu_2(Htrz)_{4.}(trz)_2)^{2+}$, $(Cu_2(H\text{-}trz)_6)^{4+}$, $(Cu_4(Htrz)_{8.}(trz)_4)^{4+}$, and $(Cu_4(Htrz.)_{12})^{8+}$ were 23364.77 kJ/mol, -9666.44 kJ/mol; -30669.09 kJ/mol; and -23356.11kJ/mol respectively [10]. The computational studies on structure and stability showed that structure of 1, 2, 4 H - triazole Fe (II) complexes were similar to structure data 1, 2, 4 H triazole Cu (II) [11]. Results of computational chemistry calculation on the molecular formulas of Fe (II) Htriazole for deprotonated and non-deprotonated ligands showed that complexes with deprotonated ligands were more stable than undeprotonated ligands [12]. The computational chemistry studies on 1, 2 , 4 Htriazole Fe (II) Chloride complexes have been carried out using the B3LYP and 6-31G(d) [13].

Kitchen et al [14] conducted a study for complex compound with triazole derivatives with single-nucleated $[Fe.(Rdpt)_3]$ (BF_4). The result showed only one is ST namely the $[Fe(pldt)_3](BF_4)_2$. 1½H_2O complex. Wolny et al [15] studied the vibrational properties of the $[Fe_3$(4(2-hidroksietil) 1,2,4 triazol$)_6](CF_3SO_3)_6$ complex. The results showed that the complex formed with ST characteristics in the Fe^{2+} ion with FeN_6 skeleton while at the terminal it has FeN_3O_3 skeleton which does not show TS properties. Cirera et al [16] studied complexes with the two types of ligand of styrylpyridine and NCX with X are S, Se, and BH_3 for $[Fe(stpy)_4.(NCX)_2]$.

The ab initio computational model is a calculation model only uses the basic theory (first principles) without using experimental data. The theories have developed in the ab initio calculation model include the HF and the DFT. This study computational calculation using HF theory with UHF and DFT methods with B3LYP and TPSSh methods.

2 Computational Method

The study of chemical properties can be carried out using various equipment in the laboratory. This method can be carried out through the stages of synthesis of complex compounds, then the characterization of various properties of the complex compounds have been synthesized is carried out. Another method used to study the properties of complex compounds uses computational chemistry. At beginning of its development, results were very far from the results obtained in the laboratory.

This study is a research uses computational chemistry calculation methods. The computational with Gaussian-09 Rev D. 01 [17], while the visualization of computational calculations uses the J mol [18]. The Fe-N bond length and distance between Fe(II) ions determined using Avogadro software [19]. The computational chemistry using the function UHF and basis set 6-31G (d). The 1, 2, 4 triazole Fe(II) has a polymer structure so that the calculation computationally using molecular modeling with two and four Fe(II) ions.The model of a complex compound with two Fe(II) ions is the complex of $[Fe_2(Htrz)_6(trz)_3]BF_4$, while the model compound with four Fe(II) ions is $[Fe_4(Htrz)_{10}(trz)_5](BF_4)_3$ complex.

3 Results and Discussion

The computational chemistry calculations is one of the methods used in studying the properties of an atom or molecule. A lot of data obtained from computational chemistry calculations include: the amount of energy, electron density, eigenvalue, wave function, vibration frequency, and rotation frequency. The data is loaded in the output file which is the result of computational chemistry calculations. The output data can be visualized in the form of the observed compound structure using Jmol or Avogadro software. The visualization results can provide an overview of the resulting structure through the geometry optimization process. The structure of the $[Fe_2(Htrz)_{6.}(trz)_3]BF_4$ visualized LS and HS is shown in Fig 1.

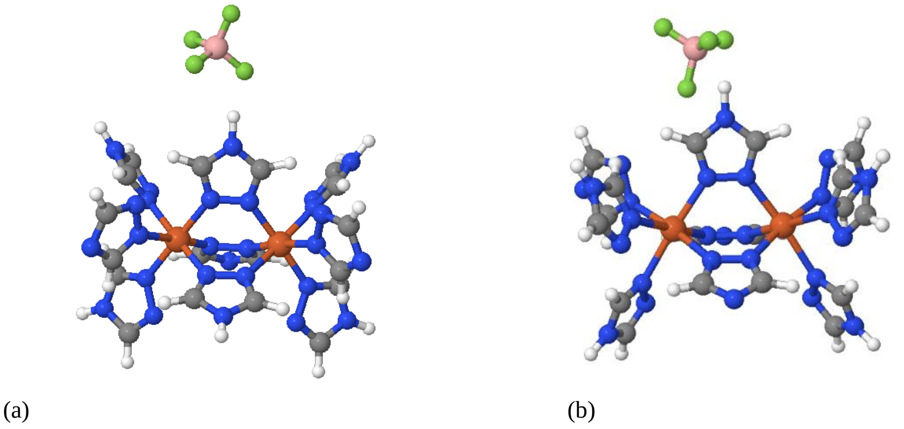

Fig. 1. The structure of the [[$Fe_2(Htrz)_{6.}$ $(trz)_3]BF_4$ at (a) LS and (b) HS.

Structure of the $[Fe_2(Htrz)_{6.}(trz)_3]BF_4$ in Figure 1 shows that structure of the complex in LS is similar to the structure in HS. This data shows that the change in the spin state of the Fe^{2+} ion does not give a large change in the structure so that the structure in the two states is similar. The computational chemistry were also performed on structure of the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$. When compared structure of the $[Fe_{2.}(Htrz)_{6.}(trz)_3]BF_4$ complex and structure of the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$ complex shows different similarities only regarding the number of Fe^{2+} ions and the number of ligands which is involved. This fact shows the consistency of the structure of the 1,2,4 H-triazole Fe(II), which is described by the number of Fe (II) ions as many as two Fe^{2+} or four Fe^{2+} ions. Structure $[Fe_4(Htrz)_{10}$ $(trz)_5](BF_4)_3$ at the LS state is similar to the structure of complex at the HS state. The structure of the $[Fe_4(Htrz)_{10.}(trz)_{5.}](BF_4)_3$ visualized presented in the Figure 2.

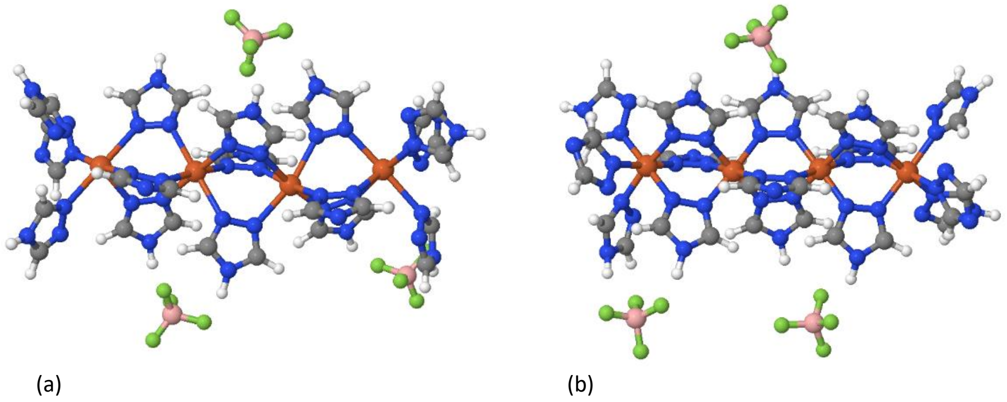

Fig. 2. The structure of the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$ in: (a) LS and (b) HS.

Based on results for visualization structure of the $[Fe_{2.}(Htrz)_{6.}(trz)_3]BF_4$ complex and the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$ complex presented in Figure 1 and Figure 2 at LS and HS conditions. The height indicates that similarity of the structure of the two complex compound structures. To deepen the study of the structure of complex, a study of data on Fe-N bond length and distance between Fe(II) ions was carried out. The reason using the two structure data is the data on Fe-N bond length and the distance between Fe^{2+} ions are very close to Fe^{2+} ions which undergo a change in spin state. So the change in spin state of the Fe(II) ion is predicted to have an effect on the two structure data. Distance between Fe^{2+} ions in $[Fe(Htrz)_2trz]BF_4$ are showed in Table 1.

Table 1. Distance between Fe^{2+} resulting from a geometric optimization of $[Fe (Htrz)_2trz]BF_4$ complex

The number of Fe(II)	Distance Fe (II) (Å)	
	LS	HS
2	3.792	4.043
4	3.823 – 3.839	3.995 – 4.008

The distance data between Fe^{2+} ions in the $[Fe_{2.}(Htrz)_{6.}(trz)_3]BF_4$ and the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$ is presented at LS state and HS state. The distance between Fe^{2+} ions in the $[Fe_{2.}(Htrz)_{6.}(trz)_3]BF_4$ at LS state is 3.792Å and at HS state is 4.043Å, while the distance between Fe^{2+} ions in the $[Fe_4(Htrz)_{10} (trz)_5](BF_4)_3$ at the LS state of 3.823Å – 3.839Å and the HS state is 3.995Å – 4.008Å. The experimental measurement results showed that distance Fe^{2+} in the LS of 3.65 and 3.87Å in the HS state [7], while other studies obtained data on the distance between Fe ions (II) at the LS 3.63 and at HS 3.83Å [8]. The data on the distance between Iron(II) ions confirmed that the change in spin state of the Iron(II) ion resulted a change in structure data. In addition to distance data between Iron(II) ions, this study also presents data on Fe - N bond length data. The bond length of Fe - N is predicted to change when there is a change for spin state of the Iron(II) ion. This happens because the Fe-N bond is very close to Iron(II) ion. The Fe-N bond length data in $[Fe (Htrz)_2trz]BF_4$ are showed in the Table 2.

Table 2. The Fe - N bond length resulting geometric optimization of $[Fe(Htrz)_2trz]BF_4$ complex

The number of Iron(II)	The distance between Iron(II) ions (Å)	
	LS	HS
2	2.047 – 2.123	2.173 – 2.372
4	2.064 – 2.228	2.140 – 2.502

The Fe-N bond lengths are presented in $[Fe_{2.}(Htrz)_{6.}(trz)_3]BF_4$ complex and the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$ at LS state and HS state. The Fe-N bond length in the $[Fe_2(Htrz)_6 (trz)_3]BF_4$ complex at LS state was 2.047Å – 2.123Å and at HS state was 2.173Å – 2.372Å, while Fe-N bond length in the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$ complex at LS state was 2.064Å – 2.228Å and at HS state was 2.140Å – 2.502Å. The results of the experimental study showed Fe – N bond length at LS state were 1.827(5) – 1.981(6)Å and at HS state was 2.04(2) – 2.042(5)Å [9]. These data indicate the Fe - N bond length in LS state is smaller than the HS state.

4 Conclusion

Visualization of the computational chemistry results shows that the structure of the $[Fe_2(Htrz)_{6.}(trz)_3]BF_4$ and the $[Fe_4(Htrz)_{10}(trz)_5](BF_4)_3$ complex in the LS state is similar to the HS state. The structure of the $[Fe_{2.}(Htrz)_{6.}(trz)_3]BF_4$ and the structure of the $[Fe_4(Htrz)_{10.}(trz)_5](BF_4)_3$ shows the BF_4^- anion is not directly bound to the Fe(II) cation but is outside and interacts directly with the H atom of the triazole ligands. The results of the measurement of distance Iron (II) in $[Fe_2(Htrz)_{6.}(trz)_3]BF_4$ for the LS state was 3.792Å and the high spin state was 4.043Å. The distance between Iron(II) ions in $[Fe_4(Htrz)_{10.}(trz)_5](BF_4)_3$ complex at LS state was 3.823Å – 3.839Å and at high spin state was 3.995Å – 4.008Å. The Fe - N bond length in the $[Fe_{2.}(Htrz)_{6.}(trz)_3]BF_4$ at the LS state was 2.047Å – 2.123Å and the HS state was 2.173Å – 2.372Å. The Fe-N bond length in the $[Fe_{4.}(Htrz)_{10.}(trz)_5](BF_4)_3$ complex at LS state was 2.064Å – 2.228Å and the HS state was 2.140Å – 2.502Å.

Acknowledgments. This work was supported by The ministry of Education, Culture, Research, and Technology of the Republic of Indonesia (grant. 130/ SP2H/ LT/DRPM/2021) and the Institut Teknologi Bandung (ITB) for its help in calculating on the HPC server.

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