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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF THE SPIN TRANSITION SYSTEM $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$ COMPLEX

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ABSTRACT

Octahedral complex of iron(II) with two different electronic state of high-spin and low-spin is potential as a molecular switch in the development of electronics technology. Changes between the two states are known as spin transition which can be observed as a change in the magnetic properties due to external disturbances such as temperature, pressure and radiation. The complex tris-(pq) iron(II) has been synthesized and single crystals are successfully grown. This complex has a chemical formula $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$, crystallized in monoklin system with space group P21/c, cell parameters are $a = 18.579(4)$, $b = 10.952(3)$, $c = 19.285(6)$ Å and $\beta = 93.605$ (10)°. Steric effect of benzene ring on the cluster causes the length of pq ligand bond Fe-N_{quinoline} approximately 0.1 Å longer than the bond length of Fe-N_{pyridil}. Therefore geometry of octahedral is distorted to tetragonally. The measurement of susceptibility magnetic at temperatures 5-300 K show this complex has spin transition character with transition temperature 168 K. Spin transition is observed as a change in mole fraction of high-spin slowly from 0.01 at 5 K up to 0.98 at temperatures of 300 K is marked change in the magnetic moment value of 0.87 to 5.35 BM.

Keywords: complex, magnetic, spin transition, structure, synthesis

INTRODUCTION

The study of molecular materials with properties or composition of the relevant properties for practical use in various fields such as molecular electronics, data storage and display devices have been developed since 30 years ago [1-3]. The molecular switches are components essentially needed in the development of molecular electronics [4-5]. The complex of iron(II) with the character of the spin transition is the most potential candidate as a molecular switch that spin transitions are marked changes real magnetic properties of diamagnetic ($S = 0$) in the low-spin state becomes paramagnetic ($S = 2$) in high-spin state [6]. The spin transition can be owned by a complex of iron(II) and the ligand with field strength is medium [7]. Ligands 2,2-(2-pyridil)quinoline (pq = C₁₄H₁₀N₂) is derived ligand 2,2'-bipyridine (bpy) resulting from the substitution of benzene groups in cis position to one nitrogen atom of bpy. Bpy ligand is strong

field ligands, with the benzene group is expected to result in a pq ligand with medium field ligand so a complex of iron(II) with pq ligands can show the spin transition [8]. The complex of iron(II) with pq ligands has been observed since long time ago. The resulting complex involves the complex of bis-(pq) iron(II) with the formula $[\text{Fe}(\text{pq})_2\text{X}_2]$; X = Cl⁻, Br⁻, NCS⁻, ClO₄⁻ and tris-(pq) iron(II) with the chemical formula $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$. Both complexes are in the high-spin state at room temperature up to liquid nitrogen temperature [8].

It was reported that there are two modifications of structure $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ based on patterns of X-ray diffraction powder. Both complexes show different magnetic properties, the first stable at high-spin state whereas the second indicates the spin state changes in the temperature range 89-300 K [9]. Until now, there has been no publication of a single crystal structure of a complex of iron (II) with pq ligands.

In this paper has been studied the complex structure of tris-(pq) iron(II) based on the analysis of X-ray diffraction single crystal and magnetic properties through the measurement of magnetic susceptibility at 5-330 K temperatures.

EXPERIMENT

Synthesis of Complex $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$. In the 50 mL flask was weighed 0.36 g of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and are covered by a rubber septum and flow the N₂ gas. Into the flask is added 5 mL of ethanol using a syringe. On the other flask weighed 1.02 g of pq ligand and dissolved in 10 mL of hot ethanol. Then a solution of ligand added to the flask containing a solution of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The mixture is heated until the solution volume is reduced and the remaining half. Crystal red-orange color formed one day later and then filtered, washed with ethanol and dried in vacuum desiccator containing P₂O₅. pq ligand synthesized from o-2-aminobenzaldehyde and acetylpyridil in accordance with the published [8].

X-ray Diffraction Measurements. A single crystal of $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$ with a size of 0.05 x 0.08 x 0.03 mm³ chosen for the measurement of X-ray diffraction. Data of X-ray diffraction collected on a Bruker SMART APEX diffractometer at a temperature 295 (2) K using ω -scan technique with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensities data were collected at the diffraction angle range of approximately 1.62-27.49° for 14.990 reflections. Correction absorption and polarization-Lorentz (Lorentz-Polarization) is used to reduce the reflection data. The molecular structure of complex solved and refined using the program SHELXTL [10]. The molecules described by using ORTEP [11].

Magnetic Properties Measurement. Measurement of magnetic properties with a continuous change in temperature is done by using a MPMS-7 (Magnetic Properties Measurement System). Approximately 5-30 mg of sample put into gelatin capsules. Then the

capsule containing the sample is inserted into a transparent straw with a depth of about 2/3 length of a straw. Straw is placed next to the sticks contained in the MPMS-7. Measurement process carried out by the method of ZFC (Zero Field Cool) that the temperature of sample is derived from room temperature to 5 K without magnetic field. By the time the temperature had reached 5 K, the magnetic field began to be used for 1000 Oe and the measurement process starts from the temperature 5 K up to approximately 330 K with increase in temperature 1-10 K/step. From these measurements the magnetic properties can be calculated the corrected molar susceptibility values (χ_M'). Then based on the corrected molar susceptibility values (χ_M') so the value of magnetic moment (μ) can be calculated by using the equation:

$$\mu = [8\chi_M'T]^{1/2} \text{ BM} \quad (1)$$

with μ is magnetic moment in BM (Bohr Magneton) unity and T is temperature in Kelvin degree(K). To identify the spin transition, the content of iron(II) on high-spin state as mole fraction at various temperature is determined using the equation:

$$(\square)T = XHS(\square)2HS) + (1 - XHS) (\square)2LS) \quad (2)$$

XHS is the mole fraction of high-spin iron(II), \square HS is the limit value of magnetic moment of iron(II) on high-spin state. It be determined equal to 5.4 BM, \square LS is the limit value of magnetic moment of iron(II) on low-spin state. It be determined equal to 0.7 BM [11].

RESULTS AND DISCUSSION

Synthesis of Complex $[Fe(pq)_3](ClO_4)_2$. The Complex of iron(II) with three molecules of pq ligands and perchlorate anions obtained as red crystals in 77% yield. The complex is soluble in methanol and ethanol, while in the water through decomposition to form a yellow solution and white precipitate detected as pq ligand.

The content of C, H, N elements indicates the complex contains three molecules of ligand pq. This is supported by the content of iron(II). Therefore, based on the contents of their constituent elements, chemical formula is most appropriate for this complex is $[Fe(C_{14}H_{10}N_2)_3](ClO_4)_2$ or $[Fe(pq)_3](ClO_4)_2$. The data of elements content C, H, N and iron(II) is presented in Table 1.

Table 1. The content of constituent elements of the complex $[Fe(pq)_3](ClO_4)_2$

	The element in percentage			
	Fe	C	H	N
Practical	6,45	57,23	3,62	9,24
Theoretical	6,39	57,75	3,46	9,62

Crystal Structure of $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$. The molecular structure of the $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$ with atomic numbering scheme is presented in Figure 1. The central metal ions of iron(II) binds three molecules of pq ligands with octahedral geometry. pq ligands consisting of two rings and one pyridil benzene ring attached to a cluster in one branch of pyridil. Ring pyridil that bind benzene ring is named as quinoline. The size of a large pq ligand causes repulsion between the pq molecules in the complex. Therefore, to minimize the repulsion between pq ligands, this complex structure adopted meridional isomer Fe-Npyridil-1-3-5 and Fe-Nquinoline 2-4-6.

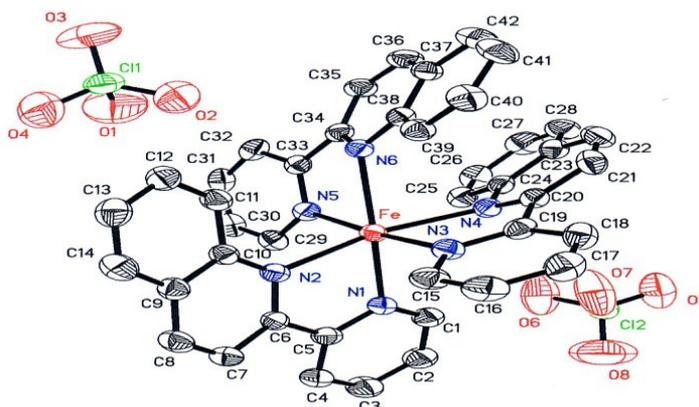


Figure 1. The structure of complex molecules $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$. For clarity picture, H atoms not shown

Bond distances $\text{Fe-N2} = 2.232(3)$ is longer than the distance of Fe-N1 bond of $2.164(3)$ Å. Similarly, the bond distances $\text{Fe-N4} = 2.263(3)$ longer than the bond distances $\text{Fe-N3} = 2.164(3)$ Å and the bond distances $\text{Fe-N6} = 2.310(3)$ longer than the bond distances $\text{Fe-N5} = 2.164(3)$ Å. The difference is due to the sterik effect of benzene rings on quinoline that hindering donor atoms Nquinoline approached the central metal ions of iron(II). Therefore the bond distances Fe-Nquinoline are longer than the bond distances of Fe-Npyridil. The sterik effects of benzene ring, also causes the bond angles $\text{N5pyridil-Fe-N2quinoline}$ (91.5°); $\text{N5pyridil-Fe-N4quinoline}$ (103.18°) and $\text{N3pyridil-Fe-N6quinoline}$ (100.18°) are greater than the 90° . Data length and angle of this bond indicates that the geometry of octahedral complex $[\text{Fe}(\text{pq})_3]^{2+}$ is distorted. Charge cations of $[\text{Fe}(\text{pq})_3]^{2+}$ was balanced by two perchlorate anion $(\text{ClO}_4)^-$. Both anions have a tetrahedral geometry with the angle around the chlorine atom for $105.6-119.3^\circ$.

This complex crystallizes in monoklin system with space group $P21/n$ and cell parameters are $a = 18.579(4)$, $b = 10.952(3)$, $c = 19.285(6)$ Å and $\beta = 93.605(10)^\circ$. Single crystal data are summarized in Table 2.

The Magnetic Properties of $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$. At low temperatures 5-100 K, a complex of iron(II) is on low-spin state with magnetic moment values obtained almost constant 1.0 BM. Increasing the temperature from 105 K causes spin transition of the iron(II) on low-spin to high-

spin state. At 168 K temperature, the mole fraction of iron (II) on low-spin state (XLS) equal to the mole fraction of iron (II) high spin state (XHS) = 0.5. The temperatures when XLS = XHS = 0.5 is known as the transition temperature ($T_{1/2}$). According to increasing of temperature, the mole fraction of iron(II) on high-spin state increase and achieve value of 0.9 with the magnetic moment of 5.2 BM at 205 K temperature.

Table 2. The single crystal data of $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$ complex

Empirical formula	$\text{C}_{42}\text{H}_{30}\text{Cl}_2\text{FeN}_6\text{O}_8$
Molecular Weight	873.47
Temperature (K)	293
Wavelength (Å)	0,71073
Crystal system	Monoclin
Space group	P21/c
Unit cell parameters	$a = 18.579(4)$, $b = 10.952(3)$ $c = 19,285(6)$ Å, $\beta = 93,605(10)^\circ$
Volume (Å ³)	3916,29(18)
The number of molecules in unit cell (Z)	4
Density (ρ in $\text{g}\cdot\text{cm}^{-3}$)	1,481
Crystal size (mm)	0,08 x 0,05 x 0,03
The value of 2 theta for data collection (°)	1,62-27,49
Limiting indices	$-24 \leq h \leq 24$, $-14 \leq k \leq 14$ and $-24 \leq l \leq 2$

This means that the spin transition of iron(II) in the $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$ complex from the low-spin to high-spin state took place in the region 105-205 K with transition temperature at 168 K. This transition temperature is higher than the transition temperature of iron (II) in a similar complex of $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ i.e approximately 150 K [8]. The difference of transition temperature is expected due to the formation of hydrogen bonding network between the H atom from H_2O to O from ClO_4^- which also form hydrogen bonding with H atoms from the pq ligand in complex. This hydrogen bonding network increases the stability of complex on high-spin state. Therefore, the transition temperature of iron(II) in the $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ lower than the $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$. The curve of mole fraction iron(II) on high-spin state in the temperature range 5-300 K are presented in Figure 2. The curve is the mole fraction of iron(II) on high-spin state (X_{HS}) against temperature (K) is known as the spin transition curve.

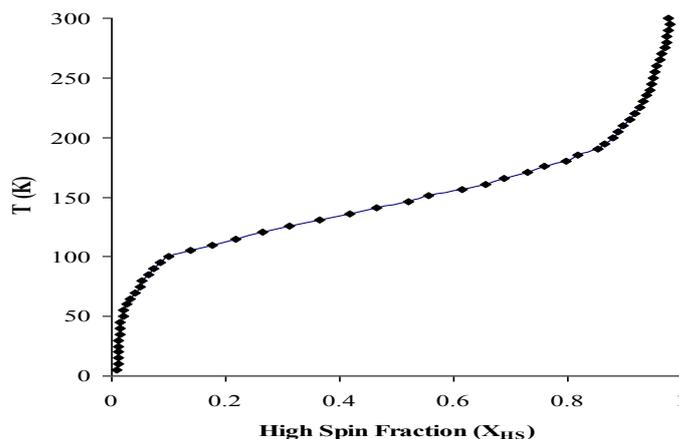


Figure 2. The curve of spin transition of iron(II) in the complex of $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$

At the temperatures range from 210 K to room temperature (300 K) this compound is on high spin state with the value of magnetic moment about 5.3 BM. This is consistent with the long Fe-N bond in the molecule structure of 2,16-2,31 Å corresponding to the distance Fe-N on high-spin state [12-13].

CONCLUSION

The complex compounds of tris-(pq) iron(II) with the formula of $[\text{Fe}(\text{pq})_3](\text{ClO}_4)_2$ successfully grown single crystals in the solvent methanol. The formula of this complex is determined based on the content of the C, H, N elements and supported by single crystal molecular structure.

The molecular structure of this complex has a distorted octahedral geometry and adopt meridional isomers. Distortion occurs due to the steric effects of benzene ring that causing the length bond of Fe-N_{quinoline} is longer than the distance of Fe-N_{pyridil} bond and the bond angles Fe-N_{pyridil}-N_{quinoline} is greater than should be 90 °.

The spin transition takes place gradually in the temperature region 105-205 K with transition temperature 168 K.

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