SYNTHESIS AND MAGNETIC PROPERTIES OF BINUCLEAR COMPLEX \([N(n-C_4H_9)_4][Mn^{II}Fe^{III}(ox)_3]\)

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ABSTRACT

Binuclear complex, \([N(n-C_4H_9)_4][Mn^{II}Fe^{III}(ox)_3]\) \((ox=oxalate)\), has been synthesized and characterized. Binuclear complex with formula of \([N(n-C_4H_9)_4][Mn^{II}Fe^{III}(ox)_3]\) was synthesized by forming precursor \(K_3[Fe(ox)_3]\) which was followed by adding manganese chloride and tetrabutyl ammonium chloride. Characterization of the complex was made by microanalysis, FT-IR spectroscopy, x-ray diffraction and Magnetic Susceptibility Balance. Magnetic moment of binuclear complex \([N(n-C_4H_9)_4][Mn^{II}Fe^{III}(ox)_3]\) is 7.81 BM. The compound has higher magnetic moment than the previously reported compound with different organic cation, \([N(n-C_5H_{11})_4][Mn^{II}Fe^{III}(ox)_3]\). This behavior might be associated with the decreasing range among layers on polymeric network.

Keywords: Binuclear complex; oxalato network; iron complex; magnetic properties; X-ray powder diffraction

INTRODUCTION

Molecular magnet based on polynuclear complexes has superior magnetic properties than mononuclear complexes. For example, the magnetic moment of \([N(n-C_5H_{11})_4][Mn^{II}Fe^{III}(Ox)_3]\) is 7.5 BM [1], while the magnetic moment of its respective mononuclear complex \(K_3Fe(Ox)_3\) is 5.8 BM [2]. Interactions among metal ions in the polynuclear complex improve their total magnetic moment.

The magnetic moment of polynuclear complexes is a function of the size of organic cation. Decreasing the cation size will increase the magnetic moment followed by the increase in temperature of paramagnetic-antiferomagnetic transition.

Studies on the effect of organic cation size to magnetic moment of polynuclear complexes have been reported. For an example, Matheriine et al. (1996) reported that binuclear complex \([N(n-C_5H_{11})_4][Mn^{II}Fe^{III}(ox)_3]\) had paramagnetic-antiferomagnetic transition at 27 K and effective magnetic moment 7.71 BM. The crystal structure of the complex was investigated later [3].

Tetra-Butylamine \([N(n-C_5H_{11})_4]^+\) is an organic cation which is smaller than tetra-pentylamine, \([N(n-C_5H_{11})_4]^+\). Therefore, when the former cation replaces the \([N(n-C_5H_{11})_4]^+\) in \([N(n-C_5H_{11})_4][Mn^{II}Fe^{III}(Ox)_3]\), the magnetic moment of the complex will increase. This paper reports the research results of the substitution and its effect on the complex magnetic moment. The polyanion complex was synthesized from \(K_3Fe(Ox)_3\) precursor.

EXPERIMENTAL SECTION

Materials

All chemicals were reagent grade and were used as commercially obtained, such as MnCl₂.4H₂O, \([NH_4]_2Fe(H_2O)_2(SO_4)_2.4H_2O\), H₂SO₄ 6M, methanol,
Fig 1. X-Ray diffraction of K₃[Fe(ox)₃].3H₂O

Fig 2. The spectrum of K₃[Fe(ox)₃].3H₂O

Table 1. Comparison of characteristic peaks K₃[Fe(ox)₃].3H₂O which was synthesized and matched to standard reference of [Fe(C₂O₄)₃]³⁻

<table>
<thead>
<tr>
<th>K₃[Fe(ox)₃].3H₂O</th>
<th>Standart reference of [Fe(C₂O₄)₃]³⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.78</td>
<td>19.81</td>
</tr>
<tr>
<td>26.83</td>
<td>26.17</td>
</tr>
<tr>
<td>28.33</td>
<td>28.06</td>
</tr>
<tr>
<td>36.02</td>
<td>36.58</td>
</tr>
<tr>
<td>42.57</td>
<td>43.77</td>
</tr>
<tr>
<td>52.06</td>
<td>55.23</td>
</tr>
<tr>
<td>61.1</td>
<td>61.29</td>
</tr>
</tbody>
</table>

H₂C₂O₄.2H₂O, K₂C₂O₄.H₂O, H₂O₂, tetra-butyl ammonium chloride and aquadest.

Instrumentation

Metal content was determined by Absorption Atomic Spectroscopy Shimadzu AA8801S. Elemental analyses (C, H, N) were performed on Fison EA 1108 microanalytical analyzer at Universiti Kebangsaan Malaysia. The FT-IR spectra was recorded on Shimadzu FTIR-8400 spectrometer in the 4000 – 400 cm⁻¹ spectral regions and Absorption Atomic Spectroscopy at Institut Teknologi Sepuluh Nopember, Powder X-ray diffraction measurements was performed Philip X’Pert PN-1830 X-Ray, at Research Center Institut Teknologi Sepuluh Nopember while magnetic susceptibility was measured by Magway MSB from Sherwood Scientific LTD at Universitas Airlangga.

Procedure

**Synthesis Complex K₃[Fe(ox)₃].3H₂O**

10.06 g ammonium ferrous sulphate hexahydrate was dissolved in 30 mL of hot water and acidified with dilute sulphuric acid. A hot solution of 6.36 g of oxalic acid dihydrate in 50 mL of aquadest was added. Cautiously the mixture was heated to boiling and then allowed the yellow precipitate of iron(II) oxalate, FeC₂O₄.2H₂O, to settle. The precipitate was washed with 30 mL water by decantation. A warm solution of 6.62 g potassium oxalate monohydrate in 18 mL of aquadest was added. 10 mL hydrogen peroxide was added, the solution was stirred continuously and the temperature was kept below 40 °C. Then the mixture was heated, the brown precipitate was formed. Saturated solution of 1.62 g oxalic acid dihydrate in 13 mL of aquadest was added until the precipitate just redissolved. The solution was filtered, and then 20 mL of methanol was added. It was left to crystallize in the dark. When the green crystal of the complex has appeared, the solution filtered and the crystals were washed in ethanol, then with acetone. The crystals were allowed to dry at room temperature in the dark. The product was stored in glass specimen tube and wrapped in aluminium foil [4].

**Synthesis Complex Binuclear [N(n-C₄H₉)]₂[Mn Fe(ox)₃]**

An aqueous solution of 0.34 g MnCl₂.4H₂O in 10 mL of aquadest was added dropwise to an aqueous solution 0.99 g of K₃[Fe(ox)₃].3H₂O in 10 mL aquadest at room temperature. The solution was evaporated at ambient temperature for 1 h. An aqueous of tetrabutyl ammonium chloride was then slowly added to the solution during stirring. After approximately 12 h, the product was collected by filtration, washed with H₂O and EtOH, and dried in vacuo [5].

RESULT AND DISCUSSION

Complex K₃[Fe(ox)₃].3H₂O

This complex is synthesized on two phases. The first phase is a synthesis of Fe(II)oxalate complex. The second phase is a forming of green crystalline
The metal ion and C, H and N contents of binuclear complex

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mn</th>
<th>Fe</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N(n-C₄H₉)₄][MnᴵⅢFeᴵⅡ(ox)]₃</td>
<td>8.77</td>
<td>8.61</td>
<td>42.97</td>
<td>5.66</td>
<td>2.35</td>
</tr>
<tr>
<td>8.91*</td>
<td>9.08*</td>
<td>42.79*</td>
<td>5.83*</td>
<td>2.69*</td>
<td></td>
</tr>
</tbody>
</table>

*Calculated

1688 cm⁻¹, and for ν(Fe-O) bands at 472 cm⁻¹ [7]. The spectrum of the complex is shown in Fig. 2.

The absorption peak at 3688.02 cm⁻¹ is indicated by stretching vibration of OH. Stretching vibration C=O from oxalate as shown at 1658.84 cm⁻¹. Stretching vibration Fe-O has been observed at 459.07 cm⁻¹. This spectrum is similar to spectrum which was reported [6]. It is indicated that K₃[Fe(ox)₃]·3H₂O has formed.

### Binuclear Complex [N(n-C₄H₉)₄][MnᴵⅢFeᴵⅡ(ox)]₃

Binuclear complex [N(n-C₄H₉)₄][MnᴵⅢFeᴵⅡ(ox)]₃ was synthesized by forming precursor K₃[Fe(ox)]₃ which was followed by adding manganese chloride and tetrabutyl ammonium [N(n-C₄H₉)₄]⁺, solvend by aquadest as solvent. Yellow crystalline binuclear complex [N(n-C₄H₉)₄][MnᴵⅢFeᴵⅡ(ox)]₃ was resulted from this reaction.

The reaction of the process is represented as follows:

\[
2K₃[Fe(ox)]₃ \cdot 3H₂O + 2MnCl₂ \cdot 4H₂O + 2[N(n-C₄H₉)₄]Cl → 2[[N(n-C₄H₉)₄][MnᴵⅢFeᴵⅡ(ox)]₃] + 6KCl + 7H₂O
\]

The formula of the complex resulted from elemental content is listed in Table 2. This table shows that the content of binuclear complex experiment suitable to the calculated content of binuclear complex [N(n-C₄H₉)₄][MnᴵⅢFeᴵⅡ(ox)]₃.

This complex was further characterized by X-Ray Powder Diffraction. They are listed in Fig. 3.

The diffraction pattern of the complex was used as precursor to get binuclear complex [N(n-C₄H₉)₄][MnᴵⅢFeᴵⅡ(ox)]₃. However, the binuclear complex was further characterized by X-Ray Powder Diffraction. It is listed in Fig. 1.

The diffractogram of K₃[Fe(ox)]₃·3H₂O has similar pattern to iron(III) oxalate’s diffraction on 14-0807 International Centre for Diffraction Data Reference. The characteristic peaks of K₃[Fe(ox)]₃·3H₂O which were synthesized and matched to standard reference of [Fe(OC₃H₅)]²⁺ is listed Table 1.

The formula of the compound is also supported by infrared spectrum. The absorption peak at 3560 cm⁻¹ indicated by a stretching vibration of OH [6]. Stretching vibration C=O from free oxalate ligand is shown at 1830 cm⁻¹, and ν(Fe-O) bands at 472 cm⁻¹ [7]. The spectrum of the complex is shown in Fig. 2.
The complex was analyzed by infrared spectrum to support the formula. The spectrum of the function group to support the formula was reported. Stretching vibration C-O indicated oxalate as bridge ligand at 1627, 1330 and 800 cm\(^{-1}\) [10-11]. Stretching and bending vibration C-H aliphatic from tetra butyl was observed at 2936.6 and 1432 cm\(^{-1}\). The bands at frequency 472.7 and 410.9 cm\(^{-1}\) indicated bond between Fe-O and Mn-O [12]. The spectrum of the complex is shown in Fig. 4.

The analysis of infrared spectrum can indicate the function group of binuclear complex [N(n-C\(_4\)H\(_9\))\(_3\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\), which is listed is Table 4.

The absorption at 2970.48 cm\(^{-1}\) indicates stretching vibration of C-H butyl which was bonding to ammonium. At the same time, \(v(\text{CO})\) stretching at 1627.97; 1346.36; and 898.86 cm\(^{-1}\) shifted to lower frequency suggests that oxalate as bridge ligand. Another band appeared in spectra of the complex at 408.92 and 486.08 cm\(^{-1}\) is due to stretching vibration Mn-O and Fe-O.

The further analysis of binuclear complex [N(n-C\(_4\)H\(_9\))\(_3\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\), which was a synthesis showed similar result to binuclear complex [N(n-C\(_3\)H\(_7\))\(_2\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\) was reported previously, so we can infer that the complex has been formed. The similar characteristic of both [N(n-C\(_3\)H\(_7\))\(_2\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\) and [N(n-C\(_4\)H\(_9\))\(_3\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\) suggests that their structures are similar too.

### Table 4. Infrared spectrum of binuclear complex [N(n-C\(_4\)H\(_9\))\(_3\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\)

<table>
<thead>
<tr>
<th>Function Group</th>
<th>Absorption Areas (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v(\text{C=O})) oxalate as bridge ligand</td>
<td>1627.97, 1346.36, 898.86</td>
</tr>
<tr>
<td>(v(\text{C-H})) butyl which was bonding to ammonium</td>
<td>2970.48, 1446.66</td>
</tr>
<tr>
<td>Mn-O</td>
<td>408.92</td>
</tr>
<tr>
<td>Fe-O</td>
<td>486.08</td>
</tr>
</tbody>
</table>

### Magnetic Properties of complex [N(n-C\(_4\)H\(_9\))\(_3\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\)

Magnetism of the bimetallic tris-oxalato [N(n-C\(_4\)H\(_9\))\(_3\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\) can be observed by analyzing the moment of magnetic value by Magnetic Susceptibility Balances.

The value of moment magnetic complex was measured at 7.81 BM. This value having higher value than binuclear complex [P(n-C\(_3\)H\(_11\))\(_2\)] [Mn\(^{III}\)Fe\(^{III}\)(ox)]\(_3\) was reported [13] giving value of 7.71 BM. This proves that decreasing range among layers on polymeric network by substituting organic cation [P(n-C\(_3\)H\(_11\))\(_2\)] with [N(n-C\(_4\)H\(_9\))\(_3\)] can increase compound magnetic interaction.

The calculated magnetic moment related to the spin of metal ion. In this case, Mn\(^{II}\) and Fe\(^{III}\) give a number of spins which is calculated as follows S\(_T\)=S\(_Mn\)+S\(_Fe\) (S\(_Mn\)=5/2; S\(_Fe\)=5/2). The produced binuclear complex [N(n-C\(_3\)H\(_7\))\(_2\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\) is high spin, this indicates that binuclear complex [N(n-C\(_3\)H\(_7\))\(_2\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\) is paramagnetic.

It was reported [13] that complex with [MnFe(ox)]\(_3\) anionic gave antiferromagnetic interaction. The magnetic moment calculated for this interaction was represented as \(\mu=g(S_{T}(S_{T}-1)1/2)\) (g=2.00023). This equation gives effective moment of [N(n-C\(_4\)H\(_9\))\(_3\)] [MnFe(ox)]\(_3\) at 8.94 BM.

The magnetic moment of bimetallic tris-oxalato with [MnFe(ox)]\(_3\) anionic and organic cation, [N(n-C\(_4\)H\(_9\))\(_3\)] or [N(n-C\(_3\)H\(_7\))\(_2\)] was reported [13] giving lower value than the magnetic moment calculated. It caused [MnFe(ox)]\(_3\) anionic having different metal ions but the same spin, S\(_Mn\)=S\(_Fe\)=5/2. This gives alternative noncholinierar chirality, so it makes spin canting and gives different value of gyromagnetic (g) value, which influences the magnetic moment calculated [14].

### CONCLUSION

The analyzed infrared, X-Ray Diffraction and microanalysis conclude that the binuclear complex [N(n-C\(_4\)H\(_9\))\(_3\)] [Mn\(^{II}\)Fe\(^{III}\)(ox)]\(_3\) has been formed. These complex was synthesized by forming precursor K\(_3\)[Fe(ox)]\(_3\) which is followed by adding manganese chloride and tetrabuthylammonium. The value of
magnetic moment complex was measured at 7.81 BM. This value having higher value than binuclear complex \([N(n-C_5H_{11})_4][Mn^{II}Fe^{III}(ox)_3]\) was reported [12] which gives value 7.71 BM. This thing proves that decreasing range among layers on polymeric network with substituting organic cation \([N(n-C_5H_{11})_4]^+\) with \([N(n-C_4H_{9})_4]^+\) can increase compound magnetic interaction. Binuclear complex \([N(n-C_4H_{9})_4][Mn^{II}Fe^{III}(ox)_3]\) which is produced is high spin. This indicates that binuclear complex \([N(n-C_4H_{9})_4][Mn^{II}Fe^{III}(ox)_3]\) is paramagnetic.

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