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311

SHORT COMMUNICATION

SYNTHESIS AND CHARACTERIZATION OF [Fe(PICOLINATE)₃][MnNi(OXALATE)₃].CH₃OH POLYMERIC COMPLEX

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ABSTRACT

Polymeric complex [Fe(picolinate)₃][MnNi(oxalate)₃].CH₃OH has been successfully synthesized using H-tube technique. The chemical composition of the synthesized product was determined by Elemental Analysis and Atomic Absorption Spectrometry. Infrared spectrum shows that the oxalate ligand acts as a bridging ligand. The crystalline product exists in the form of monoclinic structure and space group P2₁ₙ as shown on the pattern of X-Ray Diffraction and has a similar structure with [Fe(bpp)₂][MnCr(oxalate)₃] complex. The magnetic susceptibility of the polymeric complex exhibits high spin and paramagnetic behavior.

Keywords: polymeric complex; bridging oxalate; picolinate ligand; paramagnetic behavior

ABSTRAK

Kompleks polimer [Fe(pikolinat)₃][MnNi(oksalat)₃].CH₃OH telah berhasil disintesis dengan teknik tabung H. Rumus molekul kompleks diperoleh dari analisis unsur, spektroskopi serapan atom, Fourier Transform Infra Red (FTIR). Analisis FTIR menunjukkan oksalat sebagai ligan jembatan. Produk kristalin dikarakterisasi dengan difraksi sinar-X. Kompleks membentuk struktur monoklin dengan kelompok ruang P2₁ₙ. Kompleks polimer memiliki struktur yang sama dengan[Fe(bpp)₂][MnCr(oksalat)₃] bpp = bipiridin. Pengukuran suseptibilitas kompleks terhadap temperatur menunjukkan kompleks spin tinggi dan bersifat paramagnetik.

Kata Kunci: kompleks polimer; jembatan oksalat; ligan asam pikolinat; paramagnetik

INTRODUCTION

The polymeric complex of oxalate is widely used as the magnetic material, optic material, heterogeneous catalyst and energy storage material [1]. This complex is also reported as the material exhibiting photoluminescence properties [2]. The improvement of the polymeric complex properties by inserting the mono nuclear complex to the oxalate polymeric network has been conducted to obtain the superior magnetic properties [3].

Pyridine-2 carboxylic acid (picolinate acid) is a useful tool for constructing crystalline architectures due to its rigid and planar nature and its proton donating and acceptability capabilities for hydrogen bonding via the oxygen atoms of its carboxylate groups [4]. A part from the picolinate ligand having a number of potential donor oxygen and nitrogen atoms, it has been subjected to study of the coordination chemistry by both inorganic and bioinorganic chemists during the past few years [4-5].

In this study, we describe the preparation, spectroscopic, structural characterization, and magnetic studies of such a polymeric complex by inserting the cationic complex of $[Fe(picolinate)_3]^{2+}$ to the polymeric network of $[MnNi(ox)_3]^{2-}$ oxalate polymer.

EXPERIMENTAL SECTION

Materials

All chemicals and solvents used in this experiment were of the reagent grade. Picolinate (2-pyridin carboxylic), $MnCl_2.4H_2O$, $NiCl_2.4H_2O$, oxalic acid, methanol reagents and chemicals were purchased from commercial sources and used as received. $FeCl_2.6H_2O$

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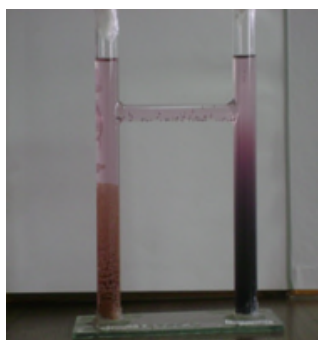**Fig 1.** Crystal growth occurred in H-tube reactor

Table 1. Metal ion contents and elemental analysis data of the polymeric complex

FeMnNiC$_{25}$H$_3$N$_{19}$	%Fe	%Mn	%Ni	%C	%H	%N
Experiment	6.64	6.16	7.43	36.23	5.73	2.59
Theoretical calculation	6.71	6.59	7.07	35.93	5.03	2.28

was prepared following the method described for FeCl$_2$ [7].

Instrumentation

Carbon, hydrogen and nitrogen analyses were performed using Fison EA 1108 Elemental Analyzer. The content of metal ions was determined by Atomic Absorption Spectroscopy. IR spectra of KBr pellets were recorded on SHIMADZU FTIR Spectrometer. Magnetic susceptibility measurements were performed at heating rate of 1 Kmin^{-1} in the range temperature 5-300 K using magnetometer Quantum Design SQUID (Superconductor Quantum Interface Device) MPMS-7 (Magnetic Properties Measurement System). Data collection of the complexes was performed on Diffraction Shimadzu, detector using CuKα (λ=1.74 Å). Intensity data were collected in the θ range 5-60° at 297 K.

Procedure

The MnCl$_2$.4H$_2$O (0.16 g, 1 mmole) solution in methanol (3 mL) was added into the NiCl$_2$.4H$_2$O (0.20 g, 1 mmole) solution in 3 mL of methanol. The mixture was then added by oxalic acid (0.38 g, 3 mmole) in 5 mL of methanol. The mixed solution was stirred for 30 min in room temperature and nitrogen atmosphere. The green solution was placed in the right side of the H-tube. The FeCl$_2$.6H$_2$O (0.23 g, 1 mmole) in methanol was added to the picolinate solution (0.37 g, 3 mmole) in methanol while following the tube with N$_2$ gas. This solution was placed in the left side of the H-tube as illustrated in Fig. 1.

RESULT AND DISCUSSION

The polymeric complex was synthesized by the reaction of [Fe(picolinate)$_3$]$^{2+}$ dan [MnNi(ox)$_3$]$^{2-}$ in the presence of methanol as a solvent. The reaction yielded a green crystalline solid with the randement of 59 %. The solubility test of the polymeric complex showed that the complex did not dissolve in methanol, ethanol, acetone and chloroform. However, the complex was dissolved in formamide. The correlation of the elemental analysis data and metal ion contents between the experimental data and theoretical calculation is shown in Table 1.

The polymeric complex was analyzed by FTIR to obtain the absorption peaks representing the functional group of the complex. This analysis could be used to make sure that the polymeric complex has been formed. The IR spectrum of the complex is shown in Fig. 2. Based on the previous report, the presence of oxalate as the bridging ligand in the polymeric complex is shown by the infra red absorption bands at wave number of 1627, 1330 and 800 cm^{-1} [8-9]. The high frequency region of the IR spectra of the complex exhibits a multiplet in the 2963 cm^{-1} region corresponding to the C-H stretching vibrations of the pyridine ligand as well as strong broad absorption centered at 3423 cm^{-1} indicating the occurrence of hydrogen bonds in the compound [10]. The strongest absorption in the IR spectra of complex is located in the region 1550-1432 cm^{-1}, which is the characteristic of the salts of C$_2$O$_4$$^{2-}$ anion [11]. This absorption has been assigned to vibrational modes representing combinations of C-O and C-C stretching modes. A strong absorption at 1720 cm^{-1} (non coordinated carbonyls of the oxalate ligand). Strong intensity peaks at 1611 cm^{-1} (coordinated C-O groups) is observed in the IR spectrum of the complex. This result is supported by the absorption bands at 500–400 cm^{-1} which corresponds to the Fe-N, Mn-O and Ni-O bonds [12]. The OH bond from the carboxylic functional group is shown by the absorption peak at 3423.1 cm^{-1}. The stretching vibration of C-H (pyridine) appears in the wavenumber of 2964 cm^{-1}. The oxalate group as the bridging ligand is shown by the peaks in wavenumber of 1612, 1363 and 822 cm^{-1}. The Fe-N bond and Ni-O bonds are indicated by the absorption bands at 469.7 and 410.9 cm^{-1}, respectively.

The refinement result which is performed by Le Bail method to the diffraction data from XRD of [Fe(picolinate)$_3$][MnNi(ox)$_3$].CH$_3$OH polymeric complex in the range of *2θ* between 10°–60° with monoclinic crystal structure and space group of *P2$_{1/n}$* dan Z = 4 shows the match between the data from X-ray diffraction (black dots) and calculation (red lines). It is indicated by the fact that the diffraction dots is affordable
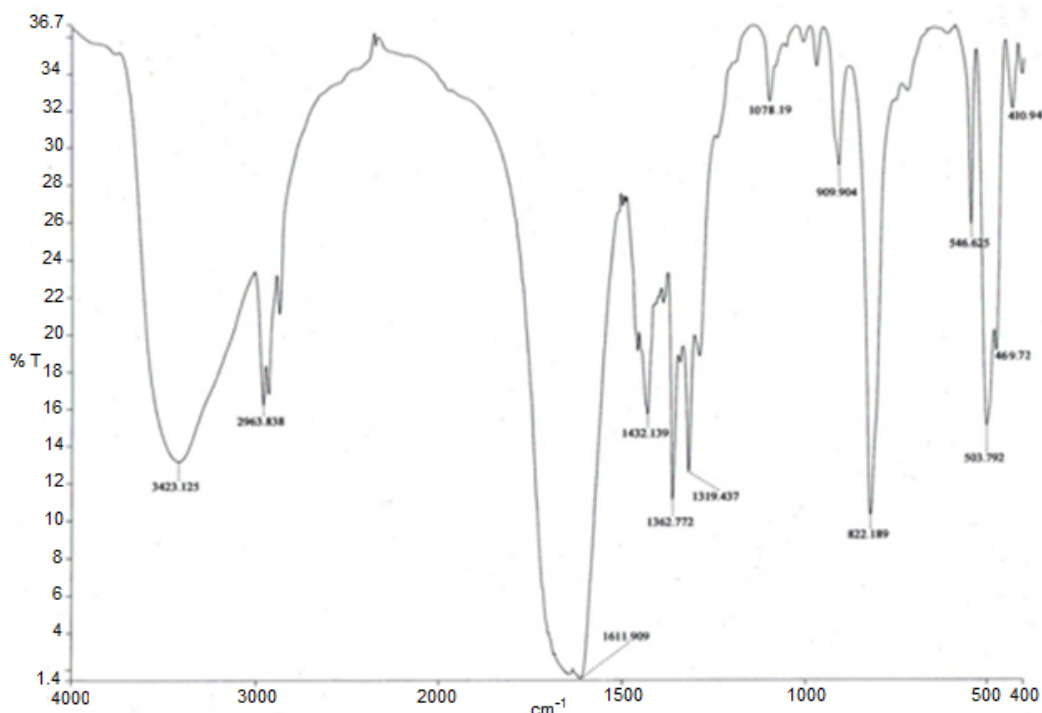
Fig 2. Spectrum of [Fe(picolinate)$_3$][MnNi(ox)$_3$].CH$_3$OH polymeric complex
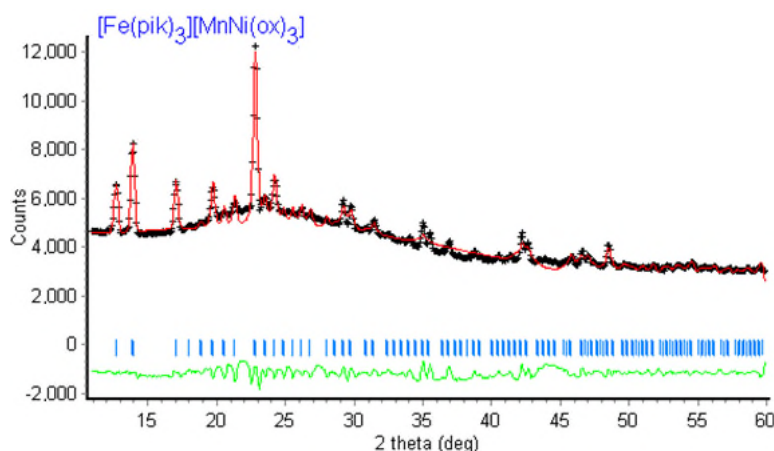
Fig 3. Le Bail plot of [Fe(picolinate)$_3$][MnNi(ox)$_3$].CH$_3$OH polymeric complex. The black dots (+) are the plot of experimental data form X ray diffraction, the red line is calculation pattern, the blue vertical lines are the expected Bragg positions and the green line is the differences between the calculation pattern and experimental data (the differences between black dots (+) and red line)

by the calculated line and the differences between the two are very small (the flat green line below the diffraction pattern). Refinement result obtained that *Rp = 4.67%, Rwp = 6.18%* and $\chi^2=1.43$ are in the acceptable range for the refinement process. From the refinement process, it is obtained that the *Rp, Rwp* dan *χ* are in the acceptable range for the refinement process. This indicates that there is compatibility between the synthesized polymeric complex with the reference complex. This refinement result is presented in Fig. 3.

The magnetic susceptibility profile of [Fe(picolinate)$_3$][MnNi(ox)$_3$].CH$_3$OH polymeric complex to the temperature measured at 5-300 K is presented in Fig. 4. In temperature of 300 K, the magnetic moment value is 8.1 Bohr Magneton which matches with the value for high spin. The magnetic value stays constant until the temperature of 140 K. Above this temperature, the magnetic moment value decreases up to 3.3 Bohr Magneton at 5 K. The three of paramagnetic transition metal ions existed in the complex exhibit spin value (S)
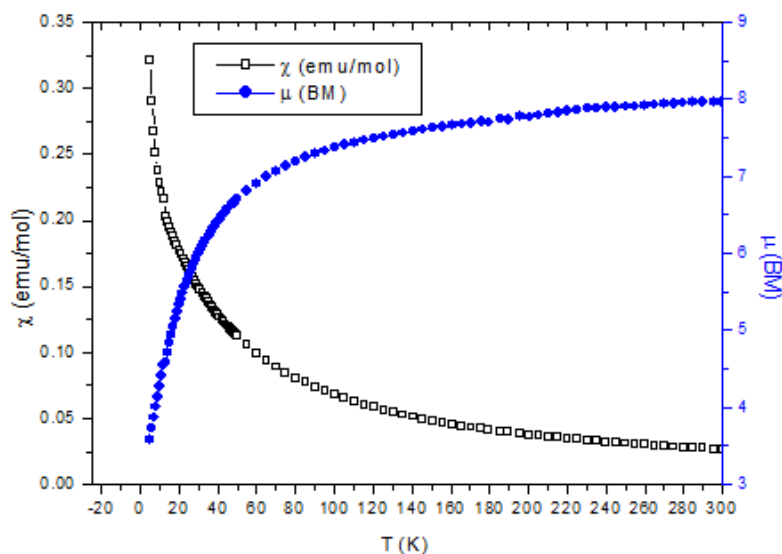
Fig 3. Plot of magnetic susceptibility and magnetic moment to the temperature of [Fe(picolinate)$_3$][MnNi(ox)$_3$].CH$_3$OH polymeric complex

of 2, 5/2 and 1, respectively. The magnetic moment of the complex is about 8.2 Bohr Magneton which is close to the expected value indicatin that the three metal ions can interact.

CONCLUSION

[Fe(picolinate)$_3$][MnNi(ox)$_3$].CH$_3$OH polymeric complex has been successfully synthesized. The molecular formula of the polymeric complex is obtained based on elemental analysis, metal ions contents analysis and FTIR spectra. The X-ray diffraction shows that the solid has crystalline structure. The complex crystallizes in monoclinic structure with the space group of $P2_{1/n}$. The [Fe(picolinate)$_3$]$^{2+}$ complex which is inserted to the [MnNi(ox)$_3$]$^{2-}$ oxalate polymeric network does not show the spin transition properties. The complex exhibits high spin properties.

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