Synthesis and Spectroscopic Characterization of Heterometallic Ni/Zn Containing 1, 10-Phenanthroline and Azide Ligands

การสังเคราะห์และการพิสูจน์เอกลักษณ์ทางสปกโตรสโกปิกของสารเชิงซ้อนโลหะต่างชนิด นิกเกิล/สังกะสี ที่ประกอบด้วยลิแกนด์ 1, 10-ฟีแนนโทรลีน และเอไซด์

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ABSTRACT

Heterometallic compound of nickel and zinc metals containing 1,10-phenanthroline and azide ligands has been synthesized by direct method of $Ni(OAc)_2 \cdot 4H_2O$, $Zn(OAc)_2 \cdot 2H_2O$, 1,10-phenanthroline and NaN_3 at room temperature. The compound has been characterized by infrared spectroscopy, electronic spectroscopy, thermogravimetric analysis, atomic absorption spectroscopy and elemental analysis. These results confirm a formula of $NiZnC_{26}H_{19}N_{13}O_2$.

บทคัดย่อ

การสังเคราะห์สารเชิงซ้อนที่ประกอบด้วยโลหะต่างชนิด โดยการทำปฏิกิริยาโดยตรงระหว่าง นิกเกิล และสังกะสี กับลิแกนด์1,10-ฟีแนนโทรลีน และเอไซด์ ที่อุณหภูมิห้อง ผลิตภัณฑ์ที่สังเคราะห์ได้เป็นสารเชิงซ้อนที่ประกอบด้วยโลหะที่ต่างกันสองชนิดได้แก่ นิกเกิล และสังกะสี ประกอบด้วยลิแกนด์ 1,10-ฟีแนนโทรลีน และเอไซด์ จากการพิสูจน์เอกลักษณ์ด้วยเทคนิค อินฟาเรดสเปกโตรสโกปี อิเล็กโทรนิกสเปกโตรสโกปี การวิเคราะห์เชิงความร้อน การวิเคราะห์หาปริมาณโลหะ และการวิเคราะห์เชิงธาตุ ผลการทดลองที่ได้สามารถทำนายสูตรโมเลกุลเป็น $NiZnC_{26}H_{19}N_{13}O_2$

Key Words: Heterometallic compound, Nickel, Zinc

คำสำคัญ: สารเชิงซ้อนของโลหะต่างชนิด นิกเกิล สังกะสี

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Introduction

Coordination compounds of pseudohalide ligand (N_3^-, NCO^- and SCN^-) are interesting materials which have shown the variety of topologies and structural diversity such as 1-dimension, 2-dimension and 3-dimension [Cortés et al., 1997; Rahaman *et al.,* 2005]. These compounds are widely used in magnetism [Villanueva *et al.,* 2001]. Among pseudohalide ligands, azide ligand (N_3^-) is a powerful tool in the construction of coordination compound. The importance of azide ligand is due to the characteristic of azido-bridges. The coordination mode of ligand in end-to-end mode results in antiferromagnetic whereas end-on mode gives to ferromagnetic behavior [Ribas *et al.,* 1999]. 1,10-Phenanthroline (phen) is an example of alpha-diimine chelating bidentate ligand. The rigidity and planarity of ligand efficiently provide intra and intermolecular π-π stacking interactions through its aromatic rings [Dubler *et al.,* 1984]. This interaction is potential to stabilize the coordination compound and the compounds can act as building blocks for the synthesis of metallo-dendrimers and supramolecular assemblies [Khavas, Amani and Safari, 2008; Amani, Safari, Khavasi and Mirzaeiet, 2007]. In the past decade, heterometallic of nickel and manganese metals containing 1,10-phenanthroline ligand has been synthesized. This compound shows three dimension networks through hydrogen bonds [Aggrawal, Kashap and Singh, 2009]. In this research, we have synthesized and characterized new heterometallic Ni/Zn mixed-ligand complex with azide and the *N,N*-chelating aromatic amine 1,10-phenanthroline.

Objectives of the study

In this work, we have synthesized and characterized new heterometallic Ni/Zn mixed-ligand complex with azide and the *N,N*-chelating aromatic amine 1,10-phenanthroline.

Methodology

General methods and materials

$Ni(OAc)_2 \cdot 4H_2O$ and NaN_3 were purchased from Sigma-Aldrich. $Zn(OAc)_2 \cdot 2H_2O$, 1,10-phenanthroline and organic solvents were purchased from CARLO ERBA. Elemental analysis of carbon, hydrogen and nitrogen was performed on a Perkin Elmer model 2400 elemental analyzer. IR spectrum was recorded as KBr dics in the region 4000-400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Solid–state (diffuse reflectance) electronic spectrum was measured as polycrystalline sample on a Perkin-Elmer Lambda 2s spectrometer, over the range 8000-18000 cm^{-1}. Thermogravimetric analysis was carried out on a Pyris Diamond TG-DTA, Perkin Elmer instrument with a heating rate of 10 ^{o}C/min in flowing nitrogen gas. Melting point was observed in capillary tube on Electrothermal 9100. Metal content was determined using an Atomic Absorption Spectrometer AA-6501 F, Shimadzu.

Preparation of compound

A methanol solution (5.0 mL) of 1,10-phenanthroline (0.11 g, 0.4970 mmol) was added into a methanol solution (5.0 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (0.14 g, 0.5433 mmol). The mixture was stirred for 30 min at room temperature followed by adding aqueous solution (5.0 mL) of NaN_3 (0.07 g, 1.0600 mmol). After stirring for 30 min, a methanol solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.22 g, 1.10 mmol) was added into the mixture solution and stirred for another 5 h. Green powder was precipitated and filtered off. Green powder was insoluble in organic solvents. Yield 78% (m.p. > 250 °C). IR (KBr disc, cm^{-1}): 3046 (w) 2027 (s), 1622(w), 1586(w), 1515 (w), 1424 (s), 726 (s).

Anal. Calc. for $NiZnC_{26}H_{19}N_{13}O_2$: C, 46.64; H, 2.86; N, 27.19%. Found: C, 46.03; H, 2.65; N, 27.58%. AAS; Zn: Ni =1:1.

Results

Synthesis and spectroscopic analysis

Heterometallic compound has been synthesized by direct method in the reaction of $Ni(OAc)_2 \cdot 4H_2O$, $Zn(OAc)_2 \cdot 2H_2O$, 1,10-phenanthroline and NaN_3. The green powder compound is insoluble in common organic solvents. The metal content was determined by AAS which is found in the molar ratio 1:1 of nickel and zinc metals. The infrared spectrum of the compound is shown in Figure 1. The broad peak about 3500 cm^{-1} is assigned to O-H stretching of water molecule which is found in the spectrum due to the moisture in the instrument. The weak peak at 3046 cm^{-1} is described to the C-H stretching vibration. The strong peak at 2027 cm^{-1} is assigned to the asymmetric stretching vibration of azide ligand. The N-N asymmetric stretch for terminal azides generally falls at 2030 cm^{-1} [Ribas *et al.,* 1999; Pettinari, 2001; Maji *et al.,* 2001]. The N-N asymmetric stretching vibration of bridging azide ligand could overlap in the main peak at 2027 cm^{-1}. The weak peak at 1622 is described to the C=N stretching vibration. The weak peak at 1568 cm^{-1} is described to the asymmetric stretching vibration of acetate [Wang, Wang, Wang and Gao, 2009]. The strong peak at 726 cm^{-1} is characteristic of the aromatic C-H out-of-plane bending vibration.

Electronic spectrum is represented in Figure 2. The two absorption bands at 586 nm and 951 nm are described to $^3A_{2g}$ to $^3T_{1g}(F)$ and $^3A_{2g}$ to $^3T_{2g}(F)$ transitions, respectively. The transition of $^3A_{2g}$ to $^3T_{1g}(P)$ is obscured by charge-transfer band of 1,10-phenanthroline ligand. This results is indicated to the

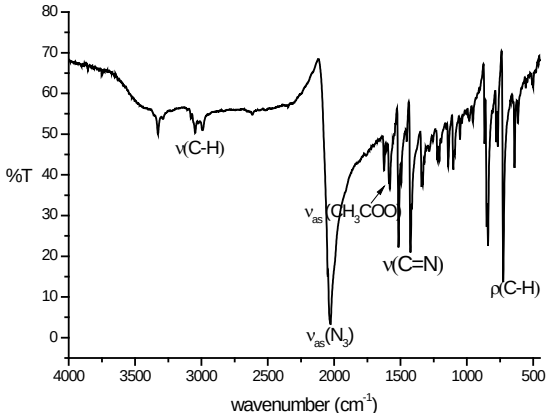
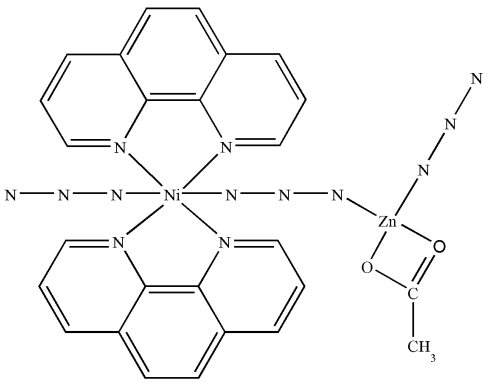


Figure 1 Infrared spectrum of $NiZnC_{26}H_{19}N_{13}O_2$

octahedral geometry around nickel(II) center [Lemus-Santana et al., 2011]. The elemental analysis suggests the product as a formula of $NiZnC_{26}H_{19}N_{13}O_2$. The expected compound is shown in Scheme 1.



Scheme 1 The expected molecular structure of $NiZnC_{26}H_{19}N_{13}O$

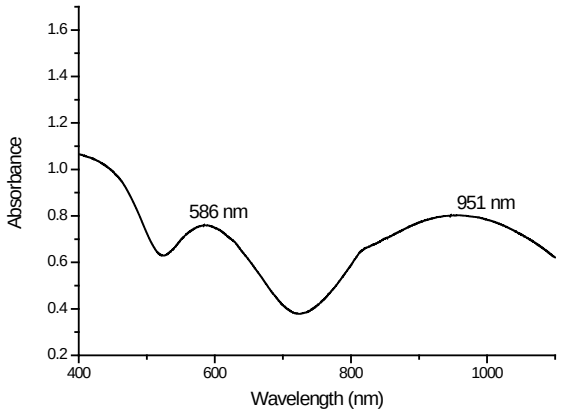


Figure 2 Electronic spectrum of $NiZnC_{26}H_{19}N_{13}O_2$

Thermogravimetric analysis

Thermogravimetric analysis of the compound is represented in Figure 3. The observed weight loss of 62.77 % (calculated = 62.25 %) takes place in the temperature ranges 268-312 °C. This result is described to the loss of two 1,10-phenanthroline and one acetate molecules. As a results, 1,10-phenanthroline and acetate molecules may coordinate to the metal centers with close energy resulting in the weight loss takes place at the same temperature.

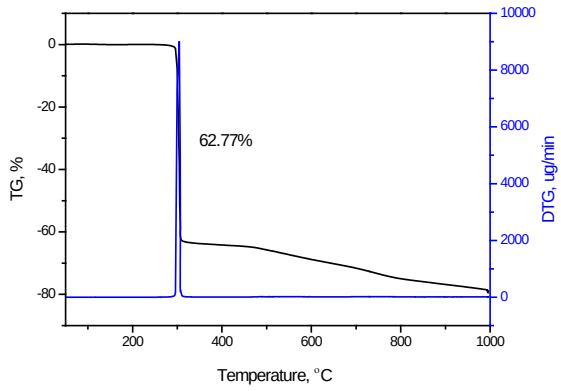


Figure 3 Thermogravimetric analysis of $NiZnC_{26}H_{19}N_{13}O_2$

Discussion and Conclusions

New heterometallic Ni/Zn compound can be synthesized by direct method. The compound is composed of nickel and zinc metals which is confirmed by AAS. The result from infrared spectroscopy, electronic spectroscopy, thermogravim etric analysis, atomic absorption spectroscopy and elemental analysis are confirmed the product as a formula of $NiZnC_{26}H_{19}N_{13}O_2$.

Acknowledgements

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