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Synthesis and Characterization of Coordination Compounds of Silver(I) Nitrite with Ligands Ethylenethiourea and *N,N'*-diethylthiourea

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ABSTRACT

Coordination compound of silver (I) nitrate and ethylenethiourea (*etu)* in 1 : 4 stochiometry have been reported [1]. Coordination compound A and B being silver (I) nitrite with *etu* and silver(I) nitrite with *N,N'*-diethylthiourea (*detu)* respectively, have never been done. The purpose of this study is to synthesize and characterize coordination compounds A and B. Synthesis of coordination compounds A with 1 : 4 and B with 1 : 2 ratio stoichiometry respectively. Both of synthesis was conducted in acetonitrile directly. The obtained compound characterized by using melting point, electrical conductivity measurement, Scanning Electron Microscopy Energy-dispersive X-ray spectroscopy *(SEM-EDX)*, qualitative nitrite test, free energy calculation and structures prediction using *Spartan'14 v1.1.0*. Coordination compounds of A and B have been investigated that it had colorless needle and prism crystals, having the melting point of 189°C and 103-105°C, free energy of -289.2567 and -1182.8101 kJ/mol respectively. Electrical conductivity measurement and qualitative nitrite test showed that the obtained compound for A is ionic and for B is molecular. *EDX* analysis gave empirical formula prediction for two coordination compounds, where A is $C_{12}H_{24}AgN_9O_2S_4$ and for B is $C_{15}H_{36}AgN_7O_2S_3$.

Key words: Synthesis, silver (I) nitrite, *etu*, *detu*

INTRODUCTION

The valence-shell electron configurations for closed shell metal ions give +1 and +2 oxidation state. Closed shell metal ion can be conducted with thiourea (*tu*) and it's derivatives ligands [1-6]. Ligands coordinate through sulfur, nitrogen, or both of these atoms. One of this ligand is ethylenethiourea (*etu*). Coordination compound of $AgNO_3$ and *etu* has been synthesized in 1 : 4 and reported as $[Ag(etu)_4](NO_3)\cdot H_2O$ [7]. *Etu* coordinated through sulfur atom as dimer coordination compound and forming distorted tetrahedral geometry about silver atom [8].

One of derivatives of *etu* is *N,N'*-diethylthiourea (*detu*). Coordination compound of silver(I) bromide and *detu* has been reported as $[Ag(detu)_3Br]$ with distorted tetrahedral geometry [9]. Silver(I) nitrite structure resembles silver(I) nitrate. Based on resonance structure, nitrate ion coordinates through oxygen atom only, while nitrite ion coordinates through nitrogen and oxygen atoms [10].

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The existence of coordination compounds A being silver(I) nitrite with *etu* and B being silver(I) nitrite with (*detu)* has never been reported.

EXPERIMENT

Chemicals and instrumentation

Chemicals used for research which purchased from Merck and pro analysis as purity grade were sodium nitrite, silver(I) nitrate, *detu*, *etu*, methanol, potassium hydroxide (KOH) pellets, sulfanilic acid, citric acid α-naphthylamine, acetonitrile and aquadest.

Instrumentation applied for analysis were analytical scale (Sartorius Element ELT103), melting point apparatus (Fischer-John), conductometer (Omega Engineering, INC), computational chemistry program (Spartan'14 v1.1.0), and Scanning Electron Microscopy Energy-dispersive X-ray spectroscopy (SEM-EDX FEI type INSPECT-50).

Procedure reaction

Experiments are divided to 3 steps: synthesis silver(I) nitrite, synthesis coordination compounds A and B, and characterization of coordination compounds.

Synthesis of silver nitrite

Synthesis of silver(I) nitrite was conducted by dissolving sodium nitrite (0.35 g; 5.00 mmol) and silver nitrate (0.85 g; 5.00 mmol) respectively in water (4.0 mL). Both were mixed in dark room. The formed precipitate was washed with methanol, filtered with a Buchner filter, and then dried in a desiccator containing KOH pellets to constant weight. The dried precipitate was characterized by melting point measurement and qualitative nitrite ion test [11].

Synthesis of coordination compound A

Coordination compound A was synthesized by direct reaction method. Synthesis was done by dissolving *etu* (0.041 g; 0.40 mmol) in acetonitrile (8.00 ml) then dripped into silver nitrite solids (0.015 g; 0.10 mmol). Furthermore, the solution was stirred in ultrasonic water bath 60 ^{o}C for 2 hours. The resulting solution was filtrated, the filtrate was evaporated gradually and decrease in temperature to obtain crystals.

Synthesis of coordination compound B

Synthesis of coordination compound B was conducted in same procedure with compound A. Silver nitrite (0.015 g; 0.10 mmol) and *detu* (0.025 g; 0.20 mmol) were dissolved respectively in acetonitrile (4.0 mL). Both were reacted and stirred in ultrasonic water bath at 60 ^{o}C for 2 hours. The solution was filtrated, and then the filtrate was evaporated at a gradual decrease in temperature to obtain crystals.

Characterization of coordination compounds A and B

Characterization of synthesized crystals was done by using melting point measurement, electrical conductivity, qualitative nitrite ion test, and SEM-EDX. Possible structures were obtained based on the characterization, optimized and calculated free energy using Spartan'14 v1.1.0.

RESULT AND DISCUSSION

Based on Merck index melting points of silver nitrite, *detu*, and *etu* are 139-140^{0}C, 76-78 ^{o}C and 203-204 ^{o}C respectively. Melting point of coordination compounds of A is 89 ^{o}C and B is 103-105 ^{o}C. These indicated that both compounds are novel, pure, and stable.

Electrical conductivity and qualitative nitrite ion tests are used to determine whether the compound formed is an ionic or a molecular one. All the summarized results were required in **Table 1**.

Table 1. Calculation of Concentration for Electrical Conductivity Test

No	Solution	Molar mass (g/mole)	Mass (g)	Solvent volume (mL)	Moles (mmol)	Concentration (M)
I	$AgNO_2$	153.87	0.27×10^{-2}	10	1.78×10^{-2}	1.78×10^{-3}
	$[Ag(etu)_4](NO_2)$	561.87	0.98×10^{-2}	10	1.78×10^{-2}	1.78×10^{-3}
II	$AgNO_2$	153.87	5.58×10^{-4}	10	3.63×10^{-3}	3.63×10^{-4}
	$[(NO_2)Ag(detu)_3]$	550.618	2.0×10^{-3}	10	3.63×10^{-3}	3.63×10^{-4}

Results of electrical conductivity of solvent, silver nitrite solution, and solution of coordination compounds of A and B are given in **Table 2**. Results of electrical conductivity showed that coordination compound of A is an ionic and B is a molecular one.

Table 2. Electrical Conductivity Results

No	Solutions	Concentration (M)	Electrical conductivity value (μS/cm)
I	Acetonitrile	-	2.00
	$AgNO_2$	1.78×10^{-3}	97.6
	Coordination compound of A	1.78×10^{-3}	40.0
II	Acetonitrile	-	0.62
	$AgNO_2$	3.63×10^{-4}	125.6
	Coordination compound of B	3.63×10^{-4}	6.12

Based on qualitative nitrite ion test, it could be investigated that coordination compounds A is classified as ionic whereas B as molecular, respectively. This is evidenced by the *Griess Illosvay* test and produced a red solution for coordination compound A, and colourless solution for compound B. The resulting coordination compounds A and B were found colorless needle and prism crystals, as shown in Figure 1(a) and (b).

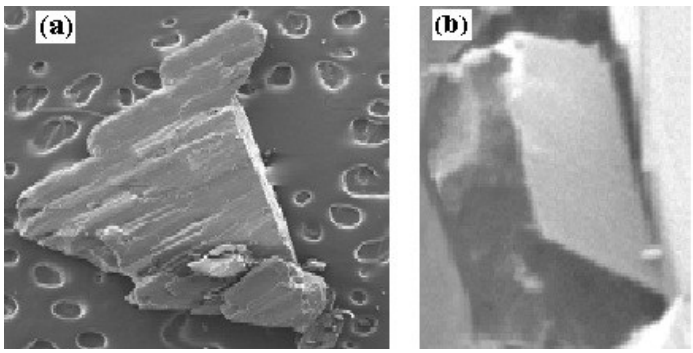

Figure 1. SEM results of (a) Coordination Compound of A (b) Coordination Compound of B

EDX analysis was used to determine empirical formula of the compounds. Based on the empirical formula, electrical conductivity, and qualitative nitrite ion tests, chemical formula of the compounds may be determined. This chemical formula was used to predict possible structures of the compounds. EDX spectra in Figure 2(a) and (b) show the atoms that arrange the crystals are Ag, S, O, N, and C.

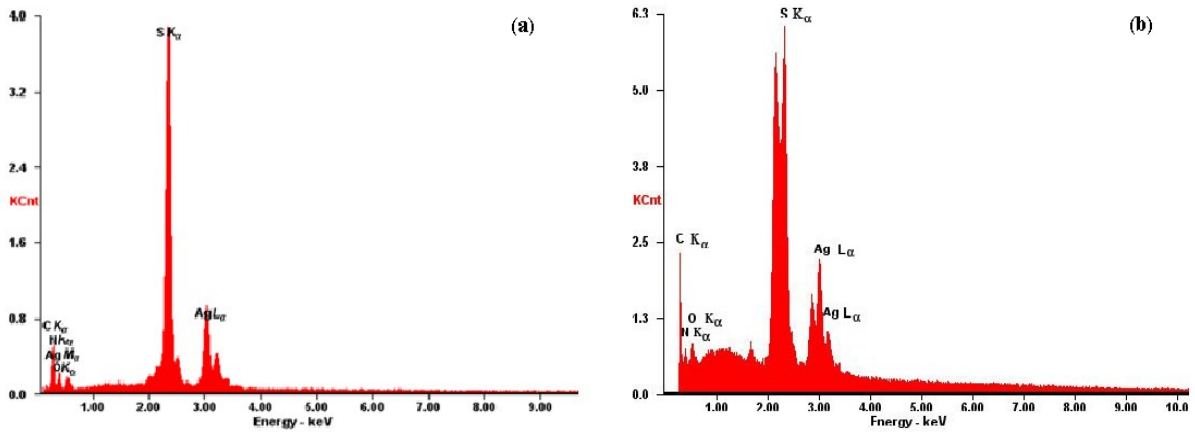

Figure 2. (a) EDX Spectrum of A; (b) EDX Spectrum of B

Predicted structure of coordination compounds can be given by comparing the percentage of the atoms arrange coordination compounds of *EDX* analysis results that are expressed as a percentage of mass (Wt%) and the percentage of atoms (At%) which can be showed in **Table 3**. Empirical formula for A is $C_{12}H_{24}AgN_9O_2S_4$ and for B is $C_{15}H_{36}AgN_7O_2S_3$.

Table 3. Comparison of Weight and Atomic Percentage of EDX Analytical Results with Teoritical Quantification of Coordination Compounds of A and B

Elements of A	*Wt%*		*At%*		Elements of B	*Wt%*		*At%*	
	EDX	Theoretical	EDX	Theoretical		EDX	Theoretical	EDX	Theoretical
C	33.69	25.64	53.67	42.86	C	34.71	32.71	52.65	53.57
N	15.52	22.40	21.21	32.14	N	20.18	17.81	25.84	32.14
O	05.50	05.68	06.58	07.14	O	7.23	05.81	07.98	07.14
S	25.06	22.78	14.95	14.29	S	17.82	17.47	10.13	10.71
Ag	20.24	19.14	03.59	03.57	Ag	20.07	19.59	3.39	3.57

Based on characterization results, the possible chemical formula of compound A is $[Ag(etu)_4](NO_2)$. Cation of that compound is $[Ag(etu)_4]^+$ with distorted tetrahedral and square planar possible structures. Free energy calculation by *Spartan'14 v1.1.0*, showed that distorted tetrahedral has -289,2567 kJ/mol and square planar structure has -563,6349 kJ/mol, respectively. Free energy of the distorted tetrahedral possible structure closed to the $[Ag(etu)_4](NO_3)\cdot H_2O$ (-222,4780 kJ/mol) [8]. Silver atom with four coordination number with square planar structure has never been reported despite having a negative free energy. Therefore, $[Ag(etu)_4](NO_2)$ coordination compound has a complex cation with distorted

tetrahedral structure. The structure prediction of coordination compound of A has been shown at Figure 3(a).

Coordination compound formed of B may be a nitro compound $[Ag(NO_2)(detu)_3]$, or nitrito compounds $[Ag(ONO)(detu)_3]$ and $[Ag(O_2N)(detu)_3]$. They have free energy of -874.3394 kJ/mol, -922.1857 kJ/mol and -1182.8101 kJ/mol respectively. Possible structures are nitrito compounds because they have lower free energy than the nitro one. Free energy of $[Ag(O_2N)(detu)_3]$ is about 260 kJ/mol lower than that of $[Ag(ONO)(detu)_3]$. Therefore $[Ag(O_2N)(detu)_3]$ is resemble with $[(NO_2)Ag(SbPh_3)_3]$ structure [10]. Structure prediction of coordination compound of B has been shown at Figure 3(b).

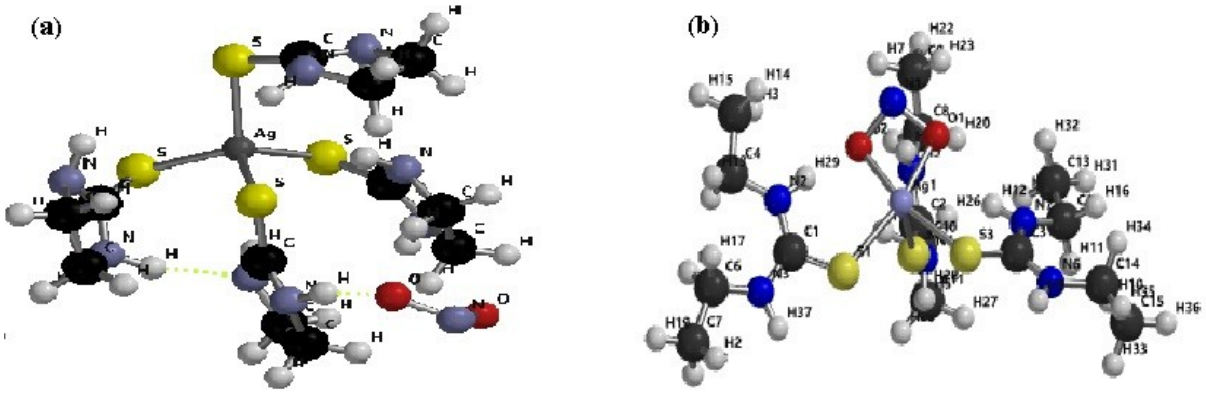

Figure 3. (a) Structure Prediction of A as $[Ag(etu)_4](NO_2)$
(b) Structure Prediction of B as $[(NO_2)Ag(detu)_3]$

The result of synthesis has been shown that sulfur donor atom coordinated to silver according to HSAB (Hard and Soft Acids Bases). Sulfur donor atom of *etu* and *detu* as soft base allows coordinating with silver atom which acts as soft acid [12].

CONCLUSION

Coordination compounds of A and B with 1 : 4 and 1 : 2 stoichiometry ratio in acetonitrile obtained as ionic and a molecular one respectively. Chemical formula of coordination compounds A is $[Ag(etu)_4](NO_2)$ and that of B is $[(NO_2)Ag(detu)_3]$. Both of free energies are -289.2567 kJ/mol and -1182.8101 kJ/mol respectively.

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