

Synthesis and Characterization of Complex Compounds from Cadmium(II) Chloride and Cobalt(II) Chloride with *N,N'*-Diethylthiourea

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ABSTRACT

The synthesis of ionic complexes of cadmium(II) chloride and cobalt(II) chloride with *N,N'*-diethylthiourea (*detu*) ligands has not been previously reported. Therefore, in this research, the synthesis was carried out to study the structure and characterization of the two ionic complex compounds. The cadmium(II)-*detu* ionic complex was synthesized using the direct reaction method with a ratio between Cd(II) salt and *detu* ligand of 1:2. Meanwhile, the cobalt(II)-*detu* ionic complex was synthesized with a ratio between Co(II) salt and *detu* ligand of 2:4. The cadmium(II)-*detu* and cobalt(II)-*detu* ionic complexes have melting points of 105-108 °C and 122-125 °C, respectively. The electrical conductivity of the cadmium(II)-*detu* and cobalt(II)-*detu* complexes showed that the complexes were ionic. The FTIR analysis showed the shifting of the C=S functional group's band to the smaller wavenumber, which indicates the coordinating *detu* ligand to the cadmium(II) and cobalt(II) through the S atom. The indirect evidence from ¹H-NMR showed that CH₃ and CH₂ only slightly shifted between the free *detu* ligand and the Cd-*detu* and Co-*detu* complexes.

Keywords: Cadmium(II), Cobalt(II), *N,N'*-diethylthiourea, ionic complex, *detu*.

INTRODUCTION

Cadmium(II) ion complex with *N,N'*-diethylthiourea (*detu*) ligand which is a derivative of thiourea is very interesting to be studied, especially its properties, crystal structure, coordination pattern and biological activity. Cadmium(II) ion is an ion of group 12 metals and a soft metal that is rich in electrons [1]. Cadmium(II) ion complexes with polydentate ligands that have antibacterial activity include [Cd(cepha)Cl]_nH₂O [2], [Cd(A1-5)₂] (where 4-((4-bromo-phenylimino)-methyl)-benzene-1,2,3-triol (A1), 4-((3,5-di-*tert*-butyl-4-hydroxy-phenylimino)-methyl)-benzene-1,2,3-triol (A2), 3-(*p*-tolylimino-methyl)-benzene-1,2-diol (A3), 4-((4-bromo-phenylimino)-methyl)-benzene-1,2-diol (A4), 4-((3,5-di-*tert*-butyl-4-hydroxy-phenylimino)-methyl)-benzene-1,3-diol (A5)) [3], [CdLX₂] (X = Cl⁻, Br⁻, I⁻, and L = *bis*(3(4-dimethylaminophenyl)-allilidine)-1,2-diaminoethane) [4], [CdL₂(H₂O)₂] (L = 5-benzoyl--hydroxy-2-methyl-6-phenyl-2H-pyridazine-3-one) [5]. Cadmium(II) complex compounds can prevent RNA polymerase activity and are easily combined with biomolecules such as proteins [4]. On the other hand, cobalt(II) ion is an ion of metal group 9 period 4 which has been widely used as an antibacterial agent. Complexes of cobalt(II) ion which are applied

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as antibacterial include $[\text{CoL}_2\text{Cl}_2]$ ($\text{L} = 2\text{-(thiazol-2-ylimino)thiazolidine-4-one}$) [6], $[\text{Co}(\text{Im})_6](\text{NO}_3)_2$ ($\text{Im} = \text{imidazole}$) [7], $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ and $[\text{Co}(\text{phen})_2(\text{Cyt})\text{H}_2\text{O}]\text{Cl}$ [8].

Cadmium(II) and cobalt(II) ions which have antibacterial activity will be complexed with *N,N'*-diethylthiourea (*detu*) ligand. The *detu* ligand is an ambidentate ligand that has two types of donor atoms, namely S and N [9]. The formation of coordination bonds between cadmium(II) and *detu* ligands involves a Lewis acid-base reaction, the cadmium(II) acts as a Lewis acid that will accept electrons, while the *detu* ligand acts as a Lewis base that will donate electrons. Based on the hard-soft acid-base theory, the cadmium(II) ion which is a soft acid will form stable coordination with the *detu* ligand through the S atom which is a soft base [10],[11]. Several complex compounds of *detu* ligands such as $[\text{CuCl}_2(\text{detu})_2]$, $[\text{CuAc}_2(\text{detu})_2]$, $[\text{CoCl}_2(\text{detu})_2]$, $[\text{ZnCl}_2(\text{detu})_2]$ have been shown to have antibacterial activity [12]. The metal complexes with thiourea-derived ligands exhibit antibacterial activity by inhibiting enzymes contained in bacterial cells [13]. These facts indicate that the ionic complex of cadmium(II)-*detu*, which is our target in this study, has the potential to be an antibacterial agent candidate.

An understanding of the coordination formed in the cadmium(II)-*detu* ionic complex may be based on the cadmium(II) complex with other thiourea-derived ligands that have been previously studied. Thiourea-derived ligands (*tu*) include *N*-methylthiourea (*metu*), *N,N'*-dimethylthiourea (*dmtu*), *N,N,N',N'*-tetramethylthiourea and *N,N'*-diethylthiourea (*detu*), and other molecules with more H atoms of the amine group replaced by another alkyl group (Fig. 1). The molecular complex compounds of cadmium(II) ions with *tu* ligands and their derivatives that have been successfully synthesized include $[\text{Cd}(\text{detu})_2\text{Cl}_2]$, $[\text{Cd}(\text{detu})_2\text{Br}_2]$ [14], $[\text{Cd}(\text{detu})_2\text{I}_2]$ [15], $[\text{Cd}(\text{tu})(\text{SO}_4)(\text{H}_2\text{O})_2]_n$, $[\text{Cd}(\text{dmtu})(\text{SO}_4)(\text{H}_2\text{O})_2]$ [16], $[\text{Cd}(\text{detu})_2(\text{OOCCH}_3)_2] \cdot \text{H}_2\text{O}$ [17], $[\text{Cd}(\text{metu})_2(\text{NCS})_2]$, $[\text{Cd}(\text{metu})_2(\text{CN})_2]$ [18], and $[\text{Cd}(\text{detu})_4\text{SO}_4]$ [19]. Meanwhile, the structure of the ionic complexes of thiourea-derived ligands, especially *detu*, can be determined by referring to the previous studies, including $[\text{Zn}(\text{detu})_4](\text{CN})_2$ [9], $[\text{Cd}(\text{diaz})_4]\text{SO}_4$ [20] and $[\text{Co}(\text{detu})_4](\text{ClO}_4)_2$ [21]. Spectroscopic studies from previous studies have shown that the *detu* coordinates with the cadmium(II) ion through the S atom of the ligand, with the geometry around the central atom being tetrahedral, square-base pyramid, or octahedral [16]. On the other hand, cobalt(II) ions with thiourea-derived ligands generally tend to form a tetrahedral geometry, although some have been reported to have octahedral geometries [22].

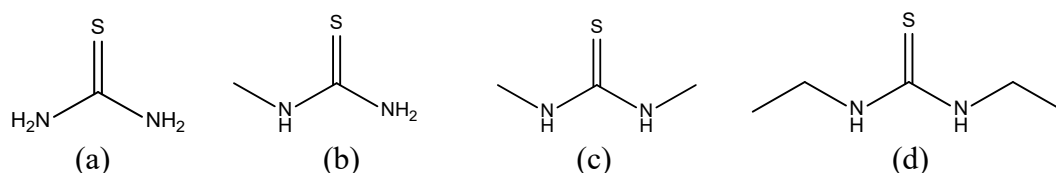


Figure 1. Structure of (a) Thiourea (*tu*), (b) *N*-Methylthiourea (*metu*), (c) *N,N'*-Dimethylthiourea (*dmtu*), (d) *N,N'*-Diethylthiourea (*detu*)

In addition to having antibacterial activity, thiourea-derived ligand complexes have many applications, including being a corrosion inhibitor, as a precursor in polymerization reactions, as plant protection agents, and as pesticides. Moreover, thiourea ligands and their derivatives are potentially applied in the pharmaceutical industry because of their biological activities, including antiparasitic, anticancer, antioxidant, antibacterial, and antifungal properties [23],[24],[25],[26],[27]. The reported antibacterial activity of metal complexes with *detu*

ligands is a molecular complex, while the antibacterial activity test of the ionic complexes of *detu* ligands has not been carried out. Whereas the ionic complex of *detu* ligand binds to many *detu* molecules, thus allowing the complex to have better antibacterial activity.

Based on our literature study, ionic complexes with the central atom of cadmium(II) and cobalt(II) with *detu* ligands have not been reported. Therefore, we reported the synthesis and characterization of cadmium(II)-*detu* and cobalt(II)-*detu* ionic complexes. Synthesis of the cadmium(II)-*detu* ionic complex was carried out by direct reaction between a solution of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and a solution of *detu* in methanol. Meanwhile, the synthesis of cobalt(II)-*detu* ionic complex was carried out by reacting CoCl_2 solution with *detu* solution in acetone solvent. The formed crystals were characterized by melting point test, electrical conductivity test (DHL), FTIR, and $^1\text{H-NMR}$.

EXPERIMENT

Chemicals and instrumentation

The precursors used in this study were $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, *detu*, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, methanol, and acetone which was purchased from Merck. All materials are used without going through a purification treatment first.

Instrumentation applied for analysis in this study were melting point test (Fisher Scientific), electrical conductivity test (CyberScan CON 400 (EC)), FTIR (Fourier Transform Infrared (FTIR) Merk Shimadzu (IR Prestige 21)), and $^1\text{H-NMR}$ (Nanalysis NMReady-60e). The FTIR spectrum was measured at wavenumbers $4000\text{-}500\text{ cm}^{-1}$, while the $^1\text{H-NMR}$ spectrum was recorded with an electromagnetic radiation frequency of 60 MHz using deuteriochloroform (CDCl_3). Qualitative analysis of chloride ion was identified in aqueous solution Cd-*detu* and Co-*detu* using silver nitrate 0,1 M as an identifier.

Synthesis Procedure Cd-*detu* dan Co-*detu* complex

The Cd-*detu* complex was synthesized by dissolving the *detu* ligand (26.45 mg; 2 mmol) in 25 mL of methanol, solid cadmium chloride monohydrate (20.13 mg; 1 mmol) was added to the *detu* solution at room temperature. Meanwhile, to synthesize the Co-*detu* complex, it was done by first dissolving the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salt (47.58 mg; 2 mmol) into 5 mL of acetone and then adding it to the *detu* solution (52.90 mg; 4 mmol in 5 mL of acetone) dropwise, and added with 5 mL of acetone at room temperature. Then each clear solution was stirred for 4 hours at $60\text{ }^\circ\text{C}$ under reflux, after which the solution was cooled to room temperature. The resulting solution was covered with aluminum foil and slowly evaporated in the refrigerator. Colourless crystals of Cd-*detu* (24.13 mg) and blue crystals of Co-*detu* (60.04 mg) were formed after several days, washed with methanol, and dried with filter paper. The formed crystals were carried out for further characterization.

RESULT AND DISCUSSION

The direct synthesis method of $[\text{Cd}(\text{detu})_4(\text{SO}_4)]$ [19] was modified to obtain Cd-*detu* complex using cadmium chloride salt as cadmium source and heating under reflux. The Cd-*detu* crystal was obtained at a good yield of up to 51.8% with a melting point of $105\text{-}108\text{ }^\circ\text{C}$ (Table 1). Co-*detu* crystal at 59.8% yield was obtained from acetone with a narrow melting point range as shown in **Table 1**. The melting points of the as-synthesized complexes show different values from the reactants used in the synthesis, which is an early indication that the crystals formed are different compounds from the reactants. Qualitative chloride ion test standard procedure using silver nitrate solution giving a white precipitate of silver chloride.

Solution of the Cd-*detu* gave a positive result either the Co-*detu* solution. It means that the chloride ion acts as a counter anion in the obtained crystals.

Table 1. Melting Points of Reactants and the As-synthesized Complex Compounds

Compound	Melting points (°C)	
	Merck	Experiment
CdCl ₂ .H ₂ O	568	>300
CoCl ₂ .6H ₂ O	56	50-54
<i>detu</i>	76	68-71
Cd- <i>detu</i>	-	105-108
Co- <i>detu</i>	-	122-125

*The melting point instrument can measure the maximum at 360 °C

Measurement of electrical conductivity or electrical conductivity aims to determine whether the complex formed is molecular or ionic. The measurement of the electrical conductivity of the precursor and the synthesized complex was carried out at the same concentration. The electrical conductivity data of the reactants and the synthesized Cd-*detu* and Co-*detu* complexes are presented in **Table 2**. The electrical conductivity of the very high synthesized Cd-*detu* complex compounds has a big difference with the conductivity values of *detu* and methanol, as well as the conductivity value of the Co-*detu* complex which is closer to the conductivity value of the CoCl₂ salt solution. Qualitative chloride and conductivity results suggested that the Cd-*detu* and Co-*detu* complexes are ionic. These results are in line with [Zn(*detu*)₄](CN)₂ [9] which is an ionic complex, where the complex has a high electrical conductivity value.

Table 2. Electrical Conductivity Test Results

Solution	Concentration (mg/mL)	Electrical Conductivity (μS)
CdCl ₂	1.00	251.00
<i>detu</i>	1.00	6.38
Methanol	-	0.77
Cd- <i>detu</i>	1,00	142.80
Acetone	-	6.24
CoCl ₂	0.10	44.1
Co- <i>detu</i>	0.10	32.6

The results of the IR test for the *detu* ligand, the as-synthesized Cd-*detu*, and Co-*detu* complexes are shown in **Figure 2** and tabulated in **Table 3**. The FTIR results for the cadmium complex with *detu* ligands have been reported previously [15],[19]. Our data showed a shift in the bands of ν(C=S), ν(N-H) secondary, and ν(C-N). The shift of the ν(C=S) band which is very prominent in the synthesized Cd-*detu* and Co-*detu* ionic complexes and other complexes that have been reported by previous researchers occurs to a smaller wave number. This is due to a decrease in the character of the C=S double bond because of the coordination of the S atom to the central Cd atom [11]. The shift of the secondary ν(N-H) band and ν(C-N) bands occurs at a larger wave number due to the changes in the molecular structure between *detu* before and after forming a complex. It can be seen that the secondary ν(N-H) band on the *detu* ligand is

wider, which is due to the presence of intramolecular hydrogen bonds [15]. This interaction was lost when it formed a complex, as evidenced by the formation of a sharper secondary $\nu(\text{N-H})$ band. While the band formed at wave number 2879-3028 cm^{-1} shows $\nu(\text{C-H})$ of $-\text{CH}_3$ and $-\text{CH}_2-$.

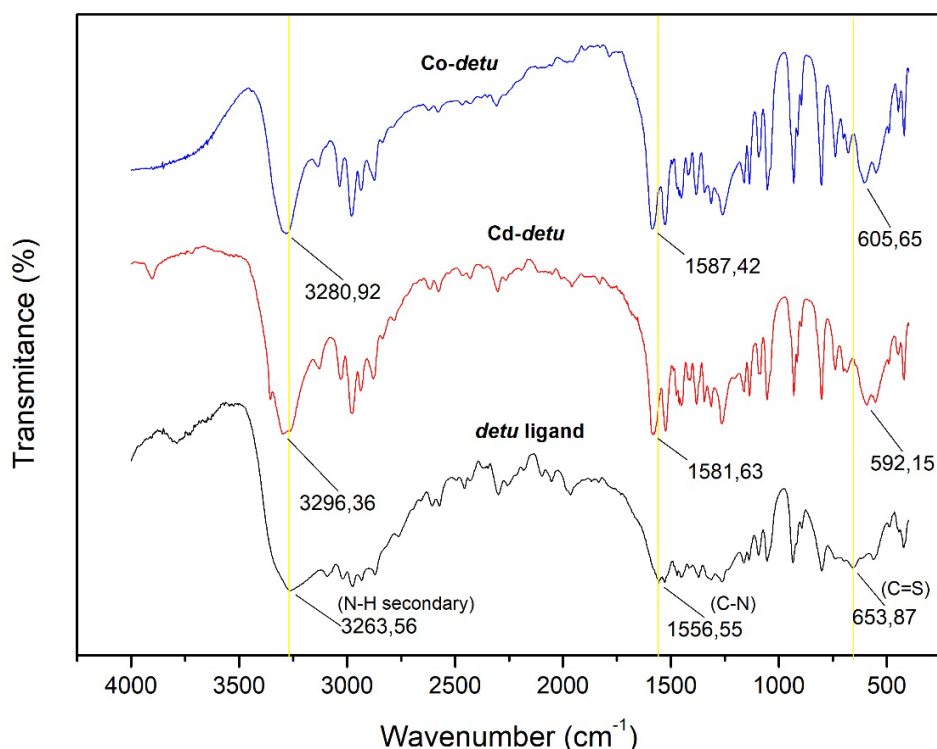


Figure 2. FTIR spectra of *detu* ligand, the as-synthesized *Cd-detu*, and *Co-detu*

Table 3. FTIR Frequency Data

Bonding	IR Frequency (cm^{-1})				
	<i>detu</i>	<i>Cd-detu</i> complex	<i>Co-detu</i> complex	$[\text{Cd}(\text{detu})_2\text{Cl}_2]$, [14]	$[\text{Cd}(\text{detu})_4\text{SO}_4]$ [19]
$\nu(\text{C}=\text{S})$	653	592	605	647	616
$\nu(\text{N-H})$ secondary	3263	3296	3280	3273	3218
$\nu(\text{C-N})$	1556	1581	1587	1578	-

The $^1\text{H-NMR}$ spectra of CH_3 and CH_2 of free *detu* ligand, *Cd-detu*, and *Co-detu* complexes are presented in **Figure 3** and the chemical shift of proton on CH_3 and CH_2 was tabulated in **Table 4**. The shift occurs due to the indirect effect of the formation of a coordination bond between the ligand donor atom and the central atom so that the electrons are attracted towards the central atom. However, the NMR data of the *detu* ligand and *Co-detu* complex only showed a shift in the NMR value of CH_2 , this was due to the distance of CH_3 which was quite far from the central atom so that it was not affected by the bond formed between the donor atom of the ligand and the central atom of Co(II) .

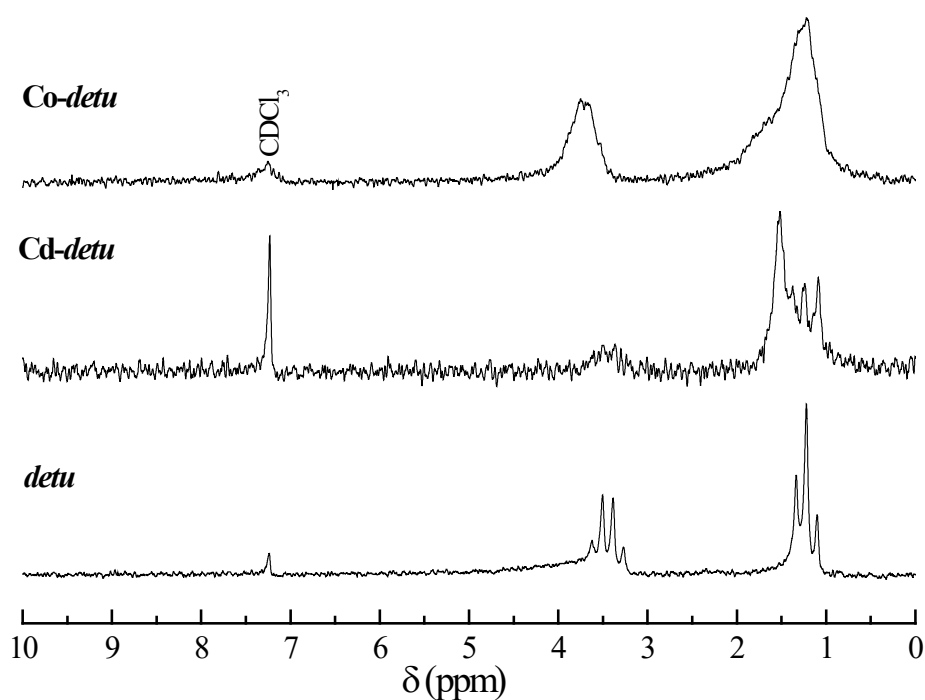


Figure 3. $^1\text{H-NMR}$ of *detu*, the as-synthesized *Cd-detu*, and *Co-detu*

Table 4. $^1\text{H-NMR}$ Chemical Shift Data

Species	NMR Shift (ppm)	
	$\delta(\text{CH}_3)$	$\delta(\text{CH}_2)$
<i>detu</i> Ligand	1.22	3.35
<i>Cd-detu</i> complex	1.24	3.45
<i>Co-detu</i> complex	1.25	3.67

The characterization results show that the two as-synthesized complexes indicated the formation of ionic complexes. The central atom will coordinate with the *detu* ligand through the S atom and no hydrogen bond interactions are detected. Regarding the reported ionic complexes with thiourea-derived ligands such as $[\text{Zn}(\text{detu})_4](\text{CN})_2$ [9], $[\text{Cd}(\text{diaz})_4]\text{SO}_4$ [20] and $[\text{Co}(\text{detu})_4](\text{ClO}_4)_2$ [21], the possible structure prediction of both complex are shown (Figure 3).

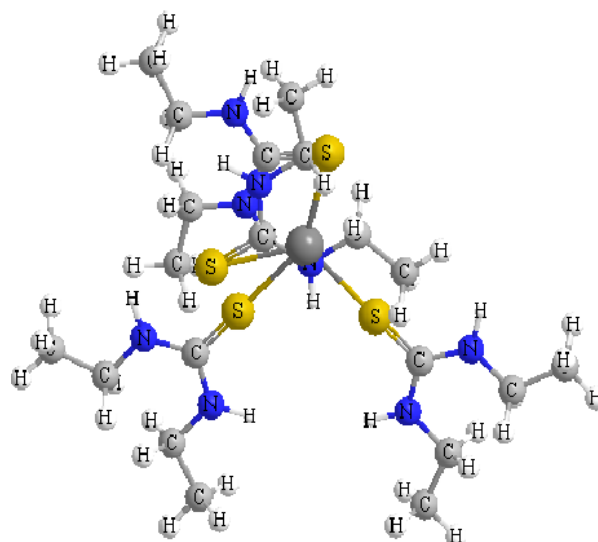


Figure 3. Predicted structure of the M-detu complex ion. (● = Cd(II)/Co(II))

CONCLUSION

Complex Cd-detu and Co-detu have been successfully synthesized and characterized. The obtained crystals (Cd-detu and Co-detu) were ionic with melting points of 105-108 °C and 122-125 °C, respectively. FTIR and ¹H-NMR analyses indicated a large shift of the (C=S) band of the complexes to a smaller wavenumber due to the bonding of the S atom to the central atom of cadmium(II) or cobalt(II). However, further single-crystal XRD characterization and refinement are critical to studying the environmental coordination of both complexes.

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