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Structure Prediction and Ultrasonic Assisted Synthesis of Coordination Compound Cadmium (II) Bromide with *N,N'*-diethylthiourea Ligand

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Abstract

Cadmium (II) halides with *N,N'*-diethylthiourea (*detu*) ligands at a stoichiometry of 1: 2 tend to form molecular complexes $[Cd(detu)_2X_2]$ with a distorted tetrahedral geometry at the central atom. Generally, these complex compounds are prepared by the conventional method of reflux for 4 hour. The use of ultrasonic waves for complex synthesis can be an alternative to make the reaction time more efficient and environmentally friendly. The aim of this study was to synthesize and characterize complex compounds from $CdBr_2$ and *detu* ligands using the ultrasonication method that have not previously reported. The synthesis of complex compounds was carried out by reacting $CdBr_2$ and *detu* (1:2) in methanol solvent. In the synthesized compounds, a melting point test, electrical conductivity test, Fourier Transform Infrared (FTIR), Scanning Electron Microscope-Energy Dispersive Xray (SEM-EDX), qualitative test of bromide ion and calculation of free energy using *Spartan'14* software were carried out for the complex structure prediction. The complex compound resulted has colorless needle crystals with a melting point of 93-94 °C. The results of the EDX analysis provide the empirical formula $C_{10}H_{24}CdBr_2N_4S_2$. The electrical conductivity test data and the bromide ion qualitative test proved that the synthesized complex compound was a molecular complex compound with the molecular formula $[Cd(detu)_2Br_2]$. The complex compound has two possible structures, namely a distorted tetrahedral and a square planar. Free energy calculations showed that complex compounds with a distorted tetrahedral structure and a square planar have free energies of -527.5574 kJ/mol and -408.7424 kJ/mol, respectively.

Keywords: $CdBr_2$; characterization; coordination compound; *detu*; ultrasonication.

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1. INTRODUCTION

Cadmium (II) complex has growing interest due to their photoluminescence, optical and other functional properties (Blumbergs et al., 2021; Genchi et al., 2020; Alizadeh & Amani, 2016). Cadmium (II) is the transition metal that belongs to group 12 of periodic tables with d^{10} configuration that has a variety of coordination geometries that are particularly useful for the construction of coordination frameworks. One of the cadmium salts is cadmium (II) halide, that forms stable coordination complex compounds with soft donor atom ligands from groups 15 and 16 (Armaghan et al., 2020). The cadmium (II) as a center atom in complex compounds is a soft Lewis acid with main coordination numbers 4, 5, and 6 (Borsari, 2014). An example of ligand that has N donor atom (element of group 15) and S donor atom (element of group 16) is thiourea (*tu*) ligand with its derivatives found in Figure 1. Based on the substituent groups bound to thiourea (*tu*), there are several derivatives of *tu* such as N-methylthiourea (*metu*), N-ethylthiourea (*ettu*), N,N'-dimethylthiourea (*dmtu*), N,N'-tetramethylthiourea (*tmtu*), N,N'-dietethylthiourea (*detu*) and so on (Shakeel et al., 2016).

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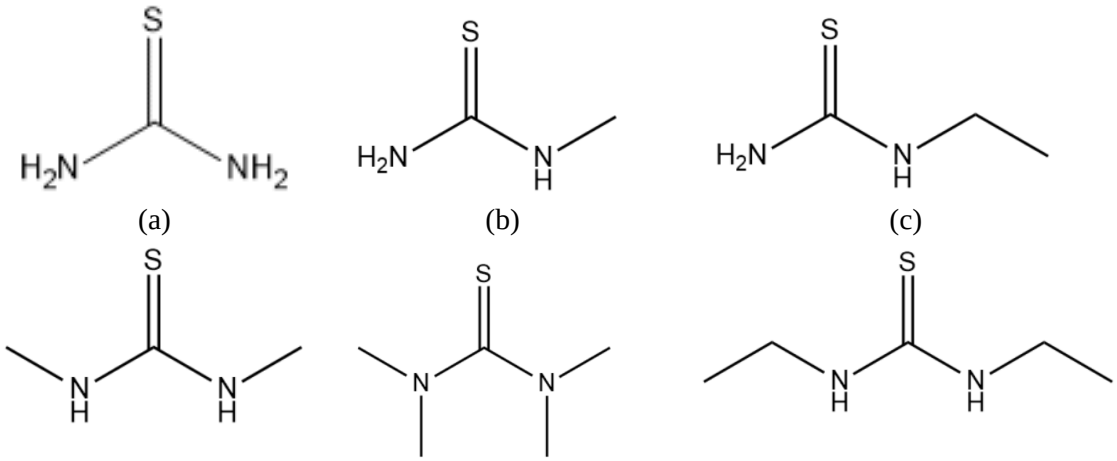

Figure 1. Structure of : (a) *tu*, (b) *metu*, (c) *ettu*, (d) *dmtu*, (e) *tmtu* dan (f) *detu*

Complex compounds of Cd(II) halides with *tu* and derivative ligands, respectively, have been reported including $[CdX_2(tu)_2]$ (X=Cl, Br, I) (Marcos et al., 1998; Ushasree & Jayavel, 2002); $[Cd(metu)_2Cl_2]$ and $[Cd(ettu)_2Cl_2]$ (Moloto dkk., 2003); $[Cd(dmtu)_2X_2]$ (X= Cl, Br, I) (Moloto, et al., 2009; Ahmad, et al., 2011) also $[Cd(tmtu)_2X_2]$ (X= Cl, Br, I) (Mahmood, et al., 2012; Nawaz et al., 2010). In each of these complex compounds, the Cd (II) center atom has a coordination number of 4 by binding two halide ligands and two S donor atoms from two *tu* ligands and their derivatives. The *tu*-derived complex was identified as an isostructural molecular complex with geometry around the central atom distorted tetrahedral. Meanwhile, with similar characteristics, complex compounds of Cd(II) halides with *detu* ligands that have been reported are $[Cd(detu)_2Br_2]$ (Marcotrigiano, 1976), $[Cd(detu)_2I_2]$ (Ahmad, et al., 2012) and $[Cd(detu)_2Cl_2]$ (Moloto et al., 2003; Wahyuni et al., 2022).

In such halide complexes, the *N,N'*-dietiltiourea (*detu*) ligand acts as a monodentate ligand, and halide ion as a terminal ligand. *Detu* ligand was classified as a thiourea disubstituent compound with two ethyl groups replacing the two H atoms of each NH_2 group, as shown in Figure 1. The presence of alkyl substituents as electron-driving groups can increase the electronic effect on the N atom so that it is theoretically more electron-rich and easy to donate its electrons as a ligand (Azizah, et al., 2020). Alkyl group substitution can also improve the steric effect of ligands (Alizadeh & Amani, 2016).

The role of anions can affect the structure of complex compounds (Althaf, et al., 2011). The size of bromide ions is smaller than iodide ions, so the repulsion caused between *detu* ligands to complex compounds that have bromo ligands is smaller than iodo ligands. As a result of this repulsion, the structure of the complex compound obtained can be different (Marcotrigiano, 1976; Borsari, 2014).

The synthesis of Cd(II)-*detu* complex compound was previously carried out by direct reaction method using methanol as solvent at 60 ^oC for 4 hours (Marcotrigiano, 1976; Wahyuni et al., 2022). The process produces an ionic complex compound, with high electrical conductivity. In this study, Cd(II) complexes with *detu* ligand were synthesized using Cd(II) bromide precursor with the assistance of ultrasonic wave. The use of ultrasonic waves as an alternative in the synthesis of coordination compounds can increase the collision ratio between chemical species and thus influence the success of chemical synthesis (Alfanaar & Notario, 2019). Compared to the conventional method, the used of ultrasound induced extreem conditions that can drive chemical or physical changes during reaction, also promote formation of nanosized particles by the instantaneously formation of a plethora of crystallization nuclei (Etaiw et al., 2021).

Structure prediction of the Cd(II)-*detu* complex compound was carried out based on the characterization results of melting point test, electrical conductivity test, a qualitative test of bromide ions, functional group analysis, morphology and elemental composition and free energy calculation using *Spartan'14* programs.

2. MATERIALS AND METHOD

Materials and Tools

The materials used for the synthesis of the complex include $CdBr_2.4H_2O$, *N,N'*-diethylthiourea, methanol and $AgNO_3$, which were obtained from Merck without further purification. The tools used were test tubes, beakers, stir bars, magnetic stirrers, watch glass, glass funnels, spray bottles, dropper drops, flasks, aluminum foil, analytical scales, melting point apparatus (Fisher-John), ultrasonicator tubs (BRANSON 1510), SEM-EDX (FEI Inspect S-50-AMETEK), FTIR (Shimadzu, IR Prestige 21) and conductometer (Omega Engineering, INC).

Synthesis of complex compound Cd-*detu*

Cadmium bromide (0.034 g; 0.10 mmol) and *detu* ligand (0.026 g; 0.20 mmol) were dissolved in 5 mL methanol, respectively. Each solution was vibrated separately in an ultrasonic bath for 15 minutes. The *detu* ligand was slowly added to the cadmium bromide solution and then further vibrated in a 42 kHz ultrasonic bath for 60 minutes at room temperature.

Characterization of complex compound Cd-*detu*

Melting Point Test

The synthesized crystals were placed on a Fischer Scientific hotplate. The sample is then heated by slowly increasing the temperature from 40°C to 100°C. The melting point test is carried out by observing the temperature when the crystals begin to melt until they melt completely.

Electrical Conductivity Test

Cadmium bromide (0.003 g; 0.01 mmol) and the synthesized complex compound (0.005 g; 0.01 mmol), each dissolved in methanol (10 mL) to obtain a solution with a concentration of 0.001 M. Measurement of electrical conductivity solvents, cadmium bromide solutions, and solutions of complex compounds synthesized using a conductometer.

Qualitative Test of Bromide Ion

Qualitative analysis of bromide was done using silver nitrate in the sample. Slight amount of complex compound was dissolved with water. A few drops of analytical grade silver nitrate solution were added. Yellow precipitate formed confirm presence of bromide as a counter anion (Tariq, et al., 2021).

Functional Group Analysis using FTIR

FTIR analysis was performed to confirm the successful synthesis of the complex by identifying functional groups. Sample and solid potassium bromide with a ratio of 1:10 were crushed until homogeneous, which were then formed into transparent pellets and stored in the IR sample holder. The pellet was then measured for its transmittance at wave numbers 4000-500 cm^{-1}.

Morphology and Elemental Analysis using SEM-EDX

The morphology of the samples was analyzed using Scanning Electron Microscope (SEM) with a voltage of 255 kV and magnification up to 10000x. A total of 5 mg of sample was put into a 3 mm sample container and then coated with a mixture of gold and palladium to make the sample more conductive to electron radiation from the EDX instrument (Mukhopadhyay, 2018).

Free Energy Analysis using Wavefunction Spartan'14

The *Spartan'14* wavefunction licensed software is used to determine the free energy of various possible structures of complex compounds based on the empirical formulas obtained. Various predictions of the structure of complex compounds and complex compounds because of previous research, were drawn based on coordinate data using the *Spartan'14* program and then optimized with the apply energy minimizer menu so that free energy is generated from each optimized structure. Then the free energy of each predicted structure is compared with the free energy of the complex compounds that have been reported. The chosen structure is the lowest free energy, in accordance with the experimental facts, and has the free energy closest to the complex compounds that have been reported (Fariati et al., 2016).

3. RESULTS AND DISCUSSION

Melting Point of Complex Compound

The complex compound was synthesized by a direct reaction between $CdBr_2$ and *detu* ligand at a ratio of 1:2 in methanol solvent. Synthesis took place in an ultrasonic bath for 60 minutes at room temperature. Ultrasonic waves in a liquid medium can produce a cavitation effect which accelerates reactions in solution with the principle of breaking intermolecular

reactions to produce nano-sized particles (Hui, et al., 2014). After 10 days of evaporation, colorless and shiny needle crystals were formed. Complex compounds with the central atom in closed cell groups are colorless because the d orbitals are completely filled with electrons, so there are no d-d transitions that cause colored complex compounds (Setiawan et al., 2017)**.**

The melting points of the reactants and the synthesized products are given in Table 1. Based on the melting point data, the synthesized complex is a new, pure, and stable compound. This result is supported by the melting point range of the complex compounds which differ by more than 10 ^{0}C from their precursors. A very sharp melting point in the range of less than 2 ^{0}C indicates that the complex compound obtained has minimal impurities (Young, 2013). Impurities from excess precursor or unwanted compound will broaden the range of melting point as they usually weaken the original crystal structure hence it progressed far from the eutectic temperature (Nichols, 2022).

Table 1. Melting point measurement results

Compounds	Melting point (°C)
$CdBr_2$	566
detu	78
Synthesized compound $CdBr_2$: *detu* = 1: 2	93-94

Electrical Conductivity of Complex Compound

The molecular properties of complex compounds were identified by comparing the electrical conductivity of the solvent, $CdBr_2$ solution and the synthesized complex solution. Based on the electrical conductivity values in Table 2, it shows that the synthesized complex compounds have an electrical conductivity value that is between the electrical conductivity of the solvent and its salt. The difference in the value of the electrical conductivity of the synthesized complex compound to the solvent of 34.32 µS/cm is closer than that of the salt, which is 38.00 µS/cm. Therefore, it can be stated that the complex compounds synthesized are molecular in nature because the value of the electrical conductivity tends to be close to that of the solvent (Fariati, et al., 2016).

Presence of Bromide Ions

The electrical conductivity test data was strengthened by a qualitative test of bromide ions on the resulting complex compounds. The qualitative analysis was done using the classic identification of halides. Water-soluble halogen compounds release halide ions when they dissociate or hydrolyze, which quickly react with silver ions (Ag^+) to produce any precipitate (Tariq, et al., 2021). The results obtained are given in Table 3.

The results of the qualitative test did not give a yellow precipitate of AgBr, proving that the bromide ion is not a counterbalance anion, but coordinates with the central atom as a ligand. The resulting complex compounds are molecular or neutral complex compounds (Fariati et al., 2019). This supports the results of the electrical conductivity tests that have been carried out.

Functional Group of Complex Compounds

The shift in wave number occurs due to a change in the molecular structure between the ligand and its complex compounds. The central atom of Cd(II) is coordinated with the *detu* ligand through the S atom, resulting in a change in the wave number ν(C=S) at 667.37cm^{-1} (Ajibade, 2013). Meanwhile the typical peak of compound that show direct vibration of metal complex is seen in the fingerprint area (Ismiyarto, et al., 2021).

Table 2. Electrical conductivity result

Solutions	Concentration (M)	Electrical conductivity (µS/cm)
Methanol	-	3.98
Cadmium (II) bromide, $CdBr_2$	0.001	76.30
Synthesized complex compounds	0.001	38.30

Table 3. Bromide ion qualitative test results

Solutions	Observations
$AgNO_3$	Colorless
Complex compound	Colorless
Complex compound + $AgNO_3$	No yellow precipitate of AgBr

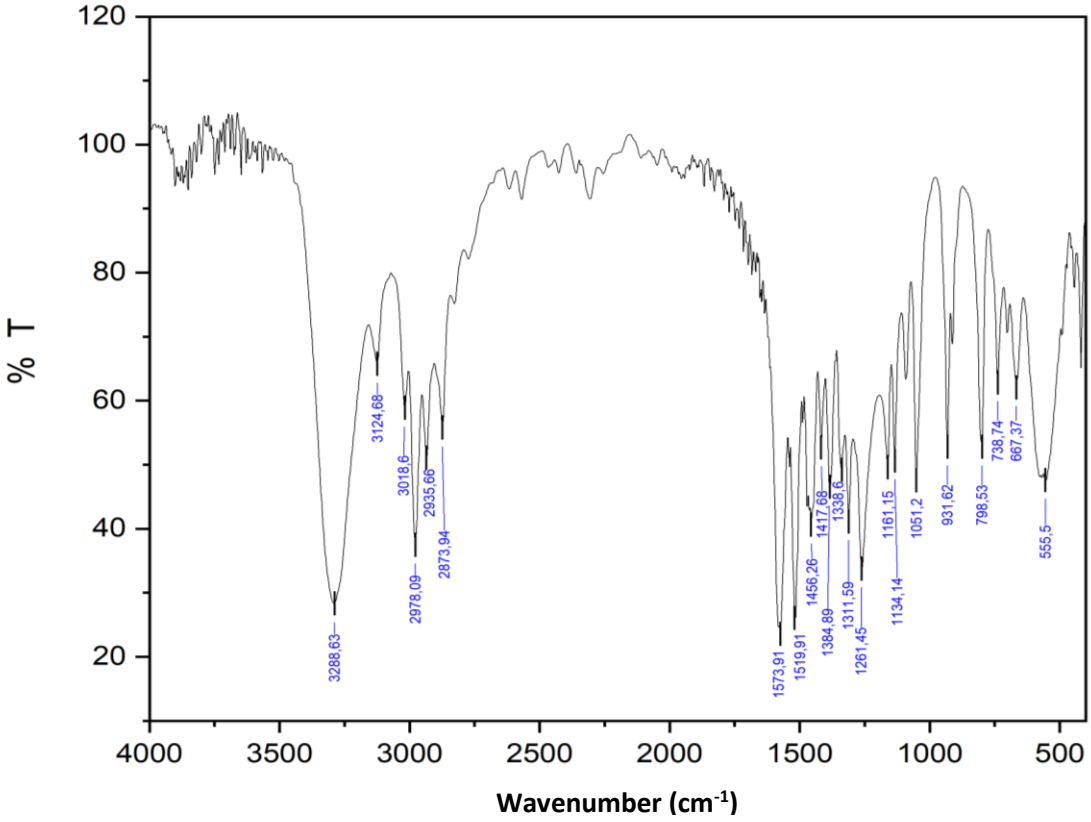

Figure 2. FTIR spectrum of the synthesized complex compound

Table 4. Comparison of Ligand and Complex Compounds Wavenumber

Functional group	Wavenumber (cm^{-1})		
	***detu* ligand (Wahyuni et al., 2022)**	**Complex $[Cd(detu)_2Br_2]$ (Marcotrigiano, 1976)**	**Synthesized complex**
ν (C=S)	653.87	-	667.37
ν (C-N)	1556.55	-	1573.91
ν (N-H)	3263.56	3290	3288.63

The vibrations of functional group ν(C-N) and ν (N-H) were observed at wave numbers 1556 cm^{-1} and 3263 cm^{-1}, in free *detu* ligand (Wahyuni et al., 2022). At the synthesized complex compound, the functional group of ν(C-N) was shifted by 17 cm^{-1}, while ν(N-H) was shifted by 25 cm^{-1} higher than ligand, as shown at Table 4. In previous studies, ν(N-H) of Cd-*detu* complex were observed also at higher wave numbers than the ligand (Marcotrigiano, 1976). The functional groups in complex compounds shift towards higher wave numbers due to changes in the molecular structure of the ligand before and after bonding with the metal. The peak of ν(N-H) from complex compound are not as wide as those of ligands due to the loss of intramolecular interactions of the hydrogen bonds (Wahyuni et al., 2022).

Morphology and elemental composition of complex compound

Analysis of the synthesized complex compounds with the SEM-EDX instrument

produced photos of the crystal surface and EDX spectra. The picture informs that the synthesized crystal is in the form of a prism. Various anions can affect the crystal morphology of the cadmium complex formed. In previous studies, cadmium nanoparticles with halides produced a pyramid-like morphology with a hexagonal base (Gaur & Jeevanandam, 2015). The SEM results of the synthesized complex compounds are shown in Figure 3.

The EDX spectrum provides qualitative information about the constituent elements of complex compounds and quantitative information related to atomic percentage (%At) and weight percentage (%Wt) data. The ratio of the percentage of elemental atoms making up a complex compound shows the empirical formula of the complex compound. The EDX spectrum of the synthesized complex compound is shown in Figure 4.

The results of the EDX spectrum showed the atomic peaks that make up the synthesized complex compound, namely C, N, S, Br, and Cd atoms. The Cd and Br elements come from salts, while the C, N, and S elements come from ligands. The composition of the constituent elements of complex compounds as a result of EDX analysis and theoretically is given in Table 5.

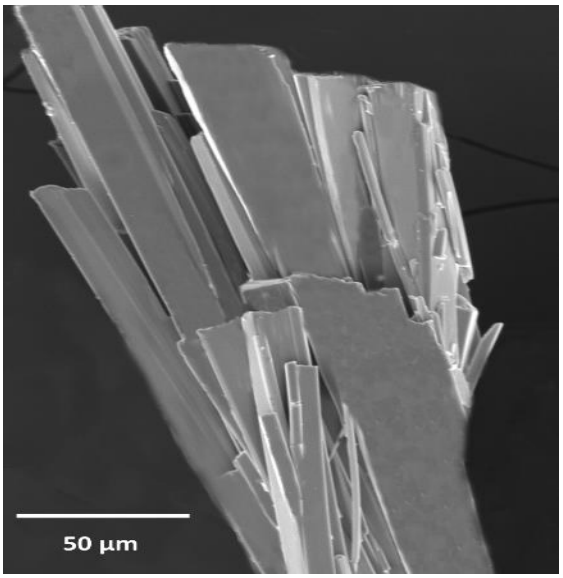

Figure 3. SEM result of complex crystal

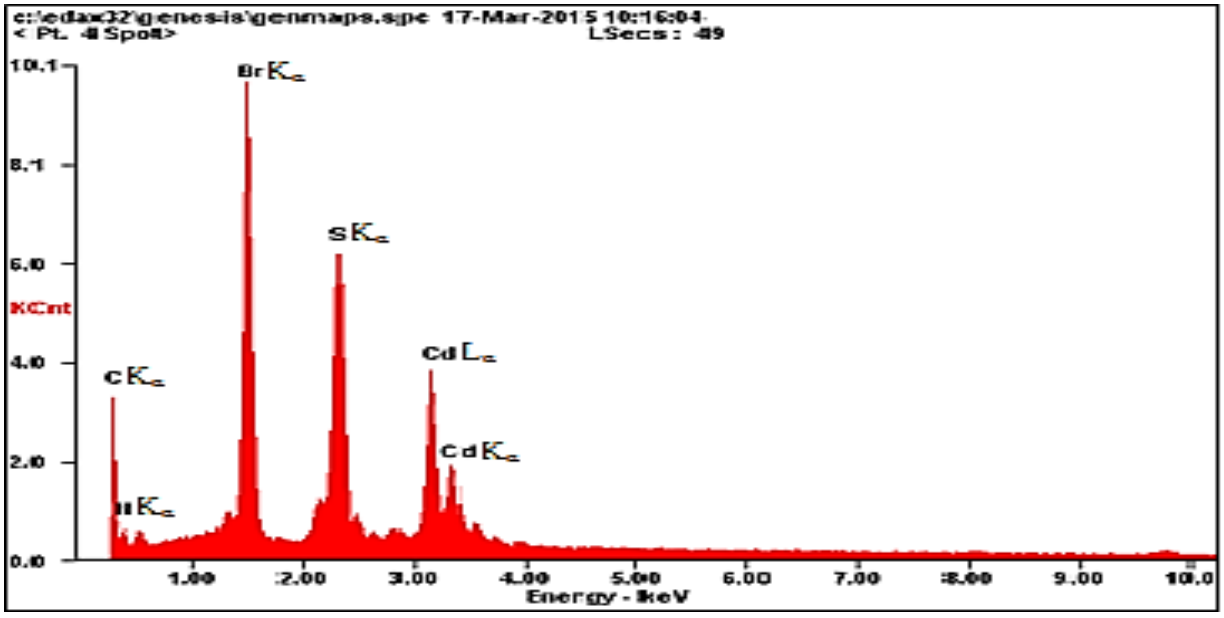

Figure 4. EDX spectrum of synthesized complex

Table 5. Elemental composition of complex compounds from EDX results

Element	%Wt		%At	
	Experimental	Theoretical	Experimental	Theoretical
C	30.60	23.43	62.71	52.63
N	09.44	10.93	16.03	21.52
S	10.40	12.51	07.87	10.52
Cd	18.89	21.93	04.08	5.26
Br	30.67	31.18	09.31	10.52

note: %At = atomic percentage, %Wt= weight percentage

Based on Table 5, it was found that the synthesized complex is pure, consisting solely of the elements C, N, S, Cd and Br with the nominal rasio of %At as 62.71 %; 16.03%, 7.87%; 4.08%; and 9.31%. Analysis using EDX has the disadvantage that it cannot detect the presence of elements with atomic numbers less than 12. In addition, H atoms cannot be detected in EDX analysis because H atoms only have one electron involved in bond formation. The synthesized complex compound at a stoichiometry of 1: 2 has the smallest percentage ratio of Cd: S: Br atoms, 1: 1.93: 2.2 rounded up to 1: 2: 2. The ratio of the percentage of atoms corresponds to the initial stoichiometry synthesis and produce the empirical formula of the complex compound, namely $C_{10}H_{24}CdBr_2N_4S_2$. The empirical formula is in line with previous research (Ahmad, et al., 2012).

Structure prediction of complex compound

EDX analysis of complex compounds produces the empirical formula $C_{10}H_{24}CdBr_2N_4S_2$. Based on the empirical formula and various characteristic test results, two predictions of the structure of the synthesized complex compound were obtained which fulfilled the stoichiometry of 1: 2. The predicted structure of the complex compound has the molecular formula [Cd(*detu*)$_2$Br$_2$] with a distorted tetrahedral geometry and a planar quadrilateral whose structure is shown in Figure 5 (a) and (b). The complex compounds modeled in Figure 5 are isostructured with the facts of previous studies (Ahmad, et al., 2012). Therefore, complex compounds with this structure tend to form. Optimization of the prediction of the structure of complex compounds and the results of previous studies using the *Spartan'14* programs produced free energy data as shown in Table 6.

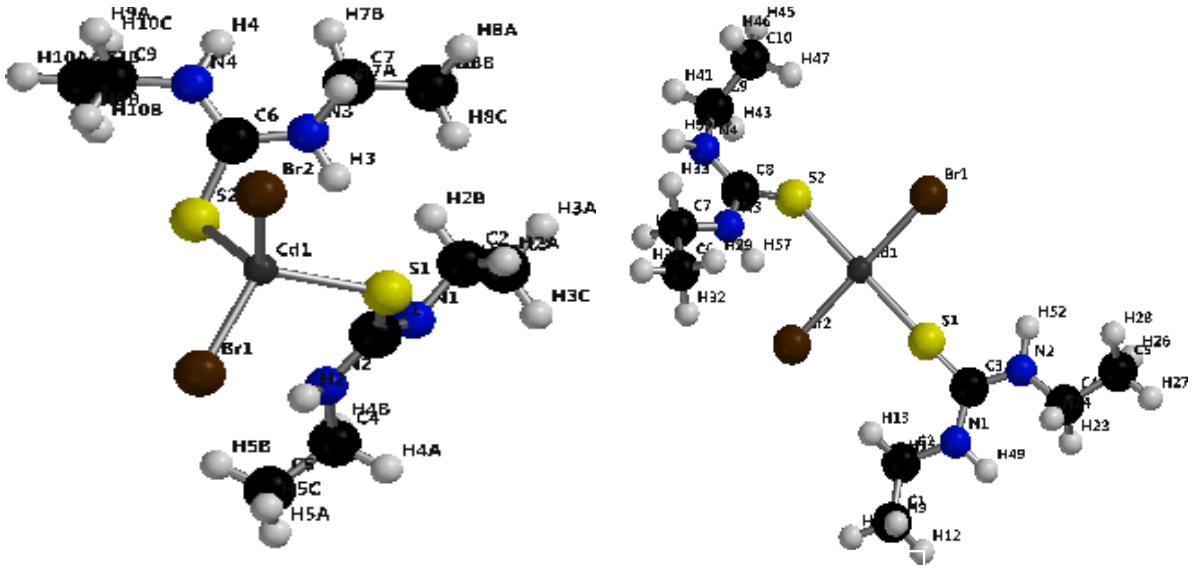

Figure 5. Structure predictions of [Cd(*detu*)$_2$Br$_2$] based on *Spartan'14* programs: (a) distorted tetrahedral (b) square planar.

Table 6. Free energy of complex compound [Cd(*detu*)$_2$X$_2$] (X= Br, I)

Molecular formula	Geometry structure	Free energy (kJ/mol)
[Cd(*detu*)$_2$Br$_2$]*	Distorted tetrahedral	-527.5574
[Cd(*detu*)$_2$Br$_2$]*	Square Planar	-408.7424
[Cd(*detu*)$_2$I$_2$]**	Distorted tetrahedral	-527.1549

Note: (*): synthesized complex
(**): previously complex reported (Ahmad, et al., 2012)

Table 7. Bond length of complex compound

Parameter	Synthesized complex [Cd(*detu*)$_2$Br$_2$]	Previously reported [Cd(*detu*)$_2$I$_2$] (Ahmad et al., 2012)
Bond length (Å)		
Cd-X(1)	2.448	2.690
Cd-X(2)	2.449	2.690
Cd-S(1)	2.409	2.410
Cd-S(2)	2.415	2.410
Bond angle (^{0})		
S(1)-Cd-S(2)	110.56	110.08
S(1)-Cd-X(1)	111.26	109.57
S(1)-Cd-X(2)	109.66	109.70
X(1)-Cd-X(2)	107.98	108.48

The structure prediction of [Cd(*detu*)$_2$Br$_2$] with a distorted tetrahedral geometry is in accordance with the experimental facts, has the lowest free energy and approaches the free energy of complex compounds that have been reported (Ahmad, et al., 2012). Based on the free energy data, the complex compound [Cd(*detu*)$_2$Br$_2$] with a distorted tetrahedral structure is the acceptable structure because it has the lowest free energy, which is -527.5574 kJ/mol. Those free energy is close to the complex compound [Cd(*detu*)$_2$I$_2$] with the same structure, which is -527.1549 kJ/mol. The smaller different in both free energy, the more closer prediction of the modeled structure to the actual structure, and the isostructure with the complex compounds that have been reported.

The lengths and bond structures of the synthesized complex compounds and complex compounds that have been reported can be found with the *Spartan'14* program. Processing results can be seen in Table 7. Based on the data in Table 7, the complex compound [Cd(*detu*)$_2$Br$_2$] has a deviation of the normal tetrahedral angle (109,28^o). Bond angle Br-Cd-Br of synthesized complex [Cd(detu)$_2$Br$_2$] smaller than the bond angle I-Cd-I of [Cd(*detu*)$_2$I$_2$]. The electronegativity of the bromide atom is greater than that of the iodide (Gao et al., 2022). This causes the strength of the Br atom to attract the electron density of the Cd-Br bond to be greater than the strength of the I atom to attract the electron density of the Cd-I bond so that the electron density of the Cd-Br bond can be considered thinner than the electron density of the Cd-I bonds. As a result, the bond electron pair repulsions with the more electronegative atom are weaker than the bond electron pair repulsions with the less electronegative atom. The Br-Cd-Br bond angle is smaller than the I-Cd-I bond angle (Palmer & Parkin, 2015). The size factor also determines the size of the bond angles around the central atom. The large size of the substituents tends to occupy a large space, so that it is offset by an enlarged bond angle. The atomic radius of I is larger than that of Br, so the I-Cd-I bond angle is larger than that of Br-Cd-Br (Ghosh & Biswas, 2002).

The Br-Cd-S bond angle is greater than the I-Cd-S bond angle which results in the Cd-S bond length of [Cd(*detu*)$_2$Br$_2$] being shorter than [Cd(*detu*)$_2$I$_2$]. Bond length of Cd-Br from synthesized complex compound [Cd(*detu*)$_2$Br$_2$] was shorter than Cd-I of [Cd(*detu*)$_2$I$_2$] because the covalent radius of the Br atom (114 pm) is shorter than that of the I atom (133 pm).

4. CONCLUSION

Molecular complex compound [Cd(*detu*)$_2$Br$_2$] successfully synthesized with stoichiometry 1:2 using ultrasonic waves. The coordination of the Cd(II) central atom with the detu ligand resulted in a significant shift in wavenumber on ν(C=S), ν(C-N) and ν(N-H) become 667,37 cm^{-1}, 1573,91 cm^{-1}, and 3288,63 cm^{-1}. The resulting complex compound has an empirical formula $C_{10}H_{24}CdBr_2N_4S_2$ with melting point 93-94 ^{o}C. Based on the results of free energy analysis using the *Spartan'14* program, the geometry around the central Cd(II) atom is distorted tetrahedral.

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