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Comparative Study of Synthesis and Characterization of Complex Compounds of Co(II) and Fe(III) Metal Ions with Ligands N-Etilisopropyldithiocarbamate and Its Application as an Additive in Lubricants

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Abstract. The aim of the synthesis and characterization of Co(II) and Fe(III) metal ions with N-Ethylisopropyldithiocarbamate ligands is to produce dithiocarbamate complex molecules that can be utilized in pharmacology, industry, agriculture, and chemistry in the future. The in situ method, which involves reacting secondary amines with carbon disulfide in ethanol solvent (dithiocarbamate ligands) and metals dissolved in ethanol solvent (metal ions), was used to synthesize complicated chemicals. Melting point, conductivity value, FT-IR, and UV-Vis analyses were used to characterize complicated compounds. The resulting Co(II)-N-Etilisopropyldithiocarbamate complex compounds are black in color and Fe(III)-N-Ethylisopropyldithiocarbamate are dark green, with a yield of 64.12% and 41.87%, respectively, with different conductivity values,≠0 (electrolyte compound). From the results of the FT-IR analysis, the presence of Co-S bonds was identified at the absorption band of 362.62 cm^{-1} and Fe-S at the absorption band of 354.90 cm^{-1}. Maximum wavelength absorption UV-Vis, Co(II) (λmax = 330 nm) > Fe(III) (λmax = 310 nm). Characterization results based on the measurement of kinematic viscosity values, Fe(III)-N-ethylisopropyldithiocarbamate complex compounds are more effective as the additives in lubricants than Co(II)-N–Ethylisopropyldithiocarbamate at a temperature of 100 ^oC.

Introduction

The study of the use of complex compounds of dithiocarbamate (DTC) is still being developed due to its wide use in various spheres of human life. In the field of chemistry, these compounds are most widely used as chelates for elemental or resin analysis (Li et al., 2022); in agriculture, they are used as fungicides (Bolado et al., 2021), For various crops, dithiocarbamates-based pesticides are utilized as fungicides (Wang et al., 2020). In industry field, dithiocarbamate can be used as a catalyst to remediate vanadium pollution (Huang et al., 2022).

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In addition, dithiocarbamate compounds are used as additives in lubricants in industry (Ranggina et al., 2023), and as corrosion inhibitors (Pham et al., 2022). In pharmacology, dithiocarbamate compounds have been proposed as anti-trypanosomatid drugs, primarily for the therapeutic control of protozoa that cause major infectious diseases in humans, including African trypanosomiasis, leishmaniasis, and Chagas disease (de Freitas Oliveira et al., 2019), as antifungal (Anggraini et al., 2020), anti-bacterial *Salmonella typhi* and *Escherichia coli* (Sanuddin et al., 2022), anti-tuberculosis (Yunus et al., 2023), anti-cancer and anti-covid-19 virus (Irfandi, Riswandi, et al., 2022), and treatment of HIV (Ajiboye et al., 2022).

Dithiocarbamate compounds consist of two sulfur donor atoms bonded to one carbon atom, which can form complexes with transition metals, and become neutral complexes of type M(DTC)X, where X is the number of ligands attached to the metal. Dithiocarbamate compounds readily react with many metal salts such as copper, iron, cobalt, and nickel and will form octahedral complexes. The use of dithiocarbamate compounds depends on the chelating properties of dithiocarbamate ligands to metal ions. (Pratiwi et al., 2022).

Metal and ligand complexing cannot be separated from the HSAB (Hard and Soft Base) principle, hard acids with hard bases, soft acids, and soft bases. In this case, dithiocarbamate is a soft base so dithiocarbamate will prefer soft acids (Duwila et al., 2023). Fe (III) metal ions in the HSAB principle are classified as hard acids and Co (II) is a soft acid. In ionic form, Fe and Co metals are very dangerous, but if complexed they will provide enormous benefits. For example, Co (II) and Fe (III) ions complexed with N-Heptylmethyl dithiocarbamate ligands have the potential to act as anti-tuberculosis agents (Hasminisari, 2015). Ahmed et al., (2024) synthesized a complex compound of dithiocarbamate ligand with metal ions Co (II), Ni (II), Zn (II), and Cd (III) and carried out a test for antibacterial resistance to Escherichia coli.

The additives added to lubricants have a significant impact on engine performance. According to Ranggina et al., (2023), additives have the ability to preserve the viscosity of lubricants while also serving as anti-wear, cleansers, and corrosion preventers. The antioxidant capabilities of lubricant additives can be enhanced by dithiocarbamate (Parenago et al., 2017).

From some of the above descriptions of dithiocarbamate complex compounds, this study will examine the ability of metal ions from transition elements, namely Co (II) and Fe (III) which based on the HSAB principle have different abilities to interact with ligands. When the two metal ions are reacted with ligands that have aliphatic alkyl, namely N-ethyl isopropyl dithiocarbamate, to form complex compounds. In addition, the use of complex compounds of Mn (II) metal with N-Ethylisopropyldithiocarbamate ligand has the potential as an additive for lubricants and is effective at temperatures of 100 ^{o}C (Ranggina et al., 2023). The objective of this study is to evaluate the potential of Co(II) and Fe(III) metal complex compounds with N-ethyl isopropyldithiocarbamate ligands as additives in lubricant.

Experimental

Material and Methods

The materials used in this study were N-Etilisopropyl-amine, Carbon Disulfide (CS_2), $FeCl_3.6H_2O$, $CoCl_2.6H_2O$, ethanol 96%, ethanol p.a., distilled water, Whatman 42 filter paper, and acetone. The tools used in this study are: glassware commonly used in laboratories, analytical balance, desiccators, ovens, electric heaters, magnetic stirrers, melting point measuring equipment model ELEKTROTERMAL 9100, conductometer, Jenwey UV-Vis spectrophotometer, and Infra-Red spectrophotometer model SHIMADZU 8201 PC.

Procedures

Synthesis of N-Etilisopropyldithiocarbamate Co(II) Complex Compounds

$CoCl_2$. $6H_2O$ of 0.4759 grams (2 mmol) and N-ethylisopropylamine of 0.5229 grams (6 mmol) were each dissolved with 10 mL of 96% ethanol. The amine solution was added with CS_2 (0.36 mL (6 mmol) in 10 mL of 96% ethanol) slowly at 15 ^{o}C, then stirred for 15 minutes.

The metal solution of $CoCl_2$. $6H_2O$ was mixed into the N-ethylisopropyldithiocarbamate ligand solution while stirring slowly for 30 minutes. After the precipitate was formed, it was filtered. The precipitate was then washed and recrystallized using ethanol p.a to obtain crystals. The precipitate was then dried in a desiccator for one week, then weighed and analyzed.

Synthesis of Fe(III) Complex Compound N-ethyl isopropyl dithiocarbamate

$FeCl_3.6H_2O$ as 0.5406 grams (2 mmol) and N-ethyl isopropylamine as 0.5229 grams (6 mmol) were each dissolved with 10 mL of 96% ethanol. The amine solution was added with CS_2 (0.36 mL (6 mmol) in 10 mL of 96% ethanol) slowly at 15 ^{o}C, then stirred for 15 minutes. FeCl.. $6H_2O$ was mixed into the N-Ethylisopropydithio carbamate ligand solution while stirring slowly for 30 minutes. Afte the precipitate was formed, it was filtered. The precipitate was then washed and recrystallized using ethanol p.a to obtain crystals. The precipitate was then dried in a desiccator for one week, then weighed and analyzed.

Characterization Analysis of Complex Compounds

The characterization of dithiocarbamate complex compounds is done by determining their melting point using the melting point apparatus, measuring their electrical conductivity using a conductometer, analyzing them using FT-IR (Fourier Transform Infrared) in the region of 4000-300 cm^{-1}, and using UV-Vis spectrophotometer and observed their absorption at a wavelength of 200–800 nm.

Test Additives in Lubricants

The potency of dithiocarbamate complex compound was tested by kinematic viscosity tests at 40 °C and 100 °C. Before being inserted into the capillary tube, 0.05 grams (0.1%); 0.08 grams (0.16%); and 0.1 grams (0.20%) of each complex compound that has been synthesized are dissolved in 50 mL of acetone. After that, the capillary tube is inserted into the kinematic viscosity bath for 30 minutes, and the flow time is measured.

Result and Discussion

Synthesis of Complex Compounds

Synthesis of complex compounds is generally done by reacting metal ions with ligands. In this study, synthesized complex compounds were synthesized by reacting metal ions Mn^{2+} and Fe^{3+} with an N-Ethylisopropyl dithiocarbamate ligand. The ligand was first synthesized by reacting N-ethylisopropylamine of 0.5229 grams (6 mmol) with CS_2 solution of 0.36 mL (6 mmol) using ethanol solvent.

The synthesis of Co(II) complex compound with N-Ethylisopropyldithiocarbamate was carried out by reacting $CoCl_2 .6H_2O$ as much as 0.4759 grams (2 mmol) dissolved in ethanol with N-Isopropyldithiocarbamate ligand solution. The resulting black-colored Co(II)-N-Ethylisopropyldithiocarbamate complex compound was 0.5269 grams and the yield obtained was 64.12%.

The synthesis of Fe(III) complex compounds with N-ethylisopropyldithiocarbamate was carried out by reacting $FeCl_3.6H_2O$ as much as 0.5406 grams (2 mmol) dissolved in ethanol with a solution of N-isopropyl dithiocarbamate ligand. The resulting Fe(III)-N-ethyl isopropyldithiocarbamate complex compound is dark green as much as 0.3415 grams and the yield obtained is 41.87%.

Characterization of Complex Compounds

Melting Point Measurement. The metal ion and the type of ligand determine the results of measuring the melting point of dithiocarbamate complex compounds. The results obtained for the measurement of the melting points of the complex compounds Fe(III)-N-ethylisopropyl-DTC and Co(II)-N-ethylisopropyl-DTC are very close, namely 397 °C and 398.5 °C. This is because the two metal ions are located in the same period and have similar chemical and physical properties, making it possible to have adjacent melting points. The Fe(III)-N-ethylisopropyl-DTC complex has a smaller melting point than Co(II)-N-ethylisopropyldithiocarbamate; this is due to the larger charge of the Fe^{3+} ion compared to the Co^{2+} metal ion. The higher the charge of the metal ion, the stronger the interaction between the ligand and the metal, resulting in a high melting point (Yunus et al., 2023).

Conductivity Measurement. Conductivity measurements are carried out to determine the electrical conductivity of synthesized complex compounds. The difference in conductivity of the solvent with the resulting complex compounds can be used to determine whether the measured complex compounds are electrolytic or non-electrolytic. Complex compounds are classified as electrolytes when the difference between the solvent (acetone) and the complex compound is ≥ 75 and are classified as non-electrolytes when the difference is ≤ 75 (Ranggina et al., 2023). The results obtained from this analysis are shown in Table 1.

Table 1. Conductivity Test Results of Solvents and Synthesised Complex Compounds.

No.	Solution	Conductivity (mv)
1.	Acetone	505,3
2.	Fe(III)-N-ethylisopropyl dithiocarbamate in acetone	647,5
3.	Co(II)-N-ethylisopropyl dithiocarbamate in acetone	516,4

Conductivity values in Table 1 showed that the Co(II)-N-ethylisopropyldithiocarbamate complex had a conductivity value difference of less than 75, while the Fe(III)-N-ethylisopropyldithiocarbamate compound was greater than 75. So, it can be concluded that Co (II)-N-ethylisopropyldithiocarbamate, is a non-electrolytic compound (charge = 0), and Fe (III)-N-ethylisopropyldithiocarbamate is an electrolytic compound (charge ≠ 0). The conductivity value difference is determined by the type and charge of the metal ion, which is the central atom that bonds the ligand. Complex compounds will have high conductivity values when the charge of metal ions is large.

Analysis using a UV-Vis spectrophotometer. Analysis using a UV-Vis spectrophotometer was performed at wavelengths of 200-800 nm. But before the absorbance measurement, the complex compounds Fe(III)-N-ethylisopropyldithiocarbamate as much as 0.0144 grams, and Co (II)-N-ethyl-isopropyl-DTC as much as 0.0105 grams each were dissolved with 20 mL of acetone.

The UV-Vis spectrum produced by dithiocarbamate compounds usually consists of two main absorption peaks, namely, the absorption peak is in the region of 250-300 nm, which arises due to the transition of the electrons of $\pi \longrightarrow \pi^*$ the N$\cdots$C bond. The second is the absorption peak in the region below 250 nm, which arises due to the transition of electrons π ⟶ π* in the S⋯C⋯S bond (Prihantono et al., 2020). The UV-Vis spectral results of the two resulting complex compounds are shown in Figures 1 and 2. If the spectrum of UV-Vis analysis results in Figures 1 and 2 is observed, it can be seen the difference in spectral peaks due to differences in metal ions but the same ligand, although the difference is not significant.

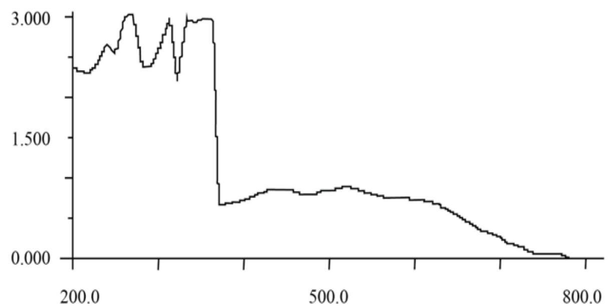

Figure 1. UV-Vis spectrum of Fe(III)- N-Ethylisopropyl-DTC.

Based on the UV-Vis spectrum in Figure 1, there are peaks at wavelengths of 240 nm, 270 nm, 310 nm, and in Figure 2 there are peaks at wavelengths of 240 nm, 290 nm, and 330 nm. The transition of electrons from the n → π * orbital in the N=C=S group can be seen through the absorption region above 300 nm (Irfandi, Santi, et al., 2022). The reaction between the CS_2 compound and the N-Ethyl isopropylamine ligand was successfully synthesized. The maximum wavelength absorption of Co(II) > Fe(III) is influenced by the binding between the metal and its ligand will decrease if the radius of the metal ion gets smaller and the atomic number gets bigger.

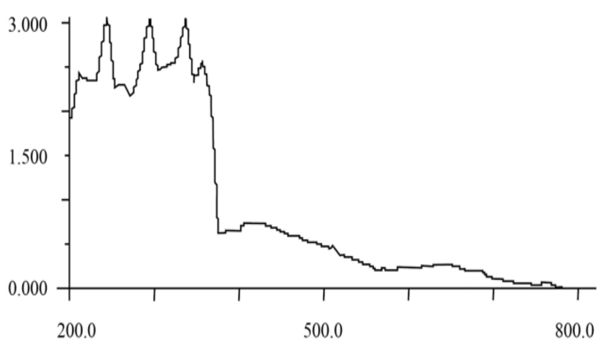

Figure 2. UV-Vis spectrum of Co(II)- N-Ethylisopropyl-DTC.

Analysis Using FT-IR. Functional groups bound in complex compounds can be identified from the results of FT-IR analysis in the frequency range of 4000-300 cm^{-1}, and 500-300 cm^{-1} (long distance) to show the bond vibration of the functional group contained in the crystal of complex compounds. The IR spectra of the near and far Fe(III)-N-ethylisopropyldithiocarbamate complexes are shown in Figures 3 and 4. As for the compound Co(II)-N-ethylisopropyl-DTC in Figures 5 and 6. Based on FT-IR analysis for close range (4000-300 cm^{-1}) Fe(III)-N-ethylisopropyl-DTC, and Co(II)-N-Ethylisopropyl-DTC complexes in Figures 4 and 6, it can be seen that both have Spectra showing that the uptake for each of their functional groups is almost the same of the two complex compounds, there is a strong absorption peak at the wavenumber 2970.38 cm^{-1} which states that the compound has an aliphatic C-H group reinforced by the absorption of methylene groups for both complex compounds at 1473.62 cm^{-1} and methyl groups for Fe(III)-N-Ethylisopropyl-DTC complex at 1419.61 cm-1 while the Co(II)-N-Ethylisopropyl-DTC 1334,74 cm^{-1}.

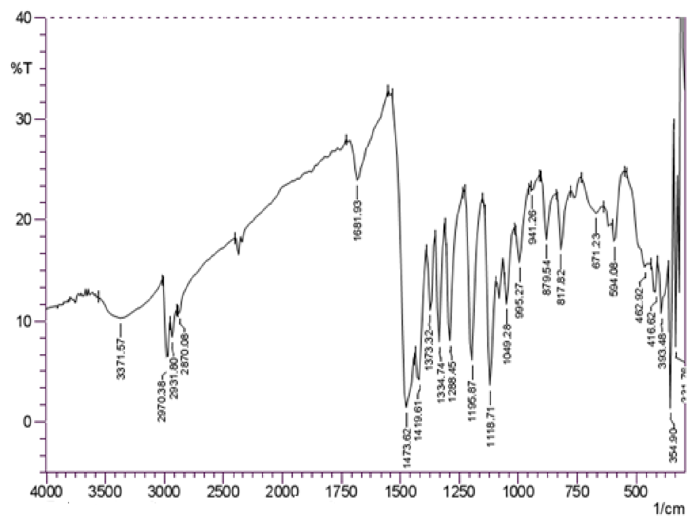

Figure 3. IR Spectrum of Fe (III) N-Ethyisopropyl-DTC.

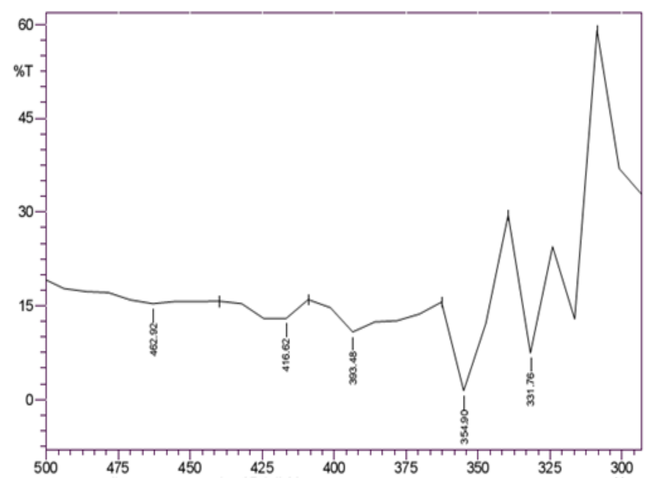

Figure 4. Far IR Spectrum Fe (III) N-Ethyisopropyl-DTC.

Absorption of 1195, 87 cm^{-1} for Fe(III)-N-Ethylisopropyl-DTC complex, and absorption of 1203.58 cm^{-1} for Co(II)-N-Ethylisopropyl-DTC complex showed N-C-S range vibration. In addition, the presence of

C-S group was reinforced by the presence of absorption at 594.08 cm^{-1} for Fe(III)-N-Ethylisopropyl-DTC complex, 725.23 cm^{-1} for Co(II)-N-Ethyl isopropyl-DTC complex (Adeyemi et al., 2021). The spectrum of FT-IR analysis results at long-range (500-300 cm-1) Fe(III)-N-ethylisopropyl-DTC, and Co(II)-N-ethylisopropyl-DTC complexes seen in Figures 4 and 6, shows the binding between the ligand and the metal. The sequence of uptake for both complexes is Co-S and Fe-S respectively, which amount to 362.62 cm-1 and 354.90 cm^{-1}. The presence of C-S groups from the spectra of the two complexes, appearing as a single uptake indicates bidentate coordination of ethyl isopropyl-DTC ligands with their respective metals (Baba & Raya, 2010).

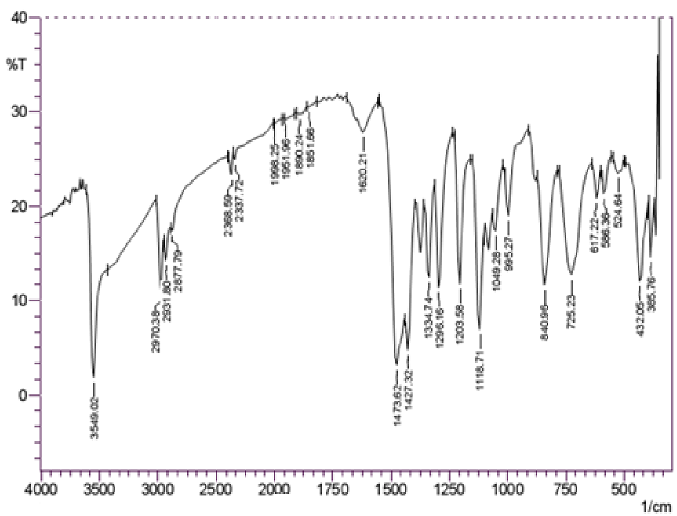

Figure 5. IR Spectrum of Co (II) N-Ethyisopropyl-DTC.

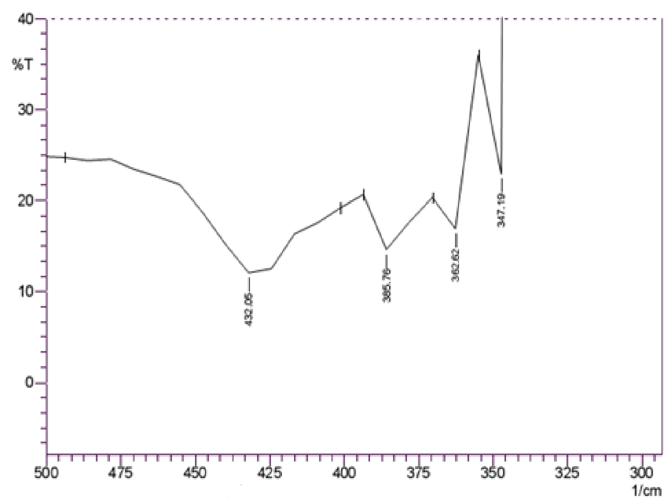

Figure 6. Far IR Spectrum Co(II) N-Ethyisopropyl-DTC.

Based on the analysis data of both complex compounds, the complex bond strength of Co(II)-N-Ethylisopropyl ditiocarbamate is greater than Fe(III)-N-Ethylisopropyl dithiocarbamate. N-ethyl isopropyl dithiocarbamate ligand is typically known as an electron donor. The bond length will be shorter when viewed from the metal ion, as the atomic radius decreases, which means more energy is needed to break the bond.

Approximate Structure of Complex Compounds with Dithiocarbamate Ligands. Based on the analysis of the characterization of complex compounds, the structure of complex compounds can be estimated as follows.

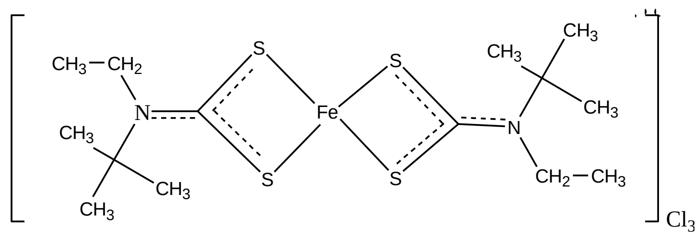

Figure 7. Structure of Fe (III)- N-Ethylisopropyl-DTC.

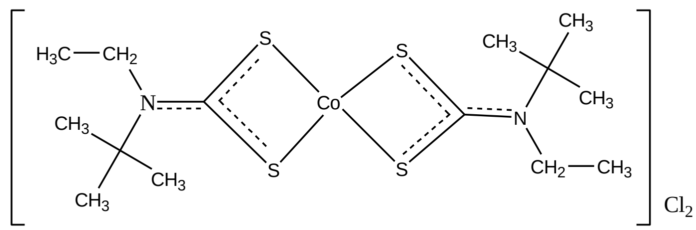

Figure 8. Structure of Co(II)- N-Ethylisopropyl-DTC.

The measurement of Lubricant Additives' Viscosity

Characterization of the potential of Dithiocarbamate complex compounds as additives in lubricants has been done by testing the viscosity, by comparing the addition of Dithiocarbamate complex compounds as additives and without addition (standard). The viscosity of the lubricant can be used to determine whether liquid flow is resistant. One of the determining factors in the viscosity value of a lubricant is temperature because if the lubricant temperature is too high, it will result in a lack of efficiency from the lubrication (Lubis, 2018). Complex compounds that have been synthesized compared their potential as additives based on the viscosity value of lubricants at a temperature of 40 ^{o}C and 100 ^{o}C temperatures shown in Table 2 and Table 3.

The kinematic viscosity values of lubricants are shown in Table 2 shows the value of viscosity without the addition of complex compounds is 128.46 cSt. After the addition of complex compounds with variations in concentration, the viscosity value of Fe(III)-N-ethyl isopropyl-DTC compounds at a concentration of 0.1% greater than the standard, but as the concentration of complex compounds increases the viscosity value decreases (smaller than the standard).

Table 2. Viscosity Test at 40 °C.

No.	Compound Name	Concentration (%)	Viscosity (cSt)
1.	Standar	Standar	128,46
2.	Fe(III)-N-etilisopropil-DTC	0,10	135,55
		0,16	70,49
		0,20	89,60
3.	Co(II)-N-etilisopropil-DTC	0,10	73,46
		0,16	99,05
		0,20	103,69

Similarly, the viscosity values of Co (II)-N-ethylisopropyl-DTC complex compounds at all concentrations are smaller than the standard (lubricants without complex compounds). It can be concluded that the complex compounds Fe(III)-N-ethylisopropyl-DTC and Co-(II)-N-ethylisopropyl-DTC are not effective as the additives in lubricants at a temperature of 40 °C, this is due to the coordination bond between the metal with dithiocarbamate ligand is not easily broken at low temperatures.

Table 3. Viscosity Test at 100 °C.

No.	Compound Name	Concentration (%)	Viscosity (cSt)
1.	Standar	Standar	128,46
2.	Fe(III)-N-etilisopropil-DTC	0,10	135,55
		0,16	70,49
		0,20	89,60
3.	Co(II)-N-etilisopropil-DTC	0,10	73,46
		0,16	99,05
		0,20	103,69

Table 3 is the result of kinematic viscosity at a temperature of 100 °C both standard and the addition of complex compounds with a concentration variation of 0.1%; 0,16%; 0,20%. The table shows a standard viscosity value of 14.04 cSt, and after the addition of the complex compound Co(II)-N-ethyl isopropyl-DTC, the viscosity value decreases further than the standard. In contrast to the addition of complex compounds Fe(III)-N-ethylisopropyl-DTC, increased compared to without the addition of complex compounds. Based on these results, it can be concluded that the complex compound Fe(III)-N-Ethylisopropyl-DTC is more effective than Co(II)-N-Ethylisopropyl-DTC, although it does not show an increasing trend as the concentration of complex compounds increases. This is due to the difference in size of complex metal ions, which affects the bond length, where Fe(III) > Co(II). Metal and ligand bonds can become tenuous as the bond length in the molecule, so it is easily broken and the viscosity value of the lubricant will increase (Siskayanti & Kosim, 2017).

Conclusion

The results showed that complex compounds of Fe(III) and Co(II) metal ions with N-Ethylisopropyl-DTC ligands could be synthesized. The synthesis of Fe(III)-N-Ethylisopropyl-DTC complex produced is dark green with a bath of 41.81% and melting point of 397 °C, while the synthesis of Co(II)-N-Ethylisopropyl-DTC complex produced is black with a bath of 64.12% and melting point of 398.5 °C. The results of the characterization of complex compounds Fe(III) and Co(II) based on the conductivity value, Co(II)-N-Ethylisopropyl-DTC, is a non-electrolytic compound (charge = 0), and Fe(III)-N-Ethylisopropyl -DTC is an electrolytic compound (charge ≠ 0). The spectrum of FT-IR analysis results at a long distance (500-300 cm^{-1}) for both complex compounds showed the presence of binding between ligands and metals. The sequence of uptake of both complexes is Co-S, Fe– S respectively amounting to 362.62 cm^{-1} and 354.90 cm^{-1}. And judging from the spectrum of UV-Vis analysis results, the maximum wavelength absorption of Co (II) (λ_{maks} = 330 nm) > Fe(III) (λmax = 310 nm). While based on the results of the characterization of metal complex compounds Fe(III) and Co(II) with N-Ethylisopropyl-DTC can be used as additives in lubricants and more effective at a temperature of 100 °C where the complex compound Fe(III)-N-Ethylisopropyl-DTC greater than Co(II)-N-Ethylisopropyl-DT..

Conflict of Interest

The authors declare that there is no conflict of interest.

Acknowledgments

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