SYNTHESIS AND INVESTIGATION OF COORDINATION COMPOUNDS OF Co(II) ION WITH 2-HYDROXY-1-NAPHTHALDEHYDE AND 1,2-PHENYLENEDIAMINE

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Abstract.
A new metal complex compound with the composition $[Co(2\text{-}hnaph)_2(1,2\text{-}phen)_2]\cdot Cl^{-}\cdot C_2H_5OH$ was synthesized by the interaction of 2-hnaph (2-hydroxy-1-naphthaldehyde), 1,2-phen (1,2-phenylenediamine), and $CoCl_2\cdot 6H_2O$ in ethyl alcohol solutions. The composition, molecular and crystal structures of this metal complex compound were investigated using differential scanning calorimetry (DSC), IR spectroscopy, and X-ray diffraction analysis (XRD). DSC analysis revealed that the thermal decomposition of the organic component in the complex varies, beginning at 75°C and ending in the temperature range of 370°C. A reaction occurs between the oxygen of the carbonyl group in the aldehyde form of 2-hnaph and the amino (NH_2) groups of 1,2-phen, resulting in the release of one water molecule ($>C=O + -NH_2 \rightarrow >C=N- + H_2O$). Analysis of two-dimensional fingerprint region plots revealed that H...O/O...H, H...H, and H...C/C...H interactions make the greatest contribution to the Hirshfeld surface. In the complex compound, H...H interactions account for 47.2%, H...C/C...H for 34.4%, and H...Cl/Cl...H for 9.2%, which is the expected state for molecules dominated by oxygen atoms. The complex compound contains H...H (47.2%), H...C/C...H (34.4%), and H...Cl/Cl...H (9.2%), which is the expected state for molecules dominated by oxygen atoms.

Keywords: 2-hydroxy-1-naphthaldehyde, 1,2-phenylenediamine, cobalt (II) chloride hexahydrate, alcohol, complex, ligand, Hirshfeld.

1. Introduction

Currently, due to environmental pollution by various waste products and the increase in toxic gases in the atmosphere as a result of industrial production, favorable conditions are emerging for the survival and reproduction of harmful microorganisms (viruses, bacteria, and fungi). This situation increases the need for new medicinal preparations that can actively affect harmful microorganisms. Along with natural medicinal preparations, synthetic medicinal preparations are also being effectively used in medical practice. It is possible to synthesize new biologically active substances with significant efficacy from several intermediate compounds. In this case, due to the phenomenon of synergism, toxicity may decrease while beneficial properties increase. Taking these circumstances into account, we aimed to synthesize mixed-ligand complex compounds of 2-hydroxy-1-naphthaldehyde and 1,2-phenylenediamines with bioactive metals and study their physicochemical properties.

As known from the literature, ligands such as 2-hydroxy-1-naphthaldehyde (2-hnaph) and 1,2-phenylenediamine (1,2-phen) are considered intermediate products in organic synthesis. Additionally, 2-hnaph is used as an analytical reagent for determining palladium and beryllium, as well as in the synthesis of adipic dihydrazones with antibacterial activity [Yuet al., 2006; Koizumi&Fukuju, 2011]. In medical practice, it is used to synthesize drugs that inhibit bacterial cells [Fernández-G&Espinosa-P. 1994]. Mixed-ligand metal complexes of 2-hnaph and 1,2-phen with Cu metal were synthesized, and their anti-cancer activity was studied [Parveenet al., 2020; Konieczny et al., 2019]. The literature presents the synthesis conditions and molecular structure of a new water-soluble metal complex of 2-hnaph and 1,2-phen with biologically active metals (Zn, Cu, Fe) based on X-ray structural analysis (XSA) [Jayamaniet al., 2018; Mahapatraet al.,2016]. Mixed-ligand metal complexes of both 2-hnaph and 1,2-phen with other biologically active ligands were obtained, and their physicochemical properties were studied [Zick&Geiger, 2016; Tziotzi et al., 2016]. This paper presents the synthesis, thermal (DSC), IR spectroscopic, X-ray structural analysis (XSA), and Hirshfeld surface analyses of a new metal complex compound of 2-hnaph and 1,2-phen with cobalt metal.

Currently, numerous research studies are being conducted on the synthesis of ligands, sorbents, and ion exchangers containing nitrogen, oxygen, sulfur, and phosphorus donor atoms [Eshqurbonov&Safarova, 2025; Eshkurbonov&Safarova,2024; Eshkurbonov&Rakhmonkulov, 2022]. The ligands, sorbents, and ion exchangers synthesized in this research work are particularly distinguished by their ability to selectively sorb d-metal ions from solutions [Eshkurbonov et al., 2025].When treating soybean seeds before sowing and during the growing season with biologically active substances, potassium and sodium humates, humic and fulvic acids, essential amino acids, and microelement stimulants, seedling emergence accelerated, resistance to unfavorable conditions increased, rapid growth and development occurred, photosynthetic activity improved, and a high and quality yield was obtained [K.M.Tadjiev et al., 2026]

Research methodology.

Chemicals, instruments, and calculations. All reagents were obtained from commercial sources and used without purification. The crystal structure determination was carried out using an Oxford diffraction Xcalibur-R CCD (CuKα radiation, λ=1.54184 Å, ω-scanning mode, with a graphite monochromator at 293K) [Xcalibur 2009]. The structure was solved using the SHELX-97 software package [Sheldrick 1997]. Molecular diagrams were generated using the MERCURY software package [Macrae et al., 2008].

Experimental part

In this experiment, the reagents 2-naphthaldehyde and 1,2-phenylenediamine were dissolved in alcohol. When solutions of 2-naphthaldehyde, 1,2-phenylenediamine (1,2-phen), and $CoCl_2·6H_2O$ were mixed in a molar ratio of 2:2:1, a turbid solution was obtained. This solution was stirred in a mechanical stirrer for 40-45 minutes at a temperature of 30-35°C, causing it to clarify. The resulting solution was left to evaporate at room temperature with the container partially open. After approximately 10-12 days, brown crystals formed. The resulting crystals were washed with ethyl alcohol. Suitable monocrystals were selected and analyzed by X-ray diffraction (XRD). According to the XRD data, both coordination and a chemical reaction occurred between the two ligands and the cobalt atom. A chemical reaction took place between the aldehyde form of 2-naphthaldehyde and the amino group of 1,2-phenylenediamine. In the resulting complex compound, the oxidation state of the Co atom changed from +2 to +3, indicating that oxidation occurred, while the nitrogen atom of the amine group of 1,2-phenylenediamine was reduced from -2 to -3. Thus, an oxidation-reduction reaction also took place. The chloride anion in the outer sphere formed a cationic complex by neutralizing the central atom. The proposed reaction equation for the synthesized single crystal is as follows (Fig1).

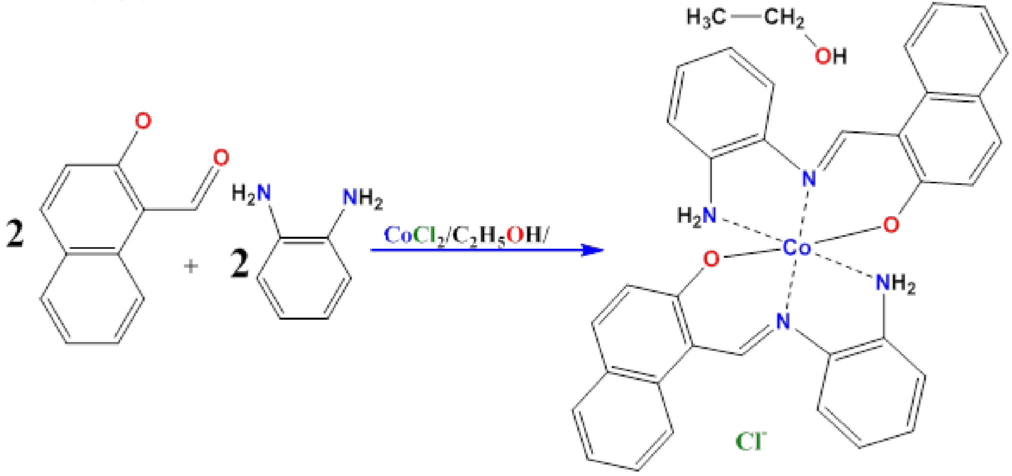

Fig 1. Synthesis scheme of the complex $[Co(2\text{-hnaph})_2(1,2\text{-phen})_2]·Cl^-·C_2H_5OH$

Results anddiscussion

When studying melting temperatures, it was determined that the resulting complex melts at a higher temperature (226.8°C) compared to the complex ligand (134.3°C). To investigate the thermal nature of the obtained complex crystal form, DSC analysis was conducted (Figure 2).

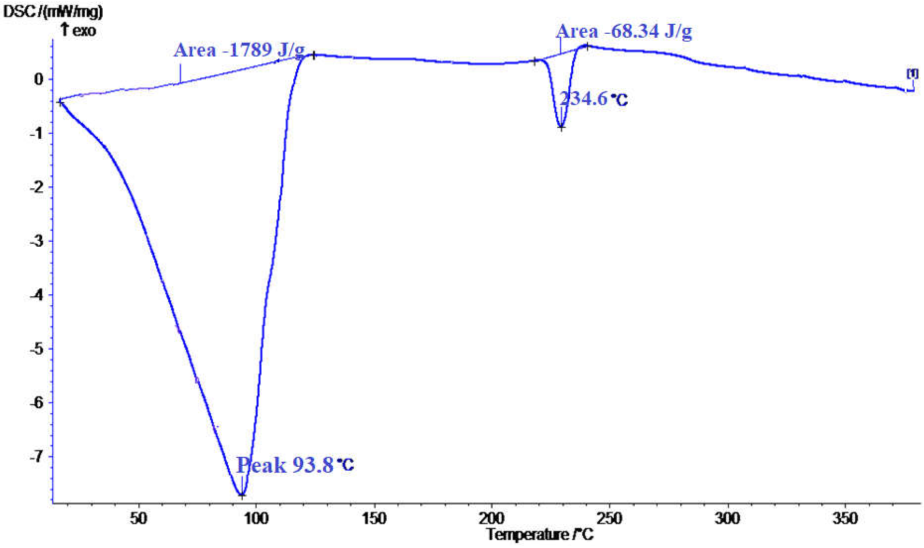

Fig 2. DSC analysis of the complex formed by cobalt (II) chloride with 2-naph and 1,2-phen

DSC analysis revealed that the thermal decomposition of the organic component in the complex varies, starting at 75°C and ending in the temperature range of 370°C. The DSC curves are explained by endo- and exo-effects, which indicate the breaking of existing chemical bonds and the formation of new ones during this process. According to the results, the nature of the DSC curves for the obtained complex is consistent. The first DSC curve of the complex exhibited an endothermic effect at 93.8°C with $\Delta Q = -1789$ J/g, while the second curve showed an endothermic effect at 226.8°C with $\Delta Q = -68.34$ J/g. The endothermic effect at 93.8°C is attributed to the separation of ethyl alcohol and chloride ions in the outer sphere, whereas the endothermic effect at 234.6°C leads to the melting of the substance and its subsequent decomposition. Based on the analysis of the research results, it was concluded that ethyl alcohol and chloride ions are located in the outer sphere of the complex compound. Based on the analysis of the research results, it was concluded that ethyl alcohol and chloride ions are located in the outer sphere of the complex compound.

When studying the IR spectra of ligands 2-hnaph, 1,2-phen, and the obtained complex, it was found that the IR spectra of 2-hnaph and 1,2-phen are identical to the data presented in the literature. The IR spectrum of the complex revealed absorption bands characteristic of additional functional groups. The absorption bands caused by the stretching vibrations of the C=O group (1820-1650 cm^{-1}) in the free ligand 2-hnaph molecule and the scissoring vibrations (1640-1550 cm^{-1}) characteristic of the -NH$_2$ group in the 1,2-phen molecule are also present in the complex compound. This is because the resulting complex compound contains a -C=N- group, which also gives absorption frequencies close to the aforementioned groups (1650-1600 cm^{-1}). The presence of absorption bands in the complex compound at 3100-3500 cm^{-1} indicates the presence of an -O-H group in the complex. Additionally, small changes were observed in the regions corresponding to the two substituted aromatic rings (1,2-phen) and the two substituted naphthalene rings (2000-1700cm^{-1}). The presence of absorption frequencies corresponding to the Me-O and Me-N bonds in the complex compound confirms the formation of the complex compound (Fig. 3).

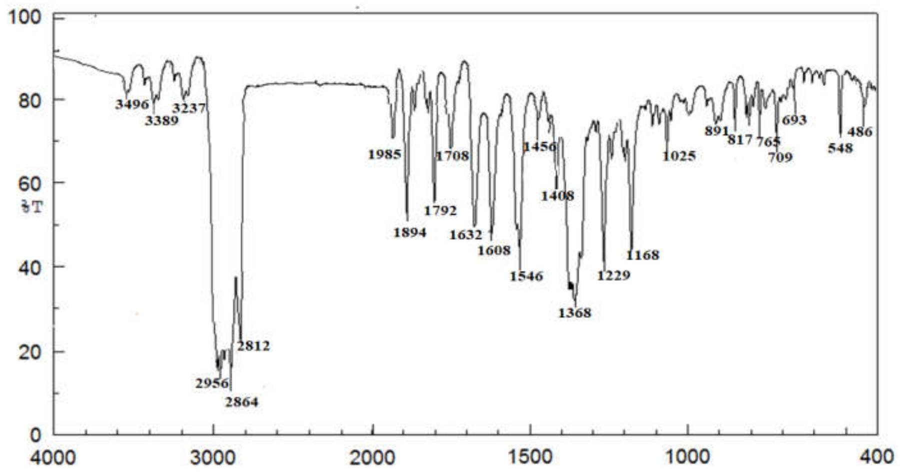

Fig 3. IR spectrum of the complex compound [Co (2-hnaph)$_2$ (1,2-phen)$_2$]·Cl-·C_2H_5OH.

We have summarized the data on the absorption lines observed in the IR spectra of ligands and newly synthesized complex compounds and presented them in Table 1.

Table 1. IR spectra of ligands and complex compounds

Vibration description →	**-OH**	**Aromatic and naphthalene group**	**-NH$_2$**	**ν_{as}(C=O)/ ν_s(C=O)**	**Me-O**	**Me-N**
Ligand and complex ↓						
2-hnaph	3185	2000-1700	-	1665, 1460, 1374	-	-
1,2-phen	-	2000-1700	1645	-	-	-
[Co(2-hnaph)$_2$(1,2-phen)$_2$]·Cl$^-$ ·C_2H_5OH	3100-3500	2000-1700	1632	1629, 1608, 1456, 1368	548	486

The changes in the melting point of the ligand and the resulting complex compound, as well as the results of DSC and IR spectroscopic analysis, allow us to conclude that a new complex compound based on cobalt chloride, 1,2-phen and 2-hnaph has been obtained.

The molecular and crystal structure of the synthesized metal complex compound was studied using X-ray diffraction analysis, which fully confirmed the data from DSC analysis and IR spectral analysis mentioned above. The composition of the synthesized complex was proven to be [Co(2-hnaph)$_2$(1,2-phen)$_2$]·Cl-·C_2H_5OH. It has been established that the complex compound is a new chelate complex compound with a mono-nuclear mixed ligand, and its molecular and crystal structure have been studied (Fig. 4).

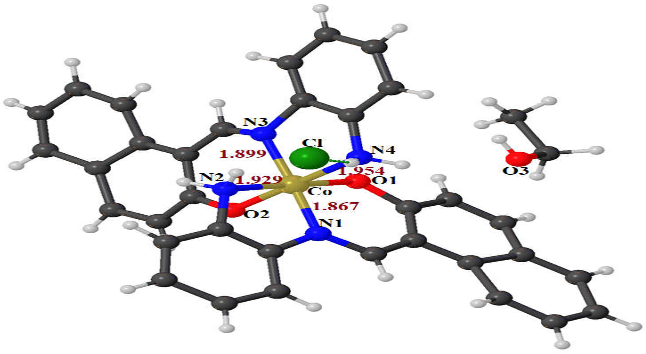

Fig 4. Molecular structure of the complex [Co(2-hnaph)$_2$(1,2-phen)$_2$]·Cl-·C_2H_5OH

In the newly obtained complex, the central atom has a distorted octahedral structure and is hybridized in the sp^3d^2 state. In the complex compound, 2-hnaph and 1,2-phen react with each other as a single ligand, binding to the central atom as a tridentate ligand, resulting in the formation of a chelate complex with six- and five-membered rings. A reaction occurs between the oxygen of the carbonyl group in the aldehyde form of 2-hnaph and the amino (NH_2) groups of 1,2-phen, leading to the release of one water molecule ($>C=O + -NH_2 \rightarrow >C=N- + H_2O$). The newly formed ligand is connected to the central atom through one oxygen atom and two nitrogen atoms. The O1-Co bond length is 1.899 Å, while the N1-Co and N2-Co bonds are 1.879 and 1.982 Å in length, respectively. Based on ligand field theory, during the process of saturating the primary and additional valences of the central atom, one amino group of 1,2-phen is coordinated with the central atom at a relatively longer distance.

Hirshfeld surface analysis of the newly obtained complex compound based on X-ray diffraction data was performed using the Crystal Explorer17.5 program [Turner et al., 2017]. The analysis revealed that the dnorm field volume is 777.67 Å3, with a surface area of 603.39 Å2, and dimensions ranging from -0.3859 (red) to 1.7735 arbitrary units (blue). The analysis was conducted by calculating the outer (d_e) and inner (d_i) distances to the nearest nucleus. On the Hirshfeld surface, points with low impact are shown in blue, while points with high impact are shown in red (Fig. 5). Analysis of two-dimensional fingerprint region plots revealed that H...O/O...H, H...H, and H...C/C...H interactions contribute the most to the Hirshfeld surface. In the complex compound, H...H interactions account for 47.2%, H...C/C...H for 34.4%, and H...Cl/Cl...H for 9.2%, which is the expected distribution for molecules dominated by oxygen atoms (Fig. 5).

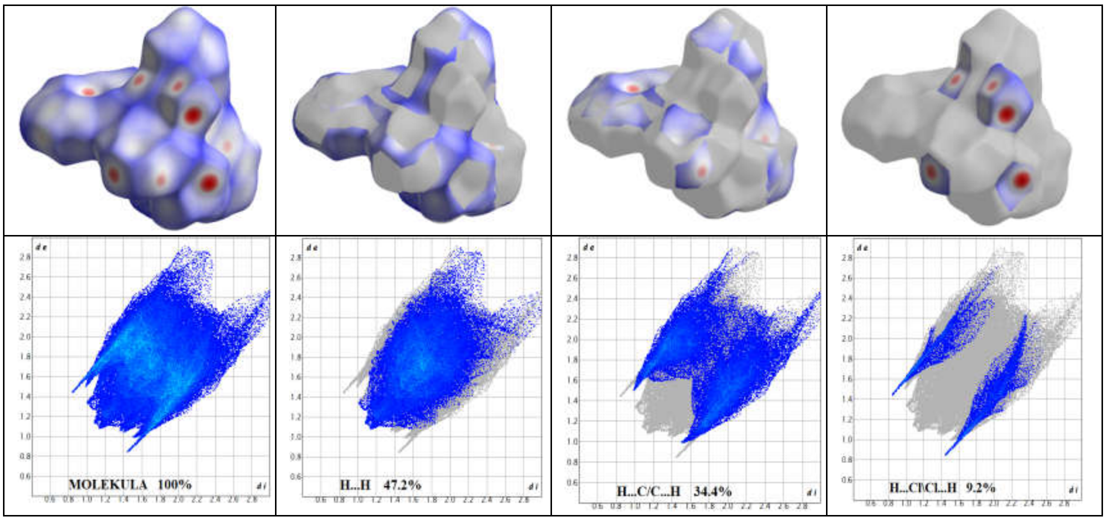

Fig 5. The three-dimensional Hirshfeld surface mapped according to dnorm and the two-dimensional fingerprint plot representing H...H, H...C/C...H, and H...Cl/Cl...H interactions in the complex crystal with the composition $[Co\ (2\text{-hnaph})_2(1,2\text{-phen})_2]\cdot Cl^-\cdot C_2H_5OH$

Among the remaining interactions in the complex compound, H...O/O...H (5.2%) and H...N/N...H (3.5%) interactions are also significant, while the contributions of C...C (0.3%) and N...C/C...N (0.1%) interactions are less substantial (Figure 6).

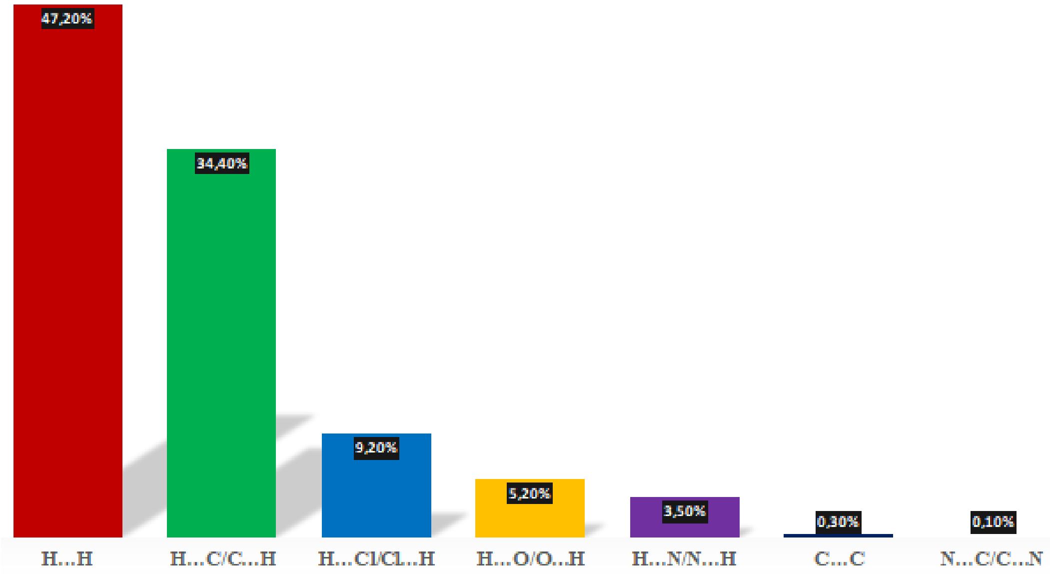

Fig 6. Hirshfeld fingerprint diagram of the complex with the composition
[Co (2-hnaph)$_2$(1,2-phen)$_2$]·Cl⁻·C_2H_5OH

Conclusion

As a result of the conducted research, a complex compound of 2-hnaph and 1,2-phen with cobalt (II) chloride was synthesized. The optimal synthesis conditions were determined to be intensive mixing of a mixture prepared from reagents (2-hnaph, 1,2-phen, and $CoCl_2{\cdot}6H_2O$) for 40-45 minutes at a temperature of 30-35°C, followed by leaving the resulting clear solution to evaporate at room temperature. The composition, molecular and crystal structures of the complex compound were determined using DSC analysis, IR spectroscopy, and XRD.

It was established that the obtained complex compound is an octahedral complex in the form of a mononuclear chelate. Analysis of the Hirshfeld surface revealed that H...H (47.2%) and H...C/C...H (34.4%) interactions constitute the main influences.

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