Cumhuriyet Sci. J., 44(2) (2023) 289-295
DOI: https://doi.org/10.17776/csj.1210668

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Synthesis and Characterization of Tetradentate Schiff Base Ligand Containing 3,4-Diamino Benzophenone and Investigation of Complex Formation with Ni (II), Cu (II) and Co (II) Metal Ions

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Research Article

History
Received: 27/11/2022
Accepted: 07/05/2023

ABSTRACT

Compound that is a novel tetradentate Schiff base ligand [(3,4-bis(((E)-4-(diethylamino)-2-hydroxybenzylidene)amino)phenyl)(phenyl) methanone] (1), 4-(diethylamino) It was synthesized by the reaction of (3,4-diaminophenyl)(phenyl)methanone with -2-hydroxybenzaldehyde. Complex reactions with Co(II) (1a), Cu(II) (1b) and Ni(II) (1c) metals were prepared based on the obtained Schiff base ligand. The synthesized Schiff base and its Ni(II), Cu(II) and Co(II) complexes were featured using FT-IR, UV-*vis*, photoluminescence, mass and ^{1}H and ^{13}C-NMR spectroscopy. The characterization processes show that the tetradentate Schiff base compound coordinates with metal ions, oxygen of the hydroxyl group and nitrogen of the azomethine group.

Keywords: Tetradentate Schiff base, Metal complex, Diaminobenzophenone.

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Introduction

The complex structures of Schiff base compounds with metals, obtained by the reaction of aromatic or aliphatic amines with substituted salicylaldehydes, represent a series of compounds that contain donor atoms such as nitrogen, sulfur and oxygen and have a wide study area [1–3]. Schiff base compounds, with intermolecular hydrogen bonding or proton transfer, are highly studied compounds in biochemistry [4]. Schiff bases and metal complexes have many applications in analytical, biological, pharmacology and industry [1,5]. Metal complexes synthesized from Schiff base compounds have an interesting side due to their antifungal, antibacterial and antitumor properties as well as their spectroscopic properties [6].

They coordinate with the transition metals O and N, which are involved in the biological activities required in living life. These structures play a very important role in life [7]. Schiff base compounds are accepted as the most important organic compound class because they have a wide range of studies in biological fields [7,8]. Extensive studies in this field of application have generated great interest in metal complexes derived from Schiff bases. Metal complexes obtained from Schiff bases are among the molecules with the most comprehensive study area due to their easy synthesis [9]. Some complexes of Schiff bases, which have applications in clinical and analytical fields, are molecules that model oxygen transport systems in biological activities [10]. It is known that complexes formed from tetradentate Schiff bases form stable complex structures with the N2O2 donor system [7,11]. Schiff base compounds induce substrate chirality, modulate metal-centered electronic events, and allow increased solubility and stability in homogeneous or heterogeneous catalysts [12].

The synthesis of aromatic Schiff bases has higher efficiency than aliphatic Schiff bases due to the partially stable strength of the imine bond given by the aryl groups attached to the N and C atoms. Metal complexes of imidazole-based aromatic Schiff bases have high performance in antimicrobial activity [11].

It is reported that metal complexes obtained from salen [bis(salicylidiene)ethylenediamine] compounds, which are a special type of Schiff bases, formed by the reaction of diamine-containing compound and aldehyde, are used as catalysts in most of the electrochemical reduction, molecular modification and reactions [13,14]. The best known of the salen compounds is bis(salicylaldehyde)ethylenediamine [15].

Salines have an acidic and tetradentate 2N, 2O) structure [16]. The application areas of metal complexes synthesized from salen compounds are quite wide. There are reactions in which they act as reactants and catalysts such as diels-Alder transformations, alkene epoxidation, electrochemical reduction, nucleic acid modification and hydroxyl addition [17,18].

Within the scope of this study, a new compound (1) of tetradentate Schiff bases, which is considered very valuable in terms of analytical and biological activity, was synthesized. Complex compounds with Co(II) (1a), Cu(II) (1b) and Ni(II) (1c) metals were synthesized using the obtained tetradentate salen ligand. The structural characterization of ligand and complex compounds was carried out in accordance with the literature.

Materials and Methods

The chemicals used in the study were obtained from institutional companies (Aldrich or Merck) and were used directly without any processing. Schiff base ligand (1) and complex structures (1a,1b,1c) were prepared in accordance with the literature. No purification process was applied. The synthesized salen-type Schiff base ligand and the structure of the compounds obtained from the reaction of this ligand and metals were characterized using spectroscopic methods such as FT-IR, ^{1}H-NMR, and ^{13}C-NMR. Structural analysis of materials, FT-IR (ATR) measurements, Perkin Elmer Spectrum 400 Spectrophotometer, light absorption properties, Hitachi U3900h UV-*vis* spectrophotometer, emission properties HORIBA Jobin Yvon Triax 550 CCD, Photoluminescence Spectrophotometer, structure magnetic determination of molecule and ^{1}H-NMR, and ^{13}C-NMR (NMR) Bruker AVANCE III 400 Mhz NMR Spectrophotometer was used. Graded cups were used in sample preparation. 1 cm optical path quartz cuvette was used in the analysis.

Synthesis of Schiff Base Ligand

In the synthesis of the salen type Schiff base compound; 2.83 mmol of 4-(diethylamino)-2-hydroxybenzaldehyde was dissolved in methanol. It was stirred on a magnetic stirrer until the dissolution process was complete. 1.41 mmol (3,4-diaminophenyl)(phenyl)methanone was added to the prepared solution. The new mixture was refluxed for 48 hours. After the solvent was removed, the product was left to dry under room conditions (Fig. 1).

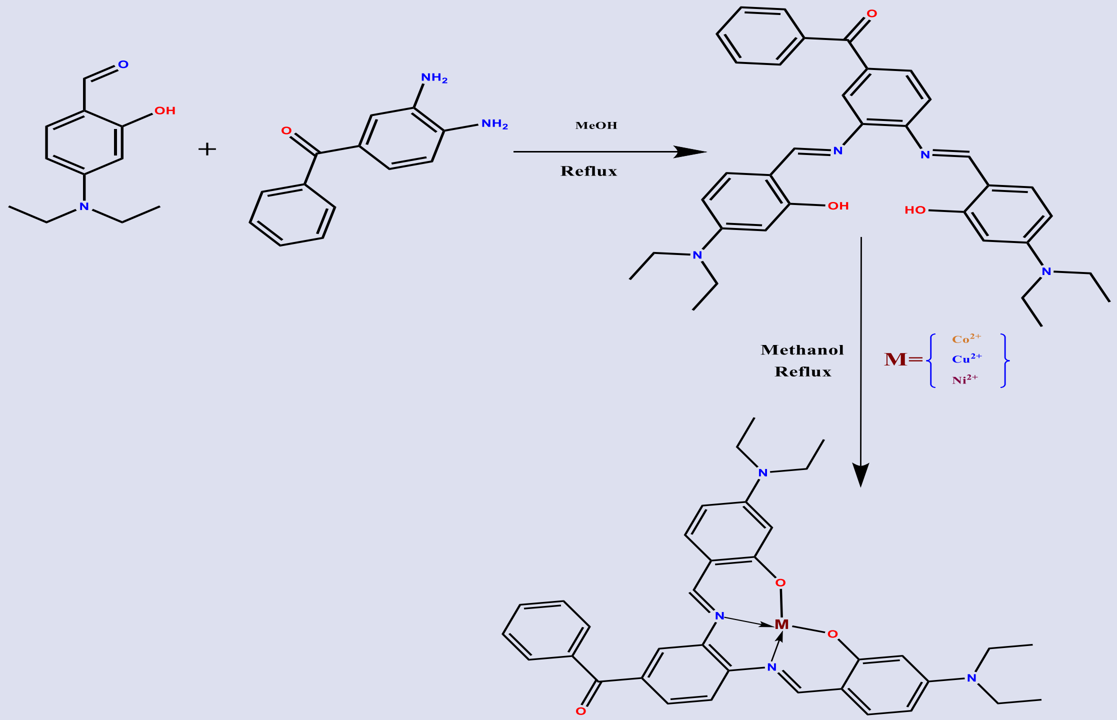

Figure 1 Synthesis of Schiff base ligand and metal complexes.

Synthesis of Metal Complexes

The complexation was performed by taking the salen type Schiff base ligand with the metal ion solution (1/1) ratio. The refluxing solutions of the ligand (0.53 mmol) in methanol (30 ml) were refluxed by adding $CoCl_2.6H_2O$ (0.53 mmol), $Cu(CH_3COO)_2$ (0.53 mmol) and $Ni(CH_3CO_2)_2{\cdot}4H_2O$ (0.53 mmol), respectively. The reaction solution was refluxed for 24 hours and then cooled to room temperature. The resulting product was filtered off and left to dry at room conditions (Fig. 1).

Data of the compounds synthesized within the scope of the work;

1: [(3,4-bis(((E)-4-(diethylamino)-2-hydroxybenzylidene)amino)phenyl)(phenyl)methanone], $C_{35}H_{38}N_4O_3$, Yield: 81%, Color: Dark red-viscous oil, Molecular Weight: 562.71, Mass spectrum (LC/MS, m/z): Calcd.: 562.29, found: 562.65 $[M]^{+}$. 562.29 (100.0%), Elemental Analysis (%):Calcd.: C, 74.71; N, 9.96; O, 8.53, found:C, 74.44; N, 9.67; O, 8.37

1a: $C_{35}H_{36}CoN_4O_3$, Yield: 88%, Melting point: 167 ^{c}C, Color: black powder, Molecular Weight: 619.63, Mass spectrum (LC/MS, m/z): Calcd.: 619.21, found: 619.27 $[M]^{+}$. 619.21 (100.0%), Elemental Analysis (%):Calcd.: C, 67.84; N, 9.04; O, 7.75, found:C, 67.57; N, 9.00; O, 7.44

1b: $C_{35}H_{36}CuN_4O_3$, Yield: 79%, Melting point: 205 °C, Color: brick color powder, Molecular Weight: 624.24, Mass spectrum (LC/MS, m/z): Calcd.: 623.21, found: 623.33 $[M]^+$. 623.21 (100.0%), Elemental Analysis (%):Calcd.: C, 67.34; N, 8.98; O, 7.69, found: C, 67.21; N, 8.38; O, 7.55

1c: Yield: $C_{35}H_{36}NiN_4O_3$, 84%, Melting point: 284 °C, Color: Bordeaux powder, Molecular Weight: 619.39, Mass spectrum (LC/MS, m/z): Calcd.: 618.21, found: 618.29 $[M]^+$. 618.21 (100.0%), Elemental Analysis (%):Calcd.: C, 67.87; N, 9.05; O, 7.75, found: C, 67.59; N, 9.01; O, 7.47

Results and Discussions

Within the scope of the study, firstly, the salen type Schiff base was synthesized. Complex structures were synthesized by reacting the obtained ligand with Co(II), Cu(II) and Ni(II) metals. Structural characterization of complexes synthesized from Salen-type Schiff base and its interaction with metals was performed by spectroscopic methods such as ^{1}H-NMR, ^{13}C-NMR, UV-*vis* and FT-IR analysis. In the results of the analyses performed, the spectroscopic data meet the expectations regarding the compounds and confirm the structures.

FT-IR Spectra of Schiff Base Ligand and Metal Complexes

When the FT-IR spectrum of the ligand is examined, the peak of the OH stretching vibration is around 3300 cm^{-1}, the peak of the azomethine (C=N) vibrations is at 1603 cm^{-1}, and the peak of the C=O stretching vibration is at 1645 cm^{-1}. As a result of the ligand binding with the metals, the peak of the OH stretching vibration disappeared. The peak belonging to the azomethine group is observed at 1611, 1610 and 1606 cm^{-1} for Co, Cu and Ni metals, respectively. The peak of C=O stretching vibrations is observed at 1637, 1649 and 1641 cm^{-1} for Co, Cu and Ni metals, respectively. In addition, weak peaks are observed in the range of 400-600 cm^{-1} because of the bonding of metal and O and N atoms. FT-IR data of ligand and complex structures are shown in Table 1.The disappearance of the absorbance peak of the OH group in the FT-IR spectrum of the ligand and the weak peaks in the range of 400-600 cm-1 after complexation with metals indicate that the targeted compounds were synthesized successfully.

Table 1 FT-IR data of ligand (1) and complex (1a, 1b, 1c) structures.

Compounds (cm^{-1})	*νC=O*	*νC=N*	*νC=C*	*νC-H Aliphatic*	*νO-H*	*νN-M*	*νO-M*
1	*1645*	*1603*	*1564*	*2971*	*3300-3500*	*-*	*-*
1a	*1637*	*1611*	*1557*	*2971*	*-*	*588*	*461*
1b	*1649*	*1610*	*1566*	*2968*	*-*	*586*	*457*
1c	*1641*	*1606*	*1557*	*2968*	*-*	*591*	*452*

The shifts in the spectrum of the azomethine group (-C=N) of the ligand at 1603 cm-1 show that the metal ions are bound through the (-C=N) group. FT-IR data of ligand and complex structures show that the metal is bound via phenolic oxygen and imino nitrogen. In addition, the FT-IR results of the study are consistent with the literature[19,20].

The FT-IR spectrum of the Schiff base ligand is given in Fig. 2 and the FT-IR spectra of the complex structures are given in (Fig. 3-5).

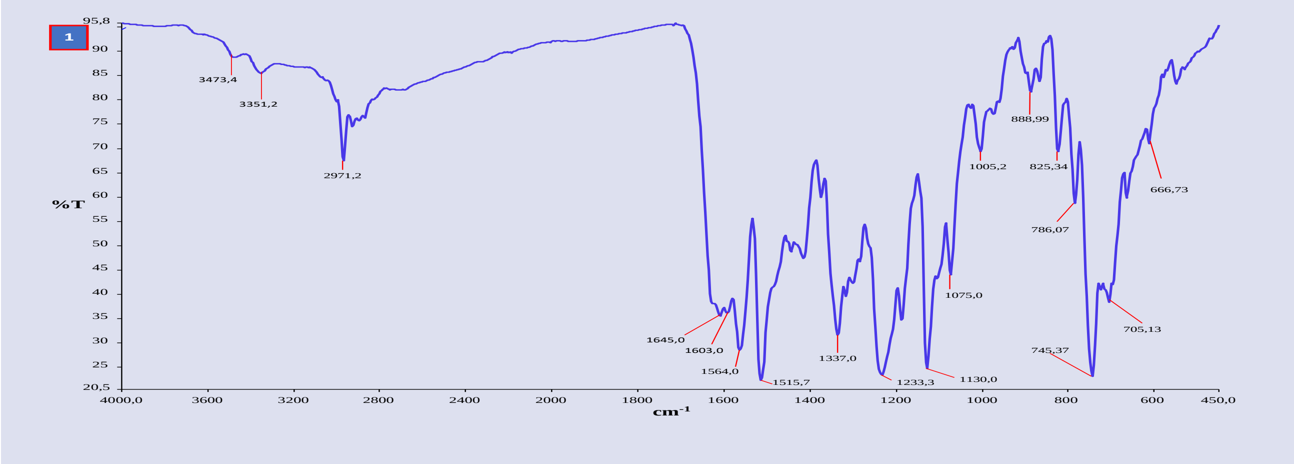

Figure 2 FT-IR spectrum of the Schiff base ligand.

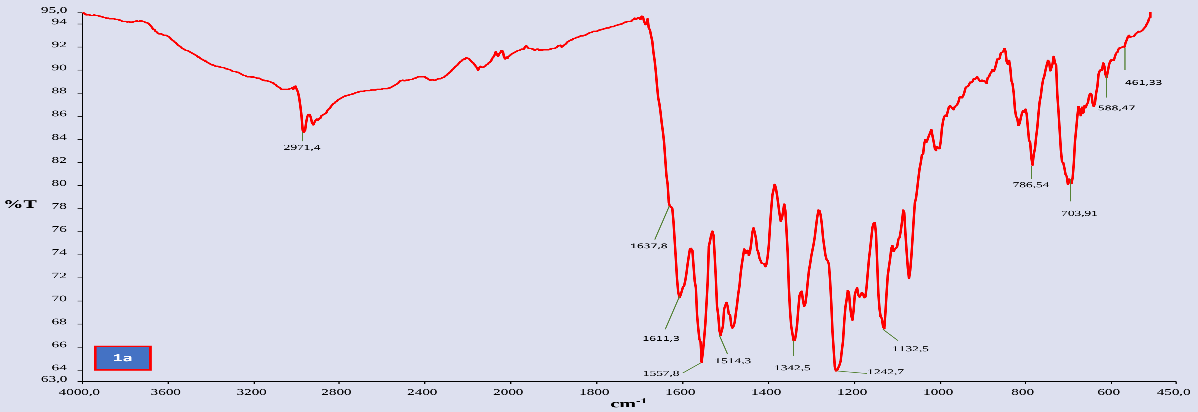

Figure 3 FTIR spectrum of the Co(II) - Ligand complex structure.

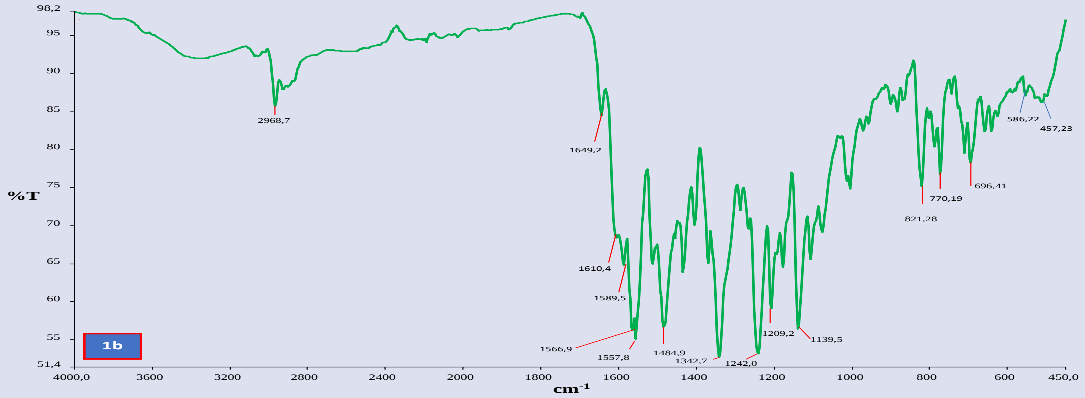

Figure 4 FTIR spectrum of the Cu(II) - Ligand complex structure.

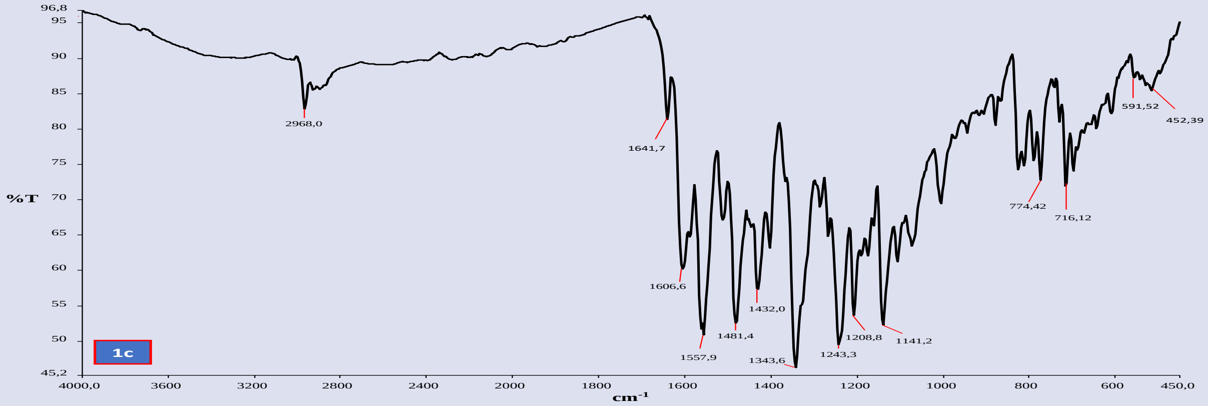

Figure 5 FTIR spectrum of the Ni(II) - Ligand complex structure.

^{1}H-NMR and ^{13}C-NMR Spectra of Compounds

When the ^{1}H-NMR [^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70, 9.44, 8.40, 8.27, 7.80, 7.73, 7.59, 7.48, 7.28, 7.21, 7.01, 6.28, 6.22, 6.03, 5.94, 3.34, 3.24, 3.20, 1.13, 1.11, 1.05]; The signal observed in the range of δ1.05-1.13 ppm is the signal of protons belonging to the ($-CH_3$) group. The signal observed in the range of δ3.20-3.34 ppm is the signal of protons belonging to the ($-CH_2-N-$) group. The signal observed in the δ5.94-8.40 ppm range is the signal of the protons in the ring structures. The signal of the proton of the azomethine (-HC=N-) group is seen at δ9.44 ppm. Signals of protons belonging to the (-O-H) group attached to the aromatic ring are seen at δ11.70 ppm.

In the ^{13}C-NMR spectrum (^{13}C NMR (101 MHz, $CDCl_3$) δ 194.30, 162.00, 160.00, 153.30, 145.63, 139.91, 136.90, 134.77, 134.20, 131.50, 129.86, 127.72, 125.79, 112.73, 100.48, 47.76, 12.85); The signal for the "C" atoms of the end ($-CH_3$) group is seen at δ12.85 ppm. The signal of "C" atoms belonging to the ($N-CH_2-$) group is located at δ47.76 ppm. The signal seen in the range of δ100.48-153.30 ppm are the signal belonging to the "C" atoms in the ring structures. Signal at δ160.00 ppm is signal belonging to the "C" atom of the azomethine (-HC=N-) group. Signal at δ162.00 ppm is signal belonging to the "C" atom of the (-C-OH) group. The signal at δ194.30 ppm is the signal for the "C" atom of the (-C=O) carbonyl group.

The signal of δ11.70 ppm protons of the OH group on the aromatic ring disappeared in the ^{1}H-NMR spectrum of the complex structure formed by the binding of the diamagnetic square plane structure Ni metal and the ligand. This indicates that the coupling (C-O-M) between the metal and the ligand has taken place. The data obtained within the scope of the study are similar to the data obtained from the " Tetradentate Schiff base ligands of 3,4-diaminobenzophenone: Synthesis, characterization and thermodynamics of complex formation with Ni(II), Cu(II) and Zn(II) metal ions" study of Asadi et al. in 2011[20].. In addition, the signal of the azomethine (-HC=N-) group proton at δ9.44 ppm is seen as a sharp singlet (δ9.05 ppm) after complexing with the metal. This indicates that in the presence of a planar ligand in the complex structure, binding occurs in a similar magnetic environment. Similarly, in the ^{13}C-NMR spectra, the signal of the "C" atom of the azomethine group at δ160.00 ppm was observed at δ163.67 ppm after complexation. The resulting shift indicates that the expected complexation has taken place.

UV-vis Spectra of Schiff Base Ligand and Metal Complexes

When the electron spectrum of the ligand is examined (Fig. 3), the intense band seen at λmax=345 nm can be attributed to molecular orbitals localized on the C=N group and π→π* transitions involving the benzene ring. The weak shoulder band seen around 400 nm can be attributed to the n→π* transition involving the C=N chromophore and the molecular orbitals of the benzene ring [20].

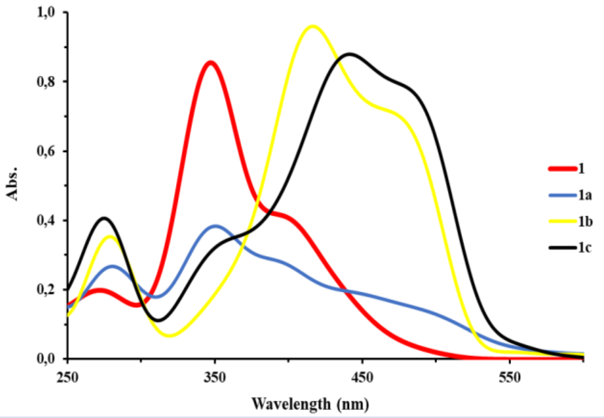

Figure 6 Uv-*vis* spectra of Schiff base ligand and metal complexes.

The absorbance bands of the ligand change when complexed with the metal (Fig. 3). As a result of the bonding of metal and nitrogen, the electron pair on the nitrogen stabilizes. In this case, the energy of the non-bonding orbital decreases and the transitions shifted to the longer wavelengths, or the absorbance band seen can be attributed to the π→π* transition, which includes the absorbance bands of the metal-ligand bond. Even at high concentration of complexes, d-d bands are hidden by a dense charge transfer band (Metal Ligand Charge Transfer) (Table 2).

Table 2 Ligand (1) ve kompleks (1a, 1b, 1c) yapıların elektronik spektral verileri.

Compounds	π→π* (C=N) (nm)	n→π* (nm)	π→π* (Metal-Ligand transition) (nm)
1	345	400	-
1a	350	-	465
1b	415	-	475
1c	440	-	480

Photoluminescence Spectra of Schiff Base Ligand and Metal Complexes

The ligand (1) showed a redshift with a 200 nm stokes shift value in response to the absorbance of π-π* transitions at 345 nm and gave emission at 545 nm. It showed a weak emission band at 740 nm with a stokes shift of 340 nm versus the absorbance at 400 nm of n-π* transitions. Photoluminescence spectra of Schiff base ligand and metal complexes are given in Fig. 4. Excitation and Emission spectra of Schiff base ligand and metal complexes are given in (Fig. 8-11).

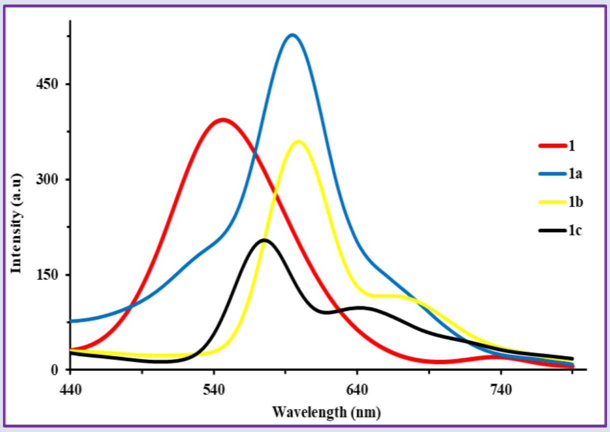

Figure 7 Photoluminescence spectra of Schiff base ligand and metal complexes.

The absorbance of the complex structures formed by the ligand with Co (1a), Cu (1b) and Ni (1c) metals at 350, 415, 440 nm of π-π* transitions, respectively, is 595, 600 with a stokes shift of 245, 185, 135 nm, respectively. showed a redshift tendency with the emission bands it showed at 675 nm. Similarly, the metal-ligand π-π* transitions exhibited a redshift by showing emission bands at 675, 685, 650 nm with a stokes shift of 210, 210, 170 nm versus absorbances at 465, 475, 480 nm. Absorption, photoluminescence and Stokes shift data of ligand and complex structures are given in Table 3.

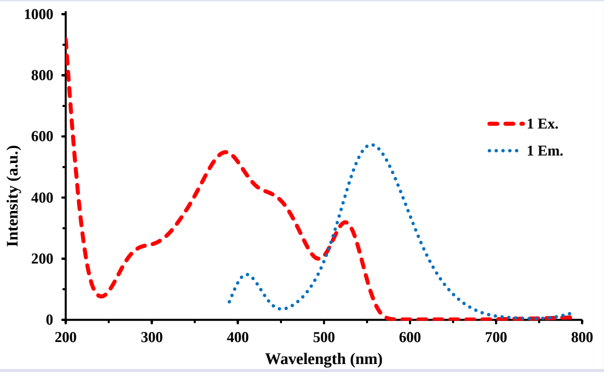

Figure 8 Excitation and Emission spectrum of Schiff base ligand

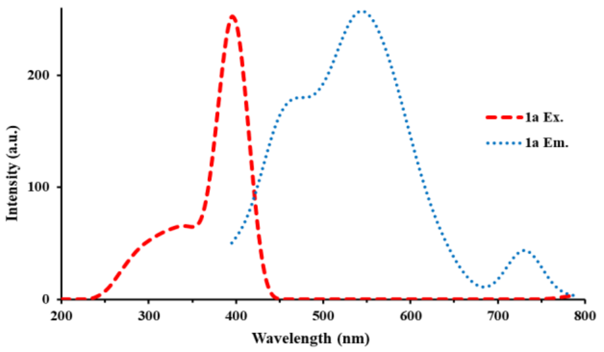

Figure 9 Excitation and Emission spectrum of the Co(II) - Ligand complex structure.

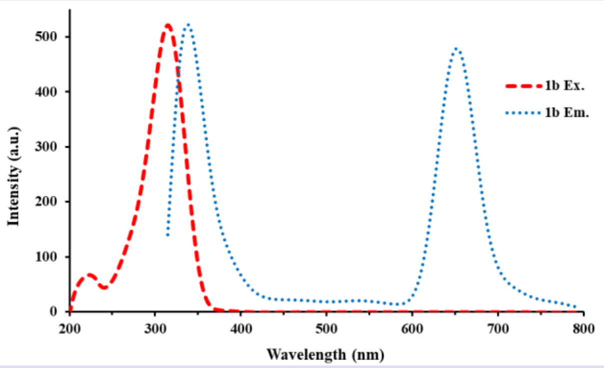

Figure 10 Excitation and Emission spectrum of the Cu(II) - Ligand complex structure.

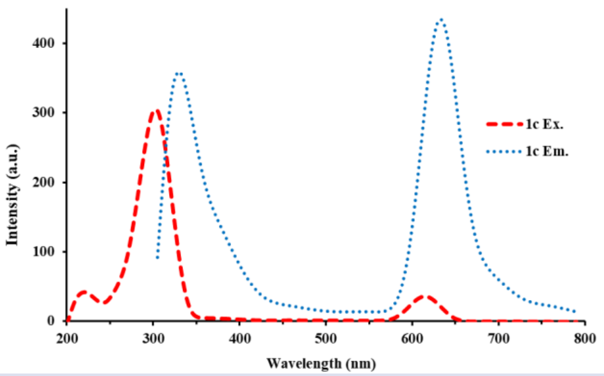

Figure 11 Excitation and Emission spectrum of the Ni(II) - Ligand complex structure.

Table 3 Absorption, photoluminescence, and Stokes shift data of ligand (1) and complex (1a, 1b, 1c) structures.

Compounds	λmax, nm		
	Absorption	Emission	Stokes shifts
1	345, 400	545, 740	200, 340
1a	350, 465	595, 675	245, 210
1b	415, 475	600, 685	185, 210
1c	440, 480	575, 650	135, 170

Conclusions

Elemental analyzes of the complexes obtained as a result of the reaction of Salen type Schiff base ligand and the reaction of this ligand with Co(II), Ni(II) and Cu(II) metals were made by FT-IR, ^{1}H, ^{13}C NMR, UV-*vis* methods. The OH Group peak at 3300-3500 cm^{-1} in the FT-IR spectrum of the Schiff base ligand was not seen in the FT-IR spectra of the complex structure consisting of metal-ligand interaction formation. This indicates that the associations between ligand and metal are lost due to chelation. From the FT-IR spectra, it was concluded that the ligand (**1**) coordinates to the metals via two azomethines N, and the Schiff base with the N2O2 region acts as a tetradentate ligand, with two phenolic OHs bonding to the metal leaving its proton. Absorption bands seen around 450 nm in the UV-*vis* spectrum of complex structures belong to the metal-ligand charge transition. This shows that the salen type Schiff base ligand and metal ions interact, and targeted complex structures are formed.

Conflicts of interest

There are no conflicts of interest in this work.

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