

Nickel (II) Complexes Synthesis, Characterization and its Larvicidal, and Antifeedant Activities

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Abstract

In this study the synthesis of Nickel complexes with various organic ligands by using ethanol as a solvent. This method offers efficient and mild reaction conditions. The synthesized complexes were characterized by UV- Visible and IR spectroscopy. The synthesized complexes are also evaluated for larvicidal, antifeedant, and mosquito larval growth and regulation activities. Complex **1b** was highly active against *Culexquinquefasciatus* LD₅₀ value of 18.52 µg/ml than complexes **1a** and **1c** with the LD₅₀ value of 59.97 and 84.73 µg/ml. Among the complexes **1a-1c** the complex **1c** was less active in contradiction of *Culexquinquefasciatus* with the LD₅₀ value of 84.73 µg/ml respectively. Complex **1a** exhibited high toxicity associated with former complexes **1b** and **1c**. Complex **1a** produced 80% mortality in 24hr at 100 µg/ml respectively. Toxicity was restrained as death percentage at 24hr. Complex **1b** produced 43% mortality in 24hr at 100 µg/ml. Among the synthesized complexes **1a-1c** the complex **1a** was highly active with the LD₅₀ value of 46.08 µg/ml.

Keywords

Nickel complexes, *Culexquinquefasciatus*, Larvicidal activity, Antifeedant activity.

Introduction

The key division of inorganic chemistry, coordination chemistry, which would be the analysis of the structures, configurations and transformations of complexes produced by ligands coordinated with a transition metal base, can be interrelated with a large portion of inorganic chemistry. In the erection of molecular substances, transition metal complexes play a key role, that show scarce conducting and magnetic properties and find applicability in material chemistry, supramolecular and biochemistry[1-4]. Due to their anticarcinogenic, antibacterial and antifungal properties, nickel (II) complexes of macrocyclic ligands are biologically essential and noteworthy [5]. They have also been checked for their therapeutic properties since they maintain

a certain amount of cytotoxic activity[6]. In metalloenzyme processes, particularly therapeutic enzymes, the electron transfer processes of metal ions are of massive importance. The redox properties include oxidation and previously recorded decreases in the central metal ion with ligands[7]. Due to the existence of the solvent, context electrolyte and the composition of the chelating ligand with the complexes, the redox potential of the Ni (I)/Ni (II) and Ni (II)/Ni (III) couples has been shown to be distinctly pretentious[8].

As templates of redox active nickel-including enzymes [9-10] and as electrocatalysts [11-12], nickel (II) compounds that can be reversibly reduced to nickel (I) species have been intriguing. Ni(I) should not be assisted by each form of ligand framework, and Ni(0) is in several cases explicitly modelled on the reduction of a Ni(II) complex, such as $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. The bulk of Ni(I) species with modest O and N ligands are thermodynamically and kinetically insecure with Ni(0) and Ni(II)[13-14] unequal reverence. Another challenge is that a Ni (II) complex's one-electron decrease will moderately contribute to a Ni (II) being a stable anion radical than a Ni (I) complex. The respectable approach of differentiating such organisms is EPR spectroscopy, with monomeric Ni(I) complexes classically exchanging greatly anisotropic spectra and radical Ni(II) species possessing isotropic spectra of $g \sim 2.0$ [13-14].

The characterization and coordination activity of organic ligands with its metal ion nickel (II) was stated in this paper. The factors that alter the structure of complexes and its geometries have been justified and structures anchored on the theoretical of magnetic moments and certain other spectral findings have been established.

Experimental

Chemicals and reagents

All of the chemicals were bought from Merck, Sigma-Aldrich, and used without further cleaning. Pre-use solvents were dried and distilled. For analytical TLC, Merck's pre-coated silica gel plates with a fluorescent indicator have been used. Chromatography of the flash column using silica gel (Merck). For TLC and column chromatography, ethyl acetate-hexane was used as the eluting solvent. In open capillary tubes, melting points have been measured and were uncorrected. On a Shimadzu UV - 1280 (200-800 nm) spectrometer, the UV-Visible spectrum

was recorded. On a Shimadzu 8201pc (4000-400 cm⁻¹) spectrometer, the FT-IR spectra (KBr) are recorded.

Synthesis of Bis-(N-aminoethylethanolamine)-Nickel (II) Complex (1a).

The compounds N-aminoethylethanolamine (0.01mol, 1mL) in 5ml ethanol is stirred in a magnetic stirrer with NiCl₂.4H₂O (0.005mol, 1g) in 5mL ethanol for one hour at 60°C. Skybluecoloured precipitate was formed. The solvent ethanol was evaporated under vacuum. The crude product was confirmed through TLC. The product was further purified by recrystallization from ethanol.

Bis-(N-aminoethylethanolamine)-Nickel (II) chloride(1a).

Skyblue solid; mw: 394.01; mp: >360°C; UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (abs): 225 (0.21), 359 (0.02); IR (cm⁻¹): 3426.21 (OH), 3238.61 (NH), 2925.86 (CH), 1467.97 (C-N) 1063.84 (C-O), 789.99 (CHbend), 630.03 (Disubstituted); Elemental analysis: Calculated. for: C₁₂H₃₂Cl₂NiN₄O₂: C, 36.14; H, 8.09; N, 14.22 %; Found: C, 36.12; H, 8.10; N, 14.23; %

Synthesis of Bis-(3-methyl-1H-pyrazol-5(4H)-one)-Nickel (II) complex (1b).

The compounds 3-methyl-1H-pyrazol-5(4H)-one (0.01mol, 0.98g) in 5mL ethanol is refluxed over a water bath in a magnetic stirrer with NiCl₂.4H₂O (0.005mol, 1g) in 5ml ethanol for three hours at 60°C. Then 30ml of 10% NaOH solution was added. Pale green coloured precipitate was formed. It is filtered and dried. The product was confirmed through TLC. The product was further purified by recrystallization from ethanol.

Bis-(3-methyl-1H-pyrazol-5(4H)-one)-nickel (II) (1b)

Pale green solid; mw: 353.86; mp: >360°C; UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (abs): 252 (1.42); IR (cm⁻¹): 3433.42 (NH), 2928.32 (CH), 1631.73 (C=O), 1458.31 (C-N) 820.93 (CHbend), 626.65 (Disubstituted); Elemental analysis: Calculated. For C₁₀H₁₆Cl₂NiN₄O₂: C, 33.94; H, 4.56; N, 15.83; %. Found: C, 33.96; H, 4.55; N, 15.82; %.

Synthesis of Bis-(1,3-cyclohexanedione)-Nickel (II) complex (1c).

The compounds 1,3-cyclohexanedione (0.01mol, 1.12g) in 5mL ethanol is refluxed over a water bath in a magnetic stirrer with NiCl₂.4H₂O (0.005mol, 1g) in 5mL ethanol for three hours

at 60°C. Then 30ml of 10% NaOH solution was added. Green coloured precipitate was formed. It is filtered and dried. The product was confirmed via TLC. The product was further purified by recrystallization from ethanol.

Bis-(1,3-cyclohexanedione)-nickel (II) (1c)

Pale green solid; mw: 282.95; mp: >360°C; UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (abs): 225 (3.95), 244 (0.79), 271 (0.85) and 276 (0.87); IR (cm⁻¹): 2940.85 (CH), 1639.52 (C=O), 1186.56 (C-O), 865.55 (CHbend), 610.95 (disubstituted moiety); Elemental analysis: Calculated. For C₁₂H₁₆NiO₄: C, 50.94; H, 5.70; %. Found: C, 50.95; H, 5.69; %.

Larvicidal activity

On a dead/alive basis, judgments were made. Evaluations are based on a 0-100 percentage scale, which is 0 equal to no action and 100 equal to absolute destruction. The bioassay was replicated three times and an average of these replicates is the product of bioactivity. The values are contrasted with the favourable Permethrin control values. Using probit study, the LD50 values of certain active title compounds were analysed and the findings were tested using the programme SPSS v16.

Larvicidal Activity against Mosquito (*Culexquinquefasciatus*).

At the preliminary test concentration of 100µg/mL against the fourth-instar *Culexquinquefasciatus*, the larvicidal operation was evaluated by the water dipping system under conditions of (27 ±2) °C, 10:14 photoperiod (light:dark), and 50-70 percent relative humidity. 24 hours after treatment, all test beakers holding twenty larvae of *Culexquinquefasciatus* were tested. The findings indicate an overall mortality percentage.

Antifeedant activity

For assessing ichthiotoxic ability, fingerlings (1.5–2.0 cm) of marine adapted *Oreochromismossambicus* were used. Ten fingerlings, each comprising one L of sea water and a chosen concentration of compound, were introduced in experimental and control glass bowls. Immediate reflexes and mortalities for the first 6 hours and then at 1 hours for the next 12 hours

were consistently observed. The amount of dead and live fish was counted after 24 hours of exposure. The results were recorded by average percentage mortality.

Results and Discussion

The synthesis of the complexes **1a-1c** was prepared in conjunction with the synthesis protocols shown in Schemes **1-3**. The condensation process using N-aminoethylethanolamine associated with $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ in the ethanol medium was synthesised by Complex 1a (Scheme 1). Complex 1b was synthesised with 3-methyl-1H-pyrazol-5(4H)-one reacted by condensation with $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$. (Scheme 2). Complex 1c was formulated by 1,3-cyclohexanedione reacted by condensation (Scheme 3) with $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$. The compounds were verified by UV and IR spectra recording.

A wavelength spectrum of 200 to 800 nm was analysed with the UV-VIS model of complex 1a. At 225 and 359 nm, three main bands were noticed with absorbance values of 0.21 and 0.02 respectively.

To classify the presence of functional groups in the complex, the FT-IR range of complex 1a was carried out on the basis of peak values in the field of infrared radiation. At KBr cm^{-1} the main bands were observed: 3426.21, 3238.61, 2925.86, 1467.97, 1063.84, 789.99 and 630.03. The peak at 3426.21 cm^{-1} reveals the absorption resulting from stretching Ni-OH. The peak at 3238.61 cm^{-1} reveals the absorption resulting from stretching Ni-NH. The peak at 2925.86 cm^{-1} reveals the absorption resulting from stretching C-H. The peak of 1467.97 cm^{-1} is equal to the C-N stretching frequency. The 1063.84 cm^{-1} peak confirms the extended C-O bond vibration in the flow of alcohol. The peak at 789.99 cm^{-1} shows the aliphatic C-H bonds' bending vibration. The peak in the aliphatic compound at 630.03 cm^{-1} refers to the disubstituted moiety. In addition, the spectrum also registered some poor absorption bands.

An excitation wavelength of 200 to 800 nm was analysed with the UV-VIS profile of complex 1b. At 252 nm with absorbance values of 1.42 respectively, one major band was noticed

To classify the functional groups present in the complex, the FT-IR spectrum of complex 1b was carried out on the basis of the peak values in the infrared radiation area. At KBr cm^{-1} : 3433.42, 2928.32, 1631.73, 1458.31, 820.93 and 626.65, the main bands were observed. The

peak at 3433.42 cm^{-1} reveals the absorption resulting from stretching Ni-NH. The peak at 2928.32 cm^{-1} reveals the absorption resulting from stretching C-H. At 1631.73 cm^{-1} , the peak correlates to the presence of the stretching frequency of Ni-CO. The peak at 1458.31 cm^{-1} is the same as the C-N stretching frequency. The highest at 820.93 cm^{-1} shows the aliphatic C-H bonds' bending vibration. The peak in the aliphatic compound at 626.65 cm^{-1} refers to the disubstituted moiety. In addition, the spectrum also registered some poor absorption bands.

A wavelength spectrum of 200 to 800 nm was analysed with the UV-VIS profile of complex **1c**. At 225, 244, 271 and 276 nm, four main bands were noted, with absorbance values of 3.95, 0.79, 0.85 and 0.87 respectively.

To classify the functional groups present in the complex, the FT-IR spectrum of complex **1c** was carried out on the basis of the peak values in the infrared radiation field. At VKBr cm^{-1} : 2940.55, 1639.52, 1186.56, 865.55 and 610.95.80., the main bands were detected. The peak at 2940.55 cm^{-1} reveals the absorption resulting from stretching C-H. The peak correlates to the presence of the Ni-CO stretching frequency at 1639.52 cm^{-1} . At 1186.56 cm^{-1} , the peak correlates to the C-O stretching frequency. The peak at 865.55 cm^{-1} demonstrates aliphatic C-H bonds bending vibration. The peak in the aliphatic compound at 610.95 cm^{-1} refers to the disubstituted moiety. In addition, the spectrum also registered some poor absorption bands.

Magnetic Susceptibility Measurement

The magnetic susceptibility of the Gouy process using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant for all nickel complexes at room temperature was noted and listed in Table 1. After adding diamagnetic corrections for the ligand components with pascal constants, the individual magnetic moments were determined. For the nickel complexes, the room temperature μ_{eff} values were 1.71–1.88 B.M. With the octahedral geometry around the central metal ion, the magnetic susceptibility of the complexes is accurate.

Larvicidal activity

Complex **1b** was highly active against *Culexquinquefasciatus* LD_{50} value of 18.52 $\mu\text{g/ml}$ than complexes **1a** and **1c** with the LD_{50} value of 59.97 and 84.73 $\mu\text{g/ml}$. Among the complexes **1a-1c** the complex **1c** was less active in contradiction of *Culexquinquefasciatus* with the LD_{50} values of 84.73 $\mu\text{g/ml}$ respectively. The synthesized complex **1b** was highly active and **1a** was moderately active compared to the positive control *Permethrin* with the LD_{50} value of 60.03 $\mu\text{g/ml}$. The results are abridged in Table 2.

Antifeedant activity (Ichthyotoxicity activity)

Complex **1a** displayed extraordinary toxicity related with other complexes **1b** and **1c**. Complex **1a** produced 80% mortality in 24hr at 100 µg/ml respectively. Toxicity was calculated at 24hr as the number of deaths. Complex **1b** produced 43% mortality in 24hr at 100 µg/ml. The results are shortened in Table 3. Among the manufactured complexes **1a-1c** the complex **1a** was extremely active with the LD₅₀ of 46.08 µg/ml.

Conclusion

It can be inferred from the present analysis that the potency of the Nickel complex with organic ligand (3-methyl-1H-pyrazol-5(4H)-one) showed significant activity in larvicidal and also less toxic in antifeedant, bioassays. Complex **1b** showed significant activity against mosquito larvae compared with positive control and complex **1a** showed significant antifeedant activity. Therefore, these complexes might be a potential pesticide for *Culex quinquefasciatus* mosquito larvae.

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Scheme 1. One-pot two component synthesis of Bis-(N-aminoethylethanolamine)-nickel (II) chloride (1a).

Scheme 2. One-pot two component synthesis of Bis-(3-methyl-1H-pyrazol-5(4H)-one)-nickel (II) (1b).

Scheme 3. One-pot two component synthesis of Bis-(1,3-cyclohexanedione)-nickel (II) (1c).

Table 1. Magnetic moment values of the Nickel (II) complexes (**1a-1c**)

Complex	Magnetic moment (B.M.)
1a	1.84
1b	1.88
1c	1.71

Table 2. Larvicidal activity of synthesized complexes (**1a-1c**)

Comp.No.	Mortality (%)Room temp				LD ₅₀ (µg /mL)
	Concentration(µg /mL) ^a				
	100	50	25	10	
1a	80±1.78	42±0.67	20±1.87	0±0.00	59.97
1b	100±0.00	80±1.42	68±1.54	34±1.23	18.52
1c	60± 1.64	30± 0.54	10± 0.34	0± 0.00	84.73
Permethrin	-	-	-	-	60.03
DMSO	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0± 0.0

^aValue were the means of three replicates ± SD.

Table 3. Antifeedant activity of synthesized complexes (**1a-1c**)

Comp.No.	Mortality (%)Room temp				LD ₅₀ (µg /mL)
	Concentration(µg /mL) ^a				

	100	50	25	10	
1a	80±1.54	60±0.56	40±1.21	18±1.87	46.08
1b	43±0.87	20±0.07	0±0.00	-	>100
1c	60±2.12	44±1.47	20±0.67	0±0.00	75.96
DMSO	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0± 0.0

^aValue were the means of three replicates ± SD.

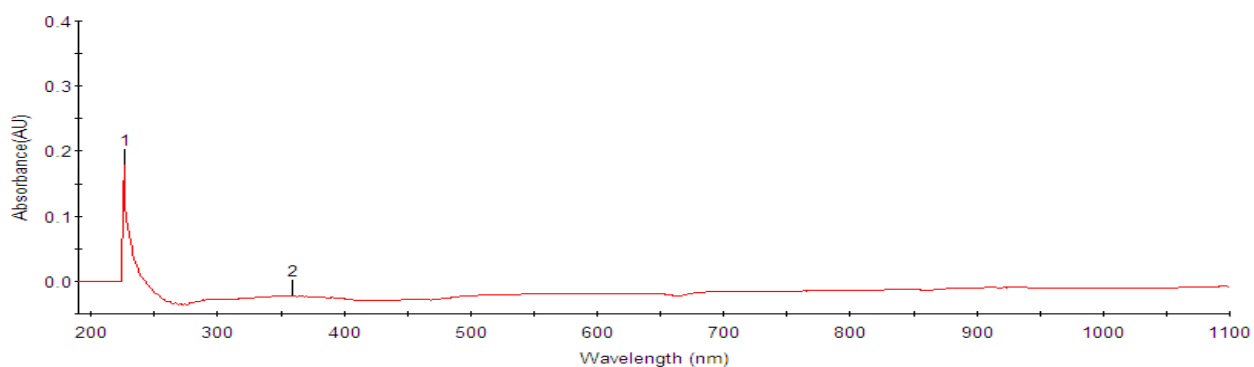


Figure. 1. UV spectrum of complex 1a.

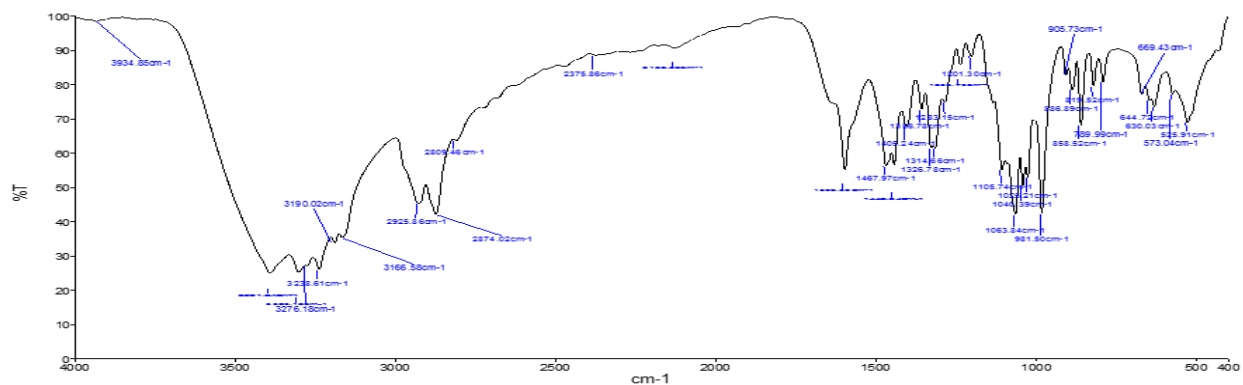


Figure. 2. IR spectrum of complex 1a.

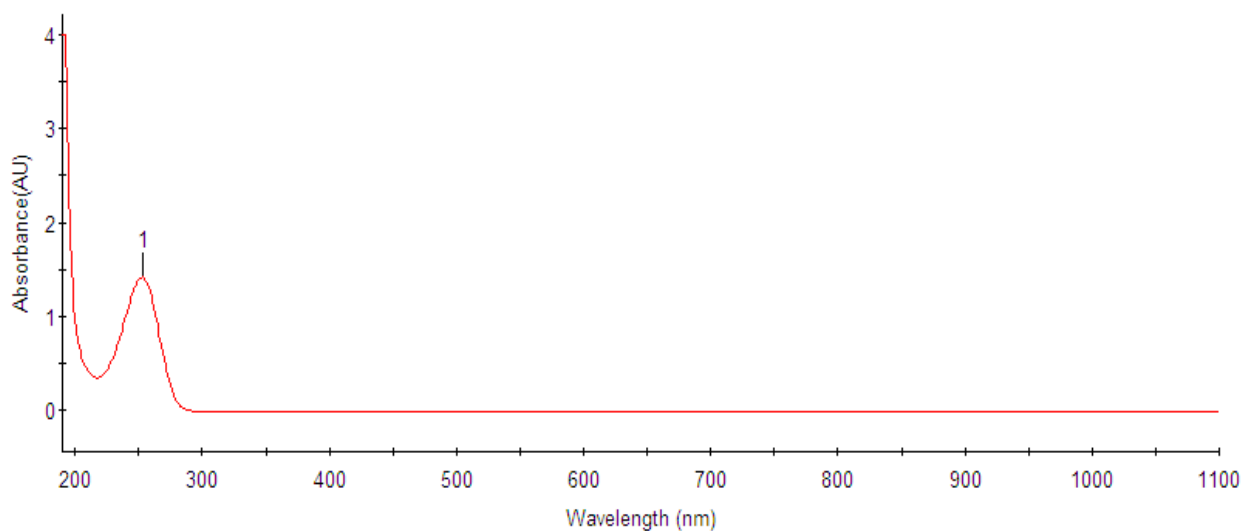


Figure 3. UV spectrum of complex 1b.

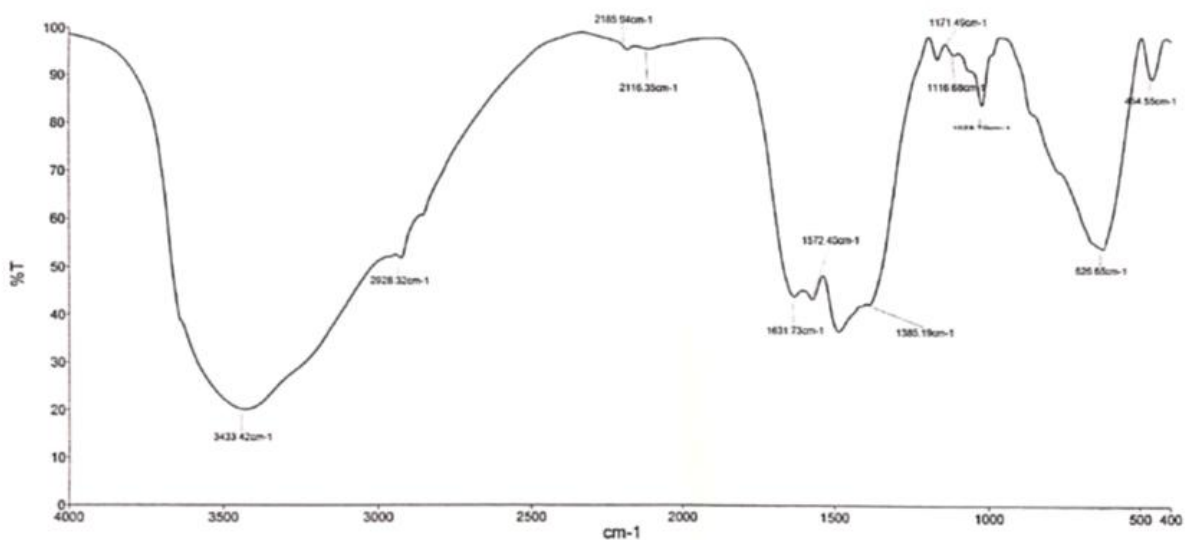


Figure 4. IR spectrum of complex 1b.

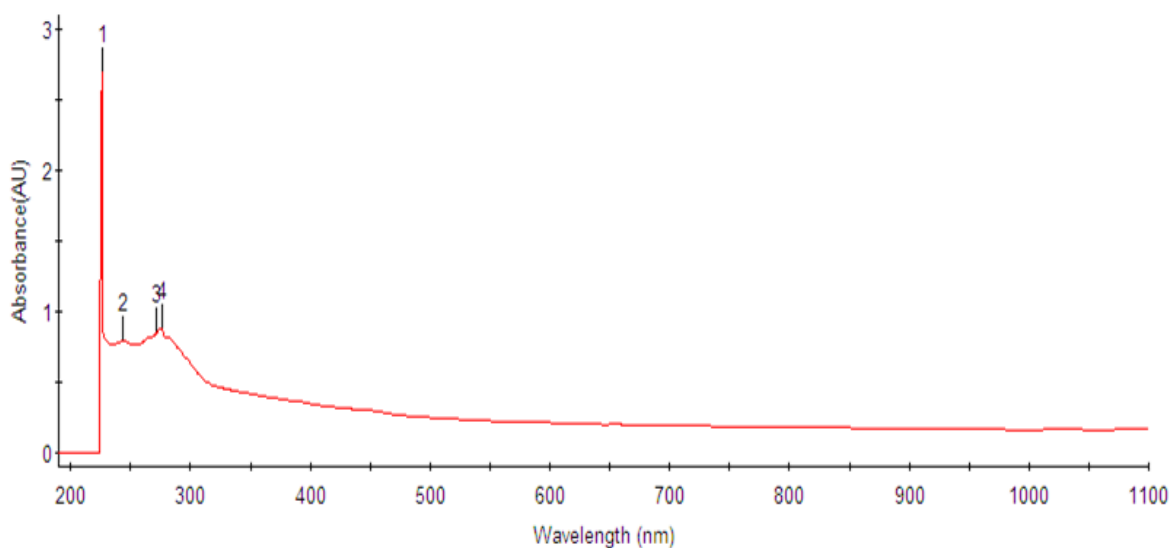


Figure. 5. UV spectrum of complex 1c.

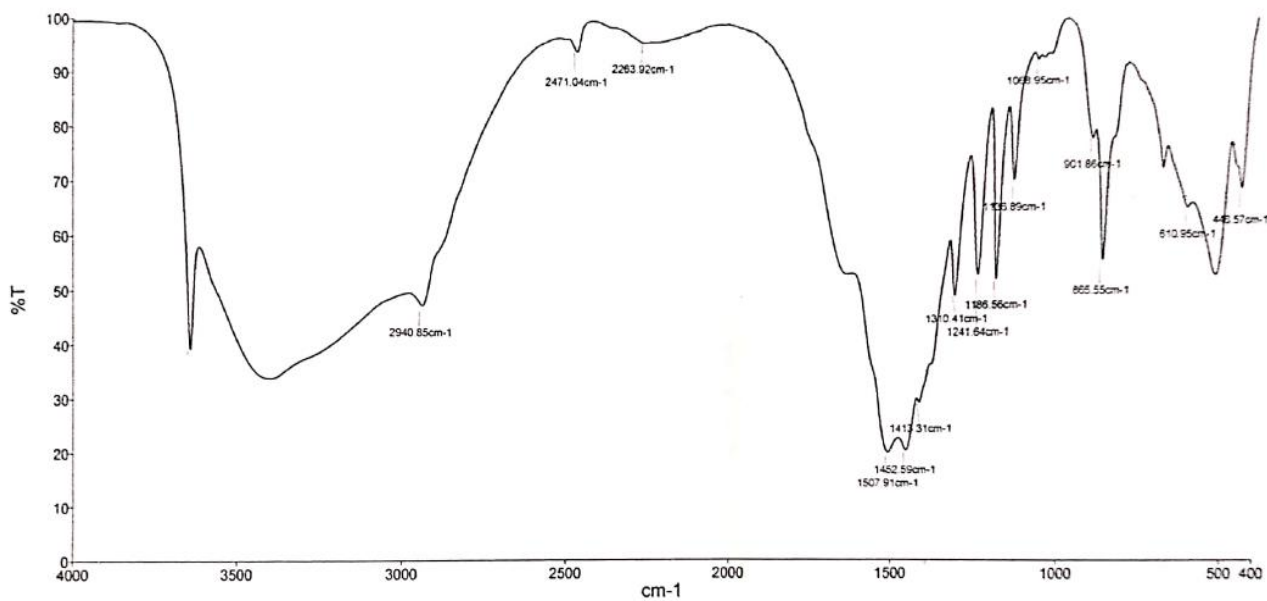


Figure. 6. IR spectrum of complex 1c.