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Synthesis and Characterization of Mixed Ligand Complexes of Co(II) And Ni(II) with Hippuric Acid, Ammonium Thiocyanate and Hydroxyl Ammonium Chloride

*Gongden J. J, Usman N. U, Uduah V, Lohdip Y.N and Solomon L.D
Department of Chemistry, Faculty of Natural Sciences, University of Jos, Nigeria

Abstract:- Mixed ligands/Coordinate complexes are still largely investigated. This is because of their very wide range of uses and applications.The mixed ligand complexes of Co (II) and Ni (II) with hippuric acid, ammonium thiocyanate and hydroxyl ammonium chloride were synthesized in a 1:2:2:2 stoichiometric ratio by a modified direct combination method. The resulting complexes were characterized by preliminary tests and spectroscopic methods. The physicochemical parameters such as melting point, boiling point, pH, electrical conductivity and colour of the complexes were determined. The solubility in water, ethanol, and methanol were also studied at 25°C. The characterization of the prepared mixed-ligand complexes was done using FT-IR, UV-VIS, XRD, crystallography and XRF spectroscopic methods. The percentage yield obtained were 42.90% and 40.70% Co (II) and Ni(II) complexes respectively. Both complexes were soluble in methanol, but slightly soluble in water and ethanol at 25°C.This implies that the ionic complexes formed are generally polar, since they are quite soluble in polar solvents such as water, ethanol and methanol. The complexes were acidic with pH values of 3.24 and 3.30 for Co(II) and Ni(II) respectively. The melting and boiling points of the complexes were (190 and 206)°C and (50 and 80.2)°C for Co(II) and Ni(II) respectively. The low melting and boiling points of the synthesized complexes may be due to the nature of the bond in the complexes since they are not completely ionic and possibly the properties of the central metals. The electrical conductivities were found to be (1.2×10^{-1} and 1.1×10^{-1}) us/cm for Co(II) and Ni(II) complexes. This indicates that the complexes are non-electrolytes. Elemental analysis corresponds to metal: ligand stoichiometry for Co (II) and Ni II) complexes are 1:2:2:2. Cobalt (II) complex was blue while Nickel (II) complex was pale green. The FT-IR spectra shows that the prepared Co(II) and Ni(II) complexes havetentative coordinate points at OH and N atoms. The maximum absorption based on the UV-VIS spectra indicates 225.50nm and 301.50nm for Co(II) and Ni(II) complexes respectively. This confirms the formation of complexes at those regions. The X-ray diffraction shows that all the complexes have sharp peaks which is a strong indication that they are crystalline. The crystallographic examinations showed that the complexes exhibitoctahedral structures. The X-ray fluorescence data indicates the presence of Co_3O_4 in the prepared Co(II) complex and NiO in Ni(II) complex. This shows that Co(II) and Ni(II) complexes were synthesized. The results obtained from this research workopines that Co(II) and Ni(II) complexes were successfully synthesized and characterized. These synthesized complexes may be applied in the area of agriculture, medicine and chemical industries.

Keywords:- *Co (II) and Ni (II) complexes; Synthesis; Characterization; Crystallography; spectroscopy;Mixed ligands.*

I. INTRODUCTION

Coordination compounds are formed by the reaction between Lewis acids and Lewis bases. Transition metals behave as Lewis acids due to a partially filled d-orbital and therefore are capable of accepting electron pairs. Co (II) and Nil (II) with a d^7 and d^8 configurations are known in four coordinate (tetrahedral) and six coordinate (octahedral) stereochemistry.

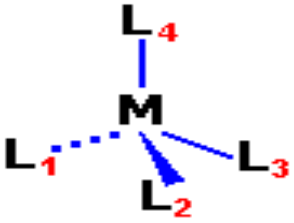

Fig. 1(a): Tetrahedral

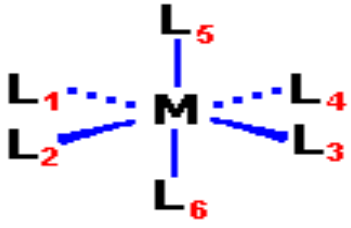

Fig. 1(b): Octahedral

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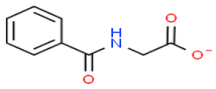
The ligands L1 to L6 corresponds to thiocyanate ion (CNS^-), hippurate ion, ammonia (NH_3), hydroxide (OH^-) and chloride (Cl^-)ions, which corresponds to the hippuric acid, ammonium thiocyanate, hydroxyl ammonium chloride respectively. The donor atoms from these ligands would be C, N, O, Cl respectively. This is because of the presence of lone pair electrons on the atom which provide electron to the vacant d-orbitals of the central transition metals in the complexes. Some organic ligands can be extracted from green plants. Gongden et al., (2020), reported the synthesis of potassium ferric oxalate with ethanedioate ($C_2O_4^{2-}$) – a bidentate ligand extracted from spinach leaves. Oxalate ions bonds easly to Ni and Fe metals. Just like oxalate ion, hippurate ligand is also bidentate. It can coordinate through the -N and O sites to the central metal of Co (II) and Ni (II).



Hippurate ion

$$M+L_3+L+L_2 \longrightarrow ML_3LL_2$$

Where M = Central metal; L = Mixed ligands (organic & inorganic)

As applied to the transition metals, coordination compounds are among the most extensively investigated areas in the field of inorganic chemistry. Mixed ligand complexes differ from traditional complexes in the sense that they are having at least two different kinds of ligands associated with the same metal ion in a complex. These complexes exhibit extensive and interesting spectral and magnetic properties in addition to widely varying structures and stoichiometries (Bekele et al., 2020). The presence of more than one type of ligand in a complex increases chance of variation in properties expected for the complex.Transition metal complexes have generated for many years due to their potential in organic synthesis (Gelman, *et al*., 2000) as well as their medical properties including antitumor and antimicrobial activities (Manav, et al., 2004), and catalytic performance (Sizhong, et al., 2003).

There is increasing interest in organometallic complex synthesis, especially in the area of mixed ligands-metal complex formation. The wide applications of these complexes havealso motivated many researchers to get involved in this field. For example, Phthalocyanine is a class of coordination complexes that the dyes and pigments industry extensively use to impart specific coloration to fabrics; Some cyanide complexes also find their use in electroplating and as protective layers on surfaces. There are complexes that find their application in photography; EDTA is another complex compound used in determining the hardness of water; some coordination compounds find their application as catalysts and additives in polymer industries as well (Sher Ali et al., 2015).

Cobalt is an essential trace element in animal nutrition in the form of vitamin B_{12} and is essential for human health as it stimulates the production of red blood cells. Nickel is associated with several enzymes and it plays a role in physiological processes as a co-factor in the absorption of iron from the intestine (Jose-Ramiro et al., 2020). Research on the metal complex is now well known as an interdisciplinary field of study, combining the effort and contributions from chemists, physicists, biologists, and medical researchers. Transition metal ions readily form stable complexes with molecules containing nitrogen, oxygen, sulfur, phosphorous or halogen as donor atoms. The metal ions are soft acids in which the electron density is easily polarized. As such they can be bonded readily with soft and highly basic reagents to form stable metal complexes.

During the past couple of decades, numerous metallic complexes have been successfully designed and synthesized by judicious choice of the metal ion and ligands (Hirotsu, *et al*., 2010). The conjugated ligands combined with electron rich metals can generate low energy electronic interactions between the metal center and ligand, resulting in interesting optical or electronic properties (Williams *et al*., 2009).A complexes ion is one that contains a central ion or atom linked to other atoms or molecules which are called ligands. Ligands attached to the central metal by more than one point of attachment are called chelating ligands and these ligands are called multidentate, and their complexes are called chelates, the ligand directly bound to the metal are said to be in the inner coordinating sphere. The ions that balance out the charge remaining on the complex after the coordination number of the central metal has been "Satisfied" are said to be outer sphere ions (Ali & Van Lier, 1999).

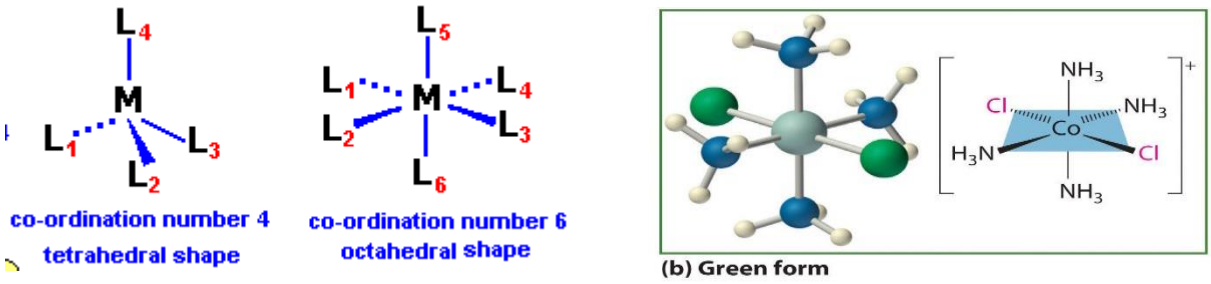


Fig. 2(b): Octahedral arrangement of ligands

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Inorganic complexes, with their metal-Ligand (where ligand: neutral covalent molecules; ionic inorganic compounds; organic molecules or ions), lie at the interface betweenclassical organic and inorganic chemistry (Uduah et al., 2020). Synthetic chemists have reached a high level of specialization and nowadays extremely complicated and attractive compounds. The development of complex multistep synthesis not only does make accessible a variety of biologically active compounds, but also allows the discovery of how reagent or reaction strategies. Although some inorganic species can be obtained in pure form from nature, most are synthesized in chemical plants and in the laboratory.

The methods used in preparation of complexes are numerous and new methods keep emerging due to advancement in technology. Some of these methods are; Self Propagating High Temperature Synthesis (SHS),Microwave synthesis,direct method of synthesis,hydrothermal Method of Synthesis, temperature-difference method, temperature-reduction technique, metastable-phase technique, and reduction and oxidation method(Lawal, 2015).The aim of this research is to synthesize and characterize mixed ligand complexes of cobalt (II) and nickel (II) using hippuric acid, ammonium thiocyanate and hydroxyl ammonium chloride as the mixed-ligands.

II. METHODOLOGY

A. Reagents and Chemicals

All the reagents used were of analytical or chemical grade purity. Solvents were purified and dried according to the standard procedures. The synthesis method of the complexes was best on " direct method" as proposed by (Lawal, 2015).

General Method for the Preparation of the Complexes of the Type [M(X)(L)]

$$M^{2+} + X + L \rightarrow [M(X)\,(L)]$$

Where, M = Co (II); Ni (II) ions;

X = hippuric acid;

L = ammonium thiocyanate; hydroxyl ammonium chloride

The percentage yield of Co (II) and Ni (II) complexes was calculated using the formula below

$$\%\ yield = \frac{mass\ of\ the\ Metal\ Complex}{Mass\ of\ the\ Metal\ salt + Ligands} \times 100$$

B. Characterization of Co (II) and Ni (II) Complexes

Physicochemical properties such as conductivity measurement, total dissolve solid, colour, solubility, pH, melting point and boiling point were first carried out on Co (II) and Ni (II) complexes formed at the Post Graduate Laboratory of the Department of Chemistry, Faculty of Natural Sciences, University of Jos, Plateau State, Nigeria, using standard laboratory procedures. Instrumental methods were then applied to characterize the complexes.Elemental analyses of the complexes were carried out by X-ray fluorescent (XRF) and FT-IR spectroscopy. Finally, the synthesized complexes obtained were further characterized using UV-vis spectrophotometer, XRD and crystallographic technique.

III. RESULTS AND DISCUSSION

A. Percentage Yield of Cobalt Complex and Nickel Complex

Plate 1a and 1b shows the two complexes of the synthesized crystals of Co (II) and Ni (II) complexes.From the calculation of the percentage yield 6g of cobalt complex was obtain which is equivalent to 42.9%. The good percentage yield may be attributed to the high solubility of cobalt in water (Jurgen, 1996). While 5.7g Nickel complex was obtain which is equivalent to 40.7%. This may have attributed to the high solubility of Nickel in water as well (Jurgen, 1996).

Plate 1(a): Synthesized Cobalt (II) complex

Plate 1(b): Synthesized Nikel (II) complex

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Parameter	*Co*	*Co Cmpl*	*Ni*	*Ni Cmpl*
Water (25^0C)	++	+	++	+
Ethanol (25^0C)	++	+	++	+
Methanol (25^0C)	++	++	++	++
pH at (25^0C)	6.50	3.24	6.33	3.3
Melting point (^0C)	1495	190	1453	50
Boiling point (^0C)	2870	206	2732	80.2
Electrical conductivity (us/cm)	-	$1.2x10^{-1}$	-	$28701.1\ x10^{-1}$
Colour	Red	Blue	Green	Pearl green

Table 1: Physical Properties of Pure Co(II), Ni (II) and Co(II), Ni (II) Complexes

+ Slightly soluble, ++ soluble

Table 1 shows the physical properties of the synthesized complexes of Co (II) and Ni (II). Both complexes are soluble in water, ethanol and methanol solvents at 25ºC and atmospheric pressure. Both complexes show very low melting and boiling point compared to the control complexes. The large disparity in melting and boiling points may be ascribed to the method of synthesis, impurities and environmental factors. This low melting and boiling point may also be due to the nature of the bond in the complexes since they are not completely ionic and possibly the properties of the central metals. Co (II) and Ni (II) complexes have pH values of 3.24 and 3.30 respectively. These pH values indicates that both complexes are acidic. The highly acidic nature of the complexes can be ascribed to the nature of ligands/ electron donors coordinating round the central metal. The electrical conductivities were found to be (1.2×10^{-1} and 1.1×10^{-1}) us/cm for Co (II) and Ni (II) complexes. This indicates that the complexes are non-electrolytes. Cobalt (II) complex is a blue needle-like crystalline solid, while Nickel (II) complex is pale green needle-like crystalline solid.

B. Spectroscopic Results

- **UV-vis spectra result of synthesized Co (II) and Ni (II) complexes**

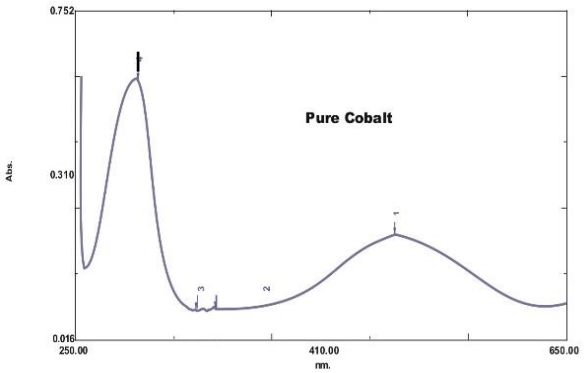

Fig. 3(a): UV-vis of pure Co (II)

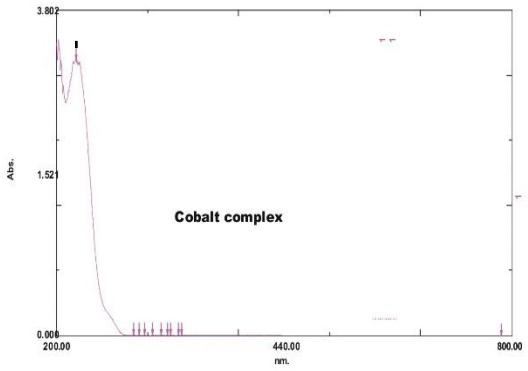

Fig. 3(b): UV-vis of synthesized Co (II) complex

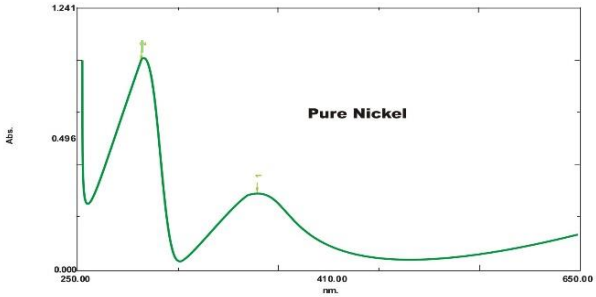

Fig. 4(a): UV-vis of pure Ni (II)

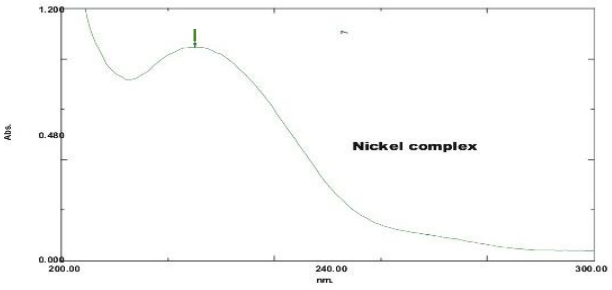

Fig. 4(b): UV-vis of synthesizedNi (II) complex

The scanned UV-vis spectrum (Figure 3a) of the pure cobalt shows a peak absorption at0.254, 0.088 and 0.599 and at a wavelength of 510.50, 364.50 and 301.50nm respectively. The crystal is found to be red in colour in the region between 500-520nm. This result is slightly different from the result of the scanned UV- vis spectrum of cobalt complex (Figure 3b) which shows absorptions of 0.002 and 3.215 and a wavelength of 360.50 and 225.50nm. The crystal complex is found to be colourless in the region between 230-300nm. The slight difference may be attributed to the difference in their appearance, pure cobalt is a red crystalline solid, while the cobalt complex is a colourless crystalline solid, this might be as a result of the mixed ligands that are present in the cobalt complex.

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The scanned UV-vis spectrum (Figure 4a) of the pure nickel shows a peak absorption at 0.367 and 0.995 and at a wavelength of 393.5 and 301.50nm, the crystal is found to be violet in the region between 380-435nm. This result is slightly different from the result of the scanned UV-vis spectrum of the nickel complex (Figure 4b) which shows absorptions at 0.035 and 1.015 and at wavelength of 365.00 and 225.00nm respectively. The crystal complex is found to be transparent in the region between (230-300nm). The slight difference in their wavelength may attributed to the difference in their appearance. The pure nickel is green crystalline solid while the nickel complex is a colourless crystalline solid, this might be as a result of mixed ligands that are present in the nickel complex.

C. FT-IR spectra result of synthesized Co (II) and Ni (II) complexes

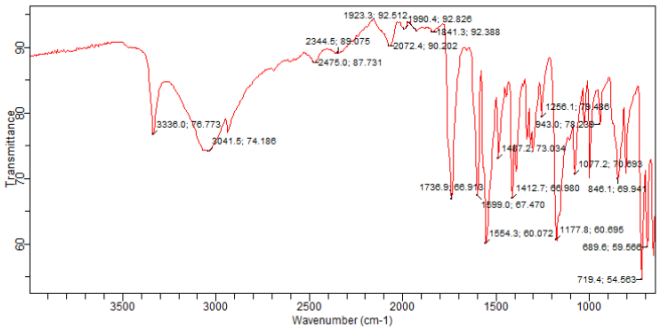

Fig. 5: FT-IR Spectrum of Cobalt Complex

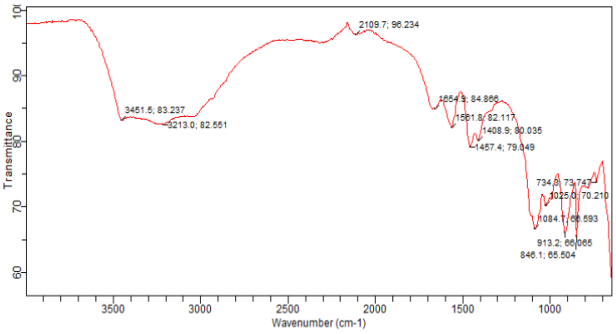

Fig. 6: FT-IR Spectrum of Nickel Complex

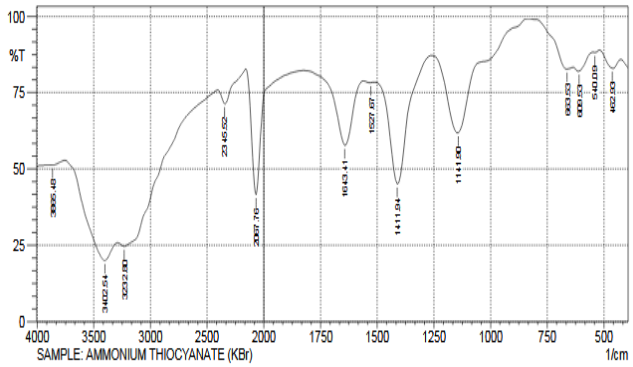

Fig. 7: FT-IR Spectrum of Ammonium Thiocyanate ligand

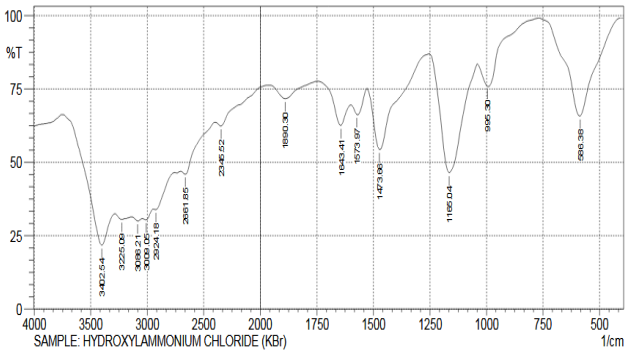

Fig. 8: FT-IR Spectrum of Hydroxyammonium chloride ligand

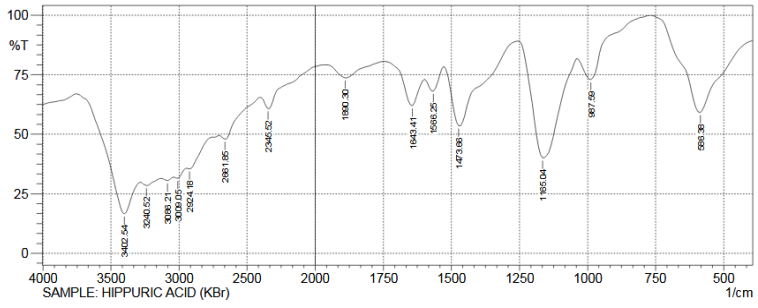

Fig. 9: FT-IR Spectrum of Hippuric Acid ligand

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The FT- IR analysis of both the ligands and the complexes were recorded on FTIR- ATR (Shimadzu 8400S model) utilizing KBr disc process and all samples were scanned over a range of 750-400cm^{-1} The FT-IR spectra of the complexes provided information on the coordination mode between the ligands and the metal ion IR spectra. The IR spectra of Co (II) and Ni (II) complexes and ligands (L) are given in Figure 4, 5, 6, 7 and 8 respectively while the IR spectral data of all the complexes and the ligands are summarized in Table 2. The infrared of the complexes are quite complex due to the presence of the numerous functional groups in the molecules, therefore, their interpretation is based on the most important region in the spectra of the mixed ligands Co(II) complex and the free ligands reveal that a broad band in the region 3500-3200cm^{-1} due to the stretching vibration of OH group. The (O-H) stretch observed in the complex 3041 cm^{-1} is significantly lower than the free ligands 3402 cm^{-1}. The complex showed absorption bands of 2073 cm^{-1} corresponding to v(CN) stretch, 1412 cm^{-1} corresponding to symmetric stretching of v(COO-) while the free ligands showed absorption bands of 2345 cm^{-1} corresponding to C≡N stretch, 1643 cm^{-1}. corresponding to C=C stretch. The complex showed v(N-H) bands at 3240-3225 cm^{-1} which is significantly higher than the free ligands (ammonium thoicyanate, hydroxyl ammonium chloride and hippuric acid (240-3225cm^{-1}) clearly suggest possible coordination to the metal through OH and N atoms.

The spectra of the mixed-ligand Ni(II) complex and the free ligands reveal that a broad band in the region ≈3500- 3200 cm^{-1} due to the stretching vibration of OH group. The (O-H) stretch observed in the complex 3071 cm^{-1} is significantly lower than the free ligands 3402cm^{-1}. The complex show absorption bands of 2109 cm^{-1} corresponding to v(CN) stretch, 1416cm^{-1}corresponding to symmetric stretching of v(COO-) while that of free ligands showed an 7absorption bands at 2345 cm^{-1} corresponding to C≡N stretch, 1643 cm corresponding to c=c stretch. The complex showed v(N-H) bands at 3338 - 3213 cm^{-1}, significantly higher than the free ligands (ammoniunthiocyanate, hydroxyl ammonium chloride and hippuric acid (3240 - 3225 cm^{-1}) suggesting that possible coordination might have occurred to the metal through OH and N atoms.

Complexes& free ligands	**OH Stretch**	**C=C Stretch**	**V(CN) Stretch**	**C-H Stretch**	**(N-H) cm^{-}**	**V(COO^{-})**
Co(L_3LL_2)	3041	-	2072	-	3338	1412
Ni(L_3LL_2)	3071	-	2109	2937	3338	1416
Ammonium Thiocyanate	3402	1643	2067	-	3232	1461
Hydroxyl ammonium Chloride	3402	1643	-	2924	3225	1473
Hippuric acid	3402	1643	-	2924	3240	1473

Table 2: FT-IR Spectral data of Co(II) and Ni(II) Complexes and the ligands

- **XRF and XRD spectra result of synthesized Co (II) and Ni (II) complexes**

The following compounds are present in the two complexes (SiO_2, K_2O, Fe_2O_3, Nb_2O_5 and Sb_2O_3), this might be attributed to the same kind of ligands that was used for the complexation, while Co_3O_4 is present in the cobalt complex, NiO is present in nickel complex and indicating that Co(II) and Ni(II) was successfully synthesized.

Elements	**Cobalt Complex**	**Nickel Complex**
SiO_2	2.7234	7.5890
K_2O	3.0064	7.0366
Fe_2O_5	1.1017	2.1322
Nb_2O_3	1.00105	1.0076
Sb_2O_3	0.0054	0.0007
CO_3O_4	4.2632	-
NiO	-	6.3902
ZnO	-	-

Table 3: Elemental Analysis of Cobalt and Nickel Complexes

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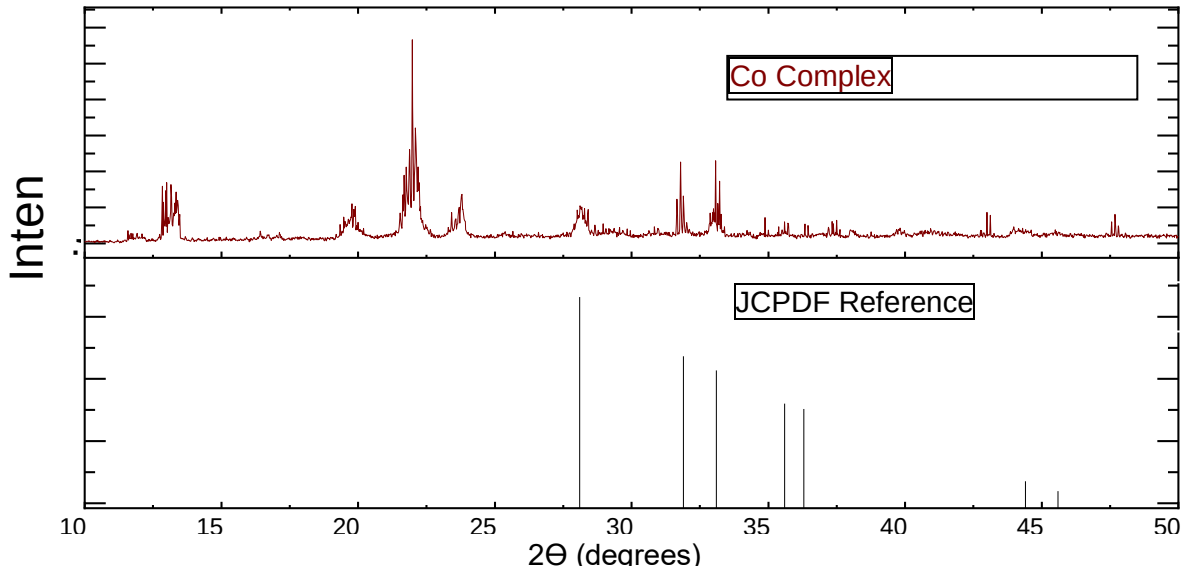

Fig. 10: The XRD Spectrum of Cobalt Complex

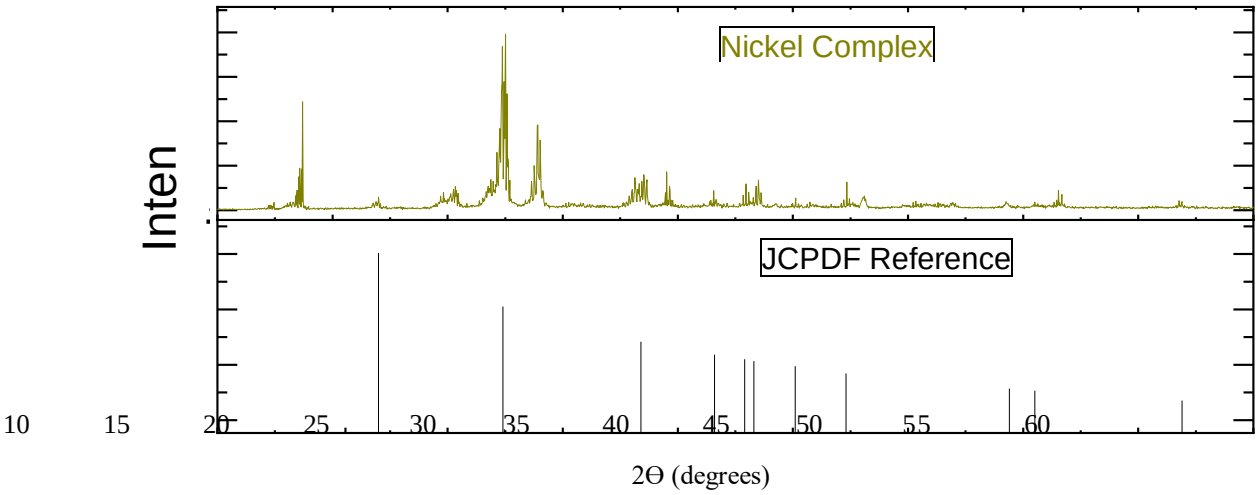

Fig. 11: The XRD Spectrum of Nickel Complex

The peak at 45.6º indicate the presence of Cobalt on the complex. Numerous other peaks indicate the presence of cobalt containing compounds 35.6º (JCPDS NO 85 - 0446), Co_2N at 28.1º and 44.4º, Cl_2, peaks at 33.1º, and 36.3º indicate the presence of Cl_2 and Cl -based compounds as $CoCl_2$ presence is observed. Nitrogen peak at 31.9º (JCPDS NO 73 - 2330) and 44.2º (JCPDS NO 73 - 2332) indicates the presence of N_2 and N -based compounds such as N_2O_4at 45.6º, 47.6º (JCPDS NO 74 - 2264) and Co_2N at 28.1º, 37.3º and 44.4º

From the XRD analysis of the nickel complexes, it is observed that the complex possesses Ni peak at 45.5º (JCPDS NO 88 - 0800) suggest the presence of chlorine and chlorine-based compounds in the complex as observed by the presence of Cl_2O at 32.9º and 51.9º (JCPDS NO 88 - 1457) and ClO_2 at 22.4º, 31.6º and 33.3º (JCPDS NO 79 - 2398). The presence of oxygen in these compounds is indicated by an oxygen peak at 37.3º corresponding to oxygen peak in standard value (JCPDS NO 85 - 0424). Nitrogen peaks at 28.4º, 35.1º suggest the presence of nitrogen and nitrogen-based compounds such as ammonium and oxides of nitrogen. This is further proven by the presence of N_2O_4 at 170º (JCPDS NO 76 - 0444). The presence of the above-mentioned peaks indicates that nickel complex has been synthesized.

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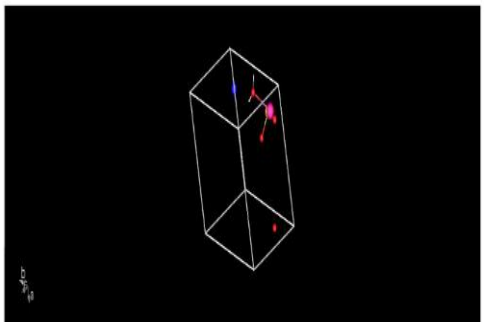

Fig. 12: Crystallographic Structure of Cobalt Complex

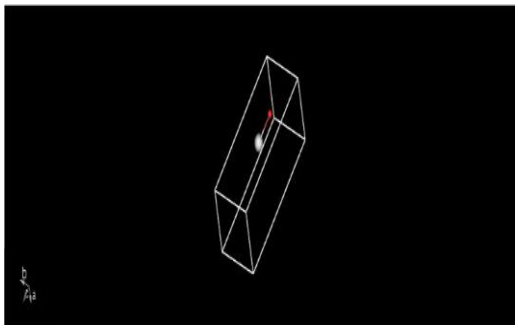

Fig. 13: Crystallographic Structure of Nickel Complex

From the result of the crystallographic studies of cobalt (II) and Nickel (II) complexes have an octahedral structure.

IV. CONCLUSION

Elemental analysis corresponds to metal: ligand stoichiometry for Co (II) and Ni (II) complexes are 1:2:2:2. The X-ray fluorescent data indicates that Co(II) and Ni(II) complexes has been successfully synthesized. The complexes have low melting and boiling points, acidic, soluble in methanol and do not conduct electricity.They have a coordination point at OH and N atoms, they are found to be crystalline with an octahedral structure.

Based on the above analysis the structure of the complexes has been proposed as follows;

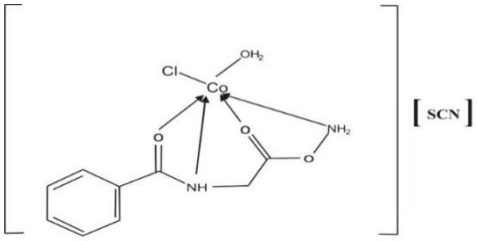

Fig. 12: Proposed structure of synthesized Co (II) Complex

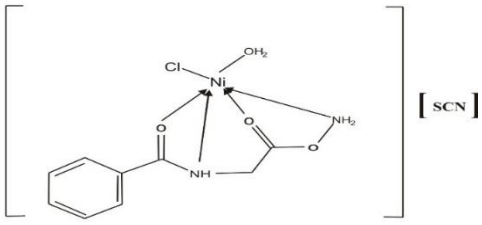

Fig. 13: Proposed structure of synthesized Co (II) Complex

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