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Synthesis and Spectroscopic Determination of Cu(II) and Co(II) Metal Complexes with Pthalamide and 2,4-Dinitrophenylhydrazine

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ABSTRACT

Copper (II) and Cobalt (II) metal complexes were derived from the synthesis of pthalamide and 2,4-dinitrophenylhydrazine. Both synthesized metal complexes were found to be soluble in acetone and butanol, slightly soluble in n-hexane and propan-1-ol, partially soluble in ethanol and methanol, and insoluble in water. The synthesized Cu (II) and Co (II) metal complexes were characterized by IR, Uv-Vis, TGA, XRD and Magnetic Susceptibility. The IR spectral bands observed for both Cu (II) and Co (II) metal complexes are3287.5cm^{-1} (N-H) stretch, 708.19 cm^{-1} (N-M) stretch, 1729.5cm^{-1} (C=O) stretch, 1610.20cm^{-1} (C=C) stretch, 1043.65cm^{-1} (N-N) stretch and 3101.1cm^{-1} (C-H) ar-stretch, 1334cm^{-1} (NO_2) stretch for Cu (II) complex while 3145.9cm^{-1} (C-H) ar-stretch, 1341cm^{-1} (NO_2) stretch for Cu (II) complex. The electronic transitions found from the Cu-Complex were 236.95nm (n- π*) assigned to C=O, 207.29nm (π- π*) assigned to C=C, 400.82nm (n- π*) assigned to NO_2 and a band of 472nm assigned to the LMCT. The Co-Complex also has bands at 237.8nm (n- π*) assigned to C=O, 215.58nm (π- π*) assigned to C=C, 401.82nm (n- π*) assigned to NO_2 and 465nm assigned to the LMCT. The decomposition of the synthesized complexes were to be 205^{o}C and 202^{o}C for Cu-Complex and Co-Complex respectively. The thermal decomposition of the complexes were also observed by TGA. The XRD results showed that the Cu-Complex is crystalline while the Co-Complex is amorphous and the Magnetic Susceptibility of the complexes was also confirmed for their paramagnetic nature.

Keywords: Decomposition, Determination, Metal Complexes, Spectroscopic, Synthesis

INTRODUCTION

The continues resistance of bacteria to many antibiotics and fungi to many antifungal becomes a serious issue of concern, so the quest for developing antimicrobials with new strategy is a non-stop task that would lead to endless exploitation and exploration of new synthetic compounds. It is this that made inorganic chemists researchers decided to discover the chemistry relation of metal together with organic compounds (Ere *et al.*, 2020).

Antimicrobial resistance today is count as one among the leading death cases with global annual deaths of five million lives (Murray *et al.*, 2022). In these years, the ineffective of the therapeutic drugs is as a result of the antimicrobial resistance of these bacterial infections (Laxminarayan *et al*., 2013). The increase in the levels of this resistance is due to the narrow reserves of these antimicrobial agents to challenge them. This risks the sustainability of active public health concerns to these infections with resistant ability (So *et al*., 2012; Smith and Coast 2013). *E. coli* is among the abundant commensals found in the intestine and excreted in the feces of animals and humans (Hu *et al*., 2021). It is an unscrupulous pathogen which lead to food-borne, urinary tract and bloodstream infections, together with meningitis in new born babies (Mellata 2013). Findings on the globally recent load of resistance of bacteria stated that *E. coli* is the death leading cause because of its resistance (Bailey *et al*., 2010). The previous findings mostly set from hospital reported the high rates of multidrug resistance amongst isolates of *E. coli* ranged from 29% to 45% (Nji *et al*., 2021 and Shrestha *et al*., 2022).

It's approximately been estimated that 100 million people were affected worldwide by Tuberculosis, a disease which is contagious that cause deaths in humans and is categorically be considered a deadly all over the world with annual deaths of 1.5 million. 20% were attributed approximately to the resistant to drugs for fighting TB. (Yufanyi *et al*., 2020).

METHODOLOGY

Materials

Glass wares used 250 mL round bottom flask. 250 mL, 100 mL and 50 mL beakers, and measuring cylinders. Also filter papers, refluxing apparatus, spatula, magnetic stirrer, analytical weighing balance (KERRO BL20001 made from

U.K), Uv Spectrophotometer (PerkinElmer UV WinLab Data Processor and View Version 1.00.00 made in Netherlands), FTIR Spectroscopy (FTIR Cory 630) Agitec, X-ray Diffractometer (X-ray Diffractometer Thermo scientific model: ARL'XTRA X-ray and serial number 197492086 made from Thermo fisher Scientific Company Switzerland), Thermogravimetric Analyzer (PerkinElmer MSE-TGA 4000 made in Netherlands) and Melting point apparatus (CHNT-85L17, U.K) were used. Ethanol, Pthalamide, 2,4-Dinitrophenylhydrazine, Cu (II) Sulphate, Cobalt (II) chloride hexahydrate and distilled water were used in the work were all of analytical grade.

Procedure for the synthesis of Cu (II) complex.

Pthalamide (1.507 g) was weighed into 250 ml round bottom flask, 10 ml ethanol was added and stirred, given a white color solution. (2,4-DNPH) 1.506 g was mixed with 10 ml ethanol in 50 ml beaker and transferred into 250 ml round bottom flask, given an orange color solution. $CuSO_4$ (1.505 g) was weighed and dissolved using 10 ml ethanol in 50 ml beaker then transferred onto the mixture in the 250 ml round bottom flask and the orange color is still maintained by the mixture. 30 minutes from the start of the reflux the color changed to greenish brown. After the mixture was refluxed for 2.15 hours at 95ºC, the color turned to deep green (Mustapha *et al*., 2014; Miloud *et al*., 2020 and Ere *et al*., 2020).

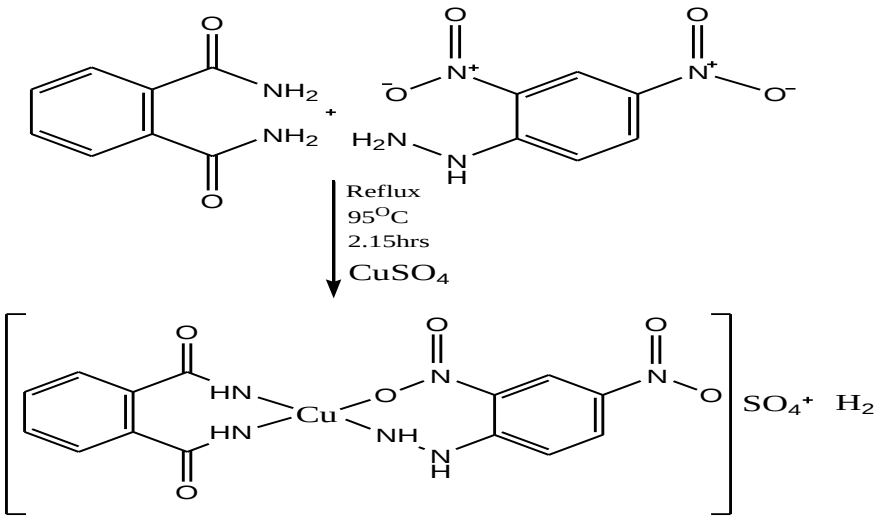

Fig. 1: Synthetic route of the reaction of Cu-Complex

Procedure for the synthesis of Co(II) complex

Pthalamide (1.501 g) was weighed into 250 ml round bottom flask, 10 ml ethanol was added and stirred, given a white color solution. (2,4-DNPH) 1.503 g was mixed with 10ml ethanol in 50 ml beaker and transferred into 250 ml round bottom flask, given an orange color solution. $CoCl_2$ (1.502 g) was weighed and dissolved using 10 ml ethanol in 50 ml beaker then transferred onto the mixture in the 250 ml round bottom flask given a greenish brown color. 40 minutes from the start of the reflux the color changed to very deep green. After the mixture was refluxed for 2.15 hours at 95ºC, the color observed to be black (Mustapha *et al*., 2014; Miloud *et al*., 2020 and Ere *et al*., 2020).

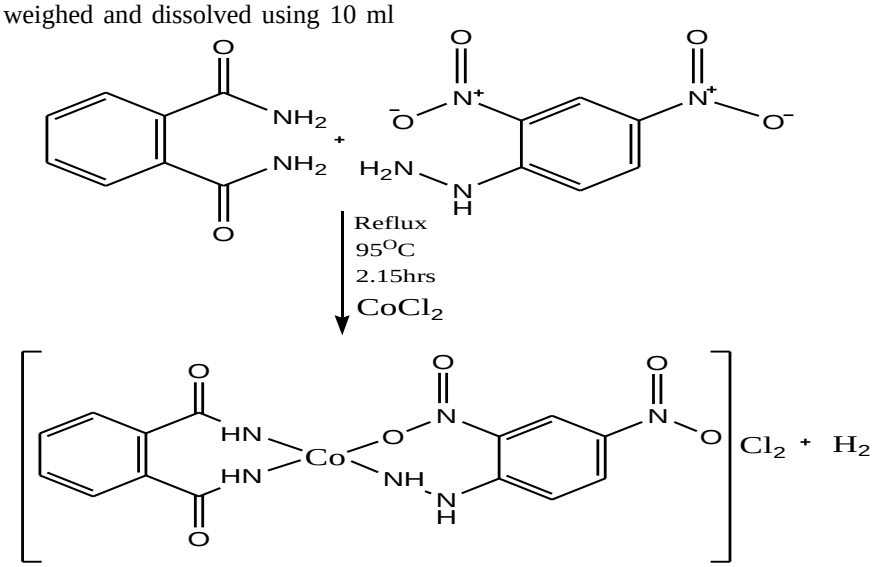

Fig. 2: Synthetic route of the reaction of Co-Complex

RESULTS AND DISCUSSION

From Table 1, the synthesized Cu(II) and Co(II) complexes are solids, so the decomposition temperatures of these synthesized complexes were found to be 205ºC and 202ºC for Cu-Complex and Co-Complex respectively. This is in line with the research findings of Mustapha *et al.,* 2014 and Suleiman *et al.,* 2022. The synthesized copper (II) complex gave a dark green colour while cobalt (II) gave a black colour.

Table 2 shows the solubility test of both Cu-Complex and Co-Complex. The synthesized copper (II) complex gave a dark green colour while cobalt (II) gave a black colour. Both the synthesized Cu (II) and Co (II) complexes are soluble in acetone and butanol, slightly soluble in n-hexane and propan-1-ol, partially soluble in ethanol and methanol, and insoluble in water.

Table 3 shows the magnetic susceptibility of the complexes. Both complexes possessed magnetic susceptibility values below 1000 and they are therefore classified as paramagnetic compounds.

Table 1: Some Physical Properties of the Complexes

S/N	Complex	F.W (g/mol)	Phase State	Decomp. Temp. (ºC)	Color
1	Cu	421.81556	Solid	205	dark green
2	Co	417.20276	solid	202	Black

Table 2: Results of solubility tests of the Complexes

SN	Solvent used	Cu-Complex	Co-Complex
1	Water	Insoluble	Insoluble
2	Ethanol	Partially soluble	Partially soluble
3	Methanol	Partially soluble	Partially soluble
4	Acetone	Soluble	Soluble
5	Propan-1-ol	Slightly soluble	Slightly soluble
6	Butanol	Soluble	Soluble
7	Hexane	Slightly soluble	Slightly soluble

Table 3: Magnetic Susceptibility of the synthesized complexes

S/N	Complex	R_1	R_o	W_o	W_1	L_1	C	Xg
1	Cu	052	-037	0.738 g	0.839 g	2.8 cm	1	1541×10^{-9}
2	Co	543	-037	0.378 g	0.840 g	2.8 cm	1	6339×10^{-9}

From Figures 3 and 4, the observed IR bands at 3287.5cm^{-1} for both copper and cobalt complexes could be attributed to the (N-H) stretching and this is in good agreement with the results obtained by Hussain *et al.* (2019). The N-H stretch at 3287.5cm^{-1} for both the complexes is also in line with the results obtained by Reiss *et al.* (2021), Sulaiman, (2021), Badma and Lakshmi, (2014), Mustapha *et al*. (2014), Sanaa *et al.* (2019) and also Seher *et al*. (2020) observed N-H stretch at this related band. The IR spectra observed at 3101.1cm^{-1} and 3145.9cm^{-1} for copper and cobalt complexes respectively indicated the presence of C-H stretch in aromatic ring and this in agreement with results obtained by Sanaa *et al.*, 2019 and the Royal Society of Chemistry correlation table 2015. The bands observed for complexes at 1729.5 cm^{-1} were assigned to C=O stretch, this observed band is in agreement with the results obtained by Kudrat *et al*. (2015), Sanaa *et al.* (2019), Seher *et al*. (2020) and also with the Royal Society of Chemistry correlation Table (2015). The N-N stretch for both copper and cobalt complexes were found at 1043.65cm^{-1} is in good agreement with the results obtained by El-Gammal *et al*. (2021), Mustapha *et al*. (2014), Suleiman *et al.* (2022) and Sanaa *et al.* (2019) revealed findings with the above related band. The 708.19cm^{-1} observed bands for both copper and cobalt complexes were attributed N-M stretch while that of M-O were observed at 832.4 and 805.1 for both copper and cobalt complexes as seeing from Figures 3 and 4, the observed related band was found by Mustapha *et al*. (2014) and Suleiman *et al*. (2022). The strong bands observed ranges from 1334cm^{-1}, 1535cm^{-1} and 1341cm^{-1} 1513cm^{-1} were attributed to the NO_2 stretch. The C=C stretch in aromatic for the complexes were found exactly at 1610.20cm^{-1}. These bands observed were related to the bands observed by Seher *et al.* (2020).

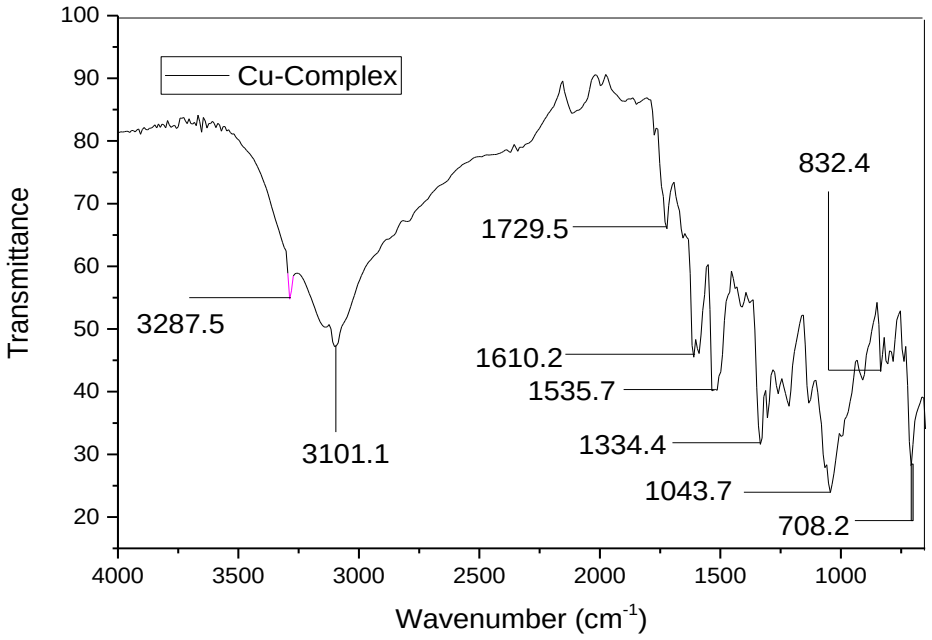

Figure 3: Cu-Complex IR-Spectra

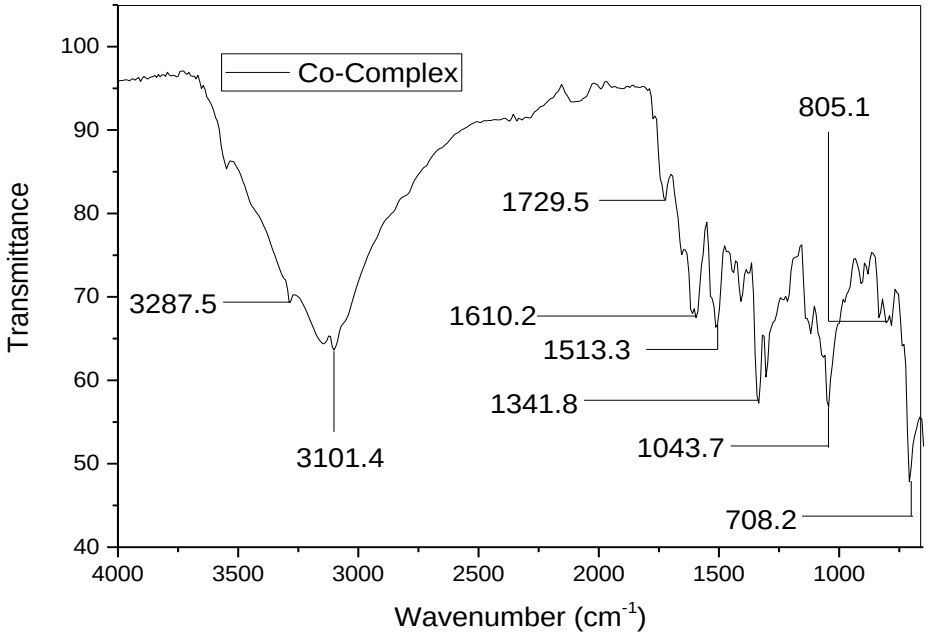

Figure 4: Co-Complex IR-Spectra

Figures 5 and 6 shows the electronic transitions found from the Cu-Complex were 236.95nm (n - π*) assigned to C=O, 207.29nm (π - π*) assigned to C=C, 400.82nm (n - π*) assigned to NO_2 and 472nm assigned to the MLCT. The Co-Complex also has a band at 237.8nm (n - π*) assigned to C=O, 215.58nm (π- π*) assigned to C=C, 401.82nm (n - π*) assigned to NO_2 and 465nm assigned to the MLCT (Mustapha *et al*., 2014; Reiss *et al*., 2021 and Suleiman *et al*., 2022).

The decomposition temperatures of the synthesized complexes were found to be 205^{o}C and 202^{o}C for Cu-Complex and Co-Complex respectively. The thermal decomposition of the complexes was also observed by TGA (Reiss *et al.*, 2021; Yosuva, 2013) as can be seeing from Figures 7 and 8.

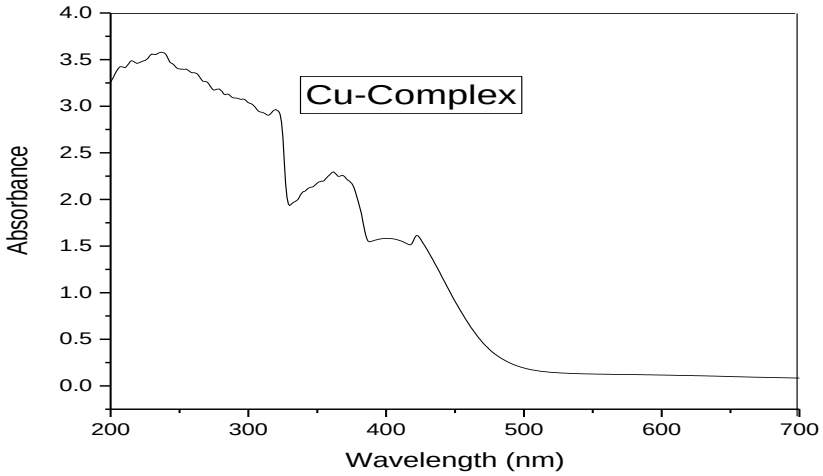

Figure 5: Uv-Vis Spectra of Cu-Complex

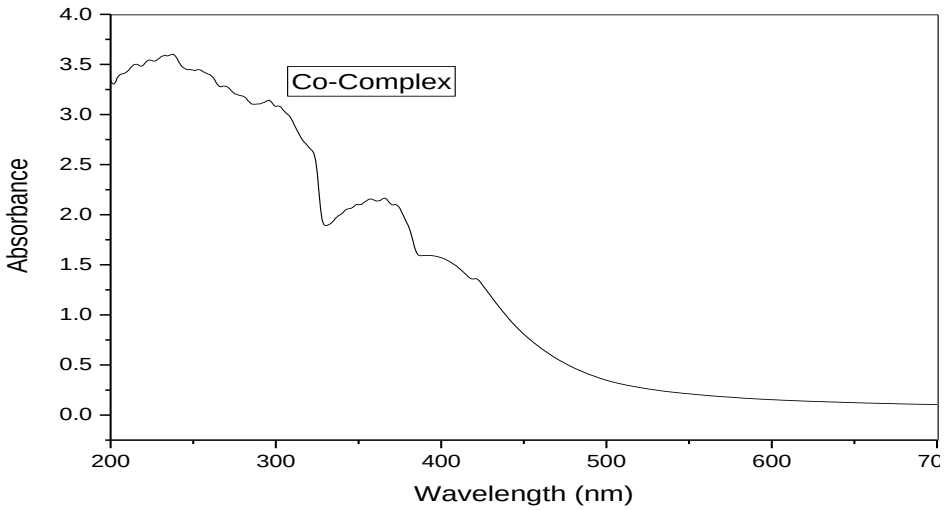

Figure 6: Uv-Vis Spectra of Co-Complex

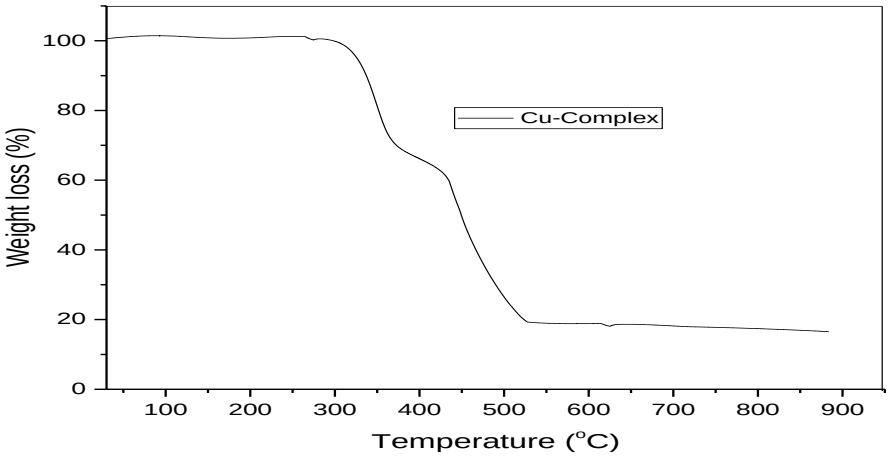

Figure 7: Cu-Complex TGA Spectra

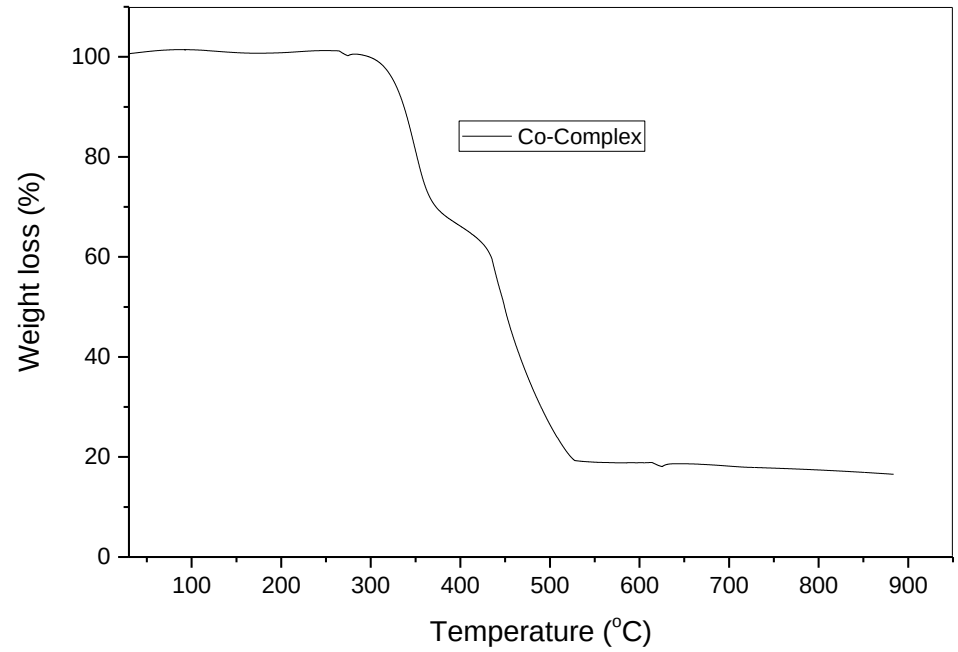

Figure 8: Co-Complex TGA Spectra

Figures 9 and 10 shows the XRD results of the synthesized metal complexes, where the Cu-complex was found to be crystalline compound. The diffraction angle observed from the Cu-complex is 12.29º with a d-spacing of 7.195, this result is in line with the results obtained by Sanaa *et al.*, 2019. For the Co-complex, it has a diffraction angle of 21.53º and a d-spacing of 4.123 with a full-width at half maximum (FWHM) of 34.18 and this confirmed its amorphous nature compared to Cu-complex with 0.19 FWHM.

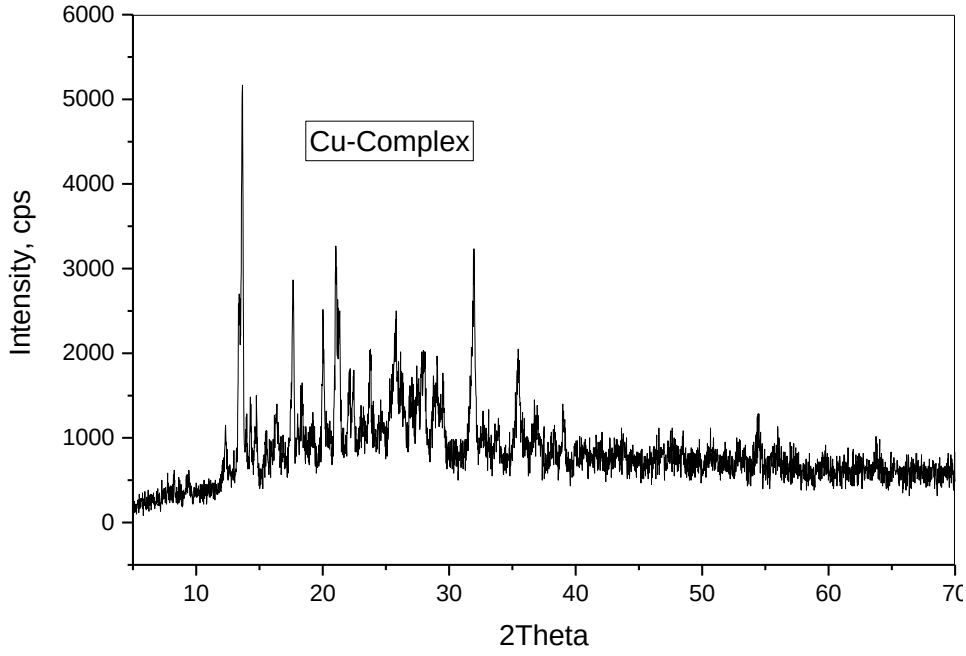

Figure 9: Cu-Complex XRD Spectra

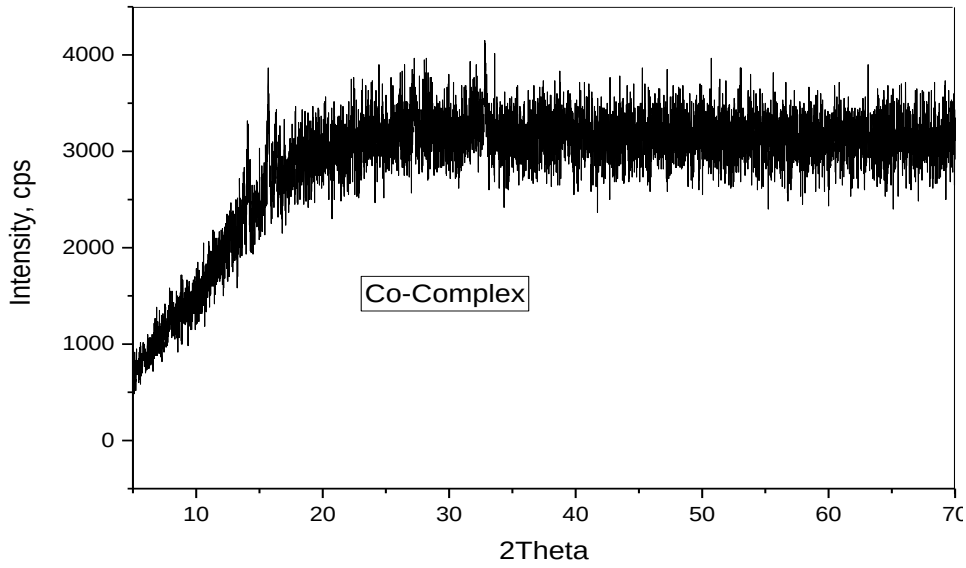

Figure 10: Co-Complex XRD Spectra

CONCLUSION

The metal complexes of copper and cobalt were synthesized from phthalamide and 2,4-dinitrophenylhydrazine ligands. The solubility of the synthesized metal complexes indicated that the complexes are soluble, partially soluble, slightly soluble and insoluble in some solvent. All the synthesized metal complexes of copper and cobalt were accessed in term of their colour, state, and their decomposition temperatures. Base on the spectroscopic analysis UV spectrophotometry conducted revealed the electronic transition occurred within the complexes, IR spectroscopy gave the functional groups presents and the new generated from the chelation through the formation of N-M and O-M bonds, TG analysis showed where the decomposition started and where it stopped which is the stability point, XRD analysis aimed in giving the crystallinity nature of the synthesized metal complexes.

This is part publication, in the next publication the Conductivity measurement and the Antimicrobial screening of the complexes will be carried out.

Recommendation

Base on the literature surveyed, the anticancer investigation of these synthesized complexes need to be carried out together with the cytotoxic effect of these complexes in further research. Antimalarial, antiulcer, antidiabetic and hypertension need to be carried out in further research. The crystallographic study of these new synthesized metal complexes need to be carried for their structures to be assessed. Drug formulation also need to be carried out to allow us benefit from our vast nature blessing endowment. Another important aspect to be determined is the fluorescence and confocal microscopy through which the cellular distribution and uptake processes can best be verified if cells treated with the synthesized metal complexes if it possess luminescence properties, visualization using fluorescence microscopy will be possible, that can be examined in the nucleus or in the cytoplasm's other organelles.

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