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Synthesis, Characterization and Antioxidant Studies of some Transition Metal Complexes with Chalcone Derivative (2-Chloroacetophenone) and 2-Hydroxybenzaldehyde

Jamila Musa Kankara

Department of Basic Studies, College of Liberal Studies, Hassan Usman Katsina Polytechnic, Katsna Katsina State, Nigeria.
Author Email: jamilakankara779@gmail.com

ABSTRACT

Chalcone derivatives and their complexes have been attracting researcher's attention due to their numerous numbers of biological activities and their uses as alternative inexpensive and synthetic compounds for treating metabolic diseases. Hence, this research focuses on the synthesis of chalcone derivatives complexes, characterization and their antioxidant activities evaluation. The complexes were prepared by claisen-schmidt condensation using Co(II), Ni(II) and Zn(II) chloride salts and were characterized using melting point/decomposition temperatures, solubility test, conductivity measurement, FT-IR and antioxidant evaluation was conducted using 1,1-diphenyl-2-dipicrylhydrazyl radical assay. The antioxidant activity of the cobalt complex was found to have better scavenging activity with IC50 of 7.89µg/ml than that of the standard vitamin C control with 10.77µg/ml. Similarly, zinc complex shows a better scavenging activity with an IC50 of 10.12µg/ml and nickel complex was the one with lowest scavenging activity against the standard vitamin C control with and IC50 of 29.91µg/ml. From the results obtained, it can be concluded that the chalcone derivatives complexes shows strong activity on free radical scavenging effect and the characterization of the compounds confirmed that the complexes were successfully synthesized.

Keywords: Antioxidant, chalcones, characterization, complexes

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INTRODUCTION

Chalcone (1,3-diphenyl-2-propen-1-one) with characteristic yellow primary colour is a reactive intermediate for the synthesis of many heterocyclic organic compounds and acts as a ligand for the synthesis of metal complexes (Adebayo et al., 2022). Chalcone occurs in (E) and (Z) isomers constituted by two aromatic ring connected by three α,β-unsaturated carbonyl system (Chopra, 2016). The (E)-isomer is the most thermodynamically stable and predominant configuration among other chalcone (Adebayo et al., 2022).

They are important reactive intermediates that constituted a major class of oxygen containing heterocyclic compound (Albuquerque et al., 2014). Chalcones and their derivatives are well-known due to their wide range of biological activities such as antiviral (Biradar et al., 2010), anti-inflammation (Nowakowska, 2007), antitumor (Kumar et al., 2010), antimitotic (Kamal et al., 2012), antimicrobial (Husain et al., 2013), antioxidant (Mirande et al., 2000), anti-diabetic (Rammohan et al., 2020) and antimalarial (Liu et al., 2001) activities.

The reason for the biological activities may be attributed to the presence of reactive keto vinyl group (Atlam et al., 2017). This article reported the preparation of chalcone derivative, synthesis and characterization of some transition metal complexes of Co (II), Zn (II) and N i(II) using 2-chloroacetopenone and 2-hydroxybenzaldehyde. The prepared ligands and metal complexes were analyzed for antioxidant using DPPH free radical scavenging activity method.

MATERIALS AND METHODS

All the chemicals and solvents used in this research were of analytical grade (sigma Aldrich) and were used as purchased from chemical suppliers without any further purification. Melting/decomposition temperature were determined using BUCHI-510 melting point machine, conductivity measurements was recorded using Jenway 4010 model conductivity meter and the Fourier transform infrared spectrum was taken using Cary 630 agilent technology model at the Instrumental Laboratory Department of Pure and Industrial Chemistry, Bayero University Kano.

Preparation of the Ligand (Chalcone Derivative)

Exactly 0.568g (3.67 mmol) of 2-chloroacetophenone was measured and dissolved in 20ml of ethanol, it was continuously stirred with the aid of magnetic stirrer until a pale-yellow solution was formed. 0.5g of 2-hydroxybenzaldehyde was weighed and dissolved in 20ml of ethanol and 2ml of 30% NaOH was added in drop-wise and stirred. The solution was then added in drop-wise to the solution of 2-chloroacetophenone. The mixture was stirred in an ice cold water bath until it solidifies. The solidified mass was kept in cold condition for overnight, the solidified mass was then separated and dried at room temperature and the dried mass is the (Ligand and Gaber, 2015).

Synthesis of metal complexes

Exactly 1.266 g of 2-Chloroacetophenone was weighed and dissolved in 20 ml of ethanol, 2 ml of 30% of NaOH solution was added and continuously stirred with a magnetic stirrer for 15 min. 1.0 g of 2-hydroxybenzaldehyde was dissolved separately in 20 ml of ethanol and was added in drops to the solution of 2-Chloroacetophenone. The mixture was stirred for 60 min in cold water bath to obtain the Chalcone derivative, 0.324 g of Cobalt (II) chloride was dissolved in 20 ml of ethanol, and the solution was added to the chalcone derivative. The mixture was refluxed for 2hrs and a purple precipitate (complex) was formed. It was filtered and the filtrate was kept in a beaker and allowed to evaporate to dryness at a room temperature (Tabti et al., 2018). The above procedure was repeated with 0.650 g of Nickel (II) chloride and 0.704 g of Zinc acetate.

Solubility test

Little amount of the chalcone derivative and its Co(II), Ni(II) and Zn(II) complexes were taken in different test tubes each, a small amount of a particular solvent was added to each of the test tubes and were shaken for about 5 min. The solubility of the compounds in each of the test tube was recorded at room temperature. This procedure was repeated using other solvents of different polarities available (i.e. both polar and non-polar solvents) (Mahapatra et al., 2019).

Determination of melting point

A very little amount of each of the prepared chalcone derivative and its Co (II), Ni (II) and Zn (II) complexes was introduced into a capillary tube for melting point determination. The tube was inserted into the Gallen Kamp melting point apparatus. The temperatures at which the prepared compounds melt or decompose were recorded (Kannan et al., 2019).

Conductivity measurements

The 0.001M of each complex was dissolved in 10 ml of Dimethylsulfoxide (DMSO) and the corresponding specific conductance value at different temperatures were recorded using Janway conductivity meter model 4010. From the specific conductance value recorded, the molar conductance of each complex at different temperatures was calculated using the expression below;

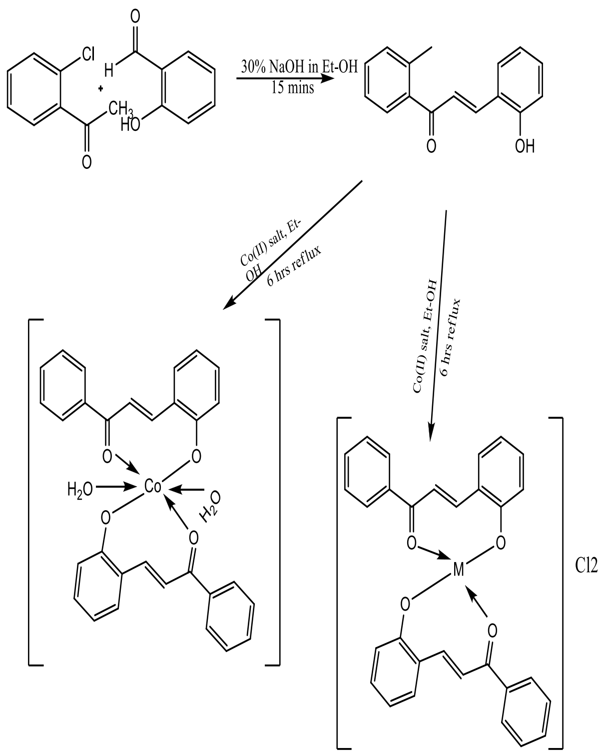
$$\lambda = \frac{1000Sc}{M}$$

Where; λ is molar conductivity
Sc is specific conductance
M is molarity.

Fourier transforms Infrared Spectroscopy

The prepared chalcone derivative (ligands) and its metal complexes: Co (L), Ni(L) and Zn(L) were taken for FT-IR analysis at the Instrumental Laboratory Department of Pure and Industrial Chemistry Bayero University Kano.

Antioxidant assay



Where; M = Zn and Ni

Figure 1: Synthesis of ligand and its complexes

The ligand and its metal complexes and vitamin C control concentrations of 500µg/ml, 250 µg/ml, 125 µg/ml, 31.3 µg/ml, 15.6 µg/ml and 7.8 µg/ml were prepared. The absorbance of the samples and DPPH solution was taken in a 96well microplate. About 50 µL of each of the sample concentration was placed in triplicate in the microplate in decreasing order of concentrations. The absorbance was measured at 517 nm. It was mixed with 100 µL of DPPH solution and the DPPH solution was also placed in empty wells in triplicate in the microplate. It was incubated for 30 min in the U.V spectrophotometer at 25°C and the absorbance was measured at 517 nm wavelengths(Kannan et al., 2019). The percentage scavenging activity (% SCA) was calculated using the equation below;

$$\% \text{ Scavenging Activity} = 1 - \frac{As - Ab}{Ac} \times 100$$

Where; Ab is the absorbance of the blank sample; Ac is the absorbance of the DPPH control and
As is the absorbance of the sample and DPPH solution

The SC_{50} values were calculated using SPSS Software. SC_{50} values are the scavenging concentration of each of the sample required scavenges 50% of DPPH free radical.

RESULTS AND DISCUSSION

Physical data of the synthesized chalcone derivatives and its complexes

The Claisen-schmidt condensation reaction of the 2-chloroacetophenone and 2-hydroxybenzaldehyde yield (E)-1-(2-Chlorophenyl)-3-(2-hydroxyphenyl) prop-2-en-1-one ligand (80%) which was pale-yellow in colour.

Table 1: Physical data.

Compounds	Colour	Yield (%)	M.P/DT (ºC)	Mol. Wt (calc.d)
($C_{15}H_{11}ClO_2$)	Pale yellow	80	198	258.04
[$Co(L)_2(H_2O)_2$]	Light brown	81	225	610.98
[$Zn(L)_2$].$2H_2O$	Gold	70	292	652.08
[$Ni(L)_2$]Cl_2	Dark brown	72	231	645.77

The Meta l (II) complexes were synthesized refluxing the ligand with metal chlorides as shown in the scheme 1 above. The complexes appeared to be light brown, gold and dark brown for Co (II), Zn (II) and Ni (II) respectively. The colour of the ligand may be due to charge transfer and that of the complexes may be attributed to the d-d electron transition or both (Sulpizio et al., 2018). The chalcone derivative (ligand) melts at 198ºC while the complexes decomposes at temperatures of 225ºC, 292ºC and 231ºC for Co(II), Zn(II) and Ni(II) respectively, this indicates the possible coordination of the metals used and the compounds become more stable upon complexation (Salga and Yusuf, 2017) (Table 1).

Table 2: Solubility test

Compounds	Water	Ethanol	Mesthanol	DMSO	Chloroform	Propanol	Acetone	Ether
L	IS	SS	SS	S	S	S	S	S
[$Co(L)_2(H_2O)_2$]	SS	SS	SS	S	S	S	S	S
[$Zn(L)_2$].$2H_2O$	IS	IS	SS	S	SS	S	S	S
[$Ni(L)_2$]Cl_2	IS	SS	SS	S	S	S	S	S

Solubility test of the ligand and its metal complexes

The solubility test of the ligand and its metal complexes showed different solubility behaviors in some common solvents of varying polarity and most of the compounds were found to be slightly soluble in ethanol and methanol and the complexes were highly soluble in dimethylsulphoxides (DMSO) which may be attributed to the high dielectric constant of the solvents (Sani and Baba, 2016). The result is shown in (Table 2).

Molar conductance of the synthesized complexes

The molar conductivity measurement of the 0.001M solution of the complexes was measured within the temperature of (40 ºC – 120 ºC) range. The ligand in DMSO solution lies within the range of 10.9-32.9 $\Omega^{-1}cm^2mol^{-1}$ which signifies that the ligand is non-electrolyte and the complexes have their molar conductivity measured between 50.1-60.9 $\Omega^{-1}cm^2mol^{-1}$ which signifies that the complexes were electrolytes and hence they are conductors of heat and electricity (Imran et al., 2013). The result is represented in (Table 3).

Table 3: Molar conductivity measurements.

Compounds	40ºC	60 ºC	80 ºC	100 ºC	120 ºC
$[Co(L)_2(H_2O)_2]$	51.2	51.6	51.6	51.7	51.9
$[Zn(L)_2].2H_2O$	50.6	50.8	50.9	51.1	51.1
$[Ni(L)_2]Cl_2$	59.9	60.3	60.5	60.6	60.9

FT-IR Spectra

The FT-IR measurement of the ligands and its metal complexes was conducted. The appearance of the medium vibrational stretching band for OH group in ligand at 3413cm^{-1} where as strong and broad absorption band at 3063cm^{-1} confirmed the formation of the Co (II) to ligand complex. The coordinated water molecule in the complex was confirmed by the presence of strong absorption band at 3079cm^{-1}. The absorption bands observed at 1700-1670cm^{-1}, 1529-1500cm^{-1} and 1235-1212cm^{-1} confirmed the corresponding functional groups C=O, C=C and C-O respectively. The characteristic band observed at 691cm^{-1}, 668cm^{-1} and 691cm^{-1} demonstrated the Co-O, Zn-O and Ni-O bonds stretching present in the formed complexes. The result is summarized in (Table 4).

Table 4: FT-IR spectral data.

Compounds	υ (O-H)	υ(C=O)	υ(C-O)	υ(M-O)
$(C_{15}H_{11}ClO_2)$	3413	1681	1235	-
$[Co(L)_2(H_2O)_2]$	3079	1700	1212	691
$[Zn(L)_2].2H_2O$	3372	1670	1208	668
$[Ni(L)_2]Cl_2$	-	1596	1238	691

Antioxidant assay

The DPPH free radical scavenging activities of the chalcone derivative (ligand) and its metal complexes were evaluated and expressed in percentage scavenging activities IC_{50} as summarizes in (Table 5). The copper complex of the chalcone derivative was identified to be the best DPPH free radical scavenger among the compounds investigated with an IC_{50} of 7.89µg/ml. The cobalt and zinc complexes exhibited higher radical scavenging activity than the standard vitamin C with 10.77µg/ml. This is due to the fact that the lower the IC_{50} the higher the antioxidant activity of the compound and the activity may be due to the metal ion chelation (Chavan et al., 2016).

Table 5: Antioxidant evaluation of the ligand and its complexes.

Compounds	IC_{50}(µg/ml)
$(C_{15}H_{11}ClO_2)$	30.55
$[Co(L)_2(H_2O)_2]$	7.89
$[Zn(L)_2].2H_2O$	10.12
$[Ni(L)_2]Cl_2$	29.91
Vitamin C	10.77

Conclusion

From the result obtained in this research, it can be concluded that the chalcone derivatives ligand and its Co (II), Zn (II) and Ni (II) Complexes were fully synthesized. The ligand was found to be coordinated to the metal through carbonyl oxygen and oxygen-carbon. The proposed geometry was octahedral. Moreover, the ligand and the metal complexes have shown a good and promising antioxidant activity against DPPH free radical with cobalt and zinc complexes with the highest scavenging activity than that of the vitamin C standard control. This is displayed due to the complexation that takes place thereby making the compounds more powerful and reducing the radicals.

Recommendation

The researcher is hereby recommend that, ^{1}H and ^{13}C NMR spectroscopy, X-ray crystallography and mass spectrometric analyses should be carried out and other biological activity tests such as antitumor, antibacterial, antiviral, antifungal among others to be carried out on the compounds to broaden the biological application of the compounds synthesized.

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