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Research Article

Synthesis, Spectroscopic Characterization and Antibacterial Studies of Co(II), Ni(II) and Cu(II) Complexes with Bis(Indolyl) Methane derived from 2-Methylindole and *p*-Vanillin

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Abstract : The Bis (Indolyl) Methane (BIM) has been prepared from 2-methylindole and *p* -vanillin. The ligand was characterized by elemental analysis, IR, mass, ^{1}HNMR, ^{13}CNMR and electronic data. The Cobalt(II), Nickel(II) and Copper(II) complexes of the ligand (BIM) were prepared and characterized by analytical spectroscopic methods. The molar connductivity data reveal that the chelates are non-electrolytes. The free ligand (BIM) and its metal complexes were screened for their antibacterial activities. The results indicated that the metal complexes are better antibacterial agents as compared to the free ligand BIM.

Keywords *:* Bis (Indolyl) Methane, Metal Chelates, Antibacterial Activity, Spectroscopic Study

INTRODUCTION

Indole and its derivatives are attractive compounds[1] and exhibit a range of bioactivities[2-10]. In addition, Bis(Indolyl) Methanes are cruceferous substances useful for promoting beneficial estrogen metabolism in men and women[11]. On the other hand, Bis(Indolyl) Methanes (BIM) have also found application as colorimetric sensors, particularly for various metals and fluoride[12]. The chelating ligands containing O and N donor atoms show brod biological activity and have special interest on bonding to metal ions[13]. Since the discovery of Cisplatin[14], many complexes have been synthesized and tested on a number of biological systems[15]. Copper complexes are know to have a broad spectrum of biological action[16]. These investigations led to the conception that the BIM ligand of *p*-vanillin would possess antibacterial properties. In this study, we report the synthesis and spectroscopic characterization of a BIM ligand derived from the condensation of 2-Methylindole and *p*-Vanillin and its Co(II), Ni(II) and Cu(II) complexes followed by their antibacterial screening against different species of bacteria. To our knowledge, antibacterial activity of the BIM and its complexes were not studied.

EXPERIMENTAL

Materials and methods : All reagents and solvents were pourchased from Acros, Aldrich and were used without further purification. Melting points were determined on a Kofler melting-point apparatus and are uncorrected. The microanalysis of C, H and N were estimated by elemental analyzer Thermo Scientific Flash 2000 at Lorraine University (France). Metal contents present in the complexes were determined by EDTA titration.The molar conductance of the complexes was measured using conductometer type Lamork AD 3000. Infrared Spectra were recorded an a Perkin-Elmer FTIR type 1650 spectrophotometer. The spectra were recorded as KBr pellets Thermogravimetric analyses were carried out using a NETZSCH STA 409 PC/PG thermal analyzer under nitrogen atmosphere with a heating rate 10°C/min. The UV-vis absorption spectra were measured on a Shimadzu 1600 spectrophotometer. The spectra of ^{1}H NMR and ^{13}C NMR were recorded in solution in dimethylsulfoxide (DMSO-$_{d6}$) on a Bruker spectrometer (^{1}H at 400 MHz, ^{13}C at 100 MHz). The chemical shifts are expressed in parts per million (ppm) by using tetramethylsilane (TMS) as internal reference. The multiplicities of the signals are indicated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quadruplet; and m, multiplet, and coupling constants are expressed in Hertz. The mass spectra were performed using Maldi Tof mass spectrophotometer at Lille University (France)

Synthesis of the ligand 4-(Bis (2-methyl-1H-indol-3-yl) methyl)-2-methoxyphenol (BIM) : Ligand BIM was prepared using a method reported in the literature[17].A mixture of 2-methylindole **1**(10mmol), *p*-vanillin **2**(5mmol) and glacial acetic acid (5ml) was reflux for 1h. The reaction mixture was cooled, and poured into water. The precipitated solid was filtered off, washed with water, dried and recrystallized of methanol, washed with diethylether and dried in a vacuum over anhydrous calcium chloride.A pink solide (85% Yield), mp =232°C.UV/vis(MeOH) : λ= 284nm. IR (KBr, cm^{-1}): 3479(O-H) ; 3370 (N-H) ; 1610 (C=C) ; 1254 (C-O) Phenolic. ^{1}HNMR (400MHz, DMSO-$_{d6}$) δppm: 2.06 (6H, s, 2 CH_3) ; 5.81 (1H, s, CH) ; 6.51-7.20 (11H, m, Ar-H) ; 8.70 (1H, s, Ar-OH) ; 10.67 (2H, s, N-H). ^{13}CNMR (100MHz, DMSO-$_{d6}$) δppm : 157,02, 136.06 ; 134.99 ; 131.83 ; 129.49 ; 128.20 ; 119.41 ; 118.45 ; 117.81 ; 113.22 ; 112.46 ; 110.21 ; 54.88 ; 37.70 ; 11.66. MS(Maldi) (Calcd : 396.48): 395.0816 (100%) [M-1]$^{+}$. Anal. calcd. For$C_{26}H_{24}N_2O_2$: C, 78.76 ; H, 6.06 ; N, 7.07 ; Found : C, 78.17 ; H, 6.72 ; N, 6.64.

Synthesis of metal complexes : The appropriate transition metal chloride salt ($CoCl_2.6H_2O$ or $NiCl_2.6H_2O$ or $CuCl_2.2H_2O$, 1mmol) dissolved in anhydrous ethanol (10ml) was stirred with ligand BIM(0.792g,2mmol) in anhydrous ethanol (15ml) and refluxed for 2h. After cooling to room temperature, the complexe precipitated. It was collected by filtration, washed with diethylether and dried under vacuum in the presence of anhydrous $CaCl_2$.

Complexe 1 :[{4-(Bis (2-methyl-1H-indol-3-yl) methyl)-2-methoxyphenolato} $_2Cl_2(H_2O)_4$ Co] : A purple solide (70% Yield), mp>300°C.^{1}HNMR (400 MHz, $DMSO_{d-6}$) δ:2.02 (12H, s, $4CH_3$) ; 3.48(s, 6H, $2OCH_3$) ; 6.83 (22Har+ 2CH, m) ; 11.76 (4H, s, 4NH). Λ_m : 38.46 Ω^{-1} cm^2 mol^{-1}. UV/vis (MeOH, nm) : λ= 282, 504. IR (KBr, cm^{-1}) : $3312(H_2O)$; 3179(NH) ; 1614 ; 1586 ; 1457 ; 748(C= C) ; 505(M-O) ; 434(M-OMe). MS(Maldi) Calcd : 994.89 ; Found : 995.73 $[M+1]^+$ Anal. calcd. For$C_{52}H_{48}N_4O_4$ $CoCl_2.4H_2O$: C, 62.72.76 ; H, 4.82 ; N, 5.62, Co, 6.83 ; Found : C, 62.33 ; H, 5.07 ; N, 4.98 ; Co, 6.03.

Complexe 2 :[{4-(bis (2-methyl-1H-indol-3-yl) méthyl)-2-methoxyphenolato} $_2Cl_2$ $(H_2O)_4$ Ni] :A dark red solide (54% Yield), mp>300°C.^{1}HNMR (400 MHz, $DMSO_{d-6}$) δ:2.06 (12H, s, $4CH_3$) ; 3.50(s, 6H, $2OCH_3$) ; 7.07 (22Har+ 2CH, m) ; 12.09 (4H, s, 4NH). Λ_m : 24.33 Ω^{-1} cm^2 mol^{-1}. UV/vis (MeOH, nm) : λ= 276, 328, 508. IR (KBr, cm^{-1}) : $3381(H_2O)$; 3183(NH) ; 1616 ; 1591 ; 1518 ; 1457 ; 751, (C= C) ; 502(M-O) ; 435 (M-OCH_3). MS(Maldi) Calcd : 994.65 ; Found : 994.87 $[M]^+$ Anal. calcd. For$C_{52}H_{48}N_4O_4$ $NiCl_2.4H_2O$: C, 67.74; H, 4.82 ; N, 5.63 ; Ni, 5.90; Found : C, 67.15 ; H, 4.02 ; N, 5.88 ; Co, 6.15.

Complexe 3 :[{4-(bis (2-methyl-1H-indol-3-yl) methyl)-2-methoxyphenolato} $_2(H_2O)_4$ Cu] :A red solide (75% Yield), mp>300°C.^{1}HNMR (400 MHz, $DMSO_{d-6}$) δ: 2.05 (12H, s, $4CH_3$) ; 3.17(s, 6H, $2OCH_3$) ; 7.57 (22Har+ 2CH, m) ; 12.50 (4H, s, 4NH). Λ_m : 23.33 Ω^{-1} cm^2 mol^{-1}. UV/vis (MeOH, nm) : λ= 278, 508. IR (KBr, cm^{-1}) : $3354(H_2O)$; 3183(NH) ; 1615 ; 1588 ; 1511 ; 751, (C= C) ; 507(M-O) ; 436(M-OMe). MS(Maldi) Calcd : 928.50 ; Found : 923.08 $[M-5]^+$ Anal. calcd. For$C_{52}H_{48}N_4O_4$ $Cu.4H_2O$: C, 67.20; H, 5.16 ; N, 6.03, Cu, 6.83, 6.83 ; Found : C, 67.60 ; H, 5.20 ; N, 6.06 ; Co, 6.87.

Antibacteriel studies : The test microorganisms ; *Escherichia coli* ATCC25922, *Pseudomonas aeruginosa* ATCC27853, *Bacillus subtilis* ATCC663, *Staphylococcus aureas* ATCC25923and *Staphylococcus epidermidis* ATCC43300 were obtained from the Laboratory of Antibiotic therapy and Hygiene of the Pasteur Institute of Algeria).Antibacterial activity of the ligand and metal complexes were tested in vitro against a three Gram-positive bacteria (*B. subtilis*, *S. aureus*, *S. epidermidis*) and two Gram-negative bacteria (*E. coli*, and *P. aeruginosa*) by the disc diffusion method[18] using nutrient agar medium.The test organisms were grown on nutrient agar medium in petri plates. The compound were prepared in MeOH and soaked in filter paper disc of 9mm diameter. The concentration of ligand and the complexes used in this study was 5 mg/ml and 1mg/ml. The discs were placed on the previously seeded plates and incubated at 37°C and the diameter (mm) of inhibition zone around each disc was measured after 24h for antibacterial activity. A blank disc was soaked in the solvent (MeOH) and implanted as negative control on each plate along with standard drugs.

RESULTS AND DISCUSSION

The formation of BIM ligand and its complexes were confirmed on the basis of results of molecular ion peak in mass spectra, elemental analysis, the caracteristic bands in the FT-IR, UV-Vis and resonance signals in the ^{1}HNMR. The results obtained data of the ligand show good agreement with theoretical values
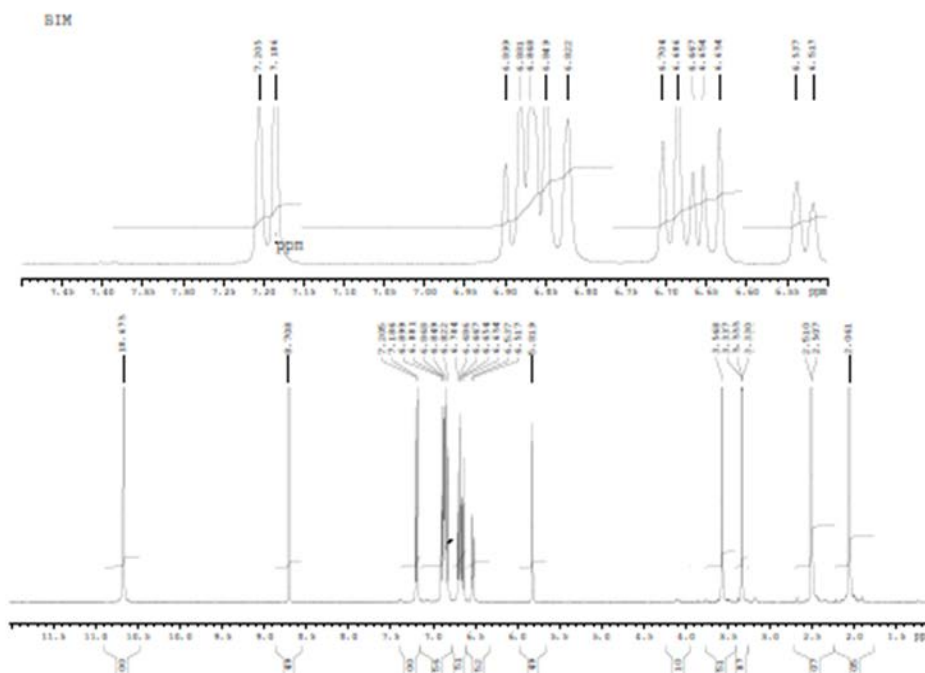
Ligand and characterization : BIM ligand (Scheme 1) was prepared by the direct solution reaction, as reported in the literature[17].

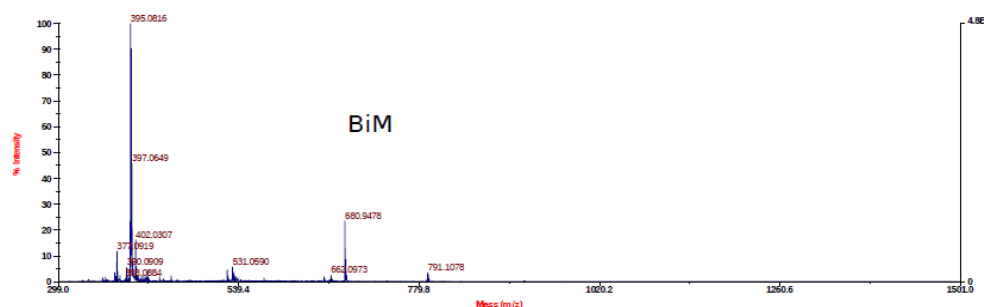**Scheme 1 :** Formation of BIM ligand

The results of elemental analyses (C, H, N) are in good agreement with those calculated for the suggested formula. The structure of the ligand under study is given below in **Scheme 1**

^{1}HNMR,^{13}CNMR and Mass spectra : The singlet at 2.06ppm in the proton NMR spectra of the ligand BIM can be attributed to the protons of the CH_3-groups of indol moiety. The singlet peak at 3.56ppm may be assigned to the protons of CH_3O-groups of the benzene ring. The singlet at 5.81ppm can be attributed to the proton of the CH. The multiplet at 6.51-7.20ppm are characteristic of the protons of the benzene and indole ring. In additio, the chemical shifts of the proton on phenol (OH) and secondary amine (NH) are around 8.70ppm and 10.67ppm, respectively **(figure1).**
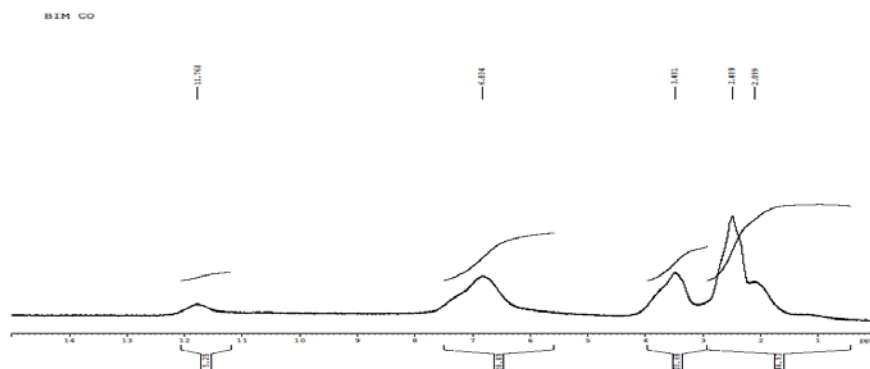

Figure1 : The ^{1}HNMR spectrum of ligand

The mass spectrum of the ligand BIM **(figure 2)** showed molecular ion peak at 395. 0816[M-1] [+.] ; 397.0649 [M+1] [+.] (90%), which correspondind to its formula $C_{26}H_{24}N_2O_2$ base peak at m/z(%) : 395(100%), peak at 680(20%), peak at 791(4%) which confirms the suggested structure. The IR and UV-vis data of BIM ligand will be discussed with its metal complexes.

Figure 2 : The Maldi Tof mass spectrum of ligand BIM

Metal complexes and characterization : The reaction of metal ions with the BIM in anhydrous ethanol in (1 :2) molar ration takes place. The isolated solid complexes of Co(II), Ni(II) and Cu(II) were subjected to elemental analyses (C, H, N), Mass, thermal analysis, IR, UV-vis and ^{1}HNMR spectral studies, molar conductance to identify their formula and their molecular structure. The results of elemental analyses, which agree well with those required by the proposed formula. All complexes were stable at room temperature and insoluble in water and most organic, soluble in MeOH and DMSO. The ^{1}HNMR spectrum of Co(II) Ni(II) and Cu(II), complexes recorded in DMSO-$_{d6}$. The signal at 8.70ppm in the [1] HNMR spectrum of the ligand due to OH proton, disappeared in the spectrum of all the complexes (figure 3). This is a clear indication that the phenolate group is coordinated to the metal ion through the phenolate oxygen after deprotonation. A broad band observed at 11.76ppm ,10.67ppm and 12.50ppm may be attributed to the proton N-H group of indole moiety for Co(II), Ni(II) and Cu(II), respectively. On comparing the position of other proton signals in the complexes with those of the ligand signals , it can be concluded that these signal are in the expected region and shift only slightly due to the coordination of the ligand to the metal ion.
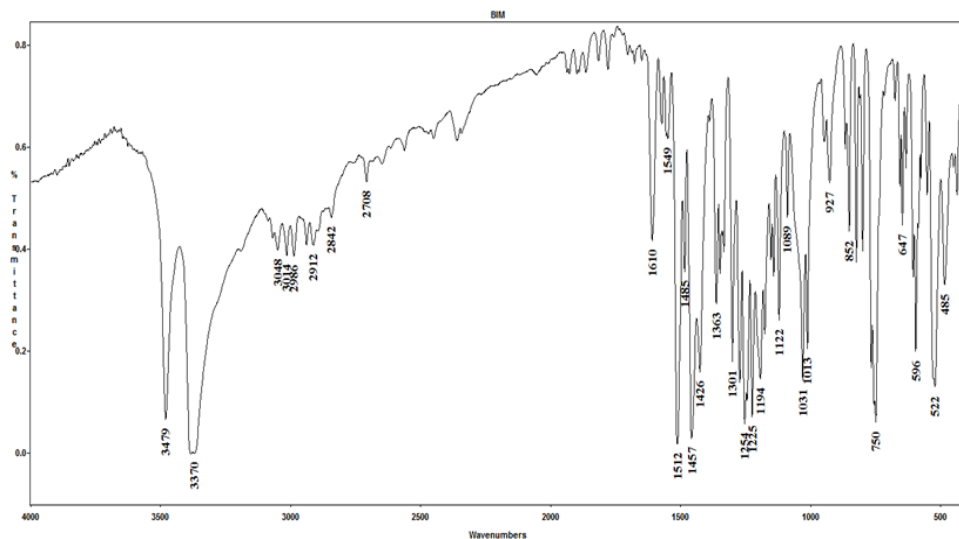

Figure 3 : The ^{1}HNMR spectrum of complexe1

Molar conductivity measurements : The chelates were dissolved in MeOH and the molar conductivities of their solutions (10^{-3} M) at room temperature were measured. The data 23.33, 24.33 and 38.46 Ω^{-1} cm^2 mol^{-1}showed that the molar conductance values of the Co(II), Ni(II) and Cu(II), complexes were relatively low, indicating the non electrolytic nature of these complexes[19].

IR spectra : The Infrared spectra of the free ligand and its metal complexes were obtained over a spectral range of 4000-400 cm^{-1}. The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in chelation. Characteristic peaks in the spectra of the ligand and complexes were considred and compared.
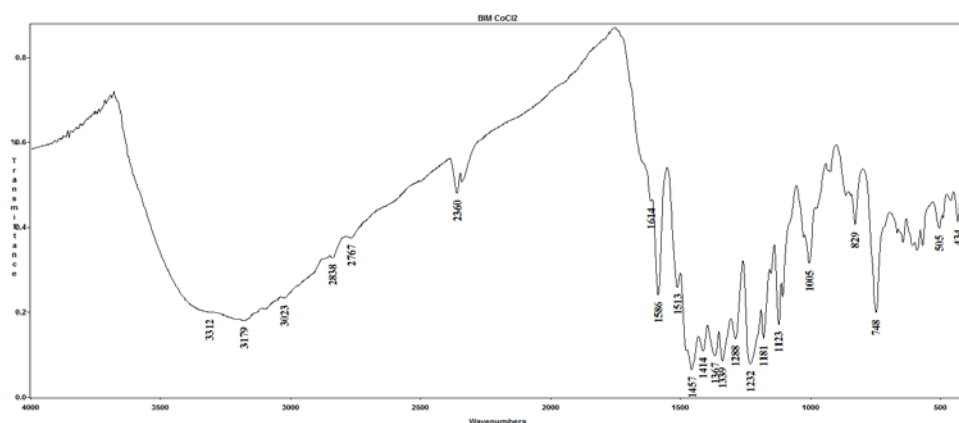
The IR spectra of the free ligand **(Figure 4)** shows two broad bands at 3479 cm^{-1} and 3370 cm^{-1},which can be attributed to ν(OH) and ν (N-H) streching vibrations of the phenolic-OH and indol moiety respectively.
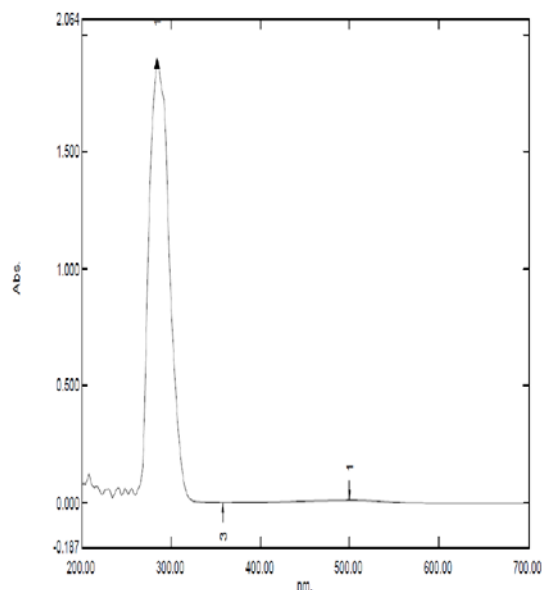

Figure 4 : IR spectra of ligand BIM

The IR spectra of metal complexes exhibited a broad band at 3400-3100 cm^{-1} which were assigned to ν(OH) from water molecules and ν (N-H) of ligand BIM respectively[20]. A reference spectrum of complexe 1 has been shown in Figure 5

The strong phenolic ν(C-O) of the free ligand BIM is observed at 1254 cm^{-1}, upon chelation, this band is shiffted to lower value by 24-29 cm^{-1}, indicating that coordination bonds were betwen the metal ion and the oxygen atoms of the phenol hydroxyl and the methoxy group for these complexes[21].The coordination is further supported by the apperance of new non-ligand bands in the range of 502-507cm^{-1}dueto ν (M-OH) and 434-436 cm^{-1} due to ν (M-OMe) [22,23].
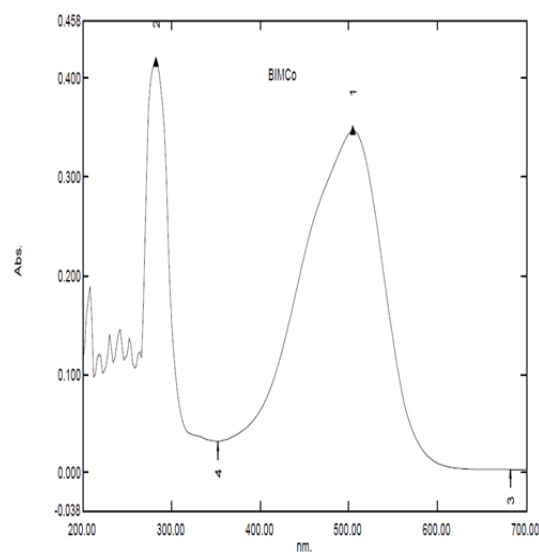

Figure 5 :IR spectra of complexe 1

Electronic spectra : The electronic spectral data of the ligand and its metal complexes are recorded in MeOH solution in the wavelenght range 200-700nm. The electronic spectra of the free ligand BIM **(Figure 6)** showeds one band at 284nm characteristic of π- π* transition due to transition involving molecular orbital located in the indole ring display. This speak has been relatively unaffected in the spectra of the complexes ; this is indicating that, the indole ring has nil role in complexation.The spectra of Co(II) (Figure 7), Ni(II) and Cu(II) complexes reveal a new bands at 504, 508 and 508nm which can be attributed to d-d transition within the complexes respectively.
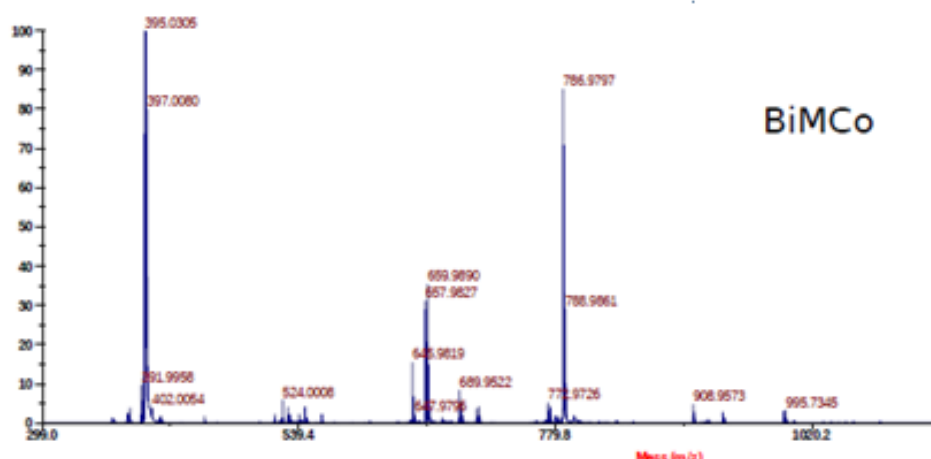
Figure 6 : UV-vis spectra of ligand BIM   **Figure 7 :** UV-Vis spectra of complexe1

Mass : The Maldi Toff mass spectra of Co(II), Ni(II) and Cu(II) BIM complexes have been recorded. All the spectra exhibit parent peaks due to molecular ion $[M^{+\cdot}] = 396$. The intensity ratios of the observed peaks around 787, 789,658, 660 for Ni and at 786, 788, 657, 659 for Co(II) (Figure 8) corresponding to isotopic chloride, and not observed for Cu.The proposed molecular formula of the complexes was confirmed by comparing their molecular formula weight with m/z values. The molecular ion $M^{+\cdot}$ peak obtained from these compounds are : 395[M-1] $^{+\cdot}$, 397[M+1] for the ligand ; 994.87 [$M_{Ni}+1$]; 995.73 [$M_{Co}+1$] and 923.08 [$M_{Cu}-5$]
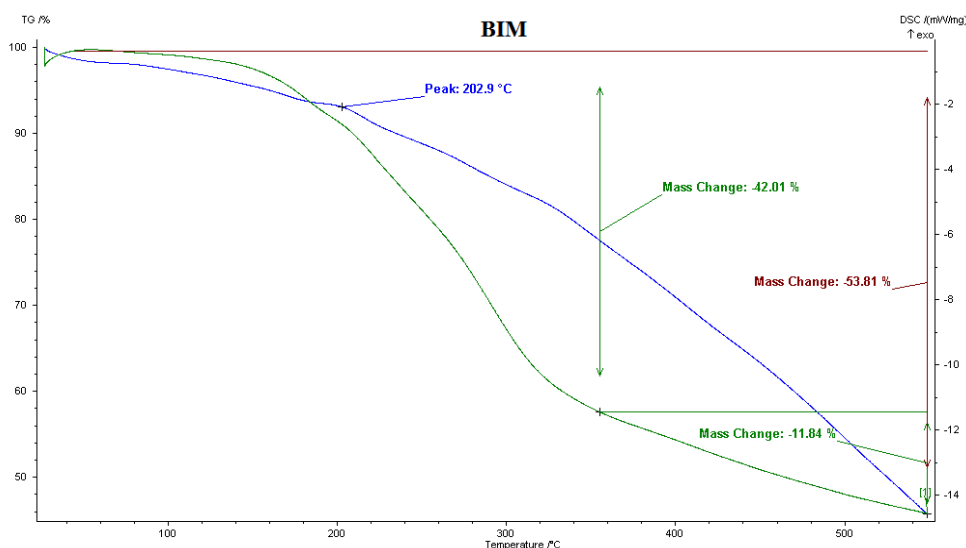

Figure 8 : The Maldi Toff mass spectrum of complexe1

Thermal analysis : The TGA curve **(Figure 9)** indicates that the BIM ligand begins to decompose at 209.9°C .The TGA curves displays two stages of mass loss within the temperature range of 167-360°C and exhibits a mass of 42.01% corresponding to the loss of $C_{11}H_6N_2$ (Calc 41.97%). The second stage occurs at 360-570°C with a mass loss of 11.84%, corresponding to the loss of CO_2 (Calc 11.11%).The TGA curves indicate that the complexes Co(II), Ni(II) and Cu (II) begin decomposition

at 281.2, 256.1 and 303.5°C, respectively. A comparison of thermogravimetric curves for the ligand and its metal complexes shows that the complexes are more thermally stable than the BIM ligand.

Figure 9 : Thermogravimetric curves (DTA and TGA) of BIM ligand

The order of thermal stability is found to be Cu(II) >Co(II)>Ni(II)>BIM ligand The thermogravimetric analysis data for the ligand and its complexes are presented in **Table1**.
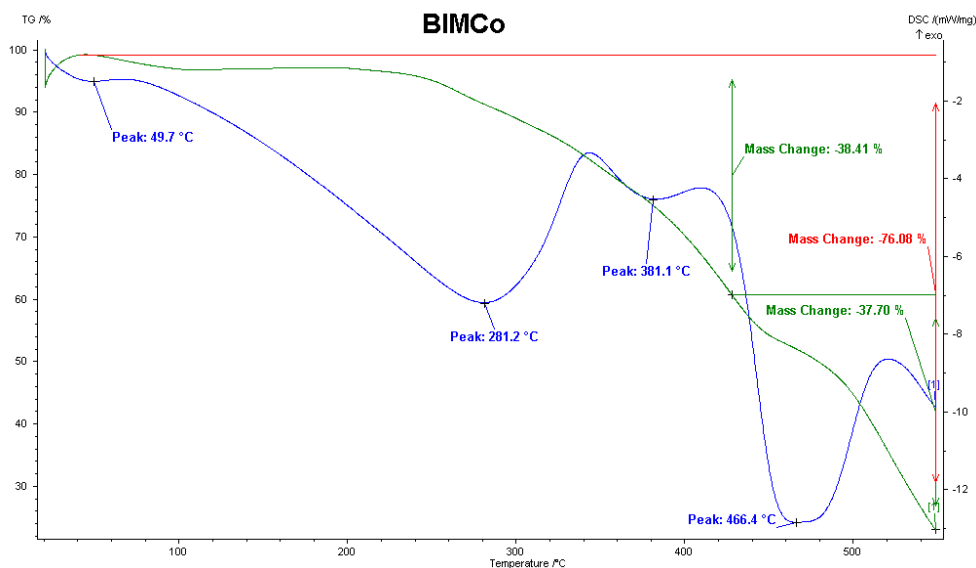
Table 1 : Thermal analyses (DTA and TGA) of the metal complexes.

Compounds	Temp. range (°C)	weight loss% Calc(Found)	Assignments	DTG max °C	Steps
Ligand	167-360 360-570	41.91 (42.01) 11.11 (11.84)	$C_{11}H_6N_2$ CO_2	202.9	1st 2nd
Complexe 1	40-450 450-570	38.43 (38.41) 37. 72(37.70)	$4H_2O$, Cl_2, $C_{19}H_{11}N$ $C_{23}H_{25}N_3O_2$	49.7 281.2 381.2 466.4	1st 2nd 3rd 4th
Complexe2	40-248 248-338 338-570	7.24 (7.73) 19.42 (19.40) 31.39 (31.06	$4H_2O$ $C_8H_{12}NCl_2$ $C_{18}H_{18}N_3O_2$	60 256.1 488.9	1st 2nd 3rd
Complexe3	40-290 290-328 328-570	9.52 (9.07) 10.35 (10.39) 46.65 (48.67)	$5H_2O$ C_7H_{12} $C_{30}H_{17}N_3O_2$	60 303.5 430.7	1st 2nd 3rd

The TG curve of Co(II) complexe (Figure 10) shows two stages of decomposition within the temperature range of 40-570°C. The first step at 40-450°C corresponds to the loss of four water molecules of hydrations, Cl_2 and $C_{19}H_{11}N$ with a mass loss of 38.41% (Calc 38.43%). A bove 450°C, weight loss of 37.70% (Calc 37.72%) has been observed betwen the temperature range 450°C-570°C corresponding of the $C_{23}H_{25}O_2N_3$.The TG curves of Ni(II) and Cu(II) chelates show three stages of decomposition within temperature range of 40-570°C. The first step at 40-290°C corresponds to the loss of water molecules of hydration.The subsequent two steps involve the loss of ligand molecule.
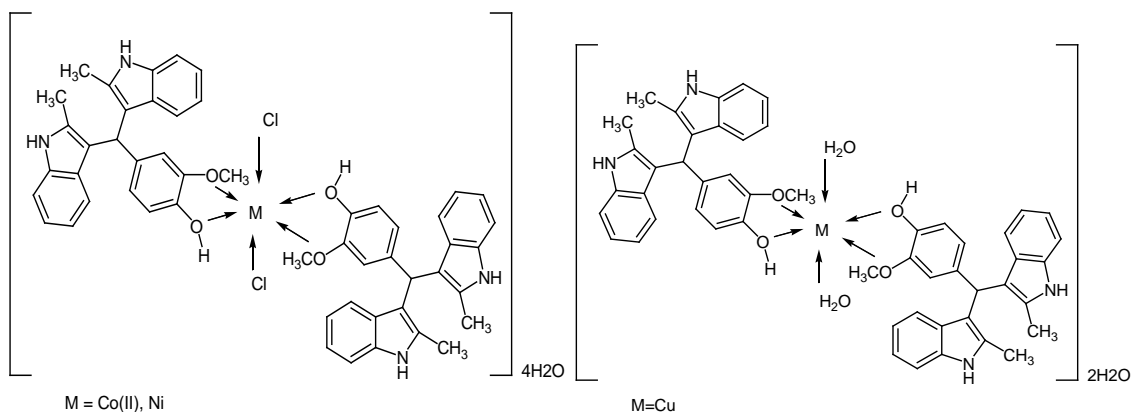
The overall weight loss amounts to 50.46% (Calc 50.81%) and 59.06% (Calc 59.00%) for Ni(II) and Cu(II) chelates respectively.

Figure 10 : Thermogravimetric curves (DTA and TGA) of complexe 1

Structural interpretation : From the spectral data, thermal and the elemental analyses, the structures proposed are based on octahedral geometry and the ligand is a neutral bidente coordinates to the metal via phenolic-OH, OCH_3 for Co(II), Ni(II) and Cu(II).Proposed structures of Co(II), Ni(II) and Cu(II) metal complexes.

Antimicrobial studies : The ligand and its complexes were screened separately for their antibacterial activity against *Escherichia coli* (G⁻), *Pseudomonas aeruginosa* (G⁻),*Bacillus subtilis* (G⁺), *Staphylococcus aureas* (G⁺)and *Staphylococcus epidermidis* (G⁺), using a filter paper method[18] and agar medium ; the concentration of the tests solutions was 5mg/ml and 1mg/ml. The results of the bacterial study of the synthesize compound are display in **Table 2**

All the tested compound showed activity againt the bacterial strains,*B.subtilis* (G⁺) and*S.aureus* (G⁺). All the tested compound except for complexe1, are found to have no biological activity againt *P. aeruginosa* (G⁻). With *S.epidermdis* (G⁺), Bim and complexe 1 showed moderate activity while the either compound showed no activity. The complexe 1 has the best antibacterial activities of all complexes against five bacterial and shows better activity against *S.aureus* (G⁺).

Table 2 : Inhibitory zone (diameter) mm of ligand and its complexes against tested bacterial strains by the disc diffusion Gram-negative Gram-positive method.

Compounds	Microorganisms									
	B.subtilis mg/ml		*E.Coli mg/ml*		*P. aeruginosa*		*S.aureus mg/ml*		*S.epidermidis*	
	5	1	5	1	5	1	5	1	5	1
L	12	11	10	NA	NA	NA	13	11	11	10
Complexe 1	25	21	27	23	17	13	30	26	17	15
Complexe 2	19	12	13	10	NA	NA	17	12	NA	NA
Complexe 3	16	14	NA	NA	NA	NA	17	14	NA	NA
MeOH	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

*Note : the data in the Table 2 ares average values of three experiments, the diameter of the filter paper is 9 mm. NA: Not active

Antimicrobial data suggests that the metal complexe1 is better antibacterial agent as compared to either compounds.On comparing the activity of the tested complexe 1 with its parent ligand BIM, the obtained data indicated that the activity is increased upon complexation. This result may be explained by the basis of chelation theorie[24]. Reports have shown that $CuCl_2.2H_2O$, $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ have no inhibitory activity on bacteria species[25].

CONCLUSION

In this work, the condensation of 2-methyl indole and *p*-vanillin to yield the BIM has been reported. The presence of N and O donor atoms renders this compound interesting for study its coordination behaviour with transition metals ion. Three new complexes with cobalt, nickel and copper have been synthesized and characterized by using elemental, mass spectra, IR, UV-Vis ^{1}HNMR and molar conductance. All the data collected in agreement with the proposed structures.

The obtained results suggested that the ligand behaves as a neutral bidente ligand with different coordination sites OH and OCH_3 groups for Co (II), Ni(II) and Cu(II). Antibacterial study reveals that metal complexes have more biological activity than free BIM ligand. Complexe Co(II) shows best antimicrobial activity against all microorganism as compared to either compounds.

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