Coordination Compounds of Carbonyl Oxygen and Indole Nitrogen Bidentate Ligand; Synthesis, Structural Characterisation and Biological Activity

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Abstract

The synthesis of the bisaldehyde ligand 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)malonaldehyde (B) and its coordinated compounds with Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) ions are reported. The synthetic route of B was completed by adopting the Vilsmeier-Haack reaction. This was based on the mixing of 1,1,2-trimethyl-1H-benzo[e]indole with phosphoryl trichloride and N, N-dimethylformamide (anhydrous) that gave the aminomethylenemalondialdehyde. The use of POCl3 and DMF was aimed to give the Vilsmeier-Haack intermediate, which was kept at 5°C and then heated with stirring at 85°C. The addition of an aqueous NaOH solution (35%) to the reaction mixture resulted in the isolation of B. The monomeric coordinated compounds are isolated from the mixing of B with selected metal ions (Cr(III), Mn(II), Fe(II), Co(II) Ni(II) and Cu(II)) in a mixture of EtOH/DMF medium in a 1:1 mole ratio of M:L. The structural characterisation of the prepared compounds was performed through a range of physicochemical methods (FT-IR, electronic spectroscopy, mass and 1H, 13C-NMR spectra, elemental microanalysis, magnetic susceptibility and molar conductance). The analytical and spectroscopic data indicated the isolation of six-coordinate monomeric complexes with the general formula; [Cr(B)Cl)2(H2O)2]Cl, [Mn(B)Cl)2(H2O)2] and four-coordinate monomeric complexes of the general formula [Fe(B)(Cl)2] and [M(B)Cl)(H2O)]Cl (where M(II)= Co, Ni and Cu). The antimicrobial activity of the ligand and its coordinated compounds was explored towards G+ and G- bacterial strains and fungal species. The collected data indicated that the coordinated compounds became potentially more active, compared with B.

Keywords: Bisaldehyde ligand; Vilsmeier-Haack approach; Monomeric coordinated compounds; Structural characterisation; Biological activity.

Introduction

The importance of the formation of compounds bearing bisaldehyde functional moieties is related to their role in the development of synthetic chemistry (organic, natural products and inorganic chemistry), biology and industry [1,2]. Further, the synthesis of such compounds represents a key route in the formation of precursors that are used in the fabrication of supramolecules and nanotechnology [3,4]. Natural product species are a crucial type of organic material and aromatic aldehydes or ketones materials are among them [3]. These compounds have been included in the fragrance and cosmetics industries, and food technology. More, the reaction of carbonyl compounds (aldehydes and ketones) with a primary amine resulted in the synthesis of the Schiff base [5-9]. The formation of the interesting bisaldehyde compound 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)malonaldehyde was achieved through the Vilsmeier-Haack reaction [10]. Molecular docking studies for the title compound to N-methyl-D-aspartate (NMDA) receptor and its anticonvulsant effects against seizures elicited have been explored [11]. The *in vivo* data (using rats) indicated this compound showed excellent anticonvulsive activity and may represent a potential human anticonvulsant agent. More, this compound is an important precursor that may use to generate a range of Schiff base ligands including the chalcogensemicarbazones that are used as complexation agents. The involvement of the chalcogen groups in the coordination with the metal centres has been reported [12-17]. Metal complexes derived from Mannich bases in which the carbonyl oxygen group of the cyclohexanone moiety is involved in the coordination with the metal centres were reported previously by our group [18,19]. More, to the best of our knowledge, there are no reported publications on the use of 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)malonaldehyde as a complexation agent. Therefore, this paper is tailored to report the potential ability of B as a complexation agent in which one of the carbonyl oxygen of the bisaldehyde moieties and the indole nitrogen group is involved in the coordination with the metal centre. Upon complex formation, the impact of the required steric and electronic parameters that influenced the structural preference of the metal centre is a key role in the determination of the coordination geometry of the isolated complexes. Therefore, monomeric six- and four-coordinated complexes are reported. The

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antibacterial and antifungal activities of the ligand and its coordinated compounds were also investigated. The experimental data indicated that the coordinated compounds became potentially more active, compared with B.

Materials and methods

All laboratory-grade reagents and solvents used in this study were purchased from commercial sources and used without further purification. The FTIR spectra of compounds were recorded using KBr and CsI discs from 4000–250 cm^{-1} on a Shimadzu Fourier Transform Infrared Spectrometer (FTIR-600). The mass spectrum for the ligand was determined using the electrospray method (positive mode) with the Agilent mass spectrometer Sciex ESI mass analysis. The ^{1}H- and ^{13}C-NMR spectra of the ligand were acquired in DMSO-d$_6$ with a Brucker-500 MHz. For the ^{1}H-NMR study, tetramethylsilane (TMS) was used as an internal standard to measure chemical shifts. A Shimadzu UV-Vis 1800 spectrophotometer was used to analyze electronic spectra of compounds from 200–1100 nm for 10^{-3} M solutions in DMSO at ambient temperature. The melting points (mp) of the synthesized compounds were determined in an open capillary tube on Melting Point Apparatus SMP$_{30}$. Elemental analysis (C.H.N.) for the ligand and their metal complexes was performed using EuroEA 3000 machine. A Shimadzu (A.A) 680G atomic absorption spectrophotometer and a potentiometric titration technique on a 686-titro processor-665 Dosimat-Metrom Swiss were used to determine metal and chloride percentages for compounds, respectively. The magnetic moments were performed on a Sherwood Scientific Devised at 308 K. A Eutech Instruments Cyberscan con 510 digital conductivity meter was used to measure molar conductance for complexes.

Synthesis

Synthesis of 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)malonaldehyde (B)

The formation of B was based on a method published in [10,11] with a modification and as follows;

To a mixture of 1,1,2-trimethyl-1H-benzo[e]indole (1.0g, 4.78mmol) in 5ml of anhydrous dimethylformamide that was kept in an ice bath, was added dropwise a solution of phosphoryl chloride (1.76ml, 19.12mmol) in anhydrous dimethylformamide (3ml). The mixture was kept stirring below 5°C in an ice bath over a period of 1h. The reaction mixture was then stirred at 85°C for 3h and then poured into the icy water. The pH was adjusted to *ca.* 8.0 by adding an aqueous solution of NaOH (35%). The yellow solid that formed was collected by filtration and washed with hot water. The resulting solid product was recrystallized from ethanol and yellow crystals that formed were air-dried. Yield: 1.8g (91%), m.p =198-200°C. FT-IR (KBr) cm^{-1}; 3140 ν(N-H), 1679 ν(C=O), 1628 cm^{-1} ν(C=C)$_{\text{aliphatic,}}$ 1598 δ(N-H) and 1222 ν(C-N). The ^{1}H-NMR spectrum (400MHz, DMSO-d$_6$) of B showed peaks at δ_H (ppm); 13.44 (1H, br., N-*H*), 9.77 (2H, s, C$_{1,1'}$-*H*). 8.18-8.16 (1H, d, C$_{11}$-*H*, *J*=8.48Hz), 8.02-8.0 (1H, d, C$_{13}$-*H*, *J*=8.16Hz), 7.97-7.90 (2H, dd, C$_{8,14}$-*H*, *J*=8.72; 8.68Hz), 7.64-7.60 (1H, t, C$_{13}$-*H*, *J*=7.08Hz), 7.51-7.47 (1H, t, C$_{12}$-*H*, *J*=7.28Hz), 1.92 (6H, s, C$_{15,15'}$-*H*). The ^{13}C-NMR spectrum (100MHz, DMSO-d$_6$) of B showed peaks at δ_H (ppm); 22.24 and 52.92 assigned to C$_{15,15'}$) and (C$_4$), respectively. peaks detected at 109.13, 114.68, 122.87, 125.24, 127.79, 127.84, 130.15, 130.24, 132.20, 133.20 and 137.88 ppm were correlated to (C$_5$), (C$_2$), (C$_9$), (C$_{13}$), (C$_{11}$), (C$_{12}$), (C$_8$), (C$_7$), (C$_{14}$), (C$_6$) and (C$_{10}$), respectively. Chemical shifts at 179.6 and 190.64ppm attributed to (C$_3$) and the carbonyl groups (C$_{1,1'}$), respectively.

Synthesis of B metal complexes

An analogue procedure was adopted to prepare the complexes of $[Cr(B)Cl)_2(H_2O)_2]Cl$, $[Mn(B)(Cl)_2(H_2O)_2]$, $[Fe(B)(Cl)_2]$ and $[M(B)(Cl)(H_2O)]Cl$ (where M(II)= Co(II), Ni(II) and Cu(II)). The formation of $[Cr(M)(Cl)_2(H_2O)_2]Cl$ is reported as an example of the preparation of other complexes and as follows;

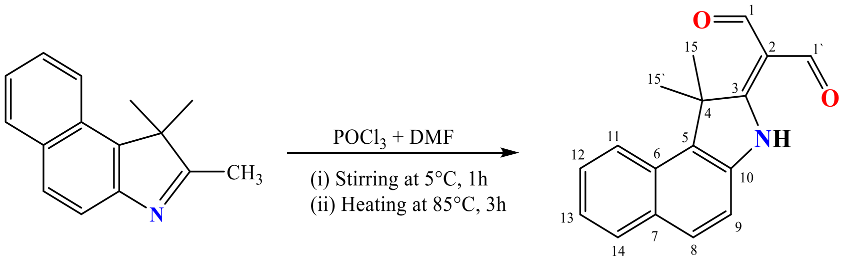
A solution of chromium(III) chloride hexahydrate (0.10g, 3.76mmol) in 5ml of ethanol was added drop-wise with stirring to a mixture of B (0.10g, 3.76mmol) in a 10ml mixture of DMF and ethanol (8:2; v/v). The resulting mixture was heated at 65-70°C for 4h, during which time a deep coloured solution was generated. Upon standing at room temperature, a deep green solid was crushed out of the solution. The solid was collected by filtration, washed with ethanol (5ml), diethyl ether (5ml) and air-dried. Yield: 0.12g (75%), m.p = >300 °C.

Biological Activity

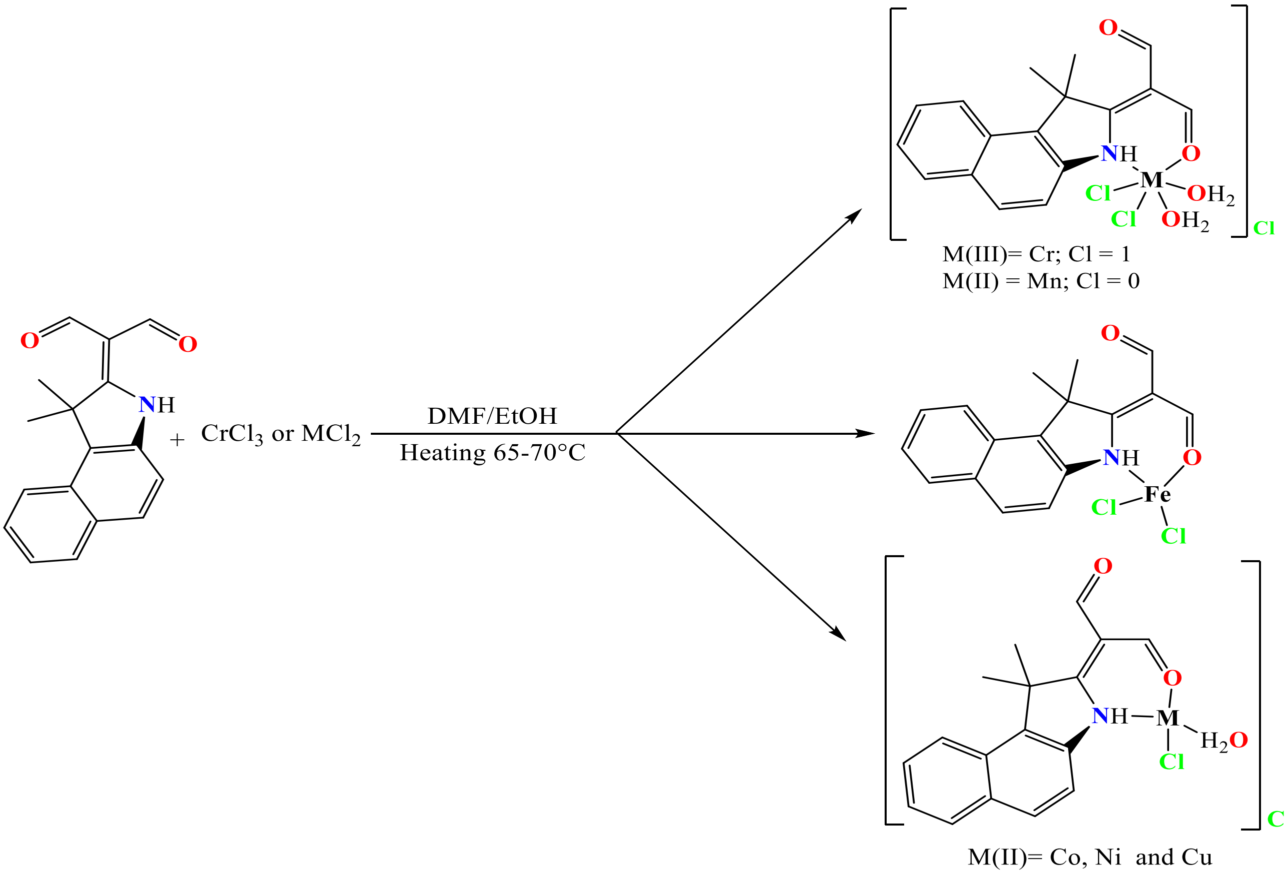
The well diffusion method was used to investigate the efficiency of B and its coordination compounds against pathogenic bacteria under aerobic circumstances. The inhibitory activity against all pathogenic microorganisms was tested using Mueller-Hinton agar. After growing each microorganism in (*Escherichia coli, Klebsiella pneumonia, Staphylococcus aureus and Bacillus subtitles*) in a nutrient broth, the agar plates were inoculated with (1.5×10^{8} (CFU)/ ml for bacteria in comparison to 0.5 McFarland tube. In the Mueller-Hinton agar plate, wells (6mm) were cut and 100 μL of the tested compounds were added to each well. For bacteria, plates were incubated at 37°C for 24h. The diameter of inhibitory zones (mm) was used to assess activity [63]. For the fungi, potato dextrose agar was used as a nutrient. After growing the microorganism in potato dextrose broth (*Candida albicans*), agar plates were inoculated with 1.5×106 (CFU)/ ml, wells (6mm) were cut and 100μL of ligand and its metal complexes were added to each well. The plates were incubated at 28°C for 72h. The diameter of inhibitory zones (mm) was used to assess the activity of the tested compounds.

Results and Discussion

The preparation of 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)malonaldehyde (B) and its metal complexes are reported. The formation of B was achieved by adopting the Vilsmeier-Haack reaction. The mixing of 1,1,2-trimethyl-1H-benzo[e]indole with phosphoryl trichloride and N, N-dimethylformamide at 5°C gave the aminomethylenemalondialdehyde (the Vilsmeier-Haack Intermediate), which then heated at 85°C. Upon neutralising the reaction mixture with an aqueous NaOH solution (35%), the required bisaldehyde ligand was obtained in an excellent yield (**Scheme 1**). The collected data indicated that the ligand (B) behaves as a bidentate species in which one of the carbonyl oxygen-aldehyde and the indole nitrogen donor atoms are involved in the coordination with the metal centres. The monomeric coordinated compounds in a 1:1 mole ratio of M:L were obtained from the reaction of B with selected metal ions (Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)) using a mixture of EtOH/DMF medium in a 2:8 (v/v) ratio at reflux, **Scheme 2**. Further, it is found the complexation reaction is solvent and temperature-dependent and impure compounds and/or unidentified residues were collected upon using different solvents or temperatures. The prepared compounds (ligand and complexes) were characterised using a range of physical and analytical techniques. These include spectroscopic tools (^{1}H, ^{13}C-NMR and mass spectroscopy (for ligand), metal ratio (**Table 1**), FT-IR (**Table 2**) and UV-Vis spectroscopy (**Table 3**)), chloride and metal ratio and micro-elemental analyses, magnetic susceptibility, conductances and melting points. The collected data indicated the isolation of six-coordinate monomeric electrolyte and non-electrolyte complexes with $[Cr(B)(Cl)_2(H_2O)_2]Cl$ and $[Mn(B)(Cl)_2(H_2O)_2]$, respectively. More, the formation of four-coordinate non-electrolyte and electrolyte monomeric complexes of the general formula $[Fe(B)(Cl)_2]$ and $[M(B)Cl)(H_2O)]Cl$ (where M(II)= Co, Ni and Cu), respectively was also concluded. The molar conductance that was determined in DMSO solutions is placed in **Table 1**.



Scheme 1: Preparation route and reaction conditions of B.



Scheme 2: Synthesis route of monomeric complexes.

Table 1: The common physical properties and elemental analyses of B and its complexes.

Comp.	yield %	m.p.°C	Colour	Elemental analyses; found/ (calc.) %					Λ_M ($cm^2\Omega\ mol^{-1}$)
				C	H	N	M	Cl	
B	91	198-200	Yellow crystal	(76.95) 76.15	(5.65) 5.82	(5.27) 4.98	-	-	-
$[Cr(B)(H_2O)_2Cl_2]Cl$	75	>300	Green	(41.27) 42.06	(4.55) 4.13	(3.01) 3.12	(11.17) 11.02	(22.84) 22.45	34.7
$[Mn(B)(H_2O)_2(Cl_2)]$	71	>300	Orange-yellow	(42.59) 42.36	(5.14) 5.19	(3.10) 3.22	(12.18) 11.95	(15.71) 15.42	12.3
$[Fe(B)Cl_2]$	70	>300	Deep-brown	(39.46) 39.88	(3.93) 4.80	(2.88) 2.94	(11.47) 11.29	(13.14) 13.87	6.67
$[Co(B)(H_2O)(Cl)]Cl$	93	204-207	Green	(42.22) 42.11	(5.09) 5.18	(3.08) 3.55	(12.95) 13.12	(15.58) 15.14	38.7
$[Ni(B)(H_2O)(Cl)]Cl$	72	>300	Greenish-yellow	(42.24) 42.35	(5.10) 5.01	(3.08) 3.14	(12.90) 12.67	(15.58) 15.42	39.9
$[Cu(B)(H_2O)(Cl)]Cl$	94	163-165	Deep-green	(45.35) 45.11	(4.52) 4.83	(3.31) 3.19	(15.00) 15.24	(16.73) 16.89	40.1

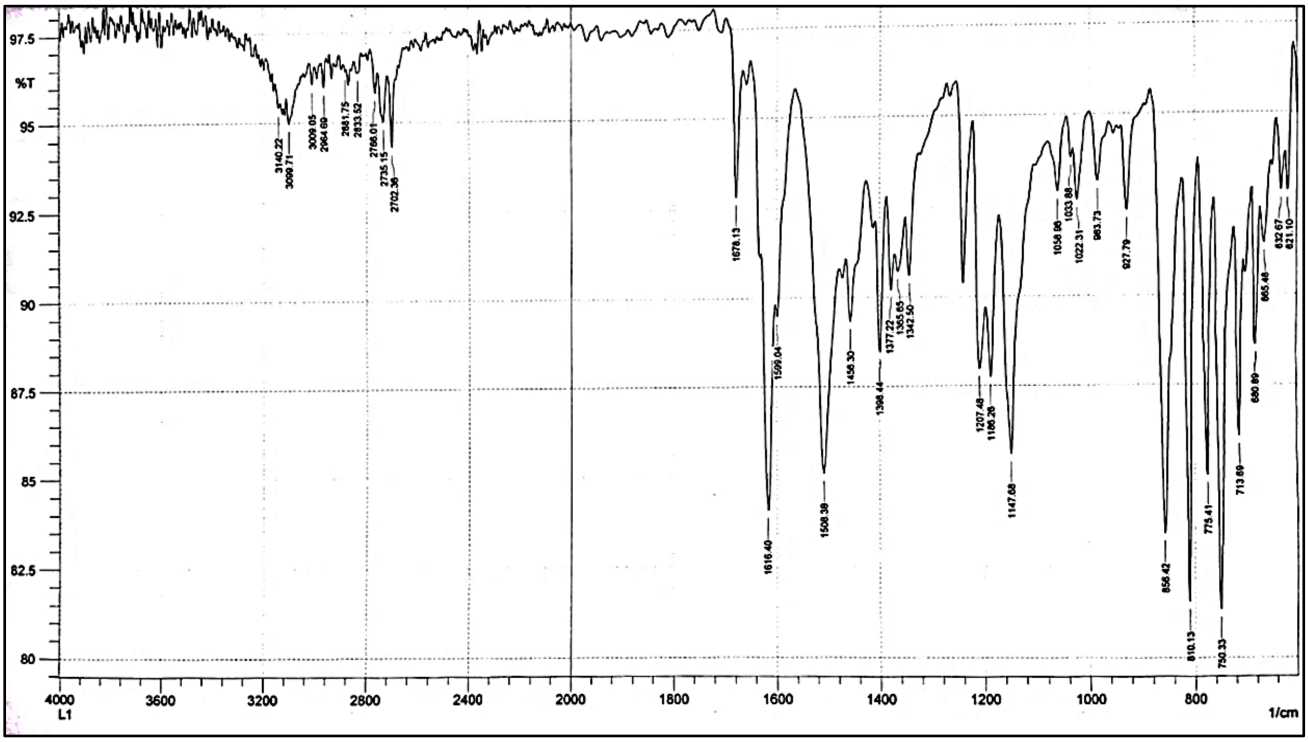


Figure 1: The FT-IR spectrum of B.

Table 2: The FT-IR spectral data of B and its complexes (cm^{-1}).

Comp.	ν(N-H)	ν(C-H)Aro. ν(C-H)Ali.	ν(C=O)	ν(C=C) Ali.. ν(C=C)Aro.	δ(N-H)	ν(C-N)	ν(M-O)	ν(M-N)	$\nu(H_2O)$ $\nu(M-OH_2)$	ν(M-Cl)
B	3140	3101 2966	1679	1628 1508	1598	1222	-	-	-	-
$[Cr(B)(H_2O)_2(Cl)_2]Cl$	3134	3010 2976	1680 1654	1620 1598	1512	1240	516	418	3383 702	271 291
$[Mn(B)(H_2O)_2(Cl)_2]$	3192	3010 2931	1680 1656	1618 1598	1510	1240	545	447	3454 708	266 271
$[Fe(B)(Cl)_2]$	3101	3007 2931	1680 1654	1620 1596	1510	1238	545	405	-	264 273
$[Co(B)(H_2O)(Cl)]Cl$	3186	2980 2933	1680 1654	1620 1579	1512	1240	516	418	3396 715	268
$[Ni(B)(H_2O)(Cl)]Cl$	3257	3008 2933	1680 1654	1618 1598	1512	1240	522	437	3471 700	285
$[Cu(B)(H_2O)(Cl)]Cl$	3197	3080 2976	1680 1645	1591 1544	1512	1244	518	437	3419 705	289

FT-IR data of B and complexes

The FT-IR spectrum of 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)malon- aldehyde (B), **Figure 1**, recorded a band at 1679cm^{-1} due to the ν(C=O) moiety, which indicated the two carbonyl groups are equivalent in the solid state. The spectrum showed a peak at 3140cm^{-1} attributed to the ν(N-H) of the indole ring. Bands recorded at 1628 and 1598cm^{-1} correlated to the conjugated ν(C=C) of the aliphatic and δ(N-H), respectively. The spectrum showed bands at 1508 and 1222 cm^{-1} assigned to $\nu(C=C)_{aromatic}$ and ν(C-N), respectively. The FT-IR spectral data of the prominent bands for the prepared complexes are placed in **Table 2**. The spectra of complexes, that compared with the spectrum of the ligand (B), indicated the involvement of one of the carbonyl oxygen and the indole nitrogen in the coordination to the metal centre. The spectra revealed two carbonyl moieties, the coordinated and the non-coordinated. The band that related to the ν(C=O) of the coordinated carbonyl has suffered a low shift and appeared at 1654-1645cm^{-1} in complexes (compared with that of B at 1679cm^{-1}). The shift to the low wavenumber is related to the reduced bond order as a result of the π–back bonding from M-L (dπ-pπ*) [16-18]. The uncoordinated carbonyl band is seen as a distinct band at 1680cm^{-1} in the spectra of complexes. However, this band is overlapped and is detected as a shoulder about 1680cm^{-1} in the spectrum of $[Cu(B)(H_2O)(Cl)]Cl$. The spectra confirmed the involvement of the indole nitrogen group in the coordination with the metal centres. This is supported by the shift of a high and a low wavenumber that occurred to the ν(N-H) in the spectra of the complexes, compared with that of B at 3140cm^{-1}. Complexes of $[Mn(B)(H_2O)_2(Cl)_2]$, $[Co(B)(H_2O)(Cl)]Cl$, $[Ni(B)(H_2O)(Cl)]Cl$ and $[Cu(B)(H_2O)(Cl)]Cl$ revealed a higher wavenumber shift for the N-H group, and the other complexes indicated a low wavenumber shift (**Table 2**). Further, the spectra recorded bands related to the ν(C-N) of the coordinated indole nitrogen moiety that suffered a shift to a high wavenumber and appeared at 1238-1244cm^{-1} (compared with that of B at 1222cm^{-1}) [17-21]. The spectra of the coordinated complexes recorded additional peaks between 700-200 cm^{-1} that were not seen in the B spectrum. Bands that are attributed to ν(M-O) carbonyl were detected at 516, 545, 545, 516, 522 and 518cm^{-1} for ν(Cr-O), ν(Mn-O), ν(Fe-O), ν(Co-O), ν(Ni-O) and ν(Cu-O), respectively [12-14]. The $\nu(M\text{-}OH_2)$ band for the aqua water molecules for the $\nu(Cr\text{-}OH_2)$, $\nu(Mn\text{-}OH_2)$, $\nu(Co\text{-}OH_2)$, $\nu(Ni\text{-}OH_2)$ and $\nu(Cu\text{-}OH_2)$ were detected at 702, 708, 715, 700 and 705cm^{-1}, respectively[12]. The FT-IR data revealed bands that belong to ν(Cr-Cl), ν(Mn-Cl), ν(Fe-Cl), ν(Co-Cl), ν(Ni-Cl) and ν(Cu-Cl) at 271;291, 266;271, 264;273, 268, 285 and 289cm^{-1}, respectively [17-21]. The appearance of two M-Cl peaks in the spectra of Cr(III), Mn(II) and Fe(II)-complex confirmed the two chlorido moieties adopt the *cis* configuration. Finally, bands related to ν(OH) of the aqua water molecules were detected at 3383, 3454, 3396, 3471 and 3419cm^{-1} in the complexes of Cr(III), Mn(II), Co(II), Ni(II) and Cu(II), respectively [14].

NMR and mass spectra of B

The ^{1}H- and ^{13}C-NMR of the bisaldehyde 2 - (1, 1-dimethyl-1, 3-dihydro-2 H-benzo[e]indol-2-ylidene) malonaldehyde (B) were obtained in DMSO-d_6 on a Brucker-400 MHz instrument. The assignment of peaks is based on the numbering fashion reported in **Scheme 1**. The ^{1}H NMR spectrum of 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)malonaldehyde is shown in **Figure 2,** with an expansion of the aromatic region. The spectrum indicated the expected chemical shifts with the correct number of protons. The broad peak that is equivalent to one proton was recorded at 13.44ppm and is attributed to the N-H of the indole ring (1H, br., N-*H*). The downfield appearance of this peak could be referred to as the intra-hydrogen bonding within the heteroatoms of the molecule and/or inter-hydrogen bonding with the NMR solvent. The singlet, with two protons ratio, at 9.77ppm is related to (2H, s, $C_{1,1'}$-*H*). The appearance of one peak indicates the two aldehydic groups are equivalents in solution as they are in the solid state. The doublet signal, with one proton integration, at 8.18-8.16ppm is assigned to (1H, d, C_{11}-*H*, *J*=8.48Hz). The one proton equivalent peak at chemical shift 8.02-8.0 ppm, which appeared as a doublet, is assigned to (1H, d, C_{13}-*H*, *J*=8.16Hz). A chemical shift that appeared as a doublet of the doublet with two protons ratio at 7.97-7.90 ppm is correlated to (2H, dd, $C_{8,14}$-*H*, *J*=8.72; 8.68Hz). The two signals that appeared as a triplet at 7.64-7.60 and 7.51-7.47 ppm with one proton integration for each are attributed to (1H, t, C_{13}-*H*, *J*=7.08Hz) and (1H, t, C_{12}-*H*, *J*=7.28Hz), respectively. The singlet peak observed at 1.92 ppm with a six protons ratio is attributed to the two methyl groups (6H, s, $C_{15,15'}$-*H*). Chemical shifts for the NMR solvent and the traces of water in the solvent have been recorded at around 2.49 and 3.34 ppm respectively. The ^{13}C-NMR spectrum of B was obtained in the DMSO-d_6 solvent and presented in **Figure 3**. The spectrum indicates resonances in the aliphatic region at δc= 22.24 and 52.92 ppm assigned to ($C_{15,15'}$) and (C_4), respectively. The resonances that correlated for the aromatic are detected as expected between 109.13 to 137.88 ppm. The chemical shifts that attribute to (C_3) and ($C_{1,1'}$) were observed at 179.66 and 190.64ppm, respectively. The spectrum indicated the two carbonyl groups of the bisaldehydes are equivalent.

The electrospray (+) mass spectrum of B is placed in **Figure 4**. The fragmentation sequence and assignment of the title compound are placed in **Scheme 3**. The spectrum indicated the parent ion peak with the expected isotope distribution pattern at m/z=265.1amu (80.2%). This fragment was assigned to (M)+, calculated 265.11amu for $C_{17}H_{15}NO_2$. The basic ion peak is detected at 222.3amu (100%). This fragment correlated to $(M\text{-}(CH_3\text{-}CH{=}NH))^+$, calculated 222.07amu for $C_{15}H_{10}O_2$. Fragments observed at m/z = 236.5 (100.1%), 194.3 (69.3%), 178.3 (44.6%), 152.1 (47.5%), 96.8 (14.9%) and 69.1 (17.8%) attributed to $[M\text{-}(C_2H_4)]^+$, $[M\text{-}(CH_3\text{-}CH{=}NH{+}CO)]^+$, $[M\text{-}(CH_3\text{-}CH{=}NH{+}CO_2)]^+$, $[M\text{-}(CH_3\text{-}CH{=}NH{+}CO{+}CHCH)]^+$, $[M\text{-}(CH_3\text{-}CH{=}NH{+}CO{+}C_8H_2)]^+$, and $[M\text{-}(CH_3\text{-}CH{=}NH{+}CO{+}C_8H_2){+}(C_2H_4)]^+$, respectively.

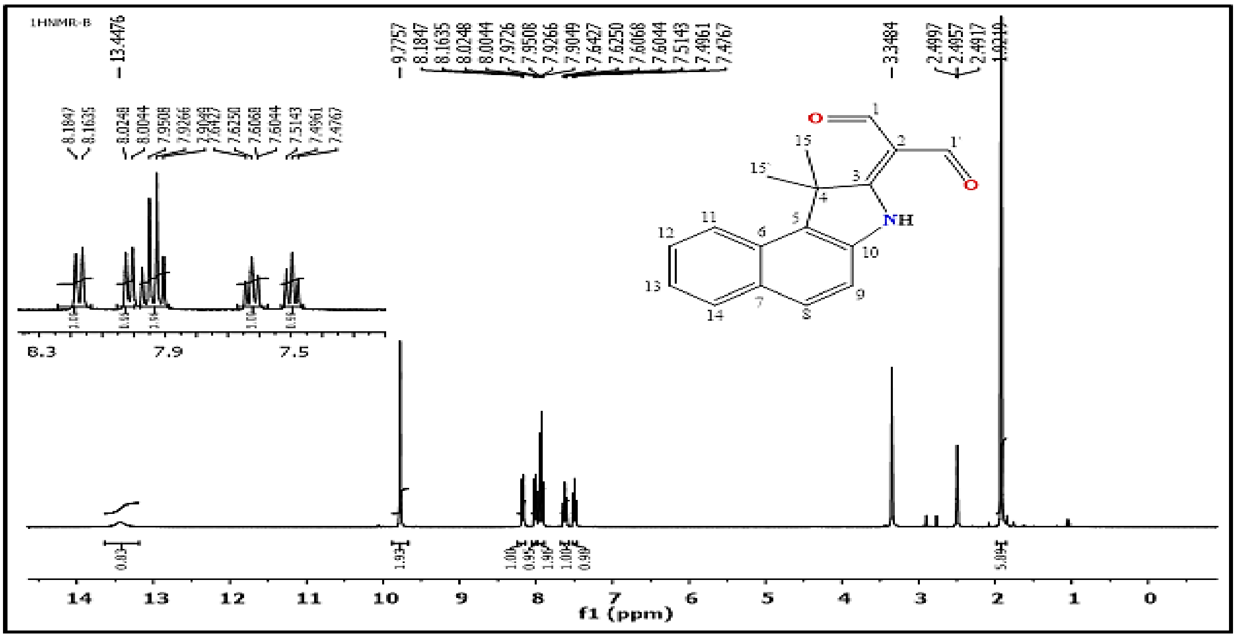


Figure 2: 1H-NMR spectrum of B in DMSO-d6 solution.

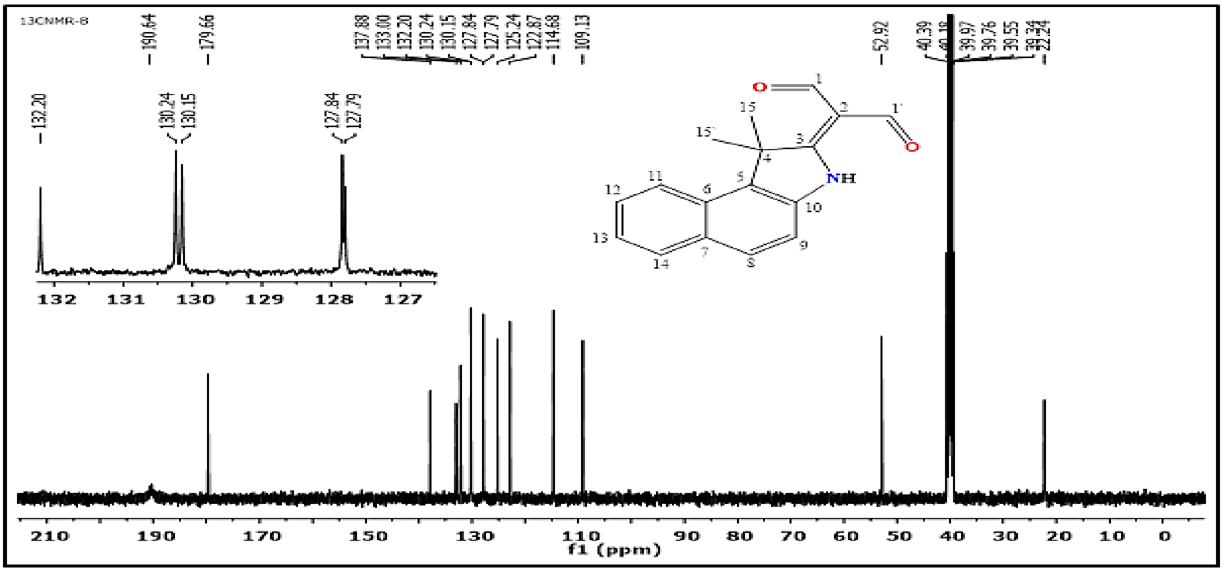


Figure 3: 13C-NMR spectrum of B in DMSO-d6 solution.

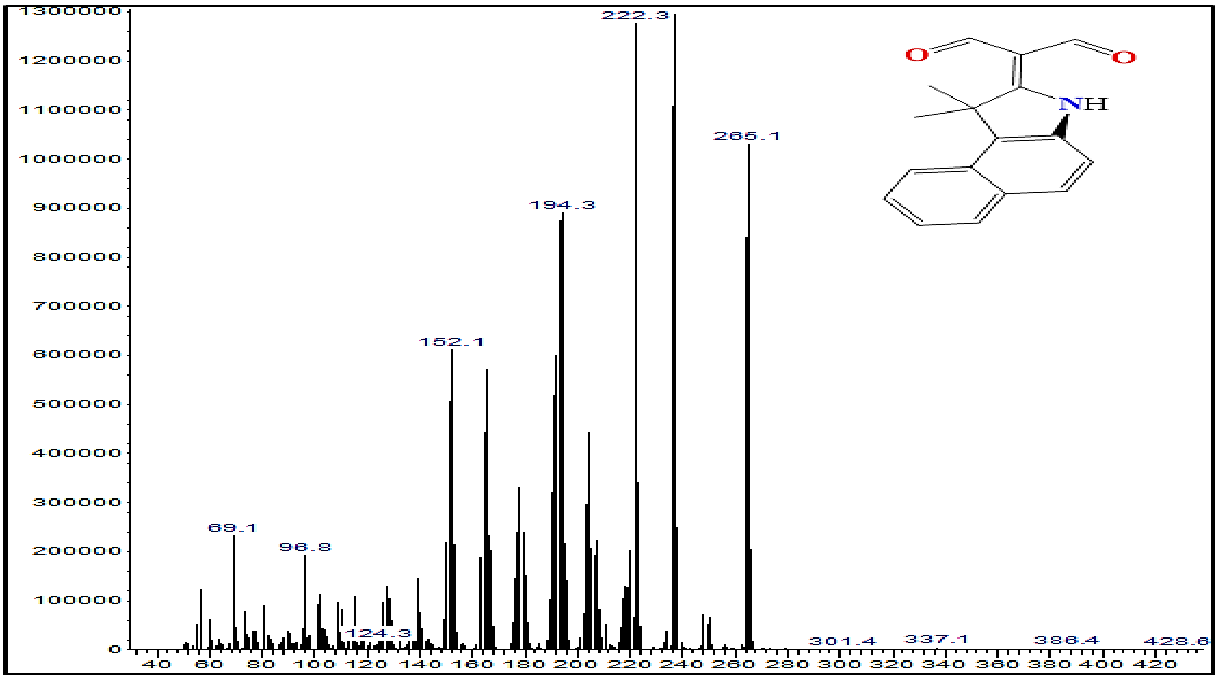
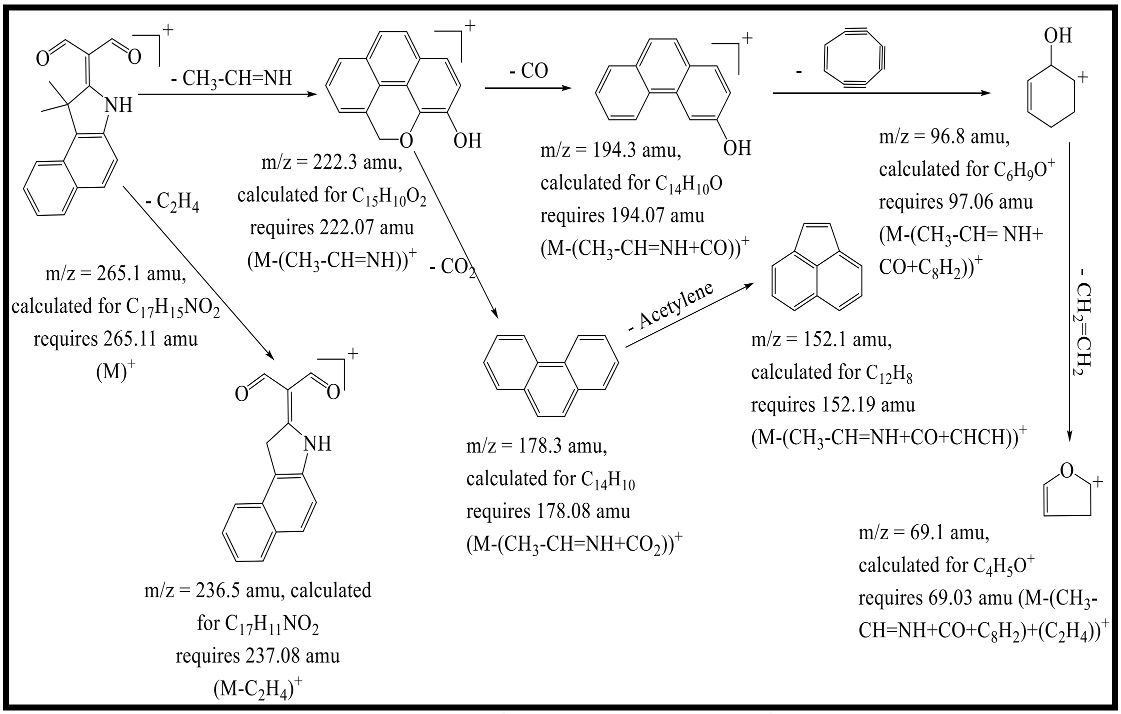


Figure 4: The electrospray (+) mass spectrum of B.



Scheme 3: The fragmentation pattern of B.

Table 3: Electronic spectral data of B and its complexes in DMSO solutions.

Comp.	μeff (BM)	Band Position λ_{nm}	Wave number (cm^{-1})	Extinction coefficient ε_{max}(dm^3 mol^{-1} cm^{-1})	Assignment
B	-	253	39526	1940	Ligand Field
		288	34722	1762	
		300	3333	1867	
		373	26810	1655	
$[Cr(B)(H_2O)_2(Cl)_2]Cl$	3.13	242	41322	1648	Ligand Field
		288	34722	1457	Ligand Field
		300	3333	1550	C.T
		375	26667	1438	C.T
		610	16393	10	$^4A_2g \rightarrow {}^4T_1g$
		908	11013	4	$^4A_2g \rightarrow {}^2Tg$
$[Mn(B)(H_2O)_2(Cl)_2]$	1.92	289	34602	942	Ligand Field
		300	3333	1023	C.T
		374	26738	987	C.T
		880	11364	9	$^6A_1g \rightarrow {}^4T_2g^{(G)}$
		908	11013	20	$^6A_1g \rightarrow {}^4T_1g$
$[Fe(B)(Cl)_2]$	5.09	289	33557	731	Ligand Field
		300	33333	811	C.T
		374	26738	846	C.T
		874	11442	9	$^5E \rightarrow {}^5T_2$
		908	11013	15	
$[Co(B)(H_2O)Cl]Cl$	2.54	260	38462	1199	Ligand Field
		289	34602	1586	Ligand Field
		300	33333	1606	C.T
		375	26667	1477	C.T
		625	16000	69	$^4A_2^{(F)} \rightarrow {}^4T_1^{(F)}$
		676	14793	89	$^4A_2^{(F)} \rightarrow {}^4T_1^{(p)}$
$[Ni(B)(H_2O)Cl]Cl$	3.09	289	34602	2096	Ligand Field
		300	33333	2066	C.T
		374	26738	1763	C.T
		704	14205	20	$^3T_1 \rightarrow {}^3T_1^{(P)}$
		799	12516	35	$^3T_1 \rightarrow {}^1E$
$[Cu(B)(H_2O)Cl]Cl$	1.81	288	34722	1323	Ligand Field
		299	33445	1209	C.T
		371	26954	846	C.T
		941	10627	28	$^2B_2 \rightarrow {}^2E$
		1011	9891	20	$^2B_2 \rightarrow {}^2A_1$

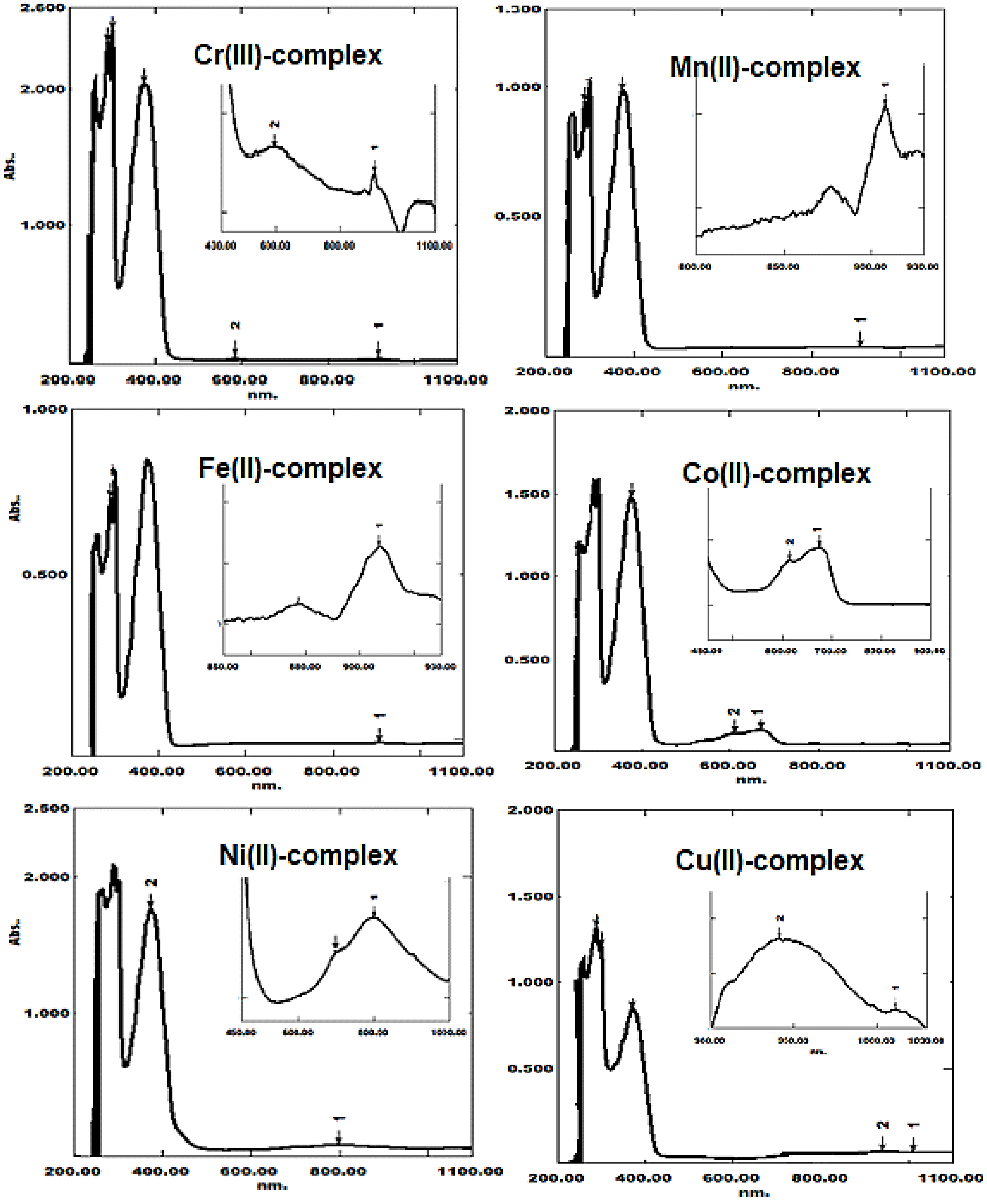


Figure 5: The electronic spectra of complexes in DMSO solutions.

Electronic spectra and magnetic moment measurements

The electronic spectral data of B and its complexes were acquired in DMSO solvents (con. = 1 x 10^{-3} M). The electronic spectrum of B recorded peaks at 253, 288,300 and 373nm correlated to $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$ and charge transfer transition, respectively [13, 14]. The spectra of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) monomeric complexes revealed peaks around 242-289nm related to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ (ligand field transitions), **Table 3** and **Figure 5.** The spectra of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) indicated an extra peak at 300-375 nm assigned to charge transfer (C.T) [13,14,22]. The Cr(III) complex indicated bands in the visible region at 610 and 908nm correlated to $^4A_2g^{(F)}\rightarrow{}^4T_1g$ and $^4A_2g^{(F)}\rightarrow{}^4T_2g^{(F)}$, respectively suggesting a distorted octahedral geometry about the metal centre [14]. The proposed octahedral geometry is supported by the magnetic moment value of 3.13 B.M. In the Mn(II)-complex, peaks at 880 and 908nm are attributed to $^6A_1g\rightarrow{}^4T_2g^{(G)}$ and $^6A_1g\rightarrow{}^1T_1g$ that supported a distorted octahedral geometry around the metal centre [13,14]. The Fe(Ⅱ)-complex revealed a peak, that split at 874 and 908nm, correlated to $^5E\rightarrow{}^5T_2$ indicating a distorted tetrahedral structure around the entre atom [23, 24]. The magnetic moment value of 5.09 B.M is following Fe(II)-complexes in which the geometry about the metal centre is tetrahedral [23]. Peaks observed at 625 and 676nm in the spectrum of Co(II)-complex correlated to$^4A_2^{(F)}\rightarrow{}^4T_1^{(F)}$ and $^4A_2^{(F)}\rightarrow{}^4T_1^{(p)}$, respectively confirming a distorted tetrahedral coordination sphere around the metal centre [23, 24]. The magnetic moment value of 2.54 BM is in agreement with Co(II)-complexes in which the coordination sphere about the metal atom is a distorted tetrahedral [23]. In the Ni(II)-complex, peaks at 704 and 799nm are attributed to $^3T_1 \rightarrow {}^3T_1^{(P)}$ and $^3T_1 \rightarrow {}^1E$ that supported a distorted tetrahedral geometry around the metal centre [22, 24]. The split broad peak with two hubs at 941 and 1011nm in the spectrum of Cu(II)-complex referred to as the $^2B_2 \rightarrow {}^2E$ and $^2B_2 \rightarrow {}^2A_1$ confirms a distorted tetrahedral structure around the metal centre [24]. The magnetic value of 1.81 B.M of the complex is another evidence of the formation of a distorted tetrahedral complex [23].

Biological activity

The prepared compounds (ligand and coordinated complexes) were examined against four types of bacteria; *Staphylococcus aureus* and *Bacillus subtilis* (G-positive) and *Escherichia coli* and *Klebsiella pneumonia* (G-negative) and one fungi species *Candida albicans*. The observed activity was expressed in millimetres (mm). This was based on the measuring of the inhibition zone diameters and correlated with the DMSO solvent that was used as a control, which showed no activity against the bacterial strains and fungi species [17-19]. The antibiotics Ceftriaxone and Fluconazole were introduced as reference drugs for bacteria and fungi species, respectively. The tested ligand and complexes showed different antimicrobial activity against the examined bacteria. The experimental data indicated that the coordinated compounds became potentially more active, compared with B. The Fe(II) complex of B-ligand showed higher antimicrobial activity against *Bacillus subtilis* compared to Ceftriaxone. In addition, the referenced drug showed higher activity compared to the tested compounds, see **Table 4** and **Fig.6.** The anti-fungal data of the tested complexes indicated the activity of these complexes, compared to fluconazole. Moreover, the iron complex showed higher activity than the antifungal **(Table 4 and Fig, 6).**

Table 4: The biological activities of compounds against bacterial strains and fungal species.

Comp.	Inhibition zones (mm)				
	Bacterial strains				Fungi species
	Staphy. aureus	*Bacil. subtilis*	*Esch coli*	*Kleb. pneumonia*	*Candida albicans*
DMSO	-	-	-	-	-
Ceftriaxone	23	20	23	22	-
Fluconazole	-	-	-	-	20
B	16	17	16	16	16
$[Cr(B)(H_2O)_3Cl]Cl_2$	17	18	17	17	20
$[Mn(B)(H_2O)_4] Cl_2$	17	18	19	18	19
$[Fe(B)(H_2O)_2Cl_2]$	20	23	19	17	22
$[Co(B)(H_2O)_4] Cl_2$	19	21	18	17	17
$[Ni(B)(H_2O)_4] Cl_2$	16	17	22	18	17
$[Cu(B)(H_2O)_2] Cl_2$	16	19	20	17	18

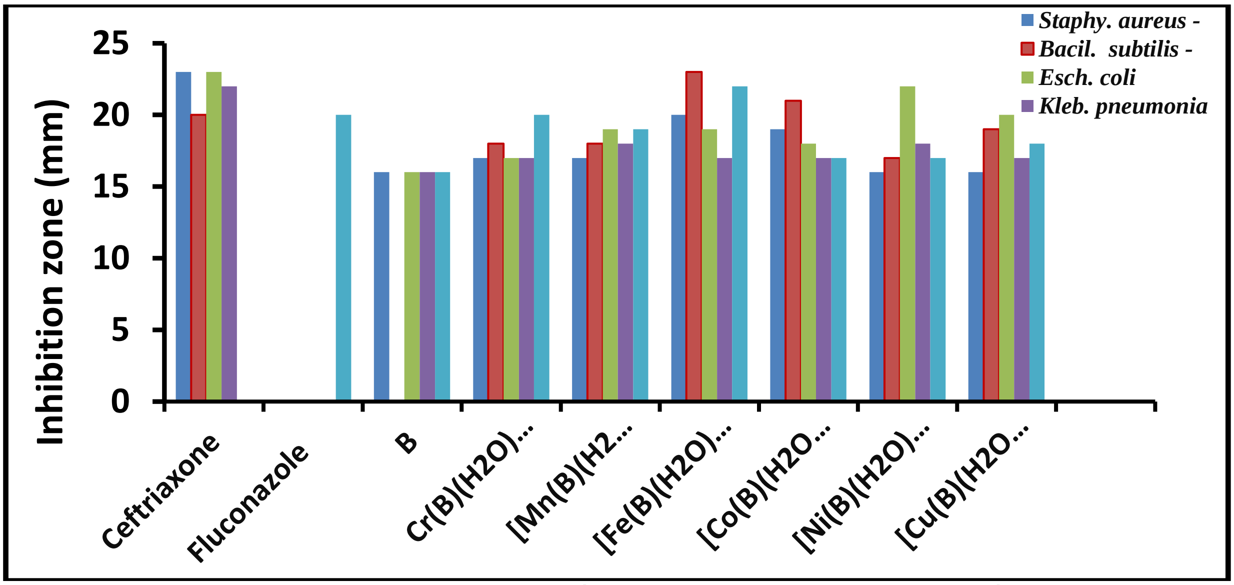


Figure 6: The inhibition zone diameter (mm) for compounds against bacterial and fungal species.

Conclusions

This paper reports the formation of coordinated complexes derived from the bisaldehyde ligand 2-(1,1-dimethyl-1,3-dihydro- 2 H - benzo [e] indol - 2 - ylidene)malonaldehyde (B). The formation of B was achieved by adopting the Vilsmeier-Haack reaction. The mixing of 1,1,2-trimethyl-1H-benzo[e]indole with phosphoryl trichloride and the anhydrous N, N-dimethylformamide gave the aminomethylenemalondialdehyde. The use of $POCl_3$ and DMF was aimed to give the Vilsmeier-Haack Intermediate. The monomeric coordinated compounds were isolated from the mixing of B with selected metal ions (Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)) in a mixture of EtOH/DMF (2:8; v/v) medium in a 1:1 mole ratio of M:L. The ligand (B) is a potentially bidentate species in which one of the carbonyl oxygen-aldehyde and the indol nitrogen donor atoms are involved in the coordination with the metal centres. The prepared compounds (ligand and complexes) were characterised using a range of physical and analytical techniques. These tools confirmed the entity of the ligand and complexes, in which monomeric six- and four-coordinated complexes are reported. The antimicrobial activity of the prepared compounds was also investigated.

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