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Spectral, Thermal and In Vitro Antibacterial Studies on Cadmium(II)–bis(2,2/-methylidenephenol)diaminoethane

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Abstract: The objective of this work is to prepare a new synthetic protocol of the cadmium(II) complex of bis(2,2'-methylylidenephenol)diaminoethane (H_2BMPDE) and study the antimicrobial bioefficacy. In this work, we report the extractive method for the synthesis of cadmium(II) complex of bis(2,2'-methylidenephenol)diaminoethane from salicylaldehyde, ethylenediamine, hydrochloric acid, and cadmium sulfate in a single, simple step. The ligand and the complex were characterized by FTIR, UV-Vis, ^{1}H and ^{13}C NMR, magnetic moment, GC-MS, thermal and elemental analysis. The chemical data indicated the formation of 1:1 (metal:ligand) mole ratio and distorted tetrahedral geometry was suggested as based on spectral data and magnetic moment. The results of preliminary antibacterial study revealed that Cd(II) H_2BMPDE complexes prepared from different acids (HCl, HNO_3, H_2SO_4) were effective against clinically important Gram-negative bacteria (*Escherichia coli, pseudomonas, Klebsiella*) and Gram-positive bacterium (*Staphylococcus aureus*).The result indicated a new synthetic protocol for the synthesis of H_2BMPDE complexes. On the application, H_2BMPDE and its complexes could be considered as a potential antibacterial agent with further investigative analysis.

Keywords: Cadmium H_2BMPDE; physicochemical studies; stability studies; antimicrobial bioefficacy.

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INTRODUCTION

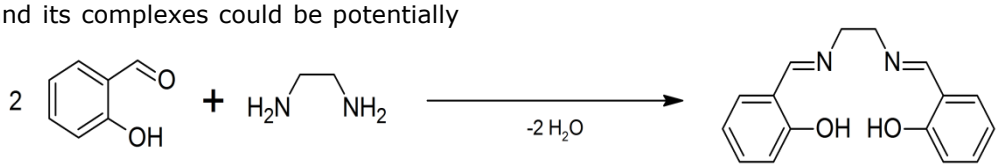
Cadmium, among various metals, transition and non-transition, requires special attention owing to its deleterious effects in nature. Anthropogenic activities such as mining and smelting have gradually increased its concentration in the environment (1). This thus calls for the development of suitable chelating agent for complexation and immobilization of cadmium(II) ion in matrices and even in organisms. Studies (1-3) have shown that certain group of compounds known as the phytochelatins naturally present in living cells effectively complex cadmium(II) ion in metabolically less active cellular part by acting as a chelating agent and protecting the cells from cadmium toxicity. There is inherent softness and lack of ligand field stabilization energy in cadmium as a consequence of its d^{10} electronic configuration leading to diverse co-ordination chemistry as it can toggle between various oxidation states (4-7). This exceptional ability of cadmium resulting from its flexible co-ordination number in complexes has paved way for its wide applications in catalytic and exchange reactions, in the development of fluorescence materials when complexed with conjugated π substrates having phenyl rings and in biological studies (3,8-9).

The development of the area of bioinorganic chemistry has increased and many researchers have worked on Schiff bases with strong donor atoms such as oxygen and nitrogen due to their strong coordination abilities with transition metal ions. Similarly several authors have worked on H_2BMPDE, its derivatives and H_2BMPDE complexes of transition metals of the first series. Several studies of H_2BMPDE complexes has shown that it exhibits unique and excellent photoluminescence property, catalytic ability, antimicrobial activities, magnetic drugs and in

environmental cleaning (carbonic anhydrase cycle) (10-13).

Abou-Melha and Faruk (14) noted that the co-ordination of a ligand to metal ion synergistically increase the biological activity of the ligand and decrease the cytotoxic effect of ligand and metal ion as a consequence of chelation. In their study, Brown and co-workers (15) observed that a compound with long lipophilic chain would interact with cellular components and enhance transport of the compound to the active required site, thereby increasing the biological activity. The observation was explained on the basis of the greater lipophilic nature of the complexes than the ligand a consequence of chelation (15). H_2BMPDE and its complexes could be potentially bacteriostatic due to the presence of azomethine group and the phenolic hydroxyl in the molecule. Biswas and co-workers (16) studied the in vitro antibacterial and antifungal effects of cadmium(II) complexes of hexamethyltetraazacyclotetradecadiene and isomers of its saturated analogue and noted the antibacterial potency of the macrocyclic ligand and complexes.

In this reasearch, we report the synthesis, spectral and thermal characterization as well as antibacterial bioefficacy of cadmium(II) complex derived from the condensation of Schiff base salicylaldehyde and ethylenediamine in 2:1 ratio (Scheme 1).



Scheme 1. Synthesis of bis(2,2′ – methylidenephenol)diaminoethane (H_2BMPDE)

EXPERIMENTAL SECTION

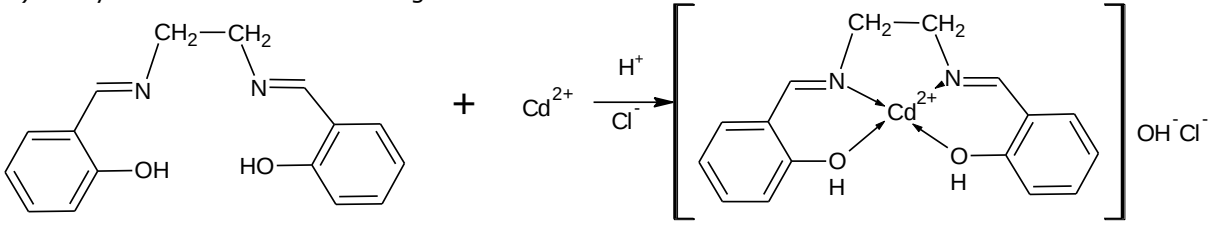
Analytical grade of all the chemicals and solvents used for the syntheses were obtained from Merck Company and were not purified unless otherwise stated. The ligand (H_2BMPDE) was synthesized according to the modified Takeshima procedure (17) by condensation of salicylaldehyde and ethylenediamine in 2:1 mole ratio and used as 0.5% solution in absolute ethanol throughout the analysis. A stock solution of Cd(II) was prepared using $CdSO_4.8/3H_2O$.Stock solutions of mineral acids (HCl, HNO_3 and H_2SO_4) were prepared by diluting the concentrated acids and were standardized using appropriate standard bases. Solutions for antibacterial bioefficacy and sensitivity tests were prepared from nutrient broth powder and Mueller Hinton powder while aliquot of 0.5 Mac Farland standard was used as control (18).

Physical measurements

The electronic spectra of the ligand and complexes were recorded in dimethyl formamide on a Genesis 10S UV-Vis spectrophotometer. Infrared spectra of the ligand and the complexes were recorded on Perkin-Elmer FTIR-8400S Fourier transform infrared spectrometer (Shimadzu, Japan) in the range of 4000-400 cm^{-1} as KBr disks. Differential scanning calorimetry (DSC) analysis was determined using NETZSCH DTA 404PC Differential scanning calorimeter. ^{1}H NMR and ^{13}C NMR and spectra were carried out on a Bruker AVANCE II 400 MHz NMR spectrometers using tetramethylsilane (TMS) as an internal reference. Elemental CHN analyses were performed using Vario-Elemental Microcube ELIII. Magnetic susceptibility was measured on a Johnson Matthey magnetic susceptibility balance Alfa product, Model No. MKI and diamagnetic corrections calculated using Pascal's constant. The conductivity measurements were carried out in DMF at room temperature using HQ4d conductivity meter. Microanalysis of the ligand and complexes were done at the Department of Chemistry, Rhodes University, South Africa.

Synthesis of the metal complex

An aliquot of a sample solution containing 100 µg of Cd(II) was transferred into a 50 mL calibrated extraction bottle and volume made up to 5 mL with an acidic solution at a concentration of 0.0001 M. Exactly 0.5 mL of the ligand solution in absolute ethanol was added and 5 minutes for color development allowed. The complex formed was extracted with 5 mL of chloroform. The organic extract was allowed to dry and product was recrystallized using carbon tetrachloride, dried, and the metal complex from HCl was characterized while others were kept for antimicrobial studies.



Scheme 2. Synthesis of cadmium(II)-bis(2,2′ – methylidenephenol)diaminoethane complex.

Physical and analytical data

Ligand; M.p (127 ^{o}C ± 1). Appearance: yellow crystals; molecular formula: $C_{16}H_{16}N_2O_2$; formula weight: 268; percentage yield: 65%). Elemental analysis (ligand) calc. C, 71.64%; H, 5.97%; N, 10.44%; found: C, 70.89%; H, 6.05%; N, 10.41%. FTIR (Ligand): 3401 cm^{-1} ν(O-H) aromatic, 3042 cm^{-1} ν(C-H) aromatic, 2913 cm^{-1} ν(C-H) aliphatic, 1615 cm^{-1} ν(C=N) iminic, 1285 cm^{-1} ν(C-O) phenolic; ^{1}H-NMR (ppm) (Ligand): 7.4 (1H, N=C(H) methine protons of azomethine); 7.11 (3H, the hydrogen of aromatic ring); 6.5 (1, N-H protons); 3.5 (4H, $=NCH_2CH_2N=$ methine or methylene protons). ^{1}H-NMR (ppm) (Cd complex): 8.4 (1H, N=C(H) methine protons of azomethine); 7.0-7.3 (3H, hydrogen of aromatic ring); 6.9(1, N-H protons); 3.90(4H, $=NCH_2CH_2N=$ methine or methylene protons). ^{13}C-NMR (ppm) (ligand): 221.44 (bonded to phenolic oxygen); 152.65 (aromatic carbons); 48.69 (methylene carbon); molar conductivity of complex: 32.00 μS; electronic spectrum of the ligand (DMF, nm, ε =mol^{-1} dm^3 cm^{-1}) 260 (ε =3.0 x10^2), 285 (ε =3.6 x 10^2), 335 (ε = 4.7 x 10^2).

Cd complex: M.p (Cd complex) >300 °C; appearance: yellow crystals; molecular formula: $C_{16}H_{16}N_2O_2$ Cl(OH)Cd; formula weight: 432.91; percentage yield: 40%). Elemental analysis (Cd complex): calc. C, 44.36%; H, 3.96%; N, 6.47%; found: C, 71%; H, 5.71%; N, 10.41%; FTIR (Cd complex): 3009 cm^{-1} ν(C-H) aromatic, 2915 cm^{-1} ν(C-H) aliphatic, 1624 cm^{-1} ν(C=N) iminic, 1414 cm^{-1} ν(C-O) phenolic, 556 cm^{-1} ν(Cd-N), 655 cm^{-1} ν(Cd-O). ^{13}C-NMR (ppm) (Cd complex): 165.28 (bonded to phenolic oxygen); 116.74, 118.63, 131.33, 132.21 (aromatic carbons); 160.91 (azomethine carbon); 59.60 (methylene carbon). Electronic spectrum of the Cd complex (DMF, nm, ε =mol^{-1} dm^3cm^{-1}) 230 (ε =9.20 x10^2), 310 (ε =4.36 x 10^3), 405 (ε =3.36 x 10^3). From magnetic measurement the complex was diamagnetic.

Thermal Analysis

The cadmium complex and reference pan were placed at separate furnaces maintained using separate heaters. The sample and reference were maintained at same temperature and the difference in thermal power required in maintaining them at the same temperature measured and plotted as a function of temperature. About 5.00 mg of sample was weighed into an alumina crucible and mass was indicated. The TA Blue DSC sample press was used to close the crucible. The enclosed sample was placed side by side with the empty alumina crucible as reference. The instrument was purged with ultra pure N_2 gas at regulated pressure between 100 and 140 Kpa gauge (15 and 20 Psig). The gas flow rate was set at 50 mL per minute and experiment was run from room temperature to 800 °C at scan rate of 10 °C min.

Gas Chromatography-Mass Spectrometry (GC–MS) Analysis

Mass spectra of the ligand and the complexes were performed by NARICT, Zaria using mass spectrometer (GCMS – QP2010 Plus Shimadzu, Japan) coupled with a gas chromatograph. The samples were dissolved in dimethyl formamide and filtered through a 1-mL syringe. A 1 μL aliquot of each sample was then injected into the GC-MS instrument. The carrier gas was nitrogen for desolvation, nebulization pressure of 108 kpa, injection temperature was 250 °C, oven temperature was 80 °C, solvent cut time was 2.50 minutes, start time was 3 minutes and ionization energy was 70 eV. The process involves electron ionization which accelerates electrons to 70 eV and pass them through a section which contains vaporized sample M which exited from GC to MS thereby generating radical cation $[M]^+$. The spectrum of the compound was generated since the ionization process was sufficiently energetic leading to fragmentation. The spectrum generated gave a characteristic fingerprint for the compound required and the mass to charge ratio (m/z) values of the prominent ions can be deconvulated from spectral libraries or using a fragmentation tree (19). The molecular formula determination also referred to as the elemental composition of the compound was generated by decomposing monoisotopic peaks by finding molecular formulas that are well very close to the measured peak mass (20). During GC-MS analysis, the mass spectrum was generated and represented as peaks. Two of the peaks are the most important namely base peak and molecular ion peak. The base peak otherwise regarded as parent peak was the largest analyzed peak and other peaks are regarded as relative abundance or percentage of the base peak. The analyzed molecule prior to fragmentation was shown by molecular ion peak always used as a reference point in fragment identification (21).

Antibacterial studies

Both gram negative bacteria (*Escherichia coli, pseudomonas, Klebsiella*) and gram-positive bacterium (*Staphylococcus aureus)* were used for *in vitro* screening of the antibacterial effect of the ligand and the complex. The bacterial strains were obtained from the department of Microbiology Ebonyi State University, Abakaliki. Antimicrobial test was performed on four bacteria (*Staph-aureus, Klebsiella, E-coli and Pseudomonas aeuroginosa*) as described (18). The media employed in the study was prepared by dissolving separately 2 g of the nutrient broth powder and 38 g of the Mueller Hinton agar powder in 250 mL and 1 L of distilled water respectively. The two media were sterilized in an autoclave at 121 °C for 15 minutes and thereafter left overnight in a refrigerator after cooling. Cultures of the micro-organisms were prepared in sterile nutrient broth and incubated for 24 hours at 37 °C. About 0.1 mL of the cultures left overnight in sterile tubes with caps was made up to 10 mL with sterile distilled water. Also, 10 mg/mL of the complex solutions prepared from different acids (HCl, HNO_3 and H_2SO_4) in ethanol

was used as solvent. The positive control was an aliquot of 0.5 MacFarland standard (10 µg of broad spectrum ampicillin) equivalent of test organism. The cultures of micro-organism was stretched on the surface of a dried Mueller Hinton agar plate and allowed for 20-25 minutes for pre-diffusion of the organism into the agar. Sterile No 4 cork borer was used to make 8 mm hole in the inoculated agar plate. The compounds were introduced into the four (4) different holes made on the innoculated agar plate whereas the control drug (ampicillin) was placed at the centre. The inoculated plates were incubated at 37 °C for 18-24 hours. The zones of inhibition of microbial growth that appeared around the walls of the compounds were examined, measured and recorded in millimeters (mm).

The evaluation of the antimicrobial activity followed after the incubation period by the measurement of the diameter of the inhibition zones. Activity index (%) (Calculated as percent activity index bacteria) is illustrated in Equation 1.

$$\frac{A}{B} \times 100 \qquad \text{(Eq. 1)}$$

where A = zone of inhibition of test compound in diameter, B = zone of inhibition of standard in diameter.

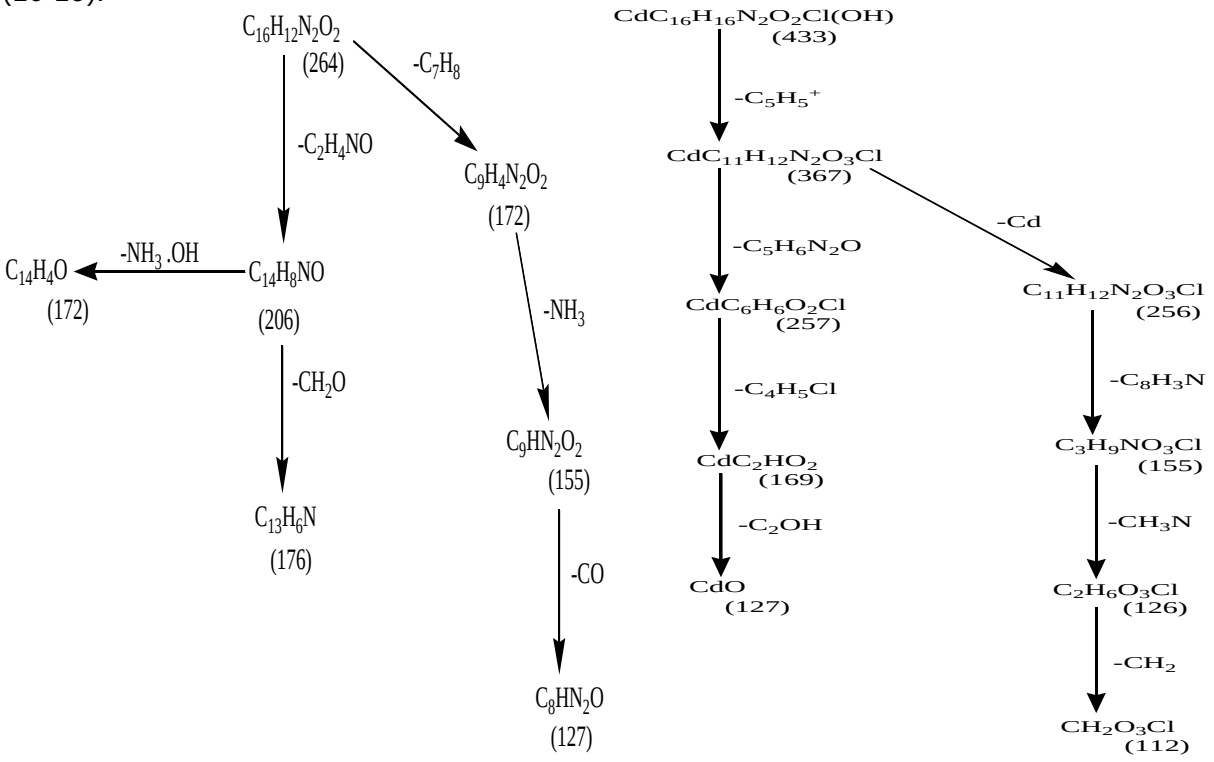
RESULTS AND DISCUSSION

The UV-Vis spectrum of the free H_2BMPDE ligand (Figure 1) exhibits three absorption bands at 260, 285 and 335 nm. The absorption band at 260 and 285 nm could be assigned to $\pi - \pi^*$ transition of the benzene ring and azomethine or imine chromophore respectively (11, 22-23). The band at 335 nm was attributed to $n - \pi^*$ transition of the non-bonding electrons resident in the nitrogen of the azomethine group (C=N) in the ligand (intraligand charge transfer (CT) transition) (22-25).

The electronic spectrum of Cd(II) H_2BMPDE consists of three bands in the region of 42553, 32258 and 24691 cm^{-1}. The band at 24691 cm^{-1} suggested a distorted tetrahedral structure (Figure 2) (26-27). The other band at 42553 and 32258 cm^{-1} was due to charge transfer transition (26-28).

The ligand exhibited the characteristic C=N stretching frequency at 1615 cm^{-1}. The shifting of ν(C=N) band to higher values by 9 cm^{-1} (from 1615-1624 cm^{-1}) indicates the participation of the two azomethine nitrogen atoms in bonding (29). The corresponding phenolic C—O stretching frequency occurs at 1285 cm^{-1} for the ligands and at 1414 cm^{-1} for the complex. The shift in C—O stretching frequency confirms the participation of the phenolic O in C—O—M bond formation (30). The ν(-OH) stretching vibration frequency of 3401 cm^{-1} observed in the ligand disappeared in the complex an indication that the hydroxyl group was not involved in complexation. The bands due to ν(Cd(II)—N) observed only in the complexes occurred at 556 cm^{-1} while 655 cm^{-1} was attributable to ν(Cd(II)—O) bond (31).

GC-MS result indicated the formation of M^+ ion for the ligand and the complex at 264 and 433 respectively with various fragmentations as represented in Scheme 3.



Scheme 3. Fragmentation pattern of H_2BMPDE and its complex.

The DSC curve of Cd(II) H_2BMPDE shows three peaks at 123.9 °C, 321.6 °C and 598.6 °C. The first weak endothermic peak at 123.9 °C corresponds to morphological transformation while the second sharp endothermic peak at 321.6 °C corresponds to the melting point of the complex and then broad exothermic peak at 598.6 °C corresponds to the decomposition of the complex. From DSC studies (Table 1), negative value of ΔS shown in the first step indicated the reaction was slower than expected thereby establishing nonspontaneous nature. Similarly, positive value of ΔG in some steps supports the nonspontaneous nature of the degradation process (32). The positive value of enthalpy indicates the endothermic nature of the degradation process (33). The degree of denaturation entropy and denaturation enthalpy was high and indicated that the stability of these drugs is high. The values of ΔS^{o}_{m} was derived from the relation in Equation 2

$$\Delta S^{o}_{m} = \Delta H^{o}_{m}/\mathrm{T_m}.. \quad \text{(Eq. 2)}$$

$\Delta G^{o}(T)$ is calculated from the modified Gibb`s Helmholtz equation (34) as shown in Equation 3:

$$\Delta \mathrm{G^o(T)} = \Delta \mathrm{H^o_m}\left(1 - \frac{\mathrm{T}}{\mathrm{T_m}}\right) + \Delta \mathrm{Cp}[(\mathrm{T} - \mathrm{T_m}) - \mathrm{T\ In}\left(\frac{\mathrm{T}}{\mathrm{T_m}}\right)] \quad \text{(Eq. 3)}$$

The denaturation entropies and enthalpies ΔS° (T) and ΔH° (T) respectively were derived from Kirchoff's laws (34) as shown in Equations 4 and 5.

$$\Delta \mathrm{H^o(T)} = \Delta \mathrm{H^o_m} + \Delta \mathrm{Cp(T - T_m)} \quad \text{(Eq. 4)}$$

$$\Delta \mathrm{S^o(T)} = \Delta \mathrm{S^o_m} + \Delta \mathrm{Cp\ In}(\frac{\mathrm{T}}{\mathrm{T_m}}) \quad \text{(Eq. 5)}$$

The stability of any given system is determined using the free energy ΔG° (T) which is the overall contribution of the enthalpic and entropic terms. These temperature-dependent parameters, enthalpic change, entropic change and heat capacity change are determined using the calorimetric method (DSC) or Van't Hoff method. Consequently, DSC studies the stability of biomolecules and helps in the proper understanding of biomolecular interactions and design of drugs.

The ^{1}H NMR spectra of H_2BMPDE and its metal complexes were recorded in $CDCl_3$ at room temperature using tetramethylsilane (TMS) as the internal reference standard.

^{1}H NMR analyses of ligand

The ^{1}H NMR spectrum of H_2BMPDE displayed the hydrogen of aromatic rings as complex multiplets at 7.11 ppm (3H) due to coupling of 4 hydrogen atoms in the ring whereas the methine proton of the ethylene bridge was observed as doublet at 3.5 ppm (4H) illustrating the symmetrical nature of the ligand. The appearance of triplet peak at 6.5 ppm (2H) was assigned to N-H proton. The azomethine proton was shown as quartet (1H) at 7.4 ppm (22,36).

^{1}H NMR analyses of complex

In Cd(II) H_2BMPDE, the singlet at 8.4 ppm (2H) was assigned proton of the azomethine group which was shifted downfield as a consequence of complexation between the metal and the ligand. The spectrum between 7.0-7.3 ppm was assigned to the hydrogen of aromatic ring. The triplet at 6.9 ppm integrated for 1 proton was assigned to the N-H group. The singlet at 3.90 ppm integrated for four protons was assigned to the proton of the ethylene bridge (37).

^{13}C NMR analyses of the ligand

The line pattern centered at 78 ppm was due to the solvent $CDCl_3$. H_2BMPDE is a symmetrical molecule and as such less than expected resonances appear in ^{13}C. The peaks at 221.44 ppm, 152.65 ppm, and 48.69 ppm are due to quaternary carbon atom bonded to oxygen of phenolic group (-C-O), imine bonded carbon (-N=C-H) due to SP^2 hybridization(37) and methylene carbon(-NCH_2CH_2N-) due to electronegative oxygen atom respectively (24, 35, 37).

^{13}C NMR analyses of the complex

In ^{13}C NMR spectrum of Cd(II) H_2BMPDE complex, peaks were observed at 165.28, 160.91, 132.21 131.33, 118.67, 118.63, 116.74 and 59.60 ppm. The peaks at 165.28, 160.91, 118.67 and 59.60 ppm were assigned to the quaternary carbon bonded to oxygen of the phenolic group, imine-bonded carbon atom, quaternary carbon bonded to imine and the methylene carbon (due to SP^3 hybridized carbon atom), respectively (37). The peaks at 132.21, 116.74, 118.63 and 131.33 ppm were assigned to methine carbon (C-H) of the aromatic ring. The upfield shift of 56.16 ppm between the ligand and the complex at the quaternary carbon bonded to oxygen of the phenolic group and downfield shift of 0.91 ppm between the ligand and the complex at the methylene carbon confirmed the involvement of C-O and NCH_2CH_2N group in bond formation. Generally, the less than expected signals in the ^{13}C NMR spectra were as the result of the symmetrical nature of the molecule (24).These observations are in line with the study of Pervaiz *et al* (37) on the synthesis and characterization of bimetallic post transition complexes for antimicrobial activity though little differences

observed could be because of the different synthetic protocols. This study is solution synthesis whereas the bimetallic study followed the constituent combination method hence the difference in the structure. The synthesis of the complex of H_2BMPDE in a 1:1 ratio was observed in the study of Yang *et al.,(*11) on the synthesis of dye sensitized cells from zinc metal and H_2BMPDE.

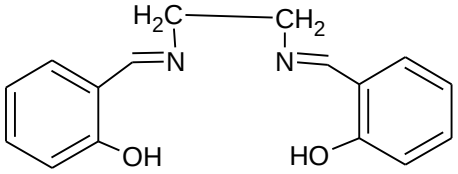


Figure 1: Structure of H_2BMPDE.

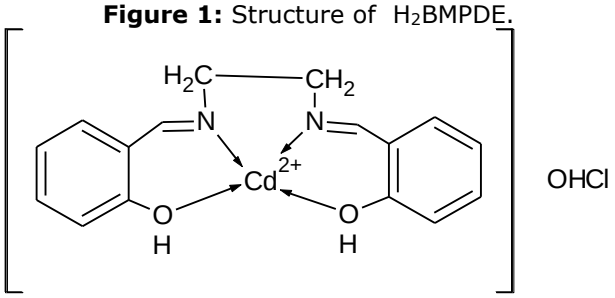


Figure 2: Proposed structure of Cadmium(II)H_2BMPDE

Table 1: Thermodynamic Data on the DSC Decomposition of H_2BMPDE Complexes.

	T	T_m	ΔH_m^o	ΔCp	ΔS_m^o	$\Delta G^o(T)$	$\Delta S^o(T)$	$\Delta H^o(T)$
Cd(II) H_2BMPDE	128.7	123.9	-124.3	12.2	-1.003	-0.028	-65.74	-0.539
	337	321.6	212.3	36	0.660	0.044	227.7	2.349
	598	598.6	28.57	8.5	0.048	-0.163	23.47	0.039

Legend:T(°C)=Temperature,T_m(°C) $= Transition\ midpoint\ temperature$, ΔH_m^o(J/K) $= calorimetric\ enthalpy$, ΔCp(°C)=change in heat capacity, ΔS_m^o(J/K) $= entropy\ change$, $\Delta G^o(T) = free\ energy\ change$, $\Delta S^o(T)$=denaturation entropy, $\Delta H^o(T)$= denaturation enthalpy.

Table 2: Antimicrobial activity of H_2BMPDE and its complexes.

H_2BMPDE /Metal complex	**Micro-organism Zone of inhibition**			
	P. aeruginosa	***K. pneumoniae***	***E. coli***	***S. aureus***
Cd(II) H_2BMPDE H_2SO_4	22	16	20	20
Cd(II) H_2BMPDE HCl	12	10	8	R
Cd(II) H_2BMPDE HNO_3	8	18	8	10
H_2BMPDE	R	08	06	06
Ampiclox (standard)	21±2	44±2	34±2	21±2

Table 3: Activity Index of H_2BMPDE and Complexes in Comparison to Standard Ampiclox.

H_2BMPDE /Metal complex	**Activity Index (%)**			
	P. aeruginosa	***K. pneumoniae***	***E. coli***	***S. aureus***
Cd(II) H_2BMPDE H_2SO_4	104.76	36.36	58.82	95.23
Cd(II) H_2BMPDE HCl	57.14	22.73	23.53	-
Cd(II) H_2BMPDE HNO_3	38.09	40.90	23.53	47.62
H_2BMPDE	-	18.18	17.65	28.57

The ligand and the complexes are shown to possess antimicrobial activities against the listed micro – organism possibly because of the presence of azomethine group (C=N). Studies have also shown (36) that ligands with hetero donor atoms (N and O) inhibiting enzyme activity and enzymes that need N or O groups for their activity are more susceptible to deactivation by metal ions on complexation. As shown in Tables 2 and 3, complexes of cadmium prepared from H_2SO_4 had the highest inhibition property for *Pseudomonas.*

CONCLUSION

This study revealed that cadmium forms octahedral complex with H_2BMPDE and at acid concentration of 10^{-4} M there was no deprotonation of the phenolic hydroxyl groups thereby enhancing the antimicrobial bioefficacy. Therefore, H_2BMPDE and its complexes synthesized using extractive technique based on the results could be considered a potential antibacterial agent.

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