

Synthesis, studies and biological activity of diphenylchlorophosphate schiff base metal complex

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Abstract: N,N-bis(benzaldehydediphenylphosphate)-p-phenylenediamine was synthesized and the structure was elucidated on the bases of elemental analysis, ¹HNMR, UV-VIS, IR, and Mass spectroscopy. The zinc complex was prepared and its structure was elucidated on the bases of elemental analysis, electronic, IR spectra and conductance measurements. Also, the biological activity of a N,N-bis(benzaldehyde-diphenylphosphate)-p-phenylenediamine and its Zinc complex were studied.

Keywords: Molar conductance, diphenylchlorophosphate, Schiff base, antifungal, antibacterial, Zn complex.

1. Introduction:

Schiff base compounds containing the azomethine (imine) group (–RC=N–) are usually prepared by the condensation of a primary amine with an active carbonyl compound. ^(1,2) It has been often used as chelating agents (ligands) in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known

that O, N and S atoms play a key role at the active sites of numerous metalloproteins in the coordination with metals. ⁽³⁾

Schiff bases are well known for their biological applications as antibacterial, antifungal, anticancer and antiviral agents ^(4, 5). Also, Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer herbicidal applications, ⁽⁶⁾ antitubercular activities ⁽⁷⁾ and chelating abilities which give it attracted remarkable attention. ⁽⁸⁾ A mixture of p-phenylenediamine and benzaldehyde were heated in ethanol until the mixture boiled; the residue on cooling was crystallized from ethanol to give N,N-bis(benzaldehyde)-p-phenylenediamine of type (I). ⁽⁹⁾

Schiff base (ethyl 4(2-hydroxybenzylidene-amino) benzoate) and its Cu complex were prepared and X-ray crystal structure of the Schiff base was studied. The nature of bonding in the isolated Schiff base and its Cu complex were elucidated by examining the elemental analysis, UV–VIS, IR and molar ratio methods. ⁽¹⁰⁾

In the present work, N,N'-bis(benzaldehydediphenylphosphate)-p-phenylenediamine of type (II) was prepared by direct reaction of N,N-bis(benzaldehyde)-p-phenylenediamine of type (I) with diphenyl chlorophosphate.

N,N'-bis(benzaldehydediphenylphosphate)-p-phenylenediamine of type (II) and its Zn complex were elucidated by examining the elemental analysis, UV–VIS, IR, TGA and molar ratio methods.

2. Experimental

2.1. Materials

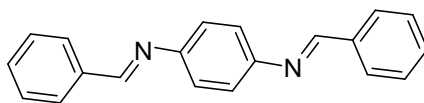
Diethylether, absolute Ethanol and dioxane from Prolabo Company. P-phenylene diamine and benzaldehyde were supplied by Merck Company. Diphenylchlorophosphate is chemically pure grade products of B. D. H.

Company. Zinc acetate was chemically pure grade, products of B. D. H. Company.

2.2. Instruments:

IR spectra were obtained as KBr disc on a Perkin. Elmer FTIR spectrophotometer 57928 RXIFT-IR system. The electronic spectra were recorded by Perkin Elmer Lambda 35 Spectrophotometer using DMF as solvent. The mass spectra were performed by Hewlett Packard mass spectrometer model MS 5988. Metal analyses were determined by atomic absorption (AAS Vario6). Conductance TDS Engineered system, U.S.A, was employed for the conductometric titration) at Al-Azhar university, Cairo, Egypt. While Elemental analysis and $^1\text{H-NMR}$ spectra which recorded by a Varian, USA, Gemini 200 MHz Spectrometer in DMSO- d_6 were taken at Micro-analytical Center, Cairo University, Cairo, Egypt and Magnet susceptibility measurement of the complexes were determined at room temperature by the Faraday method at Faculty of Science, Cairo University, Cairo, Egypt.

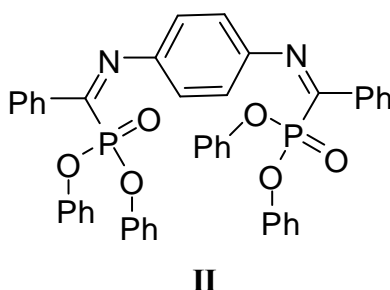
2.3. Synthesis of N,N'-bis(benzaldehyde)-p-phenylenediamine of type (I): A mixture of phenylenediamine and benzaldehyde were heated in 50ml absolute ethanol until the mixture boiled; the residue on cooling was crystallized from ethanol to give solid compound of type (I).⁽⁹⁾



I

2.4- Preparation of N, N'-bis(benzaldehydediphenylphosphate)-p-phenylenediamine of type (II): Diphenyl chlorophosphate was added to a well stirred solution of the equimolar amounts of Schiff-base of type

(I) in the presence of triethylamine, as a base in 100 ml. of nonpolar solvent such as dry dioxane. After complete addition, the reaction mixture was heated under reflux for 3 hours. The solid formed ($\text{Et}_3\text{N HCl}$) was filtered off and the filtrate was evaporated in vacuum gave (II) as crystalline compound. ⁽¹¹⁾



2.5. Preparation of complex

2.5.1. Studying the Molar ratio

2.5.1.1. Conductometric Titration

The conductometric titration Figure (1) is performed by titrating 25 ml. of 1×10^{-3} M Zn^{2+} ion solution with increasing volume of 1×10^{-3} complexing agent solution N, N'-bis(benzaldehydediphenylphosphate)-p-phenylenediamine of type (II), using ethanol as solvent, and the conductance is then recorded after stirring the solution for about 2 minutes. By plotting the conductance value Vs milliliters of the reagent added and applying the least square equation the ratio was 2:1 as shown in figure 1. ⁽¹²⁾

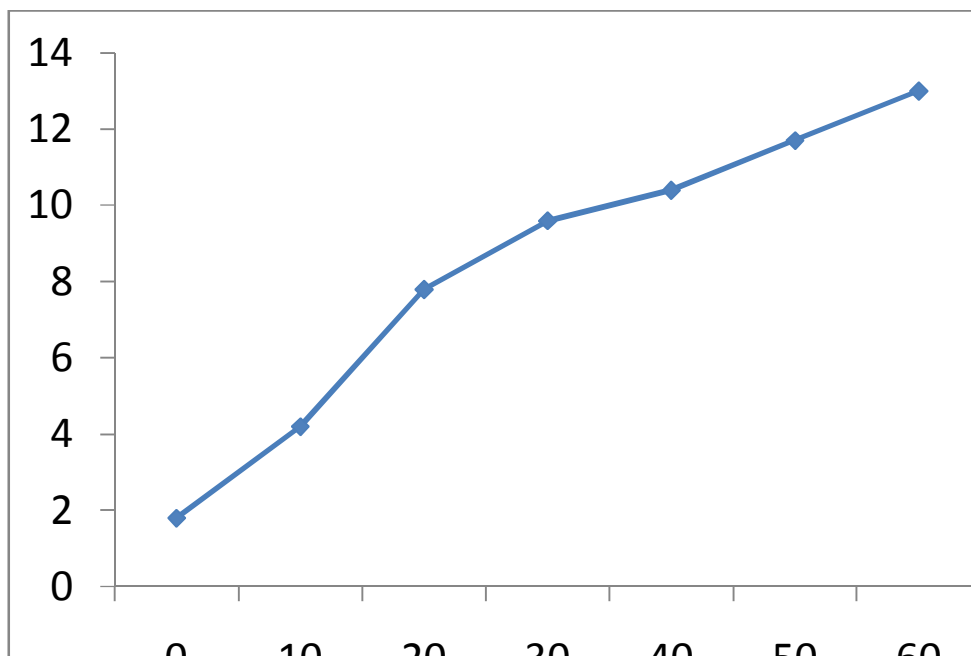
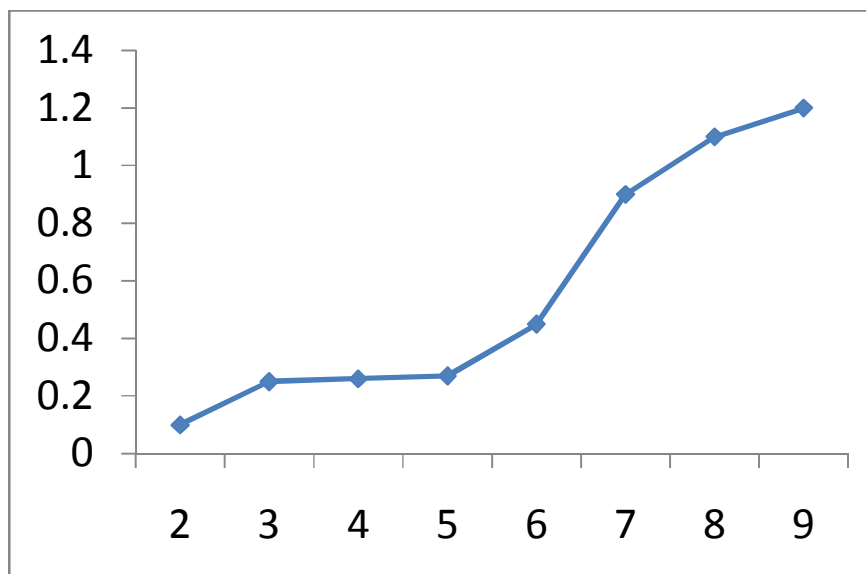


Figure 1: Conductometric titration of ligand (II)($1 \times 10^{-3} \text{ M}$) with Zn^{2+} ($1 \times 10^{-3} \text{ M}$) system.

2.5.1.2. Spectroscopic Molar ratio testing

In the present investigation, 2 ml of Zn^{+2} ions kept constant at $1 \times 10^{-4} \text{ M}$. while that the ligand (II) was varied from 0.2×10^{-4} to $2.2 \times 10^{-4} \text{ M}$ using ethanol as solvent. The absorbance of the mixed solutions was measured and plotted Vs the molar ratio [ligand] / [metal ion]. The results obtained are represented graphically in Figure (2).⁽¹³⁾ Which indicate the formation of the complex by 1:2 ligand to metal.

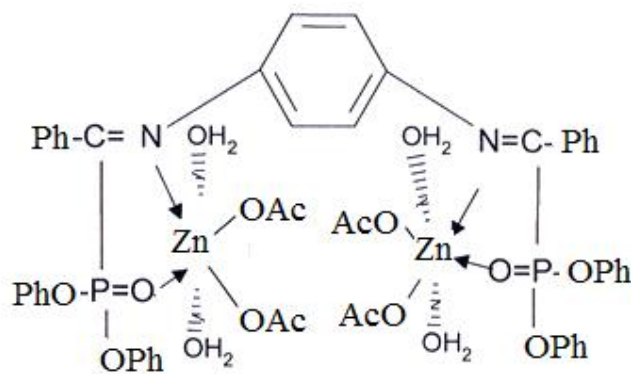


[ligand] / [Zn²⁺]

Figure 2: Absorption spectra of Zn (II) complex molar ratio method

2.5.2. Preparation of Schiff-base metal complex of type (III)

A solution of the Zinc acetate was added to organophosphorus Schiff base derivatives type (II) in 50ml absolute ethanol in (2M: 1L) molar ratio. After the complete addition of the metal salt; the reaction mixture was heated under reflux for about two hrs. The solid compound (III) obtained was filtered off giving products.



III

Octahedral structural of tetradentate aqua N,N' -bis(benzaldehydediphenylphosphate)-*p*-phenylenediamine di Zinc(II)

3. Results and Discussions

3.1. The structure of N, N' -bis(benzaldehydediphenylphosphate)-*p*-phenylenediamine of type (II) was elucidated on the bases of:

3.1.1. Elemental analysis.

The structural assignment of the isolated compound was based on the elemental analysis which is in good agreement with the proposed structures (II), Table (1).

Table1: Microanalytical data of N, N' bis(benzaldehydediphenylphosphate)-*p*-phenylenediamine of type (II)

No.	Reactants		Mp ^o c	Yield %	Color	MF	Elemental Analysis	
							Cal./Found	
							%N	%P
II	Schiff -base I	Diphenyl chloro phosphate	210	68	Yellow	$C_{44}H_{34}N_2O_6$ P_2	3.7 3.6	8.2 7.8

3.1.2. 1H -NMR spectrum

The ^1H NMR spectrum of compound (II) in DMSO solution exhibits several signals in the region 6-7.8 ppm. The para-disubstituted phenyl ring represent A_2X_2 system in which absorption protons appears as two doublets at $\delta = 6.8$ ppm and at $\delta = 7.8$ ppm. Also another singlet signal at $\delta = 7.1$ ppm characteristic for the protons of phenyl ring. While the azomethine protons appeared at $\delta = 8.3$ ppm in (the spectrum of the parent Schiff-Base were disappeared due to replacement reaction on this group with eliminated HCl).

3.1.3. Electronic spectrum.

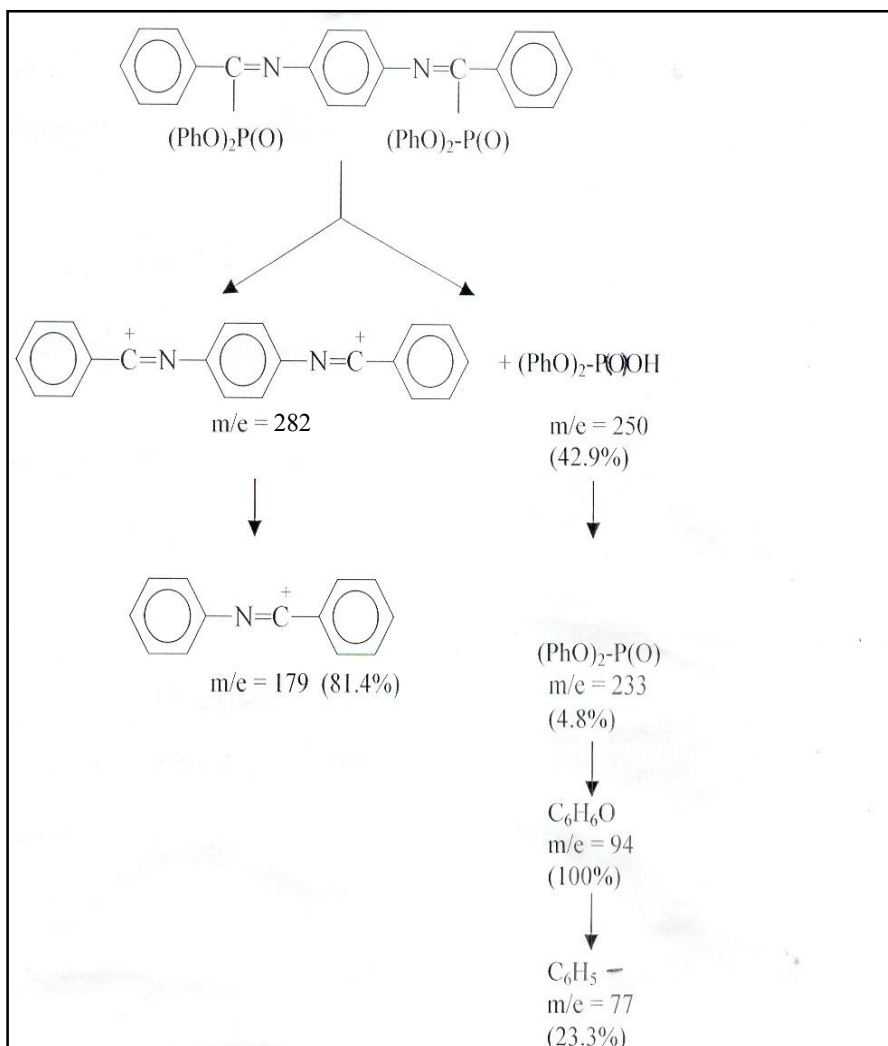
The Electronic spectra of the prepared compound (II) in DMSO as a solvent, exhibits the vibration band at 212 nm correspond to ($^1\text{La} \leftarrow ^1\text{A}$) transitions of phenyl ring and vibration band at 240.4 correspond to ($^1\text{Lb} \leftarrow ^1\text{A}$) transitions of phenyl ring. Also the band 251 nm correspond to the π - π^* transitions of the azomethine groups finally while the band at 297 nm correspond to n- π^* transitions.

3.1.4. IR spectrum.

The band at 1596 cm^{-1} may be assigned as ν -CH=N stretching mode of vibrations which is shifted to lower wave length in comparison with parent Schiff-Base ^(14,15). The bands observed at 3038 , 2860 and 1238 cm^{-1} which belong to CH stretching mode of vibrations of aromatic , aliphatic CH groups ν -C-N stretching mode of vibrations respectively⁽¹⁶⁾. A sharp peak at 1568 cm^{-1} is due to ν C=C stretching mode of vibrations. The band at 1492 and 1456 cm^{-1} are due to the CH deformation mode of vibrations of CH bond. The peak at 1186 cm^{-1} characteristic for $\nu\text{P}=\text{O}$ stretching mode of vibrations and 1070 cm^{-1} may be assigned as $\nu\text{P}-\text{O}-\text{C}$ stretching mode of vibrations.

3.1.5 Mass spectrum.

The gas-mass spectrum of compound (II), exhibits one peak indicating the purity of the compound. The spectrum exhibits many ion peaks where the base peak at m/e , 94 (100%) is due to C_6H_5O . The ion peak at m/e 108 (36.9%) corresponds the M^+ (C_6H_5P). The ion, peak at $m/e = 250$ (42.9%) can be attributed to M^+ ($C_{12}H_{11}PO_2$) where the intense peak is common for phenyl phosphorus compounds containing more than one phenyl group attached to the phosphorus atom. On the other hand the peak corresponding the phenyl ring was appeared at $m/e=77$ (23.3%).



Scheme 1: Fragmentation of Ligand (II)

3.2. The structure of Schiff base Zinc complex (Ia) was elucidated on the bases of:

3.2.1. Elemental analysis

The elemental analysis and the physical properties of metal diphenylchlorophosphate Schiff-Base complex are shown in table (3) Comparison of both the calculated and the found percentage of the elemental analysis indicates that the composition of the prepared complex coincide well the proposed structure.

Table 2: Microanalytical data of organophosphorus Schiff Base metal complex

No.	Reactants		Color	Mp ^o c	Yield, %	MF	Elemental Analysis		
	Ligand	Metal					Found/(Cal.)		
							%N	%P	%M
III	II (0.74q m ; 0.001 m)	Zn(OA c) ₂ .H ₂ O (0.45q _m ; 0.002m)	Colour less	>360	77	C ₅₂ H ₅₄ N ₂ O ₁₈ P ₂ Zn ₂	1.9 2.4	4.8 5.2	11.2 11

3.2.2. Electronic spectrm

The spectra of the Zn-L complex reveals a bands in the long wave length at 389.8, 470 and 508.6nm, can be assigned to the CT from the ligand to the Zn atom, transition in the Zn-L complex suggesting the octahedral structure of the complex. In addition to a band at 206 nm corresponding to (${}^1L_a \leftarrow {}^1A$) transition, a band at 254nm due to (${}^1L_b \leftarrow {}^1A$) transitions of benzene ring, a band at 265.6nm characteristic to $\pi\text{-}\pi^*$ transitions and a band at 303-325nm due to $n\text{-}\pi^*$ transitions of azomethine groups.

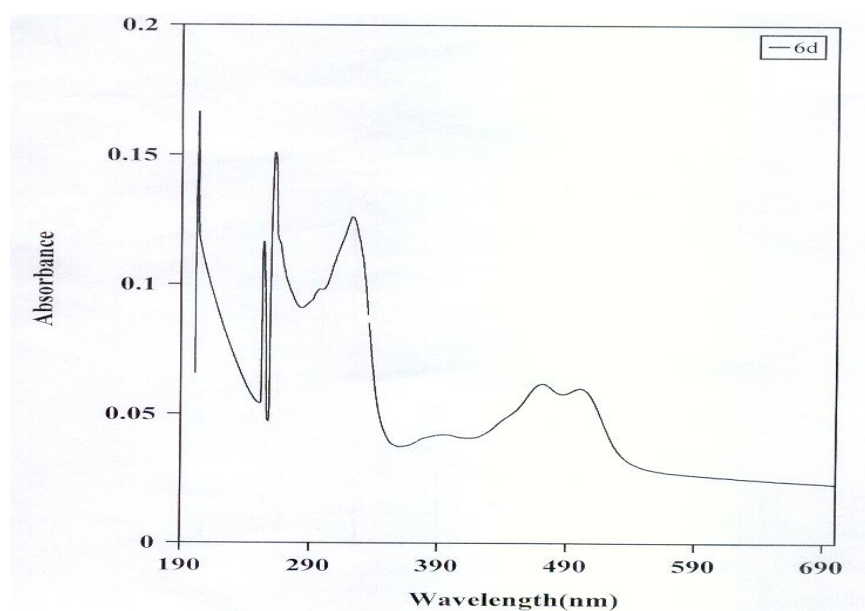


Figure 3: UV spectra for L-Zn complex

3.2.3. IR spectrum

The IR spectra exhibit a band at 3402 cm^{-1} in the spectra of Zn-L complex, can be attributed to the stretching mode of vibration of water molecules associated with the complex.⁽¹⁷⁾

The band observed at 2928 cm^{-1} can be attributed to the stretching mode of vibrations of the aliphatic C-H bonds of the acetate groups. This is further supported by the presence of $\nu\text{ C=O}$ band at 1652 cm^{-1} spectra. The band observed at 1552 cm^{-1} , can be attributed to the stretching mode of the vibrations of the azomethine group. This band suffers shifts to lower frequencies indicating that the nitrogen atom of the azomethine group participates in the coordination sphere.

The band located at 1456 cm^{-1} , can be assigned to the inplane bending deformation mode of vibrations of the aromatic C-H-bonds. The band observed at 1456 cm^{-1} , can be attributed to the stretching mode of vibrations of C-N bond. The band observed at 1232 cm^{-1} , can be attributed to stretching mode of vibrations of the C-O bonds. The band at 1178 cm^{-1} can be attributed to stretching mode of vibration of P=O bonds. The band observed at 1098 cm^{-1} , can be attributed to the stretching mode of vibrations of the P-O-C bonds. The region $1000\text{-}700\text{ cm}^{-1}$ is rich of peaks characterizing the out of plane of vibrations of benzene rings.

The general features of the IR spectra of metal diphenylphosphate Schiff-Base complexes indicate large electronic disturbance on complex formation and hence the bands appear is broad, less intense, and shift to lower frequencies, then those of the free ligand. The broadening and shift in the position of azomethine, and P=O groups support the involvement of these groups in the complexing process. The IR spectra indicate that the ligand behaves as bidentate ligand. Also the IR spectra cut clearly involvement of the participation of the acetate, azomethine and phosphoryl groups in complex.

3.2.4. Molar conductance

The Molar conductance of the complex was carried out in DMSO solution of 10^{-3} M concentration the result obtained is $9 \text{ ohm}^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$ for Zn-L complex. The very low values of the molar conductance suggest that all anions associated with the metal complex were involved in the coordination sphere complex. Hence this complex is neutral and behaves as non electrolytes.

3.2.4. Magnetic properties

The Zn-L complex shows the expected diamagnetic behavior, and hence there are no unpaired electrons.

3.3. Biological activity

In testing antibacterial and antifungal activity of these compounds we used more than one test organism to increase the chance of detecting antibiotic principles in the test materials. The sensitivity of microorganisms to antibiotics and other antimicrobial agents can be determined by the filter paper disk method.⁽¹⁸⁾

3.3.1. Antibacterial activity

The antimicrobial activity of the prepared compounds was examined with different species of gram positive (*Enterobacter Sp.* and *Sarcina Sp.*) gram negative bacteria (*Salmonella Typhi*).

3.3.2. Antifungal activity

The antimicrobial activity of the prepared compounds was examined with different species fungi (*Aspergillus terreus* and *Aspergillus flavus*) and bacteria (*Salmonella Sp.*, *Enterobacter Sp.*, and *Sarcina Sp.*). The activity of some compounds against gram positive, gram negative bacteria and fungi are summarized in table (4).

Table 4: Antimicrobial activity

Compound No.	Antibacterial activity			Antifungal activity	
	<i>Salmonella</i> Sp.	<i>Enterobacter</i> Sp.	<i>Sarcina</i> Sp.	<i>Aspergillus terreus</i>	<i>Aspergillus flavus</i>
I	-	-	+	-	-
II	-	-	+	-	-
III	-	-	-	-	-

Standard for antibacterial activity Ampicillin 25mg antifungal activity mg costa 30mg.

+ : Less active.

++ : moderate active.

+++ : Highly active.

4. Conclusion

A mixture of phenylenediamine and benzaldehyde were heated to give N,N'-bis(benzaldehyde)-p-phenylenediamine of type (I) which reacted with diphenylchlorophosphate to give N,N'-bis(benzaldehydediphenylphosphate)-p-phenylenediamine of type (II) which reacted with cobalt acetate as tetradentate ligand two from oxygen and two from azomethine nitrogen. In the case Zn-L complex the formula $[Zn_2(L)(OAc)_4] \cdot 2H_2O$ was supported by elemental analysis. The IR spectra indicate that the ligand acts as tetradentate ligand UV and magnetic moment support the octahedral structure arrangement for the Zn-L complex.

The result of all previous physiochemical measurements show that the structure of 2metal:1ligand complex. Finally the four compounds I, II and III show biological activity on both bacterial and fungal activity.

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