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Derivatives of phosphate Schiff base transition metal complexes: synthesis, studies and biological activity

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Abstract

We report the synthesis and structural characterization of series of tetra- and hexacoordinate metal chelate complexes of phosphate Schiff base ligands having the general composition LMX_n·H₂O and L₂MX_n (L = phosphate Schiff base ligand; M = Ag⁺, Mn²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, or Fe³⁺ and X = NO₃⁻, Br⁻ or Cl⁻). The structure of the prepared compounds was investigated using elemental analysis, IR, ¹H and ³¹P NMR, UV–vis, mass spectra, solid reflectance, magnetic susceptibility and conductance measurements as well as conductometric titration. In all the complexes studied, the ligands act as a chelate ligand with coordination involving the phosphate–O-atom and the azomethine–N-atom. IR, solid reflectance spectra and magnetic moment measurement are used to infer the structure and to illustrate the coordination capacity of ligand. IR spectra show the presence of coordinated nitrate and water molecule, the magnetic moments of all complexes show normal magnetic behavior and the electronic spectra of the metal complexes indicate a tetra- and octahedral structure for Mn²⁺, octahedral structure of Fe³⁺ and both square-planar and distorted octahedral structure for Cu²⁺ complexes. Antimicrobial activity of the ligands and their complexes were tested using the disc diffusion method and the chosen strains include *Staphylococcus aureus*, *Pseudomonas aereuguinosa*, *Klebsiella penumoniae*, *Escherichia coli*, *Microsporum canis*, *Trichophyton mentagrophyte* and *Trichophyton rubrum*. Some known antibiotics are included for the sake of comparison and the chosen antibiotic are Amikacin, Doxycllin, Augmantin, Sulperazon, Unasyn, Septrin, Cefobid, Ampicillin, Nitrofurantion, Traivid and Erythromycin.

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Keywords: Phosphate Schiff base ligands; Transition metal complexes; Spectroscopic techniques; Magnetic measurements; Biological activity

1. -Introduction

The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural lability and are sensitive to molecular environment [1]. The environment around the metal center 'as coordination geometry, number of coordinated ligands and their donor group' is the key factor for metalloprotein to carry out a specific physiological function [2]. About 20 Zinc enzymes are known in which Zinc is generally tetrahedrally four coordinate and bonded to hard donor atoms such as nitrogen or oxygen [3]. Manganese plays an important role in several biological redox-active system [4], a number of copper proteins including enzymes have been reported and proteins containing iron participate in oxygen transport [5]. The preparation of model complexes having similar spectroscopic features is perhaps the most important step to understand the structure and behavior of these biological systems. Schiff base metal complexes attract considerable interest and occupy an important role in the development of the chemistry of chelate systems [6,7] due to the fact that especially these with N₂O₂ tetradentate ligands, such systems closely resemble metallo-proteins. Survey of the literature reveals an excellent work devoted to synthesis and characterization of many metal complexes of Schiff base [8-13], furthermore the coordination compounds of phosphonic acid and their esters with transition metal ions have been the subject of several studies due to the fact that complexes of such compounds exhibit biological activity [14-17]. The present paper deals with the preparation and characterization of phosphate Schiff base derivatives followed by studying their complexation with di-and trivalent transition metal ions which have been the subject of several studies due to the fact that these ligands and their metal complexes exhibit different biological activity and very industrial applications.

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Table 1

Compd. No.	Molecular formula (M.wt)	Colour	m.p.(°C)	Analysis% found (calcd.)		
				N	Р	
Ia	C ₂₅ H ₂₀ NPO ₃ (413)	Yellowish green	146	2.90 (3.39)	7.62 (7.51)	
\mathbf{I}_{b}	$C_{26}H_{22}NPO_4$ (443)	Pale yellow	148	2.70 (3.16)	7.86 (7.00)	

Analytical and physical data of bidentate phosphate Schiff base ligands $(I_{a,b})$

2. Experimental

2.1. Preparation of phosphate Schiff base 'ligand'

At first, two Schiff base derivatives were prepared by literature method [18] via condensation of aniline with benzaldehyde and *p*-methoxybenzaldehyde, respectively. Secondly, the phosphate Schiff base derivatives 'ligands' $(\mathbf{I}_{a,b})$ were prepared by direct reaction of Schiff base with diphenyl chlorophosphate in 1:1 molar ratio in presence of tertiary amine to absorb the liberated hydrogen chloride using acetonitrile as solvent. In a typical experiment, a solution of diphenyl chlorophosphate (5.2 ml, 0.025 mmol) in 25 ml acetonitrile was added dropwise to a well stirred solution of Schiff base (4.53 g of benzalaniline; or 5.28 g of *p*-methoxy benzalaniline; 0.025 mmol) in 25 ml acetonitrile containing triethylamine (3.5 ml, 0.025 mmol). After complete addition, the reaction mixture was heated under reflux for 2 h, the formed solid 'triethylaminhydrochloride' was filtered and the filtrate was evaporated in vacuum. The obtained solid $(\mathbf{I}_{a,b})$ gave analytical data which are summarized in Table 1.

2.2. Preparation of metal complexes

For the preparation of metal complexes, a hot ethanolic solution of metal halide or nitrate was added dropwise to ethanolic solution of phosphate Schiff base derivatives ($I_{a,b}$) in 1:1 and 1:2 molar ratio (M:L), respectively and the resulting solution was refluxed for 2 h. After evaporation of the solvent, the colored solid obtained was recrystallised to give

Table 2

Analytical and	physical data of	phosphate Schiff base con	mplexes in 1:1 molar ratio
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 (\mathbf{II}_{a-l}) and (\mathbf{III}_{a-j}) . The microanalytical data for complex derivatives are listed in Tables 2 and 3.

2.3. Antimicrobial activity

The phosphate Schiff base 'ligands' $(I_{a,b})$ and their metal complex derivatives (II_{a-1}) and (III_{a-j}) were evaluated for their antibacterial activity against *Klebsiella penumoniae*, *Escherichia coli*, *Pseudomonas aereuguinosa* and *Staphylococcus aureus* and also for their antifungal activity against *Trichophyton mentogrophrtes*, *Microsporum canis* and *Trichophyton rubrum* using the disc diffusion method [19,20]. Moreover some of known antibiotic were evaluated for their antibacterial activity as well as phosphate derivatives and some comparison were discussed. The chosen antibiotic are Amikacin, Doxycllin, Augmantin, Sulperazon, Unasyn, Septrin, Cefobid, Ampicillin, Nitrofurantion, Traivid and Erythromycin. The obtained data are collected in Tables 4–6.

2.4. Physical measurements

The elemental C, H and N analysis were carried at microanalytical laboratory of Cairo university, phosphorus analysis were determined gravimetrically by Voy method [21], metal contents were determined volumetrically by titration against standard EDTA after complete decomposition of the complexes with nitric and perchloric acids in a kjeldahl flask [22]. IR spectra were recorded on a Perkin–Elmer FT-IR type 1650 spectrophotometer with KBr disc. Mass spectra were performed by Hewlett-Packard mass spec-

Compd. No.	Molecular formula (M.wt)	Colour	m.p. (°C)	Analysis% fo	$\mu_{\rm eff}$ B.M.		
				Р	N	M	
IIa	C ₂₅ H ₂₀ NPO ₃ Cl ₂ Hg (684.59)	Grey	151	4.33 (4.53)	2.10 (2.05)	28.70 (29.30)	Diamag.
II _b	C ₂₅ H ₂₀ NPO ₃ Cl ₂ Cd (596.41)	Greenish blue	299	4.27 (5.20)	1.80 (2.35)	18.81 (18.85)	Diamag.
II _c	C ₂₅ H ₂₂ N ₂ PO ₇ Ag (600.87)	Green	124	6.95 (5.16)	5.20 (466)		Diamag.
\mathbf{II}_{d}	C ₂₅ H ₂₀ NPO ₃ Cl ₂ Mn (538.94)	Greenish black	125	4.80 (5.75)	2.50 (2.60)	10.37 (10.19)	5.46
IIe	C ₂₅ H ₂₀ NPO ₃ Br ₂ Zn (638.19)	Greenish grey	121	4.33 (4.86)	2.10 (2.19)	10.00 (10.25)	Diamag.
\mathbf{II}_{f}	C ₂₅ H ₂₁ NPO ₃ Cl ₃ Fe (593.35)	White	>330	6.03 (5.22)	2.15 (2.36)	8.76 (9.41)	5.82
IIg	C ₂₆ H ₂₂ NPO ₄ Cl ₂ Hg (714.59)	Reddish brown	147	4.20 (4.34)	2.10 (1.96)	27.42 (28.07)	Diamag.
\mathbf{H}_{h}	C ₂₆ H ₂₂ NPO ₄ Cl ₂ Cd (626.41)	Reddish brown	297	4.46 (4.95)	2.30 (2.23)	18.91 (17.95)	Diamag.
II _i	C ₂₆ H ₂₂ NPO ₄ Cl ₂ Cu (577.55)	Pale green	120	5.32 (5.37)	2.80 (2.42)	10.14 (11.00)	2.03
II _i	C ₂₆ H ₂₂ NPO ₄ Cl ₂ Mn (568.94)	Green	110	5.70 (5.45)	3.00 (2.46)	8.73 (9.66)	5.54
IIk	C ₂₆ H ₂₂ NPO ₄ Br ₂ Zn (668.19)	Black	154	4.47 (4.64)	2.80 (2.10)	8.64 (9.79)	Diamag.
\mathbf{II}_{l}	C ₂₆ H ₂₄ NPO ₅ Cl ₃ Fe (623.35)	Yellow	>330	5.58 (4.97)	2.42 (2.25)	9.20 (8.96)	5.85

Table 3 Analytical and physical data of phosphate Schiff base complexes in 1:2 molar ratio

Compd. No.	Molecular formula (M.wt)	Colour	m.p. (°C)	Analysis% fo	$\mu_{\rm eff}$ B.M.		
				Р	N	М	
IIIa	C ₅₀ H ₄₀ N ₂ P ₂ O ₆ Cl ₂ Cd (1009.41)	Blue	167	6.11 (6.14)	3.00 (2.77)	10.95 (11.14)	Diamag.
III _b	C ₅₀ H ₄₀ N ₂ P ₂ O ₆ Cl ₂ Cu (960.55)	Greenish black	158	6.08 (6.45)	2.40 (2.91)	5.65 (6.62)	1.80
III _c	C ₅₀ H ₄₀ N ₂ P ₂ O ₆ Cl ₂ Mn (951.94)	Reddish brown	151	7.44 (6.51)	3.00 (2.94)	5.82 (5.77)	5.16
III _d	C ₅₀ H ₄₀ N ₂ P ₂ O ₆ Br ₂ Zn (1051.19)	Pale brown	122	6.95 (5.90)	2.58 (2.66)	5.48 (6.22)	Diamag.
III _e	C ₅₂ H ₄₄ N ₂ P ₂ O ₈ Cl ₂ Hg (1157.59)	Reddish brown	147	5.37 (5.36)	2.50 (2.42)	17.27 (17.33)	Diamag.
$\mathbf{III}_{\mathrm{f}}$	C ₅₂ H ₄₄ N ₂ P ₂ O ₈ Cl ₂ Cd (1069.41)	Reddish brown	164	5.95 (5.80)	3.70 (2.62)	11.47 (10.51)	Diamag.
III _g	C ₅₂ H ₄₄ N ₂ P ₂ O ₈ Cl ₂ Cu (1020.55)	Green	120	6.09 (6.08)	2.20 (2.74)	5.80 (6.23)	1.87
III _h	C ₅₂ H ₄₄ N ₂ P ₂ O ₈ Cl ₂ Mn (1011.94)	Green	164	6.85 (6.13)	2.90 (2.77)	5.12 (5.43)	6.03
III _i	C ₅₂ H ₄₄ N ₂ P ₂ O ₈ Br ₂ Zn (1111.19)	Dark green	156	5.89 (5.58)	3.30 (2.52)	6.76 (5.88)	Diamag.
III _j	$C_{52}H_{44}N_2P_2O_8$ Cl ₃ Fe (1048.35)	White	>330	6.57 (5.91)	3.11 (2.67)	4.77 (5.33)	5.95

trometer model MS 5988, ¹H and ³¹P NMR spectra were performed at the microanalytical center at Cairo University. UV–vis spectra were performed by Perkin–Elmer Lambda 20 spectrophotometer at Al-Azhar University. Magnetic susceptibilities measurements were measured by the Gouy method at room temperature using an oxford faraday magnetometer at Qanal University. The solid reflectance spectra were measured on a shimadzu 3101 pc spectrophotometer at Cairo University. The conductmetric titrations was carried out using engineered system of designs USA and the biological screening was carried out at microbiology laboratory, Bab Al-sheria University hospital, Al-Azhar University.

Table 4

Antibacterial activity of phosphate Schiff base derivatives and their metal complexes

Compd.	Gram positive	Gram negative					
No.	Staphylococcus aureus	Pseudomonas aereuguinosa	Klebsiella penumoniae	Escherichia coli			
Ia	R	R	R	R			
\mathbf{I}_{b}	R	R	R	R			
IIa	++++	++	+	++			
II _b	++	+++	+++	++			
\mathbf{H}_{d}	R	R	R	R			
IIe	R	R	R	R			
\mathbf{H}_{f}	+	R	R	R			
\mathbf{H}_{g}	+++	+	++	+			
\mathbf{H}_{h}	++	++	+++	++			
\mathbf{H}_{i}	+	++	R	R			
IIj	R	R	R	R			
\mathbf{H}_{k}	R	R	R	R			
\mathbf{II}_{l}	R	R	R	R			
III _a	+	R	R	R			
III _b	+	R	R	R			
III _c	+++	++	+	+			
$\mathbf{III}_{\mathrm{f}}$	++	R	++	+			
III_{g}	+	+	R	R			
III _h	R	R	R	R			
III _i	R	R	R	R			
III _i	R	++	R	+			

R, Resistance; +++, Highly active; +, Less active; ++++, Very active; ++, Moderate active.

Table 5									
Antifungal	activity	of sc	ome	phosphate	Schiff	base	metal	complex	es

Compd.	Fungi							
No.	Microsporum canis	Trichophyton mentagrophyte	Trichophyton rubrum					
IIa	R	++	+					
II _b	++	+	+++					
\mathbf{II}_{g}	++	++	++					
\mathbf{II}_{h}	++++	++	+++					
II_i	R	R	R					
IIj	R	R	R					
III _a	++	++	+++					
\mathbf{III}_{j}	R	R	R					

3. Results and discussion

The treatment of diphenyl chlorophosphate with benzalaniline and *p*-methoxybenzaniline, respectively led to the replacement of azomethine proton giving the corresponding phosphate Schiff base derivatives ($I_{a,b}$) which have two donor sites, nitrogen and oxygen atoms, and so, they may function as bidentate ligand (Fig. 1).

3.1. Characterization of phosphate Schiff base ligands

Structure elucidation of the prepared compounds $(I_{a,b})$ was accomplished on the bases of elemental analysis (Table 1), IR, ¹H and ³¹P NMR, Mass and UV–vis. Spectroscopic data.

(1) The analytical data of the isolated compounds $(I_{a,b})$ have been given in Table 1 which are in good agreement with the proposed structure.

$R-N = C-R^{-}$		R	R
(O - P(OPh))	Ia	C_6H_5	C ₆ H ₅
$0 - 1 (011)_2$	Ib	C ₆ H ₅	C ₆ H ₄ O CH ₃ -P

Fig. 1. Phosphate Schiff base ligands $(I_{a,b})$.

Antibiotic name	Cocci (gram positive)	Bacilli (gram negative)							
	Staphylococcus aureus	Pseudomonas aereuguinosa	Klebsiella penumoniae	Escherichia coli					
A mikacin	R	+++	+++	++					
Doxycllin	+++	R	+++	R					
Augmantin	+++	R	+++	+++					
Sulperazon	+++	+++	+++	R					
Unasyn	+++	R	R	++					
Septrin	R	R	++	R					
Cefobid	R	R	R	R					
Ampicillin	R	++	R	++					
Nitrofurantion	+++	R	+++	R					
Traivid	R	R	+++	+++					
Frythromycin		P	P	P					

 Table 6

 Antibacterial activity of some known antibiotics

(2) IR spectra showed the characteristic stretching vibrations $\nu_{C=N}$ and $\nu_{P=O}$ at (1673–1614 cm⁻¹) and (1279–1220 cm⁻¹), respectively [8,23].

(3) The ¹H NMR spectra were used to substantiate the proposed structures ($\mathbf{I}_{a,b}$), thus ¹H NMR spectra showed that the characteristic azomethine proton signal for shift bases at $\delta = 8.6$ ppm [8,9] had disappeared. Also the spectra for the compounds ($\mathbf{I}_{a,b}$) in DMSO-d₆ solution showed the aromatic protons signal at 7.2–7.1 ppm regions and a signal at 3.9 ppm region for \mathbf{I}_b only due to the presence of the methoxy group [9]. ³¹P NMR spectra for compound \mathbf{I}_b show a signal at $\delta = -11.6$ due to the non bonding electrons on oxygen phosphate group [24].

(4) The mass spectra for the compounds ($\mathbf{I}_{a,b}$) were characterized by a peak corresponding to Schiff base fragmentation (M -233), the mass spectrum of the ligand \mathbf{I}_a show intense peak at m/e 180 (0.54%) corresponding to Ph-c⁺=N-Ph ion and the mole peak at m/e 412.4 (0.26%) (calculated 413). For the ligand \mathbf{I}_b its mass spectrum is characterized by intense peak at m/e 233 (4.3%) corresponding to O=P⁺(OPh)₂ ion, m/e 210 (0.6%) due to PhNC⁺C₆H₄OCH₃ ion and an intense peak at m/e 250 (47.1%) corresponding to (PhO)₂ P (O) (OH). Intense peak of this type is very common in phenyl–phosphorus compounds containing more than one phenyl group attached to the phosphorus atom [25].

(5) The UV–vis spectra of phosphate Schiff-base ligands ($I_{a,b}$) in DMF solution show two intense bands in the region 200–400 at 265 and 294 nm can be assigned to π – π * and n– π * transition over the whole conjugated system [26].

3.2. Characterization of phosphate Schiff base metal complexes

The reaction of phosphate derivatives $(\mathbf{I}_{a,b})$ with metal halide or nitrate led to the formation of (\mathbf{II}_{a-l}) and (\mathbf{III}_{a-j}) derivatives. The elemental analysis were satisfactory and show that the complexes have a ligand-to-metal ratio of 1:1 and 2:1. A comparison of the spectra of the free ligands $(\mathbf{I}_{a,b})$ with those of the metal complexes has been carried out to investigate the mode of bonding of the ligands.

In the IR spectra of the free ligands $(I_{a,b})$, the band centered around (1673-1614 cm⁻¹) and (1279-1220 cm⁻¹) which characteristic for $v_{C=N}$ and $v_{P=O}$, respectively are shifted to a lower frequencies at (1640-1574 cm⁻¹) and $(1249-1074 \text{ cm}^{-1})$ upon coordination to transition metals [8,23] with the appearance of other modes of vibrations at $(565-493 \text{ cm}^{-1})$ and $(477-414 \text{ cm}^{-1})$ corresponding to ν_{M-N} and ν_{M-O} [23,27] which are absent in the free ligand spectra. This confirms the involvement of azomethine nitrogen and phosphate oxygen in complex formation. For the nitrato complex compound (\mathbf{II}_{c}) the band observed at 1491, 1384 and 1072 cm⁻¹ is due to $\nu_{N=O}$, $\nu_{asy NO_2}$ and ν_{sy} NO_2 , the frequency difference (107 cm⁻¹) is an agreement with the unidentate coordination mode of the nitrate anion [28,29]. A very broad band at about 3300–3446 cm^{-1} is present in the spectra of the complexes $\mathbf{II}_{c.f.l}$. The presence of this broad band is associated with coordinated and/or solvated water molecule [30,31]. The presence of coordinated water in this complexes has been inferred on the basis of a medium intensity band at 728–777 cm^{-1} (OH-rocking) [31]. The other stretching vibration in the ligand are much less affected by complex formation indicating that the ligand behave as bidentate chelating ligand and both the azomethine nitrogen and phosphate oxygen are the two sites of coordination. The data collected in Table 7.

¹H-NMR spectra for the complex derivatives ($\mathbf{II}_{b,e,h,k}$) and ($\mathbf{III}_{a,f,i}$) show signal at 7–7.4 ppm due to aromatic protons and a signal at 3.3–3.9 ppm due to the methoxy protons for compounds ($\mathbf{II}_{k,h}$) and ($\mathbf{III}_{f,i}$) [8,23], see Table 8. Also, the signal given by ³¹P nucleus in the NMR spectra appears at $\delta = -11.6$ and -11.7 for compounds \mathbf{II}_h and \mathbf{III}_f . The significance of this negative chemical shift than in the reference compound is due to that the phosphorus nucleus is more effectively shielded by the electron in the complex compounds than in the reference (85% phosphoric acid).

3.3. Determination the composition of the metal complexes

The stoichiometry of the metal complexes is confirmed by conductometric titration of each of the metal ions and Schiff base ligands in ethanol medium. The experimental

Table 7 Characteristic infrared stretching vibrations (cm^{-1}) of phosphate Schiff base metal complexes

Compd.	$\nu_{C=N}$			$\nu_{P=O}$			ν_{M-N}	vм–о
No.	Free	Coord.	Shift	Free	Coord.	Shift		
IIa	1614	1575	39	1279	1136	143	493	433
II _b		1575	39		1117	62	493	430
IIc		1591	23		1220	59	517	414
\mathbf{H}_{d}		1591	23		1222	57	519	414
IIe		1589	25		1249	30	519	438
\mathbf{II}_{f}		1591	23		1194	85	503	430
\mathbf{II}_{g}	1673	1592	81	1220	1204	16	518	480
\mathbf{H}_{h}		1615	58		1206	14	505	477
\mathbf{II}_{i}		1589	84		1218	2	505	448
IIj		1595	78		1205	15	505	446
\mathbf{H}_{k}		1638	35		1204	16	518	414
\mathbf{II}_{l}		1591	82		1200	20	502	430
III _a	1614	1574	40	1279	1134	145	565	436
III _b		1589	25		1219	60	544	438
III _c		1575	39		1139	140	564	438
\mathbf{III}_{d}		1565	49		1219	60	544	414
III _e	1673	1591	82	1220	1204	16	545	415
$\mathbf{III}_{\mathrm{f}}$		1590	83		1203	17	547	416
III_{g}		1589	84		1204	16	521	417
III _h		1638	35		1205	15	505	417
\mathbf{III}_{i}		1636	37		1204	16	505	416
\mathbf{III}_{j}		1591	82		1202	18	527	419

procedure involved the titration of 25 ml of 1×10^{-3} M of metal ion solution with increasing volume of 1×10^{-3} M of ligand solution with continuous magnetic stirring. The conductivity values were corrected for the effect of dilution during the titration then were plotted versus the milliliters of reagent added and the least square equation is applied [32]. The resulting curves are smooth straight lines for all the points and the well defined breaks are coincident with the stoichometric ratio of complexes formed in solution and the results are in a good agreement with 1:1 and 2:1 molar ratio suggested for these complexes. The low molar conductance value of the isolated complexes measured in DMF solution at room temperature suggest their nonelectrolytic

Table 8

 $^1\mbox{H-NMR}$ spectra data of diamagnetism phosphate Schiff base metal complexes

Compd. No.	Chemical shifts δ in ppm				
	Ar	-OCH ₃			
II _b	7.1–7.3	_			
IIe	7–7.4	-			
II _h	7.1–7.4	3.9			
IIk	7–7.3	3.8			
III _a	7.1–7.3	-			
III _f	7–7.4	3.8			
III _j	7–7.3	3.3			

nature [33], accordingly the halide ions or nitrate group contribute to the coordination sphere in the complexes under investigation except the Fe^{3+} complex compound III_i which its value corresponding to 1:1 electrolyte [28]. Moreover, the composition of metal complexes was determined using spectroscopic studies as the molar ratio method [34]. Cu^{2+} complexes were chosen as example of metal complexes under investigation. A series of 2 ml solution was prepared in which the Cu²⁺ ion concentration was kept constant at 1×10^{-3} M while that of the ligand was regularly varied from 0.2×10^{-3} to 2.2×10^{-3} M in ethanol using the same concentration of the ligand present in the examined solution as a blank. A plot of the absorbance as a function of molar ratio of [lig.]/[Cu²⁺], one obtains straight lines, each two interesting at a certain ratio indicating the formation of 1:1 and 1:2 metal ligand species. This is an agreement with all above results.

3.4. Magnetic susceptibility and electronic spectra measurements

A comparison of the electronic spectra of the free ligands with those of the corresponding metal complexes show some shift were detected, this can be considered as evidence for the complex formation, the data were collected in Table 9.

Additionally the solid reflectance spectra of metal complexes show different bands at different wavelengths each one is corresponding to certain transition which suggests the geometry of the complex compounds. Table 10 show the different assignment of the complex compounds.

The magnetic moment values of Mn^{2+} complexes under study are found to be 5.16–6.03 B.M. The reflectance data of Mn^{2+} complexes \mathbf{II}_d and \mathbf{II}_j show the observed bands at 12150–19305 cm⁻¹ attributable to ${}^{6}A_1 \rightarrow {}^{4}T_1$, ${}^{6}A_1 \rightarrow {}^{4}T_2$ (G) and ${}^{6}A_1 \rightarrow {}^{4}E$ transition, respectively suggest a tetrahedral stereochemistry for these complexes [35]. While, for compounds \mathbf{III}_c and \mathbf{III}_h , the observed bands at 12165–19569 cm⁻¹ due to the transition ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$, ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ (G) and ${}^{6}A_{1g} \rightarrow {}^{4}E_g$ suggest high spin octahedral geometry around the metal ion [36–38]. The magnetic moment values of Fe³⁺ complexes \mathbf{II}_f , \mathbf{II}_l and \mathbf{III}_j are found to be 5.82–5.95 B.M. indicating it to be high-spin type paramagnetic, it lies within the octahedral range which

Table 9								
The UV-vis,	spectra	data o	f the	phosphate	Schiff	base	metal	complexes

Compd. No.	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	Compd. No.	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
IIa	266	294	II	266	_
II _b	267	294	IIi	266	293
II _c	263	-	\mathbf{H}_{k}	267	293
II _d	267	294	\mathbf{II}_{l}	262	-
IIe	261	294	III _a	269	297
\mathbf{H}_{f}	261	-	III _b		247
IIg	269	293	$\mathbf{III}_{\mathrm{f}}$	269	293
II _h	263	293			

Table 10 Significant solid reflectance data of Schiff base phosphate metal complexes

Complex compound		Peak position Assignment (cm ⁻¹)	
II _d	C ₂₅ H ₂₀ NPO ₃ Cl ₂ Mn	12 150 17 528 19 305	
II _f	C ₂₅ H ₂₂ NPO ₄ Cl ₃ Fe	12 845 16 051 17 559 19 685	
II _i	C ₂₆ H ₂₂ NPO ₄ Cl ₂ Cu	12 128 15 987 19 361	${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ Charge transfer
IIj	C ₂₆ H ₂₂ NPO ₄ Cl ₂ Mn	12 845 17 730 19 305	
\mathbf{II}_{l}	C ₂₆ H ₂₄ NPO ₅ Cl ₃ Fe	12 903 15 974 17 550 19 627	${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$ ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g} (G)$ ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}$ ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g} (D)$
III _b	$C_{50}H_{40}N_2P_2O_6\ Cl_2\ Cu$	12 812 15 974 19 550	${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ Charge transfer
III _c	$C_{50}H_{40}N_2P_2O_6\ Cl_2\ Mn$	12 224 14 577 18 814	
III _g	$C_{52}H_{44}N_2P_2O_8\ Cl_2\ Cu$	12 453 15 060 19 569	${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ Charge transfer
$\mathbf{III}_{\mathrm{h}}$	$C_{52}H_{44}N_2P_2O_8\ Cl_2\ Mn$	12 165 12 437 19 569	
III _j	$C_{52}H_{44}N_2P_2O_8\ Cl_3\ Fe$	12 642 16 012 17 543 19 474	

very close to spin only value of 5.90 B.M. as the ground term is ${}^{6}A_{1g}$ and thus supports octahedral stereochemistry its reflectance spectra shows weak bands and are of low intensity in the region 12 642–19 685 cm⁻¹ may be assigned to transition ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$, ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ (G), ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}$ and ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ (D) transition [27,33,38]. The magnetic moments of Cu²⁺ complexes general range from 1.80–2.03 B.M. No absorption band is observed below 10 000 cm⁻¹ in any complex under study which rules out the possibility of tetrahedral geometry [33,39]. The electronic spectrum for Cu^{2+} complex II_i exhibits three absorption bands from 12 128–19 361 cm⁻¹ due to the transition.

 ${}^{2}B_{1} \rightarrow {}^{2}B_{2}$, ${}^{2}B_{1} \rightarrow {}^{2}E$ and charge transfer, respectively corresponding to square-planar configuration [33,39]. Additionally, the electronic spectrum for Cu²⁺ complexes III_{b} and III_{g} show the absorption bands in the region 12 453–19 569 cm⁻¹ due to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$, ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ and charge transfer transition suggesting a distorted octahedral geometry for these compounds [40]. Zn²⁺, Hg²⁺ and Cd²⁺ complexes are diamagnetic as expected for d¹⁰ system, their complexes are four- as well as six-coordinated as inferred from elemental analysis and spectral data.

4. Conclusion

On the bases of the presented results we suggest that the phosphate Schiff-base ligand coordinate to metal ions through the N,O system to give octahedral Fe^{3+} , square-planar and distorted octahedral Cu^{2+} , tetrahedral and octahedral Mn^{2+} and octahedral Cd^{2+} , Zn^{2+} and Hg^{2+} environment around the metal ion anchor depending on the molar ratio of metal to ligand in the reaction and hence the structure of phosphate Schiff base metal ions is given in Fig. 2.

4.1. Evaluation of biological activity

The question about the involvement of metal ligand complexes in medical treatment are of special interest. To assess the biological potential of the synthesized compounds, the phosphate Schiff base ligands and their metal complexes were tested against the selected bacteria and fungi. The antimicrobial data were collected in Tables 4 and 5. The synthesized compounds were found to be possess remarkable bactericidal and fungicidal properties, it is however interesting that the biological activity gets enhanced on undergoing complexation with the metal ions.

From structure point of view of the prepared compounds with their effects on microbial tested, it is clear that formation of the chelate derivatives in 1:2 molar ratio (M:L) sometimes increase the biological activity as appeared from the Mn^{2+} complexes II_d and III_c and Fe^{3+} complexes II_1 and III_j . So the enhanced activities of the metal complex derivatives compared to the free ligands may be due to the increase in the number of phosphate group around the central metal atom arising from chelation in 1:2 molar ratio (M:L) and hence, the central metal atom was not only the responsible for biological activity because some metal complexes are enhanced the activity and other reduced this activity with respect to the parent ligands.

Finally, to complete the evaluation of biological activity of the synthesized compounds, some comparison with the known antibiotic were performed and the data are collected in Table 6. This table shows that the effect of Hg^{2+} complex II_a against gram positive bacteria is greater than the



Fig. 2. The structure formula of phosphate Schiff base metal complexes.

effect of all tabled antibiotics. The effect of free ligands $(I_{a,b})$ or the chelate derivatives containing Zn^{2+} as central metal atom toward all tested bacteria is equal to the effect of antibiotic 'cefobid' that is resistance only. The antibiotic 'Erythromycin' has resistance effect only on gram negative bacteria, while the effect of some phosphate metal complexes are more and more.

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