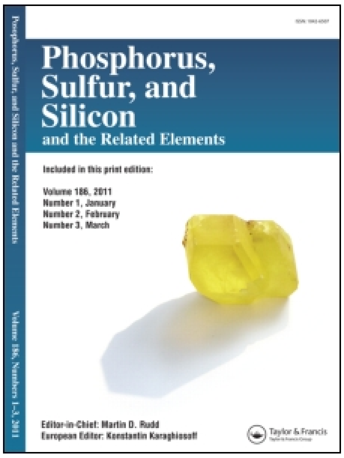

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Preparation and Biological Activity of Some Novel Tetrachlorocyclodiphosph (V) Azane Pyridazine Derivatives and Its Metal Complexes

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Preparation and Biological Activity of Some Novel Tetrachlorocyclodiphosph (V) Azane Pyridazine Derivatives and Its Metal Complexes

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1,3 - diphenyl-2,2,4,4-tetrachloro-2,4-bis(4-Cyano-5,6-dimethyl-py-ridazin-3(2H)-one) cyclodiphosph(V)azane ***(III)***, *reacts with stoichiometric amounts of transition metal salts such as Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and* UO_2*(II) to afford colored complexes in a moderate to high yield. The complexes have been investigated in solution by the spectrophotometric molar ratio and conductometeric methods. The formula of the isolated complexes was suggested based on elemental analyses, IR, molar conductance, UV-Vis,* ^1H *NMR, mass spectra, solid reflectance, and magnetic susceptibility measurements. From the elemental analyses data, 1: 2 (III : M) ratio is suggested and the complexes are found to have the general formula* $[(MX_n)_2(III)(H_2O)_m].yX$ *where M = Mn(II) (X =* $OCOCH_3$*, n = 2, m = 4, y=0), Fe(III) (X = Cl, n = 2, m = 2, y=2), Fe(II) (X =* SO_4*, n = 1, m = 2, y=0), Co(II) (X =* $OCOCH_3$*, n = 2, m = 4, y=0), Ni(II) (X =* $OCOCH_3$*, n = 2, m = 4, y=0), Cu(II) (X =* $OCOCH_3$*, n = 2, m = 4, y=0), Zn(II) (X =* $OCOCH_3$*, n = 2, m = 4, y=0), Cd(II) (X = Cl, n = 2, m = 4, y=0), and* UO_2*(II) (X =* NO_3*, n = 1, m = 0, y=2). The IR and* ^1H *NMR spectral data revealed that III behaves as a neutral bidentate ligand coordinated to the metal ions through oxygen (O) and nitrogen N atoms. The UV-Vis, solid reflectance, and magnetic-moment data have shown that the ligands are coordinated to the metal ions in an octahedral manner. The molar conductance data show that the complexes are nonelectrolytes while the Fe(III) and* UO_2*(II) complexes are 1:2 electrolytes. The in vitro–biological activity of some newly synthesized compounds against gram-positive and gram-negative bacteria was studied.*

Keywords Cyclodiphosph(V)azane; electronic; infrared (IR); metal complexes; magnetic moment

INTRODUCTION

Hetero-functional ligands containing soft and hard donor sites have attracted considerable attention as they are expected to generate

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transition metal complexes, which are efficient for various catalytic transformations.[1–4] Transition metal complexes bearing P, S-donor ligands have been used as catalysts for hydroformylation[2,3] and hydrogenation[4]reactions. Heterofunctional diphosphazanes of the type X_2 PN(R)P(E)X_2 containing phosphorus and other donor atoms such as sulfur, oxygen or nitrogen would display interesting coordination chemistry.[5–8] Phosphazanes are an established class of P–N compounds and are known for their stability and ease of synthesis.[9–11] The nature of the highly polar P–N bond with P–and N-donor sites makes a compound of kind versatile in both coordination and organometallic chemistry.[12–15] Although a few phosph(V)azanes have been used as ligands for transition elements, their coordination chemistry is so far largely unexplored.[12,13] In particular, the interaction between cobalt, nickel, and copper atoms and P-containing ligands is not well established.[16] The aim of the present work is to prepare cyclodiphosph(V)azanes derivatives by the reaction of hexachlorocyclodiphosph(V)azanes **(I)**[17,18] with nucleophilic reagents such as 4-Cyano-5, 6-dimethylpyridazin-3(2H)-one (**II**),[19] and the complexation behavior of one of these derivatives with some transition metals was studied as well as comparing the biological activity of these compounds towards different microoganisms.

RESULTS AND DISCUSSION

The Ligand

The ligand (Figure 1) was found to be soluble in $CHCl_3$, acetone, ethanol, THF, methanol, DMSO, DMF, acetonitrile, ethyl acetate, insoluble in diethyl ether and water, and slightly soluble in benzene and*n*-hexane. The formula of the ligand (L) was elucidated by elemental analyses (Table I), IR, electronic, ^{1}H and ^{31}P NMR techniques.

IR Spectra

The assignments of the important bands of the free ligand are given in Table II. The spectra reveal the characteristic bands of the ν(P-O-C) stretching vibrations of the ligand at 1200, 1102, 1050, and 926 cm^{-1}, which is similar to those assigned by Seiceira[20] and Nakamoto.[21] The band observed at 2218 cm^{-1} is ascribed to the ν(C≡N) stretching vibration which appeared at 2197 cm^{-1}in compound (II).[19] The shift of this band to higher frequency in the ligand is considered as an evidence for the ligand formation. The ν(P-Cl) stretching vibration is observed at

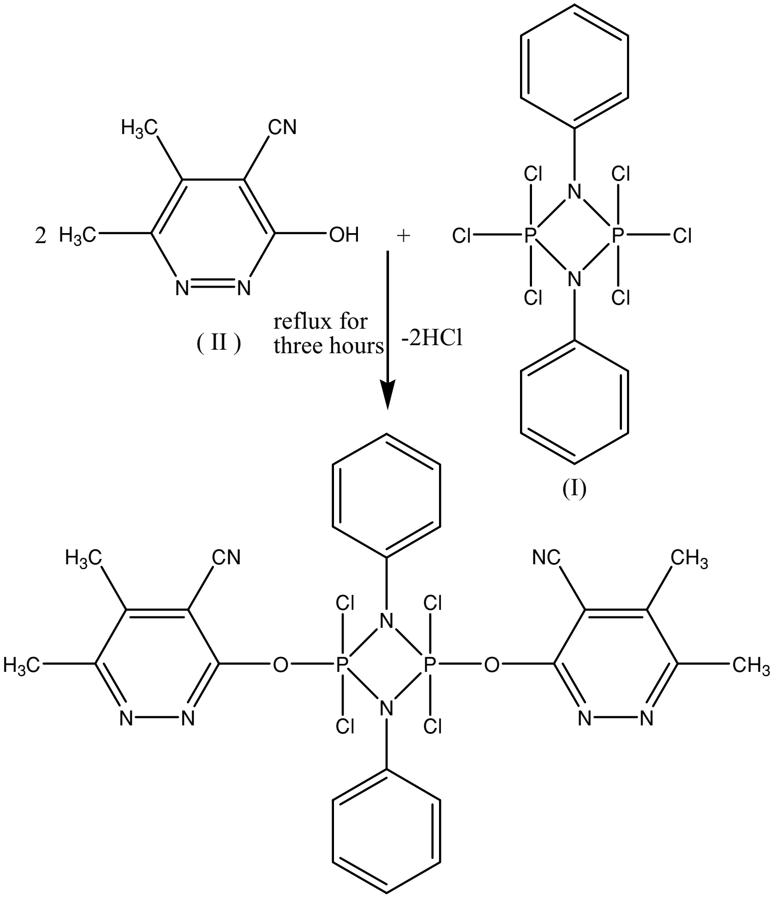


FIGURE 1 Formula of ligand (III): 1,3-diphenyl-2,2,4,4-tetrachloro-2,4-bis(4-Cyano-5, 6-dimethylpyridazin-3(2H)-one) cyclodiphosph(V)azane.

490 cm^{-1}.[22] The band at 1221 cm^{-1} was assigned to the ν(P-N) stretching vibration.[22]

Electronic Spectra

The fact that the expected band at 269 nm,[22,23] characteristic for the delocalization of the nonbonding electrons on the nitrogen atoms within the phosphazo ring of the dimeric formula was observed in the spectrum of ligand **(III)**, suggested the presence of the phosphazo ring. The bathochromically shifted band observed at 288 nm for the ligand (III)

TABLE I Elemental Analyses, Yields, Colors, and Melting Points of Ligand (III) and Its Corresponding Metal Complexes

Compd. No	Mol. Formula (M. wt.) [M.p. °C]	(Yield %) Color	Elemental analyses Found (Calc.), %					Λ_m (Ω^{-1} mo^{-1} cm^2)
			C	H	N	P	M	
III	$C_{26}H_{22}Cl_4N_8P_2O_2$ (682.26) [192]	(82.38) White	45.71 (45.73)	3.23 (3.24)	16.37 (16.42)	9.04 (9.08)	—	—
IV$_a$	$C_{34}H_{42}Cl_4Mn_2N_8O_{14}P_2$ (1100.38) [265]	(78.24) Yellow	37.04 (37.11)	3.81 (3.85)	10.08 (10.18)	5.53 (5.63)	10.00 (9.99)	17.25
IV$_b$	$C_{26}H_{30}Cl_{10}Fe_2N_8O_6P_2$ (1078.73) [213]	(64.31) Brown	28.36 (28.95)	2.74 (2.80)	10.28 (10.39)	5.73 (5.74)	10.35 (10.35)	130.32
IV$_c$	$C_{28}H_{36}Cl_4Fe_2N_8O_{14}P_2$ S_2 (1088.21) [>300]	(86.05) Brown	30.15 (30.90)	3.26 (3.33)	10.08 (10.30)	5.67 (5.69)	10.28 (10.26)	17.85
IV$_d$	$C_{34}H_{42}Cl_4Co_2N_8O_{14}P_2$ (1108.37) [>300]	(81.69) Rose	36.81 (36.84)	3.76 (3.82)	10.10 (10.11)	5.59 (5.59)	10.64 (10.63)	19.28
IV$_e$	$C_{34}H_{42}Cl_4N_8Ni_2O_{14}P_2$ (1107.89) [>300]	(80.12) Green	36.85 (36.86)	3.76 (3.82)	10.02 (10.11)	5.50 (5.59)	10.41 (10.60)	20.15
IV$_f$	$C_{34}H_{42}Cl_4Cu_2N_8O_{14}P_2$ (1117.59) [>300]	(87.67) Green	36.52 (36.54)	3.71 (3.79)	10.01 (10.03)	5.50 (5.54)	11.26 (11.37)	17.76
IV$_g$	$C_{34}H_{42}Cl_4N_8O_{14}P_2Zn_2$ (1121.28) [>300]	(68.48) Yellow	36.52 (36.42)	3.63 (3.78)	9.94 (9.99)	5.51 (5.52)	11.54 (11.66)	18.57
IV$_h$	$C_{26}H_{30}Cd_2Cl_8N_8O_6P_2$ (1120.96) [>300]	(74.16) Yellow	27.68 (27.86)	2.67 (2.70)	10.00 (10.00)	5.52 (5.53)	20.00 (20.06)	18.26
IV$_i$	$C_{26}H_{26}Cl_4N_{12}O_{20}P_2U_2$ (1506.37) [>300]	(73.26) Yellow	20.47 (20.73)	1.72 (1.74)	11.05 (11.16)	4.06 (4.11)	—	135.21

TABLE II IR Spectra of Cyclodiphosph(V)azane Complexes (IVa–i)

No.	νOH	νP—O—C	νC≡N	νP—Cl	νPNP	νP—N	νM—N	νM—O
III$_a$	—	1272(m), 1225(m), 1092(m), 1003(m)	2218(s)	494(m)	850(m)	1225(m)	—	—
IV$_a$	3348(br)	1225(m), 1086(m), 1008(m), 939(m)	2207(s)	480(m)	822(m)	1225(m)	211(m)	530(m)
IV$_b$	3334(br)	1243(m), 1003(m), 1015(m), 929(m)	2205(s)	510(m)	922(m)	1215(w)	216(m)	535(m)
IV$_c$	3330(br)	1223(m), 1069(m), 1006(m), 941(m)	2206(s)	535(m)	941(m)	1223(m)	211(m)	520(m)
IV$_d$	3338(br)	1224(m), 1077(m), 1005(m), 939(m)	2204(s)	532(m)	823(m)	1224(m)	211(m)	533(m)
IV$_e$	3358(m)	1225(m), 1067(m), 1001(m), 960(m)	2206(s)	523(m)	989(m)	1225(m)	212(m)	525(m)
IV$_f$	3340(br)	1224(m), 1067(m), 1008(m), 938(m)	2206(s)	509(m)	937(m)	1217(m)	211(m)	528(m)
IV$_g$	3324(br)	1224(m), 1077(m), 1005(m), 939(m)	2205(s)	545(m)	909(m)	1219(m)	214(m)	530(m)
IV$_h$	3347(br)	1224(m), 1067(m), 1008(m), 924(m)	2205(s)	540(m)	822(m)	1224(m)	213(m)	534(m)
IV$_i$	3336(br)	1226(m), 1064(m), 1004(m), 955(m)	2207(s)	473(m)	932(m)	1226(m)	213(m)	520(m)

relative to that of the dimer **(I)** is explained to be due to the replacement for one chlorine atom of each phosphorus atom by the 4-Cyano-5, 6-dimethylpyridazin-3(2H)-one **(II)**. The new band observed at 349 nm is attributed to the n-π^* transition of attached compound **(II)**, which is absent in the corresponding dimer **(I)**, and this is considered as an evidence for the ligand formation.

Mass Spectrum

The mass spectrum of the ligand **(III)** shows the fragmentation pattern in Figure 2. The spectrum showed the molecular ion m/e peak at 679 (abundance 0.30%) corresponding to molecular weight of the ligand (III). The base peak was observed in the spectrum at 64.

^{1}H-NMR Spectrum

The ^{1}H-NMR spectrum of the ligand (III) showed the following characteristic proton signals at: $\delta = 6.80$–7.90 ppm is assigned for aromatic protons Ar-H and two sharp singlet signal bands at $\delta = 2.50$ and 2.80 ppm corresponding to the protons of CH_3 group.

Spectrophotometric Measurements of Solution Stoichiometry

The absorption spectra of the Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and UO_2(II) complexes IV_{a-i} are shown in Figure 3. The diagrams in Figure 4, consist of two linear portions intersecting at 1:2 [ligand]/[M^{2+} or M^{3+}], where M^{3+} is Fe(III) and M^{2+} corresponding to Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and UO_2(II), respectively, indicating the formation of 2M: 1L species. This is in agreement with the elemental analyses and conductometric analyses data.[22]

Electronic Spectra and Magnetic Properties

The UV—Vis spectra of complexes in DMF solution showed absorption bands between 269 nm and 288 nm, which is characteristic of phosphazo four-membered rings.[24,25] However, the absorptions were red shifted with respect to the ligands depending on the types of metal ions present. The spectra of the Fe(III), Fe(II), and Cu(II) complexes further display a band in the range 360–445 nm, which might be assigned to charge transfer transition (most probably L→M CT).[26] For the Co(II) complex, however, a d–d bands are observed at 600 nm and 675 nm which may attributed to the transitions $^4T_1g\ (F) \rightarrow {}^4T_2g\ (P)$

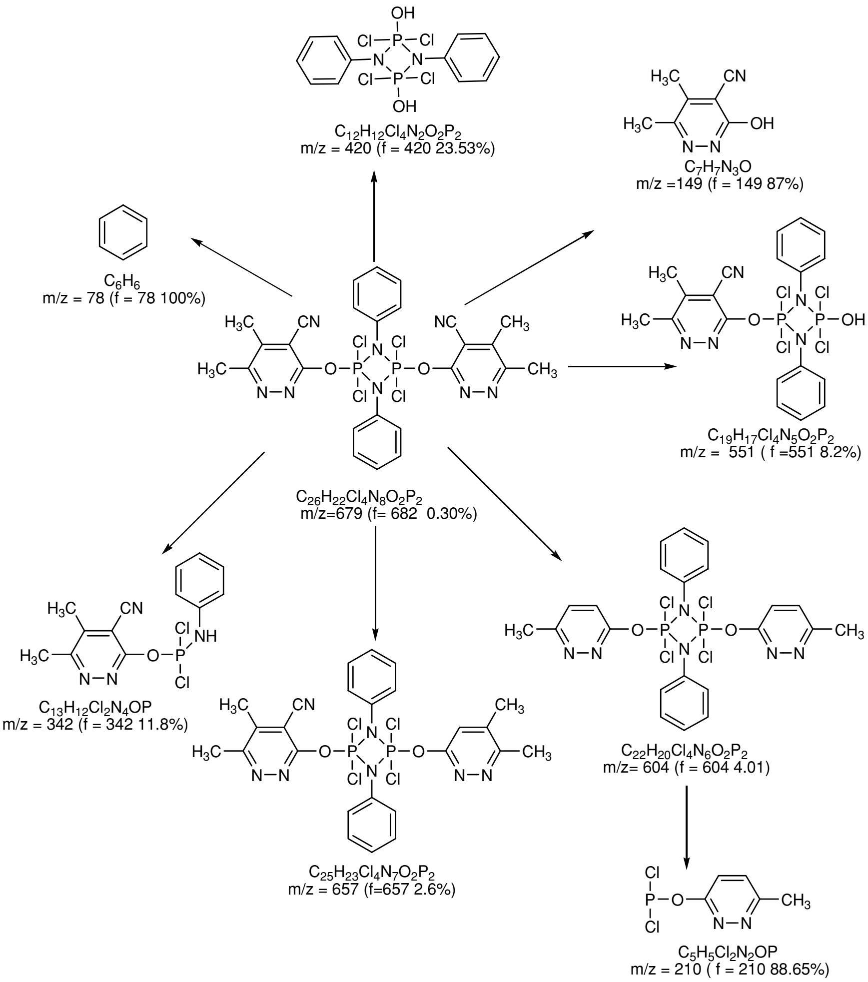


FIGURE 2 Possible fragmentation pathways of III ligand.

and ^4T_1g (*F*) →^4A_2g (*F*), respectively, typical of octahedral structure around Co(II) ion.[26]

The diffuse reflectance spectra of the complexes show bands at 240–250 nm, which are associated with interligand transitions.

The diffuse reflectance spectrum of Mn(II) complex shows three bands at 15,662, 22,235, and 26,432 cm^{-1} assignable to $^4T_{1g} \rightarrow {}^6A_{1g}$, $^4T_{2g}$ (G)→$^6A_{1g}$ and $^4T_{1g}$ (D)→$^6A_{1g}$ transitions, respectively.[27] The magnetic moment value is 5.34 μB. which indicates the presence of Mn(II) complex in octahedral structure.

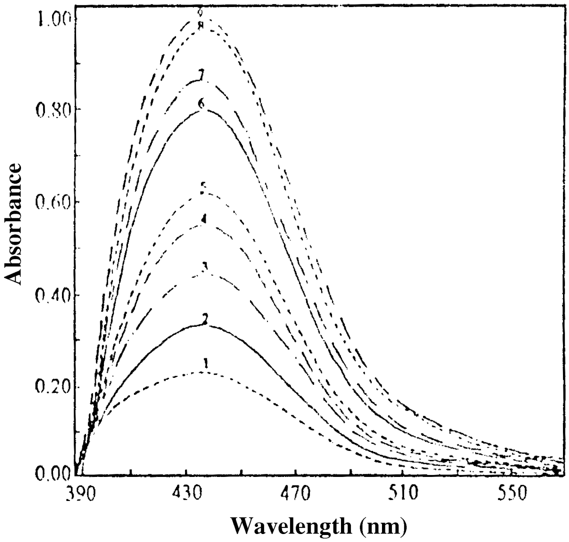


FIGURE 3 Absorption spectra of Cu(II)-III Complex, molar ratio method.

It is observed from the diffuse reflectance spectra of the Fe(III) complexes that they exhibit a band at 21,150–21,196 cm^{-1}, which may be assigned to the $^6A_1g \rightarrow T_2g$ transition in octahedral geometry.[27] The spectra also show spitted bands at 14,937–15,683 and 17,567–18,363 cm^{-1}, which assigned to the $^6A_1g \rightarrow {}^5T_1g$ transition. The observed magnetic moment of the Fe(III) complex is 5.67 μB for III ligand, respectively, which confirm the octahedral geometry.[28] The bands observed at 29,154 and 24,952–26,120 cm^{-1} can be attributed to ligand-to-metal charge transfer band for the Mn(II) and Fe(III) complexes, respectively.[27]

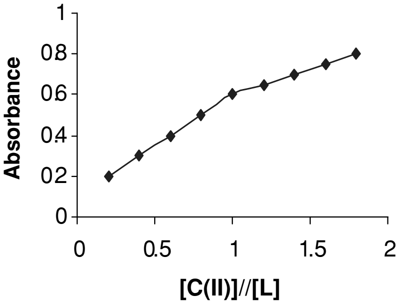


FIGURE 4 Results of molar ratio method for Cu(II) Complex.

The diffuse reflectance spectrum of Fe(II) complex displays two absorption bands at 15,173 cm^{-1} and 22,224 cm^{-1}, which are assigned to $^5T_2g \rightarrow ^5E_g$ transitions.[29]Also, the band at 25,643 cm^{-1} is assigned to L→M charge transfer.[29] The observed magnetic moment of 4.98 B.M. is consistent with an octahedral geometry.[29]

The electronic spectrum of the Co(II) complex displays two bands at 15,314 cm^{-1} and 17,480 cm^{-1} assigned to the $^4T_1g \rightarrow ^4T_1g$ (*P*) and $^4T_1g \rightarrow ^4T_2g$ (*F*) transitions, respectively, which arise due to ligand field transition of the pseudo octahedral component of the Co(II) complex. The observed magnetic moment value is $\mu_{\text{eff}} = 5.04$ B.M. at room temperature which confirms the octahedral structure of this cobalt complex.[29] The band observed at 22,623 cm^{-1} refers to L→ M CT band.

The solid reflectance spectrum of the Ni(II) complex shows bands at 23,252, 17,484 and 18,918 cm^{-1}, suggesting the existence of $^3A_2g \rightarrow ^3T_1g$ (*P*), $^3A_2g \rightarrow ^3T_1g$ (*F*) and $^3A_2g \rightarrow ^3T_2g$ transitions, respectively, with an octahedral spatial configuration. The observed magnetic moment of the complex is 2.84 B.M., which confirms the octahedral structure of this complex.[30]

The solid reflectance spectrum of the Cu(II) complex gave a band at 16,800 cm^{-1}, which may be assigned to $^2Eg \rightarrow ^2T_2g$.[31] The observed magnetic moment of the Cu(II) complex is 1.95 B.M., which confirms the octahedral structure of this complex. The band observed at 22,935 cm^{-1} refers to L→MCT band.

The Zn(II) and Cd(II)complexes are diamagnetic as expected and its geometry is most probably octahedral similar to the Mn(II), Fe(III), Fe(II), Co(II), Ni(II), and Cu(II)complexes of the ligand (III).[32]

The electronic spectrum of the yellow UO_2(II) complex **(IV_i)** arises from the electronic transition of metal→ligand charge transfer. This is an allowed transition and produces a broad, intense absorption band at 20618 cm^{-1} for complex **(IV_i)**, tailing into the visible region. This produces the intense yellow color, where the UO_2(II) complexes are diamagnetic as expected.[33]

Mössbauer Measurements

The Mössbauer spectra were measured at room temperature for iron complexes. The spectra revealed the presence of Fe ions in $[(FeCl_2)_2(L)(H_2O)_4]$ and $[FeSO_4)(L)(H_2O)_4]$ in ferric and ferrous state respectively in octahedral coordination.[34] The Mössbauer parameters are listed in Table III and Figure 5.

TABLE III Mössbauer Parameters for Iron Complexes of the III Ligand

Complex	Isomer shift (IS) (mm/s)	Quadrupole splitting (QS) (mm/s)
$[(FeCl_2)_2III(H_2O)_4].2Cl$	0.46	0.74
$[(FeSO_4)_2III(H_2O_4)]$	1.8	4.2

IR Spectra

The most characteristic IR spectral bands of the metal chelates together with those of the free ligand are collected in Table II. The results of IR spectra of the metal complexes show absorption bands of both $\nu_{C\equiv n}$ and ν_{p-o-c} at lower frequencies than those of the free ligand **III**, indicating that the metal ions are coordinated to the nitrogen and oxygen atoms of both C≡N and P-O-C[20,21]groups of the ligand **III**. In all of the metal complexes, there are new medium to weak bands appearing at lower frequencies between 440–480 cm^{-1} and 500–552 cm^{-1}, which were assigned to ν(M–N) and ν(M–O) stretching modes, respectively.[22,30] These stretches were not present in the spectra of the ligand. The appearance of bands at 3340–3444 cm^{-1} and 796–832 cm^{-1} is due to the stretching vibration and out of plane bending of coordinated water molecules in the spectra of the metal complexes.[30]

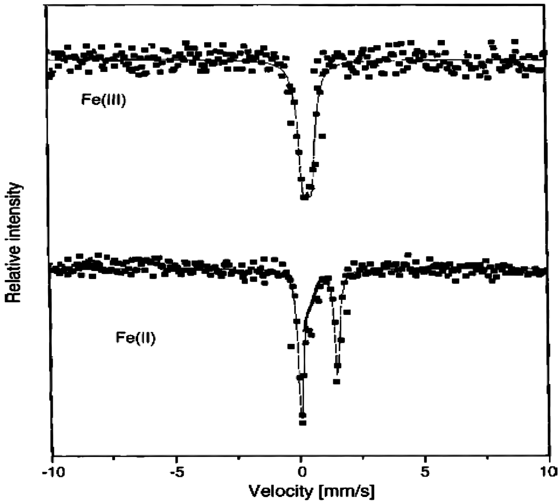


FIGURE 5 Mössbauer spectra of the iron complexes.

The bands observed at 1464–1461 and 1579–1602 cm^{-1} in complexes (IV_a, IV_d-IV_e) were assigned to ν(sym.OCO) and ν(asym. OCO), respectively, which indicated that the acetate groups coordinate as a monodentate to the central metal cation in (IV_a, IV_d-IV_e) complexes respectively.[22]This is supported with the observed characteristic ν(M-O) band.

IR spectrum of the sulfato **(IV_c)** complex of **III** shows bands at 1186, 1045 and lower frequency regions, which indicate bidentate nature of this anion.

The spectra of nitrato complex **(IV_i)** gave additional bands around 1230, 1040 and 870 cm^{-1}, which are consistent with the monodentate nature of this group.[32] Theν(U=O) vibration in the uranyl complex **(IV_i)** is observed as expected as a very strong band at 928 cm^{-1} is a good agreement with those known for many dioxouranium (IV) complexes.[21]

The characteristic bands corresponding to the ν(PNP), ν(P–N) and ν(P–Cl) which were associated with all the investigated complexes are collected in Table II.

Conductometric Titration

In order to follow up the behavior of the ligand III in solution with Co(II), Ni(II), and Cu(II), we investigated these systems using conductometric titration method.

In this method, 25 ml (10^{-4} M) of M(II) or M(III), where M(III) is Fe(III) and M(II) is Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and UO_2(II) solution in absolute ethanol was titrated with (10^{-3} M) of III solution absolute ethanol at room temperature 25°Cand represented in Figure 6. The curves were plotted between the conductance of the solution and the volume of ligand added. The results show that the break in the curve occurred when the 2:1 (M: L) species are formed in solution. The conductance of the reaction mixture was increase continuously with increasing the amount of the ligand III added in all the complexes under investigation. The reason for increase in conductivity after 2:1 (M: L) complex forms may be due to the presence of the ligand in ionic form in the medium (ethanol) which arises the conductivity.[22,35,36]

Molar Conductance Data

The molar conductance (Table I) of Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO_2(II) complexes were measured in DMF solvent. It is expected that the complexes are neutral where the nitrate groups are coordinated to the metal ions, and give low value in conductivity. The measured values were 130 and 135Ω^{-1} cm^2 mol^{-1},

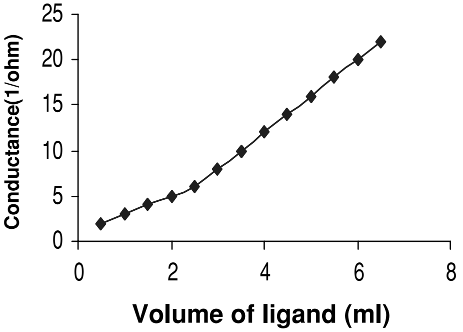


FIGURE 6 Conductometric titrations for Cu(II) complex.

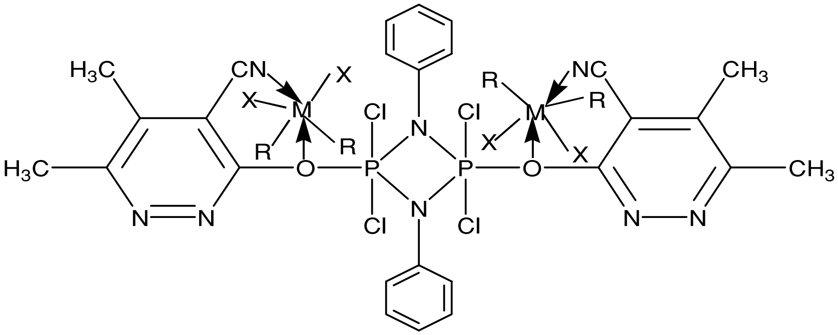
for complexes Fe(III) and UO_2(II), respectively, which are higher than the expected value. This may be due to the fact that the DMF solvent replaced the Cl^- and NO^{3-} anions in the complexes, which results in the 1:2 electrolytes due to the uncoordinated chloride or nitrate ion.[37]

Structural Interpretation

From all of the above observations, the formulas of these complexes may be interpreted in accordance with complexes of ligands with a similar distribution of sites such coordination cyclodiphosph(V)azanes of thiophene[35] and pyrazole.[36] The structural information from these complexes is in agreement with the data reported in this article based on the IR, molar conductance, ^{1}H NMR, UV-Vis, mass, solid reflectance, thermal analysis, and magnetic-moment measurements. Consequently, the structures proposed are based on octahedral geometric structures. III ligand always coordinates via the nitrogen (C≡N) and the oxygen (P-O-C) forming two-binding chelating sites. The octahedral geometry is brought by the two anions (CH_3COO^-, Cl^- or NO_3^-) and two coordinated water molecules. According to the above data and similar to those proposed previously, the formulas of the complexes are shown in Figures 7–10.

Bioactivity

The in vitro antimicrobial activity of the newly prepared compounds **III**, **(IV_a–IV_i)** against two groups of microorganisms, including three strains of gram-positive bacteria and three strains of gram-negative bacteria, was investigated in comparison with ampicillin. The ten tested compounds were capable of inhibiting the growth of both gram-positive and gram-negative bacteria, and they could be considered as



No.	M	R	X
IVa	Mn	H_2O	OAc
IVd	Co	H_2O	OAc
IVe	Ni	H_2O	OAc
IVf	Cu	H_2O	OAc
IVg	Zn	H_2O	OAc
IVh	Cd	H_2O	Cl

FIGURE 7 The proposed formula of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes of an octahedral structure of the ligand III.

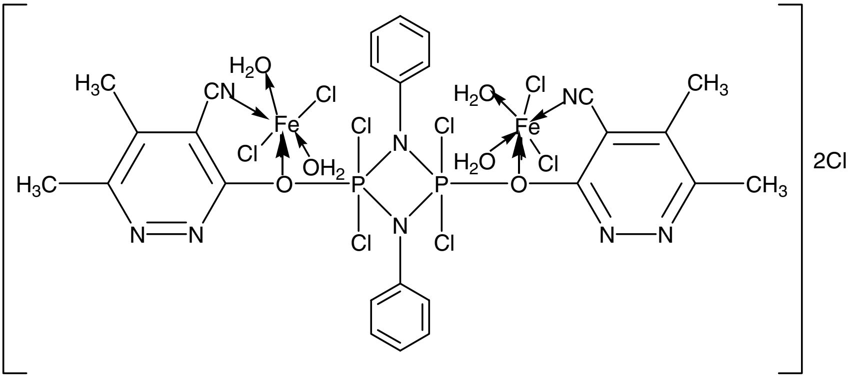


FIGURE 8 The proposed formula of Fe(III) complex **IVb** of an octahedral structure of the ligand III.

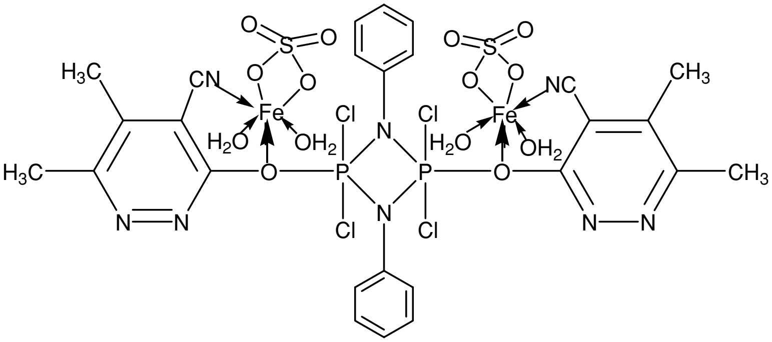


FIGURE 9 The proposed formula of Fe(II) complex **IVc** of an octahedral structure of the ligand III.

promising antimicrobial agents. Table IV shows the results of the bioassay. In conclusion, we have reported here the importance of the tested compounds as antibacterial agents. Further studies should be made to elucidate their mechanism of action.

EXPERIMENTAL

Melting points were recorded on Griffen melting point apparatus, England, and are uncorrected. Elemental analyses of C, H, and N were carried out at the Microanalytical Research Center, Faculty of Science, Cairo University and phosphorus was determined gravimetrically as phosphoammonium molybdate using R. Voy method.[38] The mid-infrared and the Ultraviolet measurements have been carried out at

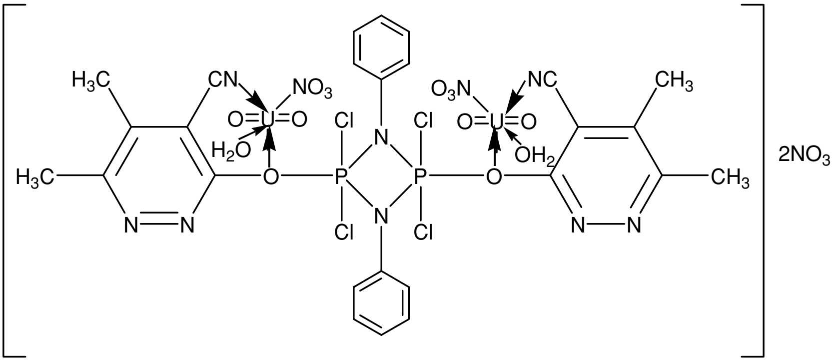


FIGURE 10 The proposed formula of UO_2(II) complex **IVi** of an octahedral of the ligand III.

the chemistry Department, Faculty of Science, and Al-Azhar University. The infrared spectra are recorded on Shimadzu-440 infrared spectrophotometer using KBr technique. Ultraviolet spectra were recorded on PerkinElmer Lambda-3B Ultraviolet-Visible spectrophotometer-meter using dimethylformamide as a solvent.^{1}H NMR spectra were measured on Varian Em-360-60 MHz spectrophotometer using TMS as internal standard, the chemical shift (δ) is in ppm. The mass spectra were performed by Shimadzu-Ge-Ms-QP 100EX using the direct inlet system, Cairo University. Metal contents were determined complexometerically using standard EDTA titration.[39] Mössbauer measurements were performed in the Physics Department, Faculty of Science, Al-Azhar University, at room temperature in a transmission geometry employing ^{57}Co as a radioactive source. The spectra were analyzed using a computer program based on Lorentzian distribution. The isomer shifts were expressed relative to a metallic iron absorber.

Preparation of 4-Cyano-5, 6-dimethylpyridazin-3(2H)-one (II)

4-Cyano-5, 6-dimethylpyridazin-3(2H)-one**(II)** has been prepared and purified using the method described elsewhere.[19]

Preparation of 1,3-diphenyl-2,2,2,4,4,4,-hexachlorocyclodiphosph (V)azane (I)

Hexachlorocyclodiphosph(V)azane derivatives **(I)** have been prepared and purified using the method previously.[17,18,22,35,36]

TABLE IV Antimicrobial Potentialities of the Tested Compounds Expressed as Size (mm/mg Sample) of Inhibition Zone Compounds

	Compounds									
Test Organisms	III$_a$	IV$_a$	IV$_b$	IV$_c$	IV$_d$	IV$_e$	IV$_f$	IV$_g$	IV$_h$	IV$_i$
Bacillus subtilis	16	12	13	15	16	14	15	15	12	12
Staphylococcus aureus	16	12	12	13	13	14	14	14	13	11
Streptococcus faeculis	15	11	13	14	12	14	13	14	13	11
Escherichia coli	15	12	13	16	12	13	15	13	12	12
Neisseria genorrhes	16	12	12	15	13	12	14	14	12	12
Pseudomonae aeruginosa	15	13	13	14	12	11	14	16	13	12
Ampicillin	+	+	+	+	+	+	+	+	+	+

Preparation of 1,3-diphenyl-2,2,4,4-tetrachloro-2,4-bis (4-Cya-no-5, 6-dimethylpyridazin-3(2H)-one) cyclodiphosph(V)azane (III)

The solid of 4-Cyano-5, 6-dimethylpyridazin-3(2H)-one**(II)** (0.01 mmol) was added in small portions to a well stirred solution of the hexachlorocyclodiphosph(V)azane **(I)** (0.005 mmol) in 100 ml acetonitrile over a half-hour period. After the complete addition, the reaction mixture was heated under reflux for 2 h with continuous stirring. After completion of the reaction (HCl gas ceased to evolve), the reaction mixture was filtered, while hot and the filtrate was left to cool at room temperature. The obtained solid was filtered washed several times with acetonitril, diethylether, and dried in vacuo to give the corresponding cyclodiphosph(V)azane pyridazine derivatives **III** the data obtained are listed in Table I.

Preparation of Pyridazine-cyclodiphosph(V)azane Complexes (IVa-i)

A solution of the metal salts (0.002 mol) in 50 mL dry ethanol was added dropwise to a solution of pyridazine-cyclodiphosph(V)azane (0.002 mol) in 100 mL absolute ethanol in a 2:1 metal to ligand molar ratio at room temperature with continuous stirring. After complete addition of the metal salt solution, the reaction mixture was heated under reflux for about 2 h under dry conditions. The complexes obtained were washed with dry ethanol then with dry diethyl ether and dried in vacuo. The products obtained give elemental analyses consistent with the proposed formula.

Bioassay: Measurement of Antimicrobial Activity Using the Diffusion Disc Method

A filter-paper sterilized disc saturated with a measured quantity of the sample was placed on a plate containing a solid bacterial medium (nutrient agar broth), which was heavily seeded with the spore suspension of the tested organism. After inoculation, the diameter of the clear zone of inhibition surrounding the sample was taken as a measure of the inhibitory power of the sample against the particular test organism.[40–42]

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