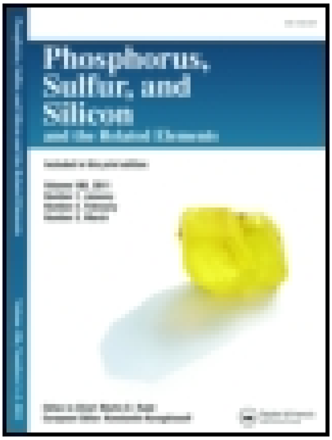

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Spectral and Biological Activity Properties of Some New Aminocyclodiphosph(V)azane Derivatives and Their Complexes

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Spectral and Biological Activity Properties of Some New Aminocyclodiphosph(V)azane Derivatives and Their Complexes

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The ligand aminocyclodiphosph(V)azane derivative (III) and its complexes with Co(II), Ni(II), Cu(II) and Pd(II) ions were prepared and characterized by microanalytical, FTIR, ^{1}H and ^{31}P NMR, UV/Visible, analysis and magnetic moments. The ligand acts in a tetrahedral manner forming 2:1 metal to ligand ratio. Electronic spectra and magnetic susceptibility measurements reveal octahedral geometry for Co(II), Ni(II) and Cu(II) complexes and square planar geometry for Pd(II) complex. The powder XRD studies confirm the amorphous nature of the complexes. The free ligand (III) and its metal complexes have been tested in vitro against Alternarie alternate, Aspergillus flavus, Aspergillus nidulans *and* Aspergillus niger fungi *and* Streptococcus, Staph, Staphylococcus *and* Escherchia coli *bacteria in order to assess their antimicrobial potential. The results indicate that the ligand and its metal complexes possess antimicrobial properties.*

Keywords ^{31}P NMR; aminocyclodiphosph(V)azane; metal complexes

INTRODUCTION

The reaction of hexachlorocyclodiphosph(V)azanes with aromatic and aliphatic amines, active methylene containing compounds, and bifunctional reagents have been investigated in some detail.[1–3] Little is known about the interaction of hexachlorocyclodiphosph(V)azane with aminothiophene derivatives and their metal complexes. In the present work, the interaction of 1,3-di-phenyl-2,2,2,4,4,4-hexachlorocyclodiphos-(V)azane**(I)** with 2-amino-3-cyano-4,5-dimethylthiophene **(II)** and its metal complexes have been reported.

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RESULTS AND DISCUSSION

The yields of the complexes are lower than those of the ligand. The low yields may be due to the steric hindrance around the coordination centre. The ligand and their complexes are soluble in common organic solvents such as DMF, DMSO, and THF. The results of the elemental analyses, given in Table I, are in accord with the composition suggested for the ligand and their metal complexes. The formula of the free ligand was investigated using elemental analyses, IR, UV, ^{1}H, and ^{31}P NMR.

IR Spectra

The assignment of the important bands of the free ligand is given in Table II. The spectra reveal the characteristic bands of the $\nu_{\text{P-NH}}$ stretching vibrations of the ligand at 2606 cm^{-1}, which is similar to those assigned by Abd-Ellah[2] and Pustinger.[4] The band appeared at 3389 cm^{-1} is attributed to the ν_{NH} stretching vibration. The band observed at 2219 cm^{-1} is ascribed to the $\nu_{\text{C}\equiv\text{N}}$ stretching vibration, which appeared at 2198 cm^{-1} in compound (II).[5] The shift of this band to higher frequency in the ligand is considered as an evidence for the ligand formation. The $\nu_{\text{P-Cl}}$ stretching vibration is observed at 490 cm^{-1}.[6,7] The band at 1243 cm^{-1} was assigned to the νP—N stretching vibration.[8,9] Bands appear in the range 1625–1395 cm^{-1} may be attributed to $\nu_{\text{C=C}}$ of the aromatic rings and attached compounds (II).[10] Moreover, the IR spectra showed weak band at 635 cm^{-1} due to the $\nu_{\text{C-S}}$ stretching vibration of thiophene ring. The weak band observed at 3175 cm^{-1} is due to aromatic C—H stretching vibrations.[11]

Electronic Spectra

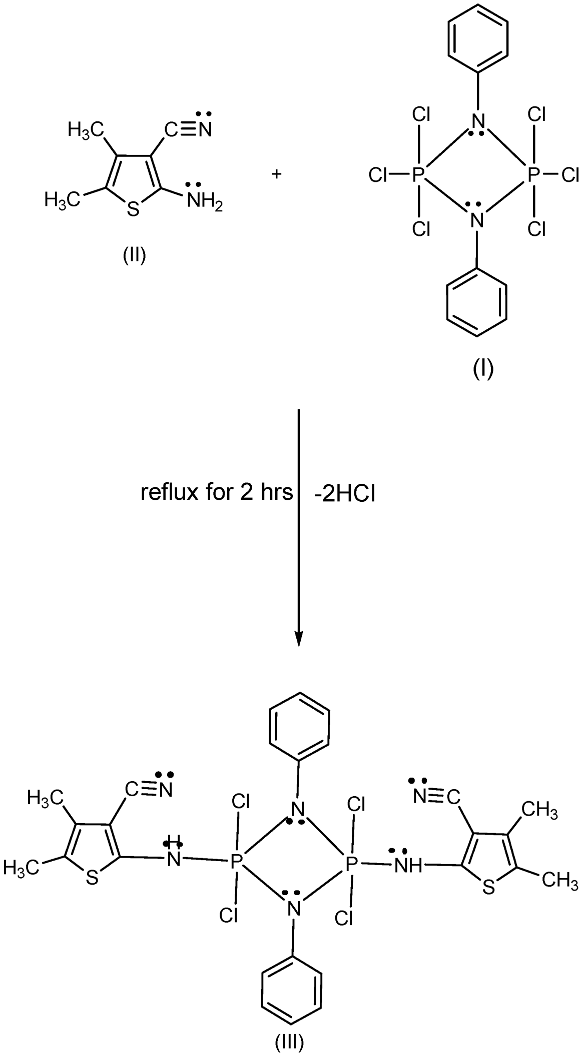
The electronic spectrum of the ligand (III) showed an absorption band at longer wavelength 282 nm than that associated with its dimer (I) at 277 nm.[12] This bathochromic shift could be expected due to the replacement of one chlorine atom of each phosphorus atom of the phosphazo ring of dimer **(I)** by chromophoric group containing conjugated system such as 2-amino-3-cyano-4,5-dimethylthiophene **(II)** Scheme 1. It is worthwhile that the expected band at 275 nm,[25] characteristic for the delocalization of the nonbonding electrons on the nitrogen atoms along the phosphazo ring of the dimeric structure was observed in the spectrum of ligand **(III)** at 282 nm, indicated the presence of the phosphazo ring. Moreover, the new band observed at 355 nm corresponding to n-π^* the transition of attached compound **(II),** was absent in its dimer **(I),** that is considered as an evidence for the ligand formation.

TABLE I Elemental Analyses, Yields, Colors and Melting Points of the Metal Complexes

Compd. no.	Mol. formula (m. wt.)	Color	M.p. °C (Yield%)	Elemental analyses found (calcd.) (%)						Λ_m (Ω^{-1} mol^{-1} cm^2)
				C	H	N	P	S	M	
IVa	$C_{26}H_{24}Cl_4N_6P_2S_2$ (688.4)	Yellow	194 (95.8)	45.87 (45.36)	3.54 (3.51)	12.28 (12.21)	9.00 (9.00)	9.10 (9.32)	—	—
IVa	$C_{36}H_{48}Cl_4Co_2N_6O_8P_2S_2$ (1078.56)	Green	>300 (88.8)	36.15 (40.09)	4.08 (4.49)	7.72 (7.79)	5.74 (5.74)	5.94 (5.95)	10.90 (10.93)	17.42
IVb	$C_{36}H_{48}Cl_4N_6Ni_2O_8P_2S_2$ (1078.08)	Brown	>300 (87.7)	40.09 (40.11)	4.48 (4.49)	7.48 (7.80)	5.73 (5.75)	5.92 (5.95)	10.83 (10.89)	11.86
IVc	$C_{36}H_{48}Cl_4Cu_2N_6O_8P_2S_2$ (1087.78)	Dark brown	>300 (89.6)	39.73 (39.75)	4.42 (4.45)	7.40 (7.73)	5.57 (5.69)	5.87 (5.90)	11.63 (11.68)	16.89
IVd	$C_{26}H_{24}Cl_4N_{10}O_{12}P_2Pd_2S_2$ (1149.26)	Dark brown	>300 (87.6)	27.16 (27.17)	2.10 (2.10)	12.18 (12.19)	5.38 (5.39)	5.58 (5.58)	—	9.86

TABLE II IR Spectra of Ligand and Its Metal Complexes

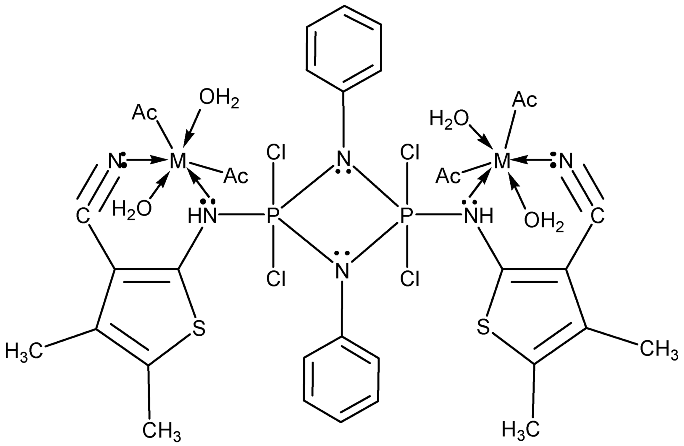
Compd. no.	ν_{NH}	$\nu_{P\text{-}NH}$	$\nu_{\text{disubstituted ring}}$	$\nu_{C\equiv N}$	ν_{OCOCH3}	$\nu_{P\text{-}N}$	$\nu_{P\text{-}Cl}$	$\nu_{M\text{-}N}$	$\nu_{M\text{-}O}$
III	3389 (br)	2606 (w)	780 (m)	2219 (m)	—	1243 (m)	540 (m)	—	—
IVa	3361 (br)	2600 (v.w)	774 (m)	2203 (m)	1470 (m) 1619 (m)	1220 (m)	450 (m)	252 (m)	550 (m)
IVb	3326 (br)	2600 (v.w)	772 (m)	2206 (m)	1488 (m) 1622 (m)	1225 (m)	445 (m)	300 (m)	555 (m)
IVc	3279 (br)	2600 (v.w)	772 (m)	2208 (m)	1563 (m) 1661 (m)	1209 (m)	460 (m)	265 (m)	559 (m)
IVd	3279 (br)	2600 (v.w)	772 (m)	2208 (m)	—	1223 (m)	460 (m)	303 (m)	—



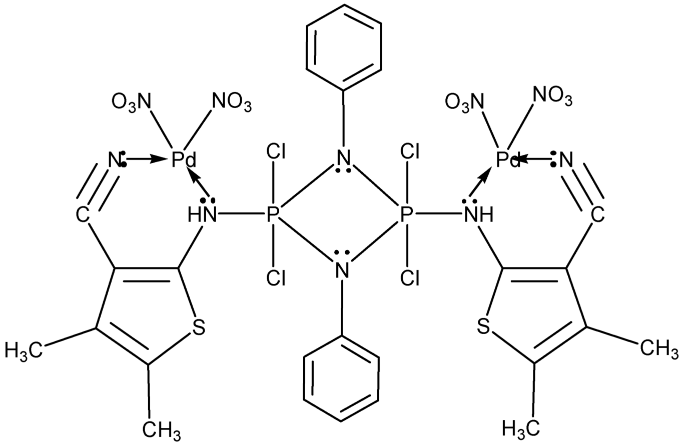
SCHEME 1 Formula of ligand III: 1,3-diphenyl-2,2,4,4-tetrachloro-2,4- bis (2-amino-3-cyano-4,5-dimethylthiophene) cyclodiphosph(V)azane.

^{1}H and ^{31}P NMR Spectra of Ligand(III)

The ^{1}H NMR spectrum of the ligand **(III)** showed characteristic proton signals at $\delta = 7.93$ ppm corresponding to phenyl protons and the signal at $\delta = 10.49$ ppm due to N-H proton, which was disappeared on the addition of D_2O because of the proton exchange. Two sharp singlet



Where M is Co^{2+}, Ni^{2+} or $Cu^{+2}$and Ac = acetate



SCHEME 2 The formula of the four complexes.

signal bands at $\delta = 2.50$ and 2.80 ppm were assigned to the protons of the methyl groups in two different environments. The ^{31}P NMR of the ligand records a signal at $\delta = 25.92$ ppm, which supports the phosphazo ring structure.

Metal Complexes

All the complexes are polycrystalline solids and the elemental analysis results (Table I) agree well with the binuclear structure shown in Scheme 2. The purities of all these compounds were checked by TLC by dissolving the appropriate complex in DMF and using ethyl acetate (80%) – methanol (15%) – acetic acid (5%) as eluant. Only one spot was observed in each case after developing in an iodine chamber, indicating that the compounds were pure.

Conductimetric Titrations

The calculated molar ratio [L]/[M] are plotted against the corrected molar conductance values. The results indicate that the conductance increases with the addition of the metal ion solutions due to the release of the highly conducting hydrogen ions because of chelation. Inspection of the titration curves shows the presence of two distinctive breaks at metal to ligand molar ratios of 2M:1L.[2,3]

Magnetic and Electronic Spectral Studies

On complexation the lower-energy band observed at 345 nm in the spectrum of the free ligand **III**, which was assigned to, is shifted to a red shift, while the other one at 282 nm of the π-π^* transition is slightly shifted to a blue shift.

The magnetic susceptibility measurement at room temperature of the green Co(II) complex **IVa**, gave magnetic moment value μ_{eff} of 5.04 B.M., this high value may be due to orbital contribution corresponding to three unpaired electrons are expected for a week field ligand. The electronic spectra of the Co(II) complex as nujol mulls and/or solution in ethanol table 3 showed. Two Peaks at 705 nm and 554 nm, which may be assigned to $^4T_{1g}(F) \rightarrow {}^4A_{1g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and is consistent with the octahedral geometry.[1,3] The peaks observed at 255 nm, 310 nm and 380–405 nm regions, were assigned to $\pi \rightarrow \pi^*$ and n$\rightarrow \pi^*$ transitions, respectively. Finally, the low value of molar conductance (5.0 Ω^{-1} mol^{-1} cm^2) suggests a non-electrolytic nature of this complex in DMSO. The high melting point of the Co(II) complex (>300°C) suggest the existence of a strong covalent bonding between the Co(II) ion and the ligand under investigation.

The deep brown Ni-complex **IV$_\mathbf{b}$** gives value μ_{eff} 2.92 B.M. that is indicative of two unpaired electrons. The electronic spectrum of the Ni (II) complex **IV$_\mathbf{b}$** shows absorption band at 712 nm which may be investigated to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$, week bands observed on the high and low energy sides of the 712 nm band have been assigned to spin forbidden bands.[1,3] The value of molar conductance in DMSO (6.0 Ω^{-1} mol^{-1} cm^2) indicating a non-electrolytic nature around the Ni(II) ion. The high melting point of the Ni(II) complex (>300°C) suggest the existence of a strong covalent bonding between the Ni(II) ion and the ligand under investigation.

The Cu(II) complex **IVc** gave a band at 576 nm, suggesting the existence of a transition from d_{xy}, d_z^2 and d_{xz}, d_{yz} transfer to the antibonding and half-filled $d_{x2}-d_{y2}$ level which is consistent with an octahedral configuration.[13] The observed magnetic moment of the Cu(II) complex is 2.04 B.M., which confirms the octahedral structure of this complex. In addition, the value of molar conductance in DMSO (7.0 Ω^{-1} mol^{-1} cm^2) suggests a non-electrolytic nature of this complex. The high melting point of the Cu(II) complex (>300°C) suggest the existence of a strong covalent bonding between the Cu(II) ion and the ligand under investigation.

Palladium complex **(IV$_d$)** has three spin allowed singlet–singlet d–d transitions, which are $^1A_1g\rightarrow{}^1A_2g$ (716 nm), $^1A_1g\rightarrow{}^1B_1g$ (498 nm) and $^1A_1g\rightarrow{}^1Eg$ (415 nm).[14,15] These transitions are from the lower lying d orbital to the empty $_{dx^2-y^2}$ orbital. The strong band at 375 nm is assignable to a combination of M→L (charge transfer) and d–d bands. The molar conductance value of Pd(II) complex (6.0 Ω^{-1} mol^{-1} cm^2) indicating that this complex is non-electrolytic in nature. The high melting point of the Pd(II) complex (>300°C) suggest the existence of a strong covalent bonding between the Pd(II) ion and the ligand under investigation.

It is concluded from the above results that the proposed formula of the investigated complexes coordination with metal ions occurs through the nitrogen of the NH and C≡N groups as shown in the Scheme 2.

IR Spectra

The most important vibrational bands of the ligand and its metal complexes are given in Table II. The results of IR spectra of the metal complexes show absorption bands of both $\nu_{C\equiv N}$ and $\nu_{N\text{-}H}$ at lower frequencies than those of the free ligand **III**, indicating that the metal ions are coordinated to the nitrogen atoms of both C≡N and NH groups of the ligand **III**. Further, in all the metal complexes, there were new medium to weak bands observed at lower frequencies in the range (252–305 cm^{-1}) were assigned to $\nu_{M\text{-}N}$ and two bands at 550–559 cm^{-1} were attributed to $\nu_{m\text{-}o}$ for **IV$_{a\text{-}d}$**.[1–3] The bands observed at 1563–1470 cm^{-1}, 1 and, 1619–1561 cm^{-1} in both Co (II), Ni(II) and Cu(II) complexes were attributable to ν_{sym}OCO and ν_{asym}OCO respectively, which indicated that the acetate groups coordinate as a monodentate to the central metal cation of Co(II), Ni(II), and Cu(II) complexes, respectively. This is supported with the observed characteristic $\nu_{M\text{-}O}$ band.[1–3]

The spectra of nitrato complex **(IV$_d$)** gave additional bands around 1232, 1045, and 877 cm^{-1}, which are consistent with the monodentate nature of this group.[10]

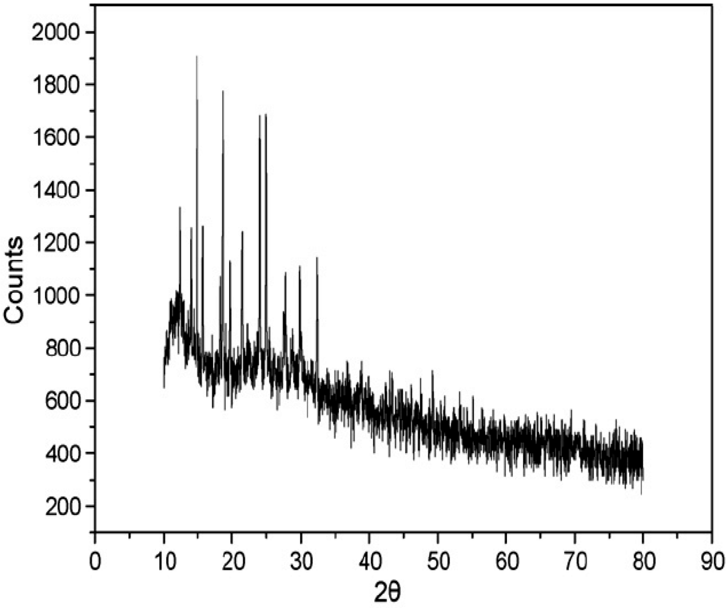


FIGURE 1 X-ray powder diffraction of Cu(II) complex.

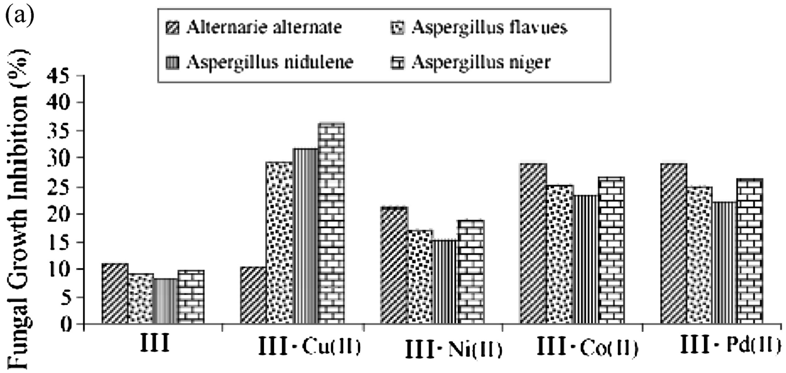
Moreover, the characteristic vibrational bands corresponding to the $\nu_{\text{P-NH}}$, $\nu_{\text{P-N}}$, and $\nu_{\text{p-Cl}}$ which were associated with all the complexes under investigation are given in Table II.

Powder X-ray Diffraction

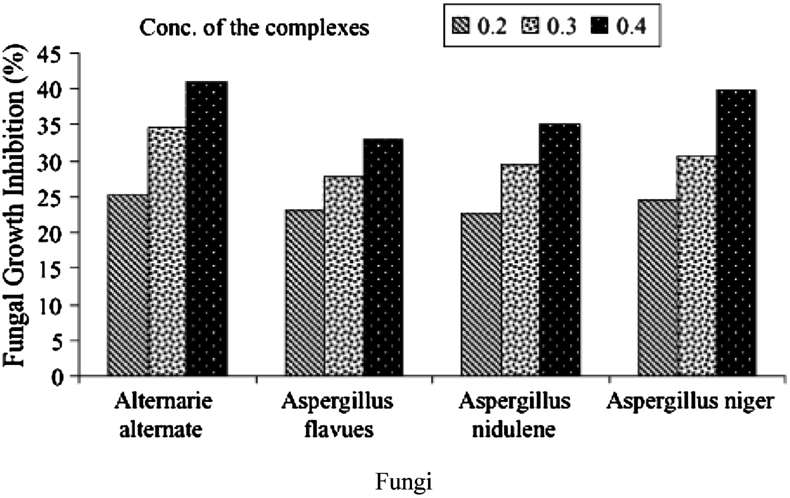
X-ray patterns of the Cu(II) complex **IVc** recorded at $2\theta = 0$–90 range was shown in Figure 1. All the complexes are powder solids (amorphous). The resulted complexes are slightly soluble in DMF and DMSO and are decomposed in diluted solutions of all strong acids. Attempts to prepare single crystals were unsuccessful.

Antimicrobial Activities

The free ligand and its respective metal chelates were screened against *A. alternate*, *A. flavus*, *A. nidulence,* and *A. niger* fungi and *Strepproteus*, *Staph*, *Staphylococcus* and *E. coli* bacteria to asses their potential antimicrobial agents. The results are quite promising. It is clear from the antifungal screening data (Figure 2a), that the metal complexes are more fungitoxic than the chelating agent itself. The bacterial screening results (Figure 2b) reveal that the free ligand **(III)** showed the maximum activity against *Streproproteus* bacteria. Its copper, cobalt, and palladium complexes also showed the maximum activity against *Streproproteus* bacteria whereas the nickel complex showed the maximum activity against *Staphylococcus* bacteria. In general, the activity was the least against *Staph* bacteria. The antimicrobial data reveal that the complexes are more bioactive than the free ligand. The enhanced activity of the metal complexes may be ascribed to the increased lipophilic

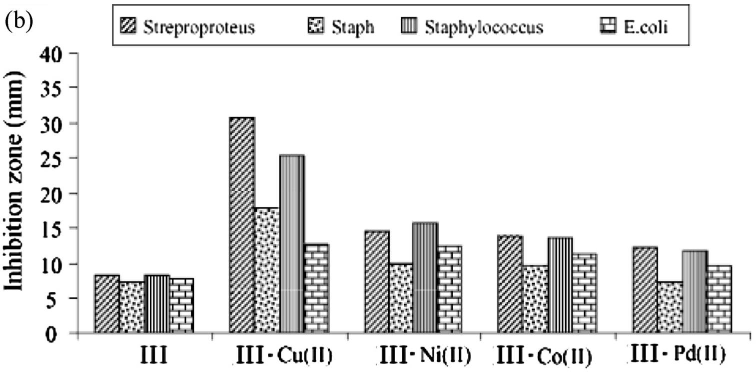


Antifungal agent potential of III and its complexes at 0.4% concentration

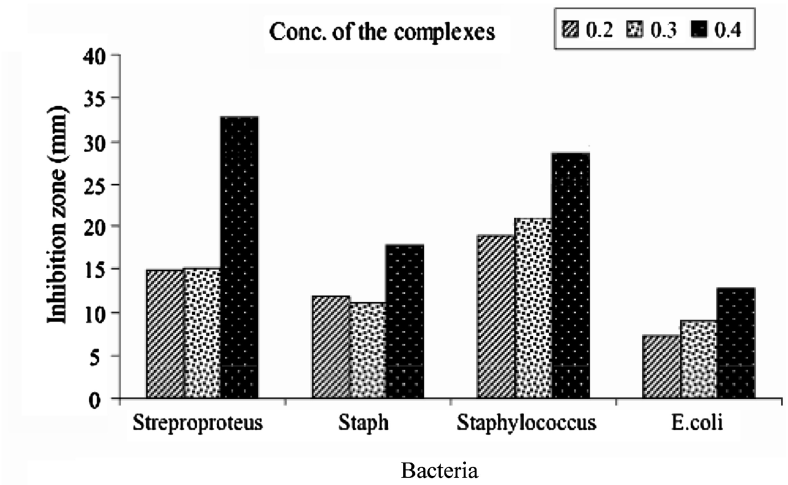


Effect of concentration of Cu(II)-III complex on its antifungal potential

FIGURE 2 (a) Antifungal screening and (b) antibacterial screening. (*Continued*)



Antibacterial agent potential of III and its complexes at 0.4% concentration



Effect of concentration of Cu(II)-III complex on its antibacterial potential

FIGURE 2 (*Continued*)

nature of these complexes arising due to chelation.[16] It was also noted that the toxicity of the metal chelates increases on increasing the metal ion concentration. It is probably due to faster diffusion of the chelates as a whole through the cell membrane or due to the chelation theory. The bounded metal may block enzymatic activity of the cell or else it may catalyze toxic reactions among cellular constituents. It can be concluded from all the results given above that the ligand acts as tetradentate chelating agent, coordinates with transition metal ions to give square planar/tetrahedral environments, around the metal ion anchor.

EXPERIMENTAL

Starting Materials

The preparation and purification of hexachlorocyclodiphosph-(V)azanes **(I)** has been reported.[2,3] The preparation of 2-amino-3-cyano-4,5-dimethylthiophene **(II)** was carried out according to the Gewald method.[5]

Synthesis of Ligand (III)

The solid of 2-amino-3-cyano-4,5-dimethylthiophene **(II)** (3.04 g; 0.02 mol) was added in small portions to a well-stirred solution of the hexachlorocyclodiphosph(V)azane **(I)** (4.57 g; 0.01 mol) in 100 ml acetonitrile over 0.5 h 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 (bright yellow) was filtered washed several times with acetonitrile, followed by ether and then dried in vacuo to give the corresponding aminocyclodiphosph(V)azane derivative **(III)** (Scheme 1).

Preparation of the Solid Metal Complexes

A solution of the salts (0.002 mol) in 50 ml acetonitrile was added dropwise to a solution of aminocyclodiphosph(V)azane derivative **(III)** (0.001 mol) in 50 ml acetonitrile at room temperature with continuous stirring. After the complete addition of the metal salt solution, the reaction mixture was heated under reflux for 3 h. Then, the reaction mixture was evaporated to give solid compounds, which recrystallized from acetonitrile to give the products **IVa-c**. The analytical data of both ligand and its metal complexes are listed in Table I.

Measurements

Elemental analysis of C, H, and N and S were carried out using the Perkin-Elmer 2400 apparatus and phosphorus was determined grave-metrically as phosphoammonium molybdate using the R. Voy method.[17] Infrared spectra were recorded in the solid state on a Mattson 5000 FTIR spectrometer using KBr disc technique. The absorbance of solutions was measured in the UV/VIS range (200–800 nm) using Unicam spectrophotometer model UV 2–100 and 1 cm matched quartz cells. The ^{1}H NMR spectra were recorded on a Varian Spectrometer at 90 (22.5) MHz, using TMS as an internal reference. ^{31}P NMR spectra were run, relative to external H_3PO_4 (85%), with a Varian FT-80 spectrometer at 365 MHz. Magnetic measurements were recorded by the Gouy method at room temperature using a magnetic susceptibility balance (Johnson Mathey), Alfa product. Model No. (MK). The conductometric measurements in solutions were carried out using conductivity TDS model 72. The X-ray powder diffraction analyses were carried out by using Rigku Model ROTAFLEX Ru-200. Radiation was provided by copper target (Cu anode 2000 W) high intensity X-ray tube operated at 40 kV and 35 MA. Divergence slit and the receiving slit were 1 and 0.1, respectively.

Biological Activity

Antibacterial Screening

In vitro anti-microbial (anti-bacterial) activities of the synthesized ligand and its metal complexes were tested using paper disc diffusion method.[18] The nutrient agar medium (peptone, beef extract, NaCl and agar-agar) and 5 mm diameter paper discs of Whatman No. 1 were used. The test compound was dissolved in methanol in 0.05–0.40% concentrations. The filter paper discs were soaked in different solutions of the compound, dried, and then placed in the Petri plates (9 mm diameter) previously seeded with the test organisms *Streptococcus*, *Staph*, *Staphylococcus* and *Escherchia coli*. The plates were incubated for 24–30 h at 27 ± 1°C and the inhibition zone (mm) was measured around each disc. As the organism grows, it forms a turbid layer, except in the region where the concentration of antibacterial agent is above the minimum inhibitory concentration and a zone of inhibition is seen. The size of the inhibition zone depends upon the culture medium, incubation conditions, rate of diffusion, and the concentration of the antibacterial agent.

Antifungal Screening

The antifungal activity of the complexes was checked by dry weight method for the *Alternarie alternate*, *Aspergillus flavus*, *Aspergillus nidulans,* and *Aspergillus niger* fungi. The complexes were directly added to the growth medium in varying concentration (0.05–0.40% (w/v)). The actively growing mycelia (of the test fungi) were placed on the medium with the help of inoculum needle and incubated at 27 ± 1°C for 7 days. The medium with the test solutions served as "treated" while without them as "control" or "check." The resulting mycelia mats in each set were carefully removed, washed, dried, and then weighed separately. The fungal growth was calculated from the following relation:

$$\text{fungal growth inhibition }(\%) = C_g - T_g/C_g \times 100 \tag{1}$$

where C_g is the average growth in the "control" or "check" set and T_g is the average growth in the treated set.

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