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# Phosphorus, Sulfur, and Silicon and the Related Elements

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## New

Tetrachlorocyclodiphosph(V)azane Complexes of Co(II), Ni(II), and Cu(II): Preparation, Characterization, Solid State Electrical Conductivity, and Biological Activity Studies

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## New Tetrachlorocyclodiphosph(V)azane Complexes of Co(II), Ni(II), and Cu(II): Preparation, Characterization, Solid State Electrical Conductivity, and Biological Activity Studies

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Tetrachlorocyclodiphosph(V) az ane of thiazole,  $H_2L$  (1,3-diphenyl -2,4-bis(3-phenyl -2,4-bis(3-p 2-iminothiazole)-2,2,4,4-tetrachlorocyclodiphos(V) azane, reacts with stoichiometric amounts of transition metal salts such as Co(II), Ni(II), and Cu(II) to afford colored complexes in a moderate to high yield. The structure of the isolated complexes was suggested based on elemental analyses, IR, molar conductance, UV-Vis, <sup>1</sup>H and <sup>31</sup>P NMR, mass spectra, solid reflectance, magnetic susceptibility measurements and dark electrical conductivity of solid state from room temperature up to 450 k. The data obtained obeyed the relation  $\sigma = \sigma^{\circ} \exp(-E/2kT)$  over the temperature range 30-150°C. The observed conductivities of the different complexes follow the order Co < Ni < Cu. It is clear that this trend is depending on the decreasing of the ionic radii and the increasing stability of metal complexes. The calculated mobility of charge carriers is ranged from  $10^{-5}$  to  $10^{-9}$  cm<sup>2</sup>/V s suggesting that the conduction of the studied complexes takes place by hopping mechanism. The solid-state electrical conductivity obtained reveals that the metal complexes behave as semiconducting materials. The powder XRD studies confirm the amorphous nature of the complexes. From the elemental analyses data, 1: 2  $(H_2L; M)$  ratio is suggested and the complexes are found to have the general formula  $[(MX_2)_2(H_2L)(H_2O)_m]$ .  $nH_2O$  where M = Co(II) (X = SCN, n = 2, m = 0), Ni(II) (X = Cl, n = 4, m = 4), and Cu(II) (X = Cl, n = 2, m = 0). The complexes have been investigated in solution by the spectrophotometric molar ratio and conductometric methods. IR spectra show that the ligand is coordinated to the metal ions in a bidentate manner with NN donor sites of the imine NH and thiazole N. The UV-Vis, solid reflectance, and magnetic-moment data have shown that the ligand is coordinated to the metal ions in an octahedral, tetrahedral, or square planar manner. The molar conductance data show that the complexes are nonelectrolytes. The prepared complexes showed high to moderate bactericidal activity compared with the ligand.

**Keywords** Electrical conductivity; electronic; IR; magnetic moment; <sup>31</sup>P NMR; tetrachlorocyclodiphosph(V)azane metal complexes

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## INTRODUCTION

In recent years, the structural feature of four-membered  $N_2P_2$  ring compounds in which the coordination number of P varies from three to five have attached considerable attention.<sup>1,2</sup> Heterocycles with P–C, P–N, P–O, and P–S bonds, in addition to their great biochemical and commercial importance,<sup>3,4</sup> play a major role in some substitution mechanisms as intermediates or as transition states.<sup>3,4</sup> The reaction of hexachlorocyclod-iphosph(V)azanes with aromatic and aliphatic amines, active methylene containing compounds, and bifunctional reagents have been investigated in some detail.<sup>5–7</sup>

The present work aims chiefly to prepare the metal complexes of tetrachlorocyclodiphos(V)phazanes of thiazole. In this work, novel tetrachlorocyclodiphosph(V)azanes of thiazole (H<sub>2</sub>L) was prepared and its behavior towards some transition metal ions was studied using different techniques such as elemental analyses, IR, <sup>1</sup>H NMR, and <sup>31</sup>P NMR, solid reflectance, mass spectra, molar conductance, magnetic moment, UV-Vis, and mass spectra. The DC electrical behavior of 1,3-diphenyl-2,4-bis(3-phenyl-2-iminothiazole)-2,2,4,4tetrachlorocyclodiphos(V)azane compound and its cobalt(II), nickel(II), and copper(II) complexes at different temperatures is investigated. The mechanism of conduction is explained. Also, the bactericidal activities of these compounds were studied. The proposed structure for H<sub>2</sub>L is shown in Figure 1.

## **EXPERIMENTAL**

All chemicals used were of analytical reagent grade. They included  $Co(SCN)_2$ ,  $Ni(CH_3COO)_2 \cdot 4H_2O$ , and  $CuBr_2$ , 3-phenyl-2aminothiazole and phosphorus pentachloride supplied from BDH. The solvents used were ethanol, benzene, dimethylformamide (DMF), and deuterated dimethyl sulfoxide (DMSO).

## **Preparation of Ligand**

The solid of 3-phenyl-2-aminothiazole (II) (1.76 g, 0.01 mmol) was added in small portions to a well stirred solution of the 1,3-diphenyl-2,2,2,4,4,4-hexachlorocyclodiphosph(V)azane (I) (3.56 g, 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

 $NH_2$ 



FIGURE 1 Structure of ligand H<sub>2</sub>L:1,3-diphenyl-2,2,4,4-tetrachloro,2',4'bis(2-imino-3-phenylthiazole) cyclodiphosph(V)azane.

(bright yellow) was filtered washed several times with acetonitrile, and dried in vacuo to give the corresponding 1,3-diphenyl-2,4-bis(3phenyl-2-iminothiazole)-2,2,4,4-tetrachlorocyclodiph-os(V)azane (H<sub>2</sub>L) (Figure 1). Yield = 88.6%; m.p. =  $196^{\circ}$ C; elemental analysis calculated (found) for  $C_{30}H_{24}N_6P_2S_2Cl_4$  (736.44): C = 48.9% (48.3%), H = 3.3%(3.2%), N = 11.4% (11.2%), P = 8.4% (8.4%), S = 8.7% (8.7%).

### Preparation of Complexes

A hot solution (60°C) of the metal salts  $[Co(SCN)_2 (0.35 g;$ (0.002 mol)], [Ni(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O (0.497; 0.002)] or [CuBr<sub>2</sub> (0.466; 0.002)] in 50 mL absolute ethanol was added dropwise to a hot solution of 1,3-diphenyl-2,4-bis(3-phenyl-2-iminothiazole)-2,2,4,4tetrachlorocyclodiphos(V)azane (H<sub>2</sub>L) (0.736 g; 0.001 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 hot metal-salt solution, the reaction mixture was heated under reflux for about 2 h under dry conditions. The complexes obtained were washed with absolute ethanol then with dry diethyl ether and dried in vacuo. The analytical data of both ligand and its metal complexes are listed in Table I.

## Methods

Microanalytical analysis of C, H, N, and S were carried out and phosphorus was determined gravimetrically as phosphoammonium molybdate using the R. Voy method.<sup>8</sup> Infrared spectra were recorded in the solid state on a Mattson 5000 FTIR spectrometer using KBr disc technique. The absorbance of solutions were measured in the UV/VIS range (200-800 nm) using Unicam spectrophotometer model UV 2-100 and 1 cm matched quartz cells. The <sup>1</sup>H NMR spectrum of the ligand was recorded on a Varian FT-290.90 MHz spectrometer in deutrated DMSO using TMS as an internal standard. <sup>31</sup>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 Matthey), Alfa product, Model No. (MK). Diamagnetic corrections were calculated from Pascal's constants. The conductometric measurements in solutions were carried out using conductivity TDS model 72. Metal contents were determined by titration against standard EDTA after complete decomposition of the complexes with agua regia in a Kieldahl flask several times. The X-ray-diffraction patterns of the samples were recorded with a Rikagu Geigerflex diffractometer using Cu K $\alpha$  radiation. The Antimicrobial activity was performed using DMF as solvent at Fermentation Biotechnology and Applied Microbiology (FERM-BAM) Center, Al-Azhar University, Egypt. The test was done using diffusion agar technique. Conductivity measurements were made on discs having 1mm thickness of 1,3-diphenyl-2,4-bis(3-phenyl-2-iminothiazole)-2,2,4,4-tetrachlorocyclodiphos(V)azane and its complexes sandwiched between two copper electrodes. The conductivity cell used was the same as that reported before.<sup>9</sup> The electrical conductivity was measured in the temperature range 30–150°C. The activation energies were calculated using the equation  $\sigma = \sigma^{\circ} \exp(-E/2kT)$ .

## **RESULTS AND DISCUSSION**

The ligand was found to be soluble in  $CHCl_3$ , acetone, ethanol, THF, methanol, DMSO, DMF, ethyl acetate, and insoluble in diethyl ether and water, slightly soluble in benzene and *n*-hexane. The structure of

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	M.n.		Yield		Elem	iental analy	ses% found	l (calc.)		IL off	۸m
Compound M. F. (mol. wt.)	(°C)	Color	(%)	С	Н	N	Р	$\mathbf{S}$	М	(B.M)	$(\Omega^{-1} mol^{-1} cm^2)$
$({ m H_2L})~{ m C_{30}H_{24}Cl_4N_6P_2S_2}\ (736.44)$	212	Bright yellow	88.6	48.3(48.9)	3.3(3.3)	11.2(11.4)	8.3(8.4)	8.7 (8.7)	I	I	I
$egin{array}{l} [{ m Co}_{20}){ m SCN}_4({ m H}_2{ m L})].{ m 2H}_2{ m O}\ { m C}_{34}{ m H}_{28}{ m Cl}_4{ m Co}_2{ m N}_{10}{ m O}_2{ m P}_2{ m S}_6\ (1122.67) \end{array}$	262	Green	82.4	36.2 (36.5)	2.2 (2.5)	12.2(12.5)	5.3(5.5)	17.0 (17.1)	$10.3\ (10.5)$	5.26	13.45
$\begin{array}{l} [\mathrm{Ni}_2(\mathrm{Ac})_4(\mathrm{H}_2\mathrm{L})(\mathrm{H}_2\mathrm{O})_2].4\mathrm{H}_2\mathrm{O}\\ \mathrm{C}_{38}\mathrm{H}_{52}\mathrm{Cl}4\mathrm{N}_6\mathrm{Ni}_2\mathrm{O}_{16}\mathrm{P}_2\mathrm{S}_2\\ (1234.13)\end{array}$	267	Pale yellow	80.0	36.7 (36.9)	4.1 (4.2)	6.6 (6.8)	5.2(5.0)	5.4(5.2)	9.4 (9.5)	2.98	12.68
$\begin{array}{l} [\mathrm{Cu}_{2}\mathrm{Br}_{4}(\mathrm{H}_{2}\mathrm{L})] \ .2\mathrm{H}_{2}\mathrm{O} \\ \mathrm{C}_{30}\mathrm{H}_{28}\mathrm{Br}_{4}\mathrm{Cl}_{4}\mathrm{Cu}_{2}\mathrm{N}_{6}\mathrm{O}_{2}\mathrm{P}_{2}\mathrm{S}_{2} \\ (1219.18) \end{array}$	298	Black	06	29.8 (30.4)	2.1 (2.3)	6.8 (6.9)	5.5(5.1)	5.3(5.3)	$10.4\ (10.4)$	1.89	14.96

the ligand  $(\rm H_2L)$  was elucidated by elemental analyses, IR, electronic,  $^{1}H$  PNMR techniques, 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  $\nu_{P-NH}$ stretching vibrations of the ligand at 2620 cm<sup>-1</sup> which is similar to those assigned by Abd-Ellah et al.<sup>10</sup> and Pustinger et al.<sup>11</sup> The band appeared at 3053 cm<sup>-1</sup> is attributed to the  $\nu_{NH}$  stretching vibration. The  $\nu_{P-Cl}$  stretching vibration is observed at 522 cm<sup>-1</sup>.<sup>12,13</sup> The band at 1223 cm<sup>-1</sup> was assigned to the  $\nu_{P-N}$  stretching vibration.<sup>14,15</sup> Bands appear in the range 1622–1409 cm<sup>-1</sup> may be attributed to  $\nu_{C=C}$  of the aromatic rings and attached compounds (II).<sup>16</sup> Moreover, the IR spectra showed weak band at 621 cm<sup>-1</sup> due to the  $\nu_{C-S}$  stretching vibration of thiazole ring. The weak band observed at 2929 cm<sup>-1</sup> is due to aromatic C–H stretching vibrations.<sup>17</sup>

## **Electronic Spectra**

The fact that the expected band at 272 nm,<sup>18</sup> characteristic for the delocalization of the nonbonding electrons on the nitrogen atoms within the phosphazo ring of the dimeric structure was observed in the spectrum of ligand (H<sub>2</sub>L), suggested the presence of the phosphazo ring. The bathochromically shifted band observed at 284 nm for the ligand 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 2-amino-3-phenylthiazole. The new band observed at 350 nm is attributed to the n- $\pi^*$  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 possible fragmentation pathways of ligand  $(H_2L)$  (Scheme 1) showed the expected fragments, which confirm the proposed structure of this ligand. The base peak was observed in the spectrum at 92.

## <sup>1</sup>H and <sup>31</sup>P-NMR Spectrum

The <sup>1</sup>H NMR spectrum of the ligand (H<sub>2</sub>L) showed the following characteristic proton signals at:  $\delta$  (7.51) ppm is assigned for aromatic protons Ar—H and abroad signal at  $\delta$  (8.97) ppm is assigned for N—H proton, which disappeared on the addition of D<sub>2</sub>O due to the proton exchange.

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	$\nu(MBr)$	
	$\nu({\rm SCN})$	
	$\nu(M-N)$	
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	$\nu({ m H}_2{ m O})~({ m coord.})$	
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$H_2L$ and	$\nu$ (P–NH)	
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s = strong; m = medium, sm = small; w = weak; vw = very weak; br = broad.

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694 m631 vw 624 w

522 m 556 m 464 m464 m

1223 m 1228 m 1227 m1217 m

2620 w2600 vw2600 vw2600 vw

3053 br 3026 br 3028 br 3001 m

3400 m 3390 br 3500 m

 $[Ni_2(Ac)_4(H_2L)\,(H_2O)_4\,].4H_2O$  $[C_{02})SCN)_4(H_2L)].2H_2O$ 

 $[Cu_2Br_4(H_2L)]].2H_2O$ 

 $H_2L$ 

542 wI

831 w, 753 s



SCHEME 1 Fragmentation pattern for ligand (H<sub>2</sub>L).

The <sup>31</sup>P NMR of the ligand records a signal at  $\delta = 14.4, 10.6$  ppm, which supports the phosphazo-ring structure.

## **Metal Complexes**

The complexes were found to be soluble in DMSO, DMF and THF and insoluble in CHCl<sub>3</sub>, ethanol, diethyl ether, and water; they were slightly

soluble in acetone. The chemical behavior of  $H_2L$  towards transitionmetal cations was our goal in this article. The metal cations selected for this purpose were Co(II), Ni(II), and Cu(II). When a mixture of one mol of  $H_2L$  in dry ethanol was reacted with two moles of the metal salts in acetonitrile, a change in color was observed and the complex compounds precipitated. The products were purified by washing with absolute ethanol, and gave elemental analysis compatible with the general formula  $[(MX_2)_2(H_2L)(H_2O)_m]$ . nH<sub>2</sub>O, where M = Co(II) (X = SCN, n = 2, m = 0), Ni(II) (X = OCOCH<sub>3</sub>, n = 4, m = 4), and Cu(II) (X = Br, n = 2, m = 0). Accordingly, the complexes are prepared following the general equation:

$$2MX_n + H_2L + mH_2O \rightarrow [(MX_2)_2(H_2L)(H_2O)_m] . nH_2O$$
(1)

where M = Co(II) (X = SCN, n = 2, m = 0), Ni(II) (X = OCOCH<sub>3</sub>, n = 4, m = 4), and Cu(II) (X = Br, n = 2, m = 0).

The analytical data of the isolated complexes are listed in Table I. Further, the proposed structures of the complexes of  $H_2L$  is confirmed using different physicochemical tools such as IR, molar conductance, UV-Vis, solid reflectance, magnetic moment, XRD, and solid state electrical conductivity.

### IR Spectra

A detailed interpretation of the IR spectra of H<sub>2</sub>L and the effect of binding with Co(II), Ni(II), and Cu(II) ions on the vibrational frequencies of the free  $H_2L$  ligand are discussed. The IR spectra of the free ligand and its metal chelates were carried out in the 4000–400  $cm^{-1}$  range (Table II). IR spectrum of the ligand revealed a medium band at 1595  $cm^{-1} \nu_{(C=N)}$  thiazole ring, which is shifted to lower frequency at about  $10 \text{ cm}^{-1}$  after complexation, which also indicates that it has been affected upon coordination to metal ions. In the IR spectrum of all the complexes, IR band is observed between 624-694 cm<sup>-1</sup>, which is attributed to the  $\nu_{(M-N)}^{19}$  stretching vibrations. There are also two bands affected after complexation belonging to the thiazole skeleton stretching and benzene  $\nu_{(C=C)}$  stretching vibration at 1279 and 1409 cm<sup>-1</sup>, respectively, which clearly shows that ligands coordinated to the metal ions from nitrogen atom of imine NH and nitrogen atom of thiazole groups.<sup>20</sup> The results of IR spectra of the metal complexes show absorption bands of both  $\nu_{C=N}$  and  $\nu_{N-H}$  at lower frequencies than those of the free ligand  $H_2L$ , indicating that the metal ions are coordinated to the nitrogen atoms of both C=N and NH groups of the ligand H<sub>2</sub>L. Practically unchanged  $\nu_{(C-S-C)}$  vibration at 1027 cm<sup>-1</sup> of the thiazole  $ring^{21,22}$  indicates that the thiazole group does not coordinate to metal from the sulfur atom.

The acetato complex has band at 1593 cm<sup>-1</sup> and 1409 cm<sup>-1</sup> can be assigned to  $\nu_{\rm as}(\rm CO_2)$  and  $\nu_{\rm s}(\rm CO_2)$  fundamental stretching bands, respectively, which are in agreement with the acetate group being monodentate<sup>23</sup> because the difference  $\Delta$  ( $\Delta = \nu_{\rm as}(\rm CO_2) - \nu_{\rm s}(\rm CO_2)$ ] is 1593–1409 = 148 cm<sup>-1</sup>. The band at 1409 cm<sup>-1</sup> is due to the  $\nu_{\rm s}(\rm CO_2)$  mode of both acetate and H<sub>2</sub>L ligand.

The  $\nu(Cu-Br)$  band is observed at 464 cm<sup>-1</sup>, which showed terminal rather than bridging bromine for the bromo complex.<sup>23</sup> In the complex with NCS<sup>-</sup> group, it seems to be that NCS<sup>-</sup> coordinated through the nitrogen atom, since  $\nu(NCS)$  are observed in region of 2066 cm<sup>-1.24,25</sup> All complexes showed broad band around 3500–3390 cm<sup>-1</sup> due to  $\nu(OH)$ from water molecules. This band is absent in the ligand.<sup>26</sup>The appearance of a medium-to-strong bands in the stretching vibration region between 831 and 753 cm<sup>-1</sup> in the spectra of the Ni(II) complex were attributed to coordinated water molecules.<sup>23</sup> The presence of acetate, thiocyanate, or bromide ions in the structural configuration of the complexes suggests that H<sub>2</sub>L act as a bidentate monoanionic molecule during complexation with the metal ions. The characteristic bands corresponding to the  $\nu_{P-NH}$ ,  $\nu_{P-N}$  and  $\nu_{P-C1}$  which were associated with all the investigated complexes are collected in Table II.

From these observations, it was suggested that the imine nitrogen and the nitrogen atom in thiazole ring are involved in the complexation reaction as donor atoms.

## Spectrophotometric Measurements of Solution Stoichiometry

The absorption spectra of the  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  complexes are shown in Figure 2. The diagrams in Figure 3, consist of two linear portions intersecting at 1:2 [ligand]/[ $M^{2+}$ ], where  $M^{2+}$  corresponding to  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  respectively, indicating the formation of 2M: IL species.<sup>27</sup> This is in agreement with the elemental analyses and conductometric analyses data.

## **Conductometric Titration**

In order to follow up the behavior of the ligand in solution with Co (II), Ni (II), and Cu (II), we investigated these systems using conductometric titration method.<sup>27</sup> In this method. 25 ml ( $10^{-4}$  M) of M(II) where M(II) is Co(II), Ni(II) and Cu(II) solution in absolute ethanol was titrated



FIGURE 2 Absorption spectra for Co(II), Ni(II) and Cu(II) Complexes.

with  $(10^{-3} \text{ M})$  of ligand solution absolute ethanol at room temperature  $25^{\circ}$ C and represented in Figure 4. 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 complexes under investigation. The reason for increase in conductivity after 2:1 (M: L) complexes forms may be due to the presence of the ligand in ionic form in the medium (ethanol) which arises the conductivity.

#### Molar Conductance Data

The molar conductance values in DMF at 25°C (Table I) for the complexes were found to be in the range 7.85–18.30  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>. The relatively low values indicate the non-electrolytic nature of these complexes. This can be accounted for by the satisfaction of the bivalent



FIGURE 3 Results of molar ratio method for Co(II), Ni(II) and Cu(II) Complexes, respectively.

of the metal by the acetate, bromide. or thiocyanate. This implies the coordination of the anions to the metal ion centers.

## **Electronic Spectra and Magnetic Properties**

The UV-Vis spectra of the complexes in DMF  $(1 \times 10^{-3} \text{ M})$  show a sharp and intense band in the region 269–281 nm, which is characteristic of phosphazo four-membered rings.<sup>27</sup> However, the absorptions that were red or blue shifted with respect to the ligands depending on the types of metal ions present. The spectra of the Ni(II), and Cu(II) complexes



FIGURE 4 Conductometric titrations for (a) Co(II), (b) Ni(II) and (c) Cu(II) complexes, respectively.

further display a band in the range 360–439 nm, which might be assigned to charge-transfer transition (most probably L $\rightarrow$ M CT).<sup>28</sup> For the Co(II) complex, however, a d–d bands are observed at 600 and 675 nm which may attributed to the transitions  ${}^{4}T_{1}(F) \rightarrow {}^{4}T_{2}(P)$  and  ${}^{4}T_{1}(F) \rightarrow {}^{4}A_{2}(F)$ , respectively, which is typical of tetrahedral structure around Co(II) ion.<sup>27</sup>

The diffuse reflectance spectrum of the Co(II) complex displays three bands at 13,501, 18,250, and 22,953 cm<sup>-1</sup> assigned to the <sup>4</sup>T<sub>1</sub>  $(F) \rightarrow {}^{4}T_{2}(F) (\nu_{1}), {}^{4}T_{1} (F) \rightarrow {}^{4}A_{2}(F) (\nu_{2})$ , and  ${}^{4}T_{1} \rightarrow {}^{4}T_{2}(P) (\nu_{3})$  transitions, respectively. The band observed at 26,520 cm<sup>-1</sup> refers to L $\rightarrow$  MCT band. From the observed magnetic moment value ( $\mu_{eff} = 5.26$  B.M.) together with the band position in the solid reflectance spectra, the Co(II) complex is tetrahedral with largely covalent bonds between the organic ligand and Co(II) ion.<sup>29</sup>

The Ni(II) complex reported herein is high spin with a room temperature magnetic-moment value of 2.89 B.M., which confirms the octahedral structure of this complex.<sup>29,30</sup> The solid reflectance spectrum of the complex shows three bands at 14,993, 17,483, and 21,552 cm<sup>-1</sup>, which are assigned to the  ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(P)(\nu_{1})$ ,  ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)(\nu_{2})$ , and  ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g(P)(\nu_{3})$  transitions, respectively, confirming the octahedral geometry of the Ni(II) complex.<sup>29</sup>

The solid reflectance spectrum of the Cu(II) complex gave a band at 17,361 cm<sup>-1</sup>, was assigned to  ${}^{2}B_{2} \rightarrow {}^{2}E$  transition. The bands observed in the range 426–414 nm were assigned to the charge transfer via L $\rightarrow$ M (Cu<sup>2+</sup>). The observed magnetic moment of the Cu(II) complex is 1.89 B.M., which confirms the square planner structure of this complex.<sup>27</sup>



**FIGURE 5** Plots of In  $\sigma$  versus 1000/T for Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> cyclodiphos(V)azane complexes.

## Solid-State Electrical Conductivity

Figure 5 shows the relation between log  $\sigma$  against 1/T for 1,3diphenyl-2,4-bis(3-phenyl-2-iminothiazole)-2,2,4,4-tetrachlorocyclodiphos(V)azane compound and its complexes. A linear behavior was obtained for all samples. The conductivity of the free ligand is increased on complexing with transition metal ions. This behavior is attributed to the inclusion of the various metal cations in the  $\pi$ -electron delocalization of the ligand.<sup>31</sup> The observed conductivities follow the order Co < Ni < Cu. Theoretically, if we consider the charge/radii, the stability of the metal complexes increases as the size of the metal ion decreases or the value of the ratio charge/radii increases. This means that the stability increases towards the copper complex. It is apparent that increasing stability of the complexes will increase the number of dislocated electrons on the ligand molecule and then increase the conductivity<sup>32</sup> as given in (Table III). To explain the conduction mechanism of the ligand and its complexes, it is necessary to determine

Compound	$\sigma(\rm Ohm^{-1}~cm^{-1})$	E(ev)	$n(\mathrm{cm}^{-3})$	$\mu({\rm cm^2/V~s})$
$\begin{array}{c} \\ \hline H_2L \\ [Co_2)SCN)_4(H_2L)].2H_2O \\ [Ni_2(Ac)_4(H_2L) (H_2O)_4].4H_2O \\ [Cu_2Br_4(H_2L)]].2H_2O \end{array}$	$\begin{array}{c} 1.6 \times 10^{-8} \\ 1.8 \times 10^{-8} \\ 2.2 \times 10^{-8} \\ 2.8 \times 10^{-8} \end{array}$	$0.34 \\ 0.42 \\ 0.49 \\ 0.61$	$\begin{array}{c} 8.8\times 10^{19}\\ 13.0\times 10^{18}\\ 1.9\times 10^{18}\\ 1.6\times 10^{16}\end{array}$	$\begin{array}{c} 1.4\times 10^{-7}\\ 8.5\times 10^{-9}\\ 7.6\times 10^{-8}\\ 1.2\times 10^{-5}\end{array}$

the mobility of charge carriers  $\mu$ . If the density of charge carriers is known, then the mobility can be calculated using the relation  $\sigma = eNm$ , e is the electron charge. The charge carrier concentration was determined using the relation,

$$n = 2[2\mu m^* kT/h^2]^{1/2} \exp(-E:kT).$$
(2)

where  $m^*$  is the effective mass of charge carrier. The calculated mobilities are ranged from  $10^{-5}$  to  $10^{-9}$  cm<sup>2</sup>/V s suggesting that the conduction iminothiazole-cyclodiphos(V)azane ligand and its metal complexes takes place by hopping mechanism.<sup>33</sup>

## **X-Ray Powder Diffraction**

X-ray powder diffraction patterns in the  $5^{\circ} < 2\theta < 90^{\circ}$  of the compounds were carried in order to obtain an idea about the lattice dynamics of the compound. By comparison of the obtained X-ray powder diffraction patterns shown in Figure 6, the X-ray powder diffraction pattern throws light only on the fact that each solid represents a definite compound of a definite structure which is not contaminated with starting materials. This identification of the complexes was done by the known method.<sup>34</sup> Such facts suggest that the prepared compounds are amorphous.

#### Structural Interpretation

2-Iminothiazole)-2,2,4,4-tetrachlorocyclodiphos(V)azane ( $H_2L$ ) form (2M: 1L) complexes with the Co(II), Ni(II), and Cu(II) metal cations. The structural information from these complexes is in agreement with the data reported in this article based on the IR, molar conductance, UV-Vis, mass, solid reflectance, XRD, solid state electrical conductivity, magnetic moment, and spectrophotometric molar ratio and conductometric methods. The design and synthesis of a new bidentate ligand derived from 3-phenyl-2-aminothiazole for use in square planar, tetrahedral, or octahedral molecular templates have been successfully demonstrated.



FIGURE 6 XRD diagrams of: (A) Co (II), (B) Ni(II), and (C) Cu(II) complexes.

The synthesis of the ligand and its complexes proved as straightforward as expected, giving high yields of the free ligand and its complexes in simple, one-pot reactions. As anticipated, the ligand coordinates equatorially to four- or six-coordinate transition metal ions to give tetrahedral (Co(II)), octahedral (Ni(II)), and square planar (Cu(II)), environments around the metal ion anchor. The proposed general structures of the complexes are shown in Figure 7. H<sub>2</sub>L ligand always coordinates via the thiazole-N and imine-NH forming two-binding chelating sites.

## **Biological Activity**

The disc diffusion method was used to measure the antimicrobial activity of the complexes.<sup>35,36</sup> The compounds under test were dissolved in dimethylformamide (DMF) (2% w/v) and added at a concentration of 0.5 mL/disc to Whatman number 3 filter paper, 5 mm diameter. The biological activity of the H<sub>2</sub>L, its complexes and traivid and tavinic (as standard compounds), were tested against bacteria because bacteriums



FIGURE 7 The proposed structure of the Co(ll), Ni(II) and Cu(lI) Complexes. Where X = SCN or Br,  $M = Co^{2+}$  or  $Cu^{2+}$ , Ac = acetate.

can achieve resistance to antibiotics through biochemical and morphological modifications.<sup>36</sup> The antimicrobial activity was examined with different species of gram-positive bacteria such as *Staphylococcue Pyogones*, gram-negative bacteria such as *Pseudomonas aereuguinosa* and *Escherichia coli*, and fungi (*Candida*). The data obtained are summarized in Table IV. The data obtained reflect the following findings:

- 1. The H<sub>2</sub>L ligand has moderate activity in comparison with *Staphylococcus Pyogones* and is less active in comparison with *Escherichia coli* and Pseudomonas aereuguinosa. The remarkable activity of the ligand may arise from the thiazole-N and the imine -NH groups, which may play an important role in the antibacterial activity,<sup>37</sup> as well as the presence of two imine groups which imports in elucidating the mechanism of transformation reaction in biological systems.<sup>36</sup>
- 2. Antibacterial activity of the complexes towards the different organisms shows a high-to-moderate activity.

					-2-				- <b>G</b>			1000-1A						
	$H_2L$ (	mg/ml	(T)	Co(II)	[mg/m]	L)	[Ni(II)	(mg/m	[(י]	[Cu (]	II) (mg/	mL)]	Tavenic	a (mg/1	mL)	Traiv	id <sup>a</sup> (mg	/mL)
Compound	5	2.5	1	5	2.5	1	5	2.5	1	5	2.5	1	5	2.5	1	5	2.5	1
S. P. P.A. Fungs (Candida) E.C.	$\begin{array}{c} + \\ + \\ + \\ + \end{array} + \left. \right  \begin{array}{c} + \\ + \end{array}$	$^+_+$ +   +	+     +	$^{+}_{+} ^{+}_{+} ^{+}_{+} ^{+}_{+}$	+ + + + +	+ +   +	$^{+}_{+}^{+}$	+ +   +	+ +   +	$^+_{+} ^+_{+} ^+_{+} ^+_{+}$	+ + +   +	+     +	$\begin{array}{c} + & + & + \\ + & + &   & + \\ + & + & + \end{array}$	+ +   +	+ +   +	$+ \\ + \\ + \\ + \\ + \\ + \\ + \\ + \\ + \\ + \\$	+ +   +	

TABLE IV Antimicrobial Activity of H<sub>3</sub>L and Corresponding Metal Complexes

 $^{a}$ Standard materials. Inhibition value = 0.1–0.5 cm beyond control = +; Inhibition value = 0.6–1.0 cm beyond control = ++; Inhibition value = 1.1-1.5 cm beyond control = + + +; S.P. = Staphylococcus Pyogones; E.S. = Escherichia coli; and P.A. = Pseudomonas value = 1.1-1.5 cm beyond control = + + +; S.P. = Staphylococcus Pyogones; E.S. = Escherichia coli; and P.A. = Pseudomonas value = 1.1-1.5 cm beyond control = + + +; S.P. = Staphylococcus Pyogones; E.S. = Staphyloaereuguinosa. 3. The activity of the ligand and its complexes increases as the concentration increases because it is a well known fact that concentration plays a vital role in increasing the degree of inhibition.<sup>38</sup>

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