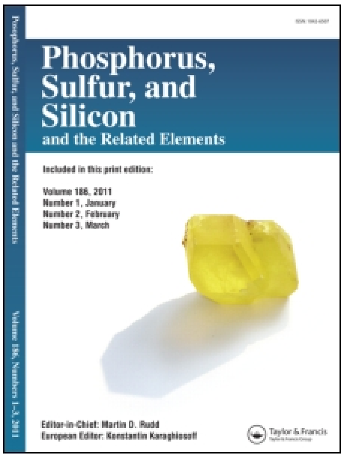

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Complexes of Co(II), Ni(II), Cu(II), and Pd(II) with Sulfametrole-Cyclodiphosph(V)azane Derivatives

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To cite this Article Alaghaz, A. M. A.(2008) 'Complexes of Co(II), Ni(II), Cu(II), and Pd(II) with Sulfametrole-Cyclodiphosph(V)azane Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 11, 2807 — 2826
To link to this Article: DOI: 10.1080/10426500802016661
URL: http://dx.doi.org/10.1080/10426500802016661

Phosphorus, Sulfur, and Silicon, 183:2807–2826, 2008
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802016661

Complexes of Co(II), Ni(II), Cu(II), and Pd(II) with Sulfametrole-Cyclodiphosph(V)azane Derivatives

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Novel [1,3-di-[N_1-4-methoxy-1,2,5-thiadiazole-3-yl-sulfanilamide(sulfametrole)]-2,,4-bis-[1,3-dithiole-2-thione-4,5-dithiolate]-2′,4′-dichlorocyclodiphosph(V)azane] ***(III)****, was prepared and their coordinating behavior towards the metal ions Co(II), Ni(II), Cu(II), and Pd(II) was studied. The structures of the isolated products are proposed based on elemental analyses, IR, UV, ^1H, and ^{31}P NMR, ESR, magnetic susceptibility, molar ratio, conductometric titration and electrical conductivity measurements. The prepared complexes showed high to moderate bactericidal activity compared with the ligand.*

Keywords complexes; Cyclodiphosph(V)azane; dithiolate; sulfametrole;

INTRODUCTION

Sulfonamides are the oldest class of antimicrobials and are still the drug of choice for many diseases such as cancer and tuberculosis.[1,2] Cyclophosphamide and its derivatives are examples of phosphorus compounds that are some of the most effective anticancer agents with proven activity against a large variety of human cancers.[3] The reaction of hexachlorocyclodiphosph(V)azanes with amino compounds, active methylene containing compounds and bifunctional reagents have been investigated in some details.[4,5] Little is known about the interaction of sulfametrole-hexachlorocyclodiphos-ph(V)azane with 1,3-dithiole-2-thione-4,5-disodiumthiolate and their metal complexes. The proposed structure for III is shown in Scheme 1.

Received 6 November 2007; accepted 27 February 2008.

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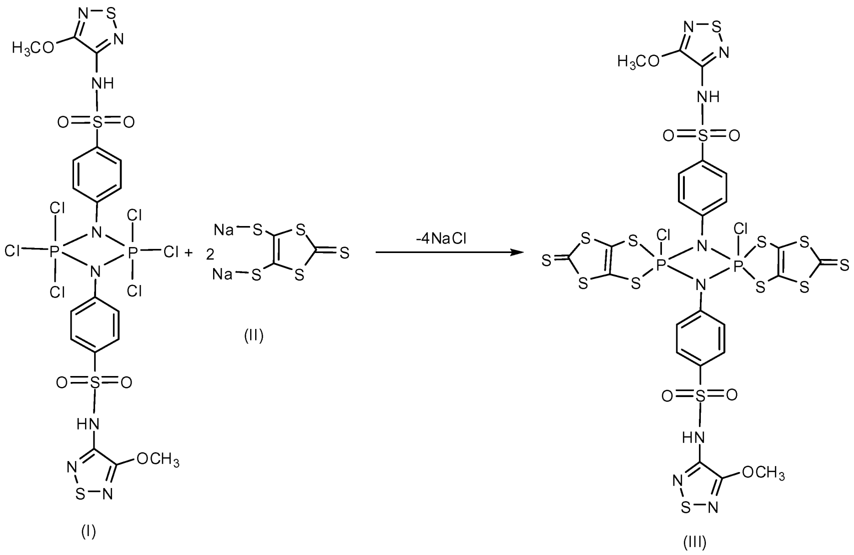


SCHEME 1 Proposed structure of **III** ligand III: 1,3-di-[N_1-4-methoxy-1,2,5-thiadiazole-3-yl- sulfanilamide]-2,,4-bis-[1,3-dithiole-2-thione-4,5-dithiolate]-2′,4′ dichlorocyclodiphosph(V)azane (III).

RESULTS AND DISCUSSION

The ligand was found to be soluble in $CHCl_3$, acetonitrile, 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 the ligand **(III)** was elucidated by elemental analyses, IR, electronic, ^1H, and ^{31}P NMR techniques. The assignment of the proposed structure for **III** is based on the elemental analyses data listed in Table I. The UV spectra of III in DMF showed absorption bands at 284 nm, which is characteristic for phosphazo four-membered rings.[6] The infrared spectra of the **III** ligand showed the characteristic bands which are summarized in Table II. The ^1H—NMR spectrum of the ligand **(III)** showed the following characteristic proton signals at: δ (7.20) ppm is assigned for aromatic protons Ar-H and abroad signal at δ (10.54) ppm is assigned for N—H proton, which disappeared on the addition of D_2O due to the proton exchange. The ^{31}P NMR of the ligand records a signal at $\delta = 25.93$ ppm, which supports the phosphazo ring structure. Further insight concerning the structure of the ligand was obtained from its mass spectra. The mass fragmentation pattern of the ligand showed a base peak at m/z 92 (100%), together with peaks at m/z 155

TABLE I Elemental Analysis Data of the Ligand III and Its Metal Complexes (IV_a-IV_d)

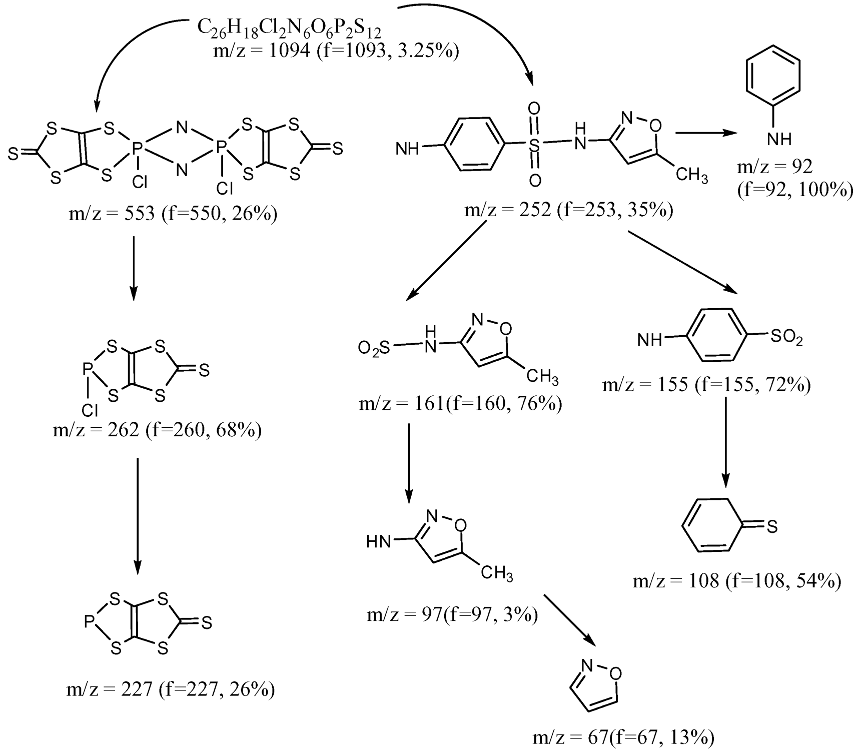
(Compound number)M.F.	MW	Color	Yield % (mp°C)	Elemental analysis data found (calculated)% C	H	N	Cl	S	P	M
(III) $C_{24}H_{16}Cl_2N_8O_6P_2S_{14}$	1094.2	Red	82	26.31	1.41	10.23	6.49	41.02	5.60	—
			(244)	(26.34)	(1.47)	(10.24)	(6.48)	(41.03)	(5.66)	
(IV_a) $C_{25}H_{27}Cl_6Co_2N_8O_{10}P_2S_{14}$	1440.97	Brown	66	20.42	1.41	8.53	14.54	31.12	4.21	8.10
			(>360)	(20.84)	(1.89)	(7.78)	(14.76)	(31.15)	(4.30)	(8.18)
(IV_b) $C_{25}H_{27}Cl_6N_8Ni_2O_{10}P_2S_{14}$	1440.49	Light Brown	71	20.34	1.40	7.64	14.37	31.12	4.30	8.12
			(>360)	(20.84)	(1.89)	(7.78)	(14.77)	(31.16)	(4.30)	(8.15)
(IVc) $C_{25}H_{27}Cl_6Cu_2N_8O_{10}P_2S_{14}$	1450.2	Deep Brown	76	2069	1.82	7.45	14.62	30.55	4.25	8.76
			(>360)	(20.71)	(1.88)	(7.73)	(14.67)	(30.96)	(4.27)	(8.76)
(IV_d) $C_{25}H_{19}Cl_2N_{12}O_{18}P_2Pd_2S_{14}$	1570.09	Black	79	19.11	1.21	10.70	4.52	28.46	3.94	—
			(>360)	(19.12)	(1.22)	(10.71)	(4.52)	(28.59)	(3.95)	

TABLE II Characteristic IR Stretching Vibration Bands (cm^{-1})^{a} of the Ligand (III) and Its Metal Complexes (IV$_{a}$-IV$_{d}$)

Compd.	$\nu_{(OH)}$	$\nu_{(NH)}$	$\nu_{(C=N)}$	$\nu_{(C=C)}$	$\nu_{(SO2)asym.}$	$\nu_{(P-N)}$	$\nu_{(SO2)}$ sym	$\nu_{(C-S)}$	$\nu_{(PNP)}$	$\nu_{(C-S)}$	$\nu_{(P-S)}$	$\nu_{(P-Cl)}$	$\nu_{(M-N)}$	$\nu_{(M-Cl)}$	$\nu_{(M-O)}$
III	—	3168 br	1538 m	1435 m	1401 s	1162 m	1080 m	963 m	893m, 817m	829 w	626 m	651 m	—	—	—
IV$_{a}$	3486 br	—	1600 s	1406 m	1392 m	1134 m	1060 s	924 s	860w, 920 s	888 m	607 w	521 m	480 w	318 w	239 m
IV$_{b}$	3475 br	—	1614 s	1410 m	1378 m	1127 m	1072 v. s	1000.s	872 w, 922 w	893 w	605 m	532 m	482 w	315 m	238 m
IV$_{c}$	3427 br	—	1606 s	1404 m	1390 m	1133 m	1070s	1022 s	832 w, 906 w	897 w	604 m	490 m	530 w	270 m	254 m
IV$_{d}$	3424 br	—	1601 m	1405 s	1379 m	1164 m	1068 v. s	1022 s	890 w, 933 w	897 w	609 s	488 m	570 w	—	261 s

[a] v. s = very strong; s = strong; m = medium; w = weak; br = broad.

(72%) and m/z 161 (76%). The other possible fragmentations are given in Scheme 2.



SCHEME 2 Possible fragmentation pathways of **III** ligand.

Spectrophotometric Measurements of Solution Stoichiometry

The absorption values of the Co^{2+}, Ni^{2+}, Cu^{2+}, and Pd(II) complexes are shown in Table III. The diagrams in Figure 1, consist of two linear portions intersecting at 1: 2 [ligand]/[M^{2+}], where M^{2+} corresponding to Co^{2+}, Ni^{2+}, Cu^{2+}, and Pd(II) respectively, indicating the formation of 2 M: 1 L species.[7] 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^{2+}, Ni^{2+}, Cu^{2+}, and Pd(II), we investigated these systems using

TABLE III Absorption Data of Ligand (III) Solution with the Addition of Metal M^{2+} (M^{2+} = Cu) Solution, Where [Cu_2Cl_4(III)] (IV_c)

Molar ratio(M^{+2}: III)	Conc. of III (10^{-4}M)	Conc. of III (10^{-4}M)	Cu(II)
0	0	2.0	0.159
2:0.25	0.25	2.0	0.163
2:0.50	0.50	2.0	0.170
2:0.75	0.75	2.0	0.174
2:1.00	1.0	2.0	0.180
2:1.25	1.25	2.0	0.181
2:1. 50	1.50	2.0	0.182
2:1.75	1.75	2.0	0.182
2:2.00	2.0	2.0	0.182
2:2.25	2.25	2.0	0.183
2:2.50	2.50	2.0	0.183
2:0.75	2.75	2.0	0.183
2:3.00	3.0	2.0	0.183

conductometric titration method.[7] In this method, 50 ml (10^{-4}M) of M(II), where M(II) is Co(II), Ni(II), and Cu(II) solution in absolute ethanol was titrated with (10^{-3}M) of ligand solution absolute ethanol at room temperature 25^{o}C and represented in Figure 2. 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 a rises the conductivity.

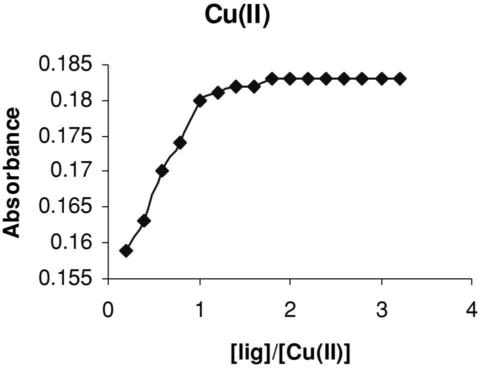


FIGURE 1 Results of molar ratio method for Cu(II) complex.

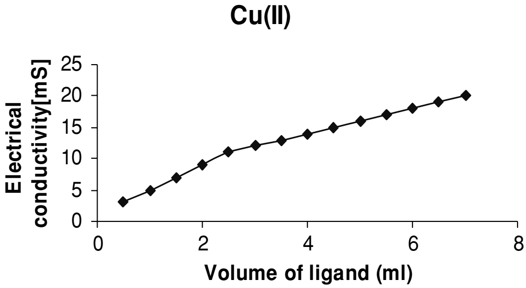
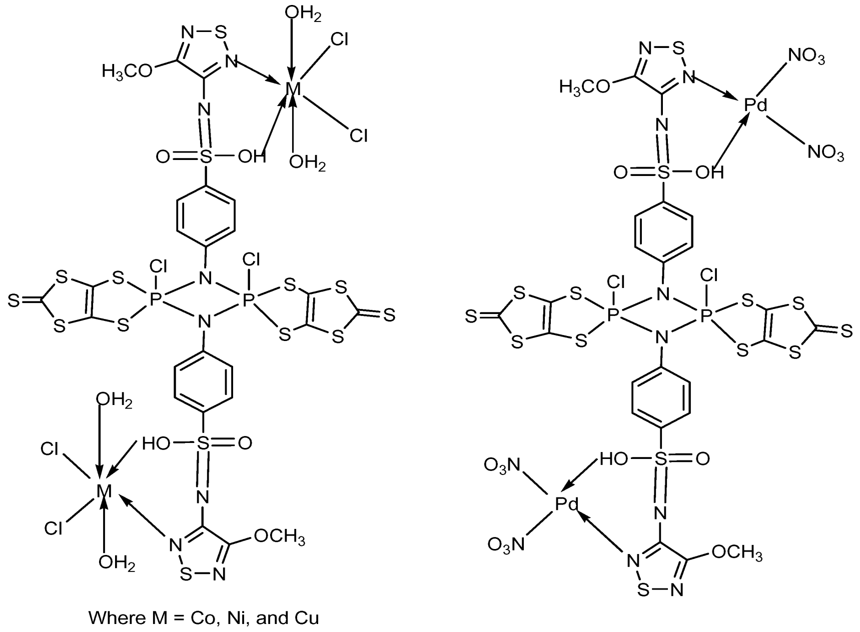


FIGURE 2 Conductometric titrations for Cu(II) complex.

Metal Complexes

All the complexes are polycrystalline solids and the elemental analysis results (Table I) agree well with the binuclear structure shown in Scheme 3. 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



SCHEME 3 Suggested structures of **III** metal complexes.

that the compounds were pure. All the complexes have high melting points (>360°C) suggesting the existence of a strong covalent bonding between the Co(II), Ni(II), Cu(II), or Pd(II) ions and the ligand under investigation.

The chemical behavior of **III** towards transition-metal cations was our goal in this article. The metal cations selected for this purpose were Co(II), Ni(II), Cu(II), and Pd(II). When a mixture of one mol of III in acetonitrile was reacted with two moles of the metal salts in acetonitrile, a change in color was observed and the complex compounds precipitated.[7] The products were purified by washing with acetonitrile, and gave elemental analysis compatible with the general formula:

$$[M_2X_4III(H_2O)_m], \tag{1}$$

where:

M(II)	X^-	m
Co	Cl	4
Ni	Cl	4
Cu	Cl	4
Pd	NO_3	0

Accordingly, the complexes are prepared following the general equation:

$$2\ MX_2 + III = H_2O \xrightarrow[\text{reflux for 2hours}]{\text{acetonitrile (solvent)}} [M_2X_4III\left(H_2O\right)_m] \tag{2}$$

where;

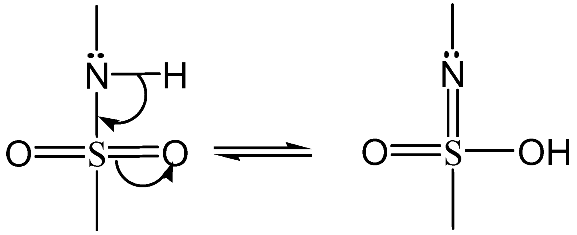
M(II)	X^-	m
Co	Cl	4
Ni	Cl	4
Cu	Cl	4
Pd	NO_3	0

The analytical data of the isolated complexes are listed in Table I.

Further, the proposed structures of the complexes of III is confirmed using different physico-chemical tools such as IR, molar conductance, UV-Vis, molar ratio, ESR, magnetic moment, conductometric titration, and electrical conductivity measurements. Biological activities of III and its metal complexes were done and compared with standard drugs.

IR Spectra

A comparative study of the IR spectra of the complexes with that of the free ligand and those of the complexes of related ligands gives some positive information regarding the binding sites of the sulfadrug-cyclodiphosph(V)azane. The IR data are listed in Table II. The SO_2 group modes of the ligand appear as medium to small bands at 1401 cm^{-1} (ν_{asym}) and 1080 cm^{-1} (ν_{sym}). In the complexes, the asymmetric and symmetric modes are shifted to 1378–1392 cm^{-1} and 1060–1072 cm^{-1} for the asymmetric and symmetric modes, respectively, upon coordination to the transition metals.[8] The stretching vibration band ν(NH) of the sulfonamide group, which in the free ligand is found at about 3183cm^{-1}, disappeared or was hidden under the broad bands at 3486–3324 cm^{-1} in the spectra of the isolated complexes, as the result of the presence of coordinated water molecules. The presence of coordinated water molecules renders it difficult to confirm the enolization of the sulfonamide group. The blue shift of the SO_2 stretching vibration to lower frequencies may be attributed to the transformation of the sulfonamide to the enol form as a result of complex formation to give a more stable six-membered ring. This transformation would result in the loss of the amide proton and the appearance of the absorption peak for enol ν(OH) stretching mode at 2922–2976 cm^{-1} for the complexes, together with a change in position and intensities of the sulfone group. This is supported by the ^1H NMR data. The enolic OH group is formed through the following tautomerism.[4,5,9]



The lower frequencies of the enolic OH groups can be taken as evidence for the participation of this group in complex formation. The strong band located at 1638 cm^{-1} is assigned to the ν(C=N) stretching vibrations of thiadiazole N atom. After complexation, this band is shifted to lower wavenumbers (24–38 cm^{-1}), indicating coordination via the thiadiazole N atom, as previously reported. [10] However, a medium intensity band in the 480−570 cm^{-1} region may reasonably be assigned to the M-N stretching vibration.[11] Bands appearing in the regions 2880−2920 and 1410−1440 cm^{-1} in all the complexes may be due to ν(C—H) and δ(C—H), respectively. The spectrum of $[Pd_2(III)(NO_3)_2]$ shows bands at 1450 cm^{-1} (υ_1), 1030 cm^{-1} (υ_2), 1362 cm^{-1} (υ_4), and 710 cm^{-1} (υ_5) with υ_1–υ_4 separation of 88 cm^{-1}, characteristic of monodentate nitrato group.[12] Bands appearing in the chloro complexes in the regions 270−318 cm^{-1} are assignable to ν(M—Cl).[11] Another band appeared between 230 and 240 cm^{-1}, which is assigned to the interaction of enolic sulfonamide OH oxygen to the metal atom, i.e., the stretching vibrationsν(M—O).[7] The appearance of a medium-to-strong band in the stretching vibration region between 820–860 $cm^{-1}$and 780–794 cm^{-1} in the spectra of the metal complexes were attributed to coordinated water molecules.[13] The band at 1375−1378 cm^{-1} in all the complexes is due to the $\nu(CH_3)$ frequency, is not affected upon complexation. The aliphatic protons are not greatly affected upon complexation. This is supported with the observed characteristic $\nu_{M—O}$ band. Moreover, the characteristic vibrational bands corresponding to the ν_{PNP}, $\nu_{P—N}$, $\nu_{P—S}$, $\nu_{P—Cl}$, $\nu_{C=S}$, $\nu_{C=C}$ and $\nu_{C—S}$ which were associated with all the complexes under investigation are given in Table II. It is obvious from the IR data that **III** behaves as a neutral bidentate ligand coordinated to the metal ions through the thiadiazole N and enolic sulfonamide OH atoms.

^{1}H and ^{31}P–NMR Spectra

The ^{1}H–NMR spectrum of the diamagnetic Pd(II) complex showed the same characteristic proton signals for the **III** ligand and the data are listed in Table IV. The signal characteristic for amide —NH proton (δ = 7.72 ppm) disappeared in the spectrum of the isolated Pd(II) complex and a new band appeared at δ = 11.11 ppm. The absence of this signal is attributed to the transformation of the amide-NH group to the enolic form. This is also supported by the disappearance of the band at δ = 11.11 ppm when using deuterated solvent.[9] The ^{31}P NMR of the

TABLE IV ^{1}H and ^{31}P-NMR Spectra of III and Its Pd(II) Complex

	δ,ppm				
	^{1}H -NMR				^{31}P-NMR
	OH	NH	ArH	$-OCH_3$	phosphazo ring
III	—	10.54	7.20	3.47	25.93
$[Pd_2(NO_3)_4(III)]$	11.11	—	7.67	3.82	24.32

Pd(II) complex records a signal at $\delta = 24.32$ ppm, which supports the phosphazo ring structure**.**

From the above IR and ^1H NMR studies, we suggest that the ligand **III** is present in the complexes in the enol form.

Magnetic and Electronic Spectral Studies

On complexation the lower-energy band observed at 355 nm in the spectrum of the free ligand **III**, which was assigned to n-π^* transition is shifted to a red shift, while the other one at 284 nm of the $\pi - \pi^*$ transition is slightly shifted to a blue shift.

The magnetic susceptibility measurement at room temperature of the green Co(II) complex $\mathbf{IV_a}$, gave magnetic moment value μ_{eff} of 5.14 B.M.,[11] this high value may be due to orbital contribution corresponding to three unpaired electrons are expected for a week field ligand. 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. [11] The peaks observed at 255 nm, 310 nm, and 380−405 nm regions, were assigned to $\pi \rightarrow \pi^*$ and n→ π^* transitions, respectively. Finally, the low value of molar conductance (11.33 $\Omega^{-1}cm^2\ mol^{-1}$**)** suggests a non-electrolytic nature of this complex in DMSO.[12]

The electronic spectrum of the Ni (II) complex $\mathbf{IV_b}$ shows absorption band at 702 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 710 nm band have been assigned to spin forbidden bands.[11] The value of molar conductance in DMSO (10.34 $\Omega^{-1}cm^2mol^{-1}$) indicating a non electrolytic nature around the Ni (II) ion.[11] Also, the value of magnetic moment (2.87 B. M.) is taken as additional evidence for the presence of octahedral geometry around the Ni(II) ion. [11]

The Cu(II) complex $\mathbf{IV_c}$ gave a band at 560 nm, suggesting the existence of a transition from $d_{xy} \rightarrow d_z^2$ and $d_{xz} \rightarrow d_{yz}$ transfer to the antibonding and half-filled $d_x^2 - d_y^2$ level which is consistent with an octahedral configuration.[11] The observed magnetic moment of the Cu(II) complex is 1.76 B.M.,[11] which confirms the octahedral structure of this complex. Also, the value of molar conductance in DMSO (8.20 $\Omega^{-1}cm^2mol^{-1}$) suggests a non-electrolytic nature of this complex.[12]

Palladium complex **($\mathbf{IV_d}$)** has three spin allowed singlet–singlet d–d transitions, which are $^1A_1 \rightarrow {}^1A_2$ (662 nm), $^1A_1 \rightarrow {}^1B_1$ (495 nm), and $^1A_1 \rightarrow {}^1E$ (443 nm).[14] These transitions are from the lower lying d orbital to the empty $_{dx2-y2}$ 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 the Pd(II) complex (6.93 $\Omega^{-1}cm^2mol^{-1}$**)** indicates that this complex in DMSO is non electrolyte in nature. [12] Also, the diamagnetic nature of this complex is taken as additional evidence for the presence of square-planar geometry around the Pd(II) ion. [13]

ESR Spectrum of Cu(II) Complex

X-band ESR spectrum of the Cu(II) ($\mathbf{IV_c}$) complex, was recorded in the solid state at 25°C. The spectrum exhibits one broad band with $g = 2.11$ for complex ($\mathbf{IV_c}$). The shape of the spectrum is consistent with the octahedral geometry around the Cu(II) environment in the complex ($\mathbf{IV_c}$).[15]

Thermal Studies

Thermogravimetric studies (TGA) for the complexes were carried out within a temperature range from room temperature up to 1000°C. TGA results are in a good agreement with the suggested formulae resulted from microanalyses data (Table I). The determined temperature ranges and percent losses in mass of the solid complexes on heating are given in Table V, which revealed the following findings:

The Co(II) complex of **III** ($\mathbf{IV_a}$) gives a decomposition pattern as follows; the first stage is one step within the temperature range of 30–175°C, representing the loss of four coordinated water and HCl gas with a found mass loss of 7.34% (calcd. 7.53%). The second stage is four steps between (175–1000°C) representing the decomposition of the organic part with losses of 3HCl gas with found mass loss of 82.45% (calcd. 82.07%). At a temperature higher than 1000°C, and at the end of the thermogram, the metal oxide 2CoO was the residue 10.21% (calcd. 10.40%), which is in good agreement with the calculated metal content obtained and the results of elemental analyses (Table I).

The thermogram of the Ni(II) complex of **III** ($\mathbf{IV_b}$) shows that the first weight loss is between 125 and 230°C representing the loss of four coordinated water molecules and HCl gas with a found mass loss of 7.52% (calcd. 7.53%) and second stage at (230–1000°C) representing the decomposition of the organic part in addition to the loss of 3HCl with a found mass loss of 82.14% (calcd. 82.10%) leaving behind nickel oxide as the product of decomposition, found 10.34% (calcd. 10.37%).

The Cu(II) complex of **III** ($\mathbf{IV_c}$) is thermally decomposed in two stages. The first stage corresponds to a mass loss of 14.64% (calcd. 14.72%) within the temperature range 25–240°C represents the loss of four coordinated water, 3 HCl and O_2 gases. The second stage, 240–1000°C with a found mass loss of 74.53% (calcd. 74.31%), is reasonably accounted for the decomposition of the organic part of the complex and HCl gas leaving out 2CuO as a residue with a found mass loss of 10.83% (calcd. 10.97%).

TABLE V Thermonanalytical Results TG of the Metal Complexes (IV_{a-d})

Comp. no.	Complex	TG range (°C)	Found (calcd. %)		Assignment
			Mass loss	Total mass loss	
IV_a	$[Co_2(III)(Cl)_4(H_2O)_4]$	30–175	7.34 (7.53)	—	Loss of four coordinated H_2O and HCl
		175–1000	82.45 (82.07)	89.79 (89.6)	Loss of 3HCl, organic part of the complex and formation of 2CoO.
IV_b	$[Ni_2(III)(Cl)_4(H_2O)_4]$	125–230	7.52 (7.53)	—	Loss of four coordinated H_2O and HCl
		230–1000	82.14 (82.10)	89.66 (89.63)	Loss of 3HCI, organic part of the complex and formation of 2NiO.
IV_c	$[Cu_2(III)(Cl)_4(H_2O)_4]$	25–240	14.64 (14.72)	—	Loss of four coordinated H_2O, 3HCl and O_2
		240–1000	74.53 (74.31)	89.17 (89.03)	Loss of HCl, organic part of the complex and formation of 2CuO.
IV_d	$[Pd_2(III)(NO_3)_4]$	30–245	10.00(10.06)	—	Loss of $2HNO_3$ and O_2
		245–1000	74.57(74.35)	84.57 (84.41)	Loss of two HNO_3, organic part of the complex and formation of 2PdO.

The Pd(II) complex of **III ($\mathbf{IV_d}$)** is thermally decomposed in two stages. The first stage corresponds to a mass loss of 10.00% (calcd. 10.06%) within the temperature range 30–245°C represents the loss of two nitric acid and O_2 gases. The second stage, 230–1000°C with a found mass loss of 74.57% (calcd. 74.35%), is reasonably accounted for the decomposition of the organic part of the complex and HNO_3 gas leaving out 2PdO as a residue with a found mass loss of 15.43% (calcd. 15.59%).

From the above thermogravimetric analyses, the overall weight losses for the Co(II), Ni(II), Cu(II) and Pd(II) complexes agree well with the proposed formulae obtained by elemental analyses, IR, ^{1}H and ^{31}P NMR, EPR, solid reflectance, magnetic susceptibility molar ratio method, and conductometric titration measurements.

From the above findings, we propose that the coordination occurs through the nitrogen of the heterocyclic ring and the enolic OH group to give the structures shown in Scheme 3.

Solid-State Electrical Conductivity

Figure 3 shows the relation between log σ against $1/T$ for (III) 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 π-electron delocalization of the ligand.[20] The observed conductivities follow the order Co < Ni < Cu < Pd. Theoretically, if we consider the charge/radii, the stability of the metal complexes

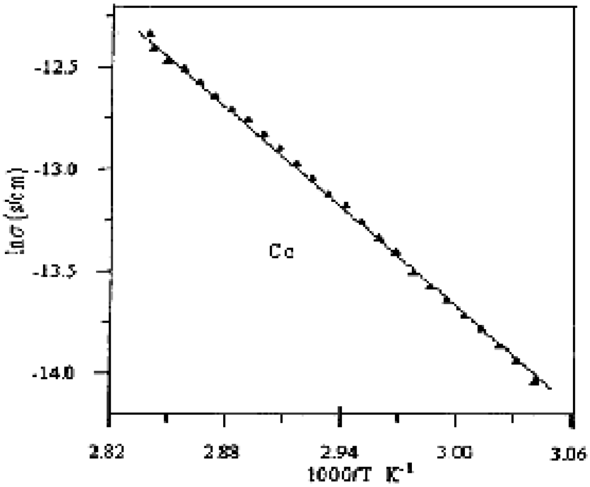


FIGURE 3 Plots of In σ versus 1000/T for Co^{2+} complex (IV_a).

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[21] as given in (Table VI). To explain the conduction mechanism of the ligand and its complexes, it is necessary to determine the mobility of charge carriers μ. If the density of charge carriers is known, then the mobility can be calculated using the relation $\sigma = eN$m, *e*is the electron charge. The charge carrier concentration was determined using the relation,

$$n = 2[2\mu m * kT/h^2]^{1/2} \exp(-E/kT), \tag{3}$$

where m^* is the effective mass of charge carrier. The calculated mobilities are ranged from 10^{-5} to 10^{-9} cm^2/Vs, suggesting that the conduction of sulfadrug-cyclodiphos (V)azane ligand and its metal complexes takes place by hopping mechanism.[22]

Biological Activity

The disc diffusion method was used to measure the antimicrobial activity of the complexes.[23] 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 III, its complexes and traivid and tavinic (as standard compounds), were tested against bacteria because bacteriums can achieve resistance to antibiotics through biochemical and morphological modifications.[24] 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 VII. The data obtained reflect the following findings.

TABLE VI Values of the Electrical Conductivity (σ) and Thermal Activation Energy of the Ligand (III) and Its Co(II), Ni(II), Cu(II), and Pd(II) Complexes at 303 K

Compound	σ(Ohm^{-1} cm^{-1})	E(eV)	n(cm^{-3})
III	1.53×10^{-8}	0.32	9.26×10^{19}
Co_2(III)Cl_4	1.72×10^{-8}	0.38	12.85×10^{18}
Ni_2(III)Cl_4	2.13×10^{-8}	0.43	1.74×10^{18}
Cu_2(III)Cl_4	2.62×10^{-8}	0.56	1.29×10^{16}
Pd_2(III) $(NO_3)_4$	3.24×10^{-8}	0.76	0.79×10^{16}

1. The III 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 isoxazole-N and the enolic OH of sulfonamide groups, which may play an important role in the antibacterial activity,[25] as well as the presence of two imine groups, which is important in elucidating the mechanism of transformation reaction in biological systems.[26]
2. Antibacterial activity of the complexes towards the different organisms shows a high-to-moderate activity.
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.[26]

EXPERIMENTAL

All chemicals used were of analytical reagent grade. They included $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, and $Pd(NO_3)_2.2H_2O$, sulfametrole and phosphorus pentachloride supplied from BDH. The solvents used were acetonitrile, $CHCl_3$, acetone, ethanol, dimethyformamide (DMF), tetrahydrofuran (THF), methanol, ethyl acetate, diethyl ether, benzene, *n*-hexane, and deutrated dimethyl sulfoxide (DMSO). The 1,3-dithiole-2-thione-4,5-disodiumthiolate (II) was prepared by the literature method.[23]

Preparation of Ligand

A solution of 1,3-dithiole-2-thione-4,5-disodiumthiolate **(II)** (2.42 g, 0.01 mmol) was added to a well-stirred mixture of 1,3-di-[N_1-4-methoxy-1,2,5-thiadiazole-3-yl-sulfanilamide]-2,2,2,4,4,4-hexachlorocyclodiphosph(V)azane **(I)** (4.21 g, 0.005 mmol) as a base in 100 ml of acetonitrile. After completing the addition, the reaction mixture was heated under reflux for 3 h. The solid formed (sodium chloride) was filtered off, and the filtrate was evaporated under vacuum to give a solid compound that was recrystallized from DMF to obtain a red crystalline compound **(III)**. The whole process of the chemical reactions and the structures of compounds**I**, **II** and **III** are shown in Scheme 1.

Preparation of Complexes

A hot solution (60°C) of the metal salts [$CoCl_2{\cdot}6H_2O$ (0.47 g; 0.002 mol)], [$NiCl_2{\cdot}6H_2O$ (0.47 g; 0.002 mol)], [$CuCl_2{\cdot}2H_2O$ (0.34 g; 0.002 mol)], or

TABLE VII Antimicrobial Activity of III and Corresponding Metal Complexes

	III (mg/mL)			Co(II) (mg/mL)			[Ni(II) (mg/mL)			[Cu(II) (mg/mL)			Tavenic[a] (mg/mL)			Traivid[a] (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.	++	++	—	++	++	+	++	++	+	++	+	+	+++	++	+	++	+	—
Fungus Candida	—	—	—	+	—	—	+	—	—	+	—	—	—	—	—	—	—	—
E.C.	++	+	+	+++	++	+	++	++	+	++	++	+	+++	++	+	++	+	—

[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*; ES. = *Escherichia coli*; and P. A. = *Pseudomonas aereuginosa*.

[$Pd(NO_3)_2{\cdot}2H_2O$ (0.50 g; 0.002 mol)]in 50 mL acetonitrile was added dropwise to a hot solution of III (1.09 g; 0.001 mol) in 100 mL acetonitrile 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 resultant polycrystalline solid products **(IV_{a-d})** were filtered and recrystallized from DMF. The analytical data of both ligand and its metal complexes are listed in Table I.

METHODS

Elemental analyses were determined at the Microanalytical Unit of Cairo University (Egypt) using CHNS-932 (LECO) Vario EL elemental analyzers. The phosphorus content was determined gravimetrically as phosphoammonium molybdate.[24] Analyses of metal ions after the dissolution of the solid complex in hot concentrated nitric acid, HNO_3, then diluting with distilled water and filtering to remove the precipitated ligand. The solution was neutralized with ammonia solution and the metal ions were then titrated with EDTA.[25] The infrared spectra were recorded on a Shimadzu FT-IR spectrometer using KBr discs. ^1H NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer. The samples were dissolved in DMSO-d6 using tetramethylsilane as an internal standard. ^{31}P NMR spectra were run, relative to external H_3PO_4 (85%), with a Varian FT-80 spectrometer at 365 MHz. The solid reflectance spectra were measured using a Shimadzu PC3101 UV-VIS-NIR scanning spectrophotometer. The mass spectra were obtained by a Shimadzu-Ge-Ms-Qp 100 EX mass spectrometer (Shimadzu, Japan), using the direct inlet system, at Cairo University (Egypt). The conductometric measurements in solutions were carried out using conductivity TDS model 72. The magnetic susceptibilities of the complexes in the solid state were recorded on a Sherwood Scientific magnetic susceptibility balance. Diamagnetic corrections were calculated from Pascal's constants. ESR spectra recorded on the Bruker, Model: EMX, X-band spectrometer. The magnetic field was calibrated with a 2,2-diphenyl-1-picrylhydrazyl sample. The thermogravimetric analyses (TGA) were recorded on a Shimadzu TGA-50H. TGA was carried out in a dynamic nitrogen atmosphere (20 mL min^{-1}) at a heating rate of 10°C min^{-1}. The ultraviolet spectra were recorded on a Perkin Elmer Lambda 3B UV-VIS spectrophotometer. Conductivity measurements were made on discs having 1-mm thickness of **III**, and its complexes were sandwiched between two copper electrodes. The conductivity cell used was the same as that reported before.[26] The electrical conductivity was measured in the temperature range 30°C –150°C.

The activation energies were calculated using the equation $\sigma = \sigma^\circ$ exp (-*E*/2*kT*). The biological activity experiments were carried out at Bab-Al-Sheria University Hospital (Al-Azhar Microbiology Laboratory University).

CONCLUSION

From all of the above observations, the structure of these complexes may be interpreted in accordance with complexes of ligand III with a similar distribution of sites such coordination hexachlorocyclodiphosph(V)azanes of sulfadimidine and sulfametrole.[5] The structural information from these complexes is in agreement with the data reported in this article based on the IR, molar conductance, ^{1}H, ^{31}P NMR, UV-Vis, mass, thermal analysis, and magnetic-moment measurements. The Co(II), Ni(II), and Cu(II) complexes of this ligand have octahedral structure. III ligand always coordinates via the isoxazole-N and enolic sulfonamide-OH forming two-binding chelating sites.

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