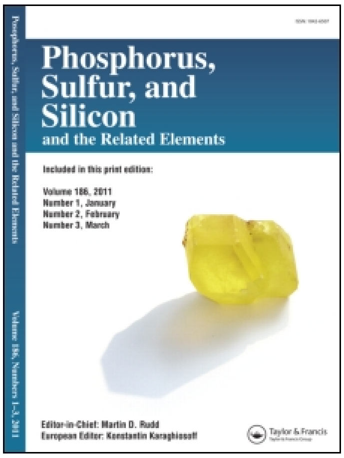

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New Cyclodiphosph(V)azane Complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and UO_2 (II): Preparation, Characterization, and Biological Activity Studies

Gehad G. Mohamed[a]
[a] Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

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New Cyclodiphosph(V)azane Complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and UO_2 (II): Preparation, Characterization, and Biological Activity Studies

Gehad G. Mohamed
Chemistry Department, Faculty of Science, Cairo University,
Giza, Egypt

Hexachlorocyclodiphosph(V)azane of sulfamethoxazole, H_2L, reacts with stoichiometric amounts of transition metal salts such as Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and UO_2(II) to afford coloured complexes in a moderate to high yield. The structure of the isolated complexes was suggested based on elemental analyses, IR, molar conductance, UV-Vis, ^1H NMR, mass spectra, solid reflectance, magnetic susceptibility measurements, and thermogravimetric analysis (TGA). From the elemental analyses data, 1:2 (H_2L:M) ratio is suggested and the complexes are found to have the general formula $[(MX_n)_2(H_2L)(H_2O)_m]$ where M = Fe(III) (X = Cl, n = 3, m = 2), Co(II) (X = Cl, n = 2, m = 4), Ni(II) (X = Cl, n = 2, m = 4), Cu(II) (X = Cl, n = 2, m = 4), Zn(II) (X = Cl, n = 2, m = 4), and UO_2(II) (X = NO_3, n = 2, m = 0). The IR and ^1H NMR spectral data revealed that H_2L behaves as a neutral bidentate ligand coordinated to the metal ions through enolic sulfonamide OH and isoxazole 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. The thermal data reveal that the coordinated water and anion molecules are lost in the first two steps while the ligand molecules are lost in the subsequent steps, leaving metal oxide residues. Different thermodynamic activation parameters are calculated using the Coats-Redfern equation. The prepared complexes showed high to moderate bactericidal activity compared with the ligand.

Keywords Phosphorus pentachloride; sulfamethoxazole; transition metal complexes

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.[1,2] Heterocycles with P—C, P—N, P—O, and P—S bonds, in addition to their great biochemical and commercial importance,[3,4] play a major role in some substitution mechanisms

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Address correspondence to Gehad G. Mohamed, Chemistry Department, Cairo University, Giza, Egypt. E-mail: ggenidy@hotmail.com

as intermediates or as transition states.[3,4] Also, some *P*-containing heterocycles had been found to be potentially carcinostatics[3] among other pharmacological activities. The introduction of tervalent *P* centers in the ring enhanced the versatility of the heterocycles in complexing with both hard and soft metals. Since the tervalent *P* centers could stabilize transition metals in low oxidation states, such complexes could be potential homogeneous or phase-transfer catalysts in various organic transformations.[3]

There is considerable current interest in compounds containing spiro and ansaorganic P rings.[5] Although the ammonolysis of some 1,3-diaryl-2,4-dichlorocyclodiphosph(V)azanes had been investigated in some detail,[5] little was known about the interaction of hexachlorocyclodiphosph(V)azanes with bifunctional reagents.[5] The reaction of bifunctional reagents with cyclodiphosph(V)azanes could give rise in principle to four types of structures named spiro, ansa, cross-linking, and only one functionality attached, while the other remains free. Spiro, ansa, and cross-linking structures of phosphazanes were now well-studied synthetically, spectroscopically, and crystallographicaly.[5] The reaction of hexachlorocyclo-diphosph(V)azanes with amino compounds, active-methylene-containing compounds, and bifunctional reagents had been investigated in some details.[6,7] Little was known about the interaction of hexachlorocyclodiphosph(V)azanes with therapeutic sulfonamides.[6,7]

Sulfonamides were the oldest class of antimicrobials and were still the drug of choice for many diseases such as cancer and tuberculosis.[8] Cyclophosphamide and its derivatives were examples of phosphorus compounds which were one of the most effective anticancer agents with proven activity against a large variety of human cancers.[9] Hexachlorocyclodiphosph(V)azanes of sulfonamides and their complexes had been prepared.[6,10–11] The present-work aims chiefly to prepare the metal complexes of hexachlorocyclodiphos(V)phazanes of sulfamethoxazole. In this work, novel hexachlorocyclodiphosph(V)azanes of sulfamethoxazole (H_2L) was prepared and its behavior towards some transition metal ions was studied using different techniques such as elemental analyses, IR, ^{1}H NMR, solid reflectance, molar conductance, magnetic moment, mass spectra, UV-Vis, and TGA. Also, the bactericidal activity of these compounds were studied. The proposed structure for H_2L is shown in Figure 1.

EXPERIMENTAL

All chemicals used were of analytical reagent grade. They included $FeCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2$, and

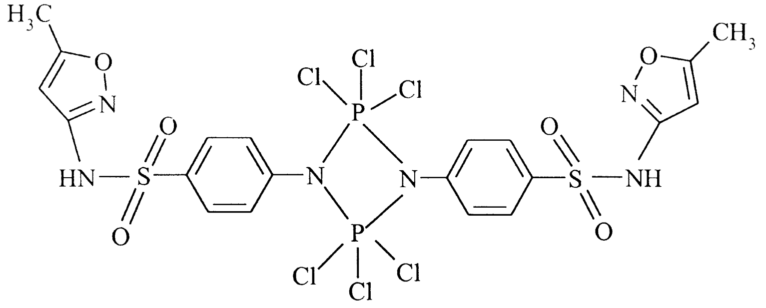


FIGURE 1 Proposed structure of H_2L ligand.

$UO_2(NO_3)_2{\cdot}2H_2O$, sulfamethoxazole, and phosphorus pentachloride supplied from BDH. The solvents used were ethanol, benzene, dimethyformamide (DMF), and deutrated dimethyl sulfoxide (DMSO).

Synthesis of Cyclodiphosph(V)azane of Sulfamethoxazole (H_2L)

The H_2L ligand was prepared using the methods of Chapmann and Kirsanov.[12] Sulfamethoxazole [4-amino-N-(5-methyl-3-isoxazolyl)-benzene sulfonamide] (0.1 mol, 28.60 g) in 100 mL cold dry benzene was added in small portions to a stirred cold solution of phosphorus pentachloride (0.1 mol, 20.85 g) in 100 mL cold dry benzene during half hour at 15°C. After the addition was completed, the reaction mixture was heated under reflux for three hours under anhydrous conditions with continuous stirring (the experiment was done in a well-ventilated area because benzene is a cancer suspect agent). After the completion of the reaction (HCl gas ceased to evolve), the reaction mixture was cooled to room temperature and the solids obtained were filtered, then washed several times with dry benzene and dry diethyl ether to give crystalline 1,3-di[(N-5-methyl-3-isoxazolyl)sulfanilamide]-2,2,2,4,4,4-hexachlorocyclodiphosph(V)azane (H_2L).

Synthesis of Complexes

A hot solution (60°C) of the metal salts (10 mmol) in 50 mL dry ethanol was added dropwise to a hot solution of sulfa drug-cyclodiphosph(V)azane (5 mmol) 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 two hours 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 analysis consistent with the proposed structures.

Instrumentation

The elemental analysis were carried out in the Microanalytical Center at Cairo University. The infrared spectra were recorded on a Shimadzu FT-IR spectrometer using KBr discs. The molar conductance measurements were carried out using a Sybron-Barnstead conductometer. ^{1}H NMR spectra were performed on a Varian Gemini 200 MHz spectrometer. The samples were dissolved in DMSO-d_6 using tetramethyl-silane as internal references. The solid reflectance spectra were measured using a Shimadzu PC3101 UV-VIS-NIR scanning spectrophotometer. The magnetic susceptibilities of the complexes in the solid state were recorded on Sherwood Scientific magnetic susceptibility balance. The TGA were recorded on a Shimadzu TGA-50H. TGA was carried out in a dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of 10°C min^{-1}. The ultraviolet spectra were recorded on a Perkin-Elmer Lambda–3B UV-VIS spectrophotometer. The mass spectra were performed using a Shimadzu-Ge-Ms-Qp 100 EX mass spectrometer using the direct inlet system. Metal contents were determined complexometrically by standard EDTA titration. The *P* content was determined gravimetrically as phospho-ammonium molybdate using the Voy method.[13] The biological activity experiments were carried out at the Microbiology Laboratory at Bab-Al-Sheria University Hospital, Al-Azhar University.

RESULTS AND DISCUSSION

In the present investigation, novel hexachlorocyclodiphosph(V)azane of sulfamethoxazole were prepared using the methods of Chapmann and Kirsanov.[12] Phosphorus pentachloride reacted in cold, dry benzene with sulfamethoxazole to give 3-di[(N′-5-methyl-3-isoxazolyl)sulfanilamide]-2,2,2,4,4,4-hexachlorocyclodi-phosph(V)azane (H_2L) in 70% yield. The assignment of the proposed structure for H_2L is based on the elemental analyses data listed in Table I. The UV spectra of H_2L in DMF showed absorption bands at 270 nm, which is characteristic for phosphazo four-membered rings.[5,7,10–11] The infrared spectra of the H_2L ligand showed the characteristic bands which are summarized in Table II. The ^{1}H NMR spectra of the ligand showed characteristic proton signals, which are listed in Table III. A broad signal appeared at $\delta = 7.65$ ppm, which is characteristic of a–NH proton signal. Further insight

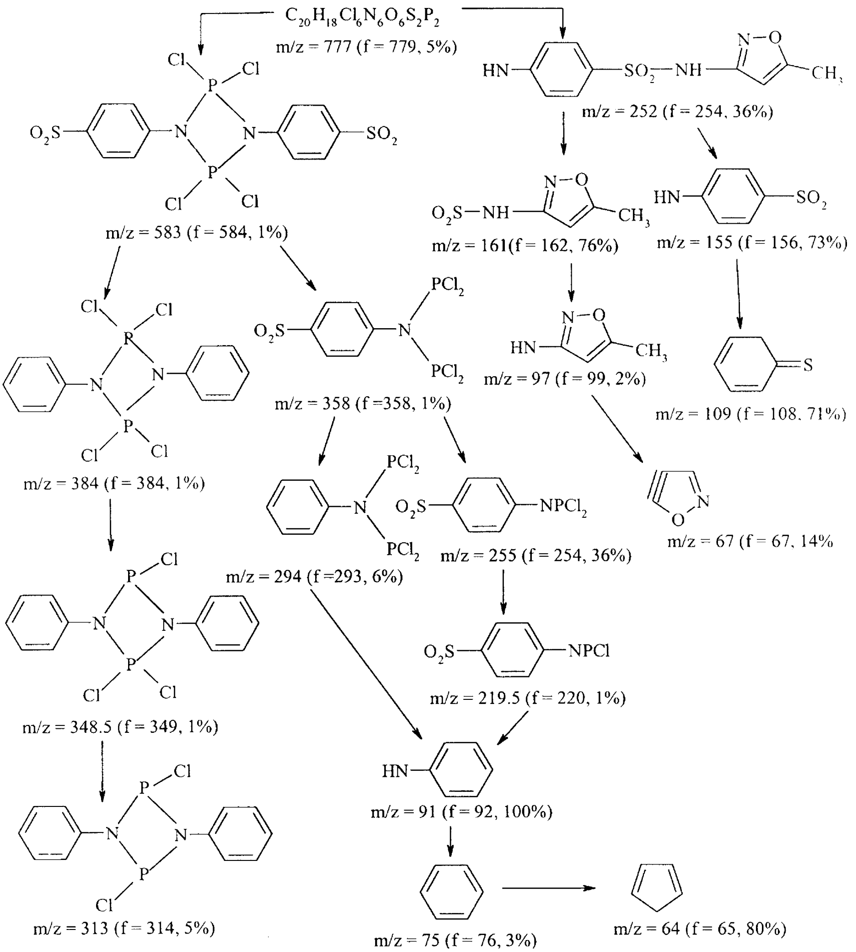
TABLE I Analytical and Physical Data of H_2L and Its Complexes

Compound	M.p. (°C)	Clour (% yield)	% Found (Calcd.) C	H	N	S	P	M	μ_{eff} (B.M.)	$\Lambda_m\ \Omega^{-1}$ $mo^{-1}\ cm^2$
H_2L	180 ± 2	White	30.50	2.65	10.61	8.05	7.65	—	—	—
$C_{20}H_{18}Cl_6N_6O_6P_2S_2$		(70)	(30.89)	(2.32)	(10.81)	(8.24)	(7.98)			
$[(FeCl_3)_2(H_2L)(H_2O)_2]$	>300	Yellow	21.41	2.26	7.03	5.31	5.63	9.52	5.20	16.52
$C_{20}H_{22}Cl_{12}Fe_2N_6O_8P_2S_2$		(54)	(21.09)	(1.93)	(7.38)	(5.62)	(5.45)	(9.84)		
$[(CoCl_2)_2(H_2L)(H_2O)_4]$	>300	Blue	21.93	2.13	7.38	5.41	5.12	10.86	4.87	17.50
$C_{20}H_{26}Cl_{10}Co_2N_6O_{10}P_2S_2$		(62)	(21.64)	(2.34)	(7.57)	(5.77)	(5.59)	(10.64)		
$[(NiCl_2)_2(H_2L)(H_2O)_4]$	>300	Green	21.42	2.56	7.20	5.90	5.22	10.42	2.95	10.40
$C_{20}H_{26}Cl_{10}N_6Ni_2O_{10}P_2S_2$		(60)	(5.77)	(21.64)	(2.34)	(7.57)	(5.59)	(10.64)		
$[(CuCl_2)_2(H_2L)(H_2O)_4]$	>300	Yellow	20.99	2.45	7.65	5.32	5.32	11.00	2.13	15.50
$C_{20}H_{26}Cl_{10}Cu_2N_6O_{10}P_2S_2$		(68)	(21.47)	(2.33)	(7.51)	(5.54)	(5.54)	(11.36)		
$[(ZnCl_2)_2(H_2L)(H_2O)_4]$	>300	White	21.78	2.53	7.18	5.49	5.26	12.01	diam.	9.87
$C_{20}H_{22}Cl_{10}N_6O_{10}P_2S_2Zn_2$		(53)	(21.41)	(2.32)	(7.46)	(5.71)	(5.53)	(11.60)		
$[(UO_2)_2(H_2L)(NO_3)_4]$	>300	Brown	15.48	1.35	5.67	3.85	4.20	—	diam.	17.35
$C_{20}H_{22}Cl_6N10O_{22}P_2S_2U_2$		(55)	(15.33)	(1.15)	(5.37)	(4.09)	(3.96)			

TABLE II IR Spectra (4000–400 cm^{-1}) of H_2L and Its Complexes. s = Strong, m = Medium, sm = Small, w = Weak, br = Broad

Compound	ν(OH) (enolic)	ν(C=N)	ν(SO$_2$) (asym)	ν(SO$_2$) (sym)	ν(P—N)	ν(P—Cl)	ν(H$_2$O) (coord.)	ν(M—O)	ν(M—N)
H_2L	—	1630 s	1350 m	1050 sm	1180 s	580 s	—	—	—
$[(FeCl_3)_2(H_2L)\text{-}(H_2O)_2]$	2984 m	1616 s	1334 m	1036 m	1168 s	590 m	836 w, 794 m	572 m	470 w
$[(CoCl_2)_2(H_2L)\text{-}(H_2O)_4]$	2850 m	1618 s	131 m	1038 s	1172 s	574 s	830 s, 790 s	550 sm	450 w
$[(NiCl_2)_2(H_2L)\text{-}(H_2O)_4]$	2950 s	1620 s	1316 m	1040 s	1170 s	578 m	860 m, 780 s	486 m	454 m
$[(CuCl_2)_2(H_2L)\text{-}(H_2O)_4]$	2932 m	1608 s	1336 m	1042 s	1174 s	574 s	820 m, 790 m	544 m	470 w
$[(UO_2)_2(H_2L)\text{-}(NO_3)_4]$	2890 m	1616 m	1334 m	1060 w	1168 m	574 s	840 m, 794 m	550 w	460 w

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 (73%) and m/z 161 (76%). The other possible fragmentations are given in Scheme 1.



SCHEME 1 Possible fragmentation pathways of H_2L ligand.

Metal Complexes

The chemical behavior of H_2L towards transition-metal cations was our goal in this article. The metal cations selected for this purpose were

TABLE III ^{1}H NMR Spectra of H_2L and Its Zn(II) Complex

	δ, ppm				
	OH	NH	ArH	CH ring	-CH_3
H_2L	—	7.65 br	7.20–7.80 (d, J = 7.5 Hz)	6.20 s	2.30 s
$(ZnCl_2)_2(H_2L)(H_2O)_4$	11.03 s	—	6.34-7.58 (d, J = 7.5 Hz)	6.09 s	2.29 s

Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and UO_2(II). When a mixture of one mole of H_2L in dry ethanol was reacted with two moles of the metal salts in dry ethanol, a change in clour was observed and the complex compounds precipitated. The products were purified by washing with dry ethanol, and gave elemental analysis compatible with the general formula $[(MX_n)_2(H_2L)(H_2O)_m]$, where M = Fe(III) (X = Cl, n = 3, m = 2); Co(II) (X = Cl, n = 2, m = 4); Ni(II) (X = Cl, n = 2, m = 4); Cu(II) (X = Cl, n = 2, m = 4); Zn(II) (X = Cl, n = 2, m = 4); and UO_2(II) (X = NO_3, n = 2, m = 0). Accordingly, the complexes are prepared following the general equation:

$$2MX_n + H_2L + mH_2O \rightarrow [(MX_n)_2(H_2L)(H_2O)_m]$$

where M = Fe(III) (X = Cl, n = 3, m = 2); Co(II) (X = Cl, n = 2, m = 4); Ni(II) (X = Cl, n = 2, m = 4); Cu(II) (X = Cl, n = 2, m = 4); Zn(II) (X = Cl, n = 2, m = 4); and UO_2(II)(X = NO_3, n = 2, m = 0).

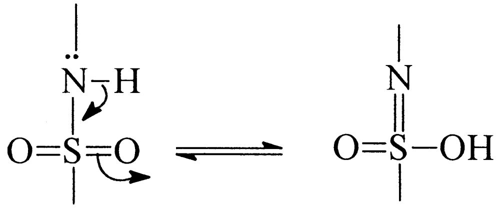
The analytical data of the isolated complexes are listed in Table I. Further, the proposed structures of the complexes of H_2L is confirmed using different physico-chemical tools such as IR, molar conductance, UV-Vis, solid reflectance, magnetic moment, and thermal analysis. Biological activities of H_2L 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 sulfamethoxazole-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 1350 cm^{-1} (ν_{asym}) and 1050 cm^{-1} (ν_{sym}). In the complexes, the asymmetric and symmetric modes are shifted to 1336–1316 cm^{-1} and 1060–1036 cm^{-1} for the asymmetric and symmetric modes, respectively, upon coordination to the transition metals.[14]

The stretching vibration band ν(NH) of the sulfonamide group, which in the free ligand is found at about 3150 cm^{-1}, disappeared or was hidden under the broad bands at 3492–3080 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 2850–2984 cm^{-1} for the complexes, together with a change in position and intensities of the sulfone group. This is supported by the ^{1}H NMR data. The enolic OH group is formed through the following tautomerism:[6,7,11]



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 1630 cm^{-1} is assigned to the ν(C=N) stretching vibrations of isoxazole N atom. After complexation, this band is shifted to lower wavenumbers (10–22 cm^{-1}), indicating coordination via the isoxazole N atom, as previously reported.[15]

In all of the metal complexes, there are new medium-to-weak bands which appeared at lower frequencies between 486–572 and 450–470 cm^{-1}, which were assigned to ν(M—O) and ν(M—N) stretching modes.[16] The appearance of a medium-to-strong bands in the stretching vibration region between 820–860 and 780–794 cm^{-1} in the spectra of the metal complexes were attributed to coordinated water molecules.[17] In the UO_2(II) complex, two additional bands at 940 and 835 cm^{-1}, were assigned to $\nu_{as}(UO_2)$ and $\nu_s(UO_2)$ modes, respectively. This observation indicates that the O=U=O moiety virtually exists in this complex.

It is obvious from the IR data that H_2L behaves as a neutral bidentate ligand coordinated to the metal ions through the isoxazole N and enolic sulfonamide OH atoms.

Molar Conductance Data

The molar conductance data of the complexes ($\Lambda_m = 9.87$–$17.5\ \Omega^{-1}\mathrm{mo}^{-1}\ \mathrm{cm}^2$) in 10^{-3} M DMF solutions at 25°C, listed in Table I, revealed that the complexes are nonelectrolytes.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of the diamagnetic Zn(II) complex showed the same characteristic proton signals for the H_2L ligand and the data are listed in Table III. The signal characteristic for amide –NH proton ($\delta =$ 7.65 ppm) disappeared in the spectrum of the isolated Zn(II) complex and a new band appeared at $\delta = 11.03$ 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 $\delta =$ 11.03 ppm when using deuterated solvent.[11]

Electronic Spectra and Magnetic Properties

The UV-Vis spectra of the complexes in DMF (1×10^{-3} M) show a sharp and intense band in the region 269–281 nm, which is characteristic of phosphazo four-membered rings.[11] 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 Fe(III), Ni(II), Cu(II), and UO_2(II) complexes further display a band in the range 360–439 nm, which might be assigned to charge-transfer transition (most probably L → M CT).[16] For the Co(II) complex, however, a d—d bands are observed at 600 and 675 nm which may attributed to the transitions $^4T_{1g}\ (F) \rightarrow^4 T_{2g}(P)$ and $^4T_{1g}\ (F) \rightarrow^4 A_{2g}\ (F)$, respectively, which is typical of octahedral structure around Co(II) ion.[18]

The diffuse-reflectance spectra of the complexes show bands at 249–250 nm, which are associated with interligand transitions.

From the diffuse reflectance spectrum of the Fe(III) complex, it is observed that a band at 22,779 cm^{-1} may be assigned to the $^6A_{1g} \rightarrow T_{2g}(G)$ transition in octahedral geometry.[19–21] Two bands, also, observed at 15,649 and 17,482 cm^{-1}, can attribute to $^6A_{1g} \rightarrow ^5T_{1g}$ transition. The measured magnetic-moment value of 5.20 B.M. confirm octahedral geometry involving d^{2}sp^3 hybridization in the Fe(III) ion.[19–21] The diffuse reflectance spectrum of the Co(II) complex displays three bands at 13,501, 18,250, and 22,953 cm^{-1} assigned to the $^4T_{1g}\ (F) \rightarrow\ ^4T_{2g}(F)\ (\nu_1)$, $^4T_{1g}\ (F) \rightarrow ^4A_{2g}(F)\ (\nu_2)$, and $^4T_{1g} \rightarrow ^4T_{2g}(P)\ (\nu_3)$ transitions, respectively. The band observed at 26,520 cm^{-1} refers to L → M CT band. From the observed magnetic moment value ($\mu_{\mathrm{eff}} = 4.70$ B.M.) together with the band position in the solid reflectance spectra, the Co(II) complex is octahedral with largely covalent bonds between the organic ligand and Co(II) ion.[21,22]

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.[20,21] The solid reflectance spectrum of the complex shows three bands at 14,993, 17,483, and 21,552 cm^{-1}, which are assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2), and$^3A_{2g} \rightarrow {}^3T_{2g}$ (P) (ν_3) transitions, respectively, confirming the octahedral geometry of the Ni(II) complex.[23] The solid reflectance spectrum of the Cu(II) complex gave a band at 17,361 cm^{-1}, suggesting the existence of a transition from d_{xy}, d_z^2 and d_{xz}, d_{yz} transfer to the antibonding and half-filled $d_{x^2-sy^2}$ level which is consistent with an octahedral configuration.[11] The observed magnetic moment of the Cu(II) complex is 2.12 B.M., which confirms the octahedral structure of this complex.

The Zn(II) and UO_2(II) complexes are diamagnetic and analogous to similar previously published data;[11] they propose to have octahedral structure.

Thermal Studies

Thermogravimetric studies for the complexes were carried out within the temperature range from room temperature up to 1000°C. The calculated and found mass losses were listed in Table IV. Different thermodynamic parameters are calculated and listed in Table V. The determined temperature ranges and percent losses in mass of the solid complexes on heating are given in Table IV, which revealed the following findings:

The Fe(III) complex gives a decomposition pattern of two steps. The first step within the temperature range of 150–450°C, representing the loss of O_2 and 6HCl gases, and $C_{20}H_{16}Cl_6N_6O_2P_2$ molecule with a found mass loss of 78.47% (calcd. 78.91%). The energy of activation (Table V) is amounted to 60.80 kJ mole^{-1}. The second step between 450–750°C with an activation energy of 82.97 kJ mole^{-1} represents the decomposition of the remaining organic part with found mass loss of 6.92% (calcd. 7.03%) leaving Fe_2O_3 residue (found 14.61%, calcd. 14.06%).

The thermogram of the Ni(II) complex shows that the first weight loss within the temperature range 50 to 250°C representing the loss of 4 HCl and $2O_2$ gases, and $C_{18}H_{16}Cl_6N_2O_2P_2$ molecule with found mass loss of 66.85% (calcd. 66.10%) in two successive steps. The activation energies of these two steps are amounted to 54.43 and 88.94 kJ mol^{-1} for the first and second steps, respectively. The third step within the temperature range 350–700°C may attributed to the decomposition of $C_2H_2N_4O_4S_2$ molecule with found mass loss of 18.63% (calcd. 18.94%),

TABLE IV Thermogravimetric Data of H_2L Metal Complexes

Complex	TG range (*C)	DTG_{max} (*C)	% Found (Calcd.)		Assignment	Metallic residue
			Mass loss	Total mass loss		
$[(FeCl_3)_2(H_2L)\text{-}(H_2O)_2]$	150–450	320	78.47 (78.91)	85.39 (85.94)	-Loss of 6HCl, O_2 and $C_{20}H_{16}Cl_6N_6O_2P_2$.	Fe_2O_3
	450–750	560	6.92 (7.03)		-Loss of S_2O.	
$[(NiCl_2)_2(H_2L)\text{-}(H_2O)_4]$	150–350	190, 270	66.85 (66.10)	85.48 (85.04)	-Loss of 4HCl, $2O_2$ and $C_{18}H_{16}Cl_6N_2O_2P_2$.	Ni_2O_3
	350–700	490	18.63 (18.94)		-Loss of $C_2H_2N_4O_4S_2$.	
$[(CuCl_2)_2(H_2L)\text{-}(H_2O)_4]$	50–250	79, 180	19.85 (19.14)	82.41 (81.48)	-Loss of 4HCl, $2O_2$ and $C_{18}H_{16}Cl_6N_2O_2P_2$.	Cu_2SO_3
	250–950	310, 600	62.56 (62.34)		-Loss of $C_2H_2N_4O_4S_2$.	
$[(ZnCl_2)_2(H_2L)\text{-}(H_2O)_4]$	50–220	70, 180	19.50 (19.10)	86.23 (85.56)	-Loss of 4HCl and $2O_2$.	2ZnO
	220–900	310, 670	66.73 (66.46)		-Loss of $C_{20}H_{18}Cl_6N_6O_4P_2S_2$.	
$[(UO_2)_2(H_2L)\text{-}(NO_3)_4]$	40–150	70	7.68 (7.92)	65.93 (65.49)	-Loss of $2NO_2$ and O_2.	$2UO_2$
	150–800	260, 650	58.25 (57.57)		-Loss of $2NO_2$, O_2 and $C_{20}H_{18}Cl_6N_6O_6S_2P_2$.	

TABLE V Thermodynamic Data of the Thermal Decomposition of the Complexes

Complex	TG range (°C)	E^* (kJ mol^{-1})	A (S^{-1})	ΔS^* (JK^{-1} mol^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
$[(FeCl_3)_2(H_2L)(H_2O)_2]$	150–450	60.80	3.67×10^5	−23.65	85.65	75.62
	450–750	82.97	2.14×10^8	−52.82	36.46	56.12
$[(NiCl_2)_2(H_2L)(H_2O)_4]$	150–240	54.43	7.63×10^8	−30.75	78.55	94.37
	240–350	88.94	1.07×10^7	−45.76	49.76	40.53
	350–700	142.0	2.51×10^5	−87.56	122.0	102.3
$[(CuCl_2)_2(H_2L)(H_2O)_4]$	50–130	40.50	3.82×10^9	−19.98	50.23	48.56
	140–250	87.25	1.09×10^{10}	−40.95	115.2	77.35
	250–420	54.82	2.51×10^7	−66.83	203.0	115.3
	550–950	135.0	4.03×10^{12}	−57.76	183.6	85.76
$[(ZnCl_2)_2(H_2L)(H_2O)_4]$	50–120	43.55	2.15×10^7	−93.88	77.46	68.19
	150–220	65.82	5.07×10^{10}	−58.67	66.55	91.62
	220–400	137.7	2.49×10^8	−102.0	36.87	63.25
	500–900	52.87	1.82×10^{11}	−93.82	125.3	74.45
$[(UO_2)_2(H_2L)(NO_3)_4]$	40–150	51.60	1.59×10^{11}	−76.64	28.96	40.51
	150–450	62.90	4.39×10^9	−45.69	59.87	71.02
	550–800	102.0	6.55×10^7	−99.86	88.95	82.36

leaving behind Ni_2O_3 as the product of decomposition. The activation energy of this step is 142 kJ mol^{-1}.

The Cu(II) and Zn(II) complexes are thermally decomposed in four successive stages. The first and second steps correspond to a mass losses of 19.85% (calcd. 19.14%) and 19.50% (calcd. 19.10%) within the temperature range 50–250°C for the Cu(II) and Zn(II) complexes, respectively. These mass losses are accounted for the loss of 4HCl and $2O_2$ gases. The activation energies of these two steps are amounted to 40.50 and 87.25 kJ mol^{-1} (for Cu(II) complex) and 43.55 and 65.82 kJ mol^{-1} (for Zn(II) complex) for the first and second steps, respectively. The third and fourth steps, within the temperature range 220–950°C, found mass losses of 62.56% (calcd. 62.34%) and 66.73% (calcd. 66.46%) for the Cu(II) and Zn(II) complexes, respectively. These are reasonably accounted to the decomposition of the organic part of the complex leaving Cu_2SO_3 and 2ZnO as a residue with activation energies of 54.82 and 135.0 kJ mol^{-1} (for Cu(II) complex) and 137.7 and 52.87 kJ mol^{-1} (for Zn(II) complex) for the third and fourth steps, respectively.

The UO_2(II) complex gives three pattern decomposition steps. The first step, is within the temperature range of 40–150°C, may be accounted to the loss of two nitrate groups as $2NO_2$ and O_2 gases with a found mass loss of 7.68% (calcd. 7.92%). The energy of activation (Table V) is amounted to 51.60 kJ mole^{-1}. The second and third steps between 150–800°C, with an activation energies of 62.90 and

102.0 kJ mole^{-1}, represents the decomposition of the organic part of the ligand with a found mass loss of 58.25% (calcd. 57.57%) leaving a $2UO_2$ residue.

Kinetic Studies

The kinetic parameters such as activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*), and free-energy change of the decomposition (ΔG^*) were evaluated graphically by employing the Coats-Redfern relation:[24]

$$\log\left[\frac{\log\{W_r/(W_r - W)\}}{T^2}\right] = \log\left[\frac{AF}{\theta E^*} - \left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT}, \qquad (1)$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T, R is the gas constant, E is the activation energy in $kJ \cdot mol^{-1}$, θ is the heating rate, and $(1-(2RT/E^*)) \cong 1$. A plot of the left-hand side of Equation (1) against 1/T gives a slope from which E^* was calculated and A (Arrhenius constant) was determined from the intercept. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and the free energy change of activation (ΔG^*) were calculated (Table V).

According to the kinetic data obtained from DTG curves, all the complexes have negative entropy, which indicates that activated complexes have more-ordered systems than reactants. From Table V, it is obvious that the Ni(II) complex shows a higher thermal stability than those of a Cu(II) complex. This can be discussed in terms of repulsion among electron pairs in the valence shell of the central ion. The high electronegativity of Cu(II) compared to that of Ni(II) leads to a higher repulsion between bonding pairs in the valence shell of copper ion giving lower stability.[21,25]

Structural Interpretation

From all of the above observations, the structure of these complexes may be interpreted in accordance with complexes of ligands with a similar distribution of sites such coordination hexachloro-cyclodiphosph(V) azanes of sulfadimidine and sulfametrole.[11] The structural information from these complexes is in agreement with the data reported in this article based on the IR, molar conductance, ^1H NMR, UV-Vis, mass, solid reflectance, thermal analysis, and magnetic-moment measurements. Consequently, the structures proposed are based on an octahedral geometric structures. H_2L ligand always coordinates via the isoxazole-N and enolic sulfonamide-OH forming two-binding chelating sites. The octahedral geometry is brought by the two anions (Cl or NO_3) and two coordinated water molecules. According to the above data and similar

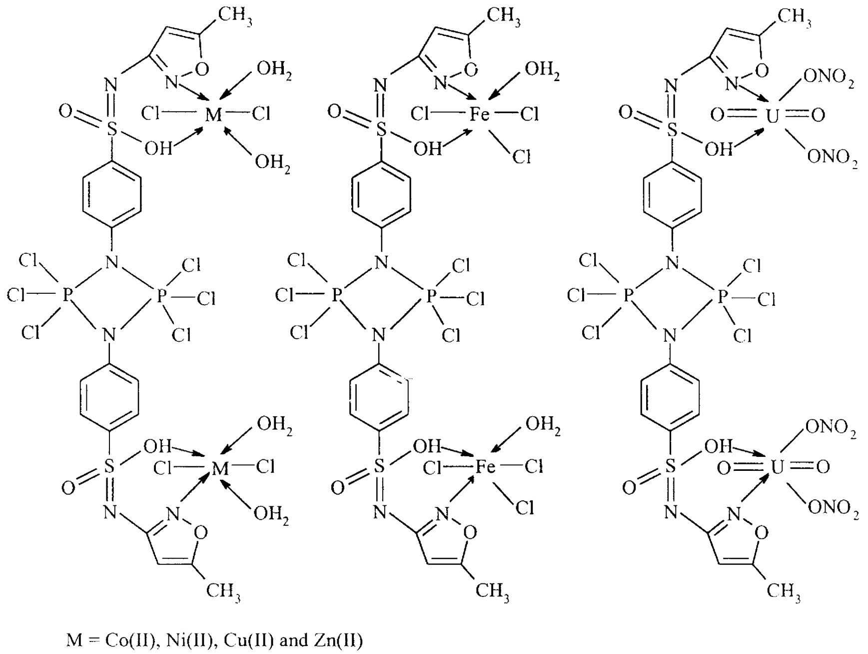


FIGURE 2 Suggested structures of H_2L metal complexes.

to those proposed previously, the structures of the complexes are shown in Figure 2.

Biological Activity

The disc diffusion method was used to measure the antimicrobial activity of the complexes.[26,27] 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_2L, 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.[27] 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 VI. The data obtained reflect the following findings:

1. The H_2L ligand has moderate activity in comparison with Staphylococcus Pyogones and is less active in comparison with Escherichia

TABLE VI Antibacterial Activity of H_2L and Its Metal Complexes

	H_2L (mg/mL)			Fe (III) (mg/mL)			Co(II) (mg/mL)			Ni(II) (mg/mL)			Cu(II) (mg/mL)			Zn(II) (mg/mL)			UO_2(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	5	2.5	1	5	2.5	1	5	2.5	1
S.P.	+++	++	+	++	+	+	++	+	+	+++	++	+	++	++	+	+++	++	++	++	++	+	+++	++	+	++	+	−
P.A.	++	+	−	++	++	+	++	+	−	++	++	+	++	+	−	++	+	+	++	+	+	+++	++	+	++	+	−
Fungs (Candida)	−	−	−	+	−	−	+	−	−	+	−	−	+	−	−	+	+	−	+	−	−	−	−	−	−	−	−
E.C.	++	+	+	+++	++	+	++	++	+	++	++	+	++	++	+	++	++	+	+++	++	+	+++	++	+	++	+	−

[a] Standard materials.

Inhibition values = 0.1–0.5 cm beyond control = +.

Inhibition values = 0.6–1.0 cm beyond control = ++.

Inhibition values = 1.1–1.5 cm beyond control = + + +.

S.P. = Staphylococcue Pyogones.

E.C. = Escherichia coli.

P.A. = Pseudomonas aereuguinosa.

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,[28] as well as the presence of two imine groups which imports in elucidating the mechanism of transformation reaction in biological systems.[27]

2. Antibacterial activity of the complexes towards the different organisms show 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.[29]

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