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Preparation and spectroscopic characterization of novel cyclodiphosph(V)azane of N^1 -2-pyrimidinylsulfanilamide complexes Magnetic, thermal and biological activity studies

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Abstract

Hexachlorocyclophosph(V)azane of sulfadiazine, (sulfupyrimidine) [N^1 -2-pyrimidinylsulfanilamide] (H_2L^1), was prepared and reacted with sulfur and glycine to give (H_2L^2) and (H_2L^3) ligands, respectively. The prepared ligands; H_2L^1 , H_2L^2 and H_2L^3 , react in 1:2 [ligands]:[metal ions] molar ratio with transition metals to give coloured complexes in a relatively good yields. The complexes were characterized using different physicochemical techniques, namely elemental analyses, IR, UV–vis, mass, ¹H NMR, molar conductance, magnetic, solid reflectance and thermal analysis. The spectral data reveal that all the ligands behave as neutral bidentate ligands and coordinated to the metal ions via pyrimidine-N and enolic sulfonamide OH. The molar conductance data reveal that the complexes are non-electrolytes while UV–vis, solid reflectance and magnetic moment data have been shown that the complexes have octahedral geometry. The thermal behaviour of the complexes is studied and the thermodynamic activation parameters are calculated. The ligands and their complexes show high to moderate bactericidal activity. © 2006 Elsevier B.V. All rights reserved.

Keywords: Sulfadiazine; Phosphorus pentachloride; Sulfur; Glycine; Transition metals; Thermal analysis; Biological activity

1. Introduction

No congeners in the periodic table of the elements form compounds of a greater structural variety than nitrogen and phosphorus [1]. This was due in part to the ability of these nonmetals to form single, double, and triple bonds with each other. It was, however, also due to the strength of P-N bonds, which render most phosphorus-nitrogen compounds exceptionally thermally stable [2]. While the unsaturated cylophosphazenes and their polymeric products were of the oldest and best-known class of P-N compounds [3], the saturated phosphazanes also had a well-established chemistry [4]. The reaction of cyclophosphazenes [CIPNR]₂ were interesting class of heterocycles with two reactive phosphorus centers [5]. It was also interested in designing compounds with multiple cycladiphosphazane unites to be used as ligands for complexation. We needed the mono substituted cyclodiphosphazanes to represent a few examples of this type [5]. The bis-cyclodiphosphazane and tetrakis-

* Corresponding author. *E-mail address:* csharaby@hotmail.com (C.M. Sharaby). cyclodiphosphazane had been prepared [5]. The cyclodiphosphazanes of sulfonamides had been prepared and their ability to form more biologically active complexes had been studied [6–9]. In continuation to our interest to prepare hexachlorocyclodiphosph(V)azane of sulfa drugs [6–9], the present paper aims chiefly to prepare hexachlorocyclodiphosph(V)azane of sulfadiazine H_2L^1 or its disulfo and diamino substituted hexachlorocyclodiphosph(V)azane, H_2L^2 and H_2L^3 , respectively. The behaviour of these three ligands towards transition metal ions was studied. The characterization of the prepared compounds was performed using different physicochemical methods. Also the biological activity of the prepared ligands and their complexes were studied.

2. Experimental

2.1. Reagents

Chemicals were procured from Aldrich or BDH. They were purified when required. Solvents were purified according to standard procedures.

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2.2. Synthesis of H_2L^1 , H_2L^2 and H_2L^3 ligands

1,3-di-[N^1 -2-pyrimidinylsulfanilamide]-2,2,2.4,4,4hexachlorocyclodiphosph(V)azane (H₂L¹) was prepared using the methods of Chapman et al. [10] and Zhumurova and Kirzanov [10], sulfadiazine [N^1 -2-pyrimidinylsulfanilamide] (0.1 mol, 25.0 g) in 100 ml cold dry benzene was added in small portions to a well stirred cold solution of phosphorus pentachloride (0.1 mol, 20.95 g) in 100 ml cold dry benzene during half an hour at \simeq 15 °C under dry conditions. After completion of the reaction (HCl gas ceased to evolve), filtration and removal of all solvent in vacuo, a residue was obtained which on crystallization, yielded white crystals of (H₂L¹) (37 g, 80.5%) with mp = 162 °C.

2.2.1. 1,3-di- $[N^1$ -2-pyrimidinylsulfanilamide]-2,4-disulfo-2,4-dichlorocyclodiphosph(V)azane(H_2L^2)

The sulphur solid (0.7 g) was added in excess to a well stirred solution of H_2L^1 (7.68 g, 0.1 mol) in 100 ml acetonitrile. After the addition was completed, the reaction mixture was heated under reflux for 1 h with continuous stirring under anhydrous conditions. The reaction mixture was filtered while hot at vacuo, a residue was obtained which on washing several times with acetonitrile and dry diethyl ether, yielded yellow crystals of H_2L^2 (3 g, 35.80%), with mp = 192 °C.

2.2.2. 1,3-di- $[N^1$ -2-pyrimidinylsulfanilamide]-2,4-di-[aminoacetic acid]-2,4-dichlorocyclodiphoph(V)azane (H₂L³)

Glycine (1.50 g, 0.02 mol) was added in small portions to a well stirred solution of H_2L^1 (7.68 g, 0.01 mol) in 100 ml acetonitrile during half hour. After the addition was completed, the reaction mixture was heated under reflux for 3 h. After the completion of the reaction (HCl gas ceased to evolve), the reaction mixture was filtered while hot and the solid obtained was washed several times with acetonitrile, diethyl ether and dried in vacuo to give the corresponding aminoacyclodiphazane derivative (H₂L³), (5.5 g, 60%) with mp = 210 °C.

2.3. Synthesis of the complexes

A solution of metal salts (10 mmol) in 50 ml dry well stirred ethanol was added dropwise to the solution of H_2L^1 , H_2L^2 and H_2L^3 (5 mmol) in 100 ml dry ethanol at room temperature. The reaction mixture was heated under reflux for 2 h. The product was separated and washed several times with ethanol and diethyl ether and dried under vacuo.

2.4. Instrumentation

Microanalytical determinations (C, H, N and S) were carried out in the Microanalytical center, Cairo University. The IR spectra were recorded on a Shimadzu FT-IR spectrometer (KBr technique). ¹H NMR spectra (DMSO- d_6) were measured on a Varian Gemini 200 MHz spectrometer, using TMS as internal standard. The electronic spectra were measured using a Shimadzu PC 3101 spectrophotometer. The magnetic susceptibilities of the complexes in the solid state were recorded on a Sherwood Scientific Magnetic Susceptibility Balance using Faraday method. Thermogravimetric analysis was performed under a nitrogen atmosphere using a Shimadzu TGA-50H with a flow rate of 20 ml min⁻¹. The UV-vis spectra were recorded on a Perkin-Elmer Lambda 3B UV-vis spectrophotometer. Mass spectra were recorded with the aid of a Shimadzu-Ge-Ms-QP 100 EX mass spectrometer (Japan) using a direct insertion probe (DIP) at temperature range 50-800 °C. Mössbauer measurements were performed at Physics Department, Faculty of Science, Al-Azhar University, employing ⁵⁷Co as a radioactive source. The spectra were analyzed using a computer program based on lorentzian distribution. The isomer shift were expressed relative to a metallic iron absorber. Metal contents were determined complexometerically using standard EDTA titration [7]. The phosphorus content was determined gravimetrically as phosphoammoniummolybdate [7]. 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.

3. Results and discussion

3.1. The ligands

In the present investigation, novel hexachlorocyclodiphosph(V)azane of sulfadiazine (H_2L^1) was prepared using the methods of Chapman et al. [10] and Zhumurova and Kirzanov [10]. Phosphorus pentachloride was reacted with sulfadiazine in cold dry benzene to give 1,3-di- $[N^1-2$ -pyrimidinylsulfanilamide]-2,2,2,4,4,4-hexachlorocyclodiphosph(V)azane (H_2L^1) in 80.5% yield. The reaction of solid sulfur with H_2L^1 in acetonitrile give 1,3-di- $[N^1-2$ -pyrimidinylsulfanilamide]-2,4disulfo-2,4-dichlorocyclodiphosph(V)azane (H_2L^2) in 35.80% yield, while the reaction of glycine with H_2L^1 in acetonitrile gave a cyclosubstitution at the phosphorus atoms to give 1,3-di- $[N^1-2$ -pyrimidylsulfanilamide]-2,4-(diaminoacetic acid)-2,4-dichlorocyclodiphosph(V)azane (H_2L^3) in 60% yield.

The analytical data suggest the structures of the three prepared ligands H_2L^1 , H_2L^2 and H_2L^3 as given in Fig. 1.

The structural elucidation of the ligands; H_2L^1 , H_2L^2 and H_2L^3 , was accomplished on the basis of elemental analyses (Table 1), UV–vis, IR, ¹H NMR and mass spectroscopic data. The UV spectra of the ligands in DMF solvent showed absorption bands at 269, 270 and 270 nm, which are due to the electron delocalization within the four membered ring of the dimeric structure for the ligands H_2L^1 , H_2L^2 and H_2L^3 , respectively [7,11]. The IR spectra for the ligands H_2L^1 , H_2L^2 and H_2L^2 , $\nu(P-Cl)$, $\nu(P-N)$, $\nu(SO_2)$, $\nu(C-N)$ and $\nu(NH)$ which are summarized in Table 2.

Further the band at $623-625 \text{ cm}^{-1}$ was characteristic to $\nu(P=S)$ for H_2L^2 and other bands characteristic to $\nu(P-O-C)$, $\nu(C=O)$ and $\nu(P-N-H)$, respectively, for H_2L^3 ligand are listed in Table 2. ¹H NMR (DMSO- d_6), showed the characteristic



Fig. 1. The proposed structures for H_2L^1 , H_2L^2 and H_2L^3 ligands.

proton signals, which are listed in Table 3. A broad signal appeared between δ 6.28–7.3 ppm which is characteristic of -NH proton signal for H_2L^1 , H_2L^2 and H_2L^3 ligands. Further insight concerning the structures of the prepared ligands were obtained from their mass spectra. The possible fragmentation pathways of H_2L^1 , H_2L^2 and H_2L^3 ligands (Schemes 1–3) showed a base peak at m/z 95, m/z 95 and m/z 186 (100%), respectively. H_2L^1 ligand showed a peaks at m/z 673 (4%), m/z580(3.4%), m/z 384(2.3%) and m/z 383(2%) which confirm the dimeric structure of H_2L^1 ligand (Fig. 1). H_2L^2 ligand showed a peaks at m/z 578 (41%), m/z 379 (13.6%), m/z 346 (1.0%) and m/z 342 (46%) which confirm the proposed structure of H₂L² ligand (Fig. 1). Also the mass fragmentation of H_2L^3 ligand showed peaks at m/z 680 (47%) m/z 522 (8.24%) and m/z 388 (3.2%) which confirm the proposed structure of H₂L³ ligand (Fig. 1).

3.2. Metal complexes

The results of the elemental analyses listed in Table 1 are in good agreement with those calculated for the suggested formulae

of the complexes $[(MX_n)_2 (H_2L^1 \text{ or } H_2L^2 \text{ or } H_2L^3) (H_2O)_z]$. The formation of these complexes may proceed according to the following equation:

$$2MX_{n} + H_{2}L^{1}orH_{2}L^{2}orH_{2}L^{3} + zH_{2}O$$

$$\rightarrow [(MX_{n})_{2}(H_{2}L^{1}orH_{2}L^{2}orH_{2}L^{3})(H_{2}O_{z})],$$

$$M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II),$$

$$X = Cl, n = 2, z = 4, \quad M = Fe(II), X = SO_{4}, n = 0, z = 4,$$

$$M = Fe(III), X = Cl, n = 2, z = 2,$$

$$M = UO_{2}(II), X = NO_{3}, n = 2, z = 0$$

3.2.1. Molar conductance

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The molar conductance values in DMF at 25 °C (Table 1) for the complexes were found to be in the range 7.85–18.30 Ω^{-1} mol⁻¹ cm². The relatively low values indicate the non-electrolytic nature of these complexes [7,9]. This can be accounted for by the satisfaction of the bi- or tri-valency of the metal by the chloride, nitrate or sulphate. This implies the coordination of the anions to the metal ion centers.

Table 1 Analytical and physical data of H_2L^1 , H_2L^2 and H_2L^3 , ligands and their corresponding metal complexes

Compound		Colour (% yield)	% Found (calco	$\mu_{\mathrm{eff.}}$	$\Omega_{\rm m} \left(\Omega^{-1} \right)$					
	(°C)		С	Н	Ν	S	Р	М	(μ _B)	$mol^{-1} cm^2$)
$\overline{H_2L^1, (C_{20}H_{16}Cl_6N_8O_4P_2S_2)}$	162	White (80.5)	31.62 (31.15)	2.48 (2.09)	14.42 (14.53)	8.40 (8.32)	7.87 (8.03)	_	_	_
$[(FeCl_3)_2(H_2L^1)(H_2O)_2], C_{20}H_{20}Cl_{12}Fe_2N_8O_6P_2S_2$	>300	Brownish yellow (58)	21.60 (21.23)	1.83 (1.78)	9.32 (9.90)	5.15 (5.67)	5.90 (5.47)	10.13 (9.87)	5.65	18.30
$[(MnCl_2)_2(H_2L^1)(H_2O)_4], C_{20}H_{24}Cl_{10}Mn_2N_8O_8P_2S_2$	>300	Yellowish brown (52)	22.40 (21.94)	2.71 (2.21)	10.13 (10.23)	5.60 (5.86)	6.03 (5.66)	9.49 (10.03)	5.42	9.58
$[(FeSO_4)_2(H_2L^1)(H_2O)_4], C_2OH_{24}Cl_{16}Fe_2N_8O_{16}P_2S_4$	>300	Yellow (60)	20.35 (20.94)	2.32 (2.11)	9.42 (9.77)	11.39 (11.18)	4.98 (5.40)	9.38 (9.74)	5.20	10.50
$[(CoCl_2)_2(H_2L^1)(H_2O)_4], C_{20}H_{24}Cl_{10}Co_2N_8O_8P_2S_2$	>300	Brown (67)	21.73 (21.79)	2.27 (2.19)	9.82 (10.16)	5.63 (5.82)	5.87 (5.62)	10.22 (10.65)	5.13	12.40
[(NiCl ₂) ₂ (H ₂ L ¹)(H ₂ O) ₄], C ₂₀ H ₂₄ Cl ₁₀ N ₈ Ni ₂ O ₈ P ₂ S ₂	>300	Brown (68)	21.99 (21.79)	2.04 (2.19)	9.73 (10.16)	5.52 (5.82)	6.03 (5.62)	10.13 (10.65)	3.2	11.30
$[(CuCl_2)_2(H_2L^1)(H_2O)_4], C_{20}H_{24}Cl_{10}Cu_2N_8O_8P_2S_2$	>300	Yellow (70)	21.16 (21.60)	2.24 (2.18)	9.63 (10.08)	5.43 (5.77)	5.77 (5.57)	10.89 (11.43)	2.09	7.85
$[(ZnCl_2)_2(H_2L^1)(H_2O)_4], C_{20}H_{24}Cl_{10}N_8N_8O_8P_2S_2$	>300	White (73)	21.89 (21.52)	2.53 (2.15)	10.30 (10.50)	5.33 (5.74)	5.63 (5.56)	11.23 (11.66)	Diam.	11.30
$[(CdCl_2)_2(H_2L^1)(H_2O)_4], C_{20}H_{24}Cd_2Cl_{10}N_8O_8P_2S_2$	>300	Yellow (55)	20.38 (19.85)	2.06 (2.00	9.06 (9.26)	5.66 (5.30)	4.93 (5.12)	18.20 (18.58)	Diam.	14.22
$[(UO_2)_2(H_2L^1)(NO_3)_4], C_{20}H_{16}Cl_6N_{12}O_{20}P_2S_2U_2$	>300	Brownish yellow (52)	15.00 (15.41	1.42 (1.03)	10.42 (10.78)	4.61 (4.11)	3.67 (3.97)	-	Diam.	12.5
H_2L^2 , $C_{20}H_{20}Cl_2N_8O_4P_2S_2$	192	White (36)	34.24 (34.64)	2.61 (2.33)	15.93 (16.16)	19.73 (18.49)	8.53 (8.93)	-	-	-
$[(FeCl_3)_2(H_2L^2)(H_2O)_2], C_{20}H_{20}Cl_8Fe_2N_8O_6P_2S_4$	>300	Yellowish brown (60)	22.54 (22.79)	2.22 (1.91)	10.78 (10.63)	12.30 (12.17)	5.48 (5.88)	10.28 (10.60)	5.82	13.95
$[(CdCl_2)_2(H_2L^2)(H_2O)_4], C_{20}H_{24}Cd_2Cl_6N_8O_8P_2S_4$	>300	Yellowish white (63)	21.50 (21.22)	2.01 (2.14)	9.62 (9.90	11.00 (11.33)	5.07 (5-47)	19.41 (19.86)	Diam.	11.85
H_2L^3 , $C_{24}H_{22}Cl_2N_{10}O_8P_2S_2$	210	White (60)	36.95 (37.17)	3.05 (2.86)	18.36 (18.06)	8.07 (8.27)	8.15 (7.99)	-	-	-
$[(FeCl_3)_2(H_2L^3)(H_2O)_2], C_{24}H_{26}Cl_8Fe_2N_{10}O_{10}P_2S_2$	>300	Yellow (58)	24.93 (25.38)	2.70 (2.31)	12.45 (12.33)	5.26 (5.65)	5.73 (5.45)	10.18 (9.83)	5.86	14.50
$[(CdCl_2)_2(H_2L^3)(H_2O)_4], C_{24}H_{30}Cd_2Cl_6N_{10}O_{12}P_2S_2$	>300	White (60)	24.07 (23.74)	2.14 (2.49)	11.32 (11.54)	5.47 (5.28)	4.92 (5.10)	18.99 (18.52	Diam.	9.76

Table 2 IR spectra (4000–400 cm⁻¹) of the H_2L^1 , H_2L^2 and H_2L^3 ligands and their metal complexes

Compound	$\nu(NH)$	ν (P=NH)	ν(C=O)	ν(C=N)	$\nu(SO_2)$ (asym.)	v(SO ₂) (sym.)	ν(PN)	$\nu(H_2O)$ (coord.)	ν(PC l)	$\nu(P=S)$	ν(M -O)	ν(M —N)
$H_2L^1 [C_{20}H_{16}Cl_6N_8O_4P_2S_2]$	3368 br	_	_	1618 sh	1348 s	1084 m	1156 sh	_	570 sh	_	550 m	_
$[(FeCl_3)_2(H_2L^1)(H_2O)_2]$	3375 sh	-	-	1594 m	1326 sh	10.92 m	1158 sh	844 m, 796 sh	574 sh	-	520 s	502 m
$[(MnCl_2)_2(H_2L^1)(H_2O)_4]$	3388 br	-	_	1600 m	1332 sh	1060 s	1170 w	820 s, 782 s	575 m	_	524 s	480 w
$[(FeSO_4)_2(H_2L^1)(H_2O)_4]$	3372 br	-	-	1596 m	1322 w	1090 s	1156 br	826 s, 790 s	572 m	-	500 w	490 w
$[(CoCl)_2(H_2L^1)(H_2O)_4]$	3388 br	-	_	1600 m	1324 w	1052 m	1188 br	850 m, 780 m	574 m	_	510 w	460 w
$[(NiCl_2)_2(H_2L^1)(H_2O)_4]$	3378 br	-	_	1605 m	1320 w	1046 m	1188 br	820 m, 780 m	574 m	_	524 m	480 w
$[(CuCl_2)_2(H_2L^1)(H_2O)_4]$	3376 sh	-	_	1594 m	1326 sh	1092 sh	1156 sh	842 m, 796 sh	572 m	_	556 s	500 m
$[(CdCl_2)_2(H_2L^1)(H_2O)_4]$	3375 br	_	_	1590 sh	1326 m	1080 sh	1168 sh	812 m, 782 m	572 sh	-	510 w	475 w
$[(UO_2)_2((NO_3)_4(H_2L^1)]$	3375 br	-	_	1608 m	1325 w	1100 s	1168 br	840 m, 795 m	566 m	_	_	480 w
$H_2L^2 [C_{20}H_{16}Cl_2N_8O_4P_2S_4]$	3380 br	_	_	1618 sh	1348 m	1086 m	1168 br	-	572 sh	625 m	_	_
$[(FeCl_3)_2(H_2L^2)(H_2O)_2]$	3385 br	-	_	1595 m	1326 w	1090 br	1158 sh	810 s, 785 s	574 sh	625 m	530 w	490 w
$[(CdCl_2)_2(H_2L^2)(H_2O)_4]$	3390 br	_	_	1590 sh	1328 w	1086 m	1150 m	820 s, 794 m	572 w	623 m	584 m	470 w
$H_2L^3[C_{24}H_{22}Cl_2N_{10}O_8P_2S_2]$	3375 br	2690 br	1650 m	1618 sh	1342 sh	1088 m	1146 m	-	572 w	_	_	-
$[(FeCl_3)_2(H_2L^3)(H_2O)_2]$	3383 br	2700 br	1652 m	1598 m	1324 w	1092 br	1160 m	830 s, 780 s	575 sh	-	550 s	470 w
$[(CdCl_2)_2(H_2L^3)(H_2O)_4]$	3386 br	2715 br	1652 m	1596 m	1326 sh	1092 sh	1150 w	842 m, 796 sh	568 m	-	485 m	425 m

sh: sharp, m: medium, s: small, w: weak, and br: broad.

Table 3 Characteristic ¹H NMR spectra for the ligands H_2L^1 , H_2L^2 and H_2L^3 and their Cd(II) complex

Compound	Chemical shift, δ (ppm)	Assignment
H_2L^1	7.12 7.60 6.97 8.47 9.80	d, 4H, ArH's, <i>J</i> = 8.80 Hz d, 4H, ArH's, <i>J</i> = 8.40 Hz br, 2H, -SO ₂ NH s, CH, hetero br, H, heterocycle proton
$[(CdCl_2)_2(H_2L^1)(H_2O)_4]$	6.60 7.60 4.21 7.66 8.48 3.48	d, 4H, ArH's, $J = 8.60$ Hz d, 4H, ArH's, $J = 8.40$ Hz br, H, OH enolic s, CH, hetero br, 2H, heterocycle proton br, 8H, coordinated H ₂ O protons
H_2L^2	6.60 7.60 6.28 7.90 8.48	d, 4H, ArH's, <i>J</i> = 8.90 Hz d, 4H, ArH's, <i>J</i> = 8.50 Hz br, 2H, —SO ₂ NH t, CH, hetero br, 2H, heterocycle proton
$[(CdCl_2)_2(H_2L^2)(H_2O)_4]$	6.50 7.00 5.80 7.00 8.40 3.45	d, 4H, ArH's, <i>J</i> = 8.70 Hz d, 4H, ArH's, <i>J</i> = 8.40 Hz br, H, OH enolic t, CH, hetero s, 2H, heterocycle proton br, 8H, coordinated H ₂ O protons
H ₂ L ³	6.59 7.60 2.50 7.30 8.30 6.98 8.40	d, 4H, ArH's, J = 8.90 Hz d, 4H, ArH's, J = 8.70 Hz s, 2H, glycine CH ₂ protons br, 2H, -SO ₂ NH br, 2H, glycine NH protons t, CH hetero s, 2H, CH heterocycle protons
$[(CdCl_2)_2(H_2L^3)(H_2O)_4]$	6.50 7.60 2.50 5.97 8.30 6.99 8.40 3.49	d, 4H, ArH's, <i>J</i> = 8.80 Hz d, 4H, ArH's, <i>J</i> = 8.80 Hz s, 2H, glycine CH ₂ protons br, H, OH enolic br, 2H, glycine NH protons t, CH hetero s, 2H, CH heterocycle protons br, 8H, coordinated H ₂ O protons

3.2.2. IR spectra and mode of bonding

The IR spectra of the ligand and its metal complexes were carried out in the range of $400-4000 \text{ cm}^{-1}$ and the important bands were listed in Table 2. The IR spectra of the complexes were compared with those of the free ligands in order to determine the possible coordination sites that may involved in chelation. There were some guide peaks, in the spectra of the ligands, which were of good help for achieving this goal.

The stretching vibration band; ν (NH), of the sulfonamide group, which found at 3368–3380 cm⁻¹ in the free ligands, were shifted to higher frequencies in the spectra of the isolated complexes. The presence of coordinated water molecules renders it difficult to confirm the enolization of the sulfonamide group. The SO₂ group modes of the ligands appear as medium to sharp bands at 1348, 1348 and 1342 cm⁻¹ ($\nu_{asym}(SO_2)$) and 1094, 1086 and 1088 cm⁻¹ ($\nu_{sym}(SO_2)$) for H₂L¹, H₂L² and H₂L³ ligands, respectively. In the complexes, the asymmetric and symmetric modes are shifted to $1320-1332 \text{ cm}^{-1}$ and $1046-1100 \text{ cm}^{-1}$, respectively, upon coordination to the transition metals [6–9]. The blue shift of the SO₂ stretching vibration to lower frequencies may be attributed to the transformation of the sulfonamide (-SO₂NH) to give the enol form (-SO(OH)=N) as a result of complex formation to give more stable six-membered ring

[6–9]. The strong and sharp bands at 1618 cm^{-1} of the pyrimidine-N; ν (C=N) in the free ligands are shifted to $1595-1605 \text{ cm}^{-1}$ in the metal complexes. This indicates the participation of the pyrimidine-N in complex formation. The presence of medium-to-strong bands in the region between 810-850 and $769-780 \text{ cm}^{-1}$ in the spectra of the metal complexes were attributed to coordinated water molecules. New bands were found in the spectra of the complexes in the regions 485-556 and $425-502 \text{ cm}^{-1}$ which were assigned to ν (M–O) and ν (M–N) stretching vibrations, respectively [12].

Therefore, the IR data reveal that H_2L^1 , H_2L^2 and H_2L^3 ligands behave as neutral bidentate ligands and bind to the metal ions through enolic sulfonamide OH and pyrimidine-N.

3.2.3. ¹H NMR spectra

The ¹H NMR spectra of H_2L^1 , H_2L^2 and H_2L^3 and their Cd complexes were recorded in dimethylsulphoxide (DMSO-*d*₆) using trimethylsilane (TMS) as internal standard. The chemical shifts of the different types of protons of H_2L^1 , H_2L^2 and H_2L^3 ligands and their Cd complexes are listed in Table 3. It was found that the $-SO_2NH$ signal is found at $\delta = 6.97$, 6.28 and 7.30 ppm in the spectra of H_2L^1 , H_2L^2 and H_2L^3 ligands, respectively. This signal is disappeared and a new signal was appeared at $\delta = 4.21$, 5.80 and 5.97 ppm in the spectra of Cd complexes of H_2L^1 , H_2L^2 and H_2L^3 ligands, respectively. This was attributed to the enolization of the $-SO_2NH$ to -SO(OH)=N and coordination of the enolized OH to the metal ions [6–9].

Also, the spectra of the complexes showed a broad signals at δ 3.48, 3.45 and 3.49 ppm for Cd complexes with H₂L¹, H₂L² and H₂L³ ligands, respectively, which attributed to the presence of coordinated water molecules.

3.2.4. Electronic spectra and magnetic moment

The UV-vis spectra of the ligands and the complexes were recorded in DMF solution in the wavelength range from 200 to 800 nm. The spectra showed a sharp and intense band in the 270 nm region, which is characteristic for phosphazo fourmembered rings of the ligands. The blue or red shifts of the band in the region (267–276 nm) with respect to the ligands depend on the type of metal ions coordinated to the ligand [6–9]. The spectra of the complexes further display a band in the range 388–401 nm, which might be assigned to charge transfer transition from the ligand to metal ions (L \rightarrow M) [9].

The diffuse reflectance spectrum of Mn(II) complex shows three bands at 15,644, 22,222 and 26,455 cm⁻¹ assignable to ${}^{4}T_{1g} \rightarrow {}^{6}A_{1g}$, ${}^{4}T_{2g}$ (G) $\rightarrow {}^{6}A_{1g}$ and ${}^{4}T_{1g}$ (D) $\rightarrow {}^{6}A_{1g}$ transitions, respectively [13]. The magnetic moment value is 5.42 μ_{B} . which indicates the presence of Mn(II) complex in octahedral structure.











It is observed from the diffuse reflectance spectra of the Fe(III) complexes that they exhibit a band at 21,008–21,276 cm⁻¹ which may be assigned to the ${}^{6}A_{1g} \rightarrow {}^{5}T_{2g}$ (G) transition in octahedral geometry [14,15]. The spectra also show a spitted bands at 14,947–15,673 and 17,574–18,315 cm⁻¹ which assigned to the ${}^{6}A_{1g} \rightarrow {}^{5}T_{1g}$ transition. The observed magnetic moment of the Fe(III) complexes is 5.65, 5.82 and 5.86 μ_B for H₂L¹, H₂L² and H₂L³ ligands, respectively, which confirm the octahedral geometry. The bands observed at 29,154 and 24,937–26,041 cm⁻¹ can be attributed to ligand-to-metal charge transfer band for the Mn(II) and Fe(III) complexes, respectively.

The diffuse reflectance spectrum of the Fe(II) complex displays two absorption bands at 13,157 and 17,636 cm⁻¹ which are assigned to ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$ transitions [16]. Also the band at 28,735 cm⁻¹ is assigned to L \rightarrow M charge transfer. The observed magnetic moment of 5.2 μ_{B} is consistent with an octahedral geometry [16].

The electronic spectrum of the Co(II) complex shows two bands at 16,051 and 22,075 cm⁻¹ assigned to the ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}$ (P) and ${}^{4}T_{1g} \rightarrow {}^{4}T_{2g}$ (F) transitions, respectively, indicating octahedral geometry. The band observed at 26,178 cm⁻¹ refers to L \rightarrow Co charge transfer. The observed magnetic moment value is 5.13 μ_{B} at room temperature which confirms the octahedral geometry of this complex [16,17].

For Ni(II) complex, the electronic spectrum shows three bands at 16,339, 17,636 and 20,964 cm⁻¹, suggesting the existence of ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (P), ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) and ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ transitions, respectively. The observed magnetic moment of the complex is 3.2 μ_B which confirms the octahedral structure of this complex [7,17]. The spectrum also displays band at 26,315 cm⁻¹ which assigned to L \rightarrow M CT band.

The electronic spectrum of the Cu(II) complex exhibits a band at 17,605 cm⁻¹ which may be assigned to ${}^{2}E_{g} \rightarrow {}^{3}T_{2g}$ transition [18]. The spectrum also displays and at 28,571 cm⁻¹ refers to $L \rightarrow M$ CT band. The observed magnetic moment of the Cu(II) complex is 2.09 μ_{B} which confirms octahedral geometry around the Cu(II) ion [18].

The Zn(II), Cd(II) and UO₂(II) complexes are diamagnetic and they proposed to have octahedral structure as those previously published [19,6-9].

3.2.5. Mössbauer measurement

The Mössbauer spectra of iron complexes of ligands H_2L^1 , H_2L^2 and H_2L^3 were measured at room temperature (Table 4 and Fig. 2). The observed isomer shift values indicate the presence of iron in its +2 and +3 oxidation states. A comparative study of the isomer shift values of these iron complexes with

Table 4 Mössbauer parameters of iron complexes of $H_2L^1,\,H_2L^2$ and H_2L^3 ligand

Complex compound	Isomer shift (m/m/s) (IS)	Quadrupole splitting (mm/S) (QS)
$[(FeSO_4)_2(H_2L^1)(H_2O)_4]$	1.39	2.7
$[(FeCl_3)_2(H_2L^2)(H_2O)_2]$	0.48	0.58
$[(FeCl_3)_2(H_2L^2)(H_2O)_2]$	0.47	0.56



Fig. 2. Mössbauer spectra of iron complexes of H_2L^1 , H_2L^2 and H_2L^3 .

those already present in the literature indicates the coordination number of Fe(II) and Fe(III) complex are six. On the bases of quadruple splitting data (QS), the iron complex exist in octahedral configuration [20].

4. Thermal analysis (TGA)

Table 5 shows the TGA results of the thermal decomposition of the metal complexes of the ligands under study. While the thermodynamic activation parameters are listed in Table 6.

 $[(FeSO_4)_2(H_2L^1)(H_2O)_4]$ complex was thermally decomposed in five decomposition steps within the temperature range of 50-1100 °C. The first decomposition step with an estimated mass loss of 6.83% (calcd. mass loss = 6.28%) within the temperature range 50-200 °C, may be attributed to the liberation of the four coordinated water molecules. The activation energy was $63.60 \text{ kJ} \text{ mol}^{-1}$. The remaining decomposition steps (four steps) found within the temperature range 200-1100 °C with an estimated mass loss of 67.35% (calcd. mass loss = 67.22%) which are reasonably accounted for by the removal of H_2L^1 ligand as gases. The activation energies were 92.04, 85.67, 136.80 and $185.7 \text{ kJ} \text{ mol}^{-1}$ for the second, third, fourth and fifth steps, respectively. The thermograms of $[(FeCl_3)_2(H_2L^1)(H_2O)_2]$, $[(CuCl_2)_2(H_2L^1), (H_2O)_4]$ and $[(CdCl_2)_2(H_2L^1)(H_2O)_4]$ complexes show five decomposition steps within the temperature range 30–1000 °C. The first two steps of decomposition (in case of Fe(III) and Cd(II) complexes) or three steps of decomposition (in case of Cu(II) complex) within the temperature range 30-350 °C corresponds to the loss of 4–6 HCl, $3H_2O$ and O_2

Table 5
Thermogravimetric data of H_2L^1 , H_2L^2 and H_3L^3 metal complexes

Complex	TG range ($^{\circ}C$)	DTG_{max} (°C)	n ^a	% Found (calco	l.)	Assignment	Metallic residue	
				Mass loss	Total mass loss			
$\overline{[(\text{FeSO}_4)_2(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_4]}$	50-200	120	1	6.73 (6.28)		Loss of 4H ₂ O	25.60	
	200-1100	275, 390, 660, 875	4	67.35 (67.22)	74.18 (73.50)	Loss of H ₂ L ¹	2FeSO ₄	
$[(FeCl_3)_2(H_2L^1)(H_2O)_2]$	30-250	70, 210	2	22.68 (22.18)		Loss of 6HCl and O ₂	F 0	
	250-1000	330, 560, 850	3	63.79 (63.87) 86.47 (86.05)		Loss of H_2L^1	Fe ₂ O ₃	
$[(CuCl_2)_2(H_2L^1)(H_2O)_4]$	30-220	60, 185	2	12.31 (12.86)		Loss of 2HCl, 3H ₂ O and 1/2O ₂		
[(CuCi2)2(11212)(1120)4]	220-350	290	1	6.67 (6.56)		Loss of 2HCl	Cu ₂ SO ₃	
	350-800	490, 670	2	61.45 (61.88)	80.43 (81.39)	Loss of H_2L^1	2 9	
$[(CdCl_2)_2(H_2L^1)(H_2O)_4]$	30-180	120	1	11.54 (11.66)		Loss of 2HCl, 3H ₂ O and 1/2O ₂		
	180-260	230	1	6.68 (6.04)		Loss of 2HCl	2CdO	
	260-600	290, 370, 510	3	60.75 (60.96)	78.79 (78.83)	Loss of H ₂ L ¹		
$[(CdCl_2)_2(H_2L^2)(H_2O)_4]$	30-200	90	1	11.98 (12.64)		Loss of 2HCl, 3H ₂ O and 1/2O ₂		
	200-360	248	1	6.70 (6.45)		Loss of 2HCl	2CdO	
	360-1000	530, 850	2	58.82 (58.27)	77.50 (77.36)	Loss of H_2L^2		
$[(CdCl_2)_2(H_2L^3)(H_2O)_4]$	30-210	108	1	11.63 (11.79)		Loss of 2HCl, 3H ₂ O and 1/2O ₂		
	210-340	230	1	5.80 (6.02)		Loss of 2HCl	2CdO	
	340-800	530	1	60.89 (61.09)	78.32 (78.90)	Loss of H_2L^3		

^a *n*: number of decomposition steps.

gases with a mass loss of 22.68% (calcd. mass loss = 22.18%), 18.98% (calcd. mass loss = 19.42%) and 18.22% (calcd. mass loss = 17.87%) for Fe(III), Cu(II) and Cd(II) complexes, respectively. The activation energy values were 33.45-108.4 kJ mol⁻¹.

The last steps (250–1000 °C) correspond to the loss of the organic ligand molecule (H_2L^1) leaving Fe₂O₃, Cu₂SO₃ and CdO as a residue with an activation energies 99.86–152.3, 155.6–198.7 and 92.97–136.9 kJ mol⁻¹ for Fe(III), Cu(II) and

Table 6

Thermodynamic data of the thermal decomposition of H_2L^1 , H_2L^2 and H_2L^3 metal complexes

Complex	Decomp. temp. (°C)	E^* (kJ mol ⁻¹)	$A(s^{-1})$	ΔS^* (kJ mol ⁻¹)	$\Delta H^* (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta G^* (\text{kJ mol}^{-1})$
	50–150	63.60	1.67×10^{7}	-43.05	75.05	55.43
	220-300	92.07	$3.04 imes 10^{10}$	-72.22	56.96	76.62
$[(FeSO_4)_2(H_2L^1)(H_2O)_4]$	340-460	85.67	1.67×10^{7}	-102.3	87.95	89.53
	570-760	136.8	$4.84 imes 10^{12}$	-98.87	106.5	102.5
	830–960	185.7	6.53×10^9	-135.6	146.3	142.7
	30-100	64.73	3.67×10^9	-36.95	68.45	84.77
$[(FeCl_3)_2(H_2L^1)(H_2O)_2]$	150-250	108.4	2.67×10^{5}	-65.97	79.06	64.53
	280-380	152.3	4.59×10^{10}	-97.68	112.3	122.4
	500-670	99.86	6.82×10^{11}	-112.6	143.6	154.2
	780–900	145.6	7.14×10^9	-153.7	98.99	165.3
[(CuCl ₂) ₂ (H ₂ L ¹)(H ₂ O) ₄]	30–90	49.85	1.98×10^{11}	-39.85	52.73	38.66
	100-220	97.65	3.52×10^{8}	-68.95	95.53	87.55
	220-400	84.89	$4.09 imes 10^{12}$	-97.85	143.6	135.4
	460-530	155.6	2.51×10^6	-107.7	193.2	168.3
	600-750	198.7	7.08×10^{10}	-154.3	223.6	200.1
	50-150	33.45	$3.05 imes 10^6$	-73.78	67.96	58.69
	180-250	75.02	5.27×10^{11}	-98.77	86.15	90.67
$[(CdCl_2)_2(H_2L^1)(H_2O)_4]$	250-320	117.7	4.49×10^{9}	-132.3	76.87	103.4
	320-430	92.97	$6.08 imes 10^{10}$	-163.4	145.3	87.45
	440-600	136.9	3.56×10^{13}	-203.5	165.2	115.6
	50-180	53.26	2.83×10^8	-29.78	45.13	38.56
$f(C_1C_1) = (I_1 I_2)(I_1 O_1)$	200-300	77.95	3.49×10^{12}	-59.95	95.26	67.53
$[(CdCl_2)_2(H_2L^2)(H_2O)_4]$	400-600	94.82	1.50×10^{9}	-88.66	176.3	125.4
	750–900	175.2	6.04×10^{13}	-107.3	203.6	95.67
	30–150	48.69	2.95×10^9	-56.44	38.46	34.62
$[(CdCl_2)_2(H_2L^3)(H_2O)_4]$	200-290	75.23	4.19×10^{7}	-85.19	79.98	61.52
[(edel2)2(112E)(112O)4]	450-650	152.6	5.65×10^{10}	-106.7	100.5	95.96

Cd(II) complexes, respectively. The overall weigh loss amounts to 86.47% (calcd. mass loss = 86.05%), 80.43% (calcd. mass loss = 81.39%) and 78.79% (calcd. mass loss = 78.83%) for Fe(III), Cu(II) and Cd(II) complexes, respectively.

On the other hand, $[(CdCl_2)_2(H_2L^2)(H_2O)_4]$ and $[CdCl_2)_2(H_2L^3)(H_2O)_4]$ complexes exhibit four and three decomposition steps, respectively, within the temperature range 30–1000 °C. The first decomposition step occurs within the temperature



Fig. 3. (a) Suggest structural formulae of H_2L^1 ligand. (b) Suggest structural formulae of H_2L^2 ligand. (c) Suggest structural formulae of H_2L^3 ligand.

Test organisms	(Comp	ound	l																						
H_2L^1		$[(FeCl_3)_2(H_2L^1)_2(H_2O_2)]$				[(M	nCl ₂) ₂	$(H_2L^1$)(H ₂ O) ₄]	$[(FeSO_4)_2(H_2L^1)(H_2O)_4]$] [$[(CoCl)_2(H_2L^1)(H_2O)_4]$				$[(NiCl_2)_2(H_2L^1)(H_2O)_4]$			St				
Conc. (mg/ml)	-	1	2.5	5	1	2.5	5		1	2.5	5		1	2.5	5		1		2.5	5	1	2.5	5	1	2.5	5
Escherichia coli	+	++	++	++	++	++	++		++	++	++		+	++	++		+	+	+++	+++	++	++	++	++	+++	+++
Staphylococcus aurei	ıs -	+	++	++	+	++	++		+	++	++		+	++	++		+	+	++	+++	+	+	+	+++	+++	+++
Salmonella typhi	+	+	+	++	+	+	+		+	++	++		+	+	++		+	+	+++	+++	++	+++	+++	++	++	+++
Bacillus subtillus	-	+	+	+	+	+	+		+	+	+		+	+	+		+	-	++	+++	+	+	+	++	+++	+++
Aspergillus terreus	()	0	+	0	0	+		0	0	+		0	0	0		+	-	+	++	0	0	0	++	+++	+++
Aspergillus flavus	+	+	+	+	0	+	+		0	0	+		0	0	0		0		0	+	0	0	0	+++	+++	+++
Test organisms	Com	npoun	ıd																							
	[(Cu	$(Cl_2)_2$	(H_2L)	L ¹)(H ₂	O) ₄]	[(Cd	$Cl_2)_2(H_2)$	$^{2}L^{1})(H_{2})$	O)4]	[(U	O ₂) ₂ ((NO ₃) ₄ (H ₂	L ¹)]	H ₂	L ²		[(F	eCl ₃)	$_2(H_2L)$	$(H_2O)_2$	[(Cd	$Cl_2)_2(H$	$H_2L^2)(H_2O)_4]$	St.		
Conc. (mg/ml)	1	2.5	5			1	2.5	5		1	2.5	5		1	2.5	5	1	2.5	5		1	2.5	5	1	2.5	5
E. coli	++	++	+	+		++	++	+++		+	++	++		++	++	++	+	++	++	-	++	+++	+++	++	+++	+++
S. aureus	+	+	+			++	++	+++		+	+	+		++	++	+++	+	++	++	-+	++	+++	+++	+++	+++	+++
S. typhi	++	++	+	++		+++	+++	+++		+	+	+		++	++	+++	+	++	++	-	++	++	+++	++	++	+++
B. subtillus	+	+	+			++	++	++		+	+	+		+	++	++	+	+	+		++	++	++	++	+++	+++
Aspergillus terrens	0	+	+			+	++	++		0	0	+		0	+	+	+	+	+		+	++	++	++	+++	+++
A. flavus	+	+	+			+	+	+		0	0	0		0	+	+	+	+	+		+	++	+++	+++	+++	+++
Test organisms	С	ompo	ound																							
	Н	$_2L^3$						[(FeC	l3)2(H	2L ³)(H	$(120)_2$					[(CdCl	2)2(H2	2L ³)(I	$H_2O)_4$]			St.			
Conc. (mg/ml)	1			2.5		5		1		2.5		5				1		2.5		5			1	2.5		5
E. coli	+-	+		+++		+++		++		++		++				++		++		++			++	+++		+++
S. aureus	+-	+		++		++		+		+		++				++		++		++			+++	+++		+++
S. typhi	+-	+		++		+++		+		++		++				++		++		+++			++	++		+++
B. subtillus	+			+		+		+		+		+				+		++		++			++	+++		+++
A. terreus	+			+		++		0		+		+				+		++		++			++	+++		+++
A. flavus	0			0		+		0		0		+				+		+		+			+++	+++		+++

Table 7 The antibacterial and antifungal activity of H_2L^1 , H_2L^2 , H_2L^3 ligands and their metal complexes

St.: references standard; Chloramphenicol was used as a standard antibacterial agent and Grisofluvine was used as a standard antifungal agent; *tested was done the diffusion agar technique. Well diameter: 1 cm $(100 \,\mu l \text{ of each conc.}, \text{ was tested}); +: inhibition values = 0.1-0.5 \text{ cm beyond control}; ++: inhibition values = 0.6-1.0 \text{ cm beyond control}; ++: inhibition values = 1.1-1.5 \text{ cm beyond control}; 0: not detected.$

range 30-210 °C and corresponds to the loss of 2HCl, 3H₂O and $1/2O_2$ gases with an estimated mass loss 11.98% (calcd. mass loss = 12.64%) and 11.63% (calcd. mass loss = 11.79%) for Cd(II) complexes with H_2L^2 and H_2L^3 ligands, respectively. The energy of activation was 53.26 and $48.69 \text{ kJ mol}^{-1}$ for Cd(II) complexes with H_2L^2 and H_2L^3 ligands, respectively. While, the subsequent steps involve the loss of 2HCl and ligand molecules within the temperature range 200-1000 °C with an estimated mass loss 65.52% (calcd. mass loss = 64.72%) and 66.69%(calcd. mass loss = 67.11%) for Cd(II) complexes with H_2L^2 and H_2L^3 ligands, respectively. The energies of activation were 77.95, 94.82 and 175.2 kJ mol⁻¹ for the second, third and fourth steps in case of [CdCl₂)₂(H₂L²)(H₂O)₄] complex, respectively, 75.23 and 152.6 kJ mol⁻¹ for the second and third steps, respectively, for the $[(CdCl_2)_2, (H_2L^3) (H_2O)_4]$ complex. The overall weight loss amounts to 77.50% (calcd. mass loss = 77.36%) and 78.32% (calcd. mass loss = 78.90%) for Cd(II) complexes with H_2L^2 and H_2L^3 ligands, respectively.

5. Kinetic data

The thermodynamic activation parameters such as activation energy (E^*), enthalpy of activation (ΔH^*), entropy (ΔS^*) and free energy change of the decomposition (ΔG^*) were evaluated graphically by employing the Coats–Redfern relation [21]. The data are listed in Table 6. It was shown from the data that all the complexes have negative entropy values, which indicate that the activated complexes are formed spontaneously.

6. Structural interpretation

From the satisfactory microanalyses, magnetic, molar conductance, thermal analysis and various spectral data, the structure can be interpreted in accordance with complexes of ligands with the same coordination sites like hexachlorocyclodiphosph(V)azane of sulfadimidine [6], sulfameterol [7], sulfamethoxazole [9] and sulfaguanidine [8]. It is concluded that H_2L^1 , H_2L^2 and H_2L^3 ligands act as a neutral bidentate ligands coordinated to the metal ions through enolized -SO(OH)=N and pyrimidine-N. The structures proposed are based on an octahedral geometric structures. The molar conductance data reveal that the complexes are non-electrolytes while the thermal analysis (TGA) data show that the complexes decomposed in three to five steps where the coordinated water and anions are removed in the first steps followed by the ligands. Therefore, from the above data and in accordance to those previously published, the structures of the complexes are shown in Fig. 3.

7. The antimicrobial activity

The synthesized compounds were tested against the bacterial species namely *Escherichia coli*, *Staphylococcus aureus*, *Salmonella typhi* and *Bacillus subtillus*. Also the antifungal activity against *Aspergillus terreus* and *Aspergillus flavus* were carried out. The organisms were tested against the activity of different concentrations of the compounds, results are depicted in Table 7. The results showed that Co(II) and Cd(II) complexes enhanced the activity towards *E. coli* more than the H_2L^1 free ligand and the other metal complexes gave the same activity as the H_2L^1 free ligand. Co(II), Ni(II) and Cd(II) complexes showed a remarkable activity towards *S. aureus* than the H_2L^1 free ligand while the other tested metal complexes gave the same or lower activity as the H_2L^1 free ligand.

Also Co(II), Ni(II), Cu(II) and Cd(II) complexes showed a very high activity towards *S. typhi* than the H_2L^1 free ligand, while the other metal complexes gave the same activity or lower than the free ligand H_2L^1 . Co(II) complex, enhanced the activity towards *B. subtillus* than the free ligand H_2L^1 .

Comparison of the biological activities of the synthesized compounds and the standard antibiotic (Chloramphenicol) showed that the free ligand H_2L^1 showed lower activity towards the investigated bacterial than the standard.

The metal complexes of Co(II), Ni(II) and Cd(II) enhanced the activity towards some investigated bacteria than the standard antibiotic Chloramphenicol and in the same time they showed the same activity towards some of the investigated bacteria as the standard.

Ligand H_2L^2 showed a higher or the same activity towards the investigated bacteria than the first ligand H_2L^1 . This might be due to the replacement of four chlorine atoms in H_2L^1 by two sulphur atoms in H_2L^2 ligand. Also the free ligand H_2L^2 showed the same activity as Chloramphenicol towards *S. aureus* and *S. typhi* and showed lower activity towards the investigated fungi than the standard antibiotic Grisofluvine.

While Cd(II) complex enhanced the activity towards *E. coli* and *S. aureus* than the free ligand H_2L^2 and this complex showed the same activity as the standard antibiotic Chloramphenicol. Also Cd(II) complex showed a remarkable higher activity towards *A. terreus* and *A. flavus* than the free ligand H_2L^2 and the same activity towards *E. coli*, *S. aureus*, *S. typhi* and *Aspergillus ftavus* as that of the standards Chloramphenicol and Grisofluvine.

 H_2L^3 free ligand showed the same activity towards *E. coli* and *A. terreus* than the free ligands H_2L^1 and H_2L^2 . This might be reasonably accounted to the replacement of four chlorine atoms in H_2L^1 ligand by two glycine molecules in H_2L^3 free ligand.

Cd(II) complex showed a remarkable higher activity towards *B. subtillus*, *A. terreus* and *A. flavus* than the free ligand H_2L^3 and the standard Chloramphenicol.

From all of the above results we can conclude that some metal complexes enhanced the activity of the ligands and showed higher activity than the investigated standard antibiotics.

References

- (a) D.E.C. Corbridge, Phosphorus: An Outline of its Chemistry, Biochemistry and Technology, 5th ed., Elsevier, Amsterdam, 1995;
 (b) N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed., Butterworth-Heinemann, Oxford, 1998.
- [2] S. Ingo, P. Luke, Grocholl, S. Lother, Inorg. Chem. 39 (2000) 3037.

(c) C.E. Allen, Coord. Chem. Rev. 130 (1994) 137.

[3] (a) J.E. Mark, H.R. Allcock, R. West, Inorganic Polymer, Englewood Cliffs, Prentice Hall, NJ, 1992;
(b) R.H. Neilson, P. Wisian-Neilson, Chem. Rev. 88 (1988) 541;

947

- [4] (a) R.R. Holmes, J.A. Former, Inorg. Chem. 2 (1963) 380;
 - (b) T.G. Hill, R.C. Haltiwanger, M.L. Thompson, S.A. Katz, A.D. Norman, Inorg. Chem. 33 (1994) 1770;
 - (c) O.J. Scherer, G. Schnable, Angew. Chem. Int. Ed. Engl. 15 (1976) 772;
 (d) S.S. Kumaravel, S.S. Krishnamurthy, T.S. Gameron, A. Linden, Inorg. Chem. 27 (1988) 4546;

(e) A.R. Davies, A.I. Dronsfield, R.N. Haszeldin, D.R. Taylor, J. Chem. Soc. Perkin Trans. 1 (1973) 379;

- (f) W. Zeiss, W. Schwarz, H.Z. Hess, Naturforschung 33b (1980) 959; (g) D. Dou, E.N. Duesler, R.T. Paine, Inorg. Chem. 38 (1999) 788.
- [5] J.J. Praveen Kommana, K.C. Vittal, Kumaraswamy, Polyhedron 22 (2003) 843.
- [6] C. Sharaby, Ph.D. Thesis, Faculty of Science, Al-Azhar University (Girls), Cairo, Egypt, 1992.
- [7] C.M. Sharaby, Synth. React. Inorg. Met.-Org. Chem. 35 (2005) 133.
- [8] C.M. Sharaby, Spectrochem. Acta (Part A) 62 (2005) 326.
- [9] G.G. Mohamed, Phosphorus Sulfur Silicon Related Elements 180 (7) (2005) 1569.
- [10] I.N. Zhumurova, A.V. Kirzanov, Zh. Obshch. Khim. 32 (1962) 2576.
- [11] (a) I.M. Abd Ellah, E.H.M. Ibrahim, A.N. El Khazandar, J. Phosphorus Sulfur 29 (1987) 239;

(b) I.M. Abd-Ellah, E.H.M. Ibrahim, A.N. El-Khazandar, J. Phosphorus Sulfur 31 (1987) 13.

- [12] R.J. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, 1st ed., Plenum Publisher, New York, 1997, p. 168.
- [13] G.M. Abu El-Reash, K.M. Ibrahim, M.M. Bekheit, Bull. Chem. Soc., Fr. 128 (1991) 149.
- [14] G.G. Mohamed, N.E.A. El-Gamel, F.A. Nour El-Dien, Synth. React. Inorg. Met.-Org. Chem. 31 (2) (2001) 347.
- [15] G.G. Mohamed, N.E.A. El-Gamel, Spectrochim. Acta (Part A) 61 (2005) 1089.
- [16] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th ed., Wiley, New York, 1999.
- [17] G.G. Mohamed, M.A. Zayed, N.E.A. El-Gamel, Spectrochim. Acta (Part A) 58 (2002) 3167.
- [18] A.B.P. Lever, Inorganic Electronic Spectroscopy, 1st ed., Elsevier Publisher, London, New York, 1968, p. 267.
- [19] Z.M. Zaki, Spectrosc. Lett. 31 (4) (1998) 757.
- [20] N.N. Greenwood, T.C. Gibb, Mössbauer Spectroscopy, 1st ed., Chapman and Hall Ltd. Publishers, London, 1671, p. 248.
- [21] A.W. Coats, J.P. Redfern, Nature 201 (1961) 68.