



Ligating Properties of Sulfaquinoxaline with some Transition Metal Ions

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Abstract Sulfaquinoxaline metal complexes with transition metals (Cr(III), Mn(II), Co(II), Cu(II), Hg(II), Fe(III), Zn(II), Cd(II), Ni(II), Zr(VI)) have been prepared. IR spectra proved that sulfaquinoxaline ligand acts as tetradentate ligand. All complexes of sulfaquinoxaline have octahedral geometry which has been proved by magnetic measurements and spectral results. The hyperchemistry method is used for confirmation of the active site of sulfaquinoxaline coordination. Some of the complexes being prepared were studied using mechanisms of thermal decomposition. The kinetic and thermodynamic parameters of the thermal decomposition steps, E_a , ΔH^* and ΔS^* , were estimated from DTA thermograms. For some strains, the activity of sulfaquinoxaline complexes is greater than industrial sulfaquinoxaline.

Keywords Sulfaquinoxaline; Complexes; Thermogravimetric study; Spectroscopic analysis

Introduction

Sulfaquinoxaline (Figure 1) is considered to be an antiprotozoal and antimicrobial antibiotic that used for treating many coccidial infections [1-2] (coccidiosis) in swine, cattle, fowl, and other animals. Sulfa drug used for stopping fowl typhoid occurred by sensitive organisms beside fowl cholera which occurred by *Pasteurella multocida* [3-4]. Previous work in sulfaquinoxaline metal complexes fell to synthesis sulfaquinoxaline complexes with (Ni, Co, Cu, Sn, Cd) [5-7]. The previous studies showed that Cu and Co sulfaquinoxaline have a very high cytotoxic effect on a colon tumor cell line with low concentration that reduces the survival to 50% [8]. The complexation properties, thermal behaviors and biological activity were studied. The mechanism of decomposition was discussed from TGA and DTA curves, the thermodynamic parameters are evaluated and discussed.

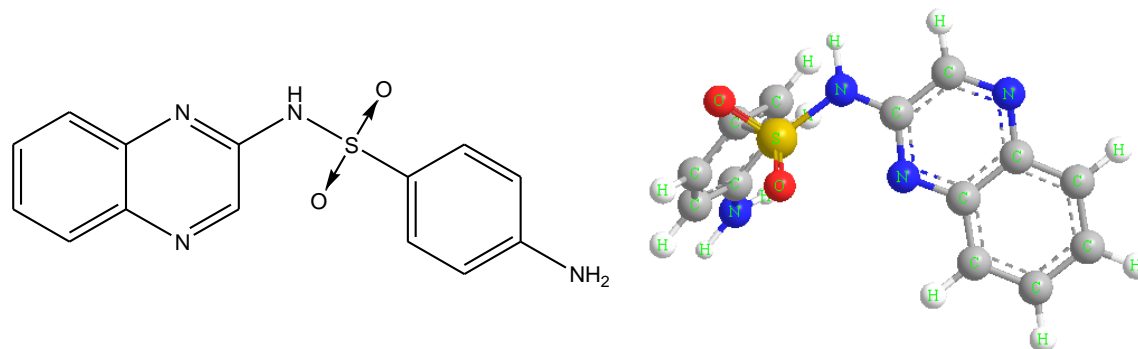


Figure 1: Structure of sulfaquinoxaline (HL)

Experimental Section

Similarly all complexes of metal sulfaquinoxaline were prepared. This occurred by dissolving the chlorides inorganic salts of transition metal ions in 40 mL bidistilled water but ligand was dissolved in ethanol. The ethanolic solution of ligand was mixed with solution of metal chloride in different ratio (M:L). The reaction mixture in each case was refluxed for about 5 min then left over-night, then the precipitated complexes were filtered, washed several times with a mixture of EtOH-H₂O and dried in a vacuum desiccator over anhydrous CaCl₂. There were two methods used to determine the metal contents first: depending on atomic absorption technique using model 6650 Shimadzu-atomic absorption spectrophotometer and second: complexometrically by using standard EDTA solution and appropriate indicator as given [9]. The chloride content of complexes were determined by using the familiar Volhard method [10].

Table 1: Elemental analysis, m.p, formula, stoichiometries and color of simple sulfaquinoxaline complexes

Complexes	Color	Calculated/(Found)%					
		C	H	N	S	M	Cl
[Cr ₂ (HL)Cl ₆ (H ₂ O) ₂] (2:1)	Dark Green	25.75 (25.60)	2.47 (2.57)	8.58 (8.80)	4.91 (4.95)	15.92 (15.90)	32.57 (32.50)
[Mn ₃ (HL) ₂ (H ₂ O) ₆ (OH) ₄] (3:2)	Pale Brown	35.72 (35.70)	4.28 (4.32)	11.90 (11.95)	6.81 (6.84)	17.50 (17.61)	- -
[Fe ₂ (HL)Cl ₆ (H ₂ O) ₂] (2: 1)	Dark Brown	25.45 (25.47)	2.44 (2.42)	8.48 (8.55)	4.85 (5.10)	16.90 (16.82)	32.19 (32.17)
[Co ₂ (HL) ₃ Cl ₄ (H ₂ O) ₂] (2:3)	Pale Pink	42.15 (42.71)	3.37 (3.32)	14.05 (14.11)	8.04 (8.09)	9.85 (9.77)	11.85 (11.99)
[Ni ₂ (HL) ₂ (OH) ₄ (H ₂ O) ₂] (2:2)	Green	40.03 (40.09)	4.08 (4.11)	13.34 (13.30)	7.63 (7.60)	13.97 (13.90)	- -
[Cu ₂ (HL) ₃ Cl ₂ (H ₂ O) ₂] (2: 3)	Green	44.44 (44.66)	3.55 (3.41)	14.81 (14.70)	8.47 (8.50)	11.20 (11.09)	6.25 (6.38)
[Zn ₂ (HL) ₃ Cl ₄ (H ₂ O) ₂] (2:3)	Yellow	42.21 (42.32)	3.46 (3.38)	13.74 (13.68)	7.86 (7.82)	10.69 (10.73)	11.59 (11.68)
[Cd ₂ (HL) ₂ Cl ₄ (H ₂ O) ₂] (2:2)	Yellow	32.93 (32.85)	2.96 (2.88)	10.97 (10.82)	6.28 (6.32)	22.01 (22.11)	13.88 (13.77)
[Hg ₂ (HL) ₃ Cl ₄ (H ₂ O)] (2:3)	Orange	34.50 (34.39)	2.62 (2.55)	11.50 (11.42)	6.58 (6.52)	27.44 (27.42)	9.70 (9.73)
[(ZrO ₂) ₂ (L) ₂ (HL)Cl(OH)] (2:3)	Black	42.11 (42.09)	2.95 (2.99)	14.03 (14.09)	8.03 (8.08)	15.23 (15.12)	2.96 (2.99)

Physical Measurements

Perkin Elmer spectrophotometer, Model 1430 which it is range of 200-4000 cm⁻¹ was used to determine IR spectra of the sulfaquinoxaline and their metal complexes, also by using Unicam UV/Vis spectrometer [11] spectra of sulfaquinoxaline and the solid complexes were measured in Nujol mull spectra. The magnetic measurements were determined at room temperature (298 K) using Faraday's method. ESR spectra were determined by using reflection spectrometer operating at (9.1-9.8) GHz in a cylindrical resonance cavity with 100 KHZ modulation and g values were determined by comparison with DPPH signal. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the ligand (sulfaquinoxaline) and their complexes was recorded on Shimadzu DTA/TGA-60 thermal analyzer with heating rate 20°C/min under nitrogen atmosphere of flow rate 20 ml/min. The biological activity of sulfaquinoxaline and their metal complexes were examined against 5 microorganisms representing different microbial categories, {two Grampositive (*Staphylococcus Aureas* ATCC6538P and *Bacillus subtilis* ATCC19659), two Gram negative (*Escherischia coli* ATCC8739 strain and *Pseudomonas aeruginosa* ATCC9027)



and *candida albicans* as a fungi. Hyperchem computer program using PM3 semi-empirical and Molecular Mechanics Force Field (MM+) is applied for ligand.

Result and Discussion

Table 2 summarizes the assignments of sulfaquinoxaline bonding sites and its metal complexes. It is showed from the elemental analysis of the complexes that all complexes contain water molecules in their structures. Sulfaquinoxaline complexes give broad bands in the 3400–3580 cm^{-1} region except Zr complex suggesting coordination with water. Coordinated water in these complexes is indicated by the presence of metal-oxygen bands at 422-450 cm^{-1} region [12]. The sharp band of O=S=O stretching vibration of sulfaquinoxaline is assigned at 1350 cm^{-1} but for metal complexes is shifted to (1384-1416 cm^{-1}) range that suggesting that ligand coordination with these metal ions occurs through the oxygen of sulfonyl group. The sharp band of N-H stretching vibration of secondary NH group of sulfaquinoxaline appears at 3192 cm^{-1} while for simple complexes appears at (3240-3361 cm^{-1}) range for all complexes except Zr complex, (the band disappeared) this large shift mean that there is metal ligand coordination occurred through nitrogen of secondary amino group. The sharp band at 3318 cm^{-1} corresponding to symmetrical stretching vibration while the band at 3356 cm^{-1} corresponding asymmetrical stretching vibration of N-H of hydrogen bonded NH_2 for spectrum of sulfaquinoxaline while for metal complexes assigned at range of (3360-3437 cm^{-1}) and (3420-3576 cm^{-1}) for symmetrical and asymmetrical stretching vibration respectively. This shift means that there is ligand coordination with metal ions through nitrogen of terminal amino group. The band at 1637 cm^{-1} corresponding to stretching vibration of C=N of sulfaquinoxaline but the complexes show this band at (1637-1642 cm^{-1}) range so the shifting is not significant so there is no metal ligand coordination. The narrow band of C-N stretching vibration appeared at 1308 cm^{-1} of spectrum of sulfaquinoxaline while for simple complexes is correspond to (1307-1315 cm^{-1}) that meaning that there is no shift occurred in the band and so no metal ligand coordination occurred. The sharp band of CH stretching vibration of the spectrum of sulfaquinoxaline appears at 2942 cm^{-1} but for simple complexes appears at (2920-2955 cm^{-1}) range. The absorption band at 1598 cm^{-1} is assigned to C=C aromatic bending vibration of sulfaquinoxaline while for complexes appears at (1592-1594 cm^{-1}) range.

Electronic Spectral and Magnetic Studies

The violet chromium-complex: $[\text{Cr}_2(\text{HL})\text{Cl}_6(\text{H}_2\text{O})_2]$ give by the electronic absorption spectra three bands at 288, 320 and 354 nm as result of ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{p})$ transition, respectively, Table(3). So that, this complex has octahedral geometry [13]. Its room temperature μ_{eff} value of 6.61 that suggested the existence of Oh configuration. The brown manganese complex $[\text{Mn}_3(\text{HL})_2(\text{H}_2\text{O})_6(\text{OH})_4]$ show by electronic absorption spectrum three bands at 300, 337 and 366 nm, Tables (5). So this complex has octahedral geometry in which due to $\pi - \pi^*$ the first band appear while the second one is assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$, while the third is due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ transition. Such Oh geometry is further deduced from the μ_{eff} values which equals, 5.62 B.M. The bands of brown iron-complex $[\text{Fe}_2(\text{HL})\text{Cl}_6(\text{H}_2\text{O})_2]$ appeared by using electronic absorption spectra at 305, 334 and 367 nm, Table (3). This means that the geometry of iron complex is octahedral. These bands appeared as result of CT ($t_{2g} \rightarrow \pi^*$) and CT ($\pi \rightarrow e_g$) that have μ_{eff} value of 4.66. The presence of O_h configuration for each iron complex is typified by μ_{eff} value. Cobalt complex $[\text{Co}_2(\text{HL})_3\text{Cl}_4(\text{H}_2\text{O})_2]$ gave bands at 285, 314 and 371 nm by electronic absorption spectra, Tables (3). As result of charge transfer nature of bands are assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ transition deduced the octahedral geometry [14] of complex with magnetic moment value equal to 3.69 at room temperature. There are three bands appeared by green electronic absorption spectra for Nickel-complex $[\text{Ni}_2(\text{HL})_2(\text{OH})_4(\text{H}_2\text{O})_2]$ at 287, 318 and 373 nm as result of ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ transition, Tables (3). So the complex has octahedral geometry which given by the μ_{eff} value which equal 2.64 B.M. The green electronic spectra of copper complex $[\text{Cu}_2(\text{HL})_3\text{Cl}_2(\text{H}_2\text{O})_2]$, Tables (3), showed three bands at 304, 343 and 362 nm. The band is assigned to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}(\text{D})$ transition which mean octahedral environment. The octahedral [14] geometry is typified by the μ_{eff} value which equal 1.62 B.M. The electronic absorption spectra of zirconium complex $[(\text{ZrO}_2)_2(\text{L})_2(\text{HL})\text{Cl}(\text{OH})]$ gave three bands at 291, 346 and 372 nm, Tables (3). The nature of geometry is octahedral as result of metal ligand charge



transfer excitations and assigned to ($\pi \rightarrow \pi^*$) and CT ($n \rightarrow \pi^*$) [15]. Such Oh geometry is further deduced from the μ_{eff} values 2.76 B.M.

The electronic absorption spectra of Zn(II), Cd(II) and Hg(II) complexes $[\text{Zn}_2(\text{HL})_3\text{Cl}_4(\text{H}_2\text{O})_2]$, $[\text{Cd}_2(\text{HL})_2\text{Cl}_4(\text{H}_2\text{O})_2]$ $[\text{Hg}_2(\text{HL})_3\text{Cl}_4(\text{H}_2\text{O})]$ gave bands at 314, 364 nm, 327, 371nm and 308, 349nm respectively (Table 3) which referred to ligand \rightarrow metal charge transfer. There is no d-d transition could be observed due to the d^{10} - configuration of Zn(II), Cd(II) and Hg(II) and so the stereochemistry around these metals in its complexes cannot be determined from ultraviolet and visible spectra. So the geometry of these complexes are determined by comparing their spectra with those of similar environments, an octahedral structure is suggested for these complexes.

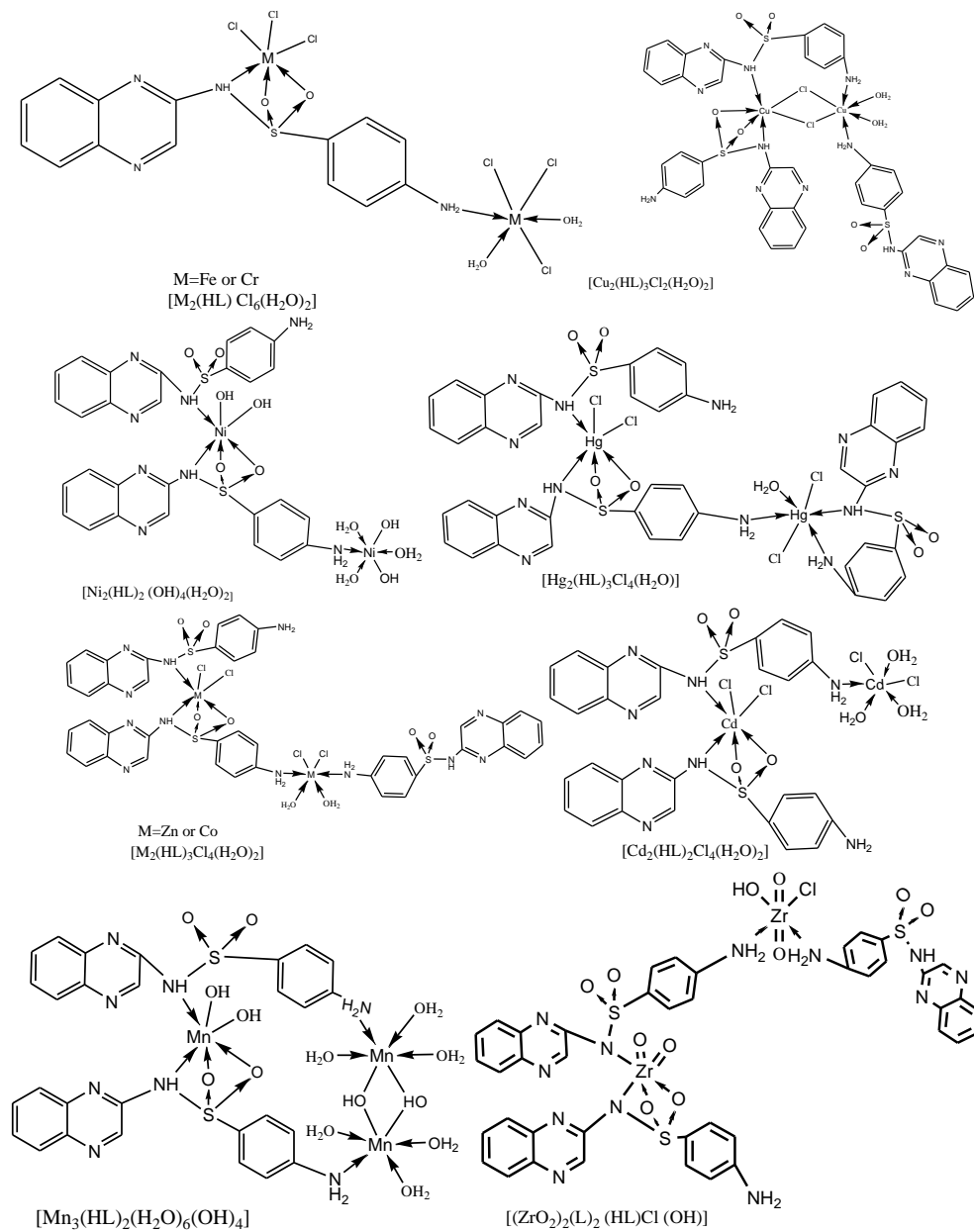


Figure 2: Proposed structures of sulfaquinoxaline complexes



Table 2: Fundamental infrared bands (cm^{-1}) of sulfaquinoxaline and its simple metal complexes

Compound	ν_{NH} 2oamine	ν (O=S=O)	$\nu(\text{NH})$ 1oamine sym	$\nu(\text{NH})$ 1oamine asym	ν (C=N)	ν (C- N)	ν (CH) stretch	$\nu(\text{NH})$ 1oamine bend
Sulfaquinoxaline	3192	1350	3318	3356	1637	1308	2942	1598
$[\text{Cr}_2(\text{HL})\text{Cl}_6(\text{H}_2\text{O})_2]$ (2:1)	3075	1416	3361	3438	1640	1311	2927	1592
$[\text{Mn}_3(\text{HL})_2(\text{H}_2\text{O})_6(\text{OH})_4]$ (3:2)	3255	1414	3360	3437	1640	1310	2927	1592
$[\text{Fe}_2(\text{HL})\text{Cl}_6(\text{H}_2\text{O})_2]$ (2: 1)	3075	1416	3360	3442	1639	1314	2944	1592
$[\text{Co}_2(\text{HL})_3 \text{Cl}_4(\text{H}_2\text{O})_2]$ (2:3)	3075	1415	3360	3400	1640	1311	2940	1594
$[\text{Ni}_2(\text{HL})_2(\text{OH})_4(\text{H}_2\text{O})_2]$ (2:2)	3075	1415	3360	3438	1639	1311	2940	1593
$[\text{Cu}_2(\text{HL})_3 \text{Cl}_2(\text{H}_2\text{O})_2]$ (2: 3)	3075	1416	3360	3437	1642	1314	2942	1592
$[\text{Zn}_2(\text{HL})_3\text{Cl}_4(\text{H}_2\text{O})_2]$ (2:3)	3375	1414	3360	3438	1639	1311	2920	1593
$[\text{Cd}_2(\text{HL})_2\text{Cl}_4(\text{H}_2\text{O})_2]$ (2:2)	3075	1415	3360	3437	1638	1310	2940	1593
$[\text{Hg}_2(\text{HL})_3\text{Cl}_2(\text{H}_2\text{O})]$ (2:3)	3074	1415	3360	3437	1640	1311	2940	1593
$[(\text{ZrO}_2)_2(\text{L})_2(\text{HL})\text{Cl}(\text{OH})]$ (2:3)	-	1384	3360	3436	1636	1307	2950	1592

Table 3: Nujol mull electronic absorption spectra λ_{max} (nm), room temperature effective magnetic moment values (μ_{eff} 298 K) and geometries of sulfaquinoxaline metal complexes

Complex	λ_{max} (nm)	μ_{eff}	Geometry
$[\text{Cr}_2(\text{L})\text{Cl}_3(\text{H}_2\text{O})_3]$ (2: 1)	288,320, 354	6.61	O_h
$[\text{Mn}_3(\text{HL})_2(\text{H}_2\text{O})_6]$ (3: 2)	300, 337, 366	5.62	O_h
$[\text{Fe}_2(\text{L})\text{Cl}_6(\text{H}_2\text{O})_2]$ (2:1)	305, 334, 367	4.66	O_h
$[\text{Co}_2(\text{L})_3 \text{Cl}_6(\text{H}_2\text{O})_6]$ (2:3)	285, 314, 338	3.69	O_h
$[\text{Ni}_2(\text{L})_2(\text{H}_2\text{O})_4]$ (1: 1)	287, 318, 373	2.64	O_h
$[\text{Cu}_2(\text{L})_3 \text{Cl}_4(\text{H}_2\text{O})_2]$ (2:3)	304, 343,362	1.62	O_h
$[(\text{ZrO}_2)_2(\text{L})_2(\text{HL})\text{Cl}(\text{OH})]$ (2:3)	291,346,371	2.76	O_h
$[\text{Zn}_2(\text{L})_3\text{Cl}_4(\text{H}_2\text{O})_2]$ (2: 3)	314,364	diamagnetic	O_h
$[\text{Cd}_2(\text{HL})_2\text{Cl}_2(\text{H}_2\text{O})_2]$ (1: 1)	327,371	diamagnetic	O_h
$[\text{Hg}_2(\text{L})_3\text{Cl}(\text{H}_2\text{O})]$ (2:3)	308,348	diamagnetic	O_h

From hyper-chem program charge density of sulfaquinoxaline atoms is calculated, Figure 3 confirmed sulfaquinoxaline coordination through oxygen of sulfonyl group and nitrogen of both primary and secondary amine, which has highest charge.

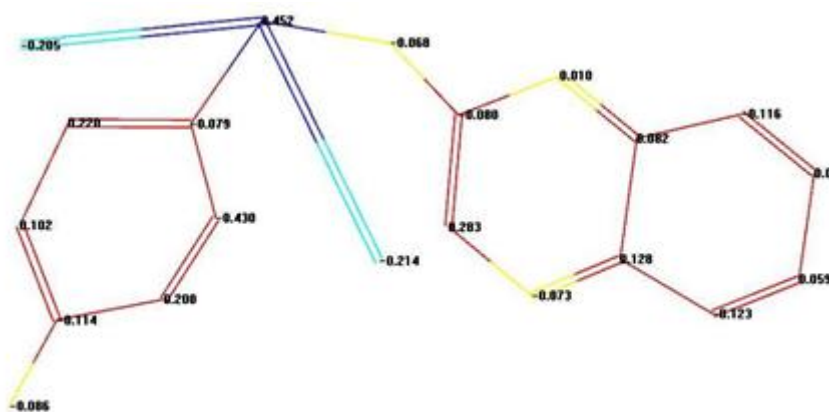


Figure 3: Charge density of sulfaquinoxaline

Electron Spin Resonance of Copper and Cobalt Complex

The room temperature polycrystalline X-band ESR spectral pattern of $[\text{Cu}_2(\text{HL})_3\text{Cl}_2(\text{H}_2\text{O})_2]$ complex is isotropic nature with $g_s = 2.13$ and value of $A = 165$. The presence of ESR signals at $g < 4$ may assign the spin-spin interaction between the Cu atoms show the diametric nature of complex.

From the studies of single crystal ESR spectra on the $[\text{Co}_2(\text{HL})_3\text{Cl}_6(\text{H}_2\text{O})_6]$ complex we conclude that the nature of complex is anisotropic with two g values : $g_{\parallel} = 2.07$, $g_{\perp} = 2.0035$. The A values obtained through minimization method which accounted for second order effect are: $A_{\parallel} = 50$ and $A_{\perp} = 80$. It was reported that in tetragonal octahedral Co-complex the g values is affected by π bonding ability of equatorial and axial ligand. The data of ESR of complex show anisotropic g values which based on structural consideration that allowed us to determine the g and A tensors in a good agreement with experimental findings,

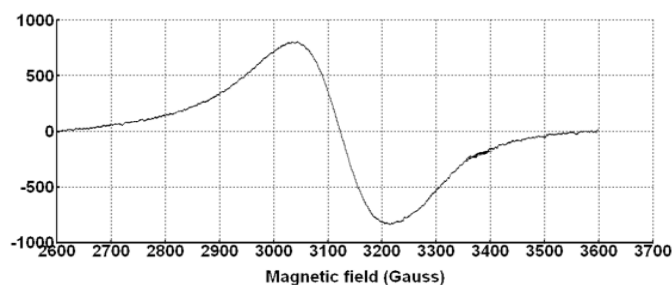


Figure 4: ESR of copper sulfaquinoxaline complex

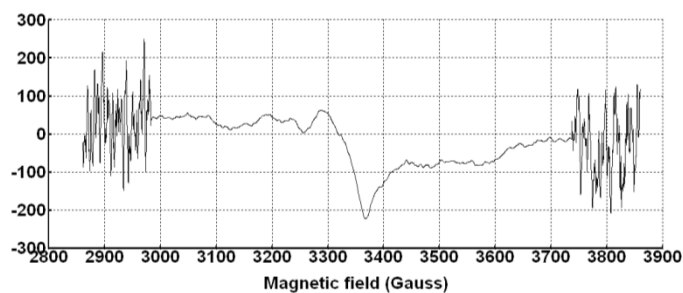


Figure 5: ESR of cobalt sulfaquinoxaline complex



Result and Discussion

Biological Activity

To study biological activity of sulfaquinoxaline and its complexes, we depend on five micro organisms that represent different microbial classes. Those five organisms involved {two Gram-positive (*Staphylococcus aureus* ATCC6538P and *Bacillus subtilis* ATCC19659), two Gram negative (*Escherichia coli* ATCC8739 strain and *Pseudomonas aeruginosa* ATCC9027) bacteria and *Candida albicans* as fungi were used., in this study there are four complexes of different metal ions are used (Zn, Cu, Co, Fe) and two different broadly antibiotics (Ciprofloxacin and Clotrimazole) are used as references (Table 4).

From the data we conclude that: Sulfaquinoxaline ligand showed similar activities for all five micro organisms. All investigated compounds showed higher activity for *Staphylococcus aureus* except $[\text{Fe}_2(\text{HL})\text{Cl}_6(\text{H}_2\text{O})_2]$ which showed similar activity for it. The activities for all compounds are similar to *Candida albicans*, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Bacillus subtilis*. The positive antibacterial activity of all investigated compound higher than anti fungal activity, the activity of compounds are lower than references. The activity of free ligands have lower activity [16] than most of metal complexes, the increased activity of metal chelates could be discussed depending on the bases of overtones concept and chelation theory [17]. As result of chelation, the polarity of metal ion is decreased to a larger extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with the donor groups which lead to raising the delocalization of p- and d-electrons over the whole chelate and enhances the lipophilicity of the complex. The cell permeability the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials on the basis that liposolubility is an important factor that controls antimicrobial activity. The increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking of metal binding sites on the enzymes of the microorganism.

Table 4: The antibacterial activity of the free ligands and its complexes against some reference strains expressed in absolute activity (AU)

Complexes	<i>Candida albicans</i>		<i>Escherichia coli</i>		<i>Pseudomonas aeruginosa</i>		<i>Staphylococcus aureus</i>		<i>Bacillus subtilis</i>	
	Blank	Cpd	Blank	Cpd	Blank	Cpd	Blank	Cpd	Blank	Cpd
Sulfaquinoxaline	9	9	9	9	9	9	9	9	9	9
$[\text{Fe}_2(\text{HL})\text{Cl}_6(\text{H}_2\text{O})_2]$	9	9	9	9	9	9	9	9	9	9
$[\text{Co}_2(\text{HL})_3\text{Cl}_4(\text{H}_2\text{O})_2]$	9	9	9	9	9	9	9	26	9	9
$[\text{Cu}_2(\text{HL})_3\text{Cl}_2(\text{H}_2\text{O})_2]$	9	9	9	9	9	9	9	22	9	9
$[\text{Zn}_2(\text{HL})_3\text{Cl}_4(\text{H}_2\text{O})_2]$	9	9	9	9	9	9	9	21	9	9
Ciprofloxacin(as reference)	-	-	9	30	9	30	9	30	10	30
Clotrimazole (as reference)	9	18	-	-	-	-	-	-	-	-

Thermal analysis

The thermal behavior some biologically active compound has been reported from Masoud *et al* [18-21]. The thermal studies of ligand and its investigated compounds were determined by thermograms (TGA), in case of sulfaquinoxaline the decomposition occurred in two steps 50-700 °C range. The first step of decomposition starts at 48 °C and ends at 389.1 °C with a corresponding weight loss 60.8% which accompanied by endothermic effect from DTA curve. The last step of decomposition is observed at 389-684°C with a corresponding weight loss 17.90% that exhibit exothermic effect. Table (5,6), Figure (6,7).



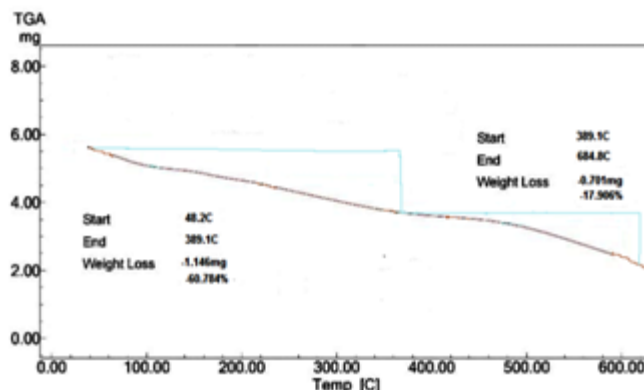


Figure 6: TGA of sulfaquinoxaline ligand

In case of $[\text{Co}_2(\text{HL})_3 \text{Cl}_4(\text{H}_2\text{O})_2]$ complex, Table(5,6) (Figure 8,9), there is no weight loss up to 27.6°C. The decomposition occurred in 4 steps, the first step of decomposition starts at 27°C and ends at 114°C with a corresponding weight loss 12.97%. The second step of decomposition occurred at (114-156) °C range with 3.35% weight loss. In case of third stage the decomposition starts at 156 °C and ends at 198 °C with a weight loss 7.66%. In the last step the weight loss was of 15.009% from decomposition at (198-346) °C range. The DTA data showed two peaks at 85.2 and 550.5 °C first one is endothermic and second is with exothermic effect.

In case of $[(\text{ZrO}_2)_2(\text{L})_2(\text{HL})\text{Cl}(\text{OH})]$ complex, Table (5,6) (Figure 8), there is no weight loss up to 28 °C. TGA curve showed that the decomposition occurred 4 steps. In the first step the decomposition starts at 28°C and ends at 101°C with a corresponding weight loss 12.57%. The decomposition in second step include 13.98% weight loss and occurred at (101-150)°C. In case of third step the decomposition starts at 150°C and ends at 346°C with a corresponding weight loss 23.03%. In last step the decomposition starts at 346°C and ends at 423°C. The DTA data showed two peaks at 86.4 and 517.3 °C first one is with endothermic effect and second one is with exothermic effect.

Table 5: DTA analysis of sulfaquinoxaline and its metal complexes

Complex	Type	T _m (°C)	E _a kJ mol ⁻¹	n	α _m	ΔS [#] kJ K ⁻¹ mol ⁻¹	ΔH [#] kJ mol ⁻¹	Z
Sulfaquinoxaline	Endo	104.2	3.38	1.99	0.50	-0.30	-31.41	0.004
	Exo	451.1	22.64	1.28	0.59	-0.31	-139.8	0.006
$[\text{Cu}_2(\text{HL})_3 \text{Cl}_2(\text{H}_2\text{O})_2]$	Endo	87.4	9.59	1.53	0.55	-0.29	-25.33	0.013
	Exo	567.2	51.44	1.05	0.62	-0.31	-174.1	0.011
$[\text{Zn}_2 (\text{HL})_3\text{Cl}_4(\text{H}_2\text{O})_2]$	Endo	58.9	12.07	2.02	0.50	-0.29	-24.71	0.017
	Exo	580.3	35.17	1.15	0.61	-0.31	-183.5	0.007
$[(\text{ZrO}_2)_2(\text{L})_2(\text{HL})\text{Cl} (\text{OH})]$	Endo	86.4	11.08	1.51	0.55	-0.29	-24.92	0.015
	Exo	517.3	66.24	1.31	0.58	-0.30	-156.9	0.015
$[\text{Mn}_3(\text{HL})_2 (\text{H}_2\text{O})_6(\text{OH})_4]$	Endo	80.6	11.21	1.51	0.55	-0.29	-23.15	0.017
	Exo	518.6	55.78	1.23	0.59	-0.30	-158.1	0.013
$[\text{Ni}_2 (\text{HL})_2(\text{OH})_4(\text{H}_2\text{O})_3]$	Endo	79.2	13.38	2.54	0.45	-0.28	-22.61	0.020
	Exo	479.7	63.59	1.15	0.51	-0.30	-145.1	0.015
$[\text{Co}_2(\text{HL})_3 \text{Cl}_4(\text{H}_2\text{O})_2]$	Endo	85.2	9.36	1.62	0.54	-0.29	-24.68	0.013
	Exo	550.5	25.04	1.02	0.63	-0.31	-172.02	0.005



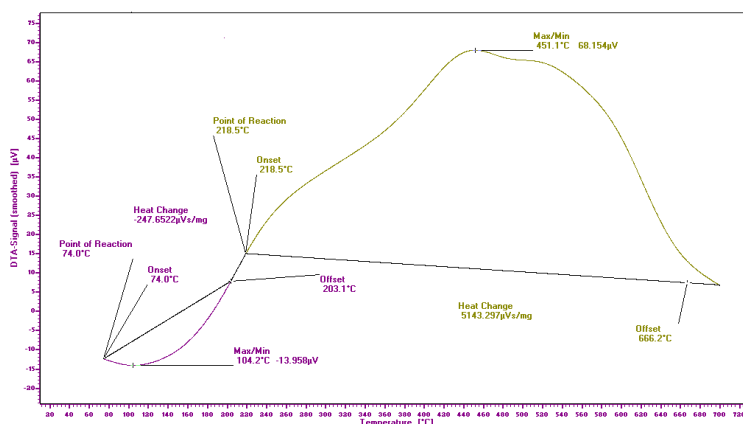
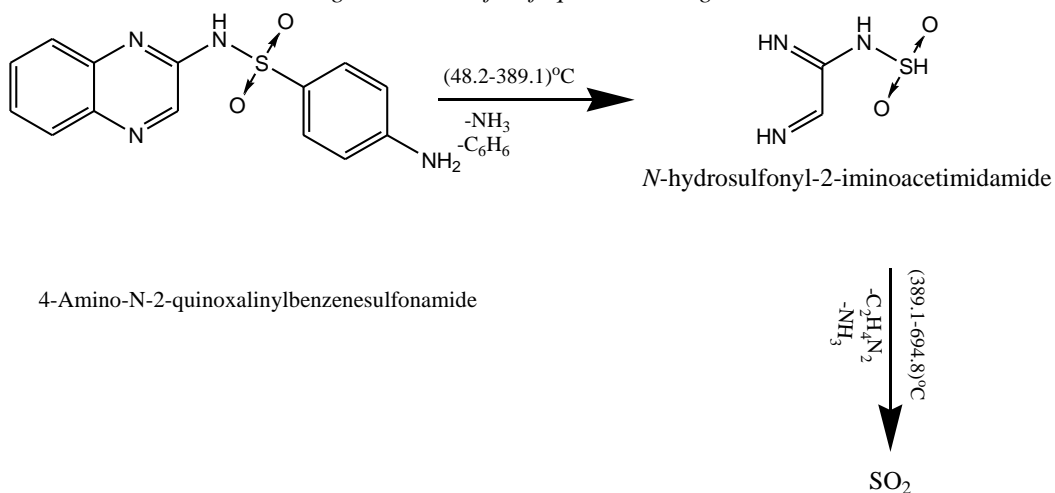


Figure 7: DTA of sulfaquinoxaline ligand



Scheme(1): Thermolysis of sulfaquinoxaline

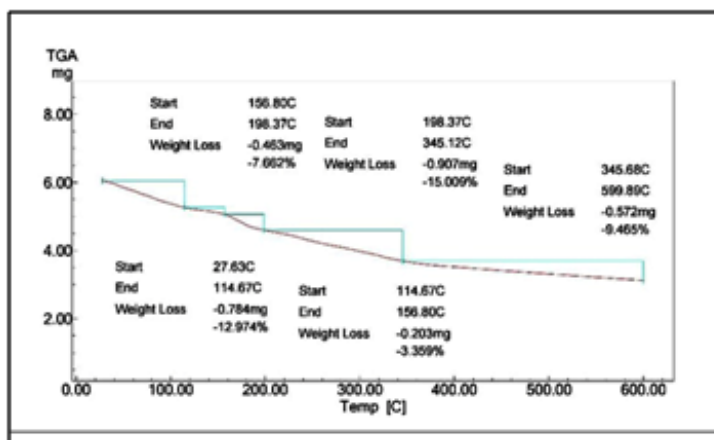


Figure 8: TGA of Co Sulfaquinoxaline complex

Table 6: TGA analysis of sulfaquinoxaline and its metal complexes

Complex	Temp. (°C) TGA	Wt. Loss %		Assignment
		Calc	Found	
Sulfaquinoxaline	48.2-389.1°C	59.60	60.87	Elimination of NH ₃ and 2C ₆ H ₆
	389.1-684.6 °C	17.20	17.71	Elimination of C ₂ H ₄ N ₂ and NH ₃
[Cu ₂ (HL) ₃ Cl ₂ (H ₂ O) ₂]	18.86-106.16°C	11.49	11.37	Loss of 2H ₂ O and C ₆ H ₇ N
[Zn ₂ (HL) ₃ Cl ₄ (H ₂ O) ₂]	106.16-147.52°C	11.90	11.29	Loss of 3C ₆ H ₆
	147.52-257.51 °C	20.80	20.78	Loss of C ₂ H ₄ N ₂ and 2SO ₂
	257.51-316.10 °C	17.03	17.12	Loss of C ₆ H ₇ N, 2HCl and S
[(ZrO ₂) ₂ (L) ₂ (HL) Cl (OH)]	26.52-76.47 °C	12.05	11.97	Elimination of 3HCl, NH ₃ and 2H ₂ O
	76.47-172.11 °C	13.93	14.12	Elimination of HCl and 3C ₆ H ₆
	171.11-225.18 °C	24.02	23.87	Elimination of 3C ₂ H ₄ N ₃ , 2C ₆ H ₅ SO ₂ and NH ₃
	225.18-338.70 °C	16.35	16.41	Elimination of 4NH ₃ and C ₆ H ₅ S
[Mn ₃ (HL) ₂ (H ₂ O) ₆ (OH) ₄]	28.96-101.76 °C	12.34	12.57	Loss of HCl , H ₂ O and NH ₃
	101.76-150.86 °C	14.08	13.98	Loss of 3C ₆ H ₆ N ₂
	150.86-346.99 °C	23.34	23.04	Loss of 2C ₆ H ₆ , 3C ₂ H ₄ , NH ₃ and SO ₂
	346.99-423.74 °C	2.57	2.69	Loss of C ₆ H ₇ N, 3NH ₃ and 2SO ₂
[Ni ₂ (HL) ₂ (OH) ₂ (H ₂ O) ₅]	27.01-60.97 °C	14.79	14.80	Elimination of 8H ₂ O
	60.97-261.43 °C	6.05	6.02	Elimination of 2C ₆ H ₆
	261.43-356.85 °C	10.35	10.31	Elimination of 2C ₂ H ₄ N ₂
	356.85-419.98 °C	7.48	7.51	Elimination of 2NH ₃ , 2H ₂ O and 2C ₆ H ₆
	419.98-513.70 °C	2.91	2.94	Elimination of S, SO and 2NH ₃
[Co ₂ (HL) ₃ Cl ₄ (H ₂ O) ₂]	24.55-56.97 °C	6.23	6.40	Loss of 3H ₂ O
	56.97-256.33 °C	6.63	6.49	Loss of 4H ₂ O and 2NH ₃
	256.33-334.25 °C	16.73	16.85	Loss of 2C ₈ H ₆ N ₃
	334.25-434.64 °C	26.40	26.44	Loss of 2C ₆ H ₅ SO and 2NH ₃
[Co ₂ (HL) ₃ Cl ₄ (H ₂ O) ₂]	27.63-114.67 °C	12.84	12.97	Elimination of 3HCl ,2H ₂ O and NH ₃
	114.67-156.80 °C	3.40	3.36	Loss of HCl and 3C ₆ H ₆
	156.80-198.37 °C	7.69	7.66	Elimination of NH ₃ ,3C ₂ H ₄ N ₂ and C ₆ H ₅ SO ₂
	198.37-345.12 °C	14.98	15.01	Loss of C ₆ H ₅ SO and 2NH ₃



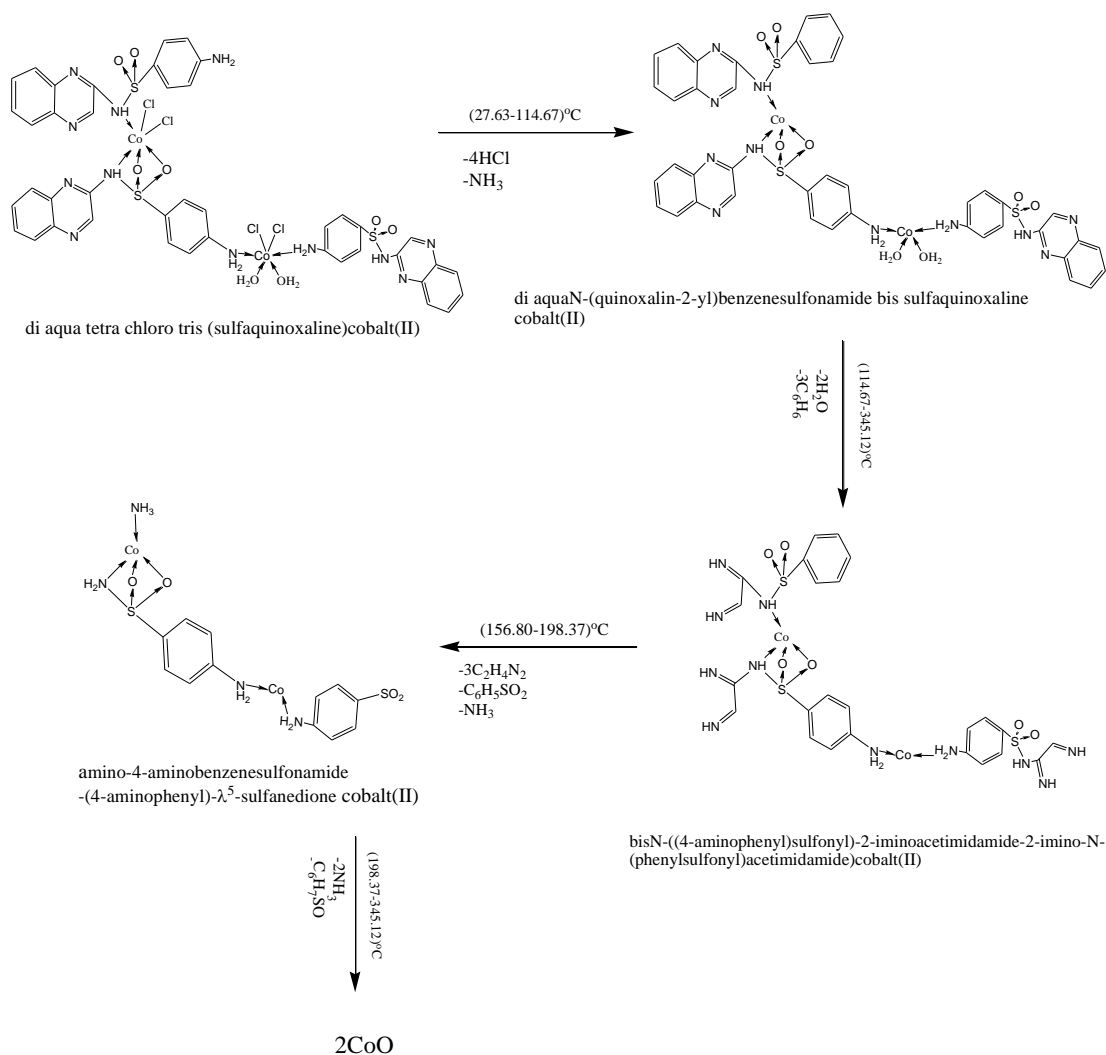
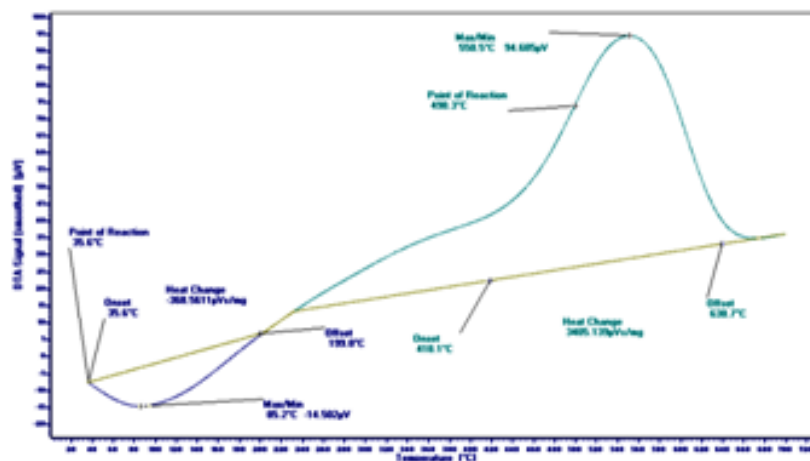
Scheme(2):Thermolysis of $[\text{Co}_2(\text{HL})_3 \text{Cl}_4(\text{H}_2\text{O})_2]$ 

Figure 9: DTA of Co sulfaquinoxaline complex



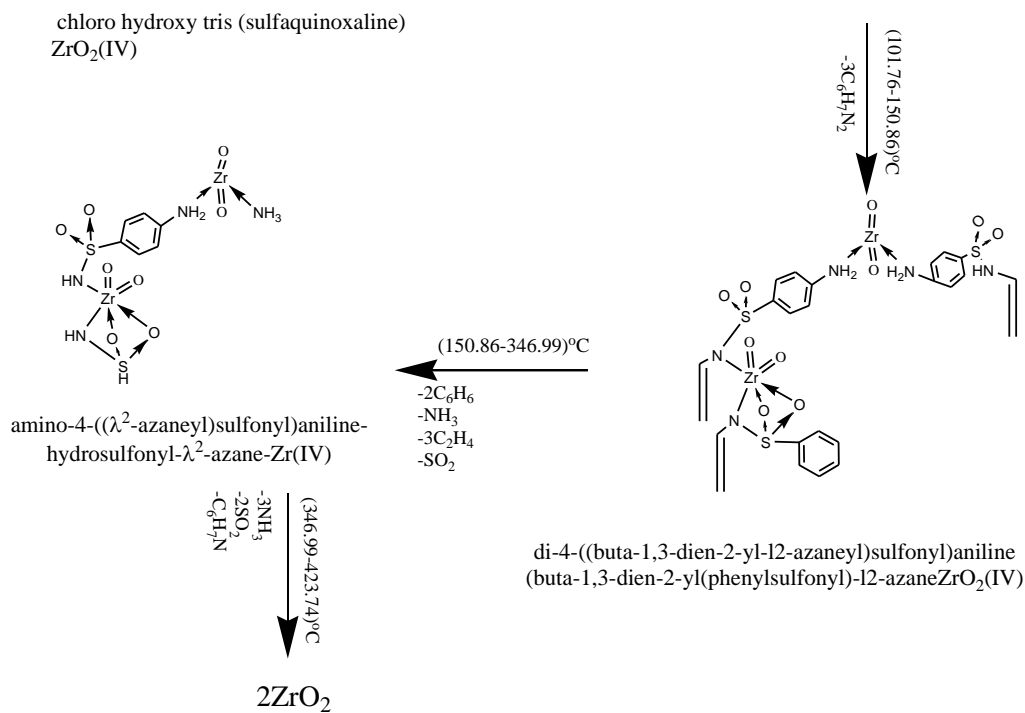
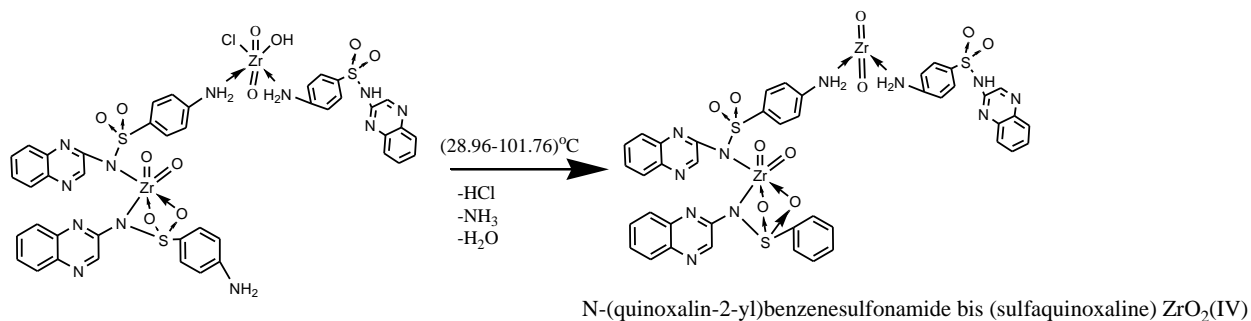
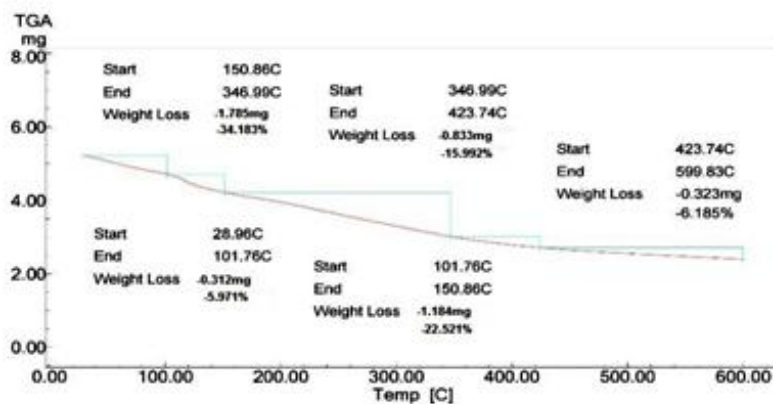
Scheme (5): Thermolysis of [(ZrO₂)₂(L)₂(HL) Cl(OH)]

Figure 10: TGA of Zr Sulfaquinoxaline complex



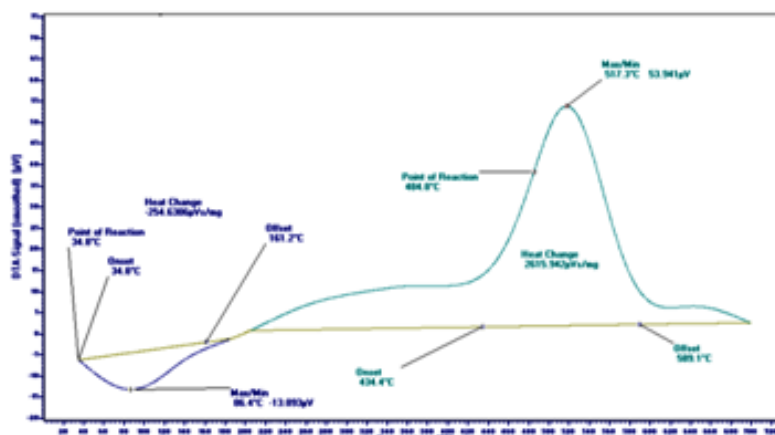
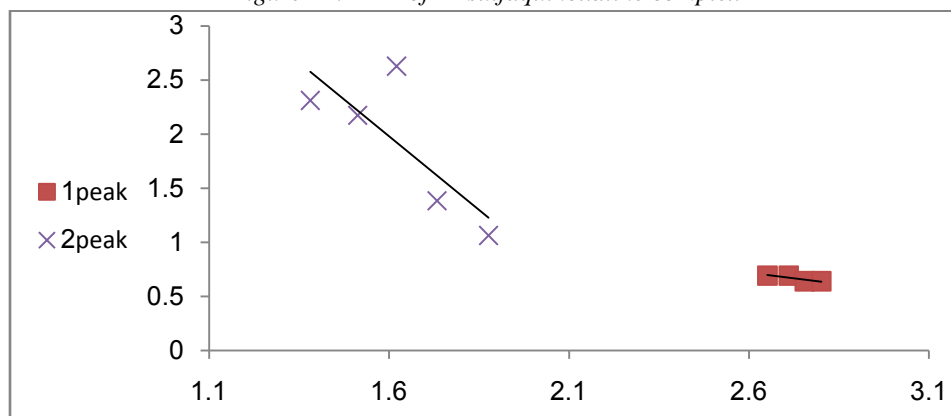


Figure 11: DTA of Zr sulfaquinoxaline complex

Figure 12: $\ln\Delta T$ against $10^3/T$ relation for Sulfaquinoxaline ligand

Conclusion

Sulfaquinoxaline metals complexes are synthesized and characterized by different spectroscopic methods. All complexes have Oh geometry and these results confirmed by Nujol and ESR spectra. Sulfaquinoxaline act as a tetradentate ligand. Also have different sites available for coordination which carries more electronegative charges and the computational study discuss these results. The thermal decomposition of the complexes ended with the formation of metal oxides as a final product. Sulfaquinoxaline complexes show higher activity than commercial sulfaquinoxaline for *Staphylococcus aureus* except $[\text{Fe}_2(\text{HL})\text{Cl}_6(\text{H}_2\text{O})_2]$ complex.

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