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Spectroscopic and Antibacterial Studies of Mixed Ligand Complexes of Transition Metal (II) Ions with Sulfadoxine and 1,10- Phenanthroline

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Abstract

The mixed ligand complexes of Co(II), Ni(II) and Cu(II) with Sulfadoxine and 1,10-phenanthroline were synthesized and characterized by elemental analysis, Infrared (IR), mass spectrometry, ¹H-NMR, and Ultraviolet (UV) spectroscopy. Some physical parameters were obtained using molar conductance measurement and melting point determination. Based on the analytical and spectroscopic data, the complexes were proposed to have the formula [M L₁ L₂ Cl₂].nH₂O, where M= Co, Ni or Cu; L₁= sulfadoxine, L₂=1,10- phenanthroline, n = 0 and 2. The spectroscopic data showed that sulfadoxine coordinated through (N-H) and (O=S=O), while 1,10- phenanthroline coordinated through two nitrogen atoms making them bidentate ligands. The kinetic and thermodynamic parameters such as: activation energy (E_a), enthalpy of reaction (ΔH^{*}), entropy change (ΔS^{*}) and free energy change (ΔG^{*}) were estimated from the differential thermal analysis curves. Free ligand 1,10-phenanthroline showed antibacterial activity, but sulfadoxine had no effect and all complexes showed antibacterial activity.

Keywords: Synthesis, Characterization, Mixed ligand, Sulfadoxine, Metal Ion.

INTRODUCTION

The Mixed ligand complexes play an important role in a lot of chemical and biological systems like water softening, ion exchange resin, electroplating, dyeing, antioxidant, photosynthesis in plants, removal of undesirable and harmful metals from living organisms and many of these metal complexes shown good biological activity against pathogenic microorganisms (Mrinalinil and Manihar Singh, 2012; Rajasekar *et al.*, 2012). 1,10-Phenanthroline is one of the most popular bidentate N,N chelating agent, so far used in the development of coordination chemistry of heterocyclic nitrogen donor ligands (Sangeetha *et al.*, 2012; El-Sharief *et al.*, 2003). Its rigidity makes it an entropically better chelating molecule than 2,2'-bipyridine and has been exploited to make a variety of simple geometrically diverse complexes (Accorsi *et al.*, 2009). Complexes containing 1,10-phenanthroline display exciting photochemical, photophysical properties (Azar *et al.*, 2017) and are used as fluorescent sensors for the selective detection of cations (Schmittel and Lin., 2007) anions (Liu *et al.*, 2008), and oxygen (Baleizao, 2008). Literature survey fell to reveal any previous work or literature regarding on the complexation of 1,10-phenanthroline and sulfadoxine with metals Sulfadoxine (sulphadoxine) [4-amino-N-(5,6-dimethoxy-Pyrimidin-4-yl)benzenesulfoamide or 4,5 dimethoxy-6- Sulfanilamidopyrimidine]. Sulfadoxine is an ultra-long-lasting sulfonamide. It has a half-life of 120 to 200 hours (Vardanyan and Hruby, 2006). The biological activity of sulpham drugs as well as the ligands derived from them has been known for a long time, and their activities has been reported to increase on complexation with metal ions (Nair and Regupathy, 2009). This is true as the resultant structural changes that normally occur on complexation with the metal, center alters and sometimes improves the activities of the substance (Adediji *et al.*, 2009).

MATERIALS AND METHODS

Materials

All chemicals, solvents, metal(II) chlorides (i.e. Cobalt chloride hexahydrate, Nickel chloride hexahydrate and Copper chloride dihydrate) and 1, 10-Phenanthroline were available from BDH and were used without further purification. Pure sample of sulfadoxine was obtained from Shaphaco Pharmaceutical Company at Sana'a-Yemen.

Preparation of the drug metal complexes

Generally, the solid complexes were prepared by adding an ethanolic solution of hydrated metal chlorides to an ethanolic solution of mixed ligands of sulfadoxine and 1,10-phenanthroline in a 1:1:1 mole ratios. The mixture of each was refluxed on hot plate at 60°C with constant stirring for 2 hours until the colored precipitates were

formed. The precipitated solids were filtered off, washed with ethanol absolute, then washed by DMF and air-dried.

Spectral measurements

IR spectra of the complexes were measured in the rang 200-4000 cm^{-1} by using (FT/IR-140, Jasco, Japan) at Sana'a University.

The electronic spectra of the complexes were measured in the rang 200-800 nm by using UV-VIS spectrophotometer (specord200, Analytik Jena, Germany) at Sana'a University.

The proton NMR spectra were recorded on a Varian FT- 300 MHz spectrometer in d_6 -DMSO solvent, using TMS as internal standard, at Cairo University, Giza, Egypt.

Mass Spectra were recorded on JEOL JMS600 spectrometer, at Micro analytical center, Egypt.

C, H, N and S analysis for complexes have been carried out in Vario EL Fab. CHNS Nr. 11042023, at Central Laboratory, Faculty of Science, Cairo University, Egypt. Chloride was determined gravimetrically by silver nitrate (Vogel, 1989). The amount of coordinated and uncoordinated water were determined gravimetrically using weight loss method (Vogel 1989) and by thermal analysis methods.

Physical Measurements

The molar conductance of 10^{-3} M solutions of the ligands and their metal complexes in DMSO solvent were measured on Jenway conductivity meter model 4510. All the measurements were taken at room temperature on freshly prepared solutions. Stuart Scientific electrothermal melting point apparatus was used to measure the melting points of the metal complexes in glass capillary tubes in degrees Celsius.

The metal content was measured by using Perkin-Elmer 2380 flame atomic absorption spectrophotometer at the central lab of the Ministry of Oil, Sana'a-Yemen.

TLC was carried out on Silica Gel GF₂₅₄ plates (m-kieselgel G., 0.2 mm thickness) with a 3:1 v/v ethylacetate / petroleum ether solution as eluent mobile at room temperature. The plates were scanned under ultraviolet light 254 nm lamp (Szafran *et al.*, 1991).

The mass susceptibility (χ_g) of the solid complexes was measured at room temperature using Gouy's method by a magnetic susceptibility balance from Johnson Metthey and Sherwood model at Cairo University Central Lab (Suberu, 2004).

Thermal Analysis

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) experiments were conducted by using Shimadzu DTA-50 and Shimadzu TGA-50H thermal analyzers, respectively, (at Micro Analytical Center, Cairo University.). All experiments were

performed under nitrogen at a flow rate of 30 ml/min and a 10°C/min heating rate in a temperature range 20-800°C.

Biological Screening

The ligands and their metal complexes were tested for their antibacterial activity against four species of bacteria (*Staphylococcus aureus*, *Bacillus*, *Escherichia coli*, and *Pseudomonas aeruginosa*), using filter paper disc method (Amin and Yamany, 2012). The screened compounds were dissolved individually in DMSO (dimethyl sulfoxide) in order to make up a solution of 1000 µg/ml concentration for each of these compounds. Discs saturated with DMSO are used

as solvent control. Gentamicin 120µg/ml was used as a reference substance for these bacteria (Skehan and Storeng, 1990).

RESULTS

Synthesis of the complexes

The synthetic Co(II), Ni(II) and Cu(II) with sulfadoxine and 1,10-phenanthroline complexes are investigated. Some physical properties, conductivity, analytical data and their composition are summarized in (Tables 1 and 2).

Table 1. Some physical properties of the complexes

complex	Color (Yield%)	M.P. (°C)	TLC		Solubility								
			No. of spots	R _f	H ₂ O	MeOH	EtOH	Acetone	CCl ₄	CHCl ₃	DMF	DMSO	
[Co(phen)(Sfd)Cl ₂]	darkblue (20)	340	one	0.17	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	S.
[Ni(phen)(Sfd)Cl ₂]	lightgreen (22)	316	one	0.13	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	S.
[Cu(phen)(Sfd)Cl ₂].2H ₂ O	Dark green (31)	345	one	0.15	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.	S.

R_f = Retention factor in Thin Layer Chromatography; S= Soluble; Ins.= Insoluble

Table 2. Elemental Analysis of the complexes

Complex (Molecular formula)	F. Wt	A _m Ω ⁻¹ cm ² mol ⁻¹	Element Analysis, Found Calculated %					
			C	H	N	S	M	Cl
[Co(phen)(Sfd)Cl ₂] (C ₂₄ H ₂₂ Cl ₂ N ₆ CoO ₄ S)	620.38	12	46.30 (46.46)	3.35 (3.57)	13.68 (13.54)	4.98 (5.16)	9.30 (9.49)	11.60 (11.42)
[Ni(phen)(Sfd)Cl ₂] (C ₂₄ H ₂₂ Cl ₂ N ₆ NiO ₄ S)	620.14	15	46.54 (46.48)	3.78 (3.57)	13.40 (13.55)	4.97 (5.17)	9.59 (9.46)	11.45 (11.43)
[Cu(phen)(Sfd)Cl ₂].2H ₂ O (C ₂₄ H ₂₆ Cl ₂ N ₆ CuO ₆ S)	661.02	19	43.51 (43.60)	4.02 (3.96)	12.51 (12.71)	4.84 (4.85)	9.69 (9.61)	10.57 (10.72)

Molar conductance

The molar conductance values of the synthetic complexes obtained in DMSO as a solvent at room temperature are listed in (Table 2).

Infrared Spectra

Sulfadoxine in these complexes behave as neutral bidentate molecule, through oxygen of sulfone group and nitrogen atom of amino group (O and N donor atoms). Therefore, in these complexes one metal ion is coordinated

with two ligands 1,10-phenanthroline molecule and Sulfadoxine molecule (Figures 1, 2 and 3) and (Table 3).

Mass Spectra

The mass spectra of Co, Ni and Cu complexes with 1,10-phenanthroline and sulfadoxine were the molecular ion peaks at m/e 620.65(29%), 620.09(16%), and 660.90(30%), respectively, are similar to that calculated 620.38, 620.14 and 661.02.

Table 3. Significant IR spectral bands (cm⁻¹) of 1,10-phenanthroline, sulfadoxine ligands and their complexes

1,10-phenanthroline	Sulfadoxine	[Co(phen)(Sfd)Cl ₂]	[Ni(phen)(Sfd)Cl ₂]	[[Cu(phen)(Sfd)Cl ₂].2H ₂ O]	Assignment
-	3468 ^s , 3241 ^s	3371,3230 ^w	3450,3230 ^w	3361,3200 ^m	v(NH)
-	3311 ^s	3310 ^w	3313 ^w	3314 ^w	v(NH ₂)
-	-	-	-	3150 ^{br}	v(OH)H ₂ O
1134 ^s	-	1110 ^m	1100 ^w	1117 ^w	Benzene ring + pyridine ring stretch
3010 ^m	2998 ^w	3056 ^{w,br}	2965 ^{w,br}	3059 ^{w,br}	v CH-arom.
-	2877 ^m	2973 ^{w,br}	2856 ^{w,br}	2973 ^{w,br}	v CH-aliph.
-	1080 ^m	1050 ^w	1042 ^w	1047 ^m	v(C-N)
-	1214 ^s	1206 ^m	1210 ^m	1203 ^m	v(C-O)
-	1374 ^s	1310 ^s	1323 ^m	1344 ^m	v(O=S=O)
1588 ^s	1654 ^s	1430 ^m	1458 ^m	1423 ^m	v(C=N)
-	-	421 ^m	492 ^m	425 ^m	v(M-N)
-	-	592 ^m	674 ^m	677 ^m	v(M-Cl)

s = strong; m = medium; br = broad; w = weak; w,br = weak and broad

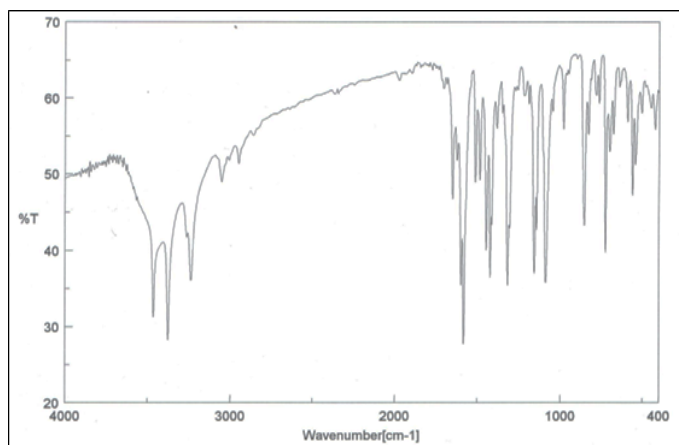


Fig. 1. Infrared Spectrum of [Co(phen)(Sfd)Cl₂] complex

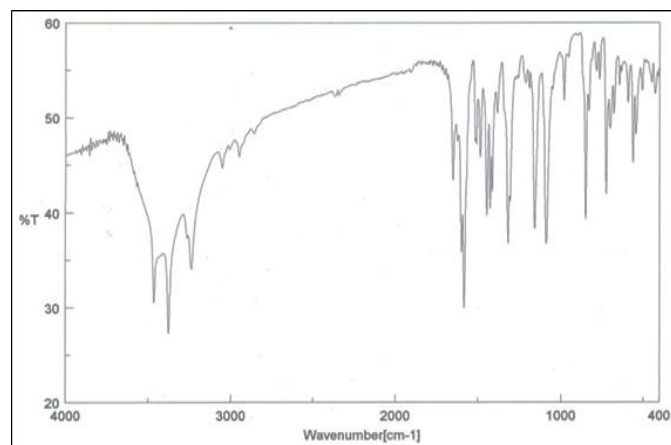


Fig. 2. Infrared Spectrum of [Ni(phen)(Sfd)Cl₂] complex

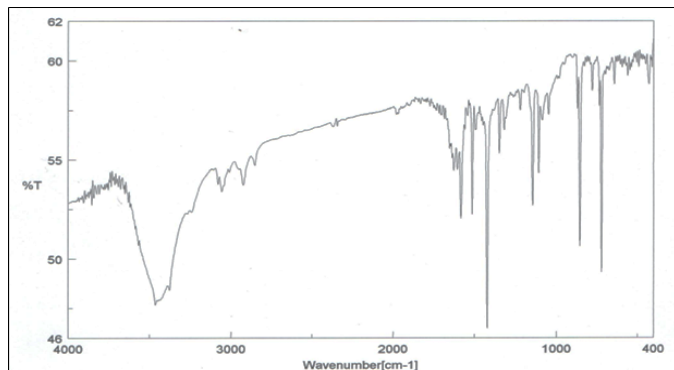


Fig. 3. Infrared Spectrum of $[\text{Cu}(\text{phen})(\text{Sfd})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ complex

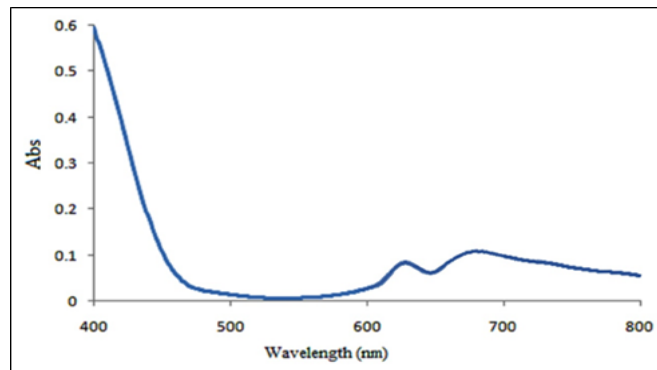


Fig. 5. UV-visible Electronic Spectrum of $[\text{Ni}(\text{phen})(\text{Sfd})\text{Cl}_2]$ complex

Magnetic and Electronic Spectral Studies

The results are shown in Table 4, and (Figures 4,5, and 6).

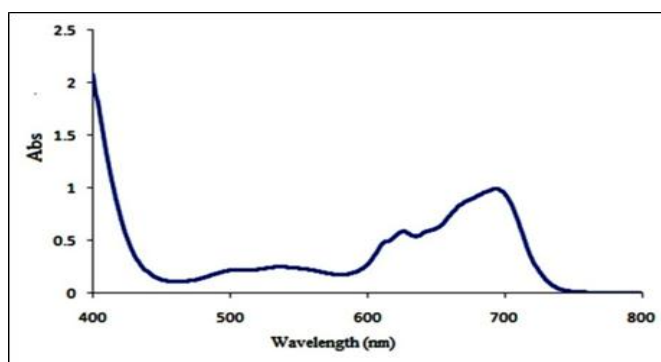


Fig. 4. UV-visible Electronic Spectrum of $[\text{Co}(\text{phen})(\text{Sfd})\text{Cl}_2]$ complex

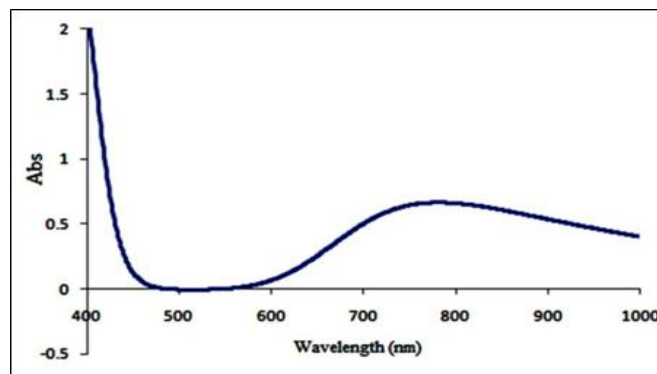


Fig. 6. UV-visible Electronic Spectrum of $[\text{Cu}(\text{phen})(\text{Sfd})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ complex

Table 4. Magnetic moment, electronic spectral data for the Sulfadoxine complexes

Complex	μ_{eff} (B.M.)	L→M charge transfer (cm^{-1})	d-d transition bands (cm^{-1})	Assignments	Supposed structure
$[\text{Co}(\text{phen})(\text{Sfd})\text{Cl}_2]$	5.15	22827	18560 16102 14501	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g} \rightarrow {}^4A_{2g}$ ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$	Octahedral
$[\text{Ni}(\text{phen})(\text{Sfd})\text{Cl}_2]$	2.86	21794	16200 14705	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	Octahedral
$[\text{Cu}(\text{phen})(\text{Sfd})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	1.79	24120	12820	${}^2eg \rightarrow {}^2T_{2g}$	Distorted Octahedral

Table 5. Characteristic parameters of thermal decomposition ($10^{\circ}\text{C min}^{-1}$) for Co(II), Ni(II) and Cu(II) complexes with 1,10-phenanthroline and sulfadoxine

Comp.	Step	TGA				DTA		Reaction
		Δm % found (calc.)	T_i/C°	T_f/C°	T_{DTG}	T_{dta}	Heat	
[Co(phen)(Sfd)Cl ₂]	1	7.10 (7.14)	26	175	170	172	endo	-1.25Cl
	2	9.30 (9.29)	175	287	230	232	endo	-[0.75Cl + OCH ₃]
	3	4.99 (5.00)	287	415	356	353	endo	- OCH ₃
	4	64.57 (64.55)	415	654	576	571	exo	-[C ₂₁ H ₁₆ N ₆ OS]
Final residue (CoO + C) : 14.03% (14.01)								
[Ni(phen)(Sfd)Cl ₂]	1	5.70 (5.72)	24	262	241	237	endo	- Cl
	2	15.76 (15.72)	262	468	379	381	exo	- Cl + 2OCH ₃
	3	55.78 (55.86)	468	755	612	610	exo	-[C _{16.5} H ₁₆ N ₆ OS]
Final residue(NiO + 5.5C) : 22.75% (22.69)								
[Cu(phen)(Sfd)Cl ₂].2H ₂ O	1	5.39 (5.45)	23	101	80	76	endo	-2H ₂ O
	2	2.69 (2.68)	101	179	158	156	endo	-0.5Cl
	3	5.38 (5.36)	179	325	203	218	endo	-Cl
	4	12.10 (12.07)	325	450	427	426	exo	-[0.5Cl + 2OCH ₃]
	5	4.22 (4.24)	450	480	473	472	exo	-N ₂
	6	56.33 (56.34)	480	632	533	534	exo	-C ₂₁ H ₁₆ N ₄ OS
Final residue (CuO + C) : 13.88% (13.85)								

endo=endothermic peak, exo= exothermic peak

Thermal Analysis

Co(II) complex

The TG thermograms and DTG curves of [Co(phen)(Sfd)Cl₂], [Ni(phen)(Sfd)Cl₂], and

[Cu(phen)(Sfd)Cl₂].2H₂O were obtained in (Figure 7a,b , Figure 8a,b and Figure 9a,b and Table 5, 6) respectively.

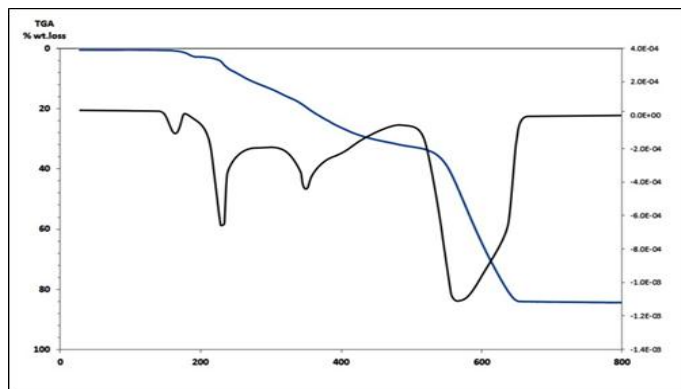


Fig. 7a. TG and DTG thermograms of [Co(phen)(Sfd)Cl₂] complex

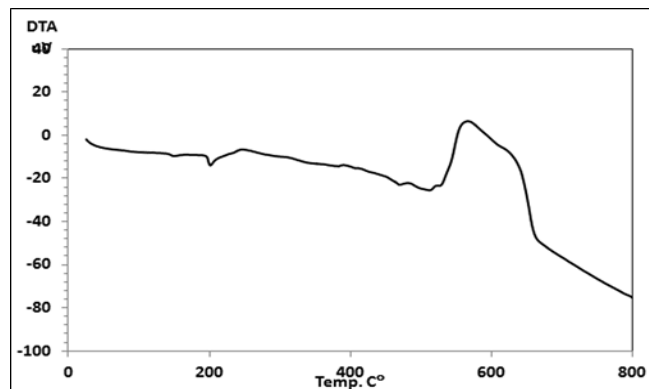


Fig. 7b. DTA thermogram of [Co(phen)(Sfd)Cl₂] complex

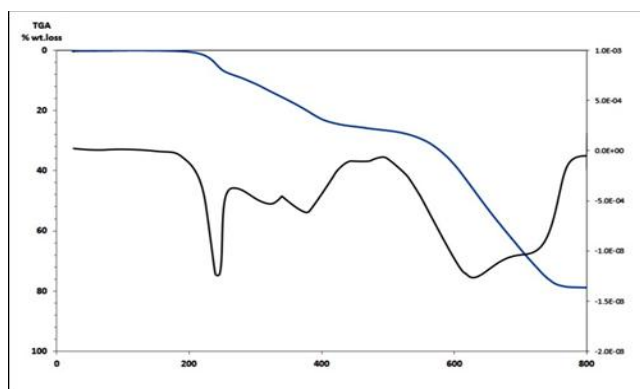


Fig. 8a. TG and DTG thermograms of [Ni(phen)(Sfd)Cl₂] complex

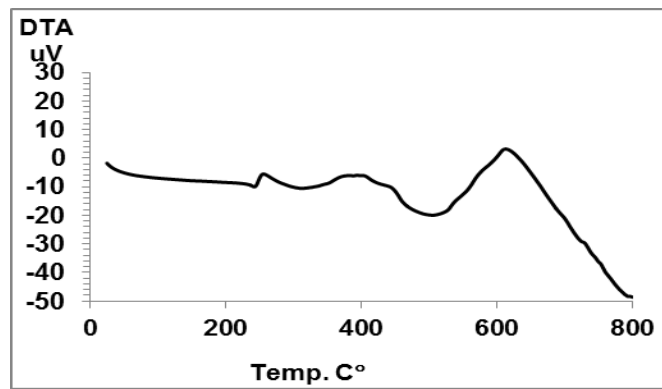


Fig. 8b. DTA thermogram of [Ni(phen)(Sfd)Cl₂] complex

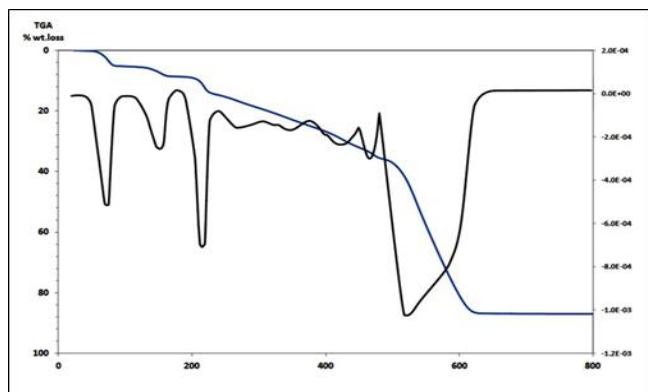


Fig. 9a. TG and DTG thermograms of [Cu(phen)(Sfd)Cl₂].2H₂O complex

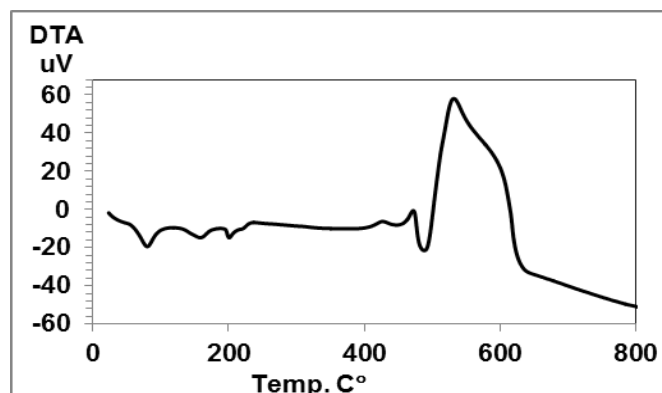


Fig. 9b. DTA thermogram of [Cu(phen)(Sfd)Cl₂].2H₂O complex

Table 6. Kinetic and thermodynamic parameters of the thermal decomposition for Co(II), Ni(II) and Cu(II) complexes with 1,10-phenanthroline and sulfadoxine

Comp.	Step	r	n	Z s ⁻¹	T _{max} K	E kJ.mol ⁻¹	ΔS* J.K ⁻¹ mol ⁻¹	ΔH* kJ.mol ⁻¹	ΔG* kJ.mol ⁻¹
[Co(phen)(Sfd)Cl ₂]	1	0.9981	1.5	3.10x10 ¹⁰	443	104	-47.4	100.3	121.1
	2	0.9927	1.9	6.40x10 ¹⁵	503	98	53.3	38.8	22.5
	3	0.9976	3	1.19x10 ³	629	111	-192.2	105.7	226.6
	4	0.9753	2.1	2.14x10 ⁶	849	250	-132.4	242.9	335.3
[Ni(phen)(Sfd)Cl ₂]	1	0.9915	2	7.22x10 ⁹	514	112	-60.7	107.7	138.9
	2	0.9922	0.5	2.43x10 ⁷	562	124	-108.8	119.3	180.4
	3	0.9901	1.4	3.67x10 ²²	885	203	178.1	195.6	38.0
[Cu(phen)(Sfd)Cl ₂].2H ₂ O	1	0.9799	2.9	3.02x10 ³	353	45	-179.7	42.1	105.5
	2	0.9888	2	3.99x10 ⁵	431	55	-140.8	51.4	112.1
	3	0.9991	1.1	6.20x10 ¹⁶	476	63	-118.8	59.1	115.6
	4	0.9920	1.6	5.69x10 ¹⁰	700	131	-46.1	125.1	157.4
	5	0.9985	3	8.90x10 ¹⁵	746	201	52.8	194.7	155.3
	6	0.9911	2.1	2.21x10 ⁷	806	187	-112.6	180.2	271.0

r= correlation coefficient of the linear plot , n=order of reaction , Z = pre-exponential factor

Antibacterial studies

The results of the highest-to-lowest effective activities can be summarized in Table 7.

Table 7. Effect of the ligands and their complexes on the growth

Compound (1000 µg/ml)	Bacteria (Zone of inhibition in mm)			
	gram-positive		gram-negative	
	<i>Staphylococcus aureus</i>	<i>Bacillus</i>	<i>Pseudomonas Aeruginosa</i>	<i>Escherichia coli</i>
1,10-phenanthroline	++	+++	++	++
sulfadoxine	-	-	-	-
[Co(phen)(Sfd)Cl ₂]	-	++	-	-
[Ni(phen)(Sfd)Cl ₂]	-	-	-	-
[Cu(phen)(Sfd)Cl ₂].2H ₂ O	++	++	++	+
Gentamicin 120 µg/ml	++	+	++	+

(-) No zone of inhibition were observed; Moderately sensitive, (+) Inhibition zone of 2-5; Sensitive, (++) Inhibition zone of 6-10; Highly sensitive, (+++) Inhibition zone of 11-15.

DISCUSSION

The elemental analysis showed that the formed complexes of Co(II), Ni(II) and Cu(II) with sulfadoxine and 1,10-phenanthroline are of 1:1:1 (metal: 1,10-phenanthroline : sulfadoxine) molar ratio.

Co (II), Ni(II) and Cu (II) complexes with 1,10-phenanthroline and sulfadoxine have molar conductivity values of 12, 15 and 19 Ω⁻¹ mol⁻¹ cm², respectively, which indicated the non-ionic nature of these complexes (Thakar *et al.*, 2013).

A comparison of IR spectra of free ligands with that of their complexes leads to that the sulfoxide O=S=O stretching which occurs at 1374 cm⁻¹ in free ligand (Ajibade *et al.*, 2006) is also shifted to lower wavelength thus oxygen of sulfone group is coordinated with metals (Sunil *et al.*, 2011; Kim and Takizawa, 1975). The absorption band at 3241 and 3454 cm⁻¹ are assigned to symmetric and asymmetric N-H stretching frequencies in free ligand (Ferraro, 1971). Similar bands are shifted to lower and higher wavelengths in the metal complexes, such changes clearly indicate that the lone pair of NH is involved in the complexation with metals, so the infrared spectra display

bands at 492-412 cm⁻¹ attributed to M-N vibrations (Silverstein and Webster, 1998).

The bands in the range 677-592 cm⁻¹ are assigned to M-Cl bonds in Co(II), Ni(II) and Cu(II) complexes, respectively (Gamo, 1961). A broad band at 3510-3100 cm⁻¹ for Cu(II) complex is attributed to νOH (H₂O) (Mahmoud and Bountis, 2014). 1,10-phenanthroline behaves as a neutral bidentate molecule, strong band appearing at 1134 cm⁻¹ is assigned to benzene and pyridine ring stretching vibrations in the free 1,10-phenanthroline (Hassan *et al.*, 2013). This band shows a slight shift by 16-33 cm⁻¹ and a shift of ν(C=N) of the 1,10-phenanthroline from 1588 cm⁻¹ to lower frequency in the complexes due to the nitrogen atoms coordinated to the metal (El-Ghamry *et al.*, 2013; Cotton and Wilkinson, 1972).

In the ¹H-NMR spectra of [Co(phen)(Sfd)Cl₂], [Ni(phen)(Sfd)Cl₂] and [Cu(phen)(Sfd)Cl₂].2H₂O, the chemical shifts were observed at 4.75, 4.46 and 4.64 ppm (br s, NH), respectively, compared with free sulfadoxine at 3.99 ppm (Ajibade *et al.*, 2006). The characteristic proton signals between 3.25 and 3.82 ppm (s, 6H, -OCH₃) which support the presence of a methoxy groups of the sulfadoxine in the complexes (Ajibade *et al.*, 2006), and multiple signals between 6.37 and 7.93 ppm (m, 13H,

pyridine ring of 1,10-phenanthroline and aromatic ring of sulfadoxine). In the ^1H NMR spectra of $[\text{Cu}(\text{phen})(\text{Sfd})\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ The signal at 3.13 ppm was assigned to coordinated water molecules.

The Co(II) complex exhibited three bands at 18560, 16102 and 14501 cm^{-1} which were consistent with octahedral geometry and were assigned to $^4T_{1g} \rightarrow ^4T_{1g}(P)$ (ν_3), $^4T_{1g} \rightarrow ^4A_{2g}$ (ν_2) and $^4T_{1g} \rightarrow ^4T_{2g}(F)$ (ν_1), transitions, respectively (Al-Maydama *et al.*, 2008). Moment of 5.15 B.M was supportive of octahedral geometry since moments in the range 4.7-5.2 B.M. were reported for octahedral Co(II) complexes (Idemudia and Ajibade, 2010).

Furthermore, the Ni(II) complex showed two absorption bands at 16200 and 14705 cm^{-1} typical of 6-coordinate octahedral geometry, assigned to $^3A_{2g} \rightarrow ^3T_{1g}(P)$ (ν_3) and $^3A_{2g} \rightarrow ^3T_{1g}(F)$ (ν_2) transitions, respectively (Idemudia and Ajibade, 2010). An observed moment of 2.86 B.M. was complimentary of octahedral geometry since moments in the range 2.9-3.3 B.M (Al-Maydama *et al.*, 2008).

The Cu(II) complex had an absorption band at 12820 cm^{-1} which assigned to $^2eg \rightarrow ^2T_{2g}$. The broadness of the band could be attributed to the overlapping of several bands as a result of strong Jahn-Teller distortion expected in a d^9 ion which enhances the distortion of the octahedral geometry (Figgis, 1966). The magnetic moment value of this complex (1.79 B.M.) was found to be within the range reported for the d^9 -system containing one unpaired electron.

The TG thermogram of $[\text{Co}(\text{phen})(\text{Sfd})\text{Cl}_2]$ is characterized by four degradation steps in the range 26-175, 175-287, 287-415 and 415-654°C. The first step at T_{DTG} of 170°C ill-defined is consistent with the evolution of 1.25Cl atom (cal. 7.14%, found 7.10%). The activation energy calculated is $104\text{ kJ}\cdot\text{mol}^{-1}$. (OCH_3) may be eliminated in the second step together with 0.75Cl atom (cal. 9.29%, found 9.30%), with the activation energy ($98\text{ kJ}\cdot\text{mol}^{-1}$). The apparent T_{DTG} (230°C) and the endothermic peak (T_{dta}) at 232°C. The third step which corresponds to the loss of OCH_3 fragment (cal. 5.00, found 4.99%) has activation energy of $111\text{ kJ}\cdot\text{mol}^{-1}$. The fourth step has a broad exothermic peak of T_{dta} at 571°C which corresponds to the loss of $\text{C}_{21}\text{H}_{16}\text{N}_6\text{OS}$ fragment, has activation energy of $250\text{ kJ}\cdot\text{mol}^{-1}$. The final ill-defined residue is CoO and C fragments (cal. 14.01%, found 14.03%). ΔS^* , ΔH^* and ΔG^* calculated are (-47.4, 53.3, -192.2 and -132.4 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), (100.3, 38.8, 105.7 and 242.9 $\text{kJ}\cdot\text{mol}^{-1}$) and (121.1, 22.5, 226.6, 335.3 $\text{kJ}\cdot\text{mol}^{-1}$), respectively.

The TG and DTG curves of $[\text{Ni}(\text{phen})(\text{Sfd})\text{Cl}_2]$ show relatively rapid decomposition in the first (24-262°C), second (262-468°C) and third (468-755°C) steps with T_{DTG} peaks at 241°C, 379°C and 612°C. The sharp T_{DTG} peak observed for the first step at 241°C is preceded

with a small endothermic peak (T_{dta}) in DTA curve at 237°C. 5.70%, 15.76% and 55.78% mass losses in the first, second and third steps correspond to the release of (Cl), (Cl + 2OCH_3) and ($\text{C}_{16.5}\text{H}_{16}\text{N}_6\text{OS}$) fragments (Cal. 5.72%, 15.72% and 55.86), respectively. The final residue is NiO and 5.5 C fragments (cal. 22.69%, found 22.75%). The activation energies calculated for the first, second and third steps are 112, 124 and $203\text{ kJ}\cdot\text{mol}^{-1}$ and the values (-60.7, -108.8 and $178.1\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), (107.7, 119.3 and $195.6\text{ kJ}\cdot\text{mol}^{-1}$) and (138.9, 180.4, $38.0\text{ kJ}\cdot\text{mol}^{-1}$) are their entropy, enthalpy and free energy changes of activation, respectively.

The TG and DTG curves of $[\text{Cu}(\text{phen})(\text{Sfd})\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ show six steps of a continuous mass loss with sharp, weak and broad DTG peaks, indicating slow mass losses. The first-step (23-101°C) with 5.39% mass loss at a T_{dtg} (80°C) and the endothermic peak (T_{dta}) at 76°C was assigned to the release of two uncoordinated water molecules (cal. 5.45%). The remaining mass losses 2.69%, 5.38% and 12.10%, 4.22%, 56.33% occur in the second (101-179°C), third (179-325°C), fourth (325-450°C), fifth (450-480°C), sixth (480-632°C) steps are due to the release of (0.5Cl), (Cl), (0.5Cl and 2OCH_3), (N_2) and ($\text{C}_{21}\text{H}_{16}\text{N}_4\text{OS}$) fragments (cal. 2.68%, 5.36%, 12.07%, 4.24% and 56.34%, respectively) at the T_{dtg} peaks of 158, 203, 427, 473 and 533°C and T_{dta} peaks at 156, 218, 426, 472 and 534°C. The activation energies calculated of these six steps are 45, 55, 63, 131, 201 and $187\text{ kJ}\cdot\text{mol}^{-1}$, respectively, and the values (-179.7, -140.8, -118.8, -46.1, 52.8 and -112.6 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), (42.1, 51.4, 59.1, 125.1, 194.7 and $180.2\text{ kJ}\cdot\text{mol}^{-1}$) and (105.5, 112.1, 115.6, 157.4, 155.3 and $271.0\text{ kJ}\cdot\text{mol}^{-1}$) are their entropy, enthalpy and free energy changes of activation, respectively. The residue at the end of the decomposition reaction is CuO and C (Cal. 13.85%, found 13.88%) (Weder *et al.*, 2002; Agwara *et al.*, 2010).

In vitro antibacterial activities results of 1,10-phenanthroline and sulfadoxine free ligands and their metal complexes clearly show that the compounds have both antibacterial against the tested bacteria in the presence of the standards Gentamycin as antibacterial agent (Suberu, 2004; Piruthiviraj, 2016).

The lowest activity of the drugs was attributed to a probable lipophilic nature which made permeation through lipid bacteria membrane impossible as indicated. Generally, the metal(II) complexes were mostly more effective than the free drugs due to chelation which increases lipophilic character, increasing its permeation through lipid layers of the bacterial membrane as documented (Anacona and Lopez, 2012).

In general, because metal can undergo ligand exchanges, metal complexes are pro-drugs, ligand substitution can activate the metal complex toward binding to target molecules. It should be recognized that a metal is

not just a metal, the metal ion plus its ligand determine the biological activity (Kassa, 2015).

In our paper, sulfadoxine have not been given positive results with tested bacteria. 1,10-phenanthroline ligand have slightly more antibiotic activity than their complexes against the tested microorganisms under identical experimental conditions. The best activity of 1,10-phenanthroline was attributed to its ability to form hydrogen bond with the cellular content of the bacteria thereby causing the death of the organism (Al-Noor *et al.*, 2012).

It is known that chelation tends to make ligands act as more powerful and potent bactericidal agents (Raja *et al.*, 2011; Chandra *et al.*, 2015). The complexes show minor activity against selected strains of microorganisms. It has been suggested that the ligand with nitrogen and oxygen donor systems inhibit enzyme activity. Coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups within the chelate ring system (Verma *et al.*, 2012).

CONCLUSION

We report the preparation, characterization, thermal and antibacterial studies of Co(II), Ni(II) and Cu(II) complexes of 1,10-phenanthroline and sulfadoxine. The complexes formulated as $[M L_1 L_2 Cl_2] \cdot nH_2O$, L_1 = sulfadoxine, L_2 = 1,10-phenanthroline, $n = 0$ and 2. They are six coordinated complexes. The complexes were characterized by elemental analysis, 1H NMR, mass, electronic and IR spectroscopy. Spectroscopic analyses confirmed the sulfadoxine coordination amide nitrogen and oxygen of sulfone group. Also, 1,10-phenanthroline was proposed to be a bidentate ligand and coordinated through N atoms. The thermal study, kinetic and thermodynamic parameters were estimated from the DTG curves. The antibacterial screening of complexes showed varied activities.

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CONFLICT OF INTEREST

There is no conflict of interest.

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