

SYNTHESIS, SPECTRAL AND THERMAL STUDIES OF METAL COMPLEXES OF 2,4-DIHYDROXYACETOPHENONE SALICYLOYL HYDRAZONE (DHASH)

¹S.D.Deshmukh, ²P.R.Mandlik

¹Lecturer, ²Associate Professor

¹ Department of Chemistry, Government polytechnic, Amravati, India ,

¹ Department of Chemistry, Shri Shivaji Science College, Amravati- 444603, India.

Abstract : Co(II), Cu(II), Fe(III) and Zr(IV) complexes of 2,4-dihydroxyacetophenone salicyloyl hydrazone (DHASH) have been synthesized and characterized by elemental analysis, molar conductance, magnetic moments, electronic, ¹H NMR, Mass, IR spectra, ESR, and thermal studies. The molar conductivity data of the complexes show them to be non-electrolyte. The IR data suggest that the ligand acts as dibasic tridentate (ONO) (enol form) donor towards Co(II), Cu(II), Zr(IV) and tribasic tetradentate (ONOO) (enol form) donor towards Fe(III) complexes while the electronic spectral data together with magnetic moment suggest square planer geometry for Co(II), Cu(II) and octahedral geometry for Fe(III), Zr(IV) complexes. The TG analysis suggests high stability for most of the complexes followed by thermal decomposition in different steps. The kinetic parameters for their decomposition have been evaluated by using the Freeman Carroll and Sharp-Wentworth methods. ESR spectra of copper complexes were recorded and discussed.

Keywords: - Salicyloyl hydrazone, complexes, thermal analysis.

1. INTRODUCTION

In the recent years, there has been enhanced interest in the synthesis and characterization of hydrazine Schiff base metal complexes containing Schiff base as ligand due to their physiological, pharmacological and biological activity [1-3]. Schiff base hydrazones possessing azomethine proton (-NHN=CH-) play an important role for new drug development. High stability of the coordination compounds and their good solubility in common solvent, Schiff bases have been widely used as ligands [4]. It is well known that O and N atoms play a key role at the active sites of metal complexes in which they are bonded to metal ions [5].

We report here the synthesis and characterization of Co(II), Cu(II), Fe(III) and Zr(IV) complexes of Schiff base ligand derived from the condensation of 2,4-dihydroxyacetophenone and salicyloyl hydrazide. The newly synthesized compounds are characterized by elemental, molar conductance, magnetic moments, spectral (IR, ¹HNMR, UV, Mass, ESR) and thermal analysis.

2. EXPERIMENTAL

2.1. Reagents and materials

All the chemicals used were analytical reagent grade and solvents were dried and distilled before use according to standard procedure. Metal salts were purchased from Merck, Sigma-Aldrich, S.D. Fine and were used as received. The precursor salicyloyl hydrazide (C₆H₄(OH)CONHNH₂) was prepared by the reported procedure [6] by refluxing methyl salicylate with hydrazine hydrate in 1:1 molar ratio containing 10 mL ethanol for 2 hours. The pure product was characterized by its melting point. M.P. 150°C.

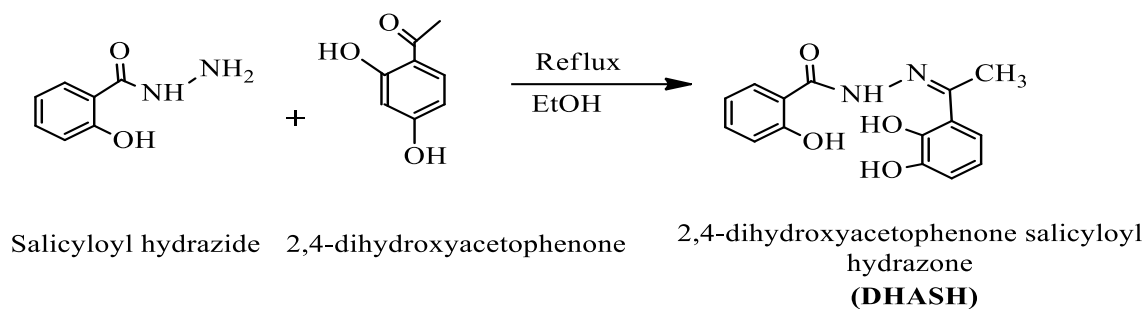
2.2. Physical measurements

C, H, N content of the ligand were determined by Perkin Elmer CHN 2400 elemental analyzer. The infrared spectra of the ligand and its complexes were recorded in the range 4000 cm⁻¹ to 400 cm⁻¹ with a Bruker IF566V KBr and polyethylene medium for manganese complex. ¹H-NMR spectra of the ligand were recorded in DMSO-d₆ solution on a Bruker 400 FT-NMR spectrophotometer. Thermal analysis of complexes was carried out by heating in air at a rate of 10°C per minute on a Perkin Elmer thermobalance. The magnetic susceptibility values were recorded at room temperature by Gouy method using Hg[Co(NCS)₄] as a calibrant type magnetic balance. The molar conductance of the complexes was determined in dimethylsulphoxide using solution of about 10⁻³ mol concentration. The electronic spectra of the ligand and complexes were recorded on a shimadzu UV/Vis spectrophotometer in the region 200-1100 nm. ESR spectra of copper complex at room temperature and liquid nitrogen temperature were carried by using JES-FA 200 ESR spectrometer.

2.3. Synthesis of salicyloyl hydrazone ligand (LH₃)

A hot ethanolic solution of salicyloyl hydrazide (1.52 g, 0.01 mol) was added to an ethanolic solution of 2,4-dihydroxyacetophenone (1.52 g, 0.01 mol). The reaction mixture was refluxed in a water-bath for 4-6 hours. The yellow coloured product was filtered off and recrystallized from hot ethanolic solution. Yield 76%, M. P. 220°C. It was characterized by elemental analysis, IR, UV, ¹HNMR and mass spectra.

¹H-NMR- δ13.33(2H, S, Phenolic C₂-OH), δ11.44(1H, S, imino NH), δ6.98- δ7.99(7H, M, Aromatic proton), δ2.53(3H, S, Methyl, N=CCH₃), δ9.82(1H, S, Phenolic C₄-OH [7]. The schematic representation of synthesis of LH₃ is shown in reaction scheme 1.

Fig.1. Synthesis of LH₃ ligand

2.4. Synthesis of Co(II), Cu(II), Fe(III) complexes

Equimolar quantities (0.02M) of the metal salt and ligand were dissolved separately in ethanol and refluxed for about 6-8 hrs. in water bath. The solid products obtained on cooling were filtered off, washed several time by diethyl ether and dried at room temperature over CaCl₂.

2.5. Synthesis of Zr(IV) complex

Zirconyloxychloride octahydrate (0.64g, 0.002 mol) was dissolved in methanol (15ml) and to this a methanolic solution of anhydrous sodium acetate (0.32g, 0.004 mol in 15ml) was added and stirred for 5 min. The separated sodium chloride was filtered off. The respective ligand (0.002 mol) was dissolved separately in hot DMF-methanol (1:4 v/v). To these solutions, the solution containing oxozirconium(IV) diacetate was added and the reaction mixture was refluxed for 4-6 hours. The product obtained was filtered, washed several times with hot water followed by methanol and dried over fused calcium chloride.

3. RESULTS AND DISCUSSION

All the complexes are coloured, non-hygroscopic solid and stable in air. They are insoluble in water and common organic solvents but soluble in coordinating solvents like DMF and DMSO. The analytical data (Table1) of the complexes indicates 1:1 stoichiometry. The molar conductance values of 10⁻³m solutions of complexes lie in the range 7.61-19.6 ohm⁻¹cm²mol⁻¹ indicating the non-electrolyte nature of the complexes.

Table 1. Analytical and physical data of ligand and its metal complexes-

Compound	Formula weight	Colour	M % Found (calc.)	C % Found (calc.)	H % Found (calc.)	N % Found (calc.)
LH ₃	286.28	Yellow	-	62.85 (62.93)	4.77 (4.93)	9.65 (9.79)
[Co(LH) ₂]	686.4	Brown	17.17 (17.45)	52.49 (52.51)	3.52 (3.99)	8.16 (8.80)
[Cu(LH) ₂]	695.63	Green	18.27 (18.35)	51.80 (51.72)	3.48 (3.41)	8.05 (8.17)
[Fe(L)(H ₂ O) ₂]	714.24	Black	15.64 (15.60)	50.45 (50.57)	3.67 (3.70)	7.84 (7.81)
[Zr(LH) ₂]	659.76	Yellow	13.83 (13.84)	54.61 (54.44)	3.67 (3.61)	8.49 (8.41)

3.1. IR Spectra

In order to study the bonding mode of ligand to metal in the complexes, IR spectrum of free ligand were compared with those of metal complexes. The structurally significant IR bands for free ligand and its complexes have been reported in Table 2. The band at 3300 cm⁻¹ due to intermolecular hydrogen bonded $\nu(\text{OH})$ group in the free ligand spectrum disappeared in spectra of all the complexes [8] and the $\nu(\text{C-O phenolic})$ band at 1273 cm⁻¹ shifted to higher frequency by 22-34 cm⁻¹, suggest the co-ordination of ligand through phenolic oxygen via deprotonation [9]. The vibrational band at 1620 cm⁻¹ assigned to $\nu(\text{C=N})$ in the spectrum of ligand show downward shift by 14-23 cm⁻¹ in the spectra of complexes confirming co-ordination through azomethine nitrogen [9]. The co-ordination through the azomethine nitrogen atom is further supported by the upward shift of $\nu(\text{N-N})$ vibrational frequency by 26-40 cm⁻¹ in the spectra of complexes [10]. The spectra of metal complexes do not show the band due to $\nu(\text{N-H})$ and $\nu(\text{C=O})$ frequency indicating the coordination of ligand to metal in enol form [7]. It is supported due to the presence of $\nu(\text{C-O enolic})$ and $\nu(\text{C=N-N=C})$ (azine) group frequencies in their spectra indicating the tribasic tetradentate nature of the ligand in these complexes. The coordination of water in Fe(III) is indicated by the appearance of bands at 3460, 1616, 833 and 756 cm⁻¹ assignable to $\nu(\text{OH})$, $\delta(\text{H}_2\text{O})$, $p_r(\text{H}_2\text{O})$ and $p_w(\text{H}_2\text{O})$ mode, respectively [8]. Also in addition to above bands all complexes display the bands in the far-infrared region at 505-547 and 447-489 cm⁻¹ assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations [11].

Table 2. Infrared spectral data (cm⁻¹) of the ligand and its metal complexes

Ligand/Complexes	$\nu(\text{OH})$	$\nu(\text{N-H})$	$\nu(\text{C-O})$ Phenolic	$\nu(\text{C=N})$	$\nu(\text{N-N})$	$\nu(\text{C=O})$	$\nu(\text{C-O})$ enolic	$\nu(\text{M-O})$	$\nu(\text{M-N})$
LH ₃	3300	3209	1273	1620	1033	1643	-	-	-
[Co(LH) ₂]	-	-	1300	1606	1059	-	1257	505	447
[Cu(LH) ₂]	-	-	1296	1602	1066	-	1242	532	462
[Fe(L)(H ₂ O) ₂]	-	-	1295	1597	1059	-	1246	532	489
[Zr(LH) ₂]	-	-	1307	1606	1073	-	1257	547	455

3.2. Mass Spectral studies of ligand and its complexes

The mass spectra of ligand DHASH, Co(II), Cu(II), Fe(III) and Zr(IV) complexes have been recorded. The molecular ion peaks obtained from various complexes are as follows (1) m/e=285.2 (LH₃) (2) m/e =687.43 [Co(LH)₂] complex (3) m/e =696.64 [Cu(LH)₂] complex (4) m/e =717.74 [Fe(L)(H₂O)₂] complex (5) m/e = 658.99 [Zr(LH)₂] complex. This data is in good agreement with the proposed molecular formula of the complexes. In addition to the peaks due to the molecular ion, the spectra exhibit peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peak intensity gives an idea of the stability of the fragments. Mass spectra of DHASH complexes are shown in Fig 3.1-3.5.

Fig. 3.1 Mass spectrum of Ligand DHASH.

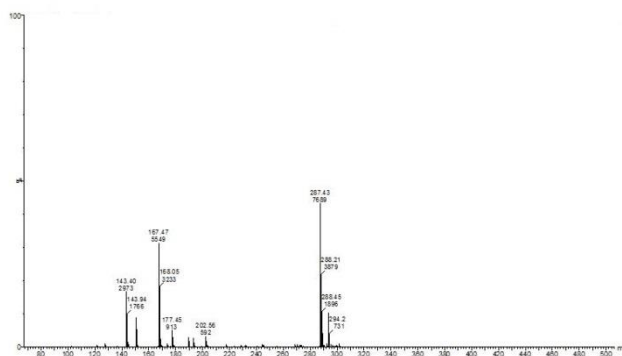


Fig. 3.2 Mass spectrum of Co(II) DHASH complex.

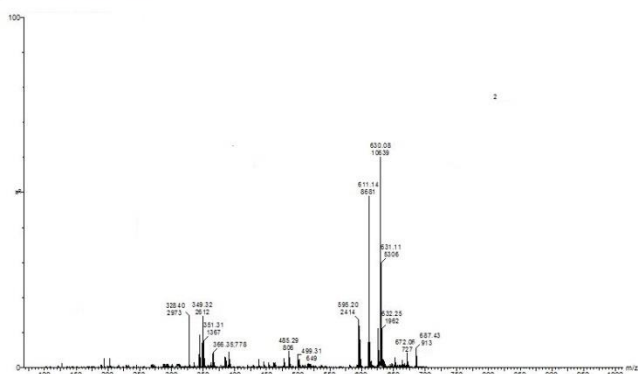


Fig. 3.3 Mass spectrum of Cu(II) DHASH complex.

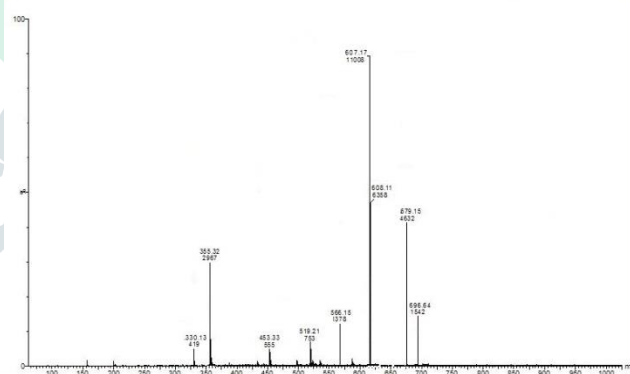


Fig. 3.4 Mass spectrum of Fe(III) DHASH complex.

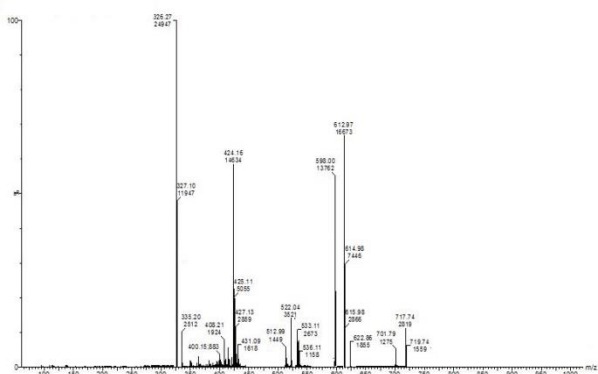
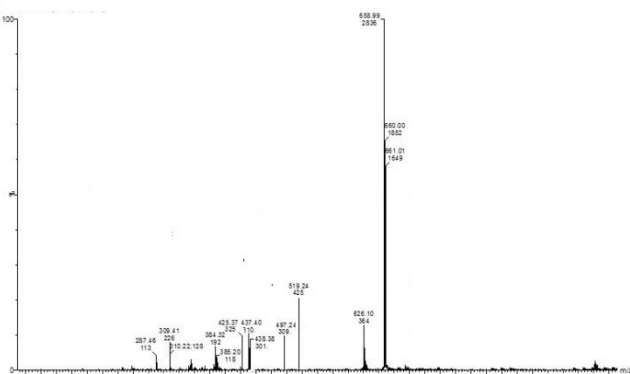


Fig. 3.5 Mass spectrum of Zr(IV) DHASH complex.



3.3. Electronic spectra and magnetic moment

UV spectrum of Co(II) complex shows band at 27027 cm⁻¹ and 19569 cm⁻¹ assigned to INCT and ¹A_{1g}→¹B_{1g} transitions respectively. These bands clearly suggest square planar geometry for Co(II) complex [12]. Electronic spectra of Cu(II) complex exhibited bands at 28986 cm⁻¹, 18587 cm⁻¹ and 15528 cm⁻¹ assigned to charge transfer, ²B_{1g}→²A_{1g} and ²B_{1g}→²E_g transitions respectively suggesting square planar geometry around Cu(II) ion. Electronic spectra of Fe(III) complex exhibits three absorption bands at 12804, 17668 and 22222 cm⁻¹ which may be assigned to ⁶A_{1g}(S)→⁴T_{1g}(G), ⁶A_{1g}(S)→⁴T_{2g}(G) and ⁶A_{1g}(S)→⁴E_g, ⁴A_{1g}(G) transitions respectively, suggesting an octahedral geometry[13]. The electronic spectra and magnetic moments of the metal complexes are listed in table 4. The magnetic moment values in Co(II), Cu(II) and Fe(III) complexes are lower than the spin only value due to an exchange interaction between two metal centres indicating some amount of antiferromagnetic interaction [14]. The slightly low value of magnetic moment for all complexes indicates dimeric structure. The electronic spectra of Zr(IV) complex show a single broad band at 23542 cm⁻¹, which may be assigned due to LMCT [15].

Table 4. Electronic absorption spectra and magnetic measurements data of complexes

Sr. No.	Compounds	Electronic spectra		Molar cond. (Ω ⁻¹ cm ² mol ⁻¹)	Mag. Moment μ _{eff} (BM)
		Absorption bands (nm)	Absorption bands (cm ⁻¹)		
1	[Co(LH)] ₂	370, 511	27027, 19569	7.61	2.07
2	[Cu(LH)] ₂	345, 538, 644	28986, 18587, 15528	9.52	1.32
3	[Fe(L)(H ₂ O)] ₂	781, 566, 450	12804, 17668, 22222	19.7	5.14

3.4. Thermal Analysis

The decomposition pattern of DHASH and its metal complexes (Fig. 4) reveals a three-step decomposition pattern for Fe(III) complex and two step for Co(II), Cu(II) and Zr(IV) complexes. The weight loss corresponding to two coordinated water molecules each in Fe(III) complex is observed in the first step in the 160-240°C region (obs./calcd.: Fe(III) : 5.11/5.02). The Co(II), Cu(II) and Zr(IV) complexes remain stable up to ~300°C indicating absence of coordinated and lattice water molecules. The thermal degradation of the ligand molecule is observed in the temperature range 310-450°C, followed gradual weight loss upto ~620°C is due to the part and complete decomposition of coordinated ligand respectively. Above 620°C nature of the curve is almost horizontal the complexes indicating the formation of corresponding metallic oxides. The thermal decomposition data of the compounds is given in table 5. The half decomposition temperature decreases in the following order- Co(II) > Cu(II) > Fe(III) > DHASH > Zr(IV).

Table 5. Thermal decomposition data of DHASH and its complexes.

Complex	Half decomposition temperature (°C)	Step	Decomposition Temperature (°C)	Activation Energy Ea (kJ mole ⁻¹)		Overall Order of Reaction (n)	Entropy Change -ΔS (J/mol/K)	Free Energy Change ΔF (kJ/mol)	Apparent Entropy Change S* (kJ)
				FC*	SW**				
LH ₃	380°C	I	210°C-400°C	23.48	23.13	0.93	-289.06	113.95	-16.79
[Co(LH)] ₂	500°C	I	260°C-420°C	14.47	32.47	0.96	-318.43	114.13	-34.49
		II	421°C-520°C	9.63	17.25		-334.67	114.38	-34.01
[Cu(LH)] ₂	420°C	I	240°C-420°C	13.34	17.17	0.94	-340.65	119.96	-27.19
		II	421°C-620°C	16.07	17.48		-256.92	96.48	-27.38
[Fe(L)(H ₂ O)] ₂	400°C	I	160°C-240°C	13.73	17.39	1.00	-318.74	113.49	-39.83
		II	241°C-360°C	20.06	16.32		-309.57	116.95	-40.21
		III	361°C-580°C	7.62	19.87		-345.17	112.65	-38.74
[Zr(LH) ₂]	330°C	I	260°C-360°C	9.56	19.23	0.90	-267.06	93.75	-32.88
		II	361°C-580°C	30.21	15.24		-330.69	133.71	-34.05

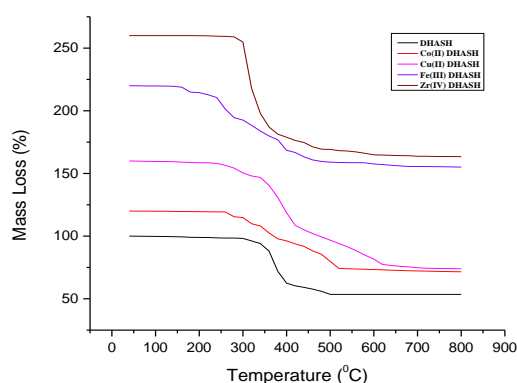


Fig.4. Thermogram (TGA) of DHASH and its complexes

3.5. ESR Spectra

An isotropic spectrum is obtained for Cu(II) complex in dimethylformamide at liquid nitrogen temperature. The g_{\parallel} and g_{\perp} values are computed using tetracyanoethylene (TCNE) free radical as 'g' marker. Important ESR parameters are $g_{\parallel} = 2.169$, $g_{\perp} = 2.046$, $g_{av} = 2.087$, $G = 3.662$, $A_{\parallel} = 168.60$, $A_{\perp} = 84.30$, $A_{av} = 112.40 \text{ cm}^{-1}$. The observed g value of the complex indicates that the unpaired electron is present in $d_{x^2-y^2}$ orbital as it follows the trend $g_{\parallel} > g_{\perp} > 2.0023$ and G value less than 4.0 suggest the ground state having small exchange coupling [16]. The g_{\parallel} value is an important function for indicating the covalent character of (M-L) bonds. For ionic, the g_{\parallel} is < 2.0023 while for covalent g_{\parallel} is > 2.0023 . In the present complexes, g_{\parallel} is more than 2.0023, indicating covalent Cu-L bond. ESR spectra of Cu(II) complex recorded in the solid state liquid nitrogen temperature (LNT) are shown in Fig. 5.

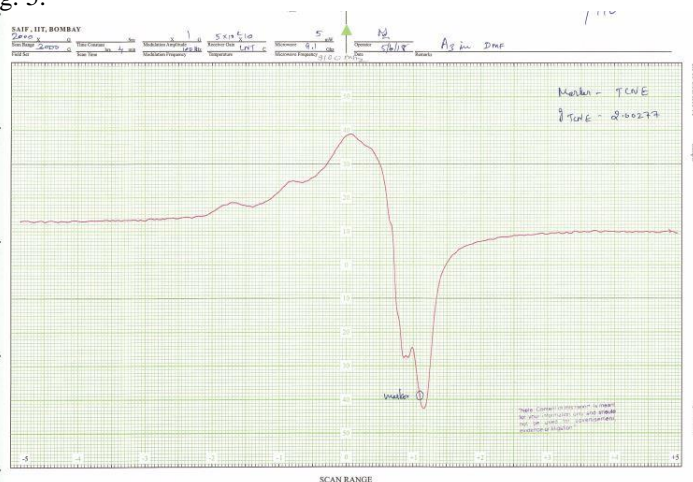


Fig.5. ESR spectrum of Cu(II) DHASH complex at LNT.

4. ANTIMICROBIAL ACTIVITY

Evaluation of antimicrobial activity of ligand DHASH and all compounds were carried out against *Staphylococcus aureus*, *Streptococcus pneumoniae*, *Escherichia coli* and *Klebsiella pneumoniae*. Ligand shows no activity against *S. aureus*, *S. pneumoniae* and *E. coli* and *K. Pneumoniae*. An inhibition zone for gram-positive bacteria is found in the range of 13-18 mm, for gram negative bacteria 16-18 mm. It is observed that, Co(II) and Cu(II) are effective against all the bacteria whereas Fe(III) and Zr(IV) are found to be bacteriostatic towards gram-positive and gram-negative bacteria respectively. Thus ligand exhibit a bacteriostatic behaviour against all the bacterial strains and the activity of the ligand was found to be enhanced after coordination with metal ions. The antimicrobial investigation data are summarized in Table 6.

Table 6. Antibacterial activity of ligand (DHASH) and their complexes

Ligand and its complexes	Diameter of inhibition of zone (in mm) ^a				% Activity index			
	<i>S. aureus</i>	<i>S. pneumoniae</i>	<i>E. coli</i>	<i>K. Pneumoniae</i>	<i>S. aureus</i>	<i>S. pneumoniae</i>	<i>E. coli</i>	<i>K. Pneumoniae</i>
DHASH	-	-	-	-	-	-	-	-
Co-DHASH	15	18	18	16	52	78	47	47
Cu-DHASH	18	16	16	18	62	70	42	53
Fe-DHASH	16	13	-	-	55	57	-	-
Zr-DHASH	18	15	-	-	62	65	-	-
DMSO	-	-	-	-	-	-	-	-
Antibiotic (Standard)	29	23	38	34	100	100	100	100

-: no activity,

^a values, including diameter of the well (8mm), are means of three replicates

5. CONCLUSION

Salicyloyl hydrazone (DHASH) and its Co(II), Cu(II), Fe(III) and Zr(IV) complexes were synthesized and characterized by elemental analysis, different spectral data, molar conductance, magnetic measurements and thermal gravimetric analysis. The DHASH ligand acts as dibasic tridentate ONO donor in Co(II), Cu(II) and Zr(IV) metal complexes a tribasic tetradentate ONOO donor towards Fe(III) complex. Thermal data show degradation pattern of the complexes. TG studies also guide to thermodynamic, kinetic and reactivity behaviour of compounds and metal-ligand interaction. Based on elemental, spectral, molar conductance, magnetic moments and thermal data suggested square planer geometry for Co(II), Cu(II) complex and octahedral geometry for Fe(III) and Zr(IV) complex.

6. REFERENCES

- [1] Suvarapu, L.N. Seo, Y.K. Baek, S.O. and Ammireddy, R. 2012. Review on analytical and biological applications of hydrazones and their metal complexes. E-Journal Chem., 9(3): 1288-1304.
- [2] Gwaram, N.S. Ali, H.M. Khaledi, H. Abdulla, M.A. Hadi, A.H.A. Lin, T.K. Ching, C.L. and Ooi, C.L. 2012. Antibacterial Evaluation of Some Schiff Bases Derived from 2-Acetylpyridine and Their Metal Complexes. Molecules, 17, 5952-5971.
- [3] Kumar, S. Dhar, D.N. and Saxena, P.N. 2009. Applications of metal complexes of Schiff bases- A review. J. Sci. Ind. Res., 68(3), 181-187.
- [4] Ahmed, A.A. BenGuzzi, S.A. and Agoob, A.O. 2009. Synthesis and characterisation of some N₂-O₂-Schiff bases and their metal complexes. RASAYAN J. Chem., 2(2), 271-275.
- [5] El-Nawawy, M.A. Farag, R.S. Sobbah, I.A. and Abu-Yamin, 2011. Synthesis, spectroscopic, thermal studies and biological activity of a new sulfamethoxazole Schiff Base and its copper complexes. Int. J. Pharm. Sci. Res., 2(12), 3143-3148.

- [6] Singh, B. Srivastava, K.K. Narang, K. and Singh, V.P. 1999. Synthesis and Spectral Studies of Copper(II) Sulphate complexes with some Acetophenone Acylhydrazones. *Synth. React. Inorg. Met-Org. Chem.*, 29, 1867-1881.
- [7] Ahmed, A. H. Hassan, A. M. Gumaa, H. A. Mohamedand, B. H and Eraky, A. M. 2016. Nickel(II)-oxaloyldihydrazone complexes: Characterization, indirect band gap energy and antimicrobial evaluation. *Cogent Chemistry*. 2, 1-14.
- [8] Jain, R. K. and Mishra, A. P. 2012. Microwave synthesis, spectral, thermal, and antimicrobial activities of some transition metal complexes involving 5-bromosalicylaldehyde moiety *Current Chemistry Letters*. 1, 163-174.
- [9] Dey, K. Bandopadhyay, D. Bhattacharya, P. K. and Chakraborty, K. 1996. Synthesis and characterisation of iron(III) complexes of salicylaldehyde 4-methoxybenzoyl hydrazone. *Indian J. Chem.* 35A, 107-111.
- [10] Singh, N. K. Srivastava, A. and Kayastha, A. M. 2000. Synthesis, characterization and in -vitro antitumour studies. *Indian Journal of Chemistry*. 39A, 1074-1078.
- [11] Mishra, A. P. Sharma, N. and Jain, R. K. 2013. Microwave Synthesis, Spectral, Thermal and Antimicrobial Studies of Some Ni(II) and Cu(II) Schiff Base Complexes *Open J. Syn. Theory and Applications*. 2, 56-62.
- [12] Singh, V. P. Singh, S. and Katiyar, A. 2009. Synthesis, physico-chemical studies of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with some p-substituted acetophenone benzoylhydrazones and their antimicrobial activity *J. Enzyme Inhibition and Medicinal Chem.* 24(2), 577-588.
- [13] Anitha, C. Sheela, C. D. Tharmaraj, P. and Shanmugakala, R. 2013. Studies on Synthesis and Spectral Characterization of Some Transition Metal Complexes of Azo-Azomethine Derivative of Diaminomaleonitrile. *Int. Inorg. Chem.* 2013, 1-10.
- [14] Ahmed, A.H. and Ewais, E.A. 2012. Physicochemical and antimicrobial investigation on some selected arylhydrazone complexes. *J. Chem. Pharm. Res.* 4(7), 3349-3360.
- [15] Singh, H.L. and Singh, J. 2013. Synthesis of New Zirconium(IV) Complexes with Amino Acid Schiff Bases: Spectral, Molecular Modeling, and Fluorescence Studies. *Int. J. Inorg. Chem.* 2013, 1-10.
- [16] Kumar, D. Chadda, S. Sharma, J. and Surain, P. 2013. Syntheses, Spectral Characterization, and Antimicrobial Studies on the Coordination Compounds of Metal Ions with Schiff Base Containing Both Aliphatic and Aromatic Hydrazide Moieties. *Bioinorg. Chem. and Applications*. 2013, 1-10.

