



# SYNTHESIS, SPECTRAL CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF SCHIFF BASE METAL COMPLEXES DERIVED FROM DAPSONE AND SALICYLALDEHYDE

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## ABSTRACT

Complexes of Cr(III), Mn(III) and Fe(III) with Schiff base derived by the condensation of dapsone with salicylaldehyde were synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, spectral studies (IR, <sup>1</sup>H NMR, UV-Visible), mass, TGA. Elemental analysis data suggest the 1:1 [M:L] stoichiometry ratio in all the metal complexes. The molar conductance measurements reveal the non-electrolytic nature of the complexes. The electronic spectral data support octahedral geometry for all the synthesized complexes. The thermal degradation pattern of the compounds has been analyzed from the thermograms and the kinetic parameters have been evaluated. The Schiff base ligand and its complexes have been tested *in vitro* to evaluate their antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Klebsiella pneumoniae* using well-diffusion method. It has been found that the Schiff base ligand and its complexes show significant antimicrobial activity against all tested bacterial species.

**Keywords:** Dapsone, salicylaldehyde, Schiff base, well-diffusion

## 1. Introduction

Sulfone Schiff base ligands are the condensation products of aldehydes or ketones with sulfone analogues. 4,4'-diaminodiphenylsulphone (DDS), popularly called Dapsone, is a creamy white crystalline

powder that is lightly soluble in water but freely soluble in alcohol and dilute mineral acids. It is an antibiotic sulpha drug that is commonly used to treat leprosy, dermatitis, herpeticiformis and pneumocysticariipneumonia.

Dapsone shows efficient pharmacological activity against *Mycobacterium leprae* that occur as cross activity in HIV inflamed sufferers; it reveals application in numerous fields (Vijayalakshmi, Chitra and Balaramesh, 2015). For the treatment of leprosy infections, dapsone is a pharmaceutical drug most commonly used in combination with rifampicin and clofazimine as multidrug therapy (MDT). This antileprosy drug is a very potent chelating agent and its effective coordination to metal ion may have important biological implication (Lakshmi, Syed Tajudeen, and Geetha, 2011). The current study focused on the synthesis of heterocyclic Schiff base ligand and its Cr(III), Fe(III) and Mn(III) complexes and its thermal and spectroscopic characterization.

## 2. Experimental method

### 2.1. Material and reagents

All the metal salts and solvents used were analytical reagent grade supplied by SD Fine and Merck. Pure sample of dapsone was obtained from Shah Scientific Pvt. Ltd. Mumbai. Solvents were purified and dried before use by literature method (Furniss, Hannaford, Smith and Tatchell, 1989). The ligand used in the present work is not commercially available, hence were synthesized in laboratory. Manganese acetate dihydrate was prepared by the oxidation of  $Mn(OAc)_2 \cdot 4H_2O$

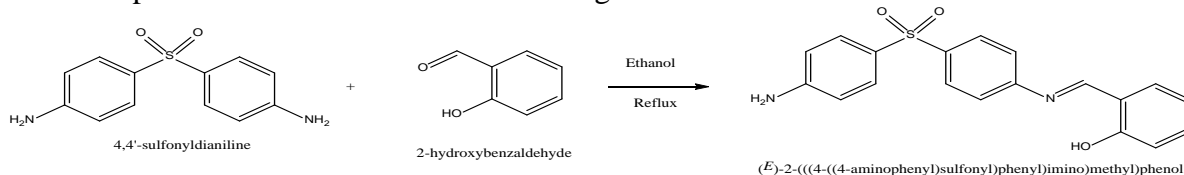
using Christensen's method (Christensen, 1901) while all other metal salts are commercially available and used as receive.

The amounts of metal present in the complexes were estimated by metal oxide method (Aswar, Bahad, Paradhi and Bhawe, 1988). The molar conductance of the complexes in dimethyl formamide (DMF) solution ( $10^{-3}$  M), was measured using equiptronic digital conductivity meter EQ-660 with a cell constant of  $1.00\text{cm}^{-1}$  at room temperature.  $^1\text{H-NMR}$  spectra of the ligand were recorded in DMSO- $d_6$  solution on EM-360, 60 MHz NMR spectrometer. The infrared Fourier-transform infrared (IR) spectra of ligand and complexes were recorded as KBr pellets using Shimadzu spectrometer (IRAffinity-1S). Mass spectra of synthesized compounds were carried out on

Thermo scientific TSQ 8000 Gas Chromatograph- Mass Spectrometer. The thermal analysis was performed with a Perkin Elmer (TGS-2 model) thermal analyzer at a heating rate of  $10^\circ\text{C min}^{-1}$  in the temperature range  $40\text{-}500^\circ\text{C}$

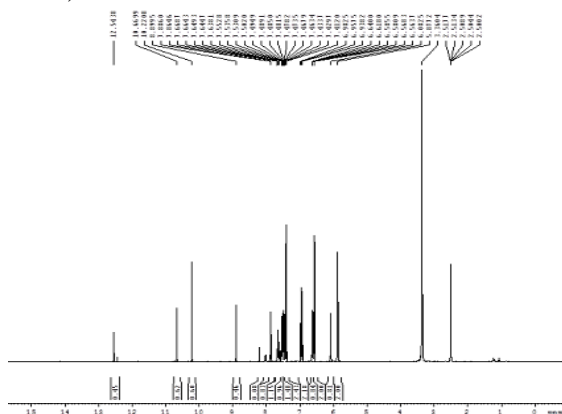
## 2.2. Synthesis of Ligand ( $L^2H$ )

Equimolar (0.01m) solutions of Salicylaldehyde (2ml) and dapsone (2.48g) were separately dissolved in ethanol and refluxed for two hours. The volume of reaction mixture was reduced to one third and cooled at  $0^\circ\text{C}$ . The solid residue was filtered off and recrystallized by ethanol. The purity of the compounds were checked by thin layer chromatography (TLC). General scheme for the synthesis of Schiff base ligand is shown in Figure 1.



**Figure 1: Synthesis of Schiff base ligand.**

Yield: 81%. The  $^1\text{HNMR}$  spectra of Schiff base ligand was recorded in DMSO- $d_6$  using TMS as an internal standard. The  $^1\text{H NMR}$  spectrum of Ligand  $L^2H$  (Figure 2) shows following peaks.  $^1\text{H NMR}$  (DMSO- $d_6$ )  $\delta$  ppm: 12.54 (s, 1H, phenolic OH), 8.89 (s, 1H, azomethine proton), 5.87-7.88 (m, 12H, aromatic), 3.36 (s, 2H, - $\text{NH}_2$ ) (Halli, Patil, 2011, Patil, Jadhav and Patil, 2012).



**Fig. 2 -  $^1\text{H NMR}$  Spectrum of Ligand  $L^2H$**

## 2.3. Synthesis of complexes

The complexes were synthesized by adding equimolar ethanolic solution of the ligand and respective metal salt, i.e.,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ . Few drops of 1N KOH were added to the reaction mixture and the reaction mixture was refluxed in water bath for about 10-12 h. The coloured solids obtained were filtered off, washed several times with ethanol followed by petroleum ether and finally dried over fused calcium chloride.

## 3. Results and Discussion

In the present study, all the complexes are found to be coloured solids, air stable and non-hygroscopic. The analytical data indicate 1:1 metal: ligand stoichiometry. The complexes are insoluble in water and common organic solvents but soluble in coordinating solvents like DMF and DMSO. Lower values of molar conductance indicate that complexes are nonelectrolytes. The analytical and physical data of ligand and its complexes are given in Table 1.

**Table 1: Analytical and physical data of ligand and its metal complexes**

Compounds	Molecular formula	FormulaWt.	Color	M.P.( <sup>o</sup> C)	%C	%H	%N	%M
L <sup>2</sup> H	C <sub>19</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> S	352.41	Yellow	240 <sup>o</sup> C	64.76(63.91)	4.58(4.66)	7.95(7.82)	--
[Cr(L <sup>2</sup> ) Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	Cr <sub>19</sub> H <sub>21</sub> C <sub>12</sub> CrN <sub>2</sub> O <sub>6</sub> S	528.34	Brown	>300 <sup>o</sup> C	43.19(43.31)	4.01(4.85)	5.30(5.52)	9.84(10.02)
[Mn(L <sup>2</sup> ) (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	C <sub>23</sub> H <sub>27</sub> MnN <sub>2</sub> O <sub>10</sub> S	524.43	Black Cherry	>300 <sup>o</sup> C	47.76(47.88)	4.70(4.28)	4.84(4.34)	9.50(9.42)
[Fe(L <sup>2</sup> ) Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	C <sub>19</sub> H <sub>21</sub> C <sub>12</sub> FeN <sub>2</sub> O <sub>6</sub> S	530.98	Black	>300 <sup>o</sup> C	42.88(41.99)	3.98(4.02)	5.26(5.36)	10.49(10.68)

### 3.1. IR Spectra

To study the binding modes of ligand toward metal ion, IR spectral data of Schiff base ligand was compared with the complexes (Table 2). After complexation, the band due to azomethine vibration in free L<sup>2</sup>H ligand was shifted to a lower wave number and appeared at 1596-1601 cm<sup>-1</sup> in metal complexes, indicating the involvement of azomethine nitrogen in the coordination to the metal center (Xavier and Srividya, 2004, Conpolat, 2014, Sharma and Shah, 2013, Nida, Javed and Muhammad, 2009, Gupta, Singh, Varshney and Varshney, 2003). The ligand showed a strong band at 3328 cm<sup>-1</sup> due to the phenolic -OH group (Conpolat, 2014). This band was absent in the spectra of all the metal complexes, indicating involvement of

this group in the formation of the complexes. The appearance of the M-N bands at 405-435 cm<sup>-1</sup> and the M-O bands at 518-536 cm<sup>-1</sup> in the complexes indicate that the ligand was coordinated through O and N atoms (Hakim, Ahmad, Salima and BenGuzzi, 2008, Bharti, Malik, Sharma N and Sharma S, 2013). A medium sharp doublet due to NH<sub>2</sub> stretching vibration is observed at 3452-3460 cm<sup>-1</sup> and 3367-3379 cm<sup>-1</sup> (Kumaran, Priya, Gowsika, Jayachandramani and Mahalakshmi, 2013, Ghazizadeh, Badiei and Sheikhshoae, 2013). Two prominent bands, one around 1300-1303 cm<sup>-1</sup> and other around 1134-1145 cm<sup>-1</sup> are observed due to asymmetric and symmetric SO<sub>2</sub> stretching vibration (Nida, Javed and Muhammad, 2009).

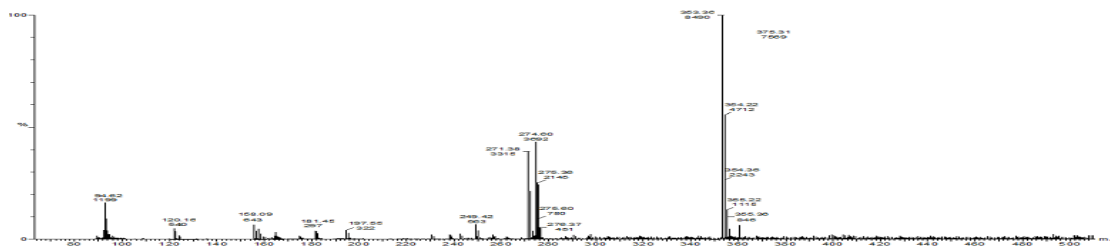
**Table 2: IR spectral data (cm<sup>-1</sup>) of ligand and its metal complexes.**

Compound	v(O-H) hydrogen bonded	v(NH <sub>2</sub> )	v(C=N)	v(SO <sub>2</sub> )	v(M-O)	v(M-N)	asymym
L <sup>2</sup> H	3228	3460, 3367	1614	1300	1145	--	--
[Cr(L <sup>2</sup> ) Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	--	3459, 3379	1596	1303	1136	518	435
[Mn(L <sup>2</sup> ) (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	--	3456, 3367	1597	1300	1134	536	405
[Fe(L <sup>2</sup> ) Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	--	3452, 3379	1601	1301	1134	523	424

### 3.2. Mass Spectra

Mass spectrometry has been successfully used to determine the molecular ion peak for Schiff base ligand. The various fragmentation peaks obtained for ligand,

Cr(III), Fe(III), and Mn(III) complexes are in good agreement with the proposed structure. Mass spectrum of ligand shown in Figure 3.

**Fig. 3: Mass spectrum of Ligand L<sup>2</sup>H**

**3.3. Electronic Spectra**

The electronic absorption spectra of metal complexes were recorded in DMSO in the range 200-800 nm. The electronic spectrum of Cr(III) complex shows bands at 288, 482 and 611 nm corresponding to transition  ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ ,  ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ , and  ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$  respectively, indicating octahedral geometry around Cr(III) ion (Sibous, Bentouhami and Khan, 2013). For Mn(III) complex band appears at 275, 579 and 797 nm for transition  ${}^5B_{1g} \rightarrow {}^5E_g$ ,  ${}^5B_{1g} \rightarrow {}^5B_{2g}$  and  ${}^5B_{1g} \rightarrow {}^5A_{1g}$ . All these transitions indicate

octahedral geometry for Mn(III) complex (Alhadi, Shaker, Yehye, Ali and Abdullah, 2012, Hankare, Gavali, Bhuse, Delekar and Rokade, 2004). The electronic spectrum of Fe(III) complex shows bands at 762, 537 and 343 nm corresponding to transition  ${}^6A_{1g} \rightarrow {}^4T_{1g}(D)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  and LMCT transition respectively, indicating octahedral geometry around Fe(III) ion (Sibous, Bentouhami and Khan, 2013) The absorption region, band assignment and proposed geometry of the complexes are given in Table 3.

**Table 3: Electronic absorption spectral data of the complexes**

Compounds (B.M)	$\mu_{eff}$ $\Omega^{-1}cm^2mol^{-1}$	Molar conductance (nm)	Absorption Band assignment	Geometry
$[Cr(L^2)Cl_2(H_2O)_2].H_2O$	3.64	10.12	288,482,611	
			${}^4A_{2g} \rightarrow {}^4T_{2g}(F), {}^4A_{2g} \rightarrow {}^4T_{1g}(F), {}^4A_{2g} \rightarrow {}^4T_{1g}(F)$	octahedral
$[Mn(L^2)(OAc)_2(H_2O)_2].H_2O$	5.10	12.25	275, 579, 797	
			${}^5B_{1g} \rightarrow {}^5E_g, {}^5B_{1g} \rightarrow {}^5B_{2g}, {}^5B_{1g} \rightarrow {}^5A_{1g}$	octahedral
$[Fe(L^2)Cl_2(H_2O)_2].H_2O$	5.50	8.24	762, 537, 343	
			${}^6A_{1g} \rightarrow {}^4T_g(D), {}^6A_{1g} \rightarrow {}^4T_g$	LMCT octahedral

**3.4. Thermal Analysis**

Thermal analysis is performed to determine the thermal stability of complex and its degradation pattern in which the change in the weight of the substance is recorded as function of temperature or time. Thermogravimetric analysis (TGA) was performed in nitrogen atmosphere with heating rate  $10^\circ C \text{ min}^{-1}$  and thermograms were recorded in temperature range 40-500°C. Using this technique several kinetic parameters such as activation energy (Ea), order of reaction (n), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy change ( $S^*$ ) were calculated. The thermal data have been analyzed using Freeman- Carroll and Sharp-Wentworth methods (Ozawa 1975, Patel and Patel 1993).

Thermogram of ligand  $L^2H$  and its complexes is given in Figure 4 while kinetic parameters are assigned in Table 4. The TG curves of complexes show three step decomposition patterns. The complexes lose their weights in the temperature range 60-120°C indicating the presence of one lattice water. Further weight loss observed in the temperature range 130-220°C corresponding to the presence of two coordinated water molecules [%wt. loss, obs/cal.: Cr(III): 6.86/6.81; Mn(III): 6.27/6.22; Fe(III): 6.81/6.76]. The complexes show sudden loss in weight in range 230-440°C which is due to the loss ligand molecule. Above 450°C, the curve is almost horizontal indicating the formation of corresponding metal oxides.

**Table 4: Thermal decomposition data of ligand and its complexes**

Compound	Half decomposition temperature (°C)	Apparent Ea (kJ/mol)	reaction-order (n)	$\Delta S$ (J/mol/K)	$\Delta F$ (kJ/mol)	$S^*$ (kJ)	Order of		Entropy change	Free
							FC	SW		
$[Cr(L^2)Cl_2(H_2O)_2].H_2O$	330			8.11	8.23	0.99	-277.74	94.95	-37.67	
$[Mn(L^2)(OAc)_2(H_2O)_2].H_2O$	350			11.72	11.63	0.92	-281.62	99.87	-38.01	

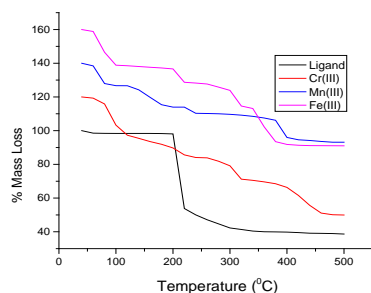


Fig. 4: Thermograms of ligand (L<sup>2</sup>H) and its complexes.

### 3.5. Antimicrobial activity

Antibacterial screening of Ligand (L<sup>2</sup>H) and its complexes against *E. coli*, *S. aureus*, *P. aeruginosa* and *K. pneumoniae* strains were carried out. Almost all complexes showed a good zone of inhibition against *E. coli*. *P. aeruginosa* and *K. pneumoniae* were found to be resistant towards Mn(III) complex. However Mn(III) complex has shown moderate antibacterial activity towards *E. coli* and *S. aureus*. The Fe(III) complex was found to be

bactericidal against *S. aureus* while bacteriostatic in nature against all other bacterial species. Cr(III) complex was found to be moderate in activity against *K. pneumoniae*. Results of studies of antibacterial effect of ligand and their metal complexes are summarized in Table 5. Photographic plates showing zones of inhibition in *E. coli* and *K. pneumoniae* are presented as figures 5 and 6 respectively.

Table 5: Results of antibacterial effect of ligand and its metal complexes

Compounds	<i>E. coli</i> (mm)	<i>S. aureus</i> (mm)	<i>P. aeruginosa</i> (mm)	<i>K. pneumoniae</i> (mm)
L <sup>2</sup> H	S <sub>22</sub>	S <sub>23</sub>	S <sub>20</sub>	S <sub>25</sub>
[Cr(L <sup>2</sup> ) Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	S <sub>18</sub>	R	S <sub>12</sub>	S <sub>16</sub>
[Mn(L <sup>2</sup> ) (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	S <sub>14</sub>	S <sub>20</sub>	R	R
[Fe(L <sup>2</sup> ) Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	R	S <sub>11</sub>	R	R

S- Sensitive (Bactericidal) R- Resistant (Bacteriostatic)

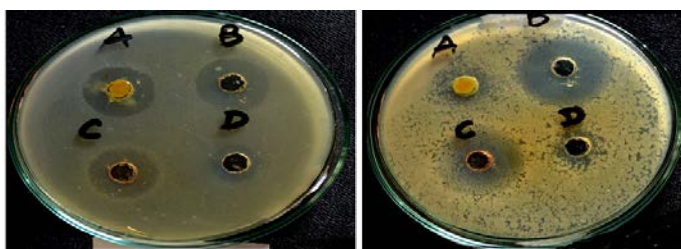


Figure 5: Photographic plate 1 showing zones of inhibition in *E. coli* Figure 6: Photographic plate 2 showing zones of inhibition in *K. pneumoniae*

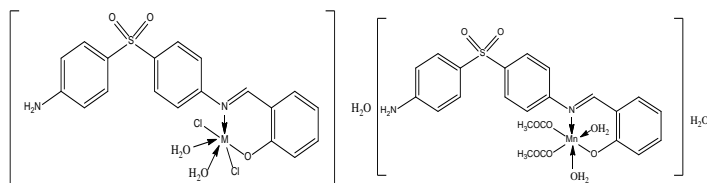
### 4. Conclusion

The present article includes the synthesis and characterization of new Schiff base ligand and its Cr(III), Mn(III) and Fe(III) complexes. Characterization of compounds includes IR, mass, <sup>1</sup>H NMR, and TGA. Electronic spectrum

suggests octahedral geometry for all synthesized complexes. It is observed that ligand coordinates to metal ion through hydroxyl oxygen, and azomethine nitrogen and acts as a monobasic bidentate ligand (metal ligand ratio 1:1). The thermal data show that complexes were highly stable and their thermal

decomposition, as well as thermodynamic parameters, were studied. The Schiff base ligand and its complexes have been tested in vitro to evaluate their antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and

*Klebsiella pneumoniae* using well-diffusion method. It has been found that the Schiff base ligand and its complexes show significant antimicrobial activity. On the basis of spectral data, the proposed structures of complexes are shown in Figures 7 & 8.



M= Cr(III) or Fe(III)

**Fig 7: Proposed structure for Cr(III) and Fe(III) complexes** **Fig 8: Proposed structure for Mn(III) complex**

### Acknowledgement

The authors are thankful to Principal, Jagadamba Mahavidyalaya, Achalpur, for providing necessary laboratory facilities, Director RSIC, Chandigarh, for recording  $^1\text{H}$  NMR spectra and mass spectra and Director CDRI, Lucknow, for elemental analysis. The authors express sincere thanks to Principal and Head, Department of Microbiology, Adarsha Mahavidyalaya, Dhamangaon Rly., for antimicrobial activity.

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