

# Synthesis, Spectral Characterisation, and Thermal study of Cr(III), Fe(III) complex derived from Hydrazone Schiff Base

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## Abstract

New hydrazone Schiff base ligand of (5-bromo-2-hydroxybenzylidene)-4-oxopiperidine-1-carbohydrazide ( $H_2L$ ) was designed and synthesized by the condensation reaction of 4-oxo-1-carboxopiperidone hydrazide with 5 bromosalicylaldehyde. The hydrazone ligand This ligand reacts with Cr(III) and Fe(III)chloride salts to obtain (1)  $[Cr(L)(H_2O)_2Cl]$  (2)  $[Fe(L)(H_2O)_2Cl]$  complexes. The ligand was characterized by elemental and spectral techniques such as Infrared, UV-vis,  $^1H$  and  $^{13}C$  NMR, mass) and supporting analysis molar conductance, magnetic susceptibility, powder XRD, TG analyses also performed for the confirmation of structure. The ligand and metal stoichiometric ratio found as 1:1 (M:L) in the complex. The spectral, thermo-analytical data displays octahedral geometry to complexes. X-ray diffraction data inferred nanocrystalline nature of metal complexes. The newly synthesized ( $H_2L$ ) ligand and Cr(III) and Fe(II) complexes are thermally stable at high temperature.

**KEYWORD-** Metal complexes, Spectral characterisation, ONO hydrazone, XRD diffraction, Thermal properties.

## I. INTRODUCTION

The Schiff bases of hydrazone find enormous applications in the field of biological science and medicinal field due to its antibacterial, antifungal, antidepressant [1-4]. The coordinating behaviors of hydrazone based Schiff bases are attracted to as they can coordinate to the metal ions as tridentate by ONO etc. The transition metals have enhance most of the above pharmacological properties due to its versatility. The catalytic applications of such hydrazone and its metal complexes are greatly enhances pharmacological, catalytic and by their subtle steric structural frameworks of complexes [5-10]. Importance associated with the hydrazone Schiff base ligand and their its Cr(III), Fe(III) metal complexes, and our interest in screening of metal complexes of hydrazine based ligand encouraged us to prepare a new tridentate 5-bromo-2-hydroxybenzylidene-4-oxopiperidine-1-carbohydrazide (I) (Scheme 1)

## I. EXPERIMENTAL

### 2.1 Material and Method

All chemicals were of analytical grade used without purification. The solvents were purified by standard methods. The completion of reaction while synthesizing compounds was checked by TLC Merck's.

IR spectra of compounds were recorded on advance Bruker spectrophotometer. The magnetic susceptibility were performed on Sherwood balance MK-1. NMR and  $^{13}C$  spectra of ligand were on adv. Bruker NMR spectrometer, and ESI-mass spectrum of ligand was recorded on Waters Micro mass Q-T. The absorbance spectra of the complexes were recorded on a Shimadzu spectrometer. The thermal curve ligand and its metal complexes were performed on TGA-4000 analyzer Perkin-Elmer balance. The molar conductivities of compounds was performed by using 180-Elico conductivity meter.

Table1. Analytical data of hydrazone ligand, Cr(III) and Fe(III) complexes

Compounds	Molecular Formula	Mol. wt.	Elemental analysis found (calcd.) %					
			C	H	N	Cl	Br	M
Ligand [ $H_2L$ ]	$C_{13}H_{14}N_3O_3Br$	340.17	46.02	4.25	12.40	---	23.70	---
$[Cr(L)(H_2O)_2Cl]$	$CrC_{13}H_{16}N_3O_5BrCl$	461.63	33.94 (33.82)	4.00 (3.49)	9.40 (9.10)	7.75 (7.67)	17.40 (17.30)	11.30 (11.26)
$[Fe(L)(H_2O)_2Cl]$	$FeC_{13}H_{16}N_3O_5BrCl$	465.48	34.00 (33.54)	3.50 (3.44)	9.25 (9.00)	7.25 (7.61)	17.25 (17.16)	12.00 (11.99)

### 2.5. Synthesis of ONO hydrazone Schiff base ligand:

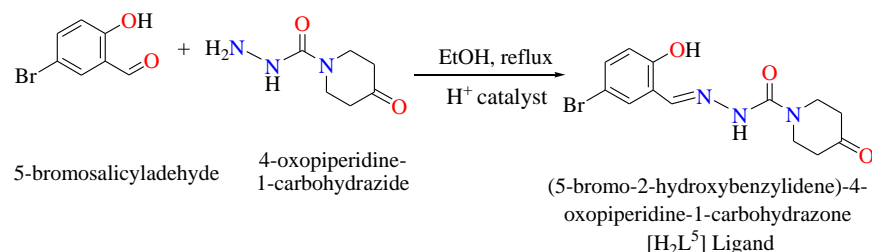
To a round bottom flask, equimolar amounts of 4-oxo-1-carboxopiperidone hydrazide (3.15-gram, 0.020 mole) and 5-hydroxy salicylaldehyde (4.02gram, 0.020 mole) refluxed together with a addition of two drops of con.  $H_2SO_4$ . The reaction mixture was continuous refluxed for 2 h. and cooled later to room temperature where bright yellow spongy product obtained. The product was filtered and washed with ethanol and recrystallized by DMF. The structure of ligand was confirmed by C-H-N-S analyser, IR, NMR ( $^1H$  and  $^{13}C$ ), HR-Mass spectroscopy. Yield: 7.17gm (85%). M.P:250-252°C. The ligand was soluble in DMF and DMSO.

#### Micro analytical data for $[C_{13}H_{14}N_3O_3Br]$ :

**Elemental analysis (%)**: Calc. C, (45.90); H, (4.15); Br, (23.49); N, (12.35); found C, 45.99; H, 4.20; N, (12.45).

**FT-IR** ( $cm^{-1}$ ): 3332  $\nu$ (OH broad), 3270  $\nu$ (N-H), 1659  $\nu$ (C=O amide), 1625  $\nu$ (C=N), 1174  $\nu$ (C-Br), 723  $\nu$ (1,2 aryl subst.)

**UV-visible** (DMSO,  $c=2 \times 10^{-4}$  mol  $dm^{-3}$ ):  $\lambda$  max  $\epsilon=41$  nm, 331 nm, 210 nm.



**Scheme 1. Synthesis of hydrazone base ligand (H<sub>2</sub>L)**

### 2.5. Synthesis of Cr(III) metal complexes – a conventional method

An equimolar amount of ligand and metal salt (0.020 mol each) [Cr(III)Cl<sub>3</sub>.6H<sub>2</sub>O, Fe(III)Cl<sub>3</sub>], were dissolved separately in 20 mL of hot DMSO and dry ethanol, respectively. Both the solutions were filtered and mixed them in warm conditions. The resulting reaction mixture was then heated at ca. 80 °C in alcoholic ammonia in an oil bath for 4-5 hrs. After cooling the reaction mixture, the separated solid product obtained was filtered, washed several times hot ethanol and dried under vacuum over CaCl<sub>2</sub>. The proposed compositions, empirical formula, molecular weight, elemental analysis and molar conductance data of metal complexes are presented in table 1.

## 3. RESULTS AND DISCUSSION

### 3.1. Infrared spectral study

The bonding between the ligand and metal ions can be concluded by comparing the IR spectra of metal complexes with the free ligand spectrum to confirm the chelation involved in complexes. The relevant IR frequencies observed in the spectra of the ligands and all of their metal complexes along with assignment are given in table 2 and spectra are shown in fig.1-3. The [H<sub>2</sub>L] ligand shows a broad band at 3332 cm<sup>-1</sup> due to ν(O-H) hydroxyl group. This band disappears in the spectra of the complexes indicating that deprotonation of the group has taken place, followed by coordination of phenolate oxygen atom to the metal ions. This is further authenticated by the upward shifting of ν(C-O) phenolic band by 68-40cm<sup>-1</sup> from 1230 cm<sup>-1</sup>, in all the metal complexes suggesting coordination through phenolic oxygen atom to the metal ions through C-O-M bond formation. The shift of amide carbonyl ν(C=O) to lower frequency side by 41-64 cm<sup>-1</sup> suggesting the coordination of oxygen atom of amide ν(C=O) to metal ions as such without undergoing enolization. However, disappears of both this bands in Cr(III), Fe(III), Zn(II) complexes indicate enolization followed by coordination to the metal ion after deprotonation [11-12].

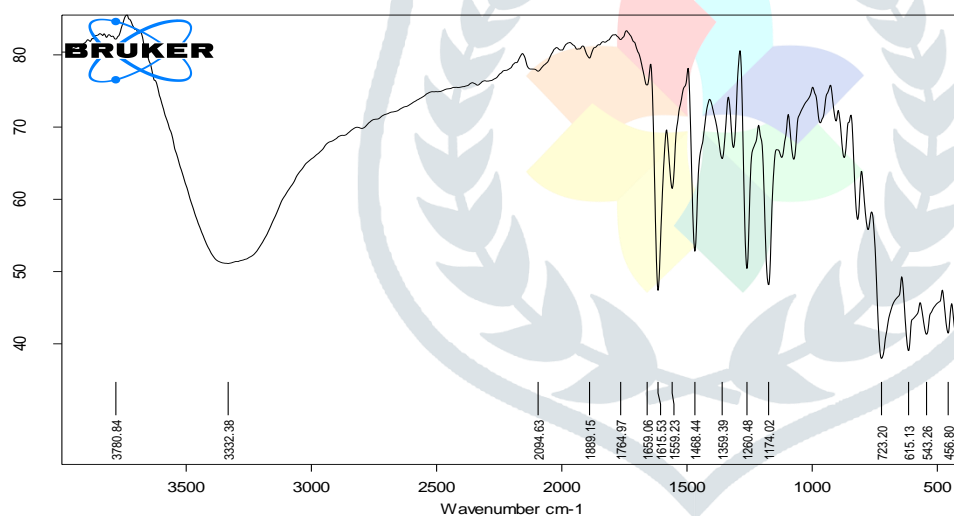


Fig.1 FT-IR (cm<sup>-1</sup>) spectra of hydrazone ligand

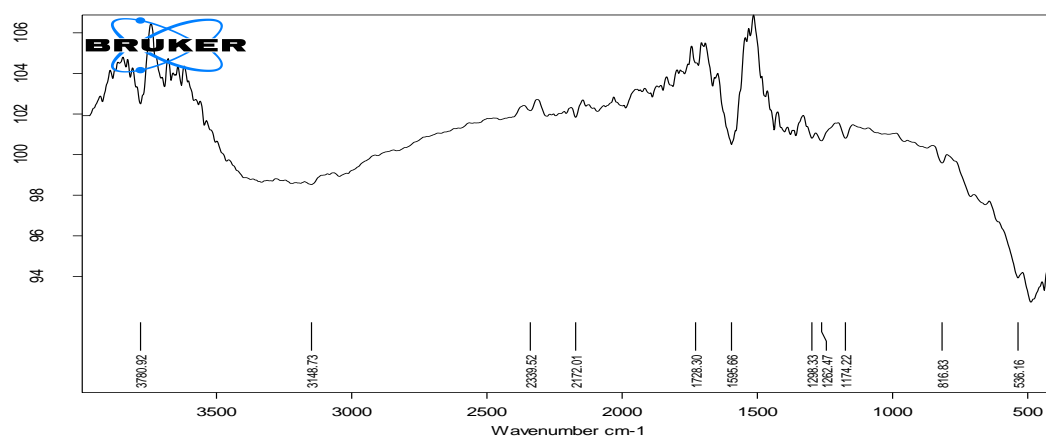
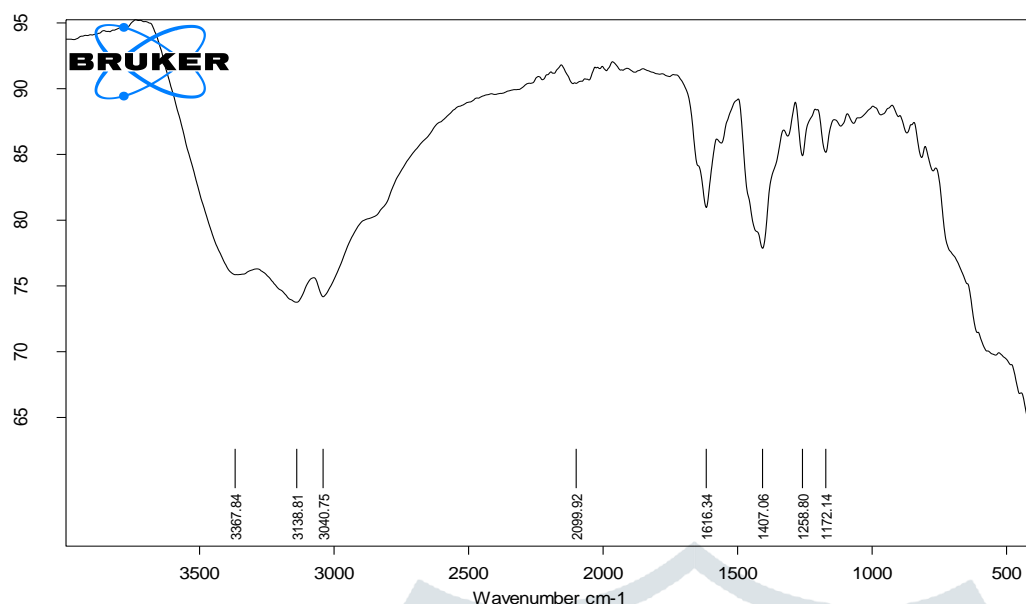


Fig.2 FT-IR (cm<sup>-1</sup>) spectrum of Cr(III) complexFig.3 FT-IR (cm<sup>-1</sup>) spectrum of Fe(III) complexTable 2. FT-IR (cm<sup>-1</sup>) spectral data of free ligand (H<sub>2</sub>L) and Zn(II) complex

Compound (cm <sup>-1</sup> )	$\nu(\text{OH})$	$\nu(\text{N-H})$	$\nu(\text{C=O})$ amide	$\nu(\text{C=N})$ azomethin	$\nu(\text{C-O})$ Phenoli	$\nu(\text{C-O})$ enolic	$\nu(\text{N-N})$	$\nu(\text{H}_2\text{O})$ coord.	$\nu(\text{M-O})$	$\nu(\text{M-N})$
[H <sub>2</sub> L] ligand	3332	3270	1659	1625	1300	---	950	---	---	---
[Cr(L)Cl(H <sub>2</sub> O) <sub>2</sub> ]	---	---	1595	1614	1314	1262	952	848	536	439
[Fe(L)Cl(H <sub>2</sub> O) <sub>2</sub> ]	---	---	1616	1600	1258	1230	980	859	575	440

### 3.4. Magnetic and electronic spectral studies

The Cr(III) complex shows three bands at 17544, 25000, 37313cm<sup>-1</sup> due to  ${}^4A_{2g} \longrightarrow {}^4T_{2g}$ ,  ${}^4A_{2g} \longrightarrow {}^4T_{1g}(\text{F})$  and  ${}^4A_{2g} \longrightarrow {}^4T_{1g}(\text{P})$ , transitions, respectively suggested a octahedral stereochemistry. The magnetic moment of complex was found to be 3.92 B.M. considerable for d<sup>3</sup> (<sup>4</sup>F ground term) with three unpaired electrons for high spin octahedral geometry around Cr(III) ion. The ligand field parameters Dq, B,  $\beta$  and  $\nu_2/\nu_1$  have been evaluated and values are found to be 1754cm<sup>-1</sup>, 645 cm<sup>-1</sup>, 0.70 and 1.43 respectively. The interelectronic repulsion factor B value was found lower (645cm<sup>-1</sup>) than for free ion and other ligand field parameters indicated the presence of covalent character in the M-L bond in the complex [13-14].

### 3.6. Thermal analysis:

The simultaneous TG-DTG curve of (H<sub>2</sub>L) ligand and its metal complexes are presented in figs.4-6 and thermal data summarized in table 3. The [H<sub>2</sub>L] ligand and its metal complexes was thermally analyzed in dynamic condition of the temperature range of 45oC-700 °C. The ligand exhibits a peak (broad DTGmax) appears at 350 °C maximum in N<sub>2</sub> atmosphere. The mass loss found 90.20.2% (theor.90.01%) due to the fragmented species (-H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>). Upon continued heating, found that temperature between 375oC-700 °C mass losses 9.80% (10.00%) of carbon residues left in crucible. The TG-DTG curve of [Cr(L)(H<sub>2</sub>O)<sub>2</sub>Cl] complex in first decomposition step shows at (broad DTG max =140°C) with a mass loss of 8.10% (calcd.7.29%) due to the loss of two coordinated water molecules. The second decomposition step showed mass loss of 27.50 % (Calcd. 27.10%) at 250 oC (DTG<sub>max</sub>) and regarded as the removal of one mole of chloride and non-coordinated Br ion. In third stage of decomposition, maximum mass loss of organic moiety of ligand 42.00% (calcd.42.62%) about at 500oC. Finally, TG curve attain a horizontal level for the formation of stable metal oxide [ $\frac{1}{2}\text{Cr}_2\text{O}_3$ ] 22.40% (calcd.24.49%).

TG-DTG curve of [Fe(L)(H<sub>2</sub>O)<sub>2</sub>Cl] complex shows mass loss of 8.12% (calc.7.73%) at 100°C (broad DTG<sub>max</sub>) which display the loss of two coordinated water molecules. In second step degradation occurred at 240 °C (DTG<sub>max</sub>) with a mass loss of 27.10 % (calcd. 26.85%) which are due to the removal of one mole of chloride and non-coordinated molecule. The third stage of degradation observed at 510°C with mass loss of 42.00% (calc.40.00%) which are conformity of the removal of organic moiety and leaving the final residue of [ $\frac{1}{2}\text{Fe}_2\text{O}_3$ ] found 22.78% (calc. 25.42%) [15-20].

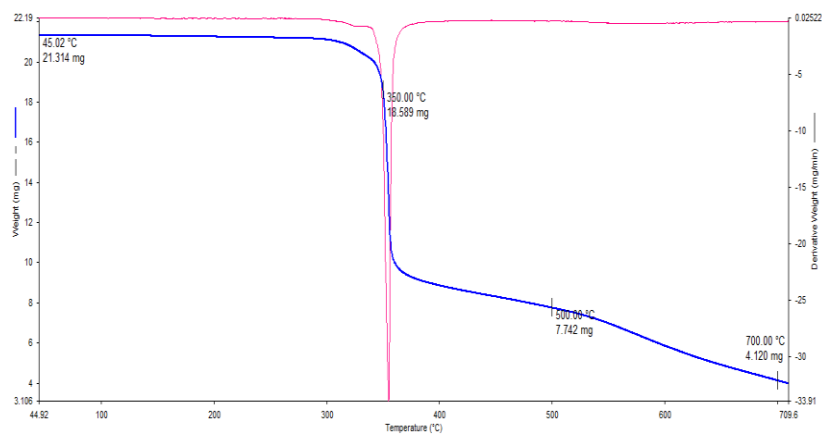


Fig.4 TG-DTG curve of hydrazone ligand

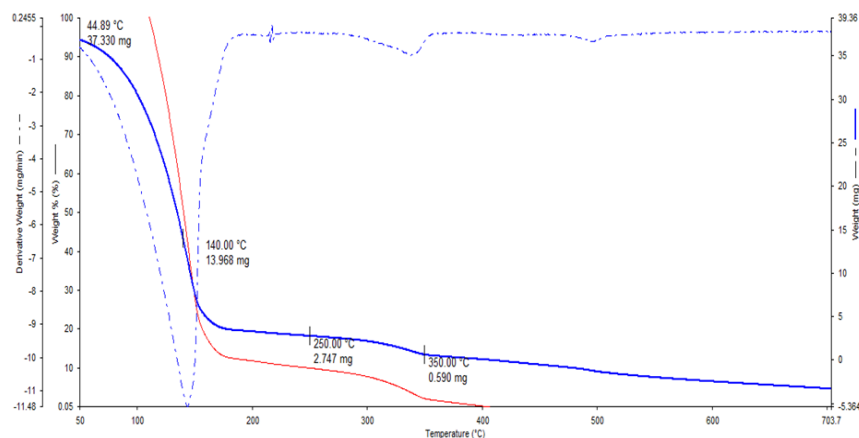


Fig.5 Thermogravimetric data of Cr(III) complex

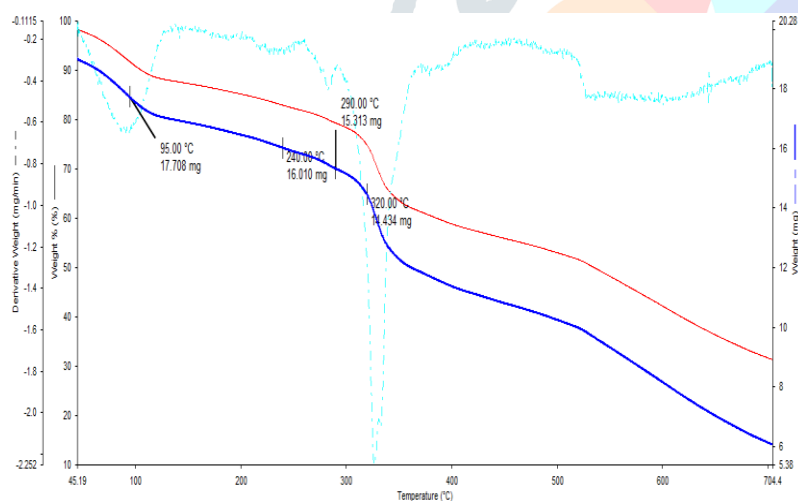
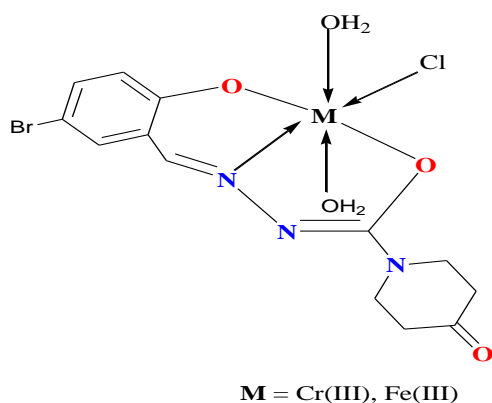


Fig.6. Thermogravimetric data of Fe(III) complex

Table 3. Thermogravimetric data of (H<sub>2</sub>L) ligand and its metal complexes

Compounds	Stages	Temp.range (°C)	DTG <sub>max</sub> (°C)	% Mass loss		Decomposition Assignments
				Exptl.	Calcd.	
(H <sub>2</sub> L)ligand	I	45-350	350	90.20	90.01	Loss of H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> species
	II	350-700	--	9.80	10.00	obtained carbon residue
[Cr(L)Cl(H <sub>2</sub> O) <sub>2</sub> ]	I	45-140	140	8.10	7.29	Loss of two coordinated H <sub>2</sub> O molecules
	II	140-250	250	27.50	27.10	Loss of one coordinated Cl & non coordinated Br
	III	250-500	500	42.00	40.62	Loss of organic moieties (C <sub>17</sub> H <sub>23</sub> N <sub>4</sub> O)
	IV	500-703	--	22.40	24.49	Obtained metallic oxide residue of (1/2Cr <sub>2</sub> O <sub>3</sub> )
[Fe(L)Cl(H <sub>2</sub> O) <sub>2</sub> ]	I	45-95	100	8.12	7.73	Loss of two coordinated H <sub>2</sub> O molecules
	II	95-320	240	27.10	26.85	Loss of one coordinated Cl & non coordinated Br
	III	240-510	510	42.00	40.00	Loss of organic moieties (C <sub>17</sub> H <sub>23</sub> N <sub>4</sub> O)
	IV	510-704	---	22.78	25.42	Obtained metallic oxide residue of (1/2Fe <sub>2</sub> O <sub>3</sub> )

All thermal and spectral parameter of newly synthesised Cr(III) and Fe(III) complexes proposed octahedral structure shown in Scheme 2.



Scheme 2. Octahedral structure of Cr(III) and Fe(III) complexes

## CONCLUSION

The synthesis of hydrazone schiff base ligand and its Cr(III) and Fe(III) complexes based on single step reaction with better yield. The octahedral geometry for the Cr(III) and Fe(III) complexes have been inferred on the basis of IR, electronic spectra and magnetic moment data where ligand behaves as dibasic, tridentate and enolate oxygen coordinating to metal ions in addition to phenolate oxygen, azomethine nitrogen.

In TG analysis ligand decomposes in single and complexes in three step; finally ligand converted to carbon and metal complexes converted to respective metal oxides.

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## Disclosure statement

Declaration of Competing Interest- The author declares that this our original work and we don't have any conflict of interest towards its publication.

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