

# **Synthesis, characterization, thermal and kinetic studies of nickel (II), copper (II) and zinc (II) chelates with multidentate ligand.**

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**ABSTRACT:** Complexes of Ni(II), Cu(II) and Zn(II) with an asymmetric tridentate Schiff base prepared by condensation of ethyl 2-amino-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate with (3Z)-3-(hydroxyimino)butan-2-one were synthesized and characterized on the basis of elemental analysis, molar conductance measurements, magnetic susceptibility values, UV-Vis, IR and NMR spectral data wherever possible. Spectral studies show that the ligand behaves as tridentate chelating agent and bonded to the metal ion through azomethine nitrogen, ester carbonyl and the enolic oxygen atom. Electronic spectra and magnetic susceptibility measurement reveal octahedral geometry for Ni (II), tetrahedral configuration for Zn (II) complex, and square planar structure for Cu (II) complex. The complexes are found to be non-electrolytic in nature on the basis of low molar conductance. The thermal behavior (TGA/DTA) of the complexes were studied and kinetic parameter was determined by the Coats-Redfern method.

**KEYWORDS:** Asymmetrical tridentate, Transition metal complexes, Thermal analysis

## **I INTRODUCTION**

Schiff bases [1-3] which are formed as condensation products of primary amines with carbonyl compounds where the presence of a lone pair of electrons in a  $sp^2$  hybridized orbital of the nitrogen atom is of chemical and biological importance. They are excellent chelating agents with the metal ion and this is a result of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group. They are with many applications such as biological [4] pharmacological activities [5], analytical in potentiometric sensors [6] for specific metal ions, and industrial applications [7] (e.g catalysis, hydrogenation of olefins, or as an effective corrosion inhibitor which is based on their ability to spontaneously form a monolayer on the surface to be protected). There is great interest in synthesis and characterization of ligand which contain O, N, O sequence and their metal complexes so the present work was oriented towards the synthesis of a polydentate ligand with its metal complexes.

## **II MATERIALS AND METHODS**

The entire chemical used in the project work was of AR grade and was recrystallised while the solvent was purified and double distilled before use. Metal content was determined by the standard methods [8]. Molar conductance was measured in DMF ( $10^{-3}$  M solution) on an ELICO Digital Conductivity meter Model CM-180. The IR spectra were recorded in KBr disc on a Perkin Elmer Model 1600 FTIR spectrophotometer. The electronic spectra of the complex in DMF were recorded on UV-Systronic spectrophotometer. The  $^1\text{H}$  NMR spectra were recorded in DMSO on a VXR-300S Varian Supercon NMR Spectrometer using TMS as the internal reference. Magnetic susceptibility measurements were carried out by employing the Gouy method using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant. Thermogravimetric studies of the complex were done on Netzch-429 Thermoanalyser recording at a rate of  $10^\circ\text{C min}^{-1}$ .

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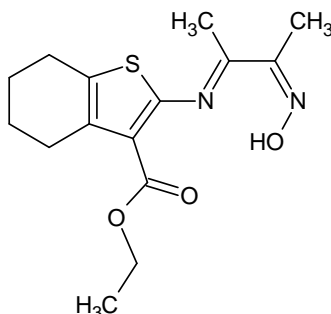
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**Preparation of ligand** : L=Ethyl 2-[(E)-[(3Z)-3-(hydroxyimino)butan-2-ylidene]amino]-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate Fig.1

Ethyl 2-amino-4, 5, 6, 7 tetrahydrobenzo(b)thiophene 3-carboxylate is prepared according to a reported method[9]. To a solution of this thiophene derivative (0.01mol) prepared in ethanol (20ml), a solution of (3Z)-3-(hydroxyimino)butan-2-one (0.01mol) in ethanol (10ml) was added in small portion with constant stirring. The resulting solution was refluxed on a water bath for about four hours. On cooling the solution, the Schiff base crystallized. It was then filtered, washed and vacuum dried. Further purification was done by crystallization from ethanol (MP 156°C).



**FIGURE 1:** ethyl 2-[(E)-[(3Z)-3-(hydroxyimino)butan-2-ylidene]amino]-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate

**Preparation of metal complexes:** The metal complexes were prepared by the following general procedure. To a magnetically stirred and warmed ethanolic solution (20ml) of the ligand (0.01mol) added an ethanolic solution of metal (II) chloride in appropriate ratios dissolved in ethanol (10ml) in small parts. After complete additions of the metal salt solution, the pH was adjusted to 7.5 by adding ethanolic ammonia. It was then refluxed for about six hours in a water bath and the resulting solution was reduced to half the initial volume and allowed to stand overnight. The complex formed was filtered, washed successively with aqueous ethanol and ether. Finally, the complex was dried in vacuum over P<sub>4</sub>O<sub>10</sub>.

### III. RESULTS AND DISCUSSIONS:

Analytical data gave clear evidence that condensation of the ethyl 2-amino-4, 5, 6, 7 tetrahydrobenzo (b) thiophene 3-carboxylate and (3Z)-3-(hydroxyimino)butan-2-one occurred in 1:1 molar ratio and the structure of the novel Schiff base formed has been elucidated on the basis of UV-visible, infrared and proton NMR spectral studies. The UV spectrum of the present ligand in ethanol exhibit at 230 and 305nm characteristic of hydroxyimine form, these band can be assignable to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition respectively of the azomethine group. The infrared spectrum of the ligand exhibit a broadband spreading well over the region 3000-3300  $\text{cm}^{-1}$  and centered at 3200 $\text{cm}^{-1}$ , which can be attributed to hydrogen bonded hydroxyimino  $\nu(\text{NOH})$ . A strong band appearing at 1720 $\text{cm}^{-1}$ , medium intensity band appearing at 1630 $\text{cm}^{-1}$  and 1596 $\text{cm}^{-1}$  could be assignable to ester carbonyl group, azomethine  $\nu(\text{C}=\text{N})$  and oximino  $\nu(\text{C}=\text{NOH})$  vibration. The  $\nu(\text{N}-\text{O})$  stretching vibration are observed in the form of medium intensity band at 987 $\text{cm}^{-1}$ . The strong band at 2930 $\text{cm}^{-1}$  is assign to  $\nu(\text{C}-\text{H})$  of cyclohexane where as medium intensity band at 608 $\text{cm}^{-1}$  is of  $\nu(\text{C}-\text{S})$  mode of thiophene moiety [10].

Proton NMR spectral data of the ligand supported the conclusion drawn on the basis of UV and IR spectral data .the absence of NH<sub>2</sub> proton signal in the NMR spectrum of ligand in DMSO-d<sub>6</sub> indicates successful Schiff base formation by replacement of the C=O group of (3Z)-3-(hydroxyimino)butan-2-one. A signal at 11.85 $\delta$  reveals the oximino proton since it is expected to be rather acidic and therefore the weakest shielded proton in the molecule. The signals appearing at 1.50 $\delta$  (d) and 4.30 $\delta$  (m) can be attributed to methyl and methylene proton respectively of the ester group. A multiplet at 1.7 $\delta$  is due to four hydrogen of tetrahydrobenzothiophene.

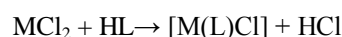
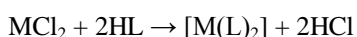
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Ligand (HL) ethyl 2-{(E)-[(3Z)-3-(hydroxyimino)butan-2-ylidene]amino}-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate formed well defined complexes with the metal salts. Formation of the complexes can be symbolized as follows:



M = Ni(II)

M = Cu(II), Zn(II)

HL = ethyl 2-{(E)-[(3Z)-3-(hydroxyimino) butan-2-ylidene]amino}-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate  
 Formulation of the complexes has been based on their elemental analytical data, molar conductance values, and magnetic susceptibility data. The stoichiometry of the complexes 1:1 (Metal: ligand) of Cu (II) and Zn (II) complexes, where as 1:2 (metal: ligand) of Ni (II) complex as shown in **Table-1**. All the complex are insoluble in water, while partly soluble in methanol, ethanol, and chloroform and highly soluble in DMF and DMSO. The complexes are all stable up to 190°C indicating high thermal stability and hence strong metal to ligand bond. The results of the electrical conductance measurements of the soluble complex in DMF show that they are non-electrolyte in nature[11]

**TABLE -1**  
**Physico-Chemical characteristic of Schiff Base ligand and its metal complexes**

Compound	Colour	F.Wt	Elemental analysis (%) Found(calcd)					Molar Cond. ( $\Omega^{-1}cm^2mol^{-1}$ )
			C	N	S	Cl	M	
L	yellow	308.39	58.23 (58.42)	10.03 (9.08)	9.85 (10.40)	-	-	-
NiL <sub>2</sub>	Brown	673.47	52.82 (53.50)	7.95 (8.32)	8.95 (9.52)	-	7.45 (8.32)	7.62
CuLCl	Black	406.39	42.85 (44.33)	7.02 (6.89)	6.82 (7.89)	7.85 (8.72)	15.23 (15.64)	19.32
ZnLCl	yellow	408.25	43.89 (44.13)	7.23 (6.86)	7.66 (7.85)	7.92 (8.68)	14.82 (16.02)	12.16

The UV spectral bands characteristic of the ligand is only marginally red shifted in the spectra of the metal complexes indicating that no structural alteration of the ligand occurs on coordination with the metal ions. In the metal complexes, the  $\nu(C=N)$  is displaced to lower wave number by about 20-25  $cm^{-1}$  on bond stabilization of the azomethine moiety upon coordination. The bond corresponding to the ester  $\nu(C=O)$  has been shifted to lower frequency by about 25-30  $cm^{-1}$  in the metal complexes indicating coordination by ester function [12]. A broad band at 3200  $cm^{-1}$  which is assigned to the enolic OH group of the (3Z)-3-(hydroxyimino)butan-2-one moiety, the broadness of this band indicates the presence of hydrogen bond and this band disappear in the complexes indicates deprotonation of an enolic group, which lead to a six-membered ring structure around metal ions. A strong band around 2930  $cm^{-1}$  due to  $\nu(C-H)$  of cyclohexane did not show any appreciable change in metal complexes. Infra spectra of the complexes also showed non-ligand band in the region 430-460  $cm^{-1}$  and 510-520  $cm^{-1}$ , which could be assigned to  $\nu(M-O)$  and  $\nu(M-N)$  modes respectively [13]. The medium band observed in the range 385- 395  $cm^{-1}$  can be assigned to the presence of  $\nu(M-Cl)$  in complexes [14] which was recorded on Plytec 30 spectrometer using CsI disc. Absence of  $\nu(M-S)$  band in the far infrared spectra of the metal complexes gives direct evidence to non-involvement of ring sulphur in bond formation.

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spectral data of IR is given in Table-2. Comparison of the <sup>1</sup>H-NMR spectra of the ligand and its complexes reveal that the ligand behaves as a tridentate mono negative ONO donor. The disappearance of the signal at 11.85δ was ascribed to the fact that the ligand underwent deprotonation of the oximino group during complexation. Signals due to the other proton were found in the expected region and shifted by about 0.20 to 0.50δ in the spectra of the metal complexes.

**TABLE -2: IMPORTANT IR SPECTRAL BANDS OF SCHIFF BASE AND ITS METAL COMPLEXES**

Tentative assignment	ν(O-H)	ν(C-H)	ν(C=O)	ν(C=N)	ν(M←N)	ν(M←O)	ν(M-O)	ν(M-Cl)
HL	3210br	2930m	1720s	1670s	-----	-----	-----	-----
[NiL <sub>2</sub> ]	-----	2935m	1695s	1648s	445m	512m	590m	
[CuLCl]	-----	2932m	1692s	1646s	452m	520m	610m	430m
[ZnLCl]	-----	2932m	1694s	1645s	458m	527m	618m	440m

The electronic spectra of Ni(II) complex shows absorption band at 11010, 17520 and 28240 cm<sup>-1</sup>, which may be assigned to the <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F)(ν<sub>1</sub>), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F)(ν<sub>2</sub>) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P)(ν<sub>3</sub>) transition respectively indicating octahedral geometry [15]. The magnetic moment value of 3.38 BM supports octahedral geometry. The ν<sub>2</sub>/ν<sub>1</sub> value in the Ni(II) complex is 1.734 and it lies in the range (1.60-1.82) for octahedral Ni(II) complexes. The electronic spectral parameters values are as follows Dq=1101 cm<sup>-1</sup>, B=848.6 cm<sup>-1</sup>, β = B'/B=0.82, β<sub>0</sub> = 17% and CFSE = -157.83 KJmol<sup>-1</sup>. The low value of Racah parameters compare to the free-ion value of 1030 to 944 cm<sup>-1</sup> of the complex and β<sub>0</sub> value of 17% indicates the covalent nature of Ni-L bond. The magnetic moment value of 3.22 BM supports octahedral geometry. The spectrum of Cu(II) complex shows a broad band at 18990 cm<sup>-1</sup> attributed to <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub> transition which strongly favours the square planar geometry around the central metal ion [16]. The broadness of the band indicates distorted square planar geometry. The Zn(II) complex is diamagnetic and there is no d-d transition. The elemental analyses are in good agreement with the proposed formula suggesting tetra-coordinated Zn(II) complex preferred tetrahedral geometry [17].

**TABLE -3  
THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TGA/DTA) OF COMPLEXES**

Complexes	Temperature Range (°C)	Weight loss (%) Exp.(Theo)	Decomposition Product	DTA peak (°C)
[NiL <sub>2</sub> ]	195-330	54.82(55.61)	2C <sub>8</sub> H <sub>13</sub> S O + 4CH <sub>3</sub>	275(exo)
	380-490	34.06(33.29)	2C <sub>5</sub> N <sub>2</sub> O+(O)	450(exo)
	>490(Residue)	11.12(11.09)	NiO	
[CuLCl]	200-375	45.25(46.09)	C <sub>8</sub> H <sub>13</sub> S O + 2CH <sub>3</sub>	275(exo)
	420-500	35.20(34.34)	C <sub>5</sub> N <sub>2</sub> OCl	475(exo)
	>500(Residue)	19.55(19.57)	CuO	
[ZnLCl]	195-390	46.52(45.87)	C <sub>8</sub> H <sub>13</sub> S O + 2CH <sub>3</sub>	340(exo)
	430-525	33.95(34.18)	C <sub>5</sub> N <sub>2</sub> OCl	485(exo)
	>525(Residue)	19.53(19.94)	ZnO	

Thermal decomposition of the complexes was studied by TG technique in a nitrogen atmosphere. The TGA/DTA data of complexes are given in Table-3 and the thermogram of the metal complexes is shown in figure:2. There is no weight loss up to 190°C and this ruled out the presence of any water molecule in the complexes. The thermogram of Ni(II) complex indicated that it was stable up to 190°C. Thermal decomposition took place in the temperature range of 195-490°C. First TG loss was observed in 195-330°C with the loss of substituted thiophene moiety 2C<sub>8</sub>H<sub>13</sub>SO and methyl molecule 4CH<sub>3</sub> (theo. 55.61%. exp., 54.82%) followed by an exotherm at 275°C. Second TG loss was in the temperature range of 380-490°C with a loss of remaining ligand fragments 2C<sub>5</sub>N<sub>2</sub>O+(O) (theo. 33.29%. exp., 34.06%) followed by an

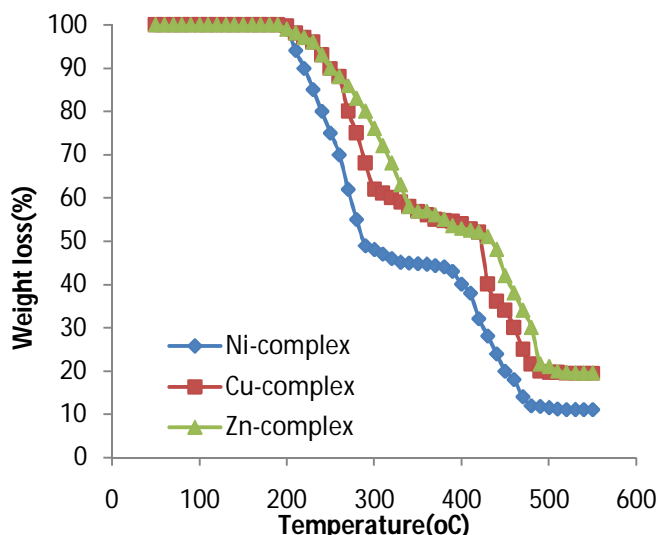
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exotherm at 450°C. The residue left was of weight correspond NiO (theo. 11.09%. exp., 11.12%). The thermogram of Cu(II) complex indicated that it was stable up to 200°C. Thermal decomposition took place in the temperature range of 200-500°C. First TG loss was observed in 200-375°C with the loss of C<sub>8</sub>H<sub>13</sub>SO and 2CH<sub>3</sub> (theo. 46.09%. exp., 45.25%) followed by an exotherm at 275°C. Second TG loss was in the temperature range of 420-500°C with a loss of remaining ligand fragments C<sub>5</sub>N<sub>2</sub>OCl (theo. 29.86%. exp., 28.70%) followed by an exotherm at 475°C. The residue left was of weight correspond to CuO. (theo. 19.57%. exp. 19.55%). The thermogram of Zn(II) complex indicated that it was stable up to 195°C. Thermal decomposition took place in the temperature range of 195-525°C. First TG loss was observed in 195-390°C with the loss of C<sub>8</sub>H<sub>13</sub>SO and 2CH<sub>3</sub> (theo. 45.87%. exp., 46.52%) followed by an exotherm at 340°C. Second TG loss was in the temperature range of 430-525°C with a loss of remaining ligand fragments C<sub>5</sub>N<sub>2</sub>OCl (theo. 34.18%. exp. 33.95%) followed by an exotherm at 485°C. The residue left was of weight correspond to ZnO. (theo. 19.94%. exp., 19.53%).



**Fig. 2 Thermogram of metal complexes**

The kinetic parameters such as activation energies ( $E^*$ ), enthalpy ( $\Delta H^*$ ), entropy ( $\Delta S^*$ ) and free energy change of decomposition ( $\Delta G^*$ ) were evaluated graphically by employing the Coats-Redfern relation [18].

$$\text{Log} \left[ \frac{\log \{W_f / (W_f - W)\}}{T^2} \right] = \log \left[ \frac{AR}{\theta E^*} \left( \frac{1 - 2RT}{E^*} \right) \right] - \frac{E^*}{2.303RT}$$

Where  $W_f$  is the mass loss at the completion of the reaction,  $W$  is the mass loss up to the temperature  $T$ ,  $R$  is the gas constant,  $E^*$  is the activation energy in  $\text{kJmol}^{-1}$ ,  $\theta$  is the heating rate and  $(1 - (2RT/E^*)) \approx 1$ . A plot of the left-hand side of Eq. (1) against  $1/T$  gives a slope from which  $E^*$  was calculated and  $A$  (Arrhenius constant) was determined from the intercept. The entropy of activation ( $\Delta S^*$ ), enthalpy of activation ( $\Delta H^*$ ) and the free energy of activation ( $\Delta G^*$ ) were calculated using the following equation:

$$\Delta S^* = 2.303 R \log (A h / k T) \quad (2)$$

$$\Delta H^* = E^* - RT \quad (3)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (4)$$

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Where  $k$  and  $h$  are the Boltzmann and Plank constants respectively. The calculated values  $E^*$ ,  $A$ ,  $\Delta S^*$ ,  $\Delta H^*$  and  $\Delta G^*$  for the decomposition steps are given in Table-4

**TABLE -4**  
**KINETIC DATA ON COMPLEXES**

Complexes	Temp Range (K)	$E^*$ (kJmol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	$\Delta S^*$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H^*$ (kJmol <sup>-1</sup> )	$\Delta G^*$ (kJmol <sup>-1</sup> )	$r$
[NiL <sub>2</sub> ]	468-603	116.16	4.114x10 <sup>10</sup>	-46.78	111.60	137.24	0.914
	653-763	192.27	2.158x10 <sup>13</sup>	2.98	186.70	184.54	0.950
[CuLCl]	473-648	67.63	1.723x10 <sup>5</sup>	-149.75	63.07	145.14	0.960
	693-773	164.93	5.266x10 <sup>13</sup>	10.12	158.71	151.14	0.979
[ZnLCl]	468- 663	61.09	2.601x10 <sup>4</sup>	-166.41	56.00	158.01	0.979
	703-798	214.06	1.65x10 <sup>14</sup>	19.53	207.76	192.95	0.962

The correlation coefficient of the Arrhenius plots of the thermal decomposition steps was found to lie in the range 0.91-0.98, showing a good fit with the linear function. In the present studies, the numerical values of activation energy, frequency factor, and entropy of activation indicate about the smoothness of the feasibility and reaction rate of the initial reactants and intermolecular stage compounds. The calculated values of the activation energy of the complexes are relatively low indicating an autocatalytic effect of the metal ions on the thermal decomposition of the complexes [19,20]. The negative values for the entropy of activated complexes have more ordered or more rigid structure than the reactants or intermediate and the reaction is slower than normal. These values are comparable with other observation[21]. The order of stability of complexes on the basis of activation energy is NiL<sub>2</sub> > CuLCl > ZnLCl (on the basis of first decomposition stage) and ZnLCl > NiL<sub>2</sub> > CuLCl (on the basis of second decomposition stage).

## IV CONCLUSION

Based on the above analytical and physico-chemical properties it has been observed that a new ligand ethyl 2-[(2E, 3Z)-4-hydroxypent-3-en-2-ylidene] amino}-4, 5, 6, 7-tetrahydro-1-benzothiophene-3- carboxylate behaves as a tridentate chelating agent and bonded to the metal ion through azomethine nitrogen, ester carbonyl and enolic oxygen atom. Electronic spectra and magnetic susceptibility measurement reveal octahedral geometry for Ni (II) complex, a square planar structure for Cu(II) complex, tetrahedral configuration for Zn(II) complexes and Structures proposed for the complexes are designated in Figure 3-5 below.

Proposed structure of complexes

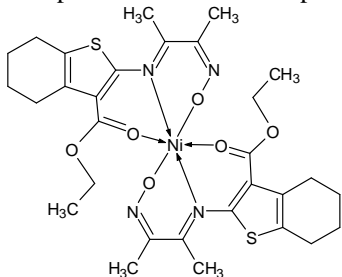


Fig.3; Structure of [NiL<sub>2</sub>] complex

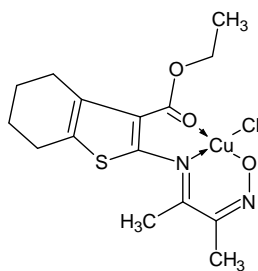


Fig.4. Structure of [CuLCl] comple

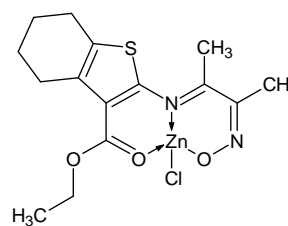


Fig.5. Structure of [ZnLCl] complex



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