

## **Synthesis, characterization of some transition metal complexes of unsymmetrical tetradentate schiff base and their antimicrobial studies**

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### **ABSTRACT**

*A new series of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes with tetradentate unsymmetrical Schiff base ligand derived from Dehydroacetic acid, 2-hydroxy benzaldehyde (L) and 6-methyl-1,3,5-triazine-2,4-diamine have been reported. The complexes have been characterized by elemental analysis, magnetic susceptibility measurements, conductrometry, electronic and infrared spectra, X-ray diffraction, <sup>1</sup>H-NMR spectra and thermogravimetric analysis. The ligand and its complexes were screened for their antibacterial activity against bacterium Staphylococcus aureus, B.subtilis (Gram positive) and Escherichia coli, K.pneumoniae (Gram negative). The result indicated that the complexes exhibited good antibacterial activities.*

**Keywords:** *Dehydroacetic acid, Unsymmetrical Schiff bases, Transition metal complexes, Thermal analysis, Powder X-ray diffraction.*

### **INTRODUCTION**

Tetradentate Schiff bases are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry [1]. Schiff bases of 6-methyl-1,3,5-triazine-2,4-diamine reported to have variety of applications including biological, clinical and analytical fields [2-5]. Metal complexes make the compounds effective as a stereospecific catalysts towards oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry, Schiff base complexes play a vital role in designing metal complexes related to synthetic and natural oxygen carriers. [4,6-8] Many asymmetrical tetradentate bis-Schiff bases of 1, 2-diamines with different aldehyde/ketone have been prepared and studied intensively. However much less attention has been focused on asymmetrical tetradentate Schiff bases derived from 1, 2-diamines and different aldehydes / ketones. In particular, those derived from heterocyclic 1, 2- diamines have been under-investigated. It is worthwhile to mention here that asymmetrical Schiff bases of this type are difficult to obtain and not easily isolated.

A search of literature reveals that no work has been done on the transition metal complexes of the asymmetrical Schiff bases derived from 6-methyl-1,3,5-triazine-2,4-diamine, dehydroacetic acid and 2-hydroxybenzaldehyde. In this communication we report the synthesis of asymmetrical tetradentate Schiff bases formed by the condensation of 6-methyl-1,3,5-triazine-2,4-diamine, dehydroacetic acid and 2-hydroxybenzaldehyde (Fig.1). The solid complexes of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with these ligands have been prepared and characterized by different physico-chemical methods.

## MATERIALS AND METHODS

### Reagents and solvents

Dehydroacetic acid obtained from Merck was used as supplied 2-hydroxy benzaldehyde and 6-methyl-1,3,5-triazine-2,4-diamine of AR grade were used for synthesis of ligand. AR grade metal nitrate were used for the complex preparation.

### Synthesis of ligand

The ligand was prepared by a modification of the reported methods [9-15]. Asymmetric tetradentate Schiff base ligand has been synthesized via a stepwise approach. In the first step mono-Schiff base compound was prepared by refluxing 50ml solution of 10mmol of dehydroacetic acid and 20mmol 6-methyl-1,3,5-triazine-2,4-diamine in super dry ethanol for about 4h. Mono-Schiff base thus formed was then refluxed with 10mmol 2-hydroxy benzaldehyde to prepare asymmetric ligand. Asymmetric Schiff base thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol. (Yield:69%).

### Synthesis of metal complexes

To a hot ethanol solution (25ml) of the ligand (0.005mol), methanolic solution (25ml) of metal Nitrate (0.0025mol) was added with constant stirring. The pH of reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 3 h. The precipitated solid metal complex was filtered off in hot condition and washed with hot methanol, ethanol, petroleum ether (40°-50°) and dried over calcium chloride in vacuum desiccator.(yield: 57%)

### Physical Measurement

IR spectra were recorded on FTIR(ATR)-BRUKER-TENSOR37 spectrometer using KBr pellets in the range of 4000-400  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (varian mercury 300MHZ) spectra of ligand were measured in  $\text{CDCl}_3$  using TMS as internal standard. X-RD were recorded on BRUKER D8 Advance. TGA- DTA were recorded on Shimadzu. The carbon, hydrogen and nitrogen contents were determined on Elementar model vario EL-III. The UV-visible spectra of the complexes were recorded on model UV-1800, SHIMADZU spectrometer. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using  $10^{-4}$  M solution in DMSO. Magnetic susceptibility measurements of the metal chelates were done on a Guoy balance at room temperature using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant.

## RESULTS AND DISCUSSION

Schiff bases of 6-methyl-1,3,5-triazine-2,4-diamine and its complexes have a variety of applications including biological, clinical and analytical. The coordinating possibility of 6-methyl-1,3,5-triazine-2,4-diamine has been improved by condensing with a variety of carbonyl compounds. An attempt has been made to synthesize asymmetric Schiff bases from 6-methyl-1,3,5-triazine-2,4-diamine and dehydroacetic acid with 2-hydroxybenzaldehyde. Physical characteristics, micro analytical, and molar conductance data of ligand and metal complexes are given in (Table 1 and 2)The analytical data of complexes reveals 2:1 molar ratio (metal: ligand) and corresponds well with the general formula  $[\text{ML}(\text{H}_2\text{O})_2]$  (where M= Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)). The magnetic susceptibilities of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes at room temperature are consistent with high spin octahedral structure with two water molecules coordinated to metal ion. The presence of two coordinated water molecules was confirmed by TG-DT analysis. The metal chelate solutions in DMSO show low conductance and supports their non-electrolyte nature (Table 1).

### $^1\text{H-NMR}$ spectra of ligand

The  $^1\text{H-NMR}$ . spectra of free ligand at room temperature shows the following signals. 2.14  $\delta$  (s, 3H,  $\text{C}_6\text{-CH}_3$ ), 2.35  $\delta$ (s, 3H,  $\text{C}_6$ .methyl H 6-methyl-1,3,5-triazine-2,4-diamine ), 2.48  $\delta$  (s, 3H,  $\text{N}=\text{C-CH}_3$ ), 6.31  $\delta$  (s, 1H, phenolic OH), 6.94-7.60  $\delta$  (m,4H, Aromatic  $\text{H}_a$ ,  $\text{H}_b$ ,  $\text{H}_c$ ,  $\text{H}_d$  protons of phenyl ring).

### IR Spectra

The IR spectrum of free ligands shows characteristic bands at 3283, 1661, 1549, 1463,1393 and 1124  $\text{cm}^{-1}$  assignable to  $\nu$  OH (intramolecular hydrogen bonded),  $\nu$  C=C(aromatic),  $\nu$  C=N (azomethine),  $\nu$  C-N (aryl azomethine) and  $\nu$  C-O (phenolic) stretching modes respectively[16-19] The absence of a weak broad band in the 3200-3400  $\text{cm}^{-1}$  region, in the spectra of the metal complexes suggests deprotonation of the intramolecular hydrogen

bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by downward shift in  $\nu$  C-O (phenolic) [20] with respect to free ligand. On complexation, the  $\nu$  (C=N) [21] band is shifted to lower wave number with respect to free ligand, denoting that the nitrogen of azomethine group is coordinated to the metal ion. The  $\nu$  C-N band is shifted to lower wave number with respect to free ligand. The IR spectra of metal chelates showed new bands in between the 500-600 and 400-500  $\text{cm}^{-1}$  regions which can be assigned to  $\nu$  M-O and M-N [22] vibrations respectively. The IR spectra of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) show a strong band in the 3050-3600  $\text{cm}^{-1}$  region, suggesting the presence of coordinated water in these metal complexes. The presence of coordinated water is further confirmed by the appearance of non-ligand band in 830-840  $\text{cm}^{-1}$  region, assignable to the rocking mode of water. The presence of coordinated water is also established and supported by TG/DT analysis of these complexes. Hence it is concluded that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

### Thermogravimetric analysis

Thermal decomposition studies of complex have been carried out as to corroborate the information obtained from the IR spectral studies to know the presence of water molecule in these complexes as well as to know their decomposition pattern. The simultaneous TG/DT analysis of Cr(III) and Fe(III) was studied from ambient temperature to 1000  $^{\circ}\text{C}$  in nitrogen atmosphere using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference. An analysis of the thermogram of the complexes indicated that Cr(III) complexes shows two step decomposition. The first weight loss 7.70%, in between temp. 33-60 $^{\circ}\text{C}$  could be correlated with the loss of two coordinated water (calculated 8.01%). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 65-470 $^{\circ}\text{C}$  with 77.74% mass loss corresponds to decomposition of the complex (calcd. 76.50%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide Cr<sub>2</sub>O<sub>3</sub> obs. 14.54% (calcd. 14.90%). An analysis of the thermogram of the complexes indicated that Fe(III) complexes shows two step decomposition. The first weight loss 7.64%, in between temp. 33-70 $^{\circ}\text{C}$  could be correlated with the loss of two coordinated water (calculated 7.82%). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 70-470 $^{\circ}\text{C}$ , with 77.10% mass loss corresponds to decomposition of the complex (calcd. 76.50%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide Fe<sub>2</sub>O<sub>3</sub> obs. 15.24% (calcd. 14.70%). The kinetic and thermodynamic viz the energy of activation (E<sub>a</sub>), frequency factor (Z), entropy change (- $\Delta S$ ) and free energy change ( $\Delta G$ ) for the non-isothermal decomposition of complexes have been determined by employing Horowitz-Metzger method [23] and Coats-Redfern method [24] and values are given in Table 3. The Calculated values of the given activation energy of the complexes are relatively low, indicating the autocatalysis effect of metal ion on the thermal decomposition of the complex. The negative value of activation entropy indicate that the activated complexes were more ordered than the reaction were slow. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer transitions[25].

### Magnetic measurements and electronic absorption spectra

The electronic absorption spectrum of the Cr(III) complexes in DMSO solution shows the region 17667 $\text{cm}^{-1}$  and 37594 $\text{cm}^{-1}$  assignable to the transition  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  and charge transfer bands. All Cr(III) complexes were diamagnetic in nature. these data and magnetic moment suggest octahedral geometry around Cr(III) [26]. The electronic absorption spectrum of the Fe(III) complexes shows bands at 37453 $\text{cm}^{-1}$  assignable to the charge transfer bands. All Fe(III) complexes were diamagnetic in nature. these data and magnetic moment suggest octahedral geometry around Fe(III)[27]. Co(II) complexes shows bands at 18348 $\text{cm}^{-1}$  and 37174 $\text{cm}^{-1}$  assignable to  ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$  and charge transfer transitions. All Co(II) complexes were diamagnetic in nature. these data and magnetic moment suggest octahedral geometry around Co(II)[28]. Ni(II) complexes shows bands at 13175 $\text{cm}^{-1}$  and 38610 $\text{cm}^{-1}$  are assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  and charge transfer transitions. The absence of band below 10,000  $\text{cm}^{-1}$  and All Ni(II) complexes were diamagnetic in nature indicates octahedral geometry[29]. Cu(II) complexes shows bands at 29498 $\text{cm}^{-1}$ . These transitions may be assigned to charge transfer transitions. All Cu(II) complexes were diamagnetic in nature indicates octahedral geometry[30]. Zn(II) complexes did not show any d-d bands and their spectra were dominated by the charge transfer bands at 29411 $\text{cm}^{-1}$ . All Zn(II) complexes were diamagnetic in nature indicates octahedral geometry[31].

### Molar Conductivity Measurements

The metal(II) and (III) complexes were dissolved in DMSO and the molar conductivity of 10<sup>-4</sup> M of their solution at room temperature were measured. The lower conductance values of the complexes support their non-electrolytic nature of the compounds.

**Table 1. Physical characterization, analytical and molar conductance data of compounds**

Compound	Molecular formula	Mol.Wt.	M.P. Decomp temp. °C	Colour	Molar Conduc Mho. Cm <sup>3</sup> mol <sup>-1</sup>
L		379.37	>300	Yellow	----
L Cr		431.37	>300	Gray	40.28
L Fe		435.21	>300	Brown	40.58
L Co		438.3	>300	Pink	19.63
L Ni		438.06	>300	Green	28.25
L Cu		442.92	>300	Blue	13.62
L Zn		444.76	>300	White	19.33

**Table 2. Elemental Analysis of Co(II) Complex:-**

Compound	Found (Calculated)			
	C	H	N	M
L	60.76	4.48	19.15	0
	-60.15	-4.5	-18.46	
L-Co	52.1	3.95	15.94	13.4
	-52.06	-3.9	-15.97	-13.44

### Powder x-ray diffraction

The x-ray diffractogram of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of L was scanned in the range 20-80° at wavelength 1.543 Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of Cr(III) complex of L had twenty one reflections with maxima at 2θ = 13.52° corresponding to d value 2.180Å. The diffractogram of Fe(III) complex of L had twenty one reflections with maxima at 2θ = 13.681° corresponding to d value 3.254Å. The diffractogram of Co(II) complex of L had seventeen reflections with maxima at 2θ = 39.977° corresponding to d value 1.198Å. The diffractogram of Ni(II) complex of L had sixteen reflections with maxima at 2θ = 10.761° corresponding to d value 4.116Å. The diffractogram of Cu(II) complex of L had twenty one reflections with maxima at 2θ = 14.891° corresponding to d value 2.995Å. The diffractogram of Zn(II) complex of L2 shows seventeen reflections with maxima at 2θ = 10.724° corresponding to d value 4.140 Å. The x-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% has been indexed by using computer programme [32]. The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of Cr(III) complex of L yielded values of lattice constants, a=9.9812 Å, b=8.9774 Å, c = 19.3429 Å and unit cell volume V=1501.03 Å<sup>3</sup>. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠ γ required for sample to be Monoclinic were tested and found to be satisfactory. Hence it can be concluded that Cr(III) complex has Monoclinic crystal system. The unit cell of Fe(III) complex of L yielded values of lattice constants, a=9.9785 Å, b=10.1484Å, c = 16.9833Å and unit cell volume V=1489.43 Å<sup>3</sup>. The unit cell of Co(II) complex of L yielded values of lattice constants, a=9.9804 Å, b=10.6471 Å, c = 16.1026Å and unit cell volume V=1481.87Å<sup>3</sup>. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠ γ required for sample to be monoclinic. The unit cell of Ni(II) complex of L yielded values of lattice constants, a=8.3219 Å, b=9.9871 Å, c = 14.9793Å and unit cell volume V=1244.97Å<sup>3</sup>. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = γ = β required for sample to be monoclinic. The unit cell of Cu(II) complex of L yielded values of lattice constants, a=9.8558 Å, b=9.0270 Å, c = 20.2809Å and unit cell volume V=1562.64Å<sup>3</sup>. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠ γ required for sample to be monoclinic. The unit cell of Zn(II) complex of L yielded values of lattice constants, a=9.9216Å, b=8.928 Å, c = 19.5717Å and unit cell volume V=1501.39Å<sup>3</sup>. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠ γ required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complex of L has monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method [33] and found to be 1.12, 1.04, 1.12, 0.72, 1.04 and 1.3 gcm<sup>-3</sup> for Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes respectively. By using experimental density values, molecular weight of complexes, Avogadro's number and volume of the unit cell were calculated. Number of molecules per unit cell were calculated by using equation ρ = nM/NV and was found Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes respectively. With these values, theoretical density were computed and found to be 1.12, 1.04, 1.12, 0.72, 1.04 and 1.3 gcm<sup>-3</sup> for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error [34].

Table 3 The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CR)

Complex	Step	N	Method	Decomp. Temp. (°C)	Ea (kJ mole <sup>-1</sup> )	Z (S <sup>-1</sup> )	ΔS (JK <sup>-1</sup> mole <sup>-1</sup> )	ΔG (kJ mole <sup>-1</sup> )	Correlation coefficient
L <sub>2</sub> -Fe	I	1.9	HM	170	3.76	7.4 X 10 <sup>2</sup>	-168.5	12.73	0.989
			CR		10.51		1.59	-244.37	23.53
	II	0.9	HM	420	9.2	1.44X10 <sup>1</sup>	-159.27	22.47	0.997
			CR		31.58	3.98	-240.48	51.61	0.996
L <sub>2</sub> -Cr	I	2.4	HM	195	4.19	7.96X10 <sup>2</sup>	-167.49	13.62	0.98
			CR		11.13		1.86	-243.51	24.83
	II	2.2	HM	450	10.01	1.56X10 <sup>1</sup>	-158.25	23.77	0.99
			CR		48.73	3.65X10 <sup>05</sup>	-337.29	78.06	0.998

Table 4: Antibacterial activity of compounds

Bacterium	Diameter of inhibition zone (mm)				
	(L)				Tetracyclin
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
<i>E. coli</i>	6	7	8	6	13
<i>S. Aurious</i>	11	10	7	4	12
<i>B.Subtilis</i>	10	11	9	9	10
<i>K.Pneumoniae</i>	9	7	10	6	16

Table 5: Antibacterial activity of compounds

Bacterium	Diameter of inhibition zone (mm)				
	(LM)				Tetracyclin
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
<i>E. coli</i>	17	13	12	10	25
<i>S. Aurious</i>	17	16	12	8	22
<i>B.Subtilis</i>	24	20	16	12	39
<i>K.Pneumoniae</i>	17	16	13	10	22

### Antibacterial activity

Antibacterial activity of ligand and metal complexes were tested *in vitro* against bacteria such as *E. Coli*, *B.Subtilis*, *S. Aurious* And *K.Pneumoniae* by paper disc plate method [35] The compounds were tested at the concentrations 1250ppm 2500ppm 5000ppm and 10000ppm. DMSO and compared with known antibiotics *viz* *Tetracyclin*. (Table 4 and 5). From Table 4, it is clear that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes [36] Such enhanced activity of metal chelates is due to the increased lipophilic nature of the metal ions in complexes. The increase in activity with -concentration is due to the effect of metal ions on the normal cell process. The action of compounds may involve the formation of hydrogen bond with the active centre of cell constituents, resulting in interference with the normal cell process

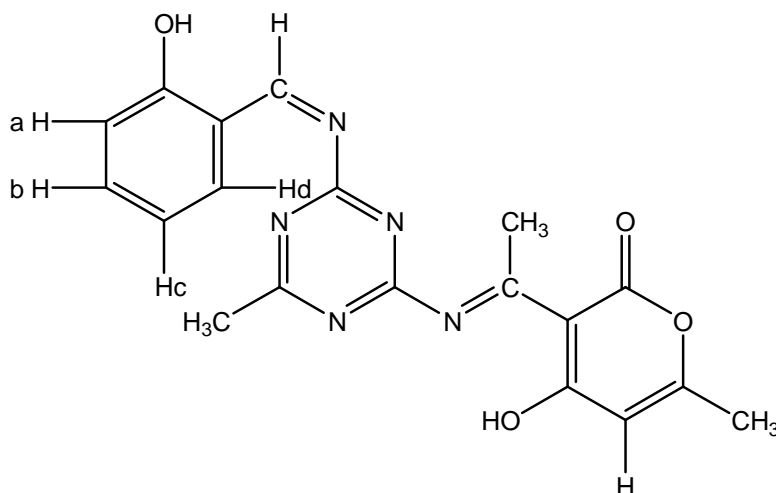
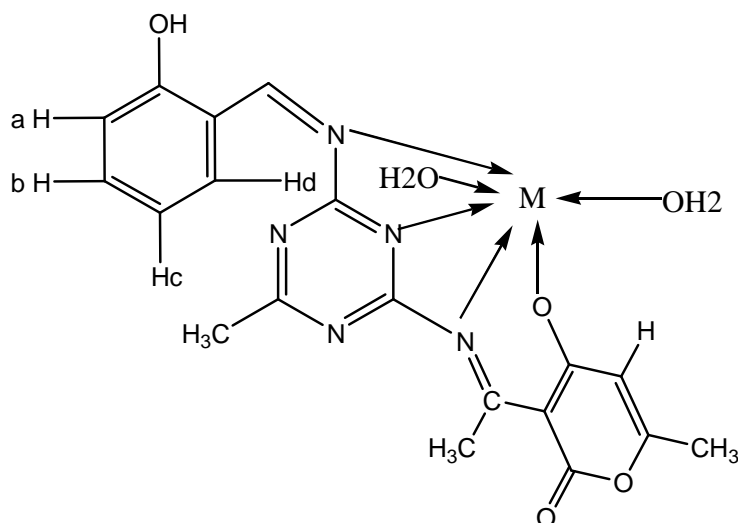


Figure 1. Structure of ligand



**Figure 2. The proposed Structure of the complexes**  
when  $M = \text{Cr(III)}, \text{Fe(III)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$  and  $\text{Zn(II)}$

### CONCLUSION

In the light of above discussion we have proposed octahedral geometry for Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume that the ligand behave as dibasic, NNNNO tetradentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig.2. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The X-ray study suggests monoclinic crystal system for Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes.

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