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Synthesis, and characterization of Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes with novel Schiff base ligand derived from 4-Hydroxy-3-(1-((5-phenyl-1,3,4-oxadiazol-2-yl)imino)ethyl)-2H-chromen-2-one

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ABSTRACT:

A novel bi-dentate Schiff's base ligand (L), 4-hydroxy-3-(1-((5-phenyl-1,3,4-oxadiazol-2-yl)imino)ethyl)-2H-chromen-2-one(3) were synthesized by condensation of primary heterocyclic aromatic amines 5-phenyl-1,3,4-oxadiazol-2-amine(2) with 3-acetyl-4-hydroxychromen-2-one (1). The characterization of these compounds was carried out using IR, ¹H NMR, ¹³C NMR, and mass spectrometry. Complexes of Cu(II), Ni(II), Zn(II), Cd(II), and Hg(II) were synthesized and analyzed through mass spectrometry, IR spectroscopy, electronic spectra, and X-ray diffraction (XRD) analysis. The magnetic moments and molar conductance of the Cu(II) and Ni(II) complexes were studied using standard methods. Based on magnetic and spectral data, an octahedral geometry around these metal ions has been proposed. The results confirm that the Cu(II) and Ni(II) complexes crystallize in a monoclinic system with monomeric octahedral geometry. In contrast, the Zn(II), Cd(II), and Hg(II) complexes exhibit a monomeric tetrahedral geometry.

KEYWORDS: 3-acetyl-4-hydroxychromen-2-one, 5-phenyl-1, 3, 4-oxadiazol-2-amine, Schiff base ligand, spectra, magnetic moments, molar conductance etc.

INTRODUCTION:

Schiff bases and their metal complexes are important in coordination chemistry. They are appreciated for their simple synthesis and versatility and manifold varieties of applications [1]. Schiff base metal complexes have been extensively studied in the field of coordination chemistry due to their direct synthesis, availability of reactants, electronic properties, and good solubility in common solvents [2]. Salen-type bidented donor ligands are a motivating area of research in coordination chemistry. Metal-based Schiff bases are more potent than regular Schiff bases. Transition metals play an important role in pharmacology [3]. Schiff base molecules offer potential sites for bioactive compounds due to their involvement in proton transfer equilibrium and intermolecular hydrogen bonding. Metal complexes of Schiff base ligands have demonstrated a wide range of applications in analytical, biological, clinical, and industrial fields. Recently, these complexes have stored remarkable attention, not only because of their diverse applications and fascinating spectroscopic properties, but also due to their significant antibacterial, antifungal, and antitumor activities [4-8].

The literature review reveals extensive research on lanthanide complexes of Schiff bases derived from 8-formyl-7-hydroxy-4-methyl-2H-chromen-2-one [9]. Experimental studies have also focused on metal complexes with Schiff bases derived from 3-formyl-4-hydroxychromen-2-one and semicarbazone [10]. Significant work has been conducted on metal complexes of Schiff bases derived from 4-hydroxy-3-(1-(arylimino) ethyl) chromen-2-one and primary aromatic amines [11].

However, there has been limited investigation into Schiff bases derived from 4-hydroxy-3-(1-(arylimino) ethyl) chromen-2-one and primary heterocyclic aromatic amines. In the present paper, we report the preparation of 3-acetyl-4-hydroxychromen-2-one from 4-hydroxychromen-2-one using a previously reported method with some modifications [12]. This compound was then condensed with primary aromatic 5-(phenyl)-1,3,4-oxadiazol-2-amine to synthesize novel Schiff base 4-hydroxy-3-(1-((5-phenyl-1,3,4-oxadiazol-2-yl)imino)ethyl)-2H-chromen-2-one. Complexes with Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) metal ions

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were synthesized using this stated ligands. Their structures were characterized through various analytical methods, including magnetic susceptibility measurements, IR and ¹HNMR spectroscopy, electronic spectral analysis, and powder XRD techniques. The findings align with the ligand-field splitting energy (10Dq).

EXPERIMENTAL SECTION:

1. Material and Measurements Techniques: All chemicals and solvents used in the synthesis of the novel ligand and its complexes were of analytical reagent (AR) grade. Elemental analysis (CHNS) was carried out using a Vario EL-III analyzer. The FTIR spectra were obtained on a Spectrum RX-I spectrophotometer, employing KBr pellets. The proton NMR (¹H NMR) spectra of the ligand were recorded in a mixture of CDCl₃ and DMSO. Mass spectrometric data were acquired using a Bruker Esquire 3000 instrument. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TA/SDT-2960, while powder X-ray diffraction (PXRD) patterns were recorded on a Philips 3701 system. UV-visible spectra of the complexes were measured using a spectrophotometer (Jasco UV-530).

2 Synthesis of a ketone 3-acetyl-4-hydroxychromen–2–one (1): The reaction mixture of 4-hydroxychromen-2-one (8.1 g, 0.05 moles) in acetic acid (44 mL) and phosphorous oxychloride (15 mL) was added. The mixture was subjected to reflux heating for a duration of 30 minutes. After cooling the reaction flask, the precipitate was collected and recrystallized from ethanol, to obtain 3-acetyl-4-hydroxychromen-2-one, as white needles [12], in a yield of 7.1 g (88%), mp 134-36°C.

3 Synthesis of 5-phenyl-1,3,4-oxadiazol-2-amine(2): 5-phenyl-1,3,4-oxadiazol-2-amine have synthesized with slight modification in reported procedure [13-15] starting form a mixture of benzoic acid (0.01 mol) and semicarbazide hydrochloride (0.01 mol) in POCl₃ (20 mL) in a round-bottom flask and refluxed for 7-8 hrs. The reaction mixture was concentrated, cooled, and then poured onto crushed ice while stirring. The obtained precipitate was stirred for 15 min in the same solution and further treated carefully with 50% aqueous potassium hydroxide solution. Finally, the precipitate was collected by filtration process under vacuum, washed with water and dried it. The precipitate was filtered off and recrystallized from ethanol. The melting point was well in agreement with earlier reported values.

4 Preparation of novel Schiff base Ligand (L), 4-hydroxy-3-(1-((5-phenyl-1,3,4-oxadiazol-2-yl)imino)ethyl)-2H-chromen-2-one(3): The novel Schiff base was synthesized by heating an equimolar mixture 0.01 moles of 3-acetyl-4-hydroxychromen-2-one and 0.01 moles of 5-phenyl-1,3,4-oxadiazol-2-amine was dissolved in 50 ml of dry methanol in a round-bottom flask. The reaction mixture was then refluxed for 4-5 hours. Upon cooling, the Schiff base solidified and was subsequently filtered, washed with dry methanol, and dried. The solid was purified through recrystallization from methanol and dried in a vacuum desiccator. The purity of the ligand was checked using m. p. determination, thin-layer chromatography (TLC), and elemental analysis. Yield: 74%; Colour: white; Melting Point: 253-255 ^OC; Further characterization was performed using IR, ¹H NMR, ¹³C NMR, and mass spectrometry. (Scheme-1)



(i) Ac-OH, (ii) POCl₃, (iii) Semicarbazide, (iv) Et-OH, (v) POCl₃ (vi) aq.KOH

Scheme-1: Synthesis of Novel Schiff's Base(L)

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5 General procedure for the synthesis complexes (4): A solution of 0.01 moles of a metal (II) salt in 20 mL of methanol at 50°C was added drop wise to a solution of 0.02 moles of a Schiff base ligand (in slight excess) in 30 mL of hot methanol at 50°C in a 100 mL round-bottom flask. (Scheme-2)



Scheme-2: Synthesis of Metal Complexes

The mixture was refluxed for two hours on a water bath at 60°C. After cooling, no precipitation was observed then, 10% alcoholic ammonia solution was added drop wise until precipitation occurred, with different metal complexes forming at various pH levels. The precipitated complex was digested for an additional hour. The progress of the reaction was monitored using TLC. The precipitated complex was filtered, washed with methanol, hot ethanol, and petroleum ether (40-60°C) to remove unreacted Schiff base and metal (II) salt. The resulting solid metal (II) complex was dried in a vacuum desiccator over calcium chloride [16, 17]. (Yield 67-85%).

RESULTS AND DISCUSSION:

The Schiff base ligand (L) was synthesized as outlined in Scheme 1. The synthesis begins with the acetylation of commercially available 4-hydroxy coumarin using acetic acid and phosphorus oxychloride in a fume hood for safety, following a procedure from the literature [12], resulting in compound (1). The ligands 4-hydroxy-3-(1-((5-phenyl-1, 3, 4-oxadiazol-2-yl)imino)ethyl)-2H-chromen-2-one (3) is then synthesized (Yield: 74%) through the condensation of compound (1) with a heterocyclic aromatic amine, such as 5-phenyl-1,3,4-oxadiazol-2-amine (2). The structures of the ligands (L) in both solid and solution states are investigated using various spectroscopic techniques. The physical, analytical, and spectral data for the ligand and its complexes are presented in Table 1.

Ligand/	Molecular	PH of	Color	M.P.	Mol.	Sol ⁿ	Elemental Analysis Found [Calc.]			
Metal	formula	range		°C	Wt.	cond.	С	Н	Ν	Μ
Complex						μ_{v}				
1	$C_{19}H_{13}N_3O_4$		White	253-	347.09		65.70	3.77	12.10	
				255			(65.73)	(3.75)	(12.12)	
2	[Ni(C ₁₉ H ₁₂ N ₃ O ₄) ₂ (7.0 -8.0	Yellowish	>300	787.37	15.20	57.54	3.54	10.58	7.12
	$H_2O)_2]$		Green				(57.97)	(3.58)	(10.67)	(7.45)
3	[Cu(C ₁₉ H ₁₂ N ₃ O ₄) ₂ (7.0 -8.0	Green	>300	792.22	16.51	57.14	3.24	10.31	7.88
	$H_2O)_2]$						(57.61)	(3.56)	(10.61)	(8.02)
4	$[Zn(C_{19}H_{12}N_3O_4)_2]$	7.0-7.5	yellowish	285	758.02	14.50	59.97	3.24	10.88	8.36
			White				(60.21)	(3.19)	(11.09)	(8.63)
5	$[Cd(C_{19}H_{12}N_3O_4)_2]$	7.0-7.5	White	288	805.06	20.09	56.27	2.78	9.99	13.73
							(56.69)	(3.01)	(10.44)	(13.96)
6	$[Hg(C_{19}H_{12}N_3O_4)_2]$	7.0-7.5	White	>300	893.23	14.19	49.84	2.56	9.19	22.05
							(51.10)	(2.71)	(9.41)	(22.46)

Table 1: Physical and analytical data of ligand (L) and metal complexes

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Fig.-4 Mass spectra of Ligand (L)

All these synthesized metal complexes are stable at room temperature, insoluble in water, but limited solubility in ethanol, methanol, chloroform, and fully soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The results from elemental analysis, magnetic moment measurements, and molar conductance data (Table 1) are consistent with the general formula $[M(L)_2]\cdot 2H_2O$ for Ni(II) and Cu(II) complexes and for Zn(II), Cd(II) and Hg(II) complexes it is $[M(L)_2]$. The bi-dentate ligand coordinates through the azomethine nitrogen and the phenolic oxygen of the coumarin moiety, following de-protonation. Molar conductance values in DMSO at a concentration of 10^{-3} M fall within the range of 14.19-16.51 Ω^{-1} , indicating the non-electrolytic nature of the complexes [18]. The elemental analysis of the entire complexes shows a 1:2 metal-to-ligand ratio, suggesting a monomeric structure.

The Ni(II) complex exhibits a magnetic moment of 3.08 B.M. at room temperature, which aligns with the high-spin octahedral geometry [19], though it is slightly higher than the expected 2.83 B.M. due to spinorbit coupling [20]. This suggests that the Ni(II) complex, when coordinated with ligands L, likely adopts a monomeric octahedral configuration. For the Cu(II) complex, the observed magnetic moment of 1.78 B.M. at room temperature indicates one unpaired electron, which is typical for an octahedral geometry [21]. The Zn(II), Cd(II), and Hg(II) complexes were confirmed to be diamagnetic through magnetic susceptibility measurements, consistent with earlier experimental findings [22,23]. Based on the stoichiometry, conductance, magnetic, infrared, and electronic data, the Ni(II) and Cu(II) complexes are most likely to adopt an octahedral configuration, whereas the Zn(II), Cd(II) [24], and Hg(II) [25] complexes are more likely to favor a tetrahedral geometry.

eu (ii) complexes at foolit temperature										
Sr.	Metal	χм	χ _{A x 10} ⁶	μ_{eff}	Electronic Absorption			Ligand field parameters		
No.	Complexes	x10 ⁶	(CGS)	В.	Maxima	cm ⁻¹				
		(CGS)		М.	V1 V2 V3		LFSE	LFSE		
								10 Dq cm ⁻¹	Kcal Mol ⁻¹	
1	[Ni (L)2]	3609.39	3974.77	3.08	11363	16393	27777	11363	32.53	
					(880)	(610)	(360)			
2	[Cu (L)2]	962 17	1327 55	1 78	12821	16129	27027	1282	36.70	
		702.17	1527.55	1.70	(780)	(620)	(370)	1202	30.70	

 Table No. 2: Magnetic susceptibility, Electronic Absorption and Ligand field parameters data of Ni (II) and Cu (II) complexes at room temperature

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The ligand IR spectrum (KBr, cm⁻¹) shows a broad absorption band at 3507 cm⁻¹, corresponding to the phenolic -O-H stretching vibration in the Schiff base. The carbonyl stretching (>C=O) of the lactone is observed at 1716 cm⁻¹. The ligand shows a high-intensity band at around 1598 cm⁻¹, attributed to the >C=N- of the oxadiazole ring, and a band at 1613 cm⁻¹, indicating the imine v(C=N) stretching vibration, suggesting Schiff base formation. The bands at 1269 and 1067 cm⁻¹ are due to C-O-C stretching in the oxadiazole, while the intense band between 1361-1238 cm⁻¹ is assigned to >C–O and phenolic v(C-O) vibrations. Bands between 1590-1450 cm⁻¹ and 1422 cm⁻¹ are associated with v(C=C) of the aromatic ring. The in-plane deformation (wagging) of the aromatic ring C-H is seen at 722 cm⁻¹, and the out-of-plane deformation of the aromatic ring C-H is observed at 567 cm⁻¹. Table-3 (Fig.-1)

The ¹H NMR spectrum (CDCl₃, 300 MHz) of ligand shows a singlet at δ 2.14, corresponding to 3 protons of the imine –CH₃ group. The aromatic protons of the ligand (Ar–H) resonate as a multiplet in the region of δ 7.96-7.18. A broad singlet at δ 14.72 is attributed to 1 proton of the O–H group. (Fig.-2) Mass Spectra [M+1] +: 348.18.

The ¹³CNMR (CDCl₃) (300 MHz) of ligand displays shows characteristic chemical shifts at δ 81.12 for the C³ carbon, δ 125.50–116.64 for the aromatic carbons, δ 154.43 for the C⁹ carbon, δ 163.40 for the lactone carbon, and δ 170.0 for the C⁴ carbon of the coumarin moiety. Additionally, a peak is observed at δ 20.13 for the imine -CH₃ carbon and at δ 175.99 for the imine carbon. For the 1, 3, 4-oxadiazol ring moiety, the 1, 3, 4-oxadiazol ring carbon appears at δ 167.04, while the aromatic carbons of the phenyl ring bonded to C² of 1, 3, 4-oxadiazol ring are found between δ 138.42–126.33. (Fig.-3)

Mass Spectra $[M+1]^+$ of ligand 'L' shows a peak at m/z 348.18 which confirms the formation of Schiff base (HPOAC). (Fig.-4)

The v(C=N) stretching frequency in the free ligand, originally observed at 1613 cm⁻¹, shifts to medium to weak bands in the range of 1596-1594 cm⁻¹ in the metal complexes. This downward shift suggests that the metal ion coordinates with the azomethine nitrogen. The decrease in the band's frequency by 15-20 cm⁻¹ upon complexation indicates that the imine group of each ligand is coordinating to the metal ion through its nitrogen. This phenomenon can be explained by the involvement of the azomethine nitrogen in bonding with the metal ion [26, 27]. (Fig.-5 & Fig.-6)

		Bond vibrational modes (stretching $-v$)								
Sr. No.	Ligand / Complex	Lactone	Azo- methine	Enolic	Oxadiazole ring		New Peaks			
		(C=O)	(C=N)	(C-O)	(C=N)	C-O-C	M-O	M-N		
1	L ₁	1716	1613	1361	1598	1269	_	_		
2	$Ni(L_3)_2$	1718	1595	1378	1600	1270	500	428		
3	$Cu(L_3)_2$	1716	1596	1375	1598	1268	560	480		
4	$Zn(L_3)_2$	1718	1595	1378	1600	1270	502	380		
5	$Cd(L_3)_2$	1718	1596	1380	1600	1270	498	425		
6	$Hg(L_3)_2$	1716	1596	1380	1600	1270	520	480		

Table-3: Infrared Absorption Frequencies (cm⁻¹) of Metal Complexes

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Fig.-6 IR Spectrum of Cu(II) Complex of Ligand (L)

2200

2000

1800

1600

The medium-intensity absorption bands in the 1402-1375 cm⁻¹ region in the spectra of metal complexes are attributed to the enolic C–O stretching frequency. In the corresponding free ligands, these bands appear in the 1388-1360 cm⁻¹ region. The upward shift by 14-20 cm⁻¹ in the enolic C–O stretching frequency, along with the disappearance of the phenolic –OH absorption in the IR spectra of metal complexes, indicates that the enolic oxygen and phenolic –OH groups are involved in metal complex formation via de-protonation, as confirmed by a bathochromic shift [28,29]. The band assigned to the lactam C=O stretching frequencies in the corresponding free ligands were observed in the 1716-1708 cm⁻¹. The unchanged position of v(C=O) indicates that the lactone is not involved in the coordination.

In the present Schiff base ligands (L), strong to medium intensity stretching bands in the range of 1269 cm⁻¹ and 1067 cm⁻¹ are indicative of C—O—C aromatic ring stretching. Additionally, absorption bands around 1622-1615 cm⁻¹ correspond to the vibrational modes of the >C=N- group in the 1,3,4-oxadiazole ring. In all complexes, the >C=N- and C—O—C stretching bands appear either at the same or nearly the same frequencies as in their corresponding ligands. This consistency suggests that the imine nitrogen and oxygen of the 1,3,4-oxadiazole ring are not involved in coordination.

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The presence of coordinated water molecules in Cu(II) and Ni(II) complexes is indicated by a broad band in the range of 3600-3400 and a peak at 985-948 cm⁻¹ [30]. This band is absent in the IR spectra of Zn(II), Cd(II), and Hg(II) complexes. Further the presence of coordinated and non-coordinated water molecules is confirmed by the TGA studies of Cu(II) and Ni(II) complexes. The appearance of two strong bands at 561-495 cm⁻¹ and at 484-380 cm⁻¹ are assignable to v(M-O) and v(M-N) vibrations respectively [31,32].

In thermal studies, no weight loss was observed after heating at 120°C for 1 hour, suggesting the presence of coordinated water. TG analysis indicates that the percentage weight loss corresponds to the loss of two coordinated water molecules in Cu(II) and Ni(II) complexes. The dehydration process in these complexes is a single-step event, as evidenced by a single endothermic peak observed between 200-220°C [33]. (Fig.-7 & Fig.-8)

The Ni (II) complex exhibits three distinct absorption bands consistent with octahedral geometry. These are observed in the regions of 11363-10989 cm⁻¹ (V₁), 16393-17241 cm⁻¹ (V₂), and 26351-27777 cm⁻¹ (V₃), corresponding to three spin-allowed transitions: namely, ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ (F), ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F), and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (P), indicative of charge transfer phenomena. These transitions suggest a distorted octahedral field [34, 35]. Figure-9 illustrates these phenomena, and Table 2 provides detailed spectral data.



The electronic absorption spectra of the Cu (II) complex show a broad band between 16,260-16,666 cm⁻¹, another band from 12,987-13,333 cm⁻¹, and a charge transfer band between 27,027-29,411 cm⁻¹, indicating a ${}^{2}E_{g} > {}^{2}T_{2g}$ transition. These features are consistent with those of octahedral or pseudo-octahedral Cu (II) complexes in previous studies. [36, 37] The spectra of Cu (II) complexes with ligand L are shown in Figure 10. The complex has a magnetic moment of 1.78 BM at room temperature, equivalent to one unpaired electron BM support the octahedral structure (Table 2).

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 bie-4. Lore data of the Cu (II) complexes with figure									
Complex	g_	g_{\perp}	g_{av}	G					
$[Cu(L)_2.2(H_2O)_2]$	2.27	2.08	4.106	3.47					

Table-4: ESR data of the Cu (II) complexes with ligand (L)

The ESR spectra of the Cu(II) complexes were recorded at room temperature, as shown in Table 4. The anisotropic G values were calculated using Kneubuhl's method, where $G = (g|| - 2.003) / (g \perp - 2.003)$, which measures the exchange interaction between Cu(II) centers. In the Cu(II) complex, the unpaired electron with a ${}^{2}B_{1g}$ ground state resides in the d_{x2-y2} orbital of the ligand, following the trend $g|| > g \perp > ge$ (ge = 2.0036, the free ion value). The axial spectrum, characterized by $g|| > g \perp > 2.03$, is consistent with a distorted octahedral geometry around the Cu(II) ion [19]. The spectra of [Cu(L)₂(H₂O)₂] exhibited a pronounced peak at $g \perp = 2.07 \pm 0.02$ and a broad, shallow quadruplet at $g|| = 2.28 \pm 0.04$. These spectral features are indicative of Cu²⁺ ions in axially distorted octahedral sites [20]. The calculated G values for the present complexes, ranging from 3.13 to 3.66, suggest a negligible exchange interaction between copper centers, as G < 4 [21]. (Fig.-11)



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In conclusion, the literature review demonstrates that metal complexes with ligands consistently display a crystalline nature, as confirmed by their X-ray diffraction patterns. The presence of sharp and distinct peaks in these patterns (Fig.-12- Fig.-16) indicate a highly crystalline structure, particularly within a monoclinic system [38]. Furthermore, the exact determination of peak positions and their respective interplanar distances (d-spacing), calculated using Bragg's equation, further supports this finding. Moreover, investigations into metal complexes with Schiff bases [39, 40] affirm that these complexes reliably crystallize in the monoclinic crystal system.

CONCLUSION

In conclusion, the comprehensive analysis, including elemental analysis, molar conductivity measurements, magnetic susceptibilities, electronic absorption, infrared spectral studies, and XRD studies, confirms that the Cu(II) and Ni(II) complexes exhibit a crystalline monoclinic system with monomeric octahedral geometry (Structure-I). In contrast, the Zn(II), Cd(II), and Hg(II) complexes demonstrate a monomeric tetrahedral geometry (Structure-II). Furthermore, the results indicate that the Cu(II) complexes possess superior antibacterial and antifungal activities compared to the Ni(II) complexes.



ACKNOWLEDGEMENT

The authors extend their sincere gratitude to the Principal of the research Centre Deogiri College Aurangabad and the Principal of Swa. Sawarkar Mahavidyalaya, Beed, Maharashtra for providing the necessary laboratory facilities. We would also like to thank MIT College Aurangabad, as well as Private Analytical Laboratories Pune and Hyderabad, for their invaluable assistance in conducting the required analysis.

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