

Synthesis, Physico-Chemical Characterization, Antibacterial and Antifungal Activities Studies of a New Schiff Base Ligand and its Transition Metal Complexes

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Summary: The complexes of Co(II), Cu(II) and Zn(II) with the Schiff base 2-[(E)-{[4-(4-aminophenoxy)phenyl]imino}methyl]-6-ethoxyphenol (LH) have been synthesized and their structure have been elucidated on the basis of elemental analyses, IR, ¹H- and ¹³C-NMR spectra, electronic spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA). Mononuclear complexes with a metal:ligand ratio of 1:1 have been prepared with Co⁺² and Zn⁺² salts, whereas the copper(II) complex is dinuclear which have a metal:ligand ratio of 2:1. According to the results, it is suggested that the ligand is coordinated to each metal atom by the phenolic oxygen and the azomethine nitrogen atoms. The synthesized compounds were tested for antimicrobial activity against in vitro antibacterial (*Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhimurium*) and antifungal activities (*Candida globrata* and *Candida tropicalis*) by the minimum inhibitory concentration (MIC) method. All of the selected compounds showed weak antimicrobial activity against test microorganisms (256-1024 µg/mL).

Key words: Schiff base, Transition metal complexes, Antimicrobial activity, 4,4-diaminodiphenylether.

Introduction

Recently, several metal complexes of Schiff bases containing N, O and N, S donors have been synthesized and studied [1, 2]. Schiff bases and their metal complexes play a key role in our understanding of the coordination chemistry of transition metal ions [3]. In addition, the presence of nitrogen and oxygen donor atoms in the complexes makes these compounds effective and stereospecific catalysts for oxidation, reduction hydrolysis and they also show biological activity and other transformations of organic and inorganic chemistry [2]. It is well known that some drugs have higher activity when administered as metal complexes than as free ligands [2].

In the present paper, we report the synthesis and characterization of a new Schiff base ligand and its complexes with cobalt(II), copper(II) and zinc(II) ions. All compounds were characterized by elemental analyses, IR, ¹H and ¹³C-NMR spectra, electronic spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA).

Experimental

Elemental analyses (C, H, N) were carried out using LECO-932 CHNSO by Technical and Scientific Research Council of Turkey (TUBITAK). IR spectra were recorded on a Mattson 1000 FT-IR

spectrometer as KBr pellets. ¹H and ¹³C-NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR spectrometer. Electronic spectra were obtained on a Shimadzu 1700 UV spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using Hg[Co(SCN)₄] as a calibrant; diamagnetic corrections were calculated from Pascal's constant. TGA curves were recorded on a Shimadzu TG-50 thermo balance.

Preparation of the ligand (LH)

To a solution of (1,66 g, 10 mmol) 3-methoxysalicylaldehyde in 10 ml absolute EtOH, 4,4-diaminodiphenylether dissolved in 30 ml absolute EtOH were added dropwise at 78 °C with continuous stirring for 20 h and monitoring of the course of the reaction with IR. The precipitate was filtered off after overnight, washed with hot ethanol and dried at room temperature.

Preparation of the Co(II), Cu(II) and Zn(II) complexes

A sample of the ligand (LH) (0,35 g, 1.00 mmol) was dissolved in absolute (20 ml) ethanol by heating. A solution of the acetate salt of metal [Co(AcO)₂].4H₂O (0,26 g, 1.00 mmol),

[Cu(AcO)₂].H₂O (0,40 g, 2.00 mmol), and [Zn(AcO)₂].2H₂O (0,26 g, 1.00 mmol) in 20 ml of hot ethanol was added dropwise to the ligand solution under reflux at 60 °C with continuous stirring at for 15 h. The precipitated complex was filtered off after overnight, washed with water and cold ethanol several times and dried at room temperature.

Antimicrobial activity

In order to determine both antibacterial and antifungal activity, the synthesized compounds and the control drugs were dissolved in absolute dimethylsulfoxide (DMSO). Further dilutions were done at the required quantities of 1024, 512, 256, 128, 64, 32, 16, 8, 4, 2, and 1 µg/mL on the microorganisms at the studied concentrations. Stock solutions were prepared in DMSO having no effect on the microorganisms in the studied concentrations. Antimicrobial activities of compounds were determined using the broth dilution method proposed by the National Committee for Clinical Laboratory Standards (CLSI). MIC, which is the lowest concentration of a compound that completely inhibits microbial growth, was determined by a standard broth dilution technique adapted from the CLSI. As quality control strains 1 gram-positive bacterium, 1 gram-negative bacterium, and 2 yeast-like fungi were used. Tested microorganisms were gram-positive *Staphylococcus aureus* ATCC 6538P, *Bacillus subtilis* ATCC 6633, gram-negative *Escherichia coli* ATCC 25922, *Salmonella typhimurium* NRRL B 4420, and the yeast like fungi; *Candida glabrata* ATCC 66032 and *Candida tropicalis* ATCC 13803. Ampicillin (Mustafa Nevzat) and Fluconazole (Pfizer) were used as antibiotic reference for bacteria and yeast, respectively (obtained from Department of Biology, Firat University, Turkey).

Antibacterial and antifungal assays

Bacterial cultures were obtained in Mueller-Hinton broth (Difco) for all the bacterial strains after 24 h of incubation at 37 ± 0.1 °C. Yeasts were propagated in Sabouraud dextrose broth (Difco) after incubation for 24 h at 25 ± 0.1 °C. Testing was carried out in Mueller-Hinton broth and Sabouraud dextrose broth at pH 7.4 for bacteria and yeast, respectively. The final inoculum size for bacteria and fungi was 10⁵ CFU mL⁻¹. Test compounds were dissolved in DMSO at an initial concentration of 1024 µg/mL and then serially diluted in culture medium to 1 µg/mL. A set of tubes containing only inoculated broth was kept as control. Antibacterial

activity was determined after incubation for 24 h at 37 °C for bacteria and after incubation for 48 h at 25 °C for the yeasts. MIC was defined as the lowest concentration of the compounds that inhibited the visible growth of a microorganism. Every experiment in the antibacterial and antifungal assays was replicated two times to define the MIC values.

Results and Discussion

The ligand (LH) was prepared by reacting equimolar amounts of 3-ethoxysalicylaldehyde with 4,4-diaminodiphenylether in absolute ethanol (Scheme-1). The structures of the ligand and the complexes were established from their IR, ¹H and ¹³C-NMR spectra, electronic spectra, elemental analyses, magnetic susceptibility measurements and thermogravimetric analyses (Tables 1-5). According to results obtained, the metal to ligand ratio in the cobalt(II) and zinc(II) complexes is 1:1, whereas the metal to ligand ratio in the copper(II) complex is 2:1. The complexes are intensely coloured stable solids Fig. 1.

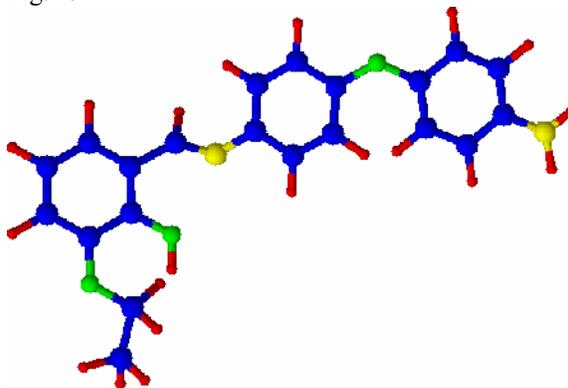


Fig. 1: Conformation of the ligand.

Elemental analyses

A summary of the elemental analysis data for the ligand and the complexes are given in detail as following: For LH: % calculated C,72.40; H,5.79; N,8.04; found C,72.54; H, 5.22; N, 8.30. For [Co(L)(AcO)(H₂O)₂]: % calculated C,55.10; H,5.23; N,5.59; found C,55.73; H, 5.68; N, 5.86. For [Cu₂(L)(AcO)₃(H₂O)₂].H₂O: % calculated C,45.96; H,4.86; N,3.97; found C,45.69; H, 4.90; N, 3.75. For [Zn(L)(AcO)(H₂O)₂]: % calculated C,54.39; H,5.16; N,5.52; found C,54.63; H, 4.56; N, 5.80.

The elemental analysis results agree with the calculated values showing that the Co(II) and Zn(II) complexes have 1:1 metal:ligand ratios, whereas the Cu(II) complexes has 2:1 metal:ligand ratio.

According to results obtained from IR, TGA and elemental analysis, two water molecules are also coordinated to metal ions. The elemental analysis confirmed the compositions of the above synthesised compounds.

IR spectra

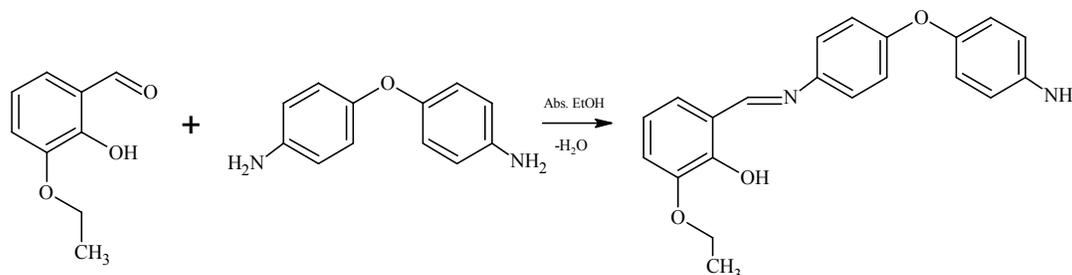
The important infrared spectral bands for synthesized complexes and ligand are given in Table-2. The strong band observed in the free ligand at 1614 cm^{-1} , is due to characteristic of the azomethine (C=N) group [2, 4, 5]. This band of the ligand at 1614 cm^{-1} was shifted to lower frequencies after complexation, which is 1604 , 1606 and 1607 cm^{-1} for cobalt(II), copper(II) and zinc(II) complexes respectively [2, 4, 6-8].

A medium intensity band around $3340\text{-}3560\text{ cm}^{-1}$ in the spectra of the free ligand due to $\nu(\text{OH})$ was absent in the spectra of all the complexes, indicating the deprotonation of Schiff base prior to coordination through its oxygen atom [2, 5]. This is further supported by an increase in the absorption frequency of the phenolic C-O band from 1278 cm^{-1} in the spectra of the free ligand to $1320\text{-}1324\text{ cm}^{-1}$ in the spectra of the complexes, indicating that the other coordination site of the Schiff base is the phenolic oxygen [2, 5, 6, 9]. The cobalt(II), copper(II), and zinc(II) complexes show the broad diffuse band centered at $3550\text{-}3440\text{ cm}^{-1}$ due to the stretching and

bending modes of lattice and coordinated water [5, 10, 11]. In addition, weak bands are detectable at $840\text{-}830\text{ cm}^{-1}$ regions which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion [12]. The shoulder at $1543\text{-}1541\text{ cm}^{-1}$ in the complex may be attributed to the $\nu_{\text{as}}(\text{CO})$ of the CH_3COO^- group [13].

^1H and ^{13}C -NMR spectra

^1H and ^{13}C -NMR spectrum of the ligand (LH) and its diamagnetic Zn(II) complex were recorded in DMSO- d_6 and data are given in Table-3 and 4. In the spectra of the Zn(II) complex a sharp singlet appeared at 8.50 ppm and has been assigned to the azomethine proton (CH=N). The position of the azomethine signal in the complexes are downfield in comparison with that of the free ligand, suggesting deshielding of the azomethine proton due to its coordination to zinc through the azomethine nitrogen [2, 6]. Comparison of the chemical shifts of the ligand with those of the complex shows that the signal due to the phenolic proton (OH) is absent in the complex, suggesting the coordination of the phenolic oxygen to the metal ion after deprotonation [2, 6, 8]. More detailed information about the structures of the ligand and its Zn(II) complex were provided by ^{13}C -NMR spectra data that C-OH, CH=N and C-N carbon atoms are observed at 156.42 , 169.46 and 144.19 ppm . The results confirm the proposed structure of Zn(II) complex (Fig. 2).



Scheme-1: Synthesis of the ligand.

Table-1: Analytical and physical data of the ligand and the complexes.

Compounds	Formula	F.W.(g/mol)	Color	Yield (%)	μ_{eff} (B.M)	λ_{max} , nm	
						d-d	C-T
LH	$\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3$	348.39	Orange	95	—	—	—
$[\text{Co}(\text{L})(\text{AcO})(\text{H}_2\text{O})_2]$	$\text{CoC}_{23}\text{H}_{26}\text{N}_2\text{O}_7$	501.39	Red	65	4.13	663	403
$[\text{Zn}(\text{L})(\text{AcO})(\text{H}_2\text{O})_2]$	$\text{ZnC}_{23}\text{H}_{26}\text{N}_2\text{O}_7$	507.87	Yellow	57	*Dia	—	412
$[\text{Cu}_2(\text{L})(\text{AcO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	$\text{Cu}_2\text{C}_{27}\text{H}_{34}\text{N}_2\text{O}_{12}$	691.63	Light brown	65	*Dia	537	412

Dia = Diamagnetic

Table-2: Characteristic IR bands of the ligand and the complexes (in cm^{-1}).

Compounds	$\nu(\text{O-H})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{AcO})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$
LH	3440-3560	—	—	1614	1278
$[\text{Co}(\text{L})(\text{AcO})(\text{H}_2\text{O})_2]$	—	3440-3550	1541	1604	1321
$[\text{Cu}_2(\text{L})(\text{AcO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	—	3440-3550	1543	1606	1320
$[\text{Zn}(\text{L})(\text{AcO})(\text{H}_2\text{O})_2]$	—	3440-3550	1542	1607	1324

Table-3: $^1\text{H-NMR}$ spectral data of the ligand the Zn(II) complex (in ppm).

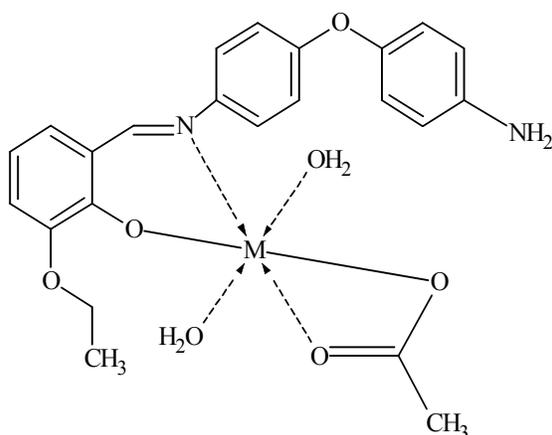
Compounds	$\delta(\text{-OH})$	$\delta(\text{NH}_2)$	$\delta(\text{AcO})$	$\delta(\text{CH=N})$	$\delta(\text{Arom-H})$
LH	13.45(s, 1H)	6.36 (s, 2H)	—	8.87 (s, 1H)	7.47-7.67(m, 11H)
$[\text{Zn(L)(AcO)(H}_2\text{O)}_2]$	—	6.23(s, 2H)	3.42 (s, 6H)	8.50 (s, 1H)	6.98-6.76 (m, 11H)

Table-4: $^{13}\text{C-NMR}$ spectral data of the ligand the Zn(II) complex (in ppm).

Compounds	$\delta(\text{C-OH})$	$\delta(\text{CH=N})$	$\delta(\text{Arom-C})$	$\delta(\text{O-CH}_3)$	$\delta(\text{C=O})_{\text{AcO}}$	$\delta(\text{-CH}_3)_{\text{AcO}}$
LH	144.34	162.26	115.10-158.46	64.34	—	—
$[\text{Zn(L)(AcO)(H}_2\text{O)}_2]$	156.42	169.46	113.74-162.05	63.68	162.05	15.20

Table-5: TGA data of the ligand and complexes.

Compounds	Temperature range ($^\circ\text{C}$)	Dehydration stage		Assignment
		Weight loss (%)	Found(calculated)	
$[\text{Co(L)(AcO)(H}_2\text{O)}_2]$	25-144	—	—	No loss
	144-340	6.93 (7.18)	—	Loss of two coordinated water molecules
$[\text{Cu}_2(\text{L})(\text{AcO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	25-110	2.65 (2.60)	—	Loss of one lattice water molecules
	110-340	5.35 (5.20)	—	Loss of two coordinated water molecules
$[\text{Zn(L)(AcO)(H}_2\text{O)}_2]$	25-142	—	—	No loss
	142-335	6.66 (7.09)	—	Loss of two coordinated water molecules



M = Co(II) and Zn(II)

Fig. 2: Suggested structure of the Co(II) and Zn(II) complexes.

Electronic Spectra

The electronic spectra of the ligand and the Co(II), Cu(II) and Zn(II) complexes were recorded in DMF at room temperature. The electronic spectra of the compounds with their assignments are given in Table-1. The band around 335 nm is due to $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base. The complexes of cobalt(II) and copper(II) show less intense shoulders at 537-663 nm, which are assigned as the d-d transitions of the metal ions. All the complexes show an intense band at 306-326 nm

which is assigned to the $n \rightarrow \pi^*$ transition associated with the azomethine linkage [6]. In addition, the three complexes exhibited absorption bands at 403-412 nm that could be due to ligand-to metal charge transfer transitions [6, 13, 14].

Magnetic properties

As known, magnetic susceptibility measurements provide information regarding the structure of the complexes. The room temperature magnetic moment values of the complexes are given in Table-1. The magnetic moment value of 4.13 B.M measured for the cobalt complex lies in the range expected for a d^7 system, which contains three unpaired electron with mononuclear octahedral geometry. [15] The zinc (II) complex is diamagnetic as expected for a d^{10} configuration. Furthermore, the copper (II) complex is diamagnetic because of the dimeric structure [16]. In order to investigate the presence of magnetic properties in the $[\text{Cu}_2(\text{L})(\text{AcO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ complex, $^1\text{H-NMR}$ instrument was employed. It was found that $[\text{Cu}_2(\text{L})(\text{AcO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ complex is paramagnetic, therefore the NMR spectra of the $[\text{Cu}_2(\text{L})(\text{AcO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ complex could not be obtained. According to results obtained from $^1\text{H-NMR}$ spectra and the magnetic moment, the magnetic properties of the complexes are different in solid and solution state. These values are in agreement with those observed for similar compounds [17, 18].

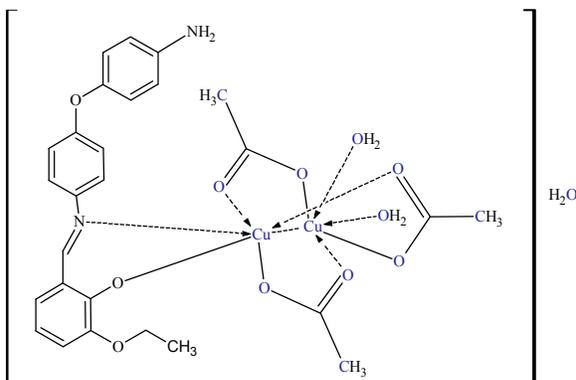


Fig. 3: Suggested structure of the dimeric Cu(II) complex.

Thermal studies

The thermal behavior of the ligand and all the complexes has been investigated using thermogravimetric techniques in the temperature range from ambient to 800 °C at a heating rate of 10 °C/min. The thermal stability data are listed in Table-5. The decomposition temperature and the weight losses of the ligand and the complexes were calculated from TGA data. The ligand is stable up to 175 °C and its decomposition starts at 175 °C and is completed at 690 °C. Thermogravimetric studies of the Zn(II) and Co(II) complexes showed no weight loss up to 142 and 144 °C respectively, indicating absence of the lattice water molecules in the complexes [19]. In the zinc(II) and cobalt(II) complexes, the first weight loss stage has a composition temperature range of 142-335 and 144-340 °C with a weight loss of 6.66% and 6.93% which corresponds to the loss of two coordinated water molecules calculated 7.09% for zinc(II) and calculated 7.18% for cobalt(II) respectively [20]. On the other hand in the copper(II) complex, the first 2.65% (calculated 2.60%) weight loss occurred in the 25-110 °C range and second, 5.35% (calculated 5.20%) in the 110-340 °C range. The results indicate the loss of one lattice water molecule in the former step and two coordinated water molecules in the latter [21]. In the complexes obtained, the lattice / coordinated water molecules are also confirmed by the results of IR spectra [12]. When the complexes are heated to higher temperature, they decompose to give oxides of the MO type [22-24].

We have designed and synthesized novel Schiff base ligand and its novel $[\text{Co}(\text{L})(\text{AcO})(\text{H}_2\text{O})_2]$, $[\text{Cu}_2(\text{L})(\text{AcO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ and $[\text{Zn}(\text{L})(\text{AcO})(\text{H}_2\text{O})_2]$ complexes in order to Fig out their antimicrobial activities. Minimum inhibitory concentration (MIC) of the synthesized compounds was determined against gram-positive *Staphylococcus aureus* ATCC

6538P, *Bacillus subtilis* ATCC 6633, gram-negative *Escherichia coli* ATCC 25922, *Salmonella typhimurium* NRRL B 4420, and yeast-like fungi *Candida glabrata* ATCC 66032 and *Candida tropicalis* ATCC 13803 using a standard broth dilution technique. Their antimicrobial activities were compared to ampicillin and fluconazole as standard drugs. The synthesized Schiff base compounds have comparable and similar inhibitory effects (low to moderate MIC values 256 and 1024 µg/mL) on the growth of tested strains (Fig. 4).

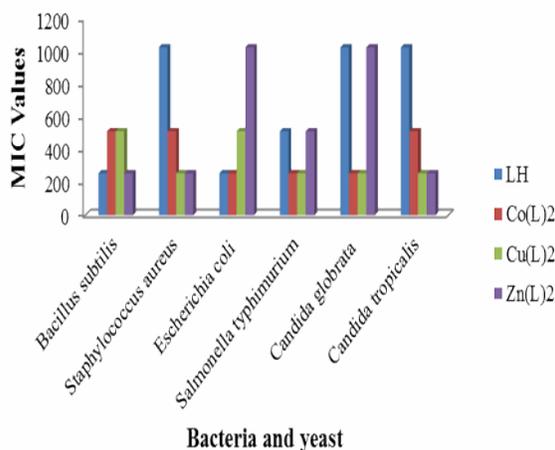


Fig. 4: Comparison of the MIC values (in µg/mL) of the complexes and the standard drugs against different bacteria.

Conclusion

The satisfactory analytical data and all of the physico-chemical studies presented above suggest that these complexes may be formulated as $[\text{Zn}(\text{L})(\text{AcO})(\text{H}_2\text{O})_2]$, $[\text{Co}(\text{L})(\text{AcO})(\text{H}_2\text{O})_2]$ and $[\text{Cu}_2(\text{L})(\text{AcO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$. Suitable mononuclear and dimeric structures have been proposed for these complexed and are shown in Fig. 2. The Schiff base ligand and its cobalt(II), zinc(II) and copper(II) metal complexes were synthesized and characterized by elemental analyses, IR, UV-Vis, ¹H and ¹³C-NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA). According to the results obtained, the zinc(II) and cobalt(II) complexes are mononuclear and octahedral, whereas the copper(II) complex is dimeric. The suggested modes of coordination are shown in Fig. 2 and 3.

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