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ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (3): 1066-1073

(International Peer Reviewed Journal)

Synthesis, Characterization and Antibacterial Activity of Cobalt (II), Nickel (II), Copper (II) Zinc (II) and Cadmium (II) Complexes with a new Hexadentate N_4O_2 Ligand

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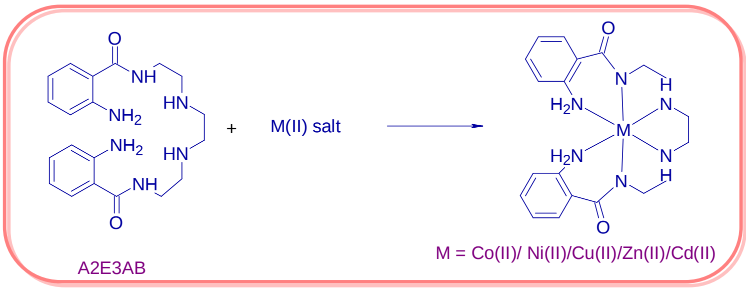
Accepted on 4th April, 2019

ABSTRACT

A new hexadentate ligand N-{2-[2(2-aminobenzoyl) amino-ethylamino)-ethylamino]-ethyl-2-aminobenzamide (A2E3AB) is prepared by the reaction between methyl anthranilate and triethylene tetraamine in dry ethanol at refluxing temperature. The Complexes of Co (II), Ni(II), Cu(II), Zn(II) and Cd(II) with this new ligand are prepared and characterized by elemental analyses, magnetic susceptibility measurements, thermal studies, IR, UV-Vis , NMR and Mass spectral investigations. The ligand A2E3AB is found to lose the amide protons and acts as a hexadentate dianionic ligand. The complexes are found to have the formula [M(A2E3AB)], where M = Co(II), Ni(II), Cu(II), Zn(II) or Cd(II).

Graphical Abstract



Keywords: Polydentate ligands, Transition metal complexes, Cobalt(II), Nickel(II), Copper(II), Zinc(II) and Cadmium(II).

INTRODUCTION

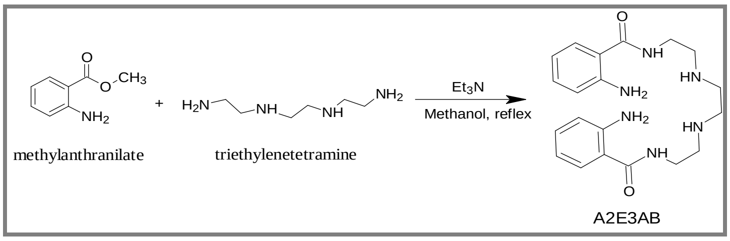
An amide group offers two potential binding atoms, the oxygen and nitrogen, for complexation of metal ions. A number of complexes have been reported with amide group ligands which exhibit diverse coordinating behavior with different metal ions [1, 2]. As a good number of organic molecules with varying molecular weights are prepared every year, there is a great scope to exploit their reactions with different metal ions. Further, investigations on the complexes of amide group containing ligands are always interesting and challenging as it is an important group in different biomolecules [**1, 2**]. As part of our research, we have developed a number of polydentate ligands containing N, O donors [**3-10**]. The coordination behavior of the amide group has been the topic of great debate [**11-13**]. The amide nitrogen is reported to be completely non-basic and does not coordinate to metal ions unless it is deprotonated. Coordination occurs through the carbonyl oxygen of the amide group. But when the reactions between amide group containing ligands and metal salts are carried out in basic medium, the amide proton is deprotonated and the amide nitrogen atom is coordinated to the metal ions. In view of the continued interest in the ligands containing amide group ligands, we report here the synthesis and characterization of the new hexadentate ligand N-{2-[2(2-aminobenzoyl)amino-ethylamino)-ethylamino]-ethyl-2-aminobenzamide(A2E3AB) and its complexes with a few bivalent transition metal ions, *viz.*, Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

MATERIALS AND METHODS

All the chemicals used were of AnalaR grade. Solvents were purified according to standard procedures before use. The purity of these compounds was checked by TLC and melting point determination. The metal ion contents in the complexes were determined by complexometric titrations using EDTA or by spectrophotometric methods. Microanalysis (C, H and N) of the complexes were carried out on a perkin-Elmer-2401 CHN analyzer. Magnetic susceptibility measurements were made on Guoy balance at room temperature, Molar conductance measurements were made in DMF using Digisum Digital DI-909 Instrument. IR spectra were recorded on Perkin-Elmer Bx series in the range of 4000-600 cm^{-1} using KBr pellets and Nujol mulls between CsI plates in the far IR region. The electronic spectra were recorded on Shimadzu UV-2401 PC Spectrophotometer. ^{1}H NMR spectra were recorded on JEOL 200 MHz spectrometer. Mass spectra (FAB) were recorded on a Joel JMS D-300 spectrometer. Thermal stabilities of the complexes were studied in the temperature range of 50° – 1000°C with a heating rate of 20°C min^{-1} in nitrogen atmosphere.

Synthesis of ligand: The ligand N-{2-[2(2-aminobenzoyl) amino-ethylamino)-ethylamino]-ethyl-2-aminobenzamide (A2E3AB) was prepared by extending the reported procedure in literature [**3**]. The two reagents, isatoic anhydride and methyl anthranilate extensively used to develop amide group. The ligand **A2E3AB** was prepared by condensation of 2 mol of the appropriate methyl anthranilate with 1 mol of triethylenetetramine as shown in scheme 1. An ethanolic (50 mL) solution of triethylenetetramine (7.3 g, 0.05 mol) was added to an ethanolic solution of methyl anthranilate (15.1 g, 0.01 mol). The mixture was refluxed by attaching $CaCl_2$ guard tube to the reflux condenser, in the presence of 5 mL (0.05 mol) of triethylamine. The volume of the reaction mixture was reduced to half by distilling out solvent under reduced pressure. The contents of the flask were cooled to room temperature and poured on crushed ice. The solution was carefully neutralized with cold dilute (4N) HCl, whereby white crystalline solid was separated. The compound was filtered, recrystallized from methanol and dried in vacuum (yield 78%, m.pt. 138°C).

Analytical and spectral data of A2E3AB: Mass *m/z* 383 $[M+H]^{1+}$. Anal. calcd. (%) for $C_{20}H_{28}N_6O_2$: C, 62.48; H, 7.34; N, 21.86. Found: C, 62.14; H, 7.16; N, 21.65. IR (KBr cm^{-1}): 3473, 3373 ν(N-H), 1674 ν (C=O), 1560 ν[(C-N)+δ (N-H)]. UV-Vis λ_{max} (nm): 235, 260, 350. ^{1}H NMR (d_6-DMSO) δ ppm: 8.2 (t, 2H), 7.73-6.54 (m, 8H), 5.69 (b, 4H), 4.07 (m, 2H), 3.56 (t, 4H), 2.83 (t, 4H), 2.50 (d, 4H). ^{13}C NMR (d_6-DMSO) δ ppm: 170, 122.2-142.6, 53.4, 51.2, 45.5.



Scheme 1. A2E3AB

Synthesis of complexes: The complexes of A2E3AB are prepared by using the following general method. A warm methanolic (20 mL) solution of corresponding metal salt (0.004 mol) was added to a warm solution of A2E3AB (1.5 g, 0.004 mol). The pH of the solution was adjusted to 8.0 by adding methanolic solution of NaOAc. The reaction mixture was heated under reflux with stirring for 4-5 h. On cooling a colored complex precipitated out, which was filtered, washed with cold methanol and dry ether and dried *in vaccuo* over fused calcium chloride. The complexes were isolated in yields of 60-70%.

Analytical and spectral data

[Co(A2E3AB)]: Mass *m/z* 464 $[M+Na]^{1+}$. Anal. Calcd. for $C_{20}H_{26}CoN_6O_2$ (%):C, 54.42; H, 5.94; N, 19.04; M, 13.35. Found: C, 54.06; H, 5.73; N, 18.89; M, 13.72. IR (KBr cm^{-1}): 3308, 3138 ν(N-H), 1682 ν(C=O), 1553 [ν(C-N)+δ (N-H)], 370 ν(M-N). UV-Vis λ_{max} (nm): 410 [$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$], 530 [$^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$], 790 [$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$]. μ : 4.86 B. M.

[Ni(A2E3AB)]: Mass *m/z* 442 $[M+1]^{1+}$. Anal. calcd. for $C_{20}H_{26}NiN_6O_2$ (%):C, 54.45; H, 5.94; N, 19.04; M, 13.30. Found: C, 54.13; H, 5.66; N, 19.14; M, 12.98. IR (KBr cm^{-1}): 3301, 3124 ν(N-H), 1680 ν(C=O), 1547 [ν(C-N)+δ (N-H)], 365 ν(M-N). UV-Vis λ_{max} (nm): 380 [$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$], 569 [$^3A_{2g}((F) \rightarrow {}^3T_{1g}(F)$), 896 ($^3A_{2g}(F) \rightarrow {}^3T_{2g}(p)$]. μ : 3.03 B. M.

[Cu(A2E3AB)]: Mass m/z 447 $[M+1]^{1+}$. Anal. calcd. for $C_{20}H_{26}CuN_6O_2$ (%):C, 53.86; H, 5.88; N, 18.84; M, 14.25. Found: C, 53.58; H, 5.43; N, 19.01; M, 13.86. IR (KBr cm^{-1}): 3275, 3121 ν(N-H), 1678 ν(C=O), 1492 ν[(C-N)+δ (N-H)], 350 ν(M-N). UV-Vis λ_{max} (nm): 645 ($^2A_{1g} \rightarrow {}^2B_{1g}$). μ : 1.82 B. M.

[Zn(A2E3AB)]: Mass *m/z* 471 $[M+Na]^{1+}$. Anal. calcd. for $C_{20}H_{26}ZnN_6O_2$ (%):C, 53.64; H, 5.85; N, 18.77; M, 14.60. Found: C, 53.22; H, 5.51; N, 18.49; M, 14.23. IR (KBr cm^{-1}): 3300, 3132 ν(N-H), 1682 ν(C=O), 1536 ν[(C-N)+δ (N-H)], 348 ν(M-N). ^{1}H NMR (d_6-DMSO) δ ppm: 8.2 (t, 2H), 7.73-6.54 (m, 8H), 6.17 (b, 4H), 4.14 (m, 2H), 3.56 (t, 4H), 2.83 (t, 4H), 2.50 (d, 4H). UV-Vis λ_{max} (nm): 220, 270, 350. Diamagnetic.

[Cd(A2E3AB)]: Mass *m/z* 495 $[M+1]^{1+}$. Anal. calcd. for $C_{20}H_{26}CdN_6O_2$ (%):C, 48.54; H, 5.30; N, 16.98; M, 22.72. Found: C, 48.07; H, 4.98; N, 17.17; M, 22.43. IR (KBr cm^{-1}): 3290, 3139 ν(N-H), 1679 ν(C=O), 1532 ν[(C-N)+δ (N-H)], 330 ν(M-N). ^{1}H NMR (d_6-DMSO) δ ppm: 8.2 (t, 2H), 7.73-6.54 (m, 8H), 6.17 (b, 4H), 4.14 (m, 2H), 3.56 (t, 4H), 2.83 (t, 4H), 2.50 (d, 4H). UV-Vis λ_{max} (nm): 220, 270, 358. Diamagnetic.

All the complexes prepared are non-hygroscopic and stable at room temperature. The complexes are insoluble in common solvents but soluble in DMSO and DMF. The characterization data are presented in the experimental section. On the basis of analytical data the metal chelates are found to have 1:1 (metal–ligand) stoichiometry. As the complexes are insoluble in common solvents, molar conductance could not be measured [3], but this very insolubility indicates that the complexes are neutral and the ligand acts as dianion.

RESULTS AND DISCUSSION

Mass Spectra: N-{2-[2(2-aminobenzoyl) amino-ethylamino)-ethylamino]-ethyl-2-aminobenzamide (A2E3AB) exhibits molecular ion peak at m/z 383 $[M+1]^{1+}$. The conspicuous fragments in the spectra of all the complexes of A2E3AB exhibit high mass peaks corresponding to the ion $[M(A2E3AB)]^{1+}$. This shows the interaction of the ligand with the metal ions. The mass spectra of representative complexes of Co(II), Ni(II),Cu(II), Zn(II) and Cd(II) showed molecular ion peaks at m/z 464 $[M+Na]^{1+}$, 442 $[M+1]^{1+}$, 447 $[M+1]^{1+}$, 471 $[M+Na]^{1+}$ and 495 $[M+1]^{1+}$ respectively. The analytical data presented in the table 1 confirm the formula of the complexes as [M(A2E3AB)].

Thermal analysis: The thermograms of the complexes of A2E3AB exhibit single stage thermal decomposition between temperature regions 315-780°C. The loss of matter in this temperature region corresponds to organic moiety. It is further evidenced by their DTA curves which give exothermic peak in the same temperature range. In all the cases the residue left corresponds to the percentage of their respective metal oxide (Co_3O_4, NiO, CuO, ZnO and CdO) as the final product [6, 14]. The percentages of metal ions calculated from the inflections on the TG curves are in good agreement with both theoretical values and those obtained from elemental analysis. The inflection on the TG curve is accompanied by either endothermic or exothermic peak in the DTA curve that corresponds to a certain phase transition/decomposition taking place as a result of heating. These results confirm the formula of the complexes as [M (A2E3AB)]. Thus A2E3AB is expected to act as a hexadentate dianion and the coordination number of the metal ions is six. The thermal stability of the complexes is found to follow the order Co(II) ≈ Ni(II) < Cu(II) > Zn(II) ≈ Cd (II).

Table 1. Thermo analytical data of complexes of A2E3AB

S. No.	Complex	Thermal Process	Temparature range, °C	Pyrolysis product %	
				Found	Calcd.
1	[Co(A2E3AB)]	[Co(A2E3AB)] → Co_3O_4	355-376	17.71	18.19
2	[Ni(A2E3AB)]	[Ni(A2E3AB)] → NiO	340-745	16.43	16.78
3	[Cu(A2E3AB)]	[Cu(A2E3AB)] → CuO	365-780	18.18	17.84
4	[Zn(A2E3AB)]	[Zn(A2E3AB)] → ZnO	320-655	17.82	18.17
5	[Cd(A2E3AB)]	[Cd(A2E3AB)]→ CdO	315-640	25.46	25.94

Infrared spectra: The IR spectrum of A2E3AB exhibits the characteristic absorptions at 3437, 3373 cm^{-1} ν(N-H) of amine ($-NH_2$), 1674 cm^{-1} ν(C=O), and 1560 cm^{-1} ν[(C-N)+δ (N-H)] [amide-II] [15]. The amine and amide stretching frequencies at 3473, 3373 cm^{-1} and 1560 cm^{-1} in the free ligand are shifted to low frequency side, i.e., to about 3300, 3130 cm^{-1} and 1550 cm^{-1} in complexes indicating their involvement in coordination. The amide carbonyl ν(C=O) stretching frequency observed at 1674 cm^{-1} in the spectrum of free ligand shifted towards higher frequency by 5-10 cm^{-1} in the spectra of complexes indicating non participation of oxygen atom in coordination. Absence of broad absorption between 3400-2500 cm^{-1} indicates the absence of water molecules that support the results of thermal analysis that is no endothermic peaks in the thermograms. In addition to these characteristic changes the spectra of all the complexes show a prominent absorption in the far IR region 330-370 cm^{-1} that may be assigned to ν(M-N) vibration [16].

^{1}HNMR spectra: The ^{1}H-NMR spectra of the ligand and diamagnetic Zn(II) and Cd(II) complexes were recorded in d_6-DMSO. The characteristic proton resonance signals of A2E3AB are found at δ 8.2_t [2H, C(O)N*H*]; $7.73\text{-}6.54_m$ [8 Hs of aromatic rings]; 5.69_b [4 Hs Ar-NH_2]; 4.07_m [2H, C-N*H*-C]; 3.56_t [4H,-CH_2-]; 2.83_t [4H, -CH_2-]; 2.50_d [4H, CH_2-]. In the ^{1}HNMR spectra of Zn(II) and Cd(II) complexes with A2E3AB there is no change in the resonance signals of aromatic protons on complexation, but the broad signals at 5.69 and 4.07 ppm shifted to downfield, 6.17 and 4.14ppm respectively indicating the coordination of 1° and 2° amine nitrogen atoms. The resonance signal corresponding to that of amide protons (8.2 ppm) is not observed in the spectra of complexes indicating the deprotonation [17] of amide proton and coordination of the nitrogen atom. Another multiplet in the range 7.28–7.52 ppm is assigned to aromatic ring protons [18]. These shifts in the resonance signals of 1° and 2° amine protons and disappearance of amide H support and confirm the coordination of the ligand A2E3AB through its six nitrogen atoms.

Magnetic moment and UV-Vis spectra: The evaluated magnetic moment values of the complexes and the electronic spectra of all the complexes were recorded in solid state as the solubility of the complexes is very poor in common solvents are presented in the experimental section. The magnetic moments of high spin octahedral Co(II) and Ni(II) complexes were found to be 4.86 and 3.03 B.M. respectively. The ground state term $^4T_{1g}(F)$ of Co(II) derived from $t_2g^5eg^2$ configuration, results in three spin allowed transitions of low intensity to $^4T_{2g}(F)$, $^4A_{2g}(F)$ and $^4T_{2g}(P)$ excited states. Ni(II), a d^8 ion, with $^3A_{2g}$ ground state term exhibits three high intensity absorptions corresponding to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. The parameters like β, B and Dq of Co(II) and Ni(II) complexes of A2E3AB have been evaluated from the electronic spectral absorptions. The β values are found to be less than 1.0, indicating that the M-L bond is covalent. The diffused reflectance spectrum of Cu(II) complex with μ_{eff} =1.82 exhibits a broad absorption at 15503 cm^{-1}. This observation coupled with the analytical, infrared spectral data and magnetic moment studies indicates that the Cu(II) complex may be proposed to have tetragonal geometry [19].

The diamagnetic Zn(II) and Cd(II) (d^{10}) complexes do not exhibit any characteristic *d-d* transitions and are also found to be diamagnetic. However, the ligand absorptions in the UV region have shifted in the spectra of the complexes (changes in n → π* transition) confirming the coordination of the ligand A2E3AB to Zn(II) and Cd(II) ions through six nitrogen atoms with octahedral geometery.

Electron Spin Resonance Spectrum: The EPR spectrum of Cu(II) complex was recorded at liquid nitrogen temperature and the bonding parameters have been evaluated using Kneubuhl's approximation [20]. The $g_{||}$, $g_{\perp}$ and g_{ave} values are found to be 2.21, 205 and 2.10 respectively. The spin-orbit coupling constant value evaluated from the spectra is found to be less than that of the free ion value of 829cm^{-1} suggesting a considerable mixing of ground and excited state terms. The same is evident from slightly higher magnetic moment value (1.82 B.M.) as compared to the spin only value of 1.73 B.M.

Antibacterial activity: The antibacterial activity of the synthesized ligand and complexes was performed by cup plate method. Freshly prepared liquid agar medium (35 mL Petri dish^{-1}) was taken into the Petri dishes and 200 µL of standardized culture (99 mL Nutrient broth media + 1 mL culture) of organism was spread on each Petri dish by L-shaped spreader with a borer (5 mm). Three bores were made on each plate. The compounds were diluted with dimethyl sulfoxide (DMSO). The Petri dishes were kept aseptically for 4 to 5 h for diffusion of the sample. After the completion of diffusion period, all Petri dishes were kept for incubation at 37°C for 24 h. After 24 h the zone of inhibition was observed for compound against two (1 Gram positive and 1Gram negative) microorganisms, namely *Staphylococcus aureus* and *Escherichia coli*. In vitro antimicrobial activities were measured from the diameter of clear inhibition zones (mm) caused by samples against the same bacteria and under the identical experimental conditions. The results are given in table 2. DMSO was used as a control.

Table 2. Antibacterial activity data of the prepared ligands and their M(II) complexes

Compounds	Inhibition Zone (mm)	
	Gram-negative	Gram-positive
	Escherichia coli	Staphylococcus aureus
A2E3AB	0.65	0.78
[Co(A2E3AB)]	16.23	19.20
[Ni(A2E3AB)]	18.36	18.76
[Cu(A2E3AB)]	23.59	21.56
[Zn(A2E3AB)]	19.23	18.89
[Cd(A2E3AB)]	12.21	11.06

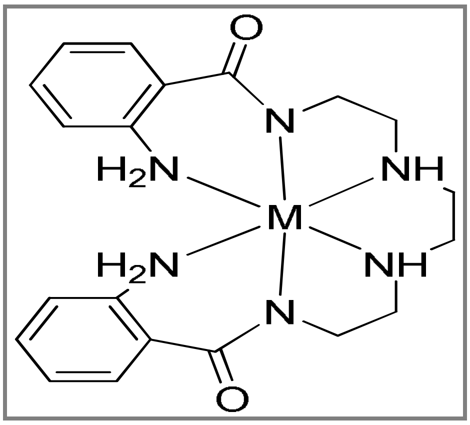
The preliminary screening for antibacterial activity of A2E3AB and complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) was determined against gram positive, *Staphylococcus aureus* and gram negative, *Escherichia coli* bacterial strains and compared with the standard antibacterial drugs ampicillin and Fluconazole. The results obtained indicate that the ligand exhibited low activity against the tested strains. The Ni(II), Cu(II) Zn(II) and Cd(II) metal complexes of the ligands were found to be more active against the bacterial strains compared to the free ligands. The activity of the Cu(II) complexes against all the bacterial strains is very promising as compared to the activity of other metal complexes. These results confirm the reports of other workers [21, 22] that biologically inactive compounds become active and less active compounds become more active upon coordination. Such enhancement in activity of the metal complexes can be explained on the basis of Overtone's concept and Tweedy's chelation theory [23]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials and the lipid solubility is considered to be a significant factor that controls antimicrobial activity. On chelation, the delocalization of π-electrons over the whole chelate ring increases and enhances the lipophilicity of the complex. This improved lipophilicity in turn increases the diffusion of the complexes into lipid membranes and blocks metal binding sites on the enzymes of the microorganisms [23].

APPLICATION

The antibacterial activity of the prepared ligand and metal complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) against one gram-negative and one gram-positive bacterial strains have been evaluated using disc diffusion method. The complexes are found to be more active than the ligand and among the metal complexes, the Cu(II) complexes exhibited better activity and comparable with the activity of the standard drugs ampicillin & Fluconazole.

CONCLUSION

The reaction between 2 moles of methyl anthranilate and 1 mol of triethylene tetraamine results in a new hexadentate ligand, N-{2-[2(2-aminobenzoyl) amino-ethylamino)-ethylamino]-ethyl-2-amino benzamide (A2E3AB). A2E3AB reacts with transition metal salts of cations [Co (II), Ni (II), Cu (II), Zn (II) and Cd (II)) in basic medium and form neutral complexes of respective metal ions. Based on the results obtained from different physicochemical and spectroscopic investigations, it is concluded that the deprotonated A2E3AB acts as a hexadentate dianionic ligand, coordinating through amine and amide nitrogen atoms. Tentative structures are proposed for all the hexacoordinated complexes as tetragonal and are shown in figure 1.



M= Co(II)/ Ni(II)/ Cu(II)/ Zn(II)/Cd(II)

Figure 1. Tentative structure of the metal complexes of ligand A2E3AB.

ACKNOWLEDGEMENTS

The authors thank the UGC-SERO, Hyderabad for financial assistance in the form of MRP to SJ (F.MRP-3589/11/MRP/UGC-SERO). Authors thank Dr. S. Jagannatha Swamy, Retired Professor of Chemistry, Kakatiya University for helpful discussions.

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