Synthesis, crystal growth, spectral, thermal studies of Copper(II) complexes

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Abstract : Most of the reaction of solid materials in high temperature environments are controlled by crystal chemistry. In other words, chemical reactivity is determined by the crystal structure and defect structure of the solid materials. The suitability of the crystal for optical application was studied by UV spectroscopy. FTIR spectral analysis was used to confirm the presence of various functional groups in the grown crystals. The thermal stability of the compound was investigated by the thermal gravimetric and differential thermal analysis.

Key words : Complexes, UV, FT IR, TGA-DTA.

Introduction

The coordination chemistry in solution of alkali metal ions was relatively little investigated, in particular if compared with the great number of results reported in the literature for complexes of transition metal ions. All the classical experimental technique were employed in determining the formation constants of weak complexes (ion pairs), so as reported in the review of Marcus and Hfter. Many transition metal complexes have been used throughout history for the diagnosis and treatment of a wide variety of disorder. The unique properties of transition metal complexes, such as their structural diversity, interesting phytochemical and photo physical properties, and their ability to form specific interaction with biomolecules, make them versatile alternatives to organic small molecules for drug discovery. Alternatively, metal complexes have also been used functional scaffolds for the development of sensory probes. Structurally, metal complexes consist of a metal center surrounded by a number of organic or inorganic ligands via coordination bonds. Metal complexes can adopt a large range of structural type, including octahedral or square-planer geometries, which are unavailable to purely organic small molecules. This feature call allow metal complex to sample region of chemical space within molecules that cannot be accessed by organic compounds. Additionally, metal complexes can perform

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ligand exchange reaction with biological molecules, forming solvent adducts that can perturb cellular function. Importantly, the liability of metal-ligands bond can be tuned by the choice of metal ion, its oxidation state and auxiliary ligands. Finally, metal complexes can coordinate ligands that are themselves biological active, leading to dual function or even synergistic effects between the metal ion and the ligands.

The most famous examples of metal based drugs are the platinum anticancer compounds, such as cis-platin and its analogues, which have been approved for the treatment of a number of human cancers. The archetypical platinum drugs target DNA via covalent interactions, forming DNA cross links that trigger cellular apoptosis. However, this relatively non-specific mode of action can lead to side effects due to damage to normal cells; furthermore, resistance to platinum drugs can often be developed. Synthesis and characterization of Cu(II) complexes with the various ligands (1-2) are presented in this paper. Although extensive work has been carried out on the synthesis and characterization of Cu(II) complexes with different organic macromolecules as ligand, no work has been reported on comparative studies of complexes of ligands (1-2). In this view, it will be worth to study the Cu(II) transition metal ion complexes of the above type of ligands.

Experimental work

Preparation of piperidin-4-ones (1)

The compound (1) was prepared by adopting the following procedure. A mixture of acetone (14.5g), benzaldehyde (53g), ethanol (20ml) and anhydrous ammonium acetate (19.3g) were heated on a waterbath with constant shaking till the content became pale orange in colour. The flask was then cooled; ether (125ml) was added to the cold mixture and filtered. Addition of concentrated hydrochloric acid (13ml) to the clear filtrate afforded the hydrochloride of piperidone (m.pt 214-216°C (lit 216-217°C), which was collected after washing several times with ethanol – ether (1:5). The base was liberated by suspending the hydrochloride in acetone and adding ammonia (1:1) till the hydrochloride dissolved and the free base (1) was generated by diluting with water, which was crystallized from ethanol. Yield: 90%, M.Pt: 104-105°C (Lit 104 – 105°C), (Anal. calc. %) for ligand: C-81.2, H-6.77, N-4.9 Molecular weight 249.2. Found C-80.9, H-6.77, N-5.88, Molecular weight 251. IR (cm⁻¹) : 3305(s), 3062(s), 2975(s), 1724(s), 1637(s), 1458(sd), 1078(b), 1002(s), 933(b), 821(b), 754(w), 698(b), 663(b), 611(s), 522(l).

Preparation of 2-thioxo-6-Methyl-tetrahydro pyrimindin-4(1H)-one (2).

A solution of phenyl ethyl ammine (1.21g) and t-Butyl acetoacetate (1.58g) were heated in the presence of O-xylene (5ml) for 1 hr. Then the reaction mixture was poured over crushed ice and separated. The product 3-oxo-N(1)-phenyl butamide was filtered and recrystallized from ethanol. The product (1.025g), Benzaldehyde (0.1g) and thiourea (0.38g) dissolved in acetonitrile were reflexed in the presence of CeCl₃·7H₂O (0.931g) as catalyzed for 6 hrs. The reaction mixture was poured over crushed ice and separated. The product was filtered and recrystallized from ethanol. Yield 50%, M.Pt:144°-147°C. (Anal. calc. %) for ligand: C-41.6, H-5.50, N-19.39 Molecular weight 143. Found C-41.6, H-5.56, N-19.44, Molecular weight 144. IR (cm⁻¹) : 3114(s), 3085(s), 2931(s), 1701(s), 1635(s), 1483(sd), 1419(b), 1240(s), 1166(b), 1039(b), 748(w), 696(b), 669(b), 655(s), 511(l).

Analysis of Complexes

The content of Copper (II) ion in the complexes were estimated by Volhard’s method. Carbon, nitrogen and hydrogen were determined by micro analytical method. Molecular mass of the complexes were estimated by Rast method, using camphor as solvent.

Physical Measurements

Molar conductivities of the complexes were measured at room temperature (20±2°C) in DMF (~10⁻³M solution). Magnetic moments of the complexes were recorded using VSM instrument. IR spectra of the complexes were recorded in the region 400-4000cm⁻¹ in a double beam Perkin Elmer FT –IR spectrometer using KBr disc technique. The electronic spectra were recorded in DMSO using Hitachi UV – visible spectrophotometer in the range of 200-1200nm. TG and DTA studies were carried out on a Shimandzu STA - 1500 instrument (heating rate 10°C/ minute) in nitrogen atmosphere. Cyclic Voltammetry was carried out with an EG and G instrument model 270/250 research electrochemistry hardware and software using
Tetrabutylammonium perchlorate as the supporting electrolyte. XRD measurements were carried out with a Jeol JDX 8030X-ray diffractometer using CuKα radiation (λ=1.54Å) instrument.

Results and Discussion

The Cu(II) complexes are in green colour and are non-hygroscopic in nature. They are insoluble in benzene, carbon tetrachloride, chloroform etc., but moderately soluble in methanol, DMF and DMSO. The analytical data and composition of the complexes are presented in Table – 1.

Table – 1 Analytical Data of Cu (II) Complexes with Ligands (1-2)

| complex | Carbon % Found (Cal) | Hydrogen % Found (Cal) | Nitrogen% Found (Cal) | Sulphur % Found (Cal) | Metal Cu % Found (Cal) | M. Wt Found (Cal) | M.Pt °C |
|---------|---------------------|------------------------|----------------------|-----------------------|------------------------|-------------------|--------|
| 1       | 38.91 (38.60)       | 5.35 (5.11)            | 7.97 (7.95)          | -                     | 12.39 (12.02)         | 528.33 (528.5)    | 200-202 |
| 2       | 14.74 (14.23)       | 4.29 (4.27)            | 13.97 (13.29)        | 8.01 (7.59)           | 15.19 (15.07)         | 421.73 (421.5)    | 280    |

Electrical Conductance

Molar conductance values of different copper (II) complexes (10⁻³M) in DMF are given in Table -2. The values are in the range of 69-90ohm⁻¹ cm² mol⁻¹. Comparison of these values with standard values, shows that all the complexes are 1:1 electrolyte behavior in nature.

Table -2 Molar Conductance of Cu(II) Complexes with Ligands (1-2) (ohm⁻¹ cm² mol⁻¹)

| Complex                  | Molar conductance |
|--------------------------|-------------------|
| [Cu (DP) (H₂O)₄NO₃]NO₃.H₂O | 90                |
| [Cu (MOTTP) (H₂O)₄NO₃]NO₃.H₂O | 84                |

Magnetic Behavior

Magnetic moments of different copper (II) complexes with ligands (1-2) are given in Table –3. These values suggest the presence of one unpaired electron. These values (1.74-1.79) are slightly higher than the spin only value 1.73 BM for one unpaired electron. This reveals that the complexes are monomeric in nature and also indicates the absence of metal-metal bonding along the axial positions. These results support an octahedral copper (II) environment. The slightly higher magnetic moments of the complexes indicates the quenching of orbital moment to some extent.

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Table – 3 Magnetic Moment of Cu (II) Complexes with ligands (1-2)

| Complex                        | Magnetic moment (μeff) |
|--------------------------------|------------------------|
| [Cu (DP) (H₂O)₄NO₃]NO₃.H₂O     | 1.74BM                 |
| [Cu (MOTTP) (H₂O)₄NO₃]NO₃.H₂O | 1.78BM                 |
Molar Mass

The molar mass of the complexes are determined by Rast method. The values obtained are in good agreement with the calculated ones for the suggested formula of the complexes. The molar mass values are presented in Table -1. The possible structure of these complexes is given as follows:

Electronic Spectra

The solid state electronic spectra of the copper (II) complexes (Table - 4) are characterized by a broad asymmetric band around 13000-16500cm\(^{-1}\)from the energy level diagram.

Table – 4 Electronic spectra of Cu(II) Complexes with Ligands (1-2) in cm\(^{-1}\)

| Complex                                           | \(2E_g \rightarrow 2T_{2g}\) |
|---------------------------------------------------|-------------------------------|
| [Cu (DP) (H\(_2\)O)\(_4\)NO\(_3\)]NO\(_3\)H\(_2\)O  | 16318                         |
| [Cu (MOTTP) (H\(_2\)O)\(_4\)NO\(_3\)]NO\(_3\)H\(_2\)O | 12453                         |

The splitting of octahedral \(2E_g\) and \(2T_{2g}\) states increases with the tetragonal component of the crystal field with the increase in energy of \(2A_{1g}\) state, this state becomes sufficiently close to \(2B_{2g}\) and \(2E_g\) states and hence the three transitions cannot be resolved properly in the spectrum. Thus, the appearance of a single band in the visible region (15000 – 17000 cm\(^{-1}\)) suggests that all three expected transitions may be buried within the single broad envelope and the distortions is not large from octahedral geometry\(^{326}\).

Infrared Spectra

The IR spectral bands of the complexes with their probable assignments in the spectra are given in Figs. 2. The moderately strong bands found around 3300cm\(^{-1}\) in the IR spectra, ligands (1&2) are attributed to
stretching mode of N-H vibration but these bands exhibit a considerable downward shift of 30-50 cm$^{-1}$ in complexes. This spectral observation suggests that the coordination of the ligands to the metal ion takes place through the lone pair of electrons of secondary amine nitrogen atom of the ligands (1&2) moiety. The observed similar decreasing trend of C-N stretching frequency of N-CH$_3$ bond in ligands (1&2) and their complexes also confirmed the coordination involvement of lone pair of electrons in the tertiary amine nitrogen atom of the ligands. The IR data also reveal that the ligands are coordinated to the metal ion through the lone pair of electrons in ring S atom and through the benzylidene carbonyl moiety respectively.

Fig. 2 IR spectrum of the Cu (II) complexes

A new band at 455 – 417 cm$^{-1}$ due to $\nu$(M-N) and the M-O-bonding is also confirmed by the presence of a new band in the region 553-511 cm$^{-1}$. The presence of water in copper (II) complexes are evidenced by presence of sharp or broad band in the region 3487 -3400 cm$^{-1}$. The O-H stretching vibration of a strong or medium intensity band in the region 1647-1574 cm$^{-1}$ due to H-O-H bending vibration.

The presence of water molecules in the complexes is shown by a broad absorption band in the 3600-3200cm$^{-1}$ region (merged with the NH absorption) due to O-H stretching vibration and a sharp medium peak at 1624 cm$^{-1}$ due to H-O-H bending vibration. The peaks corresponding to other vibrational modes of water could not be detected. The coordination of oxygen atom of water molecules to the metal ion is confirmed by the presence of a new band in the region 528 – 507 cm$^{-1}$ due to M-O bonding.

**Thermal Analysis**

The simultaneous TG & DTA measurements of the complexes [Cu(DP)(H$_2$O)$_4$NO$_3$]NO$_3$.H$_2$O and [Cu(MOTTP)(H$_2$O)$_4$NO$_3$]NO$_3$.H$_2$O are shown in Fig.3.

Fig. 3 Simultaneous TG & DTA of Cu(II) complexes
1. \([\text{Cu(DP)}(\text{H}_2\text{O})_4\text{NO}_3]\) \text{NO}_3.\text{H}_2\text{O}

Table 6 Thermal Analysis Data of Cu(II) Complexes with DP and MOTTP ligands

| Complex | DTA Peak Temp\(^{\circ}\text{C}\) | Thermogravimetry | Mass Loss % |
|---------|---------------------------------|------------------|-------------|
|         |                                 | Temperature Range \(\circ\text{C}\) | Observed | Calculated |
| 1       | 159 (+) 252 (+) 399 (-) 419 (-) | 225-336 336-441 441-590 | 12.02 | 13.04 |
|         |                                 |                  | 59.51 | 60.11 |
|         |                                 |                  | 73.13 | 74.77 |
|         |                                 |                  | 84.86 | 85.01 |
|         |                                 |                  | 96.59 | 97.01 |
| 2       | 157 (+) 510 (+) 149 (+) 471 (-) | 148-187 187-345 345-519 | 13.16 | 11.13 |
|         |                                 |                  | 78.71 | 75.11 |

The thermal analysis data of the complexes are given in Table 6. From this, it is confirmed that the complex is stable up to 225°C as shown by the TG plateau. The first decomposition stage takes place in the temperature range 225°-336°C which corresponds to the removal of one coordinated water molecule present in the complex. The dehydration process can be followed by the mass loss of 12.02% (Theoretical value 13.04%). The endothermic peak temperature is 159°C. In TG curve the second plateau temperature ranges from 336°-441°C and the corresponding mass loss is 59.51% (Theoretical value 60.11%). The endothermic decomposition peak temperature is 252°C in DTA. The third stage corresponds to the exothermic decomposition peak temperature is 252°C in DTA. The third stage corresponds to the exothermic decomposition of nitrate ion, at 399°C. The peak temperature from DTA is 590°C. The mass loss is 73.13% (theoretical value 74.77%) and 84.86% (theoretical value 85.01%) respectively. The fourth stage corresponds to the exothermic decomposition of ligand and four water molecules at 419°C which finally decomposes to Cu_2O in a violent reaction. The mass loss is 96.59% (theoretical value 97.01%). The four stage of decomposition are attributed to the stepwise removal of one water molecule, nitrate ions, four water molecules and final decomposition of metal – ligand resulting in the formation of Cu_2O as the reaction product.

The decomposition scheme of \([\text{Cu(DP)}(\text{H}_2\text{O})_4\text{NO}_3]\) \text{NO}_3.\text{H}_2\text{O} is given below as representative example.

\[
\text{[Cu(DP)(H}_2\text{O})_4\text{NO}_3]\text{NO}_3.\text{H}_2\text{O} \rightarrow_{225°-336°C} \rightarrow_{336°-441°C} \text{[Cu(DP)(H}_2\text{O})_4\text{]} \rightarrow_{441°-590°C} \text{Cu}_2\text{O}
\]

2. \([\text{Cu(MOTTP)}(\text{H}_2\text{O})_4\text{NO}_3]\) \text{NO}_3.\text{H}_2\text{O}

The first mass loss 13.16% (theoretical mass loss 13.04%) observed endothermically at 157°C can be attributed to the release of one outer molecule and the second endothermic decomposition stage is due to the removal of remaining water molecules at 510°C and the mass loss is 78.71% (theoretical value 75.11%). The third stage corresponds to the decomposition of nitrate ions. The intermediate undergoes exothermic decomposition at 149°C and 191°C, which finally decomposes to Cu_2O in a violent reaction. The peak temperature is 471°C in DTA.

\[
\text{[Cu(MOTTP)(H}_2\text{O})_4\text{NO}_3]\text{NO}_3.\text{H}_2\text{O} \rightarrow_{148°-187°C} \rightarrow_{187°-345°C} \text{[Cu(MOTTP)(H}_2\text{O})_4\text{]} \rightarrow_{345°-519°C} \text{Cu}_2\text{O}
\]
The thermal analysis of complexes \([\text{Cu(DP)(H}_2\text{O)}_4\text{NO}_3\text{NO}_3\cdot\text{H}_2\text{O}}\) and \([\text{Cu(MOTTP)(H}_2\text{O)}_4\text{NO}_3\text{NO}_3\cdot\text{H}_2\text{O}}\) has been carried out to supplement to infrared spectral data and percentage composition of the complexes. Examination of the thermal curves reveals that the complexes undergo the first stage dehydration of coordinated water molecules in the temperature range 225°-336°C and 148°-187°C, in both the complexes.

The dehydration step is followed by the decomposition of ligand along with the remaining water molecules. In both cases, the final product formed is to be copper (II) oxide.

Cyclic Voltammeteric Studies

The electrochemical behaviours of the Cu complexes and the ligands (1-2) have been investigated by cyclic voltammetric studies and the results are listed in Table -7. Comparison of the peak potentials of the ligands (1-2) and the Cu complex reveals that the metal based one – electron reduction process Cu(II) – Cu(I) occurs in the complex. The separation of the peak potentials of the peaks obtained in the forward and reverse scan indicates the quasi – reversible nature of the electrode process in the Cu(II) complex. However, in the reverse scan the Cu (II) complex exhibits an anodic peak at 0.56V. This peak is attributed to the one electron oxidation of Cu(II) i.e Cu(II) – Cu(III).

Table -7 Cyclic voltammetric data of ligands (1-2) and Copper (II) Complex

| Compounds       | E_pC (V) | E_pa (V) | ΔE_p (V) |
|-----------------|----------|----------|----------|
| DP              | 1.70     | -8.27    | 1.1      |
| MOTTP           | 1.62     | -8.16    | 2.9      |
| Copper (II) Complex | -0.69 | -0.40    | 1.22     |

X-ray (Powder) Diffraction Study

The X-ray (powder) diffraction photograph was recorded for the copper complexes with ligands (1&2). For complex \([\text{Cu(MDDP)(H}_2\text{O)}_4\text{NO}_3\text{NO}_3\cdot\text{H}_2\text{O}}\), photograph (Fig.4) reveals that 17 reflections with maximum reflection at 10.24 (2θ) with the spacing of 8.63Å. All the lines in the powder photograph were indexed based on Ito’s method. The Cu(II) complexes are crystallizes in a triclinic lattice. The agreement between observed and computed \(Q_{hkl}\) (within 1%) are displayed in Table 8-9. The direct cell dimensions calculated from the reciprocal cell dimensions are collected in Table -10. The molecules is non-centro symmetric and it is a neutral monomer in the Cu(II) is octahedrally coordinated by two each of crystallographically independent N-coordinated ligands. The NH, NCH\(_3\) groups are quasilinear with 107.0° & 101.1° bonded to the Cu(II) ion through an angle of 189.5° & 165.3° respectively. Interestingly the respective N atoms of the ligands is cis – located whereas the same are trans-positioned in the reportedCu(II) complexes.

![Fig.4 Powder XRD spectra of Cu (II) complexes](image-url)
### Table 8: X-ray (Powder) Diffraction data for complex [Cu(DP)(H$_2$O)$_4$NO$_3$]NO$_3$.H$_2$O

| $d$  | $2\theta$ | $Q_{obs} = 1/d^2$ | d-spacing [Å] | Rel. Int. [%] | $Q_{cal}$ | Index (h k l) |
|------|-----------|-------------------|---------------|--------------|-----------|--------------|
| 10.2545 | 2341.67   | 0.1171            | 8.62654       | 100.00       | 0.003475  | Q$_{100}$    |
| 12.8399 | 42.78     | 0.1673            | 6.89478       | 1.83         | 0.006092  | Q$_{010}$    |
| 14.1941 | 379.01    | 0.1338            | 6.23984       | 16.19        | 0.005270  | Q$_{001}$    |
| 14.6624 | 493.41    | 0.1840            | 6.04159       | 21.07        | 0.004211  | Q$_{101}$    |
| 18.3303 | 57.12     | 0.2007            | 4.84012       | 2.44         | 0.011809  | Q$_{111}$    |
| 20.1247 | 32.79     | 0.1673            | 4.41243       | 1.40         | 0.014486  | Q$_{101}$    |
| 20.5235 | 348.77    | 0.2007            | 4.32756       | 14.89        | 0.020662  | Q$_{012}$    |
| 22.0948 | 980.97    | 0.1840            | 4.02323       | 41.89        | 0.021702  | Q$_{301}$    |
| 22.5652 | 265.14    | 0.1338            | 3.94043       | 11.32        | 0.039592  | Q$_{122}$    |
| 23.2482 | 279.38    | 0.2844            | 3.82618       | 11.93        | 0.033403  | Q$_{310}$    |
| 25.7696 | 52.72     | 0.1338            | 3.45724       | 2.25         | 0.035153  | Q$_{122}$    |
| 26.0766 | 33.96     | 0.1338            | 3.41724       | 1.45         | 0.038131  | Q$_{310}$    |
| 29.5438 | 111.30    | 0.1506            | 3.02362       | 4.75         | 0.039385  | Q$_{122}$    |
| 30.4714 | 41.43     | 0.2007            | 2.93366       | 1.77         | 0.010769  | Q$_{111}$    |
| 30.9367 | 21.33     | 0.1338            | 2.89059       | 0.91         | 0.001746  | Q$_{102}$    |
| 36.7073 | 28.45     | 0.1338            | 2.44834       | 1.22         | 0.035489  | Q$_{310}$    |
| 37.1855 | 194.11    | 0.1171            | 2.41795       | 8.29         | 0.034568  | Q$_{122}$    |

### Table 9: X-ray (Powder) Diffraction data for complex [Cu(MOTTP)(H$_2$O)$_4$NO$_3$]NO$_3$.H$_2$O

| $d$  | $2\theta$ | $Q_{obs} = 1/d^2$ | d-spacing [Å] | Rel. Int. [%] | $Q_{cal}$ | Index (h k l) |
|------|-----------|-------------------|---------------|--------------|-----------|--------------|
| 10.3269 | 4.03     | 0.2656            | 8.55792       | 3.14         | 0.004675  | Q$_{100}$    |
| 11.2130 | 3.15     | 0.4015            | 7.89822       | 2.45         | 0.006092  | Q$_{010}$    |
| 12.7349 | 24.09    | 0.2676            | 6.89742       | 18.75        | 0.004270  | Q$_{001}$    |
| 13.6842 | 17.16    | 0.2676            | 6.42446       | 14.91        | 0.017211  | Q$_{101}$    |
| 18.1300 | 14.22    | 0.2676            | 4.92004       | 11.07        | 0.001809  | Q$_{111}$    |
| 22.9407 | 18.03    | 0.1338            | 3.87844       | 14.03        | 0.013486  | Q$_{101}$    |
| 26.2911 | 7.70     | 0.4015            | 3.38984       | 5.99         | 0.029662  | Q$_{102}$    |
| 27.2387 | 128.50   | 0.2342            | 3.27403       | 100.00       | 0.034702  | Q$_{010}$    |
| 33.2991 | 27.92    | 0.2007            | 2.69072       | 21.72        | 0.031597  | Q$_{122}$    |

### Table 10: Crystal Parameters of [Cu(DP)(H$_2$O)$_4$NO$_3$](NO$_3$)$_2$.H$_2$O

| Cell length (Å) | Angular parameters (°) | Cell Volume (Å$^3$) |
|----------------|------------------------|---------------------|
| a = 17.67      | α = 101.1              | 3345.43             |
| b = 15.62      | β = 116.7              |                     |
| c = 14.40      | γ = 107.0              |                     |
Conclusions

From the various data, the conclusions are

1. The molar conductance values of the Copper (II) complexes suggest that they are 1:1 electrolytes.
2. The UV spectral studies confirmed that the ligands are monodentate, coordinating through ring hetero atom and benzylidene carbonyl moiety.
3. The IR spectra of the complexes indicated that the presence of water molecules in the complexes and the thermal studies confirmed the coordination nature of the water molecules.
4. The effective magnetic moments of the complexes lie in the range 1.76 – 1.79BM, which reveals that the presence of one unpaired electron and the monomeric nature of the complexes.
5. The electronic spectral studies indicated an octahedral geometry of the complexes.
6. The cyclic voltammetric studies indicated that the complexes are involved in one electron transferable processes.
7. XRD shows that the complexes are crystallized in triclinic lattice.

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