

## Synthesis and Characterization of 5,5'-(6-phenoxy-1,3,5-triazine-2,4-diyl)bis(azanediyl)bis(2-hydroxybenzoic acid) and its metal complexes

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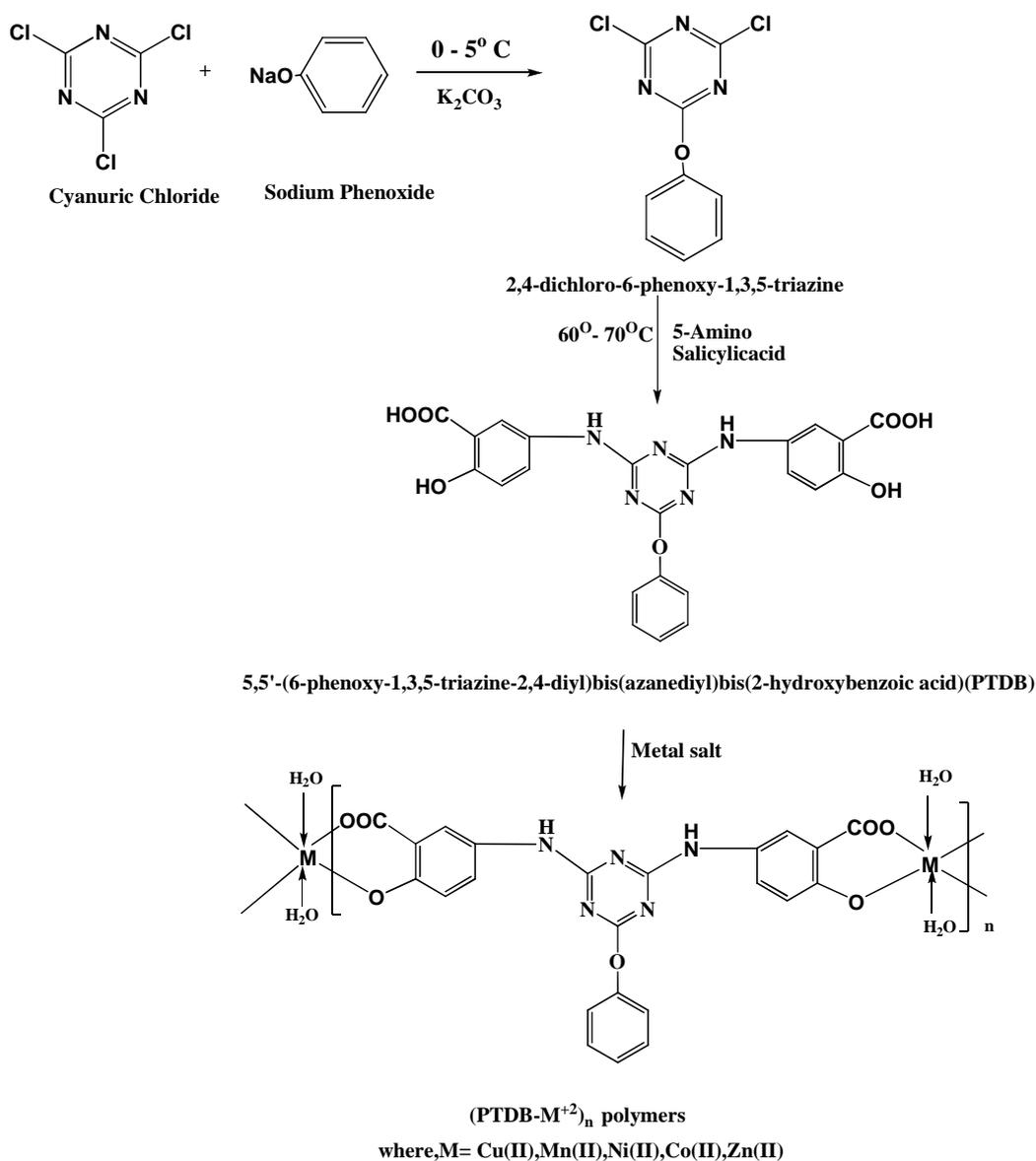
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**Abstract:**Co-ordination polymers of novel bis ligand namely 5,5'-(6-phenoxy-1,3,5-triazine-2,4-diyl)bis(azanediyl) bis(2-hydroxybenzoic acid) have been prepared with various metal complexes viz  $Zn^{+2}$ ,  $Cu^{+2}$ ,  $Ni^{+2}$ ,  $Co^{+2}$  and  $Mn^{+2}$ . The novel bis bidentate ligand (PTDB) is synthesized by condensation of 5-amino salicylic acid with 2,4-dichloro-6-phenoxy-1,3,5-triazine in presence of catalyst. All these co-ordination polymers and parent ligand are characterized by elemental analysis, IR spectra and diffuse reflectance spectral studies for their structure determination. The thermal stability was evaluated by thermogravimetric analyses(TGA). In addition, all of the coordination polymers have been characterized by their magnetic susceptibilities. The microbicidal activities of all the samples have been monitored against plant pathogens.

**Keywords:** 5-amino salicylic acid, antibacterial and antifungal activities, coordination polymers, IR, NMR, reflectance spectra and TGA.

### Introduction

Nitrogen containing heterocyclic play an important role, not only for life science industries but also in many other industrial fields related to special and fine chemistry. Among them s-triazine ring containing derivatives have been reported for applicable mostly as reactive dyes and some are used as polymers and drugs. The study of co-ordination polymers has made much progress [1-4]. Such co-ordination polymers are mostly derived from bi-chelating ligands in which metal ions and chelating agents are arrayed alternatively. Most of bichelating ligands are derived from well known chelating agents like 8-hydroxy quinoline and salicylic acid etc [5,6]. The joining segment of these two similar ligands are mainly -N=N-, SO<sub>2</sub>, -CH<sub>2</sub> -, -O- [5-10]. A promising method has been reported for the formation of coordination polymers of enhanced chelating ability by using a bidentate 8-hydroxyquinoline moiety in which two 8-hydroxyquinolanyl end groups are joined with bridge, usually at the 5,5'-position [11-13]. The literature survey reveals that bis-5-amino salicylic acid ligand having 1,3,5-triazine ring as a bridge has not been reported so far. Though 4-amino salicylic acid is excellent anti T.B agent. Thus this may afford good chelating ligand with better microbicidal activity. With this view, the present authors communicated the initial work recently. Hence it was thought to undertake such type of study. Thus the present paper deals with synthesis, characterization and chelating properties of ligand (PTDB) and its co-ordination polymers are shown in Scheme 1.



## Experimental

### Materials

All other chemicals used were of laboratory grade. 5-amino salicylic acid was prepared by method reported [14,15].

### Synthesis of 5, 5'-(6-phenoxy-1,3,5-triazine-2,4-diyl)bis(azanediyl) bis(2-hydroxybenzoic acid) (PTDB)

The 5-Amino salicylic acid (SA) (i.e. 5-Aminosalicylic acid) was obtained from local dealer.

To a suspension of 5-amino salicylic acid (3.06g, 0.02 mol), 2,4-dichloro-6-phenoxy-1,3,5-triazine (2.41 g, 0.01 mol) in an acetone–water mixture was added. Then  $\text{K}_2\text{CO}_3$  (0.02 mol) was added as an acid accepted [16]. The resulting mixture was refluxed for 3 hr with occasional shaking. The resulting suspension, which contained a colour precipitate, was neutralise and then filtered. The solid product was collected and dried to give PTDB (58% yield). The product melted with decomposition at above  $240^{\circ}\text{C}$  (uncorrected).

### Preparation of coordination polymer

All coordination polymers were synthesized by using equimolar amount of ligand PTDB and metal salt. A warm clear solution of bis-ligand (0.01 mol) in ethanol-acetone (60ml) was added drop wise in metal salt (0.01 mol) in alcoholic NaOH with stirring. The pasty precipitates were obtained at neutral pH. These were dissolved by

addition of water up to clear solution. The reaction mixture was heated on a water bath for 0.5 hr. The reaction mixture was made alkaline by the addition of dilute sodium acetate or ammonia until the precipitation was completed. The polymer separated out in the form of a suspension and was digested on a boiling water bath for about 1 hr. Finally, the resultant solid was collected by filtration and washed with hot water, dimethylformamide (DMF), and then acetone. The polymer [PTDB-M<sup>2+</sup>] (resultant product) was air-dried.

### Antimicrobial Activities

Antibacterial activity and antifungal activities of PTDB ligand and its coordination polymers were studied against gram-positive bacteria (*Bacillus subtilis* and *staphylococcus aureus*) and gram-negative bacteria (*E.coli*, *salmonella typhi* and *klebsiella promioe*) and plant pathogenic organisms used were *Aspergillus niger*, *Candida albicans*, *Trichoderma harsianum.*, *Mucor mucedo.*, and *Botrytis cinerea* at a concentration of 50 µg/ml by agar cup 520 plate method. The methanol system was used as control in this method. The area of inhibition of zone was measured in mm.

### Measurements

The C, H, N contents of metal were determined by TF-Flash-1101 EA. The metals contents of metal chelates were determined volumetrically by Vogel's method [17]. To a 100mg chelate sample, 1ml of HCl, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> each were added and then 1 gm of NaClO<sub>4</sub> was added. The mixture was evaporated to dryness and the resulting salt was dissolved in double distilled water and diluted to the mark. From this solution the metal content was determined by titration with standard EDTA solution. Infrared spectra of the synthesized compounds were recorded on Nicolet 760 FT-IR spectrometers. NMR spectrum of ligand was recorded on a Bruker spectrophotometer at 400 MHz. Magnetic susceptibility measurement of the synthesized coordination polymer was carried out on Gouy Balance at room temperature. The electronic spectra of coordination polymer in solid were recorded at room temperature. MgO was used as a reference. Antimicrobial activity of all the samples was monitored against various gram positive(+) and gram negative(-) organisms, following the method reported in the literature [18,19].

### Results And Discussion

The synthesis of bis bidentate ligand of PTDB was performed by a simple nucleophilic substitution reaction of 2,4-dichloro-6-phenoxy-1,3,5-triazine and 5-amino salicylic acid. The resulting PTDB ligand was an amorphous colour powder. The ligand is characterized by elemental analysis as well as <sup>1</sup>H NMR and IR spectroscopic techniques as given below.

### Elemental Analysis

The metal and C, H, N contents of ligand and coordination polymer (its coordination polymer) are shown in Table-1 and are also consistent with the predicted structure. The results show that the metal: ligand (M: L) ratio for all divalent metal chelate is 1:1.

**Table -1: Physico chemical parameters of the ligand PTDB and metal complexes**

| Empirical   | Formula | Mol. Cal<br>g/mol | Yield<br>% | Elemental Analysis (%) Found(Calcd) |            |              |              |
|---|---------|-------------------|------------|-------------------------------------|------------|--------------|--------------|
|   |         |                   |            | C                                   | H          | N            | M            |
| C <sub>23</sub> H <sub>17</sub> N <sub>5</sub> O <sub>7</sub>                       |         | 475               | 58         | 58.11(58.07)                        | 3.60(3.55) | 14.73(14.69) | ---          |
| C <sub>23</sub> H <sub>15</sub> N <sub>5</sub> O <sub>7</sub> Cu .2H <sub>2</sub> O |         | 572               | 60         | 48.21(48.17)                        | 3.34(3.29) | 12.22(12.17) | 11.09(11.02) |
| C <sub>23</sub> H <sub>15</sub> N <sub>5</sub> O <sub>7</sub> Ni .2H <sub>2</sub> O |         | 568               | 53         | 48.62(44.03)                        | 3.37(3.32) | 12.32(12.28) | 10.37(10.31) |
| C <sub>23</sub> H <sub>15</sub> N <sub>5</sub> O <sub>7</sub> Co .2H <sub>2</sub> O |         | 567               | 55         | 48.60(44.01)                        | 3.37(3.32) | 12.33(12.28) | 10.33(10.32) |
| C <sub>23</sub> H <sub>15</sub> N <sub>5</sub> O <sub>7</sub> Mn .2H <sub>2</sub> O |         | 564               | 62         | 48.95(44.56)                        | 3.39(3.35) | 12.41(12.36) | 09.73(09.70) |
| C <sub>23</sub> H <sub>15</sub> N <sub>5</sub> O <sub>7</sub> Zn .2H <sub>2</sub> O |         | 573               | 59         | 48.06(43.11)                        | 3.33(3.28) | 12.18(12.85) | 11.38(11.35) |

**Table -2: Spectral features and magnetic moment of metal chelates**

| Metal Chelates          | BM          | Electronic Spectral Data $\text{cm}^{-1}$ | Transitions  | IR spectral features Common for all $\text{cm}^{-1}$ |
|-------------------------|-------------|---|--|--|
| PTDB - $\text{Cu}^{+2}$ | 1.99        | 23370<br>15655                            | C.T<br>${}^2\text{E}_g$ ${}^2\text{T}_{2g}$  | 3030, Aromatic<br>1520,                              |
| PTDB - $\text{Ni}^{+2}$ | 3.75        | 22478<br>15607<br>8200                    | ${}^3\text{A}_{2g}$ ${}^3\text{T}_{1g}(\text{P})$<br>${}^3\text{A}_{2g}$ ${}^3\text{T}_{1g}(\text{F})$<br>${}^3\text{A}_{2g}$ ${}^3\text{T}_{2g}$  | 1640,<br>1710 CO<br>3450-3160 OH                     |
| PTDB - $\text{Co}^{+2}$ | 4.45        | 20660<br>18867<br>10975                   | ${}^4\text{T}_{1g}(\text{F})$ ${}^4\text{A}_{2g}$<br>${}^4\text{T}_{1g}(\text{F})$ ${}^4\text{T}_{1g}(\text{P})$<br>${}^4\text{T}_{1g}(\text{F})$ ${}^4\text{T}_{2g}$                    | 3400 Sec. NH<br>1690 COOH<br>1070 C-O-M &            |
| PTDB - $\text{Mn}^{+2}$ | 5.06        | 23045<br>18657<br>15380                   | ${}^6\text{A}_{1g}$ ${}^6\text{A}_{1g}$ ( ${}^4\text{E}_g$ )<br>${}^6\text{A}_{1g}$ ${}^4\text{T}_{2g}$ ( ${}^4\text{G}$ )<br>${}^6\text{A}_{1g}$ ${}^4\text{T}_{1g}$ ( ${}^4\text{G}$ ) | 509 O-M<br>700 N-M<br>650                            |
| PTDB - $\text{Zn}^{+2}$ | Diamagnetic |   | -----  |  |

### IR Analysis

The important infrared spectral bands and their tentative assignments for the synthesized bis-ligand and its coordination polymers were recorded as KBr disks and are shown in Table 2.

Examination of IR spectrum of ligand of PBDQ comprises the important bands due to Salicylic acid. The bands were observed at 1640, 1520, and  $3030\text{cm}^{-1}$ . The broad band in ligand and its coordination polymer at  $3160 - 3450\text{cm}^{-1}$  are due to the presence of the -OH group [20].

In the investigated coordination polymers, the -OH group of the ligand forms a coordination bond with the metal ions. whereas the band at  $509\text{cm}^{-1}$  in the IR spectrum of PTDB assigned to in-plane -OH deformation was shifted towards higher frequency in the spectra of the coordination polymer due to the formation of the M-O bond [21]. This was further confirmed by a weak band at  $1070\text{cm}^{-1}$  corresponding to C-O-M stretching, while bands around 700 and  $650\text{cm}^{-1}$  correspond to the N-M vibration [22].

### ${}^1\text{H}$ NMR Analysis

The structural analysis of the ligand (PTDB) was determined by  ${}^1\text{H}$  NMR spectrum.

NMR

|        |                       |                    |
|--------|-----------------------|--------------------|
| (DMSO) | 6.91 – 7.83 ppm (11H) | Multiplet Aromatic |
|        | 11.00 ppm (1H)        | Singlet (COOH)     |
|        | 5.35 ppm (1H)         | Singlet (OH)       |
|        | 4.0 ppm (1H)          | Singlet (NH)       |

### Magnetic Measurements

Magnetic moments of coordination polymers are given in Table 2. The diffuse electronic spectrum of  $\text{Cu}^{+2}$  complex shows two broad bands,  $15655\text{cm}^{-1}$  and  $23370\text{cm}^{-1}$ . The first band may be due to a  ${}^2\text{E}_g$   ${}^2\text{T}_{2g}$  transition, while the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the  $\text{Cu}^{+2}$  metal complex [23-25]. The  $\text{Co}^{+2}$  metal complex gives rise to three

absorption bands at 20660  $\text{cm}^{-1}$ , 18867  $\text{cm}^{-1}$  and 10975  $\text{cm}^{-1}$  which can be assigned  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$  transitions, respectively. These absorption bands and the  $\mu_{\text{eff}}$  value indicate octahedral configuration of the  $\text{Co}^{+2}$  metal complex [26,27]. The spectrum of  $\text{Mn}^{+2}$  polymeric complex comprised three bands at 23045  $\text{cm}^{-1}$ , 18657  $\text{cm}^{-1}$  and 15380  $\text{cm}^{-1}$ . These bands may be assigned to  ${}^6\text{A}_{1g} \rightarrow {}^6\text{A}_{1g}$  ( ${}^4\text{E}_g$ ),  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}({}^4\text{G})$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$  transitions, respectively. The high intensity of the bands also suggests that they may have some charge transfer character. The magnetic moment is found to be lower than normal range. In the absence of low temperature measurement of magnetic moment, it is difficult to attach any significance to this. As the spectrum of the metal complex of  $\text{Ni}^{+2}$  show three distinct bands at 22478  $\text{cm}^{-1}$ , 15607  $\text{cm}^{-1}$  and 8200  $\text{cm}^{-1}$  are assigned as  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$  transition, respectively, suggesting the octahedral environment for  $\text{Ni}^{+2}$  ion. The observed  $\mu_{\text{eff}}$  values in the range 1.99–5.06 B.M are consistent with the above moiety [28,29].

### Thermal Studies

The TGA data for the Co-ordination polymers samples at different temperatures indicate that the degradation of the co-ordination polymers is noticeable beyond 300<sup>0</sup> C. The rate of degradation becomes a maximum at a temperature between 400 and 500<sup>0</sup> C. This may be due to acceleration by metal oxides, which form in situ. Each polymer lost about 60% of its weight when heated up to 680<sup>0</sup> C. Inspection of the thermograms of all coordinated polymer samples revealed that all samples suffered appreciable weight loss in the range of 160 to 280<sup>0</sup>C. This may be due to the presence of a coordinated water molecule.

### Antimicrobial Activities

The antibacterial and antifungal data obtained from analysis are shown in Table-3 and Table- 4, respectively. The increase in antimicrobial activity may be considered in light of Overtone's concept [30] and Tweedy's chelation theory[31]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage only of lipid-soluble materials due to which liposolubility is an important factor controlling the antimicrobial activity. On complexation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of  $\pi$ -electrons over the whole chelate ring and enhances the lipophilicity of the coordination polymers. This increased lipophilicity enhances the penetration of the coordination polymer into lipid membranes and blocks the metal binding sites in the enzymes of microorganisms. These coordination polymers also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organisms.

**Table-3:Antibacterial activity of coordination Polymers**

| Compounds   | Gram +ve                 |                              | Gram -ve                  |                         |               |
|---|--------------------------|------------------------------|---------------------------|-------------------------|---------------|
|   | <i>Bacillus subtilis</i> | <i>Staphylococcus Aureus</i> | <i>klebsiella promioe</i> | <i>Salmonella typhi</i> | <i>E.coli</i> |
| PTDB  | 64                       | 70                           | 65                        | 70                      | 71            |
| (Cu PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 66                       | 75                           | 64                        | 65                      | 75            |
| (Co PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 67                       | 72                           | 70                        | 73                      | 64            |
| (Ni PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 71                       | 70                           | 80                        | 84                      | 70            |
| (Mn PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 65                       | 69                           | 71                        | 75                      | 78            |
| (Zn PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 71                       | 70                           | 76                        | 70                      | 72            |

**Table-4:Antifungal activity of coordination Polymers**

| Compounds   | Zone of Inhibition at 1000 ppm (%) |                         |                              |                     |                         |
|---|------------------------------------|-------------------------|------------------------------|---------------------|-------------------------|
|   | <i>Aspergillus Niger</i>           | <i>Candida albicans</i> | <i>Trichoderma harsianum</i> | <i>Mucor mucedo</i> | <i>Botrytis cinerea</i> |
| PTDB  | 75                                 | 74                      | 58                           | 56                  | 55                      |
| (Cu PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 77                                 | 68                      | 63                           | 73                  | 69                      |
| (Co PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 72                                 | 72                      | 70                           | 71                  | 65                      |
| (Ni PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 62                                 | 73                      | 85                           | 75                  | 77                      |
| (Mn PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 63                                 | 68                      | 69                           | 68                  | 71                      |
| (Zn PTDB (H <sub>2</sub> O) <sub>2</sub> ) <sub>n</sub> | 65                                 | 65                      | 66                           | 70                  | 76                      |

Coordination polymers exhibit higher biocidal activity as compared with the free ligands; from the comparative analysis shown in Table 3 and Table 4, respectively, it is observed that all the coordination polymer are more potent biocidals than the free ligands. From the data obtained it is clear that Cu (II) is highly active among the coordination polymer of the respective metal.

## Conclusion

The results obtained in this study allow the following conclusions. The synthesis design of new bis-ligand has been performed successfully, and analysed by normaly spectral study. A series of some novel coordination polymers from bis-ligands with transition metals have been prepared and characterized for their spectral and magnetic properties. All the synthesized coordination polymer compounds were screened for their antimicrobial activity. The coordination polymers exhibited behave toxic for gram-negative bacteria (*E.coli*, *salmonella typhi* and *klebsiella promioe*) and gram-positive bacteria (*Bacillus subtilis* and *staphylococcus aureus*), and plant pathogenic organisms (fungi) used were *Aspergillus niger*, *Candida albicans*, *Trichoderma harsianum*, *Mucor mucedo*, and *Botrytis cinerea* microorganisms. In comparison with the ligand, coordination polymers were more active against one or more bacterial strains, thus introducing a novel class of metal-based bactericidal agents. The information regarding geometry of the coordination polymer was obtained from their electronic and magnetic moment values. The magnetic moment values of coordination polymer indicate an octahedral geometry.

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