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# Studies on co-ordination polymers of 5,5'-(6-(diphenyl amino)-1,3,5-triazine-2,4-diyl) bis(azanediyl) diquinolin-8-ol

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## ABSTRACT

*Co-ordination polymers containing a novel bis ligand namely 5,5'-(6-(diphenylamino)-1,3,5-triazine-2,4-diyl) bis(azanediyl)diquinolin-8(DATBD)* ***)*** *have been prepared with metal ion like* $Zn^{+2}$, $Cu^{+2}$, $Ni^{+2}$, $Co^{+2}$ *and* $Mn^{+2}$*. The novel bis bidentate ligand (DATBD) is synthesized by condensation of 5-amino-8-hydroxyquinoline with 4,6-dichloro-N,N-diphenyl-1,3,5-triazin-2-amine in presence of base catalyst. All of these co-ordination polymers and parent ligand were 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**: 8-hydroxyquinoline, ligands(DATBD), antibacterial and antifungal activities, coordination polymers, IR, NMR, reflectance spectra and TGA.

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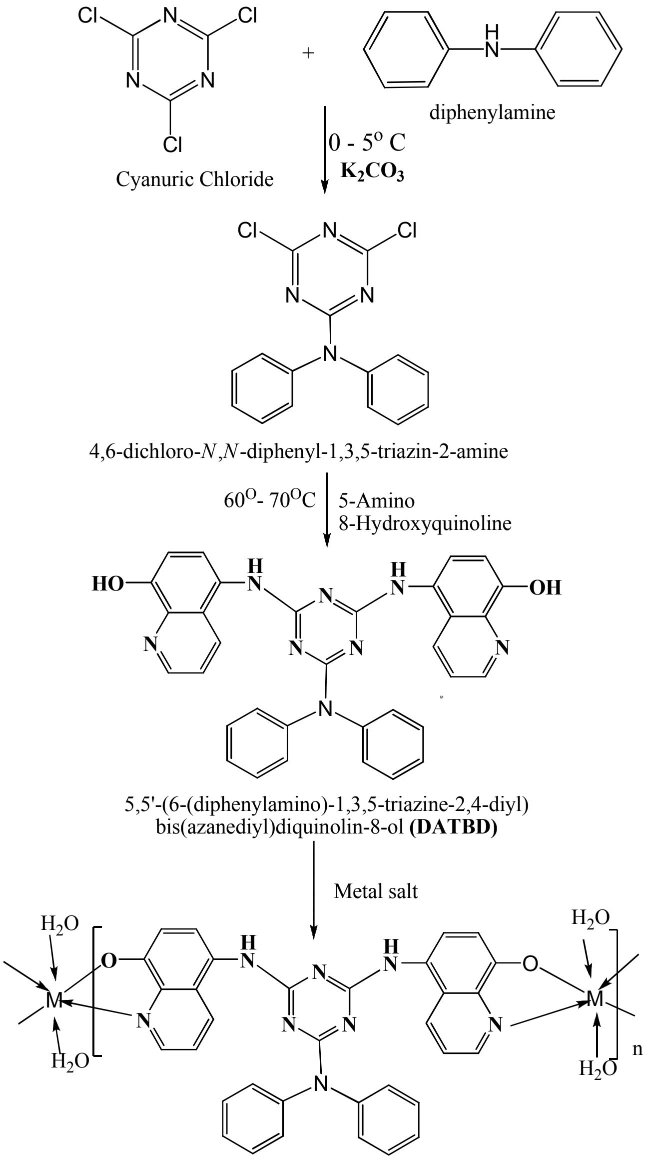
## INTRODUCTION

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 [1-3]. 5-amino 8-quinolinol is well known as an analytical reagent [4,5]. Its various derivatives are very useful in pharmaceuticals [6]. Several azo dyes based on 8-quinolinol are also reported for dyeing of textiles as well as their chelating properties [7,8]. 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-hydroxyquinolinyl end groups are joined with bridge, usually at the 5,5'-position [9–11]. The 5–Amino 8-hydroxy quinolinol is the easiest preparable precursor for the preparation of bis-ligand and thus bis-ligands based on 5–Amino 8–hydroxyquinoline have been reported for coordination polymers [11,12].ion exchange resins have also been prepared from 5–amino 8–hydroxyquinoline and amino or hydroxyl functionalized polymers[13-15]. The literature survey reveals that bis-8- hydroxyquinoline ligand having 1,3,5-triazine ring as a bridge has not been reported so far. Hence it was thought to undertake such type of study. Thus the present paper deals with synthesis, characterization and chelating properties of ligand (DATBD) and its co-ordination polymers are shown in **Scheme 1**.



**(DATBD)**-$M^{+2})_n$ polymers
where,M= Cu(II),Mn(II),Ni(II),Co(II),Zn(II)

## MATERIALS AND METHODS

### Materials

All the chemicals used were of pure grade. 5–amino 8–hydroxyl quinoline was obtained from local dealer.

### Synthesis of 5, 5'-(6-(diphenylamino)-1,3,5-triazine-2,4-diyl) bis(azanediyl)diquinolin-8-ol(DATBD)

To a suspension of 5–amino 8-hydroxyquinoline(3.2g, 0.02 mol), 4,6-dichloro-N,N-diphenyl -1,3,5-triazin-2-amine (3.16 g, 0.01 mol) in an acetone–water mixture was added. Then $K_2CO_3$ (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 precipitate, was neutralise and then filtered. The solid product was collected and dried to give DATBD(66% yield).The product melted with decomposition at above 250$^0$C (uncorrected).

### Synthesis of coordination polymer

A solution of metal (0.01 mol) in aqueous formic acid was added drop wise to a solution of DATBD (0.01 mol) in aqueous formic acid with stirring. The reaction mixture was heated on a water bath for 1.0hr. The reaction mixture was made alkaline by the addition of dilute aqueous 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 [DATBD -$M^{+2}$] (resultant product) was air-dried.

### Antimicrobial Activities

Antibacterial activity and antifungal activities of DATBD 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.

### MEASUREMENT

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, $H_2SO_4$ and $HClO_4$ each were added and then 1 gm of $NaClO_4$ 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 Brucker 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 5,5'-(6-(diphenylamino)-1,3,5-triazine-2,4-diyl) bis(azanediyl) diquinolin-8-ol (DATBD) was performed by a simple nucleophilic substitution reaction of 4,6-dichloro-N,N-diphenyl -1,3,5-triazin-2-amine and 5-amino 8-hydroxy quinoline. The resulting DATBD ligand was an amorphous colour powder. The ligand is characterized by elemental analysis as well as 1H 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:Analysis of DATBD ligand and its metal chelates**

| Empirical Formula | Mol. Cal g/mol | Yield % | Elemental Analysis (%) Found(Calcd) | | | |
|---|---|---|---|---|---|---|
| | | | C | H | N | M |
| $C_{33}H_{24}N_8O_2$ | 564 | 66 | 70.20 (70.15) | 4.28(4.25) | 19.85(19.81) | -- |
| $C_{33}H_{22}N_8O_2Cu..2H_2O$ | 661 | 72 | 59.86 (59.82) | 3.96(3.92) | 16.92(16.87) | 09.60(09.55) |
| $C_{33}H_{22}N_8O_2Ni .2H_2O$ | 658 | 65 | 60.30 (60.25) | 3.99(3.95) | 17.05(17.01) | 08.93(08.89) |
| $C_{33}H_{22}N_8O_2Co .2H_2O$ | 657 | 69 | 60.28 (60.24) | 3.99(3.95) | 17.04(17.00) | 08.96(08.92) |
| $C_{33}H_{22}N_8O_2Mn .2H_2O$ | 553 | 62 | 60.65 (60.61) | 4.01(3.96) | 17.15(17.11) | 08.41(08.37) |
| $C_{33}H_{22}N_8O_2Zn .2H_2O$ | 662 | 67 | 59.69 (59.65) | 3.95(3.90) | 16.88(16.84) | 09.85(09.81) |

**Table-2: spectral feactures and magnetic moment of metal chelates**

| Metal Chelates | BM | Electronic Spectral Data $cm^{-1}$ | Transitions | IR spectral feactures Common for all $cm^{-1}$ |
|---|---|---|---|---|
| DATBD -$Cu^{+2}$ | 1.90 | 22700<br>15885 | C.T<br>$^2Eg \rightarrow {}^2T_{2}g$ | 3200 Quinoline Moiety<br>2300<br>1640<br>1550<br>1100 C-O-M &<br>1450 O-M<br>730 M-N<br>650 |
| DATBD -$Ni^{+2}$ | 3.89 | 22990<br>14495<br>8000 | $^3A_2g \rightarrow {}^3T_1g(P)$<br>$^3A_2g \rightarrow {}^3T_1g(F)$<br>$^3A_2g \rightarrow {}^3T_2g$ | |
| DATBD -$Co^{+2}$ | 4.59 | 20710<br>19385<br>11980 | $^4T_1g(F) \rightarrow {}^4A_2g$<br>$^4T_1g(F) \rightarrow {}^4T_1g(P)$<br>$^4T_1g(F) \rightarrow {}^4T_2g$ | |
| DATBD -$Mn^{+2}$ | 5.02 | 22965<br>16385<br>15370 | $^6A_1g \rightarrow {}^6A_1g\ ({}^4Eg)$<br>$^6A_1g \rightarrow {}^4T_2g({}^4G)$<br>$^6A_1g \rightarrow {}^4T_1g({}^4G)$ | |
| DATBD -$Zn^{+2}$ | Diamagnetic | | ----- | |

### IR Analysis

The important infrared spectral bands and their tentative assignments for the synthesized ligand $H_2L$ and its coordination polymers were recorded as KBr disks and are shown in Table-2.

IR spectrum of ligand of DATBD show a broad band extended from 3200 to 2300 $cm^{-1}$ which might be responsible to phenolic -OH group bonded to N atom of 8-hydroxyquinoline moieties[20].

Several bands appeared between 1550 and 1640 $cm^{-1}$ region may arised from aromatic breathing and 3400 $cm^{-1}$ for –NH group. The IR band at 1580 $cm^{-1}$ (C=N of 8-quinolinol system) of DATBD ligand shifted to higher frequency side 1600 $cm^{-1}$ in the spectra of the metal complexes indicating involvement of nitrogen in the complexes formation[21], whereas the band at 1450 $cm^{-1}$ in the IR spectrum of DATBD 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 [22]. This was further confirmed by a weak band at 1100 $cm^{-1}$ corresponding to C–O–M stretching, while bands around 730 and 650 $cm^{-1}$ correspond to the N → M vibration [23].

### $^1$H NMR Analysis

The structure of the ligand (DATBD) was characterized by $^1$H NMR spectrum in DMSO- d6 system.

NMR

| | |
|---|---|
| (DMSO)6.6 – 8.8 ppm (20H) | Multiplet Aromatic |
| 5.3 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 $Cu^{+2}$ complex shows two broad bands, 15885 and 22700 $cm^{-1}$. The first band may be due to a $^2Eg \rightarrow {}^2T_2g$ transition, while the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the $Cu^{+2}$ metal complex [24,25]. The $Co^{+2}$ metal complex gives rise to two absorption bands at 20710 $cm^{-1}$, 19385 $cm^{-1}$ and 11980 $cm^{-1}$, which can be assigned $^4T_1g(F)\rightarrow{}^4A_2g$, $^4T_1g(F)\rightarrow{}^4T_1g(P)$ and $^4T_1g(F)\rightarrow{}^4T_2g$ transitions, respectively. These absorption bands and the $\mu_{eff}$ value indicate octahedral configuration of the $Co^{+2}$ metal complex [26,27]. The spectrum of $Mn^{+2}$ polymeric complex comprised three bands at 22965 $cm^{-1}$, 16385 $cm^{-1}$ and 15370 $cm^{-1}$. These bands may be assigned to $^6A_1g\rightarrow{}^6A_1g(^4Eg)$, $^6A_1g\rightarrow{}^4T_2g(^4G)$ and $^6A_1g\rightarrow{}^4T_1g(^4G)$ 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 $Ni^{+2}$ show three distinct bands at 22990 $cm^{-1}$, 14495 $cm^{-1}$ and 8000 $cm^{-1}$ are assigned as $^3A_2g\rightarrow{}^3T_1g(P)$, $^3A_2g\rightarrow{}^3T_1g(F)$ and $^3A_2g\rightarrow{}^3T_2g$ transition, respectively, suggesting the octahedral environment for $Ni^{+2}$ ion. The observed $\mu_{eff}$ values in the range 1.93–5.11 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 $310^0$ C. The rate of degradation becomes a maximum at a temperature between 400 and $500^0$ 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 $690^0$ C. Inspection of the thermograms of all coordinated polymer samples revealed that all samples suffered appreciable weight loss in the range of 150 to $280^0$ C. This may be due to the presence of a coordinated water molecule.

### Antibacterial(Antimicrobial) Activities

The increase in antimicrobial activity may be considered in light of Overtone's concept [30,31] and Tweedy's chelation theory[32,33]. On complication, 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 -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. The antibacterial and antifungal data obtained from analysis are shown in Table-3 and Table-4.

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

| Compounds | Gram +ve | | Gram –ve | | |
|---|---|---|---|---|---|
| | *Bacillus subtilis* | *Staphylococcus Aureus* | *klebsiella promioe* | *Salmonella typhi* | *E. coli* |
| DATBD | 30 | 29 | 32 | 32 | 33 |
| (Cu DATBD $(H_2O)_2)_n$ | 44 | 46 | 41 | 42 | 39 |
| (Co DATBD $(H_2O)_2)_n$ | 42 | 40 | 34 | 33 | 33 |
| (Ni DATBD $(H_2O)_2)_n$ | 40 | 36 | 36 | 35 | 36 |
| (Mn DATBD $(H_2O)_2)_n$ | 41 | 43 | 34 | 34 | 32 |
| (Zn DATBD $(H_2O)_2)_n$ | 40 | 42 | 39 | 42 | 33 |

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

| Compounds | **Zone of Inhibition at 1000 ppm (%)** | | | | |
|---|---|---|---|---|---|
| | *Aspergillus Niger* | *Candida albicans* | *Trichoderma harsianum* | *Mucor mucedo* | *Botrytis cinerea* |
| DATBD | 34 | 30 | 29 | 24 | 26 |
| (Cu DATBD $(H_2O)_2)_n$ | 45 | 35 | 44 | 40 | 44 |
| (Co DATBD $(H_2O)_2)_n$ | 37 | 34 | 36 | 34 | 35 |
| (Ni DATBD $(H_2O)_2)_n$ | 36 | 31 | 38 | 30 | 30 |
| (Mn DATBD $(H_2O)_2)_n$ | 37 | 31 | 36 | 30 | 35 |
| (Zn DATBD $(H_2O)_2)_n$ | 41 | 32 | 35 | 29 | 33 |

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 at present work show the following conclusions. The design synthesis of new bis-ligand have been successfully demonstrated. FT-IR, $^1$H-NMR spectral studies. We have synthesized 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 bioassay. The coordination polymers exhibited behave toxic for gram-negative bacteria (*E.coli*, *samonella 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 polymer 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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