Studies of novel Azo group containing co-ordination polymers

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ABSTRACT

Novel bis ligand namely 2,2'-(4,4'-(4,4'-sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl))bis(4,1-phenylene))bis(azanediyl)bis(oxomethylene)dibenzoic acid (SPPBA) has been prepared and characterized. The co-ordination polymers based on this bis ligand with transition metal ions like Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Mn\textsuperscript{2+} and Zn\textsuperscript{2+} were prepared and studied for their metal: ligand (M/L) ratio, IR and reflectance spectroscopies, magnetic properties, number-average molecular weight and by thermogravimetry. All the novel synthesized compounds were screened for their antibacterial and antifungal activities.

Keywords

Co-ordination polymer, Bisazo ligand, magnetic properties, Spectral studies and microbicidal activity.

Introduction

Traditionally, azo dyes are the most fundamental class of commercial dyes. The azo compounds are well colored and have been used as dyes and pigments [1, 2]. In addition, they have been studied usually because of their excellent thermal and optical properties in purposes such as toner [3, 4], ink-jet printing [5, 6] and oil-soluble lightfast dyes [7] optical recording medium [8–11]. In modern times, azo metal chelates have also paying attention due to their interesting electronic and geometrical features in link with their application for molecular memory storage, nonlinear optical elements and printing systems [9,11,12].

Recently, the study of co-ordination polymers has been made much progress [13, 14]. These polymers are known for their semiconducting catalytic properties, waste water treatment for metal recovery, in protective coating, as anti fouling paints and anti fungal properties [15, 16]. Such Coordination polymers are mostly derived from bi-chelating ligands in which metal ions and chelating agents are grouped alternatively. The joining segment of these two similar ligands are mainly –N=N–, SO\textsubscript{2}–, - CH\textsubscript{2}–, -O– [17-23]. Co-ordination polymers mostly derived from bichelating ligands in which metal ions and chelating agents arrayed alternatively [24-26]. The area in which the co-ordination polymers having azo dye moiety has been reported by one of author [DSR] [27]. In extension of previous work, the present article comprises the study of co-ordination polymers based on bisazo dye with phthalamic acid segment. Though phthalamic acid also act as good metal chelating agent.

In the present article, we report the synthesis, spectral studies and magnetic properties as well as antibacterial and antifungal activities of all the novel synthesized compounds and its metal chelates. Thus paper connecting with the studies of co-ordination polymers based on amic acid functionalized bisazo dye. The synthetic routes are shown in scheme-1.

Materials

4,4'-Sulfonyldianiline was obtained from S. D. Fine Chemical Ltd. All other chemicals used were of analytical grade.

Synthesis of (4,4'-(4,4'-sulfonylbis(4,1-phenylene))bis(diazene-2,1-diyl))dibenzoic acid (SPPBA):

A solution of 24.8g (0.1mole) of 4,4'-sulfonyldianiline in 250 ml 2N HCl was cooled in a round bottom flask, surrounded by ice and stirred with electric motor, when solution was cold, add few pieces of ice and 200 ml 1N nitrite solution was added drop wise from a dropping funnel at below 0\textdegree C with stirring. After completing the addition of nitrite mixture was stirred for about 10 mins. Then tested to make sure that it gave strong blue coloration with Congo red paper and weak blue test with starch iodide paper, added distilled water in it dilute the solution & kept it into ice-bath.

Experimental

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A solution of dil. HCl added into aniline 18.6 gm (0.2 mole) till Congo Red Paper gave blue color, now added above diluted diazonium solution into aniline solution gradually in cold situation, stirred it well and add sodium acetate solution till the neutralization of dye. Now washed the dye with cold water. The products were obtained in the form of dark red color, collected neutralization of dye. Now washed the dye with cold water. The yield-83%, M.P. 186-92°c (uncorrected). Analysis of ligand was tetra-n-butyl ammonium hydroxide (TBAH) in pyridine. The details procedure followed in titrations described here for SPPBA ligand.

**Non-aqueous conductometric titration.**

Experimental:

The ligand sample dried at 60°C was finely powdered and used for non-aqueous conductometric titration. A weighed amount of ligand sample (50 mg) was dissolved in 40 ml of anhydrous pyridine.

The solution was allowed to stand overnight for complete dissolution. This ligand solution was transferred into conductance cell and it was then stirred magnetically. The base tetra-n-butyl ammonium hydroxide (TBAH) (0.1 N), in pyridine was added to the conductance cell at regular interval of 0.01 ml of titrant beyond the stage of equivalence. The conductance measurement after addition of each volume of titrant base was carried out by allowing 2-3 minutes to lapse. During the titration the temperature of solution was maintained constant about 25°C, when the point of equivalence was exceeded, there was a continuous increase in conductance on addition of every additional aliquot of tetra-n-butyl ammonium hydroxide (TBAH) indicating the stage of complete neutralization of the –COOH groups in the given amount of ligand sample. The volume of base added is converted into millimoles of tetra-n-butyl ammonium hydroxide (TBAH) required for 100 gm of ligand. A plot of conductance against millimoles of tetra-n-butyl ammonium hydroxide (TBAH) per 100 gm of ligand was plotted. Inspection of such plot revealed two breaks. From the plot, the millimole per 100 gm of ligand sample corresponding to the break was noted. From this value, the number of –COOH groups was estimated. Each titration was reported twice as an independent experiments using different amount of the ligand sample. The two values estimated is agreed each other with 5% variation.

(I) Thus millimoles of TBAH required for complete neutralization of –COOH groups present in the sample was found by following formula using break of the titration curve. Finally two no. of COOH group calculated by:

\[
\text{No. of carboxylic groups} = \text{Mol. weight} \times 10^5
\]

Per mole of ligand per 100gm of sample

\[
E.g. \text{For (SPPBA)} = \frac{752 \times 269 \times 10^3}{X} = 2.02
\]

**Result and Discussion**

The typical conductometric titration curve of SPPBA Ligand has been shown in Fig II. Examination curves of the ligand reveal that, the two breaks observed the all curve. From the value of at second break the number of –COOH group for ligand has been calculated. It was found that the value of carboxylic group is about 2 the ligand.
Table-I Non-aqueous Conductometric titration of Estimation of – COOH groups

| Solvent: Anhydrous pyridine. |
| Reagent: 0.1 N tetra-n-butyl ammonium hydroxide (TBAH) in pyridine |

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Molecular weight gm</th>
<th>Millimoles of TBAH at break per 100 gm of sample</th>
<th>Estimated No. of – COOH group</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPPBA</td>
<td>752</td>
<td>269</td>
<td>2.02</td>
</tr>
</tbody>
</table>

**Determinant of azo group:**
The number of azo group for SPPBA ligand was estimated by method reported [33]. 35 mg. of sample was taken in the titration flask and dissolved in 25 ml. of diluted sulphuric acid (2:5 v/v) and carbon dioxide gas was passed into it for 5 minutes to displace air. 20 ml. of 0.10 N tinate chloride solutions was added into this air free solution. It was boiled for 5 minutes while maintaining the current of carbon dioxide. Cool the resulting solution and add 10 ml. of ammonium thiocyanate solution. It was titrated with standard 0.10 N ferric ammonium sulphate solutions. Blank set of 20 ml. of tinate chloride solution was also run. Number of azo group for each dye sample was estimated by this method indicates that there are two azo groups (-N=N-) present in the dye molecule. Examination of these data reveals that there are two azo groups (-N=N-) present in the dye molecules.

**Preparation of Co-Ordination Polymers**
All co-ordination polymers were synthesized by using metal acetate in general method described.

A warm and clear solution (pH–8) of SPPBA (7.52 gm, 0.01mole) in aq. NaOH (200 ml) was added to a solution of copper acetate (1.99 gm, 0.01mole) in 50% aq. formic acid (50 ml) with constant stirring. After complete addition of metal salt solution, the pH of reaction mixture was adjusted to about 5 with dilute ammonia solution. The polymer chelate was separated out in the form of suspension, digested on a water bath for one hour and eventually filtered, washed with hot water followed by acetone, dimethyl formamide (DMF) and then dried in air at room temp. The yields of all co-ordination polymers were almost quantitative.

**Measurements**

**Elemental Analysis**

The metal analysis of co-ordination polymers comprised decomposition of a weighted amount of the polymer followed by EDTA titration following standard procedures [33]. C, H, N analysis of SPPBA and its coordination polymers were carried out by C, H, N elemental analyzer (Italy).

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Table II Analytical and Spectral Data of the Co-Ordination Polymers of SPPBA

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical Formula</th>
<th>Formula Weight</th>
<th>Analyses (%) Found (Calculated)</th>
<th>% M</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% Yield</th>
<th>Dp</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPPBA</td>
<td>C₆H₁₀N₂O₅S</td>
<td>752.75</td>
<td></td>
<td>63.71</td>
<td>3.66</td>
<td>11.10</td>
<td>11.16</td>
<td>78</td>
<td>-</td>
</tr>
<tr>
<td>[Cu(SPPBA)H₂O]₄</td>
<td>Cu₂C₆H₈N₂O₅S₂H₂O</td>
<td>849.60</td>
<td></td>
<td>56.35</td>
<td>9.72</td>
<td>(9.89)</td>
<td>9.72</td>
<td>4065</td>
<td>81</td>
</tr>
<tr>
<td>[Co(SPPBA)H₂O]₄</td>
<td>Co₂C₆H₈N₂O₅S₂H₂O</td>
<td>844.99</td>
<td></td>
<td>56.70</td>
<td>9.74</td>
<td>(9.94)</td>
<td>9.74</td>
<td>4890</td>
<td>80</td>
</tr>
<tr>
<td>[Ni(SPPBA)H₂O]₄</td>
<td>Ni₂C₆H₈N₂O₅S₂H₂O</td>
<td>844.75</td>
<td></td>
<td>56.70</td>
<td>9.66</td>
<td>(9.54)</td>
<td>9.66</td>
<td>3998</td>
<td>76</td>
</tr>
<tr>
<td>[Mn(SPPBA)H₂O]₄</td>
<td>Mn₂C₆H₈N₂O₅S₂H₂O</td>
<td>841.00</td>
<td></td>
<td>56.99</td>
<td>9.66</td>
<td>(9.99)</td>
<td>9.66</td>
<td>4856</td>
<td>77</td>
</tr>
</tbody>
</table>

Table III FT-IR data of ligand SPPBA and its coordination polymers

<table>
<thead>
<tr>
<th>Compound</th>
<th>Compounds</th>
<th>IR Bands(cm⁻¹)</th>
<th>Transitions</th>
<th>Magnetic momentum(μe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPPBA</td>
<td>Penicillium expansum</td>
<td>1591 1675</td>
<td>5630 1646</td>
<td></td>
</tr>
<tr>
<td>[Cu(SPPBA)H₂O]₄</td>
<td>1575 1641</td>
<td>1556 1633</td>
<td>3385 1633</td>
<td></td>
</tr>
<tr>
<td>[Co(SPPBA)H₂O]₄</td>
<td>1565 1641</td>
<td>1556 1621</td>
<td>3389 1621</td>
<td></td>
</tr>
<tr>
<td>[Ni(SPPBA)H₂O]₄</td>
<td>1571 1650</td>
<td>1557 1624</td>
<td>3375 1624</td>
<td></td>
</tr>
<tr>
<td>[Mn(SPPBA)H₂O]₄</td>
<td>1561 1632</td>
<td>1554 1610</td>
<td>3366 1608</td>
<td></td>
</tr>
<tr>
<td>[Zn(SPPBA)H₂O]₄</td>
<td>1590 1671</td>
<td>1559 1632</td>
<td>3400 1632</td>
<td></td>
</tr>
</tbody>
</table>

*Zn- containing polymers are diamagnetic in nature

Table IV Reflectance spectral and magnetic moment data of the ligand SPPBA containing coordination polymers

<table>
<thead>
<tr>
<th>Coordination polymers</th>
<th>Absorption band(cm⁻¹)</th>
<th>Transitions</th>
<th>Magnetic moment(μe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(SPPBA)H₂O]₄</td>
<td>22750</td>
<td>Eg → T₂g(F) charge transfer</td>
<td>1.89</td>
</tr>
<tr>
<td>[Co(SPPBA)H₂O]₄</td>
<td>15560</td>
<td>T₁g(F) → A₁g, T₂g(F) → T₂g(P)</td>
<td>2.99</td>
</tr>
<tr>
<td>[Ni(SPPBA)H₂O]₄</td>
<td>14780</td>
<td>A₁g → T₂g(F)</td>
<td>4.18</td>
</tr>
<tr>
<td>[Mn(SPPBA)H₂O]₄</td>
<td>15708</td>
<td>A₁g → T₂g(F)</td>
<td>4.99</td>
</tr>
</tbody>
</table>

Table V TGA data of SPPBA containing coordination polymers

<table>
<thead>
<tr>
<th>Co-ordination polymers</th>
<th>% Weight loss at different temperatures(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(SPPBA)H₂O]₄</td>
<td>4044</td>
</tr>
<tr>
<td>[Co(SPPBA)H₂O]₄</td>
<td>4856</td>
</tr>
<tr>
<td>[Ni(SPPBA)H₂O]₄</td>
<td>4890</td>
</tr>
<tr>
<td>[Mn(SPPBA)H₂O]₄</td>
<td>3998</td>
</tr>
<tr>
<td>[Zn(SPPBA)H₂O]₄</td>
<td>4065</td>
</tr>
</tbody>
</table>

Table VI Antibacterial Activities of Co-Ordination Polymers

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Gram +Ve</th>
<th>Gram -Ve</th>
<th>Salmonella typhi</th>
<th>E.coli</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(SPPBA)H₂O]₄</td>
<td>74</td>
<td>79</td>
<td>61</td>
<td>60</td>
</tr>
<tr>
<td>[Co(SPPBA)H₂O]₄</td>
<td>65</td>
<td>64</td>
<td>64</td>
<td>72</td>
</tr>
<tr>
<td>[Ni(SPPBA)H₂O]₄</td>
<td>75</td>
<td>72</td>
<td>66</td>
<td>70</td>
</tr>
<tr>
<td>[Mn(SPPBA)H₂O]₄</td>
<td>72</td>
<td>75</td>
<td>82</td>
<td>77</td>
</tr>
<tr>
<td>[Zn(SPPBA)H₂O]₄</td>
<td>55</td>
<td>71</td>
<td>70</td>
<td>76</td>
</tr>
</tbody>
</table>

Table VII Antifungal Activities of Co-Ordination Polymers

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Penicillium expansum</th>
<th>Nigrospora Sp.</th>
<th>Trichothecum Sp.</th>
<th>Rhizopus nigricum</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(SPPBA)H₂O]₄</td>
<td>74</td>
<td>79</td>
<td>61</td>
<td>60</td>
</tr>
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<td>64</td>
<td>64</td>
<td>72</td>
</tr>
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</tr>
<tr>
<td>[Mn(SPPBA)H₂O]₄</td>
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<td>75</td>
<td>82</td>
<td>77</td>
</tr>
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<td>55</td>
<td>71</td>
<td>70</td>
<td>76</td>
</tr>
</tbody>
</table>
Antifungal Activities

The fungicidal activities of all the compounds were studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were Penicillium expansum, Nigrospora Sp., Trichothecium Sp. and Rhizopus nigricum. The antifungal activity of ligand and its coordination polymers were measured on each of these plant pathogenic organisms on a potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200 gm, dextrose 20 gm, agar 20 gm and water one liter. Five days old cultures were employed. The compounds to be tested were suspended (1000 ppm) in a PDA medium and autoclaved at 120°C for 15 min. at 15atm. pressure. These medium were poured into sterile Petri plates and the organisms were inoculated after cooling the Petri plates. The percentage inhibition for fungi was calculated after five days using the formula given below:

Percentage of inhibition = \( \frac{100(X-Y)}{X} \)

Where, \( X \) = Area of colony in control plate
\( Y \) = Area of colony in test plate

Results and Discussion

The synthesis of the novel bis ligand 2,2′-(4,4′-(4,4′- sulfonyl)bis(4,1-phenylene) bis (diazenaz-2,1-diyl))bis(4,1-phenylene)bis(azanediyl)bis(oxomethylene)dibenzoic acid(SPPBA) has not been reported previously. The ligand SPPBA was isolated in the form of a dark red crystalline powder. It was soluble in DMF, dioxane, acetone, acetic acid and dilute hydrochloric acid.

The important IR spectral features are a broad band extending from 3200-3600 cm\(^{-1}\) OH of COOH. The band around 1690 cm\(^{-1}\) may due to carbonyl group. The bands around 1660, 3400 cm\(^{-1}\) may be due to amide group. The strong band at 1625 cm\(^{-1}\) may be due to \( N= N \) group. The others bands are at their respective positions.

The NMR data of SPPBA shown in experimental part are also confirming the structure of SPPBA.

The co-ordination polymers derived from SPPBA were insoluble in common organic solvents. Hence, it is not possible to characterize the co-ordination polymers by molecular mass using conventional methods like osmometry, viscometry etc. The co-ordination polymers did not melt up to 360°C. Examination of the metal content in the polymers (Table-I) revealed that the 1:1 metal: ligand (M: L) stoichiometry for all the polymers. The broad band at 3400-3100 cm\(^{-1}\) in the IR spectrum of SPPBA.Cu\(^{2+}\) reveals certain characteristic differences. The broad band at 3400-3100 cm\(^{-1}\) for SPPBA has virtually disappeared for the spectra of polymers. However the weak bands around 3200 cm\(^{-1}\) in the spectra of SPPBA.Co\(^{2+}\), SPPBA.Ni\(^{2+}\), SPPBA.Mn\(^{2+}\) indicate the presence of water molecules which may have been strongly absorbed by the polymer sample. An indication of this aspect is made later. The weak band around 1110 cm\(^{-1}\) is attributed to the C-O-M stretching frequency. The band at 1430 cm\(^{-1}\) in the IR spectrum of SPPBA is attributed to the in-plane OH deformation [35]. The band is shifted towards higher frequency in the spectra of the polymers indicating formation of metal-oxygen bond. These feature suggest that the structure of the co-ordination polymer.

Magnetic moments (\( \mu_{\text{eff}} \)) of polymeric chelates are given in Table-II. The diffusion electronic spectrum of SPPBA.Cu\(^{2+}\) coordination polymers shows two broad bands around 15,550 cm\(^{-1}\) and 22,750 cm\(^{-1}\). The first bands may be due to \( ^2T_g \rightarrow E_g \) transition. While the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the SPPBA.Co\(^{2+}\) polymers. The higher values of \( \mu_{\text{eff}} \) of the SPPBA.Cu\(^{2+}\) polymer supports this view. The SPPBA.Ni\(^{2+}\) and SPPBA.Co\(^{2+}\) polymers give two absorption bands respectively at 14,780 and 22,750 cm\(^{-1}\) and at 15,650 and 22,110 cm\(^{-1}\) which can be assigned respectively to \( ^3A_g \rightarrow ^3T_{1g(P)} \), \( ^4T_{1g(2)} \rightarrow ^2T_{1g(P)} \) transitions. These absorption bands and the values of \( \mu_{\text{eff}} \) indicate an octahedral configuration for the SPPBA.Ni\(^{2+}\) and SPPBA.Co\(^{2+}\) Polymers.

The TGA data for the polymers are presented in Table-V. The weight loss of the polymer samples at different temperatures indicates that the degradation of the polymers is noticeable beyond 300°C. The rate of degradation becomes a maximum at a temperature lying between 400°C and 500°C depending upon the nature of the polymers. Each polymer lost about 55% of its weight when heated up to 600°C. Inspection of the thermograms of SPPBA.Cu\(^{2+}\), SPPBA.Mn\(^{2+}\) and SPPBA.Ni\(^{2+}\) samples revealed that these samples suffered appreciable weight loss in the range 150 to 280°C. This may due to the presence of water strongly absorbed by the polymers. It has also been indicated earlier that the IR spectra of these three polymer samples have OH bands at around 3200 cm\(^{-1}\) due to associated water.

On the basis of the relative decomposition (% wt. loss) and the nature of thermograms, the co-ordination polymers may be arranged in order in increasing stability as:

\[ \text{Cu} < \text{Ni} < \text{Co} < \text{Mn} \]

This trend also coincides with the stability order already reported for the metal oxinates and for co-ordination polymers of SPPBA [36].

The antimicrobial activity of SPPBA and its coordination polymers are presented in Table-VI and VII. The data suggest that all the samples are toxic to bacteria or fungus. The data also suggest that the percentage of bacteria or fungus is inhibited in the range of 63 to 85% depending upon the biospecies and coordination polymers. All the polymers have good microbicidal activity.

References