Synthesis and X-ray diffraction studies of 4-[2'-hydroxy salicylidene-5' (2"-thiazolylazo)] methoxy benzene

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The new compounds having azo Schiff base characteristics have been synthesized by condensing 5-(2'-thiazolylazo) salicylaldehyde with para-substituted aniline and subjected for structural characterization. X-ray diffraction study has been carried out for 4-[2'-hydroxy salicylidene-5'-(2"-thiazolylazo)] methoxy benzene. The structure of compound is found to be tetragonal, belonging to non-primitive system. The strain broadening effects are also examined and discussed.

[Keywords: Azo Schiff base, X-ray diffraction, Benzene]

1 Introduction

Schiff bases are considered to be a very important class of organic compounds having wide range of applications, specially in coordination complexes. In such studies, aniline has been widely used as a precursor for the preparation of bidentate Schiff bases, by simple condensation of their primary amino group with the carbonyl compounds. Bidentate and tridentate Schiff bases derived from azo-substituted salicylaldehyde and substituted anilines are the simplest ones. Schiff base and thiazol compounds bearing azo and azomethine group are known to possess bacteriostatic, anticancerous and other biochemical properties. It is necessary to know the structural details such as, solid-state properties, including space groups, cell parameters etc. of such compounds so that, modelling for useful applications can be made. The authors planned a programme of synthesis, characterization and studies of coordinating properties of such ligands. In this work, they report X-ray diffraction properties of 4-[2'-hydroxy salicylidene-5'-(2"-thiazolylazo)] methoxy benzene, which have been found to be good complexing ligands.

2 Experimental Details

All the chemicals and solvents used were of AR grade and 5-(2'-thiazolylazo) salicylaldehyde was prepared. The 4-[2'-hydroxy salicylidene-5'-(2"-thiazolylazo)] methoxy benzene ligand (Schiff base) was obtained as follows; 5-(2'-thiazolylazo)salicylaldehyde (0.01 mole) in 50 ml ethanol and para methoxy aniline (0.01 mole) in ethanol (15 ml) were mixed together and refluxed for three hours on water bath. It was then cooled and poured into the crushed ice. The separated solid was filtered, purified by repetitive re-crystallization from ethanol and finally dried in air. The purity was checked by thin layer chromatography (TLC).

The colour, yield, melting point and result of elemental analysis are as under.

Colour - light brown, yield - 70%, MP-154°C, IR - 1625 cm⁻¹ ν (C=N), 1550 cm⁻¹ ν (N=N), 1280 cm⁻¹ ν (C-O).


Fig. 1 — Structure of ligand

Structure of the ligand was tentatively fixed, as given in Fig. 1, on the basis of elemental analysis...
Table 1 — XRD data of 4-[2'-hydroxysalicylidene-5' (2''-thiazolylazo)] methoxy benzene ligand

<table>
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<tr>
<th>Peak No</th>
<th>2θ in degree</th>
<th>d(obs) Å</th>
<th>(calc) Å</th>
<th>ϕ(obs)</th>
<th>ϕ(calc)</th>
<th>hkl</th>
<th>RI</th>
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<td>1</td>
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<td>13.4726</td>
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<td>2</td>
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<td>18.85</td>
<td>4.7048</td>
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<tr>
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<td>1.5742</td>
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<td>0.4035</td>
<td>0.4040</td>
<td>305</td>
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</table>

IR, UV and 1H NMR spectral studies. The XRD spectra of ligand were recorded in the range of 2θ from 0 to 80° on Philips PW-3710 diffractometer attached to digitized computer along with graphical assembly in which CuKα radiation source, connected with the tube Cu-Ni, 25kV/20mA was used.

Table 2 — X-ray parameters of 4-[2'-hydroxy salicylidene-5'- (2''-thiazolylazo)] methoxy benzene

| Structure | tetragonal |
| Space group | 14/m mmm |
| Lattice group | 4/m |
| Symmetry of lattice | non-primitive |
| Lattice parameters | a = b = 12.4688 Å, c = 8.4974 Å |
| Bond angles | α = β = γ = 90° |
| Vol. of unit cell | 1321.11 Å³ |
| Radius of atom | 5.3991 Å |
| Vol. of atom | 658.91 Å³ |
| Packing fraction | 49.42 % |
| Density (Experimental) | 0.85 gr/cc |
| (Theoretical) | 0.80 gr/cc |
| Pore fraction | 28.52 % |
| Thickness of particle | 245.02 Å |

3 Results and Discussion

The X-ray diffraction spectrum of the Schiff base 4-[2'-hydroxy salicylidene-5'- (2''-thiazolylazo)] methoxy benzene is shown in Fig. 2. The presence of sharp reflections in XRD pattern indicates the formation of a single-phase compound. The XRD pattern shows ten reflections between 2θ range from 0 to 80° with maxima at 2θ=18.85° corresponding to the value of d = 4.7048 Å.

All main peaks have been indexed by using appropriate methodology and use of computer program (PowdMulti, Version 2.3). The indexing is confirmed on the basis of correction obtained between observed and calculated d and ϕ values based on characteristics of symmetry consideration. The method also yielded hkl (Miller indices) values. The 2θ values and relative intensities corresponding to the prominent peaks have been listed in Table 1.
Assuming the ligand as a tetragonal system, the unit cell lattice parameters are found to be $a=b=12.4688\,\text{Å}$ and $c=8.4974\,\text{Å}$, respectively, while the cell volume was $1321.11\,\text{Å}^3$. The unit cell parameters were refined by weight-fraction method. The refined parameters were used for finding out space group and Laue group, using the data from international table on X-ray crystallography. In conjunction with refined cell parameters, the condition for tetragonal system ($a=b=c$ and $a=b=c=90°$) for the ligand was tested and found to be in good agreement. The standard deviation of $Q's$ were of the order of $10^{-4}$. On the basis of the magnitude of deviation, it can be said that, the way of processing adopted for evaluation of cell parameters, is appropriate, indicating the non-primitive tetragonal structure for the sample. The observed tetragonal structure for the compound is in agreement with the report on similar compounds by Sami & Jejurkar. The experimental value of density ($\rho$) has been calculated by using the specific gravity method. The number of atoms per unit cell, $n$, was calculated by using the equation:

$$n = \rho V/N/M$$

where, $M$ is the molecular weight, $V$ is the unit cell volume and $N$ is the Avogadro number. With this $n$ value, the theoretical density was calculated and found to be in good agreement with the experimental value. The other parameters such as, pore fraction, packing fraction, particle size and radius of atoms were calculated. All the values are tabulated in Table 2.

The particle size of the sample was calculated by using an equation:

$$t = 0.9 \lambda / B \cos \theta$$

The parameters can be distinguished between natural particle size and particle size due to broadening effect. This was done by calculating full width at half maximum ($B$), corresponding to the Bragg's 20 values. The nature and behaviour of these values for the present ligand are shown in Fig. 3.

The plot of $B \cos \theta$ versus $\sin \theta$ was found to be a straight line, parallel to X-axis, indicating the absence of any strain, caused by homogeneous lattice distortion and compositional fluctuations. Hence, present ligand seems to be homogeneous with respect to the particle size distribution.

Acknowledgement

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