X-ray diffraction studies of 2-[2'-hydroxy salicylidene 5'-(2"-thiazolylazo)] phenol

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Abstract   The Schiff base, 2-[2'-hydroxy salicylidene 5'-(2"-thiazolylazo)] phenol has been synthesized by condensation of 5-(2' thiazolylazo) salicylaldehyde with 2-aminophenol The purified sample is characterized and has been subjected to X-ray diffractometry to elucidate structural information The structure of the sample is found to be tetragonal belonging to non-primitive system The strain broadening effects are also examined and discussed

The importance of Schiff bases can be related to the presence of C = N group in common with the natural systems and also to the fact that their easy formation gives us opportunity of building wands of different structures The Schiff bases containing azo and azomethine group are known to possess bacteriostatic [1] anticancerous [2] and other biochemical properties [3, 4]. It is also known that the derivatives of thiazole have been used as anticancer [5] and anthelmintic [6] agents. The fact that the enhancement of biological activity and toxicity is generally achieved by complexing these biological active compounds with metal ion [7]. It is therefore, of considerable interest to know the coordinating behaviour of Schiff bases as ligand. We have attempted here to report the synthesis of one such Schiff base, 2-[2' hydroxy salicylidene 5'-(2"-thiazolylazo) phenol and its structural parameters by X-ray diffractometry.

All the chemicals used were of reagent grade.5-(2'-thiazolylazo)salicylaldehyde was prepared as reported earlier [8] The Schiff base was synthesized by condensing this

aldehyde with 2-aminophenol in methanol medium . To a hot methanolic solution (100 cm¹) of 5-(2'-thiazolylazo) salicylaldehyde (5 g , 0.02 mole) was added methanolic solution (10cm¹)of 2-aminophenol (1 4359g ,0.02 mole) and it was refluxed for 3-4 hours on water bath . After cooling the reaction mixture was poured in ice-cold water . The separated solid was filtered , washed with water, dried and recrystallised from ethanol . The purity of the product was checked by Thin Lay Chromatography (TLC).

Colour, yield, melting point and elemental analysis are as follows :

Brick red, yield 64 % . Mp. - 137°C , IR- 1618 cm⁻¹ ($\nu C = N$), 1593 cm⁻¹ ($\nu N = N$), 1271 cm⁻¹(νC -O). Anal. Cald. for $C_{16}H_{12}N_4O_2S$, C 59.25 % , H 3.73%, N 17.27% found C 59.68%, H 3.83%, N 17.43%.

Structure of the molecule was tentatively fixed as given in Figure 1 on the basis of elemental analysis IR , UV and ¹HNMR spectral studies.

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The XRD spectra was recorded on Philips PW 3710 diffractometer attached to a digital computer along with graphical assembly The Cuk_{α} radiation (Cu- Ni 25 kV /20 mA) was used for analysis.
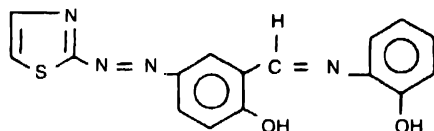

Figure 1. Structure of ligand

The X-ray diffraction pattern (XRD) of 2- | 2'- hydroxy Salicylidene 5' -(2" thiazolyla/o)] phenol is shown in Figure 2 The XRD pattern shows fifteen reflection peaks in the range of $2\theta(CuK\alpha)$ = 10 to 80° with maximum peak at 2θ = 14.835° corresponds to a value of d = 5.967 Å.
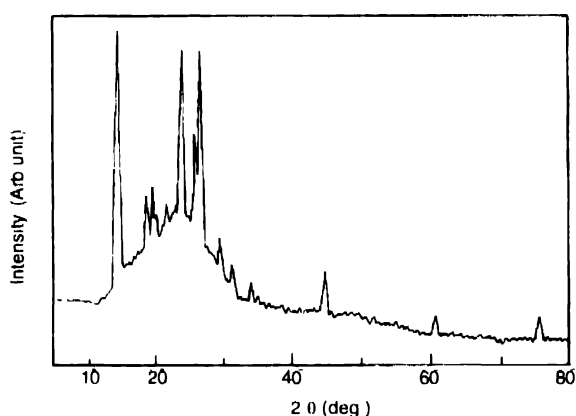

Figure 2. X-ray diffractogram of ligand

Table 1. Powder X-ray diffraction data of 2-[2'-hydroxysalicylidene 5'-(2"-thiazolyla/o)] phenol

Peak No	2θ deg	d_{ob} Å	d_{cal} Å	Q_{ob}	Q_{cal}	hkl	RI %	δ Qx10⁴
1	14.835	5 967	5 976	0 0281	0 0280	130	100	2 00
2	15.210	5 820	5 803	0 0295	0 0297	031	36 4	2 00
3	19.115	4.639	4 657	0 0465	0 0461	113	25 7	2.00
4	20 025	4 430	4 454	0 0509	0 0504	330	29 6	3 00
5	21 975	4 041	4 066	0 0612	0 0605	241	25.0	3 00
6	22 279	3 987	3 986	0 0629	0.0629	223	27 3	3 00
7	24 275	3 663	3 664	0 0745	0 0745	341	79 2	3 00
8	26 285	3 387	3.371	0.0871	0 880	342	60 7	3 00
9	26 925	3 308	3 317	0 0914	0 0909	333	98 5	3.00
10	29 895	2 986	2 988	0.1121	0 1120	460	20 1	4.00
11	31 395	2 847	2.843	0 1134	0 1137	025	11 9	4 00
12	34 030	2 632	2 634	0 1143	0 1141	163	7 4	4.00
13	44 569	2 031	2.029	0.2424	0.2429	227	13.2	5.00
14	61 315	1 511	1.512	0 4382	0 4373	159	1.4	6 00
15	76 711	1.241	1 245	0 6490	0.6447	859	5 2	7.00

The indexing of the spectrogram with respect to the prominent peaks have been carried out by using computer software by trial and error method [8]. The programme was modified in such a way that a good fit could be obtained between observed and calculated d and Q and having symmetry constraints. The method also yielded hkl (miller indices) values The relative intensities corresponding to prominent peaks have been calculated (Table 1).

Comparison of value of d and Q for present ligand shown in Table 1 reveals that there is good agreement between the calculated and observed values of d and Q on the basis of assumption of tetragonal structure. The structure yields values for lattice constant and cell volume at $a = b$ = 18.898 Å, c = 14.907 Å and V = 5323.80 Å³ respectively. In conjunction with such cell parameters, the condition [9, 10] such as $a = b \neq c$ and $\alpha = \beta = \gamma$ = 90° required for the sample to be tetragonal were tested and found to be satisfactory. Hence, it is concluded that the structure of the present ligand is tetragonal.

The experimental density of sample was determined by using specific gravity method, which further enabled to calculate the volume of unit cell. The number of atoms (n) per unit cell were calculated by using equation ($\rho = nM / NV$) and was found to be 2. The other parameters such as pore fraction, packing fraction, particle size, radius of atom were then calculated. The space group and point group of the sample were noted from International Table for X-ray Crystallography [11]. These values are presented in Table 2.

Table 2. X-ray parameters of 2-[2' hydroxy salicylidene 5'-(2" thiazolylazo)] phenol

Structure	Tetragonal
Space group	I4/mmm
Laue group	4 / m
Point group	4 / mmm
Symmetry of lattice	Non primitive
Lattice parameters	18 898 Å
	14 907 Å
Bond angles	$\alpha = \beta = \gamma$ = 90°
Vol of unit cell	5323.80 Å³
Radius of atom	8 183 Å
Vol of atom	2295.23 Å³
Packing fraction	43 11%
Density ρ (Experimental)	0 187 gr/cc
(Theoretical)	0.202 gr/cc
Pore fraction	31.07%
Thickness of particle	248.15 Å

The particle size of the sample was calculated by using a equation $t = 0.9\lambda / B \cos\theta$, where λ is wavelength of X-ra

radiation in Å, B is the half angular width in radians and θ is Bragg's diffraction angle. For the determination of particle size, the corresponding peak was enlarged for better accuracy in measuring the half width and then particle size of the sample was calculated. This parameter makes it possible to distinguish between natural particle size and particle size due to broadening effect. This was done by plotting a graph of $B \cos\theta$ versus $\sin\theta$. The nature and behavior of these values are presented
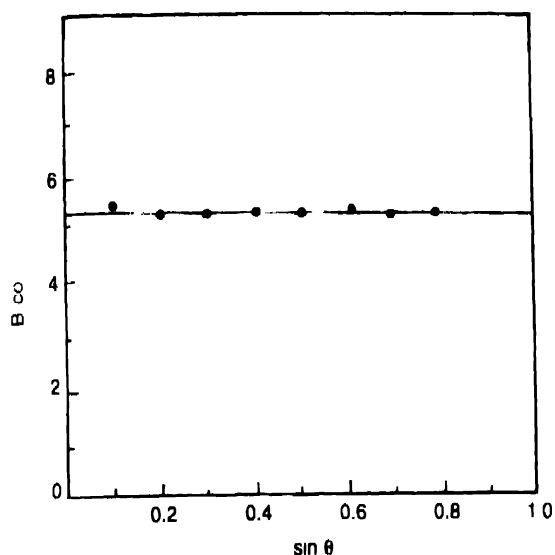

igure 3. Analysis of homogeneity

graphically in Figure 3. It is found to be straight line parallel to X axis indicating the absence of any strains caused by inhomogeneous lattice distortions and compositional fluctuations. Hence the sample under investigation is found to be homogenous with respect to the particle size distribution.

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