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

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Abstract · The ligand 2-[2'hydroxy salicylidene 5'-(2''-thiazolylazo)] benzoic acid was synthesized by condensing 5-(2'-thiazolylazo) salicylidehyde and 2-amino benzoic acid. The purified sample has been subjected to the 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

Keywords · Azo compound, X-ray diffraction.

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Thiazole derivatives have attracted considerable attention by Chemists since many of them have been used in medicinal therapy [1, 2]. Derivatives of thaizole have been widely used as antibacterial [3], antifungal [4], anticancer [5] and anthelmintic [6] agents. It is known that the activity of many enzymes depends upon the interaction of thiazole group with transition metal ion. It is therefore of considerable interest and importance to know the detail about co-ordinating behaviour of ligands containing this important functional group, we have synthesized one such ligand 2-[2'-hydroxy salicylidene 5'-(2''thiazolylazo)] benzoic acid and examined for structural properties.

All the chemicals used were of AR grade. 5-(2'-thiazolylazo) salicylaldehyde was prepared by diazotisation of 2 aminothiazole (1 g, 0.01 mole) using conc. HCl and $NaNO_2$ following the method reported earlier [7]. The diazotised solution so formed was consequently coupled with salicylaldehyde (1.28 g, 0.01 mole) dissolved in 15 ml of aqueous 2 N NaOH. The reaction mixture was stirred for 1 h at 0°C and then allowed to warm slowly at room temperature. The brown precipitate formed was filtered, washed with water and recrystallised from ethanol.

5-(2'-thiazolylazo) salicylaldehye (5g, 0.02 mole) was dissolved in ethanol (100 cm^3) to this, a solution of 2-amino benzoic acid (2.939 g, 0.02 mole) in ethanol (10 cm^3) was added and resulting mixture was refluxed for 3-4h on water bath. After cooling the solution was poured in ice-cold water, the separated solid was filtered, dried and purified by repetitive recrystallisation with ethanol. The purity of the product was checked by TLC (Thin layer chromatography).

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

Brick red, yield 60%, Mp.–137°C, IR – 1619 cm^{-1} (ν C = N), 1589 – cm^{-1} (ν N = N), 1281 cm^{-1} (ν C-O). Anal. Cald. for $C_{17}H_{12}N_4O_3S$, C: 57.94%, H: 3.43% N: 15.89% found C: 56.74%, H: 3.46%; N: 16.09%.

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

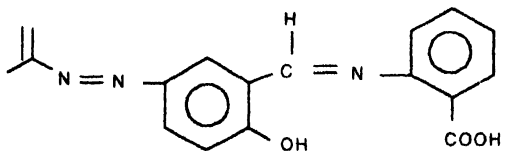

Figure 1. Structure of ligand.

The XRD (X-ray diffraction) spectra were recorded on Phillips PW 3710 diffractometer attached to a digitized computer alongwith graphical assembly in which CuKα radiation source connected with the tube Cu-Ni 25 kV/20 mA was used.

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The X-ray diffractogramme of 2-[2' hydroxy salicylidene 5'-(2" thiazolylazo)] benzoic acid (Figure 2) records twenty one reflections between 10° and 100° (2θ) with maxima at $2\theta = 27.165°$ corresponding to a value of $d = 3.280$ Å.

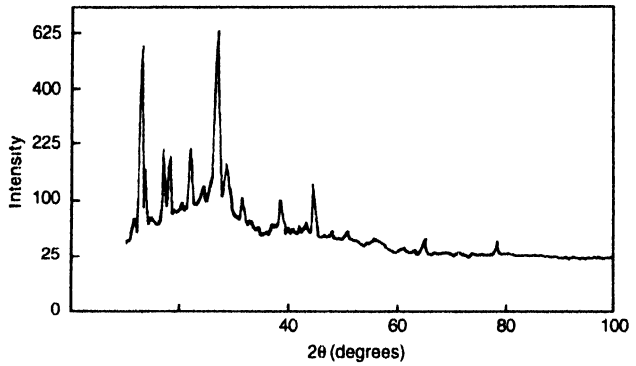

Figure 2. X-ray diffractogramme of ligand

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

The experimental density was determined by using specific gravity method. Which further enabled to calculate the volume of unit cell. The number of atoms per unit cell n were calculated by using the equation ($\rho = nM / NV$) and was found to be 2. With this number, the theoretical density was fixed. The other

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

Structure	Tetragonal
Space group	I4/mmm
Laue group	4/m
Point group	4/mmm
Symmetry of lattice	Non primitive
Lattice parameters	19 612 Å
	14.907 Å
Bond angles	$\alpha = \beta = \gamma = 90^0$
Vol of unit cell	5733.69 Å^3
Radius of atom	8 492 Å
Vol of atom	2565 18 Å^3
Packing fraction	44.74%
Density ρ (Experimental)	0 184 gr/cc
(Theoretical)	0 204 gr/cc
Pore fraction	27 43%
Thickness of particle	257 61 Å

Table 1. Powder X-ray diffraction data of 2-[2'-hydroxy salicylidene 5'-(2"-thiazolylazo)] benzoic acid

Peak No.	2θ deg	d_{obs} Å	d_{cal} Å	Q_{obs}	Q_{cal}	hkl	RI %	$\delta Q \times 10^4$
1.	12.010	7.363	7.454	0.0184	0.0180	002	5 3	2 00
2.	13.410	6.597	6.565	0 0230	0 0232	112	95.5	2 00
3.	14.165	6 247	6 287	0.0256	0 0253	221	16 2	2 00
4.	17 525	5.056	5 077	0 0391	0.0388	222	28 8	2 00
5.	18 390	4.820	4 817	0.0430	0 0431	013	26 0	2 00
6.	20.290	4 373	4.385	0 0523	0.0520	240	5.3	3.00
7.	22.195	4.001	4.010	0.0624	0.0622	142	26 4	3.00
8	24.355	3 651	3 661	0.0750	0 0746	014	11 9	3.00
9.	25.200	3.531	3.538	0.0802	0.0799	251	10.1	3.00
10.	25.920	3.434	3.436	0.0848	0.0847	143	14.4	3.00
11.	27.165	3.280	3 281	0.0930	0.0929	351	100 0	3.00
12	28 630	3 115	3 101	0.1030	0.1040	260	17 1	4.00
13.	31.625	2.826	2 823	0 1251	0.1255	125	9.6	4.00
14.	33.030	2.709	2.705	0.1362	0.1367	163	2 5	4.00
15.	38.375	2.343	2.349	0 1821	0.1813	281	8.7	5 00
16.	41.985	2.150	2.149	0.2163	0.2165	265	1.7	5.00
17.	43.625	2.073	2.072	0.2327	0.2329	573	2.3	5.00
18.	44.165	2.029	2.031	0.2428	0.2425	175	19.1	5.00
19.	51.195	1.782	1.784	0.3146	0.3141	067	1 9	6.00
20.	64.925	1.435	1.438	0.4856	0.4838	2310	3.5	7.00
21.	78.045	1.223	1.225	0.6681	0.6661	1049	2.3	7 00

parameters such as pore fraction, packing fraction, particle size, radius of atom were then calculated. Space group and point group of the ligand were noted from International Table for X-ray crystallography [9]. All these values are presented in Table 2.

Comparison of the value of d and Q reveals a 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 constants and cell volume as $a = b$ 19.612 Å, c = 14.907 Å and V = 5733.69 Å^3 respectively. These values were further refined by using weight fraction method. The refined parameters were used for finding out Space group and Laue group. In conjunction with such cell parameters, the condition [10, 11] such as $a = b \neq c$ and $\alpha = \beta = \gamma = 90^0$ 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.

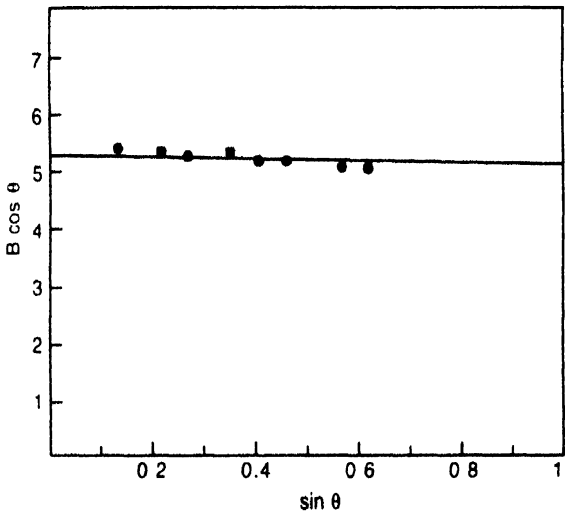

Figure 3. Analysis of homogeneity.

The particle size of the sample was calculated by using an equation $t = 0.9\ \lambda / B \cos\theta$. These parameters can distinguish between natural particle size and particle size due to broadening effect. This was done by calculating fullwidth at half maximum (B) corresponding to its Bragg's θ and thereby computing cos and sin values. The nature and behavior of these values for the present ligand are shown graphically in Figure 3.

A plot of $B \cos\theta$ *versus* $\sin\theta$ was found to be a straight line, parallel to X axis indicating an absence of any strains caused by inhomogeneous lattice distortions and compositional fluctuations. Hence, present sample seems to be homogeneous with respect to the particle size distribution.

References

[1] M Akabar Ali and S E Livingstone *Coordination Chem Rev* **13** 101 (1974)

[2] R J Sundberg and R B Martin *Chem Rev* **74** 471 (1974)

[3] N H Bhavsar, A V Kasture and K R Desai *Asian J Chem* **11** 165 (1999)

[4] S G Wadodkar and A V Kasture *J Indian Chem Soc* **61** 374 (1984)

[5] H C Gerg and R A Sharma *J Pharm Soc* **59** 348 (1970)

[6] B C Sharma *Bull Chem. Soc Jpn* **40** 2422 (1967)

[7] H H Hovind *The Anal Rev* **100** 769 (1975)

[8] R T Pattar, K R Choukimath and V G Tulasigiri *Indian J Phys* **73A** 343 (1999)

[9] J D H Donney and David Haker *Tables of Space & Group Criteria, Crystallographiques Naturalist Canadien* **67** 33 and 160 (1940)

[10] B D Cullity *Elements of X-ray Diffraction* (Massachusetts Addison - Wesley) (1956)

[11] H S Peiser, H P Rookshy, A J C Wilson *X-ray Diffraction by Polycrystalline Material* (Institute of Physics, London) (1956)