ON THE STRUCTURE OF COMPLEX SILVER LUTIDINE PER CHLORATE

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ABSTRACT. The Debye Scherrer pattern of complex Silver Lutidine per Chlorate has been obtained and analysed. The data obtained indicates that the crystal belongs to the monoclinic system with the unit cell dimensions $a = 10.96$ A.U., $b = 12.04$ A.U., and $c = 6.933$ A.U. and $\beta = 101° 26'$. There are two molecules per unit cell and the space group P_2, P_2/m or Pm can be assigned to the crystal.

INTRODUCTION

The study of complex salts containing ligands is of importance for the study of stretching force constants between the various groups of atoms in the molecules. Diamagnetic properties of such complexes are also of interest. Silver Lutidine per Chlorate $[Ag(C_7H_9N)_2 \, Cl \, O_4]$, is available in microcrystalline form, white in colour. As it is not possible to obtain single crystals suitable for complete structural analysis, the powder method has been used to establish certain crystallographic data.

EXPERIMENTAL

Filtered CuK_α radiation was obtained from a Machlett A-2 X-ray Diffraction tube running at 35KV and 15 m.A. and the specimen was contained in a very fine capillary of Lindmann glass of 0.01 mm. wall thickness and 0.5 mm. diameter. The Debye Scherrer pattern was obtained in a photographic film using a Rigaku Camera of 9 cm. diameter. The time of exposure was 4 hours. Interplanar distances were calculated with great accuracy from measurements on the photographic film. Attempts were made to index the power lines with Cubic, Tetragonal and Hexagonal systems and the data did not fit with any one of these systems of higher symmetry. Lipson's (Lipson, 1949) method was then tried which did not give a good number of constant differences indicating there by that the crystal belongs clearly to the two systems of lower symmetry namely the monoclinic or the triclinic. In such cases the De Wolffes' (1957) method or the most general method due to Ito (1950) is applicable. Here we have tried the latter method.

In the Table are listed the experimental X-ray data. As all the six parameters were to be found out the Ito's method was used and the powder pattern was indexed, Azaroff and Buerger (1958). The d values and the corresponding Q values $(1/d^2_{hkl} = Q_{hkl})$ are all given in the Table. Here Q_{hkl} is given by

$$Q_{hkl} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2klb^*c^* \cos \alpha^* + 2hlc^*a^* \cos \beta^* + 2hka^*b^* \cos \gamma^*$$

where α^*, β^*, γ^* and a^*, b^* and c^* are the reciprocal angles and axes respectively.

TABLE

No. of lines	Intensity	dA	$Q = 1/d$ hkl observed	Q hkl computed	Indices
1.	s	8.071	0.0154	0.01557	110
2.	s	6.074	0.0271	0.0276	020
3.	s	5.382	0.0345	0.03468	200
4.	w	3.966	0.0636	0.0634	121
5.	vw	3.869	0.0668	0.0672	201
6.	w	3.747	0.07122	0.0708	130
7.	s	3.580	0.07801	0.07803	300
8.	w	3.405	0.0863	0.08664	002
9.	w	3.241	0.0952	0.0948	221
10.	m	3.009	0.1105	0.1104	040
				0.1109	$\cdot 32\bar{1}$
11.	w	2.756	0.1316	0.1320	$30\bar{2}$
				0.1321	041
12.	vw	2.682	0.1390	0.1387	400
				0.1386	$40\bar{1}$
				0.1389	$31\bar{2}$
13.	w	2.606	0.1470	0.1465	$13\bar{2}$
14.	w	2.539	0.1552	0.1559	$24\bar{1}$
15.	m	2.458	0.1656	0.1662	$42\bar{1}$
				0.1663	420
16.	w	2.406	0.1728	0.1725	050
17.	m	2.344	0.1820	0.1821	401
				0.1819	$40\bar{2}$
18.	vvw	2.240	0.1978	0.1973	302
19.	m	2.152	0.2160	0.2165	142
				0.2167	500
20.	m	2.114	0.2238	0.2237	510
				0.2240	303
21.	m	2.066	0.2342	0.2346	$22\bar{3}$
22.	s	2.007	0.2486	0.2484	060
				0.2490	$44\dot{1}$
				0.2490	$50\bar{2}$
				0.2491	$440\bar{}$

TABLE—(contd).

No. of lines	Intensity	dA	$Q_{hkl}=1/d^2$ observed	Q_{hkl} computed	Indices
23.	w	1.928	0.2690	0.2691	$23\bar{3}$
				0.2689	402
				0.2685	$40\bar{3}$
24.	vvw	1.877	0.2838	0.2831	260
				0.2840	$33\bar{3}$
				0.2843	161
25.	m	1.823	0.3004	0.2999	223
26.	vvw	1.764	0.3211	0.3216	$54\bar{1}$
27.	w	1.714	0.3404	0.3404	$11\bar{4}$
				0.3404	$61\bar{2}$
28.	vvw	1.698	0.3467	0.3466	004
				0.3468	170
29.	w	1.646	0.3693	0.3698	352
30.	w	1.604	0.3887	0.3892	550
31.	vw	1.573	0.4042	0.40462	124
32.	vw	1.541	0.4214	0.4215	$37\bar{1}$
				0.4214	$33\bar{4}$
				0.4215	$55\bar{2}$
33.	vw	1.501	0.4437	0.4442	172
				0.4439	$14\bar{4}$
				0.4439	$64\bar{2}$
				0.4433	053
34.	w	1.444	0.4779	0.4774	181
35.	vw	1.410	0.5031	0.5026	$55\bar{3}$
36.	w	1.378	0.5262	0.5260	$18\bar{2}$
				0.5261	632
37.	vw	1.354	0.5448	0.5449	315
				0.5451	273
38.	w	1.323	0.5709	0.5714	453
				0.5715	$40\bar{5}$
39.	vvw	1.283	0.6073	0.6077	$36\bar{4}$
				0.6069	472
40.	vvw	1.240	0.6504	0.6502	670
				0.6069	$52\bar{5}$

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After certain trials the second, third, and the eighth reflections were taken as Q_{020}, Q_{200} and Q_{002}. It was then possible to find out the reciprocal cell dimensions as

$$a^* = 0.0731 \text{ A.U.}$$

$$b^* = 0.0831 \text{ A.U.}$$

$$c^* = 0.1472 \text{ A.U.}$$

In order to select the reciprocal cell angles α^*, β^*, γ^* (hko), (hol) and (okl) reflections were carefully examined and it was found that (hko) and (okl) reflections were present if α^* and γ^* were taken to be 90°. The angle β^* could then be calculated after studying some pairs of (hol) and (hol̄) reflections after the equation

$$\cos \beta^* = \frac{Q_{hol} - Q_{hol̄}}{4hla^*c^*}$$

Thus β^* was found out to be 78° 34'. The six parameters of the reciprocal cell having been thus found the direct cell dimensions are obtainee as

$$a = 10.970 \text{ A.U.}$$

$$b = 12.04 \text{ A.U.}$$

$$c = 6.933 \text{ A.U.}$$

$$\alpha = 90°$$

$$\beta = 101° 26'$$

$$\gamma = 90°$$

The Buerger test for the reduced cell dimensions has been applied and the dimensions are found to be the reduced ones.

The above data establishes the crystal to be monoclinic. Finally all the powder lines were indexed using the general formula given above and the pattern so indexed showed the following conditions :

hkl—no condition

hol—no condition

hko—no condition

oko—no condition

ool—even present

The probable space groups therefore are P_2 or $P_{2/m}$ or P_m. The observed density is 1.644 gms/cc. and the number of molecules per unit cell comes to be 2. The calculated density is 1.563 gms/cc.

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