

CRYSTALLOGRAPHIC DATA FOR COMPLEX COPPER LUTIDINE CHLORIDE

T. RATHO AND Mrs. M. KRISHNASWAMY

REGIONAL ENGINEERING COLLEGE, ROURKELA

(Received April 11, 1966; Resubmitted June 1, 1966)

ABSTRACT. Debye Scherrer pattern of Copper Lutidine Chloride has been photographed with the help of Rigaku Camera at room temperature. The Powder diffraction data showed that the complex belonged to the monoclinic system with $a = 13.75 \text{ \AA}$, $b = 11.56 \text{ \AA}$, $c = 10.91 \text{ \AA}$ and $\beta = 103^\circ 11'$. The number of molecules per unit cell is 4. The systematic extinctions observed are consistent with the space group $P2_1/m - C2_2h$ or $P2_1 - C2^2$.

INTRODUCTION

Copper Lutidine Chloride $[\text{Cu}(\text{C}_7\text{H}_9\text{N})_2\text{Cl}_2]$ is obtainable in the microcrystalline form, pink in colour, and the diamagnetic properties of such complexes using Lutidine as ligand is of some interest. As it is not possible to grow large crystal powder method has been resorted to, to investigate some of its crystallographic properties.

EXPERIMENTAL

When Cupric Chloride dissolved in Ethanol is treated with ethanolic solution of Lutidine, a shining pink crystalline substance separates out. This is the microcrystalline complex compound of Copper Lutidine Chloride.

Filtered $\text{CuK}\alpha$ radiation was obtained from a Machlett A-2 X-ray diffraction tube running at 15 mA, 30 K.V. and the specimen was contained in a Lindmann glass capillary tube of 0.5 mm. diameter, wall thickness 0.01 mm. The Debye Scherrer pattern of the substance was obtained on a photographic film using the Rigaku Camera of 9 cm. diameter. The time of exposure was about 12 hours.

The interplanar distances were calculated from the measurements on the diffraction pattern with great accuracy. Attempts were made to index the powder lines in terms of cubic, tetragonal and hexagonal systems.

Since the observed data did not fit into any one of these systems of higher symmetry, the Lipson's method (Lipson, 1949) was tried and this also did not give sufficient number of constant differences. This evidently shows that the crystal perhaps belongs to the lower symmetry group of monoclinic or triclinic systems. Therefore it became necessary to apply either De Wolffe's method (De Wolffe, 1957) or Ito's method (Ito, 1950).

EXPERIMENTAL DATA

The X-ray data obtained are given in Table I. Since all the six unknown parameters are to be determined, the most general method of Ito (Ito, 1950) was applied.

The powder pattern was indexed by Ito's method (Ito's, 1950, Azoroff and Buerger, 1958). The interplanar spacings and the corresponding Q values ($Q_{hkl} = 1/d^2_{hkl}$) are listed in Table II.

In Ito's method the expression relating $\sin^2\theta(Q)$ to the cell constants of a triclinic cell is

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

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

The first three lines in Table II were first taken as Q_{100} , Q_{010} , and Q_{001} . Attempts were made to index the other lines with the above assumption. Since it was not possible, the first three lines were taken again as Q_{200} , Q_{020} , and Q_{002} . It can be seen from Table I that the observed Q 's are in good agreement with the calculated Q values for the other higher orders of reflection.

TABLE I
Selection of Q_{200} , Q_{020} , and Q_{002}

Q_{hkl}	Computed	Observed	Error in Q	Q , Corrected
Q_{200}		0.0227		
Q_{400}	0.0908	0.0891	$-\frac{0.0017}{4} = -0.0004$	0.0223
Q_{600}	0.2043	—		
Q_{020}		0.0292		
Q_{040}	0.1168	0.1196	$+\frac{0.0028}{4} = +0.0007$	0.0299
Q_{060}	0.2028	—		
Q_{002}		0.03465		
Q_{004}	0.1386	0.1418	$+\frac{0.0032}{4} = +0.0008$	0.03545
Q_{006}	0.3118	0.3190	$+\frac{0.0072}{9} = +0.0008$	

From Table I one gets the reciprocal cell dimensions as

$$\begin{aligned} a^* &= 0.0747 \\ b^* &= 0.08648 \\ c^* &= 0.09412 \end{aligned}$$

Now considering the Q values for planes hol and $h\bar{o}l$ with $\beta^* \neq 90^\circ$, we have

$$Q_{hol} = h^2 a^{*2} + l^2 c^{*2} + 2hlc^* a^* \cos \beta^*$$

$$Q_{h\bar{o}l} = h^2 a^{*2} + l^2 c^{*2} - 2hlc^* a^* \cos \beta^*$$

It is seen that these quantities are symmetrical with respect to the quantity $a^{*2} + c^{*2}$. By giving proper values to h and l , the two symmetrically placed lines hol and $h\bar{o}l$ were found out. Then β^* was calculated from

$$\cos \beta^* = \frac{(Q_{hol} - Q_{h\bar{o}l})}{4c^* a^* hl}$$

This β^* was found out to be $76^\circ 49'$. The other two angles α^* and γ^* were derived in the same way and they were found to be $\alpha^* = 90^\circ$, and $\gamma^* = 90^\circ$

Therefore the six parameters of the reciprocal cells are

$$\begin{aligned} a^* &= 0.0747 & \alpha^* &= 90^\circ \\ b^* &= 0.08648 & \beta^* &= 76^\circ 49' \\ c^* &= 0.09412 & \gamma^* &= 90^\circ \end{aligned}$$

The direct cell dimensions are therefore

$$\begin{aligned} a &= 13.75 \text{ \AA} & \alpha &= 90^\circ \\ b &= 11.56 \text{ \AA} & \beta &= 103^\circ 11' \\ c &= 10.91 \text{ \AA} & \gamma &= 90^\circ. \end{aligned}$$

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

TABLE II

No. of lines	Intensity	d \AA	$Q_{hkl} = 1/d^2$ observed	Q_{hkl} computed	Indices
1.	vs	6.636	0.0227	0.0223	200
2.	w	5.852	0.0292	0.0299 0.0298	020 210
3.	vw	5.371	0.03465	0.03545 0.0355 0.0346	022 120 102
4.	vww	4.564	0.04799	0.0476 0.0474	121 102
5.	w	4.222	0.0561	0.0569	311
6.	ms	3.773	0.0703	0.0706	202
7.	w	3.538	0.0799	0.0797 0.0794 0.0801	003 321 320
8.	h	3.350	0.0891	0.0892 0.0896	400 230
9.	w	3.181	0.0988	0.0991 0.0986	402 321

TABLE II (contd)

No. of lines	Intensity	d Å	$Q_{hkl} = 1/d^2$ observed	Q_{hkl} computed	Indices.
10.	w	2 892	0 1196	0 1196 0 1192	040 420
11.	ms	2 756	0.1316	0 1311 0 1309	323̄ 141
12	vw	2 654	0 1418	0 1418 0.1420 0 1420	004 240 114̄
13.	w	2 605	0 1473	0 1470 0 1471	510 033
14.	ms	2 581	0.1501	0 1503 0 1502 0 1504	402 233̄ 512̄
15.	vw	2.505	0 1593	0 1588	303
16.	m	2 433	0 1690	0 1684 0 1685 0 1692 0 1694	224̄ 333 341 520
17.	vw	2.353	0.1806	0 1803	422
18.	vw	2 290	0 1907	0 1902 0 1905	242 601
19.	vw	2 261	0 1955	0.1954 0.1959	143 051
20.	vw	2 187	0 2091	0 2091 0 2090 0.2093	034 440 250
21.	vw	2 180	0 2105	0.2111 0.2103	106̄ 532̄
22.	m	2.104	0 2258	0 2261	333
23.	m	1.998	0 2505	0 2503	443̄
24.	vw	1.834	0 2972	0 2972 0.2979 0 2977	523 451 334
25.	vw	1.770	0 3190	0 3191 0.3197 0.3195 0.3191 0 3188 0.3194	006 305 360 310̄ 361̄ 551̄
26.	vw	1.693	0 3486	0 3488 0.3490 0 3487	026 063 535̄
27	vvw	1 676	0.3559	0 3567	326
28.	vw	1 642	0.3712	0 3704	363̄
29.	vw	1.590	0 3956	0.3955	245
30	vvw	1 544	0.4194	0.4194 0.4190	604 462
31.	vvw	1 429	0.4898	0.4899	256̄

The crystal therefore belongs to the monoclinic system.

Finally all the Q_{hkl} values were computed using the above general formula. The powder pattern so indexed showed the following conditions.

hkl —no condition ;

oko —odd absent.

This obviously leads to the probable space group $P2_1/m-C_{2h}^2$ or $P2_1-C_2^2$.

The observed density of 1.412 gms./cc. indicates 4 molecules per unit cell; calculated density is 1.372 gms./cc.

It is however not possible to throw light on the complete structure of this substance. Further work on these lines is in progress.

ACKNOWLEDGMENT

Our thanks are due to Dr. D. V. Raman Rao, Head of the Department of Chemistry, for supplying the chemically pure sample used in this work.

REFERENCES

- Azoff, L. V. and Buerger, M. J., 1958, *Powder Method*, 150
Deyo and Wait, 1960, *X-ray Powder Photography in Inorganic Chemistry*.
Ito, T., 1950, *X-ray studies in Polymorphism*, Maruzen Tokyo.
Lipson, H., 1949, *Acta Cryst.*, **2**, 43