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X-Ray Powder Diffraction Data for Tin (IV) Phthalocynine Dichloride

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ABSTRACT. The observed X-ray powder diffraction data of Tin (IV) Phthalocyanine dichloride ($C_{32}H_{16}Cl_2N_8Sn$) have been investigated together with indexing of Miller indices for monoclinic system. Using statistical error minimizing technique, the unit cell parameters were found to be a = 21.0490 (5)Å, b = 10.9730(2) Å, c = 11.3310(3) Å and β = 96.02° (2) with volume as 2602.7 Å^3. Suggested space group is $P2_1/n$ whereas the calculated X-ray density D_x is 1791.7 Kg/m^3. The above parameters are compared to an earlier investigation on single crystal sample of the same compound.

Keywords : Phthalocyanines; lattice parameters, X-ray powder diffraction.

Introdution

Phthalocyanines (PC) are a class of organic materials which exhibit optical, thermal and environmental stability. These materials have optoelectrical properties which make them plausible candidate for applications in dyes, pigments and photocopying technology (Gregory, 1991; Waring and Hallas, 1990). They can be classified into three categories as Metal-free phthalocynine, Metal phthalocyanines and Bisphthalocyanines (Engle, 1997). Thin films of metal phthalocyanines (MPc) in particular have been used as gas sensors due to the ability of these materials to readily modify their molecular structure and hence electrical and optical properties, which are known to be critically dependent upon a variety of parameters including purity, crystal structure, morphology and device temperature (Hassan and Gould, 1992). Therefore, precise information of the solid state structure could improve our understanding of their atomic arrangements and hence give further insight into the physical properties of these compounds.

The lattice parameters obtained from direct measurements of X-ray powder diffractometric data are not accurate and suffer from both systematic aberrations and statistical errors. Instrumental errors such as misalignments and miscalibration can be minimized by using a standard reference material such as high purity powdered silicon SRM 640a (Hubbard, 1983a). On the other hand, analytical correcting methods minimize random and systematic errors resulting from the specimen displacements from the

diffractometer axis and absorption of X-rays in the sample (Razik, 1985a). In the present investigation this method was applied to the X-ray powder diffraction data of Tin (IV) Phthalocyanine dichloride as an example of metal phthalocyanine in order to calculate the best values of its unit cell parameters and eompare it with an earlier single crystal study made on the same eompound (Rogers & Osborn, 1971).

Experimental Procedure

The powder Tin (IV) Phthalocyanine dichloridc ($C_{32}H_{16}Cl_2N_8Sn$) used in this study was supplied by ACROS ORGANICS, USA (C.A.S. 18253-54-8). lts basic molecular structure is illustrated in Fig.1. A Philips X-ray powder diffractometer (model PW 1710) was used for the measurements using CuKα radiation, graphite crystal monochromator, divergence slit 1°, receiving slit 0.1 mm, Soller slits and proportional counter detector. The working conditions were 40 kV and 30 mA for the X-ray tube, scan speed 0.02° per second and sample interval time 2 seconds. Threc continuous scans werc made for the sample to cover angular range (2θ) between 5° to 50°. For accurate determination of the pcak position, the diffraction angle was measured automatically by parabola fitting to five points around the maximum peak intensity and was recorded to three decimal plaees. An examplc of the X-ray diffraction pattern of the Tin (IV) Phthalocyanine dichloride is shown in Fig.2. For the calibration purposes of the X-ray diffractometer, X-ray scan was madc of high purity silicon powder certified for X-ray powder diffraction by thc National Bureau of Standards as standard referencc material (SRM 640a).

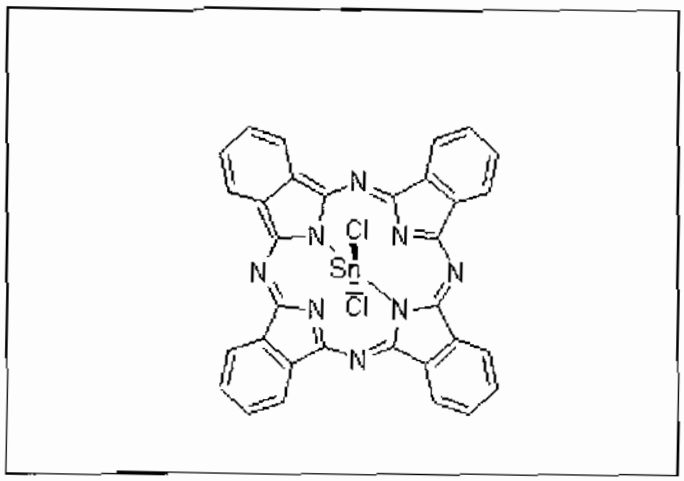

Fig. 1. Schematic representation of Tin (IV) Phthalocyanine dichloride ($C_{32}H_{16}Cl_2N_8Sn$).

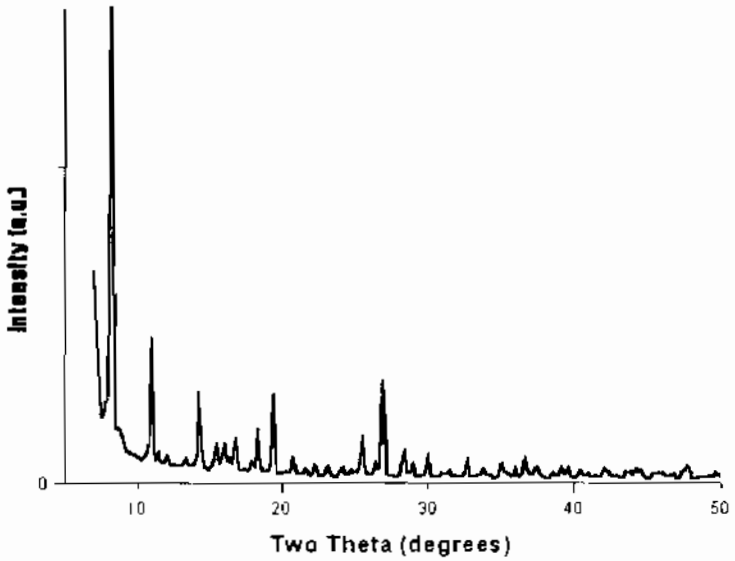

Fig. 2. X-ray diffractogram of powder Tin (IV) Phthalocyanine dichloride.

Results and Discussion

X-ray diffractogram was recorded from the silicon powder SRM 640a at 296.3 K for the calibration of the diffractometer. Using the analytical correcting method for the cubic system (Razik *et al*, 1989a & Razik *et al* 1990), the lattice constant was found to be 5.4309 (4) Å in comparison to the earlier published value 5.43074 (3) Å at 298 K hy Razik, (1985a). Preliminary indexing of the X-ray diffraction pattern of the Tin (IV) Phthalocyanine dichloride was performed by means of the computer program DICVOL (Boultif & Louër, 1991). Fifteen observed peak positions were used as input data to the program and the only possible solution proposed was that of the monoclinic symmetry. The cell parameters were ohtained as a = 21.08 (2) Å, b = 11.01(1) Å, c = 11.34 (1) Å and $\beta = 96.1^{\circ}$ (1). The output data of the DICVOL program were then linked to the CHEKCELL program which assigned the space group as $P2_1/n$ (Jean & Bernard, 2001). To refine the estimated values of the lattice parameters (a, b, c, β) , a computer program based on the analytical correction method for monoclinic system was used (Razik & El-Barakati, 1989b). The program was designed to search for a set of *h k ℓ* iudices which yields the lowest value of $\Delta \sin^2\theta$ ($\Delta \sin^2\theta = \sin^2\theta_{cle} - \sin^2\theta_{obs}$) for each diffraction line in the pattern from which the lattice parameters can be recalculated. These steps were repeated several times to obtain the best values of the lattice parameters with the lowest possible errors. Thc best estimated values are a = 21.0490 (5) Å, b = 10.9730 (2) Å, c = 11.3310 (3) Å and $\beta = 96.02^{\circ}$ (2) which can be considered as refinements to the reported parameters a = 21.104 Å, b = 11.060 Å, c = 11.392 Å and $\beta = 96.04^{\circ}$ for a monoclinic single crystal of Tin(IV) Phthalocyanine dichloride ($C_{32}H_{16}Cl_2N_8Sn$) without uncertainty determination (Rogers & Osborn, 1971). However, higher precision can be obtained by using external and internal analytical correcting method (Razik & El-Barakati, 1989b) with a suitable reference material to cover the low and high angnlar range of the X-ray

diffractogram. The observed and calculated lattice spacings (d) of the diffracting plan and tbeir differences. Miller indices and relative intensities are given in Tables 1.

Table 1. X-ray powder diffraction data of Tin (IV) Phthalocyanine dichloride ($C_{32}H_{16}Cl_2N_8Sn$)

(hkl)	d_{obs} (Å)	d_{calc} (Å)	d_{obs} (Å) d_{calc}	I/I_0
$\bar{1}01$	10.3831	10.3873	0.0042	100
011	7.8415	7.8615	0.0200	35
111	7.1704	7.1885	0.0181	7
$\bar{2}11$	6.5033	6.5190	0.0160	8
211	6.0746	6.0760	0.0014	32
002	5.6423	5.6343	-0.0080	14
020	5.4916	5.4865	-0.0051	10
$\bar{2}02$	5.1995	5.1936	-0.0059	15
220	4.8661	4.8593	-0.0068	7
202	4.7610	4.7572	-0.0038	23
$\bar{4}11$	4.5085	4.5112	0.0027	32
411	4.2198	4.2163	-0.0035	12
$\bar{4}02$	4.0514	4.0522	0.0008	4
321	3.9435	3.9435	0.0000	7
412	3.8040	3.8012	-0.0028	5
402	3.6472	3.6483	0.0011	8
013	3.5527	3.5537	0.0001	3
412	3.4596	3.4620	0.0024	22
611	3.2805	3.2791	-0.0014	33
521	3.1211	3.1220	0.0001	14
$\bar{1}32$	3.0564	3.0606	0.0042	5
503	2.9516	2.9541	0.0025	8
$\bar{7}11$	2.8672	2.8656	-0.0016	4
701	2.8221	2.8180	-0.0041	4
432	2.7169	2.7151	-0.0018	8
$\bar{3}14$	2.6335	2.6336	0.0001	4

References

Boultif, A. and **Louër, D**. (1991) Indexing of powder diffraction patterns for low – symmetry lattices by the successive dichotomy method, *J. Appl. Cryst.* **24:** 987-993.

Engle, M.K. (1997) Report kawamura inst., *Chem. Res.* **8:**11-54.

Jean, Laugier and **Beruard, Bochu** (2001), LMGP-Snite Suite of Programs for the interpretation of X-ray Experiments, ENSP/Laboratoire des Matériaux et du Génie Physique, BP 46. 38042 Saint Martin d'Hères, France.

Gregory, P. (1991) *High technology applications of organic colorants*, Plenum press, London.

Hassan, A.K. and **Gould, R.D**. (1992) Structnral studies of thermally evaporated thin films of eopper phthalocyanine, *Phys. Stat. Sol.* (a) **I32:** 91-101.

Hubbard, C.R. (1983a) New standard reference materials for X-ray powder diffraction, *Adv. X-ray. Analy.* **26:** 45-51.

Razik, N.A. (1985a) Precise lattice constant determination of cubic crystals from X-ray powder diffraetometric measurements, *Appl. Phys.* **A 37:** 187-189.

Razik, N.A. and **El-Barakati, G.G**. (1989b), Precise determination of lattice parameters of monoclinic crystal by X-ray powder diffractometery, *Indian Journal of Technology*, **27:** 459-461.

Razik, N.A., **El-Barakati, G.G**. and **Al-Heniti. S**, (1989a), Refinment of GaAs powder diffraction data, *Journal of Material Science Letters*, **8:** 1458-1460.

Razik, N.A., **El-Barakati, G.G**. and **Al-Heniti. S**, (1990), Powder diffraction data of $CdTe_xSe_{1-x}$ solid solutions, *Powder diffraction*, **5**(4): 206-209.

Roger, D. and **Osborn, R.S.** (1971) X-ray crystal structure of dichlorophthalocyaninatotin (IV), *J. Chem. Soc., Chem. Commun.*, 840-841.

Waring, N.R. , and **Hallas, G**.(1990) *The chemistry and applications of dyes*, Plenum press, London.

حيود الأشعة السينية لمسحوق ثنائي كلوريد الفيثالوسينين القصديري

غالي البركاتي ، أحمد الغامدي و صالح الحنيطي

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المستخلص. بينت نتائج قياسات حيود الأشعة السينية لمركب ثنائي كلوريد الفيثالوسينين القصديري $(C_{12}H_{18}Cl_2N_8Sn)$ أن نظام التركيب هو أحادي الميل. باستخدام الطرق الإحصائية في تقليل الأخطاء وجد أن أبعاد الوحدة البنائية التركيبية هي $a = 21.0490(5)Å$ و $b = 10.9730(2)Å$ و $c = 11.33103(3)Å$ و $\beta = 96.02^{o}(2)$ بينما الحجم هو $2602.7Å^3$ و المجموعة التماثلية المقترحة هي $P2_1/n$ والكثافة هي $1791.7\ Kg/m^3$. هذه النتائج تم مقارنتها مع دراسة سابقة على بلّورة أحادية من هذا المركب.