Short Communication

A Synchrotron X-Ray Powder Diffraction Study of the Structure of *trans*-Dichlorotitanium(IV) Tetraphenylporphyrin

A. Nørlund Christensen,[a,*] A. Grand,[b] M. S. Lehmann[c] and D. E. Cox[d,‡]

[a] Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark, [b] Department de Recherches Fondamentales, CEA-CENG, F-38041 Grenoble Cedex, [c] Institut Max von Laue–Paul Langevin, 156x, Centre de Tri, F-38042 Grenoble Cedex, France and [d] Brookhaven National Laboratory, Physics Department, Upton, New York 11973, USA

The continuing development of high-resolution powder diffraction techniques using X-ray or neutron data has recently opened up new possibilities for structure determination from powder diffraction data. Patterns with overlapping reflections may be unfolded into individual intensities, and these can be used for solving a structure by standard single-crystal methods. When a model for the structure is found, refinements of the model can be made using the Rietveld profile refinement least-squares procedure.[1] The various steps in such a procedure have been discussed recently.[2] Synchrotron X-ray radiation yields powder patterns with well-resolved reflections, but as heavy atoms often dominate the X-ray scattering in the case of many inorganic compounds, the positions of the light atoms are not always determined with good precision from X-ray powder data. It is therefore desirable to supplement X-ray data with neutron powder data, as the neutron scattering cross-sections are more evenly distributed, and it is thus the combined use of X-ray and neutron data that eventually will lead to the most precise analysis. Synchrotron X-ray analyses have recently been made for structures of organic as well as inorganic compounds.[3,4]

In an investigation of how well crystal structures may be solved and refined from powder diffraction data alone, synchrotron X-ray powder data from $C_{44}H_{28}N_4TiCl_2$ have been analyzed. This compound was chosen because it contains the heavy atoms Ti and Cl as well as a large number of carbon and nitrogen atoms in the organic part of the molecule. The average scattering contribution per atom in the compound is Ti, 17.5 %; Cl, 10.4 %; C, 1.30 %; N, 1.77 %; but the large number of carbon and nitrogen atoms in the molecule results in the total scattering contribution from the organic molecule being approximately 62.0 %. The case is well-suited to investigate if a least-squares profile refine-

ment will give an acceptable geometry for the organic molecule in a heavy-atom scattering case.

The powder pattern was measured with synchrotron X-ray radiation using the diffractometer on the X13A beam line of the Brookhaven National Synchrotron Light Source (NSLS).[5] The powder pattern was measured in the 2θ range 10–70° in step intervals of 0.01°, using a wavelength of 1.315 Å. A Ge(111) crystal was used as monochromator and an LiF(400) crystal as analyzer before the counter. The sample was a flat plate of the compound which was oscillated through a few degrees during the data collection to ensure proper particle randomization. For maximum in-
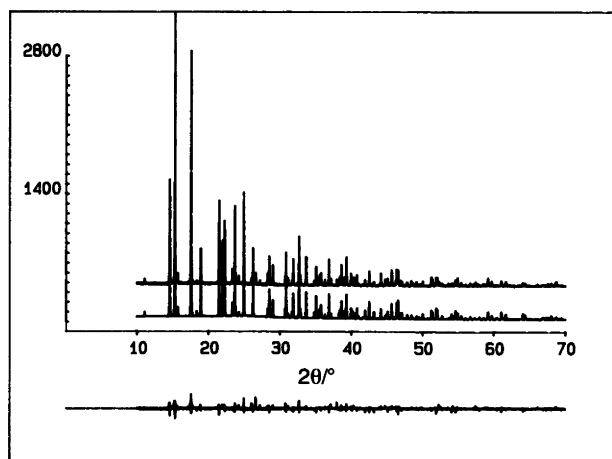

Fig. 1. Observed and calculated profiles of the synchrotron X-ray powder data (upper and lower curves, respectively). The differences are shown in the lower part of the figure. The number of structure factors used in the profile refinement was 380. Of the observed lines only 28 had contributions from two or three non-systematically overlapping reflections, and the number of completely resolved lines is thus approximately 320 in the pattern. The half-width of the lines can be calculated from the values of the profile parameters (see the footnote to Table 1). For the strongest reflection 002 at 2θ = 15.32°, FWHM = 0.074°.

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* To whom correspondence should be addressed.

Table 1. Atomic coordinates and isotropic temperature factors in $Å^2$ units. Numbers in square brackets are positional parameters from unconstrained refinements.[a]

Atom	$C_{44}H_{28}N_4TiCl_2$				$C_{44}H_{28}N_4TiBr_2$[b]			
	x	y	z	B	x	y	z	B
Ti	0	0	0	3.4(3)	0	0	0	2.65
Cl/Br	0	0	0.2306(6) [0.2305(6)]	3.6(2)	0	0	0.2484(2)	3.72
N	0.149(1) [0.150(1)]	0.041(1) 0.042(1)]	0	0.7(5)	0.1444(6)	0.0400(6)	0	2.74
C1	0.187(2) [0.187(2)]	0.132(2) 0.133(2)]	0	6.9(6)	0.1773(8)	0.1361(8)	0	2.78
C2	0.287(2) [0.286(2)]	0.142(2) 0.142(2)]	0	5.2(7)	0.2833(9)	0.1320(9)	0	3.59
C3	0.323(3) [0.324(3)]	0.039(2) 0.039(2)]	0	4.0(1.2)	0.3106(9)	0.0368(9)	0	3.61
C4	0.241(3) [0.241(3)]	−0.016(3) −0.014(3)]	0	7.3(1.3)	0.2243(8)	−0.0203(8)	0	3.01
C5	0.226(2) [0.227(2)]	−0.134(2) −0.133(2)]	0	4.7(1.0)	0.2190(8)	−0.1214(9)	0	3.30
C6	0.333(2) [0.333(2)]	−0.178(2) −0.177(2)]	0	4.2(7)	0.3147(8)	−0.1749(8)	0	2.94
C7	0.360(1) [0.360(1)]	−0.206(1) −0.206(1)	0.126(1) 0.125(1)]	4.5(4)	0.3577(7)	−0.2019(8)	0.1205(10)	5.12
C8	0.451(1) [0.452(1)]	−0.265(1) −0.265(1)	0.124(1) 0.124(1)]	3.1(5)	0.4448(8)	−0.2542(8)	0.1221(11)	5.77
C9	0.481(1) [0.481(1)]	−0.280(1) −0.280(1)]	0	1.0(5)	0.4864(8)	−0.2830(10)	0	4.97

[a]The profiles were described with a pseudo-Voigt function with a Gaussian half-width $(U \tan^2\theta + V \tan\theta + W)^{\frac{1}{2}}$ and a Lorentzian half-width $T/\cos\theta$. The R-factors are defined as follows: $R_I = \Sigma|I_{obs} - I_{calc}|/\Sigma I_{obs}$. The I values are approximate integrated intensities.[1] $R_W = (\Sigma(y_{obs} - y_{calc})^2 W/\Sigma y_{obs}^2 W)^{\frac{1}{2}}$. The y values are the profile intensities with the background y_b subtracted, and $W = 1/(y_{obs} + y_b)$. $R_E = ((N - M)/\Sigma y_{obs}^2 W)^{\frac{1}{2}}$, where N and M are the number of profile points and variable parameters, respectively. $R_I = 12.8\%$, $R_W = 7.3\%$, $R_E = 9.2\%$. $U = 0.0227(22)$, $V = -0.0147(10)$, $W = 0.0036(1)$, $T = 0.0287(5)$. Zero point offset of the diffractometer = $0.0017(2)°$. [b]From Ref. 7.

tensity it is best to use a flat plate sample in powder diffraction, but the disadvantage is that preferred orientation may occur which cannot be corrected for by oscillation of the sample over a few degrees in the plane of the sample. For example, severe preferred orientation was observed in the powder patterns of $BaC_2O_4 \cdot 0.5H_2O$ and $CaSO_4 \cdot 0.5H_2O$ measured under the same experimental conditions; however, it turned out that the pattern of $C_{44}H_{28}N_4TiCl_2$ showed negligible preferred orientation. The pattern was indexed with the program FZON[6] with a tetragonal cell, $a = 13.5956(2)$, $c = 9.8681(1)$ Å, and it was then evident that the compound was isostructural with $C_{44}H_{28}N_4TiBr_2$ $[a = 13.757(2), c = 9.880(1)$ Å, space group $I4/m]$.[7] Owing to the tetragonal symmetry it was not possible to extract non-equivalent structure factors F_{hkl} and F_{khl} from the in-

tensities I_{hkl}, and no attempts were made to solve the structure *ab initio* from the powder pattern. Instead, refinement of the structure was accomplished with the atomic parameters from the structure of $C_{44}H_{28}N_4TiBr_2$ as starting values. No absorption correction was made, since this is a constant for flat-plate data. Profile refinement of the model was made with the program EDINP[8] and neutral atom values for the atomic scattering factors.[9] The parameters refined were a scale factor, a zero-point parameter, two unit-cell parameters, four profile parameters of a pseudo-Voigt function, 23 positional parameters and 12 isotropic temperature factors. The final results are listed in Table 1, and Fig. 1 shows the observed and calculated profiles and a difference plot of the powder pattern. The fit to the individual peaks using the pseudo-Voigt function is very satis-
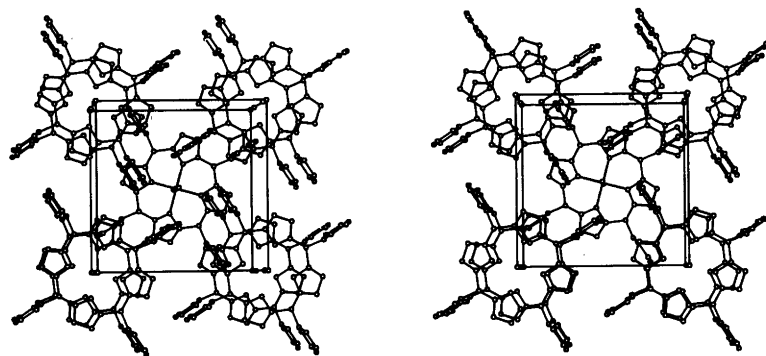
Fig. 2. Stereoscopic drawing of the structure of $C_{44}H_{28}N_4TiCl_2$.

factory. There is no tendency towards preferred orientation in the pattern and no sign of directional-dependent line-broadening of reflections due to strain, or to stacking faults, as was the case for the pattern of PbC_2O_4.[4]

The least-squares refinement was made with the interatomic distances of the organic molecule restrained to the values reported for the distances found in $C_{44}H_{28}N_4TiBr_2$.[7] These distances were included as additional observations with standard deviations of 0.01–0.02 Å. Without this restraint the C4–C5 distance had a tendency to be too large, 1.62 Å. In the restrained refinement the coordinates (Table 1) were in good agreement with the coordinates reported for $C_{44}H_{28}N_4TiBr_2$, but the standard deviations in this case were higher than for the single-crystal investigation of $C_{44}H_{28}N_4TiBr_2$, based on diffractometer data measured with $CuK\alpha$ radiation, which is not unexpected. Thus, the investigation shows that a synchrotron radiation X-ray powder pattern provides enough detailed information to allow a profile refinement of a heavy-atom structure with a large organic molecule resulting in an acceptable model for that molecule.

Fig. 2 shows a model of the structure.

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