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Towards a more reliable symmetry determination from powder diffraction: a redetermination of the low-temperature structure of 4-methylpyridine-*N*-oxide

The low-temperature structure of 4-methylpyridine-*N*-oxide was previously determined in symmetry $P4_1$ [Damay *et al.* (2006), *Acta Cryst.* **B62**, 627–633]. Using a recently published symmetry-determination method it was found that the true symmetry of the structure is $P4_12_12$. The structure was refined in the new space group using X-ray and neutron data. The previously published structure is close to the newly refined structure, but the new structure is in agreement with the results of rotational tunneling spectroscopy, and, in contrast to the structure in symmetry $P4_1$, does not require a twofold degeneracy of the tunneling bands.

1. Introduction

The 4-methylpyridine-*N*-oxide (4MPNO) molecule crystallizes in three different structures at different temperatures. While the room-temperature structure ($I4_1/amd$), and the intermediate-temperature structure ($Fddd$, $T < 139$ K) have been determined in the past (Rose, 1961; Ikeda *et al.*, 1991; Kaiser-Morris *et al.*, 1998), the low-temperature structure ($T < 91$ K) has been determined only recently from combined synchrotron and neutron powder diffraction experiments on fully hydrogenated and fully deuterated 4-MPNO, respectively (Damay *et al.*, 2006, denoted as Paper I hereafter). Indexing of the diffraction pattern revealed a unit cell that corresponds to an approximate doubling of the a and b parameters of the room-temperature unit cell. The structure was solved by simulated annealing using the program *FullProf* (Rodríguez-Carvajal, 1993), starting from the room-temperature structure. The solution was complicated by the fact that the space group of the low-temperature structure could not be determined unambiguously. Therefore, a list of candidate tetragonal subgroups of $I4_1/amd$ compatible with the unit-cell transformation $[200; 020; 001]$ was generated with the help of the *MaxSub* program on the Bilbao crystallographic server (Aroyo *et al.*, 2006). The solution was then attempted in all subgroups from the list. The only converged solution was obtained in $P4_1$. It was thus concluded that this is the correct symmetry of the structure. Once the structure was solved, it was checked by the *ADDSYM* option of the program *PLATON* (Spek, 2009) for missing symmetry, but no missing symmetry was found. This result was taken as an independent confirmation of the selected space group.¹

Recently a new space-group determination method has been proposed (Palatinus & van der Lee, 2008). Using this method, it has been shown that the true space group of the low-temperature structure of 4MPNO is $P4_12_12$. In this short communication we give the details of the procedure leading to the correct symmetry, and report the correct low-temperature structure of 4MPNO.

2. Symmetry determination

The low-temperature structure of 4MPNO was used as a test case for structure solution from powder diffraction data by a charge-flipping algorithm adapted for powder diffraction data (Oszlányi & Sütő, 2004, 2008; Baerlocher *et al.*, 2007). It turned out that the structure

¹ It must be noted that the standard tolerances in *PLATON* were set for single-crystal studies and may not be appropriate for powder studies. See §4 for the discussion of this problem.

Table 1Agreement factors for symmetry operations of the space group $P4_12_12$.

Column 'charge-flipping' contains a range of agreement factors obtained from ten structure-solution attempts. Column 'structure model' contains agreement factors obtained from the electron density generated from the structure model refined in space group $P4_1$.

Symmetry operation	Charge flipping	Published structure
4_1^+	0.03–0.05	0.00
4_3^+	0.03–0.05	0.00
2_1^+	0.05–0.09	0.00
2^{a+b}	0.17–0.25	0.05
2^{a-b}	0.14–0.22	0.05
2_1^a	0.15–0.23	0.05
2_1^b	0.16–0.24	0.05

can be solved *ab initio* by this method, and the solution matched the solution published in Paper I very closely. Later, the same example was used to test a new symmetry determination method (Palatinus & van der Lee, 2008). The new method does not rely on the statistics of the diffraction intensities, but directly on the electron density in a unit cell. The (approximate) electron density is searched for all symmetry elements compatible with the lattice parameters. The best possible position of each symmetry operation is located, and the degree of presence of the symmetry operation $\mathcal{S} = \{\mathbf{R}|\tau\}$ in the density is evaluated using the *symmetry agreement factor* φ_{sym} [see Palatinus & van der Lee, 2008, equation (7)]

$$\varphi_{\text{sym}}(\mathcal{S}) = C \cdot \frac{\sum_{\mathbf{h}} |F_{\mathbf{h}} F_{\mathbf{h}\mathcal{R}}| \Delta_{\mathbf{h},\mathcal{S}}^2}{\sum_{\mathbf{h}} |F_{\mathbf{h}} F_{\mathbf{h}\mathcal{R}}|}, \quad (1)$$

where $\Delta_{\mathbf{h},\mathcal{S}}$ is the difference in phases between structure factors $F_{\mathbf{h}}$ and $F_{\mathbf{h}\mathcal{R}}$. The normalization constant C is selected so that a random density results in $\varphi_{\text{sym}} = 1$. The most likely space group is estimated from the list of symmetry elements with sufficiently low φ_{sym} . The threshold is user-definable, but practice shows that a value of 0.25 is reasonable in most cases.

This method is particularly useful in combination with structure-solution methods solving the structure in $P1$, *i.e.* without any *a priori* assumptions about the symmetry. However, the method can also be applied to an electron density calculated from a structure model. In this case, it can be regarded as a method to check for missing symmetry elements in the structure.

At first the method was applied to the solution of the low-temperature structure of 4MPNO obtained by the powder-adapted charge-flipping algorithm (Baerlocher *et al.*, 2007), using the program *SUPERFLIP* (Palatinus & Chapuis, 2007). Surprisingly, it turned out that the structure most likely has the space group $P4_12_12$ rather than the originally proposed $P4_1$. The list of symmetry operations of the space group $P4_12_12$ with their agreement factors in the solution is given in Table 1.

Note that during the solution procedure the intensities were averaged assuming the Laue class 4, but the space group $P4_12_12$ corresponds to the Laue class $4/mmm$. It is therefore not surprising that the agreement factors of the twofold axes (see Table 1) are higher than those of the fourfold screw axis.

To confirm the hypothesis about the higher space group the structure model was analyzed in the same way. An electron density was calculated from the refined structure model in $P4_1$ using X-ray atomic scattering factors, and this density was analyzed for symmetry. The result is also shown in Table 1, and confirms that the symmetry is also contained to a very good approximation in the refined model.

Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_5\text{D}_4\text{NO}\cdot\text{CD}_3$
M_r	116
Crystal system, space group	Tetragonal, $P4_12_12$
Temperature (K)	10
a, c (Å)	15.4073 (2), 19.6748 (3)
V (Å ³)	4670.52 (13)
Z	32
Radiation type	Constant-wavelength neutron diffraction, $\lambda = 1.225300$ Å
Specimen shape, size (mm)	Cylinder, $8 \times 8 \times 30$
Data collection	
Diffractometer	3T2 diffractometer at LLB-Orphée, Saclay, France
Specimen mounting	Vanadium
Data-collection mode	Transmission
Scan method	Step
2θ values (°)	$2\theta_{\text{min}} = -0.0420$, $\theta_{\text{max}} = 125.4120$, $2\theta_{\text{step}} = 0.05$
Refinement	
R factors and goodness-of-fit	$R_p = 0.033$, $R_{\text{wp}} = 0.041$, $R_{\text{exp}} = 0.014$, $R_{\text{Bragg}} = 0.057$, $\chi^2 = 0.0810$
No. of data points	2510
No. of parameters	38
No. of restraints	0

Computer programs used: *FullProf* (Rodriguez-Carvajal, 1993).

By averaging the structure model in the higher symmetry a new structure model has been obtained that could be readily refined (Table 2). However, owing to the complexity of the structure the atoms could not be refined independently, and therefore a similar procedure was used as in Paper I. The molecules were refined as rigid bodies, except for free rotation of the methyl groups around the C—C bond. For each molecule its position and orientation was refined, and the atomic displacements were described by TLS tensors. In addition to the structural parameters the procedure also included the refinement of the pseudo-Voigt profile function parameters, and four parameters of microstrain broadening. The background was determined manually.

3. Implications for the structure interpretation

The previously published structure in $P4_1$ is close to the correct solution. Therefore, the description of the structure, as presented in Paper I, remains valid, including the discussion about structure motifs, rotations of the molecules with respect to the high-temperature structures, and the mutual orientations and interactions of the methyl groups. The distances between the methyl groups have changed only moderately (maximum change 0.186 Å, see Table 3). However, the new structure with four independent molecules is now in accordance with the results of rotational tunneling spectroscopy, where four tunneling bands have been observed (Carlile *et al.*, 1990; Ikeda *et al.*, 1991). In the old structure it was necessary to assume a twofold degeneracy of each band to explain the rotational tunneling spectrum.

4. Conclusions

The structure determination of complex structures from powder diffraction data still remains a challenge. The bottleneck of the process is frequently the space-group determination, which is often ambiguous, even if good-quality powder data are available. The process of structure solution with many possible space groups at hand

Table 3

The nearest-contact distances between the methyl groups in 4MPNO as derived from the previously published structure and from the new refinement.

The labels P1 through to PL refer to four crystallographically independent molecules, individual atoms in each molecule are numbered 1–8, with 8 referring to the C atom of the methyl group. The numbering of distances as used in Fig. 7 of Paper I is listed for reference in the second column.

Atoms	Number	Paper I	Updated distances
PK8–PL8	(1)	3.813 (4)	3.9665 (9)
PJ8–PK8 ⁱ	(2)	3.962 (4)	3.9023 (9)
PI8–PJ8 ⁱⁱ	(3)	4.159 (4)	4.0836 (10)
PI8–PL8 ⁱⁱⁱ	(4)	4.420 (6)	4.3304 (10)
PK8 ^{iv} –PL8 ^{iv}	(5)	4.153 (4)	3.9665 (9)
PI8 ^{iv} –PL8 ^v	(6)	4.230 (4)	4.3304 (10)
PI8 ^{iv} –PJ8 ^{vi}	(7)	3.968 (4)	4.0836 (10)
PJ8 ^{iv} –PK8 ^{vii}	(8)	3.933 (4)	3.9023 (9)
PL8–PL8 ^{viii}	(a)	3.870 (4)	3.8804 (9)
PJ8–PK8	(b)	3.581 (4)	3.6031 (13)
PJ8 ^{ix} –PK8 ^{ix}	(c)	3.581 (4)	3.6031 (13)
PI8–PI8 ⁱⁱ	(d)	4.043 (4)	4.0510 (14)

Symmetry codes: (i) $-\frac{1}{2} + y, \frac{5}{2} - x, -\frac{1}{4} + z$; (ii) $2 - y, 2 - x, \frac{5}{2} + z$; (iii) $-\frac{1}{2} + x, \frac{5}{2} - y, \frac{1}{4} - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$; (v) $1 + x, 2 + y, 2 + z$; (vi) $-\frac{3}{2} - y, \frac{5}{2} + x, \frac{9}{4} + z$; (vii) $y, -2 + x, 1 - z$; (viii) $2 - y, 2 - x, \frac{7}{2} + z$; (ix) $\frac{1}{2} + y, \frac{3}{2} - x, -\frac{1}{4} + z$.

is not only tedious, but also prone to errors. The determination of the low-temperature structure of 4MPNO is an illustration of the problem. Despite substantial efforts invested in the correct space-group determination, both during the structure solution (group-subgroup analysis) and after the structure refinement (searches for missing symmetry by *PLATON*), the correct symmetry was missed, and the structure was refined in a lower symmetry. When checking for the reason of the failure of *ADDSYM* to localize the missing symmetry it turned out that the deviation of the symmetry-dependent methyl groups from their ideal position was larger than the default threshold used in *PLATON*, probably due to large negative correlations between the rotation angles of the symmetry-dependent methyl groups. If the allowance threshold had been increased to 30%, *PLATON* would have indicated the correct symmetry. In general, however, the problem is quite fundamental: setting a more relaxed

threshold would detect the symmetry in the current case, but it would also indicate missing symmetry in many cases of genuine pseudo-symmetry.

The correct symmetry of the low-temperature structure of 4-methylpyridine-*N*-oxide could be determined thanks to a recently published symmetry-detection technique that does not rely on an analysis of the diffraction pattern, but uses instead an electron density of the structure solved in *P1*. This method is qualitatively different from the symmetry-determination methods based on the analysis of the diffraction pattern, and therefore does not suffer from their limitations. Since the analysis of the powder diffraction pattern for symmetry represents a particularly difficult problem, we believe that the new method is especially attractive in the field of powder diffraction.

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