

Crystal Structure of 2-[*N*-Morpholino]ethane Sulfonic Acid Hydrate, C₆H₁₅NO₅S

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Christensen, A. N., Hazell, R. G., Lehmann, M. S. and Nielsen, M., 1993. Crystal Structure of 2-[*N*-Morpholino]ethane Sulfonic Acid Hydrate, C₆H₁₅NO₅S. – Acta Chem. Scand. 47: 753–756.

The crystal structure of 2-[*N*-morpholino]ethane sulfonic acid hydrate, MES, was solved by direct methods from single-crystal X-ray diffraction data. The structure is monoclinic, space group *P*2₁/*c* (No. 14) with the lattice parameters *a* = 8.632(4), *b* = 9.985(6), *c* = 11.150(6) Å, β = 93.77(3)° and *Z* = 4. Attempts to solve the structure from synchrotron X-ray powder diffraction data were unsuccessful.

Synchrotron X-ray powder patterns have successfully been used in structure solutions of inorganic compounds, and by refinements¹ of such powder patterns combined with a similar neutron diffraction powder analysis detailed crystal structures have been obtained. Examples of structures solved and refined with the use of synchrotron X-ray powder patterns are listed in Table 1. Patterns have also been used in profile refinements of structures of compounds, isomorphous with compounds of known structures.

The procedure for solving structures from powder patterns was outlined in Refs. 2–5. The examples listed in Table 1 of solved inorganic structures are all heavy-atom structures where the heavy and possibly some of the light atoms were found from the X-ray powder patterns, and the remaining light atoms were found from the neutron diffraction powder patterns. The synchrotron X-ray powder pattern of NH₂CH₂CONHCH₂COOH, glycylglycine, was used to demonstrate that the pattern of an organic compound could be decomposed to structure factors, and that the known structure could be refined by the profile refinement methods. It was then decided to test if the structure of an organic compound with unknown structure could be solved by the method outlined above. The compound chosen was MES (2-[*N*-morpholino]ethane sulfonic acid). Unfortunately, it turned out that the synchrotron X-ray powder pattern of MES could not be used to solve the structure for two reasons: (i) The sample used contained an unidentified impurity. The extra powder lines made it impossible to index the powder pattern and to determine a unit cell and space group. (ii)

Table 1. Application of synchrotron X-ray powder patterns in structure solutions and profile refinements.

Structures solved and refined by the use of powder patterns	Structures refined in profile refinements	Refs.
I ₂ O ₄		2
	NH ₂ CH ₂ CONHCH ₂ COOH (glycylglycine)	3
PbC ₂ O ₄		4,5
	C ₄₄ H ₂₈ N ₄ TiCl ₂	6
γ-Ti(H ₂ PO ₄)(PO ₄)·2H ₂ O		7
	Al ₂ Y ₄ O ₉	8
Cr ₆ O ₂₁		9
	PbS ₂ O ₃	10
	NdSrBaCu _{2.88} O _{6.8}	11
	Nd _{1.33} Ca _{0.25} Ba _{1.42} Cu _{2.92} O _{6.8}	11
	HoBa ₂ Cu ₃ O _{7-δ}	12
	Y ₄ O(OH) ₉ NO ₃	13

When at a later stage the unit cell and space group were determined from single-crystal X-ray diffraction and the extra lines in the powder pattern could thus be eliminated, it turned out that only 65 significant structure factors could be extracted from the powder pattern out to sin θ/λ = 0.401. This number of structure factors was not sufficient for a structure determination.

Traditional single-crystal X-ray diffractometry has then been used to determine and refine the crystal structure of MES.

Experimental

Two samples of MES were used in the investigation. They were both from Sigma Chemical Co. but from two different batches. One was used in the measurement of the synchrotron X-ray powder pattern, while the other was

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used to record an in-house X-ray powder pattern and in the single-crystal X-ray diffraction measurements.

X-Ray powder diffraction. The synchrotron X-ray powder pattern of MES was measured at HASYLAB on a general-purpose diffractometer¹⁴ on the wiggler W1 beam line. The diffractometer was modified for use as a powder diffractometer.^{2,3} The in-house X-ray powder pattern of MES was measured on a Stoe diffractometer with a position-sensitive detector and Cu $K\alpha_1$ radiation. The Stoe diffractometer has a Guinier geometry for transmission diffraction and has a curved Ge monochromator that selects the Cu $K\alpha_1$ component. The diffractometer was calibrated with a standard of $\text{Ag}_6\text{Ge}_{10}\text{P}_{12}$ ($a = 10.312 \text{ \AA}$). The experimental conditions for the measurements of the two powder patterns are listed in Table 2.

X-Ray single-crystal diffractometry. Precession photographs were taken of a single crystal of MES, and the space group was determined from the photographs. The single-crystal X-ray diffraction data were measured on a Huber four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The unit cell parameters were calculated in a least-squares refinement using diffraction data from 116 reflections. The unit cell parameters and data for the single crystal investigated are listed in Table 2.

Structure determination

The in-house X-ray powder pattern of MES was indexed with the program FZON, which gave a monoclinic cell comparable to the cell found in the single-crystal diffraction measurements (Table 2). The synchrotron X-ray powder pattern of MES had extra reflections compared to the in-house X-ray powder pattern, and these extra lines hampered the automatic indexing of the pattern. However, when the extra lines were excluded the pattern could also be indexed with a monoclinic cell (Table 2).

Table 2. Experimental data and unit cell parameters for the investigated samples of MES.

Powder samples:		
Pattern source	Synchrotron	In house
$2\theta_{\min}/^\circ$	4.293	5.000
$2\theta_{\max}/^\circ$	62.558	88.780
$\Delta 2\theta/^\circ$	0.00922	0.020
$\lambda/\text{\AA}$	1.29359	1.5406
Max. $\sin \theta/\lambda/\text{\AA}^{-1}$	0.401	0.454
Diameter of capillary sample/mm	0.3	0.3
Frequency of rotation/Hz	1	2
Unit cell parameters from indexing with the program FZON ^a		
$a/\text{\AA}$	8.590	8.592
$b/\text{\AA}$	9.924	9.932
$c/\text{\AA}$	11.108	11.106
$\beta/^\circ$	93.70	93.75
Figure of merit, M_{20}	48.5	37.5
Single crystal:		
$a/\text{\AA}$	8.632(4)	
$b/\text{\AA}$	9.985(6)	
$c/\text{\AA}$	11.150(6)	
$\beta/^\circ$	93.77(3)	
Space group	$P2_1/c$ (No. 14)	
Z	4	
Size of crystal/mm	$0.05 \times 0.06 \times 0.10 \text{ mm}^3$	
Density (calcd.)/ g cm^{-3}	1.51	
Linear absorption coefficient, μ/cm^{-1}	3.4	
No. of measured reflections (two standard reflections included for every 50 reflections)	4588	
No. of independent reflections	1020	
Scan method	$\omega - 2\theta$	
Scan range in θ	$1 + 0.346 \tan \theta$	

^a Ref. 15. The synchrotron powder pattern was indexed after removal of the extra lines from the impurity.

The synchrotron X-ray powder pattern and the in-house X-ray powder pattern were decomposed to structure factors using the unit cell found with the indexing program and the space group found in the single-crystal

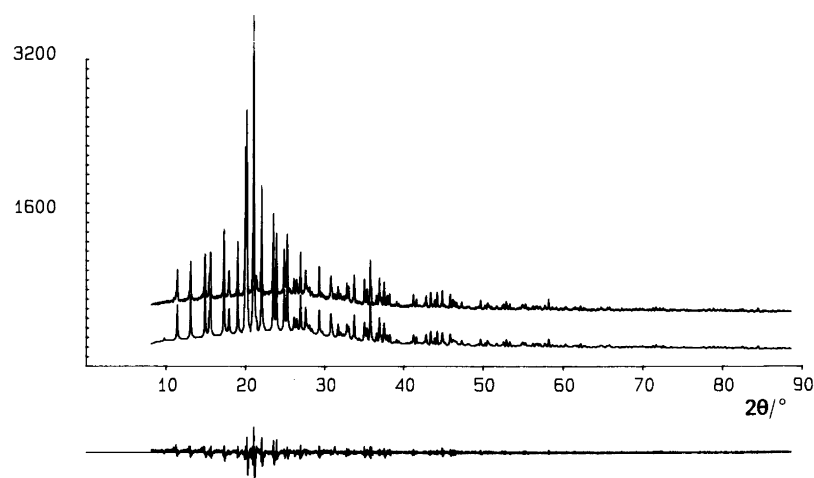


Fig. 1. Observed and calculated in-house X-ray powder pattern of MES (upper and lower curves, respectively) and difference plot below the 2θ axis.

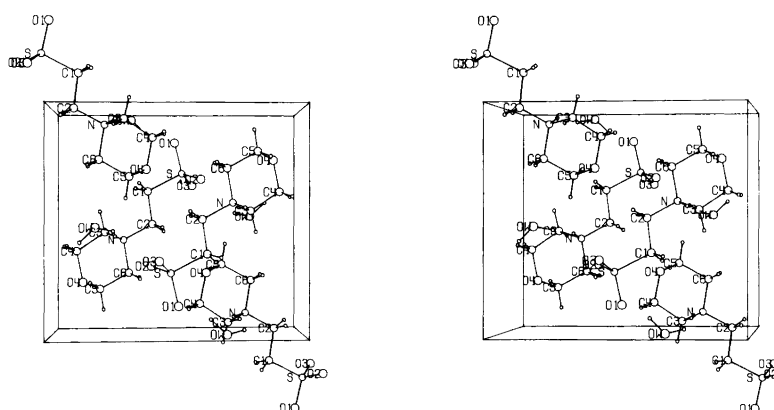


Fig. 2. Stereoscopic drawing of 2-[N-morpholino]ethane sulfonic acid hydrate along the [100] direction. The *c*-axis is along the page.

X-ray diffraction measurements using the ALLHKL program.¹⁶ Figure 1 shows the observed and calculated profiles and the difference between the profiles for the in-house powder pattern, and shows an acceptable agreement between observed and calculated pattern. Of the 644 possible reflections in the 2θ range of the pattern only 67 reflections had $F > 3\sigma(F)$. This number of structure

Table 3. Atomic coordinates and equivalent isotropic temperature factor parameters for MES.^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
S	0.7840(2)	0.7209(2)	0.4773(2)	0.036(1)
O1	0.7941(8)	0.8628(6)	0.5073(5)	0.063(4)
O2	0.6472(7)	0.6928(7)	0.4009(5)	0.058(4)
O3	0.9254(8)	0.6678(8)	0.4342(6)	0.078(5)
C1	0.7585(9)	0.6396(8)	0.6176(6)	0.038(4)
C2	0.7353(9)	0.4899(8)	0.5987(6)	0.038(4)
N	0.7412(7)	0.4182(6)	0.7179(5)	0.032(3)
C3	0.6058(8)	0.4534(8)	0.7917(8)	0.035(4)
C4	0.6158(11)	0.3696(8)	0.9054(7)	0.047(5)
O4	0.6156(6)	0.2300(6)	0.8805(5)	0.044(3)
C5	0.7458(10)	0.1951(8)	0.8150(8)	0.045(5)
C6	0.7401(9)	0.2683(8)	0.6951(7)	0.039(4)
OW	0.0282(10)	0.0242(11)	0.3109(11)	0.172(9)
H1	0.670	0.676	0.652	
H2	0.848	0.654	0.670	
H3	0.816	0.456	0.552	
H4	0.638	0.475	0.556	
H5	0.834	0.440	0.762	
H6	0.511	0.436	0.747	
H7	0.611	0.546	0.812	
H8	0.530	0.390	0.951	
H9	0.710	0.391	0.591	
H10	0.828	0.244	0.653	
H11	0.648	0.243	0.649	
H12	0.839	0.219	0.861	
H13	0.745	0.101	0.801	
H14	0.090	0.039	0.244	
H15	0.061	0.087	0.372	

^aThe positions of the hydrogen atoms are calculated assuming tetrahedral coordination of the carbon, nitrogen and oxygen atoms and bond lengths of 0.95 Å, and the positions are not refined. An isotropic temperature factor parameter $U_{\text{iso}} = 0.1$ was applied for the hydrogen atoms.

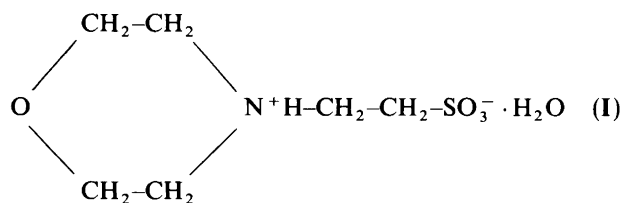
factors was too small to get a solution of the structure by direct methods using the MULTAN program.¹⁷ The similar MULTAN solution with the data from the synchrotron X-ray powder pattern had the highest peak at the position (0.83, 0.73, 0.47), less than 0.5 Å from the final sulfur atom, but it was not possible to get any further.

In the structure determination with the single crystal diffraction data a total of 1020 reflections with $I > 3\sigma(I)$ were used. The structure was solved by direct methods using the SHELX program.¹⁸ This gave the positions of all the atoms (except the hydrogen atoms) in MES, C₆H₁₃NO₄S. The positions of the hydrogen atoms were calculated assuming tetrahedral coordination of the nitrogen atom and the carbon atoms. A difference Fourier map showed an electron density that was interpreted as an oxygen atom of a water molecule, and the positions of the hydrogen atoms in this water molecule were arrived at

Table 4. Bond lengths (in Å) and angles (in degrees) for MES.

Bond lengths within the molecule			
S-O1	1.458(7)	N-C3	1.514(9)
S-O2	1.438(5)	C3-C4	1.517(11)
S-O3	1.442(6)	C4-O	1.421(9)
S-C1	1.789(7)	N-C6	1.519(10)
C1-C2	1.522(11)	C5-C6	1.521(11)
C2-N	1.508(9)	C5-O	1.424(9)
Hydrogen bonds			
OW-N	2.684(10)	OW-O1	2.707(10)
Bond angles			
O1-S-O2	111.1(4)	C2-N-C3	112.7(5)
O1-S-O3	113.3(4)	C2-N-C6	108.7(5)
O2-S-O3	114.3(4)	C3-N-C6	108.9(5)
O1-S-C1	104.5(4)	N-C3-C4	108.8(6)
O2-S-C1	106.6(3)	C3-C4-O4	112.2(6)
O3-S-C1	106.3(4)	C4-O4-C5	110.5(6)
S-C1-C2	110.2(5)	O4-C5-C6	110.6(6)
C1-C2-N	110.4(6)	C5-C6-N	109.1(6)

by packing considerations. The formula of the sample of MES investigated is thus as shown in (I).



The model of the structure was refined in a least-squares procedure using the program LINUS,¹⁹ and scattering contributions from neutral atoms.²⁰ Anisotropic thermal parameters for the non-hydrogen atoms were refined, and the positions and isotropic thermal parameters for the hydrogen atoms were not refined. Unit weights were used in the refinement. The refinements gave the final R -values of $R = 7.3\%$, and $R_w = 7.5\%$. The atomic coordinates and thermal parameters are listed in Table 3, and a list of interatomic distances is given in Table 4. A stereoscopic drawing of the structure is shown in Fig. 2.

Discussion

The single-crystal X-ray structure analysis of MES showed that the sample investigated was a hydrate. The bond lengths found in the molecule of 2-[*N*-morpholino]-ethane sulfonic acid are all in the expected ranges of bond lengths.

It was not possible to solve the structure of MES from its X-ray powder patterns. Significant structure factors could only be extracted from the lower half of the measured 2θ range, and the number of structure factors was not large enough to yield a solution by direct methods using the MULTAN program. In the upper half of the measured 2θ -range the overlap of the reflections was too great, and the intensity of the reflections too weak, for a satisfactory decomposition of the powder pattern.

The method of solving crystal structures from powder diffraction data described in Refs. 2–5 is thus applicable for heavy-atom structures (inorganic compounds), but it appears that a structure solution of organic compounds from powder patterns by the use of direct methods might be more difficult. However, synchrotron X-ray powder patterns may successfully be used in structure refinements by profile analysis in cases where the structure is known from an isomorphous compound or can be derived from packing considerations. An example of this is $\text{C}_{44}\text{H}_{30}\text{O}_6$,²¹ and the structure refinement of glycylglycine.³ It is also possible that the intensity increase

expected from the next generation of synchrotron sources might help in unravelling the necessary higher angle part of the powder patterns.

Acknowledgments. The Danish Natural Science Research Council and *Carlsbergfondet* are acknowledged for contributing financially to the four-circle diffractometer. *Teknologistyrelsen* is acknowledged for making the Stoe X-ray powder diffractometer available. Mrs. M. A. Chevallier, Mrs. C. Secher and Mr. N. J. Hansen are thanked for valuable assistance.

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Received December 16, 1992.