

Piperazine Silicate (EU 19): the Structure of a Very Small Crystal Determined with Synchrotron Radiation

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Abstract

Single-crystal diffraction data have been recorded for a very small crystal of dimensions $8 \times 18 \times 175 \mu\text{m}^3$. From these data the structure of piperazine silicate (EU 19) has been determined and refined to $R = 0.094$ for 490 observed reflections. Data collection for such a crystal has been made practicable by the high intensity of the Daresbury Synchrotron Radiation Source and the Enraf–Nonius FAST area detector diffractometer. The potential of this synchrotron radiation method for other small crystals including proteins is discussed. Crystal data: $\text{C}_4\text{H}_{12}\text{N}_2^+ \cdot \text{Si}_6\text{O}_{13}^{2-}$, $M_r = 464.6$, monoclinic, $C2/c$, $a = 13.57$ (2), $b = 4.90$ (1), $c = 22.46$ (3) Å, $\beta = 91.67$ (1)°, $V = 1493$ Å³, $Z = 4$, $D_x = 2.04$ g cm⁻³, $\lambda = 0.90$ Å, $F(000) = 952$, room temperature. The structure contains silicate double layers separated by, and hydrogen bonded to, piperazinium ions.

Introduction

The high intensity of a synchrotron radiation (SR) source should allow the recording of single-crystal intensity data for structure determination on crystals that would be considered too small for study with conventional X-ray sources. The difficulty in recording data for such very small crystals arises from (1) the very small scattering power of the crystals, and (2) the fact that crystals of this size are often rather imperfect – they have a large mosaic spread and the already weak diffraction intensity is spread over a much larger angular range. The Enraf–Nonius FAST area detector diffractometer, recently commissioned at Daresbury

Laboratory, is well suited for the measurement of these intensities.

Piperazine silicate (EU 19) was one of several compounds synthesized for use in the preparation of silica molecular sieves (Franklin & Lowe, 1987*a*); like most other compounds in this class it failed to yield crystals of good size for normal single-crystal diffraction. The SR source has therefore been used.

Experimental

Crystals of piperazine silicate (EU 19) were prepared by hydrothermal crystallization of a reaction mixture consisting of piperazine, SiO₂ and water (molar ratio 15 : 20 : 1000) in a PTFE-lined stainless-steel bomb at 423 K. Similar reaction mixtures of other amines give silica molecular-sieve precursors, and although thermal analysis and ion exchange showed that EU 19 was not a sieve precursor, they nevertheless suggested a novel structure. The largest crystals that could be grown were needles with cross sections $10 \times 15 \mu\text{m}^2$.

Very weak Weissenberg photographs (Cu K α) gave approximate cell dimensions. Intensity measurements were attempted on a CAD-4 diffractometer with Mo K α radiation (X-ray tube at 1500 W) and a reflection scan time of 90 s; of 2132 reflections measured only 103 had $I > 2\sigma(I)$. We were unable to determine the structure from this small data set.

Data were remeasured on an Enraf–Nonius FAST area detector diffractometer at the PX9.6 experimental workstation on the 5 T wiggler beamline of the SRS (Helliwell *et al.*, 1986), with the SRS

operating at 2 GeV, 10 mA. The X-ray beamline optics comprised a 750 mm 1:1 vertically focusing fused-quartz platinum-coated mirror, set at a grazing angle of 3 mrad (cut-off 0.5 Å), preceding an Si(111) 10:1 horizontally focusing monochromator and a 0.2 mm collimator. The crystal, with dimensions $8 \times 18 \times 175 \mu\text{m}^3$ was mounted on a 1 mm length of glass wool attached to a glass fibre. The crystal-to-detector distance was 39 mm, and the minimum recorded plane spacing was 1.0 Å. The *MADNES* (Pflugrath & Messerschmidt, 1986) program suite was used to collect and process data, with the dynamic masking option for intensity integration (Sjoelin & Wlodawer, 1981). An automatic indexing procedure (Jacobsen, 1976) found the crystal orientation and a triclinic unit cell; after data collection this was converted to a monoclinic cell in agreement with the earlier measurements. All the data were recorded in 6 h.

Intensity data were collected as 0.5° rotation images over a rotation range of 180° with an image integration time of 15 s. Two data collections were performed, the first at a detector tilt of $2\theta = 0^\circ$ and high-voltage gains on the image intensifier and camera of 2, the second, for the higher-resolution data, with the

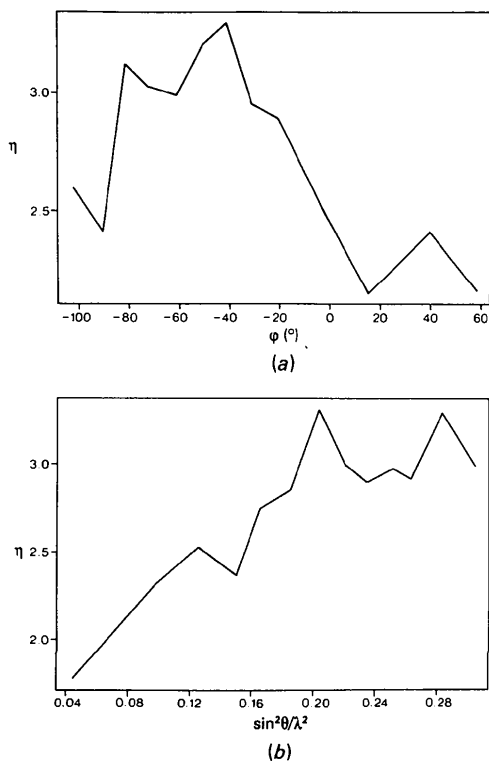


Fig. 1. (a) Variation of mosaic spread with crystal rotation, ϕ , during data collection, and (b) with $\sin^2\theta/\lambda^2$. The mosaic spread, η , is $\Delta\phi/Ld^*\cos\theta$ where $\Delta\phi$ is the measured full width of the reflections, L is the Lorentz factor, d^* the reciprocal-lattice-vector amplitude, and θ the reflection Bragg angle. The effects of beam crossfire and spectral dispersion are assumed to be negligible as they normally contribute no more than 0.1° to ϕ .

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

	x	y	z	U_{eq}
Si(1)	0.4671 (4)	0.3329 (10)	0.6835 (2)	0.0318 (36)
O(1)	0.3515 (8)	0.2805 (19)	0.6762 (4)	0.0276 (69)
O(2)	0.5247 (8)	0.1419 (20)	0.6407 (4)	0.0342 (78)
O(3)	0.4878 (7)	0.6367 (21)	0.6655 (4)	0.0341 (78)
O(4)	0.5000 (0)	0.2500 (0)	0.7500 (0)	0.0533 (119)
Si(2)	0.5627 (4)	-0.1677 (10)	0.6335 (2)	0.0332 (36)
O(5)	0.5733 (8)	-0.2217 (24)	0.5653 (4)	0.0423 (80)
O(6)	0.1660 (8)	0.3079 (22)	0.6664 (5)	0.0429 (77)
Si(3)	0.2543 (4)	0.2457 (10)	0.7110 (2)	0.0327 (35)
O(7)	0.2535 (8)	0.4464 (22)	0.7668 (4)	0.0396 (79)
N(1)	0.6621 (13)	0.3526 (32)	0.5263 (7)	0.0436 (130)
C(1)	0.6885 (17)	0.4093 (46)	0.4651 (9)	0.0569 (158)
C(2)	0.7537 (16)	0.3105 (39)	0.5625 (9)	0.0442 (140)
H(11)	0.608 (12)	0.498 (35)	0.538 (7)	0.0500 (0)
H(12)	0.636 (12)	0.149 (33)	0.519 (7)	0.0500 (0)
H(21)	0.624 (11)	0.444 (33)	0.451 (6)	0.0500 (0)
H(22)	0.724 (13)	0.568 (32)	0.469 (7)	0.0500 (0)
H(31)	0.737 (11)	0.265 (30)	0.603 (7)	0.0500 (0)
H(32)	0.791 (12)	0.521 (33)	0.569 (6)	0.0500 (0)

detector at $2\theta = 20^\circ$ with a gain of 5. The mosaic spread of the crystal, η , extracted from the individual reflection profiles, varied from 2 to 3.2° for X-rays incident in different directions on the crystal (Fig. 1); for comparison, with the same experimental arrangement we find a mosaic spread $< 0.1^\circ$ for good protein crystals.

Merging only those reflections for which a dynamic mask could be found yielded 584 independent intensities ($R = 0.08$); of these 483 had $I > 2\sigma(I)$ — i.e. nearly five times as many as in the conventional data collection. A structure solution was readily found with *MULTAN80* (Main *et al.*, 1980) and then *SHELX76* (Sheldrick, 1976). Positional and anisotropic vibration parameters for all 13 non-H atoms were refined to give $R = 0.094$ for 490 reflections with $F > 3\sigma(F)$, $wR = 0.08$, $S = 1.003$. H atoms were included at the stereochemically expected positions and refined with the C—H or N—H distances restrained; weights $1/[\sigma^2(F) + 0.00053F^2]$ were used. The atomic parameters are given in Table 1.*

Results and discussion

The structure

The numbering and connectivity are illustrated in Fig. 2 and the structure in Fig. 3. The structure consists of double layers of $(\text{Si}_6\text{O}_{13})^{2n-}$, parallel to the (001) planes, held together by strong hydrogen bonds to the piperazine cations. Figs. 2(b) and 2(c) show the two components of the double silicate layer, which are related to each other by an inversion centre at O(4);

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44419 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

each sheet is entirely composed of 8-Si-atom rings; the linking between the sheets constitutes 5-Si-atom rings.

Table 2 gives selected interatomic distances and angles. All the Si—O bond lengths lie between 1.55 (1)

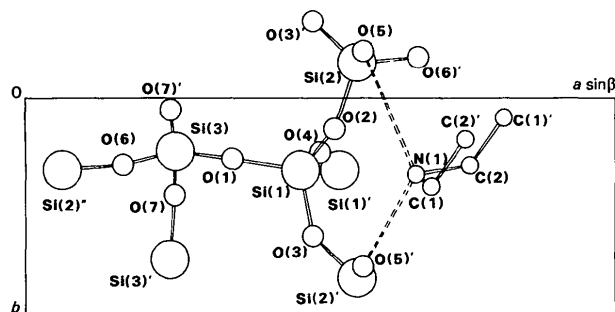


Fig. 2. *c*-Axis view of one asymmetric unit showing the atom-numbering scheme; atoms covalently bonded to atoms in the asymmetric unit are also shown and are primed. H atoms on N and C are omitted for clarity. The symmetry relations needed to derive Si(1'), etc., are given in Table 2.

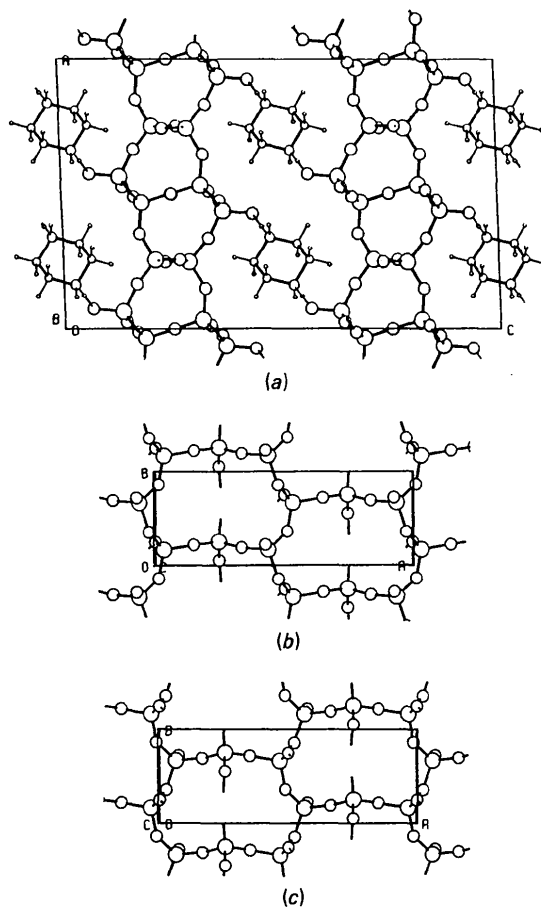


Fig. 3. (a) *b*-Axis view of the structure of EU 19: double silicate layers, parallel to the (001) planes, are held together by strong hydrogen-bonded interactions with the piperazinium cations. (b) and (c) show the two components of the double silicate layer in projection along *c*; each sheet is entirely composed of 8-Si-atom rings; the linking between the sheets constitutes 5-Si-atom rings.

Table 2. Selected interatomic distances (Å) and angles (°)

		Primed atom at
Si(1)—O(1)	1.594 (11)	
Si(1)—O(2)	1.568 (11)	
Si(1)—O(3)	1.570 (11)	
Si(1)—O(4)	1.598 (5)	
Si(2)—O(2)	1.612 (12)	
Si(2)—O(3)'	1.585 (6)	$x, y-1, z$
Si(2)—O(5)	1.566 (12)	
Si(2)—O(6)	1.569 (6)	
Si(3)—O(1)	1.562 (11)	
Si(3)—O(6)	1.568 (12)	
Si(3)—O(7)	1.595 (12)	
Si(3)—O(7)'	1.553 (11)	$0.5-x, -0.5+y, 1.5-z$
C(1)—N(1)	1.46 (3)	
C(2)—N(1)	1.48 (3)	
C(1)—C(2)'	1.48 (3)	$1.5-x, 0.5-y, 1-z$
N(1)...O(5)	3.194 (21)	
N(1)...O(5)'	2.575 (17)	$x, y+1, z$
Si(1)—O(1)—Si(3)	144.0 (7)	
Si(1)—O(2)—Si(2)	142.2 (7)	
Si(1)—O(3)—Si(2)'	144.4 (4)	$x, 1+y, z$
Si(1)—O(4)—Si(1)''	150.5 (2)	$1-x, y, 1.5-z$
Si(3)—O(6)—Si(2)''	166.0 (8)	$-0.5+x, 0.5+y, z$
Si(3)—O(7)—Si(3)'	146.7 (8)	$0.5-x, 0.5+y, 1.5-z$

and 1.61 (1) Å; O(5) is the only terminal O atom, but Si(2)—O(5) does not differ significantly from the other Si—O bond lengths. The Si—O—Si angles range from 142 to 166°. Around each N atom four atoms are approximately tetrahedrally arranged, C(1), C(2), O(5) and O(5)': N(1)—O(5)', 2.58 (2) Å, is clearly a hydrogen bond; N(1)...O(5), 3.19 (2) Å, may be a weak one.

This structure is considerably more open than the dense clathrasil, piperazine—ZSM 39, formed in crystallization at higher temperatures (453 K) (Franklin & Lowe, 1987b). As might be expected the organic moiety is readily and completely removed when EU 19 is heated in air. Above 573 K a new thermally stable (to > 1173 K) crystalline silica polymorph (EU 20) is formed. This transformation takes place pseudomorphically and probably involves cross-linking of the double sheets (Franklin & Lowe, 1987a).

Potential of the method

Limited data collections using a synchrotron source with single-counter diffractometer have been reported for other microcrystals (Bachmann, Kohler, Schulz & Weber, 1985; Eisenberger, Newsam, Leonowicz & Vaughan, 1984). Both crystallites were of good quality. The scattering power of a crystal depends on its size and complexity as shown in Table 3 and discussed by Harding (1987). By this calculation our piperazine silicate microcrystal has a scattering power comparable to that of the tiny CaF₂ crystal (Bachmann, Kohler, Schulz & Weber, 1985), and 1/300 of that of a conventional-sized crystal of similar composition. However, additionally its reflection profile is dramati-

Table 3. Comparison of crystal scattering powers (ignoring the effect of mosaic spread referred to in text)

Sample	Unit-cell scattering efficiency ^a (e ² Å ⁻⁶)	Sample volume V _s (μm ³)	Sample scattering power ^b (e ² Å ⁻³)	Approximate ratio of scattering powers
Piperazine silicate 'normal' size ^c	18 × 10 ⁻³	8 × 10 ⁶	64000 × 10 ¹²	1000
Piperazine silicate microcrystal	18 × 10 ⁻³	25 × 10 ³	200 × 10 ¹²	3
CaF ₂ microcrystal ^d	0.34	200	68 × 10 ¹²	1
Protein-lysozyme ^e 'normal' size	7.5 × 10 ⁻⁶	8 × 10 ⁶	60 × 10 ¹²	1
Protein-lysozyme microcrystal	7.5 × 10 ⁻⁶	27 × 10 ³	0.20 × 10 ¹²	0.003

Notes: (a) $\sum f^2/V_{\text{cell}}^2$, where the summation is over the atoms in the primitive unit cell with scattering factors f . (b) $V_s(\sum f^2/V_{\text{cell}}^2)$. (c) Normal size is ca 0.2 × 0.2 × 0.2 mm. (d) As used by Bachmann, Kohler, Schulz & Weber (1985). (e) Tetragonal lysozyme (Blake, Koenig, Mair, North, Phillips & Sarma, 1965). Also allowed for is 33.5wt% of solvent in the crystal.

cally different, as shown in Fig. 4, because of the difference in mosaic spread; it is evident that satisfactory measurement of reflection intensities from such a crystal is much more difficult than predicted by the simple calculation. Nevertheless the structure determination shows that it has been achieved. Such a large mosaic spread, indicative of poor crystal ordering appears to be a characteristic of many small crystals from preparations which have failed to yield larger crystals (Andrews, Hails, Harding & Cruickshank, 1987). It presumably explains why the crystals do not grow bigger, and it adds substantially to the difficulty of data collection.

The FAST electronic area detector diffractometer has allowed us to exploit the intensity of the SRS for high-resolution data collection with a comparatively short wavelength. The FAST is more effective than a single-counter diffractometer, which only measures one reflection at a time. With film, grain size and logarithmic response require densitometry with a pixel much smaller (e.g. 10 μm) than on the FAST (100 μm). Laue geometry is also being used to study microcrystal

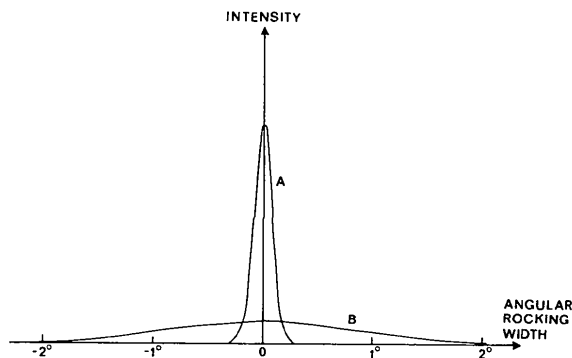


Fig. 4. *A* and *B* are hypothetical crystals of equal volume but different mosaic spread, 0.2 and 2°; the total intensity of one reflection is shown as it would be recorded on the area detector while the crystal rotates through ϕ . It is obvious that for crystal *B* the problem of distinguishing signal from noise will be much greater, even in this oversimplified case.

structures (Harding, 1987; Hedman, Hodgson, Helliwell, Liddington & Papiz, 1985; Harding, Maginn, Campbell, Clifton & Machin, 1988).

At the time the measurements were made the SRS was running in a low-current mode (single bunch) with a circulating beam of 10 mA; routinely, in multibunch mode, the injection current is 300 mA. Hence a silicate crystal volume 1/30 of that which we used, could give the same reflection intensities in multibunch mode. Diffraction data have also been recorded with the FAST diffractometer from single microcrystals of proteins (Andrews, Helliwell, Hedman & Hodgson, 1986), see Table 1; here the sample lifetime in the beam is limited. Machine enhancements are being made at the SRS to increase the intensity at the sample by a factor of 7–8, and this should allow the measurement of data from a cube of the present silicate material, with side 5 μm.

The volumes we are discussing are of the size of crystallites in a powder. New instruments for powder diffraction on the Pulsed Spallation Neutron Source (ISIS) and on SR Sources offer very high angular resolution powder data, where resolutions are limited only by the sample mosaic. These data can now be used for *ab initio* structure determination (Cheetham, 1987). Large mosaic rocking widths such as we have found may be a limitation for the powder method, but if data can be measured the single-crystal method is much better.

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More Space-Group Changes*

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Abstract

Revised structures are reported for 19 crystalline compounds, based on space groups of higher symmetry than originally reported. In four cases the Laue symmetry is changed, one from $\bar{1}$ to $2/m$ and three from $2/m$ to mmm ; in the remaining fifteen a center of symmetry has been added. For eight of these latter compounds we have obtained F values and carried out least-squares refinements in the centrosymmetric space groups, with more satisfactory results than originally reported.

Introduction

We present here revised crystal structures for nineteen additional (Marsh & Herbstein, 1983, and references therein) compounds for which the original descriptions were based on space groups of unnecessarily low symmetry. In four cases the crystal class is revised, one from triclinic to monoclinic and three from monoclinic to orthorhombic; in the remaining fifteen, centers of symmetry are added. As noted earlier (Schomaker & Marsh, 1979), the increases in Laue symmetry have involved no significant changes in the structural parameters; the additional symmetry elements have become crystallographically exact rather than approximate and, usually, unrecognized. On the other hand, the additions of centers of symmetries have removed inherent singularities associated with refining a centrosymmetric structure in a non-centrosymmetric space

group, and highly significant parameter changes usually resulted. For eight of the non-centrosymmetric-to-centrosymmetric cases we have been able to obtain the original F data and carry out successful refinements. Details follow.‡

Category 1: changes in Laue group

Methyl 8-isopropyl-3,3a,8,8a-tetrahydroindeno[2,1-c]-pyrazole-8a-carboxylate, $C_{15}H_{18}N_2O_2$

The structure of this compound was reported as triclinic, space group $P\bar{1}$, $Z = 2$ (Toupet & Messenger, 1984a; the correct value for Z is 4); the cell dimensions were subsequently corrected to: $a = 5.791$ (4), $b = 15.503$ (4), $c = 15.954$ (5) Å, $\alpha = 82.24$ (5), $\beta = 79.35$ (6), $\gamma = 79.13$ (5)° (Toupet & Messenger, 1984b). The structure is better described in $C2/c$.

The vectors $[-1,2,0]$, $[-1,0,0]$, $[0,-1,1]$ define a C -centered cell with $a' = 30.450$, $b' = 5.791$, $c' = 20.690$ Å, $\alpha' = 90.07$, $\beta' = 131.09$, $\gamma' = 90.11$ °, $Z = 8$; the corresponding transformation $x' = \frac{1}{2}(y+z)$, $y' = -x - \frac{1}{2}(y+z)$, $z' = z$ leads to coordinates that are compatible with $C2/c$ within the reported e.s.d.'s. The $C2/c$ coordinates, averaged over molecules A and B , are given in Table 1.

The c -glide plane of $C2/c$ requires the absence of reflections $0kl$ with $(k+l)$ odd in the triclinic system. The supplementary table of F 's (SUP 38963) contains

‡ Lists of observed and calculated structure factors for nine of the compounds, and anisotropic thermal parameters for ten of the compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44411 (76 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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