

The surprisingly elusive crystal structure of sodium metabisulfite

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The crystal structure of $\text{Na}_2\text{S}_2\text{O}_5$, a simple and common ionic compound, is reported here for the first time. The crystals form non-merohedral twins, with the twin domains related by a twofold axis which bisects the angle between the **a** and **c** axes of each unit cell. The structure was determined from a single-crystal fragment of a twinned crystal that had undergone cleavage along the twin boundary. In addition to the problems associated with twinning, space-group determination proved difficult as well, with the structure initially determined in the $P2_1$ space group appearing to be disordered with two rotational conformers of the metabisulfite ion occupying equivalent sites in the lattice. An analysis at low temperature provided new weak reflections which were inconsistent with the original unit cell, but indexed to the correct unit cell, allowing for space group and crystal structure determination. The apparent structure, which appeared disordered in $P2_1$, seems to have resulted from an apparently fortuitous superposition of two conformationally inequivalent $\text{S}_2\text{O}_5^{2-}$ anions in the asymmetric unit of the correct structure in the $P2_1/n$ space group. The metabisulfite ions in this structure do not adopt the C_s geometry observed in previously determined crystal structures containing $\text{S}_2\text{O}_5^{2-}$. The structures of both ions in the asymmetric unit are effectively conformational mirror images of one another with two of the O atoms on each S atom in the ion approaching an eclipsed geometry. This observation provides further evidence that the structures of sulfur-oxy anions in the solid state are dictated mainly by interionic coulombic forces rather than by intraionic bonding interactions.

1. Introduction

For a number of years we have been interested in the structure and reactivity of sulfur-oxy anions, especially those containing sulfur–sulfur bonds (Hodgeman *et al.*, 1991; Weinrach *et al.*, 1992; Carter *et al.*, 1993; Holman & Bennett, 1994). The nature of the sulfur–sulfur bond in these compounds has been the subject of both experimental and theoretical investigations, with comparisons often made between the dithionite, metabisulfite¹ and dithionate ions. In the course of our investigations we noted that the structure of potassium metabisulfite, $\text{K}_2\text{S}_2\text{O}_5$, was reported by Zachariasen (1932) in the early days of crystallographic structural investigations, solved from intensities estimated from Laue photographs, repeated by Lindqvist & Mörtzell (1957) from estimated intensities from Weissenberg photographs and determined for a third time by Chen & Wang (1984) from data collected on a single-crystal

¹ The metabisulfite ion is also commonly referred to as the pyrosulfite ion, and less commonly, as the disulfite ion.

Table 1

Experimental details.

	Sodium metabisulfite in $P2_1/n$	Sodium metabisulfite in $P2_1$
Crystal data		
Chemical formula	$\text{Na}_2\text{O}_5\text{S}_2$	$\text{Na}_2\text{O}_5\text{S}_2$
M_r	190.1	190.1
Cell setting, space group	Monoclinic, $P12_1/n1$	Monoclinic, $P12_11$
a, b, c (Å)	9.0600 (10), 5.4470 (10), 21.560 (2)	6.0730 (10), 5.4700 (10), 8.3180 (10)
β (°)	95.310 (10)	103.160 (10)
V (Å ³)	1059.4 (2)	269.06 (7)
Z	8	2
D_x (Mg m ⁻³)	2.384	2.346
Radiation type	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	49	39
θ range (°)	4.5–13.1	4.5–19.9
μ (mm ⁻¹)	1.10	1.08
Temperature (K)	153 (2)	293 (2)
Crystal form, color	Rectangular solid, colorless	Rectangular solid, colorless
Crystal size (mm)	0.3 × 0.2 × 0.2	0.25 × 0.2 × 0.15
Data collection		
Diffractometer	Bruker P4	Bruker P4
Data collection method	ω - 2θ	ω - 2θ
Absorption correction	For a cylinder mounted on the φ axis	None
T_{\min}	0.604	–
T_{\max}	0.609	–
No. of measured, independent and observed reflections	4568, 2419, 2004	1831, 1559, 1349
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.049	0.030
θ_{max} (°)	27.5	30.0
Range of h, k, l	–11 \Rightarrow $h \Rightarrow$ 11 –6 \Rightarrow $k \Rightarrow$ 7 –28 \Rightarrow $l \Rightarrow$ 28	–8 \Rightarrow $h \Rightarrow$ 8 –7 \Rightarrow $k \Rightarrow$ 7 –11 \Rightarrow $l \Rightarrow$ 11
Intensity decay (%)	6.4	7.6
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.115, 1.15	0.040, 0.110, 1.07
No. of reflections	2419	1559
No. of parameters	163	111
H-atom treatment	No H atoms present	No H atoms present
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 4.7418P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.3072P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	<0.0001	0.001
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.75, –0.78	0.56, –0.50

Computer programs: *Bruker Xscans*, *SIR97* (Altomare *et al.*, 1999), *SHELXS97* (Sheldrick, 1997), *ORTEP-3 for Windows* (Farrugia, 1997), *WinGX publication routines* (Farrugia, 1999).

autodiffractometer using a scintillation detector. Other reported structures containing the metabisulfite ion include ammonium metabisulfite, $(\text{NH}_4)_2\text{S}_2\text{O}_5$ (Baggio, 1971) and pentapotassium disulfite tris(hydrogensulfite), $\text{K}_5(\text{HSO}_3)_3(\text{S}_2\text{O}_5)$ (Magnusson *et al.*, 1983). It was therefore surprising that we found no structural investigation of the common salt of the metabisulfite ion, sodium metabisulfite, even though this material is used extensively as a waste and sewage treatment agent, and is an important component of photographic solutions, a food preservative and a common reducing agent in chemical synthesis. The absence of a structure became increasingly intriguing when, during studies of

the reaction chemistry of sodium dithionite, in which we prepared solutions of a number of sulfur-oxo salts including sodium metabisulfite, we observed what appeared to be diffraction quality crystals of $\text{Na}_2\text{S}_2\text{O}_5$ in the commercial reagent purchased from Aldrich Chemical company.

Thus, the obvious question: If small, clear crystals virtually ‘fall out’ in the manufacturing process, why has no one bothered to collect data and solve the crystal structure? We mounted a crystal and began the structural solution process. The account, which follows, chronicles the determination of the crystal structure of sodium metabisulfite – and illustrates the reasons why the structure had, in all likelihood, eluded crystallographers in the past.

2. Experimental

2.1. Materials and methods

Crystals of sodium metabisulfite were used as received from the vendor, Sigma-Aldrich Co. A minute fraction of these crystals, which are twinned, appear to have broken along the twin boundary. The crystals were screened under a binocular microscope for selection of one of these fragments consisting of a single domain of a parent twinned crystal. For ambient temperature data collection, these fragmented crystals were mounted in a quartz capillary tube and anchored to a wall with epoxy. Both ends of the capillary were sealed with epoxy to protect the crystals from water vapor, because of their hygroscopic nature. Crystals for low-temperature data collection were

glued onto a glass fiber with epoxy and placed immediately in a cold, dry nitrogen stream on the diffractometer. The density of sodium metabisulfite was measured by adding small crystals of the material to a preweighed 25 ml volumetric flask containing carbon tetrachloride, then adding sufficient bromoform to suspend the crystals, followed by diminution of the volume to the 25 mL mark and reweighing the volumetric flask. Lattice energies were calculated using GULP, the General Utility Lattice Program (Gale & Rohl, 2003). Charge distributions on the ions were obtained from density functional calculations (Carter *et al.*, 1993). Calculations were performed from coordinates generated by rotating the thio-

nate group around the sulfur–sulfur bond in 5° increments, running a separate computation for each set of coordinates. The positions of the cations and the remaining atoms in the anion were held constant in the unit cell. The dominant component of the lattice energy was coulombic, with virtually no change in short-term interaction energies.

2.2. X-ray crystallography

Intensity data were collected on a Bruker P4 diffractometer at 153 K using graphite Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in the ω - 2θ bisecting mode. The structure was solved by direct methods using *SIR97* (Altomare *et al.*, 1999) and refined by full-matrix least-squares based on F^2 using *SHELXL97* (Sheldrick, 1997) as incorporated into the *WINGX* program suite (Farrugia, 1999). All atoms were refined anisotropically. Additional crystallographic details are given in Table 1. Atomic coordinates and anisotropic thermal parameters are given as supplementary data.²

3. Results and discussion

3.1. Density problems and twinning

Numerous crystals taken directly from the commercial sample appeared to be ideal for crystallography; several produced rotation photographs that appeared to be from single crystals. In each case 25–30 centered reflections were indexed to an orthorhombic unit cell with (triclinic) lattice parameters $a = 8.304$ (2), $b = 35.4317$ (11), $c = 5.4636$ (2) \AA , $\alpha = 90.03$ (3), $\beta = 90.00$ (3), $\gamma = 90.04$ (2)°, $V = 1607.6$ (7) \AA^3 . Based on a molar mass of 190.11 g mol^{-1} , 8 formula units per unit cell were consistent with an X-ray density of 1.571 g cm^{-3} . The density listed by Weast (1973) of 1.4 g cm^{-3} was inconsistent with the X-ray density and that listed in the Sigma–Aldrich catalogue for the material used in this study was 1.480 g cm^{-3} , still quite low. We initially rationalized that this difference resulted from the hygroscopic nature of the material, which might have made it difficult to determine an accurate density.

However, we were led to reinvestigate the density problem when efforts to solve the structure from data collected based upon the orthorhombic unit cell proved fruitless. Two flotation density determinations using a carbon tetrachloride/bromoform mixture provided measured densities of 2.34 and 2.36 g cm^{-3} , significantly higher than the published values. The new measured density was, however, much more consistent with that of similar compounds obtained from crystal structures. For example, sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, has a density of 2.41 g cm^{-3} (Weinrach *et al.*, 1992).

Based upon the measured density, 12 formula units per unit cell provided an X-ray density of 2.356 g cm^{-3} . While this was very close to the measured density, the X-ray density would require 1.5 formula units per asymmetric unit in a centrosymmetric orthorhombic unit cell. The ‘ideal’ metabisulfite ion

has mirror symmetry, suggesting that the location of one of two anions along with an accompanying sodium cation on a mirror plane containing two S atoms, the sodium ion and one O atom on $-\text{SO}_3$ was possible, if not probable. Attempts to solve the structure with this constraint, however, again proved fruitless.

The inability to solve the structure, coupled with the relatively long unique axis, led us to investigate the possibility that the ‘ideal’ crystals found in the commercial reagent were actually twins. A microscopic analysis of the crystals under cross-polarizers revealed no apparent boundaries that would have been indicative of a polycrystalline material or a twin. However, while observing the crystals under the microscope, it was noted that a very small number of crystals appeared to have cleaved along an atypical cleavage plane, splitting the crystal into two halves. Fig. 1 illustrates a typical crystal of sodium metabisulfite (*A*) and a ‘cleaved’ crystal (*B*). We hypothesized that some of the crystals had split along a twin boundary and that data collection with one of these cleaved crystals would yield a structure.

3.2. Apparent disorder

A rotation photograph from a cleaved crystal yielded 27 centered reflections which were indexed to a monoclinic unit cell with (triclinic) lattice parameters $a = 6.073$ (1), $b = 5.470$ (1), $c = 8.318$ (1) \AA , $\alpha = 90.04$ (1), $\beta = 103.16$ (1), $\gamma = 89.97$ (1)°, $V = 266.06$ (7) \AA^3 . For a unit cell with two formula units of $\text{Na}_2\text{S}_2\text{O}_5$, the X-ray density was 2.346 g cm^{-3} , consistent with the measured density. Systematic absences were consistent with either the $P2_1$ or $P2_1/m$ space groups. An analysis of E -statistics strongly indicated a centrosymmetric structure, with $\text{mod}(|E^2 - 1|) = 0.953$; $P2_1/m$ was selected as the more likely space group. This selection also seemed reasonable since $\text{K}_2\text{S}_2\text{O}_5$ packs in a $P2_1/m$ lattice with very

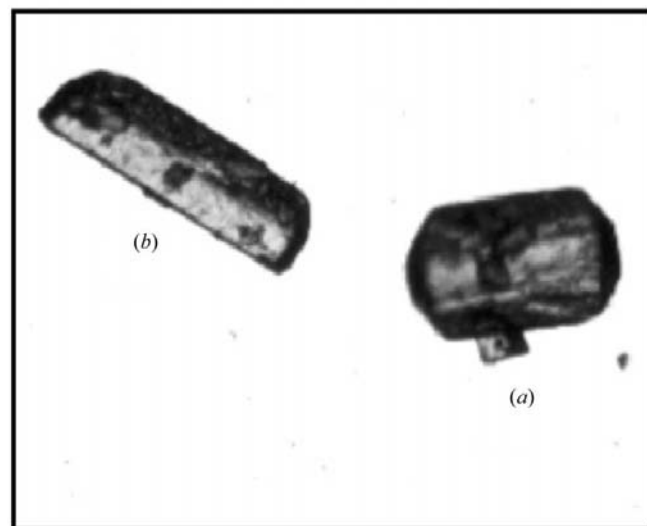


Figure 1

Crystals of sodium metabisulfite: (a) typical twinned crystal; (b) single twin domain, cleaved along the twin boundary (longest dimension approximately 0.3 mm).

² Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0141). Services for accessing these data are described at the back of the journal.

similar unit-cell parameters. However, the structure did not solve in this space group. Direct methods provided the locations of two S atoms at a reasonable internuclear distance of 2.23 Å and two Na atoms. As required by symmetry for $Z = 2$, all four heavy atoms were located on a mirror plane, but no reasonable O-atom positions appeared in a difference-Fourier map (not even the thionate O atom would be required to reside on the mirror plane). The symmetry constraints were therefore relaxed and a solution was attempted in the non-centrosymmetric space group $P2_1$. Direct methods located the positions of two S atoms with an internuclear distance of 2.22 Å, similar to the S—S distances for $K_2S_2O_5$ and $(NH_4)_2S_2O_5$ (both 2.17 Å). A difference map revealed the two O atoms bonded to the thionite ($-SO_2$) end of the anion, but six atoms appeared to be bonded to the thionate ($-SO_3$) end of the anion, appearing as two rotational conformations of the thionate group. From all appearances, the structure appeared disordered, with two rotational conformers occupying the anion locations in the lattice. The structure was refined with site occupancy factors for the two thionate groups as variables. Because of the apparently anomalous nature of the anion in this structure, we collected data on two additional crystals. Each crystal structure produced essentially the same results. Fig. 2(a) illustrates the anion determined from the structural solution; Figs. 2(b) and (c) illustrate the two apparent disordered conformations of the anion in the lattice. Independent refinement of the site occupancy factors gave values for the two conformers of 0.48 (2) and 0.54 (2), respectively, indicating a 1:1 ratio of the sites occupied by the two conformers in the lattice. The structure refined reasonably for ambient temperature data, with $wR_2 = 0.101$ and $R_1 = 0.040$ for 1359 observed reflections, and $wR_2 = 0.111$ and $R_1 = 0.050$ for all 1559 reflections. The only apparent anomaly was the large and elongated thermal ellipsoid of each O atom on the thionite

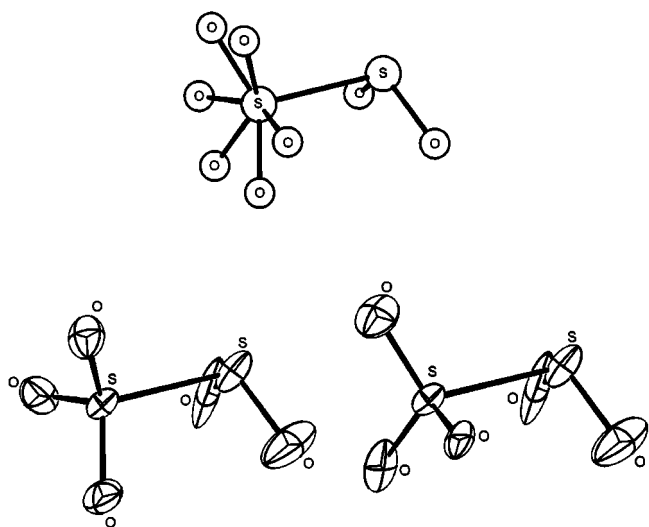


Figure 2 Apparent disordered structure of the metabisulfite ion determined in the $P2_1$ space group (top) and refined structures of the two conformers of the anion in this space group, shown with 50% probability ellipsoids (bottom).

end of the anion. While it was possible that these ellipsoids were the result of slightly different locations of the conformer in the unit cell (rotated slightly around the S—S axis), the elongations did not appear to be in the expected directions (elongated orthogonally to the S—S rotation axis).

In order to test the hypothesis that these conformers were located in a disordered fashion in the unit cell, we determined lattice energies for various rotational angles of the thionite group around the S—S bond in the structure, expecting to find the minima for the two observed conformations. Fig. 3 is a plot of calculated lattice energies as a function of rotation angle, with the eclipsed conformation at zero degrees. The crystallographically determined conformer angles are indicated with arrows on the plot; there is only a single energy minimum and neither conformer provides a lattice energy at that minimum. Based on the large ellipsoids and the inconsistencies in the lattice energies, we elected to recollect data at low temperature in order to determine if the ellipsoids were due to thermal motion, and if the structure was actually disordered. In the latter case we hypothesized that the minimum energy conformer might be observed at low temperature.

3.3. Determination of correct lattice parameters, space group and structure

Since numerous crystals had consistently yielded the same unit cell when indexing reflections were located from rotation photographs, we elected to randomly search reciprocal space to be certain that the unit cell and space group were correct. To our surprise, several fairly weak reflections (perhaps missed from film data at ambient temperature) were located which were inconsistent with the previous unit cell, but did not generate the orthorhombic unit cell observed from the crystals

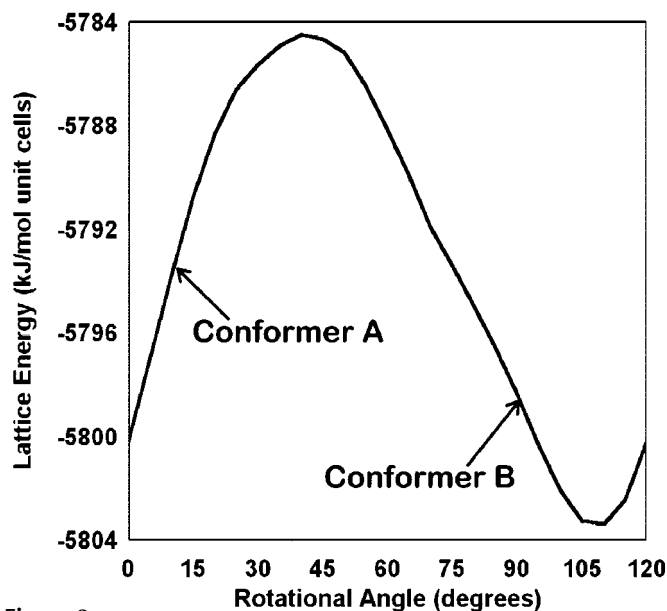


Figure 3 Lattice energies of sodium metabisulfite in the $P2_1$ space group as a function of rotation of the thionate group around the sulfur-sulfur bond. The lattice energies calculated for the conformers identified in the structural solution are indicated with arrows.

that we believed to be twinned. The entire set of 49 reflections indexed to a monoclinic unit cell with (triclinic) lattice parameters $a = 9.0597$ (11), $b = 5.4477$ (8), $c = 21.5583$ (27) Å, $\alpha = 89.992$ (10), $\beta = 95.313$ (8), $\gamma = 90.000$ (12)°, $V = 1059.42$ (19) Å³. For a unit cell with $Z = 8$, the X-ray density was 2.38 g cm^{-3} , again consistent with the measured density, but now indicating the probability of a centrosymmetric space group with two formula units per asymmetric unit. Intensity statistics indicated a centrosymmetric structure and systematic absences from data collection determined that the space group was $P2_1/n$. The structure solved readily using direct methods, refining to $wR_2 = 0.095$ and $R_1 = 0.041$ for observed reflections.

The structure showed no indications of disorder at 153 K, but this still did not rule out the possibility that the structure was disordered at ambient temperature in the $P2_1$ space group, undergoing a phase transition to an ordered structure at low temperature. To investigate this possibility, we analysed the initial set of 20 reflections used to index the $P2_1/n$ lattice in order to determine if a subset would produce the $P2_1$ unit cell.

The removal of a *single* reflection accomplished this, providing a clear reason for the persistent appearance of this lattice in our attempts to solve the structure. The index transformation matrix that resulted from this analysis, which converts the data indexed in $P2_1$ to that indexed in $P2_1/n$ is

$$\begin{pmatrix} -1 & 0 & -1 \\ 0 & 1 & 0 \\ 3 & 0 & -1 \end{pmatrix}.$$

Re-indexing the ambient temperature ($P2_1$) data produced a structural solution consistent with that collected at low temperature ($P2_1/n$). The low-temperature data set was then re-indexed with the inverse transform, generating a small subset of reflections with integer indices that reproduced the 'overlapping' structure solution determined at ambient temperature. This analysis provided strong evidence of a single structure at both temperatures. In order to rule out the 'disorder' explanation completely, data on a new crystal indexed in $P2_1$ was collected at 153 K. The structural solution was identical to that determined from ambient temperature data, with the exception that several of the thermal parameters were unreasonable, and the R factors were higher ($R_1 = 0.062$, $wR_2 = 0.16$). Thus, the ambient temperature data for the $P2_1$ structure are reported here.

3.4. Relationship between the $P2_1$ and $P2_1/n$ solutions

The re-indexing exercise described above afforded orientation matrices for both space groups and allowed for a determination of the relationship between the two lattices. Fig. 4(a) illustrates this relationship. The view is down the \mathbf{b} axes of both lattices, which have virtually identical lengths. Note that the lattices do not share a common origin; the origin/inversion centers of the $P2_1/n$ unit cell lie at the midpoints of the \mathbf{a} and \mathbf{c} axes of the $P2_1$ unit cell. Fig. 4(b) illustrates the unit cell for the $P2_1$ structure. The $P2_1/n$ structure consists of two different sub-cells, related to one another by the inversion center. The two metabisulfite anions in the $P2_1/n$ asymmetric unit have their sulfur–sulfur bonds *nearly* aligned along a vector parallel to the ac diagonal, the translation direction along the n -glide plane. The $P2_1$ solution superimposes these two sub-cells. Fig. 4(c) illustrates the results of this superposition on the positions of the two anions in the asymmetric unit in $P2_1/n$; Fig. 4(d) shows the resulting solution obtained in the $P2_1$ space group. The closed circles in Figs. 4(a) and (b) indicate the location of the screw axes in each unit cell. The locations of the screw axes in the $P2_1/n$ structure *do not* coincide with those in the $P2_1$ cell. The two components of an asymmetric unit in the $P2_1/n$ lattice constitute the contents of each subcell, related to each other by *approximate* 2_1 symmetry. The fortuitous alignment of the sulfur–sulfur bonds and the imposition of rigorous 2_1 symmetry in the $P2_1$ structure has resulted in a structural solution that appears as a single metabisulfite ion in two different conformations! Fortunately, the thionate groups in the two metabisulfite ions in the asymmetric unit were rotated sufficiently with respect to one another to allow for resolution of the positions of the O atoms, yielding the anomalous

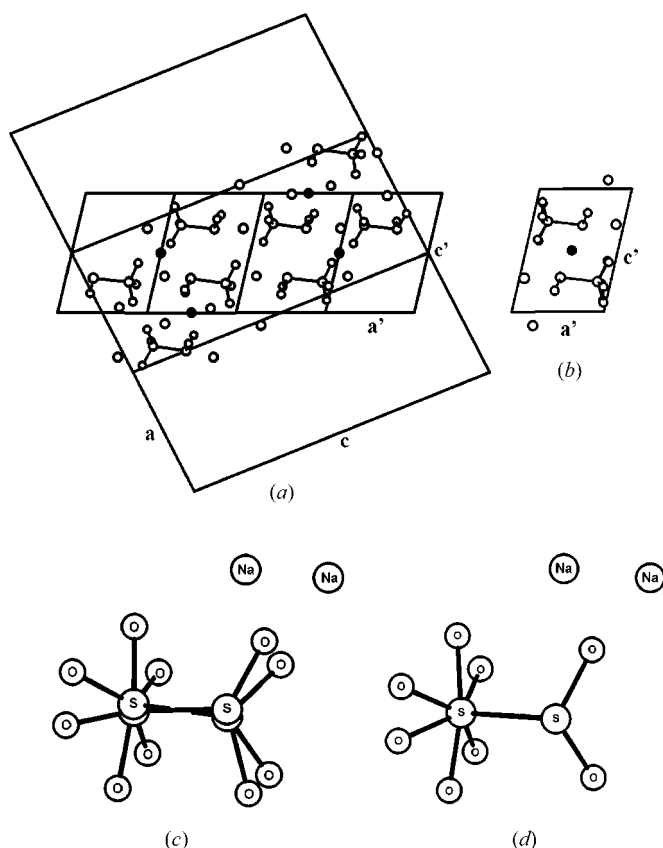


Figure 4

(a) Crystal packing of $\text{Na}_2\text{S}_2\text{O}_5$ in the $P2_1/n$ space group viewed down the unique \mathbf{b} axis. Four unit cells of $\text{Na}_2\text{S}_2\text{O}_5$ in the $P2_1$ space group are superimposed to illustrate the subcells responsible for the superpositioned structure determined in $P2_1$. The filled circles show the locations of the 2_1 axes. (b) Crystal packing of $\text{Na}_2\text{S}_2\text{O}_5$ in the $P2_1$ space group viewed down the unique \mathbf{b} axis. The filled circle shows the locations of the 2_1 axis. (c) Inequivalent ions in the $P2_1/n$ space group superimposed by an approximate $(0.25, 0, -0.25)$ translation. (d) Structure of superimposed $\text{Na}_2\text{S}_2\text{O}_5$ ions determined in the $P2_1$ space group.

Table 2

 Comparison of average bond lengths (Å) and angles (°) for Na₂S₂O₅ in *P*2₁/*n* and *P*2₁.

	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁
S–S	2.2172 (11)	2.2199 (9)
S–O (thionate)	1.463 (2)	1.464 (2)
S–O (thionite)	1.495 (2)	1.476 (8)
S–S–O (thionate)	106.41 (11)	107.7 (5)
S–S–O (thionite)	99.10 (3)	99.3 (3)
O–S–O (thionate)	112.35 (15)	112.1 (8)
O–S–O (thionite)	109.65 (15)	108.5 (3)

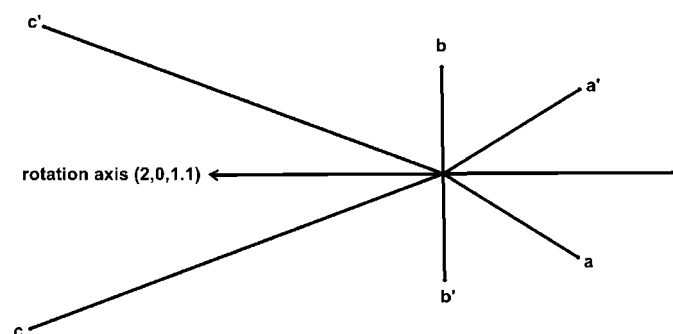
structure which subsequently led to further investigation and determination of the correct lattice parameters and space group. Table 2 compares the average bond lengths and angles for the structures refined in each space group.

3.5. Determination of twin component transformations

The determination of the correct unit cell allowed for the reinvestigation of the putative twin structure. The initial set of centered reflections were indexed into two sets, each generating the unit cell determined above in a different orientation, with orientation matrices **A**₁ and **A**₂, respectively. The matrix which transforms **A**₁ into **A**₂, **R**_{*t*}, is given by

$$\mathbf{R}_t = \mathbf{A}_2(\mathbf{A}_1)^{-1} = \begin{pmatrix} 0.929 & 0.272 & 0.253 \\ 0.273 & -0.963 & 0.036 \\ 0.252 & 0.036 & -0.968 \end{pmatrix}.$$

The eigenvectors and eigenvalues of **R**_{*t*} give the rotation axis and rotation angles which transform one reciprocal cell into the other. **R**_{*t*} has eigenvalues 1.001, –1.002 and –1.001. The non-integer matrix elements make it clear that the unit cells in the twin are *not* related by a simple rotation around a reciprocal cell axis, as is often the case. The eigenvector with the eigenvalue 1.00 is the rotation axis (0.982, 0.138, 0.128); the remaining eigenvalues give the rotation angles $\theta_1 = 1.00\pi$ and $\theta_2 = 1.00\pi$, respectively. Fig. 5 illustrates the relation between the two direct space unit cells in the non-merohedral twin, which are rotated into one another about a twofold axis that is


Figure 5

Relation between the unit-cell vectors in the sodium metabisulfite twinned crystals, showing the twofold rotation axis lying in the **a**–**c**/**a'**–**c'** plane. The coordinates of the rotation axis are given in fractional coordinates.

perpendicular to the unique axes of both unit cells (anti-parallel to one another). The rotation axis lies in the **a**–**c**/**a'**–**c'** plane and bisects the angles between the **a**, –**a'** and **b**, **b'** vectors. Note the location of the twin axis in Fig. 5 and the cleavage plane observed in Fig. 1, indicating that, as suspected, the crystal had broken along the twin boundary.

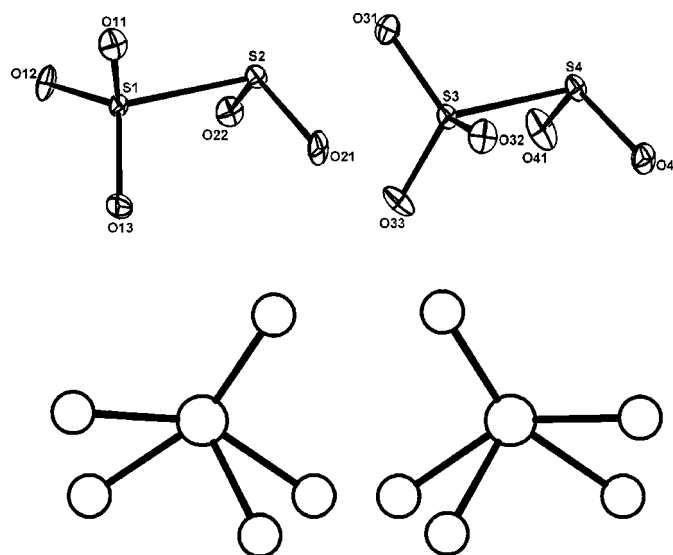
The twin law matrix, **R**_{*h*}, is given by

$$\mathbf{R}_h = (\mathbf{A}_2)^{-1} \mathbf{A}_1 = \begin{pmatrix} -0.249 & 0.001 & -0.418 \\ 0.000 & -1.001 & 0.000 \\ -2.252 & -0.003 & 0.248 \end{pmatrix}.$$

R_{*h*} transforms a reciprocal vector in the first twin, **h**₁, into a reciprocal vector in the second twin, **h**₂, and confirms that the twin rotation reverses the direction of the **b** axis.

3.6. Structures of two conformers of the metabisulfite ion

In previous work we have shown that the dithionite ion, S₂O₄^{2–}, adopts conformations which favor coulombic interactions in the lattice rather than those dictated by intramolecular bonding. The results of the structural determination reported here illustrate that the metabisulfite ion behaves similarly. In all the previously reported structures (Baggio, 1971; Chen & Wang, 1984; Magnusson *et al.*, 1983) containing the metabisulfite ion, the expected ‘staggered’ *C*_s conformation is observed, in which the projected lone pair on the thionite S atom is bisecting the angle between two of the O atoms on the thionate end of the anion, with mirror symmetry imposed crystallographically. In the structure reported here, neither conformer adopts the ‘expected’ conformation, with pairs of O atoms on the thionite and thionate ends of each anion approaching an eclipsed arrangement. The structures of both conformers are illustrated in Fig. 6. The projection of each conformer is shown directly below its thermal ellipsoid plot. The anions are virtually mirror images of one another, with


Figure 6

Top: Metabisulfite anions in the asymmetric unit of Na₂S₂O₅ in the *P*2₁/*n* space group. Displacement ellipsoids are shown at the 50% probability level. Bottom: Projections of the anions, viewed down the sulfur–sulfur bonding axis from the thionate S atom toward the thionite S atom.

Table 3Comparison of selected bond lengths (Å) and angles (°) for Na₂S₂O₅, K₂S₂O₅, (NH₄)₂S₂O₅ and K₅(HSO₃)₃(S₂O₅).

	Na ₂ S ₂ O ₅ (Conformer 1)	Na ₂ S ₂ O ₅ (Conformer 2)	K ₂ S ₂ O ₅ (Chen & Wang, 1984)	(NH ₄) ₂ S ₂ O ₅ (Baggio, 1971)	K ₅ (HSO ₃) ₃ (S ₂ O ₅) (Magnusson <i>et al.</i> , 1983)
S1—S2†	2.2179 (11)	2.2165 (11)	2.2149 (9)	2.170 (4)	2.226 (2)
S1—O11	1.465 (3)	1.456 (3)	1.4602 (8)	1.455 (6)	1.462 (4)
S1—O12	1.459 (2)	1.463 (2)	1.453 (1)	1.453 (7)	1.463 (3)
S1—O13	1.466 (3)	1.472 (2)	1.453 (1)	1.453 (7)	1.463 (3)
S2—O21	1.491 (3)	1.493(3)	1.4870 (8)	1.495 (7)	1.489 (3)
S2—O22	1.498 (3)	1.496 (3)	1.4870 (8)	1.495 (7)	1.489 (3)
S2—S1—O11	108.33 (11)	107.09 (11)	105.47 (3)	105.1 (3)	105.5 (2)
S2—S1—O12	104.39 (11)	105.29 (11)	107.16 (5)	106.7 (3)	106.7 (1)
S2—S1—O13	106.90 (11)	106.48 (11)	107.16 (5)	106.7 (3)	106.7 (1)
S1—S2—O21	99.80 (11)	98.68 (11)	99.12 (3)	98.5 (3)	98.9 (1)
S1—S2—O22	98.39 (10)	99.52 (10)	99.12 (3)	98.5 (3)	98.9 (1)
O11—S1—O12	112.78 (15)	113.28 (16)	112.78 (4)	112.8 (4)	110.5 (1)
O11—S1—O13	110.74 (16)	110.93 (15)	112.78 (4)	112.8 (4)	110.5 (1)
O12—S1—O13	113.21 (16)	113.18 (15)	112.5 (4)	112.5 (1)	112.45 (4)
O21—S2—O22	109.96 (15)	109.33 (15)	111.2 (4)	112.3 (1)	110.63 (5)

† Atomic positions for conformer 2 are the pseudo-‘mirror equivalents’ of conformer 1. For the referenced structures the atom positions correspond to those most closely related to the structures reported here.

their centroids lying along a vector essentially parallel to the diagonal glide direction. Table 3 compares these conformers with the metabisulfite anions in K₂S₂O₅, (NH₄)₂S₂O₅ and K₅(HSO₃)₃(S₂O₅). The sulfur–sulfur bond length is of particular interest, since its length has been cited as an indicator of the nature of the bonding in anions containing S–S bonds (Dunitz, 1956; Magnusson & Johansson, 1982; Peter & Meyer, 1982; Kiers & Vos, 1978; Takahashi *et al.*, 1982). The S–S bond lengths in both conformers in this study are virtually identical to that for K₂S₂O₅, in all likelihood the most accurate of the three referenced structures. As we have previously shown for the dithionite ion, the presence of a larger cation allows the anion to adopt a more symmetric conformation, since it can more readily access positive charge without distortion. The identical sulfur–sulfur bond lengths in K₂S₂O₅ and Na₂S₂O₅ provide further evidence that the changes in conformation are due to interionic rather than intramolecular interactions.

4. Conclusions

The determination of the crystal structure of sodium metabisulfite, a simple ionic compound, was substantially more difficult than anticipated. Initial attempts to solve the structure failed as a result of the tendency of the crystals to form non-merohedral rotational twins in which the rotation axis bisects the angle between the **a**–**c** vectors for each domain of the twin. The absence of a simple relationship between the twin domains precluded *a priori* determination of the twin law, which was made possible only after the final structural determination. The actual determination of the crystal structure was the result of the discovery of a small number of crystals that had fortuitously broken along the boundary plane separating the two domains of the twin. Despite the ability to collect data on single domains of the twinned crystal, the indexing of reflections located from rotation photographs consistently provided a reflection set that produced a solution

only in a non-centrosymmetric space group, despite strong indications that the crystal should be centrosymmetric. Furthermore, the resulting solution generated a metabisulfite anion that appeared to consist of two overlapping conformers, indicative of a disordered structure with approximately half of the anion sites occupied by each conformer. Lattice energy calculations, however, revealed that neither conformer produced an energy minimum for the lattice, despite the relatively strong coulombic forces characteristic of an ionic structure.

Collectively, these observations caused us to determine the structure at low temperature, revealing weak reflections consistent with a larger centrosymmetric unit cell that provided the solution reported here. The difficulties encountered in this structural determination point out the need for care in unit-cell and space-group selection. The fortuitous overlap of the two anions in the asymmetric unit, when analysed in the wrong space group, might also have generated similar overlap with the O atoms on the thionate end of the anion. The result would have been a single anion in the asymmetric unit of a structure that would have been fundamentally incorrect.

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References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

- Baggio, S. (1971). *Acta Cryst.* **B27**, 517–522.
- Carter, K. L., Weinrach, J. B. & Bennett, D. W. (1993). *J. Am. Chem. Soc.* **115**, 10981–10987.
- Chen, I.-C. & Wang, Y. (1984). *Acta Cryst.* **C40**, 1780–1781.
- Dunitz, J. D. (1956). *Acta Cryst.* **9**, 579–586.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gale, J. D & Rohl, A. I. (2003). *Mol. Simul.* **29**, 291–341.
- Hodgeman, W. C., Weinrach, J. B. & Bennett, D. W. (1991). *Inorg. Chem.* **30**, 1611–1614.
- Holman, D. A. & Bennett, D. W. (1994). *J. Phys. Chem.* **98**, 13300–13307.
- Kiers, C. T. & Vos, A. (1978). *Acta Cryst.* **B34**, 1499–1504.
- Lindqvist, I. & Mörtzell, M. (1957). *Acta Cryst.* **10**, 406–409.
- Magnusson, A. & Johansson, L. (1982). *Acta Chem. Scand. A*, **36**, 429–433.
- Magnusson, A., Johansson, L.-G. & Lindqvist, O. (1983). *Acta Cryst.* **C39**, 819–822.
- Peter, L. & Meyer, B. (1982). *J. Mol. Struct.* **95**, 131–139.
- Sheldrick, G. M. (1997). *SHELX97*. University of Göttingen, Germany.
- Takahashi, H., Kaneko, N. & Miwa, K. (1982). *Spectrochim. Acta A*, **38**, 1147–1153.
- Weast, R. C. (1973). Editor. *Handbook of Chemistry & Physics*, 53rd ed. Cleveland, Ohio: Chemical Rubber Co.
- Weinrach, J. B., Meyer, D. R., Guy, J. T., Michaliski, P. E., Carter, K. L., Grubisha, D. S. & Bennett, D. W. (1992). *J. Cryst. Spectrosc. Res.* **22**, 291–301.
- Zachariasen, W. (1932). *Phys. Rev.* **40**, 406–409.