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Key indicators

Single-crystal X-ray study
 $T = 150$ K
 Mean $\sigma(\text{O}-\text{O}) = 0.003$ Å
 R factor = 0.038
 wR factor = 0.034
 Data-to-parameter ratio = 10.5

For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

Sodium peroxodisulfate

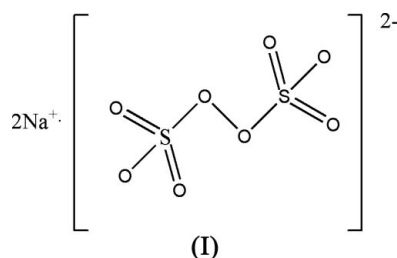
The asymmetric unit of disodium peroxodisulfate $2\text{Na}^+\cdot\text{S}_2\text{O}_8^{2-}$ consists of a single Na^+ cation and half of a peroxodisulfate dianion, the latter lying across a crystallographic inversion centre. The crystal structure is isostructural with that of potassium peroxodisulfate and it is composed of layers of molecules, partitioned by the Na^+ cations, parallel to the $(0\bar{1}1)$ plane of the triclinic cell. Neighbouring molecules within each layer are bridged end-to-end by pairs of short $\text{S}\cdots\text{O}$ intermolecular contacts [$\text{S}\cdots\text{O} = 3.074$ (2) Å].

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Comment

Sodium peroxodisulfate, (I), readily forms SO_4 radicals in hot aqueous solution. It is a powerful oxidizing and bleaching agent and it can also be used as a polymerization promoter, as well as providing a cleaner alternative to ferric chloride for copper etchant solutions (Serguchev *et al.*, 1980).



Compound (I) crystallizes from aqueous solution in the triclinic space group $P\bar{1}$, with one Na^+ cation and half of the peroxodisulfate dianion, the latter located across an inversion centre, in the asymmetric unit (Fig. 1). Its crystal structure,

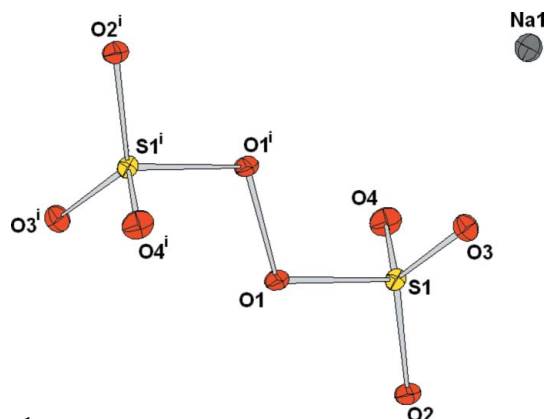


Figure 1

The structure of sodium peroxodisulfate, showing 30% probability ellipsoids [symmetry code: (i) $-x + 1, -y + 2, -z + 1$].

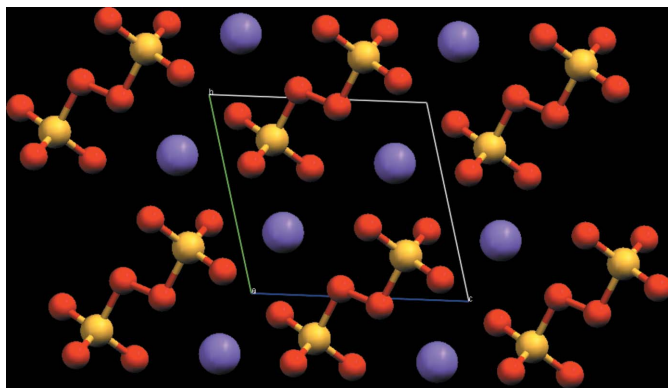


Figure 2
The packing of sodium peroxodisulfate, viewed along the a axis.

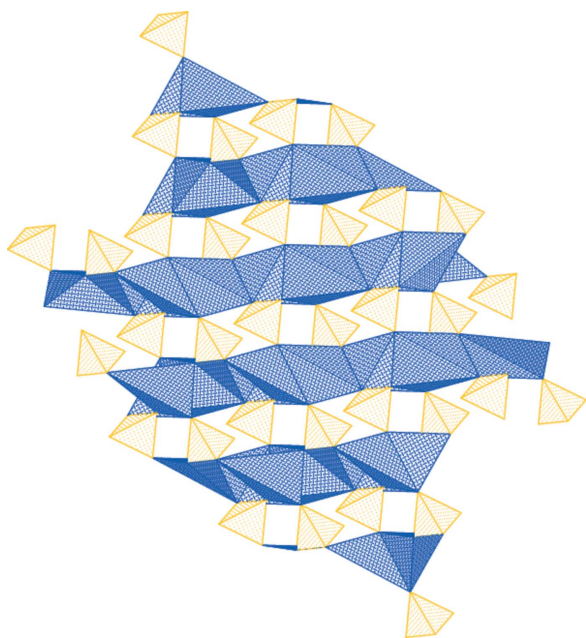


Figure 3
A polyhedral representation of the crystal structure of sodium peroxodisulfate. The structure is viewed along the c axis, with the a axis directed to the right and the b axis directed upwards. The blue polyhedra indicate the layers of distorted edge-sharing NaO_6 octahedra while the yellow tetrahedra indicate the SO_4 groups of the peroxodisulfate dianion.

which is isostructural with that of potassium peroxodisulfate, $\text{K}_2\text{S}_2\text{O}_8$, [Naumov *et al.*, 1997; ICSD (Belsky *et al.*, 2002) refcode 54024] is composed of layers of peroxodisulfate anions, which are aligned parallel to the $(0\bar{1}1)$ plane and partitioned by corrugated layers of Na^+ cations (Fig. 2).

The intramolecular $\text{S}-\text{O}$ distances and $\text{O}-\text{S}-\text{O}$ bond angles for the peroxodisulfate dianion are very similar to those reported for the potassium analogue (see Table 1). However, the cation environments for the two analogues are quite different. In potassium peroxodisulfate, the K^+ cations are coordinated by nine O atoms with interatomic distances ranging from 2.751 (3) to 3.347 (3) Å. For sodium peroxodisulfate, the Na^+ cations are coordinated by six O atoms, with $\text{Na}-\text{O}$ interatomic distances between 2.340 (2) and 2.596 (2) Å. It is interesting to note that in the sodium

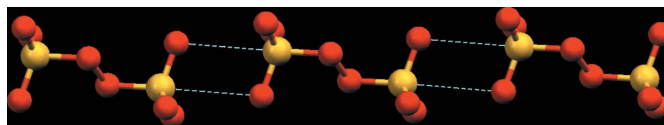


Figure 4
The dashed lines indicate short $\text{S}\cdots\text{O}$ contacts in sodium peroxodisulfate. This view is approximately perpendicular to $(0\bar{1}1)$.

analogue, the O atom involved in the intramolecular peroxo bond, O1, is not involved in the cation coordinate environment, although it does exhibit the shortest $\text{Na}-\text{O}$ distance outside this range [$\text{Na}1-\text{O}1 = 3.167$ (2) Å]. The $\text{K}1-\text{O}1$ distance in the potassium analogue [3.089 (3) Å] is of an intermediate length compared with the other O atoms defining the coordination environment. The overall effect of the $\text{Na}-\text{O}$ coordination environment in sodium peroxodisulfate is the formation of a three-dimensional network. This is indicated by the polyhedral plot shown in Fig. 3. The Na^+ cations form layers of distorted edge-sharing octahedra (shown as the blue polyhedra in Fig. 3), while the tetrahedra formed by each end of the dianions (shown as the yellow polyhedra in Fig. 3) form corner-sharing bridges between the layers.

Perhaps the most striking difference between the two structures concerns the $\text{S}\cdots\text{O}$ intramolecular contact distances. Within the layers, neighbouring anions are aligned end-to-end so that pairs of relatively short $\text{S}\cdots\text{O}$ contacts are formed. In the sodium analogue these contacts are extremely short [$\text{S}1\cdots\text{O}3 = 3.074$ (2) Å] (Fig. 4), while in the crystal structure of the potassium analogue these contacts are significantly longer [$\text{S}1\cdots\text{O}3 = 3.417$ (3) Å].

Experimental

The sample of sodium peroxodisulfate was prepared from anhydrous starting material (of 99% purity, as received from Aldrich) and recrystallized from an aqueous solution by slow evaporation. A suitable crystal was selected from the resulting batch. The sample was cooled to 150 K using an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986) during data collection.

Crystal data

$2\text{Na}^+\cdot\text{O}_8\text{S}_2^{2-}$	$Z = 1$
$M_r = 238.11$	$D_x = 2.603 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 4.780$ (2) Å	Cell parameters from 680 reflections
$b = 5.575$ (2) Å	$\theta = 7-57^\circ$
$c = 6.091$ (3) Å	$\mu = 1.02 \text{ mm}^{-1}$
$\alpha = 101.871$ (7)°	$T = 150 \text{ K}$
$\beta = 103.337$ (7)°	Needle, colourless
$\gamma = 97.418$ (7)°	$0.20 \times 0.05 \times 0.05 \text{ mm}$
$V = 151.89$ (11) Å ³	

Data collection

Bruker SMART diffractometer	590 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.021$
Absorption correction: multi-scan	$\theta_{\text{max}} = 28.9^\circ$
SADABS (Sheldrick, 2004)	$h = -6 \rightarrow 6$
$T_{\text{min}} = 0.67$, $T_{\text{max}} = 0.95$	$k = -7 \rightarrow 7$
1326 measured reflections	$l = -8 \rightarrow 7$
696 independent reflections	

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.034$
 $S = 1.06$
 590 reflections
 56 parameters

Modified Chebyshev polynomial
 (Watkin, 1994; Prince, 1982) with
 the coefficients 1.89, -1.11, 1.17
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

S1—O1	1.6392 (19)	Na1—O3 ⁱⁱ	2.380 (2)
S1—O2	1.4389 (18)	Na1—O2 ⁱⁱⁱ	2.389 (2)
S1—O3	1.4408 (19)	Na1—O2 ^{iv}	2.476 (2)
S1—O4	1.4396 (19)	Na1—O4 ^v	2.340 (2)
O1—O1 ⁱ	1.479 (3)	Na1—O4 ^{vi}	2.596 (2)
Na1—O3	2.376 (2)		
O1—S1—O2	97.30 (11)	O2—S1—O4	115.65 (12)
O1—S1—O3	105.92 (11)	O3—S1—O4	113.08 (11)
O1—S1—O4	106.87 (11)	O1 ⁱ —O1—S1	106.26 (17)
O2—S1—O3	115.78 (12)		

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y + 1, -z$; (iii) $x - 1, y - 1, z$; (iv) $-x + 1, -y + 1, -z$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $x - 1, y, z$.

Indexing with *GEMINI* (Sparks, 1999) revealed that the sample was twinned non-merohedrally with two domains. The data set was integrated using the orientation matrix of the stronger subset of reflections, corresponding to the larger domain. During refinement, the *ROTAX* procedure, as implemented in the *CRYSTALS* refinement package (Cooper *et al.*, 2002), was used to identify the relationship between the two domains. This could be expressed by the matrix $(\bar{1}00, 0\bar{1}0, 0.667 \ 0.523 \ 1)$, which corresponds to a twofold rotation about the c^* axis. Subsequent refinement indicated that the twin fraction of the second domain was 0.379 (8).

Data collection: *SMART* (Bruker Nonius, 2001); cell refinement: *SAINT*; data reduction: *SAINT* (Bruker Nonius, 2003); program(s)

used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS* and *PLATON* (Spek, 2003).

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