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Key indicators

Single-crystal X-ray study

T = 300 K

Mean $\sigma(S-N)$ = 0.001 Å

Disorder in solvent or counterion

R factor = 0.021

wR factor = 0.029

Data-to-parameter ratio = 13.2

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Calcium sodium iminodisulphonate trihydrate,
a product of flue-gas desulfurizationOne of the crystalline products resulting from the removal of
sulfur dioxide from flue gas has been shown to be calcium
sodium iminodisulfonate trihydrate, $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$.

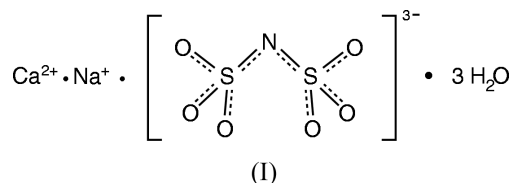
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Comment

The removal of sulfur dioxide in the flue gas from the Enstedværk power plant in Aabenraa is effected by treating the flue gas with an aerated slurry containing calcium carbonate. The primary product is gypsum, but the presence of, for example, NO, NO₂, HCl and HF in the flue gas leads to a complex chemistry, resulting in the presence of a large number of species formed through reaction. Among other compounds, sulfonic acid derivatives of ammonia and hydroxylamines are known to be present and they contribute up to 500 mg_N l⁻¹ to the total nitrogen content in the slurry filtrate. Soluble species are removed through a bleed stream of slurry filtrate that is treated in order to remove heavy metals and residual suspended matter before it is pumped through a 3 km long pipeline to a municipal waste water plant for final treatment and discharge into the sea. Large, up to 1 cm³, crystals of an unidentified compound were found in both the heavy-metal precipitation plant and the pipeline. The temperature is 313–323 K, the pH is close to 9 and the major ions present in the slurry filtrate are Ca²⁺, Na⁺, Mg²⁺, Cl⁻, SO₄²⁻, SO₃²⁻ and CO₃²⁻. Since the crystals could not be identified from a powder pattern, a single-crystal study was carried out, which showed the crystals to be the known compound calcium sodium iminodisulfonate trihydrate, $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, (I).



The compound was first reported by Divers & Haga (1892), who obtained it when attempting to make the Ca salt by treating the Na salt with the required amount of CaCl₂; this suggests that the mixed Ca/Na salt is less soluble than either the Na or the Ca salt. The iminodisulfonate ion (Fig. 1) has approximate mirror symmetry, with atoms S1, S2, N1, O2 and O6 in the mirror plane. The geometry of the imidosulfonate ion is similar to that found in the potassium salt (Barbier *et al.*, 1979; Hall *et al.*, 1980). The shortness of the S–N bond is usually attributed (*e.g.* Cruickshank, 1961) to $d\pi-p\pi$ bonding; the $[\text{N}(\text{SO}_3)_2]^{3-}$ ion has shorter S–N distances (0.064 Å) and longer S–O distances (0.018 Å) than the $[\text{HN}(\text{SO}_3)_2]^{2-}$ ion (Barbier *et al.*, 1979), indicating a greater degree of S=N

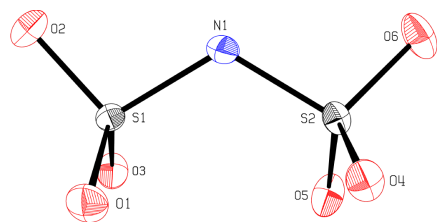


Figure 1
View of the $[\text{N}(\text{SO}_3)_2]^{3-}$ anion, showing the labelling of atoms. Displacement ellipsoids are shown at the 50% probability level. Colour code: S black, O red, and N blue.

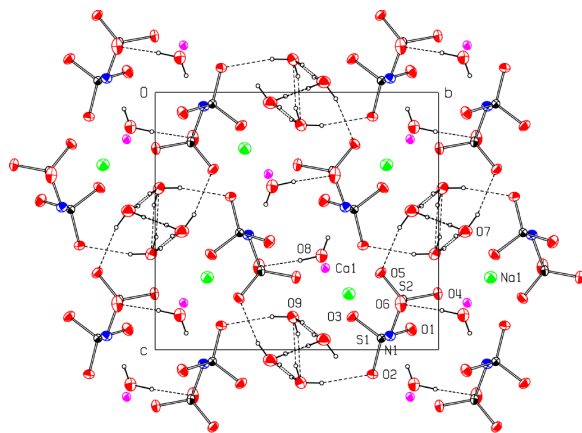


Figure 2
The cell contents, showing the hydrogen bonding; *b* is across the page and *c* down the page. Colour code: Ca magenta, Na green, S black, O red, and H open black circles.

double bonding. The Ca^{2+} ion is surrounded by five sulfonate O atoms, two water molecules and the N atom, which form a very irregular dodecahedron, with $\text{Ca}\cdots\text{O}$ distances in the range 2.391 (1)–2.756 (1) Å; the $\text{Ca}\cdots\text{N}$ distance of 2.559 (1) Å is similar to that, 2.58 Å, found in eight-coordinated CaN_8 arrangements (Hazell *et al.*, 1999). The Na^+ ion is surrounded by an octahedral arrangement of four sulfonate O atoms and two water molecules at distances in the range 2.304 (1)–2.514 (1) Å. There is an extensive system of hydrogen bonding (Table 2) involving the water molecules and atoms O2, O5 and O6 of the iminodisulfonate ion (Fig. 2). Water molecules O7 and O9 are both disordered so that one of the the associated H atoms in each case is disordered over two sites (HO7*a*/HO7*b* and HO9*b*/HO9*c*); thus, for the hydrogen bonds between O7 and O7', O9 and O9', and O7 and O9, there are two half-H atoms.

Experimental

Crystal data

$\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$
 $M_r = 291.19$
Monoclinic, $P2_1/c$
 $a = 7.4416$ (3) Å
 $b = 11.1779$ (4) Å
 $c = 10.4536$ (4) Å
 $\beta = 104.431$ (1)°
 $V = 842.11$ (6) Å³
 $Z = 4$

$D_x = 2.296$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 8369 reflections
 $\theta = 2.7$ – 29.8°
 $\mu = 1.32$ mm⁻¹
 $T = 300$ K
Plate, colourless
 $0.36 \times 0.22 \times 0.06$ mm

Data collection

Siemens SMART CCD diffractometer
 ω rotation scans with narrow frames
Absorption correction: by integration (*XPREP*; Siemens, 1995)
 $T_{\min} = 0.690$, $T_{\max} = 0.925$
12 384 measured reflections

2444 independent reflections
2112 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\max} = 29.8^\circ$
 $h = -10 \rightarrow 10$
 $k = -14 \rightarrow 14$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F
 $R = 0.021$
 $wR = 0.029$
 $S = 1.12$
2112 reflections
160 parameters
All H-atom parameters refined
 $w = 1/[\sigma_{\text{cs}}(F^2) + B + (1 + A)F^2]^{1/2}$
– $|F|^2$
where $A = 0.03$, $B = 0.1$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.50$ (7) e Å⁻³
 $\Delta\rho_{\min} = -0.50$ (7) e Å⁻³
Extinction correction: B–C
type 1 Lorentzian isotropic
(Becker & Coppens, 1974)
Extinction coefficient: 23 (5)

Table 1

Selected geometric parameters (Å, °).

S1–O1	1.467 (1)	S2–O4	1.464 (1)
S1–O2	1.465 (1)	S2–O5	1.470 (1)
S1–O3	1.465 (1)	S2–O6	1.463 (1)
S1–N1	1.604 (1)	S2–N1	1.602 (1)
O1–S1–O2	111.80 (7)	O4–S2–O6	110.67 (6)
O1–S1–O3	109.97 (7)	O4–S2–N1	110.51 (7)
O1–S1–N1	110.81 (7)	O5–S2–O6	111.49 (7)
O2–S1–O3	110.81 (7)	O5–S2–N1	109.57 (6)
O2–S1–N1	101.49 (7)	O6–S2–N1	104.75 (7)
O3–S1–N1	111.74 (6)	S1–N1–S2	118.10 (7)
O4–S2–O5	109.75 (7)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O7–HO7 <i>a</i> ...O5 ⁱ	0.85 (3)	2.02 (3)	2.850 (2)	167 (3)
O7–HO7 <i>b</i> ...O9 ⁱⁱ	0.97 (7)	1.79 (7)	2.740 (2)	166 (5)
O7–HO7 <i>c</i> ...O7 ⁱ	0.81 (4)	1.95 (4)	2.742 (3)	177 (4)
O8–HO8 <i>b</i> ...O6 ⁱⁱⁱ	0.91 (3)	1.82 (3)	2.731 (2)	173 (3)
O9–HO9 <i>a</i> ...O2 ^{iv}	0.83 (3)	2.04 (3)	2.865 (2)	169 (2)
O9–HO9 <i>b</i> ...O7 ⁱⁱⁱ	0.90 (5)	1.85 (5)	2.741 (2)	172 (4)
O9–HO9 <i>c</i> ...O9 ^{iv}	0.81 (5)	2.10 (5)	2.898 (3)	166 (5)

Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $1 - x, 1 - y, 2 - z$.

H atoms were located from a difference synthesis plotted on the surface of a sphere of radius 0.9 Å about the O atoms of the water molecules. Site-occupation factors for HO7*c* and HO9*c* were required to be 0.5 from symmetry considerations, and so those for HO7*b* and HO9*b* were also 0.5.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997) and *KRYSTAL* (Hazell, 1995); program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962) and *KRYSTAL*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

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