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Bis(diisopropylammonium) sulfate

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Bis(diisopropylammonium) sulfate, $2C_6H_{16}N^+\cdot SO_4{}^{2-}$, crystallizes in the monoclinic centrosymmetric space group $P2_1/n$. The asymmetric unit contains two crystallographically independent diisopropylammonium cations and one sulfate anion in general positions. Strong hydrogen bonding occurs between the cations and anions, forming layers parallel to $(\bar{1}01)$. Each layer is composed of ring systems that can be classified according to Etter's nomenclature as $R_4^4(12)$ and $R_{12}^{12}(36)$. IR and Raman spectroscopy confirm the presence of a nearly undistorted sulfate anion.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.056
wR factor = 0.099
Data-to-parameter ratio = 17.7

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

Comment

During our continuing study of the structures of simple ammonium salts, we have found that the diisopropylammonium cation (dip) forms simple salt structures that are dominated by their hydrogen-bonding pattern. This class of compounds seems to be an excellent model system for the investigation of the anion-dependent formation of one- or higher-dimensional hydrogen-bonded polymers.

An extremely strong hydrogen-bond acceptor, such as the $[SiF_6]^{2-}$ anion, produces a structure that is built from quasi-molecular ion pairs of one hexafluorosilicate anion and two diisopropylammonium cations, held together by only two very strong N—H$\cdots$F interactions (Reiß, 1998). The systematic study of the structural chemistry of diisopropylammonium halides (Reiß, 2000; Reiß & Koppelhuber-Bitschnau, 2002) and of the analogous hydrogen difluoride (Reiß, 2001) has shown that these are all isostructural and form hydrogen-bonded one-dimensional polymeric chains. In the case of the bulky and weak hydrogen-bond acceptor $[IrCl_6]^{2-}$ as the counter-ion to diisopropylammonium (Reiß, 2002), a three-dimensional network structure is formed. The bonding in the structure of dip$_2$[IrCl$_6$] is best described as a compromise between extremely weak hydrogen bonds on the one hand and a combination of electrostatic and hydrophobic interactions on the other hand. In fact, this structure shows a close structural resemblance to the $K_3[IrCl_6]$ structure (Coll *et al.*, 1987). In terms of crystal engineering, the ability of an anion to act as a building block for the generation of one- or higher-dimensional polymers depends mainly on two factors. One is the ability of the ion to form hydrogen bonds of various strengths and the other is its geometric and steric parameters. If this is true for the dip/anion system, it is clear that some complex oxoanions, such as sulfate, should form structures that are intermediate between the one-dimensional polymers of diisopropylammonium halides and the three-dimensional network of dip$_2$[IrCl$_6$]. The sulfate anion is known to form strong to medium hydrogen bonds to alkylammonium cations

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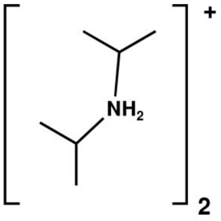
and its tetrahedral geometry is conducive to the formation of higher-dimensional hydrogen-bonded polymers (Zaworotko, 1994).



(I)

The structure of the title compound, (I), comprises a sulfate anion and two crystallographically independent diisopropylammonium cations, all in general positions. The C—C and N—C bond lengths in both cations are as expected and the conformations of the two cations are very similar. The almost exactly tetrahedral geometry of the SO_4^{2-} anion is consistent with the results of other structure determinations of hydrogen-bonded sulfates. In addition, IR and Raman spectroscopy give no indication of serious distortion of the SO_4^{2-} anion.

Each O atom of the sulfate anion accepts exactly one hydrogen bond from neighbouring ammonium groups, while each N atom of the two independent cations donates two hydrogen bonds (Fig. 1 and Table 2). To the best of our knowledge, this is the first example of a sulfate anion involving four 'equal' hydrogen bonds. This came as a surprise to us, since many groups have investigated the receptor properties of the sulfate anion with respect to macrocyclic ligands (Dietrich, 1993; Dietrich *et al.*, 1981; Hossain *et al.*, 2001) and biological systems such as the sulfate-binding proteins (Pflugrath & Quiocho, 1985). They found sulfate anions that are bound in most cases asymmetrically and which accept, at least one, forked hydrogen bond.

Hydrogen bonding occurs only in a layered region parallel to the $(\overline{1}01)$ plane. Each hydrogen-bonded layer is separated from neighbouring ones by a hydrophobic layer (Fig. 2). The hydrogen-bonded layer is built from small, hydrogen-bonded ring motifs, $R_4^4(12)$ (Etter *et al.*, 1990), perpendicular to the $(\overline{1}01)$ plane. These subunits form hydrogen bonds to two of the O atoms of the sulfate anion and to one H atom of one of the crystallographically independent dip cations. These subunits are further connected to the second crystallographically independent diisopropylammonium ion to form large ring motifs, $R_{12}^{12}(36)$, parallel to the $(\overline{1}01)$ plane (Fig. 3). The resulting hydrogen-bonded complex two-dimensional network cannot be related to any previously published ones (Beatty, 2001).

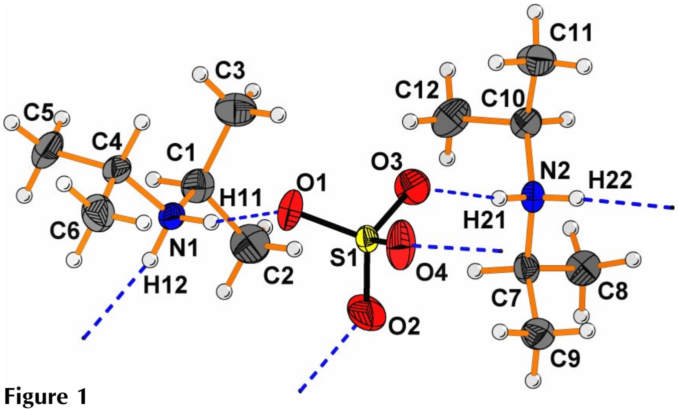


Figure 1
Diagram showing the SO_4^{2-} anion with the neighbouring dip cations. Displacement ellipsoids are drawn at the 50% probability level.

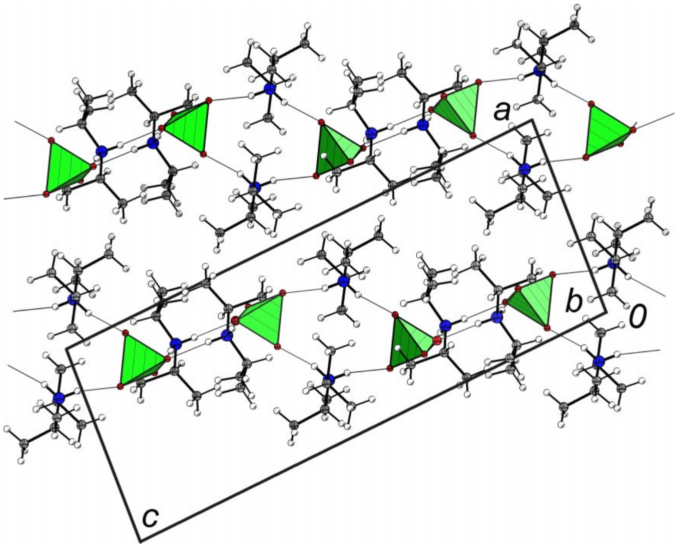


Figure 2
View along *b*, showing the layered structure of the title compound.

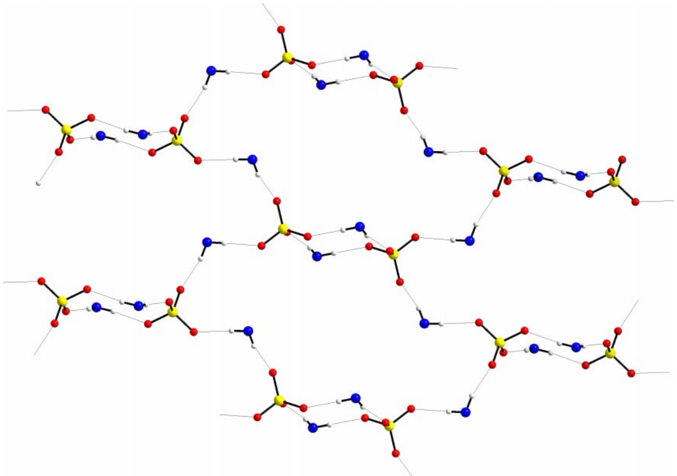


Figure 3
Diagram showing the system of hydrogen bonds built by ring systems best described, according to Etter's nomenclature, as $R_4^4(12)$ and $R_{12}^{12}(36)$.

Experimental

Diisopropylamine (1 ml) was added to sulfuric acid (96%, 1 ml), producing a colourless solution. After 1 d, the solution became viscous, and from this solution colourless needles were grown. At 298 K, the complete crystal growth process took one week. Most of the needles grew together and many swallow-tail twins were found. The measured crystal was cut from a larger specimen. Thermal analysis: in the temperature range 123 K to room temperature, no thermal effect was detected. IR (4000–560 cm^{-1}): 3404, 2982, 2878, 2707, 1613, 1504, 1399, 1156, 1065 (SO_4^{2-}, ν_3), 606 cm^{-1} (SO_4^{2-}, ν_4). Raman spectroscopy (4000–10 cm^{-1}): 2941, 1105 (SO_4^{2-}, ν_3), 1073, 981 (SO_4^{2-}, ν_1), 920, 609 (SO_4^{2-}, ν_4), 448 cm^{-1} (SO_4^{2-}, ν_2).

Crystal data

$2C_6H_{16}N^+\cdot SO_4^{2-}$
M_r = 300.46
Monoclinic, $P2_1/n$
a = 8.7869 (8) Å
b = 8.8329 (8) Å
c = 22.095 (2) Å
β = 95.21 (1)°
V = 1707.8 (3) $Å^3$
Z = 4

D_x = 1.169 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1569 reflections
θ = 5.1–18.9°
μ = 0.20 mm^{-1}
T = 293 (2) K
Block, colourless
0.30 × 0.20 × 0.15 mm

Data collection

Stoe STADI-4 CCD diffractometer
ω scans
Absorption correction: none
17 529 measured reflections
3699 independent reflections
2834 reflections with $I > 2\sigma(I)$

R_{int} = 0.043
$\theta_{\max}$ = 27.0°
$h = -10 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -25 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.099
S = 1.01
3699 reflections
209 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 1.7P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.005
$\Delta\rho_{\max}$ = 0.50 e $Å^{-3}$
$\Delta\rho_{\min}$ = −0.27 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.450 (2)	C7—C8	1.514 (3)
S1—O4	1.456 (2)	C7—C9	1.511 (3)
S1—O1	1.462 (2)	C10—C11	1.514 (3)
S1—O3	1.463 (2)	C10—C12	1.513 (3)
N1—C1	1.493 (3)	C1—C3	1.515 (4)
N1—C4	1.506 (3)	C1—C2	1.514 (4)
N2—C10	1.496 (3)	C4—C6	1.513 (4)
N2—C7	1.502 (3)	C4—C5	1.511 (3)
O2—S1—O4	109.88 (15)	O4—S1—O3	109.02 (12)
O2—S1—O1	110.34 (12)	O1—S1—O3	109.88 (11)
O4—S1—O1	108.70 (11)	C1—N1—C4	118.01 (19)
O2—S1—O3	108.99 (13)	C10—N2—C7	117.87 (18)
C10—N2—C7—C8	54.9 (3)	C4—N1—C1—C3	58.7 (3)
C10—N2—C7—C9	178.1 (2)	C4—N1—C1—C2	−178.4 (2)
C7—N2—C10—C11	−178.5 (2)	C1—N1—C4—C6	178.4 (2)
C7—N2—C10—C12	58.0 (3)	C1—N1—C4—C5	54.5 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···O1	0.87 (2)	1.88 (2)	2.732 (2)	164 (2)
N1—H12···O2^{i}	0.87 (2)	1.87 (2)	2.716 (3)	165 (2)
N2—H21···O3	0.87 (2)	1.90 (2)	2.746 (3)	166 (2)
N2—H22···O4^{ii}	0.87 (2)	1.87 (2)	2.733 (3)	177 (2)

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

The atomic coordinates of the H atoms belonging to NH_2 and CH groups, as well as their individual U_{iso} values, were refined freely; only the N—H distances were restrained, to one common value of 0.87 (2) Å. H atoms belonging to methyl groups were included in the refinement riding on their attached C atoms, and were allowed to rotate about the C—C bond. One common U_{iso} value for each group was refined freely.

Data collection: *CrysAlisCCD* (Kuma, 2000); cell refinement: *CrysAlisRED* (Kuma, 2000); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL*97.

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