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Key indicators

Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
Disorder in solvent or counterion
 R factor = 0.047
 wR factor = 0.094
Data-to-parameter ratio = 14.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

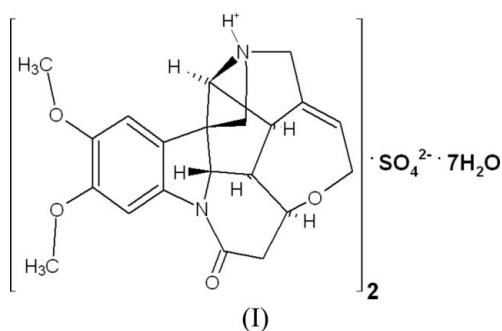
Dibrucinium sulfate heptahydrate

The crystal structure of dibrucinium sulfate(VI) heptahydrate, $2\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_4^+ \cdot \text{SO}_4^{2-} \cdot 7\text{H}_2\text{O}$, has been determined. The components are packed in layers. Puckered brucinium sheets are separated by layers consisting of hydrogen-bonded disordered sulfate(VI) anions and water molecules. Both layers, the cationic together with the anionic/water, are linked by $\text{N}-\text{H}^+ \cdots \text{O}^-$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds.

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Comment

In 1953, Eeles published some preliminary crystallographic data for dibrucinium sulfate(VI) heptahydrate, (I) (Eeles, 1953). On the basis of the number of formula units per unit cell, calculated from unit-cell dimensions and the observed density, he found that each sulfate(VI) anion must lie on a diad axis. Moreover, he postulated that seven water molecules are possibly arranged in a manner similar to that of the molecules of water in the structure of strychninium sulfate pentahydrate (Bokhoven *et al.*, 1951). However, until now the crystal structure of dibrucinium sulfate(VI) heptahydrate was unknown.



A view of the asymmetric unit of (I), together with the numbering scheme employed, is presented in Fig. 1. The geometry of the brucinium cation is comparable with that found in other crystal structures (Gould & Walkinshaw, 1984; Quinkert *et al.*, 1986; Boiadjiev *et al.*, 1992; Kuwata *et al.*, 1993; Wright *et al.*, 1994; Dijksma, Gould *et al.*, 1998; Dijksma, Walkinshaw *et al.*, 1998; Sada *et al.*, 1998; Cheung *et al.*, 1990; Allenmark & Skogsberg, 2000; Laursen *et al.*, 2003; Thunberg & Allenmark, 2003; Białońska & Ciunik, 2004; Białońska *et al.*, 2005; Smith, Wermuth, Healy *et al.*, 2005; Smith, Wermuth & White, 2005; Smith, Wermuth, Young & Healy, 2005). In compound (I), the S atom of the sulfate(VI) anion lies on a crystallographic twofold axis, and the O atoms of the anion adopt two arrangements (in the ratio 1:1) around the twofold axis. Similarly, one of the water molecules (O1W) is located on a special position. The disordered anion, *via* atom O5 and the

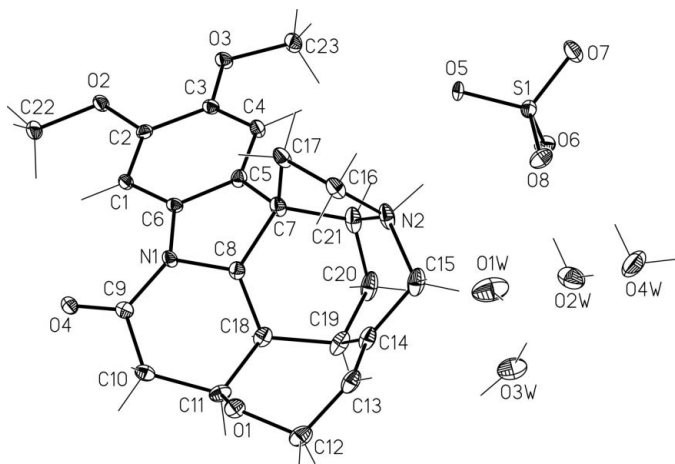


Figure 1

A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. Only one disorder component is shown for the anion.

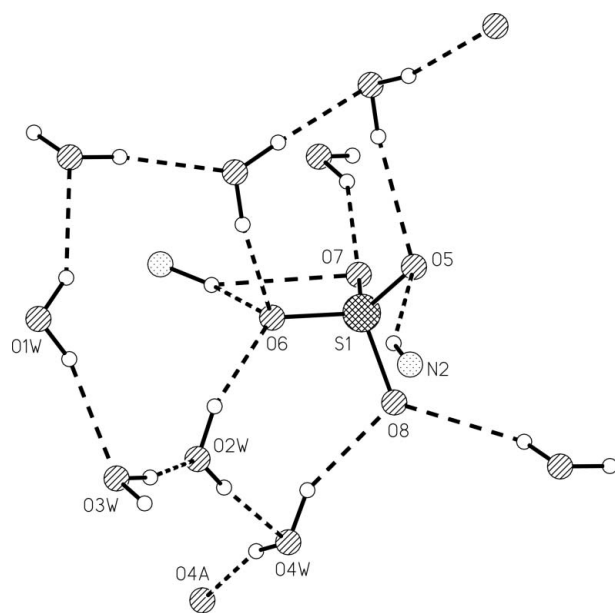


Figure 2

The hydrogen-bonded network (dashed lines) of the anionic/water layer. For clarity, one component of the disordered anion has been omitted.

two atoms O6 and O7, participates in $N-H^+ \cdots O^-$ hydrogen bonds in which the protonated amine atoms N2 and N2($-x, y, -z + \frac{1}{2}$) of the brucinium cations act as donors, respectively.

The nearest environment of the anion also consists of water molecules. Thus, each O atom of the disordered anion is involved in at least two hydrogen bonds (Fig. 2). All water molecules which do not lie on special positions, *i.e.* atoms O2W, O3W and O4W, are acceptors of one and donors of two hydrogen bonds. The O1W water molecule, as a donor of hydrogen bonds, belongs to a cyclic arrangement (Fig. 2), which also involves the O2W and O3W water molecules and atom O6 of the anion.

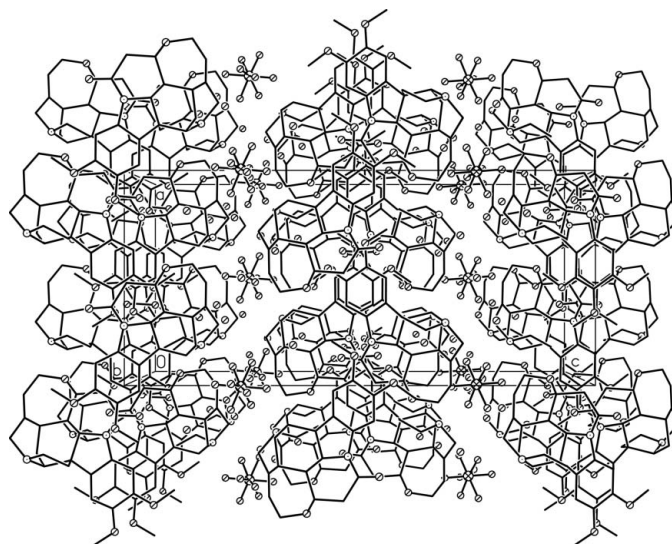


Figure 3

A packing diagram for (I), showing the puckered brucine sheets and the disordered sulfate anions between them. For clarity, the water molecules and H atoms have been omitted.

The anionic/water layer, which results from the hydrogen-bonded network of the sulfate(VI) anion and the water molecules, is separated by puckered sheets of brucinium cations (Fig. 3). Similar brucine self-assembly is found in other crystal structures containing brucinium cations (Dijkema, Walkinshaw *et al.*, 1998; Laursen *et al.*, 2003; Białońska *et al.*, 2005). Both layers, the cationic together with the anionic/water, are linked by the above-mentioned $N-H \cdots O$ hydrogen bonds and also by $O-H \cdots O$ hydrogen bonds. The O4W water molecule and the carbonyl atom O4($-x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$) of the brucinium cation participate in the $O-H \cdots O$ interlayer hydrogen bond (Fig. 2).

Experimental

Commercially available brucine and sulfuric acid were dissolved in water in a 1:1 molar ratio of alkaloid and acid. Crystals of (I) were formed after slow evaporation of the solvent at room temperature.

Crystal data

$2C_{23}H_{27}N_2O_4^+ \cdot SO_4^{2-} \cdot 7H_2O$
 $M_r = 1013.10$
 Orthorhombic, $C222_1$
 $a = 12.1765$ (9) Å
 $b = 14.2518$ (10) Å
 $c = 26.6488$ (18) Å
 $V = 4624.6$ (6) Å³
 $Z = 4$
 $D_x = 1.455$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 5256 reflections
 $\theta = 3.7$ – 28.5°
 $\mu = 0.16$ mm⁻¹
 $T = 100$ (2) K
 Block, colourless
 0.40 × 0.40 × 0.40 mm

Data collection

Kuma KM4 CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 15405 measured reflections
 4939 independent reflections

4393 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.043$
 $\theta_{max} = 27.0^\circ$
 $h = -15 \rightarrow 15$
 $k = -18 \rightarrow 17$
 $l = -33 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.094$
 $S = 1.07$
 4939 reflections
 335 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 1.9728P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$
 Absolute structure: Toda *et al.* (1985) and Flack (1983), with 2356 Friedel pairs
 Flack parameter: $-0.01 (9)$

Table 1
 Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...O6 ⁱ	0.96	1.83	2.712 (4)	151
N2—H2...O5	0.96	2.00	2.873 (4)	150
N2—H2...O7 ⁱ	0.96	2.36	3.141 (4)	138
O1W—H11W...O3W	0.88	2.04	2.834 (2)	150
O2W—H21W...O4W	0.88	1.88	2.756 (3)	175
O2W—H22W...O6	0.88	1.91	2.716 (4)	151
O2W—H22W...O6 ⁱ	0.88	2.17	2.976 (4)	152
O3W—H31W...O2W	0.88	1.89	2.748 (3)	165
O3W—H32W...O7 ⁱⁱ	0.88	1.97	2.769 (4)	150
O3W—H32W...O8 ⁱⁱⁱ	0.88	2.27	3.093 (4)	155
O4W—H41W...O4 ^{iv}	0.88	1.95	2.808 (3)	164
O4W—H42W...O8	0.88	2.00	2.801 (4)	151
O4W—H42W...O5 ⁱ	0.88	2.14	2.983 (4)	160

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

H atoms bonded to C atoms in the brucinium cation were included in their idealized positions and treated as riding in the subsequent refinement, with C—H distances in the range 0.95–1.00 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The remaining H atoms were located in difference density maps and refined with isotropic displacement parameters; in the final cycle of refinement, they were made to ride on their parent atoms. The absolute configuration of dibrucinium sulfate(VI) heptahydrate was chosen on the basis of the known absolute configuration of brucine (Toda *et al.*, 1985) and confirmed by this refinement.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97*

(Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1999); software used to prepare material for publication: *SHELXL97*.

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References

Allenmark, S. & Skogsberg, U. (2000). *Enantiomer*, **5**, 451–455.
 Białońska, A. & Ciunik, Z. (2004). *Cryst. Eng. Commun.* **47**, 276–279.
 Białońska, A., Ciunik, Z., Popek, T. & Lis, T. (2005). *Acta Cryst. C* **61**, o88–o91.
 Boiadjev, S. E., Person, R. V., Puzicha, G., Knobler, C., Maverick, E., Trueblood, K. N. & Lightner, D. A. (1992). *J. Am. Chem. Soc.* **114**, 10123–10133.
 Bokhoven, C., Schoone, J. C. & Bijvoet, J. M. (1951). *Acta Cryst.* **4**, 275–280.
 Bruker (1999). *SHELXTL-NT*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Cheung, E., Netherton, M. R., Scheffer, J. R. & Trotter, J. (1990). *Tetrahedron Lett.* **40**, 8737–8740.
 Dijkma, F. J. J., Gould, R. O., Parsons, S., Taylor, P. & Walkinshaw, M. D. (1998). *Chem. Commun.* pp. 745–746.
 Dijkma, F. J. J., Walkinshaw, M. D., Person, S. & Gould, R. O. (1998). *Acta Cryst. C* **54**, 1948–1951.
 Eeles, W. T. (1953). *Acta Cryst.* **6**, 809–810.
 Flack, H. D. (1983). *Acta Cryst. A* **39**, 876–881.
 Gould, R. O. & Walkinshaw, M. D. (1984). *J. Am. Chem. Soc.* **106**, 7840–7842.
 Kuwata, S., Tanaka, J., Onda, N., Yamada, T., Miyazawa, T., Sugiura, M., In, Y., Doi, M., Inoue, M. & Ishida, T. (1993). *Bull. Chem. Soc. Jpn.* **66**, 1501–1510.
 Laursen, J. B., Jorgensen, C. G. & Nielsen, J. (2003). *Bioorg. Med. Chem.* **11**, 723–731.
 Oxford Diffraction (2001). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Poland, sp. z o.o., Wrocław, Poland.
 Quinkert, G., Schalz, H.-G., Dzierzynski, E. M., Durner, G. & Bats, J. W. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 992–993.
 Sada, K., Miyata, M. & Yoshikawa, K. (1998). *Chem. Commun.* pp. 1763–1764.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Smith, G., Wermuth, U. D., Healy, P. C., Young, D. J. & White, J. M. (2005). *Acta Cryst. E* **61**, o2646–o2648.
 Smith, G., Wermuth, U. D. & White, J. M. (2005). *Acta Cryst. C* **61**, o621–o624.
 Smith, G., Wermuth, U. D., Young, D. J. & Healy, P. C. (2005). *Acta Cryst. E* **61**, o2008–o2011.
 Thumberg, L. 1322.
 Toda, F., Tanaka, K., Ueda, H. & Oshima, T. (1985). *Isr. J. Chem.* **25**, 338–345.
 Wright, J. L., Caprathe, B. W., Downing, D. M., Glase, S. A., Heffner, T. G., Jaen, J. C., Johnson, S., Kesten, S. R., MacKenzie, R. G., Meltzer, L. T., Pugsley, T. A., Smith, S. J., Wise, L. D. & Wustrow, D. J. (1994). *J. Med. Chem.* **37**, 3523–3533.