

## Lithium pyridine-3-sulfonate

A. van der Lee\* and M. Barboiu

Institut Européen des Membranes, UMII-cc047,  
Place E. Bataillon, 34095 Montpellier, FranceCorrespondence e-mail:  
avderlee@univ-montp2.fr

## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$ 

R factor = 0.046

wR factor = 0.068

Data-to-parameter ratio = 21.0

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

In the structure of the title lithium salt of pyridine-3-sulfonic acid,  $\text{Li}^+\cdot\text{C}_5\text{H}_4\text{NO}_3\text{S}^-$ , apart from the electrostatic interactions between the lithium cations and the pyridine-3-sulfonate anions, the three-dimensional structure contains  $\pi$ - $\pi$  interactions between pairs of pyridine moieties. The asymmetric unit contains two cations and two anions.

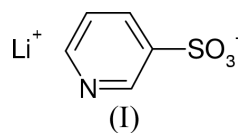
Received 5 March 2004

Accepted 16 March 2004

Online 20 March 2004

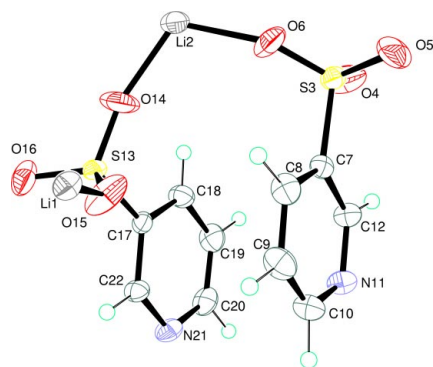
## Comment

Ligands containing sulfonate groups and guanidinium ions are capable of assembling into lamellar crystalline architectures with hexagonal frameworks (Holman *et al.*, 2001). In a recent attempt to assemble new, interesting and more or less porous networks based on sulfonate and guanidinium groups, we tried to synthesize diaminoguanidinium trifluoromethanesulfonate from diaminoguanidinium chloride and trifluoromethanesulfonic acid, but we obtained a protonated diaminoguanidinium chloride salt (van der Lee & Barboiu, 2004). In a new attempt, this time to synthesize guanidinium pyridine-3-sulfonate, we obtained the lithium salt of pyridine-3-sulfonate, lithium pyridine-3-sulfonic acid, (I). Complexes or salts based on pyridinesulfonate are very rare in the Cambridge Structural Database (CSD; Version 5.25; Allen, 2002). The structures of two pyridine-3-sulfonate complexes (Walsh & Hathaway, 1980; Brodersen *et al.*, 1980), the acid (Chandrasekhar, 1977) and one pyridine-2-sulfonate complex (García-Vázquez *et al.*, 2000) have been published.

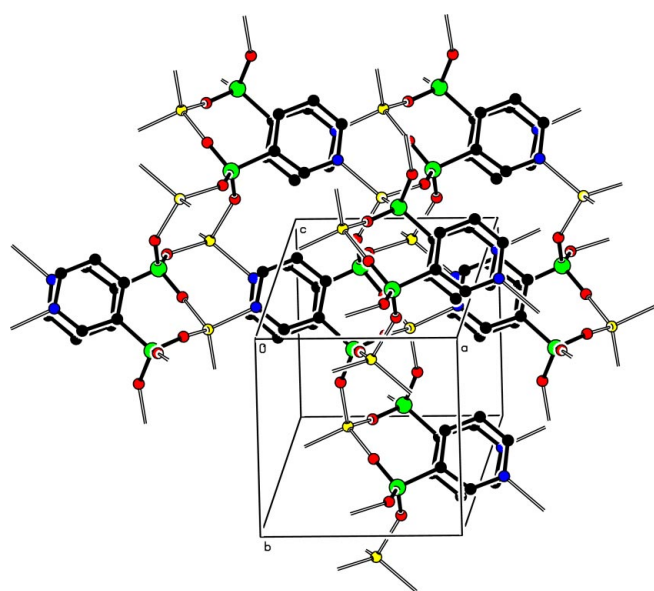


A view of the asymmetric unit of (I) is presented in Fig. 1. The asymmetric unit contains two pyridine-3-sulfonate ions and two lithium ions. Table 1 gives some selected geometric parameters. The lithium cations are tetrahedrally coordinated by three O atoms and one N atom belonging to four different ligands, the bond angles being in the range  $106.4(2)$ – $115.1(2)^\circ$ . The Li–O distances range from  $1.868(5)$  to  $1.962(4) \text{ \AA}$ , whereas the Li–N distances are  $1.996(5)$  and  $2.157(4) \text{ \AA}$ . The distance ranges in the CSD (18 entries for this particular geometry) are  $1.898$ – $2.163 \text{ \AA}$  for the Li–O distance and  $1.842$ – $2.069 \text{ \AA}$  for the Li–N distance.

Fig. 2 shows the three-dimensional structure, in which pairs of pyridine-3-sulfonate groups are held together by  $\pi$ - $\pi$  non-covalent intermolecular interactions. The distance between the centroids of two adjacent pyridine rings is  $3.80 \text{ \AA}$ , whereas the angle between the ring-centroid vector and the ring normal of one of the pyridine rings is  $20.1(2)^\circ$ , and the angle



**Figure 1**  
The asymmetric unit of (I), showing displacement ellipsoids at the 30% probability level.



**Figure 2**  
A packing diagram of (I). H atoms are not shown for clarity.

between the two phenyl rings is  $2.8(2)^\circ$ . These values can be considered to be normal for  $\pi$ - $\pi$  interactions (Janiak, 2000).

## Experimental

Single crystals of the title complex were obtained by slow evaporation of an aqueous solution of pyridine-3-sulfonic acid (500 mg, 3.15 mmol), lithium hydroxide (132 mg, 3.15 mmol) and guanidinium chloride (300 mg, 3.15 mmol).

### Crystal data

$\text{Li}^+ \cdot \text{C}_5\text{H}_4\text{NO}_3\text{S}^-$   
 $M_r = 165.10$   
 Triclinic,  $P\bar{1}$   
 $a = 7.6362(6) \text{ \AA}$   
 $b = 8.8697(9) \text{ \AA}$   
 $c = 10.397(1) \text{ \AA}$   
 $\alpha = 81.572(8)^\circ$   
 $\beta = 71.486(8)^\circ$   
 $\gamma = 82.921(7)^\circ$   
 $V = 658.33(11) \text{ \AA}^3$

$Z = 4$   
 $D_x = 1.666 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 4215 reflections  
 $\theta = 2-29^\circ$   
 $\mu = 0.43 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Prism, colourless  
 $0.52 \times 0.33 \times 0.22 \text{ mm}$

### Data collection

Oxford Diffraction XCALIBUR diffractometer  
 $\omega$  scans  
 11 562 measured reflections  
 4187 independent reflections  
 2612 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.07$   
 $\theta_{\text{max}} = 32.2^\circ$   
 $h = -10 \rightarrow 11$   
 $k = -12 \rightarrow 12$   
 $l = -14 \rightarrow 15$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.068$   
 $S = 1.21$   
 4182 reflections  
 199 parameters

H-atom parameters constrained  
 Weighting scheme: see below  
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.71 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.68 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

S3—O4	1.4421 (18)	O6—Li2	1.959 (4)
S3—O5	1.438 (2)	O14—Li2	1.896 (4)
S3—O6	1.4451 (18)	O15—Li1	1.962 (4)
S3—C7	1.772 (2)	O16—Li1 <sup>iii</sup>	1.868 (4)
S13—O14	1.430 (2)	N11—C10	1.333 (3)
S13—O15	1.4412 (19)	N11—C12	1.335 (3)
S13—O16	1.4471 (18)	N11—Li2 <sup>iv</sup>	1.996 (5)
S13—C17	1.777 (2)	N21—C20	1.340 (3)
O4—Li2 <sup>i</sup>	1.886 (5)	N21—C22	1.342 (3)
O5—Li1 <sup>ii</sup>	1.886 (4)	N21—Li1 <sup>v</sup>	2.157 (4)
O4—S3—O5	112.89 (13)	C20—N21—Li1 <sup>v</sup>	124.44 (18)
O4—S3—O6	113.56 (11)	C22—N21—Li1 <sup>v</sup>	118.89 (18)
O4—S3—C7	105.19 (10)	S3—C7—C8	121.20 (18)
O5—S3—O6	111.89 (13)	S3—C7—C12	119.83 (14)
O5—S3—C7	105.83 (12)	N11—C10—C9	122.7 (2)
O6—S3—C7	106.72 (11)	N11—C12—C7	123.34 (18)
O14—S13—O15	114.17 (14)	S13—C17—C18	121.27 (18)
O14—S13—O16	112.37 (11)	S13—C17—C22	119.29 (16)
O14—S13—C17	105.67 (11)	N21—C20—C19	123.9 (2)
O15—S13—O16	112.16 (11)	N21—C22—C17	123.3 (2)
O15—S13—C17	105.82 (12)	O15—Li1—N21 <sup>v</sup>	96.50 (18)
O16—S13—C17	105.84 (10)	O5 <sup>ii</sup> —Li1—O15	111.4 (2)
S3—O4—Li2 <sup>i</sup>	151.12 (17)	O5 <sup>ii</sup> —Li1—N21 <sup>v</sup>	111.1 (2)
S3—O5—Li1 <sup>ii</sup>	173.2 (2)	O16 <sup>iii</sup> —Li1—N21 <sup>v</sup>	115.1 (2)
S3—O6—Li2	147.00 (17)	O15—Li1—O16 <sup>iii</sup>	116.3 (2)
S13—O14—Li2	159.6 (2)	O5 <sup>ii</sup> —Li1—O16 <sup>iii</sup>	106.4 (2)
S13—O15—Li1	142.25 (19)	O6—Li2—N11 <sup>vi</sup>	108.8 (2)
S13—O16—Li1 <sup>iii</sup>	133.49 (16)	O4 <sup>i</sup> —Li2—O6	111.2 (2)
C10—N11—C12	117.4 (2)	O6—Li2—O14	111.3 (2)
C10—N11—Li2 <sup>iv</sup>	125.5 (2)	O4 <sup>i</sup> —Li2—O14	110.4 (2)
C12—N11—Li2 <sup>iv</sup>	117.07 (19)	O4 <sup>i</sup> —Li2—N11 <sup>vi</sup>	108.3 (2)
C20—N21—C22	116.6 (2)	O14—Li2—N11 <sup>vi</sup>	106.7 (2)

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

A Chebyshev polynomial (Watkin, 1994; Prince, 1982) was used in the weighting scheme;  $w = 1.0/[A_0T_0(x) + A_1T_1(x) + \dots + A_{n-1}T_{n-1}(x)]$ , where  $A_i$  are the Chebyshev coefficients listed below and  $x = F_{\text{calc}}/F_{\text{max}}$ . Robust weighting (Prince, 1982)  $W = w [1 - (\Delta F/6\sigma(F))^2]^2$ .  $A_{0-2} = 471.0, 539.0$  and  $166.0$ , respectively. H atoms were found in Fourier difference maps ( $C-H = 0.93-1.06 \text{ \AA}$ ) and allowed to ride on their parent C atoms, with  $U_{\text{iso}}(\text{H})$  values fixed at  $0.05 \text{ \AA}^2$ . Five reflections have been omitted from the refinement because they were too close to the beam stop.

Data collection: *Xcalibur* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *ORTEP-3* (Farrugia, 1997) and

PLATON (Spek, 2003); software used to prepare material for publication: CRYSTALS.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Casciaro, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–435.
- Brodersen, K., Dolling, R. & Liehr, G. (1980). *Z. Anorg. Allg. Chem.* **464**, 17–22.
- Chandrasekhar, K. (1977). *Acta Cryst.* **B33**, 143–145.
- Farrugia, L. D. (1997). *J. Appl. Cryst.* **30**, 565.
- García-Vázquez, J. A., Romero, J., Sousa-Pedrares, A., Sousa, A., Garnovskii, A. D. & Garnovskii, D. A. (2000). *J. Chem. Cryst.* **30**, 23–26.
- Holman, K. T., Pivovar, A. M. & Ward, M. D. (2001). *Science*, **294**, 1907–1911.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Lee, A. van der & Barboiu, M. (2004). *Acta Cryst.* **E60**, o89–o91.
- Oxford Diffraction (2002). *CrysAlis RED and Xcalibur Users Manual*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Prince, E. (1982). In *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Walsh, B. & Hathaway, B. J. (1980). *J. Chem. Soc. Dalton Trans.* pp. 681–689.
- Watkin, D. J. (1994). *Acta Cryst.* **A50**, 411–437.
- Watkin, D. J., Prout, C. K., Carruthers, J. R., Betteridge, P. W. & Cooper, R. I. (2001). *CRYSTALS*. Issue 12. Chemical Crystallography Laboratory, Oxford, England.