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A Refinement of the Crystal Structure of Lithium Hydrazinium Sulphate by X-ray Diffraction

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Abstract. At room temperature, crystals of lithium hydrazinium sulphate, $Li(N_2H_5)SO_4$, are orthorhombic, space group $Pna2_1$, with cell dimensions $a=9{\cdot}929$ (5), $b=8{\cdot}973$ (3), $c=5{\cdot}181$ (2) Å, $Z=4$, $D_{calc}=1{\cdot}958$ g cm^{-3}. The structure, refined by least-squares methods using three-dimensional X-ray diffractometer measurements [R(weighted) = 0·027], is the same as that proposed by Brown [*Acta Cryst.* (1964). **17**, 654–660] although more accurate. The N–H bond lengths are systematically shorter than those determined by neutron diffraction [Padmanabhan & Balasubramanian (1967). *Acta Cryst.* **22**, 532–537].

Introduction. Single crystals of lithium hydrazinium sulphate, $Li(N_2H_5)SO_4$, were prepared by evaporation from an aqueous solution of $LiCO_3$ and $(N_2H_6)SO_4$. All diffraction measurements were made at room temperature on a crystal with dimensions 0·2 × 0·2 × 0·3 mm on a Syntex four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å) monochromated by reflexion from a graphite crystal. The lattice parameters (Table 1) were refined by the method of least-squares from the 2θ settings of 15 reflexions. Intensities of 911 independent reflexions with $\sin\theta/\lambda<0{\cdot}76$ Å^{-1} were measured and corrected for Lorentz and polarization effects. No correction was made for absorption as this was considered to be negligible ($\mu=0{\cdot}603$ mm^{-1}).

The non-hydrogen atomic positions of Brown (1964) were used as a basis for the refinement. After refinement of the positional and isotropic thermal param-

Table 1. *Crystallographic data for* $Li(N_2H_5)SO_4$

	This work	Pepinsky *et al.* (1958)	Brown (1964)
Crystal system	Orthorhombic		
Space group	$Pna2_1(C_{2v}^9)$		
a	9·929 (5) Å*	9·913 (4) Å	9·94 (1) Å
b	8·973 (3)	8·969 (4)	8·99 (1)
c	5·181 (2)	5·178 (3)	5·18 (1)
Z	4		
Cell volume	461·6 (3) Å^3		
D_{calc}	1·958 g cm^{-3}		
Absorption coefficient for Mo $K\alpha$	0·603 mm^{-1}		
Crystal size	0·2 × 0·2 × 0·3 mm		
Wavelength Mo $K\alpha$	0·71069 Å		
Systematic absences	$0kl$: $k+l=2n+1$ $h0l$: $h=2n+1$		

* Throughout this work, the estimated standard deviations are enclosed in parentheses.

Table 2. *Parameters derived from the final least-squares refinement of X-ray data for* $Li(N_2H_5)SO_4$

Expressions used for the temperature factors are:
$\exp[-2\pi^2\times10^{-3}(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$ and $\exp[-2\pi^2\times10^{-3}U(2\sin\theta/\lambda)^2]$.

	Positional coordinates			Temperature factors					
	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	0·3312 (3)	0·4333 (3)	0·2533 (12)	21 (1)	19 (1)	18 (1)	−1 (1)	−1 (2)	−2 (2)
S	0·1580 (1)	0·1285 (1)	0·2500†	11·0 (1)	12·4 (1)	11·7 (1)	−1·4 (1)	−0·9 (2)	0·1 (2)
O(1)	0·1909 (2)	0·1052 (2)	0·5271 (3)	26·6 (7)	24·3 (7)	12·7 (6)	−2·5 (5)	−5·3 (5)	2·2 (5)
O(2)	0·0115 (1)	0·1540 (2)	0·2282 (5)	11·5 (4)	31·7 (7)	28·1 (8)	−0·5 (4)	−1·3 (7)	6·1 (8)
O(3)	0·2299 (1)	0·2593 (2)	0·1533 (4)	21·9 (6)	20·2 (7)	24·2 (7)	−8·9 (5)	2·2 (6)	3·9 (6)
O(4)	0·3040 (2)	0·4957 (2)	0·6023 (3)	32·0 (7)	19·4 (7)	22·0 (7)	−6·2 (6)	4·8 (6)	−8·7 (6)
N(1)	0·0235 (2)	0·4157 (2)	0·7488 (7)	30·8 (8)	27·6 (8)	35·3 (9)	−8·6 (6)	−1·0 (13)	3·5 (13)
N(2)	0·4400 (2)	0·2136 (2)	0·7381 (6)	22·1 (6)	23·5 (6)	21·8 (7)	1·6 (5)	1·5 (10)	−0·1 (10)
H(1)	0·103 (4)	0·392 (4)	0·776 (9)	16 (9)					
H(2)	0·026 (7)	0·445 (6)	0·582 (15)	65 (20)					
H(3)	0·358 (4)	0·192 (6)	0·680 (11)	40‡					
H(4)	0·446 (6)	0·234 (8)	0·895 (17)	69 (26)					
H(5)	0·462 (3)	0·282 (4)	0·616 (8)	8 (8)					

† This parameter was used to define the origin and was not refined.
‡ Not refined.

eter of these atoms with the full-matrix least-squares program *CRYLSQ* of the X-RAY 71 Program Library System, all the hydrogen atoms were located with a three-dimensional difference electron-density map. Further refinement with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms gave a residual index, R $[=\sum(||F_o|-|F_c||)/\sum|F_o|]$, of 0·022. During later cycles of refinement, the temperature factor of H(3) refined to a negative value and was set at a typical value of 0·04 and not refined further. The final cycles included an extinction correction where the corrected values of F_c were given by:

$$F_c^*(\text{corr}) = KF_c[1 + 0{\cdot}94 \times 10^{-3}\beta(2\theta)F_c^2]^{-1/2}$$

(Larson, 1967), and were weighted with the function

$$w = (0{\cdot}250 - 0{\cdot}032|F_o| + 0{\cdot}0016|F_o|^2)^{-1}.$$

Table 3. *Bond distances and angles in* $Li(N_2H_5)SO_4$

LiO_4 tetrahedron			
Li–O(1)	1·950 (5) Å	O(1)–Li–O(2)	112·3 (2)°
Li–O(2)	1·959 (3)	O(1)–Li–O(3)	114·9 (3)
Li–O(3)	1·928 (4)	O(1)–Li–O(4)	108·7 (2)
Li–O(4)	1·912 (6)	O(2)–Li–O(3)	97·8 (2)
		O(2)–Li–O(4)	108·0 (3)
		O(3)–Li–O(4)	114·7 (2)
SO_4 tetrahedron			
S–O(1)	1·487 (2) Å	O(1)–S–O(2)	108·2 (1)°
S–O(2)	1·477 (1)	O(1)–S–O(3)	109·7 (1)
S–O(3)	1·462 (2)	O(1)–S–O(4)	109·5 (1)
S–O(4)	1·465 (2)	O(2)–S–O(3)	109·3 (1)
		O(2)–S–O(4)	109·8 (1)
		O(3)–S–O(4)	110·4 (1)
(N_2H_5) ion			
N(1)–N(2)	1·427 (3) Å	N(2)–N(1)–H(1)	111 (2)°
N(1)–H(1)	0·83 (4)	N(2)–N(1)–H(2)	102 (4)
N(1)–H(2)	0·91 (8)	N(2)–N(1)–H(2′)	111 (2)
N(1)–H(2′)	2·18 (7)	H(1)–N(1)–H(2)	102 (5)
		H(1)–N(1)–H(2′)	103 (4)
		H(2)–N(1)–H(2′)	126 (4)
N(2)–H(3)	0·89 (5)	N(1)–N(2)–H(3)	111 (4)
N(2)–H(4)	0·84 (9)	N(1)–N(2)–H(4)	96 (5)
N(2)–H(5)	0·91 (4)	N(1)–N(2)–H(5)	116 (2)
		H(3)–N(2)–H(4)	116 (6)
		H(3)–N(2)–H(5)	98 (4)
		H(4)–N(2)–H(5)	121 (6)

This gave a final weighted residual index, $Rw\{=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ of 0·027. The final atomic positions and temperature factors are given in Table 2.*

* The observed and calculated structure factors are given by Anderson (1973), and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30276 (7 pp.). Copies may be obtained through the Executive Secretary, IUCr, 13 White Friars, Chester CH1 1NZ, England.

The numbering of the atoms is the same as that used by Brown (1964).

Discussion. The structure is the same as that proposed by Niizeki & Koizumi (1964), Brown (1964) and Van den Hende & Boutin (1964). The average Li–O and S–O distances are 1·937 (18) and 1·473 (9) Å respectively. The S–O(1) distance of 1·487 (2) Å lies between the two discrepant values of 1·45 (3) Å (Brown, 1964) and 1·557 Å (Van den Hende & Boutin, 1964) previously reported. Bond lengths and angles are given in Table 3.

Table 4 gives details of the hydrogen bonds. The $-NH_2$ group is involved in three single hydrogen bonds, twice as a donor and once as an acceptor. The $-NH_3^+$ group forms three hydrogen bonds, one of which [H(5)] is bifurcated. A staggered configuration exists between the $-NH_3^+$ group and the $-NH_2$ group and its lone pair.

The structure was refined to allow an accurate comparison with the neutron determination of Ross (private communication). There are no significant differences between our heavy-atom positions and those of the neutron-diffraction studies of both Padmanabhan & Balasubramanian (1967) and Ross $[Li(N_2D_5)SO_4]$, but the N–H bond lengths found by X-rays are systematically shorter than the N–H bond lengths found by neutrons [0·87 (4) Å as against 1·022 (4) Å respectively]. Ross obtained heavy-atom temperature factors which are systematically smaller than those determined by X-rays. This effect, which shows the inadequacy of the free-atom form factors, and the bonding-electron density in the N–H bonds can both be seen on the X–N difference map. A full discussion of this and other related structures is being prepared.

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References

ANDERSON, M. R. (1973). Ph. D. Thesis, McMaster Univ., Hamilton, Ontario, Canada.

BROWN, I. D. (1964). *Acta Cryst.* **17**, 654–660.

LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.

NIIZEKI, N. & KOIZUMI, H. (1964). *J. Phys. Soc. Japan*, **19**, 132–133.

PADMANABHAN, V. M. & BALASUBRAMANIAN, R. (1967). *Acta Cryst.* **22**, 532–537.

PEPINSKY, R., VEDAM, K., OKAYA, Y. & HOSHINO, S. (1958). *Phys. Rev.* **111**, 1467–1468.

VAN DEN HENDE, J. H. & BOUTIN, H. P. (1964). *Acta Cryst.* **17**, 660–663.

Table 4. *Hydrogen bond lengths and angles in* $Li(N_2H_5)SO_4$

D–H···*A*	*D*–H	H···*A*	*D*–*A*	∠*D*–H···*A*
N(1)–H(1)···O(4)	0·83 (4) Å	2·38 (4) Å	2·975 (3) Å	129 (3) °
N(1)–H(2)···N(1′)	0·91 (8)	2·18 (7)	3·043 (3)	156 (5)
N(2)–H(3)···O(1)	0·89 (5)	2·00 (7)	2·874 (3)	169 (5)
N(2)–H(4)···O(2)	0·84 (9)	2·10 (8)	2·892 (4)	158 (7)
N(2)–H(5)···O(2)	0·91 (4)	2·15 (5)	2·982 (4)	153 (3)
N(2)–H(5)···O(4)		2·48 (4)	2·954 (3)	113 (3)