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The Crystal Structure of Lithium Hydroxylammonium Sulphate

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Abstract. Crystals of lithium hydroxylammonium sulphate, $LiNH_3OHSO_4$, are orthorhombic, space group *Pbca*, with $a=18{\cdot}461$ (5), $b=7{\cdot}267$ (3), $c=6{\cdot}695$ (2) Å, $Z=8$. Crystals were grown from an aqueous solution of $(NH_3OH)_2SO_4$ and Li_2SO_4. The structure, which was refined to $R=0{\cdot}034$ from 1574 X-ray reflexions, contains sheets of $LiSO_4$ hydrogen-bonded together by the NH_3OH ions. The Li atom is surrounded by four O atoms at 1·96 Å and S by four O at 1·477 Å.

Introduction. Single crystals of $LiNH_3OHSO_4$ were grown by slow evaporation from an aqueous solution of $(NH_3OH)_2SO_4$ and Li_2SO_4 in stoichiometric quantities. Very thin hexagonal crystals were formed, but recrystallization improved the thickness to a size suitable for X-ray work. The space group was deduced from systematic absences on Weissenberg photographs and the lattice parameters were measured both for a powder sample and a single crystal; the results, with other crystal data, are given in Table 1. For determination of the structure, a single crystal measuring $0{\cdot}1\times0{\cdot}1\times0{\cdot}4$ mm was selected. The intensities were measured at room temperature on a Syntex four-circle automatic X-ray diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å) monochromated by reflexion from a graphite crystal. Intensities of 1574 independent reflexions with $\sin\theta/\lambda<0{\cdot}705$ were measured and cor-

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Table 1. *Crystallographic data for* $LiNH_3OHSO_4$

	Powder		Single crystal
Crystal system			Orthorhombic
Space group			*Pbca*
a	18·460 (8) Å		18·461 (5) Å
b	7·280 (5)		7·267 (3)
c	6·712 (3)		6·695 (2)
Z		8	
d_m		2·06 (10) g cm^{-3}	
d_x		2·027 (3) g cm^{-3}	
Absorption coefficient	5·9 (Cu $K\alpha$) mm^{-1}		0·63 (Mo $K\alpha$) mm^{-1}
Wavelength $K\alpha$	1·5406 Å		0·71069 Å
Systematic absences		$0kl$ $k=2n+1$	
		$h0l$ $l=2n+1$	
		$hk0$ $h=2n+1$	

Table 2. *Parameters derived from the final least-squares refinement*

Estimated standard deviations are in parentheses

The expressions used for the temperature factors are:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\right]$$

and

$$\exp\left[-2\pi^2U\left(\frac{2\sin\theta}{\lambda}\right)^2\right].$$

	x	*y*	*z*	*U* or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	0·2612 (2)	0·2535 (8)	0·4122 (8)	0·024 (2)	0·021 (2)	0·020 (2)	−0·002 (3)	0·000 (2)	0·004 (2)
S	0·1559 (1)	0·0520 (1)	0·1577 (1)	0·0127 (2)	0·0128 (2)	0·0138 (2)	−0·0000 (3)	0·0003 (3)	0·0005 (3)
O(1)	0·3348 (1)	0·4390 (3)	0·3394 (3)	0·022 (1)	0·025 (1)	0·021 (1)	−0·004 (1)	−0·002 (1)	0·011 (1)
O(2)	0·3289 (1)	0·0586 (3)	0·4777 (3)	0·025 (1)	0·024 (1)	0·018 (1)	0·005 (1)	0·001 (1)	0·007 (1)
O(3)	0·2076 (1)	0·2075 (2)	0·1649 (3)	0·024 (1)	0·020 (1)	0·020 (1)	−0·009 (1)	−0·002 (1)	0·002 (1)
O(4)	0·0810 (1)	0·1213 (3)	0·1458 (4)	0·015 (1)	0·021 (1)	0·029 (1)	0·005 (1)	0·002 (1)	0·002 (1)
O(5)	0·4468 (1)	0·1444 (3)	0·0716 (3)	0·034 (1)	0·034 (1)	0·036 (1)	−0·001 (1)	0·001 (1)	0·009 (1)
N	0·4446 (1)	0·0037 (4)	0·2142 (4)	0·031 (1)	0·028 (1)	0·028 (1)	−0·003 (1)	0·006 (1)	−0·000 (1)
H(1)	0·404 (2)	0·017 (5)	0·326 (6)	0·011 (9)					
H(2)	0·429 (2)	−0·109 (5)	0·146 (5)	0·012 (9)					
H(3)	0·493 (2)	0·005 (7)	0·263 (7)	0·025 (11)					
H(4)	0·400 (3)	0·085 (9)	0·001 (10)	0·087 (20)					

rected for Lorentz and polarization effects but not for absorption, which was negligible ($\mu = 0{\cdot}63$ mm^{-1}).

The structure was solved from a Patterson synthesis and the hydrogen atoms found from a difference map. The atomic parameters and temperature factors were refined by the full-matrix least-squares program *CRYLSQ* of the XRAY 71 program library. With anisotropic temperature factors for all non-hydrogen atoms $R_1\,[=\sum(|F_o|-|F_c|)/\sum|F_o|]$ was 0·034. The final $R_2\,[=(\sum\omega(|F_o|-|F_c|)^2/\sum\omega|F_o|^2)^{1/2}]$ was 0·027, where $\omega=(0{\cdot}1146-0{\cdot}0044|F_o|+0{\cdot}00004|F_o|^2)^{-1}$. Final atomic positions and temperature factors are given in Table 2.*

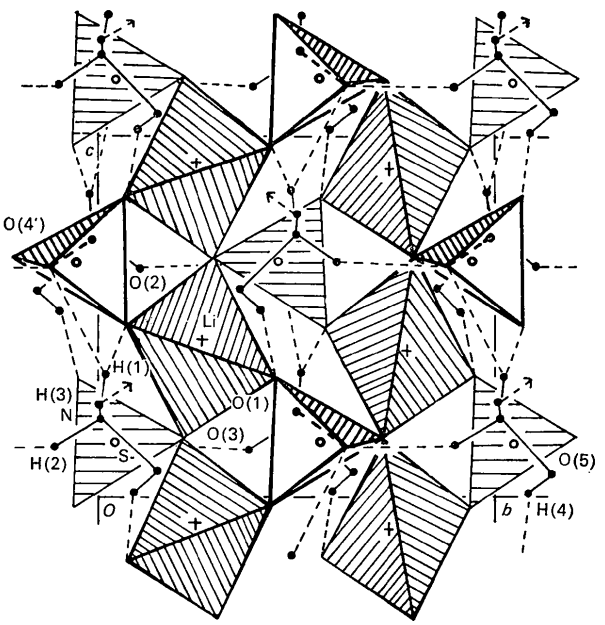

Fig. 1. Structure of $LiNH_3OHSO_4$ projected down **a**.

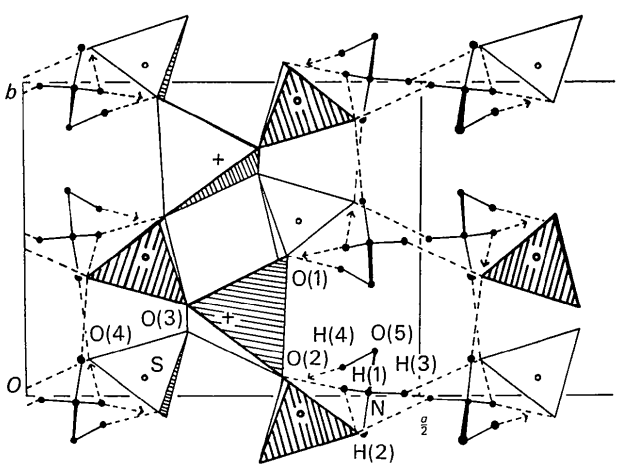

Fig. 2. Structure of $LiNH_3OHSO_4$ projected down **c**.

Description of the structure. The bond lengths and bond angles are given in Table 3.

Crystals of $LiNH_3OHSO_4$ are composed of sheets of $LiSO_4$ which are held together by hydrogen bonds from the hydroxylammonium ions. This structure is quite different from the stuffed tetrahedral framework structures of the isoelectronic $Li(N_2H_5)SO_4$ (Brown, 1964) and $Li(N_2H_5)BeF_4$ (Anderson, Brown & Vilminot, 1973) or the other compounds of the form $LiMSO_4$ and $LiMBeF_4$ (M = K, Rb, Cs, NH_4) discussed by Chung & Hahn (1972).

Table 3. *Bond distances and angles*

SO_4 tetrahedron	
S–O(1)	1·478 (2) Å
S–O(2)	1·476 (2)
S–O(3)	1·480 (2)
S–O(4)	1·473 (2)
O(1)–S–O(2)	110·3 (1)°
O(1)–S–O(3)	108·8 (1)
O(1)–S–O(4)	110·1 (1)
O(2)–S–O(3)	108·6 (1)
O(2)–S–O(4)	108·7 (1)
O(3)–S–O(4)	110·2 (1)
LiO_4 tetrahedron	
Li–O(1)	1·975 (5) Å
Li–O(2)	1·939 (6)
Li–O(3)	1·957 (5)
Li–O(3′)	1·981 (5)
O(1)–Li–O(2)	96·4 (2)°
O(1)–Li–O(3)	104·8 (3)
O(1)–Li–O(3′)	117·2 (3)
O(2)–Li–O(3)	113·1 (3)
O(2)–Li–O(3′)	103·5 (3)
O(3)–Li–O(3′)	119·7 (2)
NH_3OH ion	
N—O(5)	1·400 (4) Å
N—H(1)	1·06 (3)
N—H(2)	0·98 (4)
N—H(3)	0·96 (4)
O(5)–H(4)	1·08 (6)
H(1)–N—H(2)	102 (3)°
H(1)–N—H(3)	115 (3)
H(1)–N—O(5)	116 (2)
H(2)–N—H(3)	116 (3)
H(2)–N—O(5)	107 (2)
H(3)–N—O(5)	101 (3)
H(4)–O(5)–N	89 (3)

Views of the structure projected along **a** and **c** are shown in Figs. 1 and 2. The sulphur and lithium atoms are at the centre of oxygen tetrahedra which share corners to form the $LiSO_4$ sheets perpendicular to [100].

Two hydrogen atoms of the $-NH_3$ group and the

* A list of observed and calculated structure factors is given by Anderson (1973), and has also been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30162 (9 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Hydrogen-bond lengths and angles of the* NH_3OH *ion*

	D–H···A		D–H (Å)	H···A (Å)	D–A (Å)	D–H···A (°)
N	H(1)	O(2) }	1·06 (3)	{ 1·75 (3)	2·799 (3)	170 (3)
N	H(1)	O(4) }		{ 2·38 (4)	3·066 (4)	121 (2)
N	H(2)	O(4)	0·98 (4)	1·97 (4)	2·856 (3)	149 (3)
N	H(3)	O(4)	0·96 (4)	1·93 (4)	2·820 (3)	155 (4)
O(5)	H(4)	O(1)	1·08 (6)	1·62 (6)	2·656 (3)	158 (6)

Table 5. *Bond strengths in* $LiNH_3OHSO_4$: *bond strengths in valence units and bond lengths in* Å (*in parentheses*) *for bonds between* O *and* Li, S *and* H

Bond strengths (s) are calculated from the expression $s=(R/R_0)^{-N}$ where R is the bond length:

			H–O	Li–O	S–O			
		R_0	0·86*	1·378	1·622			
		N	2·17*	4·065	4·290			
	Li	S	H(1)	H(3)	H(3)	H(4)	Sums around anion	
O(1)	0·23 (1·975)	1·49 (1·478)				0·25* (1·62)	1·97	
O(2)	0·25 (1·939)	1·50 (1·476)	0·21* (1·75)				1·96	
O(3)	0·24 (1·957)	0·23 (1·981)	1·48 (1·480)					1·95
O(4)		1·51 (1·473)	0·11* (2·38)	0·17* (1·97)	0·17* (1·93)		1·96	
Sums around cations	0·95	5·98						

* The parameters for H apply to bonds determined by neutron diffraction and will tend to underestimate the bond strength in this case.

hydrogen atom of the –OH group form hydrogen bonds with oxygen atoms of the nearest sheet. The remaining hydrogen atom of the $-NH_3$ group, H(3), forms a hydrogen bond to O(4) of the opposite sheet. Details of the hydrogen bonds are given in Table 4.

The correctness of this structure is confirmed by the bond strength calculation (Brown & Shannon, 1973) given in Table 5. Each oxygen atom of the sheet forms one strong bond (1·5 valence units) with a sulphur atom. The equivalence of the Li–O and H···O bonds in terms of their strengths is seen in the way O(1) and O(2) complete a threefold coordination by forming one bond to each Li and H while O(3) forms two bonds to Li and O(4) accepts three rather weak hydrogen bonds. The r.m.s. deviation of the sums of the bond strengths from the valence is 0·04 valence units.

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