LARSEN, A. C. (1961). *A.C.A. Meeting, Boulder*, Colorado, Paper A5

NITTA, I., SAKURAI, K. & TOMIIE, Y. (1951). *Acta Cryst.* **4**, 289.

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

SAKURAI, K. & TOMIIE, Y. (1952). *Acta Cryst.* **5**, 293.

SOMMER, F. & WEISE, K. (1916). *Z. anorg. Chem.* **94**, 51.

Acta Cryst. (1964). **17**, 660

The Crystal Structure of Ferroelectric Lithium Hydrazinium Sulfate*

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The crystal structure of lithium hydrazinium sulfate has been determined by the heavy atom method from 0*kl*, *h*0*l* and *hk*0 data. Bond lengths and angles based on three-dimensional data are given, e.s.d. 0·008 Å and 1°.

The N–N distance found is 1·447 Å, which corresponds to previously reported values for the $N_2H_5^+$ ion. The nitrogen atoms form in the direction of the *c* axis an infinite hydrogen-bonded zigzag chain of the type NH–N with a distance of 3·018 Å. The length of one of the S–O bonds is 1·557 Å, which is considerably longer than the normally accepted value for that ion. That of another bond is 1·430 Å, which indicates a large amount of double bond character.

The structure is held together by three-dimensional network of weak hydrogen bonds. Tentative positions of the hydrogen atoms are assigned.

Introduction

The preceding article (Brown, 1964) concerns the crystal structure of the ferroelectric lithium hydrazinium sulfate.

This paper represents an independent structure analysis of the same compound, which was carried out concurrently. However, after it was submitted for publication, the work of Brown was pointed out to us by one of the editors, and Dr. Brown was so courteous as to provide us with a copy of his manuscript. In order to avoid duplication, a large amount of material has been omitted from this publication.

The intensity data

The intensities were recorded with both a Weissenberg camera and a General Electric XRD 5 diffractometer equipped with a single-crystal orienter, Cu $K\alpha$ radiation being used. To reduce the background and the accidental overlapping of β reflections and harmonics, a nickel filter and pulse-height analyzer were employed. The crystal used for data collection was carefully ground into a cylinder with a radius of 0·015 cm and with the axis coinciding with the *c* axis. For the *h*0*l* projection 30 reflections were observed, and 2 had zero magnitude. For the 0*kl* and *hk*0 projections these numbers are respectively 30 and 0, 83 and 16. The data were not corrected for absorption but the usual corrections for the Lorentz and polarization factors were applied. In a later stage of the structure determination a complete set of three-dimensional data was obtained. Fifty-three of the 505 possible reflections, for which sin θ is smaller than 0·9659 ($2\theta < 150°$), had a magnitude smaller than detectable. In all cases the intensities were measured with the counter and the specimen rotating in the ratio 2 to 1.

Structure determination

The *x* and *y* coordinates of the sulfur atoms were determined from the Patterson function $P(u,v)$ from which the peak at the origin was removed. The approximate positions of the oxygen atoms were obtained from a subsequent Fourier synthesis based on the signs as determined by the sulfur atoms alone. After the sulfur and oxygen atoms had been included in the structure factor calculations, the discrepancy index R for this projection was 0·25. Two additional Fourier syntheses revealed the positions of the nitrogen atoms and provided improved positional

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Table 1. *Atomic parameters for* $LiN_2H_5SO_4$

Coordinates are in fractions of the cell edge.

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B
S	0·1290	0·1589	0·25	0·002 Å	0·002 Å	0·002 Å	0·78 Å^2
O(1)	0·1068	0·1870	0·5434	0·006	0·006	0·007	1·10
O(2)	0·1511	0·0132	0·2296	0·008	0·008	0·008	2·35
O(3)	0·2558	0·2335	0·1626	0·007	0·007	0·007	1·91
O(4)	0·4904	0·3048	0·6016	0·008	0·008	0·009	2·70
N(1)	0·4193	0·0285	0·7405	0·010	0·010	0·010	2·36
N(2)	0·2137	0·4460	0·7346	0·008	0·009	0·009	1·92

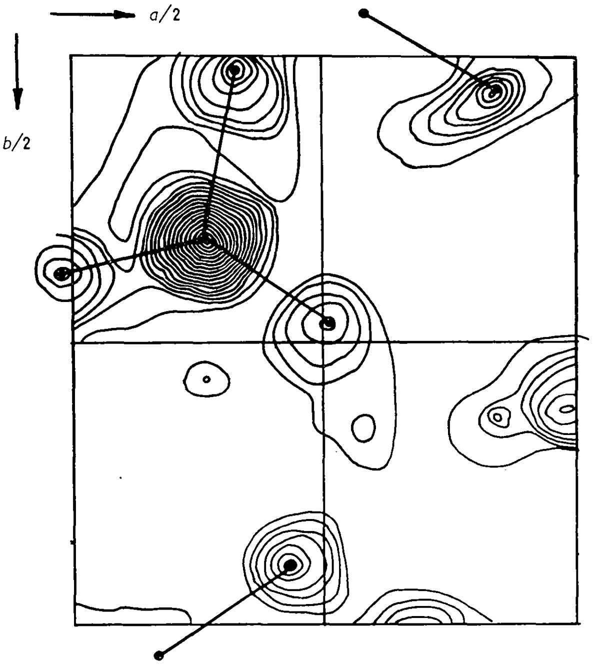

Fig. 1. F_o Fourier synthesis from $hk0$ data. Contours at arbitrary intervals.

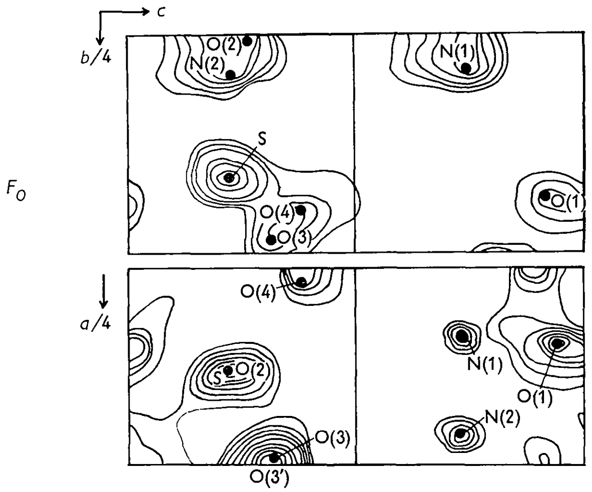

Fig. 2. F_o synthesis from (*a*) $h0l$ and (*b*) $0kl$ data; contours at arbitrary intervals.

parameters for the other atoms. The z coordinates were found in a similar manner after the sulfur atoms had been arbitrarily assumed to be located at the heights 0·25 and 0·75.

Refinement

The structural parameters were improved by using six cycles of least-squares refinement and assigning a weighting factor of $1{\cdot}0/F_o$ to each reflection. The off-diagonal terms in the least-squares matrix were ignored. For this procedure the computer program ERBR1 was used on an IBM 7090 computer. The over-all value of R, excluding the eighteen non-observed reflections, was 0·12. For the individual projections the discrepancy factors were 0·07 ($h0l$), 0·10 ($0kl$), and 0·13 ($hk0$). Fourier syntheses for the three projections as obtained here are shown in Figs. 1 and 2. For all Fourier summations the ERFR2 program of Sly, Shoemaker & Van den Hende was used.

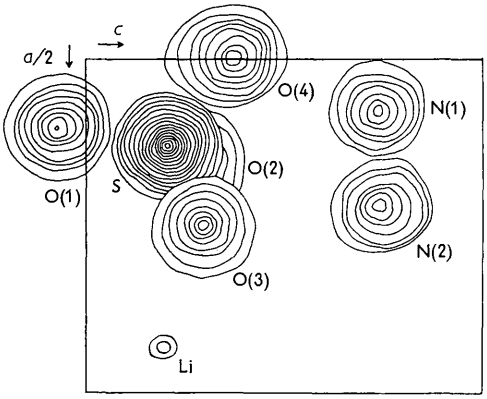

Fig. 3. Composite electron density map as obtained from the three-dimensional F_o synthesis. Contours at arbitrary intervals.

At this stage the projection data were abandoned and three-dimensional data included in the least-squares refinement; but after two cycles no shifts larger than 0·00002 of the cell edges were observed, and the refinement was stopped with an over-all R index of 0·14. Only isotropic temperature factors were applied during these calculations. The positions of the atoms thus obtained are given in Table 1. Fig. 3 shows a composite electron density map.

Discussion of the structure

The interatomic distances are given in Table 2. The N–N distance of 1·447 Å corresponds to that of the hydrazinium ion, $N_2H_5^+$, and is in good agreement with the value 1·45 found by Nitta, Sakurai & Tomiie (1951) in hydrazinium chloride. The N–N distance for hydrazine, N_2H_4, in the gaseous phase is 1·47 Å, and 1·46 Å in the crystalline state (Giguère & Schomaker, 1943), whereas values between 1·40 and 1·42 Å have been reported for the hydrazonium ion (Nitta *et al.*, 1951; Kronberg & Harker, 1942; Donohue & Lipscomb, 1947).

Table 2. *Interatomic distances*

O(2)(*a*)–N(2)(*b*)	2·959	O(1)(*a*)–N(2)(*c*)	2·915
O(2)(*a*′)–N(2)(*b*)	2·913	O(1)(*c*)–N(2)(*d*)	3·046
O(1)(*a*)–N(2)(*b*)	3·046	N(2)(*a*)–N(1)(*a*)	1·447
N(1)(*c*)–N(1)(*d*)	3·019	S(*a*)–O(1)(*a*)	1·557
O(2)(*c*)–O(3)(*b*)	2·917	S(*a*)–O(2)(*a*)	1·461
O(4)(*a*)–N(2)(*a*)	2·931	S(*a*)–O(3)(*a*)	1·430
O(4)(*a*)–N(1)(*d*)	2·903	S(*a*)–O(4)(*a*)	1·505
O(3)(*d*)–N(2)(*a*)	3·081		

The bond distances and angles for the sulfate ion are presented in Fig. 4. The average S–O distance for a sulfate ion, as obtained from the available literature, is 1·49 Å and the S–O(1) distance of 1·557 Å seemed, at first, unreasonably long. This combined with the short S–O(3) distance of 1·430 Å, suggested that the least-squares refinement might have converged to a 'false' minimum. In view of this, the sulfur atom was then placed in the center of the tetrahedron formed by the four oxygen atoms, and in another trial the oxygen atoms at equal distances from the sulfur atom, but subsequent refinement cycles returned the atoms to their original positions, which we may therefore assume to be correct.

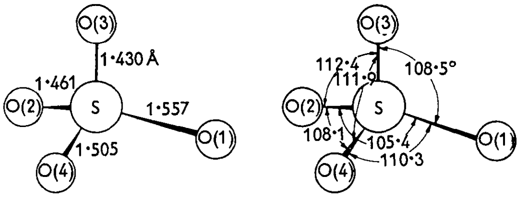

Fig. 4. Bond distances and angles for the sulfate ion.

Atom O(3) has, according to Table 2, no nearest

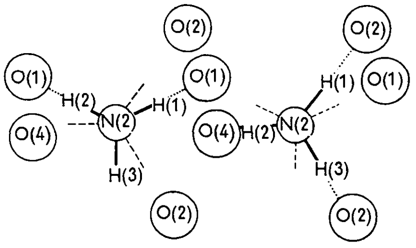

Fig. 5. Schematic view of the environment of N(1) viewed along the N(1)–N(2) axis.

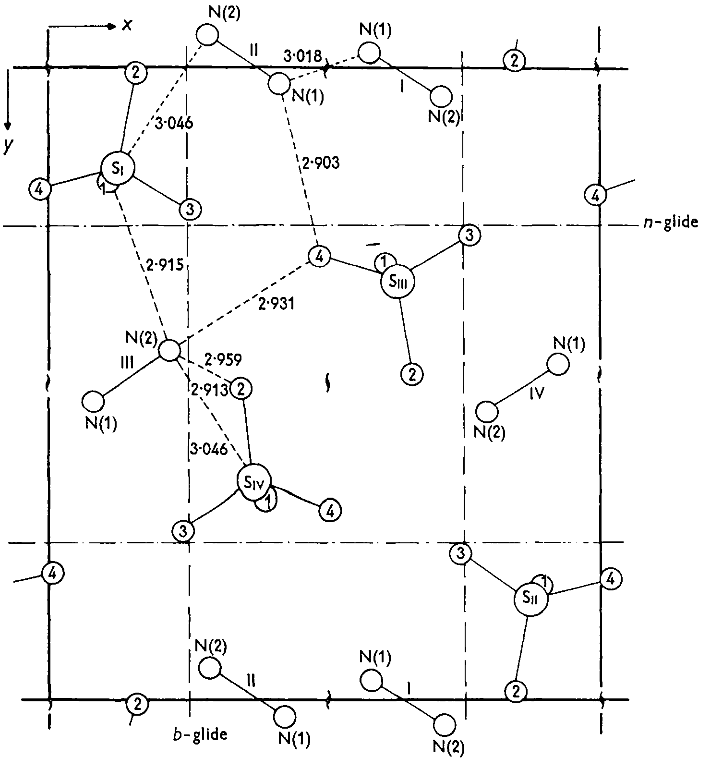

Fig. 6. A view of the structure of $LiN_2H_5SO_4$ along the *c* axis showing the short intermolecular distances.

neighbors within 3·2 Å and it is not involved in any hydrogen bonding. The short S–O(3) distance suggests a double bond. If there were no such double bond and the sulfur atom were actually shifted 0·078 Å from the center of the tetrahedron, a spontaneous polarization of 3·0 microcoulomb.cm^{-2} in the direction of the c axis should be observed. This is an order of magnitude larger than the observed value for σ_s measured at room temperature. Atom O(1), on the other hand, has two nitrogen nearest neighbors, N(1) and N(2′), at 2·915 and 3·046 Å, which suggests a bifurcated hydrogen bond.

A study of a three-dimensional electron density map and a difference Fourier synthesis was made in order to locate, if possible, the hydrogens and the lithium atoms. In the neighborhood of N(2), six positive peaks were observed in the difference map corresponding to about 0·5 e.Å^{-3}. One set (A) of three of these peaks may correspond to three half hydrogens, two of which are positioned between N(2) and O(1) and O(1′). The remaining peaks form a second set (B) of half hydrogen atoms, two of which are located between N(2) and O(2), and between N(2) and O(2) in the cell immediately (in the **c** direction), as shown in Fig. 5.

The positional coordinates of the lithium ion as obtained from the final electron density map are $x=0{\cdot}433$, $y=0{\cdot}339$, $z=0{\cdot}271$.

The present work was started at the Crystal Research Laboratory of the Pennsylvania State University under contracts with the Solid State Sciences Division of the Air Force Office of Scientific Research and with the Signal Corps Engineering Laboratories. The authors wish to thank Professor Ray Pepinsky for suggesting the problem and for his keen interest in this study.

References

Brown, I. D. (1964). *Acta Cryst.* **17**, 654.

Donohue, J. & Lipscomb, W. N. (1947). *J. Chem. Phys.* **15**, 115.

Giguère, P. A. & Schomaker, V. (1943). *J. Amer. Chem. Soc.* **65**, 2025.

Kronberg, M. L. & Harker, D. (1942). *J. Chem. Phys.* **10**, 309.

Nitta, J., Sakurai, K. & Tomiie, Y. (1951). *Acta Cryst.* **4**, 289.

Acta Cryst. (1964). **17**, 663

The Crystal Structure of Iron Pentacarbonyl: Space Group and Refinement of the Structure

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The data from iron pentacarbonyl reported by Hanson have been refined, both in the space group Cc assumed by Hanson, and in $C2/c$. The results indicate the correct space group to be $C2/c$. The required molecular symmetry is only 2, but deviations from an ideal trigonal bipyramid are not significant, within the limits of error of this determination. The bond lengths are Fe–C = 1·79 ± 0·02, and C–O = 1·12 ± 0·02 Å.

Additional calculations confirm that the bonding is Fe–C–O rather than Fe–O–C: with the latter structure worse agreement between the F_o and the F_c resulted, and highly unreasonable temperature factors were obtained.

Introduction

In the report by Hanson (1962) on the structure of iron pentacarbonyl the space group assignment was mentioned but once, namely, that it was 'probably Cc'. The alternate possibility, $C2/c$, which is also consistent with the observed absences, was apparently not considered. The required molecular symmetry (for $Z=4$) is none for Cc, and 2 (or $\bar{1}$) for $C2/c$. Upon examination of Hanson's Fig. 1 and his Table 1 it appeared that within experimental error the molecule does contain a twofold axis, and that the space group is thus $C2/c$. The deviations of Hanson's coordinates from the restrictions of $C2/c$ are given in Table 1; the average value of 0·07 Å is less than two standard deviations. Thus, it was felt that further examination of this structure was indicated in order to decide with more certainty which of the two space groups is the correct one.

There is, moreover, additional interest for reexami-

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* This situation was brought to our attention by Prof. A. W. Adamson.