

The Crystal Structure of Thiourea Nitrate

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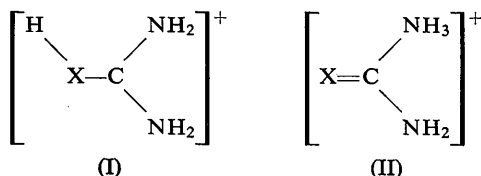
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The structure of thiourea nitrate has been determined by three-dimensional X-ray methods. Both Cu $K\alpha$ and Mo $K\alpha$ data were obtained with a single-crystal diffractometer and the final R values are 4.9% and 5.5% respectively. The space group is $P2_1/m$ and there are two molecules in the unit cell. All atoms, including hydrogen, lie on mirror planes. The whole structure is built up of layers of atoms, the atoms within each layer being linked by a network of hydrogen bonds.

Introduction

There are two possibilities for the structure of the protonated urea or thiourea cation:



Various attempts have been made to locate the position of the extra proton by infrared-spectroscopic methods, but the interpretation of the spectra has been contradictory; both structure (I) and structure (II) have been used to explain the same infrared spectra.

From the spectrum of urea nitrate Davies & Hopkins (1957) concluded that the proton is attached to one of the two NH_2 groups. Spinner (1959) came to the same conclusion. On the other hand, Janssen (1961) and Kutzelnigg & Mecke (1961*a, b, c*) came to the conclusion that the proton is attached to the oxygen or sulphur atom.

The X-ray structure analyses of the salts urea phosphate (Sundera-Rao, Turley & Pepinsky, 1957) and *N*-methylurea nitrate (Bryden, 1957) indicated that the proton of the acid becomes attached to the urea oxygen, but the results were not conclusive. The present X-ray analysis was carried out in an attempt to locate the position of the proton in thiourea nitrate and urea nitrate, and then to compare the bonding in these two compounds. (Three-dimensional intensity data have been collected for urea nitrate and work on this structure is in progress.)

Experimental

Crystals grown from an aqueous solution were mainly long monoclinic needles in the $[010]$ direction. They were extremely soft, having well-developed faces showing easy cleavage along (010) . The crystals were un-

stable in air, and the specimens investigated were sealed in thin-walled capillary tubes.

Unit-cell dimensions obtained from a single crystal mounted on the Nonius automatic diffractometer are: $a = 6.384 \pm 0.005$, $b = 6.398 \pm 0.004$, $c = 6.980 \pm 0.005$ Å; $\beta = 98.65 \pm 0.05^\circ$. The density was determined by flotation to be 1.65 g.cm^{-3} ; the calculated density is 1.65 g.cm^{-3} for 2 molecules in the unit cell.

Intensities of a single crystal were measured at room temperature on the Nonius diffractometer; 448 reflexions (hkl and $\bar{h}\bar{k}l$) were recorded with filtered Cu $K\alpha$ radiation and 662 with filtered Mo $K\alpha$ radiation.

The linear absorption coefficient for Cu $K\alpha$ radiation is 45 cm^{-1} and the optimum thickness 0.045 cm . The needle-shaped crystal measured had a cross-sectional thickness of the order of 0.01 cm ; no absorption corrections were applied.

Patterson function and space group determination

A three-dimensional sharpened Patterson function was evaluated using $I/(\sum f_j)^2$ as coefficients, the sum being



Fig. 1. Section of sharpened Patterson at $y/b=0$, showing configuration of the proposed molecule.

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taken over the atoms in the unit cell. I is the intensity of a reflexion corrected for Lorentz and polarization factors, and f_j is the scattering factor of the j th atom.

Precession photographs showed that the $0k0$ reflexions were absent for odd values of k . The allowed space groups are $P2_1$ and $P2_1/m$, the latter being centrosymmetric. The statistical test of Howells, Phillips & Rogers (1950) indicated that the structure was centrosymmetric.

Furthermore, the Patterson function showed maxima only on the sections $y/b=0$ and $y/b=\frac{1}{2}$. This indicates that the space group is $P2_1/m$, with the two molecules lying on mirror planes separated by a distance $b/2$. The molecules are further related to each other by screw axes running parallel to the b axis.

Structure determination

Investigation of the Patterson section $y/b=0$ showed the configuration of the molecule outlined in Fig. 1.

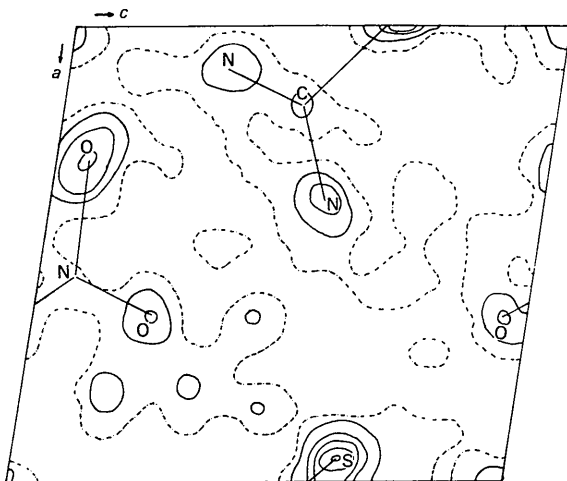


Fig. 2. Difference electron density projection showing the position of the second molecule.

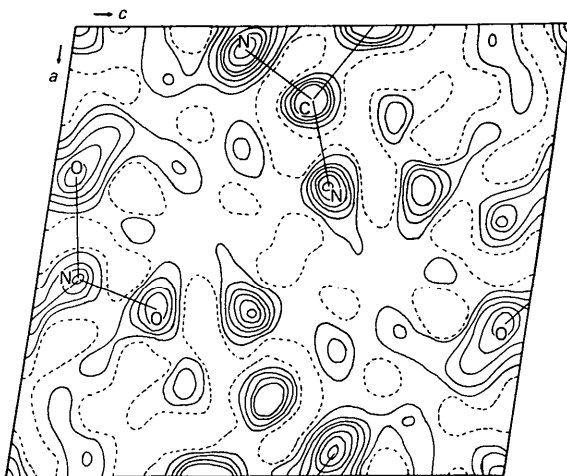


Fig. 3. Section of the sharpened Patterson at $y/b=\frac{1}{2}$.

If the location of this molecule could be assumed, the problem was then to locate the second molecule, or what amounted to the same thing, the position of the screw axis in the centrosymmetric structure had to be determined. Structure factors F_c were calculated for the $h0l$ reflexions, assuming that the molecule shown in Fig. 1 was part of a non-centrosymmetric structure. The phases thus obtained were used to make the difference electron density projection shown in Fig. 2. The second molecule is now revealed and the section $y/b=\frac{1}{2}$ of the Patterson function can easily be interpreted (Fig. 3).

Structure refinement

The three-dimensional least-squares refinement was carried out with a modification of the Busing, Martin & Levy (1962) program *ORFLS*. First the Cu $K\alpha$ data were refined, and when the Mo $K\alpha$ data were obtained, they were refined in exactly the same way. The method used was the following.

Three cycles of refinement were carried out in which the overall scale factor and the x and z coordinates of the eight independent atoms and their isotropic temperature factors were varied. The function minimized was $\sum w(|F_o| - (1/s)|F_c|)^2$, where the summation is over all the observed reflexions.

s = scaling factor

F_o = observed structure factor

F_c = calculated structure factor .

The weighting scheme was:

$$w = 1.0 \quad \text{if } |F_o| < 10$$

and

$$1/w = |F_o|/10 \quad \text{if } |F_o| \geq 10 .$$

The R index, $\sum ||F_o| - (1/s)|F_c|| / \sum |F_o|$, was 14.3% for the Cu $K\alpha$ data.

Next, three cycles of refinement were carried out with the temperature factors of five atoms in anisotropic form. (The number of parameters was limited by the size of the computer used.) The R value for Cu $K\alpha$ data dropped to 7.3%. A difference electron density section at this stage is shown in Fig. 4. The positions of the 5 hydrogen atoms are revealed; they all lie on the same plane with the other atoms.

The final refinement was carried out in several stages since not more than 30 parameters could be varied at a time. Besides the overall scale factor, the x and z coordinates of all the atoms and the anisotropic temperature factors of the non-hydrogen atoms were varied. The hydrogen atoms were assigned fixed isotropic temperature factors of 3.5 \AA^2 except H(5) which had $B=4.0 \text{ \AA}^2$. The terms β_{12} and β_{23} were kept equal to zero in accordance with the space group restrictions (Peterse & Palm, 1966).

In order to allow for the anomalous dispersion of the sulphur atom a hypothetical scatterer was superimposed over the 'normal' sulphur atom. This scatterer was assigned a constant scattering power of 0.3 elec-

trons for the Cu $K\alpha$ data and 0.1 electron for the Mo $K\alpha$ data. All other scattering factors used were those tabulated by Hanson, Herman, Lea & Skillman (1964).

Refinement was stopped when the changes in the parameters were less than the standard deviations of the parameters themselves. The positional parameters of H(5) kept oscillating slightly, however. The final R values were 4.9% for the Cu $K\alpha$ data and 5.5% for the Mo $K\alpha$ data.

Results

The final positional and vibrational parameters are shown in Tables 1 and 2, and the bond lengths and angles in Tables 3 and 4. An investigation of the Tables shows that the two sets of data yield essentially the same results. It is interesting to note, however, that the estimated standard deviations are smaller for the Mo $K\alpha$ data, where more than 200 extra reflexions were

Table 1. Fractional coordinates of the atoms

Standard deviations in the last digits are shown in parentheses.
 $y/b = \frac{1}{2}$ for all atoms.

	Cu $K\alpha$ data		Mo $K\alpha$ data	
	x/a	z/c	x/a	z/c
S	0.5169 (2)	0.6782 (2)	0.5171 (2)	0.6782 (2)
O(1)	0.8578 (5)	0.0747 (5)	0.8562 (4)	0.0739 (4)
O(2)	0.8011 (6)	0.3683 (5)	0.8008 (5)	0.3678 (5)
O(3)	0.1163 (5)	0.3060 (5)	0.1161 (4)	0.3065 (4)
N(1)	0.1212 (6)	0.7592 (6)	0.1220 (5)	0.7594 (5)
N(2)	0.3900 (7)	0.0146 (6)	0.3907 (5)	0.0153 (5)
N(3)	0.9234 (6)	0.2507 (5)	0.9238 (5)	0.2502 (4)
C	0.3250 (7)	0.8299 (6)	0.3245 (5)	0.8299 (5)
H(1)	0.310 (9)	0.113 (9)	0.314 (8)	0.106 (8)
H(2)	0.522 (10)	0.062 (8)	0.526 (9)	0.055 (7)
H(3)	0.089 (10)	0.630 (10)	0.083 (9)	0.639 (8)
H(4)	0.042 (10)	0.842 (9)	0.041 (9)	0.846 (8)
H(5)	0.441	0.549	0.452	0.572

Table 2. Vibration parameters (\AA^2) with the standard deviations in the last digits shown in parentheses

The temperature factor used was:

$$\exp[-2\pi^2(h^2a^*U_{11} + 2hka^*b^*U_{12} + \dots)]$$

Cu $K\alpha$ data	U_{11}	U_{22}	U_{33}	$2U_{13}$
	S	0.0426 (8)	0.0809 (13)	0.0439 (10)
O(1)	0.0408 (18)	0.0892 (29)	0.0391 (19)	0.0007 (15)
O(2)	0.0638 (26)	0.0942 (33)	0.0565 (24)	0.0305 (20)
O(3)	0.0353 (22)	0.1392 (44)	0.0509 (22)	0.0035 (18)
N(1)	0.0345 (22)	0.0637 (29)	0.0439 (24)	0.0024 (18)
N(2)	0.0353 (22)	0.0678 (31)	0.0417 (24)	0.0057 (18)
N(3)	0.0392 (24)	0.0527 (27)	0.0393 (24)	0.0055 (20)
C	0.0361 (26)	0.0407 (27)	0.0401 (27)	0.0062 (20)

Mo $K\alpha$ data	U_{11}	U_{22}	U_{33}	$2U_{13}$
	S	0.0412 (6)	0.0774 (8)	0.0442 (5)
O(1)	0.0361 (12)	0.0890 (22)	0.0437 (15)	0.0020 (11)
O(2)	0.0603 (18)	0.0934 (27)	0.0579 (17)	0.0296 (16)
O(3)	0.0347 (14)	0.1296 (33)	0.0507 (15)	0.0033 (11)
N(1)	0.0345 (14)	0.0577 (21)	0.0434 (15)	0.0033 (13)
N(2)	0.0339 (14)	0.0606 (21)	0.0429 (15)	0.0068 (11)
N(3)	0.0375 (14)	0.0487 (19)	0.0396 (15)	0.0066 (11)
C	0.0301 (14)	0.0359 (19)	0.0422 (17)	0.0079 (13)

recorded. This is in spite of the fact that the errors in the measurement of the Cu $K\alpha$ intensities were smaller; there was much less background associated with the Cu $K\alpha$ radiation and the count rate was appreciably higher.

Cruickshank's (1961) correction for rotational oscillation of molecules yielded values of between 0.01 and 0.02 \AA , which were applicable to the bond lengths of

Table 3. Bond distances (\AA)

Standard deviations of Mo $K\alpha$ data shown in parentheses.

	Cu $K\alpha$ data	Mo $K\alpha$ data
S—C	1.735	1.739 (4)
C—N(1)	1.321	1.312 (5)
C—N(2)	1.293	1.300 (5)
N(3)—O(1)	1.237	1.241 (4)
N(3)—O(2)	1.215	1.218 (4)
N(3)—O(3)	1.234	1.232 (4)
N(1)—H(3)	0.90	0.84 (6)
N(1)—H(4)	0.82	0.86 (6)
N(2)—H(1)	0.92	0.86 (6)
N(2)—H(2)	0.86	0.87 (6)
S—H(5)	0.96	0.79
N(1)—O(1)	2.965	2.970 (5)
N(2)—O(3)	2.874	2.877 (5)
H(5)—O(2)	2.82	2.78
H(5)—O(3)	2.61	2.48

Table 4. Bond angles ($^\circ$)

Standard deviations of Mo $K\alpha$ data shown in parentheses.

	Cu $K\alpha$ data	Mo $K\alpha$ data
S—C—N(1)	121.2	121.3 (3)
S—C—N(2)	117.3	116.9 (3)
O(1)—N(3)—O(3)	118.9	119.9 (3)
O(1)—N(3)—O(2)	121.0	120.3 (3)
C—N(1)—H(3)	116	120 (4)
C—N(2)—H(2)	122	118 (4)
C—N(1)—H(4)	114	114 (4)
C—N(2)—H(1)	128	127 (4)
C—S—H(5)	106	105

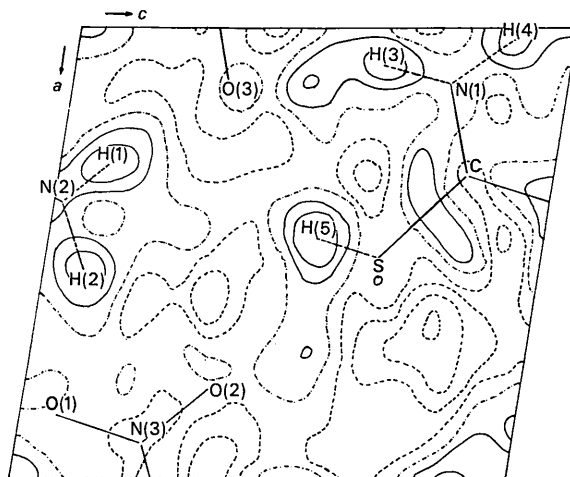


Fig. 4. Difference electron density section at $y/b = \frac{1}{2}$, showing positions of hydrogen atoms.

tallographic b axis; the inter-layer spacing is 3.2 \AA . Screw axes parallel to b relate molecules within adjacent layers.

Within the layers themselves, an extensive network of hydrogen bonds links thiourea and nitrate groups together (Fig. 5). The atoms N(1) and N(2) are in the trigonally hybridized state and form $\text{N-H}\cdots\text{O}$ bonds of lengths 2.97 and 2.88 \AA with O(1) and O(3) respectively. The other two hydrogen atoms attached to N(1) and N(2) form bifurcated hydrogen bonds with two other nitrate groups. These bonds are not equal in length, the $\text{N}\cdots\text{O}$ distances being 3.31 , 2.94 , 3.16 and 3.16 \AA . The fifth hydrogen atom also lies in the plane formed by the rest of the atoms. It is attached to the sulphur atom and lies approximately equidistant from two oxygen atoms. The line $\text{H}(5)\cdots\text{S}$ makes an angle of 105° with the C-S bond.

Theoretical considerations lead us to expect the S-C bond to be lengthened and the C-N bonds to be shortened when the S atom becomes protonated. Referring

to Table 5, we see that the S-C bond length in thiourea nitrate is indeed greater than that found in thiourea, but this difference is not large enough to be statistically significant.

The two C-N bond lengths in thiourea nitrate are not significantly different. Assuming an average C-N length of 1.306 \AA , we see that this value is significantly smaller than the 1.340 \AA determined for thiourea, with $\Delta/\sigma = 6.0$.

There is a large difference in the two S-C-N angles. A similar effect has been discovered in *s*-methylisothiurea sulphate by Stam (1962).

The values of the S-C and C-N bond lengths and the S-C-N bond angles determined for several thiourea derivatives are shown in Table 5.

The dimensions and symmetry of the nitrate anion have been discussed in several publications (Ferrari, Braibanti, Manotti-Lanfredi & Tiripicchio, 1967 and references quoted therein). The results for thiourea nitrate show no significant differences in the O-N-O

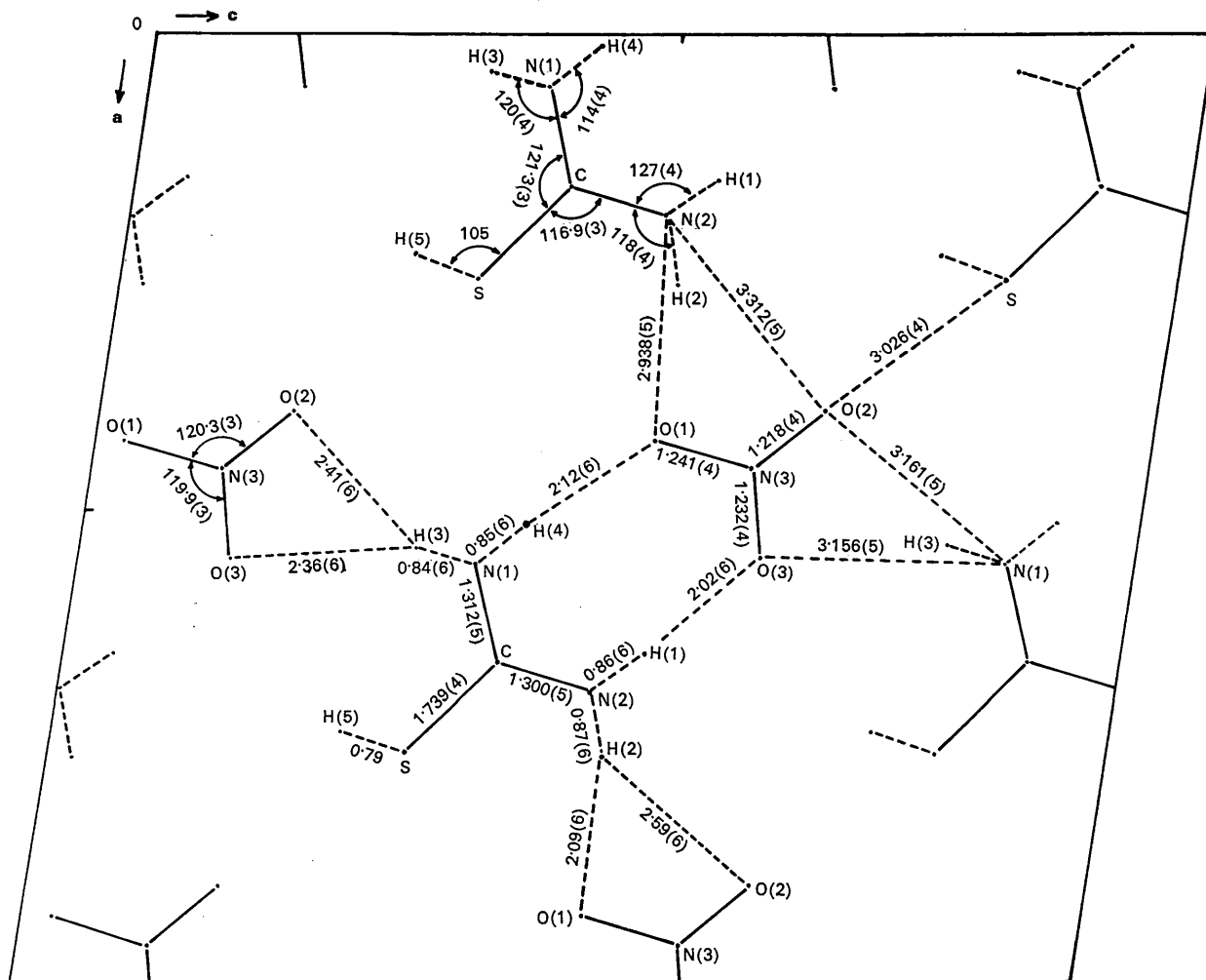


Fig. 5. Bond lengths and bond angles in thiourea nitrate

angles, but one of the N–O distances is significantly shorter than the other two. The effect of the N–H...O hydrogen bonds appears to be to 'stretch' the N(3)–O(1) and N(3)–O(3) bonds.

We wish to express our gratitude to Mrs R. Olthof-Hazekamp for preparing the input tape for the diffractometer.

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Die Kristallstruktur des α -KZnBr₃·2H₂O

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α -KZnBr₃·2H₂O crystallizes from aqueous solutions (mole proportion KBr:ZnBr₂=1.75:1), with unit-cell dimensions $a_0=6.71$, $b_0=12.42$, $c_0=13.02$ Å, $\beta=130,3^\circ$. Space-group $P2_1/c$ with $Z=4$. The structure was solved by Patterson and Fourier syntheses and by direct methods. By least-squares methods with anisotropic temperature factors the structure was refined to $R_1=5.1\%$. Zn is tetrahedrally coordinated by three bromine atoms and one water molecule.

Einleitung

Im Rahmen einer systematischen Untersuchung der Kristallstrukturen von Alkalihalogenozinkaten wurde die Struktur des α -KZnBr₃·2H₂O bestimmt.

In den bisher bekannten Strukturen der Alkalihalogenozinkate wird Zink jeweils tetraedrisch umgeben, wobei bislang nur isolierte Tetraeder bekannt geworden sind. In den Verbindungen vom Typ $A_2ZnCl_4 \cdot xH_2O$ (e.g. Jacobi & Brehler, 1968) wird Zn von vier Cl, im KZnCl₃·2H₂O (Brehler & Süsse, 1963) von drei Chlor und einem Wassermolekül umgeben. Zweck der vorliegenden Arbeit war es festzustellen, welche Koordination im α -KZnBr₃·2H₂O vorliegt.

Experimentelles

Aus wässrigen Lösungen mit einem Molverhältnis beider Komponenten von 1:1 entsteht bei Zimmertem-

peratur das β -KZnBr₃·2H₂O, das zuerst von Ephraim (1908) angegeben und dessen Struktur von Brehler & Holinski (1967) aufgeklärt worden ist. Bei einem Molverhältnis KBr:ZnBr₂ von 1,75:1 entsteht das α -KZnBr₃·2H₂O. Bei dieser Lösungszusammensetzung wurden ausserdem Kristalle der Zusammensetzung K₂ZnBr₄·H₂O und zwei Modifikationen des K₂ZnBr₄·2H₂O, von denen eine ebenfalls bei Ephraim (1908) aufgeführt ist, erhalten.

Das α -KZnBr₃·2H₂O bildet farblose nach [001] gestreckte langprismatische monokline Kristalle, die stets nach (100) verzwillingt sind. Aus Weissenbergaufnahmen solcher Kristallnadeln wurde das in Fig. 1 dargestellte reziproke Gitter erhalten. Durch Aufnahmen von Teilindividuen eines längs der Zwillingsenebene gespaltenen Kristalls konnte gezeigt werden, dass es sich dabei um eine Überlagerung von zwei um 180° gedrehten bzw. gespiegelten reziproken Einzelgittern handelt.