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Habit Modification in the System Rocksalt-Urea-Water

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The crystal structure of NaCl.Urea.H_2O ($a = 6{\cdot}50$, $b = 5{\cdot}24$, $c = 17{\cdot}55$ Å, $\beta = 90°\ 10'$, space group $I2$) has been determined in two projections. It is shown that habit modification of NaCl in the presence of urea may be explained by adsorption of units of NaCl.Urea.H_2O on (111) of NaCl. Likewise, habit modification of urea in aqueous solutions containing NaCl may be explained by temporary adsorption of NaCl.Urea.H_2O on (001) of urea. In the latter case (001) of urea and (001) of NaCl.Urea.H_2O are parallel, with [100] of urea parallel to [100] of NaCl.Urea.H_2O.

1. Introduction

The habit of a crystal is said to be modified by an 'impurity' when the presence of a (usually low) concentration of the impurity in the isotropic phase results in a habit that is different from the one observed in the absence of the impurity, without a noticeable incorporation of the latter in the modified crystal.

Habit modification of NaCl by urea in aqueous solutions is the oldest known example of this phenomenon (Romé de l'Isle, 1783). Bunn (1933) explains this and other similar cases by assuming a temporary adsorption of the impurity (in this case urea) on certain crystal faces during crystal growth. In this way deposition of particles of the host substance would be largely prevented by the impurity, and consequently the modified crystal would show predominantly those faces on which the impurity was selectively adsorbed. This selective adsorption is usually attributed to a geometric correspondence of two lattice dimensions in both crystals of the host substance and of the impurity. Bunn showed that the unit cells of urea and NaCl have several dimensions in common. Furthermore, three kinds of oriented overgrowths of urea on NaCl were obtained by him by evaporation of urea in vacuo on crystals of NaCl, indicating that the correspondence of the dimensions in question is sufficiently close to allow the adsorption to take place.

However, Seifert (1937) has already pointed out that the best correspondence of the lattice dimensions is that of [001] of urea and [001] of NaCl, which should favour the adsorption of urea on {001} of NaCl instead of on {111}! In his opinion NaCl.Urea.H_2O is the impurity rather than urea itself. This hypothesis could not be verified by Seifert, as no X-ray crystallographic data of the mixed compound were known at that time. We have determined the crystal structure of NaCl.Urea.H_2O by means of X-ray diffraction techniques, in order to test Seifert's hypothesis. Not only have we been able to confirm this hypothesis and explain the habit modification more in detail, but we have also found that the crystal structure of NaCl.Urea.H_2O affords the key to the habit modification of urea by NaCl in aqueous solutions. Here, Bunn found that {001} of urea develops instead of {111}. We thus arrive at similar conclusions to those reached by Rimsky (1960) in his simultaneous† investigation of the system NH_4Cl-Urea.

2. Determination of the crystal structure of NaCl.Urea.H_2O

Colourless, transparent crystals of NaCl.Urea.H_2O were obtained by slow evaporation of an equimolar solution of NaCl and urea. For a description of the morphology and crystal optics of the substance we refer to a paper by Kleber, von Stackelberg & Wallraf (1950). Our preliminary investigation yielded the following data, which are in accordance with those given by Kleber *et al.*

Lattice constants:
$a = 6{\cdot}50$ Å ($\pm 0{\cdot}05$), $b = 5{\cdot}24$ Å ($\pm 0{\cdot}05$),
$c = 17{\cdot}55$ Å ($\pm 0{\cdot}10$),; $\beta = 90°\ 10'$ ($\pm 3'$).
Cell volume: $V = 592$ Å^3.
Extinctions: Reflexions hkl with $h+k+l = 2n+1$ are systematically absent.
Density (exp.): 1·52.
Density (X-ray): 1·53.
Number of molecules per unit cell: 4.
Space group: $I2$.

The lattice constants were determined in a standard 2·87-cm radius Weissenberg camera, employing Cu $K\alpha$ radiation. Systematic absences were deduced from zero and first layer Weissenberg diagrams around the

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† Our results have been communicated by the senior author (C. H. MacG.) at one of the Fedorov Commemoration (1959) symposia.

two shortest axes. *I*2/*m* was eliminated as a possible space group when a piezo-electric effect was detected in a Giebe–Scheibe type circuit. From the two remaining possibilities, *I*2 and *Im*, the former was shown to be the correct one in the course of the structure determination.

In view of the fact that two of the axes in the structure are relatively short, and with no computing facilities available at the time, it was decided to solve the structure in two projections along the shortest axes.

In order to allow a correction of the X-ray intensities for specimen absorption of X-rays the crystals were originally cut out of a single crystal and subsequently shaped on a small lathe (cylindrical specimens being used). On careful examination of the zero-layer Weissenberg diagrams around the *b* axis it was discovered that the higher-order reflexions had a peculiarly split appearance. This phenomenon was traced to the formation of twin crystals as a result of the machining of the crystals on the lathe. It is only noticed on careful examination of the X-ray diagram, because the twin plane of the crystals is (100), and β is very nearly equal to 90°. These two facts cause the reflexions $h0l$ and $h0\bar{l}$ of the two individuals of the twinned crystal very nearly to coincide. Excellent diagrams, completely free from twin reflexions, could be obtained from specimens that were shaped by etching with a small wet brush.

In order to collect as large a number of intensities as possible, diagrams of the zero layer around the *a* and *b* axes were made with Mo *K* as well as Cu $K\alpha$ radiation. The latter exposures yielded integrated intensities of the reflexions of lower order, while the Mo *K* diagrams were made with the integrating mechanism of the camera switched off, in order to yield the weak high-order reflexions. The multiple-film technique was used, the film holder being loaded with three films. All intensities were corrected for the Lorentz and polarization factor and for specimen absorption. The integrated films were measured on a photometer, while the intensities on the Mo *K* diagrams were visually estimated by comparison with a calibrated scale.

Two-dimensional Patterson syntheses were calculated from the $h0l$ data and from the $0kl$ data.

Table 1. *Atomic positions and temperature factors in* NaCl.Urea.H_2O

Atom	x	y	z	B
Cl^-	0·994	0·000	0·117	$\beta_{11}=0{\cdot}0113$ $\beta_{22}=0{\cdot}0167$ $\beta_{33}=0{\cdot}0113$ $\beta_{12}=\beta_{23}=\beta_{13}=0$
Na^+	0·256	0·234	0·000	1·50
H_2O_I	0·000	0·527	0·000	1·50
H_2O_{II}	0·500	0·886	0·000	1·50
H_2O	0·003	0·943	0·411	1·50
C	0·992	0·928	0·338	1·50
N_I	0·863	0·775	0·308	2·85
N_{II}	0·114	0·040	0·296	2·85

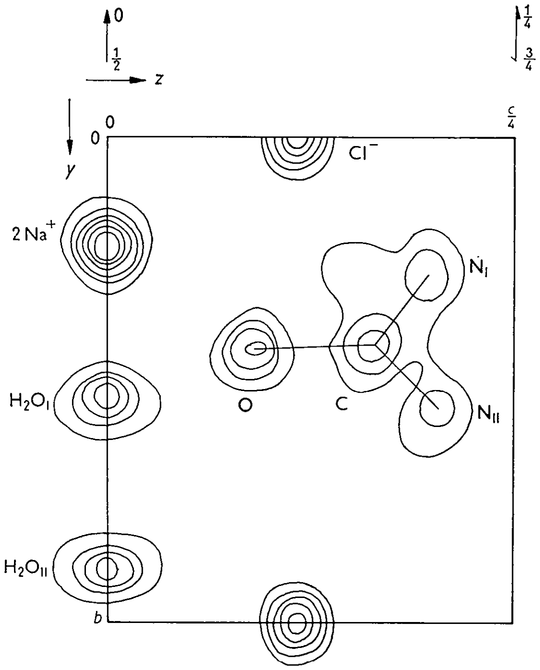

Fig. 1. Final electron-density projection along [100] for NaCl.Urea.H_2O.

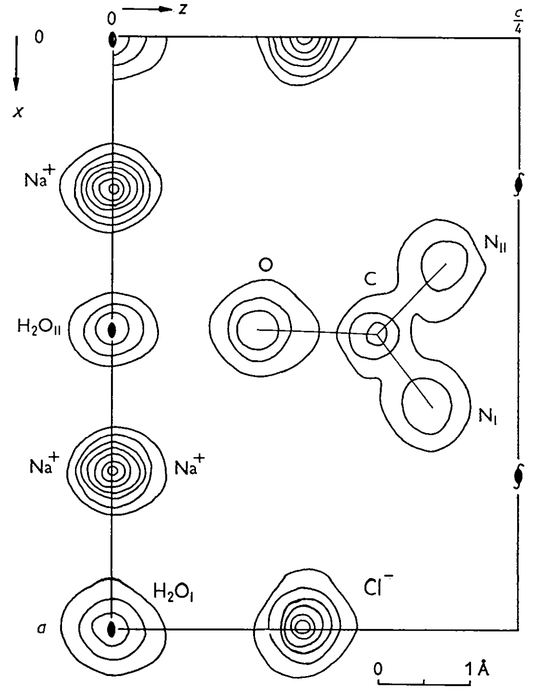

Fig. 2. Final electron-density projection along [010] for NaCl.Urea.H_2O.

These Patterson syntheses could be solved for the atomic positions of nearly all atoms.

These crude atomic positions were further refined by means of successive calculations of structure factors and difference syntheses. Individual isotropic temperature factors were introduced for the different atoms, and an anisotropic temperature factor for Cl^-. In the final stages of the refinement the observed structure factors were corrected for extinction effects, a procedure described by Jellinek (1958) being used.

Final values of the R-index amount to 0·138 for the reflexions $h0l$, and 0·145 for the reflexions $0kl$. Figs. 1 and 2 show the final electron-density maps of the two projections, Table 1 the corresponding atomic positions. For further details of the structure determination, see Palm (1961).

3. Discussion of the crystal structure of NaCl.Urea.H_2O

Figs. 3 and 4 show the crystal structure projected along the b and a axes, respectively. Fig. 3 shows that, although the true symmetry of this projection is that of the plane group $p2$, a very pronounced

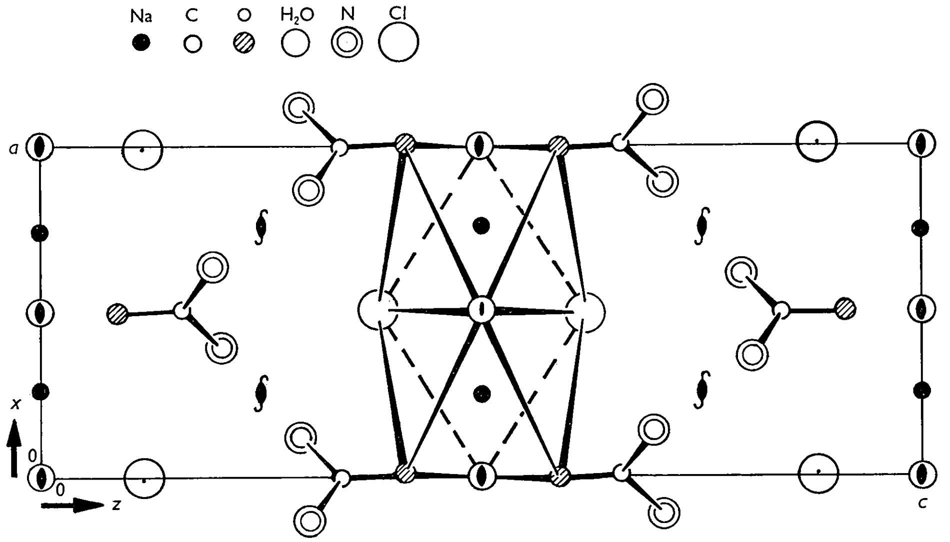

Fig. 3. The crystal structure of NaCl.Urea.H_2O, b-axis projection.

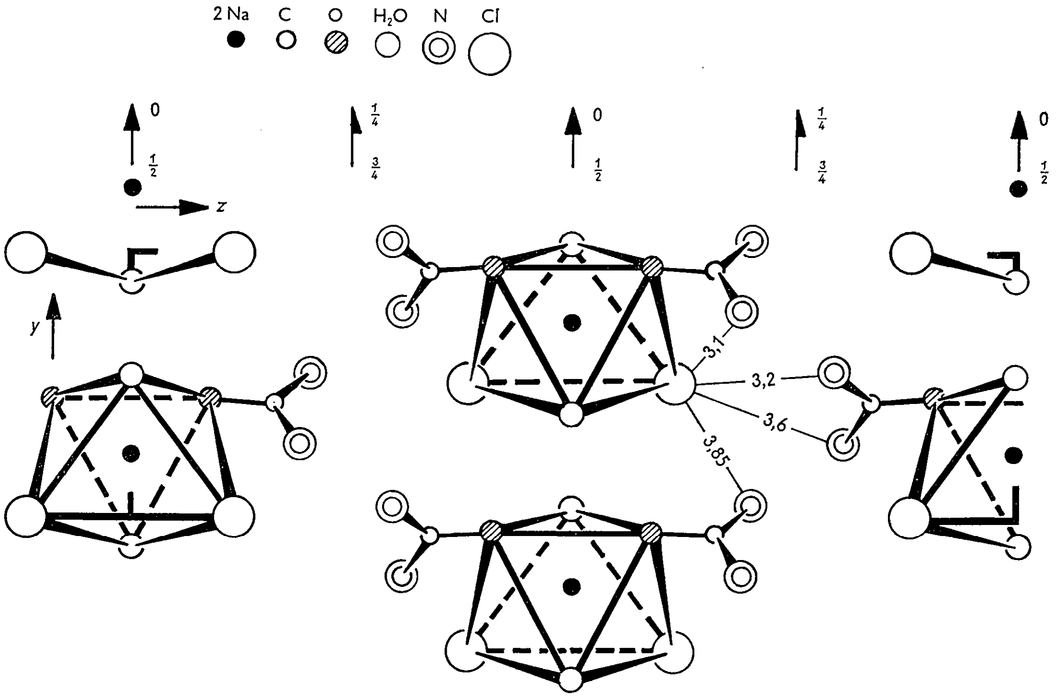

Fig. 4. The crystal structure of NaCl.Urea.H_2O, a-axis projection.

pseudosymmetry *cmm* is exhibited by this projection of the structure. Cl^-, O, and C have very small x coordinates, while z_{N_I} is nearly equal to $z_{N_{II}}$, with $x_{N_I} \simeq -x_{N_{II}}$, while $z_{Na^+}=0$ though symmetry does not demand it.

The structure can be described as follows: Na^+ ions are octahedrally coordinated by $2Cl^-$, $2H_2O$ and 2 oxygen atoms belonging to two molecules of urea. The twofold axes of the latter molecules coincide nearly, but not quite, with the direction of the c axis. The b-axis projection (Fig. 3) presents a view of these octahedra around Na^+ exactly along two opposite faces. The first of these faces, namely the one in the plane $x=0$, is formed by H_2O_{II} and the two carbonyl oxygen atoms; the other (in the plane $x=\frac{1}{2}$) consists of H_2O_I and the two Cl^- ions. This configuration is repeated by the twofold symmetry axes of the structure, so as to form an infinite chain of octahedrally coordinated Na^+ ions, which share opposite faces of their coordination octahedra with two adjoining Na^+ ions.

The a-axis projection (Fig. 4) shows the octahedral coordination of the central Na^+ ion more clearly, namely in a projection on a plane parallel to the faces shared by the octahedra. The two Na^+ ions at $z=0$, and likewise those at $z=\frac{1}{2}$, are projected as one, because $z_{Na^+}=0$. A consideration of the packing of the octahedra in the y direction shows that chains of 'occupied' (*i.e.* by Na^+) and 'vacant' octahedra alternate in that direction.

In the z direction two-dimensional, infinite networks of octahedra at $z=0$ are alternated by identical networks at $z=\frac{1}{2}$, which are the consequence of the presence of the I-lattice. The packing of the networks is such, that NH_2–Cl^- contacts occur, the shortest N–Cl^- distances between subsequent networks being 3·22 Å. The length of these distances does not exclude the possibility of hydrogen bond formation. The length of such bonds is known to vary between 3·05 and 3·3 Å. Regardless of whether or not a hydrogen bond is formed, however, it can be assumed that an attraction takes place between the negative Cl^- ions and the NH_2 groups, which are the positive side of the urea molecule, known to be a very strong permanent dipole.

A second, very short, N–Cl^- distance occurs between a urea molecule and a Cl^- ion in the same coordination octahedron, this distance being 3·05 Å. It indicates a relatively strong hydrogen bond.

It is interesting to compare the structures of $NaCl.Urea.H_2O$ and $NH_4Cl.Urea$ (Rimsky, 1960). Of course, there are very great differences between the two structures as to composition, space group, and lattice constants. However, there are some interesting resemblances too. Both structures have one long axis: $c_{NaCl.Urea.H_2O}=17·55$ Å, $b_{NH_4Cl.Urea}=17·08$ Å. Perpendicular to these long axes two sections can be distinguished in which the cations are located. The cations are coordinated by two oxygen atoms of urea molecules and by $2Cl^-$. And in both structures the twofold axis of the urea molecules coincides with the direction of the long axis, the urea molecules having NH_2–Cl^- contacts with Cl^- ions that are situated on the twofold axis of urea. (We neglect the very small deviations from the higher symmetry in $NaCl.Urea.H_2O$.) The presence of H_2O in $NaCl.Urea.H_2O$ serves to complete the octahedral coordination of Na^+, while in $NH_4Cl.Urea$ a tetrahedral coordination suffices for NH_4^+. We will elaborate on the similarity of the positions of Cl^- and urea in both structures in the discussion of habit modification of urea by NaCl.

4. Habit modification of NaCl by $NaCl.Urea.H_2O$

Crystals of NaCl with octahedral faces may be obtained from aqueous solutions containing a urea concentration of 0·2–0·5 times the NaCl concentration. It has been mentioned that Bunn's evidence in favour of the hypothesis that adsorption of urea on {111} is the cause of retarded growth of {111} is not very strong. Actually Seifert's hypothesis, assuming the presence of $NaCl.Urea.H_2O$ adsorbed on {111} of NaCl is much more plausible, because the relatively large concentration of urea required for habit modification would suggest the presence of the 1:1 compound.

On purely lattice-geometrical grounds, however, the preferential adsorption of $NaCl.Urea.H_2O$ does not seem to be likely. The (111) plane of NaCl can be described as a net of equilateral triangles with edges 3·98 Å. One may also select a rectangular centered unit area with edges 3·98 Å and 6·90 Å. The only correspondence of the lattice translations of $NaCl.Urea.H_2O$ and (111) of NaCl is that between [11$\bar{2}$] in NaCl (6·90 Å) and the a axis of $NaCl.Urea.H_2O$ (6·50 Å), the discrepancy between the two periods being 5·8%. A uniform cover of (111) of NaCl by the mixed compound therefore seems unlikely. A closer inspection of the two crystal structures shows, however, that there is a correspondence of (111) in NaCl and the asymmetric unit of the crystal structure of $NaCl.Urea.H_2O$. The distance Cl^-–Cl^- in the latter compound is 4·07 Å, very nearly along the c axis. The distance between two Cl^- ions in NaCl, along [110], is 3·98 Å, a good agreement. In directions perpendicular to these two, the disagreement between [11$\bar{2}$] of NaCl and [100] of $NaCl.Urea.H_2O$ is 5·8%, as we mentioned before. Therefore adsorption of $NaCl.Urea.H_2O$ on (111) of NaCl in a fashion as depicted in Fig. 5 seems quite likely. At left a schematic lattice plane (111) of NaCl is drawn, with the familiar stacking *ABCABC*... of successive close-packed layers of Na^+ and Cl^- indicated. If the solution contains enough urea to give rise to habit modification of a growing NaCl crystal one may envisage the following course of events: two Cl^- ions will be deposited in their proper sites on top of a layer of Na^+ ions, *i.e.* 3·98 Å apart. It is not unreasonable to assume that the Na^+ ions of the surface are solvated; then two molecules of H_2O will be present on lattice

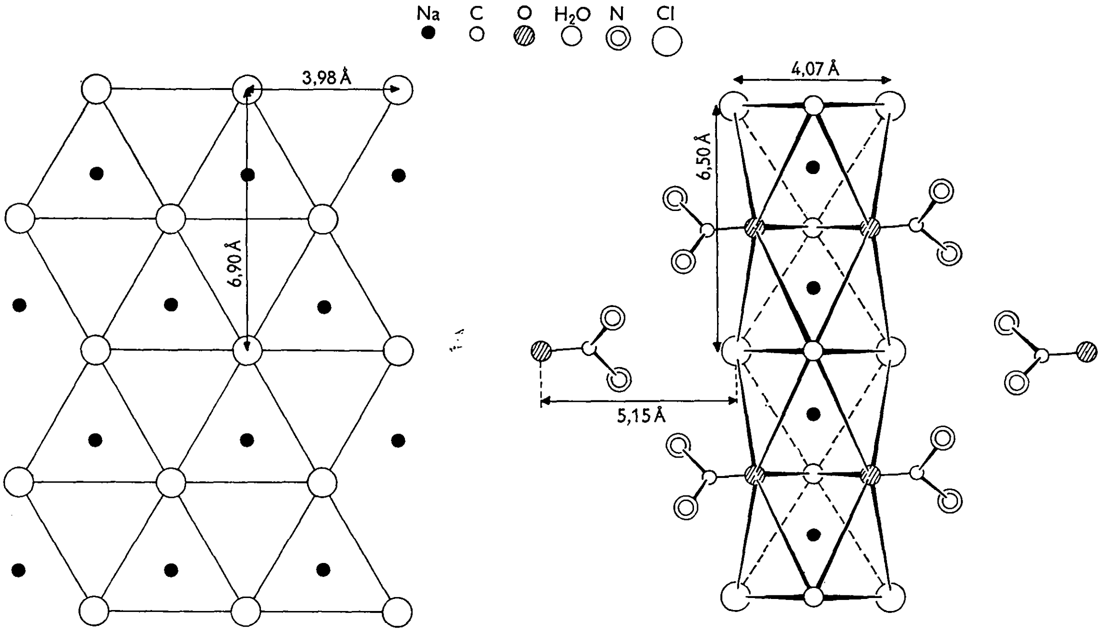

Fig. 5. Comparison of the crystal structures of NaCl (at left, projected along [111]) and NaCl.Urea.H_2O (at right, *b*-axis projection).

points at 3·98 Å from each of the two Cl^-. This configuration of two Cl^- and two H_2O on the surface of the NaCl crystal also occurs in NaCl.Urea.H_2O (*vide* the two dashed triangles in Fig. 3). In NaCl, the layer of ions following on the one consisting of two Cl^- and two H_2O would consist entirely of Na^+ ions occupying the vacant triangles of Fig. 5. However, in NaCl.Urea.H_2O the *adjacent* dashed triangles of Fig. 5 (at right) are all occupied by a Na^+ ion. So, if growth of NaCl is to proceed in the fashion of NaCl.Urea.H_2O, only one half of the Na^+ ions is in its correct cubic close-packed position, while the other half occupies an incorrect hexagonal close-packed position. The coordination of all Na^+ ions is completed by H_2O and urea as indicated in the fully drawn triangles of Fig. 5 (at right). The reason for the — at least temporary — stability of the NaCl.Urea.H_2O structure on (111) of NaCl may be found in the *a*-axis projection (Fig. 4). It may be seen that the Na^+ ions are sandwiched (in the direction of the *b* axis) between layers of $2\,Cl^- + H_2O_{II}$ and $2\,O + H_2O_I$. These two layers are being held together by the electrostatic attraction of the Na^+ ion, but also by a hydrogen bond between urea and Cl^-, the distance between Cl^- and N being very short: 3·05 Å.

The adsorption of NaCl.Urea.H_2O on (111) of NaCl must be envisaged as temporary because some Na^+ ions are situated in unstable 'hexagonal' positions with respect to the NaCl structure. It is conceivable that the tendency of an Na^+ ion to leave its 'hexagonal' site is approximately equal to the free energy required to break up the stabilizing octahedra. Then a suitable local fluctuation of energy might suffice to cause desorption of NaCl.Urea.H_2O.

5. Habit modification of urea by NaCl.Urea.H_2O

Bunn (1933) mentions that urea is bounded by {001} rather than {111} when it is crystallized from an aqueous solution containing NaCl. It is obvious that in this case NaCl.Urea.H_2O is the impurity, as no habit modification is obtained on crystallization from alcoholic solutions containing NaCl.

We will now explain this case of habit modification in terms of the crystal structures of urea and NaCl.Urea.H_2O. The crystal structure of urea has been determined in considerable detail by Vaughan & Donohue (1952) and Worsham, Levy & Peterson (1956). Urea crystallizes in the space group $P\bar{4}2_1m$ with lattice constants $a = 5{\cdot}670$ and $c = 4{\cdot}726$ Å. The only lattice plane in NaCl.Urea.H_2O showing dimensions comparable to the affected plane (001) in urea is (001):

$$a_{\text{urea}} = 5{\cdot}67\ \text{Å} \qquad a_{\text{NaCl}\cdot\text{Urea}\cdot\text{H}_2\text{O}} = 6{\cdot}50\ \text{Å}$$
$$b_{\text{urea}} = 5{\cdot}67\ \text{Å} \qquad b_{\text{NaCl}\cdot\text{Urea}\cdot\text{H}_2\text{O}} = 5{\cdot}24\ \text{Å}$$

The discrepancy between the lengths of the *a* axes is 14·6%, while the *b* axes differ by 7·6%. (Discrepancy is defined as the difference of the periods, expressed as a percentage of the period in the affected plane.)

Despite the fairly large discrepancy in lattice dimensions, adsorption of NaCl.Urea.H_2O on (001) of urea seems quite plausible on the basis of the considerable degree of structural similarity of both compounds: Fig. 6 illustrates this similarity: at the left a projection of the crystal structure of urea along [100] is shown, while at the right part of the *b*-axis projection of NaCl.Urea.H_2O is given. It is evident that the configuration of urea in both structures is

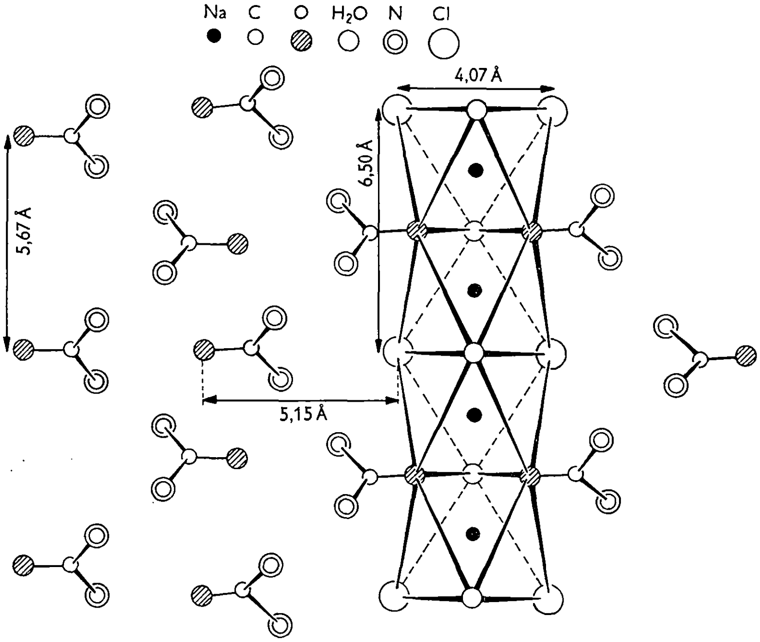

Fig. 6. Comparison of the crystal structures of urea (at left) and NaCl.Urea.H_2O, both projected along their *b* axes.

quite similar, as mentioned in section 3. In urea the individual molecules are interconnected by a network of hydrogen bonds N–H · · · O. In the direction of c_{urea} (horizontally in Fig. 6) the molecules exhibit a head-to-tail configuration in which a hydrogen bond from each of the two NH_2 groups of a molecule terminates on the oxygen atom of the next. The second H atom of each of the NH_2 groups forms a hydrogen bond with another molecule in the direction [110]. Fig. 6 shows that after attachment of urea molecules to their normal positions (*i.e.* $x_C = x_O = 0{\cdot}000$) on (001) of urea, cavities remain at $x = \frac{1}{2}$, $y = \frac{1}{2}$, in which normally the oxygen atom of the next urea molecule is accommodated. However, when NaCl is present, the cavity can be occupied by a Cl^- ion. This very configuration is present in NaCl.Urea.H_2O! Therefore further growth may proceed as in NaCl.Urea.H_2O, as shown in Fig. 6. In this way (001) of urea (and only this plane) may become temporarily inaccessible to other molecules of urea in solution, and retarded growth of (001) takes place, with a modified habit as a result. In view of the fairly large discrepancy of the lattice constants in the structures of urea and the mixed compound it does not seem very probable that (001) of urea is covered by a continuous layer of NaCl.Urea.H_2O. One must rather think in terms of Bunn's 'isolated particles here and there' or in this case 'isolated Na^+ ions with their coordination octahedra'.

In this way we arrive at the same transition configuration between urea and NaCl.Urea.H_2O as was postulated by Rimsky (1960) for the transition layer between urea and NH_4Cl.Urea, because the configuration of Cl^- and urea in the two mixed compounds show a great similarity.

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