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Rock salt–urea–water (1/1/1) at 293 and 117 K

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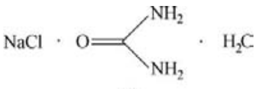
The crystal structure of $NaCl \cdot CH_4N_2O \cdot H_2O$ has been determined at 117 K and redetermined at room temperature. It can be described as consisting of alternating 'organic' and 'inorganic' planar layers. While at room temperature the structure belongs to the space group *I*2, the low-temperature structure belongs to the space group $Pn2_1m$. All water O atoms are located on positions with crystallographic symmetry 2 (*m*) in the room-temperature (low-temperature) structure, which means that the water molecules belong, in both cases, to point group *mm*2. During the phase transition, half of the urea molecules per unit cell perform a 90° rotation about their respective C—O axes. The other half and the inorganic parts of the structure remain unaltered. The relationship between the two phases is remarkable, inasmuch as no obvious reason for the transition to occur could be found; the internal structures of all components of the two phases remain unaltered and even the interactions between the different parts seem to be the same before and after the transition (at least when looked at from an energetic point of view).

Comment

In the Georg-Kerschensteiner-Gymnasium Müllheim there is a 30 year tradition of growing crystals by pupils (Georg-Kerschensteiner-Gymnasium Müllheim, 2008). In searching for more crystal growth experiments performable by grammar school students – and being aware of the existence of rock salt–glucose–water (1/2/1) crystals (Ferguson *et al.*, 1991) – we have tried to grow crystals from aqueous solutions containing rock salt and urea. The growth experiments led to large single-crystal plates, the structure of which we determined at ambient temperature and at 117 K. Structure analysis showed the crystals to be composed of rock salt, urea and water in the molar ratio 1:1:1. Actually, crystals of $NaCl \cdot CH_4N_2O \cdot H_2O$, (I), have been known for a long time (see Kleber *et al.*, 1950); their three-dimensional structure under ambient conditions was determined by Palm & MacGillavry (1963) from two Weissenberg zero-level photographs. Our own X-ray experiments confirm and refine the results of Palm & MacGillavry (1963) but show that the structure at 117 K is different from that at room temperature.



$NaCl \cdot O{=}C(NH_2)_2 \cdot H_2C$

(I)

While, in principle, our room-temperature structure of (I) is equivalent to the *I*2 structure described by Palm & MacGillavry (1963), there are, not surprisingly, some differences in detail. For example, the short Cl—N distance of 3.05 Å mentioned by Palm & MacGillavry (1963) is replaced by the more reasonable distance of 3.351 (2) Å in our investigation. Furthermore, the quality of our data allowed us to localize all H atoms in the difference Fourier maps (but see *Experimental*) and to determine the correct absolute configuration.

Palm & MacGillavry (1963) have already described the structure and its relationship to the structures of urea and NaCl. In addition to their view, we can picture the structure (Fig. 1*a*) as a stacking of toothed alternating 'inorganic' and 'organic' (001) layers (Fig. 2). The former consist of Na^+ ions, Cl^- ions and H_2O molecules, forming infinite $–Na(\mu_2\text{-}OH_2)\text{-}Na([\mu_2\text{-}Cl]_2,\mu_2\text{-}OH_2)Na–$ chains parallel to [100] with vicinal

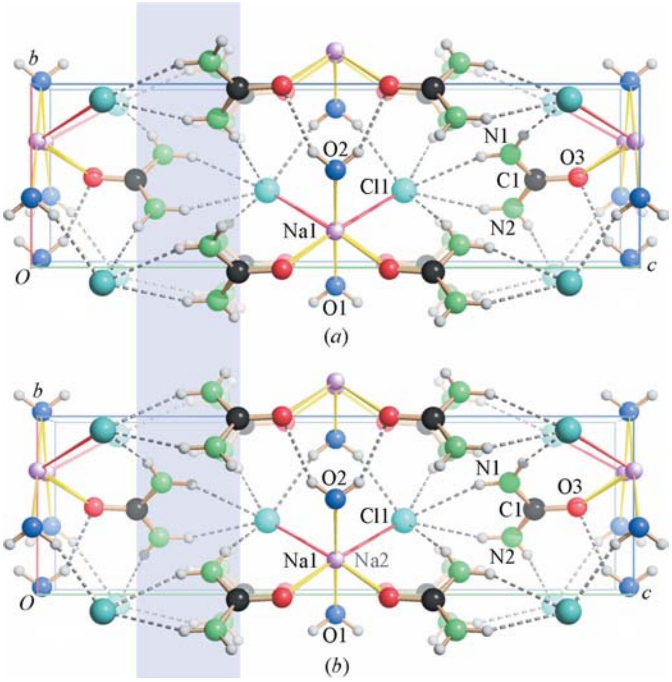


Figure 1
(*a*) The room-temperature *I*2 and (*b*) the low-temperature $Pn2_1m$ structure of (I) (view parallel to [100]). All *x* values of corresponding atoms differ by approximately 0.25 (before and after the transition, see Fig. 4). The two structures differ significantly only in the shaded range (location of one-half of the amide groups). In (*b*), atom Na2 is positioned exactly behind Na1.

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chains connected by O—H···Cl hydrogen bonds (Fig. 3). The Cl atoms form the 'teeth' of these layers. The organic layers simply contain the urea molecules, with the O3 atoms acting as 'teeth'. The interface between the two different layers is stabilized by Na—O3 bonds, by four different N—H···Cl hydrogen bonds and by O—H···O hydrogen bonds. As already mentioned by Palm & MacGillavry (1963), the Na^+ ions are octahedrally coordinated by two Cl^- ions, two water O atoms and two carbonyl O atoms (Tables 1 and 3). The Cl^- ions are twofold coordinated by two Na^+ ions in a nonlinear manner. If hydrogen bonds to Cl atoms (Tables 2 and 4) are included, an irregular sevenfold coordination results.

Within one organic layer, the orientation of the planar urea molecules alternates in the $\langle 110 \rangle$ directions by a form of local $\bar{4}$ operation, *i.e.* one molecule is transformed into the vicinal one (approximately) by mirroring at, for example, $(x, y, \frac{3}{4})$ and a subsequent rotation by 90° about a [001] axis roughly located at $(0, \frac{1}{2}, z)$ or $(\frac{1}{2}, 0, z)$. When going from one organic layer to the vicinal one in the [001] direction, there is a similar relation between two vicinal urea molecules. Here, the mirror plane is, for example, $(x, y, \frac{1}{2})$ and the rotation axis is defined by the (approximately) coinciding axes of the two carbonyl groups [close to $(0, 0, z)$ or $(\frac{1}{2}, \frac{1}{2}, z)$].

The 117 K $Pn2_1m$ structure of (I) (Fig. 1*b*) differs from the room-temperature *I*2 structure exclusively by the fact that this latter operation (and only this one) is replaced by a real mirror *m*, *i.e.* the rotation by 90° about the [001] axis drops out. This means that, in the transition from room temperature to 117 K, the inorganic layers and one of the two organic layers remain essentially the same, while in the second organic layer, all urea molecules perform a synchronized 90° flip about a [001] axis defined (approximately) by their respective carbonyl groups. While a superposition of the projections of the two structures parallel to [100] hardly shows any positional differences, small but significant differences can be seen in the second organic layers when viewed parallel to the [010] direction (Fig. 4).

The coordination polyhedra of the Na and of two of the four Cl atoms remain unaltered by the transition. For the other two Cl atoms, the absolute configuration of the coordination polyhedron (including H atoms) changes; furthermore, two of the H atoms (H11 and H21) that are 'donated' to a given Cl atom belong to two different urea molecules after the transition compared with the situation before the transition (which obviously is reversible, see *Experimental*). Thus, hydrogen bonds are broken and reformed.

There is no group–subgroup relation between the two space groups *I*2 (room temperature) and $Pn2_1m$ (117 K), the multiplicity of the general position being 4 in both cases. Instead, the relationship between the two structures is reflected in the fact that both space groups are maximal non-isomorphic subgroups to *Im*2*m*. As the different components of the structure do not change significantly during the transi-

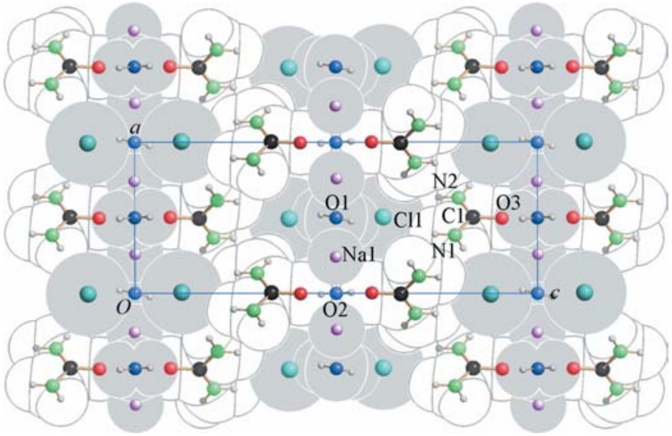

Figure 2
A ball-and-stick model superimposed on a space-filling model of the room-temperature structure of (I), as seen parallel to $[0\bar{1}0]$. In the space-filling model, the atoms of the inorganic layers have been shaded grey.

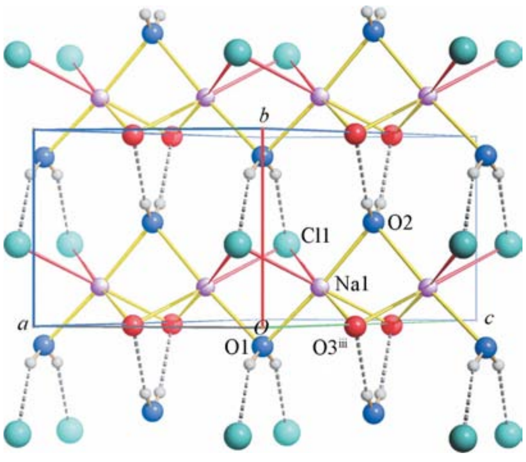

Figure 3
An inorganic layer of (I), as seen parallel to [101], with O3 atoms and O—H···O hydrogen bonds added.

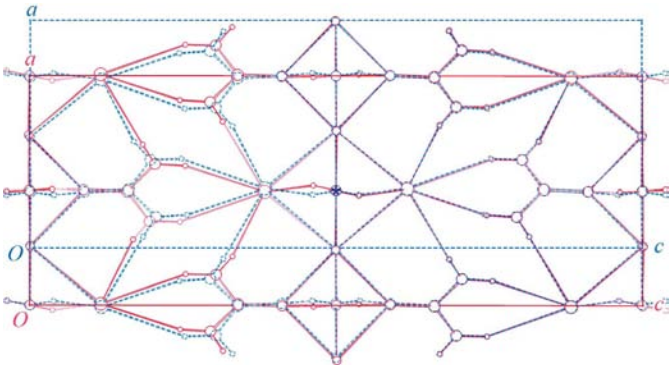

Figure 4
A superimposition of the room-temperature structure (solid lines) and the low-temperature structure (dashed lines) of (I), as seen parallel to $[0\bar{1}0]$. After aligning both *a* vectors vertically, prior to superimposition, the room-temperature structure has been rotated by 0.076° counter-clockwise to account for the difference of 0.152° between the monoclinic angle and 90°. The point of coincidence in the center is marked by a ⋆ symbol.

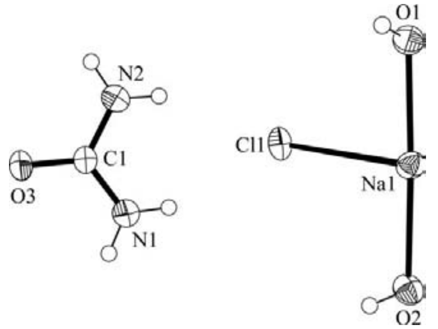

Figure 5
The molecular structure of (I) at room temperature. Displacement ellipsoids are shown at the 50% probability level.

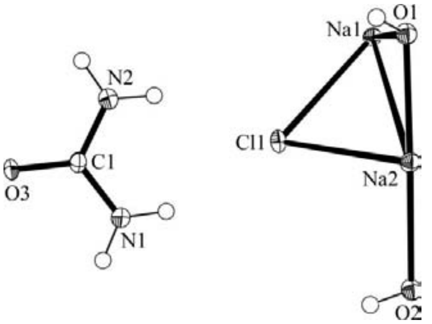

Figure 6
The molecular structure of (I) at 117 K. Displacement ellipsoids are shown at the 50% probability level.

tion and as even the interactions between these different parts seem to be unaffected in principle (at least when seen from an energetic point of view), we could find no obvious reason for the transition to occur.

Another question is how easily alkali halides, purely organic molecules and water form crystalline structures as a ‘joint venture’ as in (I). As an answer to this, a search in the 2008 release of the Cambridge Structural Database (CSD; Allen, 2002) yielded some 50 structures fulfilling this condition. However, we found only nine structures [including (I)] with a 1:1:1 composition (Table 5). In most of these, the alkali ion is ‘captured’ (*i.e.* multiply coordinated) by a cyclic part of the organic molecule. Only two structures [CSD refcodes CMHTRB (Fodor *et al.*, 1971) and KESGUL (Fan *et al.*, 2007)] do not show this feature and are as such comparable to (I). In contrast to the latter, in KESGUL the inorganic part consists of isolated NaI ‘molecules’ and isolated water molecules. Details of the CMHTRB structure are not available. Finally, it should be noted that thiourea (NH_2CSNH_2) forms structures with Cs*X* (*X* = F and Cl) and water, but the compositions are 1:4:2 and 1:4:1 in these cases (Boeyens, 1968*a*,*b*).

Experimental

Urea (40.0 g, 0.666 mol), NaCl (15.5 g, 0.265 mol) and water (40 ml) were stirred at 303 K with a magnetic stirrer until a clear solution had formed. After slow evaporation of the water at 285 K (in a refrigerator), large crystal plates formed. The experiment was repeated. The separated solution was cooled to room temperature. A seed crystal cut from one of the crystal plates obtained in the previous experiment was added and the solution was placed in a refrigerator. Large crystal plates formed comparatively rapidly in the solution. The solution was removed and the plates were dried with paper. Two small roughly isometric fragments were cut from the large crystal plates and measured in sealed capillaries. The first fragment (crystal 1) was measured first at 117 K and then at room temperature. The second fragment (crystal 2) was measured first at room temperature and then at 117 K.

Compound (I) at 293 K

Crystal data

$NaCl\cdot CH_4N_2O\cdot H_2O$
M_r = 136.52
Monoclinic, *I*2
a = 6.4845 (2) Å
b = 5.2362 (2) Å
c = 17.3497 (5) Å
β = 90.152 (2)°
V = 589.09 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.62 mm^{-1}
T = 293 K
0.4 × 0.4 × 0.4 mm

Data collection

Bruker SMART CCD area-detector diffractometer
7728 measured reflections
1752 independent reflections
1728 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.085
S = 1.25
1752 reflections
71 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.36 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 783 Friedel pairs
Flack parameter: 0.00 (7)

Table 1
Selected interatomic distances (Å) for (I) at 293 K.

Cl1—Na1$^{\rm i}$	2.8516 (8)	Na1—O3$^{\rm iii}$	2.4251 (15)
Cl1—Na1	2.9130 (8)	Na1—O3$^{\rm iv}$	2.4281 (15)
Na1—Na1$^{\rm ii}$	3.1237 (12)	O3—C1	1.252 (2)
Na1—Na1$^{\rm i}$	3.3612 (12)	N1—C1	1.323 (2)
Na1—O1	2.3430 (13)	N2—C1	1.341 (2)
Na1—O2	2.3732 (15)		

Symmetry codes: (i) $-x+1, y, -z+1$; (ii) $-x, y, -z+1$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °) for (I) at 293 K.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H12···Cl1	0.86	2.56	3.3671 (19)	157
N1—H11···Cl1$^{\rm v}$	0.86	2.52	3.3512 (19)	163
N2—H22···Cl1	0.86	2.60	3.397 (2)	155
N2—H21···Cl1$^{\rm vi}$	0.86	2.58	3.4242 (19)	168
O1—H1···Cl1$^{\rm vii}$	0.819 (15)	2.38 (2)	3.1559 (14)	159 (2)
O2—H2···O3$^{\rm v}$	0.825 (16)	2.08 (2)	2.846 (2)	154 (2)

Symmetry codes: (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (vi) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (vii) $x, y-1, z$.

Compound (I) at 117 K

Crystal data

$NaCl\cdot CH_4N_2O\cdot H_2O$
$M_r = 136.52$
Orthorhombic, $Pn2_1m$
$a = 6.4374$ (2) Å
$b = 5.1744$ (2) Å
$c = 17.2998$ (5) Å
$V = 576.25$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.63$ mm^{-1}
$T = 117$ K
0.3 × 0.3 × 0.3 mm

Data collection

Bruker SMART CCD area-detector diffractometer
15591 measured reflections
2688 independent reflections
2022 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.079$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.086$
$S = 0.95$
2688 reflections
76 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.66$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Absolute structure: Flack (1983), 1109 Friedel pairs
Flack parameter: −0.02 (6)

After solution and/or refinement, the two room-temperature (and the two low-temperature) structures turned out to be essentially the same. The two structures yielding the best reliability factors (the room-temperature structure of crystal 1 and the low-temperature structure of crystal 2) are referred to in the tables and figures. Displacement ellipsoid plots for the two structures are shown in Figs. 5 and 6. All H atoms were located in difference maps, but free refinement did not lead to positions of sufficient quality. Therefore, in both structures, the H atoms bonded to N atoms were treated as riding atoms, with N—H distances of 0.86 Å (0.88 Å) in the room-temperature (low-temperature) structure and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(N). O—H distance restraints of 0.82 Å (0.84 Å) in the room-temperature (low-temperature) structure and H···H distance restraints of 1.30 Å (1.33 Å), with $U_{\rm iso}$(H) values of $1.5U_{\rm eq}$(O) [$2U_{\rm eq}$(O)], were applied to the water molecules. The correct absolute configuration for the room-temperature structure and the correct orientation of the low-temperature structure with respect to the polar-axis direction were established by means of the Flack (1983) parameters, although these have no chemical significance.

For both structures, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SCHAKAL99* (Keller, 2004) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

We thank Mr H. P. Winkler for technical assistance in preparing the crystal fragments to be measured for structure analysis. The experimental contributions of the pupils F. Fuchs, T. Sichler and H. Bilgic performed within the scope of the SOKRATES–COMENIUS project 2006/2007 (Georg-Kerschensteiner-Gymnasium Müllheim, 2008) are gratefully acknowledged.

Table 3
Selected interatomic distances (Å) for (I) at 117 K.

Cl1—Na1	2.8481 (7)	Na2—O1	2.3223 (16)
Cl1—Na2	2.8845 (7)	Na2—O2	2.3411 (17)
Na1—Na2$^{\rm i}$	3.0842 (11)	Na2—O3$^{\rm iii}$	2.4131 (12)
Na1—Na2	3.3534 (11)	O3—C1	1.2577 (17)
Na1—O1	2.3392 (16)	N1—C1	1.336 (2)
Na1—O2$^{\rm i}$	2.3674 (17)	N2—C1	1.334 (2)
Na1—O3$^{\rm ii}$	2.4066 (12)		

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, y-\frac{1}{2}, z-\frac{1}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for (I) at 117 K.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H12···Cl1	0.88	2.55	3.3643 (14)	155
N1—H11···Cl1$^{\rm iv}$	0.88	2.48	3.3260 (14)	161
N2—H22···Cl1	0.88	2.55	3.3641 (13)	155
N2—H21···Cl1$^{\rm ii}$	0.88	2.52	3.3877 (15)	168
O1—H1···Cl1$^{\rm v}$	0.827 (15)	2.352 (18)	3.1405 (12)	159.5 (19)
O2—H2···O3$^{\rm iv}$	0.833 (15)	2.06 (2)	2.8097 (18)	150 (2)

Symmetry codes: (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $x, y-1, z$.

Table 5
Alkali halide (AX)–organic molecule–water structures with a 1:1:1 composition.

AX	Organic molecule	CSD code	C^a	Reference
NaCl	CH_4N_2O	NCUREA	No	Palm *et al.* (1963); this work
NaCl	$C_{27}H_{35}N_2O_4$	UHARUQ	Yes	Gawley *et al.* (2002)
NaBr	$C_{10}H_{17}NO_3$	CMHTRB^b	No	Fodor *et al.* (1971)
NaBr	$C_{32}H_{38}N_4O_6$	ZEXCAG	Yes	Suwinska (1995)
NaI	$C_{18}H_{23}N_2O_6$	FIRYAG	Yes	Arnold *et al.* (1987)
NaI	$C_{22}H_{31}NO_3$	KESGUL	No	Fan *et al.* (2007)
NaI	$C_{26}H_{38}N_2O_4$	VIHFUN^b	Yes	Meadows *et al.* (2000)
KI	$C_{26}H_{38}N_2O_4$	VIHGIC^b	Yes	Meadows *et al.* (2000)
KI	$C_{20}H_{40}N_2O_7$	VOWVEI	Yes	Dalley *et al.* (1992)

Notes: (a) alkali atom multiply coordinated by organic ring structure; (b) no atomic coordinates available.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3223). Services for accessing these data are described at the back of the journal.

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