atoms. The figures were prepared from the output of *ORTEP*II (Johnson,1976). Major calculations were performed on a VAX 8800 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71843 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1047]

## References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem Res.* **16**, 146–152.

Camerman, A. F., Camerman, I. R. & Duncanson, F. D. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 789–793.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Karolak-Wojciechowska, J., Mikolajczyk, M., Zatorski, A., Kiéc-Kononowicz, K. & Zejc, A. (1985). *Tetrahedron*, **41**, 4593–4602.

Kiéc-Kononowicz, K., Zejc, A., Mikolajczyk, M., Zatorski, A. & Karolak-Wojciechowska, J. & Wieczorek, M. W. (1980). *Tetrahedron*, **36**, 1079–1087.

Kwiatkowski, W., Karolak-Wojciechowska, J. & Kiéc-Kononowicz, K. (1991). *Acta Cryst.* C**47**, 1256–1259.

Lempert, K., Nyitrai, J., Zauer, K., Kálmán, A., Argay, Gy., Duisenberg, A. J. M. & Sohar, P. (1973). *Tetrahedron*, **29**, 3565–3569.

Sheldrick, G. M. (1976). *SHELXS76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

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# Guanidinium Nitrate

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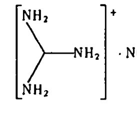
## Abstract

Crystals of $C(NH_2)_3^+.NO_3^-$ are built of sheets of guanidinium and nitrate ions linked by N—H···O hydrogen bonds of length 2.945 (6), 2.962 (8) and 2.968 (6) Å. The sheets are perpendicular to the crystallographic mirror planes; the C and N(1) atoms of the guanidinium cations, and the N and O(1) atoms of the nitrate anions, lie on these planes. It appears that pronounced changes of the crystal shape, observed at the first-order phase transition of guanidinium nitrate crystals at 296 K, are connected with shear shifts of the sheets in the crystal lattice.

## Comment

In the most recent article, the crystals of guanidinium nitrate (hereafter GN) were reported to exhibit unusual properties connected with two phase transitions observed in this substance (Szafrański, 1992). The low-temperature phase, GN1, on heating at $T_{12} = 296$ K, undergoes a transition to phase GN2; the second phase transition occurs at $T_{23} = 384$ K, where the crystals transform to the GN3 phase. The transition between the GN1 and GN2 phases has first-order character and is associated with a 20° temperature hysteresis between 276 and 296 K; the phase transition GN2–GN3 has a continuous character. One of the most interesting features of the GN1–GN2 transformation is the abrupt change in crystal dimensions; in certain directions the parameters expand or contract by nearly 45% of their initial length. The other interesting properties of the GN crystals at this phase transition were observed in calorimetric, dilatometric and dielectric measurements (Szafrański, 1992; Szafrański, Czarnecki, Dollhopf, Höhne, Brackenhofer & Nawrocik, 1993). The main aim of the present study was to determine the crystal data and the structure of the GN1 phase, which are necessary for interpretation of these phenomena. Crystals containing guanidinium cations are known to exhibit various types of molecular motions, like rotations or other forms of disorder of the cations (*e.g.* Grottel & Pająk, 1984; Grottel, Kozak, Małuszyńska & Pająk, 1992; Gima, Furukawa & Nakamura, 1984; Ratcliffe, 1985), and a cationic self diffusion was considered in order to explain the mechanism of the phase transition in guanidinium perchloate crystals (Titova & Rosolovskij, 1965; Pająk, Grottel & Kozioł, 1982). In no other guanidinium salt is a phase transition similar to that associated with the GN1–GN2 transformation reported.



GN

The GN1 crystals are built of guanidinium and nitrate ions hydrogen bonded into sheets along crystallographic planes (001), as shown in Fig. 1. The sheets are perpendicular to the mirror planes. The C and N(1) atoms of the cations and the N and O(1)

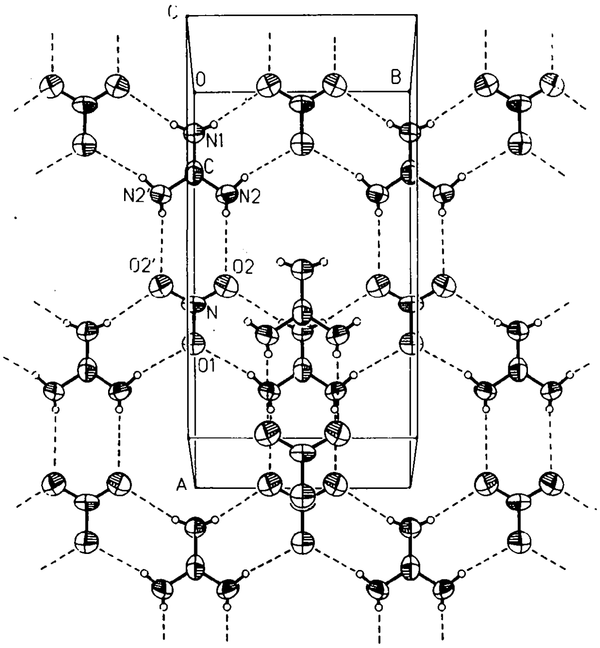


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the GN1 structure viewed perpendicular to the sheet of hydrogen-bonded ions. One cation and one anion of the neighbouring sheet are included in the drawing to show overlapping of the sheets. The displacement ellipsoids are drawn at the 50% probability level, the H atoms are represented as small circles of arbitrary size and the hydrogen bonds are indicated by broken lines.

atoms of the anions lie on the special positions, and the ions are $C_s$ symmetric. Thus, half of the formula unit constitutes the symmetry-independent part of the unit cell.

While the differences between symmetry-independent bond lengths in the cation and in the anion, as well as the valency angles in the anion, are within or slightly exceed three e.s.d.'s, the two symmetry-independent valency angles of the guanidinium cation are significantly different. Each cation and each anion is interconnected by six hydrogen bonds to three neighbouring ions arranged in a chicken-wire pattern within the sheets. Three hydrogen bonds are symmetry independent, the dimensions of which are compared in Table 3. The longest of the hydrogen bonds is that linking the ions along [100]. The neighbouring sheets are parallel, but displaced by $c.\cos\beta = 1.839\ (1)$ Å along [100]. The average distance between the sheets is $c.\sin\beta = 3.148\ (1)$ Å; however, the ions are deflected from the (001) plane in a manner which increases the distances between the closest atoms. Thus, in Fig. 1, the atom N(1) has a lower $z$ coordinate than atom N(2) and atom O(2) has a lower $z$ coordinate than atom O(1) (compare the manner of overlapping of the ions as shown in Fig. 1 to the coordinates in Table 1). The inclination angles between the (001) plane and the guanidinium and the nitrate ions are 5.1 (2) and 3.0 (2)°, respectively; the dihedral angle between the planes fitted to the ions is 2.1 (3)°. The differences in the dimensions of chemically equivalent bonds and hydrogen bonds may result from their different surroundings.

The arrangement of the sheets in this structure suggests that the pronounced changes of the crystal dimensions at $T_{12}$ can be connected with shear shifts of the hydrogen-bonded sheets. Similarly, large effects in crystal morphology were induced by the phase transition in crystals of 1,3-cyclohexanedione, also constructed of hydrogen-bonded molecules linked into planar chains arranged in parallel (Katrusiak, 1990, 1991). Also, as in the high-temperature phase of 1,3-cyclohexanedione, calorimetric results indicate the possibility of some kind of disorder in the GN2 phase (Szafrański *et al.*, 1993). Dilatometric measurements show that the GN2 phase is denser by 1.85% than the GN1 phase.

Attempts to investigate the GN2 phase by single-crystal X-ray diffraction methods proved unsuccessful. In most cases the crystals remain transparent on transformation from the GN1 to GN2 phase, but their quality is significantly affected. The reverse transformation from the GN2 to the GN1 phase visibly damages the crystals, which bend and become opaque. The crystallizations of GN carried out above $T_{12}$, directly in the GN2 phase, yield small and low-quality species which are not suitable for X-ray measurements. We are continuing structural studies of these crystals by single-crystal and powder X-ray, as well as neutron diffraction methods.

## Experimental

Crystals of GN1 were obtained by slow evaporation of an aqueous solution at 280 K. They crystallized in the form of colourless elongated prisms with well developed faces.

*Crystal data*

$C(NH_2)_3^+.NO_3^-$
$M_r = 122.08$
Monoclinic
$Cm$
$a = 12.686\ (3)$ Å
$b = 7.274\ (2)$ Å
$c = 3.629\ (1)$ Å
$\beta = 120.85\ (2)°$
$V = 287.5\ (2)$ Å$^3$
$Z = 2$
$D_x = 1.410$ Mg m$^{-3}$

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 5\text{–}20°$
$\mu = 1.135$ mm$^{-1}$
$T = 291$ K
Prisms
0.7 × 0.2 × 0.2 mm
Colourless

*Data collection*

Kuma 4-circle $\kappa$-craddle diffractometer
$2\theta$-$\theta$ scans
Absorption correction: none

$R_{\text{int}} = 0.018$
$\theta_{\text{max}} = 65°$
$h = -6 \rightarrow 15$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 4$

320 measured reflections
309 independent reflections
281 observed reflections
  [$I \geq 1.96\sigma(I)$]

2 standard reflections
  monitored every 50
  reflections
  intensity variation: ±0.5%

*Refinement*

Refinement on $F$
$R = 0.0319$
$wR = 0.0366$
$S = 1.32$
281 reflections
53 parameters
All H-atom parameters
  refined

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} = 0.2$
$\Delta\rho_{\max} = 0.18$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.16$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å$^2$)

$U_{\rm iso}$ for H atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

| | $x$ | $y$ | $z$ | $U_{\rm iso}/U_{\rm eq}$ |
|---|---|---|---|---|
| N | 0.5464 (4) | 0 | 0.0915 (12) | 0.0578 |
| O(1) | 0.6512 (4) | 0 | 0.1271 (12) | 0.0830 |
| O(2) | 0.5007 (3) | 0.1508 (2) | 0.0957 (10) | 0.0833 |
| C | 0.2000† | 0 | 0.0000† | 0.0562 |
| N(1) | 0.0971 (6) | 0 | −0.0235 (18) | 0.0850 |
| N(2) | 0.2586 (4) | 0.1533 (5) | 0.0332 (17) | 0.0806 |
| H(1) | 0.079 (3) | 0.093 (5) | −0.005 (8) | 0.032 (9) |
| H(2) | 0.299 (5) | 0.148 (4) | −0.005 (9) | 0.011 (8) |
| H(3) | 0.221 (5) | 0.236 (8) | 0.060 (15) | 0.084 (15) |

† Coordinate fixed to define origin.

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| C—N(1) | 1.264 (9) | N(2)—H(3) | 0.80 (6) |
| C—N(2) | 1.311 (4) | N—O(1) | 1.269 (8) |
| N(1)—H(1) | 0.73 (4) | N—O(2) | 1.244 (4) |
| N(2)—H(2) | 0.61 (6) | | |
| N(1)—C—N(2) | 121.6 (2) | C—N(2)—H(3) | 107 (5) |
| N(2)—C—N(2$^{\rm i}$) | 116.6 (4) | O(1)—N—O(2) | 117.97 (11) |
| C—N(1)—H(1) | 111 (3) | O(2)—N—O(2$^{\rm i}$) | 123.7 (3) |
| C—N(2)—H(2) | 116 (3) | | |

Symmetry code: (i) $x, -y, z$.

Table 3. *Hydrogen-bonding geometry* (Å, °)

| $D$ | H | $A$ | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|---|
| N(1) | H(1) | O(2$^{\rm ii}$) | 2.23 (4) | 2.945 (6) | 168 (4) |
| N(2) | H(2) | O(2) | 2.39 (6) | 2.962 (8) | 160 (4) |
| N(2) | H(3) | O(1$^{\rm ii}$) | 2.18 (6) | 2.968 (6) | 167 (6) |

Symmetry code: (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Owing to the crystals very high elasticity they could not be cut or shaped and it is possible that the defects in the samples resulted in broadening of the reflection peaks. The crystal diffraction symmetry was determined by precession and Weissenberg methods. The unit cell was chosen in the way corresponding to the crystal morphology and its microstructure. Thus, [100] lies along the sheets of hydrogen-bonded ions, which is not consistent with the Niggli cell parameter $a_N$ = 10.931 Å (*cf. Crystal Data*). As a result of all crystals having reflections broader than normal, presumably because of the low quality of the highly elastic crystals, an appropriately wider scan range of 2.0° was applied. $2\theta$-$\theta$ scan method and a variable scan speed (1.0-20.0° min$^{-1}$) depending on reflection intensity were applied. The intensities were corrected for Lp effects. The structure was solved by the Patterson method and H atoms were located from difference Fourier maps. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. Most of the calculations were performed with *SHELX*76 (Sheldrick, 1976); all calculations were performed on an IBM 486DX computer.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71808 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1064]

## References

Gima, S., Furukawa, Y. & Nakamura, D. (1984). *Ber. Bunsenges. Phys. Chem.* **88**, 939–946.
Grottel, M., Kozak, A., Małuszyńska, H. & Pająk, Z. (1992). *J. Phys. Condens. Matter*, **4**, 1837–1848.
Grottel, M. & Pająk, Z. (1984). *J. Chem. Soc. Faraday Trans.* 2, **80**, 533–560.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Katrusiak, A. (1990). *Acta Cryst.* **B46**, 246–256.
Katrusiak, A. (1991). *Acta Cryst.* **B47**, 398–404.
Pająk, Z., Grottel, M. & Kozioł, A. (1982). *J. Chem. Soc. Faraday Trans.* 2, **78**, 1529–1538.
Ratcliffe, C. I. (1985). *Can. J. Chem.* **63**, 1239–1244.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Szafrański, M. (1992). *Solid State Commun.* **84**, 1051–1054.
Szafrański, M., Czarnecki, P., Dollhopf, W., Höhne, G. W. H., Brackenhofer, G. & Nawrocik, W. (1993). *J. Phys. Condens. Matter*, **5**, 7425–7434.
Titova, K. V. & Rosolovskij, V. I. (1965). *Zh. Neorg. Khim.* **10**, 446–450.

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# *N,N'*-Bis(2-hydroxypropyl)dithiooxamide

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## Abstract

The molecular structure of *N,N'*-bis(2-hydroxypropyl)dithiooxamide, $C_8H_{16}N_2O_2S_2$, belongs to the $C_i$ point group, with only half of the molecule in an asymmetric unit. The dithiooxamide part of the molecule is planar with normal bond distances and angles. There are intermolecular hydrogen bonds