[1·369 (3) and 1·363 (3) Å respectively] are also intermediate between a single and a double bond. C(2)—O(1) [1·340 (3) Å] also has partial double-bond character and is comparable to the carbon–oxygen single bond in carboxylic acids [1·36 (1) Å]. The C(2)—O(2) distance [1·199 (3) Å] is short and is similar to the carbon–oxygen double-bond length [1·207 (6) Å] observed in conjugated systems. (*International Tables for X-ray Crystallography*, 1962). Finally the N(1)—O(1) bond [1·434 (2) Å] is close to the N—O bond in furazan *N*-oxide (Sillitoe & Harding, 1978). We can conclude from these results that the heterocycle is strongly conjugated.

The torsional angles C(2)—N(2)—C(1)—N(1) = 0·01 and N(2)—C(1)—N(1)—O(1) = −0·56° show that the heterocycle is planar. On the other hand, N(2)—C(2)—C(1)—C(31) is very small (3°), which may suggest that N(2) is sp^2 hybridized and its unshared pair would be orthogonal to the heterocycle. This assumption is supported by the very short distance (0·05 Å) of the N(2) atom from the plane of its ligands defined by C(1), C(2) and C(31).

The phenyl ring, linked to N(2), makes a dihedral angle of 66° with the heterocycle plane and cannot be conjuguated with N(2); this is suggested by the N(2)—C(31) bond [1·435 (3) Å] which is comparable to the C—N bond [1·47 Å] in the amino compounds. The other phenyl ring linked to C(1) may be partially conjugated with the heterocycle, as suggested by the dihedral angle of 35° between the two rings and the C(1)—C(21) bond length [1·466 (3) Å].

Finally, the steric repulsion between the two phenyl rings prevents planarity; their dihedral angle is 72°.

References

Bel Hadj Amor, A. & Baccar, B. (1986). *J. Soc. Chim. Tunisie*, **11**, 9–13.

Bois, C., Philoche-Levisalles, M. & Chihaoui, M. (1983). *J. Heterocycl. Chem.* **20**, 97.

Breuer, H. (1976). *Chem. Abstr.* **85**, 123953a.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press (Present distributor D. Reidel, Dordrecht.)

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Ruiz-Valero, C., Gutiérrez-Puebla, E. & Monge, A. (1985). *Acta Cryst.* C**41**, 1791–1792.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sillitoe, A. K. & Harding, M. M. (1978). *Acta Cryst.* B**34**, 2021–2022.

Acta Cryst. (1987). C**43**, 1589–1591

Structure of Acetamidinium Nitrate at 293 and 116 K

By M. Hjorth and R. Norrestam

Structural Chemistry Group, Chemistry Department B, The Technical University of Denmark, DK-2800 Lyngby, Denmark

(*Received* 11 *January* 1985; *accepted* 9 *March* 1987)

Abstract. $C_2H_7N_2^+.NO_3^-$, $M_r = 121{\cdot}10$, monoclinic, $P2_1/m$, $a = 6{\cdot}457\ (2)$, $b = 6{\cdot}442\ (2)$, $c = 6{\cdot}884\ (1)$ Å, $\beta = 97{\cdot}56\ (2)°$, $V = 283{\cdot}9\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}4167\ (5)$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}2$ cm^{-1}, $F(000) = 128$, $T = 293\ (2)$ K, $R = 0{\cdot}035$ for 360 unique observed reflections. The structure was also refined from data at 116 K [cell dimensions: $a = 6{\cdot}415\ (3)$, $b = 6{\cdot}221\ (3)$, $c = 6{\cdot}832\ (3)$ Å, $\beta = 97{\cdot}27\ (4)°$] to $R = 0{\cdot}052$ for 467 unique observed reflections. The crystals were obtained by evaporation of a methanolic solution. The crystal structure contains layers of hydrogen-bonded ions with crystallographic mirror symmetry. Two hydrogen bonds, both with an N···O distance of 2·934 (4) Å, are formed between one acetamidinium ion and one nitrate ion to form a hydrogen-bonded ion pair.

Introduction. The present study is part of a research project on the structures of acetamidines and their metal complexes [see *e.g.* Norrestam, Mertz & Crossland (1983) and Norrestam (1984)]. When attempting to prepare a chromium(III) complex with acetamidine by evaporating a methanolic solution of chromium(III) nitrate and acetamidine (molar ratio 1:4) a crystalline specimen was formed. The lack of color of the crystals and the size of the unit cell (*cf.* Table 1) suggested that the crystals formed were not a chromium complex. Furthermore, the unit-cell parameters were close to

0108-2701/87/081589-03$01.50

Table 1. *X-ray data collection and structural refinement parameters*

A second set of figures in parentheses refers to the 116 K study.

Crystal color and shape	Colorless, prismatic
Crystal size	0·12 × 0·12 × 0·20 mm
Diffractometer	Enraf–Nonius CAD-4
Determination of unit cell	
Number of reflections used	14
θ range	6·6 to 13·2°
Intensity data collection	
Max. of $(\sin\theta)/\lambda$	0·704 Å^{-1}
Range of *h*, *k*, and *l*	0,0,–9 to 7,8,9
Standard reflections	300 and $0\bar{2}0$
Intensity variation	Negligible
No. of measured reflections	946
No. of unique reflections	887 (848)
No. of observed reflections	360 (467)
Criterion for observed reflections	$\sigma/I < 0{\cdot}33$
$R_{\rm int}$	0·018 (0·035)
Absorption correction	
Min. and max. transmission	0·984 and 0·987
Determination of H atoms	From difference Fourier map
Structure refinement	
Minimization of	$\sum w(\Delta F)^2$
Anisotropic model for	Non-H atoms
Isotropic model for	H atoms
Parameters fixed	$U_{12} = U_{23} = 0$
Number of parameters	68
Weighting scheme, *w*	$(\sigma_F^2 + gF^2)^{-1}$ with $g = 0{\cdot}002$ (0·0005)
Final *R*	0·035 (0·052)
Final *wR*	0·041 (0·066)
Max. final Δ/σ	~0·4 (0·3)
Max. and min. $\Delta\rho$	0·13 and –0·18 (0·44 and –0·65) e Å^{-3}

those [$a = 5{\cdot}6887\ (5)$, $b = 6{\cdot}0436\ (6)$, $c = 7{\cdot}5788\ (7)$ Å, $\beta = 101{\cdot}080\ (7)$°, $Z = 2$, space group $P2_1/m$] found for acetamidium nitrate (Gubin, Yanovsky, Struchkov, Berimzhanov, Nurakmetov & Buranbaev, 1980) indicating that the present compound was acetamidinium nitrate. In view of the limited structural knowledge of simple acetamidinium compounds, *viz* acetamidinium chloride (Cannon, White & Willis, 1976) and bis(acetamidinium) carbonate monohydrate (Norrestam, 1984), it was considered worthwhile to carry out a complete structure determination of the title compound.

Experimental. Colorless crystals of the title compound were obtained by allowing a methanolic solution of chromium (III) nitrate hexahydrate and acetamidine to evaporate in air. Information on the X-ray diffraction data collection at 293 and 116 K is summarized in Table 1. Low-temperature data on the same crystal were collected by using a conventional nitrogen-gas-stream cooling device.

Systematic absences ($k = 2n + 1$) indicated the possible space groups $P2_1$ or $P2_1/m$. The space-group symmetry $P2_1/m$ was confirmed from intensity statistics which indicated a slight hypercentricity. Attempts to determine the structure by routine applications of direct methods failed. The room-temperature structure was eventually solved by using the non-H coordinates of the related compound acetamidium nitrate (Gubin *et al.*, 1980) as a starting point for a least-squares refinement. Later it was shown that the structure could have been easily determined with the direct-methods package *MITHRIL* (Gilmore, 1984).

The low-temperature structural parameters were determined by using the room-temperature parameters as the starting point in a least-squares refinement. The higher *R* value, 0·052, for the low-temperature (116 K) data compared with 0·035 for the room-temperature

Table 2. *Fractional atomic coordinates and isotropic temperature factors* (Å^2) (× 10^4 *for non-*H *atoms*, × 10^3 *for* H)

Equivalent isotropic temperature factors for the non-H atoms are calculated as $\frac{1}{3}$ trace **U**.

	x	*y*	*z*	$U_{\rm eq}/U_{\rm iso}$
$T = 293$ K				
O(1)	936 (4)	2500	8059 (4)	676 (11)
O(2)	−1552 (4)	2500	5638 (3)	599 (9)
O(3)	−2238 (4)	2500	8613 (4)	674 (10)
N	−955 (5)	2500	7453 (4)	465 (10)
N(1)	3808 (5)	2500	5092 (4)	478 (11)
N(2)	1178 (5)	2500	2552 (5)	488 (10)
C(2)	4728 (7)	2500	1803 (6)	591 (16)
C(1)	3172 (5)	2500	3218 (5)	398 (11)
H(1)	423 (7)	250	53 (8)	87 (14)
H(23)	557 (5)	347 (6)	202 (5)	111 (14)
H(4)	520 (7)	250	548 (6)	71 (13)
H(5)	292 (6)	250	597 (5)	48 (9)
H(6)	80 (7)	250	124 (7)	93 (16)
H(7)	6 (7)	250	340 (6)	67 (11)
$T = 116$ K				
O(1)	959 (4)	2500	8051 (4)	242 (9)
O(2)	−1549 (5)	2500	5590 (4)	212 (8)
O(3)	−2287 (5)	2500	8595 (4)	234 (8)
N	−977 (5)	2500	7434 (5)	162 (8)
N(1)	3813 (5)	2500	5078 (5)	159 (9)
N(2)	1185 (5)	2500	2490 (5)	160 (9)
C(2)	4803 (6)	2500	1790 (6)	195 (11)
C(1)	3205 (6)	2500	3176 (5)	142 (10)
H(1)	432 (11)	250	41 (11)	80 (23)
H(23)	557 (6)	384 (8)	193 (5)	55 (12)
H(4)	539 (9)	250	531 (7)	33 (13)
H(5)	290 (8)	250	589 (7)	27 (13)
H(6)	99 (6)	250	117 (6)	3 (9)
H(7)	21 (10)	250	336 (9)	49 (17)

Table 3. *Bond distances* (Å) *and angles* (°) *between the non-*H *atoms at* 293 *and* 116 K

	293 K	116 K
O(1)–N	1·237 (3)	1·260 (4)
O(2)–N	1·258 (3)	1·267 (4)
O(3)–N	1·224 (3)	1·226 (4)
N(1)–C(1)	1·301 (4)	1·309 (4)
N(2)–C(1)	1·309 (4)	1·321 (5)
C(2)–C(1)	1·489 (4)	1·481 (5)
O(1)–N–O(2)	119·6 (3)	118·8 (3)
O(1)–N–O(3)	120·2 (3)	120·7 (3)
O(2)–N–O(3)	120·2 (3)	120·5 (3)
N(1)–C(1)–N(2)	121·0 (3)	120·5 (3)
N(1)–C(1)–C(2)	119·8 (3)	119·4 (3)
N(2)–C(1)–C(2)	119·2 (3)	120·0 (3)

(293 K) data is apparently due to deterioration of the crystal upon cooling. This is possibly related to the fact that the unit-cell size decreases highly anisotropically, by 0·7, 3·4 and 0·8% for the *a*, *b* and *c* axes, respectively.

Atomic scattering factors for neutral atoms were from *International Tables for X-ray Crystallography* (1974). Programs used were *SHELX*76 (Sheldrick, 1976) and *XTAPL* (Norrestam, 1982).

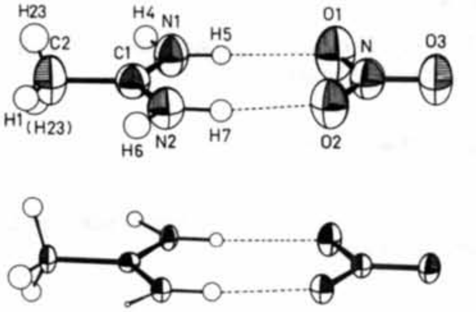

Fig. 1. Atomic labels and molecular structure of the hydrogen-bonded ion pairs. The non-H-atom positions are represented by 50% probability ellipsoids while the H positions are drawn with 10% probability. The upper figure shows the ellipsoids at 293 K and the lower one at 116 K. Hydrogen bonds are indicated by broken lines.

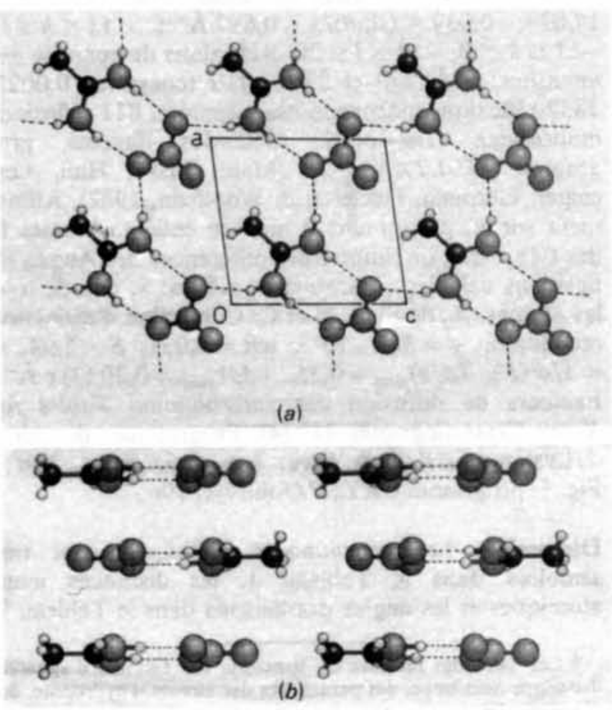

Fig. 2. Packing diagram of the crystal structure. The packing in the layer $y = \frac{1}{4}$ is shown in (*a*) and the stacking along **b** of the hydrogen-bonded ion pairs in (*b*). N and O atoms are grey-rastered, C black and H white. Hydrogen bonds are indicated by broken lines.

Discussion. Atomic coordinates at 293 and 116 K are given in Table 2,* bond distances and angles in Table 3. The atomic labels and the molecular structure are shown in Fig. 1. The geometry of the acetamidinium ion agrees well with that found in earlier studies (Cannon *et al.*, 1976; Norrestam, 1984); the two C—N distances are almost equal and the bond angles around C(1) close to 120°. In the nitrate ion there is a significant difference between the N—O(1) bond distance at the two temperatures, 1·237 (3) Å at 293 K, 1·260 (4) Å at 116 K. The shortest N—O bond length is observed for the O atom O(3), not involved in intermolecular hydrogen bonding.

Similar to acetamidium nitrate the crystal structure is built up of hydrogen-bonded ions in layers coinciding with the mirror planes of the space group. However, the relative molecular orientations are different in the two structures; two hydrogen bonds, N(1)—H···O(1) and N(2)—H···O(2), both with N···O distances of 2·934 (4) Å, are formed between one acetamidinium ion and one nitrate ion in the present structure, but only one between the corresponding ions in acetamidium nitrate. The hydrogen-bonded ion pairs in the present structure are held together within one layer by two further hydrogen bonds (Fig. 2*a*), N(2)···O(1) and N(1)···O(2), with distances 3·076 (4) and 2·970 (4) Å, respectively. The hydrogen-bonded entities are stacked on each other in alternating orientations (Fig. 2*b*). The absence of hydrogen bonds between the layers explains the anisotropic decrease of the cell dimensions on cooling as noted above.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43878 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

CANNON, J. R., WHITE, A. H. & WILLIS, A. C. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 271–272.

GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

GUBIN, A. I., YANOVSKY, A. I., STRUCHKOV, YU. T., BERIMZHANOV, B. A., NURAKMETOV, N. N. & BURANBAEV, M. Z. (1980). *Cryst. Struct. Commun.* **9**, 745–748.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

NORRESTAM, R. (1982). *XTAPL. Interactive APL-programs for Crystal Structure Calculations.* Technical Univ. of Denmark.

NORRESTAM, R. (1984). *Acta Cryst.* C**40**, 297–299.

NORRESTAM, R., MERTZ, S. & CROSSLAND, I. (1983). *Acta Cryst.* C**39**, 1554–1556.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.