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The Ammonium and Potassium Salts of Nitromalonamide

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Abstract

The ammonium and potassium salts of nitromalonamide are isomorphous. They are monoclinic, $P2_1/c$, with $Z = 4$. The ammonium salt, $C_3H_4N_3O_4^-.NH_4^+$, has $a = 7{\cdot}3522\ (9)$, $b = 12{\cdot}4391\ (9)$, $c = 7{\cdot}5608\ (9)$ Å, $\beta = 100{\cdot}376\ (9)°$, $D_m = 1{\cdot}61$, $D_x = 1{\cdot}603$ Mg m^{-3}. The potassium salt, $C_3H_4N_3O_4^-.K^+$, has $a = 7{\cdot}2228\ (8)$, $b = 12{\cdot}133\ (1)$, $c = 7{\cdot}4402\ (8)$ Å, $\beta = 99{\cdot}00\ (1)°$, $D_m = 1{\cdot}92$, $D_x = 1{\cdot}909$ Mg m^{-3}. The final residuals are 0·068 for the NH_4^+ salt and 0·052 for the K^+. The anion has a non-planar configuration.

Introduction

This structure determination is part of a study of aliphatic nitro compounds, nitronate salts and tautomeric forms of these compounds. The structure of nitromalonamide has been reported previously (Simonsen & Thorup, 1979). This structure determination has been carried out to study structural changes connected with nitromalonamide salt formation.

Nitromalonamide was prepared from malonamide by nitration as described by Ratz (1904). Evaporation of a solution made from nitromalonamide and aqueous ammonia gave suitable crystals of the ammonium salt. The potassium salt was prepared by an analogous procedure.

Values and statements which apply to the potassium salt structure are in the following text indicated by K^+; NH_4^+ is used for the ammonium salt.

Unit-cell dimensions were determined by a least-squares refinement of data from Guinier powder photographs taken with Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54059$ Å) and calibrated with an internal standard (K^+: quartz; NH_4^+: silicon).

Single crystals with dimensions 0·50 × 0·68 × 0·75 mm (K^+) and 0·44 × 0·31 × 0·80 mm (NH_4^+) were used for data collection on an Enraf–Nonius CAD-3 diffractometer employing Mo $K\alpha$ radiation and different monochromators (K^+: Zr filter; NH_4^+: graphite crystal). All reflections (K^+: hkl and $hk\bar{l}$; NH_4^+: hkl and $\bar{h}kl$) in the range $2{\cdot}5° < \theta < 30°$ were measured applying the ω-scan technique. A reflection was designated unobserved for K^+ if $I < 2{\cdot}5\ \sigma(I)$, and for NH_4^+ if $I < 2{\cdot}2\ \sigma(I)$. With these criteria for K^+ 1556 out of 1834 and for NH_4^+ 1623 out of 1981 measured reflections were regarded as observed. One of the two reflections 080 and 400 was monitored every ten reflections. Lorentz and polarization corrections were

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Table 1. *Final atomic coordinates with standard deviations* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2$)

N(4) is the N atom in the ammonium ion. (I) is the K^+ salt, (II) the NH_4^+ salt. $B_{eq} = \frac{4}{3}\sum_i\sum_j b_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j)$, as defined by Hamilton (1959).

		x	*y*	*z*	B_{eq}
K	(I)	2511 (1)	6341·5 (6)	5059 (1)	2·47
N(4)	(II)	2494 (4)	6315 (2)	5026 (4)	1·95
O(1)	(I)	4961 (3)	2753 (2)	1027 (4)	2·97
	(II)	5052 (3)	2838 (2)	1218 (4)	2·52
O(3)	(I)	4669 (3)	4919 (2)	3008 (3)	2·40
	(II)	4798 (3)	5021 (2)	2912 (3)	1·94
O(21)	(I)	−322 (3)	2842 (2)	2472 (4)	2·55
	(II)	−150 (3)	2981 (2)	2524 (4)	2·42
O(22)	(I)	46 (3)	4646 (2)	2779 (3)	2·26
	(II)	181 (3)	4747 (2)	2675 (3)	2·11
N(1)	(I)	2598 (4)	1673 (2)	1691 (4)	2·34
	(II)	2683 (4)	1809 (2)	1827 (5)	2·40
N(2)	(I)	690 (3)	3701 (2)	2324 (3)	1·67
	(II)	834 (3)	3814 (2)	2333 (3)	1·51
N(3)	(I)	2942 (4)	5386 (2)	329 (4)	2·34
	(II)	2957 (4)	5393 (2)	255 (4)	2·05
C(1)	(I)	3363 (4)	2656 (2)	1459 (4)	1·68
	(II)	3469 (4)	2755 (2)	1600 (4)	1·63
C(2)	(I)	2339 (4)	3660 (2)	1753 (4)	1·55
	(II)	2463 (4)	3752 (2)	1816 (4)	1·46
C(3)	(I)	3402 (4)	4721 (2)	1736 (4)	1·68
	(II)	3484 (4)	4786 (2)	1700 (4)	1·42

applied, but no extinction or absorption correction was made.

Both direct methods and the heavy-atom method were unsuccessful when applied to the K^+ salt, probably because the K^+ ion is situated near a semi-special position ($\frac{1}{4}, y, \frac{1}{2}$) which does not contribute to the structure factors when $h = 2n, k + l = 2n + 1$, or $h = 2n + 1, k + l = 2n$. It was then decided to investigate the ammonium salt. The structure of the ammonium salt was solved by direct methods using *SHELX* 76 (Sheldrick, 1976) and an IBM 360/165 computer. The coordinates from the NH_4^+ salt were used as the basis for the refinement of the K^+ salt. The least-squares refinement was performed on a Univac 1110 computer using the XRAY 76 system (Stewart, 1976).

The quantity minimized was $\sum w(F_o - F_c)^2$. The weighting scheme was $w = (a + F_o + bF_o^2)^{-1}$ with $a = 10{\cdot}0$ and $b = 0{\cdot}10$. Contributions from unobserved reflections were included if $F_c > F_o$. The H atoms were located from a difference Fourier map. However, most of the H atom positional parameters refined to unrealistic values, and therefore the unrefined H atom parameters were included in the structure factor calculations. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final residuals ($R = \sum||F_o| - |F_c||/\sum|F_o|$) were 0·068 ($NH_4^+$) and 0·052 ($K^+$).

Atomic parameters are given in Table 1.*

Discussion

Nitromalonamide is a planar molecule (Simonsen & Thorup, 1979). The ammonium salt of nitromalonamide and the isomorphous potassium salt have non-planar anions (Fig. 1). There is no significant difference between corresponding bond lengths and

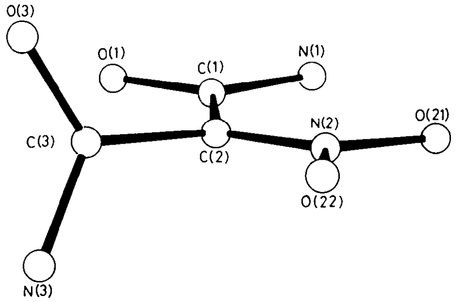

Fig. 1. Perspective drawing of the nitromalonamide anion with the atom-numbering scheme.

Table 2. *Comparison of corresponding bond lengths* (Å) *and angles* (°) *in nitromalonamide and its ammonium and potassium salts*

The estimated standard deviations are 0·004 Å and 0·3° for bond distances and angles in the two salts.

	Nitro-malonamide	NH_4^+ salt	K^+ salt
C(1)–C(2)	1·447	1·468	1·459
C(1)–N(1)	1·301	1·336	1·337
C(1)–O(1)	1·302	1·253	1·251
C(2)–C(3)	1·456	1·500	1·499
C(2)–N(2)	1·397	1·327	1·327
C(3)–N(3)	1·322	1·327	1·323
C(3)–O(3)	1·281	1·241	1·232
N(2)–O(21)	1·244	1·286	1·288
N(2)–O(22)	1·249	1·300	1·301
C(2)–C(1)–O(1)	117·9	117·6	118·0
C(2)–C(1)–N(1)	125·2	119·5	119·7
N(1)–C(1)–O(1)	116·9	123·0	122·3
C(1)–C(2)–C(3)	119·0	116·8	116·3
C(1)–C(2)–N(2)	120·2	125·5	125·5
C(3)–C(2)–N(2)	120·7	117·0	117·2
C(2)–C(3)–N(3)	123·2	117·5	117·7
C(2)–C(3)–O(3)	117·9	119·3	118·7
N(3)–C(3)–O(3)	118·9	123·2	123·6
C(2)–N(2)–O(21)	119·9	122·8	123·2
C(2)–N(2)–O(22)	120·2	119·7	119·4
O(21)–N(2)–O(22)	119·9	117·4	117·4

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35702 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Distances* (Å) *of atoms from least-squares planes* [K^+ *salt* (I), NH_4^+ *salt* (II)]

The planes are in the form $0{\cdot}27121x - 0{\cdot}05888y + 0{\cdot}96072z = 1{\cdot}45989$ (I) and $0{\cdot}24654x - 0{\cdot}02812y + 0{\cdot}96873z = 1{\cdot}63597$ (II). The coordinates x, y, and z are expressed parallel to the axial directions a, b, and c^*. The mean e.s.d. on the distances of atoms from the planes is 0·063 Å.

C(1)†	(I)	−0·007	O(21)†	(I)	−0·059
	(II)	−0·005		(II)	−0·034
N(1)†	(I)	0·070	O(22)†	(I)	0·091
	(II)	0·042		(II)	0·068
O(1)†	(I)	0·008	C(3)	(I)	0·040
	(II)	0·017		(II)	−0·004
C(2)†	(I)	−0·081	N(3)	(I)	−1·047
	(II)	−0·073		(II)	−1·113
N(2)†	(I)	−0·022	O(3)	(I)	1·132
	(II)	−0·016		(II)	1·058

† These atoms define the least-squares planes.

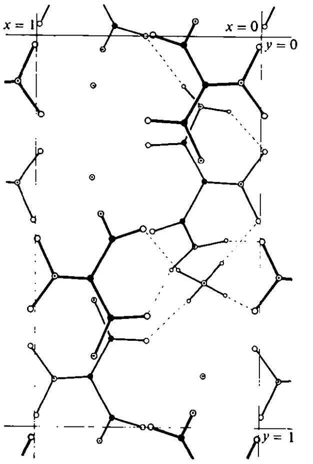

Fig. 2. View of the packing of the crystal structure (z-axis projection). The dotted lines represent the hydrogen-bonding system. Some of the symmetry-related hydrogen bonds are omitted for clarity.

bond angles in the ammonium and the potassium salts (Table 2). Analytically the anion can be divided into two parts, an amide group [C(3), N(3), O(3): part (1)] and the rest of the anion which constitutes a nearly planar system [part (2)] (Fig. 1, Table 3). Parts (1) and (2) make dihedral angles with each other of 74·21 and 76·18° in the ammonium and potassium salts respectively. For that reason, conjugation between parts (1) and (2) is impossible. This is also reflected in the significantly different lengths for C(1)—C(2) and C(2)—C(3) (Fig. 1, Table 2). The distribution of bonds and angles around the line C(2)—N(2) is rather unsymmetric compared to nitromalonamide (Table 2). Comparison of the nitromalonamide anion with nitromalonamide (Table 2) reveals some further differences: a shortening is seen for the C(2)—N(2) bond whereas N(2)—O(21) and N(2)—O(22) are elongated. Thus, the N—O single-bond character and the C—N double-bond character are enhanced.

Table 4. *The dimensions of the* $K^+\cdots O$ *ionic bonds and the* $N\cdots O$ *distances in the* $N{-}H\cdots O$ *hydrogen bonds* [K^+ *salt* (I), NH_4^+ *salt* (II)]

Estimated standard deviations are given in parentheses.

Structure	Atoms defining the distance (K^+ or N)	O	Symmetry operations for O atoms	Distance (Å)
(I)	K^+	O(1)	$1-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$	2·717 (3)
(I)	K^+	O(3)	$x,\ y,\ z$	2·913 (3)
(I)	K^+	O(3)	$1-x,\ 1-y,\ 1-z$	2·764 (3)
(I)	K^+	O(21)	$-x,\ 1-y,\ 1-z$	2·786 (3)
(I)	K^+	O(21)	$-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$	2·903 (3)
(I)	K^+	O(22)	$x,\ y,\ z$	3·056 (3)
(I)	K^+	O(22)	$-x,\ 1-y,\ 1-z$	2·844 (3)
(II)	N(4)	O(1)	$1-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$	2·889 (4)
(II)	N(4)	O(3)	$1-x,\ 1-y,\ 1-z$	2·835 (4)
(II)	N(4)	O(21)	$-x,\ 1-y,\ 1-z$	2·884 (4)
(II)	N(4)	O(22)	$x,\ y,\ z$	2·962 (3)
(I)	N(3)	O(1)	$1-x,\ 1-y,\ -z$	2·981 (4)
(II)	N(3)	O(1)	$1-x,\ 1-y,\ -z$	2·969 (4)
(I)	N(3)	O(22)	$-x,\ 1-y,\ -z$	2·905 (3)
(II)	N(3)	O(22)	$-x,\ 1-y,\ -z$	2·901 (3)
(I)	N(1)	O(3)	$1-x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z$	2·888 (4)
(II)	N(1)	O(3)	$1-x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z$	2·878 (4)
(I)	N(1)	O(21)	$x,\ y,\ z$	2·679 (4)
(II)	N(1)	O(21)	$x,\ y,\ z$	2·672 (4)

The planarity and the bond lengths of part (1) make it probable that the negative charge of the anion is to some extent delocalized over the system C(1), C(2), N(2), O(1), O(21), O(22).

As the quantitative determination of the H-atom positions was unacceptable, no values for the N—H distances are quoted. However, the hydrogen bonds are drawn on Fig. 2 as the qualitative information contained in the figure is considered to be correct. The dimensions of the N···O distances in the NH···O hydrogen bonds and the $K^+\cdots O$ ionic bonds are given in Table 4.

The planar configuration of part (2) of the anion is partly fixed by the intramolecular hydrogen bond N(1)—H···O(21) (Figs. 1 and 2). The other three amide hydrogen bonds, and for the ammonium salt also the four ammonium hydrogen bonds, make up a complicated network which stabilizes the crystal packing. The positive ions are located in channels surrounded by O atoms.

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