

Sodium 2-nitroethanaloximate forms a layered-framework structure

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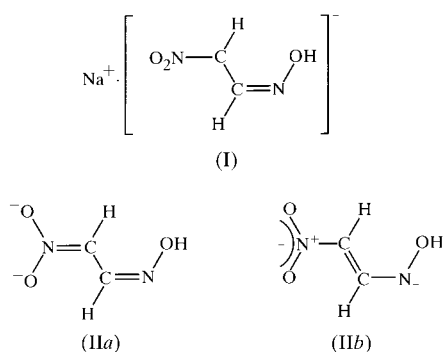
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In the title compound, [Na(C₂H₃N₂O₃)], the Na⁺ cation lies on a centre of inversion in space group *P*2₁/*m* and all the atoms of the anion lie on a mirror plane. Na is octahedrally coordinated by four O and two N atoms from six different anions and each anion is coordinated to six different Na⁺ cations, forming chains of confacial octahedra which link the anion layers. Within these layers, the individual anions are linked by both O—H...O and C—H...O hydrogen bonds.

Comment

We report here the structure of sodium 2-nitroethanaloximate, Na(O₂NCHCHNOH), (I), an unexpected coupling product derived from nitromethane, which was isolated serendipitously following attempted crystallization of an organic sodium salt from aqueous nitromethane.



Both ions of (I) (Fig. 1) lie in special positions in space group *P*2₁/*m*, with *Z'* = 0.5. Na⁺ lies at a centre of inversion, selected as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the atoms of the anion all lie on a mirror plane, selected as that at $y = \frac{3}{4}$. The overall structure thus consists of layers of anions at $y = (n/2 + \frac{1}{4})$ ($n =$ zero or integer) linked by Na⁺ at $y = (\frac{1}{2}, n/2, \frac{1}{2})$ ($n =$ zero or integer). Each Na⁺ is six-coordinate and approximately octahedral

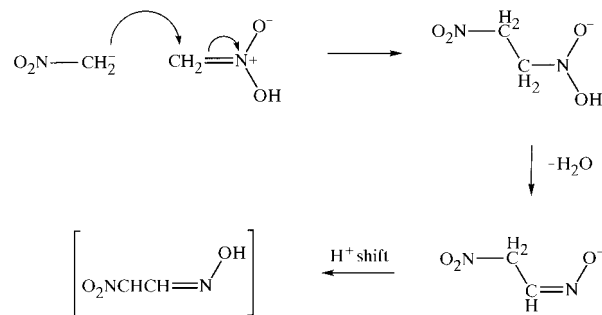
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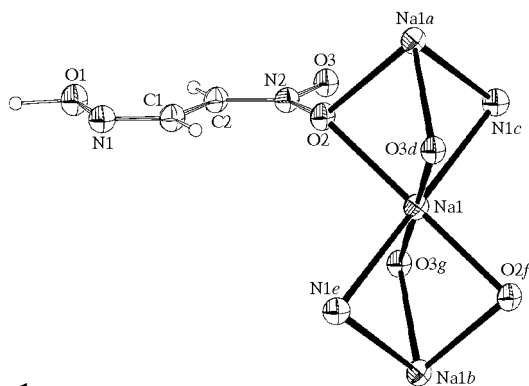
(Table 1, Fig. 1). The coordinating atoms (4O + 2N) around the Na⁺ at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ lie in the anions at $(x, \frac{3}{4}, z)$, $(-1 + x, \frac{3}{4}, z)$, $(1 - x, -\frac{1}{4}, 1 - z)$, and $(2 - x, \frac{1}{4}, 1 - z)$ (O donors), and at $(x, \frac{3}{4}, 1 + z)$ and $(1 - x, \frac{1}{4}, -z)$ (N donors). Similarly, each anion is coordinated to six different Na⁺ centres: in the reference anions, N1 is coordinated to Na⁺ at $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ and $(\frac{1}{2}, 1, -\frac{1}{2})$, O2 to Na at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 1, \frac{1}{2})$, and O3 to Na⁺ at $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{3}{2}, 1, \frac{1}{2})$. These metal–ligand interactions thus generate a chain of confacial NaN₂O₄ octahedra running parallel to [010] (Fig. 1), propagation of which by translation links all the ions into a single layered-framework structure.

In addition, the anions within each layer are linked into a continuous sheet by hydrogen bonds (Table 2, Fig. 2). Oxime O1 at (x, y, z) acts as a hydrogen-bond donor to nitro O3 at $(x, y, -1 + z)$, so generating by translation a *C*(7) chain parallel to [001]. Adjacent [001] chains are linked by C—H...O hydrogen bonds; C1 and C2 at (x, y, z) act as hydrogen-bond donors to O1 and O2 at $(-1 + x, y, z)$ and $(1 + x, y, z)$, respectively (Table 2). In this manner, the [001] chains are linked into (010) sheets built from *R*₂²(10) and *R*₄⁴(14) rings (Fig. 2). The combination of the (010) anion layers and the [010] metal–ligand chains generates the overall layer structure.

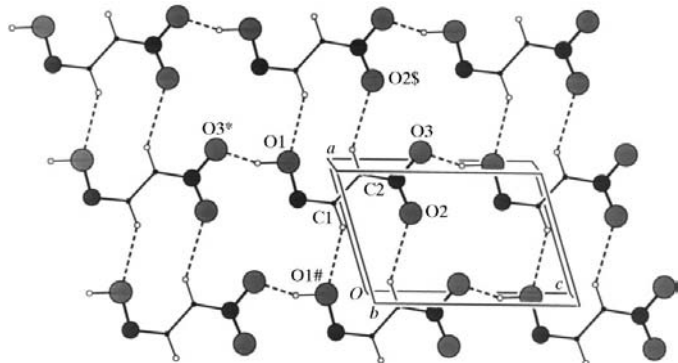
In the strictly planar anion, O1 is *cis* to C2; the bond distances (Table 1) within the anion are highly unusual in comparison with typical values for these bond types (Allen *et al.*, 1987), and they are consistent with extensive delocalization of the negative charge. The N—O bonds in the nitro group are both very long (mean distance 1.218 Å; Allen *et al.*, 1987), while the N2—C2 and C2—C1 bonds are both rather short (mean distances 1.468 and 1.455 Å, respectively); although the N—O distance in the oxime unit is unexceptional, the N1—C1 distance is somewhat long for its type (mean value 1.281 Å; upper quartile value 1.288 Å). These observations, taken together, can most simply be interpreted in terms of a dominant contribution from form (IIa) with a lesser involvement of form (IIb). The Na—O distances (Table 1) are significantly shorter than the Na—N distance. The fact that N1, O2 and O3 all act as bridging atoms between pairs of Na⁺ is consistent with the involvement of both (IIa) and (IIb); in form (IIa), N1 carries only a single lone pair and hence would not be expected to act as a bridging atom, whereas in (IIb), it carries two lone pairs.



A plausible mechanism for the formation of the anion in (I) (see Scheme above) involves nucleophilic addition of the conjugate anion of nitromethane to a neutral molecule in the enolized aci form, followed by loss of water and a proton shift.

**Figure 1**

Part of the crystal structure of (I) showing the ionic components and the coordination geometry at Na. Displacement ellipsoids are drawn at the 30% probability level. Atoms Na1a and Na1b are at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, respectively; N1c and O3d are at $(x, \frac{3}{4}, 1+z)$ and $(-1+x, \frac{3}{4}, z)$, respectively; and N1e, O2f and O3g are at $(1-x, \frac{1}{4}, -z)$, $(1-x, \frac{1}{4}, 1-z)$ and $(2-x, \frac{1}{4}, 1-z)$, respectively.

**Figure 2**

Part of the crystal structure of (I) showing the formation of the (010) sheet built from $R_2^2(10)$ and $R_4^4(14)$ rings. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(x, y, -1+z)$, $(-1+x, y, z)$ and $(1+x, y, z)$, respectively.

Experimental

The sodium salt of 3-(α -acetylbenzyl)-4-hydroxycoumarin was dissolved at ambient temperature in water and then an equal volume of nitromethane was added. When this solution was set aside to crystallize at ambient temperature, a solid orange-brown mass resulted, from which thin orange plates of (I) were isolated manually.

Crystal data

$[\text{Na}(\text{C}_2\text{H}_3\text{N}_2\text{O}_3)]$

$M_r = 126.05$

Monoclinic, $P2_1/m$

$a = 4.9640$ (15) Å

$b = 6.346$ (2) Å

$c = 7.336$ (2) Å

$\beta = 107.25$ (2)°

$V = 220.70$ (11) Å³

$Z = 2$

Data collection

KappaCCD diffractometer

φ scans, and ω scans with κ offsets

Absorption correction: multi-scan

(DENZO-SMN; Otwinowski & Minor, 1997)

$T_{\min} = 0.902$, $T_{\max} = 0.993$

1075 measured reflections

406 independent reflections

$D_x = 1.897$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 355 reflections

$\theta = 2.6$ – 25.0°

$\mu = 0.25$ mm⁻¹

$T = 150$ (2) K

Plate, orange

$0.42 \times 0.12 \times 0.03$ mm

308 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.091$

$\theta_{\text{max}} = 25.0^\circ$

$h = 0 \rightarrow 5$

$k = 0 \rightarrow 7$

$l = -8 \rightarrow 8$

Intensity decay: negligible

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.059$

$wR(F^2) = 0.162$

$S = 1.07$

406 reflections

52 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.0640P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.48$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1–N1	1.395 (5)	C2–N2	1.319 (6)
N1–Cl	1.299 (6)	N2–O2	1.300 (5)
Cl–C2	1.421 (7)	N2–O3	1.329 (5)
Na1–O2	2.398 (2)	Na1–N1 ⁱⁱ	2.587 (3)
Na1–O3 ⁱ	2.377 (2)		
O2–Na1–N1 ⁱⁱ	82.87 (10)	O3 ⁱ –Na1–N1 ⁱⁱ	84.27 (9)
O2–Na1–O3 ⁱ	80.59 (9)		

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y, 1 + z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1–H1 \cdots O3 ⁱ	1.11 (7)	1.56 (7)	2.630 (5)	160 (6)
Cl–H1A \cdots O1 ⁱⁱ	0.95	2.45	3.274 (7)	146
C2–H2 \cdots O2 ⁱⁱⁱ	0.95	2.55	3.364 (6)	145

Symmetry codes: (i) $x, y, z - 1$; (ii) $x - 1, y, z$; (iii) $1 + x, y, z$.

Compound (I) crystallized in the monoclinic system in space group $P2_1/m$ or $P2_1$ from the systematic absences; $P2_1/m$ was assumed and confirmed by the analysis. H atoms bonded to C atoms were treated as riding atoms with a C–H distance of 0.95 Å. The H atom bonded to O1 was refined isotropically. The chemical types of all the atoms in the anion were confirmed by refinement of their site-occupation factors.

Data collection: COLLECT (Nonius, 1997–2000); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2001); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1484). Services for accessing these data are described at the back of the journal.

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