

Sodium phenoxyacetate hemihydrate

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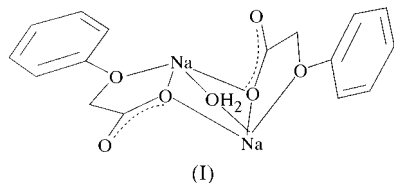
Received 13 August 2001

Accepted 17 August 2001

The structure of the hemihydrate of sodium phenoxyacetate, $\text{Na}^+ \cdot \text{C}_8\text{H}_7\text{O}_3^- \cdot 0.5\text{H}_2\text{O}$, has been redetermined at low temperature (160 K). The structure consists of ribbons containing octahedral NaO_6 units, and half of the Na_2O_2 squares within the ribbon are bridged by water molecules which lie across twofold rotation axes in $C2/c$. The phenyl substituents lie on the outside of the ribbon.

Comment

The structure of the title compound, (I), was first solved by X-ray photography ($R = 0.096$; Prout *et al.*, 1971) and has now been redetermined at 160 K ($R = 0.052$) during an investigation of the impact of impurities on the crystallization of phenoxyacetic acid. The structure consists of a ribbon-like Na–O core, running parallel to the [001] direction, which is bridged above and below by water molecules. As in the acid salt (Evans *et al.*, 2001), the phenyl groups form hydrocarbon layers on the outside of the Na–O ribbon. The ribbon consists of sodium ions surrounded by six O atoms in a distorted octahedral arrangement. The shortest Na...Na bridging distances [range 3.179 (2)–4.0384 (16) Å] are similar to those reported for other bridged systems (Albertsson *et al.*, 1973).



Hydrates of other metal salts of phenoxyacetate have been determined. Some, like the sodium salt, are oligomeric, namely the lead (Archer *et al.*, 1996; Mak *et al.*, 1985) magnesium and cobalt salts (Smith *et al.*, 1980), whereas the cadmium (Mak *et al.*, 1985) and copper (Prout *et al.*, 1968) derivatives contain discrete units.

Two structural features were identified in the CO_2^- group in the title compound. First, the distortion of the C15–C10–O1 and C11–C10–O1 *exo*-angles [123.3 (2) and 116.4 (2)°, respectively], which deviate from the trigonal angle (120°). The distortion is caused by the steric requirements of the side chain and is found throughout the phenoxyalkanoic acid series (Kennard *et al.*, 1982; Evans *et al.*, 2001). Secondly, the C–O distances for both C2–O3 and C2–O2 are identical [1.251 (3) Å], and the former of the O3–C2–C3 and O2–

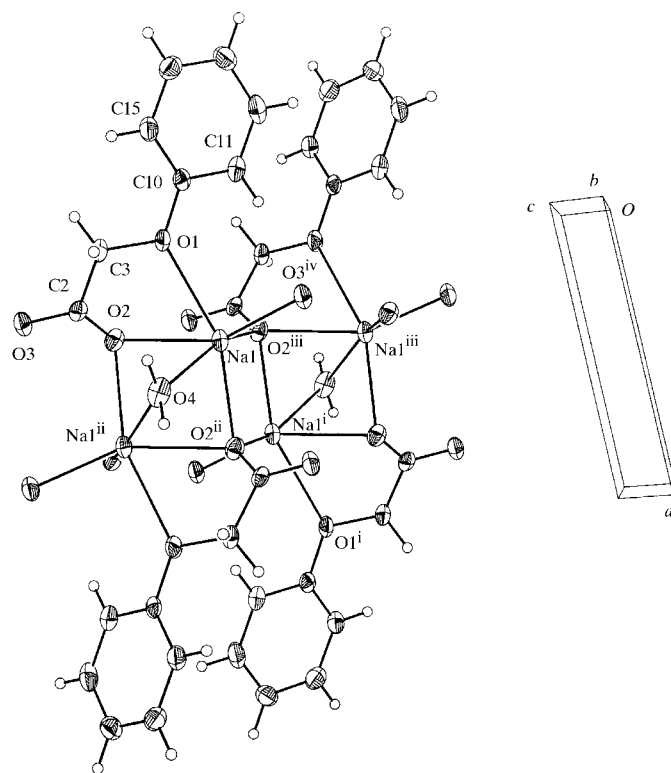


Figure 1

The molecular structure of the title compound viewed down the b axis. The unit cell is superimposed, one-fifth of the original size. Displacement ellipsoids are shown at the 60% probability level. [Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, y, \frac{1}{2} - z$; (iii) $x, -y, z - \frac{1}{2}$; (iv) $x, y, z - 1$.]

C2–C3 angles [113.6 (2) and 119.0 (2) Å] deviates from the trigonal value. In disordered carboxylic acid groups (Leiserowitz, 1976), both bond lengths are also the same, but the O–C–C angles are both close to 120°. In the title compound, the similarity of the C–O distances arises because the CO_2^- group is delocalized. However, the O2 and O3 atoms do not have similar environments, as O3 is involved in a hydrogen bond with water (see Table 2) and O2 is not. In contrast, O2 has many more contacts with sodium ions (see Table 1) as it is orientated into the Na–O core.

Experimental

A sample of powdered sodium hydrogen bis(phenoxyacetate) hydrate (Sigma–Aldrich) was dissolved in Edinburgh tap water and single crystals of sodium phenoxyacetate hemihydrate were obtained by slow evaporation of the aqueous solution.

Crystal data

Na⁺·C₈H₇O₃⁻·0.5H₂O
M_r = 183.13
 Monoclinic, *C2/c*
a = 34.149 (11) Å
b = 7.654 (3) Å
c = 6.144 (2) Å
 β = 98.02 (3)°
V = 1590.2 (10) Å³
Z = 8

D_x = 1.530 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 32 reflections
 θ = 5.3–12.3°
 μ = 0.16 mm⁻¹
T = 160 (2) K
 Needle, colourless
 0.74 × 0.26 × 0.05 mm

Data collection

Bruker *P4* diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
*T*_{min} = 0.719, *T*_{max} = 0.792
 1719 measured reflections
 1400 independent reflections
 1127 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.069
 θ_{\max} = 25.0°
h = -40 → 1
k = -9 → 1
l = -7 → 7
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.052
wR(*F*²) = 0.139
S = 1.04
 1400 reflections
 117 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0816P)^2 + 1.4634P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Na1—O1	2.537 (2)	Na1···Na1 ^{iv}	3.454 (2)
Na1—O2 ⁱⁱ	2.335 (2)	Na1···Na1 ⁱⁱ	4.038 (2)
Na1—O2 ⁱⁱⁱ	2.420 (2)	O1—C3	1.431 (3)
Na1—O2	2.459 (2)	O1—C10	1.376 (3)
Na1—O3 ⁱ	2.298 (2)	O2—C2	1.251 (3)
Na1—O4	2.513 (2)	O3—C2	1.251 (3)
Na1···Na1 ⁱⁱⁱ	3.179 (2)		
O1—Na1—O2	64.04 (7)	O2—Na1—O3 ⁱ	151.19 (7)
O1—Na1—O2 ⁱⁱ	103.40 (7)	O2 ⁱⁱ —Na1—O3 ⁱ	96.08 (7)
O1—Na1—O2 ⁱⁱⁱ	157.84 (7)	O2 ⁱⁱⁱ —Na1—O3 ⁱ	110.87 (7)
O1—Na1—O3 ⁱ	87.83 (7)	O2—Na1—O4	73.01 (7)
O1—Na1—O4	91.01 (6)	O2 ⁱⁱ —Na1—O4	156.46 (7)
O2—Na1—O2 ⁱⁱ	96.45 (7)	O2 ⁱⁱⁱ —Na1—O4	73.67 (7)
O2—Na1—O2 ⁱⁱⁱ	95.65 (7)	O3 ⁱ —Na1—O4	103.07 (7)
O2 ⁱⁱ —Na1—O2 ⁱⁱⁱ	86.86 (7)		

Symmetry codes: (i) *x*, *y*, *z* - 1; (ii) *x*, -*y*, *z* - ½; (iii) 1 - *x*, *y*, ½ - *z*; (iv) 1 - *x*, -*y*, -*z*.

The water H atoms were located in the difference map and their coordinates were freely refined, but their displacement parameters

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O4—H4···O3 ⁱ	0.85 (3)	2.00 (3)	2.809 (3)	157 (3)

Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*.

were treated as riding on oxygen (1.2*U*_{eq} of the bound atom). H atoms bonded to C atoms were treated as riding, with C—H distances in the range 0.95–0.99 Å.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank the EPSRC for a CASE award in collaboration with A. H. Marks Ltd (JE) and gratefully acknowledge G. Thomson for her comments and suggestions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1176). Services for accessing these data are described at the back of the journal.

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