

H atoms were included with isotropic displacement parameters.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Christou, V., Wuller, S. P. & Arnold, J. (1993). *J. Am. Chem. Soc.* **115**, 10545–10548.
- Du Mont, W. W., Lange, L., Karsch, H. H., Peters, E. M. & von Schnering, H. G. (1987). *Chem. Ber.* **121**, 11–13.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MOLLEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Fenske, D. & Grissinger, A. Z. (1990). *Z. Naturforsch. Teil B*, **45**, 1309–1313.
- Huffman, J. C., Stone, J. G., Krussel, W. C. & Caulton, K. G. (1977). *J. Am. Chem. Soc.* **99**, 5829–5830.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Sheldrick, G. M. (1976). *SHELXS76. Program for Crystal Structure Determination*. University of Göttingen, Germany.

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## Sodium Cholate Methanolate and Sodium Cholate 2-Propanolate

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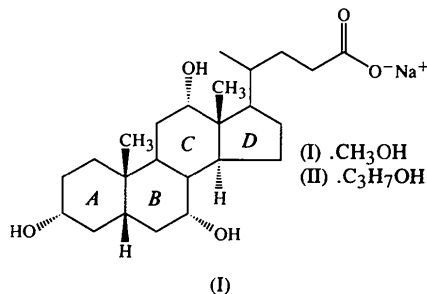
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### Abstract

The crystal structures of sodium cholate methanolate (sodium  $3\alpha,7\alpha,12\alpha$ -trihydroxy- $5\beta$ -cholan-24-oate methanol solvate,  $\text{Na}^+\cdot\text{C}_{24}\text{H}_{39}\text{O}_5^-\cdot\text{CH}_4\text{O}$ ) recrystallized from absolute methanol by diffusion of acetone, and sodium cholate 2-propanolate (sodium  $3\alpha,7\alpha,12\alpha$ -trihydroxy- $5\beta$ -cholan-24-oate 2-propanol solvate,  $\text{Na}^+\cdot\text{C}_{24}\text{H}_{39}\text{O}_5^-\cdot\text{C}_3\text{H}_8\text{O}$ ), recrystallized from 2-propanol by diffusion of acetone, have been determined. These are the second and third reported sodium cholate structures solely solvated by an organic molecule.

### Comment

Our research into methyl rotation in solid-state pseudopolymorphs led us to a number of compounds containing multiple methyl groups, including the two bile acids, cholic acid ( $3\alpha,7\alpha,12\alpha$ -trihydroxy- $5\beta$ -cholan-24-oic acid) and deoxycholic acid ( $3\alpha,12\alpha$ -dihydroxy- $5\beta$ -cholan-24-oic acid). Many solvated structures have been reported for both cholic acid (Lessinger, 1982; Lessinger & Low, 1993; Miki *et al.*, 1988; Miki, Kasai, Shibakami, Takemoto & Miyata, 1991; Nakano, Sada & Miyata, 1994; Caira, Nassimbeni & Scott, 1993, 1994*a,b*; Shibakami & Sekiya, 1994; Scott, 1995) and deoxycholic acid (Giglio, 1984). Of special note are the isostructural forms of cholic acid when solvated with methanol, ethanol and 1-propanol (Johnson & Schaefer, 1972; Jones & Nassimbeni, 1990). However, less attention has been given to cholic acid salt complexes. Until now, only four cholic acid salt structures have been reported in the literature, one with calcium (Hogan, Ealick, Bugg & Barnes, 1984), the other three with sodium (Norton & Haner, 1965; Cobbleddick & Einstein, 1980; Wahle, Stowell & Byrn, 1996). One of the sodium salts is reported to be anhydrous, while another sodium salt and the calcium salt are both hydrated structures. The third sodium salt is solvated with ethanol. We have previously reported (Wahle, Stowell & Byrn, 1996) that a search of the Cambridge Structural Database (Allen *et al.*, 1979) revealed only five sodium salt steroid complexes. Four of these sodium salts are hydrates and the fifth is an acetone/water solvate. Recently, we reported the first cholic acid salt structure solvated solely with an organic molecule (Wahle, Stowell & Byrn, 1996). Here we continue our examination of sodium cholate structures solvated solely with organic molecules by reporting two new solvates, namely, sodium cholate methanolate (NACAMEOH), (I), and sodium cholate 2-propanolate (NACA2PROH), (II).



*ORTEPII* (Johnson, 1976) diagrams of the cholate salt structures of (I) and (II) are given in Figs. 1 and 2, respectively. The rings in (I) have a geometry similar to the other cholic acid structures reported to date, with a *cis* ring junction for the *A/B* rings and *trans* ring junctions for the *B/C* and *C/D* rings. When the methanol-solvated and ethanol-solvated sodium salts are overlaid using a least-squares fit, the *A*, *B* and *C*

rings are quite similar, whereas the *D* ring and the side chains deviate slightly from one another. Even though the structures employ the same herringbone packing pattern, they are not isostructural; the *c* axis of the

methanol-solvated structure is 2 Å shorter than the *c* axis of the ethanol-solvated structure. We suspect that this difference in cell length is due to the smaller size of the methanol molecule compared with the ethanol molecule. The sodium cholate methanolate, sodium cholate ethanolate and sodium cholate 2-propanolate packing diagrams drawn using *QUANTA4.0* (Molecular Simulations Incorporated, 1994) are shown in Fig. 3.

In previous structures, the alcohol solvent molecule was often disordered (Jones & Nassimbeni, 1990; Wahle, Stowell & Byrn, 1996). Unlike the ethanol molecule in sodium cholate ethanolate, however, the methanol molecule is not disordered in (I). Hydrogen bonding between the methanol molecule, the hydroxyl O7 and O12 atoms, and the carboxylate O24 atom holds the methanol molecule in a cavity, while additional hydrogen bonding occurs between the hydroxyl O3 atom and the carboxylate O24 atom in the tail portion of the molecule (Fig. 4 and Table 3). All of the O...O distances fall within the normally accepted range for hydrogen bonds.

The  $\text{Na}^+$  atom in (I) has trigonal bipyramidal coordination involving five different O atoms from four different cholate molecules. These distances range from 2.284 (5) to 2.566 (5) Å (Table 2). Two of the coordinated O atoms are hydroxyl O3 and O7 atoms, while the other three are carboxylate O atoms, O24 and O25 from one cholate molecule and O25 from a second cholate molecule. While the geometry around the  $\text{Na}^+$  atom is not octahedral, a pentacoordinated  $\text{Na}^+$  atom was also found previously in the structures of sodium cholate monohydrate (Cobbledick & Einstein, 1980) and sodium cholate ethanolate (Wahle, Stowell & Byrn, 1996). The carboxylate O25 atom is not found to participate in

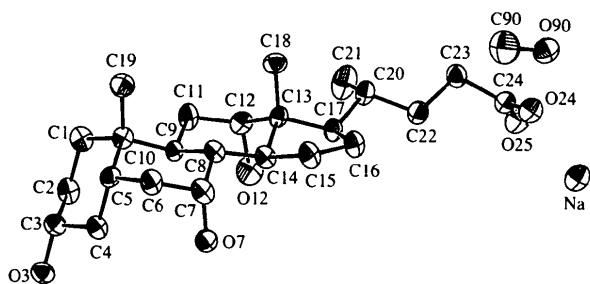


Fig. 1. ORTEP (Johnson, 1976) diagram of (I) (drawn to scale with Fig. 2) showing 50% probability displacement ellipsoids for the non-H atoms. The  $\text{Na}^+$  ion and methanol solvate molecule are also included.

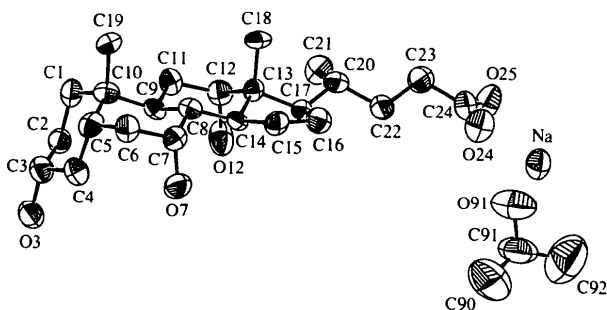


Fig. 2. ORTEP (Johnson, 1976) diagram of (II) (drawn to scale with Fig. 1) showing 50% probability displacement ellipsoids for the non-H atoms. The  $\text{Na}^+$  ion and 2-propanol solvate molecule are also included.

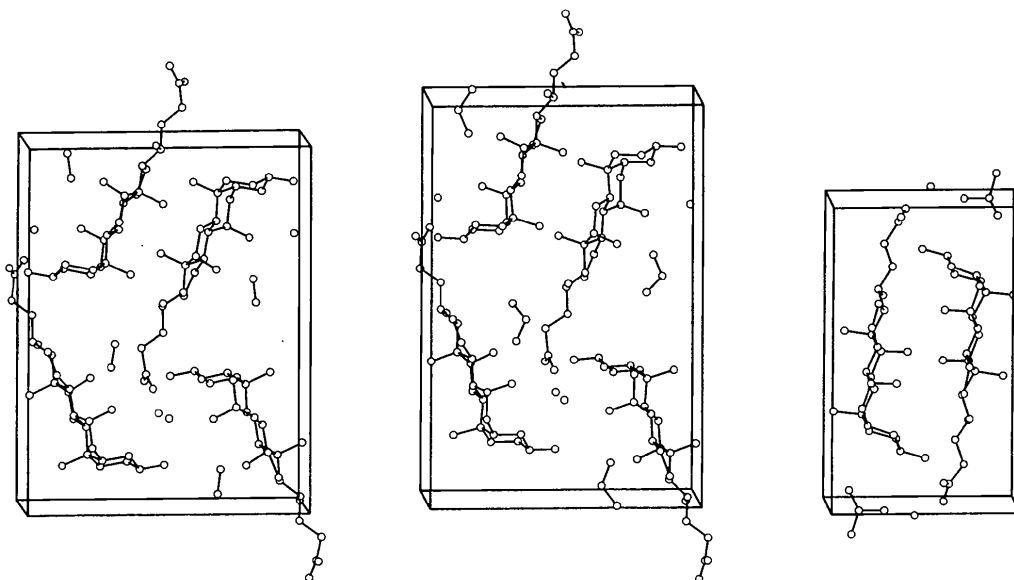


Fig. 3. Packing diagrams for the three alcohol solvates of sodium cholate. Sodium cholate methanolate (left) and sodium cholate ethanolate (Wahle, Stowell & Byrn, 1996) are viewed down the *a* axis, while sodium cholate 2-propanolate (right) is viewed down the *b* axis.

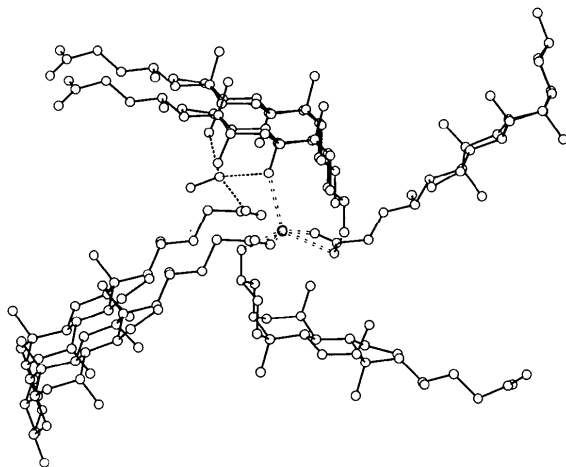


Fig. 4. Hydrogen-bonding scheme for (I). Hydrogen bonds are represented by single dashed lines and  $\text{Na}^+$  ion coordination by double dashed lines, while the  $\text{Na}^+$  ion is represented by a dark circle.

hydrogen bonding since it coordinates to two different sodium ions, whereas the carboxylate O24 atom only coordinates one  $\text{Na}^+$  ion while hydrogen bonding with the hydroxyl O3 atom.

The rings in sodium cholate 2-propanolate, (II), have a geometry similar to the other cholic acid structures reported to date, with a *cis* ring juncture for the *A/B* rings and *trans* ring junctures for the *B/C* and *C/D* rings (Fig. 2). When the 2-propanol-solvated and ethanol-solvated sodium salts are overlaid using a least-squares fit, the *B* and *C* rings are quite similar, whereas the *A* and *D* rings and the side chains deviate slightly from one another. Unlike sodium cholate ethanolate and sodium cholate methanolate, the 2-propanol-solvated structure has a layered packing pattern, similar to the layered packing pattern found in sodium cholate monohydrate (Cobbledick & Einstein, 1980). The 2-propanol molecule sits in a solvent tunnel that runs parallel to the *b* axis. The sodium cholate 2-propanolate packing diagram drawn using *QUANTA4.0* (Molecular Simulations Incorporated, 1994) is shown in Fig. 3.

As is the case with the methanol molecule in (I), the 2-propanol molecule is not disordered. Hydrogen bonding between the 2-propanol molecule and the carboxylate O24 atom holds the 2-propanol molecule in a cavity, while additional hydrogen bonding occurs between the hydroxyl O3 and the carboxylate O24 atoms in the tail portion of the molecule, and between the hydroxyl O12 and O7 atoms (Fig. 5 and Table 6). All of the  $\text{O}\cdots\text{O}$  distances fall within the normally accepted range for hydrogen bonds.

The  $\text{Na}^+$  atom in (II) has a trigonal bipyramidal coordination involving five different O atoms from three different cholate molecules and one 2-propanol molecule. These distances range from 2.234 (8) to

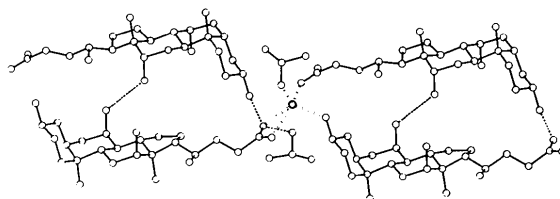


Fig. 5. Hydrogen-bonding scheme for (II). Hydrogen bonds are represented by single dashed lines and  $\text{Na}^+$  ion coordination by double dashed lines, while the  $\text{Na}^+$  ion is represented by a dark circle.

2.448 (8) Å (Table 5). Two of the coordinated O atoms are hydroxyl O3 and O91 atoms, while the other three are the carboxylate O24 and O25 atoms from one cholate molecule and O25 from a second cholate molecule. The geometry around the  $\text{Na}^+$  atom is similar to the geometry found previously in sodium cholate structures. The carboxylate O25 atom is not found to participate in hydrogen bonding since it coordinates to two different  $\text{Na}^+$  ions, whereas the carboxylate O24 atom only coordinates one  $\text{Na}^+$  ion while hydrogen bonding with the hydroxyl O3 atom. The C—C bond lengths for the sodium cholate anion average 1.533 (12) Å, while the C—C bond lengths for the 2-propanol molecule average 1.39 (2) Å. The shorter C—C bond lengths in the 2-propanol molecule are most likely a result of its large thermal motion.

## Experimental

Sodium cholate methanolate was prepared by recrystallization of sodium cholate (Sigma Chemical Co., St. Louis, MO, USA) from absolute methanol (EM Science, Gibbstown, NJ, USA) by diffusion of acetone (Mallinckrodt Specialty Chemicals Co., Paris, KY, USA). Sodium cholate 2-propanolate was prepared by recrystallization of sodium cholate from 2-propanol (Fisher Chemical, Fair Lawn, NJ, USA) by diffusion of acetone.

### Compound (I)

#### Crystal data

$\text{Na}^+ \cdot \text{C}_{24}\text{H}_{39}\text{O}_5^- \cdot \text{CH}_4\text{O}$   
 $M_r = 462.61$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 7.793 (6) \text{ \AA}$   
 $b = 15.720 (9) \text{ \AA}$   
 $c = 20.514 (12) \text{ \AA}$   
 $V = 2513 (5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.223 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 11\text{--}21^\circ$   
 $\mu = 0.093 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 Block  
 $0.70 \times 0.70 \times 0.50 \text{ mm}$   
 Colorless

#### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\theta/2\theta$  scans

$\theta_{\text{max}} = 26.05^\circ$   
 $h = 0 \rightarrow 8$   
 $k = 0 \rightarrow 19$

Absorption correction: none  
 2555 measured reflections  
 2531 independent reflections  
 1967 observed reflections  
 $[I > 2\sigma(I)]$

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.068$   
 $wR(F^2) = 0.156$   
 $S = 1.045$   
 2530 reflections  
 296 parameters  
 H atoms riding  
 $w = 1/[\sigma^2(F_o^2) + (0.0745P)^2 + 5.2593P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$l = 0 \rightarrow 25$   
 3 standard reflections  
 frequency: 83 min  
 intensity decay: 7.9%

$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL93* (Sheldrick, 1993)

Extinction coefficient: 0.0021 (5)

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (I)

	x	y	z	$U_{\text{eq}}$
Na	0.2839 (3)	0.2792 (2)	-0.01891 (12)	0.0429 (8)
O3	0.5674 (6)	0.7314 (3)	0.6101 (2)	0.0373 (10)
O7	0.1714 (6)	0.5600 (3)	0.4745 (2)	0.0410 (12)
O12	0.6391 (6)	0.4628 (3)	0.3676 (2)	0.0503 (15)
O24	0.2507 (5)	0.1884 (3)	0.0843 (2)	0.0400 (12)
O25	0.5047 (6)	0.2308 (3)	0.0518 (2)	0.0480 (12)
O90	0.0581 (7)	0.0639 (3)	0.1285 (2)	0.0460 (15)
C1	0.6627 (8)	0.4971 (4)	0.6092 (3)	0.0353 (15)
C2	0.6917 (8)	0.5921 (4)	0.5953 (3)	0.0357 (17)
C3	0.5437 (8)	0.6426 (4)	0.6225 (3)	0.0340 (17)
C4	0.3782 (8)	0.6110 (4)	0.5932 (3)	0.0323 (15)
C5	0.3432 (8)	0.5175 (4)	0.6075 (3)	0.0323 (15)
C6	0.1683 (8)	0.4900 (4)	0.5801 (3)	0.0397 (18)
C7	0.1646 (8)	0.4789 (4)	0.5062 (3)	0.0363 (17)
C8	0.3104 (8)	0.4196 (4)	0.4843 (3)	0.0297 (15)
C9	0.4881 (7)	0.4549 (4)	0.5075 (3)	0.0250 (15)
C10	0.4921 (7)	0.4599 (4)	0.5836 (3)	0.0297 (15)
C11	0.6392 (8)	0.4048 (4)	0.4790 (3)	0.0373 (17)
C12	0.6281 (8)	0.3874 (4)	0.4056 (3)	0.0330 (15)
C13	0.4562 (7)	0.3437 (4)	0.3885 (3)	0.0280 (15)
C14	0.3120 (7)	0.4040 (4)	0.4117 (3)	0.0297 (15)
C15	0.1505 (8)	0.3644 (4)	0.3815 (3)	0.0390 (18)
C16	0.2113 (8)	0.3292 (4)	0.3151 (3)	0.0373 (17)
C17	0.4129 (8)	0.3344 (4)	0.3150 (3)	0.0300 (15)
C18	0.4518 (9)	0.2555 (4)	0.4217 (3)	0.0370 (17)
C19	0.4751 (10)	0.3714 (4)	0.6147 (3)	0.0430 (17)
C20	0.4981 (8)	0.2636 (4)	0.2751 (3)	0.0343 (17)
C21	0.6952 (9)	0.2739 (6)	0.2737 (4)	0.062 (3)
C22	0.4279 (9)	0.2641 (4)	0.2054 (3)	0.0367 (18)
C23	0.4792 (9)	0.1879 (4)	0.1625 (3)	0.0377 (17)
C24	0.4097 (8)	0.2016 (4)	0.0947 (3)	0.0320 (17)
C90	0.0154 (13)	0.0759 (6)	0.1947 (4)	0.070 (3)

Table 2. Na<sup>+</sup> ion geometry ( $\text{\AA}$ , °) for (I)

Na...O3 <sup>i</sup>	2.325 (5)	Na...O25	2.376 (5)
Na...O7 <sup>ii</sup>	2.555 (6)	Na...O25 <sup>iii</sup>	2.284 (5)
Na...O24	2.566 (5)		
O3 <sup>i</sup> ...Na...O7 <sup>ii</sup>	102.07 (18)	O7 <sup>ii</sup> ...Na...O25	104.50 (18)
O3 <sup>i</sup> ...Na...O24	122.29 (19)	O7 <sup>ii</sup> ...Na...O25 <sup>iii</sup>	100.51 (19)
O3 <sup>i</sup> ...Na...O25	91.53 (18)	O24...Na...O25	52.50 (15)
O3 <sup>i</sup> ...Na...O25 <sup>iii</sup>	102.41 (18)	O24...Na...O25 <sup>iii</sup>	96.28 (17)
O7 <sup>ii</sup> ...Na...O24	127.41 (17)	O25...Na...O25 <sup>iii</sup>	148.1 (2)

Symmetry codes: (i)  $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (ii)  $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$ ; (iii)  $x - \frac{1}{2}, \frac{1}{2} - y, -z$ .

Table 3. Hydrogen-bonding distances ( $\text{\AA}$ ) for (I)

O12...O90 <sup>i</sup>	2.846 (7)	O90...O24	2.628 (7)
O7...O90 <sup>ii</sup>	2.769 (6)	O3...O24 <sup>iii</sup>	2.831 (6)

Symmetry codes: (i)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $\frac{1}{2} - x, 1 - y, z + \frac{1}{2}$ .

## Compound (II)

## Crystal data

Na<sup>+</sup>.C<sub>24</sub>H<sub>39</sub>O<sub>5</sub><sup>-</sup>.C<sub>3</sub>H<sub>8</sub>O  
 $M_r = 490.66$   
 Monoclinic  
 $P2_1$   
 $a = 10.466 (2) \text{ \AA}$   
 $b = 7.6364 (19) \text{ \AA}$   
 $c = 17.197 (2) \text{ \AA}$   
 $\beta = 90.370 (12)^\circ$   
 $V = 1374.4 (8) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.19 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Cu K $\alpha$  radiation  
 $\lambda = 1.54184 \text{ \AA}$   
 Cell parameters from 23 reflections  
 $\theta = 17-42^\circ$   
 $\mu = 0.759 \text{ mm}^{-1}$   
 $T = 295 \text{ K}$   
 Needle  
 $0.30 \times 0.08 \times 0.05 \text{ mm}$   
 Colorless

## Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: none  
 2803 measured reflections  
 2710 independent reflections  
 1123 observed reflections  
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.031$   
 $\theta_{\text{max}} = 68.13^\circ$   
 $h = -12 \rightarrow 12$   
 $k = 0 \rightarrow 9$   
 $l = 0 \rightarrow 20$   
 3 standard reflections  
 frequency: 83 min  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.063$   
 $wR(F^2) = 0.205$   
 $S = 1.088$   
 2710 reflections  
 317 parameters  
 H atoms riding  
 $w = 1/[\sigma^2(F_o^2) + (0.0702P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.068$   
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient: 0.0020 (6)  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (II)

	x	y	z	$U_{\text{eq}}$
Na	0.4525 (4)	1.3023 (6)	0.5221 (2)	0.0716 (14)
O3	0.4771 (6)	1.1605 (10)	-0.3547 (4)	0.068 (2)
O7	0.6149 (6)	1.5435 (10)	-0.1335 (3)	0.068 (2)
O12	0.5825 (6)	1.0186 (12)	-0.0004 (3)	0.081 (3)
O24	0.6077 (7)	1.3525 (11)	0.4199 (4)	0.074 (3)
O25	0.5952 (7)	1.0861 (11)	0.4635 (4)	0.084 (3)
O91	0.2834 (7)	1.1108 (14)	0.4933 (8)	0.126 (4)
C1	0.7817 (9)	1.0137 (14)	-0.2564 (5)	0.058 (3)
C2	0.6396 (9)	1.0025 (12)	-0.2809 (5)	0.053 (3)
C3	0.6091 (8)	1.1623 (14)	-0.3314 (5)	0.056 (3)
C4	0.6376 (8)	1.3276 (14)	-0.2876 (5)	0.054 (3)
C5	0.7748 (8)	1.3391 (15)	-0.2574 (5)	0.053 (3)
C6	0.7993 (10)	1.5100 (13)	-0.2115 (5)	0.058 (3)

C7	0.7509 (9)	1.5163 (13)	-0.1301 (5)	0.049 (3)
C8	0.7838 (8)	1.3513 (13)	-0.0835 (5)	0.041 (3)
C9	0.7476 (8)	1.1845 (12)	-0.1288 (5)	0.040 (3)
C10	0.8156 (8)	1.1763 (14)	-0.2107 (5)	0.048 (3)
C11	0.7739 (9)	1.0185 (12)	-0.0815 (5)	0.049 (3)
C12	0.7213 (9)	1.0252 (14)	0.0023 (5)	0.054 (3)
C13	0.7631 (8)	1.1860 (13)	0.0456 (5)	0.043 (3)
C14	0.7252 (8)	1.3463 (13)	-0.0029 (4)	0.039 (3)
C15	0.7481 (9)	1.5032 (12)	0.0507 (5)	0.051 (3)
C16	0.7166 (10)	1.4307 (14)	0.1321 (6)	0.059 (3)
C17	0.6962 (8)	1.2308 (12)	0.1236 (5)	0.044 (3)
C18	0.9099 (6)	1.1803 (15)	0.0599 (5)	0.057 (3)
C19	0.9632 (7)	1.1769 (16)	-0.2007 (5)	0.063 (3)
C20	0.7332 (9)	1.1287 (14)	0.1971 (5)	0.053 (3)
C21	0.7186 (10)	0.9297 (14)	0.1881 (6)	0.067 (4)
C22	0.6575 (8)	1.1928 (15)	0.2676 (5)	0.055 (3)
C23	0.7036 (10)	1.1254 (17)	0.3456 (5)	0.077 (4)
C24	0.6277 (10)	1.1967 (19)	0.4135 (5)	0.063 (4)
C90	0.1001 (18)	1.206 (4)	0.4324 (9)	0.245 (14)
C91	0.1491 (12)	1.122 (3)	0.4936 (8)	0.153 (9)
C92	0.1108 (17)	1.149 (3)	0.5734 (9)	0.193 (10)

Table 5.  $\text{Na}^+$  ion geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II)

$\text{Na} \cdots \text{O3}^{\text{i}}$	2.392 (8)	$\text{Na} \cdots \text{O25}^{\text{ii}}$	2.238 (8)
$\text{Na} \cdots \text{O24}$	2.431 (8)	$\text{Na} \cdots \text{O91}$	2.346 (10)
$\text{Na} \cdots \text{O25}$	2.448 (8)		
$\text{O3}^{\text{i}} \cdots \text{Na} \cdots \text{O24}$	130.0 (3)	$\text{O24} \cdots \text{Na} \cdots \text{O25}^{\text{ii}}$	94.5 (3)
$\text{O3}^{\text{i}} \cdots \text{Na} \cdots \text{O25}$	89.8 (3)	$\text{O24} \cdots \text{Na} \cdots \text{O91}$	116.9 (4)
$\text{O3}^{\text{i}} \cdots \text{Na} \cdots \text{O25}^{\text{ii}}$	111.3 (3)	$\text{O25} \cdots \text{Na} \cdots \text{O25}^{\text{ii}}$	146.7 (3)
$\text{O3}^{\text{i}} \cdots \text{Na} \cdots \text{O91}$	88.9 (4)	$\text{O25} \cdots \text{Na} \cdots \text{O91}$	87.4 (3)
$\text{O24} \cdots \text{Na} \cdots \text{O25}$	52.9 (3)	$\text{O25}^{\text{ii}} \cdots \text{Na} \cdots \text{O91}$	117.3 (3)

Symmetry codes: (i)  $x, y, 1+z$ ; (ii)  $1-x, \frac{1}{2}+y, 1-z$ .Table 6. Hydrogen-bonding distances ( $\text{\AA}$ ) for (II)

$\text{O3} \cdots \text{O24}^{\text{i}}$	2.750 (11)	$\text{O7} \cdots \text{O12}^{\text{iii}}$	3.109 (8)
$\text{O24} \cdots \text{O91}^{\text{ii}}$	2.720 (14)		

Symmetry codes: (i)  $1-x, y, -\frac{1}{2}, -z$ ; (ii)  $1-x, y, \frac{1}{2}, 1-z$ ; (iii)  $1-x, \frac{1}{2}+y, -z$ .

For both compounds, data collection: *CAD-4 Operations Manual* (Enraf-Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985) for (I); *SIR92* (Altomare *et al.*, 1994) for (II). For both compounds, program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *MolEN CIF VAX*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1236). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* **B35**, 2331–2339.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.
- Caira, M. R., Nassimbeni, L. R. & Scott, J. L. (1993). *J. Chem. Soc. Chem. Commun.* pp. 612–614.
- Caira, M. R., Nassimbeni, L. R. & Scott, J. L. (1994a). *J. Chem. Soc. Perkin Trans. 2*, pp. 623–628.
- Caira, M. R., Nassimbeni, L. R. & Scott, J. L. (1994b). *J. Chem. Crystallogr.* **24**, 783–791.
- Cobbleddick, R. E. & Einstein, F. W. B. (1980). *Acta Cryst.* **B36**, 287–292.
- Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Giglio, E. (1984). *Inclusion Compounds*, Vol. 2, edited by J. L. Atwood, J. E. D. Davies & D. D. MacNicol, pp. 207–229. London: Academic Press.
- Hogan, A., Ealick, S. E., Bugg, C. E. & Barnes, S. (1984). *J. Lipid Res.* **25**, 791–798.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Johnson, P. L. & Schaefer, J. P. (1972). *Acta Cryst.* **B28**, 3083–3088.
- Jones, E. L. & Nassimbeni, L. R. (1990). *Acta Cryst.* **B46**, 399–405.
- Lessinger, L. (1982). *Cryst. Struct. Commun.* **11**, 1787–1792.
- Lessinger, L. & Low, B. W. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 85–99.
- Miki, K., Kasai, N., Shibakami, M., Takemoto, K. & Miyata, M. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1757–1759.
- Miki, K., Masui, A., Kasai, N., Miyata, M., Shibakami, M. & Takemoto, K. (1988). *J. Am. Chem. Soc.* **110**, 6594–6596.
- Molecular Simulations Incorporated (1994). *QUANTA4.0*. Molecular Simulations Inc., Burlington, USA.
- Nakano, K., Sada, K. & Miyata, M. (1994). *Chem. Lett.* pp. 137–140.
- Norton, D. A. & Haner, B. (1965). *Acta Cryst.* **19**, 477–478.
- Scott, J. L. (1995). *J. Chem. Soc. Perkin Trans. 2*, pp. 495–502.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Shibakami, M. & Sekiya, A. (1994). *J. Chem. Soc. Chem. Commun.* pp. 429–430.
- Wahle, M. C., Stowell, J. G. & Byrn, S. R. (1996). *Acta Cryst.* **C52**, 325–328.