

between the complex and the order-disorder variation of the ethanol molecule through hydrogen bonds seem to cause the cooperative nature of this spin phase transition.

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The Structure of Sodium 3 α ,7 α ,12 α -Trihydroxy-5 β -cholan-24-oate Monohydrate (Sodium Cholate Monohydrate)

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Abstract

The structure of sodium cholate monohydrate, C₂₄H₃₉O₅·Na⁺·H₂O, has been determined with three-dimensional X-ray diffractometer data and refined by full-matrix least-squares calculations to a final *R* of 0.059 for 1579 observed reflexions. The crystals are mono-

clinic with space group *P2*₁, *Z* = 2, and unit-cell dimensions *a* = 12.197 (7), *b* = 8.214 (4), *c* = 12.559 (7) Å, β = 108.07 (4)°. The cholate ions are hydrogen bonded to form spirals parallel to the *b* axis and further hydrogen bonded across the ends of molecules to give a sandwich sheet structure. The Na ions and the disordered water molecules lie within the polar interior of the sandwich and are involved in ionic and hydrogen bonding. Each Na ion is in contact with five O atoms [Na···O ranging from 2.344 (5)–2.509 (5) Å].

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Introduction

The bile acids, which are steroids of biological interest (Fieser & Fieser, 1959), have been the subject of recent structural studies. As yet, no structural studies of their salts have been reported. Apart from the biological aspect, the bile acid salts are of interest for their reported high-temperature superconductivity (Wolf, 1976). Studies on the Na salts of 3 α ,7 α ,12 α -trihydroxy-5 β -cholan-24-oic acid (cholic acid), 3 α ,12 α -dihydroxy-5 β -cholan-24-oic acid (deoxycholic acid) and 3 α -hydroxy-5 β -cholan-24-oic acid (lithocholic acid) led to their classification as fractional or type III superconductors (Wolf, 1976; Wolf & Halpern, 1976). Commercial powdered samples of the above three acid salts were obtained from Steraloids, Inc., and crystals were obtained from a number of organic solvents. In several cases the salts formed complexes with the solvent. This property is common for neutral bile acids which form canal complexes with a large range of organic compounds. Crystal structures of a few of the complexes have been described (Johnson & Schaefer, 1972; Craven & DeTitta, 1972; Candeloro De Sanctis, Giglio, Pavel & Quagliata, 1972; Candeloro De Sanctis, Coiro, Giglio, Pagliuca, Pavel & Quagliata, 1978). Sodium cholate yielded the best quality crystals and was chosen for full structural investigation.

Experimental

Colourless acicular crystals of sodium cholate were obtained by slow evaporation from a solution in dimethylformamide. Cell dimensions were obtained by a least-squares fit to the setting angles of 11 reflexions ($2\theta > 25^\circ$) measured on a Picker FACS-I four-circle diffractometer. Crystal data are listed in Table 1. The

Table 1. *Crystal data*

| | | |
|---|---|---|
| | C ₂₄ H ₃₉ O ₅ ·Na ⁺ ·H ₂ O | C ₂₄ H ₃₉ O ₅ ·Na ⁺ * |
| FW | 448.58 | 430.57 |
| Space group | <i>P</i> 2 ₁ | <i>P</i> 2 ₁ |
| <i>a</i> (Å) | 12.197 (7) | 12.196 (8) |
| <i>b</i> (Å) | 8.214 (4) | 8.215 (8) |
| <i>c</i> (Å) | 12.559 (7) | 12.593 (8) |
| β (°) | 108.07 (4) | 107.86 |
| <i>V</i> (Å ³) | 1196.2 | 1201 |
| <i>Z</i> | 2 | 2 |
| <i>D</i> _{meas} (Mg m ⁻³)† | 1.22 | 1.167 |
| <i>D</i> _{calc} (Mg m ⁻³) | 1.245 | 1.191 |
| λ (Mo <i>K</i> α ₁) | 0.70926 Å | |
| μ (Mo <i>K</i> α ₁) | 0.110 mm ⁻¹ | |
| Crystal size | 0.35 × 0.45 × 0.35 mm | |

* Reported values for the anhydrous bile acid salt (Norton & Haner, 1965). The *a* and *c* values are interchanged.

† We were unable to determine an accurate value from one crystal since it dissolved and we had no other suitable crystals of that size.

unit-cell volume is ~ 5 Å³ smaller than the previously reported value for the supposedly anhydrous bile acid salt crystallized from acetone (Norton & Haner, 1965).

Intensities were collected on the diffractometer, using Mo *K* α radiation from a graphite monochromator. A θ - 2θ scan was employed with a scan rate of 2° min⁻¹. The scan width was 1.4° with an increment to allow for dispersion. Background counts were measured for 20 s at each side of the reflexions. Two standard reflexions were monitored every 50 measurements and no significant variation was observed. 1711 independent reflexions were measured out to $2\theta = 45^\circ$, but only the 1579 reflexions with $I > 2.3\sigma(I)$ were used in the structure refinement, where $\sigma(I) = [S + (t_s/t_b)^2 B + (0.003I^2)]^{1/2}$ with *S* the total scan count, *B* the total background count, *t_s* and *t_b* the scan and background count times, respectively, and *I* the net intensity. Lorentz and polarization factors were applied to the intensities. No correction was made for absorption.

Structure solution and refinement

The structure was solved using the computer program *MULTAN* (Germain, Main & Woolfson, 1970). The 239 reflexions with *E* values greater than 1.39 were used. After several unsuccessful attempts, allowing the program to select reflexions to fix the cell origin and enantiomorph and to choose two, three or four other reflexions in the starting set, three reflexions were input with 'known' phases (based on weak \sum_1 indications). The data set with the lowest values for the figures of merit RESID and PSI ZERO led to solution of the structure. An *E* map, calculated using the phases from this set, gave the positions of all thirty non-hydrogen atoms (excluding the disordered water molecule).

The structure was refined by full-matrix least squares, initially using isotropic temperature parameters and unit weights. A difference map indicated the presence of a disordered water molecule, occupying equally one of two positions approximately 1 Å apart. Positional and temperature parameters of each atom were allowed to refine. Further cycles of refinement were carried out using anisotropic temperature factors (except for the disordered O atom). All H atoms, apart from those of the H₂O, were located on difference maps but were not allowed to refine. The final *R* ($= \sum |F_o| - |F_c| / \sum |F_o|$) was 0.059 for the observed reflexions with a maximum shift of 0.14 σ on the last cycle of refinement. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ and $\sin \theta/\lambda$ showed that the weighting scheme $w = 1/(\sigma F_o)^2$ was satisfactory. No peaks or troughs on the final difference map were greater than 3 σ above background ($\sigma = 0.08$ e Å⁻³). The largest peaks (0.17–0.21 e Å⁻³) were in the neighbourhood of the disordered water molecule.

Table 2. Final fractional atomic coordinates ($\times 10^4$) and standard deviations (in parentheses)

| | x | y | z |
|-------|-----------|------------|-----------|
| Na | 360 (2) | 8151 | 1872 (2) |
| O(1) | 1186 (4) | 4813 (6) | -1931 (3) |
| O(2) | 2076 (4) | 6358 (6) | 2063 (3) |
| O(3) | 1488 (4) | 514 (6) | 2321 (3) |
| O(4) | 245 (4) | -2075 (6) | 8006 (3) |
| O(5) | -67 (4) | 538 (6) | 7563 (4) |
| O(6A) | 226 (8) | 8839 (14) | 69 (8) |
| O(6B) | 37 (13) | 7533 (20) | 41 (13) |
| C(1) | 3697 (6) | 2569 (8) | -43 (5) |
| C(2) | 2504 (6) | 2829 (9) | -872 (5) |
| C(3) | 2331 (5) | 4620 (9) | -1181 (5) |
| C(4) | 2538 (5) | 5626 (8) | -133 (5) |
| C(5) | 3733 (5) | 5360 (8) | 731 (5) |
| C(6) | 3912 (5) | 6467 (9) | 1759 (5) |
| C(7) | 3236 (5) | 5945 (8) | 2540 (5) |
| C(8) | 3445 (5) | 4114 (8) | 2845 (5) |
| C(9) | 3223 (5) | 3038 (8) | 1797 (5) |
| C(10) | 3962 (5) | 3553 (9) | 1056 (5) |
| C(11) | 3354 (6) | 1229 (8) | 2127 (5) |
| C(12) | 2659 (5) | 662 (8) | 2920 (5) |
| C(13) | 2920 (5) | 1749 (8) | 3954 (5) |
| C(14) | 2710 (5) | 3531 (8) | 3554 (5) |
| C(15) | 2755 (6) | 4500 (9) | 4604 (6) |
| C(16) | 2234 (6) | 3321 (9) | 5276 (5) |
| C(17) | 2081 (5) | 1654 (8) | 4672 (5) |
| C(18) | 4156 (6) | 1472 (10) | 4700 (5) |
| C(19) | 5268 (5) | 3321 (10) | 1664 (6) |
| C(20) | 2162 (6) | 221 (9) | 5466 (6) |
| C(21) | 2060 (13) | -1402 (10) | 4903 (10) |
| C(22) | 1245 (5) | 395 (8) | 6061 (5) |
| C(23) | 1315 (6) | -925 (9) | 6936 (6) |
| C(24) | 425 (5) | -770 (9) | 7541 (5) |

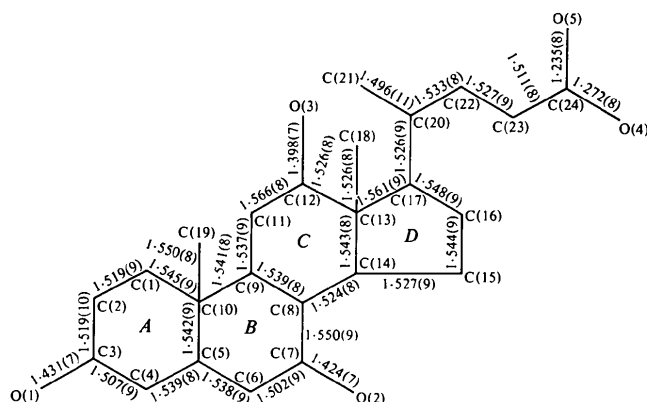
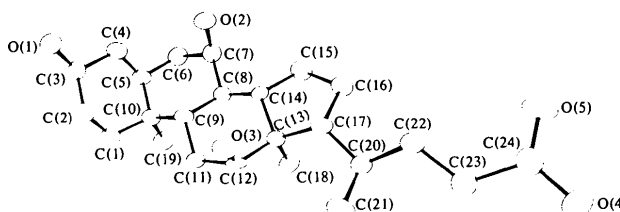
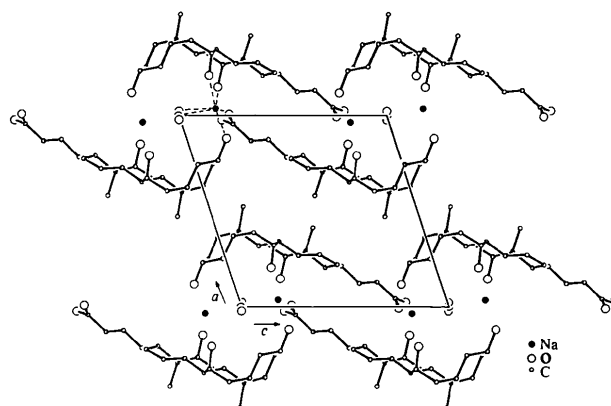


Fig. 1. Bond distances (Å).

Fig. 2. Perspective view of a molecule of the $C_{24}H_{39}O_5^-$ ion drawn by ORTEP (Johnson, 1965).Fig. 3. Molecular packing in a unit cell of $C_{24}H_{39}O_5 \cdot Na^+ \cdot H_2O$.

Scattering factors for the atoms were taken from *International Tables for X-ray Crystallography* (1974). Computer programs used in the structure analysis were those described by Einstein & Jones (1972). Fractional atomic coordinates are given in Table 2.*

Discussion

(a) General description

Bond lengths and the atom labelling are given in Fig. 1 and a perspective view of the cholate ion is shown in Fig. 2. Bond angles are given in Table 3. Fig. 3 shows a packing diagram of the structure. Hydrogen bonding of cholate ions gives continuous two-dimensional sandwich sheets with non-polar exterior surfaces. The Na ions and water molecules occur in the polar interior of

* Lists of structure factors, anisotropic thermal parameters and H atom coordinates and their B values have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34811 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the sandwich with each Na ion bonded to five O atoms. All the O atoms are involved in hydrogen bonding, with each cholate ion bonding to four others and to the disordered water molecule. Both H atoms of the water molecule may be involved in weak hydrogen bonding while the O atom is bonded to the Na ion.

(b) Sodium-ion environment

Each Na ion is in close contact with five O atoms with distances in the range 2.266–2.509 Å. Distances

Table 3. Bond angles ($^{\circ}$)

| | | | |
|------------------|-----------|-------------------|-----------|
| C(2)–C(1)–C(10) | 115.4 (5) | C(11)–C(12)–C(13) | 110.9 (5) |
| C(1)–C(2)–C(3) | 109.8 (5) | C(11)–C(12)–O(3) | 110.4 (5) |
| C(2)–C(3)–C(4) | 109.6 (5) | C(13)–C(12)–O(3) | 114.6 (5) |
| C(2)–C(3)–O(1) | 107.7 (5) | C(12)–C(13)–C(14) | 108.0 (4) |
| C(4)–C(3)–O(1) | 112.2 (5) | C(12)–C(13)–C(17) | 117.5 (5) |
| C(3)–C(4)–C(5) | 113.8 (5) | C(12)–C(13)–C(18) | 109.9 (5) |
| C(4)–C(5)–C(6) | 111.4 (5) | C(17)–C(13)–C(18) | 109.8 (5) |
| C(4)–C(5)–C(10) | 112.2 (5) | C(14)–C(13)–C(18) | 111.9 (5) |
| C(6)–C(5)–C(10) | 112.3 (5) | C(14)–C(13)–C(17) | 99.4 (5) |
| C(5)–C(6)–C(7) | 114.4 (5) | C(13)–C(14)–C(15) | 104.8 (5) |
| C(6)–C(7)–C(8) | 111.9 (5) | C(8)–C(14)–C(15) | 118.1 (5) |
| C(6)–C(7)–O(2) | 109.3 (5) | C(8)–C(14)–C(13) | 114.9 (5) |
| C(8)–C(7)–O(2) | 112.6 (5) | C(14)–C(15)–C(16) | 103.6 (5) |
| C(7)–C(8)–C(9) | 111.9 (5) | C(15)–C(16)–C(17) | 107.1 (5) |
| C(7)–C(8)–C(14) | 112.6 (5) | C(16)–C(17)–C(20) | 112.9 (5) |
| C(9)–C(8)–C(14) | 109.9 (5) | C(16)–C(17)–C(13) | 103.8 (5) |
| C(8)–C(9)–C(10) | 112.2 (5) | C(17)–C(17)–C(20) | 119.6 (5) |
| C(8)–C(9)–C(11) | 110.4 (5) | C(17)–C(20)–C(21) | 113.6 (6) |
| C(10)–C(9)–C(11) | 113.4 (5) | C(17)–C(20)–C(22) | 109.7 (5) |
| C(5)–C(10)–C(9) | 109.4 (5) | C(21)–C(20)–C(22) | 110.3 (6) |
| C(5)–C(10)–C(1) | 107.3 (5) | C(20)–C(22)–C(23) | 113.4 (5) |
| C(5)–C(10)–C(19) | 108.8 (5) | C(22)–C(23)–C(24) | 114.4 (6) |
| C(1)–C(10)–C(9) | 113.3 (5) | C(23)–C(24)–O(4) | 114.5 (6) |
| C(1)–C(10)–C(19) | 105.9 (5) | C(23)–C(24)–O(5) | 121.0 (6) |
| C(9)–C(10)–C(19) | 111.9 (5) | O(4)–C(24)–O(5) | 124.6 (5) |
| C(9)–C(11)–C(12) | 115.3 (5) | | |

(c) The water molecule

From the peak heights of an earlier electron density difference map, the water molecule appeared to be disordered between two approximately equal occupancy sites. However, the refined B_{iso} values of 4.6 (2) and 7.5 (3) \AA^2 suggest that this initial indication may be slightly in error. In both positions it is in close contact with the Na ion [$\text{Na}–\text{O}(6A) = 2.29(1)$ and $\text{Na}–\text{O}(6B) = 2.27(2)$ \AA] and hydrogen bonded to the cholate ion *via* carboxylate atom O(4) [$\text{O}(6A)\cdots\text{O}(4) = 2.70(1)$ and $\text{O}(6B)\cdots\text{O}(4) = 2.66(2)$ \AA]. In position *A* there is a longer contact of 3.09 (1) \AA to hydroxyl atom O(3) of the same anion while in position *B* there is one of 3.11 (2) \AA to hydroxyl atom O(3) of a translation-related anion which may indicate weak hydrogen bonds. The distances are near the upper limit for bonding and the H atoms would need to be close to the $\text{O}\cdots\text{O}$ line. The H atoms (site occupancy = 0.5) of the disordered water were not located from difference maps and therefore no conclusion can be made apart from noting that the angles [$\text{O}(4)\cdots\text{O}(6A)\cdots\text{O}(3) = 148$ and $\text{O}(4)\cdots\text{O}(6B)\cdots\text{O}(2) = 100^{\circ}$] do not exclude the possibility of hydrogen bonding of both H's in both positions.

Table 4. Sodium-ion environment

(a) Distances (\AA)

| | | | |
|---|-----------|--|------------|
| $\text{Na}^+\cdots\text{O}(1^{\text{II}})$ | 2.348 (5) | $\text{Na}^+\cdots\text{O}(5^{\text{IV}})$ | 2.323 (5) |
| $\text{Na}^+\cdots\text{O}(2^{\text{I}})$ | 2.509 (5) | $\text{Na}^+\cdots\text{O}(6A^{\text{I}})$ | 2.289 (10) |
| $\text{Na}^+\cdots\text{O}(3^{\text{III}})$ | 2.344 (5) | $\text{Na}^+\cdots\text{O}(6B^{\text{I}})$ | 2.266 (16) |

(b) Angles ($^{\circ}$), e.s.d. = 0.2–0.4 $^{\circ}$

| | | | |
|--|-------|--|-------|
| $\text{O}(1^{\text{II}})\cdots\text{Na}^+\cdots\text{O}(2^{\text{I}})$ | 173.0 | $\text{O}(2^{\text{I}})\cdots\text{Na}^+\cdots\text{O}(6B^{\text{I}})$ | 81.0 |
| $\text{O}(1^{\text{II}})\cdots\text{Na}^+\cdots\text{O}(3^{\text{III}})$ | 85.9 | $\text{O}(3^{\text{III}})\cdots\text{Na}^+\cdots\text{O}(5^{\text{IV}})$ | 145.7 |
| $\text{O}(1^{\text{II}})\cdots\text{Na}^+\cdots\text{O}(5^{\text{IV}})$ | 109.0 | $\text{O}(3^{\text{III}})\cdots\text{Na}^+\cdots\text{O}(6A^{\text{I}})$ | 83.7 |
| $\text{O}(1^{\text{II}})\cdots\text{Na}^+\cdots\text{O}(6A^{\text{I}})$ | 94.3 | $\text{O}(3^{\text{III}})\cdots\text{Na}^+\cdots\text{O}(6B^{\text{I}})$ | 109.5 |
| $\text{O}(1^{\text{II}})\cdots\text{Na}^+\cdots\text{O}(6B^{\text{I}})$ | 105.9 | $\text{O}(5^{\text{IV}})\cdots\text{Na}^+\cdots\text{O}(6A^{\text{I}})$ | 124.0 |
| $\text{O}(2^{\text{I}})\cdots\text{Na}^+\cdots\text{O}(3^{\text{III}})$ | 93.1 | $\text{O}(5^{\text{IV}})\cdots\text{Na}^+\cdots\text{O}(6B^{\text{I}})$ | 96.2 |
| $\text{O}(2^{\text{I}})\cdots\text{Na}^+\cdots\text{O}(5^{\text{IV}})$ | 68.4 | $\text{O}(6A^{\text{I}})\cdots\text{Na}^+\cdots\text{O}(6B^{\text{I}})$ | 27.8 |
| $\text{O}(2^{\text{I}})\cdots\text{Na}^+\cdots\text{O}(6A^{\text{I}})$ | 92.4 | | |

Symmetry code

- (i) x, y, z
 (ii) $-x, \frac{1}{2} + y, -z$
 (iii) $x, 1 + y, z$
 (iv) $-x, \frac{1}{2} + y, 1 - z$

and angles are given in Table 4. There are no other oxygen contacts within 3.8 \AA . With the usual procedures applied (Muettterties, 1974) the geometry around the Na^+ atom did not fall into the square-pyramidal, trigonal-bipyramidal or 'intermediate' geometry. Since the range was relatively large (0.243 \AA) it is not surprising that a regular pattern did not emerge. Although the coordination number of a Na ion is commonly six, five-coordinate examples are known [e.g. in 1-phenylbutane-1,3-dionato(ethyleneglycol)sodium (Bright, Milburn & Truter, 1971)]. The three hydroxyl O atoms from different cholate anions and a carboxylate O from a fourth anion and the disordered water O atom are involved.

(d) The cholate anion

Bond distances (Fig. 1) and angles (Table 3) are in reasonable agreement with those of related cholic acid structures (Hall, Maslen & Cooper, 1974; Johnson & Schaefer, 1972; Arora, Germain & Declercq, 1976; Craven & DeTitta, 1972; Candeloro De Sanctis, Giglio, Pavel & Quagliata, 1978; Schaefer & Reed, 1972).

The rings have the expected geometry with the *A/B* ring juncture *cis* and the *B/C* and *C/D* ring junctures *trans*, with the *A*, *B* and *C* rings in the normal chair conformation. The *D* ring/side chain junction geometry is *trans* to C(13) and *gauche* to C(16). Torsion angles for the rings and side chain are shown in Table 5. For rings *A*, *B* and *C* the values are in good agreement with those for related structures. In the case of ring *D* there are larger differences in the different structures reflecting the flexibility of the cyclopentane ring. The conformation of ring *D* can be described in terms of Δ , the phase angle of pseudorotation, and φ_m , the maximum angle of torsion (Altona, Geise & Romers, 1968). For the cholate ion $\Delta = 14.3^{\circ}$ and $\varphi_m = 46.6^{\circ}$, indicating an intermediate conformation between a half chair and a β envelope. These values are similar to those of 3 α ,6 α -dihydroxy-5 β -cholan-24-oic acid (Hall, Maslen & Cooper, 1974) ($\Delta = 14.3^{\circ}$ and $\varphi_m = 44.8^{\circ}$). Similarly, the side chain of cholic acids has considerable flexibility and its conformation is influenced by hydrogen bonding of the carboxyl group (Giglio & Quagliata, 1975). The torsion angles indicate that the side chain has an all-*trans* conformation similar to those in the

Table 5. Selected torsion angles ($^{\circ}$)

The sign convention of the angles is that of Klyne & Prelog (1960).

| Ring A | | Ring C | | Side chain | |
|----------------------|-----------|-------------------------|-----------|-------------------------|------------|
| C(10)–C(1)–C(2)–C(3) | 58.0 (7) | C(14)–C(8)–C(9)–C(11) | –51.4 (6) | C(13)–C(17)–C(20)–C(21) | –55.4 (9) |
| C(1)–C(2)–C(3)–C(4) | –55.7 (7) | C(8)–C(9)–C(11)–C(12) | 50.7 (7) | C(16)–C(17)–C(20)–C(21) | –177.8 (8) |
| C(2)–C(3)–C(4)–C(5) | 56.3 (7) | C(9)–C(11)–C(12)–C(13) | –52.7 (7) | C(13)–C(17)–C(20)–C(22) | –179.3 (5) |
| C(3)–C(4)–C(5)–C(10) | –55.4 (7) | C(11)–C(12)–C(13)–C(14) | 53.3 (6) | C(16)–C(17)–C(20)–C(22) | 58.2 (7) |
| C(4)–C(5)–C(10)–C(1) | 50.9 (6) | C(12)–C(13)–C(14)–C(8) | –59.5 (6) | C(17)–C(20)–C(22)–C(23) | –175.9 (6) |
| C(5)–C(10)–C(1)–C(2) | –54.5 (7) | C(13)–C(14)–C(8)–C(9) | 58.7 (6) | C(21)–C(20)–C(22)–C(23) | 58.2 (9) |
| | | | | C(20)–C(22)–C(23)–C(24) | 179.5 (6) |
| | | | | C(22)–C(23)–C(24)–O(4) | 159.9 (6) |
| | | | | C(22)–C(23)–C(24)–O(5) | –20.2 (9) |
| Ring B | | Ring D | | | |
| C(10)–C(5)–C(6)–C(7) | –52.2 (7) | C(17)–C(13)–C(14)–C(15) | 46.2 (6) | | |
| C(5)–C(6)–C(7)–C(8) | 49.6 (7) | C(13)–C(14)–C(15)–C(16) | –34.1 (6) | | |
| C(6)–C(7)–C(8)–C(9) | –50.7 (7) | C(14)–C(15)–C(16)–C(17) | 8.1 (7) | | |
| C(7)–C(8)–C(9)–C(10) | 55.2 (6) | C(15)–C(16)–C(17)–C(13) | 20.2 (6) | | |
| C(8)–C(9)–C(10)–C(5) | –56.4 (6) | C(6)–C(17)–C(13)–C(14) | –39.8 (5) | | |
| C(9)–C(10)–C(5)–C(6) | 53.9 (6) | | | | |

Table 6. Hydrogen-bond geometry

| | Distances (Å) | | | Angles ($^{\circ}$) | |
|--|---------------|------|-------|-----------------------|--|
| | O...O | O–H | H...O | O–H...O | |
| O(1 ⁱ)–H(O11)...O(4 ⁱⁱ) | 2.793 (7) | 0.90 | 2.03 | 141 | |
| O(2 ⁱ)–H(O21)...O(5 ⁱⁱⁱ) | 2.719 (6) | 1.10 | 1.67 | 157 | |
| O(3 ⁱ)–H(O31)...O(4 ⁱⁱⁱ) | 2.831 (6) | 0.89 | 1.98 | 160 | |
| O(6A ⁱ)–O(4 ⁱⁱ) | 2.705 (11) | – | – | – | |
| O(6A ⁱ)–O(3 ^{iv}) | 3.092 (11) | – | – | – | |
| O(6B ⁱ)–O(4 ⁱⁱ) | 2.665 (16) | – | – | – | |
| O(6B ⁱ)–O(2 ⁱ) | 3.106 (16) | – | – | – | |

Symmetry code

(i) x, y, z (ii) $x, 1 + y, z - 1$ (iii) $-x, \frac{1}{2} + y, 1 - z$ (iv) $x, 1 + y, z$

structures of deoxycholic acid *p*-bromoanilide (Schaefer & Reed, 1972) and the 1:1 addition compound of cholic acid and ethanol (Johnson & Schaefer, 1972), in spite of the fact that both the carboxylate O atoms are involved in hydrogen bonding. In the acids where both carboxylic O atoms are involved in hydrogen bonding the chair is *gauche* about the C(20)–C(22) bond.

(e) The hydrogen-bonding network

A packing diagram of the structure is shown in Fig. 3. All the O atoms are involved in the hydrogen bonding. Each cholate ion is linked to four others. Screw-related ions are hydrogen bonded to give a continuous zigzag chain along the *b* axis and adjacent chains are hydrogen bonded to give a sandwich sheet structure with a non-polar exterior surface. The Na ions and the disordered water molecules lie within the 'sandwich' in the polar interior. The water molecules are also involved in hydrogen bonding. In both disordered positions there is bonding to the carboxylate atom O(4) making it an acceptor of three hydrogen bonds. The other H atom of the disordered water molecule may also take part in hydrogen bonding to cholate

hydroxyl groups [see (c) above]. Relevant distances and angles for the hydrogen bonding are shown in Table 6. Between the sandwich layers only van der Waals contacts are involved.

It is not possible to relate the above structure to the temperature-related change of conductivity reportedly observed by Wolf (1976). The physical form of the salt is completely different. In Wolf's experiments, preparation of the samples was critical and the absence of water was required to observe superconductivity. Samples with oriented crystallites obtained by micelle formation with water followed by careful desiccation were used. At present it is not known if single crystals of the sodium cholate monohydrate as used in the structure determination exhibit superconductivity. Dr Suso Gyax is conducting experiments to settle this and other related questions.

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The Structure of Tetrachlorotetrakis(diphenyl sulphoxide)thorium(IV)

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Abstract

[Th(C₁₂H₁₀OS)₄Cl₄], C₄₈H₄₀Cl₄O₄S₄Th, crystallizes in the orthorhombic system, space group *Pbcn*, with $a = 17.909$ (2), $b = 13.453$ (1), $c = 19.636$ (2) Å, $Z = 4$. The structure was refined to $R = 0.041$ for 1877 counter reflexions. The Th atom is eight coordinate with dodecahedral geometry, the Cl atoms occupying the dodecahedral *B* sites and the sulphoxide O atoms the *A* sites.

Introduction

Since the original analysis of eight-coordinate geometry was given by Hoard & Silverton (1963), many structures of eight-coordinate complexes have been published. However, few examples containing two different ligands, say $4X$ and $4Y$, giving complexes of the type MX_4Y_4 have been investigated. Calculations (Kepert, 1978) have suggested that the energy equivalence between the dodecahedron and square antiprism may be upset in this case in favour of the dodecahedron where the ligands may be sorted into the two different coordination sites. Complexes of the actinide metals provide examples in which effects such as π bonding, which may also enhance dodecahedral stability (Orgel, 1960), should be small and hence provide a good test of theoretical predictions. Accordingly we have investigated the structure of tetrachlorotetrakis(diphenyl sulphoxide)thorium(IV) to provide further structural information on complexes of this type.

Experimental

The complex was prepared by the method of Alvey, Bagnall, Brown & Edwards (1973) and irregular crystals were obtained from nitromethane. Preliminary photography showed orthorhombic symmetry with systematic absences corresponding to space group *Pbcn*. In addition, reflections with $h + k = 2n + 1$ were systematically weak, consistent with the heavy atom occupying the 4(*c*) special position. Accurate cell parameters were obtained by least squares from the four-circle coordinates of 12 reflections. Owing to their irregular shape, the crystals were ground to spheres for data collection, a specimen of radius 0.17 mm being used. Data were collected on a Hilger & Watts four-circle diffractometer with $2\theta/\omega$ scans and Mo $K\alpha$ radiation. Each reflection was scanned through 0.60° in steps of 0.01° at 1 s per step, with stationary background counts of 15 s taken at each scan limit. 3416 reflections were measured to a 2θ limit of 48°, of which 1877 had intensities $> 3\sigma(F^2)$. Lorentz and polarization corrections were applied and spherical absorption corrections made. E.s.d.'s calculated as $\sigma^2(F^2) = S + (B1 + B2)T + pS^2$ where S , $B1$ and $B2$ are respectively the scan counts and two background counts, T is the correction factor for the difference between scan and background count times and p was taken as 0.05.

Crystal data

Tetrachlorotetrakis(diphenyl sulphoxide)thorium(IV), C₄₈H₄₀Cl₄O₄S₄Th, $M_r = 1182$, $a = 17.909$ (2), $b =$