Acta Cryst. (1984). C**40**, 631–635

The Structure of Helices of Rubidium Deoxycholate–Water (3/10), $3(Rb^+.C_{24}H_{39}O_4^-).10H_2O$

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(*Received* 9 *August* 1983; *accepted* 21 *November* 1983)

Abstract. $M_r = 1611{\cdot}3$, $P2_1$, $a = 19{\cdot}834\,(13)$, $b = 19{\cdot}312\,(14)$, $c = 11{\cdot}586\,(4)$ Å, $\gamma = 116{\cdot}70\,(3)°$, $V = 3965\,(4)$ Å^3, $Z = 2$, $D_m = 1{\cdot}35$, $D_x = 1{\cdot}35$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 3{\cdot}19$ mm^{-1}, $F(000) = 1712$, $T = 298$ K, $R = 0{\cdot}09_8$ and $R_w = 0{\cdot}11_1$ for 3057 observed reflections with $I \geq 2\sigma(I)$. The molecules of rubidium deoxycholate form 2_1 helices mainly stabilized by hydrogen bonds and ion–ion and ion–dipole interactions. The interior of the helix is filled with Rb^+ ions surrounded by water molecules. The helices have non-polar outer surfaces and pack together through van der Waals interactions. The structure of the helix may be considered as a possible model of a micellar aggregate for some deoxycholic acid alkali-metal salts in aqueous solutions.

Introduction. The alkali-metal salts of 3α,12α-dihydroxy-5β-cholan-24-oic acid (deoxycholic acid, DCA, Fig. 1) form micellar aggregates in aqueous solutions (Small, 1971, and references therein). The deoxycholate anion (DC^-) is amphiphilic with two faces, one polar containing two hydroxyl groups at C(3) and C(12) and the other non-polar with two angular methyl groups at C(10) and C(13). The sodium salt of DCA (NaDC) is probably the most studied among the bile salts because of its remarkable physiological role (Masoro, 1968; Small, 1971). The knowledge of the structure of the NaDC micellar aggregates is needed to understand the NaDC behaviour in aqueous solution in order to use this amphiphile, if possible, in such fields as, for example, micellar catalysis, detergency, separation science, solubilization of drugs and enhanced petroleum recovery. The geometry of DC^- is known from the crystal structures of rubidium deoxycholate (RbDC) monohydrate and several inclusion compounds of DCA (Coiro, Giglio, Morosetti & Palleschi, 1980; Popovitz-Biro, Chang, Tang, Shochet, Lahav & Leiserowitz, 1980; Giglio, 1981; Coiro, Giglio, Mazza, Pavel & Pochetti, 1982, and references therein).

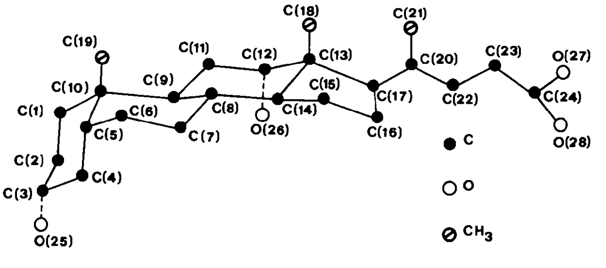

Fig. 1. Atomic numbering for the DC^- anion.

The DC^- anions and the DCA molecules form bilayers or helices stabilized mainly by hydrogen bonds and, in the case of RbDC, also by ion–ion and ion–dipole interactions. On the other hand, some pH, pNa, density and conductivity measurements were interpreted assuming that the driving force for the aggregation of NaDC molecules in aqueous solutions is the hydrogen bonding (Sugihara, Ueda, Kaneshina & Tanaka, 1977; Sugihara & Tanaka, 1976; Oakenfull & Fischer, 1977, 1978). The size of the NaDC micellar aggregates increases as a function, for example, of the ionic strength, pH, temperature and pressure so as to give rise to a gel composed of helical macromolecules (Rich & Blow, 1958; Blow & Rich, 1960). The fibres drawn from the gel give a detailed X-ray diffraction pattern which strongly suggests that the NaDC molecules are arranged in helices packed in a hexagonal lattice. On ageing, the fibres transform into hexagonal crystals of NaDC, space group $P6_5$, which can also be obtained by crystallizing NaDC from water or from water and acetone. The crystal is characterized by helices of NaDC, with sixfold symmetry, resembling those of the fibres (Campanelli, Ferro, Giglio, Imperatori & Piacente, 1983). Since the X-ray intensity distributions of the NaDC crystals, fibres and aqueous solutions are similar it is very probable that the micellar aggregates are also helices, at least when the NaDC aqueous solutions satisfy certain conditions of concentration, pH, ionic strength, *etc.*, and approach the gel phase.

There still exist controversies about many aspects of the micellar systems as, for example, the shape of the micelles and the extent of water penetration into the micelles, because of contradictory experimental evidence (Wennerstrom & Lindman, 1979; Menger, 1979). Thus, it seems important to establish without any doubt the exact structure of an amphiphile in solid

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phases, such as crystals or fibres, and to check the structural model, found in the solid state, in the study of the micellar solutions. Of course, NaDC appeared to be a very good system for our purpose of studying the structure of a micellar aggregate and, therefore, its hexagonal crystal was considered first. Unfortunately, our efforts to solve this crystal structure were unsuccessful, although we have established by means of Patterson and minimum residual analyses the occurrence of helices, very probably identical, around the 6_5 and 3_2 axes. The unit-cell parameters are: $a = b = 34{\cdot}56\ (3)$, $c = 11{\cdot}75\ (1)$ Å and the asymmetric unit is composed of 3 NaDC and 12 H_2O molecules. Six DC^- anions are packed in 11·75 Å along **c** and have their C(9)—C(13) mid-points about 8·6–8·7 Å from the 6_5 and 3_2 helical axes. The interior of the helices is filled with Na^+ ions and water molecules which give rise to hydrogen bonds and to ion–ion and ion–dipole interactions.

In order to determine the NaDC crystal structure at atomic resolution we attempted to prepare a nearly isostructural compound containing an alkali-metal ion such as Rb^+ or Cs^+, heavier than Na^+. After many trials we succeeded in obtaining suitable crystals for X-ray analysis of $3RbDC.10H_2O$, which is strictly related to the NaDC hexagonal crystal.

Experimental. $3RbDC.10H_2O$ obtained by adding little less than the equivalent amount of RbOH to DCA and filtering the resulting aqueous suspension; subsequently, acetone was added until the solution, kept at about 310 K, became cloudy; prismatic colourless crystals, elongated along **c**, crystallized by cooling; observed density by flotation in *n*-hexane and carbon tetrachloride and agrees with a $RbDC{:}H_2O$ ratio of 3/10; prismatic crystal, 0·8 × 0·4 × 0·2 mm, cell constants from least-squares refinement on 27 reflections within 2θ range 26·8–32·8°, intensities collected up to $2\theta = 140°$, automated Siemens AED single-crystal diffractometer on-line to a General Automation Jumbo 220 computer, Cu $K\alpha$ Ni-filtered radiation; $\theta/2\theta$ step scan, analysis of diffraction profiles (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979); standard reflection $\bar{6}20$, selected for orientation control and measured every 50 reflections, remained essentially constant throughout the run; 7808 independent reflections ($-24 \leq h \leq 21$, $0 \leq k \leq 23$, $0 \leq l \leq 14$) measured, 3057 reflections having $I \geq 2\sigma(I)$ used in the crystallographic calculations; Lorentz and polarization corrections applied, no correction for absorption. Patterson synthesis located Rb^+ ions; all C and O atoms of anions obtained from subsequent Fourier syntheses, together with nine peaks attributed to O atoms of water molecules; atomic coordinates, anisotropic (Rb^+) and isotropic (C and O) temperature factors refined by full-matrix least-squares with *SHELX* (Sheldrick, 1976), $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1{\cdot}0$; scattering factors including anomalous dispersion of the Rb^+ ions from *International Tables for X-ray Crystallography* (1974); H atoms generated at expected positions, those linked to O atoms considering the hydrogen bonds which can be formed; H coordinates fixed and $U(H) = U_{iso}$ of bonded atom; difference synthesis showed two peaks, nearly half the electron density of an O atom, about 1·3 Å apart; best result obtained assuming the occurrence of two water oxygens, O(10) and O(11), with occupancy 0·5; owing to the restriction of *SHELX* on the number of atoms, the refinement was continued with a program of Domenicano, Spagna & Vaciago (1969), treating the asymmetric unit in four blocks, three composed of a DC^- each and the last of Rb^+ ions and O atoms of the water molecules; $R = 0{\cdot}098$, $wR = 0{\cdot}111$, $S = 2{\cdot}25$ for 3057 reflections with $I \geq 2\sigma(I)$, $w = \sin\theta/\lambda$, max. $\Delta/\sigma = 0{\cdot}11$; max. and min. $\Delta\rho$ excursions in final difference synthesis 0·7 and −0·7 e Å^{-3}, the peaks lying very near to some atoms.*

Discussion. The final atomic coordinates are reported in Table 1. A schematic drawing of the crystal packing, viewed along **c**, is shown in Fig. 2.

The very high e.s.d.'s of the atomic parameters and the occurrence of some unrealistic bond lengths in the DC^- anions indicate that absorption corrections are necessary in order to obtain reliable intramolecular distances, which, however, are already well known, as previously mentioned. Nevertheless, our results allow us

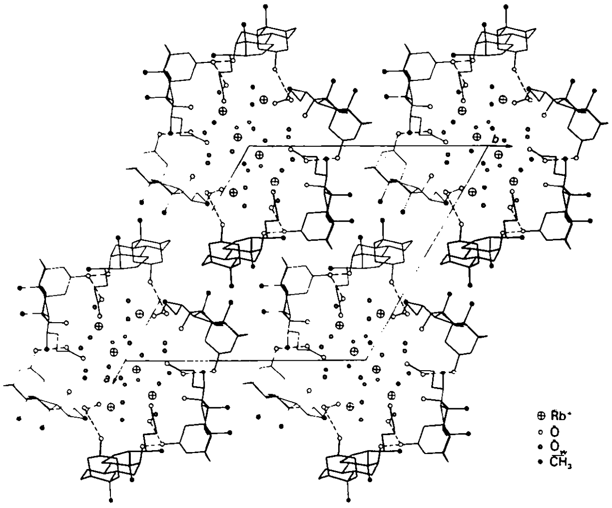

Fig. 2. RbDC crystal packing viewed along **c**. The hydrogen bonds between DC^- anions are indicated by broken lines. The thin circles represent O(10) and O(11).

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* Lists of structure factors, bond lengths and angles and short intermolecular distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39043 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

The anisotropic temperature factors ($\times 10^4$) are given in the form
$T = \exp[-(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)]$.

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Rb(1)	1555 (1)	1804 (2)	−499 (4)	48 (1)	62 (2)	−24 (4)	56 (1)	−3 (4)	217 (4)
Rb(2)	364 (2)	632 (2)	6443 (5)	70 (1)	75 (2)	3 (6)	65 (1)	−23 (6)	293 (6)
Rb(3)	2084 (2)	323 (3)	949 (8)	56 (1)	70 (4)	39 (8)	140 (3)	416 (13)	644 (17)

	x	y	z	B
O(1)	1101 (10)	1914 (10)	4715 (19)	7·9 (4)
O(2)	596 (8)	2135 (9)	7633 (15)	5·7 (3)
O(3)	816 (9)	−1268 (9)	11554 (18)	6·8 (4)
O(4)	2389 (11)	2368 (11)	7299 (19)	8·4 (5)
O(5)	2642 (13)	1089 (13)	8823 (22)	10·1 (6)
O(6)	1862 (17)	767 (17)	6175 (33)	14·8 (9)
O(7)	341 (10)	−1376 (11)	8330 (18)	7·8 (4)
O(8)	277 (11)	−602 (12)	4682 (22)	9·5 (5)
O(9)	786 (16)	139 (16)	8987 (26)	12·6 (8)
O(10)	1091 (25)	507 (27)	2300 (45)	10·0 (12)
O(11)	882 (28)	948 (30)	1706 (51)	11·6 (14)
Anion *A*				
C(1)	1664 (12)	−2888 (12)	13062 (20)	4·2 (4)
C(2)	852 (12)	−2952 (12)	13214 (21)	4·7 (5)
C(3)	303 (12)	−3803 (12)	13299 (22)	4·9 (5)
C(4)	347 (12)	−4229 (12)	12272 (21)	4·6 (4)
C(5)	1147 (12)	−4163 (12)	12098 (21)	4·6 (5)
C(6)	1157 (13)	−4626 (14)	10988 (23)	5·8 (5)
C(7)	1094 (12)	−4240 (12)	9854 (21)	4·8 (5)
C(8)	1710 (11)	−3398 (11)	9810 (19)	3·8 (4)
C(9)	1677 (10)	−2927 (10)	10857 (17)	2·9 (4)
C(10)	1741 (11)	−3306 (11)	12007 (18)	3·2 (4)
C(11)	2208 (13)	−2089 (13)	10727 (21)	4·8 (5)
C(12)	2157 (11)	−1686 (12)	9631 (23)	4·8 (4)
C(13)	2202 (12)	−2126 (12)	8512 (20)	4·0 (4)
C(14)	1615 (11)	−3005 (11)	8706 (19)	3·5 (4)
C(15)	1617 (13)	−3351 (13)	7530 (23)	4·9 (5)
C(16)	1736 (11)	−2710 (11)	6666 (20)	4·0 (4)
C(17)	1966 (11)	−1943 (11)	7372 (20)	4·0 (4)
C(18)	3022 (13)	−2051 (14)	8448 (24)	5·5 (5)
C(19)	2547 (14)	−3283 (14)	12075 (24)	5·9 (5)
C(20)	2458 (12)	−1228 (12)	6755 (22)	5·0 (5)
C(21)	2673 (18)	−518 (19)	7416 (31)	8·4 (8)
C(22)	2039 (15)	−1164 (16)	5573 (27)	7·1 (7)
C(23)	2539 (17)	−520 (17)	4813 (31)	8·0 (7)
C(24)	2086 (20)	−474 (21)	3701 (38)	9·1 (8)
O(25)	−457 (9)	−3922 (9)	13433 (16)	6·5 (4)
O(26)	1438 (7)	−1649 (8)	9650 (15)	5·2 (3)
O(27)	2134 (16)	−716 (17)	2876 (31)	12·3 (8)
O(28)	1771 (16)	−27 (17)	4107 (27)	13·2 (8)
Anion *B*				
C(1)	5190 (18)	2172 (18)	11212 (33)	8·7 (8)
C(2)	4472 (17)	1752 (18)	11536 (33)	8·4 (7)
C(3)	4263 (18)	920 (19)	11808 (30)	8·5 (8)
C(4)	4425 (14)	515 (14)	10747 (25)	6·3 (6)
C(5)	5251 (12)	1029 (12)	10386 (21)	4·8 (5)
C(6)	5444 (14)	677 (15)	9302 (26)	6·8 (6)
C(7)	5005 (13)	710 (13)	8210 (22)	5·2 (5)
C(8)	5148 (10)	1557 (10)	7944 (18)	3·5 (4)
C(9)	4970 (10)	1923 (11)	9025 (18)	3·4 (4)
C(10)	5417 (12)	1875 (12)	10129 (20)	4·5 (4)
C(11)	5155 (12)	2765 (12)	8696 (22)	4·7 (5)
C(12)	4626 (10)	2797 (11)	7748 (19)	3·6 (4)
C(13)	4726 (10)	2372 (10)	6644 (18)	3·3 (4)
C(14)	4608 (11)	1557 (11)	7002 (19)	3·7 (4)
C(15)	4600 (13)	1158 (13)	5855 (23)	5·4 (5)
C(16)	4196 (12)	1465 (12)	4976 (21)	4·6 (4)
C(17)	4100 (10)	2123 (10)	5688 (17)	3·0 (3)
C(18)	5506 (13)	2864 (13)	6116 (24)	5·7 (5)
C(19)	6294 (16)	2386 (16)	10004 (28)	7·6 (7)
C(20)	4065 (10)	2721 (11)	4850 (19)	3·7 (4)
C(21)	4104 (11)	3447 (12)	5434 (20)	4·4 (4)
C(22)	3373 (13)	2335 (13)	4110 (22)	5·1 (5)
C(23)	3283 (12)	2804 (13)	3105 (22)	5·1 (5)
C(24)	2613 (14)	2330 (14)	2367 (25)	5·8 (5)
O(25)	3482 (19)	527 (19)	12096 (32)	15·2 (10)
O(26)	3848 (7)	2468 (7)	8045 (12)	3·8 (3)
O(27)	2683 (8)	2229 (9)	1319 (17)	6·0 (3)
O(28)	1988 (12)	1940 (12)	2858 (20)	8·9 (5)
Anion *C*				
C(1)	2876 (11)	4636 (11)	9676 (21)	4·3 (4)
C(2)	2900 (11)	3857 (12)	9805 (22)	4·9 (5)
C(3)	3745 (11)	4027 (11)	9915 (20)	4·4 (4)
C(4)	4172 (11)	4488 (12)	8867 (20)	4·2 (4)
C(5)	4130 (11)	5246 (11)	8663 (20)	4·2 (4)
C(6)	4539 (12)	5673 (12)	7638 (22)	4·7 (5)
C(7)	4179 (11)	5306 (11)	6467 (21)	4·1 (4)
C(8)	3354 (9)	5150 (10)	6410 (19)	3·2 (4)
C(9)	2933 (10)	4680 (10)	7471 (18)	3·0 (4)
C(10)	3270 (10)	5107 (11)	8615 (18)	3·4 (4)
C(11)	2066 (12)	4411 (12)	7387 (21)	4·5 (5)
C(12)	1738 (10)	4005 (11)	6215 (20)	4·0 (4)
C(13)	2135 (10)	4472 (10)	5151 (17)	2·9 (4)
C(14)	2979 (10)	4677 (10)	5316 (17)	2·9 (4)
C(15)	3307 (12)	5021 (13)	4099 (20)	4·7 (5)
C(16)	2683 (12)	4574 (12)	3252 (20)	4·5 (5)
C(17)	1973 (11)	4058 (11)	3996 (18)	3·7 (4)
C(18)	2016 (12)	5204 (13)	5092 (22)	5·4 (5)
C(19)	3225 (12)	5875 (13)	8737 (22)	5·0 (5)
C(20)	1237 (11)	3886 (11)	3317 (20)	3·9 (4)
C(21)	510 (14)	3502 (15)	4092 (24)	6·4 (6)
C(22)	1153 (11)	3347 (11)	2326 (20)	4·1 (4)
C(23)	436 (12)	3105 (12)	1546 (23)	5·1 (5)
C(24)	412 (11)	2525 (12)	674 (21)	4·2 (4)
O(25)	3804 (8)	3307 (8)	9947 (14)	5·1 (3)
O(26)	1732 (7)	3251 (7)	6243 (14)	4·8 (3)
O(27)	639 (9)	2742 (9)	−300 (18)	6·5 (4)
O(28)	141 (8)	1858 (9)	1050 (16)	6·2 (4)

to determine the structure of the RbDC helix, as a model of a micelle, which is the main purpose of the present work.

The torsion angles of the side chain and ring *D* correspond in all the three DC$^-$ anions to those of a nearly *trans* side-chain conformation coupled in two of them, *B* and *C*, with an approximate β-envelope symmetry of the *D* ring, the phase angle of pseudorotation Δ being 18 (3) and 19 (4)° respectively. This situation occurs when the side-chain conformation is *trans* (Giglio & Quagliata, 1975) as in the hexagonal inclusion compounds of DCA (Candeloro De Sanctis, Coiro, Giglio, Pagliuca, Pavel & Quagliata, 1978; Candeloro De Sanctis, Giglio, Petri & Quagliata, 1979), where the DCA molecules are arranged in clockwise helices similar to those of RbDC. A *gauche* side-chain conformation and an intermediate conformation between half-chair and β-envelope for ring *D* is observed in the RbDC monohydrate, crystallized from organic solvents (Coiro, Giglio, Morosetti & Palleschi, 1980) and characterized by an assembly of bilayers, and is invariably found in the orthorhombic and tetragonal inclusion compounds of DCA (Giglio, 1981; Coiro, D'Andrea & Giglio, 1979) where the structural unit is the bilayer. However, the DC$^-$ anion *A* presents a *D* ring with a conformation closer to the half-chair [$\Delta = 8$ (4)°], but this finding could be ascribed to the low accuracy obtained in the location of the atoms.

The packing of the RbDC helices, shown in Fig. 2, is stabilized by van der Waals interactions mainly among methyl groups. The shortest contacts have been deposited. The helix formed by the DC$^-$ anions has the interior surface covered by polar groups and the outer one by non-polar groups. Its cross section is slightly ellipsoidal with the long axis approximately along the *B* anions. The backbone of the helix is composed of Rb$^+$ ions surrounded by water molecules. Strong ion–dipole interactions occur between Rb$^+$ ions and water molecules together with ion–ion interactions between Rb$^+$ and carboxylate ions. Rb(2) is linked only to oxygen atoms of water molecules and Rb(3) interacts also with the O(25)*B*($x,y,z-1$) hydroxyl group. The Rb(1)···Rb(2) ($x,y,z-1$), Rb(2)···Rb(3) ($-x,-y,\frac{1}{2}+z$) and Rb(3)···Rb(1) distances are 4·296 (6), 4·387 (5) and 3·846 (8) Å, respectively, and the cations are joined by means of water molecules O(2), O(3), O(5), O(8), O(9), O(10) and O(11). Fig. 3 shows as a projection on the *ab* plane the coordination of the Rb$^+$ ions, ranging from seven- to ninefold, and of the water molecules. It is unlikely that O(1)···O(7) ($-x,-y,z-\frac{1}{2}$) and O(4)···O(6) form hydrogen bonds owing to their rather long contacts which lie near the upper limit of the hydrogen-bonding distances. Besides the hydrogen bonds of the water molecules there are those of the oxygen atoms belonging to the DC$^-$ anions, shown in Fig. 4, which stabilize the helix even more. This close net of hydrogen bonds gives rise to an interior liquid structure compatible with that which could be formed in an aqueous solution.

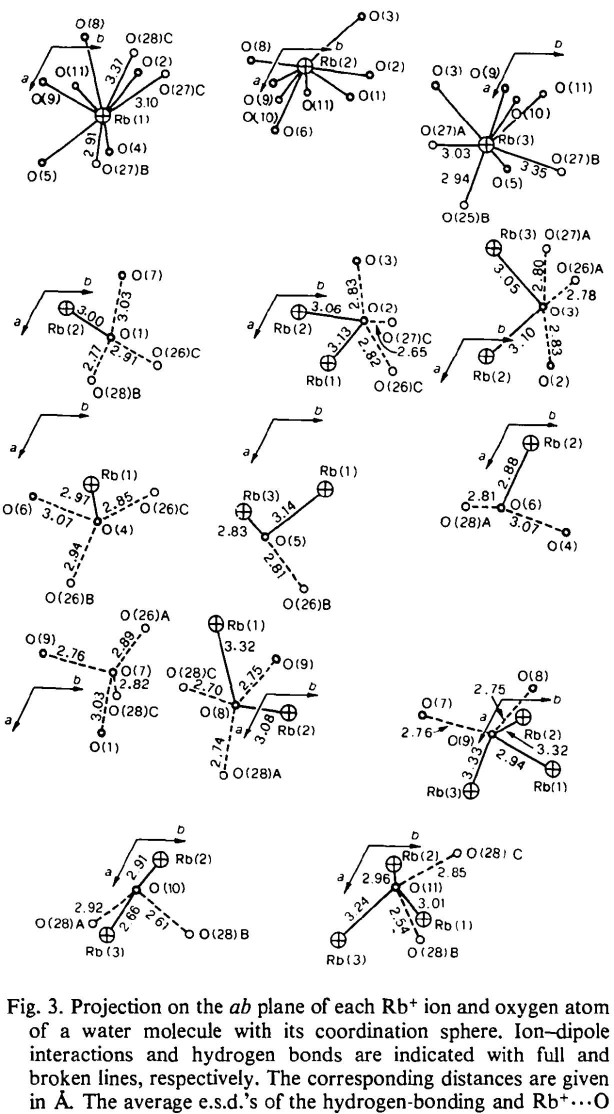

Fig. 3. Projection on the *ab* plane of each Rb$^+$ ion and oxygen atom of a water molecule with its coordination sphere. Ion–dipole interactions and hydrogen bonds are indicated with full and broken lines, respectively. The corresponding distances are given in Å. The average e.s.d.'s of the hydrogen-bonding and Rb$^+$···O distances are 0·034 and 0·030 Å, respectively, with maximum values of 0·070 and 0·067 Å.

Comparison of the RbDC and NaDC crystal structures shows the close similarity of the two molecular packings. The corners of the RbDC unit cell in the *ab* plane correspond approximately to the points (0,0), ($\frac{2}{3},\frac{1}{3}$), ($\frac{1}{3},\frac{2}{3}$) and ($-\frac{1}{3},\frac{1}{3}$) of the NaDC unit cell. The repeat of six DC$^-$ anions along the helical axis is practically identical (11·59 *vs* 11·75 Å). The distances from the helical axis of the C(9)–C(13) mid-points of the three independent DC$^-$ anions *A*, *B* and *C* are 7·4, 8·6 and 8·0 Å respectively as compared with 8·6–8·7 Å for NaDC. Moreover, the *B*-anion atomic coordinates (appropriately transformed) correspond very well to those of an *R*-factor minimum found by means of the minimum residual analysis for NaDC in space group $P6_5$. The *R* value of 0·46 obtained for 3234 observed reflections [$I > 3\sigma(I)$], without including Na$^+$ ions and water molecules and with an overall temperature factor, can be considered promising. The screw sense of the three independent DC$^-$ anions is clockwise as in $P6_5$ and the RbDC helix can be considered to be derived from the sixfold helix of NaDC.

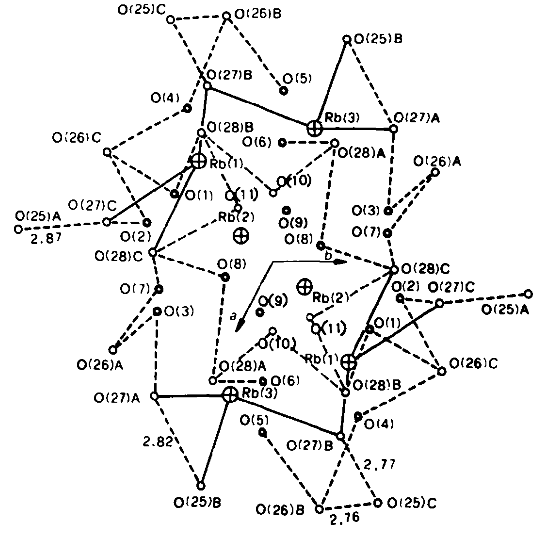

Fig. 4. Projection on the *ab* plane of the hydrogen bonds (broken lines) and the strongest ion–ion interactions (full lines) of the oxygen atoms belonging to the DC$^-$ anions. Some distances are given in Å. The average e.s.d.'s are as in the caption to Fig. 3.

Work is in progress to solve the structures of the NaDC crystal and macromolecular fibre as well as to check the helical model in aqueous solutions by means of small-angle X-ray scattering.

We thank Professor G. D. Andreetti for data collection. This work was sponsored by the Italian Consiglio Nazionale delle Ricerche–Progetto Finalizzato Chimica Fine e Secondaria.

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Crystal Structures of Ethylenediaminetetraacetato Metal Complexes. V. Structures containing the $[Fe(C_{10}H_{12}N_2O_8)(H_2O)]^-$ Anion

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(*Received* 26 *July* 1983; *accepted* 19 *December* 1983)

Abstract. (Na,Fe): $Na.[Fe(C_{10}H_{12}N_2O_8)(H_2O)].2H_2O$, $M_r = 421{\cdot}1$, monoclinic, Cc, $a = 8{\cdot}896$ (1), $b = 11{\cdot}931$ (2), $c = 15{\cdot}065$ (2) Å, $\beta = 100{\cdot}15$ (2)°, $V = 1574{\cdot}0$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}78$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7093$ Å, $\mu = 1{\cdot}083$ mm^{-1}, $F(000) = 868$, room temperature. (Ag,Fe): $Ag.[Fe(C_{10}H_{12}N_2O_8)(H_2O)].2H_2O$, $M_r = 506{\cdot}0$, monoclinic, Cc, $a = 8{\cdot}929$ (1), $b = 11{\cdot}871$ (2), $c = 15{\cdot}116$ (2) Å, $\beta = 99{\cdot}85$ (2)°, $V = 1578{\cdot}6$ (6) Å^3, $Z = 4$, $D_x = 2{\cdot}13$ Mg m^{-3}, μ(Mo $K\alpha$) $= 2{\cdot}219$ mm^{-1}, $F(000) = 1012$, room temperature. (K,Fe): $K.[Fe(C_{10}H_{12}N_2O_8)(H_2O)].H_2O$, $M_r = 419{\cdot}2$, monoclinic, $P2_1/n$, $a = 11{\cdot}361$ (2), $b = 13{\cdot}396$ (2), $c = 10{\cdot}484$ (1) Å, $\beta = 106{\cdot}00$ (2)°, $V = 1533{\cdot}8$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}82$ Mg m^{-3}, μ(Mo $K\alpha$) $= 1{\cdot}332$ mm^{-1}, $F(000) = 860$, room temperature. (Tl,Fe): $Tl.[Fe(C_{10}H_{12}N_2O_8)(H_2O)].H_2O$, $M_r = 584{\cdot}5$, triclinic, $P\bar{1}$, $a = 13{\cdot}825$ (2), $b = 8{\cdot}591$ (1), $c = 6{\cdot}807$ (1) Å, $\alpha = 87{\cdot}79$ (1), $\beta = 97{\cdot}75$ (1), $\gamma = 104{\cdot}34$ (2)°, $V = 776{\cdot}1$ (3) Å^3, $Z = 2$, $D_x = 2{\cdot}50$ Mg m^{-3}, μ(Mo $K\alpha$) $= 11{\cdot}458$ mm^{-1}, $F(000) = 554$, room temperature. Final R values are 0·047 (Na,Fe), 0·046 (Ag,Fe), 0·049 (K,Fe) and 0·040 (Tl,Fe) for 1403, 1438, 3229 and 2350 observed reflections, respectively. The Fe ion is coordinated to four O and two N atoms of one

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