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The Crystal Structure and Absolute Configuration of Cinchoninium Tetrachlorocadmate(II) Dihydrate

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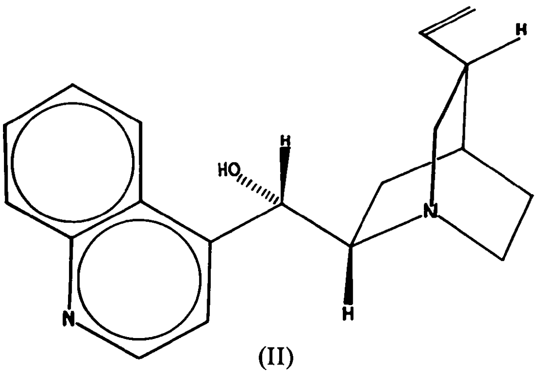
The crystal structure of the 1 : 1 complex of $CdCl_2$ with the hydrochloride of cinchonine, which crystallizes as $(C_{19}H_{24}N_2O)CdCl_4.2H_2O$, has been solved by the heavy-atom method and refined by full-matrix least-squares computations to R = 0·056 for 3871 independent reflexions measured on a diffractometer. The orthorhombic unit cell, space group $P2_12_12_1$, with a = 8·918 (2), b = 32·891 (6), c = 8·292 (2) Å contains four asymmetric units consisting of the tetrahedral $CdCl_4^{2-}$ anion, the cinchoninium^{2+} cation, and two water molecules. The units are linked spirally by hydrogen bonds between chlorine atoms, water molecules, and protonated nitrogen atoms. The absolute configuration and *erythro* configuration at C(9) have been confirmed.

Introduction

A series of cinchonine hydrochloride complexes with transition metals, formulated as $C_{19}H_{22}N_2O.MCl_2.2HCl.2H_2O$, where M = Cd, Co, Zn, Hg, Cu, was chosen as the promising object of an X-ray study aimed at determining the absolute configuration of the cinchonine molecule (II) and elucidating the metal coordination in complexes of this type.



(II)

The results of preliminary crystallographic investigations of these compounds (Chojnacki, Oleksyn & Hodorowicz, 1975; Oleksyn, Stadnicka & Hodorowicz, 1976) revealed that the first four are isomorphous.

Crystals of the Cd complex were found to be the most suitable for structure determination by the heavy-atom method. The method of crystal preparation was described by Dyrek (1976), who kindly provided us with the samples.

A well-formed prism of dimensions: 0·10 × 0·15 × 0·17 mm was mounted on a CAD-4 Enraf–Nonius automatic diffractometer.* The lattice parameters, determined together with other crystal data (Chojnacki *et al.*, 1975), were confirmed and refined in the autoindexing procedure from the setting angles of 15 reflexions.

Crystal data

$C_{19}H_{22}N_2O.CdCl_2.2HCl.2H_2O$; FW 586·66; a = 8·918 (2), b = 32·891 (6), c = 8·292 (2) Å; U = 2432·2 Å^3, Z = 4; D_m = 1·617, D_x = 1·602 g cm^{-3};

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* The measurements were carried out in the X-ray Division of the Regional Laboratory of Physicochemical Analysis and Structure Research, Kraków, Poland.

$F(000) = 1184$, space group $P2_12_12_1$; μ for Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å) = $13{\cdot}65$ cm^{-1}.

Measurements of the intensities of 3871 independent reflexions in the range $0{\cdot}5 < \theta < 30°$ were performed in the $\omega/2\theta$ scanning mode with graphite-monochromated Mo $K\alpha$ radiation. The scan width was varied with θ according to the formula: $0{\cdot}37° + 0{\cdot}92° \tan \theta$; the scan speed was varied to achieve 2500 counts above background with a maximum scan time of 150s. From the collected data, 145 reflexions with intensity $I \leq 0$ were treated as unobservable.

In order to avoid bias in the experimental data, no other reflexions were excluded, as recommended by Hirshfeld & Rabinovich (1973). The intensities of two control reflexions, recorded during data collection after every 47 reflexions, remained constant to within ±4%.

The net intensity of a reflexion and its standard deviation were calculated according to the formulae: $I = (T - 2\text{BGL} - 2\text{BGR})/\text{NPI}$, $\sigma(I) = [T + 4(\text{BGL} + \text{BGR})]^{1/2}/\text{NPI}$, where T is the total integrated intensity over the scan range, NPI is proportional to (scan speed)$^{-1}$, BGL and BGR are respectively left and right background integrated over $\frac{1}{4}$ of the scan range.

The data were corrected for Lorentz and polarization effects, but not for absorption.

Solution and refinement of the structure

The position of the Cd atom was determined from a three-dimensional Patterson synthesis. After three subsequent cycles of structure-factor calculations the positions of all non-hydrogen atoms were found in a Fourier synthesis for which $R = 0{\cdot}179$. These and all other calculations were performed with the *SHELX* system of programs (Sheldrick, 1975). Scattering factors for Cl, O, N, C and H were those used by the program, while those for Cd were taken from *International Tables for X-ray Crystallography* (1974). The corrections for anomalous dispersion of Cd atoms were from Cromer (1965).

The full-matrix least-squares refinement was carried out with $\Sigma_{hkl} w_{hkl}(|F_o|_{hkl} - K|F_c|_{hkl})^2$ as the function minimized, where K is the overall scale factor, and $w = k[\sigma^2(F_o) + |g|F_o^2]^{-1}$ (k, g are parameters to be refined).

After four cycles of isotropic refinement and three cycles with anisotropic Cd and Cl atoms, R decreased to $0{\cdot}0759$. The next four cycles of anisotropic refinement, performed in two partially overlapping, structural segments, yielded $R = 0{\cdot}0653$, and the subsequent Fourier synthesis enabled us to determine the positions of all the H atoms except H(C10). With these positions held and the U values fixed at $0{\cdot}0500$ two cycles of refinement gave $R = 0{\cdot}0631$.

At this stage, the enantiomorph (II) of the compound investigated (I) was generated by reversal of all atomic coordinates. This operation reduced R to $0{\cdot}0597$. With Hamilton's (1965) test it was shown that the ratio of R_G values {where $R_G = [\Sigma\, w(\Delta F)^2/\Sigma\, w(F_o)^2]^{1/2}$} for the two enantiomorphous structures, $R_{GI}/R_{GII} = 0{\cdot}0831/0{\cdot}0796 = 1{\cdot}044$, rejects the original enantiomorph (I) at a significance level lower than 0·5%.

The structure of the enantiomorph (II) was, therefore, accepted as the absolute configuration and refined for two cycles. The difference Fourier synthesis revealed the missing H(C10) atom. In the subsequent three cycles the positions of the H atoms and their isotropic temperature factors were refined giving $R = 0{\cdot}0561$. At this stage, the shifts of atomic parameters for non-hydrogen atoms were less than 0·1 of their estimated standard deviations, and for most of the hydrogen atoms less than 0·3 of their e.s.d.'s.

As the difference Fourier map had no peaks higher than 0·6 e Å^{-3}, the structure was assumed to be correctly refined. The final atomic positions and hydrogen isotropic temperature factors are listed in Tables 1 and 2.* The atomic coordinates and Fig. 1 depict the true chirality of the molecule.

Table 1. *The final fractional positional coordinates* (×10^4), *with their e.s.d.'s in parentheses*

	x	y	z
Cd	3282 (1)	6296·5 (1)	1532 (1)
Cl(1)	897 (2)	6321 (1)	2919 (3)
Cl(2)	3603 (2)	6781 (1)	−753 (2)
Cl(3)	3613 (3)	5628 (1)	309 (3)
Cl(4)	5518 (2)	6492 (1)	3080 (3)
N(1)	7276 (6)	6776 (2)	−792 (8)
C(2)	7075 (7)	6986 (2)	−2395 (10)
C(3)	8565 (9)	7203 (2)	−2829 (9)
C(4)	9784 (8)	7005 (2)	−1849 (10)
C(5)	9601 (8)	7142 (2)	−47 (11)
C(6)	7939 (9)	7065 (2)	420 (10)
C(7)	9655 (7)	6545 (2)	−1914 (9)
C(8)	8321 (8)	6412 (2)	−899 (8)
C(9)	7508 (7)	6022 (2)	−1472 (9)
C(10)	8770 (14)	7202 (3)	−4651 (11)
C(11)	8668 (22)	7525 (4)	−5508 (13)
O(12)	7195 (6)	6036 (2)	−3142 (6)
N(13)	10543 (6)	5037 (2)	−658 (7)
C(14)	10423 (9)	5207 (2)	−2103 (9)
C(15)	9446 (8)	5522 (2)	−2389 (8)
C(16)	8562 (7)	5668 (2)	−1163 (8)
C(17)	8681 (7)	5493 (2)	410 (8)
C(18)	7833 (9)	5614 (2)	1756 (10)
C(19)	8016 (9)	5423 (2)	3230 (8)
C(20)	9064 (8)	5112 (2)	3410 (9)
C(21)	9888 (8)	4980 (2)	2135 (9)
C(22)	9724 (7)	5168 (2)	642 (8)
O(*W*1)	2396 (7)	5561 (2)	4938 (8)
O(*W*2)	4157 (7)	6167 (3)	−3684 (8)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33069 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional and isotropic thermal parameters* $(\times 10^3)$ *for the hydrogen atoms*

The estimated standard deviations are given in parentheses.

	x	y	z	U (Å^2)
H(N1)	641 (9)	669 (2)	−56 (9)	34 (16)
H(1C2)	618 (9)	717 (2)	−238 (10)	42 (18)
H(2C2)	695 (8)	678 (2)	−326 (9)	35 (16)
H(C3)	881 (9)	744 (2)	−267 (9)	85 (27)
H(C4)	1073 (7)	708 (2)	−204 (8)	47 (19)
H(1C5)	986 (9)	742 (2)	−1 (10)	57 (21)
H(2C5)	1028 (9)	696 (2)	56 (9)	71 (24)
H(1C6)	787 (9)	697 (2)	153 (10)	57 (21)
H(2C6)	724 (9)	728 (2)	44 (10)	22 (13)
H(1C7)	956 (9)	645 (2)	−299 (10)	62 (23)
H(2C7)	1045 (9)	638 (2)	−142 (10)	40 (16)
H(C8)	855 (9)	640 (2)	−2 (9)	89 (29)
H(C9)	655 (10)	597 (2)	−83 (9)	26 (12)
H(C10)	897 (11)	686 (3)	−515 (11)	91 (28)
H(1C11)	901 (11)	783 (3)	−484 (12)	111 (34)
H(2C11)	863 (2)	763 (2)	−617 (9)	111 (31)
H(O12)	646 (11)	609 (3)	−324 (13)	65 (27)
H(N13)	1122 (9)	488 (2)	−46 (10)	55 (20)
H(C14)	1101 (9)	504 (2)	−306 (9)	88 (28)
H(C15)	925 (8)	562 (2)	−340 (10)	37 (16)
H(C18)	714 (8)	582 (2)	166 (9)	59 (21)
H(C19)	746 (8)	549 (2)	416 (10)	45 (19)
H(C20)	921 (8)	502 (2)	432 (10)	42 (18)
H(C21)	1068 (8)	474 (2)	228 (9)	55 (24)
H(1*W*1)	198 (10)	568 (2)	414 (11)	67 (24)
H(2*W*1)	293 (10)	569 (3)	534 (11)	37 (16)
H(1*W*2)	383 (6)	598 (2)	−298 (7)	31 (15)
H(2*W*2)	364 (10)	631 (2)	−284 (10)	40 (16)

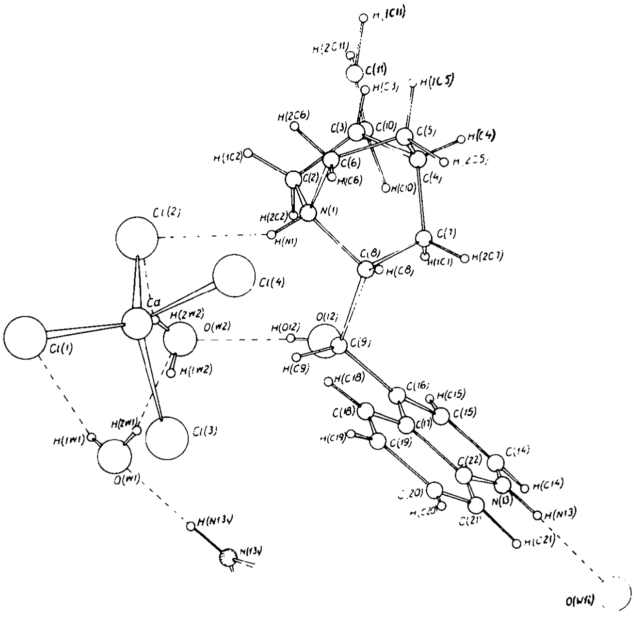


Fig. 1. The arrangement of atoms in the asymmetric unit.

Description of the structure

The bond lengths and angles are given in Tables 3 and 4. The asymmetric unit, shown in Fig. 1, consists of the tetrachlorocadmate anion, the cation of cinchonine protonated at nitrogen atoms N(1) and N(13), and two water molecules. Hence, the complex investigated is better formulated as: $(C_{19}H_{24}N_2O)^{2+}(CdCl_4)^{2-}.2H_2O$, similar to halogenometallates of protonated amines (Paulus & Göttlicher, 1969).

Table 3. *Bond lengths* (Å), *with their e.s.d.'s in parentheses*

$CdCl_4$ tetrahedron

Cd–Cl(1)	2·420 (2)	Cd–Cl(3)	2·440 (2)
Cd–Cl(2)	2·493 (2)	Cd–Cl(4)	2·456 (2)

Cinchoninium cation

N(1)–C(2)	1·508 (10)	N(1)–H(N1)	0·84 (8)
C(2)–C(3)	1·550 (10)	C(2)–H(1C2)	1·00 (7)
C(3)–C(4)	1·506 (11)	C(2)–H(2C2)	0·98 (7)
C(4)–C(5)	1·569 (12)	C(3)–H(C3)	0·81 (7)
C(5)–C(6)	1·554 (11)	C(4)–H(C4)	0·89 (7)
C(6)–N(1)	1·503 (10)	C(5)–H(1C5)	0·93 (7)
C(7)–C(4)	1·518 (9)	C(5)–H(2C5)	0·98 (7)
C(7)–C(8)	1·521 (9)	C(6)–H(1C6)	0·98 (7)
C(8)–N(1)	1·521 (8)	C(6)–H(2C6)	0·95 (7)
C(10)–C(3)	1·522 (12)	C(7)–H(1C7)	0·95 (7)
C(10)–C(11)	1·284 (15)	C(7)–H(2C7)	0·97 (7)
C(9)–C(8)	1·550 (6)	C(8)–H(C8)	0·76 (7)
C(9)–O(12)	1·413 (7)	C(9)–H(C9)	1·02 (7)
C(9)–C(16)	1·517 (8)	C(10)–H(C10)	1·20 (9)
C(16)–C(17)	1·429 (9)	C(11)–H(1C11)	1·19 (10)
C(17)–C(18)	1·406 (10)	C(11)–H(2C11)	0·65 (10)
C(18)–C(19)	1·384 (10)	O(12)–H(O12)	0·68 (6)
C(19)–C(20)	1·393 (11)	N(13)–H(N13)	0·81 (6)
C(20)–C(21)	1·359 (11)	C(14)–H(C14)	1·10 (7)
C(21)–C(22)	1·391 (9)	C(15)–H(C15)	0·91 (7)
C(22)–C(17)	1·430 (9)	C(18)–H(C18)	0·91 (7)
C(22)–N(13)	1·371 (9)	C(19)–H(C19)	0·95 (7)
N(13)–C(14)	1·327 (9)	C(20)–H(C20)	0·82 (7)
C(14)–C(15)	1·374 (10)	C(21)–H(C21)	1·06 (7)
C(15)–C(16)	1·374 (9)		

Water molecules

O(*W*1)–H(1*W*1)	0·86 (9)	O(*W*2)–H(1*W*2)	0·89 (6)
O(*W*1)–H(2*W*1)	0·72 (9)	O(*W*2)–H(2*W*2)	0·95 (9)

The Cd atom is tetrahedrally coordinated to four Cl atoms at distances in the range 2·49–2·42 Å, which is in agreement with the value reported by Paulus & Göttlicher (1969) for quinolinium tetrachlorocadmate. The bond angles in the tetrahedron vary in the range: 117·2–97·9° with a mean value of 109·3°. The observed deviations from the ideal tetrahedral geometry

Table 4. *Bond angles (°) with their e.s.d.'s in parentheses*

$CdCl_4$ tetrahedron

Cl(1)—Cd—Cl(2)	116·2 (1)	Cl(1)—Cd—Cl(4)	117·2 (1)	Cl(2)—Cd—Cl(4)	97·9 (1)
Cl(1)—Cd—Cl(3)	109·5 (1)	Cl(2)—Cd—Cl(3)	104·3 (1)	Cl(3)—Cd—Cl(4)	110·8 (1)

Cinchoninium cation

C(2)—N(1)—C(6)	110·3 (5)	C(18)—C(19)—C(20)	120·5 (7)	C(4)—C(7)—H(2C7)	118 (3)
C(2)—N(1)—C(8)	112·5 (6)	C(19)—C(20)—C(21)	120·9 (7)	H(1C7)—C(7)—H(2C7)	106 (4)
C(6)—N(1)—C(8)	107·2 (5)	C(20)—C(21)—C(22)	119·6 (6)	C(8)—C(7)—H(1C7)	111 (3)
N(1)—C(2)—C(3)	108·3 (6)	N(13)—C(22)—C(17)	118·3 (6)	C(8)—C(7)—H(2C7)	100 (3)
C(2)—C(3)—C(4)	107·1 (6)	N(13)—C(22)—C(21)	120·3 (6)	N(1)—C(8)—H(C8)	100 (3)
C(2)—C(3)—C(10)	109·4 (8)	H(N1)—N(1)—C(2)	104 (3)	C(7)—C(8)—H(C8)	110 (3)
C(4)—C(3)—C(10)	116·6 (8)	H(N1)—N(1)—C(6)	114 (3)	C(9)—C(8)—H(C8)	111 (3)
C(3)—C(4)—C(5)	108·3 (6)	H(N1)—N(1)—C(8)	109 (3)	C(8)—C(9)—H(C9)	111 (3)
C(3)—C(4)—C(7)	110·9 (6)	N(1)—C(2)—H(1C2)	111 (3)	O(12)—C(9)—H(C9)	111 (3)
C(5)—C(4)—C(7)	108·2 (6)	N(1)—C(2)—H(2C2)	110 (3)	C(16)—C(9)—H(C9)	108 (3)
C(4)—C(5)—C(6)	106·9 (6)	H(1C2)—C(2)—H(2C2)	109 (4)	C(3)—C(10)—H(C10)	111 (5)
C(5)—C(6)—N(1)	108·1 (6)	C(3)—C(2)—H(1C2)	114 (3)	C(11)—C(10)—H(C10)	126 (5)
C(4)—C(7)—C(8)	109·1 (5)	C(3)—C(2)—H(2C2)	104 (3)	C(10)—C(11)—H(1C11)	115 (5)
N(1)—C(8)—C(7)	106·6 (5)	C(2)—C(3)—H(C3)	129 (3)	C(10)—C(11)—H(2C11)	156 (5)
N(1)—C(8)—C(9)	112·6 (5)	C(4)—C(3)—H(C3)	97 (3)	H(1C11)—C(11)—H(2C11)	87 (5)
C(7)—C(8)—C(9)	115·8 (5)	C(10)—C(3)—H(C3)	98 (3)	C(9)—O(12)—H(O12)	108 (3)
C(8)—C(9)—O(12)	111·4 (4)	C(3)—C(4)—H(C4)	118 (3)	C(14)—N(13)—H(N13)	121 (3)
C(8)—C(9)—C(16)	107·0 (4)	C(5)—C(4)—H(C4)	101 (3)	C(22)—N(13)—H(N13)	116 (3)
O(12)—C(9)—C(16)	108·3 (5)	C(7)—C(4)—H(C4)	110 (3)	N(13)—C(14)—H(C14)	113 (3)
C(3)—C(10)—C(11)	122·6 (10)	C(4)—C(5)—H(1C5)	107 (3)	C(15)—C(14)—H(C14)	124 (3)
C(14)—N(13)—C(22)	122·3 (6)	C(4)—C(5)—H(2C5)	104 (3)	C(14)—C(15)—H(C15)	123 (3)
N(13)—C(14)—C(15)	121·6 (7)	H(1C5)—C(5)—H(2C5)	114 (4)	C(16)—C(15)—H(C15)	116 (3)
C(14)—C(15)—C(16)	120·0 (6)	C(6)—C(5)—H(1C5)	113 (3)	C(17)—C(18)—H(C18)	120 (3)
C(9)—C(16)—C(15)	119·9 (6)	C(6)—C(5)—H(2C5)	111 (3)	C(19)—C(18)—H(C18)	119 (3)
C(17)—C(22)—C(21)	121·3 (6)	N(1)—C(6)—H(1C6)	113 (3)	C(18)—C(19)—H(C19)	124 (3)
C(9)—C(16)—C(17)	120·6 (6)	N(1)—C(6)—H(2C6)	103 (3)	C(20)—C(19)—H(C19)	116 (3)
C(15)—C(16)—C(17)	119·5 (5)	H(1C6)—C(6)—H(2C6)	101 (4)	C(19)—C(20)—H(C20)	119 (3)
C(16)—C(17)—C(18)	124·7 (6)	C(5)—C(6)—H(1C6)	111 (3)	C(21)—C(20)—H(C20)	120 (3)
C(16)—C(17)—C(22)	118·2 (6)	C(5)—C(6)—H(2C6)	120 (3)	C(20)—C(21)—H(C21)	120 (3)
C(18)—C(17)—C(22)	117·1 (6)	C(4)—C(7)—H(1C7)	111 (3)	C(22)—C(21)—H(C21)	120 (3)
C(17)—C(18)—C(19)	120·5 (6)				

Water molecules

H(1*W*1)—O(*W*1)—H(2*W*1)	112 (4)	H(1*W*2)—O(*W*2)—H(2*W*2)	72 (4)

seem to be connected with the fact that Cl(1) and Cl(2) are involved in hydrogen bonds (Table 5, Figs. 1 and 2).

The absolute configuration of the cinchoninium cation agrees with that previously determined for the alkaloid cinchonine with chemical correlations (Turner & Woodward, 1953; Lyle & Keefer, 1967). It is also in agreement with the absolute configuration determined for quinidine (Carter, McPhail & Sim, 1967). The Newman projections along the C(4)—N(1) and C(9)—C(8) bonds [Fig. 3(*a*) and (*b*) respectively] show a mutual *cis* orientation of the C(3)—C(10) and C(8)—C(9) bonds, as well as the *erythro* configuration around C(9)—C(8).

The quinuclidinium part of the molecule has a skew conformation, the bonds C(4)—C(3), C(4)—C(5), C(4)—C(7) being rotated about −13° from the eclipsed position over the bonds N(1)—C(2), N(1)—C(6), N(1)—C(8). This angle is close to that reported by Carter *et al.* (1967) and has the same sign.

The bond lengths between N(1) and the surrounding C atoms are in the range of values reported for similar systems of atoms (*Molecular Structures and Dimensions*, 1972).

The quinolinium cation ring is planar within experimental error (Table 6). The distances N(13)—C(22), N(13)—C(14) and the angle C(22)—N(13)—C(14) are respectively: 1·371, 1·327 Å and 122·3°. These values are very close to those determined in quinolinium and isoquinolinium cations (Paulus & Göttlicher, 1969; Genet, 1965) and higher than the corresponding values, 1·31, 1·28 Å and 120°, found in

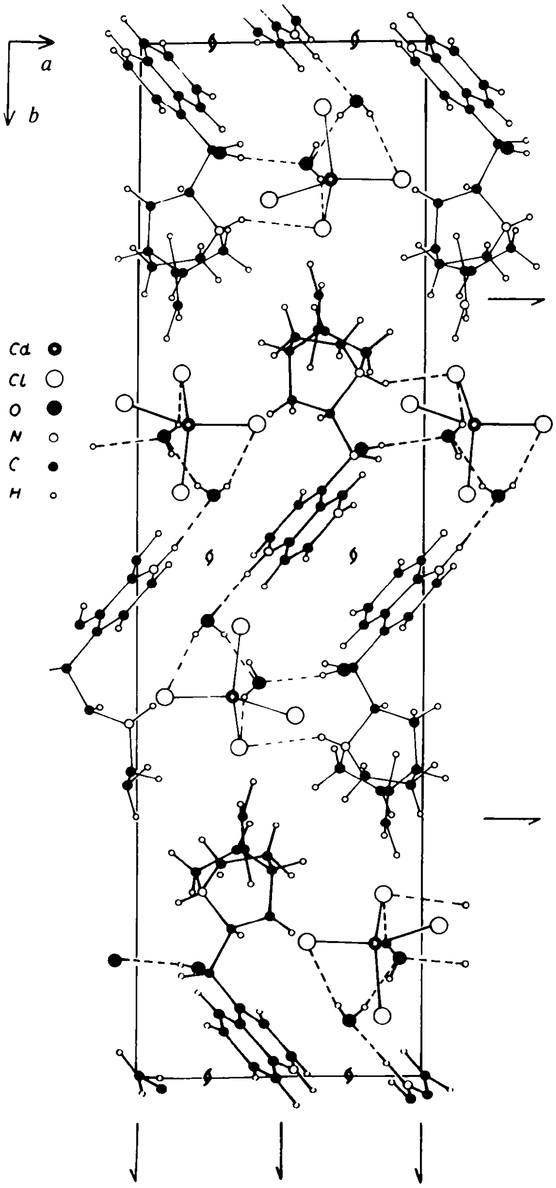
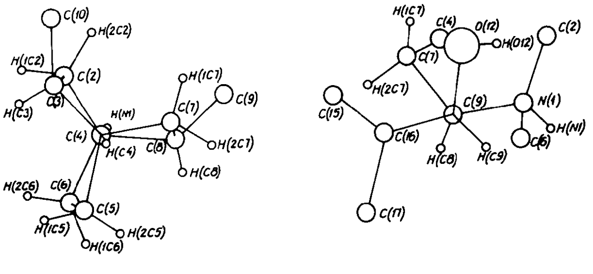


Fig. 2. The structure projected along **c**.

unprotonated quinoline (Bjorvatten & Hassel, 1962). This fact can be explained by the electron-withdrawing behaviour of the proton H(N13) leading to increase of the C—N—C angle and weakening of the N(13)—C bonds.

In view of the antimalarial activity of cinchonine it seemed interesting to compare its geometry with that postulated by Cheng (1971) for a large group of synthetic antimalarials. According to his hypothesis the antimalarial activity is related to (i) the characteristic side lengths in the triangle formed by the centre, *P*, of a planar (aromatic or heteroaromatic) ring, the O atom, and the N of the nonplanar part of the molecule, (ii) the possibility of formation of an intramolecular hydrogen bond between the O atom and the N atom of the nonplanar part. As shown in Table 7, the corresponding distances in the cinchonium cation do not contradict the first of Cheng's postulates. But his second postulate is not supported in the present crystal structure (Fig. 1).

Fig. 2, which depicts the unit-cell contents projected along **c**, shows the presence of spirals around alternate screw axes parallel to **c**, in each of which the ions and water molecules are linked *via* six distinct hydrogen bonds, details of which appear in Table 5. Adjacent spirals cohere *via* van der Waals and electrostatic forces, though there is one shortish contact of 2·60 Å between H(C14) and Cl(3) ($\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$).



(*a*) (*b*)

Fig. 3. Newman projections: (*a*) of the quinuclidinium moiety along the C(4)—N(1) line, (*b*) of the fragment of the molecule along the C(9)—C(8) bond.

Table 5. *Hydrogen-bond distances* (Å) *and angles* (°)

D	H	*A*	H···*A*	*D*···*A*	*D*—H···*A*
O(*W*1)	H(1*W*1)	Cl(1)	2·52 (8)	3·292 (7)	150 (5)
N(1)	H(N1)	Cl(2)	2·52 (8)	3·276 (7)	150 (5)
O(*W*2)	H(2*W*2)	Cl(2)	2·33 (8)	3·199 (7)	151 (5)
O(12)	H(O12)	O(*W*2)	2·11 (9)	2·780 (8)	172 (6)
O(*W*1)	H(2*W*1)	O(*W*2^{ii})	2·08 (9)	2·784 (8)	138 (6)
N(13)	H(N13)	O(*W*1^{i})	1·93 (10)	2·737 (9)	171 (6)

Symmetry code

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

Table 6. *The deviations* (Å) *of the atoms from the least-squares plane in the quinolinium part of the molecule*

The equation of the plane is $6 \cdot 3524x + 21 \cdot 7245y + 1 \cdot 9686z = 17 \cdot 52$ (x,y,z are the fractional coordinates along a, b, and c).

N(13)	−0·012	C(18)	−0·004
C(14)	−0·003	C(19)	−0·013
C(15)	0·004	C(20)	0·013
C(16)	0·001	C(21)	−0·002
C(17)	0·007	C(22)	0·009

Table 7. *Comparison of the geometries of synthetic antimalarials with the title compound*

	O–N	P–N	P–O
Antimalarials other than *Cinchona* alkaloids (Cheng, 1971)	3·18 ± 0·17 Å	4·98 ± 0·34 Å	3·85 ± 0·27 Å
Cinchoninium cation (this paper)	3·120 (8)	5·195 (10)	3·615 (9)

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The Structure of 1-Deoxy-1-thio-1,6-anhydro-β-D-glucopyranose: Thiolevoglucosan*

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$C_6H_{10}O_4S$, $M_r = 178{\cdot}21$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}654$ (1), $b = 12{\cdot}235$ (1), $c = 8{\cdot}893$ (1) Å [λ(Cu $K\alpha_1$) = 1·54051 Å], $V = 723{\cdot}99$ Å^3, $Z = 4$, $D_m = 1{\cdot}639$, $D_x = 1{\cdot}635$ g cm^{-3}. The structure was solved by *MULTAN* and refined to $R(F_o) = 0{\cdot}026$ and $R_w(F_o) = 0{\cdot}032$ for 909 reflections measured with graphite-monochromated Cu $K\alpha$ radiation. The conformation is very similar to that of the 1,6-anhydro-β-D-glucopyranose molecule, having a distorted $^1C_4$ pyranose ring and an E^0 anhydro ring. The three axial hydroxyl groups and the ring O and S atoms are all hydrogen-bonded. There is an unsymmetrical bifurcated interaction, involving a strong H···S bond, 2·38 Å, and a weak intramolecular H···O bond, 2·87 Å.

Introduction

This work is part of a series aimed at studying the effect of substituents and hetero-atoms on the fused-ring conformation and molecular dimensions of anhydro sugars. Other 1,6-anhydro sugar structures which have been studied are 1,6-anhydro-β-D-glucopyranose (levoglucosan) (Park, Kim & Jeffrey, 1971; Lindberg, 1974), 2,3-di-*O*-acetyl-1,6-anhydro-β-D-galactopyranose (Foces-Foces, Cano & García-Blanco, 1976), 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (Leung & Marchessault, 1974), 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose (Noordik & Jeffrey, 1977), and 3-ammonio-1,6-anhydro-3-deoxy-β-D-glucopyranose chloride monohydrate (Małuszyńska, Takagi & Jeffrey, 1977).

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