atomic coordinates are given in Table 1* and the bond lengths and angles in Table 2.

Discussion. The structure consists of six-coordinate monomeric $[(Cu[14]tetraeneN_4)(H_2O)_2]^{2+}$ units and NO_3^- ions. The complex cation is shown in Fig. 1. Cu has tetragonally distorted octahedral coordination geometry. The Cu atom lies at a center of symmetry, and the complex cation has point symmetry $2/m$. The four N atoms which are coordinated to Cu are necessarily planar. Their arrangement is a rectangle with sides N(1)–N(1)($x,-y,-z$) and N(1)–N(1)($-x,y,z$) equal to 2·560 (2) and 2·992 (3) Å respectively. The angles subtended by the N atoms at Cu show significant deviations from 90°: N(1)–Cu–N(1)($x,-y,-z$) in the five-membered chelate ring is 81·1 (1)° and N(1)–Cu–N(1)($-x,y,z$) in the six-membered chelate ring is 98·9 (1)°. The coordination is completed by O atoms from each of the two water molecules at a distance of 2·556 (5) Å. The Cu–O(1) bond is slightly tilted [5·4 (1)°] relative to the normal to the equatorial plane.

Because of the symmetry the five-membered chelate ring is planar, and, also, the whole macrocycle ligand, except for C(2), is almost planar. The C(2) atom is positionally disordered above and below this plane and therefore the six-membered chelate ring exists in the structure in two conformations.

The O atoms of the nitrate ions have large temperature factors, but no disorder was observed in the nitrate ions. Their point symmetry is 2.

There are no contacts shorter than the sums of van der Waals radii between adjacent molecules.

* Lists of observed and calculated structure factors, anisotropic thermal parameters for non-H atoms and positional parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36397 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

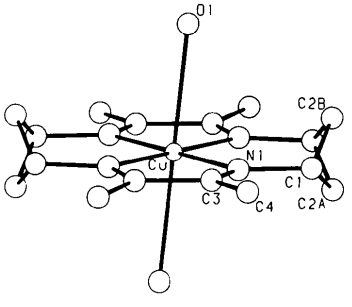

Fig. 1. View of the cation showing the atom numbering.

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Acta Cryst. (1982). B**38**, 929–932

Structure of Carfecillin (Sodium Salt)

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(*Received* 27 *April* 1981; *accepted* 21 *September* 1981)

Abstract. $C_{23}H_{21}N_2NaO_6S$, monoclinic, space group $P2_1$, $a = 8·77$ (3), $b = 6·20$ (3), $c = 21·40$ (3) Å, $\beta = 99·5$ (1)°, $V = 1147·6$ Å^3, $Z = 2$, $D_c = 1·378$ Mg m^{-3}, μ(Cu $K\alpha$) = 1·476 mm^{-1}. The final $R = 0·095$ for 1198 reflexions. The title compound is the α-phenyl ester of carbenicillin. The configuration of the asymmetric carbon to which the phenyl ester group is attached is *R*.

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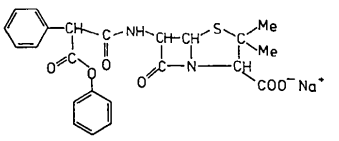
0567-7408/82/030929-04$01.00

Introduction. Carfecillin is a pro-drug of carbenicillin which is a widely used penicillin. Carbenicillin is poorly absorbed after oral administration so that its use is limited to parenteral administration. Carfecillin is well absorbed by the oral route and undergoes hydrolysis in the body to give carbenicillin (Clayton, Cole, Elson, Hardy, Mizen & Sutherland, 1975; Basker, Comber, Sutherland & Valler, 1977). Clayton *et al.* (1975) have described the synthesis of carfecillin. The molecule contains an asymmetric centre in the side chain as well as three asymmetric centres in the nucleus. The configuration of the three nuclear centres is fixed as in other penicillins by synthesis from the natural precursor, 6-aminopenicillanic acid. Deliberate resolution of the side-chain asymmetric centre is not carried out in the synthesis but the compound can be isolated from aqueous alcohols as a crystalline product which was considered, on the basis of NMR evidence, to be a single epimer in the solid state (Clayton *et al.*, 1975). This study was undertaken to establish the configuration of the side-chain asymmetric centre and to compare the crystal structure with those of other penicillins.



Carfecillin was obtained from Beecham Pharmaceuticals. 2 g starting material was dissolved in 7 cm^3 distilled water at 321 K and to this solution 18 cm^3 of ethanol and 18 cm^3 2-propanol were added slowly to prevent clouding. The solution was maintained at 277 K and protected from light for seven days. The flat plate-like crystals were filtered off and dried. NMR spectra of the redissolved crystals confirmed the same structure and configuration at the side-chain asymmetric centre as the starting material. All crystals produced were twinned. It was impossible to cleave the overlapping coincident plane and part of each twin was removed to obtain crystals of typical size 1·0 × 1·0 × 0·1 mm for use in obtaining X-ray data (Gane, 1979). The unit-cell dimensions were determined from zero-level Weissenberg photographs. Systematic absences $0k0, k = 2n + 1$, indicated space group $P2_1$.

Data for intensity measurement were obtained by the equi-inclination Weissenberg method with Ni-filtered Cu $K\alpha$ radiation (λ = 1·5418 Å) and the multiple-film technique. The crystals for these measurements were rotated about **b***. There was some reduction in intensity of reflexion at high sin θ after crystals had prolonged exposure to X-rays, and five different crystals of very similar dimensions were used. The intensities of the X-ray reflexions were measured by the Science Research Council microdensitometer at Daresbury. A total of 1208 reflexions were of measurable intensity.

Discussion. The coordinates of the non-H atoms are given in Table 1.* Bond distances and angles with e.s.d.'s are listed in Table 2. Fig. 1 gives a view of the unit-cell contents along **a**. There is a significant difference in the S–C bond lengths similar to that observed in the amoxycillin structure (Boles, Girven & Gane, 1978). The C(6)–C(7) length of 1·67 Å is significantly higher than the typical C(6)–C(7) length of 1·51 Å determined in amoxycillin and ampicillin (Boles & Girven, 1976*a*).

The major computations were carried out with *SHELX* (Sheldrick, 1975) on an ICL 1903A computer. Due to the plate-like shape of the crystal absorption corrections with the *SHELX 'ABSC'* routine were applied. The S-atom position was determined from a sharpened Patterson function and the

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36415 (11 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* (×10⁴) *and equivalent U values* (Å² × 10³) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.

	x	*y*	*z*	U_{eq}
S(1)	2614 (6)	0	1492 (3)	20 (2)
C(2)	2842 (23)	−3049 (42)	1580 (10)	17 (8)
C(3)	2004 (22)	−3992 (37)	960 (9)	23 (7)
N(4)	670 (17)	−2555 (26)	733 (7)	11 (5)
C(5)	958 (22)	−143 (47)	860 (9)	30 (8)
C(6)	−712 (23)	100 (40)	1032 (10)	27 (8)
C(7)	−712 (28)	−2592 (43)	1009 (11)	35 (9)
O(8)	−1514 (18)	−3948 (33)	1146 (9)	57 (7)
C(9)	2097 (23)	−3847 (38)	2137 (8)	23 (7)
C(10)	4622 (21)	−3547 (33)	1695 (9)	21 (7)
C(11)	3078 (22)	−4157 (40)	437 (8)	25 (7)
O(12)	3325 (18)	−6048 (24)	263 (6)	33 (6)
O(13)	3440 (15)	−2410 (22)	204 (6)	21 (5)
N(14)	−799 (17)	771 (27)	1663 (7)	20 (5)
C(15)	−2133 (20)	1481 (37)	1822 (8)	23 (7)
O(16)	−3398 (14)	1419 (22)	1454 (6)	22 (4)
C(17)	−2141 (21)	2461 (35)	2478 (8)	21 (7)
C(18)	−3141 (13)	1142 (24)	2848 (7)	28 (7)
C(19)	−2605 (13)	−878 (24)	3073 (7)	31 (8)
C(20)	−3491 (13)	−2141 (24)	3416 (7)	49 (9)
C(21)	−4913 (13)	−1383 (24)	3536 (7)	58 (11)
C(22)	−5448 (13)	638 (24)	3311 (7)	63 (11)
C(23)	−4562 (13)	1900 (24)	2968 (7)	39 (8)
C(24)	−575 (25)	2783 (45)	2908 (9)	39 (9)
O(25)	565 (15)	1680 (26)	2930 (6)	34 (5)
O(26)	−654 (16)	4472 (25)	3322 (7)	39 (6)
C(27)	441 (17)	4721 (25)	3840 (6)	47 (9)
C(28)	1219 (17)	6686 (25)	3936 (6)	56 (10)
C(29)	2253 (17)	7048 (25)	4495 (6)	59 (10)
C(30)	2509 (17)	5445 (25)	4958 (6)	87 (15)
C(31)	1730 (17)	3480 (25)	4862 (6)	88 (14)
C(32)	696 (17)	3118 (25)	4303 (6)	59 (11)
Na(33)	4871 (8)	881 (13)	457 (3)	24 (3)

Table 2. *Bond lengths* (Å) *and angles* (°)

S(1)–C(2)	1·907 (26)	C(17)–C(18)	1·515 (24)
S(1)–C(5)	1·816 (19)	C(18)–C(19)	1·395 (20)
C(2)–C(3)	1·523 (28)	C(18)–C(23)	1·395 (18)
C(2)–C(9)	1·533 (31)	C(19)–C(20)	1·395 (20)
C(2)–C(10)	1·570 (27)	C(20)–C(21)	1·395 (18)
C(3)–N(4)	1·487 (25)	C(21)–C(22)	1·395 (20)
C(3)–C(11)	1·580 (29)	C(22)–C(23)	1·395 (20)
N(4)–C(5)	1·533 (33)	C(24)–O(25)	1·206 (28)
N(4)–C(7)	1·434 (30)	C(24)–O(26)	1·381 (29)
C(5)–C(6)	1·576 (30)	O(26)–C(27)	1·350 (18)
C(6)–C(7)	1·670 (36)	C(27)–C(28)	1·395 (21)
C(6)–N(14)	1·427 (26)	C(27)–C(32)	1·395 (19)
C(7)–O(8)	1·164 (32)	C(28)–C(29)	1·395 (17)
C(11)–O(12)	1·260 (29)	C(29)–C(30)	1·395 (19)
C(11)–O(13)	1·255 (28)	C(30)–C(31)	1·395 (21)
N(14)–C(15)	1·345 (24)	C(31)–C(32)	1·395 (17)
C(15)–O(16)	1·251 (19)		
C(15)–C(17)	1·530 (26)	Na(33)···O(12)	2·334
C(17)–C(24)	1·535 (26)	Na(33)···O(13)	2·410

C(5)–S(1)–C(2)	94·8 (1·1)	O(16)–C(15)–N(14)	123·3 (1·6)
C(3)–C(2)–S(1)	105·4 (1·5)	C(17)–C(15)–N(14)	119·8 (1·4)
C(9)–C(2)–S(1)	110·3 (1·6)	C(17)–C(15)–O(16)	116·9 (1·6)
C(5)–C(2)–C(3)	110·3 (1·8)	C(24)–C(17)–C(15)	117·6 (1·6)
C(10)–C(2)–S(1)	107·2 (1·5)	C(18)–C(17)–C(15)	110·9 (1·6)
C(10)–C(2)–C(3)	112·7 (1·8)	C(18)–C(17)–C(24)	107·1 (1·4)
C(10)–C(2)–C(9)	110·8 (1·6)	C(19)–C(18)–C(17)	118·3 (1·3)
N(4)–C(3)–C(2)	107·2 (1·7)	C(23)–C(18)–C(17)	121·7 (1·4)
C(11)–C(3)–C(2)	112·5 (1·6)	C(23)–C(18)–C(19)	120·0 (1·3)
C(11)–C(3)–N(4)	109·6 (1·5)	C(18)–C(19)–C(20)	120·0 (1·2)
C(5)–N(4)–C(3)	115·4 (1·4)	C(21)–C(20)–C(19)	120·0 (1·3)
C(7)–N(4)–C(3)	121·9 (1·7)	C(22)–C(21)–C(20)	120·0 (1·3)
C(7)–N(4)–C(5)	94·0 (1·6)	C(23)–C(22)–C(21)	120·0 (1·2)
N(4)–C(5)–S(1)	105·5 (1·4)	C(18)–C(23)–C(22)	120·0 (1·3)
C(6)–C(5)–S(1)	118·7 (1·4)	O(25)–C(24)–C(17)	127·1 (2·1)
C(6)–C(5)–N(4)	90·1 (1·6)	O(26)–C(24)–C(17)	110·4 (1·8)
C(7)–C(6)–C(5)	83·9 (1·8)	O(26)–C(24)–O(25)	122·3 (1·8)
N(14)–C(6)–C(5)	116·6 (1·6)	C(27)–O(26)–C(24)	120·6 (1·5)
N(14)–C(6)–C(7)	108·6 (1·8)	C(28)–C(27)–O(26)	119·0 (1·3)
C(6)–C(7)–N(4)	90·0 (1·7)	C(32)–C(27)–O(26)	120·7 (1·4)
O(8)–C(7)–N(4)	134·6 (2·5)	C(32)–C(27)–C(28)	120·0 (1·1)
O(8)–C(7)–C(6)	135·4 (2·3)	C(27)–C(28)–C(29)	120·0 (1·3)
O(12)–C(11)–C(3)	115·0 (1·9)	C(30)–C(29)–C(28)	120·0 (1·4)
O(13)–C(11)–C(3)	116·5 (2·0)	C(31)–C(30)–C(29)	120·0 (1·1)
O(13)–C(11)–O(12)	128·1 (1·9)	C(32)–C(31)–C(30)	120·0 (1·3)
C(15)–N(14)–C(6)	121·3 (1·4)	C(27)–C(32)–C(31)	120·0 (1·4)

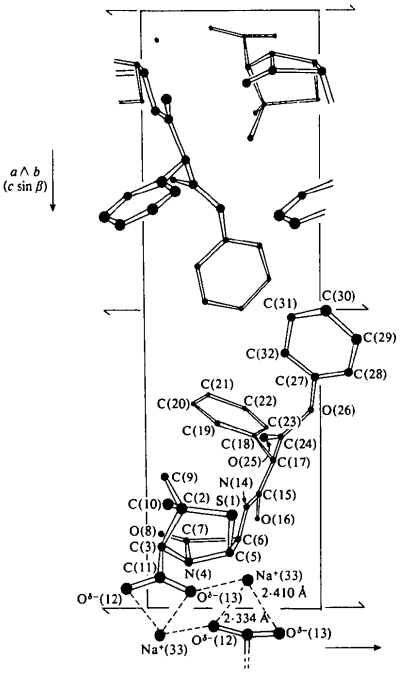


Fig. 1. The crystal structure of carfecillin viewed along **a**.

structure was solved by Fourier syntheses with the phases calculated initially from the S-atom position and then from the S atom together with those other atoms whose positions could be located from previous Fourier syntheses.

Three cycles of unweighted full-matrix least-squares refinement with individual isotropic temperature factors and refinement of scale factors resulted in $R = 0{\cdot}120$. An $(F_o - F_c)$ Fourier synthesis showed considerable anisotropic thermal vibration associated particularly with the S atom. Anisotropic refinement resulted in $R = 0{\cdot}095$, after omitting ten low-order reflexions suffering from severe extinction.* The benzene rings were refined as rigid groups and all H atoms were given isotropic temperature factors the same as the isotropic values of the atom to which they are bonded; the bond length was fixed at 1·08 Å. No further improvement could be made in F_o/F_c correlation probably due to the observed deterioration of the crystals during prolonged X-ray exposure. The highest peak in the final ΔF map was 0·51 e Å^{-3}.

Previous reports (Boles & Girven, 1976*a*,*b*; Boles *et al.*, 1978) have compared the conformation of thiazolidine rings of known penicillin structures and also the bonding geometry at the β-lactam nitrogen in some penicillins and cephalosporins. The thiazolidine ring of penicillins exists with four of its five atoms

* The temperature factors of the following atoms were non-positive-definite: C(2), C(3), N(4), C(9), C(10), O(16), C(31).

Table 3. *Mean-plane calculations*

Equations are expressed as $Px + Qy + Rz = S$ in direct space; with x, y and z given as fractions of cell edges a, b and c respectively.

P	*Q*	*R*	*S*	Deviations (Å) of atoms from planes	
(*a*) Planarity of the thiazolidine ring					
−0·3810	−0·0072	1	0·0496	S(1)	0·00
				C(2)*	0·06 (0·01)
				C(3)*	0·42 (0·01)
				N(4)	0·00
				C(5)	0·00
(*b*) Pyramidal nature of N(4)					
0·0365	0·0359	1	0·0890	C(3)	0·00
				N(4)*	0·47 (0·01)
				C(5)	0·00
				C(7)	0·00
(*c*) Deviation of N(4) and O(8) from the plane of the remaining β-lactam constituents					
0·1018	−0·0085	1	0·0958	N(4)*	0·28 (0·02)
				C(5)	0·00
				C(6)	0·00
				C(7)	0·00
				O(8)*	0·14 (0·02)

* Atoms not used to define the planes.

nearly coplanar and with the remaining atom out of this plane. In carfecillin, C(3) is 0·42 Å out of the plane defined by S(1), C(5), N(4) and C(2) (Table 3). The thiazolidine ring is therefore very similar to that in phenoxymethylpenicillin (Abrahamsson, Crowfoot-Hodgkin & Maslen, 1963) and potassium benzylpenicillin (Crowfoot, Bunn, Rogers-Low & Turner-Jones, 1949), which is characterized by C(3) out of the common plane. The distance of N(4) from the plane defined by C(3), C(5), C(7) is 0·47 Å in carfecillin, a similar value to that of 0·44 Å for methicillin methyl ester (Blanpain, Melebeck & Durant, 1977). Thus the configuration of this N atom conforms to the pyramidal arrangement which appears to be a common feature of biologically active penicillins and cephalosporins (Sweet & Dahl, 1970; Vijayan, Anderson & Hodgkin, 1973). N(4) is also significantly (0·28 Å) out of the plane of the remaining β-lactam constituents C(5), C(6) and C(7) (Table 3).

The configuration of the side-chain asymmetric C(17) in carfecillin has been assigned by comparison of the structure reported here with the crystal structures of ampicillin anhydrate (Boles & Girven, 1976*a*), ampicillin trihydrate (James, Hall & Hodgkin, 1968) and amoxycillin trihydrate (Boles *et al.*, 1978). The asymmetric centres C(3), C(5) and C(6) of the penicillin nucleus have configuration *S*, *R* and *R* respectively as in all penicillins derived from the naturally occurring precursor, 6-aminopenicillanic acid. The configuration of the side-chain asymmetric C atom in ampicillin and amoxycillin is known to be *R* because they are synthesized from the resolved amino acids, (*R*)-α-aminophenylacetic acid and (*R*)-α-amino-4-hydroxyphenylacetic acid. Comparison of the configuration of carfecillin with the ampicillin and amoxycillin structures shows that the C(17) configuration in crystalline carfecillin is also *R*.

The authors wish to acknowledge the microdensitometer facility provided by the Science Research Council and particularly the service and advice provided in this respect by Drs M. Elder and M. Pickering and Miss P. Machin at the Daresbury Laboratory. We also thank Mr N. Ward (Beecham Pharmaceuticals) and Dr R. J. Girven (formerly at Plymouth Polytechnic) for advice concerning the crystallization of carfecillin. One of us (PACG) acknowledges the award of a research assistantship by Devon Local Authority.

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Acta Cryst. (1982). B**38**, 932–934

Structure of Tribromotris(pyridine)indium(III) Pyridine Solvate

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(*Received* 2 *July* 1981; *accepted* 21 *September* 1981)

Abstract. $[In(C_5H_5N)_3Br_3.C_5H_5N]$, $C_{20}H_{20}Br_3InN_4$, monoclinic, $P2_1$, $a = 9{\cdot}635\ (5)$, $b = 14{\cdot}87\ (5)$, $c = 9{\cdot}153\ (5)$ Å, $\beta = 118{\cdot}00\ (2)°$, $Z = 2$, $D_x = 1{\cdot}923$, $D_m = 1{\cdot}91$ Mg m^{-3}. The structure has been solved from 1193 diffractometer-measured intensities with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) and refined by full-matrix least squares to $R = 0{\cdot}0668$. The crystal structure consists of 'octahedral' $InBr_3.3(C_5H_5N)$ molecules

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