

The Solid-State Conformation and Structure of Formycin B Hydrochloride

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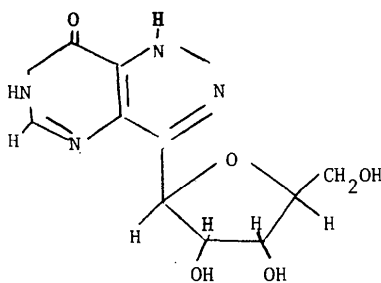
The crystal and molecular structure of formycin B hydrochloride, $C_{10}H_{12}N_4O_5 \cdot HCl$, has been determined from 1038 $Cu K\alpha$ diffractometer data. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 11.329$ (3), $b = 22.370$ (7), $c = 4.995$ (1) Å, $U = 1265.9$ Å³, $Z = 4$. The structure has been refined by the full-matrix least-squares procedures to an R index of 0.025. The formycin B cation is protonated at N(3), and the diazole proton is at N(7). The conformation around the glycosyl bond is *syn* with a torsion angle, χ , of -140.1° . There is an intramolecular hydrogen bond, $N(3)-H \cdots O(5')$, present in the molecule. The ribose ring is puckered in the $C(2')$ -*endo*-envelope conformation, and the conformation of the $C(5')-O(5')$ bond around the exocyclic bond, $C(4')-C(5')$, is *gauche-gauche*. The *syn* conformation around the glycosyl bond observed in the solid state differs from the *anti* conformation reported for the 0.01*N* aqueous hydrochloric acid solution of formycin B.

Introduction

Formycin B (I) is a nucleoside antibiotic with antibacterial and antifungal properties (Umezawa, Sawa, Fukagawa, Koyama, Murase, Hamada & Takeuchi, 1965). It is an analog of inosine with a C–C glycosyl bond, and possesses some anomalous properties which have been attributed to the nucleoside adopting a *syn* conformation around the glycosyl bond (Sheen, Martin & Parks, 1970; Ward & Reich, 1969). Experimentally, however, the glycosyl conformation of formycin B, in the solid state (Singh & Hodgson, 1975; Hodgson & Singh, 1976; Koyama, Nakamura, Umezawa & Iitaka, 1976), in aqueous solution and in 0.01*N* hydrochloric acid (Zemlicka, 1975), has been shown to be *anti*. We have, therefore, undertaken an X-ray crystallographic investigation of formycin B hydrochloride to determine the conformation of the cation of the antibiotic. The results described below show that the formycin B cation (in the hydrochloride) has the *syn* conformation.

Experimental

Colorless crystals of formycin B hydrochloride were obtained by slow evaporation at room temperature of a concentrated solution of formycin B in 1*N* hydrochloric acid. Preliminary cell constants and the space group were determined from Weissenberg and precession photography. The intensity data and precise cell constants were measured with $Cu K\alpha$ radiation on a computer-controlled Picker automatic diffractometer (FACS-I). The cell constants were obtained by the least-squares refinement of the orientation angles of 12 accurately centered reflections at a low take-off angle. The intensity data were collected by the $\theta/2\theta$ scan technique and were processed by the method of Corfield, Doedens & Ibers (1967) in a manner described elsewhere (Meyer, Singh, Hatfield & Hodgson, 1972). An absorption correction was applied with Hamilton's computer program *GONO9*. The pertinent crystallographic data are presented in Table 1.



(I)

Table 1. Crystallographic data

$C_{10}H_{12}N_4O_5 \cdot HCl$	$\mu(Cu K\alpha) = 19.8 \text{ cm}^{-1}$
$M_r = 304.6$	Crystal size: $0.38 \times 0.13 \times 0.05 \text{ mm}$
Space group: $P2_12_12_1$, orthorhombic	Scan width: $[1.9 + \Delta 2\theta(\alpha_2 - \alpha_1)]^\circ$
$a = 11.329$ (3) Å	Scan rate: 0.5 deg min^{-1}
$b = 22.370$ (7) Å	Background time: 40 s each side of peak
$c = 4.995$ (1) Å	2θ limit: 126°
$V = 1265.9$ Å ³	NO = 1038 > 3σ
$Z = 4$	$R = 0.025$
$D_c = 1.60 \text{ g cm}^{-3}$	$R_w = 0.032$
$D_m = 1.59$ (by flotation in CCl_4)	

Solution and refinement

The structure was solved by direct methods with *MULTAN* (Main, Woolfson & Germain, 1971). The H atoms were located from a difference Fourier map. The positional and thermal parameters (anisotropic for the non-hydrogen atoms and isotropic for the H atoms) were refined by the full-matrix least-squares procedure, the function minimized being $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. Examination of the data near the end of the refinement suggested that they were suffering from secondary extinction, so a correction for this effect was applied (Zachariasen, 1968). The final value of the extinction coefficient was $3.1(4) \times 10^{-7}$. The final residual, R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$), and weighted residual, R_w ($= [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$) were 0.025 and 0.032 respectively.

The scattering factors for C, N, O and Cl were taken from *International Tables for X-ray Crystallography* (1962) and those for H from Stewart, Davidson & Simpson (1965). The effects of the anomalous dispersion of Cl were included in the calculations, the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer & Liberman (1970).

Table 2. Positional parameters ($\times 10^4$; $\times 10^3$ for H) for formycin B hydrochloride

	x	y	z
Cl	946 (1)	1718 (0)	-3382 (2)
N(1)	1203 (2)	2641 (1)	1314 (6)
C(2)	248 (3)	2851 (2)	2508 (7)
N(3)	281 (2)	3263 (1)	4375 (6)
C(4)	1373 (3)	3489 (1)	5053 (7)
C(5)	2387 (3)	3262 (1)	3938 (7)
C(6)	2369 (3)	2805 (1)	1922 (8)
O(6)	3198 (2)	2575 (1)	797 (7)
N(7)	3292 (3)	3566 (1)	5025 (7)
N(8)	2920 (2)	3981 (1)	6778 (7)
C(9)	1741 (3)	3948 (1)	6809 (7)
C(1')	971 (3)	4361 (1)	8372 (7)
C(2')	323 (3)	4821 (1)	6616 (8)
O(2')	1026 (3)	5338 (1)	6279 (7)
C(3')	-804 (3)	4936 (1)	8231 (9)
O(3')	-613 (3)	5357 (1)	10318 (6)
C(4')	-1059 (3)	4340 (1)	9568 (8)
O(4')	41 (2)	4002 (1)	9469 (5)
C(5')	-2020 (3)	3958 (2)	8415 (8)
O(5')	-1751 (2)	3817 (1)	5669 (5)
HN(1)	110 (3)	232 (2)	-3 (10)
HC(2)	-46 (3)	270 (1)	212 (7)
HN(3)	-45 (3)	344 (2)	491 (9)
HN(7)	413 (4)	352 (2)	457 (12)
HC(1')	144 (3)	457 (1)	976 (7)
HC(2')	15 (2)	465 (1)	484 (7)
HO(2')	95 (5)	542 (2)	482 (13)
HC(3')	-149 (3)	506 (2)	690 (10)
HO(3')	-61 (4)	567 (2)	946 (12)
HC(4')	-128 (3)	441 (1)	1129 (9)
H1C(5')	-278 (3)	417 (1)	850 (8)
H2C(5')	-211 (3)	359 (2)	946 (9)
HO(5')	-233 (5)	365 (2)	499 (13)

The positional parameters and their associated standard deviations, as estimated from the inverse matrix of the last cycle of least squares, are presented in Table 2.*

Discussion

A computer drawing of the protonated formycin B cation is shown in Fig. 1. The extra proton is attached to atom N(3) of the pyrimidine moiety. The diazole proton remains at N(7), whereas in the formycin A cation it migrates to N(8) (Koyama, Umezawa & Iitaka, 1974).

Bond distances and bond angles

The bond distances and bond angles, involving the non-hydrogen atoms, in the formycin B.H⁺ cation (FBH⁺, hereinafter) are shown in Fig. 2, and those involving the H atoms are presented in Table 3.

A comparison of bond distances in FBH⁺ with those reported for the neutral formycin B molecule (FB,

* Lists of observed and calculated structure amplitudes, and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32655 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

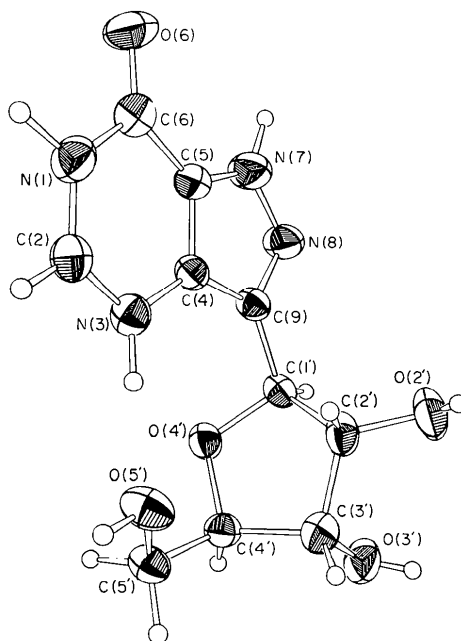


Fig. 1. A view of the formycin B.H⁺ cation. Atoms are drawn with 50% probability thermal ellipsoids (Johnson, 1965). Hydrogen atoms are drawn as small open circles for clarity.

hereinafter; Koyama *et al.*, 1976) shows that only two bond distances in the base moiety, *viz.* N(1)—C(2) and N(7)—N(8), have been affected significantly by the protonation of the base at atom N(3); the former is shortened by 0.018 Å and the latter is shortened by 0.022 Å. Surprisingly, however, the two bonds closest to the site of protonation, *viz.* N(3)—C(2) and N(3)—C(4), have not been affected at all; in FBH⁺ and FB, respectively, the bond distance N(3)—C(2) is 1.311 (4) and 1.310 (5) Å, and the bond distance N(3)—C(4) is 1.380 (4) and 1.386 (6) Å. This is unexpected since base protonation at a particular ring N atom almost always increases the bond distances associated with it. The glycosyl bond distance, C(9)—C(1'), and the bond distances in the ribose moiety of FBH⁺ are all within 3σ of those reported for FB (Koyama *et al.*, 1976), except for C(3')—C(4'), which is shorter by 0.022 Å ($\sigma = 0.007$ Å for this bond distance in FB). As is usually the case in nucleosides, the C(1')—O(4') bond, 1.434 (4) Å, is shorter than the C(4')—O(4') bond, 1.459 (4) Å.

Bond angles are generally known to be quite sensitive to distortion by perturbing forces on a molecule. It has been observed that the protonation of a pyrimidine ring N atom increases the ring angle at that site by about 5° (Singh, 1965). The ring bond angles at N(3) of 117.3 (3)° and 112.6 (4)° in FBH⁺ and FB, respectively, are consistent with this observation. The adjacent pyrimidine ring angles at C(2) and C(4) in FBH⁺ are smaller than those in FB by 4.0 and 2.7°,

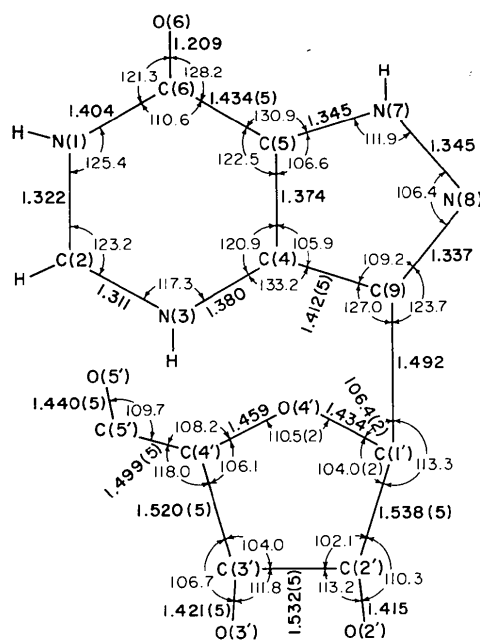


Fig. 2. Bond distances (Å) and bond angles (°) involving the non-hydrogen atoms in FBH⁺; e.s.d.'s are 0.004 Å and 0.3°, respectively, unless indicated otherwise. For clarity, H atoms on the ribose are not shown.

respectively, primarily in response to the 4.7° increase at N(3). Only two other bond angles in the purine moiety of FBH⁺, both of which are exocyclic, change significantly from the corresponding ones in FB: N(3)—C(4)—C(9) is increased by 3.5° and C(4)—C(9)—C(1') is increased by 2.2°. As is usually observed in nucleosides with the *syn* glycosyl conformation (see below) the exocyclic bond angle C(4)—C(9)—C(1') (127.0°) is larger than the exocyclic bond angle N(8)—C(9)—C(1') (123.7°) (Rao & Sundaralingam, 1970). The bond angles in the ribose moiety are in general agreement with those observed in other nucleosides with the same mode of ribose ring puckering, *i.e.* C(2')-*endo* (see below) (Prusiner, Brennan & Sundaralingam, 1973; Koyama *et al.*, 1976). The only significant difference in the endocyclic bond angles in the ribose moieties of FBH⁺ and FB, the latter with the C(2')-*endo*—C(1')-*exo* mode of ribose puckering, is at O(4'), where the bond angles are 110.5 (2) and 107.8 (4)° respectively. Among the exocyclic bond angles in the ribose moiety the largest difference between the protonated and the unprotonated formycin B is seen in the bond angle C(9)—C(1')—O(4'), which is 106.4 (2)° in FBH⁺ and 112.0 (4)° in FB. The smaller angle observed in FBH⁺ is consistent with the observed *syn* conformation around the glycosyl bond (Koyama *et al.*, 1976).

Planarity of the base

The nine-atom purine is only approximately planar, as seen from plane I in Table 4, with deviations of some atoms from the least-squares plane as high as 0.04 Å. Large deviations of similar magnitude have also been observed in both formycin A (Prusiner *et al.*, 1973) and

Table 3. Bond lengths (Å) and bond angles (°) involving the H atoms in formycin B hydrochloride

N(1)—HN(1)	0.99 (4)	HC(1')—C(1')—C(9)	110 (2)
C(2)—HC(2)	0.89 (3)	HC(1')—C(1')—C(2')	110 (2)
N(3)—HN(3)	0.96 (4)	HC(1')—C(1')—O(4')	113 (2)
N(7)—HN(7)	0.98 (5)	HC(2')—C(2')—C(1')	110 (2)
C(1')—HC(1')	0.99 (3)	HC(2')—C(2')—O(2')	109 (2)
C(2')—HC(2')	0.99 (3)	HC(2')—C(2')—C(3')	112 (2)
O(2')—HO(2')	0.76 (6)	HO(2')—O(2')—C(2')	105 (4)
C(3')—HC(3')	1.06 (4)	HC(3')—C(3')—C(2')	109 (2)
O(3')—HO(3')	0.83 (5)	HC(3')—C(3')—O(3')	113 (2)
C(4')—HC(4')	0.91 (4)	HC(3')—C(3')—C(4')	112 (2)
C(5')—H1C(5')	0.99 (3)	HO(3')—O(3')—C(3')	101 (4)
C(5')—H2C(5')	0.98 (4)	HC(4')—C(4')—C(3')	108 (2)
O(5')—HO(5')	0.83 (5)	HC(4')—C(4')—O(4')	111 (2)
HN(1)—N(1)—C(2)	118 (2)	HC(4')—C(4')—C(5')	105 (2)
HN(1)—N(1)—C(6)	116 (2)	H1C(5')—C(5')—C(4')	110 (2)
HC(2)—C(2)—N(1)	120 (2)	H2C(5')—C(5')—O(5')	109 (2)
HC(2)—C(2)—N(3)	116 (2)	H1C(5')—C(5')—H2C(5')	107 (2)
HN(3)—N(3)—C(2)	118 (2)	H2C(5')—C(5')—C(4')	110 (3)
HN(3)—N(3)—C(4)	124 (2)	H2C(5')—C(5')—O(5')	110 (3)
HN(7)—N(7)—C(5)	126 (3)	HO(5')—O(5')—C(5')	109 (4)
HN(7)—N(7)—N(8)	122 (3)		

Table 4. Deviations (Å) of atoms from the least-squares planes through the purine and the ribose atoms in formycin B hydrochloride

	Purine plane			Best ribose plane
	I	II	III	
N(1)	0.044	0.021	0.120*	C(1') -0.016
C(2)	0.004	-0.005	0.051*	C(2') 0.553*
N(3)	-0.038	0.019	-0.027*	C(3') 0.014
C(4)	-0.010	0.025	-0.006	C(4') -0.024
C(5)	-0.030	-0.009	0.003	O(4') 0.025
C(6)	-0.005	-0.014	0.068*	C(5') 1.056*
N(7)	-0.017	0.026*	0.001	
N(8)	0.016	0.085*	-0.005	
C(9)	0.036	0.101*	0.007	
O(6)	-0.011*	-0.034*		
C(1')	0.163*		0.094*	
HN(1)	0.037*			
HC(2)	-0.039*			
HN(3)	0.097*			
HN(7)	0.016*			
Cl	0.335*			
R.m.s. deviation†	0.014	0.007	0.002	0.005

* Atoms not included in the least-squares-plane calculation.

† R.m.s. deviations refer to atoms included in the least-squares-plane calculation.

formycin B (Koyama *et al.*, 1976). The substituent atom C(1') is displaced from this plane by 0.163 Å, and the chloride ion is displaced by 0.335 Å (Table 4). The six-atom pyrimidine plane, plane II in Table 4, also shows significant deviations of atoms from the least-squares plane. The dihedral angle between the six-atom pyrimidine plane and the five-atom diazole plane (plane III, Table 4) is 2.8°.

The glycosyl conformation

The conformation around the glycosyl bond, C(9)–C(1'), is *syn*, the torsion angle χ , N(8)–C(9)–C(1')–O(4') (Sundaralingam, 1969), being -140.1° . There is an intramolecular hydrogen bond between atom N(3) of the base and the terminal O atom, O(5'), of the ribose (Fig. 3), a feature commonly observed in *syn* nucleosides (Rao & Sundaralingam, 1970). It is noteworthy that the glycosyl conformation of formycin A cation in formycin A hydrobromide is also *syn* (Koyama *et al.*, 1974).

Our results for the glycosyl conformation of FBH⁺ in the solid state seem to be in conflict with those reported in solution by the circular dichroism method (Zemlicka, 1975). It was reported that the CD spectra of FB in aqueous as well as in 0.01N HCl solutions are alike, and are indicative of *anti* conformation. Although it is possible that the solid-state conformation of FBH⁺ is different from that observed in solution a more likely explanation might be that atom N(3) is not protonated to any significant degree in 0.01N HCl; this is quite probable, since in the related nucleoside inosine the *pK_a*

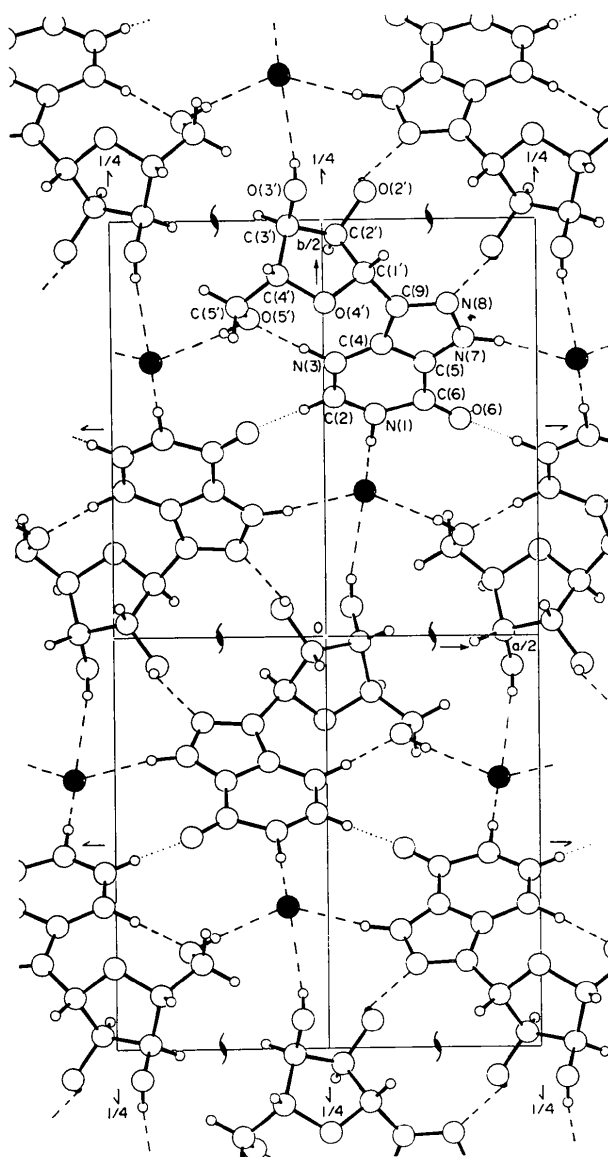


Fig. 3. Crystal structure viewed down the *c* axis. One unit cell is outlined with the origin in the middle of the cell. Chloride ions are shown as dark circles, the hydrogen bonds as dashed lines, and C(2)–H...O(6) interactions as dotted lines.

is reported to be 1.2. We might note in this connection that oxoformycin B, which also has a proton attached to atom N(3), has the *syn* conformation in the solid state (Koyama *et al.*, 1976).

The conformation of the ribose

The five-membered ribose ring is puckered in the C(2')-*endo* envelope (²*E*) conformation, with atom C(2') displaced by 0.553 Å in the same direction as atom C(5') from the best four-atom ribose plane (Table

Table 5. *Torsion angles in the ribose ring and around the C(4')-C(5') bond (°)*

τ_0 [C(4')-O(4')-C(1')-C(2')]	-25.5
τ_1 [O(4')-C(1')-C(2')-C(3')]	35.7
τ_2 [C(1')-C(2')-C(3')-C(4')]	-32.8
τ_3 [C(2')-C(3')-C(4')-O(4')]	18.4
τ_4 [C(3')-C(4')-O(4')-C(1')]	4.5
ϕ_{OO} [O(5')-C(5')-C(4')-O(4')]	-61.2
ϕ_{OC} [O(5')-C(5')-C(4')-C(3')]	59.2

4). The pseudorotation angle P (Altona & Sundaralingam, 1972) is 155° , which is in the 2T_1 range and near the ideal value of 162° for the 2E conformation. This is a favored conformation for *syn* nucleosides (Sundaralingam, 1973). The various torsion angles (Sundaralingam, 1969) are listed in Table 5. The conformation around the exocyclic bond, C(4')-C(5'), which determines the backbone conformation in polynucleotides and nucleic acids, is the familiar *gauche-gauche* (*gg*) which puts the terminal O atom O(5') on 'top' of the sugar ring. The dihedral angles ϕ_{OO} and ϕ_{OC} are -61.2 and 59.2° respectively (Table 5). It may be noted that neutral formycin B also has the *gg* conformation (Hodgson & Singh, 1976; Koyama *et al.*, 1976), but both the neutral formycin A (Prusiner *et al.*, 1973) and the protonated formycin A (Koyama *et al.*, 1974) have the *gauche-trans* (*gt*) conformation, which puts O(5') away from the sugar ring.

Hydrogen bonding and packing

The hydrogen bonding and packing in the crystal lattice, as shown in Fig. 3, are dominated by the chloride ions, each of which accepts four hydrogen bonds from four different FBH⁺ cations. The hydrogen-bond donors to the chloride ion are atoms N(1), N(7), O(3') and O(5'). The distances and angles associated with the possible hydrogen bonds are shown in Table 6, from which it appears that there is a C-H...O type interaction involving atoms C(2) and

Table 6. *Distances and angles associated with the possible hydrogen bonds*

A	H	B	A-H	H...B	A...B	$\angle AHB$
N(1)	H...	Cl	0.99 Å	2.15 Å	3.14 Å	171°
C(2)	H...	O(6)	0.89	2.20	3.00	151
N(3)	H...	O(5')*	0.96	1.74	2.69	175
N(7)	H...	Cl	0.98	2.21	3.18	172
O(2')	H...	N(8)	0.76	2.39	2.97	134
O(3')	H...	Cl	0.83	2.43	3.22	160
O(5')	H...	Cl	0.83	2.26	3.09	172

* An intramolecular hydrogen bond.

O(6). A similar C-H...O interaction involving the same atoms has also been observed in FB (Singh & Hodgson, unpublished observation). There is an intramolecular hydrogen bond, N(3)-H...O(5'), which, as stated earlier, is commonly observed, but with O(5') as the donor atom, in nucleosides with a *syn* conformation. The diazole basic N atom, N(8), accepts a hydrogen bond in FBH⁺ as it does in neutral FB, indicating that the protonation of the base at N(3) in FBH⁺ does not deplete the electron density appreciably at site N(8) (Hodgson & Singh, 1976).

The following computer programs, in addition to those mentioned in the text, were used: Robinson & Dellaca's version of Zalkin's Fourier program, Ibers's *NUCLS* least-squares refinement program, Busing, Martin & Levy's *ORFFE*, Bauer's *SADIAN* and Doedens & Ibers's least-squares plane calculation program.

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Metal Complexes in Detergent Analysis: The Crystal Structure of Bis(ethylenediamine)bis(dodecylsulphato)copper(II)

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Bis(ethylenediamine)bis(dodecylsulphato)copper(II) can be crystallized from absolute ethanol. The crystals are triclinic, space group $P\bar{1}$, $a = 5.608$ (1), $b = 8.247$ (1), $c = 21.381$ (3) Å, $\alpha = 97.30$ (3), $\beta = 95.07$ (3), $\gamma = 104.17$ (3)°, $V = 943.7$ Å³, $D_m = 1.24$, $D_x = 1.26$ g cm⁻³ for $Z = 1$. The intensities of 4448 unique reflexions were measured with an automatic diffractometer using Mo $K\alpha$ radiation. The structure was solved by standard Fourier methods and refined by full-matrix least-squares methods to a final R of 0.036 for 2858 reflexions with $I > 3\sigma(I)$. The Cu atom lies on a centre of symmetry. It is planar four-coordinated by the N atoms of two ethylenediamine ligands at a mean distance of 2.007 (2) Å. Two O atoms of the dodecylsulphato ligands occupy axial positions, 2.517 (2) Å from the Cu atom. In addition to the Cu–O bond, there are two intramolecular hydrogen bonds from each dodecylsulphato ligand to the bis(ethylenediamine)copper(II) moiety. The dodecyl chains are extended and form a highly ordered interdigitating structure. The non-bonded distances between the C atoms in one dodecyl chain and the closest C atoms in a neighbouring chain are in the range of 4.196 (5) to 4.301 (5) Å. The title compound is an example of the complexes formed between detergent anions and the bis(ethylenediamine)copper(II) ion in a recently published method for trace anionic detergent analysis.

Introduction

Analytical methods for the determination of anionic detergents most commonly involve the solvent extraction of an association complex formed between detergent anions and a cationic reagent. The reagent may be either an organic dyestuff such as the methylene-blue cation (*Standard Methods for the Examination of Water and Wastewater*, 1971) or a substitution inert metal chelate such as the tris(1,10-phenanthroline)copper(II) cation (Le Bihan & Courtot-Coupez, 1974). The association complexes formed are of the 'outer-sphere' or 'ion-pair' type first described by Bjerrum (1926). Methods using these reagents are liable to interference from other anions such as chloride and thiocyanate since these can also form extractable association complexes. The bis(ethylenediamine)copper(II) ion has recently been shown to be a more selective reagent (Crisp, Eckert & Gibson, 1975) and its use has been extended to the analysis of parts per billion concentrations of anionic detergents (Crisp, Eckert, Gibson, Kirkbright & West, 1976).

This paper describes the crystal structure of a complex formed between the bis(ethylenediamine)copper(II) ion and a typical anionic detergent. Unlike other cations used for detergent analysis, the bis(ethylenediamine)copper(II) ion forms an 'inner-sphere' association complex with detergent anions.

Experimental

Bis(ethylenediamine)bis(dodecylsulphato)copper(II) is precipitated when aqueous solutions of bis(ethylenediamine)copper(II) sulphate and sodium dodecylsulphate (BDH, specially pure) are mixed. Large purple plates were obtained by recrystallization from absolute ethanol.

Preliminary crystal data were obtained with a Supper precession camera using Zr-filtered Mo $K\alpha$ radiation. The Laue symmetry $\bar{1}$ indicated space group $P1$ or $P\bar{1}$. Space group $P\bar{1}$ was confirmed by solution of the structure.

A needle-shaped fragment of a crystal (0.08 × 0.12 × 0.66 mm) was used for the measurement of intensity