Crystal and Molecular Structure of 1-*p*-Methoxyphenyl-3-methyl-4-(D-arabinotetrahydroxybutyl)imidazoline-2-thione

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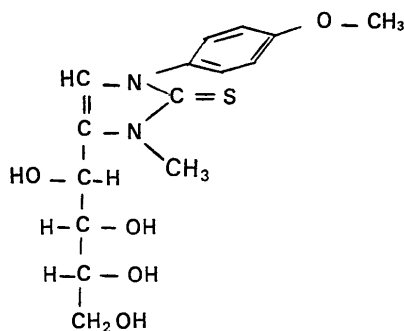
The crystal structure has been determined from three-dimensional X-ray data. The space group is $P2_12_12_1$ with four molecules in a unit cell of dimensions $a = 13\cdot571$ (6), $b = 10\cdot814$ (7) and $c = 10\cdot738$ (4) Å. The structure was solved by direct methods and refined with anisotropic temperature factors by full-matrix least-squares procedures. The final R value for 2021 independent reflexions is $0\cdot071$. The imidazoline and phenyl rings are both planar with the imidazoline plane twisted $68\cdot3°$ about the N–C(aromatic) bond with respect to the phenyl plane. The packing is dominated by the formation of hydrogen bonds.

Introduction

This work forms part of a crystal structural investigation of some *C*-glucimidazols, which have hitherto included 4-(β-D-erythrofuranosyl)imidazolidine-2-thione (Pérez-Garrido, López-Castro & Márquez, 1973), 1-*p*-chlorophenyl-4-(α-D-erythrofuranosyl)imidazolidine-2-thione (Pérez-Garrido, Conde & Márquez, 1974) and 1-methyl-4,5-(D-glucofurano)imidazoline-2-thione (Jiménez-Garay, López-Castro & Márquez, 1974). The principal aim of our investigation is to obtain the most complete information about the stereochemistry of these compounds.

The preparation and properties of 1-*p*-methoxyphenyl-3-methyl-4-(D-arabinotetrahydroxybutyl)imidazoline-2-thione have been described by García-González, Fernández-Bolaños & Fuentes-Mota (1972). The product, obtained as off-white crystals, was formulated as

Experimental

Single crystals of $SO_5N_2C_{15}H_{20}$ were prepared and kindly supplied by Professor J. Fernández-Bolaños (Departamento de Química Organica of this University).

Preliminary rotation and Weissenberg photographs indicated orthorhombic symmetry. The only observed systematic absences were $h00$ with $h = 2n + 1$; $0k0$ with $k = 2n + 1$ and $00l$ with $l = 2n + 1$, this uniquely establishing the space group as $P2_12_12_1$.

The unit-cell parameters were determined by least-squares methods from 25 accurate 2θ values measured on an automatic four-circle diffractometer. The resulting values with other crystal data are summarized below:

$a = 13\cdot571$ (6) Å	$M = 338$
$b = 10\cdot814$ (7)	$Z = 4$
$c = 10\cdot738$ (4)	$D_c = 1\cdot42$ g cm^{-3}
$V = 1575$ Å^3	$F(000) = 712$.

Intensity data were collected by the ω–2θ scan method on a Philips automated four-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å). Reflexions were collected to a maximum value of sin $\theta/\lambda = 0\cdot80$. Three reflexions, monitored at regular intervals during data collection, showed no significant variation in intensity. The intensities of 2631 independent reflexions were measured. 610 of these reflexions with $I < 2\sigma(I)$ were considered as unobserved and assigned a zero weight throughout the refinement process. Data were corrected for Lorentz-polarization effects. No correction for absorption was applied ($\mu R < 0\cdot1$).

Solution and refinement of the structure

The observed structure factors were converted into normalized structure amplitudes, $|E|$, by using the scale factor and the overall temperature factor obtained from Wilson's statistics. The $|E|$ statistics, indicated an acentric structure consistent with the space group determined from systematic absences.

The structure was solved by multisolution tangent formula refinement (Germain, Main & Woolfson, 1971) of 407 reflexions with $E \geq 1\cdot40$. The origin was fixed by the 11,11,0, 160 and 17,0,3 reflexions. An E-map calculated from the set with the highest merit figure gave 14 atoms of the structure. R was 0·39. The

structure was completed from a three-dimensional electron-density synthesis in which the phase angles were determined from the known atomic positions. The isotropic temperature factor $\exp(-B\sin^2\theta/\lambda^2)$ with $B = 2\cdot5$ Å^2 was used in calculating structure factors and the R value was 0·19.

The whole structure was then refined with full-matrix least-squares methods varying all positional parameters and temperature factors. Six cycles, of which the last three were with anisotropic thermal factors, were sufficient to reduce the discrepancy index to 0·077. A full-matrix least-squares program written by Busing, Martin & Levy (1964) was used and the Cruickshank (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) weight scheme gave the best results. A difference Fourier synthesis calculated with sin θ up to 0·35, revealed the positions of the 20 hydrogen atoms. A further cycle of refinement, including the hydrogen atoms with isotropic temperature factors equal to those of the bonded atoms and varying only the parameters of the non-hydrogen atoms, reduced R to 0·071. The shifts in the last cycle of refinement were less than 0·001σ for all non-hydrogen parameters. The correct enantiomorph was chosen in accord with the sugar configuration used in the preparation of the title compound. The atomic parameters from the final least-squares cycle are given in Table 1. The standard deviations were determined from the diagonal elements of the inverse matrix in the least-squares procedure.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31513 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Results and discussion

The molecular conformation of 1-p-methoxyphenyl-3-methyl-(D-arabinotetrahydroxybutyl)imidazoline-2-thione is shown in Fig. 1. The bond lengths and angles with the estimated standard deviations are given in Table 2.

Methoxyphenyl group

The average C–C phenyl ring bond distance is 1·39 Å. This value is close to the expected C–C bond length in aromatic rings, 1·395 ± 0·003 Å (*International Tables for X-ray Crystallography*, 1962). The bond lengths C(aromatic)–O(methoxyl) 1·37 Å and O(methoxyl)–C(methyl) 1·44 Å are similar to those reported by
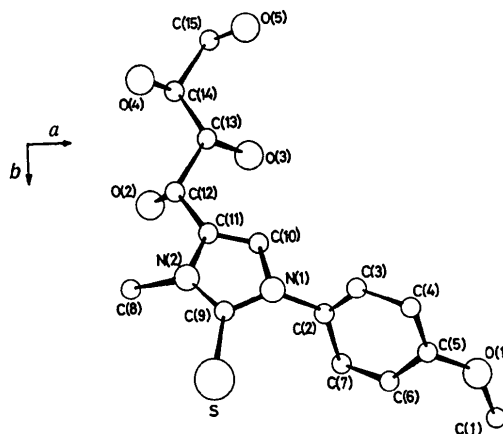

Fig. 1. Molecular conformation of 1-p-methoxyphenyl-3-methyl-4-(D-arabinotetrahydroxybutyl)imidazoline-2-thione.

Table 1. *Atomic parameters*

(a) Positional and anisotropic thermal parameters for non-hydrogen atoms with their estimated standard deviations ($\times 10^4$). The expression used is $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	4760 (1)	5448 (1)	4247 (1)	52 (1)	50 (1)	76 (1)	−19 (1)	6 (1)	7 (1)
O(1)	4599 (2)	5473 (3)	10301 (3)	46 (2)	63 (3)	51 (2)	9 (2)	−13 (2)	−15 (2)
O(2)	2149 (3)	1538 (3)	2790 (4)	44 (2)	58 (3)	77 (3)	10 (2)	−27 (2)	3 (3)
O(3)	2090 (2)	332 (4)	5173 (3)	45 (2)	73 (3)	57 (3)	−14 (2)	14 (2)	−20 (3)
O(4)	3271 (2)	−1429 (3)	2638 (3)	71 (2)	54 (3)	62 (3)	7 (2)	22 (2)	−7 (2)
O(5)	2998 (3)	−2453 (4)	5178 (4)	65 (2)	65 (3)	64 (3)	−8 (2)	−9 (2)	10 (3)
N(1)	3922 (3)	3578 (3)	5581 (3)	41 (2)	41 (2)	50 (3)	−10 (2)	8 (2)	−6 (2)
N(2)	3891 (2)	3257 (3)	3589 (3)	30 (2)	43 (2)	50 (3)	−2 (2)	6 (2)	2 (2)
C(1)	4025 (4)	6493 (5)	10774 (6)	56 (3)	66 (4)	72 (4)	2 (3)	1 (3)	−32 (4)
C(2)	4092 (3)	4098 (4)	6776 (4)	33 (2)	49 (3)	40 (3)	−5 (2)	0 (2)	−10 (2)
C(3)	4772 (3)	3541 (5)	7584 (5)	32 (2)	62 (4)	84 (4)	10 (2)	−2 (3)	−25 (3)
C(4)	4904 (3)	4017 (5)	8772 (5)	41 (2)	58 (3)	73 (4)	7 (2)	−12 (2)	−14 (3)
C(5)	4389 (3)	5068 (4)	9121 (4)	30 (2)	45 (3)	53 (3)	−3 (2)	2 (2)	−2 (3)
C(6)	3715 (3)	5622 (4)	8338 (4)	41 (2)	40 (3)	67 (4)	15 (2)	−4 (2)	−5 (3)
C(7)	3589 (3)	5143 (4)	7145 (4)	44 (2)	53 (3)	54 (3)	8 (2)	−4 (2)	0 (3)
C(8)	4077 (4)	3400 (5)	2255 (5)	55 (3)	68 (4)	44 (3)	−6 (3)	5 (2)	7 (3)
C(9)	4176 (3)	4075 (4)	4456 (4)	31 (2)	41 (3)	49 (3)	−3 (2)	2 (2)	6 (3)
C(10)	3473 (3)	2429 (4)	5396 (4)	42 (2)	38 (3)	51 (3)	−9 (2)	5 (2)	−2 (3)
C(11)	3449 (3)	2222 (4)	4159 (4)	37 (2)	36 (3)	52 (3)	−4 (2)	−1 (2)	−3 (3)
C(12)	3051 (3)	1176 (4)	3405 (5)	29 (2)	42 (3)	40 (3)	2 (2)	−7 (2)	−4 (2)
C(13)	2833 (3)	49 (4)	4240 (4)	31 (2)	48 (3)	43 (3)	−1 (2)	−1 (2)	−12 (3)
C(14)	2509 (4)	−1081 (4)	3476 (4)	50 (2)	41 (3)	49 (3)	−3 (2)	−1 (2)	−2 (3)
C(15)	2253 (4)	−2184 (4)	4283 (5)	52 (3)	51 (3)	67 (4)	−19 (2)	−7 (3)	−3 (3)

Table 1 (cont.)

(b) Positional parameters ($\times 10^3$) for the hydrogen atoms

	x	y	z
$H_1(C_1)$	325	630	1070
$H_2(C_1)$	425	685	1160
$H_3(C_1)$	410	730	1020
$H(C_3)$	540	300	740
$H(C_4)$	460	360	940
$H(C_6)$	320	620	850
$H(C_7)$	300	540	660
$H_1(C_8)$	330	350	200
$H_2(C_8)$	420	260	200
$H_3(C_8)$	460	400	200
$H(C_{10})$	340	185	605
$H(C_{12})$	360	100	280
$H(C_{13})$	350	−20	450
$H(C_{14})$	175	−105	330
$H_1(C_{15})$	160	−200	480
$H_2(C_{15})$	220	−290	370
$H(O_2)$	150	130	250
$H(O_3)$	140	−15	535
$H(O_4)$	380	−80	220
$H(O_5)$	260	−295	590

Table 2. Bond lengths and angles

(a) Bond lengths in Å (standard deviations in parentheses)

S——C(9)	1·699 (4)	N(2)—C(8)	1·462 (6)
O(1)—C(1)	1·443 (7)	C(10)—C(11)	1·347 (6)
O(1)—C(5)	1·370 (6)	C(11)—C(12)	1·493 (6)
O(2)—C(12)	1·444 (5)	C(12)—C(13)	1·542 (6)
O(3)—C(13)	1·454 (5)	C(13)—C(14)	1·536 (6)
O(4)—C(14)	1·422 (6)	C(14)—C(15)	1·515 (7)
O(5)—C(15)	1·425 (7)	C(2)—C(3)	1·401 (6)
N(1)—C(9)	1·367 (5)	C(2)—C(7)	1·379 (6)
N(1)—C(10)	1·398 (6)	C(3)—C(4)	1·387 (8)
N(1)—C(2)	1·421 (6)	C(4)—C(5)	1·386 (6)
N(2)—C(9)	1·341 (5)	C(5)—C(6)	1·379 (6)
N(2)—C(11)	1·410 (5)	C(6)—C(7)	1·393 (7)

(b) Bond angles in degrees (standard deviations in the range 0·4–0·5)

C(1)—O(1)—C(5)	117·2	C(9)—N(2)—C(8)	124·1
O(1)—C(5)—C(6)	124·3	C(8)—N(2)—C(11)	125·6
O(1)—C(5)—C(4)	114·0	C(9)—N(2)—C(11)	110·2
C(4)—C(5)—C(6)	121·7	N(1)—C(10)—C(11)	107·4
C(5)—C(6)—C(7)	118·8	N(2)—C(11)—C(10)	106·6
C(6)—C(7)—C(2)	120·5	N(2)—C(11)—C(12)	121·3
C(7)—C(2)—C(3)	120·0	C(10)—C(11)—C(12)	132·0
C(2)—C(3)—C(4)	119·7	C(11)—C(12)—O(2)	110·5
C(3)—C(4)—C(5)	119·2	C(11)—C(12)—C(13)	110·7
N(1)—C(2)—C(3)	119·8	O(2)—C(12)—C(13)	108·5
N(1)—C(2)—C(7)	120·2	O(3)—C(13)—C(12)	111·6
S——C(9)—N(1)	125·4	O(3)—C(13)—C(14)	109·7
S——C(9)—N(2)	128·3	C(12)—C(13)—C(14)	111·9
N(1)—C(9)—N(2)	106·3	C(13)—C(14)—O(4)	109·9
C(9)—N(1)—C(2)	127·0	C(13)—C(14)—C(15)	112·7
C(10)—N(1)—C(2)	123·5	O(4)—C(14)—C(15)	108·6
C(9)—N(1)—C(10)	109·5	C(14)—C(15)—O(5)	112·6

Natarajan, Sake Gowda & Cartz, 1974. The C(aromatic)–O–C(methyl) angle of 117·2° is consistent with the value given by Norment & Karle, 1962. The enlargement of C(6)–C(5)–O(1) to 124·3° is similar to that observed by Silverton (1973), Norment & Karle (1962) and Bryan (1967) and can be attributed, following Norment & Karle, to close contacts between benzenoid and methyl hydrogen atoms. Packing interactions are probably involved and may reinforce the repulsion since C(1) is fairly close (3·18 Å) to O(4) of the nearest neighbour molecule.

The phenyl group is planar as expected. The least-squares plane for the atoms of the ring and the corresponding deviations are included in Table 3. The two substituents O(methoxyl) and N(imidazole) atoms (not included in calculating the plane) lie almost in the least-squares plane of the ring, at 0·03 and 0·06 Å above and below the plane respectively.

Imidazoline ring

The bond lengths and angles in the imidazoline group agree well with the corresponding parameters from the other analogous compounds. The S–C(9), C(9)–N(1) and C(9)–N(2) distances indicate the effects of the thiourea resonance system (Jiménez-Garay, López-Castro & Márquez, 1974; Pérez-Garrido, Conde & Márquez, 1974). The N(2)–C(8) bond (1·46 Å) agrees well with the accepted N–C single bond distance of 1·47 Å.

The imidazoline ring is planar. The least-squares plane of the atoms of the ring and the corresponding deviations are given in Table 3. Three substituents S, C(methyl) and C(aromatic) lie at 0·03, 0·09 and 0·02 Å from the imidazoline plane and the C(sugar) do not show deviations from the plane.

Arabinotetrahydroxybutyl group

Bond lengths and interbond angles in the sugar chain are normal (Table 2) and agree well with the accepted values. The average C–C and C–O bond distances cf 1·52 and 1·44 Å respectively are comparable with the values reported by Cook & Bugg (1973). The four carbon atoms of the sugar chain lie in a plane (Table 3). Two oxygens (hydroxyl) are on the opposite side to the other two.

Molecular conformation and packing

The conformation of the molecule is shown in Fig. 1 and can be numerically described by the values of the torsion angles. The most important torsion angles are

Table 3. Least-squares planes in the molecule

(a) Equations of various planes in the standard orthogonal system as: $Ax + By + Cz = D$

Plane		A	B	C	D
I	Phenyl ring	0·7317	0·5838	−0·3520	−2·2142
II	Imidazoline ring	0·8925	−0·4477	0·0549	8·1887
III	C(11)–C(12)–C(13)–C(14)–C(15)	0·9425	−0·3164	−0·1069	6·5658

Table 3 (cont.)

(b) Deviations in Å from the planes

Atoms not used in the calculation of the least-squares planes are denoted by an asterisk.

	I		II		III
N(1)	−0·0556*	S	0·0316*	C(11)	0·0297
C(1)	−0·0752*	N(1)	−0·0007	C(12)	−0·0351
C(2)	−0·0099	N(2)	0·0002	C(13)	−0·0239
C(3)	0·0085	C(2)	0·0244*	C(14)	0·0354
C(4)	−0·0094	C(8)	0·0861*	C(15)	−0·0061
C(5)	0·0115	C(9)	0·0003	O(2)	−1·2410*
C(6)	−0·0126	C(10)	0·0009	O(3)	−1·1786*
C(7)	0·0119	C(11)	−0·0008	O(4)	1·2263*
O(1)	0·0294*	C(12)	−0·0209*	O(5)	0·9360*

Table 4. Selected torsion angles (°)

C(6)–C(5)—O(1)—C(1)	4·4
C(7)–C(2)—N(1)—C(9)	69·0
S——C(9)—N(1)—N(2)	0·3
C(9)–N(2)—C(8)—C(11)	4·2
C(7)–C(2)—N(1)—C(10)	67·4
C(2)–N(1)—C(10)—C(11)	1·2
N(2)–C(11)—C(10)—C(12)	0·9
O(2)–C(12)—C(11)—C(13)	59·8
O(3)–C(13)—C(12)—C(14)	56·7
O(4)–C(14)—C(13)—C(15)	58·7
O(5)–C(15)—C(14)—C(13)	49·8
N(1)–C(10)—C(11)—C(12)	1·2

given in Table 4. The dihedral angle between the mean planes of the imidazoline and the phenyl rings is 68·3°.

The packing of the molecules in the crystal is illustrated in Fig. 2. The structure consists of a three-dimensional network of molecules linked by hydrogen bonds. The shortest intermolecular distances given in Table 5 can be divided into two categories. The first of these involves a short contact from S to O(5) of another molecule related only by a translation along the b axis and another contact from O(4) to C(1) of another molecule translated along the diagonal of the bc face. The effect is to produce a two-dimensional net of molecules normal to the a axis. The second of these categories involves short intermolecular distances between atoms of molecules related by twofold screw axes, as S···O(3), O(2)···C(3), O(2)···C(6), O(2)··· O(5) and O(3)···O(4). The S···O(3) distance and the S···O(3)–H angle (Table 5) may indicate a hydrogen bond character. This hydrogen bond gives a helical

system along the a axis. For the other interactions the hydrogen bond character is not evident, although the poor resolution of the X-ray diffraction method in the determination of the hydrogen atomic positions must be taken into account.

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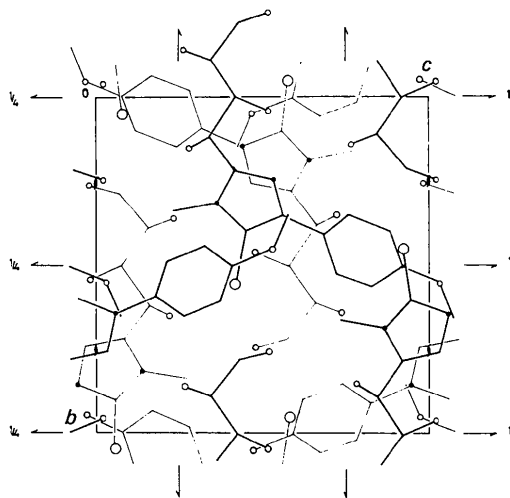COOK, W. J. & BUGG, C. E. (1973). Acta Cryst. B29, 215–222.

Fig. 2. Projection of the structure along the a axis.

Table 5. Geometry of the short intermolecular distances involving hydrogen atoms

A	B	$A\cdots B$ (Å)	A–H_A (Å)	$H_A\cdots B$ (Å)	$A\cdots H_B$ (Å)	H_B–B (Å)	$\angle H_A$–A $\cdots B$(°)	$\angle A$–H_A $\cdots B$ (°)	$\angle A\cdots H_B$ −B(°)	$\angle H_B$–B $\cdots A$ (°)
S	O(5) (i,010)	3·443 (4)	—	—	3·80 (9)	1·09 (8)	—	—	62 (4)	104 (4)
S	O(3) (iv,001)	3·329 (4)	—	—	2·29 (7)	1·09 (7)	—	—	159 (6)	14 (4)
O(3)	O(4) (iii,000)	2·941 (5)	1·09 (7)	3·03 (9)	2·54 (8)	1·09 (8)	83 (4)	75 (4)	100 (5)	58 (4)
O(2)	O(5) (iii,00Ī)	2·982 (6)	0·97 (7)	2·87 (9)	2·56 (9)	1·09 (8)	74 (5)	87 (5)	102 (5)	57 (4)
O(2)	C(6) (iii,01Ī)	3·340 (6)	0·97 (7)	3·46 (9)	2·61 (9)	0·95 (8)	89 (4)	75 (4)	134 (6)	34 (4)
O(2)	C(3) (iv,Ī01)	3·252 (5)	0·97 (7)	2·35 (7)	2·44 (7)	1·05 (7)	18 (5)	154 (6)	134 (6)	33 (4)
O(4)	H_2–C(1) (i,0ĪĪ)	3·178 (7)	1·09 (8)	3·32 (9)	2·54 (8)	1·01 (8)	88 (4)	73 (4)	121 (6)	43 (4)
O(1)	H_3–C(8) (i,001)	3·148 (6)	—	—	2·40 (9)	1·00 (8)	—	—	129 (6)	37 (4)

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

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Le Tétrachloromanganate(II) de Pyridinium 2 [C5H5NH]+.[MnCl4]2− et le Tétrabromomanganate(II) de Pyridinium 2 [C5H5NH]+.[MnBr4]2−

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$2[C_5H_5NH]^+.[MnCl_4]^{2-}$ is triclinic, space group $P\bar{1}$, $a = 12\cdot771 \pm 0\cdot005$, $b = 8\cdot158 \pm 0\cdot005$, $c = 7\cdot681 \pm \pm 0\cdot005$ Å, $\alpha = 100\cdot38 \pm 0\cdot05$, $\beta = 96\cdot43 \pm 0\cdot05$, $\gamma = 88\cdot78 \pm 0\cdot05°$, $D_c = 1\cdot496 \pm 0\cdot002$, $D_m = 1\cdot45 \pm 0\cdot04$ g cm^{-3}, $Z = 2$, $|F(000)| = 358$, $M = 357$, $\mu = 14$ cm^{-1} (Mo $K\alpha$), $R = 0\cdot056$ for 2604 unweighted reflexions. The structure contains tetrahedral $[MnCl_4]^{2-}$ ions and pyridinium $[C_5H_5NH]^+$ ions. Each of these pyridinium ions is bound by a weak hydrogen bond NH$\cdots$Cl to a $[MnCl_4]^{2-}$ ion. One pyridinium ion seems to be slightly disordered. $2[C_5H_5NH]^+.[MnCl_4]^{2-}$ and $2[C_5H_5NH]^+.[MnBr_4]^{2-}$ are isostructural. For this last compound $a = 13\cdot128 \pm 0\cdot005$, $b = 8\cdot350 \pm 0\cdot005$, $c = 7\cdot939 \pm 0\cdot005$ Å, $\alpha = 100\cdot61 \pm 0\cdot05$, $\beta = 96\cdot66 \pm 0\cdot05$, $\gamma = 87\cdot63 \pm 0\cdot05°$, $D_c = 2\cdot043 \pm 0\cdot002$, $D_m = 2\cdot06 \pm 0\cdot02$ g cm^{-3}, $Z = 2$, $|F(000)| = 502$, $M = 535$, $\mu = 103$ cm^{-1} (Mo $K\alpha$). Hydrogen bonds N-H$\cdots$Br are very weak and the two pyridinium ions are disordered. The order and the disorder for pyridinium are discussed.

Introduction

Les tétrachloro et tétrabromomanganate(II) de pyridinium sont des complexes colorés en jaune vert et présentant une forte luminescence verdâtre. Une étude infrarouge de ces composés avait montré que l'anion complexe $[MnX_4]^{2-}$ avec X = Cl ou Br présentait une structure tétraédrique et se trouvait lié au cation pyridinium $[C_5H_5NH]^+$ par liaison hydrogène (Robert, Brassy & Mellier, 1972). Une détermination des données cristallographiques de ces produits avait aussi été effectuée, mais pour confirmer ces travaux et avoir des informations structurales plus précises il était nécessaire de connaître la structure cristalline. L'étude des spectres de vibration Raman a aussi été publiée récemment (Robert, Lignou & Payen de la Garanderie, 1974).

Etude du complexe bromé

Les cristaux, très hygroscopiques ont été préparés selon une méthode décrite antérieurement (Taylor, 1934; Payen de la Garanderie, 1963). Les nouveaux paramètres cristallins et 3994 réflexions indépendantes ont été mesurés à l'aide d'un diffractomètre 4 cercles Philips PW 1100 équipé d'un tube à rayons X à anticathode de molybdène. Nous avons essayé de résoudre la structure par une méthode de multisolution à l'aide du programme *MULTAN* (Germain, Main & Woolfson,