

The Crystal Structure and Absolute Configuration of (+)-2,5-Dimethoxy-7-dimethylaminotriptycene Hydrobromide

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The crystal structure of (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide has been investigated by the X-ray method. The crystals, which are orthorhombic in the space group $C222_1$, have the unit-cell dimensions $a=8.733$, $b=13.853$ and $c=34.728$ Å. The structure has been solved by the minimum-function method. The structure parameters have been refined by the block-diagonal least-squares method to a final R value of 0.044 by using 1302 independent reflexions. The molecule is shown to have a rigid structure with a pseudo-threefold symmetry. The absolute configuration has been determined as $1R6S$ by the Cu $K\alpha$ anomalous scattering of the bromine atom.

Introduction

Triptycene derivatives have rigid conformations and are optically active when substituted asymmetrically. Recently, a series of optically active triptycene derivatives has been synthesized in Osaka University by our colleagues Ogura, Nakagawa and their coworkers. A theoretical analysis of the optical activity has been carried out in our laboratory and the absolute configuration has been deduced based on the excitation analysis of the CD spectra (Tanaka, Ozeki-Minakata, Ogura & Nakagawa, 1972). The X-ray crystal structure analysis provides an unambiguous result for the absolute configuration, and the present study has been undertaken to determine the absolute configuration of one of the substituted triptycenes.

Experimental

A crystal of (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide ($C_{24}H_{23}NO_2 \cdot HBr$) was grown in methanol solution. The crystal appeared as a hexagonal plate with developing face (001). The space group was determined from oscillation and Weissenberg photographs, and the density was measured by the flotation method in a mixture of cyclohexane and carbon tetrachloride at 20°C. The cell dimensions were calculated by a least-squares treatment based on 12 reflexions measured on a Hilger-Watt four circle diffractometer at 7°C.

Crystal data

Crystal system: orthorhombic.
Systematic absences: hkl when $h+l$ is odd
 $00l$ when l is odd.
Space group: $C222_1$
 $a=8.733 \pm 0.003$, $b=13.583 \pm 0.004$, $c=34.728$
 ± 0.005 Å; $V=4119$ Å³, $Z=8$, $D_m=1.39$, $D_c=$
 1.35 g.cm⁻³, $F_{000}=1640$.

The intensity data were obtained from a crystal of dimensions $0.2 \times 0.2 \times 0.1$ mm on a Hilger-Watt dif-

fractometer in the $\theta/2\theta$ scanning mode. 1362 independent reflexions within $\theta \leq 55^\circ$ were recorded, of which 60 with intensities less than three times their standard deviations were omitted. The linear absorp-

Table 1. Atomic coordinates

	x/a	y/b	z/c
Br	0.4660 (1)	0.3573 (1)	0.9661 (1)
C(1)	0.1343 (10)	0.3761 (10)	0.8104 (10)
C(2)	-0.1528 (11)	0.3750 (10)	0.8306 (10)
C(3)	-0.2592 (11)	0.3717 (12)	0.8612 (11)
C(4)	-0.2098 (11)	0.3733 (11)	0.8994 (11)
C(5)	-0.0549 (12)	0.3754 (10)	0.9076 (10)
C(6)	0.2235 (10)	0.3745 (10)	0.8823 (10)
C(7)	0.3624 (11)	0.5412 (10)	0.8744 (10)
C(8)	0.4048 (12)	0.6197 (11)	0.8510 (11)
C(9)	0.3604 (13)	0.6175 (11)	0.8116 (11)
C(10)	0.2747 (12)	0.5410 (10)	0.7975 (10)
C(11)	0.2721 (12)	0.2118 (10)	0.7963 (11)
C(12)	0.3617 (13)	0.3143 (13)	0.8105 (12)
C(13)	0.4127 (13)	0.1339 (12)	0.8481 (13)
C(14)	0.3709 (12)	0.2127 (10)	0.8726 (11)
C(15)	0.0003 (10)	0.3760 (9)	0.8390 (10)
C(16)	0.0508 (10)	0.3759 (9)	0.8776 (9)
C(17)	0.2776 (10)	0.4662 (9)	0.8605 (10)
C(18)	0.2315 (11)	0.4656 (9)	0.8216 (10)
C(19)	0.2298 (11)	0.2852 (9)	0.8207 (10)
C(20)	0.2798 (10)	0.2844 (9)	0.8589 (10)
C(21)	-0.3592 (11)	0.3776 (16)	0.7843 (12)
C(22)	-0.1023 (15)	0.3740 (16)	0.9760 (11)
C(23)	0.5472 (13)	0.5985 (12)	0.9262 (11)
C(24)	0.2601 (13)	0.5886 (13)	0.9381 (12)
N(1)	0.3974 (10)	0.5467 (8)	0.9162 (8)
O(1)	-0.1951 (7)	0.3748 (7)	0.7926 (7)
O(2)	0.0079 (8)	0.3764 (8)	0.9440 (7)

Atomic coordinates of assumed hydrogen atoms.

	x/a	y/b	z/c
H(C1)	0.092	0.390	0.788
H(C3)	-0.378	0.371	0.855
H(C4)	-0.289	0.373	0.922
H(C6)	0.253	0.375	0.913
H(C8)	0.471	0.678	0.862
H(C9)	0.391	0.676	0.793
H(C10)	0.242	0.544	0.769
H(C11)	0.236	0.210	0.768
H(C12)	0.396	0.076	0.792
H(C13)	0.483	0.078	0.859
H(C14)	0.407	0.212	0.901
H(N1)	0.430	0.495	0.924

Table 2. *Anisotropic temperature factors* ($\times 10^4$) and their standard deviationsThe temperature factor is in the form $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	110 (2)	53 (1)	5 (0)	- 9 (2)	2 (1)	- 7 (1)
C(1)	54 (15)	29 (8)	4 (1)	3 (21)	- 2 (6)	- 3 (4)
C(2)	67 (17)	16 (7)	6 (1)	- 15 (20)	3 (7)	0 (4)
C(3)	73 (18)	50 (9)	7 (1)	9 (26)	3 (8)	- 4 (6)
C(4)	74 (17)	34 (8)	6 (1)	- 7 (25)	8 (7)	3 (5)
C(5)	88 (17)	22 (7)	6 (1)	- 29 (22)	3 (7)	2 (4)
C(6)	55 (15)	15 (7)	5 (1)	- 1 (21)	2 (6)	- 1 (4)
C(7)	62 (18)	15 (6)	5 (1)	5 (18)	- 3 (7)	0 (4)
C(8)	111 (19)	30 (7)	6 (1)	51 (22)	- 7 (8)	0 (5)
C(9)	130 (21)	37 (8)	5 (1)	41 (24)	- 6 (8)	- 9 (5)
C(10)	101 (19)	21 (6)	5 (1)	9 (20)	1 (8)	0 (4)
C(11)	93 (19)	19 (7)	6 (1)	- 11 (21)	5 (8)	7 (5)
C(12)	135 (21)	36 (8)	9 (1)	- 69 (28)	0 (8)	11 (6)
C(13)	129 (21)	32 (7)	10 (1)	- 55 (25)	0 (9)	2 (6)
C(14)	87 (20)	16 (6)	7 (1)	- 5 (20)	- 4 (8)	0 (4)
C(15)	29 (16)	19 (6)	6 (1)	- 3 (20)	- 2 (6)	- 1 (4)
C(16)	62 (15)	7 (6)	5 (1)	8 (20)	4 (7)	- 2 (4)
C(17)	39 (16)	15 (5)	5 (1)	16 (17)	0 (7)	- 1 (4)
C(18)	49 (17)	8 (5)	5 (1)	19 (17)	3 (7)	- 1 (4)
C(19)	48 (18)	7 (6)	6 (1)	0 (18)	7 (8)	1 (4)
C(20)	37 (16)	9 (5)	6 (1)	0 (17)	2 (7)	0 (4)
C(21)	21 (16)	104 (14)	8 (1)	34 (29)	- 10 (7)	- 5 (7)
C(22)	200 (25)	97 (13)	5 (1)	62 (36)	32 (8)	- 3 (5)
C(23)	100 (20)	56 (8)	5 (1)	81 (25)	- 14 (9)	- 3 (5)
C(24)	80 (20)	54 (9)	7 (1)	- 11 (24)	13 (8)	11 (5)
N(1)	88 (16)	22 (5)	5 (1)	17 (16)	- 9 (6)	0 (3)
O(1)	73 (11)	40 (5)	5 (1)	2 (16)	- 4 (5)	- 2 (3)
O(2)	94 (14)	71 (6)	5 (1)	0 (19)	7 (5)	- 3 (3)

Table 2 (cont.)

Isotropic temperature factors of assumed hydrogen atoms

H(C1)	2.0
H(C3)	3.2
H(C4)	2.8
H(C6)	1.9
H(C8)	2.8
H(C9)	3.2
H(C10)	2.4
H(C11)	2.4
H(C12)	3.6
H(C13)	3.9
H(C14)	2.6
H(N1)	1.9

tion coefficient for Cu $K\alpha$ radiation is 30.67 cm^{-1} . No corrections were made for absorption or extinction.

Structure determination

A three-dimensional sharpened Patterson function was computed and the coordinates of the bromide ion were easily determined. The structure was solved by the minimum-function method. The atomic parameters and a scale factor were refined by the block-diagonal least-squares method, in which the temperature factor for the bromide ion only was considered to be anisotropic; the R index at this stage was 0.056. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Further refinement was performed by the block-diagonal least-squares method with anisotropic temperature factors, including assumed hydrogen atoms attached to the skeleton and the nitrogen atom, and the R index was reduced to

0.044. The atomic coordinates and their standard deviations are given in Table 1 and the anisotropic temperature factors with their standard deviations in Table 2. The computations were carried out with the programs written by Ashida and ourselves on a Hitac 5020E computer at the University of Tokyo and on a Facom 230-60 at Kyoto University. The calculated and observed structure factors are tabulated in Table 3.

Absolute configuration

The absolute configuration has been determined by application of the Bijvoet method with anomalous scattering of Cu $K\alpha$ radiation by the bromine atom. $\Delta f'$ and $\Delta f''$ values were taken from Dauben & Tem-

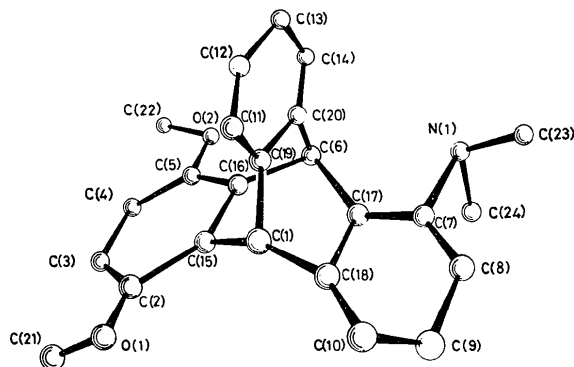


Fig. 1. The absolute configuration of *d*-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide; the $1R6S$ configuration is illustrated.

Table 3. Calculated and observed structure factors ($\times 0.25$)

L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF	L	F0	FC	DF								
1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0

pletion (1955). As shown in Table 4, the observed intensity differences between Friedel's pairs are in good agreement with those computed by assuming the atomic parameters of Table 1 referred to a right-handed axis. The absolute configuration thus determined is 1R6S (notation of Cahn, Ingold & Prelog, 1966). Fig. 1 shows the correct absolute configuration.

Results and discussion

The bond lengths and angles are shown in Tables 5 and 6 respectively. The mean estimated standard deviation in bond lengths is 0.016 Å and that in bond angles is 1°. The bond lengths of the benzene ring are normal, and the average value is 1.39 Å.

Bond lengths around the central C(1) and C(6) are 1.52~1.55 Å, which correspond to the normal single-bond length. The angles subtended at C(1) and C(6), which are less than the usual tetrahedral value of 109.5°, are C(15)-C(1)-C(18) 104.9, C(15)-C(1)-C(19) 105.3, C(18)-C(1)-C(19) 106.1, C(16)-C(6)-C(17) 104.0, C(16)-C(6)-C(20) 105.6, C(17)-C(6)-C(20) 106.5°. These results imply that a significant strain is exerted on the central carbon atoms. The strain is also reflected in the external angles of the rings. The angles on the

outer sides are larger than 120° by 5~7°:
 C(1)-C(15)-C(2) 127.2, C(1)-C(18)-C(10) 126.0,
 C(1)-C(19)-C(11) 126.4, C(6)-C(17)-C(7) 127.4,
 C(6)-C(16)-C(5) 125.3, C(6)-C(20)-C(14) 125.0°.

Table 4. Determination of absolute configuration

h	k	l	Obs.	Calcd.*
1	1	14	19.7	25.8
2	2	27	43.1	50.2
2	6	28	7.4	12.0
2	8	2	-7.3	-4.9
-2	8	-2	-6.9	-4.9
2	8	10	2.5	4.3
2	10	2	8.8	11.8
2	10	18	-7.7	-15.7
3	1	23	-8.5	-5.1
3	3	10	46.5	59.5
-3	3	-17	-2.7	-11.4
3	7	12	-10.1	-8.4
-3	7	-12	-5.2	-8.4
4	4	7	3.9	8.2
4	4	18	26.5	64.9
4	6	4	-7.6	-5.5
-4	6	-4	-12.9	-5.5
5	1	17	22.8	33.1
-5	1	-17	32.0	33.1
6	2	9	37.1	43.8

* These values are based on the atomic parameters listed in Table 1, referred to a right-handed crystal axial system.

Table 5. Bond lengths and their standard deviations

C(1)—C(15)	1.536 (14) Å
C(1)—C(18)	1.533 (15)
C(1)—C(19)	1.532 (15)
C(2)—C(3)	1.413 (17)
C(2)—C(15)	1.369 (15)
C(2)—O(1)	1.368 (13)
C(3)—C(4)	1.394 (17)
C(4)—C(5)	1.382 (16)
C(5)—C(16)	1.392 (16)
C(5)—O(2)	1.381 (14)
C(6)—C(16)	1.517 (15)
C(6)—C(17)	1.533 (15)
C(6)—C(20)	1.549 (14)
C(7)—C(8)	1.390 (16)
C(7)—C(17)	1.348 (15)
C(7)—N(1)	1.487 (15)
C(8)—C(9)	1.422 (18)
C(9)—C(10)	1.371 (18)
C(10)—C(18)	1.376 (16)
C(11)—C(12)	1.401 (18)
C(11)—C(19)	1.359 (16)
C(12)—C(13)	1.382 (18)
C(13)—C(14)	1.415 (18)
C(14)—C(20)	1.346 (16)
C(15)—C(16)	1.409 (14)
C(17)—C(18)	1.409 (15)
C(19)—C(20)	1.397 (15)
C(21)—O(1)	1.463 (18)
C(22)—O(2)	1.470 (18)
C(23)—N(1)	1.525 (16)
C(24)—N(1)	1.529 (16)

On the other hand the angles on the inner sides are smaller than 120° by $6\sim 7^\circ$ as follows: C(1)—C(15)—C(16) 112.1 , C(1)—C(18)—C(17) 114.0 , C(1)—C(19)—C(20) 113.4 , C(6)—C(16)—C(15) 114.5 , C(6)—C(17)—C(18) 112.4 , C(6)—C(20)—C(19) 113.2° .

The angles around N(1) are close to the tetrahedral value and N(1) is thus shown to be protonated, forming a quaternary ammonium salt. The four methyl groups are all oriented towards the outer sides away from the pseudo-threefold symmetry axis of the mole-

cule by steric repulsion between the substituents and H(1) and H(6). The least-squares planes for the benzene rings including the nearest bonded atoms are given by the equations:

- (1) benzene ring,
 $0.8212x + 0.5062y - 0.2633z = -3.8813$;
- (2) dimethylaminobenzene ring,
 $0.8432x - 0.4873y - 0.2270z = -7.8427$;
- (3) dimethoxybenzene ring,
 $-0.0089x + 1.000y + 0.0008z = 5.119$.

The deviations of the atoms from these planes are given in Table 7. It is remarkable that the planarities of the benzene rings including the substituent atoms are fairly good.

Table 7. Deviations from the least-squares planes

Benzene-ring plane			
C(1)	0.018 Å	C(13)	0.005 Å
C(6)	-0.011	C(14)	0.023
C(11)	0.006	C(19)	-0.015
C(12)	-0.014	C(20)	-0.012
Dimethylaminobenzene-ring plane			
C(1)	-0.046 Å	C(17)	0.018 Å
C(6)	0.054	C(18)	-0.011
C(7)	0.037	N(1)	-0.072
C(8)	0.013	C(23)	0.610*
C(9)	0.011	C(24)	-1.533*
C(10)	-0.002		
Dimethoxybenzene-ring plane			
C(1)	0.000 Å	C(15)	0.011 Å
C(2)	0.009	C(16)	0.007
C(3)	-0.027	O(1)	0.009
C(4)	-0.009	O(2)	0.018
C(5)	0.009	C(21)	0.059*
C(6)	-0.027	C(22)	-0.005*

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

Table 6. Bond angles and estimated standard deviations

C(15)—C(1)—C(18)	104.9 (0.8)°	C(1)—C(15)—C(2)	127.2 (0.9)°
C(15)—C(1)—C(19)	105.3 (0.8)	C(1)—C(15)—C(16)	112.1 (0.9)
C(18)—C(1)—C(19)	106.1 (0.8)	C(2)—C(15)—C(19)	120.7 (0.9)
C(3)—C(2)—C(15)	118.7 (1.0)	C(5)—C(16)—C(6)	125.3 (1.0)
C(3)—C(2)—O(1)	123.2 (1.0)	C(5)—C(16)—C(15)	120.2 (1.0)
C(15)—C(2)—O(1)	118.5 (0.9)	C(6)—C(16)—C(15)	114.5 (0.9)
C(2)—C(3)—C(4)	120.8 (1.1)	C(6)—C(17)—C(7)	127.4 (1.0)
C(3)—C(4)—C(5)	119.9 (1.1)	C(6)—C(17)—C(18)	112.4 (0.9)
C(4)—C(5)—C(16)	119.7 (1.0)	C(7)—C(17)—C(18)	120.2 (1.0)
C(4)—C(5)—O(2)	125.3 (1.0)	C(1)—C(18)—C(10)	126.0 (1.0)
C(16)—C(5)—O(2)	115.0 (1.0)	C(1)—C(18)—C(17)	114.0 (0.9)
C(16)—C(6)—C(17)	104.0 (0.8)	C(10)—C(18)—C(17)	120.0 (1.0)
C(16)—C(6)—C(20)	105.6 (0.8)	C(1)—C(19)—C(11)	126.4 (1.0)
C(17)—C(6)—C(20)	106.5 (0.8)	C(1)—C(19)—C(20)	113.4 (0.9)
C(8)—C(7)—C(17)	121.2 (1.1)	C(11)—C(19)—C(20)	120.2 (1.0)
C(8)—C(7)—N(1)	118.5 (1.0)	C(6)—C(20)—C(14)	125.0 (1.0)
C(17)—C(7)—N(1)	119.9 (1.0)	C(6)—C(20)—C(19)	113.2 (0.9)
C(7)—C(8)—C(9)	118.2 (1.1)	C(14)—C(20)—C(19)	121.8 (1.0)
C(8)—C(9)—C(10)	120.5 (1.2)	C(7)—N(1)—C(23)	114.9 (0.9)
C(9)—C(10)—C(18)	119.8 (1.1)	C(7)—N(1)—C(24)	110.1 (0.9)
C(12)—C(11)—C(19)	118.9 (1.1)	C(23)—N(1)—C(24)	112.8 (0.9)
C(11)—C(12)—C(13)	121.1 (1.2)	C(2)—O(1)—C(21)	117.1 (0.9)
C(12)—C(13)—C(14)	118.9 (1.2)	C(5)—O(2)—C(22)	115.6 (1.0)
C(13)—C(14)—C(20)	119.2 (1.1)		

Palmer & Templeton (1968) have analysed the crystal structure of 1-bromotriptycene and obtained the bond distances and angles of the similarly strained structure. Their values are more or less consistent with those reported in this investigation.

Karle & Estlin (1969) have analysed the crystal and molecular structure of β -chloroethyltriptycene, and have noticed a distortion from trigonal symmetry due to the presence of the chloroethyl chain at the bridge head. No such deviation has been observed in the present analysis, in spite of the presence of substituent groups on the benzene rings, and no noticeable interaction has been observed between the rings, which suggests that the cage structure is fairly rigid.

The crystal structure projected along the c axis is illustrated in Fig. 2. It can be seen that the plane of the dimethoxybenzene ring is nearly parallel to the (010) plane. Contacts between molecules are normal, as evidenced by the distances listed in Table 8.

The nitrogen atom of the protonated N -dimethylamino group is hydrogen-bonded with the bromide ion. The interatomic distance is 3.16 Å and the N-H bond makes an angle of 17.6° with the line connecting these atoms.

Table 8. Intermolecular distances < 4 Å

The Roman numerals represent the symmetry operators relevant to the atoms listed second.

Br.....C(4 ^{II})	3.67 Å
Br.....C(6 ^I)	3.61
Br.....C(14 ^I)	3.88

Table 8 (cont.)

Br.....C(22 ^{II})	3.79
Br.....C(22 ^{II})	3.78
Br.....C(23 ^I)	3.63
Br.....C(23 ^{IV})	3.85
Br.....C(24 ^I)	3.75
Br.....C(24 ^{IV})	3.85
Br.....N ^I	3.16
C(1).....C(21 ^V)	3.83
C(1).....O(1 ^V)	3.62
C(2).....C(8 ^S)	3.58
C(2).....C(9 ^S)	3.56
C(2).....C(12 ^{VIII})	3.59
C(2).....C(13 ^{VIII})	3.62
C(3).....C(8 ^S)	3.73
C(3).....C(13 ^{VIII})	3.89
C(3).....C(14 ^{III})	3.91
C(4).....C(8 ^S)	3.96
C(4).....C(23 ^{III})	3.84
C(5).....C(23 ^S)	3.92
C(8).....C(11 ^{VI})	3.93
C(8).....C(15 ^{VI})	3.60
C(8).....C(16 ^{VI})	3.82
C(8).....C(19 ^{VI})	3.77
C(8).....C(20 ^{VI})	3.98
C(9).....C(11 ^{VI})	3.85
C(9).....C(15 ^{VI})	3.84
C(9).....C(19 ^{VI})	3.96
C(9).....O(1 ^{VI})	3.59
C(10).....C(12 ^{VI})	3.85
C(10).....C(13 ^{VIII})	3.83
C(10).....C(21 ^V)	3.68
C(10).....C(21 ^{III})	3.92
C(10).....O(1 ^V)	3.92
C(11).....C(21 ^{II})	3.95
C(11).....C(21 ^V)	3.67
C(11).....O(1 ^V)	3.86
C(12).....C(15 ^{IV})	3.84

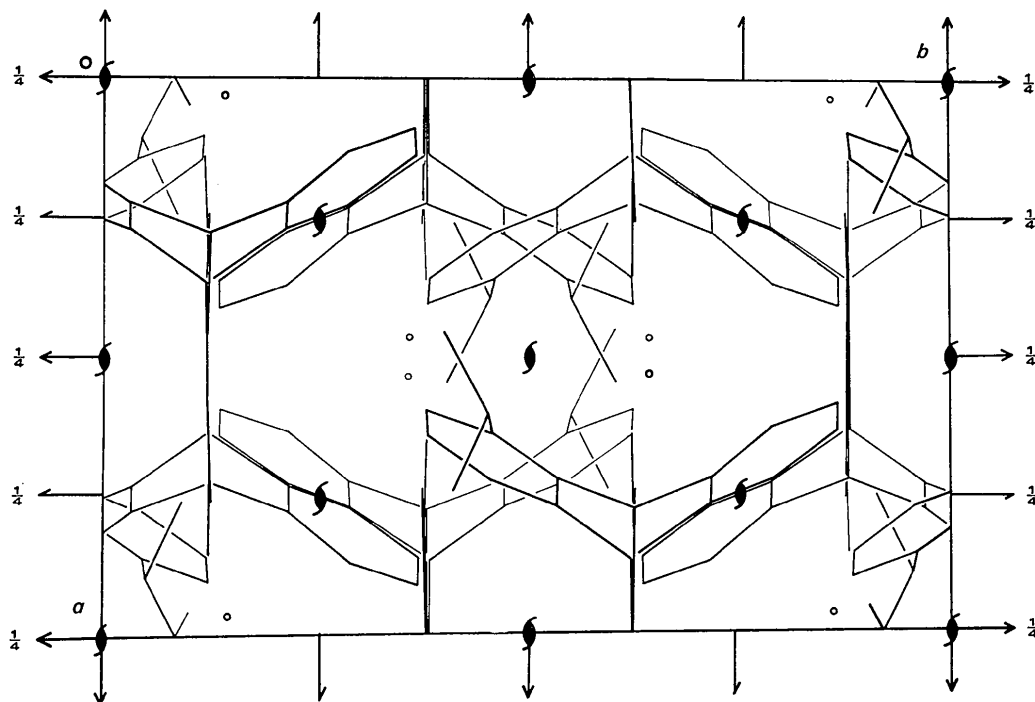


Fig. 2. The arrangement of the molecules projected along the c axis.

Table 8 (cont.)

C(12)···C(18 ^{ix})	3·98
C(12)···O(1 ^{ix})	3·61
C(13)···C(15 ^{ix})	3·60
C(13)···C(16 ^{ix})	3·84
C(13)···C(17 ^{ix})	3·94
C(13)···C(18 ^{ix})	3·72
C(14)···C(23 ^x)	3·72
C(18)···C(21 ⁱⁱ)	3·99
C(21)···C(21 ^{vi})	3·42
C(22)···C(22 ^{iv})	3·81
C(23)···O(2 ^{vi})	3·84

Symmetry code

Superscript	Symmetry operator		
i	x	y	z
ii	1+x	y	z
iii	-1+x	y	z
iv	x	1-y	2-z
v	-x	y	$\frac{3}{2}-z$
vi	-1-x	y	$\frac{3}{2}-z$
vii	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
viii	$-\frac{1}{2}+x$	$\frac{1}{2}+y$	z
ix	$\frac{1}{2}+x$	$-\frac{1}{2}+y$	z
x	$-\frac{1}{2}+x$	$-\frac{1}{2}+y$	z
xi	$\frac{1}{2}+x$	$\frac{1}{2}-y$	2-z

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The Crystal Structure of Potassium

(-)₅₈₉-Tris(1,2-benzenediolato)arsenate(V) Sesquihydrate, (-)₅₈₉-K[As(cat)₃].1·5H₂O

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The crystal structure of potassium (-)₅₈₉-tris(1,2-benzenediolato)arsenate(V) sesquihydrate, (-)₅₈₉-K[As(cat)₃].1·5H₂O, has been determined from three-dimensional data collected by a diffractometer. The crystals are orthorhombic with space group $P2_12_12_1$: $a = 12\cdot901$, $b = 24\cdot852$, $c = 11\cdot888$ Å and $Z = 8$. The structure was refined to an R value of 0·055 for the 1428 observed reflexions. The complex anion has an approximate symmetry D_3 . Each ligand molecule is coordinated to the central arsenic atom by their oxygen atoms with the average As-O distance of 1·84 Å. All the bond distances and angles are normal. The absolute configuration of the complex anion was determined by the absorption edge technique. It can be designated as Δ , in accordance with a spectroscopic assignment based on the circular dichroism spectra.

Introduction

The absolute configuration of an optically active metal complex can be determined by means of X-rays (Bijvoet, Peerdeman & van Bommel, 1951). It can also be determined non-empirically by the study of its circular dichroism (CD) associated with transitions localized principally on the ligands. Two or more electric-dipole-allowed transitions are able to couple to yield component transitions which are intrinsically optically active and which have Cotton effects whose

The absolute configuration determined in the present analysis is $1R6S$, while the structure deduced by the theory of optical rotation is the opposite of this result. The cause of this disagreement will be studied further and will be discussed in a separate paper.

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signs are determined by the phase relationships of the individual dipoles (Bosnich, 1969). The two methods should give the same result for one particular complex. The absolute configuration of (-)₅₈₉-tris(1,2-benzenediolato)arsenate(V) ion has been studied by X-ray diffraction methods and by the analysis of the CD spectrum to verify that both methods give an identical conclusion. The crystal structure of potassium (-)₅₈₉-tris(1,2-benzenediolato)arsenate(V) sesquihydrate, (-)₅₈₉-K[As(cat)₃].1·5H₂O is described in this paper.

Experimental

The crystals were prepared according to the method described by Ryschkewitsch & Garrett (1968). They

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