

Table 2. *The fractional coordinates of non-equivalent atoms in NaCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O*

	x	y	z	Number of equivalent positions
Cr	0	0	0	4
Na	$\frac{1}{2}$	0	0	4
S	0·310	0·310	0·310	8
O	0·239	0·239	0·239	8
O	0·307	0·224	-0·080	24
H <sub>2</sub> O(Cr)	0·158	0·014	0·018	24
H <sub>2</sub> O(Na)	0·042	0·136	0·302	24

sification of an alum structure depends upon the particular combination of monovalent and trivalent ions present. There does not appear to be any infallible criterion and therefore, should the details of an unknown structure be required, it would be advisable to

make an independent determination of the structure rather than to rely on any general scheme of classification of the alums.

One of us (A.H.C.L.) would like to thank the Science Research Council for the award of a studentship.

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## Molecular Nitrogen as a Ligand: The Crystal Structure of Nitrogenpentammineruthenium(II) Dichloride and Related Salts

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The X-ray crystal structure analysis of the chloride of nitrogenpentammineruthenium(II) has been carried out with diffractometer data. The salt crystallizes in the cubic system,  $a=10\cdot141$  Å, space group  $Fm\bar{3}m$ ,  $F432$  or  $F\bar{4}3m$ ; these are indistinguishable because all non-hydrogen atoms are in special positions. The structure is disordered, the nitrogen molecule randomly occupying one of the six octahedral positions around the ruthenium ion. Within the limits of accuracy imposed by the disorder, the Ru-N-N moiety is linear. An investigation has been made of the isomorphous bromide ( $a=10\cdot41$  Å), iodide ( $a=10\cdot94$  Å), tetrafluoroborate ( $a=11\cdot166$  Å) and hexafluorophosphate ( $a=11\cdot79$  Å).

### Introduction

It has been known for some years that transition metals, in the form of complexes or in the metallic form, are necessary for the fixation of molecular nitrogen. Until recently no complexes containing molecular nitrogen as a ligand had been isolated. The preparation of nitrogenpentammineruthenium(II) salts,  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{X}_2$ ,  $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  in these laboratories (Allen & Senoff, 1965; Allen, Bottomley, Harris, Reinsalu & Senoff, 1967) therefore raised questions as to the nature of nitrogen-metal bonding involved. A preliminary report of the X-ray structure analysis has appeared elsewhere (Bottomley & Nyburg, 1966).

### Experimental

The iodide and bromide were prepared by method 1, the chloride, tetrafluoroborate and hexafluorophosphate by method 3 of Allen *et al.* (1967). The iodide formed pale yellow leaf-shaped crystals elongated along

[011]. The other salts were yellow octahedra. The crystals were mounted in thin-walled glass capillaries and were all less than 0·1 mm maximum dimension. Under these conditions  $\mu R$  is approximately 0·295 for  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{I}_2$  and 0·097 for  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ , where  $\mu$  is the linear absorption coefficient ( $\text{cm}^{-1}$ ) and  $R$  is the maximum radius of the crystal treated as a sphere. Lattice parameters for the iodide, bromide, tetrafluoroborate and hexafluorophosphate were determined from rotation and zero-layer Weissenberg photographs with Mo  $K\alpha$  radiation. For the chloride, lattice parameters were obtained from a zero-layer Weissenberg photograph calibrated with aluminum using 22 Cu  $K\alpha$  and Cu  $K\beta$  reflexions with Bragg  $2\theta$  greater than  $114^\circ$  at  $25^\circ\text{C}$ . The data were treated by the method of least squares. These and other crystallographic data are summarized below:

$[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$	$M=285\cdot2$	$a=10\cdot141\pm 0\cdot001$ Å
	$V=1042\cdot90$ Å <sup>3</sup>	$Z=4$
	$D_m=1\cdot83$ g.cm <sup>-3</sup>	$D_c=1\cdot82$ g.cm <sup>-3</sup>
	(flotation in $\text{CHCl}_3/\text{CHBr}_3$ )	$F(000)=568$

[Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]I<sub>2</sub>  $M=468.1$   $a=10.94 \text{ \AA}$   
 $V=1309.3 \text{ \AA}^3$   $Z=4$   $D_c=2.37 \text{ g.cm}^{-3}$   
 $D_m=2.35 \text{ g.cm}^{-3}$  (flotation in  $\text{CHCl}_3/\text{CHBr}_3$ )  $F(000)=856$

[Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]S<sub>2</sub>O<sub>6</sub>  $M=374.6$  Orthorhombic  
 $a=10.59$ ,  $b=11.63$ ,  $c=10.47 \text{ \AA}$   
 $V=1289.5 \text{ \AA}^3$   $Z=4$   
 $D_m=1.93 \text{ g.cm}^{-3}$   $D_c=1.93 \text{ g.cm}^{-3}$  (flotation in  $\text{CHCl}_3/\text{CHBr}_3$ ).

[Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>] (BF<sub>4</sub>)<sub>2</sub>

The cell dimensions and space group of this salt were determined in this laboratory. Hodgson & Ibers (1966) have independently made a more complete study of it, and their data are given here:

$M=387.9$   $a=11.166 \text{ \AA}$   $Z=4$   $V=1392.2 \text{ \AA}^3$   
 $D_c=1.86 \text{ g.cm}^{-3}$   $D_m=1.88 \text{ g.cm}^{-3}$   $F(000)=760$

[Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]Br<sub>2</sub>  $M=374.1$   $a=10.41 \text{ \AA}$   
 [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>] (PF<sub>6</sub>)<sub>2</sub>  $M=504.2$   $a=11.79 \text{ \AA}$

For all these salts the absent spectra were:  $hkl$  when  $h+k=2n+1$  and  $k+l=2n+1$ . Space group:  $Fm\bar{3}m$ ,  $F432$  or  $F\bar{4}3m$ .

We have also recently prepared [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]S<sub>2</sub>O<sub>6</sub> by method 3 of Allen *et al.* (1967). Crystal data for this salt are given below, but the crystals may be twinned (see *Discussion*).

Absent spectra:  $hkl$  for  $h+k=2n+1$ ;  $00l$  for  $l=2n+1$ ;  $h0l$  for  $l=2n+1$ . Space group:  $Cmc2$  or  $Cmcm$ .

#### Data collection

Structure amplitudes for the iodide were obtained from  $0kl$  to  $9kl$  Weissenberg photographs (Zr-filtered Mo  $K\alpha$ ) by visual comparison of intensities with a calibrated reflexion obtained from the crystal. Data reduction was by the usual methods. 119 independent structure amplitudes were obtained ( $0 < \sin \theta < 0.5$ ), of which seven were recorded as zero. No absorption or extinction corrections were applied.

For the chloride, intensity data were collected on a manually operated Picker diffractometer (Zr-filtered Mo  $K\alpha$ ). Scanning was by the  $\omega-2\theta$  method with a scan speed of  $1^\circ.\text{min}^{-1}$ . Background was measured for

Table 1. Observed and calculated structure factors for [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]Cl<sub>2</sub>

$h$	$k$	$l$	$10 F_o$	$10 F_c$	$h$	$k$	$l$	$10 F_o$	$10 F_c$	$h$	$k$	$l$	$10 F_o$	$10 F_c$
0	0	0	—	508	1	3	7	397	403	3	3	11	142	135
0	0	2	1040	886	1	3	9	352	350	3	3	13	68	72
0	0	4	2659	2728	1	3	11	172	161	3	5	5	617	622
0	0	6	592	676	1	3	13	106	84	3	5	7	305	324
0	0	8	810	806	1	5	7	395	402	3	5	9	261	256
0	0	10	276	253	1	5	9	313	308	3	5	11	128	123
0	0	12	235	207	1	5	11	159	145	3	7	7	170	181
0	0	14	100	61	1	5	13	89	74	3	7	9	145	152
0	2	2	1934	2076	1	7	7	209	220	3	7	11	90	77
0	2	4	582	520	1	7	9	177	181	3	9	9	122	112
0	2	6	1176	1186	1	7	11	99	90	4	4	4	1113	1118
0	2	8	172	163	1	9	9	121	132	4	4	6	268	286
0	2	10	449	441	1	9	11*	79	67	4	4	8	433	436
0	2	12	82	55	2	2	2	832	-638	4	4	10	138	134
0	2	14	130	102	2	2	4	1304	1283	4	4	12	132	123
0	4	4	1674	1681	2	2	6	122	109	4	6	6	508	530
0	4	6	404	430	2	2	8	502	492	4	6	8	99	110
0	4	8	583	587	2	2	10	141	133	4	6	10	205	211
0	4	10	191	183	2	2	12	156	150	4	8	8	190	195
0	4	12	181	159	2	4	4	311	328	4	8	10*	92	60
0	6	6	745	726	2	4	6	818	829	5	5	5	526	544
0	6	8	143	149	2	4	8	108	118	5	5	7	288	300
0	6	10	283	278	2	4	10	336	331	5	5	9	214	220
0	6	12	55	47	2	4	12*	78	44	5	5	11	105	107
0	8	8	246	254	2	6	6	174	173	5	7	7	164	174
0	8	10	63	78	2	6	8	334	346	5	7	9	124	134
1	1	1	1916	1811	2	6	10	96	101	5	7	11	54	69
1	1	3	1214	1200	2	5	12	120	102	5	9	9	77	96
1	1	5	1175	1182	2	8	8*	114	56	6	6	6	133	143
1	1	7	513	518	2	8	10	126	149	6	6	8	211	230
1	1	9	430	429	2	10	10	74	49	6	6	10*	59	72
1	1	11	199	192	3	3	3	572	576	6	8	8	51	52
1	1	13	126	99	3	3	5	651	661	6	8	10	96	96
1	3	3	826	821	3	3	7	319	316	7	7	7	102	105
1	3	5	875	877	3	3	9	282	287	7	7	9	54	84

\* See text.

†  $F(000)$  calculated for all atoms except hydrogen.

40 sec before and after the peak, and the peak was measured for 100 sec. The intensities of 238 reflexions were measured a minimum of twice each. A routine check on the intensity of the 222 reflexion was used to correct for drift. The usual Lp corrections were applied and the 238 reflexions averaged to give 104 independent structure amplitudes. Of these, five had intensities of less than their standard deviation, and these were assigned an intensity equal to their standard deviation. These reflexions are asterisked in Table 1. Standard deviations, which were used to weight the reflexions in the structure refinement, were calculated using the methods of Abrahams (Abrahams, 1964; Abrahams & Bernstein, 1965). This method uses the equation  $\sigma^2(\bar{F}_{\text{meas}}^2) = V(\bar{F}^2) + C\bar{F}^4$ . No absorption or extinction corrections were applied. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), that for  $\text{Ru}^{2+}$  being corrected for anomalous dispersion.

### Structure determination

Initial attempts to solve the structure were performed on the iodide since suitable crystals of the other salts had not then been obtained. In the three possible space

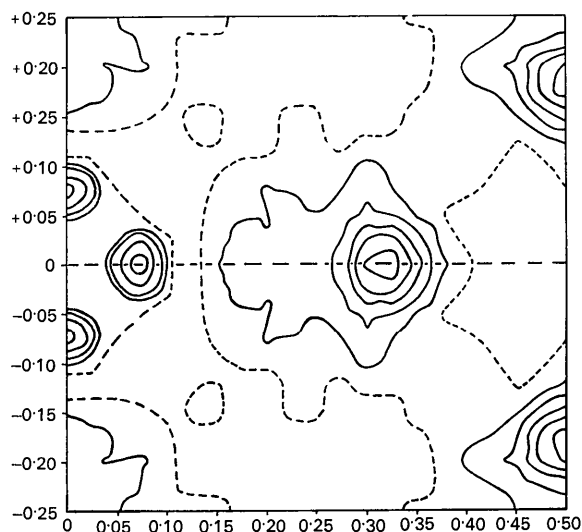


Fig. 1. Difference synthesis  $F_o - F_c^R$ ,  $F_c^R$  = structure factor calculated for all atoms except N(2) and H atoms. Contours are in  $0.1 \text{ e} \cdot \text{\AA}^{-3}$ .

groups the face-centring of any atom in a special or general position generates three others. The only feasible positions in all three space groups are the origin for  $\text{Ru}^{2+}$ , and for the anions  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$  and  $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ . For the nitrogen atoms, the only way the empirical formula can be reconciled with the space-group symmetry is by disordering in which the five nitrogen atoms of the ammonia groups and the inner nitrogen atom of the  $\text{N}_2$  molecule randomly occupy the six octahedral sites  $\pm(x_1, 0, 0; 0, x_1, 0; 0, 0, x_1)$  about the ruthenium ion. This composite nitrogen/atom at any one site is designated N(1). The remaining nitrogen atom must then randomly occupy the six positions  $\pm(x_2, 0, 0; \text{etc.})$ . This nitrogen atom is denoted N(2).

Fourier synthesis phased on  $\text{Ru}^{2+}$  and  $\text{I}^-$  revealed the position of N(1). However, all attempts to locate N(2) by least-squares refinement, Fourier and difference Fourier methods failed. The final  $R$  value was 0.098. Final values of the parameters refined and of the observed and calculated structure factors have been deposited with the American Documentation Institute.\*

With the isomorphous chloride salt, Fourier synthesis phased on  $\text{Ru}^{2+}$  and  $\text{Cl}^-$  revealed both N(1) and N(2). A site occupancy of  $\text{N}(1) = 1$  and  $\text{N}(2) = \frac{1}{2}$  per position was assumed, and full-matrix least-squares refinement, using the program of Busing, Levy & Martin (1962) as modified by Shiono (1964), minimizing the function  $\sum w(F_o - F_c)^2$ , where  $w = 1/\sigma^2$ , yielded a final  $R$  value of 0.050. On the final cycle the parameter shifts were essentially zero. The final observed structure amplitudes and calculated structure factors are given in Table 1.

Nine variable parameters were used in the refinement including the overall scale factor. Anisotropic temperature factors were used in the form:

$$\exp \left[ -\frac{1}{4}(h^2 a^{*2} B_{11} + k^2 b^{*2} B_{22} + l^2 c^{*2} B_{33} + 2hka^* b^* B_{12} + 2klb^* c^* B_{23} + 2lhc^* a^* B_{13}) \right]$$

\* Final values of the parameters refined (Table 4) and a table of observed and calculated structure factors for  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{I}_2$  (Table 3) have been submitted with the manuscript and have been deposited as Document number 9854 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make cheques or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 2. Final parameters and least-squares standard deviation for  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$

Values in square brackets and the relation  $(B_{12}) = B_{23} = B_{13} = 0$  are fixed by symmetry.

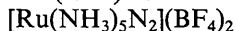
	$x/a$	$Y/b$	$Z/c$	$B_{11}$	$B_{22}$	$B_{33}$
Ru	[0]	[0]	[0]	4.77	$= [B_{11}]_{\text{Ru}}$	$= [B_{11}]_{\text{Ru}}$
$\sigma$	—	—	—	0.16		
Cl	[0.25]	[0.25]	[0.25]	6.09	$= [B_{11}]_{\text{Cl}}$	$= [B_{11}]_{\text{Cl}}$
$\sigma$	—	—	—	0.29		
N(1)	0.2071	[0]	[0]	4.48	7.65	$= [B_{22}]_{\text{N}(1)}$
$\sigma$	0.0009	—	—	0.37	0.62	
N(2)	0.3172	[0]	[0]	4.32	8.47	$= [B_{22}]_{\text{N}(2)}$
$\sigma$	0.0055	—	—	2.26	4.32	

The final values of the parameters refined, together with their standard deviations, are given in Table 2. A difference synthesis with these values revealed only a peak of  $0.5 \text{ e.}\text{\AA}^{-3}$ , at a distance of  $0.75 \text{ \AA}$  from the ruthenium ion and peaks of height  $0.1 \text{ e.}\text{\AA}^{-3}$  in the position expected for the  $\text{NH}_3$  hydrogen atoms. By symmetry, the hydrogen atoms must be disordered, and since the position of the ammonia nitrogen atom is also unknown, the hydrogen atoms have not been included in any structure factor calculations. A difference synthesis, with coefficients  $F_o - F_c^R$ , where  $F_c^R =$  structure factor calculated for all atoms except N(2), revealed a clearly defined electron density peak symmetrical with respect to the axis, in the position expected for N(2) (Fig. 1).

These parameters yield the distances Ru-N(2)  $3.221 \pm 0.06 \text{ \AA}$ , Ru-N(1)  $2.10 \pm 0.01 \text{ \AA}$ , N(1)-N(2)  $1.12 \pm 0.08 \text{ \AA}$ . Because of the disorder only the distance Ru-N(2) is structurally valid, and it is not possible to partition this distance accurately to yield bond lengths for the individual  $\text{NH}_3$  and  $\text{N}_2$  ligands.

An investigation has been made of  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$  at liquid nitrogen temperatures. From Weissenberg photographs the space group is the same as that at room temperature, and the cell dimension (uncalibrated zero layer photograph)  $a = 10.01 \text{ \AA}$ . A visual comparison of intensities revealed no changes from those on room temperature photographs. It is therefore concluded that the structure of the crystal is the same at liquid nitrogen as at room temperature.

Hodgson & Ibers (1966) found that



had a similar arrangement of ligands to that in the chloride, but with orientational disorder in the  $\text{BF}_4^-$  anion also. They estimated Ru-N(1) to be  $2.10 \pm 0.04 \text{ \AA}$ , N(1)-N(2) approximately  $1.03 \text{ \AA}$ . Because of the disorder, the different values found in the chloride and tetrafluoroborate salts cannot be considered significant.

### Discussion

Prior to the discovery of transition metal complexes containing molecular nitrogen there had been speculation as to the mode of bonding to be found in such compounds (Orgel, 1960; Dasent, 1965). The two possibilities are the 'sideways' bonding found in olefin and acetylene complexes of transition metals, and 'end-on' bonding as found in NO, CO and  $\text{CN}^-$  complexes. From the work described here the bonding is definitely 'end-on'.

Within the limits of accuracy imposed by the disorder, the Ru-N-N moiety is linear. However, the thermal vibrations of N(1) and N(2) are significantly greater perpendicular to the bond axis than along it, though the standard deviations of the thermal vibrations for N(2) are large (Table 2). The mean square displacement of N(1) from the bond axis is  $0.097 \text{ \AA}$  and for N(2)  $0.107 \text{ \AA}$ . This may indicate that the

Ru-N-N moiety is not precisely linear, but the deviation must be very small.

Fig. 2 shows the unit cell with arbitrary orientation of the nitrogen molecule. Using van der Waals radii for  $\equiv\text{N}$  from either  $\alpha$ -nitrogen,  $1.71\text{--}1.86 \text{ \AA}$  (Jordan, Smith, Streib & Lipscomb, 1964) or from cyanogen,  $1.77\text{--}1.93 \text{ \AA}$  (Parkes & Hughes, 1963), it can be shown (Fig. 3) that it is not possible to have two or more nitrogen molecules abutting. This therefore imposes a minor limitation on the complete randomness of the disorder.

The increase in cell dimensions  $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{BF}_4^- < \text{PF}_6^-$  is due solely to change in anion size. The increase does not follow that expected for the difference between twice the diameter of the anions,  $0.56, 0.84, 0.00 \text{ \AA}$  for  $\text{Cl}^-$  to  $\text{Br}^-$ ,  $\text{Br}^-$  to  $\text{I}^-$  and  $\text{I}^-$  to  $\text{BF}_4^-$  respectively, (Waddington, 1966; Kapustinskii, 1956) but is less for  $\text{Cl}^-$  through  $\text{I}^-$  and greater for  $\text{I}^-$  to  $\text{BF}_4^-$  ( $0.37, 0.53, 0.23 \text{ \AA}$ ). This could be due to the polarizability of the largest anions and the non-spherical nature of  $\text{BF}_4^-$ . An ionic radius for  $\text{PF}_6^-$  is not available.

The dithionate, for which crystal data are given in the *Experimental* section, has not yet been obtained in a form suitable for detailed investigation. All crystals so far examined have shown two diffraction peaks separated by a very small Bragg angle, and consistent

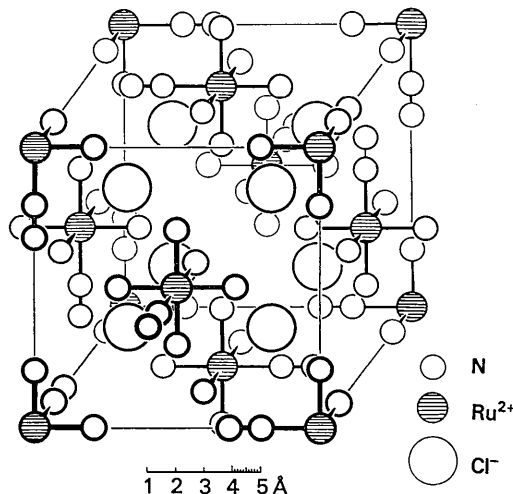


Fig. 2. Unit cell of  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ . Orientation of  $\text{N}_2$  molecule is arbitrary.

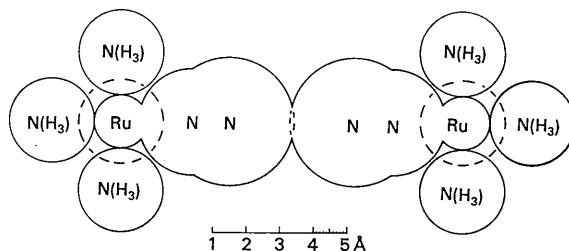


Fig. 3. Overlap of two abutting  $\text{N}_2$  molecules.

intensity measurements cannot be obtained. Further work is in progress, and it is not yet certain whether the crystals are twinned or whether two chemically different species are co-crystallizing. The space groups given are, therefore, somewhat uncertain.

The authors thank Professor J. A. Ibers for providing the results of the study of  $[\text{Ru}(\text{NH}_3)_5\text{N}_2](\text{BF}_4)_2$ , Mr I. P. Mellor and Dr J. T. Szymanski for assistance with the computer programs and Professor A. D. Allen for helpful discussions on the chemical properties of these compounds. Thanks are also due to the National Research Council of Canada for financial assistance.

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## X-ray Studies of C<sub>25</sub> Terpenoids. I. The Crystal Structure of Ophiobolin Methoxybromide

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The crystal structure and absolute configuration of ophiobolin methoxybromide, a derivative of the fungus metabolite ophiobolin, has been determined by three-dimensional X-ray analysis. The unit cell of ophiobolin methoxybromide,  $\text{C}_{26}\text{H}_{39}\text{O}_5\text{Br}$ , is orthorhombic with dimensions  $a = 13.19$ ,  $b = 22.27$ ,  $c = 8.46$  Å. The space group is  $P2_12_12_1$  with four molecules per cell. Refinement was carried out for 1499 observed reflexions by diagonal and then full-matrix least-squares calculations with anisotropic thermal parameters for bromine and isotropic ones for light atoms. The final  $R$  value was 0.11. The analysis revealed a novel skeletal structure of a new kind of terpenoid. The molecule consists of a five-, eight- and five-membered tricyclic ring system and a side chain containing a tetrahydrofuran group. Experiments on the biosynthesis of ophiobolin confirmed that this compound is the first example of a C<sub>25</sub> terpenoid.

#### Introduction

Ophiobolin is a metabolic product of the plant pathogenic fungus *Ophiobolus miyabeanus* (later it has been reclassified as *Cochliobolus miyabeanus*). Isolation of this metabolite was first reported by Ishibashi & Nakamura (1958). It has also been found that *Helminthosporium turcicum* and other *Helminthosporium* species fungi produce ophiobolin (Ishibashi, 1961, 1962a). Orsenigo (1957) reported the isolation of cochliobolin from *Cochliobolus miyabeanus*. After a report of the complete analysis of ophiobolin was published (Nozoe,

Morisaki, Tsuda, Iitaka, Takahashi, Tamura, Ishibashi & Shirasaka, 1965), Canonica, Fiecchi, Kienle & Scala (1966) reported the plane structure of cochliobolin. At present, it is generally accepted that cochliobolin and ophiobolin are one and the same compound (Fig. 1). To avoid confusion, it has been decided to call both the compounds 'ophiobolin A' (Tsuda, Nozoe, Morisaki, Hirai, Itai, Okuda, Canonica, Fiecchi, Kienle & Scala, 1967).

Ophiobolin has a pathogenic activity for plant diseases. The physiological activities of ophiobolin and its related compounds have been reported elsewhere