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THE CRYSTAL AND MOLECULAR STRUCTURE OF PYRIDINE-BORON TRIBROMIDE

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The crystal and molecular structure of pyridine-boron tribromide $C_5H_5N \cdot BBr_3$ has been determined by an X-ray diffraction method. The unit cell is monoclinic with a=9.396(3) Å, b=15.176(7) Å, c=6.558(2) Å, β=101.85(3)°, and Z=4. The space group is $P2_1/a$. Pyridine is bound to boron tribromide via nitrogen atom so that the atomic arrangement around the boron atom is tetrahedral with N–B=1.59(2) Å and B–Br=1.99(2) Å.

The molecular structure of trimethylamine complexes with boron trihalides have been determined in the solid phase.[1–3] According to these studies, the N–B bond distances of the molecular complexes are 1.58—1.61 Å and their systematic trend is not found with respect to the kind of boron trihalide. On the other hand, the crystal structures of pyridine complexes with boron trichloride and boron trifluoride have been determined by an X-ray diffraction method.[4,5] The N–B bond distance in the chloro complex (1.592 Å)[4] is considerably longer than that in the fluoro complex (1.53 Å),[5] though the heat of reaction of the former is larger than that of the latter.[6] Therefore it is interesting to know the N–B bond distance of pyridine-boron tribromide $C_5H_5N \cdot BBr_3$, the heat of reaction of which is larger than that of the chloro complex.[6]

The sample was prepared by dropwise additions of benzene solution of boron tribromide into pyridine. The single crystal used for the X-ray work was grown from the benzene solution. The structure unit is a monoclinic cell with dimension a=9.396(3) Å, b=15.176(7) Å, c=6.558(2) Å, and β=101.85(3)°. The density of the crystal is 2.39 (2) gcm^{-3} and the unit cell contains four molecules. The calculated density is 2.396

The interatomic distances and angles of the $C_5H_5N \cdot BBr_3$ molecule are listed in Table 2. The pyridine ring is planar as indicated in Table 3. The C–C bond distances of the pyridine ring are in the range of 1.38—1.40 Å with no systematic difference. The average C–C and C–N bond distances (1.38 ± 0.03 Å and 1.33 ± 0.02 Å respectively) are equal to the corresponding ones of a pyridine molecule (C–C=1.394 Å and C–N=1.340 Å)[8] within the limits of error. However, it is interesting that on the formation of a complex the C–N–C angle of a pyridine molecule (116.8°) increases by about 4° in spite of attachment of a bulky molecule to the nitrogen atom.

The N–B dative bond distance of $C_5H_5N \cdot BBr_3$ (1.59 ± 0.02 Å) is equal to that of $C_5H_5N \cdot BCl_3$[4] with no relation to the stability of their complexes. The atomic arrangement around the boron atom is tetrahedral, and the B–Br bond distance (average 1.99 ± 0.02 Å) is larger by 0.01 Å than that of a boron tribromide molecule (1.893 ± 0.005 Å).[9]

The orientation of boron tribromide to the pyridine ring is shown in Fig. 2. The molecule deforms from C_s symmetry by rotating the BBr_3 part around the N–B axis about

Table 2. Bond distances (ℓ/Å) and bond angles (φ/°) with their estimated standard deviations in parentheses.

N–B	1.59 (2)	Br(1)–B–Br(2)	110 (1)
B–Br(1)	1.99 (2)	Br(2)–B–Br(3)	112 (1)
B–Br(2)	2.01 (2)	Br(3)–B–Br(1)	110 (1)
B–Br(3)	1.96 (2)	N–B–Br(1)	107 (1)
N–C(1)	1.32 (2)	N–B–Br(2)	110 (1)
N–C(5)	1.33 (2)	N–B–Br(3)	110 (1)
C(1)–C(2)	1.40 (3)	C(1)–N–C(5)	121 (1)
C(2)–C(3)	1.38 (3)	N–C(1)–C(2)	120 (2)
C(3)–C(4)	1.38 (3)	N–C(5)–C(4)	118 (2)
C(4)–C(5)	1.38 (3)	C(1)–C(2)–C(3)	122 (2)
		C(5)–C(4)–C(3)	125 (2)
		C(2)–C(3)–C(4)	114 (2)

Table 3. Least-squares plane for the pyridine ring and individual atomic deviations from the plane (in Å unit).

$$-0.6619X + 0.2363Y - 0.7114Z + 4.1266 = 0$$

N	0.003	C(3)	0.009
C(1)	-0.004	C(4)	-0.011
C(2)	-0.003	C(5)	0.004

The X, Y, and Z are the coordinates along a, b, and c* axes, respectively.

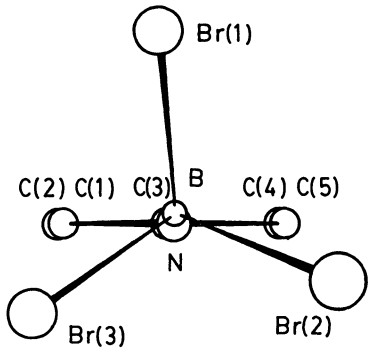

Fig. 2. Molecular structure of $C_5H_5N \cdot BBr_3$ projected parallel to the pyridine ring.

gcm^{-3}. The space group is $P2_1/a$. In total 3037 reflections were collected on a Rigaku automated four-circle diffractometer with Mo Kα radiation. The $\omega/2\theta$ scan technique was employed at a scanning rate of 4°/min in 2θ. Three standard reflections were monitored every 100 measurements. The net counts of these reflections decreased gradually and dropped to 86% at the end of the measurement, maybe because the sample is decomposed by humidity or irradiation of X-ray. Corrections for this effect and the Lorentz and polarization factors were made, but no absorption correction was applied. The 1016 reflections ($|F_o|>2\sigma(|F_o|)$) were used for the structure determination.

The atomic positions of the three bromines were obtained by the MULTAN 78 program,[7] and those of the boron atom and the pyridine ring were found from the subsequent Fourier calculations. The atomic parameters were refined by a block-diagonal least-squares method to 0.106 of R value with the introduction of anisotropic temperature factors. The hydrogen atoms were placed at the idealized positions of C–H=1.08 Å. The final atomic parameters and their estimated standard deviations are listed in Table 1.

Table 1. Final atomic coordinates with their standard deviations, multiplied by 10^4.

Atom	X	Y	Z	$B_{eq}/Å^2$
Br(1)	5735(2)	6208(1)	2055(3)	5.1(1)
Br(2)	9274(2)	6313(1)	3343(3)	4.9(1)
Br(3)	7433(3)	5667(1)	6741(3)	5.3(1)
B	7503(20)	5661(11)	3774(24)	2.6(5)
N	7556(13)	4670(8)	2990(15)	2.7(4)
C(1)	6778(18)	4075(11)	3746(26)	4.1(6)
C(2)	6711(20)	3209(13)	3011(27)	5.1(6)
C(3)	7440(23)	2946(12)	1487(27)	5.8(7)
C(4)	8245(20)	3608(13)	826(26)	5.2(7)
C(5)	8298(19)	4464(11)	1531(23)	4.1(6)

The crystal structure of $C_5H_5N\cdot BBr_3$ projected along the c-axis is shown in Fig. 1. Its structure is essentially the same as that of $C_5H_5N\cdot BCl_3$.[4]

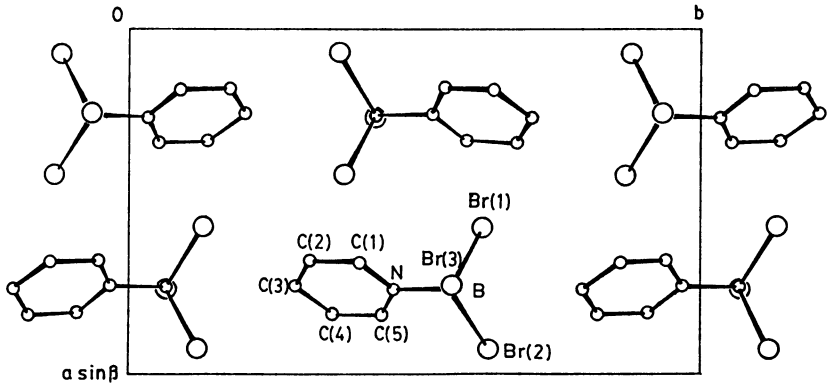

Fig. 1.
Crystal structure of $C_5H_5N\cdot BBr_3$ projected along the c-axis.

5°. The boron atom deviates about 0.1 Å from the plane of the pyridine ring. The plane formed by the three bromine atoms inclines by 84.6° to the plane of the pyridine ring, and the corresponding value is 87.1° in a pyridine-boron trichloride complex.[4] This difference may be due to that the repulsive force between the halogen and the hydrogen atoms increases with the higher atomic number of the halogen atoms.

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