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Coordinative Interactions in Chelated Complexes of Boron. XI*. Crystal Structure Determination and ^{11}B-NMR Investigations of Dihalogenoboryl-1,2,3,4-tetrahydro-1,10-phenanthrolines

GERHARD KLEBE** and DUC TRANQUI

Laboratoire de Crystallographie, Centre National de la Recherche Scientifique, 25, avenue des Martyrs, F-38000 Grenoble, France

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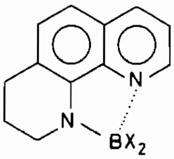
Dibromoboryl-1,2,3,4-tetrahydro-1,10-phenanthroline, $(C_{12}H_{11}N_2)BBr_2$ crystallizes with monoclinic symmetry in $P2_1/n$ with a = 7.190(5), b = 16.274(4), c = 10.931(1) Å, β = 93.39(5)°, V = 1276.9 Å^3, Z = 4. The structure was refined to a final $R_W(F)$ = 0.053 from 2202 independent reflections. The central atom is coordinated by two nitrogen and two bromine atoms in a distorted tetrahedral arrangement. The chelated complex shows a five-membered NBNCC heterocycle with two B–N bonds of different nature. The coordinative bond (1.58(2) Å) formed by intramolecular Lewis acid–base interaction is 5.9% longer than the B–N 'single' bond (1.49(2) Å) introduced by chemical substitution. The two B–Br bonds are 1.99(1) and 2.07(1) Å respectively. The chemical shifts of the ^{11}B-nuclei in $(C_{12}H_{11}N_2)BF_2$, -BBr_2, -BI_2 were registered and correlated with the crystal structure and the properties of diaminodihalogenoboranes [1].

Introduction

The trivalent compounds of boron react easily with donor molecules, such as aromatic amines to form tetravalent Lewis acid–base complexes. The crystal structure determination [2] of difluoroboryl-1,2,3,4-tetrahydro-1,10-phenanthroline (1a) revealed tetracoordinated boron arising from an intramolecular coordinative bond. The two chemically different B–N bonds display pronounced differences in length.



BX_2
BF_2 (1a)
BBr_2 (1b)
BI_2 (1c)

Several thermodynamic [3], spectroscopic [4], and single crystal diffraction studies [5] established an increase in acceptor power for the trihalides in the series $BF_3 < BCl_3 < BBr_3 < BI_3$. The detailed structure determination of the BBr_2 complex (1b) should reveal the influence of the increasing acceptor power of the boryl group on the two different B–N bonds. To correlate structural data in the crystal with those in solution ^{11}B NMR resonances of (1a)–(1c) were registered. Chemical shifts of boron have frequently been used to obtain information about the coordination of boron in its compounds in solution [6].

Experimental

The complex $(C_{11}H_{12}N_2)BBr_2$ was prepared from 1,2,3,4-tetrahydrophenanthroline [7, 8] and BBr_3 in benzene as described by Schmidt-Hansberg [9]. These compounds react initially to form the intermediate addition product 1-dibromoboryl-1,2,-3,4-tetrahydro-1,10-phenanthroline-tribromoborane, which subsequently loses BBr_3 when heated in benzene to 75 °C. Suitable crystals for X-ray diffraction were obtained from sublimation *in vacuo* (0.01 torr) through a temperature gradient of 3° to 145 °C. Due to the pronounced sensitivity to moisture the crystals were sealed in glass capillaries. The space group was determined by film-methods to be $P2_1/n$. On a Nonius-CAD4-diffractometer the lattice constants were refined from the angular setting of 25 reflec-

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*For Part X, see Ref. 1.

**Author to whom correspondence should be addressed. Present address: Institut für Kristallographie und Mineralogie der Universität Frankfurt/M, Senckenberganlage 30, D-6000 Frankfurt/Main 1, F.R.G.

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TABLE I. Final fractional coordinates and the arithmetic mean of the thermal ellipsoids projected on the principal axis, e.s.d. in parentheses.

Atom	x/a	y/b	z/c	U_{eq}
Br1	0.1167(2)	0.28566(8)	0.5607(1)	0.066(1)
Br2	0.5563(2)	0.24722(9)	0.6387(1)	0.053(1)
B	0.295(2)	0.1956(8)	0.606(1)	0.040(9)
N1	0.243(1)	0.1390(6)	0.7052(9)	0.036(7)
N10	0.306(1)	0.1303(6)	0.4988(9)	0.034(7)
C11	0.264(2)	0.0560(7)	0.541(1)	0.029(8)
C13	0.217(2)	0.0616(8)	0.667(1)	0.030(8)
C9	0.353(2)	0.1383(8)	0.385(1)	0.043(9)
C8	0.343(2)	0.067(1)	0.315(1)	0.049(10)
C7	0.301(2)	−0.0100(9)	0.356(1)	0.041(9)
C6	0.198(2)	−0.0881(8)	0.539(1)	0.041(9)
C5	0.153(2)	−0.0820(8)	0.662(1)	0.039(9)
C4	0.139(2)	0.0046(9)	0.857(2)	0.058(11)
C3	0.226(3)	0.081(1)	0.904(2)	0.102(17)
C2	0.208(2)	0.1576(9)	0.830(1)	0.057(11)
C14	0.174(2)	−0.0072(9)	0.723(1)	0.034(8)
C12	0.251(2)	−0.0168(8)	0.476(1)	0.029(8)
H9	0.37(1)	0.200(6)	0.371(8)	
H8	0.39(2)	0.065(7)	0.250(9)	
H7	0.31(1)	−0.059(6)	0.301(9)	
H6	0.20(1)	−0.143(6)	0.502(9)	
H5	0.13(1)	−0.137(6)	0.700(8)	
H41	0.00(1)	0.006(7)	0.867(10)	
H42	0.20(1)	−0.043(6)	0.904(9)	
H31	0.17(1)	0.094(6)	0.983(9)	
H32	0.36(2)	0.071(8)	0.920(10)	
H21	0.08(1)	0.181(6)	0.833(9)	
H22	0.30(1)	0.199(6)	0.862(9)	

tions: $a = 7.190(5)$, $b = 16.274(4)$, $c = 10.931(1)$ Å, $\beta = 93.39(5)^\circ$, $V = 1276.9(1.4)$ Å^3, $Z = 4$.

Intensities were collected in 6 quadrants of reciprocal space with graphite-monochromated Mo-Kα radiation up to $\sin\theta/\lambda = 0.698$ Å^{-1} in an ω-scan mode. The 8816 reflections were corrected for background [10] and scaled. After averaging over symmetry equivalent observations, 2202 unique reflections were used in the structure determination. A rough model of the structure was found using direct methods (MULTAN) [11]. The refinement of positional parameters of all atoms and the anisotropic temperature factors of all non-hydrogen atoms led to a final $R_W(F) = 0.053$. The fluoro- and iodo-derivatives (1a, 1c), studied by NMR, were synthesized as described in the literature [2, 9]. The samples for the ^{11}B NMR investigations were prepared in dried CDCl$_3$ (molecular sieve 4 Å) in a glove box under an argon atmosphere. The solutions were sealed in NMR test tubes. Spectra were registered at room temperature on a Varian XL 100 with BO$_3^-$ as the external standard. Chemical shifts were recalibrated on Et$_2$O·BF$_3$ as standard reference.

TABLE II. Bond lengths in (1b) in Å.

Atom 1–Atom 2	Distances (Å)
B–Br1	1.987(14)
B–Br2	2.072(14)
B–N1	1.490(17)
B–N10	1.584(17)
N1–C13	1.336(16)
N1–C2	1.432(18)
N10–C11	1.333(15)
N10–C9	1.313(18)
C11–C13	1.447(17)
C11–C12	1.381(17)
C13–C14	1.324(19)
C8–C9	1.395(22)
C7–C8	1.370(23)
C7–C12	1.387(17)
C6–C12	1.411(18)
C5–C6	1.406(21)
C5–C14	1.395(19)
C4–C14	1.506(21)
C3–C4	1.476(26)
C2–C3	1.483(26)

TABLE III. Bond angles in (1b) in degree.

Atom 1–Atom 2–Atom 3	Angle (degree)
Br1–B–Br2	108.0(6)
Br1–B–N10	111.9(8)
Br2–B–N10	108.4(8)
Br1–B–N1	116.8(8)
Br2–B–N1	113.0(8)
N1–B–N10	98.6(9)
B–N1–C13	113.0(10)
B–N1–C2	129.0(10)
C13–N1–C2	118.0(10)
C11–N10–C9	119.0(10)
N10–C11–C13	110.0(10)
N10–C11–C12	128.0(10)
C13–C11–C12	122.0(10)
N1–C13–C11	109.0(10)
N1–C13–C14	133.0(10)
C11–C13–C14	118.0(10)
N10–C9–C8	116.0(10)
C9–C8–C7	126.0(10)
C8–C7–C12	117.0(10)
C5–C6–C12	120.0(10)
C6–C5–C14	120.0(10)
C4–C3–C2	120.0(20)
N1–C2–C3	109.0(10)
C13–C14–C5	122.0(10)
C11–C12–C7	114.0(10)
C11–C12–C6	118.0(10)
C7–C12–C6	128.0(10)

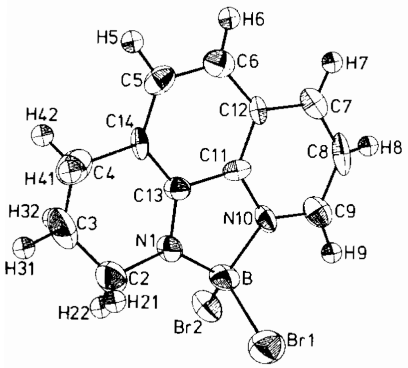


Fig. 1. ORTEP drawing of the molecule (1b), thermal ellipsoids are drawn at the 50% probability level, H atoms, shown as spheres, are at arbitrary radii.

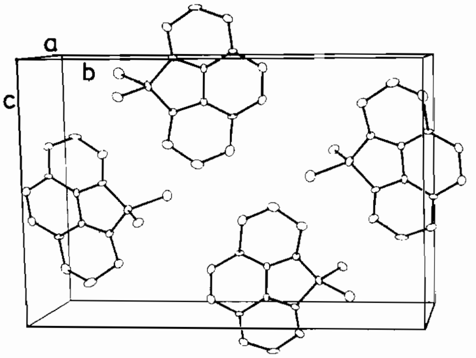


Fig. 2. Molecular packing within a unit cell.

Discussion of the Crystal Structure

The fractional coordinates of the atoms, the interatomic distances (in Å) and bond angles are given in Tables I, II and III, with the numbering scheme of Fig. 1.

Boron is located at the center of a distorted tetrahedron bonded to two bromine and two nitrogen atoms. The topological arrangement around boron is closely related to the isostructural fluoro compound. Both B–Br bonds are extended as compared with the uncomplexed trivalent BBr_3 (1.893(5) Å) [12]. This extension is more pronounced for bromine, a heavier and more polarisable substituent, than for fluorine [2]. The B–Br distances are in the same range as in other tetravalent boranes (1.99–2.05 Å) [5b, 13]. The difference in length of the two B–Br bonds is more pronounced in the present case than in the comparable fluoroderivative (B–Br 1.99(1), 2.07(1), B–F 1.369(7), 1.381(5) [2]).

The 'coordinative' B–N10 bond is only 5.9% longer than the other B–N1 'single' bond. It is comparable with distances of coordinative B–N bonds, at the lower limit of the range found for these connections in crystal structures (1.56–1.65 Å [14]). The B–N1 'single' bond is slightly extended as compared with B–N distances in trivalent aminoboranes (1.38–1.47 [15]). In comparison with the fluoro derivative (8.6%), the minor extension of coordinative bonding (5.9%), referred to as the B–N1 bond, results from the shorter B–N10 bond, for in both compounds the 'single' bond (B–N1) has the same value (within experimental error). This might be explained by a stronger Lewis acidity of the BBr_2 group as compared to the BF_2 group leading to a shorter distance between the center of the Lewis acid and the base. It is in agreement with other structural and thermodynamic studies [3, 5]. The B–N1 bond rests unaffected by the change of acceptor power of the boryl group.

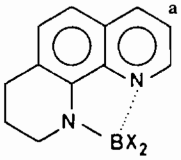
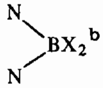
The deviation from tetrahedral arrangement around boron is due to the angle of 98° at the vertex of the five-membered NBNCC heterocycle. The other angles are rather close to those in an ideal tetrahedron.

The atoms of the aromatic system (N10, C9, C8, C7, C12, C11, C13, C14, C5, C6) form a planar arrangement. Br1 is situated 1.62 Å above, Br2 1.67 Å below this plane. Boron and N1 are found, within experimental error, in the molecular plane. The atoms C2 and C4 of the methylene bridge are very close to this plane, whereas C3 is more than half an Å apart. The conformation of the higher hydrated ring is similar to that of the SiF_3 and the $SiCl_3$ compound with the same ligand [2, 16]. In the closely related difluoroboryl complex, the deviation of C2 from the least squares plane through the major part of the ring atoms is more pronounced than in the bromo derivative. The situation in the BF_2 complex is similar to the arrangement in the $SiMe_2Cl$ and $SiMeCl_2$ derivatives, where two conformations of the higher hydrated ring (C2, C3) in the crystal were derived from structure refinement [17]. Presumably, the various conformations of the higher hydrated ring are energetically very similar, and the special conformation found in the crystal for each different complex is governed by the crystal packing forces and the substituent at N1 and N10. The molecular arrangement in the unit cell is shown in Fig. 2. The intermolecular distances are found in the range attributed to van der Waals interactions.

^{11}B NMR Spectroscopy

To correlate the structural data in the crystalline state with the properties in solution ^{11}B NMR resonance spectra of (1a), (1b) and (1c) were recorded (Table IV). The investigation of chemical shifts of

TABLE IV. Chemical Shifts of ^{11}B nuclei in (1a), (1b), and (1c) and differently substituted halogenoboranes.

Structural fragment	 [a]	$N-BX_2$ [b]	 [b]	BX_3 [b]	$N-BX_3$ [b]
X = F	6.0	17.2···18.0	0.6···1.0	9.4···11.6	−2.0··· 0.5
X = Br	8.5	25.0···28.0	6.0···7.0	38.5···44.0	−3.0··· −5.0
X = I	−25.6	0.0··· 5.0		−5.5···−8.0	−54.0···−59.8

[a] Resonance at room temperature in $CDCl_3$ with BO_3^- as external standard. [b] Chemical shifts taken from ref. 6.

the ^1H and ^{13}C nuclei in a series of differently substituted silyl- and boryltetrahydrophenanthrolines demonstrated coordinative interactions in solution [18]. The chelate complexes of silicon showed in solution DNMR phenomena which indicate the lability of coordinative bonding [19].

The empirical correlation of chemical shifts of ^{11}B nuclei to the structural environment is rather similar to that of carbon [6]. The chemical shifts of boron in (1a), (1b) and (1c) are closer to the range attributed to tetravalent diaminodihalogenoboranes than that attributed to aminodihalogenoboranes [6]. Nevertheless a low-field shift separates the present complexes from $(R_2N)_2BX_2$ derivatives. This low-field shift, in a direction towards that of trivalent species, indicates that the 'coordinative'-bond is remarkably weaker than a 'normal' B–N 'single' bond. It might result either from a smaller shielding influence of the electron density in the extended coordinative bond or from the kinetic lability of this connection (*cf.* analogous silicon complexes [19]). The displacement from the range of chemical shifts in tetravalent diaminodihalogenoboranes is more pronounced in the fluorocomplex than in the bromo-derivative. This result is in agreement with the decrease in length of the coordinative bond from (1a) to (1b) in the solid state.

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Supplementary Material Available

Listing of structure factor amplitudes, positional and thermal parameters are available from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen. Any request should be accompanied by the deposit number CSD-50463 and the full literature citation of this communication.

References

1 Part X: G. Klebe and D. Tranqui, *Acta Cryst., Sect. C,* in press.

2 Part IV: G. Klebe, K. Hensen and H. Fuess, *Chem. Ber., 116,* 3125 (1983).

3 (a) H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc., 78,* 2173 (1956).
(b) N. N. Greenwood and P. G. Perkins, *J. Chem. Soc.,* 1141 (1960).

4 (a) K. Hensen and W. Sarholz, *Theor. Chim. Acta, 12,* 206 (1968).
(b) P. H. Clippard and R. C. Taylor, *Inorg. Chem., 8,* 2802 (1969).
(c) E. J. McLauchlan and E. F. Mooney, *Spectrochim. Acta, 23A,* 1227 (1967).
(d) P. N. Gates, E. J. McLauchlan and E. F. Mooney, *Spectrochim. Acta, 21,* 1445 (1965).

5 (a) H. Hess, *Acta Cryst., B25,* 2338 (1969).
(b) P. H. Clippard, J. Hanson and R. C. Taylor, *J. Cryst. Mol. Struct., 1,* 363 (1971).
(c) K. H. Töpel, K. Hensen and M. Trömel, *Acta Cryst., B37,* 969 (1981).

6 H. Nöth and B. Wrackmeyer, 'NMR Basic Principles and Progress', Vol. 14, Springer Verl. (1978) and lit. therein.

7 I. F. Eckhard, R. Fielden and L. A. Summers, *Aust. J. Chem., 28,* 1149 (1975).

8 Part I: K. Hensen and G. Klebe, *J. Organomet. Chem., 209,* 17 (1981).

9 T. Schmidt-Hansberg, *Dissertation,* Univ. Frankfurt (1979).

10 'SDP-Program-System', Fa. Enraf-Nonius, Delft (Netherlands).

11 P. Main, L. Lessinger M. M. Woolfson, G. Germain and J. P. Declercq, 'MULTAN, A Computer Program for the Automatic Solution of Crystal Structures', Version 1980, Univ. York.

12 S. Konaka, T. Ito and Y. Morino, *Bull. Chem. Soc. Japn., 39,* 1146 (1966).

13 (a) A. L. Sayler and H. Beall, *Can. J. Chem.*, *54*, 1771 (1976).
(b) G. Allegra, E. Benedetti, C. Pedone and S. L. Holt, *Inorg. Chem.*, *10*, 667 (1971).
(c) H. Beall and W. N. Lipscomb, *Inorg. Chem.*, *6*, 874 (1967).
(d) K. H. Töpel, *Dissertation*, Univ. Frankfurt/M (1981).

14 (a) A. H. J. Wang and I. C. Paul, *Acta Cryst.*, *B33*, 2977 (1977).
(b) R. M. Spielvogel, L. Wojnowich, M. K. Das, A. T. McPhail and K. D. Hargrave, *J. Am. Chem. Soc.*, *98*, 5702 (1976).
(c) C. Svenson, *Acta Cryst.*, *B32*, 3341 (1976).
(d) W. R. Clayton, A. V. Fratini, R. Remmel and S. G. Shore, *Cyrst. Struct. Comm.*, *3*, 151 (1974).
(e) H. Y. Ting, W. H. Watson and H. C. Kelly, *Inorg. Chem.*, *11*, 374 (1972).

15 (a) H. Fussstetter, H. Nöth and W. Winterstein, *Chem. Ber.*, *110*, 1931 (1977).
(b) H. Nöth, R. Staudigl and W. Storch, *Chem. Ber.*, *114*, 3024 (1981).
(c) F. Zettler and H. Hess, *Chem. Ber.*, *108*, 2269 (1975).
(d) D. Lux, W. Schwarz and H. Hess, *Cryst. Struct. Comm.*, *8*, 33 (1979).
(e) H. Hess and B. Reiser, *Z. Anorg. Allg. Chem.*, *381*, 91 (1971).

16 Part III: G. Klebe, J. W. Bats and K. Hensen, *Z. Naturforsch.*, *38b*, 825 (1983).

17 Part V: G. Klebe, J. W. Bats and K. Hensen, *J. Chem. Soc., Dalt. Trans.*, submitted.

18 Part VI: G. Klebe, K. Hensen and J. Jouanne, *J. Organomet. Chem.*, in press (1983).

19 Part VII: G. Klebe and K. Hensen, *J. Chem. Soc., Dalton Trans.*, in press (1983).