Synthesis and crystal structure of *cis*-$[\overline{Pd\{Ph_2PCH_2C(O})Ph\}_2]$-$[BF_4][B_2F_7]$. Unexpected formation and first structural characterisation of the heptafluorodiborate anion $B_2F_7^-$

P. Braunstein*, L. Douce

Laboratoire de Chimie de Coordination, UA 416 CNRS, Université Louis Pasteur, 4 Rue Blaise Pascal, F-67070 Strasbourg Cédex (France)

J. Fischer

Laboratoire de Cristallochimie et de Chimie Structurale, URA 424 CNRS, Université Louis Pasteur, 4 Rue Blaise Pascal, F-67070 Strasbourg Cédex (France)

N. C. Craig

Department of Chemistry, Oberlin College, Oberlin, OH 44074 (USA)

G. Goetz-Grandmont and D. Matt*

Laboratoire de Chimie Minérale et Analytique, URA 405 CNRS, EHICS, 1 Rue Blaise Pascal, F-67008 Strasbourg Cédex (France)

(Received November 12, 1991)

Abstract

The reaction of *cis*-$[\overline{Pd\{Ph_2PCH{=}C(O})Ph\}_2]$ (**1**) with HBF_4/H_2O instantly leads to the formation of the cationic complex *cis*-$[\overline{Pd\{Ph_2PCH_2C(O})Ph\}_2][BF_4]_2$. When **1** was treated with commercial $BF_3 \cdot Et_2O$, containing HBF_4 as an impurity, the related compound *cis*-$[\overline{Pd\{Ph_2PCH_2C(O})Ph\}_2][BF_4][B_2F_7]$ (**2**) was formed. The structure of **2** was determined by an X-ray diffraction study. The compound crystallizes in the orthorhombic system, $P2_12_12_1$ space group, $Z=4$, cell dimensions: $a=16.474(4)$, $b=19.007(5)$, $c=12.932(4)$ Å, $V=4049.3$ Å^3, final $R=0.030$. The two chelating phosphines define puckered five membered metallocycles characterised by PCH_2 carbon atoms lying significantly out of the metal coordination plane (−0.617(7) Å for C1 and +0.779(7) Å for C21). This study establishes the first structural data for the $B_2F_7^-$ anion: the value of the $B-F_{bridge}-B$ angle is 128.1(7)°. The values of the $B-F_{bridge}$ bond lengths (1.50(1) and 1.51(1) Å) are significantly longer than the other B-F bonds (1.34-1.39 Å).

Introduction

There is a current interest in complexes containing unsymmetrical bidentate ligands combining a tertiary phosphine moiety and a weak donor functionality [1]. In molecules where such ligands act as chelates, the weak donor part may readily be displaced by incoming substrates which may then undergo stoichiometric or catalytic transformations at the metal center. Thus the 'hemilabile' ligand allows the storage of a potential vacant site suitable for the activation of a reagent [2]. The *chelate effect* of these ligands may also confer additional stability on catalyst precursors in the absence of any other substrate. Furthermore, the use of dissymmetric chelates — rather than symmetrical ones — has often proved to be of advantage for subtle electronic and steric control of the active metal centre [3].

In previous reports [4] we have described the synthesis and characterisation of complexes containing chelating phosphino-ketone ligands of the type $Ph_2PCH_2C(O)R$, a ligand type combining a soft donor center (the trivalent P atom) with a hard donor atom (the keto oxygen atom). These ligands have previously been shown to display hemilabile behaviour in some copper complexes [4a].

Here we wish to report the molecular structure of the cationic complex *cis*-$[\overline{Pd\{Ph_2PCH_2C(O})Ph\}_2]$-$[BF_4][B_2F_7]$. The preparation of the complex unexpectedly led to the formation of the $B_2F_7^-$ anion, a fluoroborate structure which has not been reported to date.

---

*Authors to whom correspondence should be addressed.

0020-1693/92/$5.00

Experimental

The preparation of the title complex was performed using standard vacuum techniques. Dichloromethane was distilled over P_2O_5 and stored under dry nitrogen. The $BF_3 \cdot Et_2O$ solution was purchased from Aldrich and used without any purification. The IR spectrum was recorded on a FT-IR Bruker IFS-66 instrument. The Raman spectrum was measured with a Coderg PH1 spectrometer. The complex *cis*-[$Pd\{Ph_2PCH=C(O)Ph\}_2$] (**1**) was prepared according to the method reported previously [5].

Synthesis of cis-[$Pd\{Ph_2PCH_2C(O)Ph\}_2$][BF_4][B_2F_7] (2)

A solution of commercial $BF_3 \cdot Et_2O$ (3 ml) was added to a solution of *cis*-[$Pd\{Ph_2PCH=C(O)Ph\}_2$] (0.200 g, 0.23 mmol) in CH_2Cl_2 (50 ml). The yellow solution immediately turned pale yellow and after *c.* 3 h pale yellow crystals precipitated (0.210 g, 0.20 mmol, 85%). These crystals were suitable for X-ray diffraction analysis. *Anal.* Calc. for $C_{40}H_{34}B_3F_{11}O_2P_2Pd$ ($M_r = 956.49$): C, 50.23; H, 3.58; Found: C, 49.86; H, 3.73%. Melting point > 220 °C. IR (KBr): 1554s (ν(C=O)), 833ms ($B_2F_7^-$), 1064s, br (BF_4^-) cm^{-1}. No NMR data are available for this complex, due to its extremely low solubility. The Raman spectrum of **2** shows two peaks of weak intensity at 707 and 253 cm^{-1}. These cannot be attributed with certainty to $B_2F_7^-$ due to their weakness and to peaks of the cation in the same region, although they have been already tentatively assigned to $B_2F_7^-$ [12].

Crystallographic data collection and structure determination of cis-[$Pd\{Ph_2PCH_2C(O)Ph\}_2$][BF_4][B_2F_7] (2)

Suitable single crystals of **2** were obtained according to the procedure described above. A single crystal of approximate size 0.22×0.24×0.32 mm was cut from a cluster and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using a Philips PW 1100/16 automatic diffractometer showed that crystals of **2** belong to the orthorhombic system. Quantitative data was obtained at −100 °C by using a locally-built gas flow device. All experimental parameters used are given in Table 1. The resulting dataset was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package was used [6] with the exception of a local data reduction program. Three standard reflections measured every hour during the entire data collection period showed no significant decay. The raw step-scan data was converted to intensities using the Lehman–Larsen method [7] and then corrected for Lorentz and polarisation factors. The structure was solved using the heavy atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as $B(H) = 1.3\ B_{eq}(C)$ Å^2 but not refined. At this stage empirical absorption corrections were applied using the method of Walker and Stuart [8] since face indexation was not possible under the cold gas stream.

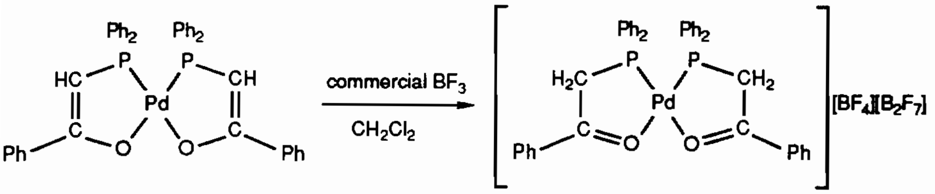
TABLE 1. Crystal data and details of data collection

Molecular formula	$C_{40}H_{34}B_3F_{11}O_2P_2Pd$
Crystal system	orthorhombic
a (Å)	16.474(4)
b (Å)	19.007(5)
c (Å)	12.932(4)
Space group	$P2_12_12_1$
V (Å^3)	4049.3
D_c (g cm^{-3})	1.569
Z	4
Temperature (°C)	−100
Diffractometer	Philips PW 1100/16
Mode	$\theta/2\theta$ flying step-scan
Scan speed (° s^{-1})	0.024
Scan width (°)	$1.10 + 0.143\ \mathrm{tg}\ \theta$
Step width (°)	0.05
Crystal dimensions (mm)	0.22×0.24×0.32
Radiation	Cu Kα (graphite monochromated)
Wavelength (Å)	1.5418
Absorption coefficient (cm^{-1})	53.13
2θ limits	6–102
No. unique reflections	2451
No. data with $I > 3\sigma(I)$	2317
Absorption min/max	0.87/1.28
R	0.030
R_w	0.048
p	0.08
GOF	1.218

Full least-squares refinements: $\sigma^2(F^2) = \sigma^2$ counts $+ (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients were taken from ref. 9a and b, respectively.

Results and discussion

Complex **2** was obtained by reaction of the bisphosphinoenolate **1** with an excess of commercial $BF_3 \cdot Et_2O$ in CH_2Cl_2. The product precipitated as pale yellow crystals within a few hours from the reaction mixture. It is practically insoluble in common solvents such as CH_2Cl_2, $CHCl_3$ and THF. The IR (KBr) spectrum of the complex shows a strong ν(C=O) band at 1554 cm^{-1}, characteristic of a coordinated ketone group [4b], and a strong absorption band at *c.* 1064 cm^{-1} due to BF_4^-.



1 2 (1)

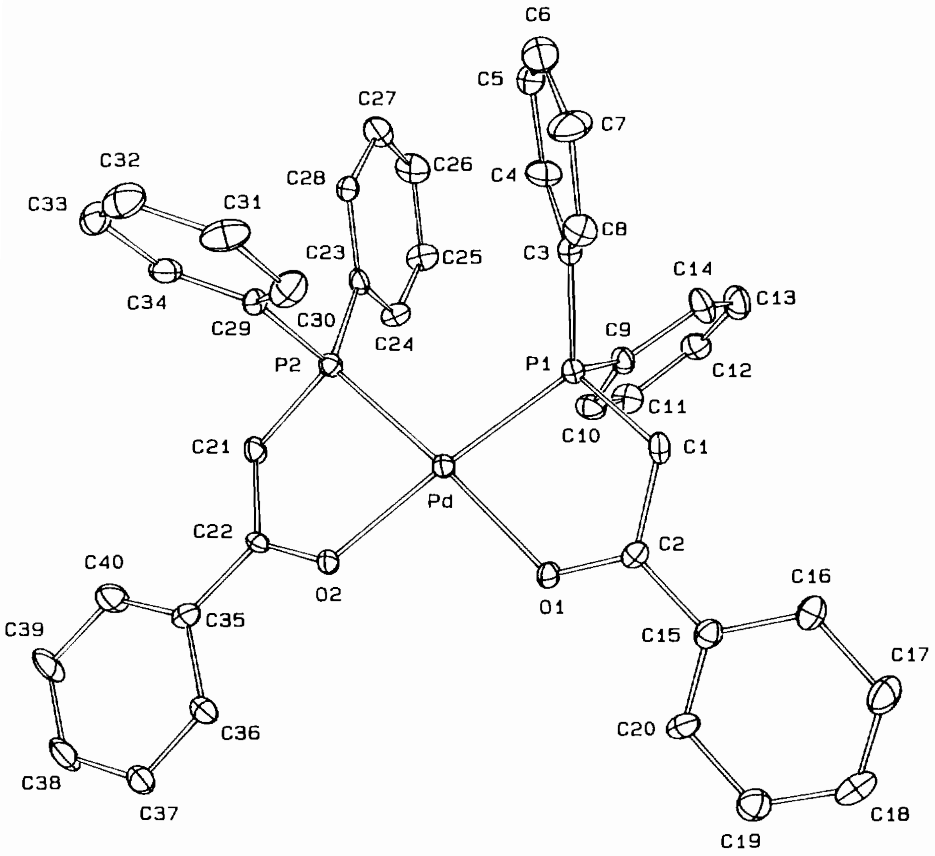


Fig. 1. ORTEP plot of the cation *cis*-$[\overline{\text{Pd}\{\text{Ph}_2\text{PCH}_2\text{C(O}})\text{Ph}\}_2]^{2+}$ showing the numbering scheme used. Ellipsoïds are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

In order to confirm the accidental protonation which occurred during this reaction, we checked, in a separate experiment, that complex **1** may instantly be protonated in THF by HBF_4/H_2O. This quantitatively gave the soluble cationic complex *cis*-$[\overline{\text{Pd}\{\text{Ph}_2\text{P-}\text{CH}_2\text{C(O}})\text{Ph}\}_2][\text{BF}_4]_2$ (**3**) which was compared with an authentic sample [4b]. Compounds **2** and **3** present quasi superimposable IR absorption bands in a large part of the spectrum, in particular in the ketone region; however an additional medium-strong absorption band appears for **2** at 833 cm^{-1} which may be assigned to $B_2F_7^-$ [10]*. The Raman spectrum of compound **2** exhibits diffusion peaks of weak intensity at 253 and 707 cm^{-1}. Although these values are in accordance with those reported earlier for $B_2F_7^-$ [11, 12], they could not be attributed with certainty because of the presence in these regions of bands due to the cation. The protonation which occurred by reacting commercial

---

*Note that the band at 833 cm^{-1} is absent in the spectrum of the isoelectronic $[F_3B(\mu\text{-OH})BF_3]^-$ anion, see ref. 10c.

TABLE 2. Positional parameters and equivalent isotropic temperature factors with their e.s.d.s

Atom	*x*	*y*	*z*	*B* (Å^2)[a]
Pd	0.88037(3)	0.77489(2)	0.79899(4)	2.112(9)
P1	0.8999(1)	0.86705(9)	0.6969(1)	2.41(3)
P2	0.7475(1)	0.75730(9)	0.7831(1)	2.26(3)
F1	0.5532(4)	0.4453(2)	0.2791(4)	6.1(1)
F2	0.4924(3)	0.3599(3)	0.1958(6)	8.0(2)
F3	0.5275(4)	0.4591(3)	0.1125(4)	7.0(1)
F4	0.6213(3)	0.3800(3)	0.1639(4)	6.2(1)
F5	0.4310(3)	−0.0717(3)	0.6320(4)	5.4(1)
F6	0.5019(3)	0.0208(3)	0.5648(4)	5.2(1)
F7	0.4101(3)	0.0359(3)	0.7022(3)	4.7(1)
F8	0.5272(3)	−0.0224(3)	0.7316(3)	4.7(1)
F9	0.5765(3)	0.0995(2)	0.4648(3)	4.5(1)
F10	0.4483(3)	0.1282(2)	0.5037(4)	4.8(1)
F11	0.5445(4)	0.1291(3)	0.6294(4)	5.8(1)
O1	1.0074(2)	0.7793(2)	0.8118(4)	2.40(9)
O2	0.8697(3)	0.6883(2)	0.8979(3)	2.20(8)
C1	0.9999(4)	0.8950(4)	0.7425(6)	2.7(1)
C2	1.0471(4)	0.8324(4)	0.7816(5)	2.4(1)
C3	0.8341(4)	0.9422(4)	0.7031(6)	2.8(1)
C4	0.7651(5)	0.9423(4)	0.6312(7)	4.6(2)
C5	0.7095(5)	0.9956(5)	0.6403(9)	5.8(2)
C6	0.7194(5)	1.0463(4)	0.7184(8)	5.6(2)
C7	0.7844(5)	1.0478(4)	0.7812(9)	5.5(2)
C8	0.8403(5)	0.9922(4)	0.7747(7)	4.3(2)
C9	0.9134(4)	0.8425(4)	0.5635(5)	3.0(2)
C10	0.9165(5)	0.7753(4)	0.5338(6)	3.7(2)
C11	0.9281(5)	0.7565(4)	0.4295(6)	4.1(2)
C12	0.9380(5)	0.8081(5)	0.3576(6)	3.6(2)
C13	0.9404(5)	0.8769(5)	0.3865(6)	4.5(2)
C14	0.9274(5)	0.8957(4)	0.4880(6)	4.1(2)
C15	1.1344(4)	0.8311(4)	0.7851(5)	3.0(1)
C16	1.1782(4)	0.8929(4)	0.7586(6)	3.2(2)
C17	1.2642(5)	0.8891(4)	0.7641(7)	4.6(2)
C18	1.3034(4)	0.8300(5)	0.7941(7)	4.4(2)
C19	1.2594(5)	0.7687(5)	0.8194(6)	4.1(2)
C20	1.1742(4)	0.7713(4)	0.8140(6)	3.3(2)
C21	0.7453(4)	0.6638(3)	0.8178(6)	2.7(1)
C22	0.8108(4)	0.6476(3)	0.8933(5)	2.0(1)
C23	0.6987(4)	0.7673(4)	0.6599(5)	2.5(1)
C24	0.7279(4)	0.7256(4)	0.5754(5)	3.0(2)
C25	0.6971(5)	0.7363(4)	0.4781(6)	3.7(2)
C26	0.6350(5)	0.7855(4)	0.4625(6)	4.1(2)
C27	0.6067(5)	0.8263(4)	0.5448(6)	4.0(2)
C28	0.6372(4)	0.8151(4)	0.6438(6)	2.8(1)
C29	0.6821(4)	0.8016(3)	0.8765(5)	2.2(1)
C30	0.7112(5)	0.8605(5)	0.9282(6)	4.4(2)
C31	0.6629(5)	0.8942(4)	1.0000(7)	4.7(2)
C32	0.5860(5)	0.8656(5)	1.0205(7)	4.7(2)
C33	0.5573(5)	0.8065(5)	0.9698(6)	4.4(2)
C34	0.6091(4)	0.7751(4)	0.8976(6)	3.5(2)
C35	0.8107(4)	0.5814(4)	0.9543(6)	2.9(2)
C36	0.8828(4)	0.5651(3)	1.0106(6)	3.0(1)
C37	0.8863(5)	0.5023(4)	1.0634(6)	3.4(2)
C38	0.8200(6)	0.4576(4)	1.0621(7)	4.9(2)
C39	0.7501(6)	0.4738(4)	1.0106(7)	4.9(2)
C40	0.7487(5)	0.5357(4)	0.9533(6)	4.2(2)
B1	0.5500(5)	0.4130(4)	0.1871(7)	2.9(2)
B2	0.4653(5)	−0.0108(6)	0.6614(7)	3.5(2)
B3	0.5177(6)	0.0971(5)	0.5417(7)	3.7(2)

[a] $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE 3. Selected bond lengths (Å) and bond angles (°)

Bond lengths and angles in the cation			
Pd–P1	2.217(2)	Pd–P2	2.224(2)
Pd–O1	2.102(4)	Pd–O2	2.092(4)
P1–C1	1.828(8)	P2–C21	1.833(7)
P1–C3	1.794(7)	P2–C29	1.825(7)
P1–C9	1.801(8)	P2–C23	1.794(7)
C1–C2	1.51(2)	C21–C22	1.49(1)
C2–O1	1.264(9)	C22–O2	1.242(8)
P1–Pd–P2	101.92(7)	O1–Pd–O2	93.8(2)
P1–Pd–O1	82.6(1)	P2–Pd–O2	81.7(1)
Pd–P1–C1	99.7(2)	Pd–P2–C21	98.2(2)
P1–C1–C2	110.1(5)	P2–C21–C22	110.4(5)
C1–C2–O1	117.9(6)	C21–C22–O2	117.9(6)
C2–O1–Pd	121.4(4)	C22–O2–Pd	121.8(4)
O1–C2–C15	119.5(7)	O2–C22–C35	120.2(6)
Bond lengths and angles in the BF_4^- anion			
B1–F1	1.34(1)	B1–F2	1.39(1)
B1–F3	1.35(1)	B1–F4	1.36(1)
F1–B1–F2	106.7(8)	F1–B1–F3	110.3(7)
F1–B1–F4	111.8(7)	F2–B1–F3	109.9(8)
F2–B1–F4	105.7(7)	F3–B1–F4	112.2(8)
Bond lengths and angles in the $B_2F_7^-$ anion			
B2–F5	1.34(1)	B2–F6	1.51(1)
B2–F7	1.38(1)	B2–F8	1.38(1)
B3–F6	1.50(1)	B3–F9	1.39(1)
B3–F10	1.38(1)	B3–F11	1.36(1)
B2–B3	2.71(1)		
F5–B2–F6	106.1(7)	F5–B2–F7	112.8(8)
F5–B2–F8	111.1(8)	F6–B2–F7	108.9(8)
F6–B2–F8	108.1(7)	F7–B2–F8	109.8(7)
F6–B3–F9	107.1(7)	F6–B3–F10	109.9(8)
F6–B3–F11	108.8(7)	F9–B3–F10	108.0(7)
F9–B3–F11	110.8(8)	F10–B3–F11	112.1(8)

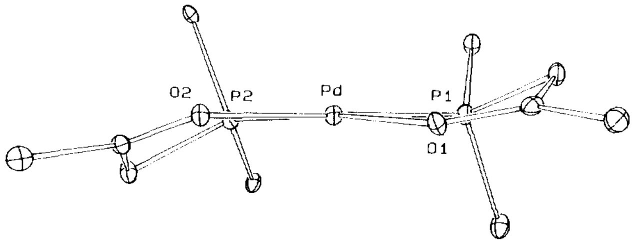


Fig. 2. Partial view of *cis*-$[Pd\{Ph_2PCH_2C(O)Ph\}_2]^{2+}$ showing the puckering of the chelate rings.

BF_3 is likely to be due to small amounts of HBF_4 present. This fast reaction is a further example of the reactivity of transition metal enolates of type **1**, a property already illustrated by reactions with other electrophilic reagents [13–15].

The structure of the cationic complex has been determined by X-ray diffraction analysis and is shown in Fig. 1. Final atomic parameters are reported in Table 2. Selected bond distances and angles are given in Table 3. This molecular structure determination confirms that the two phosphine ligands occupy *cis* positions,

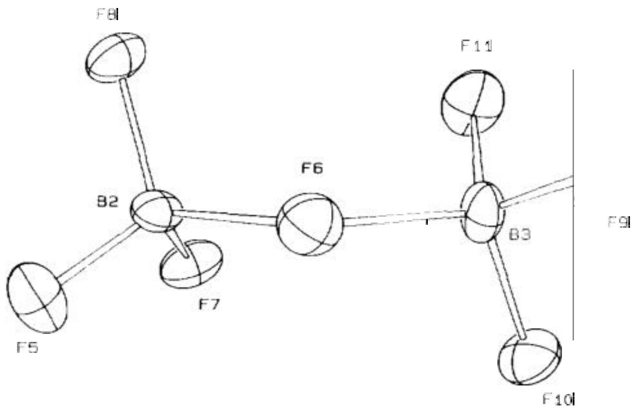


Fig. 3. ORTEP plot of the $B_2F_7^-$ anion.

confirming that no *cis–trans* isomerisation has occurred. The coordination environment of the palladium atom is nearly planar, the maximum deviation out of the P1P2O1O2 plane being 0.050 A. The Pl-Pd-P2 angle, 101.92(7)°, is significantly larger than that of the O1–Pd–O2 angle (93.8(2)°) and reflects the steric repulsion between the PPh_2 groups. The chelate rings are not planar and the puckering (see Fig. 2) is likely to be mainly due to the presence of a PCH_2 group which requires for this carbon atom an endocyclic angle near 109” (actual value 110°). Note that the two PCH_2 carbon atoms are on each side of the metal plane, a situation which obviously contributes to minimise the steric repulsions between the PPh_2 groups (the distances of Cl and C21 to the P1–P2–O1–O2 plane are −0.617(7) and +0.779(7) A, respectively). The Pd-P distances (Pd-P(1) = 2.217(2), Pd-P(2) = 2.224(2) Å) are comparable to those found in other palladium(II) complexes containing chelating P, 0 ligands [16]. The Pd–O distances (Pd-O(1) = 2.102(4) and Pd–O(2) = 2.092(4) Å) are somewhat longer than the sum of the covalent radii (2.01 Å [17]) and are comparable to Pd–O distances found in Pd(II) complexes containing labile oxygen donor groups [15]. This suggests that the ketone group may easily be displaced by competing substrates.

The structure of the $B_2F_7^-$ anion, unreported to date, is shown in Fig. 3. This anion is usually formed when BF, is added to solutions of BF_4^- in the presence of bulky cations [10,12]*. A single fluorine atom forms a bridge between two BF_3 fragments_ The structure is bent, with a $B–F_b–B$ angle of 128.1(7)° (b = bridging). This value contrasts with that deduced from some theoretical considerations [20]; note however that it compares well with that crystallographically determined for the $B–H_b–B$ angle in $B_2H_7^-$ (127.2(20)°) [21]. The geometry around each boron atom is a slightly distorted tetrahedron (range of the $F_b–B–F$ angles: 106.1(7)–109.9(8)°) with the six terminal (t) fluorine atoms arranged in a pseudo staggered conformation. As expected, the $B–F_b$ distances (1.50(1) and 1.51(1) Å) are significantly longer than the B-F, bond lengths which fall in the range 1.34(1)–1.39(1) Å. The latter bond lengths are not significantly affected by the presence of a bridging fluorine atom (for comparison see bond lengths of the BF_4^- counter anion, Table 3). It is also interesting to note that the apex-sharing bitetrahedral geometry of $B_2F_7^-$, related to that found in $B_2H_7^-$, is also similar to that observed in oxo species like $[Mo_2O_7]^{2-}$ [22].

---

*To the best of our knowledge, $B_2F_7^-$ was first reported in 1965 [10a]. In several studies, this anion has been reported to dissociate easily into BF_3 and BF_4^-; see for example refs. 18 and 19.

References

1 (a) E. Lindner and J. Dettinger, *Z. Naturforsch., Teil B,* 46 (1991) 432; (b) A. Varsbney and G. M. Gray, *Inorg. Chem.,* 30 (1991) 1748; (c) M. R. Mason and J. G. Verkade, *J. Am. Chem. Soc., ZZ3* (1991) 6309; (d) D. J. Irvine, A. F. Borowski and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, (1990) 3549.

2 (a) A. Bader and E. Lindner, *Coord. Chem. Rev., 108* (1991) 27; (b) P. Braunstein, D. Matt and D. Nobel, *J. Am. Chem. Soc., 110* (1988) *3207.*

3 (a) W. Keim, A. Bebr and G. Kraus, J. *Organomet. Chem., 251* (1983), *377;* (b) H. Hoberg, A. Ballesteros, A. Sigan, C Jegat and A. Milcbereit. *Synthesis,* (1991) 395.

4 (a) P. Braunstein, T. M. Gomes Carneiro, D. Matt, F. Balegroune and D. Grandjean, *J. Organomet.* Chem., 367 (1989) 117; (b) P. Braunstein, D. Matt, D. Nobel, F. Balegroune, S.-E. Bouaoud, D. Grandjean and J. Fischer, *J. Chem. Soc., Dalton Trans.,* (1988) *353.*

5 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.,* 25 (1986) 3765.

6 B. A. Frenz, The Enraf-Nonius CAD4-SDP, in H. Scbenk, R. Oltbof-Hazekamp, H. Van Koningveld and G. C. Bassi (eds.), *Computing in Crystallography,* Delft University Press, Delft, Netherlands, 1978, pp. 64-71.

7 M. S. Lehman and F. K. Larsen, *Acta Crystallogr., Sect. A, 30* (1974) *580.*

8 *N.* Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

9 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography,* Vol. IV, Kynocb, Birmingham, UK, 1974 (present distributor Reidel, Dordrecbt), (a) Table 2.2b; (b) Table 2.3.1.

10 (a) S. Brownstein and J. Paasivirta, Can. *J. Chem.,* 43 (1965) 1645; (b) J. J. Harris, *Inorg. Chem., 5* (1966) 1627; (c) R. Fourcade and G. Mascbexpa, *Bull. Soc. Chim. Fr.*, (1972) 4493.

11 N. C. Craig, J. Pranata, S. J. Reinganum, J. R. Sprague and P. S. Stevens, *J. Am Chem. Soc., 108* (1986) 4378.

12 N. C. *Craig, G.* F. Fleming and J. Pranata, *J. Am. Chem. Soc., 107* (1985) *7324.*

13 P. Braunstein, T. M. Gomes Cameiro, D. Matt, F. Balegroune and D. Grandjean, *Organometallics, 8* (1989) 1737.

14 F. Balegroune, P. Braunstein, T. M. Gomes Cameiro, D. Grandjean and D. Matt, *J.* Chem. *Soc., Dalton Trans.*, (1989) 582.

15 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem., 27* (1988) 2279.

16 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *J. Chem. Soc., Chem. Commun.,* (1987) 488.

17 L. Pauling, *The Nature of the Chemical Bond,* Cornell University Press, Ithaca, NY, 3rd edn., 1960.

18 J. S. Hartman and P. Stilbs, *J. Chem. Soc., Chem. Commun.,* (1975) 566.

19 M. G. Thomas, C. W. Schultz and R. W. Parry, *Inorg. Chem., 16* (1977) 994.

20 A. F. Cuthbertson, C. Glidewell and D. Liles, *THEOCHEM, 4* (1982) 273.

21 S. I. Khan, M. Y. Chiang, R. Bau, T. F. Koetzle, S. G. Shore and S. H. Lawrence, *J. Chem. Soc., Dalton Trans.,* (1986) 1753.

22 (a) W. G. Klemperer, W. Shum, V. W. Day and M. F. Fredrich, *J. Am. Chem. Soc., 99* (1977) 6146; (b) P. Braunstein, C. de Méric de Bellefon, M. Lanfranchi and A. Tiripicchio, *Organometallics, 3* (1984) 1772.