



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Möbs, Martin; Graubner, Tim; Eklund, Kim; Karttunen, Antti J.; Kraus, Florian

Bromine Pentafluoride BrF_{5} , the Formation of $[BrF_{6}]^{-}$ Salts, and the Stereochemical (In)activity of the Bromine Eone Pairs

Published in: Chemistry: A European Journal

DOI: 10.1002/chem.202202466

Published: 27/12/2022

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY

Please cite the original version:

Möbs, M., Graubner, T., Eklund, K., Karttunen, A. J., & Kraus, F. (2022). Bromine Pentafluoride BrF, the Formation of [BrF] Salts, and the Stereochemical (In)activity of the Bromine Lone Pairs. *Chemistry: A European Journal*, 28(72), Article e202202466. https://doi.org/10.1002/chem.202202466

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

WILEY-VCH



European Chemical Societies Publishing

Take Advantage and Publish Open Access



By publishing your paper open access, you'll be making it immediately freely available to anyone everywhere in the world.

That's maximum access and visibility worldwide with the same rigor of peer review you would expect from any high-quality journal.

Submit your paper today.



www.chemistry-europe.org

Bromine Pentafluoride BrF₅, the Formation of [BrF₆]⁻ Salts, and the Stereochemical (In)activity of the Bromine Lone Pairs

Martin Möbs,^[a] Tim Graubner,^[a] Kim Eklund,^[b] Antti J. Karttunen,^[b] and Florian Kraus^{*[a]}

Abstract: BrF₅ can be prepared by treating BrF₃ with fluorine under UV light in the region of 300 to 400 nm at room temperature. It was analyzed by UV-Vis, NMR, IR and Raman spectroscopy. Its crystal structure was redetermined by X-ray diffraction, and its space group was corrected to *Pnma*. Quantum-chemical calculations were performed for the band assignment of the vibrational spectra. A monoclinic polymorph of BrF₅ was quantum chemically predicted and then observed as its low-temperature modification in space group

Introduction

Bromine pentafluoride is one of the most reactive halogen fluorides, probably outperformed in its reactivity only by ClF₃.^[1–5] BrF₅ was discovered by Ruff and Menzel in 1931 and described as a colorless liquid that freezes at 211.85 K (–61.30 °C) and boils at 313.65 K (+40.50 °C).^[6] BrF₅ is the highest known binary fluoride of bromine. The existence of the hypothetical BrF₇ molecule has not yet been proven as attempts of a further oxidation of BrF₅ resulted in the formation of the [BrF₆]⁺ cation known for the compounds [BrF₆][AsF₆] and [BrF₆][Sb₂F₁₁].^[7]

The conventional synthesis of $BrF_5^{[6]}$ takes place by reacting fluorine gas with gaseous BrF_3 at 473 K in a platinum or copper vessel [Eq. (1)].

$$\mathsf{Br}\mathsf{F}_3 + \mathsf{F}_2 \xrightarrow{473\,\mathsf{K}} \mathsf{Br}\mathsf{F}_5 \tag{1}$$

The pale yellow (red if more heavily contaminated by mixtures of other bromine fluorides or Br_2) crude BrF_5 is then fractionally distilled for purification.^[6] Another synthetic route

[a]	M. Möbs, T. Graubner, Prof. Dr. F. Kraus
	Anorganische Chemie, Fluorchemie
	Philipps-Universität Marburg
	Hans-Meerwein-Str. 4, 35032 Marburg (Germany)
	E-mail: f.kraus@uni-marburg.de

- [b] K. Eklund, Prof. Dr. A. J. Karttunen Department of Chemistry and Materials Science Aalto University 00076 Aalto (Finland)
- Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202202466
- © © 2022 The Authors. Chemistry A European Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

 $P2_1/c$ by single crystal X-ray diffraction. BrF₅ reacts with the alkali metal fluorides AF (A = K, Rb) to form alkali metal hexafluoridobromates(V), A[BrF₆] the crystal structures of which have been determined. Both compounds crystallize in the K[AsF₆] structure type ($R\overline{3}$, no. 148, hR24). For the species [BrF₆]⁺, BrF₅, [BrF₆]⁻, and [IF₆]⁻, the chemical bonds and lone pairs on the heavy atoms were investigated by means of intrinsic bond orbital analysis.

for the preparation of BrF₅ is the fluorination of KBr, as described by Hyde and Boudakian.^[8] Contact with moisture or the use of unsuitable or insufficiently passivated vessel materials will also cause BrF₅ to take on a pale yellow to deep red color.^[6] In this case, fluorine can be passed through the liquid at room temperature until all the Br₂ and BrF₃ has reacted.^[7,9] After degassing, BrF₅ can be distilled onto dry NaF for storage, that reacts with traces of HF and BrF₃.^[9] Pure BrF₅ is colorless.^[6]

Compounds such as BrF₅ are hard to come by or simply unobtainable for academic research purposes, therefore we looked for a simple method for their synthesis at room temperature on a laboratory scale. While the photosynthesis of CIF₅ had already been reported in various sources,^[10-12] to the best of our knowledge no methods are yet known for the photochemical preparation of BrF₅. However, the photochemical fluorination of bromine and BrF₃, respectively, to BrF₅ should be straightforward, since the ionization energies of bromine are even lower than those of chlorine.

Due to the lower temperature of the synthesis presented here compared to the traditional routes, no or significantly less wall reactions with the vessel materials take place. Also, the decomposition of BrF_5 at higher temperatures into BrF_3 and F_2 is suppressed.^[1] Therefore, BrF_5 is obtained in nearly quantitative yield and high purity.

The crystal structure of solid BrF₅ was determined in 1957 by Burbank and Bensey,^[13] but due to the data quality a redetermination of the crystal structure was performed here. We present a modified structure model for HT-BrF₅, a novel low-temperature modification LT-BrF₅, reactions of BrF₅ with KF and RbF, and discuss the effect of the lone pair on the Br atom within the BrF₅ molecule and the $[BrF_6]^-$ anion in comparison to other species.

Chem. Eur. J. 2022, 28, e202202466 (1 of 15)



Scheme 1. A summary of the works reported here. Preparation of BrF_5 , solid-state structures of its high-temperature (HT) and low-temperature (LT) polymorph, its reactions with the alkali metal fluorides KF and RbF. Photographs of BrF_3 and BrF_5 , as well as the Lewis structures of the BrF_5 molecule and the $[BrF_6]^-$ anion, sections of the crystal structures, and the lone pairs on the Br atoms using IBOs are shown.

Results and Discussion

Scheme 1 provides an overview of the works reported in this manuscript, the photochemical synthesis of BrF₅, its high-temperature and low-temperature crystal structures, its reactions with some alkali metal fluorides and a discussion of the free valence electron pairs on the Br atoms of BrF₅ molecules and [BrF₆]⁻ anions by using intrinsic bond orbitals (IBOs).

Photochemical preparation of bromine pentafluoride

 BrF_5 was obtained by irradiation of BrF_3 and F_2 with UV light at room temperature according to Equation (2).

$$BrF_3 + F_2 \xrightarrow{h\nu, RI} BrF_5$$
(2)

The reaction can be performed either with pure fluorine gas or gas diluted with argon. The use of diluted fluorine does not entail any major disadvantages, apart from the smaller amount of F_2 being present for BrF_5 synthesis at the same overall pressure. Pure BrF_5 could be obtained at irradiation wavelengths between 300 and 400 nm in both cases. The product was characterized by X-ray diffraction, NMR, UV-Vis, Raman and IR spectroscopy and by reaction with alkali metal fluorides.

Selection of UV lamps of suitable wavelength

Various UV lamps of different wavelengths were tested for the photochemical synthesis of BrF_5 . Their emission spectra are shown in Figure 1. BrF_5 is formed independent of the used UV lamp, however, it was not possible to achieve complete conversion when the low-pressure mercury vapor lamp with a peak wavelength of 254 nm was used. Instead, yellowish samples were obtained which additionally contained BrF_3 , as was shown by Raman spectroscopy. The use of the other lamps



Figure 1. UV-Vis transmittance spectra of BrF₅ (red) and F₂ (black) as well as emission spectra of the UV lamps used: Osram Puritec HNS UV-C, ^[14] 254 nm (green), ExoTerra Reptile UVB200^[15] (blue), Nichia NVSU233B,^[16] 365 nm (cyan), Osram LuxiGen, 395 nm (magenta).^[17] An artifact due to the lamp change of the UV-Vis spectrometer at 320 nm is marked by an asterisk. Data for the emission spectra were extracted from the literature^[14-17] by using the Engauge Digitizer software.^[18]

with emission maxima at longer wavelengths resulted in all cases in pure, colorless BrF₅. This leads to the conclusion that BrF₅ is photodissociated due to its self-absorption at low wavelength and an equilibrium between BrF₅ and BrF₃ is established. However, as demonstrated by the transmission spectra of BrF₅ and F₂ in Figure 1, their absorption maxima are separated well enough, so that at higher wavelengths fluorine molecules can be photo-dissociated selectively.

NMR spectroscopy

 ^{19}F NMR spectra of the as-obtained BrF_{s} were recorded at room temperature and at 213 K and are shown in Figure 2. Two





Figure 2. ¹⁹F NMR spectra of neat BrF₅ at room temperature (top) and at 213 K (bottom), slightly above the melting point. The assignment of the observed signals to the F atoms is indicated in yellow (F_{ap}) and orange (F_{eq}).

signals with an integral ratio of 1:4 are present and assigned to the one apical, F_{apr} and the four equatorial, F_{eq} , fluorine atoms of BrF₅. Spectra recorded at 273 K or below show a splitting of the two signals into a quintet and a doublet due to ²J(¹⁹F,¹⁹F) coupling. Thus, assignments of the signals with a chemical shift of around 276 ppm to the F_{ap} atom and the one at around 139 ppm to the F_{eq} atoms are evident. The obtained spectra are in agreement with the literature.^[19] NMR spectra and data obtained from variable temperature measurements from 213 to 300 K are summarized in Figure S1 and Table S1 in the Supporting Information. NMR chemical shifts calculated at the CCSD(T)/cc-pwCVTZ level of theory agree with the experimental findings (see the Experimental Section for computational details). The chemical shift for the F_{ap} atom was calculated to be at 277 ppm and the one for the F_{eq} atoms at 138 ppm.

Vibrational spectroscopy

IR spectra of gaseous BrF_5 were recorded at room temperature at various pressures (Figures S6 and S7) in order to resolve strong fundamental vibrations as well as weaker combination modes. A spectrum together with the quantum chemically calculated modes is shown in Figure 3. The quantum-chemical calculation for band assignment of the fundamental and combination modes was performed at the CCSD(T)/cc-pVTZ level of theory.

The Raman spectrum shown in Figure 4 was recorded for liquid BrF₅. For practical reasons, no IR spectrum could be acquired on liquid BrF₅. Both the Raman as well as the gas-phase IR spectrum are in agreement with those given in the literature.^[20,21] The tetragonal-pyramidal BrF₅ molecule ($C_{4\nu}$) shows twelve normal modes of vibration. Three modes are doubly degenerate, six are non-degenerate. These are assigned



Figure 3. IR spectrum of gaseous BrF₅ at ca. 125 mbar (black line). The corresponding calculated and intensity-scaled IR bands are shown as blue lines, of which the strongest were cut at the same arbitrary value. In the region above 1500 cm⁻¹ and up to 4000 cm⁻¹, no additional bands were observed or calculated.



Figure 4. Raman spectrum of liquid BrF_5 at room temperature. No additional bands were present in the region above 800 cm⁻¹ and up to 4000 cm⁻¹.

into the irreducible representations A_1 , B_1 , B_2 , and E of the point group. All these vibrations are Raman-active, whereas only the A_1 and E vibrations are IR-active. The band assignment for the fundamental vibrations is given in Table 1. Two of the active Raman frequencies, v_5 and v_7 , were not observed in the recorded spectrum. Based on the calculated bands, it can be assumed that v_5 overlaps with v_9 , and v_7 most likely coincides with v_1 , leading to its slightly asymmetric shape. The numbering of the vibrations follows the literature.^[22]

A more comprehensive band assignment for the IR spectrum including the combination bands is given in Table S4. Raman spectra of liquid and solid BrF_5 at various temperatures are shown in Figures S2–S5, their band assignments in Tables S2 and S3. Calculated Raman spectra of the two crystalline modifications are also available in Figures S8 and S9.



Table 1. Observed fundation liquid BrF ₅ .	amental vibration frequen	cies of BrF_5 and band assignm	ent. The IR spectrum was recorded on gaseous BrF_{5} , the Raman spectrum on		
Assignment	IR	Raman	Description		
	frequency [cm ⁻	-1]			
v_1, A_1	683	687	stretching vibration $v(Br-F_{ap})$		
v_2, A_1	582	569	symmetric stretching vibration $v_s(Br-F_{eq})$		
v_{3}, A_{1}	369	365	out-of-plane bending $\pi(Br-F_{eq})$		
v_4, B_1	-	535	antisymmetric stretching v _s (Br–F _{eq})		
v_5, B_1	-	n.o.	antisymmetric deformation $\delta_a(Br-F_{eq})$		
v ₆ , B ₂	-	312	symmetric in-plane bending $\delta_s(Br-F_{eq})$		
ν ₇ , Ε	646	n.o.	degenerate stretching $v_d(Br-F_{eq})$		
ν ₈ , Ε	414	414	degenerate out-of-plane bending $\pi_{d}(Br-F_{eq})$		
ν ₉ , Ε	247	238	degenerate in-plane bending $\delta_d(\text{Br}-\text{F}_{eq})$		

Handling and reactivity

In several cases, especially during our attempts to record IR spectra on BrF₅, we visually observed a color change of BrF₅ gas from colorless to yellowish-brown, which indicated the decomposition of some traces of BrF5. The nature of the yellowishbrown species is still under investigation. Even before the color change is visible to the eye, additional IR bands appear in the region above 3690 cm⁻¹ corresponding to the rotation-vibration bands of HF. This decomposition of BrF5 does not occur when all surfaces that come in contact with it are well passivated, thoroughly baked out and as free of moisture as possible. In order to achieve this, steel apparatuses are usually baked out in a hot air bath at about 873 K in vacuo. Because it is technically not possible to bake out our IR gas cell completely, which is due to the limited thermal stress resistance of the optical windows, we suspect traces of water being the reason for the decomposition of BrF₅. To overcome this issue, we first filled the gas cell with BrF₅ or CIF₃ so that they react with "all" the moisture, then pumped of the volatiles using a vacuum of circa 10⁻³ mbar and finally filled the cell with fresh BrF₅ for the measurement.

When BrF_5 is stored in vessels made out of fluoropolymers like PFA or FEP, HF impurities are also present after some days. Both BrF_5 and moisture dissolve and diffuse through the walls of the fluoropolymer vessel so that the contamination increases over time. That is why vessels made out of passivated stainless steel, nickel or Monel should be preferred for storage and handling. When fluoropolymers are required because of their translucency, the vessels can be baked out in vacuum and then flushed with fluorine several times. This "saturates" the polymer with F_2 and temporarily displaces other contaminants such as H_2O dissolved in the fluoroplastic.

Crystal structure of HT-BrF₅

The crystal structure of BrF_5 was first published in 1957 by Burbank and Bensey.^[13] According to them, BrF_5 crystallizes in the orthorhombic space group $Cmc2_1$ (36) at 153 K. However, our diffraction data show reflections that clearly violate the extinction condition of the *C*-centering. These violations were observed not only in a powder diffraction pattern of BrF_5 recorded at 180 K, see below, but also in the single-crystal X-ray diffraction data acquired at temperatures of 200, 180, 150 and 100 K.

Below its melting point of 211.85 K (-61.3 °C), BrF₅ crystallizes in space group *Pnma* (62) but undergoes a phase transition at about 142 K as shown by variable temperature powder X-ray diffraction, see the Supporting Information. At 130 K we observed the formation of a monoclinic low-temperature (LT) modification, crystallizing in space group *P*2₁/*c* (14). The first frames collected during the X-ray diffraction experiment at this temperature showed still only the orthorhombic polymorph, then both modifications were observed, while the last frames contained only reflections of LT-BrF₅. A dataset containing only the reflections of LT-BrF₅ was collected at 100 K. Selected crystallographic data and details of the structure determinations are given in Table 2.

We solved and refined the crystal structure of the hightemperature (HT) polymorph in space group *Pnma* (62). Attempts to refine the crystal structure in the non-centrosymmetric subgroup *Pna2*₁ also lead to the essentially same structure model, however the Flack parameter of 0.46(7), the ADDSYM^[23,24] algorithm implemented in the PLATON^[25] software, as well as strong correlation of atomic coordinates clearly suggested the centrosymmetric space group *Pnma* to be the superior choice.

The following description of the crystal structure refers to the diffraction data collected at 150 K, allowing for a direct comparison with the previous structure model. In the solid state, BrF₅ adopts a square pyramidal molecular structure (Figure 5), as already indicated by NMR and vibrational spectroscopy for the liquid and gas phase. The bromine atom resides on Wyckoff position 4c (.m.) and is surrounded by the $F_{ap}(1)$ atom (4c, .m.), the F_{eq} atoms F(2) and F(3) on positions 4c (.m.), and the $F_{eq}(4)$ atom on the 8d (1) position. The Br atom is not located within the base of the pyramid, but lies with 0.1726(18) Å outside a least-squares plane spanned by the four \boldsymbol{F}_{eq} atoms, showing the putative space requirement of the lone pair of the Br atom. The bond angles between the apical and equatorial fluorine atoms F_{ap}-Br-F_{eq} are therefore smaller than 90 ° and are 83.75(11)°, 2×84.16(10)°, and 85.36(14)°. The same phenomenon is visible in the previously reported structure

Chemistry Europe European Chemical Societies Publishing

Table 2. Selected crystallographic c	data and details of the structure	e determinations of BrF ₅ at vario	us temperatures.	
		HT-BrF₅		LT-BrF₅
Formula		B	rF₅	
Molar mass [g·mol ⁻¹]		174	4.91	
Space group (no.)		Pnma (62)		P2 ₁ /c (14)
a [Å]	7.8447(13)	7.841(3)	7.8291(3)	6.3355(4)
b [Å]	6.4538(12)	6.415(3)	6.3861(2)	7.2166(4)
c [Å]	7.3062(12)	7.261(4)	7.2364(2)	7.7803(5)
β [°]	90	90	90	94.255(3)
V [Å ³]	369.90(11)	365.2(3)	361.80(2)	354.74(4)
Z	4	4	4	4
Pearson symbol	oP24	oP24	oP24	mP24
$\rho_{\rm calc} [\rm g \cdot \rm cm^{-3}]$	3.141	3.181	3.211	3.275
$\mu [{\rm mm}^{-1}]$	11.092	11.235	11.340	11.566
Color	colorless	colorless	colorless	colorless
Crystal morphology	needle	needle	needle	needle
Crystal size [mm ³]	0.784×0.274×0.248	0.665×0.299×0.285	0.784×0.274×0.248	0.665×0.299×0.285
T [K]	200	180	150	100
λ [Å] (Μο _{κα})		0.7	1073	
No. of reflections	10630	14703	11267	1286
θ range [°] (min, max)	3.811, 31.498	3.825, 33.713	2.602, 39.194	3.224, 32.568
Range of Miller indices	$-11 \le h \le 11$,	$-12 \le h \le 12$,	$-11 \le h \le 11$,	$-9 \le h \le 9$,
	$-9 \leq k \leq 9$,	$-10 \le k \le 10$,	$-9 \le k \le 9$,	$0 \le k \le 10,$
	-10 <i>≤l≤</i> 10	-11 <i>≤l≤</i> 11	-10 <i>≤l≤</i> 10	0 <i>≤l≤</i> 11
Absorption correction		mult	i-scan	
T _{max} , T _{min}	1.0000, 0.2064	0.1954, 0.0250	0.1954, 0.0250	0.1577, 0.0262
R_{int}, R_{σ}	0.0391, 0.0140	0.0515, 0.0251	0.0351, 0.0132	0.0677, 0.0180
Completeness of the data set	0.994	0.999	0.994	0.998
No. of unique reflections	663	781	674	1286
No. of parameters	34	34	34	55
No. of restraints	0	0	0	0
No. of constraints	0	0	0	0
S (all data)	1.219	1.153	1.283	1.047
$R(F)$ ($I \ge 2\sigma(I)$, all data)	0.0339, 0.0404	0.0315, 0.0392	0.0291, 0.0325	0.0337, 0.0371
$wR(F^2)$ ($l \ge 2\sigma(l)$, all data)	0.0801, 0.0837	0.0732, 0.0783	0.0715, 0.0732	0.0799, 0.0828
Largest diff. peak/hole [e Å ⁻³]	0.850/-0.490	0.599/-0.445	0.435/-0.482	1.609/-0.619



Figure 5. Left: Section of the crystal structure of BrF₅ showing the square pyramidal molecular shape. Displacement ellipsoids are shown at 70% probability at 150 K. Right: Projection of the crystal structure showing the infinite one-dimensional strands of interconnected BrF₅ molecules running parallel to the *a*-axis. Atoms are shown isotropic with arbitrary radii. Symmetry transformation for the generation of the F(4') equivalent atom: *x*, $\frac{1}{2}$ -*y*, *z*.

model, where the distance between the Br atom and the base of the pyramid was reported with 0.1734 Å (with no esds given in literature).^[13] The respective F_{ap} –Br– F_{eq} angles diverge much more with 80.4°, 2×85.4°, and 86.5°.

The Br– F_{eq} bonds range from 1.741(2) to 1.777(2) Å and are therefore slightly longer than the Br– F_{ap} bond with 1.678(2) Å. The Br– F_{eq} bond lengths of the previously reported structure show a larger deviation from the mean value with 1.7460 to 1.8206 Å, which can be attributed to the choice of the space group. However, the reported $Br{-}F_{ap}$ distance agrees with 1.6784 Å with the value redetermined here.

An intermolecular interaction is present between the Br atoms and $F_{\rm eq}$ atoms of neighboring $BrF_{\rm 5}$ molecules with a Br...F_{ea} distance of 2.880(2) Å. As expected, the F_{ea} atom involved in the intermolecular interaction is the one with the longest intramolecular Br-F_{eq} distance of 1.777(2) Å. The planes spanned by the four equatorial fluorine atoms of each of two adjacent BrF₅ molecules intersect at an angle of 106.42(6)°. As a result of this intermolecular interaction, flat, zigzag-like chains are formed running parallel to the *a*-axis. The crystal structure of BrF5 can therefore be described with the Niggli formula $\frac{1}{\infty}$ [BrF₄F₂]. To the best of our knowledge, the crystal structure of BrF₅ represents a new structure type. The formation of oligomeric molecular structures, as known for other pentafluorides such as MoF₅ (mS48), that is rings of Mo₄F₂₀, RuF₅ (mP48), differently shaped Ru_4F_{20} rings, or AuF_5 (oP48), Au_2F_{10} dimers, does not occur.[26-28] Similarity exists between the structures of BrF_{5} (oP24) and BrF_{3} (oS16) $.^{\scriptscriptstyle [29]}$ As $BrF_{5},\ BrF_{3}$ also forms one-dimensional infinite strands with a flat zigzag-like shape in its solid state. Thus, the bromine atoms are coordinated in a kite shape by F atoms and have a coordination number of 3+1. The intramolecular Br-F distances in the BrF₃ structure are in between 1.71(1) and 1.888(9) Å and therefore are in average longer than in the BrF₅ molecule, as expected for bromine in oxidation state + III. The F atom with the longest

intramolecular Br–F bond of 1.888(9) Å is the one that makes intermolecular contact with the neighboring BrF₃ molecule. The intermolecular Br–F distance is 2.451(12) Å, and thus, more than 0.4 Å shorter than in the structure of BrF₅. The shorter



Figure 6. Left: Section of the crystal structure of BrF_5 showing the cuboctahedral surrounding of a Br atom by nearest Br atoms. The green, blue and red Br atoms indicate the hexagonal layers of the cubic close packing. Right: Cuboctahedron of Br atoms and the relation of their arrangement to the pseudo-F-centered cell in blue. Bromine atoms are shown as spheres with arbitrary radii.



Figure 7. Plot of the equivalent displacement parameters vs. temperature. The displacement parameters observed at 100 K correspond to the structure of LT-BrF₅ and are therefore not directly comparable to those of HT-BrF₅. However, as the phase transition from HT- to LT-BrF₅ has no significant effect on the displacement parameters, we decided to use the data obtained at 100 K for extrapolation anyway.

intermolecular $\mbox{Br}\mbox{--}\mbox{F}$ distance is likely attributed to steric reasons.

Looking at the arrangement of the Br atoms within the crystal structure of BrF_{5r} , a structural relation to the Cu type becomes obvious and a Bärnighausen-tree is given in Figure S10. A Br atom is surrounded by 12 other Br atoms in the shape of a distorted cuboctahedron (Figure 6). The distortion that occurs is due to the formation of the chain motif adopted by the BrF_5 molecules. This leads to a deviation from the atom positions in the Cu type. In the setting chosen by Burbank and Bensey, this centering corresponds to the *C*-centering in space group $Cmc2_1$.

The structure model proposed here in space group *Pnma* is reasonable, only the comparatively large displacement ellipsoids, especially of the F_{eq} atoms, may be unexpected. In order to examine whether these are physically meaningful and to be able to exclude that artificially large displacement parameters are obtained from a flawed structure model or an incorrect absorption correction, we recorded single-crystal diffraction data at different temperatures. The obtained equivalent displacement parameters of the atoms were then plotted against the temperature (Figure 7). We observe that the extrapolated displacement parameters intersect the coordinate origin at 0 K within their standard uncertainties, implying that the strong atomic displacement is due to thermal effects indicating a "soft" molecular packing with weak intermolecular interactions.

However, the powder X-ray diffraction pattern of BrF₅ recorded at 180 K (Figure 8) shows that the compound is diffracting rather well as sharp reflections are observed up to approximately 70° 2θ which indicates a proper three-dimensional long-range order of the BrF₅ molecules within the crystal structure and that the thermal vibrations of the atoms are not severe at all.

All reflections could be assigned to the high-temperature modification of BrF_s that crystallizes in space group *Pnma*. Space group *Cmc*2₁, reported for the previous structure model,^[13] can be completely ruled out as several distinct



Figure 8. Powder X-ray diffraction pattern of HT-BrF₅ recorded at 180 K. Measured data points are shown as black dots, calculated diffraction pattern as a result of the Rietveld refinement in red, and the difference curve is in gray. Vertical black bars indicate the calculated reflection positions for HT-BrF₅ crystallizing in space group *Pnma*; blue vertical bars indicate possible reflection positions considering the extinction conditions of the previously selected space group *Cmc2*₁ for the old structure model. Rp = 3.77, Rwp = 5.42, S = 1.295.

Chem. Eur. J. 2022, 28, e202202466 (6 of 15)



reflections cannot be indexed (Figure 8). Details of the Rietveld refinement are available from Table S6.

LT-BrF₅

The phase transition from HT- to LT-BrF₅ occurs at about 142 K, as shown by variable temperature powder X-ray diffraction (Figure S11). The single-crystal structure was recorded at 100 K. The shape of the BrF₅ molecules as well as their interconnection to one-dimensional infinite strands in the low-temperature modification is similar compared to the high-temperature polymorph. The Br- F_{eq} bond lengths range from 1.744(3) to 1.779(3) Å and are therefore identical within the standard uncertainties in comparison to the high-temperature modification. The same applies to the Br-Fap bond length measuring 1.686(2) Å and to the distances of the intermolecular $Br
mathcase F_{eq}$ contacts measuring 2.881(3) Å. The Br atom is located 0.1707(16) Å below the least-squares plane defined by the F_{eq} atoms. Thus, within the standard uncertainty this distance is also identical compared to the HT structure. The major structural difference between the two polymorphs is that in LT-BrF₅, together with the deviation of the monoclinic angle from 90° , the orientation of the BrF₅ molecules within the zigzagstrands also changes (Figure 9). The intrachain Br-Br distance shortens from 4.6555(3) Å in HT-BrF₅ to 4.6447(4) Å in LT-BrF₅. The angle by which the planes spanned by the F_{eq} atoms of two neighboring BrF₅ molecules intersect decreases from 106.42(6)° in HT-BrF₅ to $103.17(7)^{\circ}$ in LT-BrF₅. The shortest distance of two Br atoms in adjacent strands decreases from 4.8257(1) Å in HT- $BrF_{\scriptscriptstyle 5}$ to 4.6489(4) Å in LT-BrF_{\scriptscriptstyle 5}. The group-subgroup relation of HT- and LT-BrF_5 is described in Figure 9 by means of a Bärnighausen tree.[30]

Solid-state quantum-chemical calculations for BrF₅

Quantum-chemical calculations on BrF_5 with dispersion-corrected hybrid density functional method (DFT-PBE0-D3/TZVP), accounting for the weak intermolecular interactions, aided in

the discovery of the low-temperature modification. Calculations on the high-temperature polymorph of BrF5 in space group Pnma showed a number of imaginary frequencies at 0 K, the largest being 33*i* cm⁻¹. Following the largest imaginary mode allowed to predict the correct space group $P2_1/c$ and Wyckoff sequence of the low-temperature modification of BrF₅ even before the single-crystal structure determination. A geometry optimization starting from the single-crystal X-ray structure of LT-BrF₅ ($P2_1/c$) and a harmonic frequency calculation resulted in a small imaginary frequency of 5.3*i* cm⁻¹, which could also arise due to accuracy limitations in the numerical integration of the DFT exchange-correlation functional. Following this mode would lead to space group Pc, but the energy is lowered only by 0.1 kJ mol⁻¹ per formula unit compared to $P2_1/c$. The intermolecular interactions in the crystal structure of LT-BrF₅ were underestimated without the empirical dispersion correction, resulting in poor prediction of the Br-F bond lengths, F-Br-F angles, the crystal structure and the lattice parameters. Without the dispersion correction, the Br...Feg contacts, responsible for the formation of one-dimensional strands, are with 3.106 Å significantly longer than in the experimentally determined crystal structure with 2.881(3) Å, and differ only slightly from the $Br-F_{ea}$ distances between the different strands, so that the motive of isolated strands was no longer discernible. The errors in lattice parameters with and without dispersion correction are shown in Table 3. Dispersion correction reduced the error in the lattice parameters to 1-2%, and the strand motive was correctly described with the shortest intermolecular Br...F_{eq} distance being 2.946 Å compared to 2.881(3) Å in LT-BrF₅.

The energetics of the two polymorphs of BrF₅ were further compared with the previously reported $Cmc2_1$ structure^[13] and a hypothetical modification in the dimeric structure of AuF₅.^[28] The previously reported $Cmc2_1$ structure showed two imaginary frequencies of 33*i* and 32*i* cm⁻¹, and was 2.9 kJmol⁻¹ per formula unit higher in energy compared to LT-BrF₅. For a hypothetical dimeric AuF₅ structure (Au₂F₁₀), imaginary frequencies of over 300*i* cm⁻¹ were present and the structure was 76 kJmol⁻¹ per formula unit higher in energy compared to LT-BrF₅, indicating that BrF₅ is energetically very unlikely to adopt a



Figure 9. Left: Crystal structures of the high- and low-temperature modifications showing the tilting of the BrF₅ molecules within the 1D infinite strands as a result of the symmetry lowering. Right: Schematic representation of the symmetry relationship between the two modifications by means of a Bärnighausen tree.

Chem. Eur. J. 2022, 28, e202202466 (7 of 15)



Table 3. Comparison of the o	calculated and	observed lattic	e parameters o	of LT- and HT-B	8rF ₅ . ^[a]					
Structure	a [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β [°]	<i>V</i> [ų]	Error [%]				
						а	b	с	β	V
LT-BrF ₅ observed (100 K)	6.336	7.217	7.780	94.3	355					
LT-BrF ₅ DFT-PBE0	8.378	6.290	8.720	100.3	452	32	-13	12	6	27
LT-BrF ₅ DFT-PBE0-D3	6.385	7.272	7.845	97.0	362	1	1	1	3	2
HT-BrF ₅ observed (150 K)	7.829	6.386	7.236	-	362					
HT-BrF ₅ DFT-PBE0	8.154	7.101	7.352	-	426	4	11	2	-	18
HT-BrF ₅ DFT-PBE0-D3	8.091	6.465	7.058	-	369	3	1	-2	-	2

[a] For HT-BrF₅, quantum-chemical calculations with DFT-PBE0-D3 were also performed and LT-BrF₅ was determined to be 1.7 kJ mol⁻¹ per formula unit lower in energy compared to HT-BrF₅ (calculations at 0 K). The structural motive is also well described by the calculation with errors between 0.9 and 1.4% for the Br–F bond lengths and an error of 2.50% for the intermolecular Br-F distance.

dimeric molecular structure like AuF_5 . All optimized crystal structures are given in CIF format in the Supporting Information.

The optimized crystal structures and their energetics obtained from the quantum-chemical calculations agree with the experimental results when a dispersion-corrected DFT method is used. DFT calculations show that the LT- as well as the HT-BrF₅ crystal structures are energetically favored over the previously reported structural model and the phase transition from HT- to LT-BrF₅ could be followed by studying the imaginary vibrational modes obtained for HT-BrF₅.

Reactions of BrF_5 with AF (A = K, Rb)

By the reaction of BrF_5 with the alkali metal fluorides AF (A = K, Rb), the corresponding alkali metal hexafluoridobromates(V), $A[BrF_6]$, are formed [Eq. (3)].^[31,32]

$$BrF_5 + AF \rightarrow A[BrF_6]$$
 (A = K, Rb) (3)

While the crystal structure of $Cs[BrF_6]$ is already known,^[33] the crystal structures of $K[BrF_6]$ and $Rb[BrF_6]$ have not been reported. Suitable crystals of these compounds were obtained by slow cooling of a saturated solution of the respective alkali metal fluoride in BrF_5 warmed to about 373 K in an air bath.

Crystal structures of the compounds $A[BrF_6]$ (A = K, Rb)

K[BrF₆] and Rb[BrF₆] crystallize isotypic to Cs[BrF₆]^[33] in the K[AsF₆] structure type in the trigonal crystal system, space group $R\bar{3}$ (no. 148, hR24), with the lattice parameters a = 7.4450(14), c = 7.287(2) Å, V = 349.80(17) Å³, Z = 3, at T = 100 K for K[BrF₆] and a = 7.576(3), c = 7.568(5) Å, V = 376.2(4) Å³, Z = 3, at T = 100 K for Rb[BrF₆]. The compounds have already been studied by Bougon and co-workers using powder X-ray diffraction methods,^[32] and two possible space groups $R\bar{3}$ and $R\bar{3}m$ have been proposed. Accordingly, two possible structure types were considered, the K[AsF₆] type in $R\bar{3}$ and the Ba[SiF₆] type in $R\bar{3}m$. We can clearly exclude space group $R\bar{3}m$ as a refinement of the crystal structures in that space group leads to a striking elongation of the displacement ellipsoids of the

fluorine atoms perpendicular to the *m* mirror plane. The crystal structure of the compounds in space group $R\bar{3}$ is shown in Figure 10 using K[BrF₆] as an example. Details of the structure solutions and refinements are given in Table 4 and the atomic coordinates and isotropic displacement parameters are given in Table 5.

The bromine atoms reside on position 3a ($\overline{3}$.) and are coordinated octahedron-like by six symmetry-equivalent fluorine atoms (18*f*, 1) forming the [BrF₆]⁻ anion with point group symmetry *S*₆. As already discussed by Seppelt and co-workers for the crystal structure of Cs[BrF₆], the lone pair of the Br atom within the [BrF₆]⁻ anion seems to show no stereochemical activity.^[33] For a discussion on the lone pair, see below. The alkali metal cations (3*b*, $\overline{3}$.) are 12-fold coordinated by fluorine atoms in a cuboctahedron-like environment.

Seppelt and co-workers observed a Br–F bond length within the [BrF₆]⁻ anions of Cs[BrF₆] of 1.854(1) Å by X-ray diffraction on single crystals and 1.847(1) Å by powder neutron diffraction.^[33] We found 1.8637(12) Å within the crystal structure of K[BrF₆] and 1.8623(15) Å for Rb[BrF₆], respectively, and quantum chemically calculated a Br–F bond length of 1.868 Å for the [BrF₆]⁻ anion in the gas phase and of both circa 1.864 Å for the calculated crystal structures of K[BrF₆] and Rb[BrF₆]. While the observed Br–F bond lengths agree within the tripled standard uncertainties for the Rb and Cs compounds, the Br–F bond length is slightly longer in the determined crystal structure of the K compound. The observed bond lengths agree with those quantum chemically calculated for the solids and the Br–F bonds are longest in the gas-phase [BrF₆]⁻ anion, as may be expected.



Figure 10. Crystal structure of K[BrF₆]. The [BrF₆]⁻ anions are shown as polyhedra, with the exception of the anion bottom left. Displacement ellipsoids are shown at the 70% probability level at 100 K.

Table 4. Selectedcrystallographdetermination of K[BrF6] and Rb[6]	nic data and detail BrF ₆].	s of the structure
Formula	K[BrF ₆]	Rb[BrF ₆]
Molar mass [g · mol ⁻¹]	233.01	279.38
Space group (no.)	R3 (148)	R3 (148)
a [Å]	7.4450(14)	7.576(3)
c [Å]	7.287(2)	7.568(5)
V [Å ³]	349.80(17)	376.2(4)
Z	3	3
Pearson symbol	hR24	hR24
$\rho_{calc} \left[\mathbf{g} \cdot \mathbf{cm}^{-3} \right]$	3.318	3.700
$\mu [\mathrm{mm}^{-1}]$	9.742	17.870
Color	colorless	colorless
Crystal morphology	needle	needle
Crystal size [mm ³]	0.29×0.22×0.15	0.2×0.08×0.02
7 [K]	100	100
λ [Å] (Μο _{κα})	0.71073	0.71073
No. of reflections	267	1195
heta range [°]	4.220 to 30.423	4.111 to 28.942
Range of Miller indices	$-10 \le h \le 8$,	$-10 \le h \le 10$,
	$-4 \le k \le 10$,	$-10 \le k \le 10$
	0 <i>≤l≤</i> 10	−10 <i>≤l≤</i> 10
Absorption correction	numerical	numerical
T _{max} , T _{min}	0.3988, 0.1359	0.1811, 0.0551
$R_{\rm int}, R_{\sigma}$	0.0318, 0.0298	0.0125, 0.0106
Completeness of the data set	1	1
No. of unique reflections	237	225
No. of parameters	14	14
No. of restraints	0	0
No. of constraints	0	0
S (all data)	1.016	0.971
$R(F)$ ($I \ge 2\sigma(I)$, all data)	0.0180, 0.0189	0.0173, 0.0254
$wR(F^2)$ ($l \ge 2\sigma(l)$, all data)	0.0420, 0.0422	0.0384, 0.0403
Largest diff. peak/hole [e Å ⁻³]	0.56/-0.31	0.38/-0.31

Chemistry Europe European Chemical Societies Publishing

Observed selected F–Br–F bond angles are 91.79(6)° within the potassium, 91.47(8)° within the rubidium, and 90.8(1)° within the cesium compound (91.3° by powder neutron diffraction). While the calculated gas-phase [BrF₆]⁻ anion shows ideal octahedral symmetry, the selected F–Br–F bond angles within the [BrF₆]⁻ anions of the quantum chemically calculated crystal structures of K[BrF₆] and Rb[BrF₆] are 91.77° and 91.30°, respectively. Therefore, observed and quantum chemically calculated that the influence of the K⁺ cations on the molecular structure of the [BrF₆]⁻ anions is seemingly the strongest and weakest for the Cs⁺ cations, as might have been expected on the basis of Pearson's concept of hard and soft acids and bases.^[34]

Raman spectroscopic investigation of the compounds $A[BrF_6]$ (A = K, Rb)

The bulk phases of the samples were analyzed by Raman spectroscopy. For both, $K[BrF_6]$ and $Rb[BrF_6]$, three bands were observed corresponding to the Raman active vibrations of the octahedron-like $[BrF_6]^-$ anion. The Raman spectra are shown in Figure 11 and the band assignments are given in Table 6.

The observed Raman bands agree with the ones reported in the literature^[32] where the assignment of bands had been carried out using O_h symmetry, while we used the crystallographic site symmetry of S_6 . We also see an agreement with the calculated Raman spectra (Figure 11). The calculated bands at 246 cm⁻¹ for K[BrF₆] and at 245 cm⁻¹ for Rb[BrF₆] are likely not

Table 5. Positions, site symmetries, atomic coordinates and equivalent isotropic displacement parameters U _{iso} for K[BrF ₆] and Rb[BrF ₆].							
Compound	Atom	Position	x	у	Ζ	U_{iso} [Å ²]	
K[BrF ₆]	Br	3a (3.)	0	0	0	0.01213(15)	
	К	3b (3.)	0	0	¹ / ₂	0.0171(2)	
	F	18 <i>f</i> (1)	0.1579(2)	0.22651(18)	0.15221(16)	0.0191(3)	
Rb[BrF ₆]	Br	3a (3.)	0	0	0	0.01903(16)	
	Rb	3b (3.)	0	0	1/2	0.01613(17)	
	F	18 <i>f</i> (1)	0.1590(2)	0.2219(2)	0.1457(2)	0.0237(3)	



Figure 11. Raman spectra of $K[BrF_6]$ (left) and $Rb[BrF_6]$ (right) at room temperature recorded with an excitation laser wavelength of 532 nm, calculated spectra shown in red. No additional bands were present in the region above 600 cm⁻¹ and up to 4000 cm⁻¹.

Chem. Eur. J. 2022, 28, e202202466 (9 of 15)



Table 6. Band assignment for the Raman spectra of K[BrF ₆] and Rb[BrF ₆]. Raman inactive vibrations are not shown. Frequencies are given in cm ⁻¹ .							
Assignment	K[BrF ₆]		Rb[BrF ₆]		Description		
	exp.	calc.	exp.	calc.			
$\begin{array}{c} A_g \\ E_g \\ E_g \\ E_g \\ A_g \end{array}$	566 452 248 248	600 456 269 246	564 452 244 244	597 452 261 245	symmetric stretching vibration v_s . (in-phase) symmetric stretching vibration v_s . (out-of-phase) symmetric in-plane bending δ_s symmetric out-of-plane bending π_s (out-of-phase)		

observed due to their small intensities in comparison to the other bands or due to band overlap.

Lone pair effects

Canonical molecular orbitals from quantum-chemical calculations are typically rather difficult to interpret when chemical bonds between two or a few atoms are considered. Many chemists like to think of localized chemical bonds, draw molecular structures with Lewis formulas, and predict the shapes of molecules with simple models such as the VSEPR theory.^[35-37] These however may bias judgment: For example, the action of BrF₅ as a Lewis acid might be unexpected as one may think that the free valence electron pair, the lone pair, on the Br atom of the BrF₅ molecule should repel an incoming F⁻ anion and therefore no $[BrF_6]^-$ anion would form based on this over-simplified view. However, BrF5 acts as a Lewis acid under formation of [BrF₆]⁻ anions according to Scheme 2, for examples see above and the literature.[31,33,38] Previous gas-phase DFT-B3LYP calculations suggest the reaction in Scheme 2 to be exoenergetic by over 300 kJmol^{-1.[39]} We obtained a gas-phase reaction energy of -299 kJmol^{-1} at the CCSD(T)/cc-pVTZ level of theory. Furthermore, we estimated the Fluoride Ion Affinity^[40-44] (FIA) of BrF_5 to be 276 kJ mol⁻¹ at the same level of theory (COF₂ as reference system). With that it is comparable to PCl₃ and PBr₃, it is stronger than AsF₃ and SF₄, weaker than SbF₃, SiF₄, BF₃ and much weaker than AsF₅, SbF₅ or Sb(OTf)₅.^[43]

In order to describe the chemical bonds of the BrF₅ and $[BrF_6]^-$ molecules, population analyses were carried out at the DFT-PBE0/TZVP level of theory by using intrinsic atomic orbitals (IAOs) and the bonding was analyzed with the aid of IBOs.^[45,46] For the gas-phase BrF₅ molecule, a local minimum is obtained in point group $C_{4\nu}$, as may be expected. The Br atom shows a positive partial charge of $+2.36 \text{ e}^-$, while the four F_{eq} atoms show negative partial charges of -0.49 e^- and the apical



Scheme 2. Lewis acid-base reaction of BrF₅ and F⁻ to $[BrF_6]^-$. The reaction might be counter-intuitive when considering the lone pair on the Br atom of BrF₅, which should repel the F⁻ anion. Also, no octahedron-like structure might be expected for the $[BrF_6]^-$ anion because of the presumed orientation and shape of the lone pair.

Chem. Eur. J. 2022, 28, e202202466 (10 of 15)

fluorine atom F_{ap} a smaller charge of $-0.40 e^-$. The high positive partial charge on the Br atom is surely also a reason why BrF₅ reacts with a fluoride anion. Figure 12 shows selected IBOs for the BrF₅ molecule. As expected, the Br–F bonds are strongly polarized covalent. The Br–F_{eq} bonds are essentially plike with a small 4 s contribution of the Br atom of 3%. The Br–F_{ap} bond is slightly less polarized in comparison and the Br 4 s orbital contributes with 19% to the bond. The shape of the lone pair on the Br atom is essentially s orbital-like with only 18% contribution from the 4p, orbital.

Quantum-chemical calculations lead to a true local minimum for the $[BrF_6]^-$ anion in O_h symmetry, that is, an "ideal" octahedron is obtained with no signs of stereochemical activity of the Br lone pair. The Br atom shows a positive partial charge of $+2.32 e^-$ which is by 0.04 e^- lower compared to the Br atom within the BrF₅ molecule. The F atoms show negative partial charges of $-0.55 e^-$. Figure 13 shows selected IBOs of the [BrF₆]⁻ anion.

The Br–F bonds in the $[BrF_6]^-$ anion become even more polarized compared to the BrF₅ molecule and the Br atom no longer contributes with its 4 s orbital to the Br–F bonds but only with its p orbitals. The lone pair of the Br atom is completely 4 s-like and therefore shows the absence of any stereochemical activity.

We calculated the $[BrF_6]^+$ cation, where there is no Br lone pair, for comparison and found a true local minimum for O_h symmetry, as expected from the literature.^[7,47] The calculated Br–F bond length is 1.67 Å which agrees with estimated



Figure 12. Intrinsic bond orbitals showing the Br–F bonds and the Br lone pair of the BrF₅ molecule. Percentages next to the IBOs indicate the contribution of each atom to that IBO. The larger a percentage, the more polarized the covalent bond. If the summation does not add up to 100%, then other atoms contribute less than 2% to the IBO. The percentages in the labels show the contributions of atomic orbitals to each IBO. F atoms are in yellow, Br atoms in reddish-brown. IBO isosurfaces are drawn so that 80% of the density is enclosed within them.

5213765, 20

2, 2, Downloaded from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/chem.202202466 by Aalto University. Wiley Online Library on [09/01/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons.



Figure 13. Intrinsic bond orbitals showing the Br–F bonds and the Br lone pair of the $[BrF_6]^-$ anion. Percentages next to the IBOs indicate the contribution of each atom to that IBO. The larger a percentage, the more polarized the covalent bond. The percentages in the labels show the contributions of atomic orbitals to each IBO (for Br–F bonding IBOs, the example orbital comprises p_y orbitals). F atoms are in yellow, Br atoms in reddish-brown. IBO isosurfaces are drawn so that 80% of the density is enclosed within them.

1.69 ${\rm \AA^{[33]}}$ based on its reported force constants. $^{[47]}$ Its IBOs of the Br–F bonds are shown in Figure 14.

In the $[BrF_6]^+$ cation the Br–F bonds are less polarized in comparison to $[BrF_6]^-$ and also in comparison to the BrF_5 molecule. The contribution of the Br 4 s orbital to the Br–F bond has increased to 37%.

For the species discussed here, $[BrF_6]^+$, BrF_5 , and $[BrF_6]^-$, the F atoms always contribute more or less the same to the Br–F



Figure 14. Intrinsic bond orbitals showing the Br–F bonds of the $[BrF_6]^+$ cation. Percentages next to the IBO indicate the contribution of each atom to the IBO. The larger a percentage, the more polarized the covalent bond. The percentages in the label show the contributions of atomic orbitals to the shown example IBO. F atoms are in yellow, Br atoms in reddish-brown. IBO isosurfaces are drawn so that 80% of the density is enclosed within them.

bonds, circa 11% with their 2s and about 89% with the respective 2p orbital. The 4s orbital contribution to the Br–F bonds goes from 37% in the $[BrF_6]^+$ cation down to 20% for Br– F_{ap} and 3% for Br– F_{eq} in the BrF_5 molecule, and reaches 0% in $[BrF_6]^-$. The 4p orbital contributions follow the inverted trend, the Br–F bonds are strongest p-like in $[BrF_6]^-$ and least in $[BrF_6]^+$.

The stereochemical inactivity of the lone pair of the Br atom within the [BrF₆]⁻ anion had been discussed previously by different researchers. Christe and co-workers reasoned wellfounded that "in a rigid molecule the space requirement of a sterically active free valence electron pair slightly exceeds that of a fluorine ligand",^[48] and that therefore anions such as $[IF_6]^$ are not octahedral as there is enough space around the I atom for the lone pair to become active because I atoms can adopt coordination numbers up to eight with F ligands, for example, in $[IF_8]^-$ anions. "In $[BrF_6]^-$ there is little or no room left for a seventh ligand and, therefore, the free valence electron pair should be sterically inactive" they concluded.[38] Seppelt and coworkers had the opinion that the 4 s electrons were particularly strongly bound to the Br atomic nucleus as the fully occupied 3d shell shields the nuclear charge incompletely. Therefore, the Br-F bonds would mainly show p character.^[33] Gillespie and coworkers reasoned that the six F atoms around the small Br atom are close packed. Therefore, no room for the lone pair is left and it belongs to the Br core.^[36,49]

A quantum-chemical calculation of the $[IF_6]^-$ anion shows that its molecular structure is not a local minimum in point group O_h . Following the imaginary mode of 39*i* cm⁻¹ leads to molecular structures in point groups $C_{2\nu}$ and C_s that are also no local minima. Finally, a true local minimum in point group C_1 is reached, and overall the energy lowered by 14 kJ mol⁻¹ compared to the ideal O_h symmetry. The IBOs of the I lone pair and the I–F bonds of the $[IF_6]^-$ anion in its energy minimum are shown in Figure 15.

The I lone pair is essentially 5 s-orbital-like with 93% 5 s and 7% 5p_x orbital contribution. It therefore shows some stereochemical activity in contrast to the Br lone pair of the $[BrF_6]^$ anion. Both reasons for the stereochemical inactivity of the Br lone pair of the $[BrF_6]^-$ anion given by Seppelt or Christe are valid and in agreement with our quantum chemical findings.



Figure 15. IBOs of the I lone pair and the I–F bonds of the $[IF_6]^-$ anion in its energy minimum in point group C_1 . Percentages next to the IBOs indicate the contribution of each atom to that IBO. The larger a percentage, the more polarized the covalent bond. The percentages in the labels show the contributions of atomic orbitals to each IBO. F atoms are in yellow, I atoms in violet. IBO isosurfaces are drawn so that 80% of the density is enclosed within them.

Chem. Eur. J. 2022, 28, e202202466 (11 of 15)



Conclusions

BrF5 was synthesized at room temperature by the photochemical reaction of BrF₃ with F₂. UV-Vis spectra of BrF₅ and F₂ were recorded to identify the region of suitable wavelength, 300 to 400 nm, to photodissociate F₂ but not the product BrF₅. BrF_5 can be obtained in yields above 90% with respect to the starting material BrF3 and pure on the basis of NMR, IR and Raman spectroscopy. NMR spectra of BrF₅ were taken at various temperatures. Quantum-chemical calculations aided in the determination of the new low-temperature modification and allowed the band assignment of the recorded IR and Raman spectra. By treating BrF₅ with KF and RbF, crystals of the compounds K[BrF₆] and Rb[BrF₆], respectively, were obtained and their crystal structures determined. The chemical bonds and the lone pairs on the Br atoms within the molecules $[BrF_6]^+$, BrF₅, and [BrF₆]⁻ were investigated by using intrinsic bond orbitals. These show that the contribution of the 4 s orbitals of the Br atoms to the Br-F bonds decreases to zero in the octahedral [BrF₆]⁻ anion where the Br lone pair is purely 4 sorbital-like. In the $[IF_6]^-$ molecule, which is not octahedral, the 5p orbitals contribute to the I lone pair, making it stereochemically active.

Experimental Section

General: All operations were performed on a Monel metal Schlenk line, which was passivated with fluorine and ClF_3 at various temperatures and pressures before use. The alkali metal fluorides were purchased from *Merck*, purified according to literature procedures,^[50] and were stored in PTFE vials in an Ar-filled glove box (MBraun).

Reaction vessels were made out of fluoropolymer (perfluoroalkoxy alkanes, PFA or perfluorinated ethylene propylene copolymer, FEP) and sealed with a bellows valve made out of Monel or stainless steel. The vessels were baked out in vacuum ($\sim 10^{-3}$ mbar) at circa 393 K for several times and then filled up to a pressure of 4 bar with diluted F₂ (F₂/Ar 20:80, *v*/*v*) for 16 h in order to saturate the polymer with fluorine.

CAUTION! Fluorine, the halogen fluorides and fluoridobromates(V) must be handled with appropriate protective gear with ready access to proper emergency treatment procedures in the event of contact. The aforementioned are potent oxidative fluorinators that are only stable under the rigorously anhydrous conditions employed in the experimental procedures outlined in the Experimental Section. They react vigorously to explosively upon hydrolysis or contact with organic materials. The utmost precautions must be taken when disposing of these materials and their derivatives.

Preparation of BrF₅ **in PFA vessels**: When only small amounts of BrF₅ around 1 g are required, the reaction can be performed in a reaction vessel with a volume of 50 to 80 mL made out of PFA or FEP and equipped with a stainless-steel valve.

For a typical synthesis 692 mg (5.08 mmol) BrF₃ was loaded into the reaction vessel (V=74 mL) and diluted fluorine (F₂/Ar 20:80, v/v, 3 bar, 1.79 mmol) was added. After irradiating the reaction mixture with a UV LED (Osram, LuxiGen-UV395, 395 nm, 1380 mW) for 6 h, the reaction vessel was cooled to 77 K and all volatiles were pumped off. The vessel was then allowed to warm to room temperature and diluted fluorine (3 bar, 1.79 mmol) was added again. This process was

repeated for three times. After the third addition of F_2 a slight excess (5.37 mmol) with respect to Br was reached. The liquid completely decolorized upon irradiation, which can be attributed to the absence of BrF₃. Bromine pentafluoride (792 mg, 4.55 mmol, 90% with respect to the starting material BrF₃) was obtained as a colorless liquid. As BrF₅, like ClF₅,^[5] tends to dissolve in the PFA/FEP vessel wall over time, the yield decreases with longer reaction times. Therefore, for larger batches requiring longer reaction times, vessels made of PFA/FEP should be avoided if possible.

Preparation of BrF₅ **in a stainless-steel reactor**: For the preparation of larger amounts of circa 60 g BrF₅ per batch, a stainless-steel (1.4571) reactor (Figure 16) with sapphire windows was used. For a typical synthesis 48.46 g (354 mmol) BrF₃ was loaded into the reactor (V=924 mL) and undiluted fluorine (1 bar, 42.7 mmol) was added. The reaction mixture was irradiated with a UV LED (Nichia, NVSU233B, 365 nm, 1450 mW) for 12 h during which the pressure dropped to circa 400 mbar. The F₂ pressure was then again increased to 1 bar and the process was repeated until the reaction mixture completely decolorized after 9.5 d of irradiation. Bromine pentafluoride (59.11 g, 338 mmol, 95% with respect to BrF₃) was obtained as a colorless liquid.

Preparation of A[BrF_6] (A = K, Rb): A PFA reaction vessel treated as described above was charged in a glove box with 40 mg of the respective dry alkali metal fluoride. The reaction vessel was then cooled to 77 K and an excess of $BrF_{\rm 5}$ (0.1 mL, 246 mg, 1.4 mmol) was condensed. The reaction mixture was then allowed to warm to room temperature and diluted fluorine was added to a pressure of 3 bar to counteract diffusion of external moisture and air. The reaction mixture was heated to circa 373 K in a hot air bath for 1 h. By slowly cooling the mixture down to room temperature, the product was obtained in form of colorless, needle shaped crystals. After a few crystals were transferred from the BrF₅ solution directly into the perfluorinated oil for the single-crystal preparation, BrF5 was removed from the reaction vessel under reduced pressure and the remaining solid was heated to 373 K in vacuum for 1 h in order to release any adsorbed BrF5. We were not able to obtain the compounds phase-pure this way, there seems to be still too much diffusion through the PFA vessels because the HF₂⁻ salts were formed in varying amounts during the syntheses.



Figure 16. Rendered graphic of the stainless-steel photoreactor (left) used for the synthesis of BrF₅. Photographs of the reactor during the reaction (middle) and the PFA vessel containing the product (right). Photographs by Martin Möbs.



NMR spectroscopy: ¹⁹F NMR spectra were recorded using a Bruker Avance III HD 300 NMR spectrometer. CFCl₃ was used as an external standard. A sample of neat BrF_5 was distilled into a thoroughly baked out 3 mm diameter FEP tube and sealed under vacuum. The sample was then placed into a regular glass NMR tube (5 mm) and stored under argon at 237 K until assayed.

Raman spectroscopy: The Raman spectra were measured with a Monovista CRS + confocal Raman microscope (Spectroscopy & Imaging GmbH) using a 532 nm solid-state laser and either a 300 grooves/mm (low-resolution mode, FWHM: <4.62 cm⁻¹) or an 1800 grooves/mm (high-resolution mode, FWHM: <0.368 cm⁻¹) grating. Sample preparation of BrF₅: A silica capillary was baked out under vacuum and flushed with diluted fluorine for several times. BrF₅ was distilled at liquid nitrogen temperature into the capillary which was then flame-sealed under vacuum. The capillary was allowed to warm to room temperature and was placed under the Raman microscope for data acquisition. Sample preparation of $A[BrF_6]$ (A = K, Rb): Samples were filled and sealed in quartz capillaries inside the glovebox and were then placed under the Raman microscope for data acquisition.

Infrared spectroscopy: The gas-phase IR spectrum of BrF₅ was recorded on a Bruker Tensor 37 FTIR with a resolution of 4 cm⁻¹ using a passivated measuring cell manufactured from 316 L stainless steel, equipped with diamond or BaF₂ windows. IR spectra of solids were recorded on a Bruker alpha FTIR spectrometer using the ATR Diamond module with a resolution of 4 cm⁻¹. The spectrometer was located inside a glovebox (MBraun) under argon atmosphere. The spectra were processed with the OPUS software package.^[51]

Single-crystal X-ray diffraction: A crystal of K[BrF₆] or Rb[BrF₆], respectively, was selected under pre-dried perfluorinated oil (Fomblin YR-1800) and mounted using a MiTeGen loop. Intensity data of a suitable crystal were recorded with an IPDS 2 diffractometer (Stoe & Cie). The diffractometer was operated with Mo_{Kα} radiation (0.71073 Å, graphite monochromator) and equipped with an image plate detector. In case of K[BrF₆], split reflections were observed for several crystals, which indicated non-merohedral twinning. Evaluation, integration and reduction of the diffraction data was carried out using the X-Area software suite.^[52] A numerical absorption correction was applied with the modules X-Shape and X-Red32 of the X-Area software suite. The structures were solved with dual-space methods (SHELXT-2014/5) and refined against F^2 (SHELXL-2018/3).^[53,54]

For the structure solution of K[BrF₆] only the non-overlapping reflections of the major twin component were used. The data were initially refined with the HKLF5 format option in SHELXL-2018/3 with all reflections (overlapping reflections and non-overlapping reflections of three twin components).^[54] The data were then processed with the HKLF5Tools^[55] program: the non-overlapping reflections of the weaker diffracting twin components were removed, the non-overlapping reflections of the major twin component were merged in point group $\bar{3}$ and the overlapping reflections were merged in point group 1. The final refinement was carried out against the detwinned dataset (created by SHELXL with the LIST 8 option as an FCF file and converted to an HKL file with HKLF5Tools).

For the determination of the crystal structure of BrF₅, a sample of the latter was prepared in a 0.3 mm quartz capillary as described for its Raman spectroscopy and mounted on a D8 Quest diffractometer (Bruker). The diffractometer was operated with monochromatized Mo–K α radiation (0.71073 Å, multi layered optics) and equipped with a PHOTON 100 CMOS detector. By cooling the sample to 200 K on the diffractometer, a polycrystalline material was obtained, as shown by the diffraction pattern in which Debye-Scherrer rings are indicated. By repeated zone melting of

the sample in the capillary with the help of a copper wire, a single crystal suitable for X-ray structure determination was obtained. Full datasets of the crystal were measured at 200, 180, 150 and 100 K respectively. Evaluation, integration, and reduction of the diffraction data was carried out within the APEX3 software suite.^[56] The data was corrected for absorption utilizing the multi-scan method of SADABS^[57] within the APEX3 software suite, the structure was solved with dual-space methods (SHELXT-2014/5) and refined against F² (SHELXL-2018/3).^[53,54] When the crystal was cooled below about 130 K, split reflections were observed in the diffraction pattern, indicating that the crystal was shattered by a phase transition. In consequence, the diffraction data recorded at 100 K is not from a single crystal but contains reflections from multiple crystallites. Using the CELL_NOW $^{\scriptscriptstyle [58]}$ indexing algorithm more than five domains with identical lattice parameters were found, of which only the two strongest were used for further processing. Only the non-overlapping reflections of the major twin component were used for the structure solution. The structure was solved with dualspace methods (SHELXT).^[53] The data were initially refined with the HKLF5 format option in SHELXL with all reflections (overlapping reflections and non-overlapping reflections of the three twin components).^[54] The data were then processed with the HKLF5Tools^[55] program: the non-overlapping reflections of the weaker diffracting twin components were removed, the nonoverlapping reflections of the major twin component were merged in point group 2/m and the overlapping reflections were merged in point group 1. The final refinement was carried out against the detwinned dataset (created by SHELXL with the LIST 8 option as a FCF file and converted to a HKL file with HKLF5Tools).

In the datasets recorded at 150, 180 and 200 K, several additional weak reflections occur at half the diffraction angle of particularly strong reflections. This can be attributed to the minor lambda-half fraction of the primary X-ray beam that is not filtered out by the monochromator and gets diffracted due to the big crystal size with significant intensity. As no subsequent correction was made, the goodness of fit values are somewhat higher than might be expected.

All atoms were refined with anisotropic displacement parameters. Representations of the crystal structures were created with the Diamond software. $^{\left[59\right] }$

Deposition Numbers 2193268 (for K[BrF₆]), 2193269 (for HT-BrF₅ at 200 K), 2193270 (for HT-BrF₅ at 150 K), 2193271 (for LT-BrF₅), 2193272 (for HT-BrF₅ at 180 K), 2193273 (for Rb[BrF₆]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Powder X-ray diffraction: A sample of BrF₅ was prepared in a 0.3 mm quartz capillary as described for Raman spectroscopy and single-crystal X-ray diffraction. The powder X-ray pattern was recorded with a StadiMP diffractometer (Stoe & Cie) in Debye-Scherrer geometry. The diffractometer was operated with Cu_{Ku1} radiation (1.5406 Å, germanium monochromator) and equipped with a MYTHEN 1 K detector. The sample was cooled to 180 K using a capillary cooling system (Osford Cryosystems). Diffraction data of the resulting polycrystalline material were collected in eight subsequent runs in a range of 15 to 71 °2 θ with an irradiation time of 80 s per 1°. Due to ice formation on the surface of the capillary during the measurement only the first tree runs were used for the refinement.

Rietveld refinements^[60] were performed using the TOPAS-Academic software (version 7).^[61] The structure model derived from the X-ray structure analysis of the single crystal was used as the starting point for the refinement. A shifted Chebyshev polynomial with 12 terms was used to describe the background, the peak profiles were fitted



with a modified Thompson-Cox-Hastings pseudo-Voigt ("TCHZ") function as implemented in TOPAS, and the zero offset was refined. To account for absorption, an intensity correction for cylindrical samples was applied as implemented in TOPAS. An eighth-order spherical harmonics function was used to account for the preferred orientation of the crystallites. The strong preferred orientation of the sample can be explained by the fact that the liquid BrF₅ was frozen directly inside of the capillary, making it impossible to grind the sample before measurement. Therefore, various different directions of crystal growth are to be expected. The same phenomenon was observed when trying to obtain single crystals of the compound. In this case, the preferred orientation was also clearly visible in the diffraction image (Figure 17).

The approach of Le Bail and Jouanneaux^[62] was used to accurately describe the peak half-width and shape anisotropy effects, and the corresponding parameters could be freely refined. The final refinement cycles converged with free refinement of all background, profile, and lattice parameters, including the coordinates and isotropic displacement parameters of all atoms.

Computational details: We carried out anharmonic force field and ¹⁹F NMR chemical shift calculations on the gas-phase BrF₅ molecule with CFOUR v2.1^[63,64] program suite. CCSD(T) coupled cluster method was used in combination with correlation-consistent polarized triple-zeta basis sets. For geometry optimizations and anharmonic frequency calculations, we used triple-valence correlation consistent basis set (cc-pVTZ)^[65,66] The structure was fully optimized within the $C_{4\nu}$ point group (wavefunction was obtained for the highest Abelian subgroup $C_{2\nu}$). The geometry of CFCl₃ was also optimized and it was used as the NMR reference species for ¹⁹F NMR chemical shifts. The ¹⁹F NMR chemical shift calculations were carried out at the optimized geometries with weighted corevalence basis sets (cc-pwCVTZ).[67,68] Anharmonic vibrational spectra were calculated within the second-order vibrational perturbation theory (VPT2).^[69] For evaluating the Fluoride Ion Affinity (FIA) of BrF₅, we optimized [BrF₆]⁻, COF₂, and COF₃⁻ at the CCSD(T)/cc-pVTZ level of theory and used the $\rm COF_2$ reference system with an experimental FIA of 208.08 kJ mol⁻¹ to estimate the FIA at an absolute scale.[43] The Z-matrices of the optimized molecular structures are included in the Supporting Information.

All solid-state calculations were performed with the CRYSTAL17⁽⁷⁰⁾ program suite. HT- and LT-BrF₅, Rb[BrF₆], and K[BrF₆] were investigated with hybrid density functional methods (DFT-PBE0)^(71,72) combined with triple-valence basis sets TZVP for Br⁽⁷³⁾ and F,⁽⁷⁴⁾ and a split-valence



Figure 17. X-ray diffraction image of a polycrystalline sample of BrF_5 obtained by cooling the liquid to 180 K.

Chem. Eur. J. 2022, 28, e202202466 (14 of 15)

basis set SVP for K^[75] and Rb^[76] (derived from molecular Karlsruhe basis sets^[77]). In case of the molecular crystals HT- and LT-BrF₅, empirical D3 dispersion correction with zero damping^[78,79] was applied for the geometry optimizations and frequency calculations to take into account weak intermolecular interactions. Atomic positions and lattice parameters were fully optimized within the space group symmetry of each system. The reciprocal space was sampled with Monkhorst-Packtype k-point grids.^[80] The employed k-point meshes are reported in Table S5. Tight truncation criteria (TOLINTEG 8, 8, 8, 8, 16) were applied for the evaluation of the bielectronic Coulomb and exchange series in all calculations. Default DFT integration grids and optimization convergence thresholds were used in all calculations. Harmonic vibrational frequencies and Raman intensities were calculated with the schemes implemented in CRYSTAL.[81-83] Raman intensities were calculated for a polycrystalline powder sample. For Rb[BrF₆] and K[BrF₆] the experimental setup of T=298.15 K and $\lambda=532$ nm was considered. For the simulation of the spectra a pseudo-Voigt band profile (50:50 Lorentzian/Gaussian) with a FWHM of 8 cm⁻¹ was used. Assignment of the vibrational bands was done with the visualization tool CRYSPLOT.^[84] The atomic positions and lattice parameters of the optimized structures are given in the Supporting Information.

Acknowledgements

We thank the precision mechanics workshop of our department for making the photoreactor and Solvay for the kind donation of fluorine. Furthermore, we would like to thank Dr. Magnus Buchner and the co-workers of our NMR service department for performing the NMR experiments. We thank Drs. Sergei Ivlev and Matthias Conrad for helpful discussions. A.J.K. and K.E. thank CSC – the Finnish IT Center for Science for computational resources. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: bromine pentafluoride · crystal structure · hexafluoridobromate · photochemistry · quantum-chemical calculations

- D. Naumann, Fluor und Fluorverbindungen, Dr. Dietrich Steinkopf Verlag, Darmstadt, 1980.
- [2] W. I. Bailey, A. J. Woytek, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, 2000.
- [3] H. Simmons Booth, J. Turner Pinkston, Chem. Rev. **1947**, 41, 421–439.
- [4] K. O. Christe, in XXIVth International Congress of Pure and Applied Chemistry, Butterworth-Heinemann, Oxford, 1974, pp. 115–141.
- [5] D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, V. E. Bedwell, *Inorg. Chem.* **1967**, *6*, 1918–1919.
- [6] O. Ruff, W. Menzel, Z. Anorg. Allg. Chem. 1931, 202, 49–61.
- [7] R. J. Gillespie, G. J. Schrobilgen, Inorg. Chem. 1974, 13, 1230-1235.
- [8] G. A. Hyde, M. M. Boudakian, Inorg. Chem. 1968, 7, 2648-2649.



5213765,

2, 2, Downloaded from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/chem.202202466 by Aalto University, Wiley Online Library on [09/01/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Ceative Commons

- [9] R. J. Gillespie, A. Netzer, G. J. Schrobilgen, Inorg. Chem. 1974, 13, 1455-1459
- [10] R. Gatti, R. L. Krieger, J. E. Sicre, H. J. Schumacher, J. Inorg. Nucl. Chem. 1966, 28, 655-657.
- [11] R. L. Krieger, R. Gatti, H. J. Schumacher, Z. Phys. Chem. 1966, 51, 240-254.
- [12] A. Šmalc, K. Lutar, Vestn. Slov. Kem. Drus. 1990, 37, 313-316.
- [13] R. D. Burbank, F. N. Bensey, J. Chem. Phys. 1957, 27, 982-983.
- [14] AG. Osram, Produktdatenblatt: PURITEC® HNS® UV-C lamps, Munich, 2018.
- [15] T. Peez, J.-N. Luy, K. Harms, R. Tonner, U. Koert, Chem. Eur. J. 2018, 24, 17686-17690
- [16] Nichia Corporation, Data Sheet: Specifications for UV LED NVSU223B(T), Anan, Tokushima, 2022.
- [17] AG. Osram, Produktdatenblatt: LED Engin, LuxiGen[™] 395 nm, San Jose, 2020.
- [18] M. Mitchell, B. Muftakhidinov, T. Winchen, Engauge Digitizer Software V 12.1, 2019.
- [19] G. L. Smith, H. P. A. Mercier, G. J. Schrobilgen, Inorg. Chem. 2007, 46, 1369-1378.
- [20] G. M. Begun, W. H. Fletcher, D. F. Smith, J. Chem. Phys. 1965, 42, 2236-2242.
- [21] R. S. McDowell, L. B. Asprey, J. Chem. Phys. 1962, 37, 165-167.
- [22] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, Hoboken, 2009.
- [23] Y. Le Page, J. Appl. Crystallogr. 1987, 20, 264-269.
- [24] Y. Le Page, J. Appl. Crystallogr. 1988, 21, 983-984.
- [25] A. L. Spek, PLATON: A Multipurpose Crystallographic Tool, Utrecht University (The Netherlands), 2019.
- [26] A. J. Edwards, R. D. Peacock, R. W. H. Small, J. Chem. Soc. 1962, 4486-4491.
- [27] J. H. Holloway, R. D. Peacock, R. W. H. Small, J. Chem. Soc. 1964, 644-648.
- [28] I.-C. Hwang, K. Seppelt, Angew. Chem. Int. Ed. 2001, 40, 3690-3693; Angew. Chem. 2001, 113, 3803-3805.
- [29] A. M. Ellern, M. Y. Antipin, Y. T. Struchkov, V. F. Sukhoverkhov, Russ. J. Inorg. Chem. 1991, 36, 792-794.
- [30] H. Bärnighausen, MATCH Commun. Math. Comput. Chem. 1980, 9, 139-175.
- [31] E. D. Whitney, R. O. MacLaren, C. E. Fogle, T. J. Hurley, J. Am. Chem. Soc. 1964, 86, 2583-2586.
- [32] R. Bougon, P. Charpin, J. Soriano, C. R. Acad. Sc. Paris, Ser. C 1971, 272, 565-568.
- [33] A. R. Mahjoub, A. Hoser, J. Fuchs, K. Seppelt, Angew. Chem. Int. Ed. 1989, 28, 1526-1527; Angew. Chem. 1989, 101, 1528-1529.
- [34] R. G. Pearson, J. Am. Chem. Soc. 1963, 85, 3533-3539.
- [35] R. J. Gillespie, R. S. Nyholm, Q. Rev. Chem. Soc. 1957, 11, 339-380.
- [36] R. J. Gillespie, P. L. A. Popelier, Chemical Bonding and Molecular Geometry, Oxford University Press, 2001.
- [37] R. J. Gillespie, Coord. Chem. Rev. 2008, 252, 1315-1327.
- [38] K. O. Christe, W. W. Wilson, Inorg. Chem. 1989, 28, 3275-3277.
- [39] C. Pak, Y. Xie, T. J. Van Huis, H. F. Schaefer, J. Am. Chem. Soc. 1998, 120, 11115-11121
- [40] J. C. Haartz, D. H. McDaniel, J. Am. Chem. Soc. 1973, 95, 8562-8565.
- [41] T. E. Mallouk, G. L. Rosenthal, G. Mueller, R. Brusasco, N. Bartlett, Inorg. Chem. 1984, 23, 3167-3173.
- K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy, J. A. [42] Boatz, J. Fluorine Chem. 2000, 101, 151-153.
- [43] P. Erdmann, J. Leitner, J. Schwarz, L. Greb, ChemPhysChem 2020, 21, 987-994.
- [44] I. Krossing, I. Raabe, Chem. Eur. J. 2004, 10, 5017-5030.
- [45] G. Knizia, J. Chem. Theory Comput. 2013, 9, 4834–4843.
- [46] G. Knizia, J. E. M. N. Klein, Angew. Chem. Int. Ed. 2015, 54, 5518-5522; Angew. Chem. 2015, 127, 5609-5613.
- [47] K. O. Christe, R. D. Wilson, Inorg. Chem. 1975, 14, 694-696.
- [48] K. O. Christe, H. Oberhammer, Inorg. Chem. 1981, 20, 296-297.
- [49] J. Pilmé, E. A. Robinson, R. J. Gillespie, Inorg. Chem. 2006, 45, 6198-6204.
- [50] G. Brauer, Handbuch der Präparativen Anorganischen Chemie in Drei Bänden, Ferdinand Enke, Stuttgart, 1975.
- [51] OPUS V7.2, Bruker Optik GmbH, Ettlingen (Germany), 2012.

- [52] X-Area 1.8.1, STOE & Cie GmbH, Darmstadt (Germany), 2018.
- [53] G. M. Sheldrick, Acta Crystallogr. Sect. A 2015, 71, 3-8
- [54] G. M. Sheldrick, Acta Crystallogr. Sect. C 2015, 71, 3-8. [55] S. I. Ivlev, M. Conrad, F. Kraus, Z. Kristallogr. 2019, 234, 415–418.
- [56] APEX3 V 2018.7-2, Bruker AXS Inc., Madison (USA), 2018.
- [57] SADABS, Bruker AXS Inc., Madison (USA), 2016.
- [58] G. M. Sheldrick, CELL NOW V 2008/4, Göttingen (Germany), 2008. [59] K. Brandenburg, H. Putz, Diamond: Crystal and Molecular Structure
- Visualization, V 4.6.8, Crystal Impact GbR, Bonn, 2019.
- [60] H. M. Rietveld, J. Appl. Crystallogr. 1969, 2, 65-71.
- [61] A. A. Coelho, J. Appl. Crystallogr. 2018, 51, 210-218.
- [62] A. Le Bail, A. Jouanneaux, J. Appl. Crystallogr. 1997, 30, 265-271.
- [63] J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews, P. G. Szalay, CFOUR V2.1, a Quantum Chemical Program Package with Contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, S. Blaschke, Y. J. Bomble, S. Burger, O. Christiansen, D. Datta, F. Engel, R. Faber, J. Greiner, M. Heckert, O. Heun, M. Hilgenberg, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, T. Kirsch, K. Klein, G. M. Kopper, W. J. Lauderdale, F. Lipparini, T. Metzroth, L. A. Mück, T. Nottoli, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the Integral Packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP Routines by A. V. Mitin, C. van Wüllen. For the current version, see http://www.Cfour.De, 2019.
- [64] D. A. Matthews, L. Cheng, M. E. Harding, F. Lipparini, S. Stopkowicz, T.-C. Jagau, P. G. Szalay, J. Gauss, J. F. Stanton, J. Chem. Phys. 2020, 152, 214108.
- [65] T. H. Dunning, J. Chem. Phys. 1989, 90, 1007-1023.
- [66] A. K. Wilson, D. E. Woon, K. A. Peterson, T. H. Dunning, J. Chem. Phys. 1999, 110, 7667-7676.
 - K. A. Peterson, T. H. Dunning, J. Chem. Phys. 2002, 117, 14.
- [68] N. J. DeYonker, K. A. Peterson, A. K. Wilson, J. Phys. Chem. A 2007, 111, 11383-11393.
- [69] V. Barone, J. Chem. Phys. 2005, 122, 014108.

[67]

- [70] R. Dovesi, A. Erba, R. Orlando, C. M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rérat, S. Casassa, J. Baima, S. Salustro, B. Kirtman, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2018, e1360.
- [71] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865–3868.
- [72] C. Adamo, V. Barone, J. Chem. Phys. 1999, 110, 6158-6170.
- [73] S. I. Ivlev, K. Gaul, M. Chen, A. J. Karttunen, R. Berger, F. Kraus, Chem. Eur. J. 2019, 25, 5793-5802.
- [74] A. J. Karttunen, T. Tynell, M. Karppinen, J. Phys. Chem. C 2015, 119, 13105-13114.
- [75] R. E. Stene, B. Scheibe, A. J. Karttunen, W. Petry, F. Kraus, Eur. J. Inorg. Chem. 2019, 2019, 3672-3682.
- [76] B. Scheibe, S. I. Ivlev, A. J. Karttunen, F. Kraus, Eur. J. Inorg. Chem. 2020, 2020, 1319-1324.
- [77] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
- [78] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
- [79] S. Grimme, A. Hansen, J. G. Brandenburg, C. Bannwarth, Chem. Rev. 2016. 116. 5105-5154.
- [80] H. J. Monkhorst, J. D. Pack, Phys. Rev. B 1976, 13, 5188-5192.
- [81] L. Maschio, B. Kirtman, M. Rérat, R. Orlando, R. Dovesi, J. Chem. Phys. **2013**, *139*, 164102.
- [82] C. M. Zicovich-Wilson, F. Pascale, C. Roetti, V. R. Saunders, R. Orlando, R. Dovesi, J. Comput. Chem. 2004, 25, 1873-1881.
- [83] F. Pascale, C. M. Zicovich-Wilson, F. López Gejo, B. Civalleri, R. Orlando, R. Dovesi, J. Comput. Chem. 2004, 25, 888-897.
- [84] "CRYSPLOT: A modern and easy to use visualization environment for plotting properties of crystalline solids as computed by means of the CRYSTAL code" can be found under http://crysplot.crystalsolutions.eu/ index.html, 2022.

Manuscript received: August 8, 2022

Accepted manuscript online: September 15, 2022 Version of record online: October 31, 2022