

FULL PAPER

An Experimental and Theoretical Study on the Novel Tetrphosphorus Triselenide Boron Triiodide (P_4Se_3) · (BI_3) Adduct

Christoph Aubauer, Thomas M. Klapötke, and Axel Schulz

Institut für Anorganische Chemie, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13 (Haus D), D-81377 Munich, Germany. E-mail: lex@cup.uni-muenchen.de

Received: 11 August 1999/ Accepted: 29 November 1999/ Published: 28 February 2000

Abstract Tetrphosphorus triselenide boron triiodide (P_4Se_3)·(BI_3) has been prepared. The product formed has been characterized by Raman and IR spectroscopy. Vibrational assignments for the normal modes of this Lewis acid-base adduct have been made on the basis of comparison between theoretically obtained and experimentally observed Raman and IR data. The geometries of several possible tetrphosphorus triselenide boron triiodide (P_4Se_3)·(BI_3) adducts have been calculated. The bonding and electron transfer from the tetrphosphorus triselenide P_4Se_3 unit to the Lewis acid BI_3 has been investigated by applying NBO analysis.

Keywords Boron halide complexes, Density functional theory, NBO analysis, Raman spectroscopy

Introduction

Recently, we have been interested in the simulation of Raman and IR spectra of phosphorus halide compounds and phosphorus boron halide adducts. Vibrational assignments for the normal modes for these Lewis acid-base adducts have been made on the basis of comparison between theoretically obtained and experimentally observed Raman and IR data. Moreover we have investigated the bonding and electron transfer within these species.[1],[2],[3]

Previous work has shown that the donor behavior of phosphorus trihalides depends on the electronegativity of the halogen substituents.[4],[5] For the phosphorus trihalides,

the order of stability for the 1:1 donor-acceptor complexes with boron trihalides is $PCl_3 < PBr_3 < PI_3$. [6] PF_3 appears to have no donor properties if only σ bonding is considered. [7] The order of the stability of the adducts formed from boron trihalides with phosphorus trihalides is $BF_3 < BCl_3 < BBr_3 < BI_3$. [8] However, the reverse order was found for the water complexes of boron halides. [9] Two effects must be considered when discussing stability of donor acceptor complexes of this type: σ - and π -donation.

Several investigations were published concerning the vibrational frequencies of α - P_4S_3 , β - P_4S_3 and the related cage-like molecules P_4S_3 , As_4S_3 and As_4Se_3 . [10] Recently, Blachnik et al. published the Lewis acid-bases adduct from the reaction of P_4Se_3 with $NbCl_5$. The crystal structure of $(P_4Se_3) \cdot (NbCl_5)$ showed that the Nb-P bonding is formed with an basal phosphorus atom. In contrast to this species the structure of β - $(P_4S_4) \cdot (NbCl_5)$, formed from P_4S_3 and $NbCl_5$, two $NbCl_5$ units are coordinated on the basal phosphorus atoms. [11]

Correspondence to: A. Schulz

Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

Table 1 Calculated and experimentally observed vibrational data of P_4Se_3 [a]

	Calculation[b]	Raman[c]	IR	Assignment
	470 (0)	484 (12)	484w	ω_1 (A_1), ν (P_{b3})
	396 (1) [e]	405 (4)	403w	ω_2 (E), ν (P_{b3} -Se ₃)
	359 (1)	364 (100, br)	358vs, br	ω_3 (A_1) ν (P_a -Se ₃)
[a] subscript b describes the basal P atoms, a the apical P atom	343 (10)	364 (100, br)	358vs, br	ω_4 (E), ν_{as} (P_a -Se ₃), ν_{as} (P_{b3})
	311 (1)	323 (14)	317vs	ω_5 (E), ν_{as} (P_a -Se ₃), ν_{as} (P_{b3} -Se ₃)
[b] in parenthesis IR intensities in $km\ mol^{-1}$	294 (6)			ω_6 (A_1), ν_s (P_a -Se ₃), ν_s (P_{b3} -Se ₃) [d]
[c] Raman intensities correspond to relative intensities.	215 (0)	213 (43)	214m	ω_7 (A_1), δ_s (P_a -Se ₃)
[d] out-of-phase (180°)	213 (0)			ω_8 (E), δ_{as} (P_a -Se ₃)
	160 (0)			ω_9 (A_2), δ (P_{b3}) (torsion)
	130 (0)	134 (19)		ω_{10} (A_1), δ (P_a -Se ₃)

Goh and co-workers recently studied the reaction of $[CpCr(CO)_3]_2$ with P_4Se_3 yielding $(Cp_4Cr_4(CO)_9) \cdot (P_4Se_3)$. The crystal structure of $(Cp_4Cr_4(CO)_9) \cdot (P_4Se_3) \cdot \frac{1}{2}C_6H_6$ revealed an opened-up confirmation of the P_4Se_3 cage.[12]

It is known that sterically demanding ligands occupy the apical position in P_4Se_3 , whereas it is assumed that attack of the basal P_3 ring results in ring opening.[13] However, recently Blachnik et al. showed that this does not have to be the case.[11] Since we are interested in P-B adducts we tried to prepare and investigate the bonding situation of the novel tetraphosphorus triselenide boron triiodide $(P_4Se_3) \cdot (BI_3)$ on which we want to report in this paper.

Results and discussion

General methods

Experiments were carried out in a dry-box under dry nitrogen. BI_3 (Aldrich) was used as received. P_4Se_3 was prepared

according to the literature.[11] CS_2 was refluxed with P_4O_{10} and distilled before used. Raman spectra were obtained on powdered solid samples contained in glass capillary tubes with a Perkin Elmer 2000 NIR spectrometer in the range 800 - 50 cm^{-1} . IR spectra were recorded on Nujol mulls between CsI plates in the range 800-200 cm^{-1} on a Nicolet 520 FT IR spectrometer. For the determination of decomposition points, samples were heated in sealed glass capillaries in a Büchi B450 instrument.

Preparations of $(P_4Se_3) \cdot (BI_3)$

$(P_4Se_3) \cdot (BI_3)$ was prepared by addition of P_4Se_3 (0.36 g, 1.00 mmol) in CS_2 to CS_2 solutions of BI_3 (0.39 g, 1.00 mmol) at room temperature. A yellow precipitate formed immediately upon addition. After stirring for 15 minutes, the precipitate was collected by filtration and washed with CS_2 until the filtrate was colorless. Traces of CS_2 were removed under dynamic vacuum at room temperature. Yield: 0.72 g (96%) of yellow solid, mp $>300^\circ C$ (decomp.).

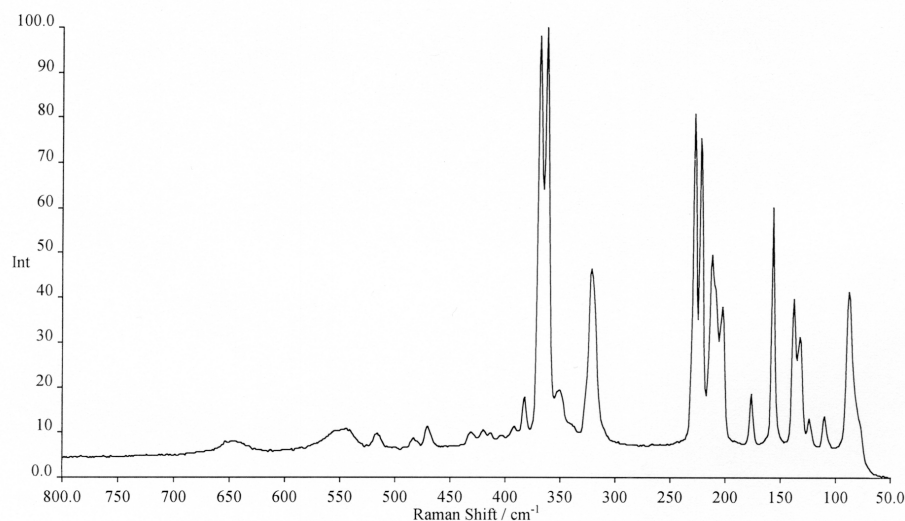
Figure 1 Raman spectrum of $(P_4Se_3) \cdot (BI_3)$ 

Table 2 Calculated and experimentally observed vibrational data for the adduct $(P_4Se_3) \cdot (BI_3)$ (IR intensities in $km\ mol^{-1}$)

apical adduct calculation [a]	basal adduct calculation [a,b]	$(P_4Se_3) \cdot (BI_3)$ Raman [a,b,c]	$(P_4Se_3) \cdot (BI_3)$ IR	assignment [d]
		646(8, br)	650w	$2 \times \omega_{11}$
545 (38)	569 (60)	558 (10)	560sh	ω_1, ν (P-B)
543 (80)	546 (103)/529(60)	544 (10)/516(9)	546vs, br/515m	ω_2, ν_{as} (BI_3)
460 (0)	490 (15)[e]	483 (8)/470 (11)	470vw	ω_3, ν_s (P_{b3})
	413 (1)	431(10)/420 (10)	429m/414vw	ω_4, ν_{as} (P_{b3})
407 (3)				ω_5, ν_{as} (P_{b3} -Se ₃), ν_{as} (P_a -Se ₃)
	400 (7)	382 (17)	391m/382m	ω_6, ν_s (P_{b3}), ν_s (P_{b3} -Se ₃), ν_{as} (BI_3)
375 (16)	371 (9)	368(98)/362(100)	370m	ω_7, ν_{as} (P_{b3} -Se ₃), ν_{as} (P_a -Se ₃)
355 (34)	359 (17)	351 (19)	350m	ω_8, ν_s (P_a -Se ₃), ν_s (P_{b3} -Se ₃), ν_s (BI_3)[f]
	336 (4)	336 (8)	336m	ω_9, ν_{as} (P_{b3}), ν_{as} (P_a -Se ₃)
319 (0)				ω_{10}, ν_{as} (P_{b3}), ν_{as} (P_{b3} -Se ₃)
315 (52)	325 (44)	322 (46, br)	324vs, br	ω_{11}, ν_s (P_a -Se ₃), ν_s (P_{b3} -Se ₃), ν_s (BI_3)[g]
	313 (4)/307 (6)	322 (46, br)	324vs, br	ω_{12}, ν_{as} (P_{b3}), ν_{as} (P_a -Se ₃)
	226 (5)	227 (81)/222(75)	230w	ω_{13}, δ_{as} (P_4Se_3)
	214 (0)	212 (49)	212vw	ω_{14}, δ_{as} (P_4Se_3)
214 (0)	210 (1)	202 (38)	206vw	ω_{15}, δ_s (P_a -Se ₃)
208 (0)				ω_{16}, δ (P_4Se_3)
155 (0)	179 (0)	176 (18)		ω_{17}, δ (P_{b3}) (torsion)
152 (0)	151 (0)	156 (60)		ω_{18}, δ_s (BI_3)
133 (0)	130 (1)/129 (0)	137 (39)/132 (31)		ω_{19}, δ_{as} (P_a -Se ₃)
	117 (1)	124 (13)		ω_{20}, δ ($(P_4Se_3) \cdot (BI_3)$)
105 (0)	103 (0)	110 (13)		ω_{21}, δ_{as} (BI_3), δ_{as} (P_a -Se ₃)
73 (0)	81 (0)	87 (41)		ω_{22}, δ ($(P_4Se_3) \cdot (BI_3)$)
	72 (0)			ω_{23}, δ ($(P_4Se_3) \cdot (BI_3)$)
72 (0)	69 (1)			ω_{24}, ν (P_4Se_3 - BI_3)
42 (0)	39 (0)			ω_{25}, δ ($(P_4Se_3) \cdot (BI_3)$)
	33 (0)			ω_{26}, δ ($(P_4Se_3) \cdot (BI_3)$)
12 (0)	13 (0)			$\omega_{27},$ torsion

[a] IR intensities in $km\ mol^{-1}$ in parenthesis

[b] second entry denotes a split due to symmetry decrease

[c] Raman intensities correspond to relative intensities

[d] subscript b describes the basal P atoms, a the apical P atom

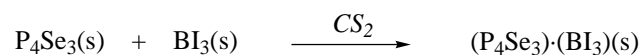
[e] ν (P_b -B)

[f] $P_b + P_a$ in-phase

[g] $P_b + P_a$ out-of-phase.

Vibrational spectroscopy

Tetraphosphorus triselenide boron triiodide was prepared from the reaction of 1 equivalent of tetraphosphorus triselenide with 1 equivalent of boron triiodide (Scheme 1) in CS_2 .



We tried to dissolve the $(P_4Se_3) \cdot (BI_3)$ in different solvents e.g. CS_2 , CH_3CN , $CFCl_3$ and SO_2 , however the solubility of $(P_4Se_3) \cdot (BI_3)$ is very small. The saturated solution of $(P_4Se_3) \cdot (BI_3)$ in CS_2 contains essentially only very small amounts of P_4Se_3 and BI_3 . Sublimation of $(P_4Se_3) \cdot (BI_3)$ results in decomposition. Therefore, we concluded that

tetraphosphorus triselenide boron triiodide exists only in the solid state.

Table 1 and 2 show the calculated and observed frequencies and their approximate assignments of all discussed species and Figure 1 the Raman spectrum of the $(P_4Se_3) \cdot (BI_3)$ adduct. The theoretically predicted vibrational frequencies for all species have been calculated with the harmonic approximation. The deviation from experimentally obtained frequencies may partly be compensated by using scaling factors. In Table 1 all frequencies are unscaled.

By means of Raman and IR spectroscopy we were able to identify the product from the reaction of P_4Se_3 and BI_3 in CS_2 unambiguously as a basal $(P_4Se_3) \cdot (BI_3)$ adduct (Figure 2). Comparison of the theoretically predicted with the experimentally observed vibrational data shows (Figure 3a and 3b):

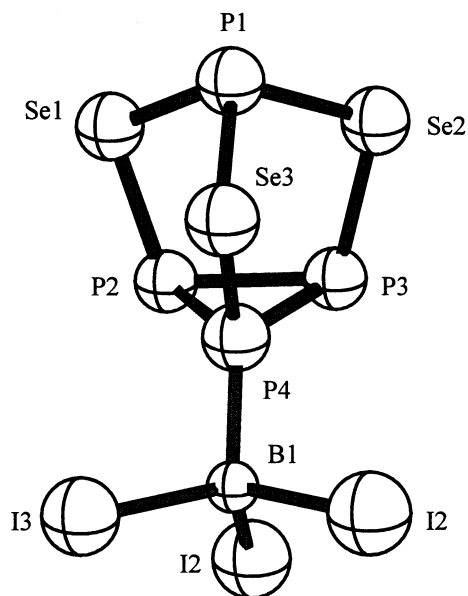


Figure 2 The basal P-B adduct

(i) the best agreement for the basal adduct (smallest deviation in the wave numbers, mean deviation 7 cm^{-1} , maximal deviation 18 cm^{-1}),

(ii) the splitting due to symmetry decrease from C_{3v} in P_4Se_3 (and the apical adduct) to C_s in the basal adduct and due to lattice effects,

(iii) the computed intensities agree between experiment and theory.

Especially ω_2 , ω_7 , ω_{12} , ω_{13} , and ω_{19} show nicely the splitting in the basal adduct due to symmetry decrease. The almost purely symmetric P-B stretching vibration (ω_1) can be observed at roughly 560 cm^{-1} . The experimental values for the corresponding modes of the related complex $(H_3P)\cdot(BX_3)$ ($X = Cl, Br, I$) are found to be in the range of $679\text{--}699\text{ cm}^{-1}$. [14], [15] With heavier halogen substituents the P-B stretching modes are shifted to lower frequencies [602 cm^{-1} (Cl_3P) $\cdot(BBr_3)$, 588 cm^{-1} (Cl_3P) $\cdot(BI_3)$, 475 cm^{-1} (Br_3P) $\cdot(BBr_3)$, 471 cm^{-1} (Br_3P) $\cdot(BI_3)$, 402 cm^{-1} (I_3P) $\cdot(BBr_3)$ and 422 cm^{-1} (I_3P) $\cdot(BI_3)$]. [3]

Four broad peaks can be assigned to asymmetric stretching vibrations of the BI_3 unit in the Raman and IR spectra (ω_2 , ω_6 , ω_8 , ω_{11}) in the range of ca. $550\text{--}510\text{ cm}^{-1}$ (Table 2), however, only ω_2 represents an almost pure asymmetric B-I stretching mode.

According to Table 2, ω_3 is almost purely an symmetric stretching mode of the P_{b3} moiety ($b = \text{basal}$), while ω_4 represents the asymmetric stretch for the P_{b3} group. The assignments of $\omega_5\text{--}\omega_{12}$ are not as straightforward as with $\omega_1\text{--}\omega_5$. These motions can be described as mixtures of stretches of the P_4Se_3 and the BI_3 units. The remaining normal modes are either symmetric and asymmetric or in-phase and out-of-phase deformation modes, except the low-lying frequency ω_{24} ,

which represents the stretching mode of the entire P_4Se_3 unit towards the BI_3 unit.

Computational methods

The structural and vibrational data of the considered species were calculated by using the density functional theory with the program package Gaussian 94. [16] For phosphorus and boron a standard 6-31G(d,p) basis set was used and for I and Se quasi-relativistic pseudopotentials (I: ECP46MWB, Se: ECP28MWB) [17] and a $(5s5p1d)/[3s3p1d]\text{-DZ+P}$ basis set. [18] The computations were carried out at the DFT level using the hybrid method B3LYP, which includes a mixture of Hartree-Fock exchange with DFT exchange-correlation. Becke's three parameter functional where the non-local correlation is provided by the LYP expression (Lee, Yang, Parr correlation functional) was used which is implemented in Gaussian 94. For a concise definition of the B3LYP functional see ref [19].

The theoretically predicted vibrational frequencies for all species have been calculated with the harmonic approximation. The deviation from experimentally obtained frequencies may partly be compensated by using scaling factors. They may also be different for various vibrational modes present in the molecule. [20]

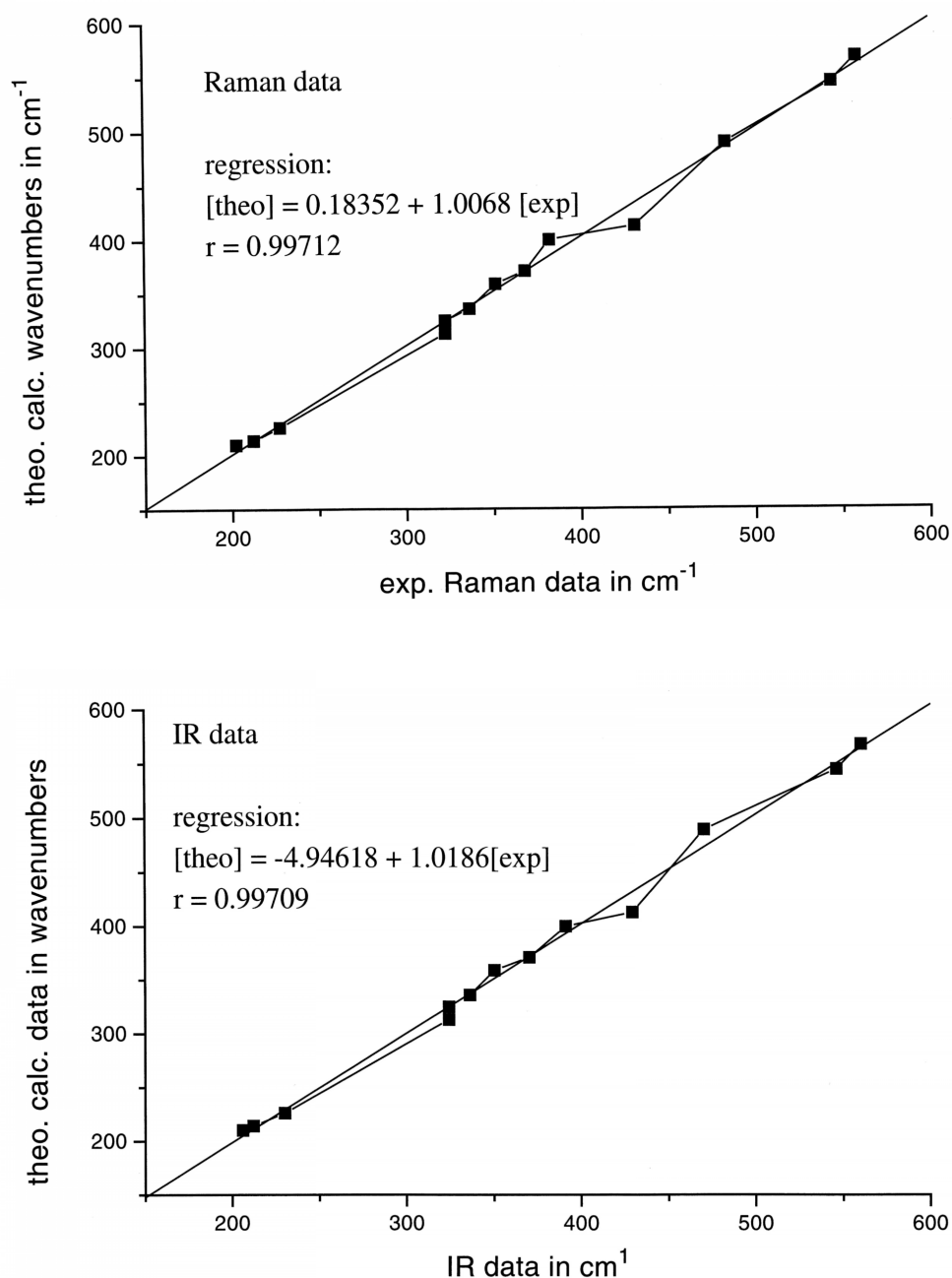
Bonding and electron transfer

A frequent object of quantum chemical studies, is the determination of the electronic configuration and net charge associated with each atom in a polyatomic molecule. Information concerning atomic charge distributions is important in rendering a chemical interpretation of the wave function, leading to a meaningful interpretation and an ability to draw analogies between different chemical phenomena.

Pearson has proposed the principle of hard and soft acids or bases (HSAB). [21] In adducts between hard acids and hard bases, the electrostatic interaction has been suggested to be the dominant source of stabilization. [22] In contrast, electron delocalization plays an important role in the interaction between soft bases and soft acids. Delocalization of electrons has been demonstrated to lead to the formation of new bonds. Hardness or softness as well as Lewis acid-bases strength of a species has often been discussed in terms of energy levels of the HOMO and LUMO.

In case of the reaction BI_3 and P_4Se_3 the LUMO (a_2'' , -0.09625 a.u.) of BI_3 represents an antibonding, over the entire molecule delocalized $p\pi$ molecular orbital with the largest coefficient for boron (Figure 4a). Figure 4b displays the HOMO (a_2' , -0.25532 a.u.) of P_4Se_3 indicating again a delocalized MO, except the coefficients in the linear combination for the apical P atom is zero. In the region of the HOMO, there is a second doubly degenerated molecular orbital (e , -0.25572 a.u.) which again describes the "lone pair electron density" within the P_3 and Se_3 unit, but again the coefficient on the apical P atom is zero (Figure 4b).

Figure 3 Linear regression for the Raman (a) and IR data (b) in comparison with the theoretically obtained data



Although this approach has been useful in understanding the chemical reactivity of molecules, in this case orbitals other than the HOMO and LUMO should also take part in a Lewis acid-base interaction and need to be considered. The unoccupied and occupied orbitals are delocalized over the entire molecule for both species, and they mix with each other induced by electron delocalization from the base (see HOMO of the adduct, Figure 4b,c). In addition, the mixing of the occupied and unoccupied orbitals weakens the conjugation between the $p\pi$ orbital of the boron and the iodine atoms,[22] making the boron orbital engage the bond formation with P_4Se_3 base.

From quantum mechanical computations, a set of delocalized molecular orbitals is obtained. Many properties can be explained more vividly within the picture of localized (bond) orbitals. Moreover, chemists are interested in chemical properties, which are in the quantum mechanical sense non-observables, such as partial charges, bond orders, etc. The calculation of these properties poses the problem of how the calculated electron density should be “distributed within a molecule”.

Natural bond orbital (NBO) analysis originated as a technique for studying hybridization, covalent and non-covalent effects in polyatomic wave functions.[23] NBO analysis is

Table 3 NPA charges and differences (in e)

	BI ₃	P ₄ Se ₃	Apical adduct	Δe	Basal adduct	Δe
B1	-0.4309		-0.7163	-0.2854	-0.7042	-0.2733
I1	0.1436		0.0511	-0.0925	0.0470	-0.0966
I2	0.1436		0.0519	-0.0917	0.0474	-0.0962
I3	0.1436		0.0512	-0.0924	0.0474	-0.0962
P1		0.1748	0.3674	0.1926	0.1954	0.0206
P2		0.0521	0.0657	0.0136	0.1431	0.0910
P3		0.0521	0.0655	0.0134	0.1431	0.0910
P4		0.0521	0.0663	0.0142	0.2597	0.2076
Se1		-0.1104	-0.0007	0.1097	-0.0926	0.0178
Se2		-0.1104	-0.0012	0.1092	-0.0926	0.0178
Se3		-0.1104	-0.0009	0.1095	0.0062	0.1166
Σe transfer P ₄ Se ₃ → BI ₃				-0.5620		-0.5623

based on a method for optimally transforming a given wave function into a localized form, corresponding to the one-center (“lone pairs”) and two-center (“bonds”) elements of the chemist’s Lewis structure picture.[24] All considered species were studied by means of NBO analysis.

It seems a bit surprising to find a negative charge on the boron atom (Table 3) and positive charges on the iodine atoms in BI₃ since the electronegativity (Allred-Rochow) would predict an opposite picture [$\epsilon(\text{I}) = 2.21$, $\epsilon(\text{B}) = 2.01$].[25] When studying the NBO analysis of BI₃ especially the natural bond orbitals (NBOs) which correspond to the widely used Lewis picture, in which two-center bonds and lone pairs are localized, three sigma bonds and one double bond are localized. The net linear NLMO/NPA bond order for the I atoms is 1.11 indicating a weak π bond character. The sigma bond system is only slightly polarized towards the iodine (Eq 1):

$$\varphi(\sigma\text{-bond}) = 0.68 h_{\text{B}} + 0.74 h_{\text{I}} \quad (1)$$

($h_{\text{B}} \approx sp^{1.75}$, $h_{\text{I}} \approx sp^{4.99}$)

In contrast to the sigma bond system, the π system is strongly polarized towards the iodine, however, the amount of π electron density transferred to the boron overcompensates

the sigma bond polarization leading to a negatively charged boron atom in BI₃ (Eq 2):

$$\varphi(\pi\text{-bond}) = 0.34 h_{\text{B}} + 0.94 h_{\text{I}} \quad (2)$$

($h_{\text{B}} \approx p^{1.00}$, $h_{\text{I}} \approx p^{1.00}$)

In addition, electron density from the iodine is back donated by intramolecular donor-acceptor interactions of the in plane p-lone pairs of the iodine with the antibonding sigma system (in the range of 10 kcal mol⁻¹). The partly occupied orbitals (φ_{BI}^*) lead to differences from the ideal Lewis-picture and thus, to a small non-covalent correction in the model of localized covalent bonds.

The other starting material P₄Se₃ represents a fairly covalent species with net linear NLMO/NPA bond order for all bonds between 0.91 (P-Se bonds) and 0.99 (P-P bonds). The NBO Lewis-picture shows four sigma bonds and one lone pair for each P atom as well as two sigma bonds and two lone pairs for each Se atom. The P-Se bonds are slightly polarized towards selenium [c.f. $\epsilon(\text{P}) = 2.06$, $\epsilon(\text{Se}) = 2.48$][25](Eq 3):

$$\varphi(\sigma\text{-bond}) = 0.67 h_{\text{P}} + 0.74 h_{\text{Se}} \quad (3)$$

($h_{\text{P}} \approx sp^{9.86}$, $h_{\text{Se}} \approx sp^{8.86}$)

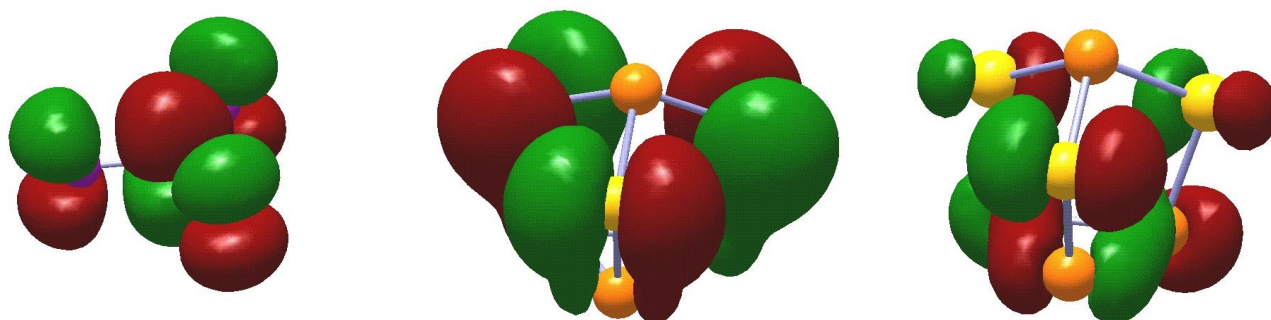
**Figure 4** (a) LUMO of BI₃; (b) HOMO of P₄Se₃; (c) HOMO-1 of P₄Se₃

Table 4 Total energies, electronic states and zero point vibrational energies of all considered species

	BI ₃	P ₄ Se ₃	Apical adduct	Basal adduct
Tot. Energy [a.u.]	-59.13760	-1393.58123	-1452.71202	-1452.71611
Electronic state	¹ A ₁ '	¹ A ₁	¹ A ₁	¹ A'
ZPE [kcal·mol ⁻¹]	2.97	6.13	9.56	9.61
S [cal·mol ⁻¹ ·K ⁻¹]	83.7	98.5	147.9	148.1
Δ ₍₃₎ H(OK) [kcal·mol ⁻¹]	-	-	4.27	1.71
Δ ₍₃₎ H(OK,zpe) [kcal·mol ⁻¹]	-	-	4.73	2.22
Δ ₍₃₎ H(298K) [kcal·mol ⁻¹]	-	-	5.43	2.89
Δ ₍₃₎ G(298K) [kcal·mol ⁻¹]	-	-	15.66	13.06

All lone pairs of P₄Se₃ can theoretically act as donor orbitals when a BI₃ molecule is approaching. There are two different types of P atoms: one apical and three basal P atoms. The lone pair on the P atoms represents an s-type orbital with a small amount of p-character (apical: 73% s + 27% p; basal: 74% s + 26% p) whereas for the Se atoms there are two different types of lone pairs: one s-type (80% s + 20% p) and one p-type (100% p) lone pair. Therefore, we have investigated three different types of adducts (Scheme 2).

- (i) (P₃Se₃)P_{ap}: → BI₃ (Figure 5a)
- (ii) (PSe₃P₂)P_{bas}: → BI₃ (Figure 2)
- (iii) (P₄Se₃)Se: → BI₃ (Figure 5b)

We were only able to localize two adduct structures: the basal and apical P-B adduct. In case of the Se-B adduct, the optimization led to separated molecules P₄Se₃ and BI₃. There is no minimum along the potential when approaching P₄Se₃ and BI₃ along the Se-B distance.

NBO analysis for the basal adduct, shows like both starting materials a fairly covalent molecule with only small amounts of polarization within the natural bond orbitals. The P-Se bonds remain almost unchanged in the adduct (see above, Eq 4):

$$\varphi(\sigma\text{-bond}) = 0.67 h_p + 0.74 h_{Se} \quad (4)$$

($h_p \approx sp^{10.11}$, $h_{Se} \approx sp^{9.48}$)

however, all P4-X (X = P3, P2, Se3, B) bonds possess about 10% more s character (ca. 20% s and 80% p) whereas the P2 and P3 bonds possess 90% p character and the remaining lone pair is made of 75% s character. The P-B sigma bond (Eq 5):

$$\varphi(\sigma\text{-bond}) = 0.79 h_p + 0.62 h_B \quad (5)$$

($h_p \approx sp^{1.34}$, $h_{Se} \approx sp^{3.38}$)

represents a strongly polarized bond with a net linear NLMO/NPA bond order of 0.70. The total valence of the boron atoms accounts to 3.6. Whereas the P4-Se3 bond remains almost unchanged (BO 0.96 vs. 0.94), the P4-P3 and P4-P2 bonds become less stable with bond orders of 0.83 (c.f. the value is 1.00 in the isolated P₄Se₃) which could explain the often observed ring-opening in basal adducts of P₄Se₃. As the adduct is a fairly covalent species, there are only weak intramolecular donor-acceptor interactions. The strongest donor-acceptor interactions (6-7 kcal mol⁻¹) describe the interaction of the p-type lone pairs localized on the I atoms with the antibonding B-Y sigma system (Y = I, P). This interaction introduces a small amount of B-I π bonding and weakens the B-Y sigma bonds. The hybridization on the boron atom can be described with close to sp³, (NBO finds 3.38 for B-P, 2.81 and 3.04 for B-I.)

The bond situation in the apical adduct is very similar to that of the basal adduct. There are two major differences. Firstly, now the P1-Se bond orbitals possess more s character in the hybrids of P1 (20%) and the bond order decreases to 0.91. Secondly, the P2-P3-P4 unit remains almost unchanged and more stable with P-P bond orders of 0.98.

It is interesting to note that in both P-B adducts almost the same amount of electron density is transferred from the P₄Se₃ unit to the BI₃ unit (Table 3), however, for the apical adduct the boron atom is slightly more negatively charged than in the basal adduct (-0.2854e vs. -0.2733e). Therefore, the three iodine atoms in the basal adduct possess a smaller positive charge than in the apical adduct leading to a total amount where both differences almost cancel each other. Comparing the charge difference of P1 in the apical adduct with the charge difference in the basal adduct it can be seen that P4 represents the slightly stronger donor than P1 which again explains why the adduct formation via P4 is favored over P1. The total amount for the charge transfer in this donor-acceptor complex amounts to 0.562 electrons. Only less than half of this value stems from the P donor atom.

Thermodynamics

At the considered level of theory (B3LYP) this adduct formation represents an endothermic reaction in the gas phase (Table 4, Scheme 3). In solid state, the lattice energy plays

Table 5 Selected structural data (distance in [Å], angle in [°]) X-ray data in brackets[29]

	BI ₃	P ₄ Se ₃	Apical adduct	Basal adduct
d (B1-I1)	2.142		2.248	2.263
d (B1-P1)			2.029	
d (B1-P4)				2.016
d (P1-Se1)		2.312 [2.30(4)]	2.308	2.327
d (P2-Se1)		2.309 [2.30(4)]	2.296	2.300
d (P4-Se3)		2.309	2.296	2.291
< (Se1-P1-Se2)		99.7 [97.5(9)]	102.9	99.9
< (P2-Se1-P1)		99.5 [100(1.3)]	95.9	100.3
< (P4-Se3-P1)		99.5	95.9	95.4
< (P4-P2-P3)		60.0 [60(0.8)]	60.0	59.0
< (I1-B1-P1)			105.1	
< (I1-B1-P4)				102.8

an important role to stabilize this adduct and therefore needs to be considered. For chemically similar compounds the lattice energy lies in the range of 25 ± 5 kcal mol⁻¹, which explains the stability of the formed adducts in the solid state.[26] In addition, the reaction entropy has a large influence on the reaction (Table 4). Only a small difference in the free molar enthalpy of about 2.6 kcal mol⁻¹ in favor of the basal adduct formation was found which is in agreement with our experiential finding.

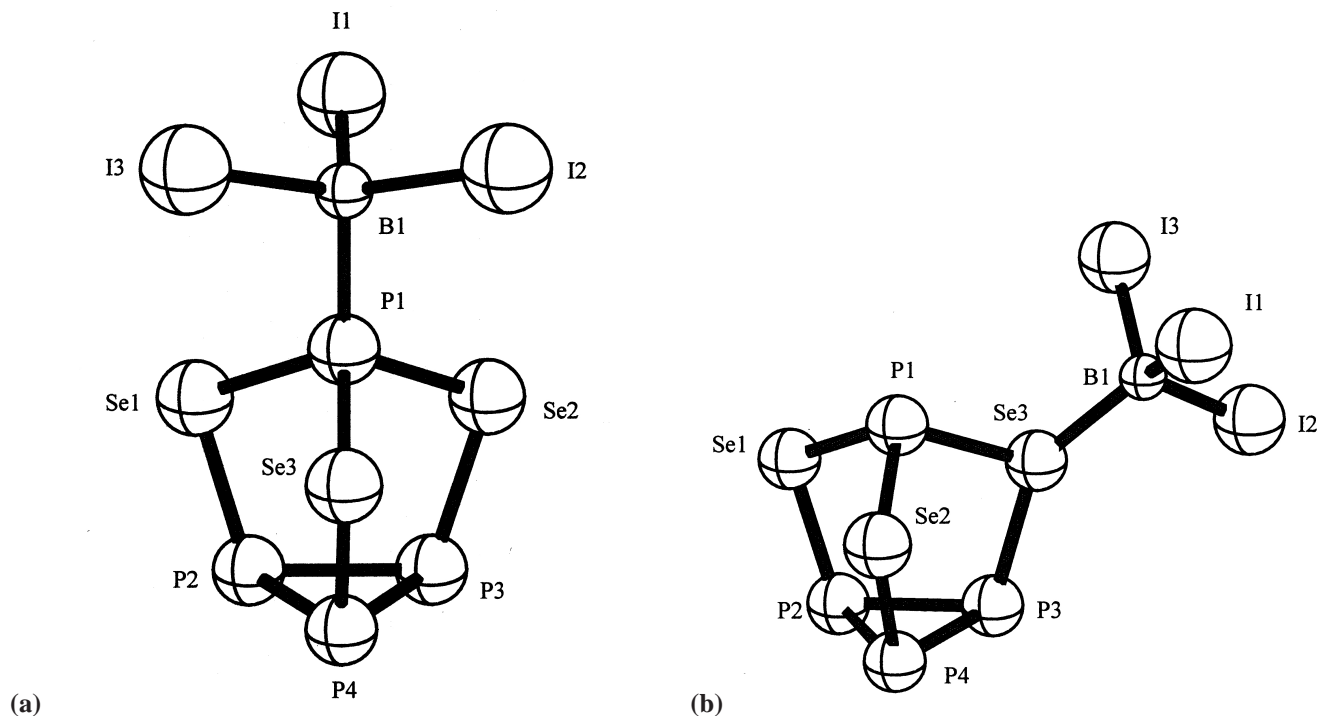
The adduct formation of (P₄Se₃)·(BI₃)(s) is assumed to be a slightly exothermic reaction although these adducts are not

stable in the gas phase. Both the electronic situation and the thermodynamics should favor the formation of the basal P-B adduct (Scheme 3).



Structure

Structural parameters obtained from density functional theory (B3LYP) calculations for main group element compounds

**Figure 5** The apical P-B adduct (a) and the Se-B adduct (b)

are in good agreement with those obtained from experimental studies. It is generally agreed that this level is sufficient to predict the relative stability of the isomers and will give reasonably reliable results for the equilibrium structures.[27]

In Table 5 selected structural data of the starting material, the basal and apical adducts are summarized. The molecular structures of all species were fully optimized at B3LYP level and are shown in Figure 2 and Figure 5. Both P-B adducts were shown to possess stable minima at B3LYP level (no imaginary frequencies) whereas no stable minimum could be found for a Se-B adduct. The apical adduct possesses C_{3v} symmetry like the P_4Se_3 adduct, but in the basal adduct symmetry is lowered to C_s symmetry. All structural parameters are in good agreement with those of other covalent Se-P compounds and P-B adducts.[3],[11] A very good agreement of the structural data was found for the starting material P_4Se_3 (Table 5). As expected for these covalently bound P-B adducts both $(P_4Se_3) \cdot (BI_3)$ adducts display only a slight change in geometry compared with the starting material P_4Se_3 . The Se-P bond distances are slightly shorter in the adducts which stems from orbital contraction due to the increased positive charge in the P_4Se_3 unit.

The estimated B-P bond distances in both $(P_4Se_3) \cdot (BI_3)$ adducts of 2.029 and 2.016 Å are comparable with that in $(Br_3P) \cdot (BBr_3)$ (2.014 Å),[3] however, significantly longer than in $[(CH_3)_3P] \cdot (BI_3)$ (1.918 Å),[28] corresponding to a bond order less than 1 (see section bonding and electron transfer). This can be explained by the larger electron transfer within $[(CH_3)_3P] \cdot (BI_3)$ due to the positive inductive effect of the methyl groups in $[(CH_3)_3P] \cdot (BI_3)$ whereas in case of $(Br_3P) \cdot (BBr_3)$ and $(P_4Se_3) \cdot (BI_3)$ bromine and selenium are more electronegative than P and therefore decrease the donor strength of the P atom.

The computed B-I bond distances in both $(P_4Se_3) \cdot (BI_3)$ adducts of 2.248 and 2.263 Å are significantly longer than in the isolated BI_3 (2.142 Å) and comparable with 2.272 Å in $[(CH_3)_3P] \cdot (BI_3)$, corresponding to a bond order slightly less than 1. As indicated by an NBO analysis, there is a significant interaction of the lone pairs on all iodine atoms of BI_3 with the unoccupied, antibonding σ^* orbital of the B-I bonds and a considerable π interaction perpendicular to the BI_3 plane. Both effects account for rather short B-I bonds in BI_3 . This intramolecular stabilization decreases dramatically in the adducts and causes longer B-I bond distances as a considerable amount of electron density is transferred from the P_4Se_3 unit to the BI_3 unit to eliminate the electron deficit on the boron center.

Conclusions

The structure, bonding and normal modes of different $(P_4Se_3) \cdot (BI_3)$ adducts have been calculated, discussed and compared with the experiment. The mean deviation in the wave numbers for the basal $(P_4Se_3) \cdot (BI_3)$ adduct is 7 cm^{-1} with a maximum deviation of 18 cm^{-1} . Comparison between

experiment and theory led to the identification of the experimentally formed adduct as a basal P-B adduct.

The adduct formation of $(P_4Se_3) \cdot (BI_3)(s)$ is a slightly exothermic reaction although these adducts are not stable in the gas phase. Both the electronic situation and the thermodynamics should favor the formation of basal P-B adduct. In this donor-acceptor interaction 0.56e are transferred from the (P_4Se_3) donor to (BI_3) acceptor.

Acknowledgement We gratefully acknowledge financial support of the Fonds der Chemischen Industrie and the University of Munich. We also wish to thank G. Spieß for Raman spectroscopic measurements and the Leibnitz Rechenzentrum for a generous allocation of CPU time. In addition we would like to thank Prof. Konstantin Karaghiosoff for helpful advice. We thank both referees for most valuable comments.

References

1. Aubauer, Ch.; Klapötke, T. M.; Schulz, A. *Int. J. Vib. Spectrosc.* **1999**, 3, ed. 2, sect. 4.
2. Aubauer, Ch.; Engelhardt, G.; Klapötke, T. M.; Schulz, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1729.
3. (a) Aubauer, Ch.; Engelhardt, G.; Klapötke, T. M.; Noeth, H.; Schulz, A.; Warchold, M. *J. Chem. Soc., Dalton Trans.* submitted; (b) Aubauer, Ch.; Klapötke, T.M.; Schulz, A. *J. Chem. Soc., Dalton Trans.* submitted.
4. Payne, D. S. *Quart. Rev.* **1961**, 15, 173.
5. Holmes, R. R. *J. Chem. Educ.* **1963**, 40, 125.
6. Armington, A. F.; Weiner, J. R.; Moats, G. H. *Inorg. Chem.* **1966**, 5, 483.
7. Parry, R. W.; Bissot, T. C. *J. Am. Chem. Soc.* **1956**, 78, 1524.
8. Cook, D. *Can. J. Chem.* **1963**, 41, 522.
9. Frenking, G.; Fau, S.; Marchand, C. M.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, 119, 6648.
10. (a) Burns, G. R. *J. Phys. Chem. Solids* **1986**, 47, 681. (b) Burns, G. R.; Clark, R. J. H. *J. Phys. Chem. Solids* **1986**, 47, 1049. (c) Burns, G. R.; Rollo, J. R. *J. Phys. Chem. Solids* **1987**, 48, 347. (d) Burns, G. R.; Rollo, J. R.; Clark, R. J. H. *Inorg. Chem.* **1986**, 25, 1145. (e) Cyvin, S. J.; Brunvoll, J. Cyvin, B. N. *Z. Naturforsch.* **1980**, 35a, 1062. (f) Cyvin, S. J.; Cyvin, B. N. *Z. Naturforsch.* **1981**, 36a, 774. (g) Bues, W.; Somer, M.; Brockner, W. *Z. Naturforsch.* **1980**, 35b, 1063.
11. Nowotnick, H.; Stumpf, K.; Blachnik, R.; Reuter, H. Z. *Anorg. Allg. Chem.* **1999**, 625, 693.
12. Goh, L. Y.; Chen, W.; Wong, R. C. S. *Z. Organometallics* **1999**, 18, 306.
13. Wachter, J. *Angew. Chem. Int. Ed. Engl.* **1998**, 37, 750.
14. Durig, J. R.; Riethmiller, S.; Kalasinsky, V. F.; Odom, J. D. *Inorg. Chem.* **1974**, 13, 2729.
15. Odom, J. D.; Riethmiller, S.; Witt, J. D.; Durig, J. R. *Inorg. Chem.* **1973**, 12, 1123.

16. *Gaussian 94*, Revision B.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. A.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, 1995.
17. Schwertfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.* **1989**, *91*, 1762.
18. Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Am. Chem. Soc.* **1991**, *113*, 1602.
19. (a) Bauschlicher, C. W.; Partridge, H. *Chem. Phys. Lett.* **1994**, *231*, 277. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (e) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
20. (a) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986; p 236. (b) Klapötke, T. M.; Schulz, A. *Quantenchemische Methoden in der Hauptgruppenchemie*, Spektrum: Heidelberg, 1996. (b) Otto, M.; Lotz, S. D.; Frenking, G. *Inorg. Chem.* **1992**, *31*, 3647.
21. (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6801.
22. Hirao, H.; Omoto, K.; Fujimoto, H. *J. Phys. Chem. A* **1999**, *103*, 5807.
23. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
24. Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.
25. Holleman, A. F.; Wiberg, E.; Wiberg, N. *Lehrbuch der Anorganischen Chemie*; 101. Aufl., Walter de Gruyter: Berlin, 1995; p 144.
26. Rossini, F. D.; Wagman, D. D.; Evans, W. H.; Levine, S.; Jaffe, I. *Selected Values of Chemical Thermodynamic Properties*; United States Government Printing Office: Washington, D.C., 1952.
27. Klapötke, T. M.; Schulz, A. *Quantum Chemical Methods in Main-Group Chemistry*; Wiley & Sons: Chichester, 1998.
28. Black, D. L.; Taylor, R. C. *Acta Cryst.* **1975**, *B31*, 1116.
29. Keulen, E., Vos, A. *Acta Cryst.*, **1959**, *12*, 323.