Se_2NBr_3, Se_2NCl_5, $Se_2NCl_6^-$: New Nitride Halides of Selenium(III) and Selenium(IV)

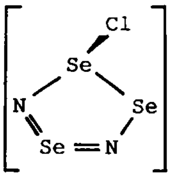
Carsten Lau, Bernhard Neumüller, Wolfgang Hiller, Martin Herker, Sergei F. Vyboishchikov, Gernot Frenking and Kurt Dehnicke*

Abstract: Se_2NBr_3, a planar molecule shaped liked dividers, was formed by the reaction of $SeBr_4$ with $N(SiMe_3)_3$, which reduced the selenium to the trivalent state. Under the same conditions, Se_2NCl_5 was obtained by the reaction of $SeCl_4$ with $N(SiMe_3)_3$, retaining the tetravalent state of selenium. The molecule is formed by two edge-sharing pseudotrigonal bipyramids with selenium as their central atoms. Se_2NCl_5 reacts with PPh_4Cl to form the $Se_2NCl_6^-$ ion by the addition of a Cl^- ion to only one of the two selenium atoms, resulting in pseudooctahedral coordination of this atom. Ab initio calculations for all the compounds reported confirm the experimentally determined structures.

Keywords
ab initio calculations · crystal structure · halogen compounds · nitrides · selenium compounds

Introduction

The chemistry of selenium and tellurium nitrogen compounds has excited great interest lately because of new synthetic possibilities, versatile coordination behaviour, and often unusual bonding situations.[1-3] The search for alternatives to tetraselenium tetranitride, limited in its synthetic use because of its explosive character and extreme insolubility, is another reason for the generation of new selenium and tellurium nitride halides.[4,5] The trivalent selenium compound Se_2NCl_3 (1), which is readily soluble in organic solvents,[6] ionic derivatives of 1, such as $[Se_2NCl_2]^+[GaCl_4]^-$ (2), with a U-shaped cation[6] like that of tetrachloroferrate(III) salt,[7] and $[Se_2NCl_2]^+[SbCl_6]^-$ (3),[8] with an S-shaped cation, have already been published. The easily accessible 3 has already been used in the synthesis of selenium-containing heterocycles.[9] Furthermore, $[Se_2NCl_4]^+[AsF_6]^-$ (4),[10] obtained from $[SeCl_3]^+[AsF_6]^-$ and tris(trimethylsilyl)amine, is known as well as 5,[11] which contains a planar Se_3N_2 five-membered ring, the cation of which was characterized by force-field calculations.[12] However, nitride halides of tellurium were not known until recently.[13] The syntheses and structures of $Te_{11}N_6Cl_{26}$,[14] containing the planar bicyclic unit Te_5N_3 as structural motif, and the ionic compound $[Te_4N_2Cl_8][AsF_6]_2$,[15] the cation of which possesses a planar Te_2N_2 four-membered ring, have only just been published.



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We report here two new molecular nitride halides of selenium(III) and selenium(IV), Se_2NBr_3 (6) and Se_2NCl_5 (7), and the salt $PPh_4^+[Se_2NCl_6]^-$, derived from 7. Thus, a direct comparison of the molecule 7, the related cation 4 and the anion $[Se_2NCl_6]^-$ (8) is possible.

Results and Discussion

A suspension of selenium tetrabromide in dichloromethane reacts with tris(trimethylsilyl)amine at 20 °C to form a red solution [Eq. (a)]. From this solution 6 is separated as metallic reddish-brown moisture-sensitive crystals, which decompose explosively on being subjected to mechanical stress in the dry state.

$$2\,SeBr_4 + N(SiMe_3)_3 \longrightarrow \underset{6}{Se_2NBr_3} + 3\,BrSiMe_3 + Br_2 \qquad (a)$$

According to the crystal structure analysis (Table 1), 6—like the corresponding chloro compound 1—forms planar molecules with C_s symmetry and the shape of dividers (Fig. 1). Since the Se–Br bonds are of different length, C_{2v} symmetry is obtained only approximately. The unit cell contains two unique molecules which are only slightly different (Table 2). The two Se–N bonds are nearly of equal length. The average value of 174 pm is significantly shortened compared with the expected value of a Se–N single bond (186 pm[16]), indicating π-bond participation as

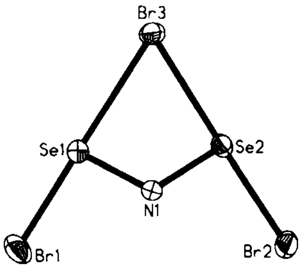

Fig. 1. Experimentally observed geometry of one of the two symmetry-independent molecules of 6.

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[*] Prof. Dr. K. Dehnicke, Dipl.-Chem. C. Lau, Priv.-Doz. Dr. B. Neumüller, Dipl.-Chem. S. F. Vyboishchikov, Prof. Dr. G. Frenking
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)
Fax: Int. code +(6421)28-8917
Prof. Dr. W. Hiller, Dipl.-Chem. M. Herker
Anorganisch-chemisches Institut der Technischen Universität München
Munich (Germany)

Table 1. Crystallographic data for compounds **6**, **7**, **8a** and **8b**.

	6	**7**	**8a**	**8b**
Formula	Se_2NBr_3	Se_2NCl_5	$C_{48}H_{40}N_2Cl_{12}P_2Se_4 \cdot 2CH_2Cl_2$	$C_{48}H_{40}N_2Cl_{12}P_2Se_4$
M_r	411.64	349.18	1617.95	1448.08
T (°C)	−60	−60	−80	−50
space group	$Pca2_1$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (pm)	1347.0(1)	811.3(1)	1135.5(1)	1237.0(2)
b (pm)	840.5(1)	1231.5(2)	1188.0(1)	1236.6(2)
c (pm)	1184.4(1)	1603.4(2)	1373.9(1)	1847.3(4)
α (°)			88.46(1)	88.07(1)
β (°)		94.92(1)	67.70(1)	87.55(1)
γ (°)			66.48(1)	85.44(1)
V (Å^3)	1340.9(2)	1596.1(4)	1555.2(3)	2813.0(9)
Z	8	8	1	2
ρ_{calcd} (g cm^{-3})	4.078	2.906	1.727	1.710
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Siemens P4
Irradiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
μ (cm^{-1})	288	108.4	31.3	32.7
2θ (°)	5.6–50.0	3.0–27.0	4.6–50.0	2.0–50.0
Scan type	ω	ω	ω	ω
Measured reflns	2112	3557	5703	11230
Independent reflns	966	3444	5453	9756
Observed reflns with $F_0 > 4\sigma(F_0)$	844	2739	4311	6629
Absorption correction	empirical (ψ-scans), extinction correction	empirical (DIFABS)	empirical (ψ-scans)	numerical
Refined parameters	109	145	335	614
Resd electron density (e Å^{-3})	−0.63; 0.65	−0.57; 0.63	−0.52; 0.43	−0.43; 0.53
R_1	0.021	0.026	0.027	0.032
wR_2 (all data)	0.048	0.061	0.068	0.069

Table 2. Experimentally determined and theoretically calculated (at MP2) bond lengths (pm) and bond angles (°) of Se_2NBr_3 (**6**), as well as interatomic contacts Se···Br < 375 and Br···Br < 370 pm. Calculated partial charges q taken from the NBO population analysis. Bond orders P according to Wiberg.

	Experimental		Calculated	Se···Br and Br···Br contacts	
	molecule 1	molecule 2			
Se1–N1	174.8(9)	175(1)	175.3	Se4a···Br2	338.8(2)
Se2–N1	173(1)	174(1)	175.3	Br6···Se2a	338.9(2)
Se1–Br1	234.7(2)	234.9(2)	230.5	Br2···Se1b	353.9(2)
Se2–Br2	242.7(2)	243.2(2)	230.5	Br3···Se4b	349.2(2)
Se1–Br3	284.9(2)	284.9(2)	262.4	Se3···Br3	353.6(2)
Se2–Br3	270.3(2)	269.4(2)	262.4	Br1···Br3c	348.6(2)
Se1-Br3-Se2	65.99(5)	66.04(5)	70.2	Br1···Br6a	356.3(2)
Se1-N1-Se2	121.0(6)	120.1(6)	118.8	Br2···Br5d	354.1(2)
Br1-Se1-N1	94.5(3)	94.1(3)	93.9	Br4···Br5e	349.1(2)
Br2-Se2-N1	92.0(3)	91.8(3)	93.9		
Br3-Se1-N1	83.9(3)	84.45(3)	85.5		
Br3-Se2-N1	88.9(3)	91.8(3)	85.5		
Br1-Se1-Br3	175.21(6)	178.16(9)	179.5		
Br2-Se2-Br3	175.49(9)	174.75(6)	179.5		
q(Se1)			+1.05	P(Se1–N1)	1.16
q(N1)			−1.01	P(Se1–Br1)	0.71
q(Br3)			−0.47	P(Se1–Br3)	0.29
q(Br1)			−0.31		

Abstract in German: *Se_2NBr_3 entsteht durch Redox-Reaktion aus $SeBr_4$ und $N(SiMe_3)_3$ in Dichlormethan. Nach der Kristallstrukturanalyse bildet diese Selenverbindung planare Moleküle in der Gestalt eines Zirkels. Dagegen entsteht unter denselben Bedingungen aus $SeCl_4$ das Nitridchlorid des vierwertigen Selens Se_2NCl_5, in dessen Molekülstruktur die Selenatome ψ-trigonal-bipyramidal umgeben sind. Mit PPh_4Cl reagiert es unter Bildung des $Se_2NCl_6^-$-Ions, in dem eines der Selenatome nun ψ-oktaedrische Umgebung erreicht. Ab-initio-Rechnungen an Se_2NCl_5 und $Se_2NCl_6^-$, in die auch das bekannte Kation $Se_2NCl_4^+$ einbezogen wird, bestätigen die experimentell ermittelten Strukturen.*

in **1**. At 234.7 and 242.7 pm, the two terminal Se–Br bonds are in good agreement with the terminal Se–Br bonds of 236 pm in the heterocubane structure of $[SeBr_4]_4$,[17] while the Se-bridging Br bond lengths of 284.9 and 270.3 pm in **6** are distinctly shorter than the Se–Br bonds of the μ_3-bridging Br atoms in $[SeBr_4]_4$ (298 pm). The packing of **6** in the unit cell is shown in Figure 2. A transfer to the centrosymmetric space group *Pbcm* is not possible because of the absence of mirror symmetry perpendicular to the *c* axis.

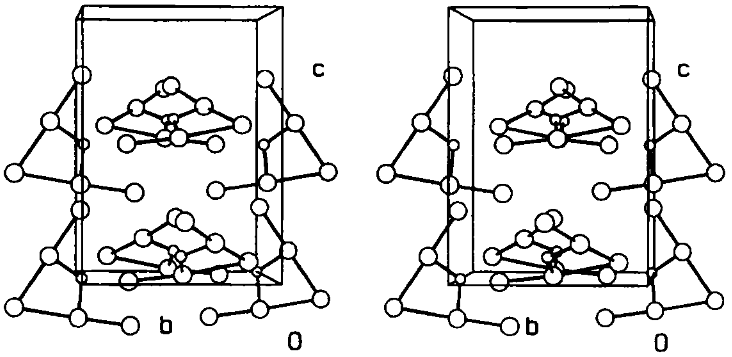

Fig. 2. Unit cell of **6** viewed along the *a* axis (ORTEP, ref. [35]).

The nitride chloride **7** with tetravalent selenium has been obtained in previous experiments by treatment of selenium tetrachloride with tris(trimethylsilyl)amine in dichloromethane at temperatures between 20 °C and 0 °C [Eq. (b)].[18] If reaction (b)

$$2\,SeCl_4 + N(SiMe_3)_3 \longrightarrow \underset{\mathbf{7}}{Se_2NCl_5} + 3\,ClSiMe_3 \tag{b}$$

is carried out in boiling dichloromethane, the nitride chloride **1** described earlier[6] will be generated. Compound **7** is reasonably soluble in dichloromethane and soluble in acetonitrile; it forms pale pink, moisture-sensitive crystals. The ^{77}Se NMR spectrum of **7** in acetonitrile shows a singlet at $\delta = 1294$; in

Table 3. Experimentally determined and theoretically calculated (at MP2) bond lengths (pm) and bond angles (°) of the cation of **4** [9], of **7**, and of the anions of **8a**, **8b**. Calculated partial charges *q* taken from the NBO population analysis. Bond orders *P* according to Wiberg.

	$Se_2NCl_4^+$ (**4**)		Se_2NCl_5 (**7**)		$Se_2NCl_6^-$ (**8a, 8b**)	
	experimental	calculated	experimental [a]	calculated	experimental [a]	calculated
Se1–N1	174.1(11)	175.8	177.1(3)	177.0	179.8(3)	184.7
Se2–N1	176.0(11)	175.8	175.9(3)	177.0	174.4(3)	171.5
Se1–Cl1			273.5(1)	264.3	269.4(1)	271.4
Se2–Cl1			275.4(1)	264.3	264.9(1)	260.5
Se1–Cl11	216.9(4)	218.7	219.1(1)	222.4	234.2(1)	237.7
Se1–Cl12	214.1(4)	213.6	217.8(1)	222.6	221.0(1)	223.2
Se2–Cl21	216.9(4)	218.7	217.5(1)	222.4	224.9(1)	229.3
Se2–Cl22	214.1(4)	213.6	218.6(1)	222.6	223.1(1)	240.8
Se1–Cl3					250.1(1)	242.6
Se1-Cl1-Se2			66.01(3)	69.7	67.85(3)	63.5
Se1-N1-Se2	117.6(2)	123.0	115.8(2)	117.1	114.8(2)	116.7
Cl11-Se1-N1	103.6(4)	105.1	103.2(1)	105.4	97.5(1)	92.2
Cl12-Se1-N1	92.8(4)	94.3	91.5(1)	89.7	91.6(1)	92.2
Cl21-Se2-N1	102.9(4)	105.1	104.0(1)	105.4	105.0(1)	113.2
Cl22-Se2-N1	93.4(4)	94.3	92.2(1)	89.7	91.5(1)	89.8
Cl1-Se1-N1			89.0(1)	86.5	87.4(1)	83.9
Cl1-Se2-N1			88.7(1)	86.5	89.8(1)	89.9
Cl3-Se1-N1					95.8(1)	92.2
Cl1-Se1-Cl11			90.42(4)	91.3	90.63(3)	90.3
Cl1-Se1-Cl12			173.16(4)	172.1	177.82(3)	174.7
Cl1-Se2-Cl21			93.07(4)	91.3	91.70(4)	92.7
Cl1-Se2-Cl22			170.75(4)	172.1	173.16(4)	173.3
Cl11-Se1-Cl12	98.5(2)	100.9	96.83(5)	96.4	91.21(3)	90.4
Cl21-Se2-Cl22	98.2(2)	100.9	95.68(5)	96.4	93.46(4)	93.6
Cl3-Se1-Cl11					166.51(3)	177.1
Cl3-Se1-Cl12					89.52(3)	90.4
Cl3-Se1-Cl1					88.87(3)	89.0
q(Se1)		+1.35		+1.31		+1.23
q(Se2)		+1.35		+1.31		+1.26
q(N1)		−1.20		−1.18		−1.08
q(Cl1)				−0.50		−0.50
q(Cl3)						−0.48
q(Cl11)		−0.165		−0.25		−0.42
q(Cl12)		−0.085		−0.22		−0.26
q(Cl21)		−0.165		−0.25		−0.41
q(Cl22)		−0.085		−0.22		−0.34
P(Se1–N1)		0.99		0.99		0.79
P(Se2–N1)		0.99		0.99		1.24
P(Se1–Cl1)				0.25		0.21
P(Se2–Cl1)				0.25		0.29
P(Se1–Cl3)						0.47
P(Se1–Cl11)		0.81		0.72		0.52
P(Se1–Cl12)		0.90		0.75		0.72
P(Se2–Cl21)		0.81		0.72		0.50
P(Se2–Cl22)		0.90		0.75		0.63

[a] Average values of the symmetry-independent species.

dichloromethane there is a singlet at $\delta = 1263$. Thus, the selenium atoms are distinctly more deshielded than in **1** ($\delta = 961$), but less than in the cations of **2** ($\delta = 1699$)[6] and **4** ($\delta = 1787$ in acetonitrile).[10]

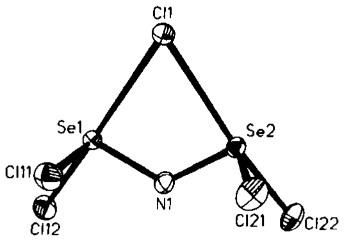

Fig. 3. Experimentally observed geometry of one of the two symmetry-independent molecules of **7**.

According to the crystal structure analysis the unit cell of **7** contains two unique but nearly identical molecules (average values in Table 3). The molecules possess almost planar Se_2NCl four-membered rings. The selenium atoms have a distorted ψ-trigonal bipyramidal environment with Cl1, Cl12 and Cl22 in axial positions with Cl-Se-Cl bond angles of 172.4 and 167.7°, respectively (Fig. 3). N1, Cl11 and Cl21 occupy the equatorial positions together with the sterically active lone pair. Naturally, the Se–Cl1 distances (274.5 pm) are considerably longer than those for the terminal chlorine atoms (218.3 pm, Table 3) because of the bridging function of Cl1. This corresponds well with the conditions in the heterocubane structure of $[SeCl_4]_4$,[19] in which Se–Cl distances of 216.4 pm for the terminal chlorine atoms and 279.4 pm for the bridging chlorine atoms have been measured. The distances between the selenium atoms and the axially arranged chlorine atoms in **7** are no longer, owing to their *trans* position to the long Se–Cl1 bond. At 177.1 and 175.9 pm, the two Se–N bonds of **7** are almost equivalent and are comparable to those of **1**[6] and **6**. The bond angle at the N atom, 115.8°, lies between sp^2 and sp^3 hybridization.

In the IR spectrum we observe the vibration ν_{asym} Se-N-Se as a doublet at 829/816 cm^{-1} because of the two unique molecules. In **1** this band has been observed at 830 cm^{-1}[6] and in the nitride bromide **6** at 831 cm^{-1}, reflecting the similarities of the bond parameters of the Se-N-Se bridges of these compounds.

The packing of the molecules **7** in the unit cell (Fig. 4) signifies a loose association to tetramers through Se···Cl contacts in which only the bridging Cl atoms Cl1 and Cl2 of the two unique molecules participate. There is only one interatomic contact from Cl1 to Se4 (306.8 pm), while Cl2 possesses the two longer contacts Cl2···Se1a of 315.8 pm and Cl2···Se3a of 311.6 pm. But all these contacts are significantly shorter than the sum of the van der Waals radii of 365 pm.[20]

Because of the fivefold coordination at the selenium atoms of **7** and their association in the solid state, Lewis acidity was expected. It was confirmed by the reaction of **7** with tetraphenylphosphonium chloride in dichloromethane at 0 °C according to Equation (c).

$$\mathbf{7} + PPh_4Cl \rightarrow \underset{\mathbf{8b}}{PPh_4[Se_2NCl_6]} \qquad \text{(c)}$$

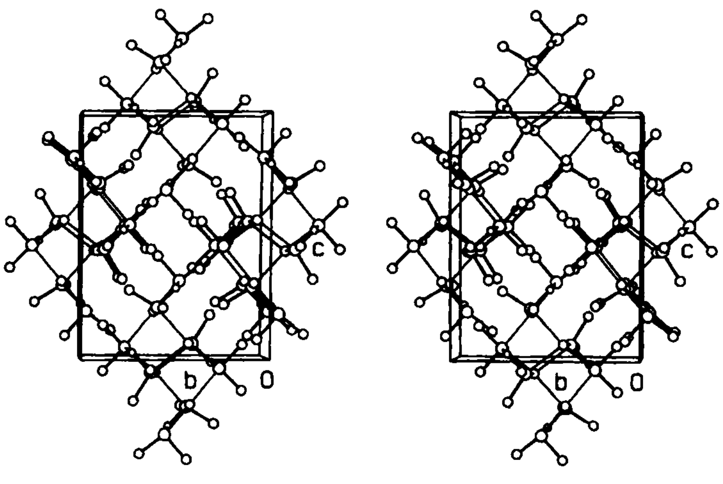

Fig. 4. Unit cell of **7** viewed along the *a* axis.

Depending on the crystallizing conditions (see Experimental Procedure) **8b** can also be obtained with one molecule of dichloromethane included per formula unit as **8a**. Like the solvent-free compound **8b**, **8a** crystallizes in the space group $P\bar{1}$. Table 4 contains bond lengths and angles determined by crystal structure analysis of the anion of **8a**.

Table 4. Selected bond lengths (pm) and bond angles (°) in **8a** taken from the X-ray structure analysis.

Se1–N1	179.9(3)	Se1-Cl1-Se2	68.23(3)
Se2–N1	174.2(3)	Se1-N1-Se2	114.7(1)
Se1–Cl1	273.0(1)	Cl11-Se1-N1	97.92(8)
Se2–Cl1	258.14(8)	Cl12-Se1-N1	92.44(9)
Se1–Cl11	232.72(7)	Cl21-Se2-N1	104.74(8)
Se1–Cl12	219.7(1)	Cl22-Se2-N1	90.75(8)
Se2–Cl21	226.06(9)	Cl1-Se1-N1	85.53(9)
Se2–Cl22	227.4(1)	Cl1-Se2-N1	91.44(8)
Se1–Cl3	251.72(8)	Cl3-Se1-N1	95.63(8)
Se2···Cl1a	309.67(9)	Cl1-Se1-Cl11	89.03(3)
Se2···Cl3a	327.4(1)	Cl1-Se1-Cl12	177.74(3)
		Cl1-Se2-Cl21	92.62(3)
		Cl1-Se2-Cl22	172.99(4)
		Cl11-Se1-Cl12	92.24(3)
		Cl21-Se2-Cl22	93.26(4)
		Cl3-Se1-Cl11	166.15(3)
		Cl3-Se1-Cl12	90.03(3)
		Cl3-Se1-Cl1	89.17(3)

The yellow, crystalline and moisture-sensitive substances are stable at −20 °C for a long time, and at least for a few hours at 0 °C. According to the X-ray structure determination, the additional chloride ion is surprisingly coordinated at one of the selenium atoms, preserving the Se-Cl-Se bridge of **7** (Fig. 5). In **8a**, two $Se_2NCl_6^-$ ions are associated to a centrosymmetric dimer by two pairs of Se···Cl contacts of 309.7 and 327.4 pm. This dimer has the shape of a distorted double cube with two corner atoms missing. These Se···Cl contacts are significantly shorter than the sum of the van der Waals radii of 365 pm.[20] The structure of **8b** contains two unique formula units, the $Se_2NCl_6^-$ ions of which do not differ much from each other and from the anion in **8a**. A significant difference arises only for the Se···Cl contacts of one of the unique $Se_2NCl_6^-$ ions, which amount to 326.6 pm for Se2···Cl1a and to 323.2 pm for Se2···Cl3a. In contrast, the contacts Se2···Cl1 (306.1 pm) and Se2···Cl3a (328.3 pm) for the second individual are comparable to those in the anion of **8a**. In an idealized way the structure of the distorted double cubes of the anions of **8a** and **8b** is realized in δ- and γ-TeI_4.[21] The addition of the chloride ion Cl3 at Se1 causes an elongation of the distance Se1–N1, leading to an asymmetric Se-N-Se bridge with mean Se–N bond lengths of 174.4 and 179.8 pm. A loss of resonance energy owing to this asymmetry could be a reason for the instability of **8**.

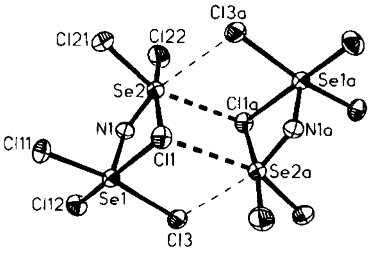

Fig. 5. Experimentally observed geometry of the centrosymmetric moiety $[Se_2NCl_6^-]_2$ of **8a**.

Figure 6 shows the unit cell of **8b** with the packing of the centrosymmetric dimers $[Se_2NCl_6]_2^{2-}$ and the PPh_4^+ ions. The anions are strung along the *b* axis, with only van der Waals contacts between them. This column-like arrangement is separated from the next chain of anions by PPh_4^+ ions.

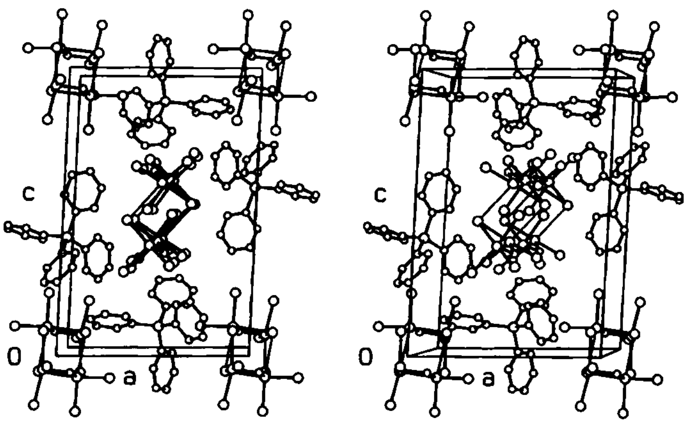

Fig. 6. Unit cell of **8b** viewed along the column-like anion structure running parallel to the *b* axis.

Comparing the structures of the cation of **4**, the molecule of **7** and the corresponding anion of **8**, a remarkably similarity is observed in the average Se–N distances of 175.1 to 177.1 pm. The bond angles around the N atom also show only a slight narrowing from 117.6° to 114.8°. The mean values of the terminal Se–Cl bonds increase only from 215.5 pm to 217.9 pm in **4** to **7**, while the anions of **8a** and **8b** show a drastic elongation to 231.5 pm. Thus the antibonding negative charge in **8a** and **8b** is distributed mainly over the periphery; this is in agreement with partially electrostatic bonds.

In order to analyze the bonding situation of the newly synthesized compounds Se_2NBr_3 (**6**), Se_2NCl_5 (**7**) and $Se_2NCl_6^-$ (**8**), we carried out quantum mechanical ab initio calculations at the MP2 level of theory[22] for **6**–**8a,b** and for the cation $Se_2NCl_4^+$ in **4**.[23] The calculated bond lengths and bond angles are shown in Tables 2 and 3. There is generally a good agreement between the theoretically predicted values and the experimental results obtained from X-ray structure analysis. The differences between the theoretically and experimentally obtained bond lengths may result partly from distortions of the molecules caused by intermolecular interactions in the crystals. This holds true in particular for the bridging halogen atoms, for which the calculated bond lengths are clearly shorter than the experimentally observed values.

The calculated structure of **6** has C_{2v} symmetry, while **4** and **7** have C_s symmetry. The pseudoaxial and equatorial Se–Cl bond lengths of **7** are nearly the same, while the corresponding Se–Cl distances of **4** show larger differences. The theoretically predicted equilibrium geometry of the anion of **8a** and **8b** is particularly interesting. The geometry optimization at the MP2 level[24] gives a structure with C_1 symmetry, which has two differently coordinated selenium atoms and different Se–N bond lengths (Fig. 7). This is in agreement with the result of the X-ray structure analysis. It follows that the unusual structure of the anions of **8a** and **8b** in the crystal is not caused by solid-state effects nor by the counterion. Rather, the C_1 form is the equilibrium geometry of the free anion. Geometry optimization at the MP2 level of $Se_2NCl_6^-$ under the constraint of C_{2v} symmetry gave a structure which is a second-order saddlepoint on the potential energy surface (two imaginary frequencies at 53.61 icm^{-1} and 35.51 icm^{-1}). The C_{2v} form is 4.4 kcalmol^{-1} higher in energy than the energy-minimum structure (Fig. 7). The transition state for the degenerate chlorine rearrangement has C_2 symmetry (one imaginary frequency at 52.61 icm^{-1}) and is only slightly distorted compared with the C_{2v} form (Fig. 7). The C_2-symmetric transition state is 4.3 kcalmol^{-1} higher in

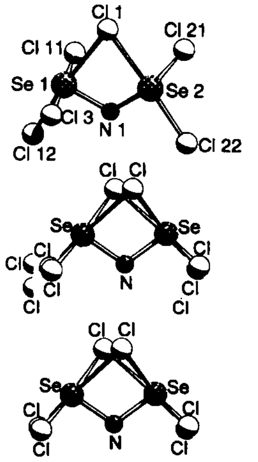

Fig. 7. Theoretically predicted geometries at the MP2 level for different forms of $Se_2NCl_6^-$ (anion of **8a, 8b**). Top: Energy-minimum structure (C_1 symmetry). Centre: C_{2v} form (second-order saddlepoint with two imaginary frequencies at 53.61 cm^{-1} and 35.51 cm^{-1}). The C_{2v} form is 4.4 kcal mol^{-1} higher in energy than the C_1 energy minimum. Bottom: Transition state for degenerate chlorine rearrangement (C_2 symmetry, one imaginary frequency at 52.61 cm^{-1}), which is 4.3 kcal mol^{-1} higher in energy than the energy minimum.

energy than the energy-minimum structure. The bond energy of Cl^- in $Se_2NCl_6^-$ is rather high; the calculated value at the MP2 level is 49.3 kcal mol^{-1}.[25]

The calculated charge distribution and the bond orders as given by the NBO method[26] indicate that the bonding between the selenium atoms and the bridging halogens in **6–8a,b** has a strongly ionic character (Tables 2 and 3). The bond orders are very low (<0.3), and the bridging halogen atoms carry a significantly higher negative charge than the other halogen atoms in the molecule. The Se–N bond orders calculated for all compounds included are about 1. The slightly higher values for **6** (P_{Se-N} = 1.19) and for the shorter of the two Se–N bonds of **8a, 8b** (P_{Se-N} = 1.24) suggest partial π bonding. The Se–N bonding is also enhanced by charge attraction between selenium and nitrogen in all compounds included in the calculations. This is indicated by the high positive and negative partial charges of Se and N, respectively (Tables 2 and 3). The partial charges at the chlorine atoms and the Se–Cl bond orders in **8a, 8b** are interesting. The chlorine atoms Cl12 and Cl22 have higher bond orders for the Cl–Se bonds and are less negatively charged than the other chlorine atoms (Table 3). Indeed, the Se1–Cl12 and Se2–Cl22 bonds are calculated to be shorter than the other Se–Cl bonds in **8a** and **8b**, which points towards a Se_2NCl_3 substructure in the molecule.

Experimental Procedure

General: All reactions were performed under an argon atmosphere by standard Schlenk techniques. CH_2Cl_2 and CH_3CN were refluxed with P_4O_{10} and CaH_2, respectively, and distilled prior to use. $SeCl_4$ and $SeBr_4$ were prepared from the elements;[30] $N(SiMe_3)_3$ (Aldrich) was distilled before use. ^{77}Se NMR spectra were recorded at 76.312 MHz on a Bruker AM400 spectrometer and referred against neat $SeMe_2$ as external reference. Infrared spectra were obtained on a Bruker IFS-88 spectrometer.

Se_2NCl_5 (7): A solution of $N(SiMe_3)_3$ (2.03 g, 8.67 mmol) in CH_2Cl_2 (9 mL) was added dropwise at 0 °C to a suspension of $SeCl_4$ (3.83 g, 17.35 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at 0 °C for 8 h. After filtration and drying in vacuo, Se_2NCl_5 (2.84 g, 8.13 mmol) was obtained as pale pink powder in 94% yield. Darkening of the compound over time has no effect on its ^{77}Se NMR spectrum. ^{77}Se NMR: CH_3CN: δ = 1294 (s), CH_2Cl_2: δ = 1263 (s); IR (Nujol, 4000–100 cm^{-1}): $\tilde{\nu}$ = 829/816 vst (ν_{asym} Se–N–Se), 585 w, 554 st (ν_{sym} Se–N–Se), 540 sh, 357 vst (ν_{asym} Se–$Cl_{2terminal}$), 330 w (ν_{sym} Se–$Cl_{2terminal}$), 202 m, 197 m (ν Se–Cl–Se), 147 m (δ Se–Cl_2); Cl_5NSe_2 (349.19): calcd: Cl 50.76, N 4.01; found Cl 50.41, N 3.98. Crystals suitable for crystallographic investigations were obtained by cooling the red filtrate at 5 °C for 1 d.

Se_2NBr_3 (6): A solution of $N(SiMe_3)_3$ (0.64 g, 2.73 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a suspension of $SeBr_4$ (2.18 g, 5,47 mmol) in CH_2Cl_2 (10 mL). After stirring for 30 min the mixture was allowed to settle for 2 h. Se_2NBr_3 was obtained as metallic reddish-brown crystals, which were used for X-ray crystallography. Because of its tendency to explode on mechanical stress Se_2NBr_3 was not isolated. IR: (Nujol, 4000–250 cm^{-1}): $\tilde{\nu}$ = 831 vst (ν_{asym} Se–N–Se), 806 w, 559 st (ν_{sym} Se–N–Se), 280 m (ν_{asym} Se–$Br_{terminal}$).

$[PPh_4][Se_2NCl_6]$ ($[PPh_4][8]$): A solution of PPh_4Cl (1.03 g, 2.75 mmol) in CH_2Cl_2 (10 mL) was added slowly to a suspension of Se_2NCl_5 (0.96 g, 2.75 mmol) in CH_2Cl_2 (10 mL) at 0 °C. Yellow crystals, unstable at temperatures above 0 °C, were formed immediately. On adding CH_3CN (20 mL), crystals of $[PPh_4][Se_2NCl_6]\cdot CH_2Cl_2$, suitable for X-ray crystallography, were yielded after cooling at −20 °C. The solvent-free compound was crystallized by the same procedure without adding CH_3CN.

Crystal structure determination [36] (see also Table 1): The crystals of **6**, **7**, **8a** and **8b** were covered with a high-boiling paraffin oil and mounted in a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections on a four-circle diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 71.073 pm). The final cell parameters were determined from 25 high angle reflections. The intensities were corrected for Lorentz and polarization effects. All structures were solved by direct methods with the programs SHELXTL Plus [31] (**6**, **7**) and SHELXTL [32] (**8a**, **8b**) and refined against F^2 by full-matrix least-squares with SHELXL 93 [33] (**6**, **7**) and SHELXTL (**8a**, **8b**). The positions of the hydrogen atoms in **8a** and **8b** were calculated for ideal positions and refined with a common displacement parameter. The calculation of the bond lengths, bond angles and U_{eq} for **6**, **8a** and **8b** was performed by the program PLATON [35]. The absolute structure of **6** was determined [Flack parameter 0.02(7)].

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[23] The geometry of **4** has already been calculated at the MP2 level by Schulz et al. [10b]. The results are very similar to our data.

[24] A geometry optimization of the anion of **8a** and **8b** at the Hartree–Fock level gives a structure with C_s symmetry as energy minimum; it has two symmetrically bridging chlorine atoms between Se1 and Se2 with identical Se–Cl bond lengths.

[25] The calculations of the energies were carried out with an additional set of diffuse functions at the atoms. The theoretically predicted bond energy of Cl^- is corrected for contributions by zero-point vibrational energy.

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