largest max./min. in the final difference Fourier synthesis: 2.275/ – 2.815 e Å^{-3}. An empirical absorption correction was applied (max./min. transmission 0.3854/0.1220). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164447 (**1**) and CCDC-164446 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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The $XeCl^+$ Ion: $[XeCl]^+[Sb_2F_{11}]^-$**

Stefan Seidel and Konrad Seppelt*

XeF_2, XeF_4, and XeF_6 are the only binary noble gas compounds that are thermodynamically stable against decomposition into the elements. $XeCl_2$, however, has only been detected in matrix,[1] not counting the single unreproduced report, in which it was claimed $XeCl_2$ could be prepared by high frequency discharge of Xe, F_2, and $SiCl_4$ or CCl_4 and that it is stable up to 80 °C.[2]

Cocrystallisates of RbCl or CsCl and, XeO_3 are known, however, which have Xe – Cl contact distances of 275(5) to 297(1) pm.[3] Quite recently $(C_6F_5Xe)_2Cl^+$ was prepared from $C_6F_5Xe^+$ and $(CH_3)_3SiCl$. In the solid state it shows contact distances between Xe and Cl of 284.7(1) and 278.4(2) pm and a Xe-Cl-Xe bond angle of 116.96(8)°. Also C_6F_5Xe–Cl has been isolated under very careful conditions starting with $C_6F_5Xe^+$ and the HCl – pyridine adduct 4-$ClC_5H_4N \cdot HCl$. Because of its instability in solution no further detailed structure information is available, but it can be assumed that it contains a real Xe–Cl bond.[4] Since the bond strength is stronger in XeF^+ than in XeF_2, salts with the $XeCl^+$ ion could be the most stable species with a Xe–Cl bond.

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We reacted $[XeF]^+[SbF_6]^-$ in HF/SbF_5 solution with small amounts of $SbCl_5$. Besides the nucleophilic Cl/F exchange [Eq. (1)], oxidation of Cl^- also takes place: An intermediate blue solution is observed, which is stable at room temperature for some time. This blue solution probably contains Cl_4^+, the first oxidation product of chlorine in the liquid phase, which has recently been identified in the form of the blue salt $[Cl_4]^+[IrF_6]^-$.[5] We did not succeed in crystallizing this blue product. After the decomposition into Cl_3^+,[5] the color of the solution changes to green and finally to orange, from which orange crystals were isolated. These melt at about –20 °C under partial decomposition.

$$XeF^+ \text{ (yellow)} + Cl^- \longrightarrow XeCl^+ \text{ (orange)} + F^- \quad (1)$$

The unit cell contains two crystallographically different, but otherwise essentially similar $[XeCl]^+[Sb_2F_{11}]^-$ units (Figure 1, only Molecule I is shown).[6] The Xe–Cl distance is much shorter (230.9(2) pm; Molecule II: 230.4(2) pm) than any

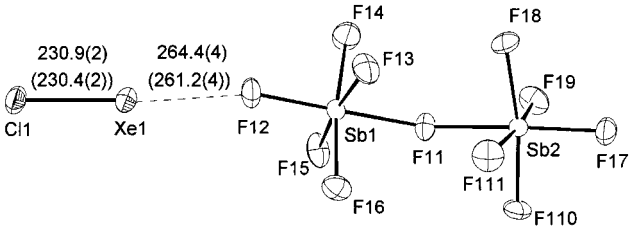

Figure 1. Ion pair $[XeCl]^+[Sb_2F_{11}]^-$ in the crystal (ORTEP representation, 50% probability ellipsoids). Ion pair I is depicted (distances in pm; numbers in parentheses: distances for ion pair II).

Xe–Cl distances measured to date in Xe–Cl compounds and corresponds to a Xe–Cl single bond, as is also predicted by ab initio calculations (230.07 pm, see Table 1). For comparison, isoelectronic ICl has a I–Cl bond length of 230.3 pm in the gaseous state and of 235.1 – 244.0 pm in the solid.[7] Similarly to the XeF^+ and KrF^+ ion,[8, 9] a contact is observed between the $XeCl^+$ ion and an F atom of the $Sb_2F_{11}^-$ ion, which leads to

Table 1. Calculated bond lengths r [pm] for the singlet state and singlet – triplet energy separation ΔE [kJ mol^{-1}] for diatomic noble gas halogen cations; CCSD approximation (numbers in parentheses: MP2 approximation).

Cation	r [pm]	ΔE [kJ mol^{-1}]
ArF^+[a]	168.2 (165.2)	55.8 (76.7)
$ArCl^+$	210.6 (208.1)	– 32.6 (– 30.9)
$ArBr^+$	238.5 (236.4)	– 101.4 (– 112.9)
ArI^+	269.4 (263.4)	– 115.7 (– 128.1)
KrF^+[b]	174.9 (173.5)	99.3 (134.9)
$KrCl^+$	217.7 (215.4)	29.4 (39.4)
$KrBr^+$	238.7 (237.9)	– 27.3 (– 35.8)
KrI^+	261.6 (260.2)	– 57.9 (– 66.5)
XeF^+[c]	189.9 (189.4)	117.9 (154.5)
$XeCl^+$	232.9 (230.7)	74.8 (86.1)
$XeBr^+$	254.4 (253.2)	21.8 (16.4)
XeI^+[d]	276.6 (275.3)	– 13.9 (– 21.7)

[a] See also ref. [12]. [b] 176.5(3) pm in $[KrF]^+[SbF_6]^-$.[9] [c] 188.8(2) pm in $[XeF]^+[SbF_6]^-$.[18] [d] See also ref. [11]. Especially in this combination of two heavy atoms the spin-orbit coupling can strongly influence the values. This is not taken into account.

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the formation of an almost linear Cl–Xe···F array with a contact distance of 264.4(4) pm (Molecule II: 261.2(4) pm).

The ^{129}Xe NMR signal (Figure 2) shows strong broadening owing to the quadrupole momentum of the $^{35/37}$Cl isotopes, but also the onset of a splitting due to the ^{129}Xe – $^{35/37}$Cl coupling

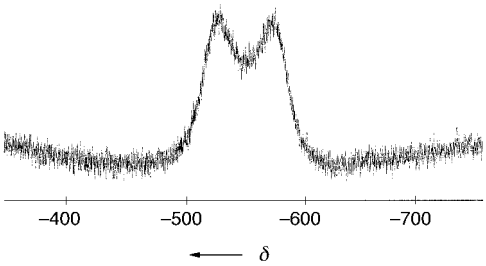

Figure 2. ^{129}Xe NMR spectrum of $[XeCl]^+[Sb_2F_{11}]^-$ in HF/SbF_5.

($I = 3/2$). The Raman spectrum is also in accord with the formula $[XeCl]^+[Sb_2F_{11}]^-$: A Raman band at 391 cm^{-1} (calculated 390.2 cm^{-1}) is clearly attributable to the XeCl vibration frequency, the other bands are typical for the $Sb_2F_{11}^-$ ion.[10] $[XeCl]^+[Sb_2F_{11}]^-$ decomposes at room temperature according to Equation (2).

$$2\,[XeCl]^+[Sb_2F_{11}]^- \longrightarrow Xe + Cl_2 + [XeF]^+[Sb_2F_{11}]^- + 2\,SbF_5 \qquad (2)$$

After the isolation of the new cation $XeCl^+$ the question arose, whether more as yet undetected diatomic noble gas halogen cations could exist. We have calculated all combinations of Ar, Kr, and Xe with F, Cl, Br, and I (Table 1) and the results are as follows: All combinations have a bound $^1\Sigma$ state. But as has been shown already by Klapötke for the XeI^+ ion, a weakly bound $^3\Pi$ state also needs to be considered, which in this case is of lower energy. Thus, the nonexistence of XeI^+ was predicted.[11] Our calculations confirm this special case and predict the same fate for all combinations of the lighter noble gases with the heavier halogens. The singlet – triplet separation is, however, large for the now known cations XeF^+, KrF^+, and $XeCl^+$.

ArF^+, $KrCl^+$, and $XeBr^+$ are undetected combinations to date, but the latter two have such a small singlet – triplet separation that the existence of these cations is unlikely, especially since a lengthening and a further weakening of the bond is expected in the condensed phase.

For the isolation of an ArF^+ salt a counterion is required that can resist the extreme oxidation force and the extreme fluoride ion affinity of ArF^+. Because of the first condition only fluoro-containing anions of elements in their highest oxidation states can be considered. The second condition is equally difficult to meet: Since an ArF_2 molecule is not a bound species according to calculations by various methods,[12] decomposition according to the reaction $[ArF]^+[XF_n]^- \rightarrow Ar + F_2 + XF_{n-1}$ is the problem. We can show that the anions HF_2^-, BF_4^-, and even AsF_6^- will not prevent this spontaneous decomposition because of their F^- donor abilities. Only $[ArF]^+[SbF_6]^-$, $[ArF]^+[AuF_6]^-$, $[ArF]^+[Sb_2F_{11}]^-$, and $[ArF]^+[Au_2F_{11}]^-$ could be isolable, since the fluoride ion affinities of SbF_5 and AuF_5 are large enough

Table 2. Calculated bond lengths r [pm] (MP2-approximation).[16]

	r(F–Ar)	r(Ar···F)
$F–Ar^+\cdots SbF_6^-$	194.9	193.0
$F–Ar^+\cdots AuF_6^-$	184.7	192.9
$F–Ar^+\cdots Sb_2F_{11}^-$ (*cis*)[a]	183.6	191.9
$F–Ar^+\cdots Au_2F_{11}^-$ (*trans*)[a]	173.9	201.6

[a] *cis* and *trans* bridging at the central Sb and Au atom, respectively. The corresponding other isomers are energetically marginally less favorable.

(see Table 2).[13] The calculations of these ion pairs is simplified by the fact that a linear F–Ar···F array can be assumed, also in the crystal, as is found in XeF^+, KrF^+, and $XeCl^+$. Thus, any further interionic interaction of these ion pairs can be neglected in a first approximation. Similar calculations have been presented recently for the KrF^+ ion with various counterions.[9] We interpret the change of the two bond lengths at the argon atom as an increased kinetic stability, that is, $[FAr]^+[SbF_6]^- < [FAr]^+[AuF_6]^- \sim [FAr]^+[Sb_2F_{11}]^- < [FAr]^+[Au_2F_{11}]^-$. But even for the most favorable case $[FAr]^+[Au_2F_{11}]^-$, the decomposition into Ar, F_2, and Au_2F_{10} is exothermic by -231 kJ mol^{-1}. The isolation of an argon compound in the condensed phase, in other words not under matrix or mass spectrometric conditions, remains a formidable task.

Experimental Section

A PFA reaction tube (polyperfluoroethylene-perfluorovinylether-copolymer) with an internal diameter of 6.5 mm was filled in a dry box (< 1 ppm H_2O) with XeF_2 (320 mg, 2 mmol), SbF_5 (2.67 g, 12 mmol), and $SbCl_5$ (60 mg, 0.2 mmol). With the help of a stainless steel vacuum line HF (650 mg, 32.5 mmol) was condensed onto the reaction mixture and the reaction tube was sealed. After brief warming to room temperature a blue solution formed, from which on slow cooling to $-30\,^\circ$C orange crystals deposited. Raman spectrum (1064 nm, $-120\,^\circ$C, solid, cm^{-1}): $\tilde{\nu} = 683$ (62), 672 (100), 649 (55), 614 (82), 493 (16), 391 (50), 383 (sh), 301 (40), 282 (19), 263 (19), 228 (38); ^{129}Xe NMR (HF/SbF_5, 17 °C, $XeOF_4$, 110.45 MHz): $\delta = -551$ (br d, separation: 5165 Hz, $\tau_{1/2} = 8084$ Hz).

Crystal structure determination: A suitable crystal was mounted on a Bruker SMART-CCD-1000 TM diffractometer with help of a special device[14] under cooling and inert gas, and measured.[6] After semiempirical absorption correction by equalizing symmetry-equivalent reflections (SADABS), the structure solution and refinement were carried out with the SHELX programs.[15, 16]

Ab initio calculations: Program Gaussian 98.[16] Møller – Plesset second-order correlation energy correction (MP2) as implemented in the Gaussian program,[17] , as well as coupled-cluster calculation with single and double substitution (CCSD). Basis sets: F, Cl, Ar: 6-311 + G(d,p), as implemented in the Gaussian program, Kr, Xe, Br, I, As, Sb: Relativistically corrected basis sets for the valence electrons and pseudo potentials for the 28 (Kr, Br, As) and 46 (Xe, I, Sb) core electrons.

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-411897 ($[XeCl]^+[Sb_2F_{11}]^-$) and CSD-411868 ($[XeF]^+[SbF_6]^-$).

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[18] $[XeF]^+[SbF_6]^-$: yellow crystals, obtained from $XeF_2/HF/SbF_5$ solution: $a = 573.8(2)$, $b = 1087.7(2)$, $c = 1095.9(2)$ pm, $\beta = 93.92(2)^\circ$, $V = 639.6 \times 10^6\,pm^3$, $Z = 4$, $P21/c$, $Mo_{K\alpha}$, $Z = 71.069$ pm, $\rho = 4.009\,g\,cm^{-3}$, $2\theta_{max} = 60^\circ$, 2000 measured, 1760 independent reflections ($R_{int} = 0.0144$), absorption correction psi-scan method by measuring seven reflections with $\chi > 80^\circ$ in 36 steps in psi, $T_{max} = 1.0$, $T_{min} = 0.76$, 83 parameters, $R_1 = 0.0189$, $wR_2 = 0.0506$.