The Cl_4^+ Ion**

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The first oxidation product of the chlorine molecule, Cl_2^+, stubbornly refuses to be prepared in a chemical system. In the diluted gas phase it can be detected by UV spectroscopy.[1] The shortened Cl–Cl distance of 189 pm and the increased valence frequency of 645.3 cm^{-1} of Cl_2^+ with respect to molecular Cl_2 (199 pm and 558 cm^{-1}, respectively) are indicative of a bond order of one and half. In comparison, cherry red Br_2^+[2–7] and light blue I_2^+ have been known for a long time and have been investigated intensively.[8, 9] I_2^+ was observed on the grounds of its color as early as 1882 on dissolution of I_2 in oleum,[10–12] but only in 1966 was it identified as such.[8]

Recently we showed that oxidation of Cl_2 with $O_2^+SbF_6^-$ yields the remarkable trapezoid-shaped $Cl_2O_2^+$ ion, which can be described as a *side-on* π complex of (singlet) O_2 to Cl_2^+[13] Since the binding between O_2 and Cl_2^+ is reversible, as has been shown by isotopic substitution, Cl_2^+ might also be obtainable, if one works under oxygen-free conditions. Therefore we chose iridium hexafluoride with an electron affinity (EA) of approximately 6.5 eV as oxidizing agent, which should just be able to oxidize Cl_2 which has a first ionization potential (IP) of 11.5 eV, if these numbers are compared with those of PtF_6 (EA 7.0 eV) and xenon (first IP 12.12 eV).[14, 15] The reaction of the latter afforded the first xenon compund "$XePtF_6$", whose exact composition still remains unknown.[16] The above calculation is based on the assumption that lattice energies of $Cl_2^+IrF_6^-$ and $Xe^+PtF_6^-$ should be quite similar.

The reaction, however, proceeds under formation of the Cl_4^+ ion [Eq. (1)]. $Cl_4^+IrF_6^-$ is obtained as a blue solid that

$$2\,Cl_2 + IrF_6 \longrightarrow Cl_4^+\,IrF_6^- \qquad (1)$$

decomposes at −78 °C to salts of the Cl_3^+ ion, which are well known with various anions.[13] Elemental chlorine can also be replaced by chlorine-containing compounds, for example, CF_2Cl_2. In spite of its instability the new compound has been characterized by a single-crystal structure determination as well as by Raman and EPR spectroscopy, and has been simulated by calculations.

According to the crystal structure determination, the compound contains a rectangular Cl_4^+ ion that shows no significant contacts to the fluorine atoms of the octahedral IrF_6^- ion (Figure 1). The short Cl–Cl distance is significantly shorter than in Cl_2, but somewhat longer than in gaseous Cl_2^+. This is in accord with the oxidation state $Cl_2^{+1/2}$. The association of both parts can be explained, similarly to $Cl_2O_2^+$, in terms of

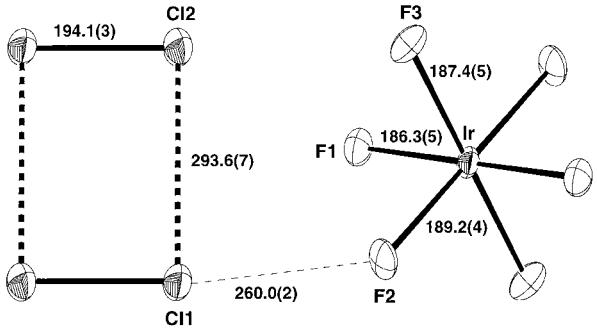

Figure 1. Structure of $Cl_4^+IrF_6^-$ in the crystal (ORTEP plot, 50% probability ellipsoids). One molecular unit with the shortest interionic distance is shown. Atoms not indexed are generated by the center of symmetry. Values in pm.

π*–π* interactions, as has been shown by ab initio and density functional theory (DFT) calculations (Table 1). A reliable prediction for the weak interaction is only possible with fairly large basis sets. The bond energy between the two parts of the cations is calculated to be approximately 100 kJ mol^{-1} with respect to $Cl_2 + Cl_2^+$ (see Table 1). This bond energy represents a very simple case of resonance energy of a system that is exclusively π-bonded.

The Raman spectrum (see Figure 2 and Experimental Section) shows the bands of the octahedral IrF_6^- ion and the Cl–Cl valence vibrations. The high intensity of the band at 175 cm^{-1}, which is possibly due to a Raman resonance, is striking, since the first and second overtone can be seen, although the excitation frequency of 1064 nm is far from the absorption in the visible region. This vibration is assigned to the symmetric stretch of the Cl_4^+ ion along the long bonds, which has also been shown by the calculations. Owing to the large amount of computing time and space needed these frequency calculations could only be done with a smaller basis set and the DFT method. This results in an elongated Cl···Cl distance and consequently in systematically lowered frequencies except for the two Cl–Cl stretching vibrations.

Table 1. Parameters for the Cl_4^+ ion determined experimentally and by ab initio and DFT calculations.

	Experiment	MP2/6-311++G(3df,3pd)[a]	Becke3LYP/6-311++G(3df,3pd)[a]
Cl-Cl [pm]	194.1(3)	194.0	195.6
Cl···Cl [pm]	293.7(3)	297.5	334.3
$\Delta H(Cl_2 + Cl_2^+ \rightarrow Cl_4^+)$ [kJ mol^{-1}]		−101.5	−104.5
ν(Cl-Cl), A_g [cm^{-1}]	578		588.8(46)
ν(Cl-Cl), B_{1u} [cm^{-1}]			562.9(0)
δ(Cl···Cl), B_{3g} [cm^{-1}]	241		115.5(19)
ν(Cl···Cl), A_g [cm^{-1}]	175		103.5(100)
ν(Cl···Cl), B_{2u} [cm^{-1}]			77.7(0)
τ, A_u [cm^{-1}]			57.0(0)

[a] See ref. [22].

The EPR spectrum shows only a noncharacteristic broad resonance. We could show with $H_2F^+IrF_6^-$, prepared by

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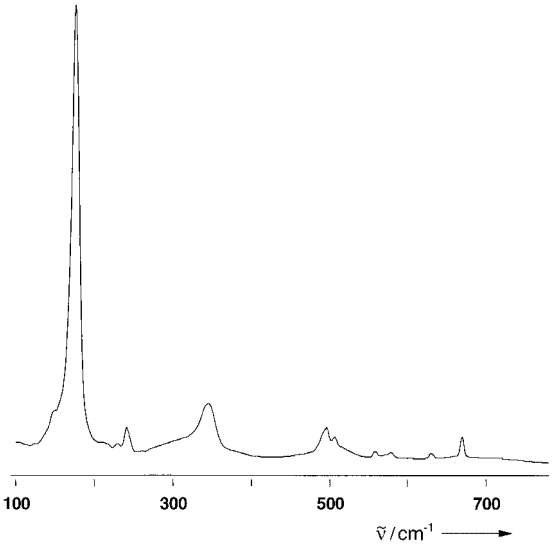

Figure 2. Raman spectrum of $Cl_4^+IrF_6^-$ at $-80\,^\circ C$. For the frequency values see Experimental Section.

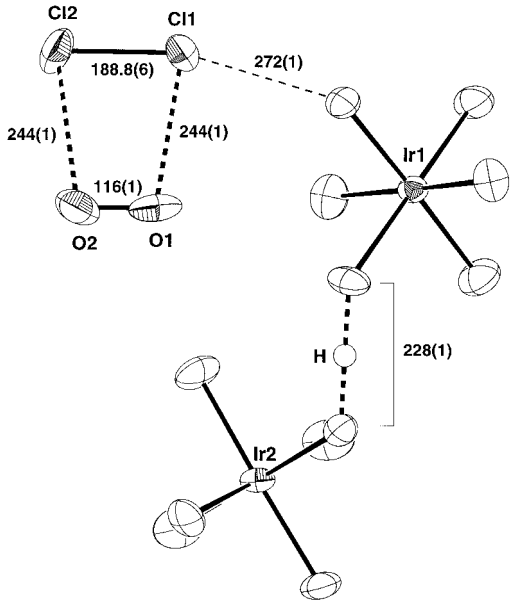

Figure 3. Structure of $Cl_2O_2^+$ $HIr_2F_{12}^-$ in the crystal (ORTEP plot, 50% probability ellipsoids). One molecular unit with the shortest interionic distance is shown. Values in pm.

reaction of IrF_6 with SO_2 in HF, that IrF_6^- gives no EPR signal. This agrees with the finding that $K^+IrF_6^-$ and $Cs^+IrF_6^-$ display temperature-independent paramagnetism.[17]

It is possible that the blue and very unstable product of chlorine with the dioxygenyl cation (under excess of Cl_2) also contains the Cl_4^+ ion.[13] A solid-state EPR spectrum of a product from Cl_2 and SbF_5 at 4.2 K is also assigned to the Cl_4^+ ion, but has fine structure.[18]

The Cl_4^+ ion is related to the I_4^{2+} ion, the dimerization product of I_2^+ in the solid state.[19, 20] This also has a rectangular structure with short (258.6(3) pm) and long bonds (324.7(3) pm).

Other parallels are the dimer of O_2 at high pressures or the diamagnetic dimer of ClO_2 below $-108\,^\circ C$.[21, 22] A difference between the latter dimers and Cl_4^+ and $Cl_2O_2^+$ is, however, that in all previous cases two electrons exist for the two (long) bonds, in the latter ones only one electron.

Cl_4^+ reacts with oxygen that diffuses slowly through the perfluoroethylene–propylene (FEP) reaction vessel to form black crystals, which are similarly sensitive and consist of $Cl_2O_2^+Hir_2F_{12}^-$ (Figure 3). The $Cl_2O_2^+$ ion present herein is identical with the cation in $Cl_2O_2^+SbF_6^-$ and $Cl_2O_2^+Sb_2F_{11}^-$ that we published recently.[13] The anion is also of interest and has a very short F-H-F bridge. It can be described either as protonated IrF_6^- ($F_5Ir\text{-}F\cdots H^+\cdots F\text{-}IrF_5^-$) or as HF_2^-, solvated by IrF_5 ($F_5Ir\cdots F\text{-}H\text{-}F^-\cdots IrF$).

Experimental Section

Method 1: IrF_6 (240 mg, 0.8 mmol) and Cl_2 (50 mg, 0.7 mmol) were condensed with help of a stainless steel vacuum line into a perfluoroethylene–propylene (FEP) reaction vessel (inner diameter 6 mm) cooled to $-196\,^\circ C$. The reaction mixture turned blue immediately. Anhydrous HF (500 mg) was condensed into the vessel, and the tube was sealed. Upon warming to $-80\,^\circ C$ a black, almost HF-insoluble solid was formed. The FEP ampule was briefly warmed, shaken, and cooled to $-90\,^\circ C$. Above the frozen solution black, needle-shaped crystals were formed. Above $-78\,^\circ C$ $Cl_4^+IrF_6^-$ decomposed.

Method 2: Similarly IrF_6 (170 mg, 0.6 mmol) and CF_2Cl_2 (800 mg, 6.7 mmol) were condensed together. Upon warming to $-90\,^\circ C$ a red solution was formed. After a few minutes a blue coloration was observed above the liquid. The solution was kept for 12 h at $-78\,^\circ C$. Within this period black, needle-shaped crystals were formed at the ampule wall above the solution.

Ab initio and DFT calculations have been done with the program GAUSSIAN 98.[23]

Raman spectrum (1064 nm, $-80\,^\circ C$, solid, cm^{-1}): $\tilde{\nu} = 669$ (8, $\nu_{A_{1g}}(IrF_6)$), 630 (1, $\nu_{E_g}(IrF_6)$), 578 (1, ν_{A_g}(Cl-Cl)), 558 (1, $\nu_{B_{1u}}$(Cl-Cl)), 525 (shoulder, $3\times\nu_{A_g}(Cl\cdots Cl)$), 506 (7), 496 (11), 345 (15, $2\times\nu_{A_g}(Cl\cdots Cl)$), 241 (10, $\delta_{F_{2g}}(IrF_b)$), 229 (1), 175 (100, $\nu_{A_g}(Cl\cdots Cl)$), 155 (shoulder); EPR spectrum ($-83\,^\circ C$, X-band): $\delta = 2.00823$, half width 300 Gauss.

Crystal structure analysis: With a special apparatus[24] a suitable crystal was mounted and measured on a Bruker-SMART-CCD-1000 TM diffractometer. Monoclinic, space group $P2_1/c$, $a = 512.2(1)$, $b = 1038.7(2)$, $c = 739.4(1)$ pm, $\beta = 93.668(3)^\circ$, $V = 392.6\times10^6$ pm^3, $T = -120\,^\circ C$, $Z = 2$, $Mo_{K\alpha}$ radiation, graphite monochromator, scan width $0-3\omega$, measurement time 10 s per frame, 3345 measured, 770 unique reflections, 53 parameters, $R(F \geq 4\sigma(F)) = 0.038$, $wR_2 = 0.102$. After a semiempirical absorption correction by equalizing symmetry-equivalent reflections (SADABS), structure solution and refinement were carried out with the SHELX programs.[25, 26]

$Cl_2O_2^+HIr_2F_{12}^-$: A sample prepared as described under Method 1 was kept in cold ethanol at $-90\,^\circ C$ for about seven days. Above the frozen solution black, needle-shaped crystals were formed on the wall of the ampule. Crystal structure analysis: Measurement as described above. Monoclinic, space group $P2_1/c$, $a = 540.24(4)$, $b = 1818.6(1)$, $c = 1191.4(1)$ pm, $\beta = 100.705(5)^\circ$, $V = 1150.1\times10^6$ pm^3. $T = -120\,^\circ C$, $Z = 4$, 9218 measured, 2031 unique reflections, 164 parameters, $R(F \geq 4\sigma(F)) = 0.037$, $wR_2 = 0.081$. The position of the hydrogen atom was assumed exactly between the F16 and F21 atoms because of their short distance. Other bond lengths [pm]: Ir1-F11 182.0(9), Ir1-F12 184.5(9), Ir1-F13 185.4(8), Ir1-F14 184.0(8), Ir1-F15 184.9(8), Ir1-F16 196.6(8), Ir2-F21 197.1(9), Ir2-F22 185.9(8), Ir2-F23 185.0(7), Ir2-F24 184.5(8), Ir2-F25 181.8(9), Ir2-F26 184.9(8).

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666, on quoting the depository numbers CSD-411351 ($Cl_4^+IrF_6^-$) and CSD-411358 ($Cl_2O_2^+HIr_2F_{12}^-$).

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[1] G. Herzberg, *Molecular Spectra and Molecular Structure*, *Vol. 1.*, Von Nostrand, Princeton, NJ, USA, **1960**, p. 520.
[2] R. J. Gillespie, M. J. Morton, *Chem. Commun.* **1968**, *24*, 1565 – 1567.
[3] A. J. Edwards, G. R. Jones, R. J. C. Sills, *Chem. Commun.* **1968**, 1527 – 1528.
[4] A. J. Edwards, G. R. Jones, *J. Chem. Soc.* (A) **1971**, 2318 – 2320.
[5] R. J. Gillespie, M. J. Morton, *Inorg. Chem.* **1972**, *3*(11), 586 – 593.
[6] W. W. Wilson, R. C. Thompson, F. Aubke, *Inorg. Chem.* **1980**, *19*, 1489 – 1493.
[7] D. K. Padma, R. D. Peacock, *J. Fluorine Chem.* **1981**, *17*, 539 – 541.
[8] R. J. Gillespie, J. B. Milne, *Inorg. Chem.* **1966**, *5*, 1577 – 1582.
[9] R. D. W. Kemmitt, M. Murray, V. M. McRae, R. D. Peacock, M. C. R. Symons, T. A. O'Donnell, *J. Chem. Soc. (*A) **1968**, 862 – 866.
[10] R. Weber, *J. Prakt. Chem*. **1882**, *25*, 224 – 231.
[11] G. Oddo, A. Sconzo, *Gazz. Chim. Ital.* **1927**, 57, 83 – 103.
[12] O. Ruff, H. Graf, W. Heller, Knoch, *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 4310 – 4327.
[13] T. Drews, W. Koch, K. Seppelt, *J. Am. Chem. Soc.* **1999**, *121*, 4379 – 4384.
[14] *Handbook of Chemistry and Physics* 76th ed., CRC, Boca Raton, FL, **1995 – 1996**, chap. 10, pp. 187 – 188.
[15] N. Bartlett, *Angew. Chem.* **1968**, *80*, 453 – 460; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 433 – 439.
[16] N. Bartlett, *Proc. Chem. Soc.* **1962**, 218; L. Graham, O. Graudejus, N. K. Jha, N. Bartlett, *Coord. Chem. Rev.* **2000**, *197*, 321 – 324.
[17] A. Earnshaw, B. N. Figgis, J. Lewis, R. D. Peacock, *J. Chem. Soc*. **1961**, 3132 – 3138.
[18] R. S. Eachus, M. C. R. Symons, *J. Chem. Soc. Dalton* **1976**, 431 – 434.
[19] R. J. Gillespie, R. Kapoor, R. Faggiani, C. J. L. Lock, M. Murchie, J. Passmore, *J. Chem. Soc. Chem. Commun*. **1983**, 8 – 9.
[20] R. Faggiani, R. J. Gillespie, R. Kapoor, C. J. L. Lock, J. E. Vekris, *Inorg. Chem*. **1988**, *27*, 4350 – 4355.
[21] F. A. Gorelli, L. Ulivi, M. Santoro, R. Bini, *Phys. Rev. Lett.* **1999**, *83*, 4093 – 4096.
[22] A. Rehr, M. Jansen, *Angew. Chem*. **1991**, *103*, 1506 – 1508; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1510 – 1512; A. Rehr, M. Jansen, *Inorg. Chem.* **1992**, *31*, 4240 – 4742.
[23] Gaussian 94, Revision E.2: M. J. Risch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. A. Montgomery. K.Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, N. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Brinkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, USA, **1995**.
[24] H. Schumann, W. Genthe, E. Hahn, M.-B. Hossein, D. van der Helm, *J. Organomet. Chem.* **1986**, *28*, 2561 – 2567.
[25] G. Sheldrick, Program for Crystal Structure Solution, Göttingen, **1986**.
[26] G. Sheldrick, SHELXS-93, Göttingen, **1993**.

$[\{Ag(t\text{BuNH}_2)_2\}_4][\{Ag(t\text{BuNH}_2)(t\text{BuN=CHCH}_3)\}_2][Ag_{12}(CF_3CO_2)_{14}]$: A Compound with an Ag_{12}^{8+} Cluster Core**

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Dedicated to Professor Herbert W. Roesky on the occasion of his 65th birthday

The tendency of silver to form subvalent compounds has been observed in the structures of, for example, Ag_3O,[1] Ag_5GeO_4,[2] Ag_5SiO_4,[3] and $Ag_6Ge_{10}P_{12}$.[4] These compounds contain octahedral Ag_6^{4+} cluster units in which two electrons of a 6-center 2-electron (6c2e) bond occupy the lowest bonding molecular orbital (a_{1g}). Furthermore, the influence of $d^{10}-d^{10}$ interactions is invoked to explain the existence of these silver clusters.[2, 3, 5]

The reaction of silver trifluoroacetate with LiNH*t*Bu leads to the formation of **1**, a molecular compound which contains two similar Ag_6^{4+} units connected to give an Ag_{12}^{8+} cluster.

$[\{Ag(t\text{BuNH}_2)_2\}_4]^{4+}[\{Ag(t\text{BuNH}_2)(t\text{BuN=CHCH}_3)\}_2]^{2+}[Ag_{12}(CF_3CO_2)_{14}]^{6-}$ **1**

Herein, in addition to the X-ray structure analysis of **1**[6] we present quantum chemical calculations to elucidate the electronic structure in the metal cluster.

Complex **1** features a central Ag_{12} cluster clamped by μ_2 bridging trifluoroacetate ligands. This core is surrounded by six silver diamine units (Figure 1). In four of them, the silver atoms (Ag(13) to Ag(16)) are linearly coordinated by two $t\text{BuNH}_2$ ligands which are formed by the protonation of the $(t\text{BuNH})^-$ units. Additionally, two $[Ag(t\text{BuNH}_2)(t\text{BuN=CHCH}_3)]^+$ ions (Ag(17) and Ag(18)) are present, the structure for Ag(17) is presented in Figure 2. A *tert*-butylamine ligand and a *tert*-butylacetateimine ligand both bind to a silver atom in this fragment. The atom N(10) has a trigonal planar coordination sphere and the N–C bond length (N(10)-C(63) = 123(3) pm) is significantly shorter than a N–C single bond.

The existence of $[Ag(t\text{BuNH}_2)(t\text{BuN=CHCH}_3)]^+$ ions could be demonstrated conclusively by electrospray ionization mass spectroscopy, however, the reaction pathway that yields these unexpected units is not yet clear. The C_2H_4 group bound to N(10) is probably generated by the cleavage of the solvent diethyl ether. In this case the resulting ethanal would react with dissolved amido or amine ligands to form imine groups which then coordinate to an Ag^+ ion or to a $[Ag(t\text{BuNH}_2)]^+$ unit.

The Ag–N bond lengths in the six complex ligands (average 214 pm) are in agreement with the values reported for

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