Noble-Gas Compounds

The First Compound Containing a Metal Center in a Homoleptic Environment of XeF_2 Molecules**

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Since Bartlett and co-workers reported that XeF_2 can act as ligand for Ag^I,[1] several coordination compounds with metal ions coordinated by XeF_2 have been prepared.[2,3] Metal centers in all the compounds of this type are coordinated simultaneously by XeF_2 molecules and $[AF_6]^-$ ions ($A = As$, Sb, P). The important feature of the compound described herein, $Ca_2(XeF_2)_9(AsF_6)_4$, is that for the first time one calcium center is coordinated to XeF_2 molecules only (a homoleptic center) while the second is coordinated to XeF_2 molecules and $[AsF_6]^-$ ions.

The reaction between $Ca(AsF_6)_2$ and XeF_2, in anhydrous HF (aHF) as a solvent, yields two compounds: $[Ca(XeF_2)_n](AsF_6)_2$; $n = 4$ and 2.5.[2] Which compound is formed depends on the mole ratio of the reactants (n corresponds the mole ratio between XeF_2 and Ca). Noted that an excess of XeF_2 is necessary ($n > 4$) in order to obtain pure $[Ca(XeF_2)_4](AsF_6)_2$, free of $[Ca(XeF_2)_{2.5}](AsF_6)_2$. We believe that at lower concentrations of XeF_2 ($n < 4$), there is always also some HF coordinated to the Ca^{2+} ion, this being lost as the solvent is removed.

In the present study a very high concentration of XeF_2 ($n > 20$) was employed to create the reaction conditions for the preparation of a possible homoleptic compound with XeF_2. A new coordination compound $Ca_2(XeF_2)_9(AsF_6)_4$ was isolated. It is clear that, with increased XeF_2 concentration, the number of XeF_2 molecules coordinated to the Ca^{2+} center will increase. The most important point is probably the mass action effect of the increased XeF_2 concentration. This effect increases the likelihood that the Ca^{2+} ion will be coordinated by XeF_2 rather than HF. As the solvent HF is removed this mass action effect is even greater.

There are two crystallographically different Ca atoms in the $Ca_2(XeF_2)_9(AsF_6)_4$ structure. Ca1 atoms (Figure 1) are in a homoleptic environment of nine XeF_2 molecules. Eight of the XeF_2 molecules donate fluorine atoms to the apexes of an Archimedean antiprism, while the ninth fluorine atom is from the $Xe3F_2$ molecule and caps one rectangular face of the antiprism. The four XeF_2 molecules that form the non-capped face of the antiprism bridge Ca1 atoms to Ca2 atoms. The coordination sphere of the Ca2 atom is also an Archimedean

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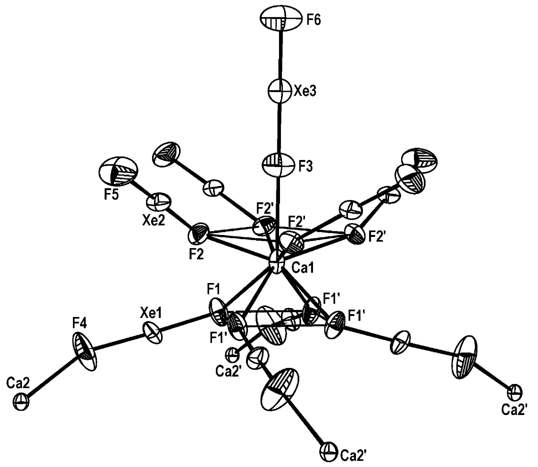

Figure 1. Coordination of the Ca1 center in $Ca_2(XeF_2)_9(AsF_6)_4$ (thermal ellipsoids set at 50% probability). Selected bond lengths [pm]: Ca1-F1 247.4(7), Ca1-F2 231.2(6), Ca1-F3 265.8(18) Xe1-F1 198.7(7), Xe1-F4 197.8(9), Xe2-F2 205.8(7), Xe2-F5 194.3(9), Xe3-F3 201.3(17), Xe3-F6 197(2)

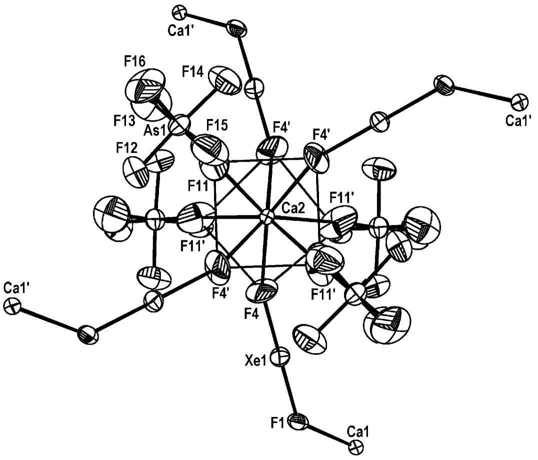

Figure 2. Coordination of the Ca2 center in $Ca_2(XeF_2)_9(AsF_6)_4$ (thermal ellipsoids set at 50% probability). Selected bond lengths [pm]: Ca2-F4 232.9(8), Ca2-F11 227.7(10), As1-F11 170.9(9), As1-F12 170.3(9), As1-F13 168.8(11), As1-F14 169.9(9), As1-F15 168.7(10), As1-F16 167.9(9).

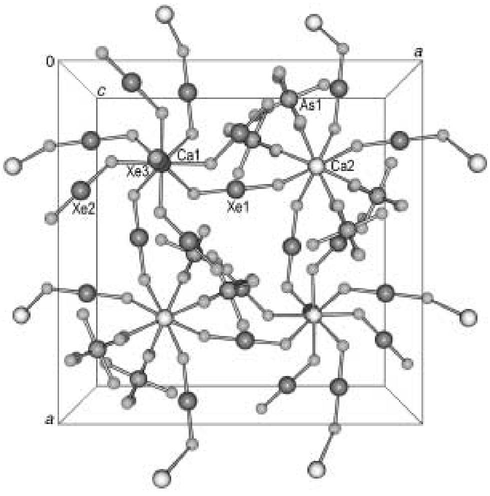

Figure 3. Position of the sixteen-member ring in the unit cell of $Ca_2(XeF_2)_9(AsF_6)_4$.

antiprism, this time composed of fluorine atoms from four monodentate $[AsF_6]^-$ units and four bridging XeF_2 molecules (Figure 2). In this way two Ca1 atoms and two Ca2 atoms are connected by XeF_2 molecules to form sixteen-member rings (Figure 3), which are further connected into wavy layers. Between the layers, stacked down the *c* axis, there are several electrostatic interactions between negatively charged fluorine atoms from $[AsF_6]^-$ units and positively charged Xe from nonbridging $Xe2F_2$ and $Xe3F_2$ molecules. These interactions hold the layers together. There are six close Xe2···F(As) contacts in the range 314.7 to 368.2 pm, while the Xe3 atom is surrounded by twelve fluorine atoms at distances between 340.8 and 379.9 pm. The Xe3 atom lies between four $[AsF_6]^-$ units with triangular faces oriented towards the Xe3 atoms. In this way the free electron pairs at the Xe3 atoms are anchored between $[AsF_6]^-$ which is reflected in a longer Ca–F(Xe3) bond (265.8(18) pm) compared to the other Ca–F(Xe) bonds in the structure (231.2(6) to 247.4(7) pm).

With respect to the different environments of the calcium atoms in the structure, the formula of the compound can be written as a salt: $[Ca(XeF_2)_5(XeF_2)_{4/2}]^{2+}[Ca(AsF_6)_4(XeF_2)_{4/2}]^{2-}$. This formulation emphasizes that, in aHF solutions of $Ca(AsF_6)_2$ with a large amount of XeF_2, calcium cations are fully surrounded by XeF_2 molecules. The $[AsF_6]^-$ ions are bulky, therefore, by grouping only linear XeF_2 molecules around one calcium cation, an energetically and sterically preferred arrangement is achieved. For the crystal packing, it is important that XeF_2 is able to bridge two calcium cations, which is less likely with more acidic cations, such as, magnesium cations[3] where more covalent character in the M–F bond is expected (electron affinity of Mg^{2+} is 15.04 eV, for Ca^{2+} it is 11.87 eV[4]). This situation means that the Lewis basicity of the fluorine atoms in the XeF_2 molecule strongly depends on the cation to which XeF_2 is already coordinated. The XeF_2 molecules, in this compound, favor the formation of a crystal-structure network, in which there are monodentate $[AsF_6]^-$ groups compensating for the overall charge of the network.

There is no significant difference between the Ca–F(Xe) and Ca–F(As) separations. Although the latter is shorter than the former (see Figure 2), owing to the electrostatic attraction of oppositely charged $[AsF_6]^-$ ion and Ca^{2+} ion, higher Lewis basicities are expected for the fluorine atoms from XeF_2 molecules. This situation is evident from the elongation of the bridging Xe–F bonds and the contraction of the terminal Xe–F bonds, while the As–F11 bridging distance (170.9(9) pm) does not show significant elongation compared to the terminal As–F bonds (ranging from 167.9 to 170.3 pm).

The high polarizability of xenon usually results in the Raman active modes of xenon fluorides and their coordination compounds having intense Xe–F stretching modes. Modes involving Ca–F and As–F vibrations are usually far less intense. The intense bands in the Raman spectrum of

$Ca_2(XeF_2)_9(AsF_6)_4$ at 548 cm^{-1} and 533 cm^{-1} can therefore be confidently attributed to Xe–F stretching modes.

According to the Rundle model of XeF_2[5] which proposes three-center molecular orbitals, and as a result of the high polarizability of XeF_2, charge from the XeF_2 molecule is transferred towards the calcium cation and it accumulates at the bridging fluorine atom giving the coordinated XeF_2 molecule some F^-XeF^+ character. This situation is also evident from the Raman spectroscopy. In free XeF_2 the totally symmetric (ν_1) stretching mode is at 497 cm^{-1},[6] where charge at fluorine ligands of 0.5 e_0 is expected.[7] When XeF_2 is coordinated to metal ion it is distorted and the band at 497 cm^{-1} is replaced by two bands. The band at higher frequency is labeled as the short-bond Xe–F stretch (at 548 cm^{-1}) and that at lower frequency is labeled as the long-bond Xe–F stretch (this band is much weaker and it is probably hidden in the band at 466 cm^{-1}). The bridging XeF_2 unit might be expected to exhibit a symmetric XeF_2 stretch at approximately 497 cm^{-1} but as can be seen from the Raman data (see Experimental Section), the observed band at 533 cm^{-1} is most likely to be associated with this vibration. The enhancement of this stretching frequency is probably a consequence of the XeF_2 molecule being anchored between two Ca^{2+} ions, and therefore more energy is required for the symmetric stretching mode.

The remaining question is whether it is possible to prepare a compound in which all the metal centers will be homoleptic and coordinated only to XeF_2 molecules. Reactions in the system $M(AF_6)_2$ with a weak Lewis acid AF_5 (e.g. A = P, V) and a medium strong Lewis base M, coupled with a large excess of XeF_2 (XeF_2: $M(AF_6)_2$ >20), in HF as solvent, will give the answer.

Experimental Section

The bulk of the product for chemical analysis and Raman spectroscopy was synthesized by the reaction of $Ca(AsF_6)_2$ (0.603 g, 1.44 mmol) and excess XeF_2 (4.105 g, 24.2 mmol) in anhydrous HF (aHF) as solvent. Both solid reagents were weighed directly into a FEP (tetrafluoroethylene-hexafluoropropylene copolymer) reaction vessel inside a dry box. After the solvent (aHF) was added, the reaction was allowed to proceed for 24 h. A crystalline white solid (1.717 g, calcd: 1.699 g) was isolated by pumping off the solvent and excess XeF_2 on a vacuum line.

Chemical analysis: free and total fluoride ion contents were determined by using an ion-selective electrode.[8,9] Calcium was determined by complexometric titration.[10] $[AsF_6]^-$ was determined gravimetrically by precipitation with tetraphenylarsonium chloride.[11] Arsenic was determined potentiometrically.[12] Calcd (%) for $Ca_2(XeF_2)_9(AsF_6)_4$: F_{total} 33.8, F_{free} 14.5, As 12.7, Ca 3.4, $[AsF_6]^-$ 32.0; found: F_{total}, 33.5, F_{free} 14.4, As 13.1, Ca 3.4, $[AsF_6]^-$ 32.3.

Raman spectrum: 690 (2.0), 591 (0.4), 548 (8.0), 533 (10.0), 491 (0.4), 466 (0.9), 377 (0.4), 368 cm^{-1} (0.4).

Crystals with composition $Ca_2(XeF_2)_9(AsF_6)_4$ were prepared in a T-shaped reaction vessel constructed from large (16 mm i.d.) and smaller (4 mm i.d.) FEP tubes joined at right angles and equipped with a Teflon valve. $Ca(AsF_6)_2$ (0.080 g, 0.19 mmol) and XeF_2 (0.653 g, 3.86 mmol) were weighed in the dry box, aHF was added and the solution decanted into the narrower arm of the reaction vessel. After several days of crystallization with a small temperature gradient, (6 K) crystals were obtained in the narrower tube and were isolated by pumping off the solvent on a vacuum line. Crystals were immersed in perfluorinated oil in the dry box. A suitable crystal was selected under the microscope and transferred into a cold nitrogen stream at the diffractometer.

Crystallographic data for $Ca_2(XeF_2)_9(AsF_6)_4$: $M_r(As_4Ca_2F_{42}Xe_9) = 2359.54$, crystal dimensions ca. 0.2 × 0.15 × 0.1 mm, tetragonal, $a = 1396.94(6)$, $c = 2207.69(14)$ pm, $V = 4.3082(4)$ nm^3, $\rho_{calcd} = 3.638$ $g\,cm^{-1}$, space group $P4/ncc$, $Z = 4$, $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), $\mu(Mo_{K\alpha}) = 10.462$ mm^{-1}, $F(000) = 4144$, $T = 200(1)$ K, no. of measured reflections 20346, of 2636 independent reflections, 2440 were considered with $I > 2\sigma(I)$, $R_{int} = 0.0595$. Data were collected on a Rigaku AFC7 diffractometer coupled with Mercury CCD area detector, ω and φ scans, multiscan absorption correction ($T_{min} = 0.176$, $T_{max} = 0.350$). Program used: Rigaku CrystalClear,[13] SIR92,[14] SHELXL-97.[15] Structure was solved by direct methods and full-matrix least-square refinement (133 parameters) of F^2 against all independent reflections was performed. Final R indices $R1 = 0.0780$ (all), $R1 = 0.0704$ [for $I > 2\sigma(I)$], $wR = 0.1391$ (all), $wR = 0.1342$ [for $I > 2\sigma(I)$], residual electron density 2614 and -2999 $e_0\,nm^{-3}$. 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 number CSD-413643.

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[1] R. Hagiwara, F. Hollander, C. Maines, N. Bartlett, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 855–866.
[2] P. Benkič, M. Tramšek, B. Žemva, *Solid State Sci.* **2002**, *4*, 1425–1434, and references therein.
[3] M. Tramšek, P. Benkič, B. Žemva, *Inorg. Chem.* **2004**, *43*, 699–703, and references therein.
[4] R. G. Pearson, *Inorg. Chem.* **1988**, *27*, 734–740.
[5] R. E. Rundle, *J. Am. Chem. Soc.* **1963**, *85*, 112–113.
[6] P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, C. G. Jones, D. F. Smith, *Science* **1963**, *139*, 842–844.
[7] J. Jortner, E. G. Wilson, C. A. Rice, *J. Am. Chem. Soc.* **1963**, *85*, 814–815.
[8] M. Ponikvar, B. Žemva, J. F. Liebman, *J. Fluorine Chem.* **2003**, *123*, 217–220.
[9] M. Ponikvar, B. Sedej, B. Pihlar, B. Žemva, *Anal. Chim. Acta* **2000**, *418*, 113–118.
[10] R. Pribil, *Applied Complexometry*, Pergamon, Oxford, **1982**, p. 200.
[11] H. M. Dess, R. W. Parry, G. L. Vidale, *J. Am. Chem. Soc.*, **1956**, *78* 5730–5734.
[12] M. Ponikvar, B. Pihlar, B. Žemva, *J. Fluorine Chem.* **2003**, *122*, 215–217.
[13] CrystalClear: Rigaku Corporation, Woodlands, Texas, USA, **1999**.
[14] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.
[15] G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**.