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The cubic $[Ti_8F_{36}]^{4-}$ anion found in the crystal structures of $K_4Ti_8F_{36}\cdot8HF$ and $Rb_4Ti_8F_{36}\cdot6HF$†

Cite this: *Chem. Commun.*, 2013, **49**, 2703

Received 29th January 2013,
Accepted 11th February 2013

DOI: 10.1039/c3cc40756j

www.rsc.org/chemcomm

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X-ray diffraction study of $K_4Ti_8F_{36}\cdot8HF$ and $Rb_4Ti_8F_{36}\cdot6HF$ reveals a novel type of octameric cubic $[M_8F_{36}]^{4-}$ anion built from eight $M^{IV}F_6$ octahedra.

In fluorides, the d transition-metal ions are usually found in octahedral coordination of six fluorine atoms. With exceptions involving heavier elements and cations with the d^8 and d^9 electronic configurations, the octahedral coordination is observed in majority of cases and it is unaffected by the oxidation state of the transition metal and by the M:F stoichiometry of the compound.[1]

Negatively charged MF_6 units could be isolated[2] or linked by sharing vertices, edges and faces. In this way larger and larger oligomeric polyanions grow before infinite 1D (chains), 2D (layers) or 3D networks are formed.[3]

Although, the number of theoretically possible compounds containing isolated oligomeric fluoro-polyanions is infinite, the number of known compounds containing oligomeric species with a high degree of MF_6 association is small.[3] The largest known example of discrete oligomeric fluoro-polyanions is octameric $[Al_8F_{35}]^{11-}$ where two tetrahedral Al_4F_{18} units (each consisting of four AlF_6 octahedra) share common fluorine atoms.[3] For M^{4+} the largest known discrete perfluoro-metallate anions with the highest rate of association are tetrameric $[Ti_4F_{18}]^{2-}$ and $[Ti_4F_{19}]^{3-}$ anions.[4–6]

During the investigation of AF–TiF_4–aHF (A = K, Rb; aHF = anhydrous HF) systems it was found that the slow crystallization of AF and TiF_4 (starting molar ratio AF : TiF_4 = 1 : 2) from aHF solutions (experimental data in ESI†) yields single crystals of $K_4Ti_8F_{36}\cdot8HF$ and $Rb_4Ti_8F_{36}\cdot6HF$. Their crystal structure determination revealed that both structures contain previously unknown octameric $[Ti_8F_{36}]^{4-}$ anions constructed from eight TiF_6 octahedral units connected into a cube (Fig. 1). In the case of non-fluorine containing compounds such species are observed in the crystal structure of $[Ti_8O_{12}(H_2O)_{24}]Cl_8\cdot HCl\cdot7H_2O$ which consists of a cubic octamer, $[Ti_8O_{12}(H_2O)_{24}]^{8+}$, where Ti atoms are bridged *via* oxygen atoms and their coordination is completed by terminal oxygen atoms of water molecules.[7] Besides the $[Ti_8O_{12}(H_2O)_{24}]^{8+}$ cubic octamer there are also other examples of non-fluorine containing compounds made of octameric species, but the geometry of octamers is different (*i.e.* β-$[Mo_8O_{26}]^{4-}$,[8–11] $[H_2Mo_8O_{28}]^{6-}$,[12] $[Al_8(OH)_{14}(H_2O)_{18}]^{10+}$,[13] $[M_8I_{28}]^{4-}$ (M = As, Sb, Bi),[14,15] $[Bi_8Cl_{30}]^{6-}$ (ref. 16), *etc.*).

Single crystals of $K_4Ti_8F_{36}\cdot8HF$ and $Rb_4Ti_8F_{36}\cdot6HF$ were grown by slow evaporation of volatiles from the corresponding saturated aHF solutions. The crystals are stable at ambient temperature only in the mother liquor. When the last traces of liquid aHF are removed they start to decompose. Their rapid decomposition could also be prevented by covering them by perfluorinated oil. The $K_4Ti_8F_{36}\cdot8HF$ and $Rb_4Ti_8F_{36}\cdot6HF$ both crystallize in the triclinic space group $P\bar{1}$ (Table S1, ESI†). The corresponding cell parameters are a = 10.2054(7) Å,

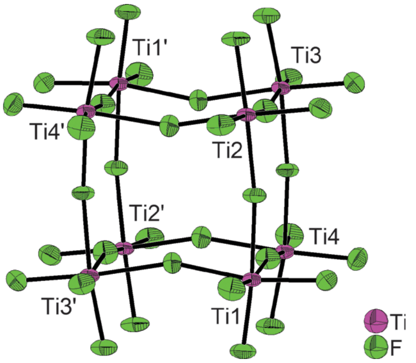

Fig. 1 The $[Ti_8F_{36}]^{4-}$ anion comprising eight TiF_6 octahedra in $K_4Ti_8F_{36}\cdot8HF$ (ellipsoids are drawn at 50% probability).

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† Electronic supplementary information (ESI) available: Detailed description of the preparation of single crystals and crystal structure determination (Table S1); interactions between A^+ (A = K, Rb) cations, HF molecules and $[Ti_8F_{36}]^{4-}$ anions and their packing (Fig. S1–S10); list of experimental in-phase Ti–F_t stretching frequencies of various $[Ti_nF_{4n+x}]^{x-}$ anions and calculated charge/n(Ti) ratios (Table S2). Further details of the crystal structure investigations may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition numbers CSD 425710 for $K_4Ti_8F_{36}\cdot8HF$ and CSD 425709 for $Rb_4Ti_8F_{36}\cdot6HF$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc40756j

b = 10.3448(1) Å, c = 10.5896(2) Å, α = 79.808(14)°, β = 65.208(11)°, γ = 60.889(11)°, V = 886.21(14) Å^3, Z = 1 for K-salt and a = 10.1991(17) Å, b = 10.4191(5) Å, c = 10.5848(7) Å, α = 89.68(6)°, β = 66.41(5)°, γ = 64.17(4)°, V = 908.2(7) Å^3, Z = 1 for Rb-salt. Their structures consist of alkali metal cations, HF molecules and $[Ti_8F_{36}]^{4-}$ anions (Fig. S1, ESI†). The $[Ti_8F_{36}]^{4-}$ anion appears as a cubic species, constructed from eight TiF_6 octahedra with the eight titanium atoms situated at the vertices of a cube (Fig. 1).

Each of the TiF_6 octahedra shares three fluorine atoms (at the *fac* position) with three neighboring TiF_6 octahedra. The $[Ti_8F_{36}]^{4-}$ anions are close to the regular cubes with similar nonbonding Ti···Ti distances which are in the range of 3.83(3)–3.93(3) Å for $K_4Ti_8F_{36}\cdot 8HF$ and of 3.86(14)–3.94(11) Å for $Rb_4Ti_8F_{36}\cdot 6HF$. The Ti···Ti···Ti angles are close to 90° (88.28(2)–91.75(2)° for K-salt and 89.41(6)–90.87(6)° for Rb-salt).

The Ti–F_t (F_t = terminal fluorine atom) bond lengths are significantly shorter than Ti–F_b (F_b = bridging fluorine atom) bond lengths. In $K_4Ti_8F_{36}\cdot 8HF$ the Ti–F_t bond lengths are 1.755(2)–1.801(2) Å and Ti–F_b are 1.9239(19)–2.0139(19) Å, while in $Rb_4Ti_8F_{36}\cdot 6HF$ the Ti–F_t bond distances are 1.754(6)–1.783(6) Å and Ti–F_b are 1.939(7)–2.005(6) Å. Both sets of distances are in agreement with those observed previously in various fluorotitanate(IV) compounds.[17,18]

It is well known that fluorine and oxygen atoms can be difficult to distinguish by X-ray diffraction, especially if the hydrogens of $[H_3O]^+$, H_2O or $[OH]^-$ species cannot be located. However, the observed bond lengths (Ti–F_b, Ti–F_t, A···FH, FH···$[Ti_8F_{36}]^{4-}$) and results of bond valence analyses exclude the presence of oxygen atoms or related species in $K_4Ti_8F_{36}\cdot 8HF$ and $Rb_4Ti_8F_{36}\cdot 6HF$.

Each $[Ti_8F_{36}]^{4-}$ anion forms 12 contacts with ten K^+ or 24 contacts with twelve Rb^+ cations, respectively (Fig. S2, ESI†). Additionally, each $[Ti_8F_{36}]^{4-}$ anion is involved in hydrogen bonding with eight (K-salt) or six (Rb-salt) HF molecules (Fig. S3, ESI†).

There are two crystallographically nonequivalent alkali metal cations in both crystal structures. In $K_4Ti_8F_{36}\cdot 8HF$ the K1 atoms form six contacts with three different $[Ti_8F_{36}]^{4-}$ anions and three contacts with HF molecules (Fig. S4a, ESI†), while K2 atoms form four contacts with three different $[Ti_8F_{36}]^{4-}$ anions and five contacts with HF molecules (Fig. S4b, ESI†). In this way the coordination number of K1 and K2 becomes equal to nine. The K1···F and K2···F bond lengths span a wide range, *i.e.* 2.659(3)–3.028(2) Å and 2.703(2)–3.042(2) Å, respectively. The corresponding bond valences are 1.138 vu (K1) and 0.991 vu (K2).

Neglecting K···F (where F belongs to the $[Ti_8F_{36}]^{4-}$ anion) contacts, the interactions between potassium cations and HF molecules lead to formation of infinite chains along the *a*-axis (Fig. S5, ESI†) where potassium atoms are linked *via* four crystallographically nonequivalent HF molecules.

The HF molecules are further involved in hydrogen bonding with fluorine atoms of the $[Ti_8F_{36}]^{4-}$ anion (Fig. S3, ESI†). The F···(H)···F distances are in the range of 2.53(2)–2.58(2) Å and hydrogen bonding could be classified as moderate, or even strong.[19]

Both crystallographically nonequivalent Rb^+ cations (Rb1 and Rb2) in the $Rb_4Ti_8F_{36}\cdot 6HF$ compound form contacts with three $[Ti_8F_{36}]^{4-}$ anions and with four (Rb1) or two (Rb2) HF molecules (Fig. S6a and b, ESI†). In this way all Rb atoms are coordinated by nine fluorine atoms. The Rb1···F (Rb2···F) contacts are in the range of 2.843(9)–3.215(10) Å (2.826(7)–3.114(8) Å). The corresponding bond valences are 0.927 vu (Rb1) and 1.015 vu (Rb2).

As a consequence of the lower amount of HF, the interactions between Rb atoms and HF molecules in $Rb_4Ti_8F_{36}\cdot 6HF$ differ from those observed in $K_4Ti_8F_{36}\cdot 8HF$. Two Rb1 atoms are bridged by two HF molecules and the Rb2 and Rb1 atoms are also connected *via* two HF molecules (Fig. S7, ESI†). Such structural units (four Rb atoms and 6 HF molecules) are not further connected into infinite chains *via* HF molecules as in the case of K-salt (Fig. S5, ESI†). Although HF bridging between closest neighbouring Rb2 atoms is absent, the nonbonding Rb2···Rb2 distances are the shortest among all nonbonding Rb···Rb distances resulting in the formation of imaginary chains (Fig. S7, ESI†).

As for potassium salt all six HF molecules in $Rb_4Ti_8F_{36}\cdot 6HF$ form hydrogen bonds with fluorine atoms of $[Ti_8F_{36}]^{4-}$ anions (Fig. S3, ESI†). The F···(H)···F distances (2.55(3)–2.57(4) Å) are in the same range as in the $K_4Ti_8F_{36}\cdot 8HF$ compound.

Packing of $[Ti_8F_{36}]^{4-}$ anions in $K_4Ti_8F_{36}\cdot 8HF$ and $Rb_4Ti_8F_{36}\cdot 6HF$ is similar, *i.e.* each $[Ti_8F_{36}]^{4-}$ anion is surrounded by twelve other anions (Fig. S8, ESI†). They are separated by K–HF chains or Rb–HF pseudo-chains (Fig. S9 and S10, ESI†).

The Raman spectra of $K_4Ti_8F_{36}\cdot 8HF$ and $Rb_4Ti_8F_{36}\cdot 6HF$ were recorded on grown crystals still covered by saturated HF solutions (Fig. 2). The same spectra were obtained on the crystals immersed in perfluorodecalin. Raman spectra of both compounds are practically identical. Five vibrational bands which do not overlap with the FEP reaction vessel could be assigned to the anion (wavenumber [intensity]: 755[100], 400[10], 237[10], 197[20] and 156[2] cm^{-1}). The most intense Raman band at 755 cm^{-1} belongs to the symmetric in-phase Ti–F_t stretching mode. The frequency of the band increases with increasing TiF_4 content and decreasing anion charge and it is very useful for

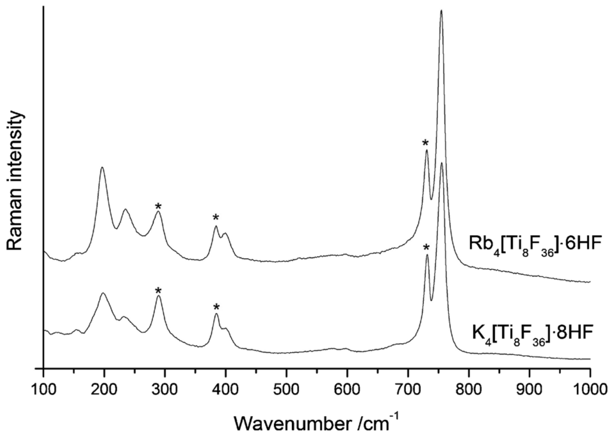

Fig. 2 Raman spectra of $K_4Ti_8F_{36}\cdot 8HF$ and $Rb_4Ti_8F_{36}\cdot 6HF$. The asterisk (*) denotes bands that could be assigned to the FEP reaction vessel.

the identification of various perfluoro-titanium anions.[20] To simplify the comparison of various $[Ti_nF_{4n+x}]^{x-}$ anions with different charges and TiF_4 contents, the total anion charge (x) could be divided by the number of TiF_6 octahedra or Ti atoms (n) present in the $[Ti_nF_{4n+x}]^{x-}$ anion. The resulting partial charges on single TiF_6 octahedra more clearly show the dependence of the in-phase Ti–F_t stretching mode on the TiF_4 content and total anion charge, *i.e.* the Raman frequency increases with increasing $x/n(TiF_6)$ value (Table S2, ESI†).

There are more than a hundred known examples of A_2MF_6 compounds (AF : MF_4 = 2 : 1; A = simple single charged cation such as alkali metal, H_3O^+, NH_4^+, O_2^+, Tl^+, Ag^+, *etc.*; M = M^{4+}) with determined crystal structures. The number of compounds with other AF : MF_4 molar ratios is much smaller and the available structural data are scarce. There is only one example of $K_3Cr_2F_{11}\cdot 2HF$[21] (AF : MF_4 = 1.5 : 1) and there are only three examples of structurally characterized AMF_5 compounds (AF : MF_4 = 1 : 1; H_3OTiF_5,[21] NH_4TiF_5,[22] $ACrF_5$, A = K, Rb, Cs[23]) built from $M^{IV}F_6$ octahedra. In the case of AMF_5 (M^{4+} = Zr, Hf, Te, Ce, Pr, Tb, Th, U and Np)[24] the coordination number of M^{4+} is higher than six.

The previous structural characterizations of AM_2F_9 compounds (with AF : MF_4 = 1 : 2 molar ratio and built from $M^{IV}F_6$ octahedra) are limited only to $H_3OTi_2F_9$,[5] $CsTi_2F_9$ (ref. 5) and $O_2Mn_2F_9$.[25] All three structures contain infinite $([Ti_2F_9]^-)_n$ double chains. The results of this study and the previous results show that the nature of the cation and incorporation of the solvent (HF) can strongly affect the geometry of the resulting anion despite the starting AF : TiF_4 molar ratio being the same. Although all crystals were grown from aHF solutions and in all cases the starting AF : TiF_4 molar ratio was equal to 1 : 2, the use of Cs^+ or H_3O^+ results in infinite double chain $([Ti_2F_9]^-)_n$ anions,[5] the use of larger cations results in $[Ti_4F_{18}]^{4-}$ oligomers[5] and the use of K and Rb results in the formation of previously unknown octameric $[Ti_8F_{36}]^{4-}$ anions. The $[Ti_8F_{36}]^{4-}$ anion reported herein is the second example of the isolated octameric unit found in fluoride compounds and the first example of cubic anion made from eight MF_6 octahedra.

It should be added that other examples of compounds with general formula AM_2F_9 (M = Nh, Te) also exist, however the coordination number around M^{4+} is higher than six.[26,27] Metals (M^{4+}) with higher coordination numbers also form compounds such as A_3MF_7, $A_5M_2F_{13}$, $A_5M_4F_{21}$, $A_7M_6F_{31}$ (M = Zr, Hf), *etc.*[28]

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