



One dimensional group 12 metal undecafluoridoditantalates



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ABSTRACT

The reactions between group 12 metals and the acidic TaF₅ were studied in the anhydrous HF (aHF) solvent. We were able to prepare and characterize the first compounds containing metal M²⁺ cations and undecafluoridodimetallate anions – M(Ta₂F₁₁)₂ (M = Cd, Hg) without the additional cations, anions or ligands included in the crystal structure. They both crystallize in *P*-1 space group with cell parameters $a = 9.1571(4) \text{ \AA}$, $b = 9.8750(3) \text{ \AA}$, $c = 10.9400(7) \text{ \AA}$, $\alpha = 94.389(4)^\circ$, $\beta = 113.124(5)^\circ$, $\gamma = 101.142(3)^\circ$, $V = 879.81(8) \text{ \AA}^3$, $Z = 2$, $T = 150 \text{ K}$ (Cd(Ta₂F₁₁)₂) and $a = 9.1381(5) \text{ \AA}$, $b = 9.8613(6) \text{ \AA}$, $c = 11.4470(7) \text{ \AA}$, $\alpha = 114.086(6)^\circ$, $\beta = 102.290(5)^\circ$, $\gamma = 100.398(5)^\circ$, $V = 877.84(11) \text{ \AA}^3$, $Z = 2$, $T = 150 \text{ K}$ (Hg(Ta₂F₁₁)₂). Metal cations connected through two anions form chains along *b* axis. M(HF)₂(TaF₆)₂nHF (M = Cd, Hg) compounds were also prepared in the MF₂/TaF₅ (M = Cd, Hg) system and their crystal structures were determined.

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1. Introduction

The undecafluoridodimetallate anions (A₂F₁₁[−]) are less common in superacid chemistry than the monomeric AF₆[−] species. They are obtained when excess parent Lewis acid AF₅ coordinates to fluoride ion in the solution to form A₂F₁₁[−] anion. Only the strongest Lewis acids AF₅ (A = As, Sb, Ru, Ir, Bi, Nb, Ta, Pt) tend to form such dimeric anions, but only systems containing Sb₂F₁₁[−] were studied more extensively. In most of those systems counter-cation is in +1 oxidation state. There are different reports on the preparation of pure M(AF₆)₂ compound prepared by the reaction between corresponding metal difluorides and AF₅ (A = As, Sb, etc.) fluoride-ion acceptors [1,2]. However crystallization from different solvents like SO₂, CH₃CN [3–5] and even anhydrous hydrogen fluoride (aHF), that is considered a weak ligand, mostly yields products with solvent coordinated to the metal center. UV–vis spectra of solutions containing Lewis acids (AsF₅, BF₃, etc.) and MF₂ in aHF show that metal centers are surrounded by HF molecules [6], that can be removed or partially removed during the isolation. A₂F₁₁[−] anions are larger than all other species in MF₂/AF₅/aHF system mentioned before therefore similar could be expected for M(A₂F₁₁)₂ compounds with metal 2+ cations. As expected all the reported compounds contain either other cations and anions (H₃O)Cd(SbF₆)(Sb₂F₁₁)₂, (H₃O)₂Cd(SbF₆)₃(Sb₂F₁₁) [7], AuXe₂F(SbF₆)(Sb₂F₁₁) [8] or just neutral ligands AuXe₂(Sb₂F₁₁)₂ [8], AuXe₄(Sb₂F₁₁)₂ [9], M(CO)_n(Sb₂F₁₁)₂ (M = Hg, Pd, Pt, Fe, Ru, Os; n = 2–

6) [10]. On the other hand no M(A₂F₁₁)₂ compound without additional ligand and with metal M²⁺ cations have been reported so far.

Our intention was to prepare and study the geometry of M(A₂F₁₁)₂ compounds without the influence of additional coordinated ligands or other cations that could influence its formation or geometry. Group 12 elements were selected because related products were observed for cadmium – (H₃O)Cd(SbF₆)(Sb₂F₁₁)₂ and (H₃O)₂Cd(SbF₆)₃(Sb₂F₁₁) [7], while Hg(Ta₂F₁₁)₂ in SO₂ solution was mentioned in the literature [11] without direct proof of its existence and composition. From all the suitable AF₅ Lewis acids TaF₅ was chosen as an acidic building block instead of widely used SbF₅ because it is not volatile at room temperature [12]. Consequently formed oligomers should have higher stability during crystallization or isolation. The only drawback of the TaF₅ is its lower solubility in aHF, which could influence its reactivity and formation of oligomeric species [13]. Ta₂F₁₁[−] anion can be rarely found in the literature and in most cases it is not structurally characterized. Examples of characterized compounds containing Ta₂F₁₁[−] anion that can be found in the literature are: O₂Ta₂F₁₁, CsTa₂F₁₁, XeFTa₂F₁₁ [14], [2,4-(OMe)₂C₆H₅][Ta₂F₁₁] [15], TBATa₂F₁₁ [16], Hg₄(Ta₂F₁₁)₂ [11].

2. Results and discussion

Synthesis in stoichiometric ratio between the MF₂ (M = Cd, Hg) and TaF₅ (1:4) in aHF led to formation of Cd(Ta₂F₁₁)₂ and Hg(Ta₂F₁₁)₂. Products are structurally related and both crystallize in triclinic *P*-1 space group.

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Metal centres in crystal structures are surrounded by eight fluorine atoms from four Ta_2F_{11} units in deformed square antiprism arrangement. (Figs. 1 and 2)

Both Ta_2F_{11} groups from asymmetric unit act as bidentate bridging ligands connecting two cadmium or mercury metal centers into chains along b axis (Figs. 3 and 4).

Cd–F distances in the crystal structure of $\text{Cd}(\text{Ta}_2\text{F}_{11})_2$ are in range from 2.251(4) to 2.410(4) Å (Fig. 1) which is similar to distances in CdF_2 (2.333 Å) [17]. Both crystallographically different $\text{Ta}_2\text{F}_{11}^-$ anions in the crystal structure are coordinated to two different cadmium atoms as bidentate bridging ligand (Fig. 5).

All Ta–F(Cd) bond distances are elongated and are in range from 1.918(4) to 1.942(4) Å. Polarization of the anion reduces non-bridging Ta–F distances which are in range from 1.821(4) to 1.851(4) Å with the Ta–F distances opposite to Ta–F(Ta) bond being the shortest. Bridging Ta–F(Ta) distances are from 2.056(4) to 2.077(4) Å. Cd to Cd distances in chain are 4.901(1) and 4.976(1) Å, which is well over the sum of Van der Waals radii, negating any possibility of direct metal–metal bonding [18].

Hg–F distances in the crystal structure of $\text{Hg}(\text{Ta}_2\text{F}_{11})_2$ are in range from 2.329(6) to 2.428(6) Å which is comparable to distances in HgF_2 2.40 Å [19]. Ta–F(Hg) distances are elongated and are in range from 1.926(7) to 1.948(6) Å. Non-bridging Ta–F distances are reduced similarly than in the crystal structure of $\text{Cd}(\text{Ta}_2\text{F}_{11})_2$. Bridging Ta–F(Ta) distances are from 2.059(6) to 2.069(6) Å. Distances between neighboring Hg atoms in the same chain are 4.902(1) and 4.961(1) Å, which is again longer than the sum of Van der Waals radii [18].

The $\text{A}_2\text{F}_{11}^-$ anions are considered weak ligands, and can be easily removed from coordination sphere of a metal cation in the presence of stronger ligands like CO [10]. On the other hand they tend to bend and orient themselves in such a way that they maximize the number of interactions with the cations through either hydrogen bonds [20,21] or act as a chelating ligands [7–9,22,23]. As a consequence of those effects, $\text{A}_2\text{F}_{11}^-$ anions are heavily distorted in practically all the crystal structures determined so far when measured by A–F–A bridge angles together with the torsion angle between two planar $\text{SbF}_{4\text{eq}}$ groups from eclipsed

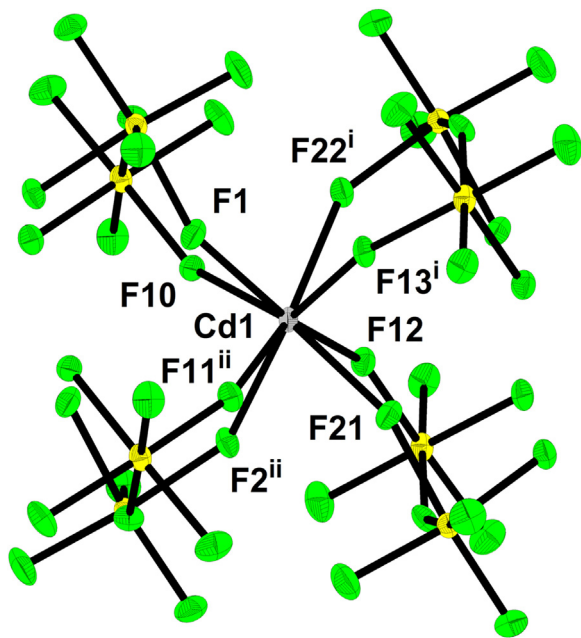


Fig. 1. Coordination sphere of Cd in the crystal structure of $\text{Cd}(\text{Ta}_2\text{F}_{11})_2$. Thermal ellipsoids are drawn at the 50% probability. Symmetry codes: (i) $2-x, 1-y, 2-z$; (ii) $2-x, 2-y, 2-z$.

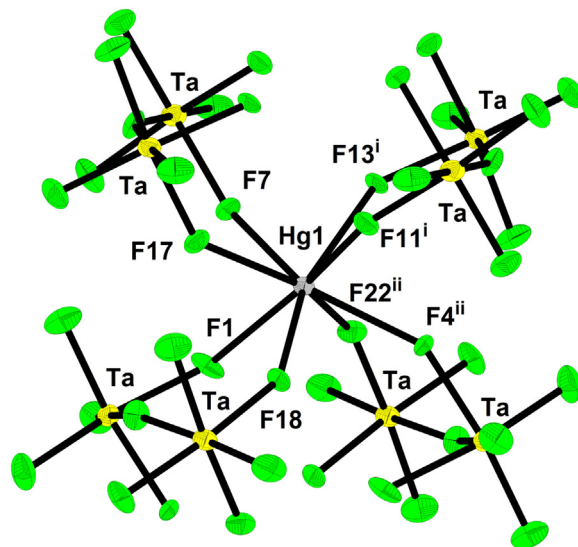


Fig. 2. Coordination sphere of Hg in the crystal structure of $\text{Hg}(\text{Ta}_2\text{F}_{11})_2$. Thermal ellipsoids are drawn at the 50% probability. Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 2-y, 1-z$.

to staggered conformation [24]. Gas phase calculations show that $\text{A}_2\text{F}_{11}^-$ anions should exist in D_{4h} symmetry [25], which is supported by recent crystal structure of the $[\text{2,4-(OMe)}_2\text{C}_6\text{H}_5][\text{A}_2\text{F}_{11}]$ ($\text{A}=\text{Nb, Ta}$). The $\text{A}_2\text{F}_{11}^-$ anion is completely linear in the described compound and is sandwiched between two arenium rings. DFT calculations for that system with $\text{Nb}_2\text{F}_{11}^-$ anion showed, that considering the interactions between a single anion and two adjacent arenium cations, a pile arrangement is theoretically favored, thus forcing the linearity of the Nb–F–Nb bridge. Conversely, the calculated structure related to one ion-pair in the gas phase shows bent Nb–F–Nb angle (159.5°) [15].

Bidentate coordination to two different metal atoms forces $\text{Ta}_2\text{F}_{11}^-$ anions to adopt even more distorted shape, which is shown in bridging Ta–F–Ta angles being $149.8(2)^\circ$ and $149.9(2)^\circ$ (dihedral angles $27.5(1)^\circ$, $23.4(1)^\circ$) in the crystal structure of $\text{Cd}(\text{Ta}_2\text{F}_{11})_2$, while the mercury analogue is slightly less distorted with Ta–F–Ta angles of $151.7(3)^\circ$ and $154.1(4)^\circ$ (dihedral angles $16.2(2)^\circ$, $23.9(2)^\circ$) (Fig. 6), probably as a consequence of slightly larger crystal radius of Hg^{2+} (1.28, Hg^{2+} ; 1.24, Cd^{2+}) [26]. Ta–F–Ta angle in related mercury compound – $\text{Hg}_4(\text{Ta}_2\text{F}_{11})_2$ is $153(1)^\circ$ [11], which is comparable to the ones obtained in the current study.

Such effects can also be seen in $(\text{H}_3\text{O})\text{Cd}(\text{SbF}_6)(\text{Sb}_2\text{F}_{11})_2$ where one $\text{Sb}_2\text{F}_{11}^-$ anion is tridentately coordinated to single cadmium cation having Sb–F–Sb angle as low as $143.1(3)^\circ$, while the other $\text{Sb}_2\text{F}_{11}^-$ anion with bidentate coordination has $147.9(2)^\circ$ angle [7]. Type of coordination influences torsion angle to a degree that cation and especially type of bonding to it dictates anion conformation in a crystal structure.

Reactions of both HgF_2 and CdF_2 with TaF_5 in 1:2 molar ratio resulted in $\text{M}(\text{TaF}_6)_2$ type of compound as expected, but crystallization of the product from solvent aHF ended up with $\text{Cd}(\text{HF})_2(\text{TaF}_6)_2 \cdot n\text{HF}$ and $\text{Hg}(\text{HF})_2(\text{TaF}_6)_2 \cdot n\text{HF}$. $\text{Cd}(\text{HF})_2(\text{TaF}_6)_2 \cdot n\text{HF}$ crystallizes in $P-1$ space group. Central cadmium atom has preferred coordination number 8 and is surrounded by 6 fluorine atoms from TaF_6 units and 2 fluorine atoms from coordinated HF molecules (Fig. 7). Basic building blocks consist of eight membered rings containing 2 cadmium, 2 tantalum and 4 fluorine atoms that are further connected into layers running along c axis. Cd–F(Ta) distances are from 2.218(4) to 2.301(4) Å, while Cd–F(HF) are 2.419(5) and 2.674(7) Å. HF(3) molecule is located outside the metal coordination sphere between two layers and is fixed in the crystal

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