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Journal of Fluorine Chemistry



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One dimensional group 12 metal undecafluoridoditantalates

ABSTRACT

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ARTICLE INFO

Article history: Received 13 June 2016 Received in revised form 21 July 2016 Accepted 26 July 2016 Available online 26 July 2016

Keywords: Undecafluoridoditantalates Hexafluoridotantalates Cadmium Mercury

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 – $M(Ta_2F_{11})_2$ (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) Å, b = 9.8750(3) Å, c = 10.9400(7) Å, $\alpha = 94.389(4)^{\circ}$, $\beta = 113.124(5)^{\circ}$, $\gamma = 101.142(3)^{\circ}$, V = 879.81(8) Å³, Z = 2, T = 150 K (Cd(Ta₂F₁₁)₂) and a = 9.1381(5)Å, b = 9.8613(6)Å, c = 11.4470(7)Å, $\alpha = 114.086(6)^{\circ}$, β = 102.290(5)°, γ = 100.398(5)°, V = 877.84(11) Å³, Z = 2, T = 150 K (Hg(Ta₂F₁₁)₂). Metal cations connected through two anions form chains along b axis. $M(HF)_2(TaF_6)_2$ mHF (M = Cd, Hg) compounds were also prepared in the MF₂/TaF₅ (M = Cd, Hg) system and their crystal structures were determined. © 2016 Elsevier B.V. All rights reserved.

1. Introduction

The undecafluoridodimetalate anions $(A_2F_{11}^{-})$ 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 $Sb_2F_{11}^{-}$ 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 $M(AF_6)_2$ 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. $A_2F_{11}^{-}$ anions are larger than all other species in MF₂/AF₅/aHF system mentioned before therefore similar could be expected for $M(A_2F_{11})_2$ 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) (Sb_2F_{11}) [8] or just neutral ligands $AuXe_2(Sb_2F_{11})_2$ [8], AuX $e_4(Sb_2F_{11})_2$ [9], M(CO)_n(Sb₂F₁₁)₂ (M = Hg, Pd, Pt, Fe, Ru, Os; n = 2-

http://dx.doi.org/10.1016/j.jfluchem.2016.07.019 0022-1139/© 2016 Elsevier B.V. All rights reserved. 6) [10]. On the other hand no $M(A_2F_{11})_2$ 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 $(A_2F_{11})_2$ 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 – $(H_3O)Cd(SbF_6)(Sb_2F_{11})_2$ and $(H_3O)_2Cd(SbF_6)_3(Sb_2F_{11})$ [7], while $Hg(Ta_2F_{11})_2$ 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 $Ta_2F_{11}^{-}$ 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 MF_2 (M = Cd, Hg) and TaF₅ (1:4) in aHF led to formation of $Cd(Ta_2F_{11})_2$ and Hg $(Ta_2F_{11})_2$. 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 Cd(Ta_2F_{11})₂ are in range from 2.251(4) to 2.410(4) Å (Fig. 1) which is similar to distances in CdF₂ (2.333 Å) [17]. Both crystallographically different $Ta_2F_{11}^-$ 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 nonbridging Ta–F distances which are in range from 1.821(4) to 1.851 (4) 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 $Hg(Ta_2F_{11})_2$ are in range from 2.329(6) to 2.428(6) Å which is comparable to distances in HgF₂ 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 Cd(Ta₂F₁₁)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 $A_2F_{11}^-$ 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, $A_2F_{11}^-$ 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 SbF_{4eq} groups from eclipsed



Fig. 1. Coordination sphere of Cd in the crystal structure of Cd(Ta₂ 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 Hg(Ta_2F_{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 $A_2F_{11}^-$ anions should exist in D_{4h} symmetry [25], which is supported by recent crystal structure of the [2,4-(OMe)_2C_6H_5] [A_2F_{11}] (A=Nb, Ta). The $A_2F_{11}^-$ anion is completely linear in the described compound and is sandwiched between two arenium rings. DFT calculations for that system with Nb₂F₁₁⁻ 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 $Ta_2F_{11}^{-}$ anions to adopt even more distorted shape, which is shown in bridging Ta–F–Ta angles being 149.8(2)° and 149.9(2)° (dihedral angles 27.5(1)°, 23.4(1)°) in the crystal structure of Cd(Ta₂F₁₁)₂, while the mercury analogue is slightly less distorted with Ta–F–Ta angles of 151.7(3)° and 154.1(4)° (dihedral angles 16.2(2)°, 23.9 (2)°) (Fig. 6), probably as a consequence of slightly larger crystal radius of Hg²⁺ (1.28, Hg²⁺; 1.24, Cd²⁺)[26]. Ta–F–Ta angle in related mercury compound – Hg₄(Ta₂F₁₁)₂ is 153(1)° [11], which is comparable to the ones obtained in the current study.

Such effects can also be seen in $(H_3O)Cd(SbF_6)(Sb_2F_{11})_2$ where one $Sb_2F_{11}^-$ anion is tridentately coordinated to single cadmium cation having Sb–F–Sb angle as low as $143.1(3)^\circ$, while the other $Sb_2F_{11}^-$ 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 HgF₂ and CdF₂ with TaF₅ in 1:2 molar ratio resulted in M(TaF₆)₂ type of compound as expected, but crystallization of the product from solvent aHF ended up with Cd(HF)₂(TaF₆)₂:nHF and Hg(HF)₂(TaF₆)₂:nHF. Cd(HF)₂(TaF₆)₂:nHF crystallizes in *P*-1 space group. Central cadmium atom has preferred coordination number 8 and is surrounded by 6 fluorine atoms from TaF₆ 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



Fig. 3. Mercury atoms connected through Ta₂F₁₁ units in the crystal structure of Hg(Ta₂F₁₁)₂.

space by moderate $F \cdots H$ -F hydrogen bonds anchored to the HF(1) molecule connected to the metal center and TaF₆ unit from the next layer (Fig. 8). However the HF is not strongly bound in the crystal structure and rapidly evaporates from it leading to total decomposition of the crystals in few hours as soon as the HF atmosphere in the reaction vessel is removed. Measurements of different crystals showed varying occupancy of HF in this position with the highest being 0.76 which is in the attached cif (Table 1).

 $Hg(HF)_2(TaF_6)_2$ nHF crystal structure is isotypic to previously described Cd(HF)_2(TaF_6)_2 nHF (Fig. 9). Hg–F(Ta) distances are from 2.298(7) to 2.368(6) Å, while Hg–F(HF) are 2.529(8) and 2.667(8) Å. The stability of mercury compound is same as in Cd (HF)_2(TaF_6)_2 nHF with HF molecules rapidly evaporating at room temperature. The highest measured occupancy of HF molecules between layers in the crystal structure is 0.58.

Assignation of bands in the synthesized products could be difficult due to the possible presence of other phases obtained during the synthesis in this system – especially MF(TaF₆), M(TaF₆)₂ and MTaF₇ as was reported in other systems [14]. Starting TaF₅ compound consists of tetramers in solid state, which was already proven by crystal structure and retains its oligomeric form even in liquid [27] and to a degree in gaseous state [28]. Raman spectrum of solid tetrameric TaF₅ has the strongest bands at 755, 727, 699, 671, 273, 254, 235 cm⁻¹ in C_{2h} symmetry [29,30].

Raman spectra of $M(TaF_6)_2$ (M = Cd, Hg) (Fig. 10, Table 2) show more bands than expected for regular TaF₆ octahedra. Different interactions of anion with cations and HF in solid state tend to



Fig. 4. Chains along b axis in the crystal structure of $Hg(Ta_2F_{11})_2$.

distort the Ta–F bonds and with it lower the symmetry of the anion resulting in some inactive vibrations to become active and may cause additional splitting. If we use assignation comparable to related compounds, Raman active bands for $M(TaF_6)_2$ (M = Cd, Hg) at 740 cm⁻¹ (Cd, Hg) could be assigned to v_1 stretching mode, while bands at 682 and 662 cm⁻¹ in cadmium and band at 672 cm⁻¹ in mercury compound can be a assigned to v_2 stretching mode. Bands at 295, 254 and 219 cm⁻¹ in Cd(TaF₆)₂ and 311 and 272 cm⁻¹ in Hg (TaF₆)₂ can be most probably assigned to v_5 bending normal modes and the rest are lattice modes.

Raman spectra measured on the $M(HF)_2(TaF_6)_2$ nHF (M = Cd, Hg) single crystals in perfluorinated oil immediately after the isolation were identical to the Raman spectra of bulk $M(TaF_6)_2$ (M = Cd, Hg).

Raman spectra of $M(Ta_2F_{11})_2$ (M = Cd, Hg) (Fig. 10, Table 2) are difficult to assign due to strong deformation of highly symmetric D_{4h} symmetry. In any case both Cd(Ta₂F₁₁)₂ and Hg(Ta₂F₁₁)₂ Raman spectra are nearly identical which can be expected from the crystal structure, where deformation in both compounds are nearly identical. Comparison to related Pd(CO)₄(Sb₂F₁₁)₂ shows similar deformation of A₂F₁₁⁻ anion [31]. Using the same similar trend bands at 750 and 740 cm⁻¹ in cadmium compound and 749 and 740 cm⁻¹ in mercury compound can be assigned to ν (TaF_{ax}), bands at 719, 694 and 674 cm⁻¹ (719, 691 and 670 cm⁻¹ for mercury) to



Fig. 5. Cadmium atoms connected through bridging $Ta_2F_{11}^-$ anions in the crystal structure of Cd(Ta_2F_{11})₂. Thermal ellipsoids are drawn at the 50% probability. Symmetry codes: (i) 2 - x, 2 - y, 2 - z.



Fig. 6. Bridging $Ta_2F_{11}^-$ anion in the structure of Hg(Ta $_2F_{11})_2$. Thermal ellipsoids are drawn at the 50% probability.

 ν (TaF_{4eq}), band at 309 cm⁻¹ (301 cm⁻¹ for mercury) to δ (TaF_{ax}), bands at 244 and 191 cm⁻¹ (247 and 188 cm⁻¹ for mercury) to δ (TaF_{4eq}) and band at 135 cm⁻¹ (131 cm⁻¹ for mercury) to δ (FTaF).

3. Conclusions

From all the so far known undecafluoridodimetallate compounds with divalent cations only $M(Ta_2F_{11})_2$ (M = Cd, Hg) exist in compound without additional ligands or ions. All the other compounds contain other ligands, anions or cations that interfere with their packing. Obtained compounds crystallize in *P*-1 space group. Ta₂F₁₁ units act as bidentate bridging ligand connecting two metal divalent cations forming one dimensional chains in the crystal structure. Dimeric anion tends to bend Ta–F–Ta angle to such a degree that it reaches the highest number of interactions with cations and are far away from ideal *D*_{4h} symmetry. On the other hand this deformation prevents the anion form forming interactions between chains therefore infinite one dimensional chains are observed.



Fig. 7. Coordination of Cd in the crystal structure of Cd(HF)₂(TaF₆)₂nHF. Thermal ellipsoids are drawn at the 50% probability. Symmetry codes: (i) 1 + x, *y*, *z*; (ii) 1 - x, 1 - y, 1 - z; (iii) 1 - x, 1 - y, 2 - z.



Fig. 8. Packing of layers in the crystal structure of Cd(HF)₂(TaF₆)₂ nHF.

4. Experimental

4.1. Apparatus, reagents and general experimental procedures

Anhydrous HF (aHF) was handled on a part of vacuum line made from Teflon, PFE, and FEP in order to diminish corrosion. Pressures were measured by means of a Monel Helicoid pressure gauge (0–3000 Torr $\pm 0.25\%$) connected to the vacuum manifold with a Teflon valve. Moisture-sensitive materials were handled in the dry argon atmosphere of a glove box (water content of ≤ 0.1 ppm; M. Braun, Germany).

Vacuum line used to carry out the reactions was coupled to a mechanical pump and oil diffusion pump. aHF was removed on the vacuum line with traps cooled by liquid nitrogen. Reaction vessels, made of PFA and equipped with Teflon valves and Teflon coated stirring bars, were used for the syntheses. Crystals were grown in a crystallization vessel, made from a T-shaped FEP reaction vessel constructed from a 16-mm i.d. length of FEP tube and a length of 4-mm i.d. FEP tubing connected to a Teflon valve. Saturated solutions in aHF were decanted from one arm of the crystallization vessel to the other. A temperature gradient was maintained between both arms in order to induce crystal growth.

Reagents. CdF₂ (99.9%, Alfa Aesar) and TaF₅ (99.9%, Alfa Aesar) were used as supplied. HgF₂ was prepared by high temperature (503 K) fluorination of HgCl₂ (99%, Merck) in 100 ml nickel autoclave. Anhydrous HF (3.5, Linde) was treated with K₂NiF₆ (Ozark-Mahoning, 99%) for several days prior to use. Caution: Reactions with anhydrous hydrogen fluoride and TaF₅ must be carried out in a well-ventilated hood and protective clothing must be worn at all times. The experimentalist must become familiar with these reagents and the hazards associated with them. Fresh tubes of calcium gluconate gel should always be on hand for the immediate treatment of Skin exposures see reference [32].

Synthesis of $M(TaF_6)_2$ (M = Cd, Hg). The Cd(TaF₆)₂ was synthesized from CdF₂ (0.136 g; 0.90 mmol) and stoichiometric amount of solid TaF₅ (0.499 g; 1.81 mmol) in aHF solvent in quantitative yield. Solvent was pumped off on the vacuum line and the product was characterized by the Raman spectroscopy.

 $Hg(TaF_6)_2$ was synthesized from HgF_2 (0.500 g; 2.10 mmol) and stoichiometric amount of solid TaF_5 (1.160 g; 4.20 mmol) in aHF solvent in quantitative yield. Solvent was pumped off on the vacuum line and the product was characterized by the Raman spectroscopy.

Synthesis of $M(Ta_2F_{11})_2$ (M = Cd, Hg). The Cd $(Ta_2F_{11})_2$ was synthesized from CdF₂ (0.030 g; 0.20 mmol) and stoichiometric amount of solid TaF₅ (0.220 g; 0.80 mmol) in aHF solvent in

	$Cd(Ta_2F_{11})_2$	$Hg(Ta_2F_{11})_2$	$Ta_4F_{20}^{b}$	Cd(HF) ₂ (TaF ₆) ₂ nHF	Hg(HF) ₂ (TaF ₆) ₂ [.] nHF
a (Å)	9.1571(4)	9.1381(5)	9.5386(3)	5.6993(3)	5.7076(1)
b (Å)	9.8750(3)	9.8613(6)	14.3655(3)	9.7763(6)	9.7665(2)
c (Å)	10.9400(7)	11.4470(7)	5.0042(1)	10.0580(6)	10.1663(2)
α (°)	94.389(4)	114.086(6)		98.691(5)	98.906(2)
β(°)	113.124(5)	102.290(5)	97.332(3)	90.432(5)	91.013(2)
γ(°)	101.142(3)	100.398(5)		103.232(5)	102.285(2)
V (Å ³)	879.81(8)	877.84(11)	680.10(3)	538.76(6)	546.29(2)
Z	2	2	2	2	2
Formula weight	703.76	1342.39	275.95	757.53	842.11
Space Group	P-1	P-1	C2/m	P-1	P-1
T (°C)	-123(1)	-123(1)	-123(1)	-123(1)	-123(1)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρcalcd (g/cm ³)	4.734	5.078	5.390	4.670	5.117
μ (mm ⁻¹)	26.166	33.750	32.298	22.401	34.177
R1	0.0316	0.0497	0.0202	0.0328	0.0364
wR2	0.0638	0.0949	0.0324	0.0934	0.0950

Table 1Crystal Data and structural Refinement^a.

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$, $wR_2 = [\Sigma (w(F_0^2 - F_c^2)^2) / \Sigma (w(F_0^2)^2)^{1/2}$.

^b redetermined.

quantitative yield. After the reaction was completed solvent was pumped off on the vacuum line. The product was characterized by the Raman spectroscopy.

The $Hg(Ta_2F_{11})_2$ was synthesized from HgF_2 (0.100 g; 0.42 mmol) and stoichiometric amount of solid TaF_5 (0.463 g; 1.68 mmol)in aHF solvent in quantitative yield. After the reaction was completed solvent was pumped off on the vacuum line. The product was characterized by the Raman spectroscopy.

4.2. Preparation of single crystals

Growth of Single Crystals of $M(Ta_2F_{11})_2$ (M = Cd, Hg). Stoichiometric amounts of MF_2 and TaF_5 were weighed in the glove box and put into the wider part of the crystallization vessel and dissolved in aHF. The crystals were grown with a temperature gradient of 28 K and were isolated by decantation of the mother liquor and were than sealed in the part of the vessel where they were grown and transferred to the glove box. The obtained crystals were immersed in perfluorinated oil (ABCR, FO5960) in a glove box. A suitable



Fig. 9. Packing of layers in the crystal structure of $Hg(HF)_2(TaF_6)_2$ nHF. Thermal ellipsoids are drawn at the 50% probability. Symmetry codes: (i) 1 + x, *y*, *z*; (ii) 1 - x, 1 - y, 1 - z; (iii) 1 - x, 1 - y, 2 - z.

crystal was selected under the microscope and transferred into the cold nitrogen stream (150 K) of the X-ray diffractometer. Such temperature was chosen, because crystals were cracking during the transfer into the cold nitrogen stream at lower temperatures.

Growth of Single Crystals of $M(HF)_2(TaF_6)_2$ nHF (M = Cd, Hg). Stoichiometric amounts of MF₂ and TaF₅ (Cd: 0.100 g CdF₂, 0.367 g TaF₅; Hg: 0.050 g HgF₂, 0.116 g TaF₅) were weighed in the glove box and put into the wider part of the crystallization vessel and dissolved in aHF. The crystals were grown with a temperature gradient of 28 K. When almost all the mother liquor had evaporated to the cooled part of crystallization vessel, cold perfluorinated oil (ABCR, F05960) was injected in the reaction vessel with a syringe and suspension of crystals in oil was transferred under the microscope and transferred into the cold nitrogen stream of the X-ray diffractometer.

4.3. X-ray structure determination

Single-crystal data for all compounds were collected on a Gemini A diffractometer equipped with an Atlas CCD detector, using graphite monochromated MoK α radiation. The data were treated using the CrysAlisPro software suite program package [33]. Analytical absorption correction has been applied to all data sets. Structures were solved with direct methods using the SHELXS program [34] or with charge-flipping method using the Superflip



Fig. 10. Comparison of Raman spectra of $Cd(Ta_2F_{11})_2$, $Hg(Ta_2F_{11})_2$, H_3OTaF_6 , TaF_5 , $Hg(HF)_2(TaF_6)_2$ nHF and $Cd(HF)_2(TaF_6)_2$ nHF.

Coi	mparison of	f Raman	bands of	f synthesized	compounds in	solid	state in	this system ⁴ .
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TaF5		H₃OTaF ₆		Cd(HF) ₂ (7 nHF	ΓaF ₆) ₂	Hg(HF) ₂ (' 'nHF	$TaF_6)_2$	Cd(Ta ₂ F ₁	1)2	Hg(Ta ₂ F	11)2
755	(100)							750	(100)	749	(100)
724	(12)	711	(100)	740	(100)	740	(100)	740	(13)	740	(20)
698	(25)			682	(18)	672	(12)	719	(8)	719	(6)
				662	(5)			694	(8)	691	(6)
								674	(8)	670	(12)
				295	(13)	311	(17)	309	(16)	301	(15)
271	(28)	284	(30)			272	(11)				
235	(7)			254	(8)			244	(6)	247	(32)
				219	(7)						
				181	(7)	200	(6)	191	(7)	188	(11)
				164	(5)	141	(24)	135	(7)	131	(8)

* Reference [38,39].

^a Vibrational frequencies are in cm⁻¹, and relative intensities are given in parentheres.

program [35] (Olex crystallographic software [36]). The electron density map, obtained by Superflip software, was analysed by EDMA program [37], which gave initial models of structures. Structure refinement has been performed with the SHELXL-2014 software [38], implemented in the program package WinGX [39]. Figures were prepared using Diamond 3.2 software [40]. The data can be ordered free of charge from the Crystal Structure Depot at FIZ Karlsruhe by quoting their CSD number (Cd(HF)₂(TaF₆)₂·nHF, 431292; Cd(Ta₂F₁₁)₂, 431293; Hg(HF)₂(TaF₆)₂·nHF, 431294; Hg (Ta₂F₁₁)₂, 431295; Ta₄F₂₀, 431296)

4.4. Raman spectroscopy

Raman Spectroscopy. Raman spectra of samples in sealed quartz capillaries or in perfluorinated oil (ABCR, FO5960) were recorded on a HORIBA JOBIN YVON LabRam-HR spectrometer equipped with an Olympus BXFM-ILHS microscope using the 632.8 nm line of a He-Ne laser for excitation. The geometry for all the Raman experiments was 1800 back scattering with a laser power of 20-0.002 mW.

Acknowledgement

The authors gratefully acknowledge the Slovenian Research Agency (ARRS) for the financial support of the Research Program P1-0045 (Inorganic Chemistry and Technology).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2016. 07.019.

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