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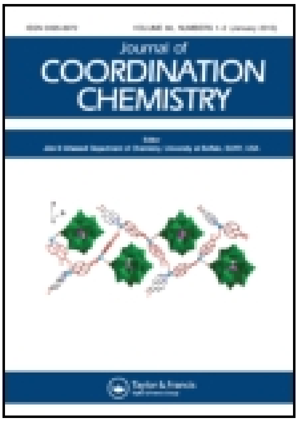

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Synthesis, structure, and thermal properties of fluorinated cesium beta-diketonates

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Synthesis, structure, and thermal properties of fluorinated cesium beta-diketonates

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Four fluorinated cesium beta-diketonates, Cs($CF_3COCHCOCF_3$) (Cs(hfac)), Cs($CF_3COCHCOCH_3$) (Cs(tfac)), Cs(OH_2)($(Me)_3CCOCHCOCF_3$) (Cs(OH_2)(ptac)), and Cs(OH_2)($PhCOCHCOCF_3$) (Cs(OH_2)(btfac)), were synthesized by interaction of the corresponding beta-diketone and Cs_2CO_3 in Et_2O. The formation of Cs($CF_3C(OH)_2CH_2C(OH)_2CF_3$)($CF_3COO$) or Cs($CF_3C(OH)_2CH_2COCH_3$)(tfac) was shown to be dependent on the reaction conditions. The compounds were characterized by elemental analysis, single crystal X-ray diffraction, and TG/DTA analysis.

All compounds have ionic structures organized into pseudo chains (in the case of Cs(hfac) and Cs($CF_3C(OH)_2CH_2COCH_3$)(tfac)) or pseudo layers (in other cases). According to the TG data Cs(hfac), Cs(tfac), Cs(OH_2)(ptac,) and Cs(OH_2)(btfac) decompose in inert atmosphere within the temperature range 30–550 °C.

Keywords: Cesium; Beta-diketonates; Single crystal X-ray analysis; Thermogravimetry; Differential thermal analysis

1. Introduction

The introduction of cesium-containing dopants into oxide film materials causes improvement of electric and electron functional characteristics. Thus, doping tin oxide films with cesium substantially improves electric conductance and sensor response to Liquefied Petroleum Gas [1]. According to a review [2], magnesium oxide films doped with cesium possess larger secondary electron emission coefficients than non-doped ones.

Film materials can be successfully formed by Chemical Vapor Deposition from the volatile metal compounds with organic ligands (MOCVD). The basic problem limiting the usage of cesium as a film dopant is the absence of suitable cesium compounds satisfying MOCVD requirements. The most important of the latter is volatility as a sufficiently high vapor pressure at relatively low temperatures.

Compounds with molecular structures are known to have high volatility since the energy of molecular interaction in their crystal lattices is very low, but very few cesium compounds with molecular structures are known [3] due to Cs^+ small charge and large radius, and consequently, high coordination numbers (>8), as well as a tendency to form ionic bonds.

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Nevertheless, volatile ionic bimetallic cesium-containing compounds Cs[ML_n] where $n = 4$, M = Sc [4], or Y [4a, 5], L = hfac ($CF_3COCHCOCF_3$); M = Ho [6] or UO [7], L = ptac $(Me)_3CCOCHCOCF_3$, or $n = 3$, M = Co, Ni, etc. [8], L = hfac, tfac ($CF_3COCHCOCH_3$), acac ($CH_3COCHCOCH_3$) were described. Many of the compounds mentioned above sublime from 150 to 250 °C.

Compounds for synthesis of cesium-containing complexes are cesium beta-diketonates [4, 5, 8]. Combination of cesium beta-diketonate with bulky neutral ligands such as for example, crown ethers, would produce a molecular crystal structure and possess sufficient volatility. Similar compounds have been obtained for sodium and potassium [9].

The successful use of cesium beta-diketonates as reagents requires knowledge of chemical and thermal properties. However, little work on the synthesis of such compounds is reported [10]; moreover, data on the structures and chemical properties of these compounds are absent.

The goal of the present work is the synthesis of fluorinated cesium beta-diketonates and investigation of the structures and thermal properties of the compounds obtained.

2. Experimental

2.1. *Synthesis*

All chemicals were commercially available products of reagent grade and used without purification.

Cesium β-diketonates were obtained by reaction of Cs_2CO_3 with corresponding beta-diketone in Et_2O. A weighed portion of cesium carbonate was placed in an Erlenmeyer flask equipped with a backflow condenser with a calcium chloride tube, and then Et_2O and beta-diketone were added. The reaction mixture was stirred at fixed temperature for a certain time. Experimental details (time, temperature, reagent proportions) are presented below. The product, if precipitated, was separated by filtration, otherwise – by evaporation of the solution.

The substances were white powders stable during storage under ambient conditions.

Cesium (1,1,1,5,5,5-hexafluoroacetylacetonate) (**1**) was obtained from 2.60 g Cs_2CO_3 (8.0 mM) and 3.33 g Hhfac (2.4 mL, 16.0 mM) in 25 mL Et_2O under 4 h at RT (25 °C). Then the solution was evaporated yielding 4.60 g (13.5 mM) Cs(hfac), yield 84%. Anal Calcd for $C_5H_1F_6O_2Cs$(%): C, 17.7; H, 0.3; F, 33.5. Found: C, 18.1; H, 0.2; F, 33.5.

Cesium (1,1,1,5,5,5-hexafluoropenta-2,2,4,4-tetraol)(1,1,1-trifluoroacetate) (**2**) was obtained from 2.60 g Cs_2CO_3 (8.0 mM) and 5.60 g Hhfac (4.0 mL, 27.0 mM) in 50 mL Et_2O under 10 h reflux (35 °C). The precipitated product was separated to give 3.46 g Cs(hfac) (10.2 mM), while evaporation of the mother liquid yielded 3.04 g of the crude product. Recrystallization of the latter from Et_2O afforded crystals of **2** and also *1,1,1,5,5,5-hexafluoropenta-2,2,4,4-tetraol* (H_4hfpt).

Cesium (1,1,1-trifluoroacetylacetonate) (**3**) was obtained from 2.85 g Cs_2CO_3 (8.7 mM) and 2.68 g Htfac (1.9 mL, 17.4 mM) in 45 mL Et_2O under 4 h reflux (35 °C). Then the solution was evaporated yielding 3.00 g (10.5 mM) Cs(tfac), yield 60%. Anal Calcd for $C_5H_4F_3O_2Cs$(%): C, 17.7; H, 0.3; F, 33.5. Found: C, 18.1; H, 0.2; F, 33.5.

Cesium (5,5,5-trifluoropentanediol-4,4-on-2)(1,1,1-trifluoroacetylacetonate) (**4**) was obtained from 3.21 g Cs_2CO_3 (9.9 mM) and 4.58 g Htfac (3.3 mL, 29.7 mM) in 40 mL Et_2O under 3.5 h reflux (35 °C). The resulting solution was evaporated to give solid product (6.60 g). Recrystallization from Et_2O yielded crystals **4**. Compound **4** was unstable at atmosphere conditions.

Cesium aqua (pivaloyltrifluoroacetonate) (**5**) was obtained from 2.60 g Cs_2CO_3 (8.0 mM) and 3.15 g Hptac (2.3 mL, 16.0 mM) in 55 mL Et_2O under 6 h reflux (35 °C). The precipitated product was separated by filtering to give 3.92 g $Cs(OH_2)$ (ptac) (11.3 mM). Anal Calcd for $C_8H_{12}F_3O_3Cs$(%): C, 27.8; H, 3.5; F, 16.5. Found: C, 27.9; H, 4.0; F, 17.0.

Cesium (benzoyltrifluoroacetonate) and *Cesium aqua (benzoyltrifluoroacetonate)* (**6**) were obtained from 1.30 g Cs_2CO_3 (4.0 mM) and 1.95 g Hbtfac (9.0 mM) in 30 mL Et_2O under 2 h reflux (35 °C). The precipitate (2.25 g) separated by filtering was a mixture of $Cs(OH_2)$ (btfac) and Cs(btfac) at the ratio of 37 : 63 (per 100%). Anal Calcd for $C_{10}H_{6.7}F_3O_{2.5}Cs$(%): C, 33.8; H, 1.9; F, 16.0. Found: C, 33.9; H, 1.7; F, 16.1.

2.2. *Methods of characterization*

Crystals suitable for single crystal X-ray diffraction analysis were obtained by slow crystallization of the synthesized substances from organic solvents: Et_2O for **1**–**4** and acetone for **5** and **6**. Suitable single crystals were mounted on a Bruker Nonius X8 Apex 4 K CCD diffractometer fitted with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 150 K for all structures by standard technique [11]. Absorption corrections were made empirically using SADABS [11]. The structures were solved by direct methods and further refined by full-matrix least-squares using the SHELXTL program package [12]. Hydrogen positions were calculated geometrically and refined in the rigid body approximation (riding model). Crystal data and the final refinement details are given in table 1. The packing diagrams were drawn using the POV-Ray program package [13].

Elemental analysis was carried out at the Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS [14a,b]. The amount of fluorine was determined according to the procedure for measurement of the mass fraction of fluorine in organic substances using the spectrophotometric method [14c]. The error of determination did not exceed 0.5%.

Thermogravimetry (TG) and Differential Thermal Analysis (DTA) data for **1**, **3**, **5** and mixture of Cs(btfac) and **6** were obtained using thermoanalizator Netzsch STA 409 PC/PG. The experiments were conducted in He flow (20 $mL\,min^{-1}$) with heating rate $10\,K\,min^{-1}$ from 298 to 883 K. Products of thermal decomposition in an inert atmosphere at 600 °C were amorphous so that no phase identification by XRD was possible.

Melting points of the compounds were determined visually using a Kofler table.

3. Results and discussion

3.1. *Synthesis*

The synthesis of cesium beta-diketonate was carried out through the substitution of carbonate by beta-diketonate in diethyl ether. Reaction temperature and molar ratios of the reagents have a dramatic influence on the process.

Table 1. Experimental details and crystallographic data for **1**–**6**.

Compound number	**1**	**2**	**3**	**4**	**5**	**6**
Identification code	*Cs(hfac)*	*Cs(H$_4$hfpt)(CF$_3$COO)*	*Cs(tfac)*	*Cs(H$_2$tfpd)(tfac)*	*Cs(OH$_2$)(ptac)*	*Cs(OH$_2$)(btfac)*
Empirical formula	$C_5H_1F_6O_2Cs$	$C_7H_6F_9O_6Cs$	$C_5H_4F_3O_2Cs$	$C_{10}H_{11}F_6O_5Cs$	$C_8H_{12}F_3O_3Cs$	$C_{10}H_8F_3O_3Cs$
Formula weight	339.97	490.03	285.99	458.10	346.09	366.07
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$		Monoclinic, $P2_1/n$		Orthorhombic, *Pcca*
Unit cell dimensions						
a (Å)	5.0137 (2)	8.8939 (3)	11.2580 (5)	21.6252 (8)	16.1090 (8)	21.0775 (13)
b (Å)	11.6863 (5)	14.0623 (4)	5.1263 (2)	5.8218 (2)	6.0850 (3)	13.7566 (9)
c (Å)	15.0413 (6)	10.9990 (3)	13.4370 (5)	24.3261 (9)	24.2640 (13)	8.4184 (4)
α (°)	77.605 (2)	90.00	90.00	90.00	90.00	90.00
β (°)	83.020 (2)	96.793 (1)	102.400 (2)	101.102 (1)	93.272 (2)	90.00
γ (°)	78.998 (2)	90.00	90.00	90.00	90.00	90.00
V, Å^3	841.94 (6)	1365.97 (7)	757.38 (5)	3005.28 (19)	2374.6 (2)	2441.0 (2)
Z, d_{cal} (g cm^{-3})	4, 2.682	4, 2.383	4, 2.508	8, 2.025	8, 1.936	8, 1.992
Absorption coefficient (mm^{-1})	4.472	2.847	4.890	2.548	3.144	3.065
F (0 0 0)	624	928	528	1760	1328	1392
Crystal size (mm)	0.50 × 0.30 × 0.05	0.40 × 0.35 × 0.25	0.40 × 0.10 × 0.03	0.40 × 0.24 × 0.15	0.35 × 0.12 × 0.03	0.40 × 0.40 × 0.08
θ range for data collection	2.06–26.37	2.31–33.15	3.10–32.54	1.40–26.37	1.48–26.43	2.43–25.33
Limiting indices	$-6 \leqslant h \leqslant 6$, $-14 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 18$	$-13 \leqslant h \leqslant 13$, $-17 \leqslant k \leqslant 21$, $-16 \leqslant l \leqslant 10$	$-16 \leqslant h \leqslant 17$, $-7 \leqslant k \leqslant 6$, $-18 \leqslant l \leqslant 20$	$-27 \leqslant h \leqslant 27$, $-4 \leqslant k \leqslant 7$, $-30 \leqslant l \leqslant 25$	$-20 \leqslant h \leqslant 19$, $-7 \leqslant k \leqslant 7$, $-30 \leqslant l \leqslant 30$	$-25 \leqslant h \leqslant 25$, $-16 \leqslant k \leqslant 16$, $-10 \leqslant l \leqslant 5$
Reflections collected/ unique (R_{int})	6995/3401 (0.0288)	14,756/5210 (0.0289)	8140/2748 (0.0286)	17,330/6152 (0.0234)	14,641/4881 (0.0359)	12,583/2219 (0.0391)
Completeness to $\theta = 25.25°$ (%)	99.5	99.9	99.9	99.8	99.9	99.0
Maximum and minimum transmission	0.2133 0.8073	0.3955 0.5363	0.2451 0.8672	0.4288 0.7011	0.4058 0.9116	0.376 0.7916
Data/restraints/ parameters	3401/0/253	5210/0/232	2748/0/101	6152/0/401	4881/4/281	2219/0/156
Goodness-of-fit on F^2	0.989	1.027	1.060	1.056	0.997	1.067
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0217$, $wR2 = 0.0472$	$R1 = 0.0234$, $wR2 = 0.0532$	$R1 = 0.0177$, $wR2 = 0.0410$	$R1 = 0.0261$, $wR2 = 0.0675$	$R1 = 0.0293$, $wR2 = 0.0617$	$R1 = 0.0471$, $wR2 = 0.1429$
R indices (all data)	$R1 = 0.0301$, $wR2 = 0.0493$	$R1 = 0.0275$, $wR2 = 0.0548$	$R1 = 0.0220$, $wR2 = 0.0421$	$R1 = 0.0280$, $wR2 = 0.0687$	$R1 = 0.0472$, $wR2 = 0.0669$	$R1 = 0.0590$, $wR2 = 0.1524$
Largest difference peak and hole (eA^{-3})	0.593/−0.699	1.022/−0.968	0.535/−0.756	1.259/−0.833	0.857/−1.102	2.842/−1.905

Cs(hfac) (**1**) was successfully obtained by reaction of Cs_2CO_3 and Hhfac in molar ratio 1 : 2 at room temperature. Boiling of these reagents in Et_2O in the presence of 50% molar excess of Hhfac gave the precipitate of **1**; the ether solution contained H_4hfpt and $Cs(CF_3C(OH)_2CH_2C(OH)_2CF_3)(CF_3COO)$ (**2**). Evaporation of the solvent and recrystallization from Et_2O led to mixture of H_4hfpt and **2**. The compounds obtained were characterized by single crystal X-ray analysis; the structure of H_4hfpt had been earlier described [15].

The possible reason for H_4hfpt formation is the nucleophilic addition of water to the carbonyl groups of Hhfac [16]. The formation of trifluoroacetate is likely to occur as a consequence of Hhfac hydrolysis in the basic medium [17]. The water hydrating beta-diketones may be present in diethyl ether or/and from air during evaporation of mother solution. Stoichiometric amount of water is formed *in situ* due to the reaction $Cs_2CO_3 + 2$ Beta-diketone = 2 Cs(beta-diketonate) + $CO_2 + H_2O$. These water molecules can react with the ligands or can be coordinated by Cs.

The boiling of 1,1,1-trifluoroacetylacetone with Cs_2CO_3 at the ratio of 2 : 1 yielded cesium trifluoroacetylacetonate (**3**) only, while the same reaction in the presence of a 50% excess of the ligand led to the formation of $Cs(CF_3C(OH)_2CH_2COCH_3)$(tfac) (**4**). The latter was unstable under storage and 5,5,5-trifluoropentanediol-4,4-on-2 formed during decomposition of **4** was easily removed by washing with nonpolar solvent such as toluene or hexane giving Cs(tfac) (**3**).

The selectivity of water nucleophilic addition to carbonyl of **3** can be explained in terms of the negative inductive effect of CF_3 such that carbon at position C2 is favored towards nucleophilic attack.

The boiling of pivaloyltrifluoroacetone and Cs_2CO_3 at a ratio of 2 : 1 in Et_2O led to formation of a stable phase of cesium aqua pivaloyltrifluoroacetonate (**5**).

The interaction of benzoyltrifluoroacetone and Cs_2CO_3 under similar conditions gave a mixture of cesium benzoyltrifluoroacetonate Cs(btfac) and cesium aqua benzoyltrifluoroacetonate $Cs(OH_2)$(btfac) (**6**) at a ratio of 63 : 37 according to TG data (see *thermogravimetric examination*) and elemental analysis data. Attempts to obtain Cs(btfac) crystals suitable for XRD had no success; only $Cs(OH_2)$(btfac) (**6**) single crystals were observed. Thus, water presence is required to form good-quality crystals (see *single-crystal XRD examination*). It should also be noted the crystals of **6** were unstable during storage and sensitive to illumination (visible light, X-rays). In our opinion, the destruction was connected with the detachment of crystallization water (see *thermogravimetric examination*).

3.2. *Single-crystal XRD examination*

All the structures show ionic character with different ionic arrangement. The crystal packing, Cs…O and Cs…F distance ranges, and average lengths are listed in table 2.

Cs(hfac) (**1**). Cesium hexafluoroacetylacetonate crystallizes in the triclinic crystal system. There are two independent cations in the structure. The nearest environment of Cs1 and Cs2 consists of 11 and 12 O and F atoms, respectively. The first coordination sphere is six and seven for Cs1 and Cs2, respectively. Zigzag bands consisting of Cs cations are located along the *a*-axis. These bands are linked with longer Cs…F contacts. If one selects the lines coinciding with the anion directions (O…O direction for example) these lines for all organic anions are collinear within 4.4°. The shortest distance between Cs cations (Cs1…Cs2) is 4.2000(3) Å. The pseudo chain structure is represented at figure 1.

Table 2. Selected Cs–O and Cs–F distances and crystal packing for **1**–**6**.

	Distance Cs–O, Å		Distance Cs–F, Å		
Compound	Range	Average value	Range	Average value	Dimensionality**
Cs(hfac) (**1**)	3.041(2)–3.407(2)	3.2⟨1⟩	3.255(2)–3.722(2)	3.4⟨2⟩	1-D
Cs(H_4hfpt)(CF_3COO) (**2**)	2.9918(13)–3.4518(12)	3.2⟨2⟩	3.2022(13)–3.6870(17)	3.4⟨2⟩	2-D
Cs(tfac) (**3**)	3.0346(14)–3.4934(14)	3.2⟨2⟩	3.0242(14)–3.5119(12)	3.3⟨2⟩	2-D
Cs(H_2tfpd)(tfac) (**4**)	3.038(2)–3.325(2)	3.16⟨8⟩	3.214(3)–3.750(2)	3.5⟨3⟩	1-D
Cs(OH_2)(ptac) (**5**)	3.094(3)–3.547(2)3.063(3)–3.554(3)*	3.2⟨2⟩3.3⟨2⟩*	3.194(2)–3.300(3)	3.26⟨5⟩	2-D
Cs(OH_2)(btfac) (**6**)	3.038(4)–3.249(5)2.990(6)–3.063(6)*	3.18⟨9⟩ 3.03⟨4⟩*	3.209(5)–3.323(4)	3.27⟨7⟩	2-D

*The distances Cs…OH_2.
**1-D = pseudo chain structure, 2-D = pseudo-layered structure.

$Cs(CF_3COO)(CF_3C(OH)_2CH_2C(OH)_2CF_3)$ (**2**). The synthesis of **1** under modified conditions resulted in formation of a new compound **2** containing an unusual form of beta-diketone. In this compound, hexafluororoacetylacetone is hydrated on both carbonyl groups, and anion is CF_3COO^-. Cs cation has four *$CF_3C(OH)_2CH_2C(OH)_2CF_3$* ($H_4$hfpt) species and three trifluoroacetate-anions. Coordination number of Cs atom is 12: six oxygens belonging to three OH of three H_4hfpt and three trifluoroacetates, and six fluorines from four H_4hfpt and two trifluoroacetates (figure 2). The whole structure is pseudo-layered with alternating organic anionic layers and cationic Cs spaces. The shortest distance between the Cs cations is Cs1…Cs1 ($2-x$, $-y$, $2-z$) of 4.5937(2) Å. The hexagonal distorted framework in Cs arrangement could be marked out in the structure.

Bond lengths and angles in H_4hfpt (either free state [15] or cocrystallizate **2**) or its anionic forms (consisting of complexes [15b, 16]) do not change significantly during formation of M–F contacts and M–O bonds or contacts.

The angle values and C–C and C–F bond lengths of CF_3COO^- of **2** and $CsH(CF_3COO)_2$ [18] are almost equal. The C–O distances in CF_3COO^- of **2** are (1.226(2) and 1.265(2) Å), while the longer bond refers to oxygen with two H-bonds.

Cs(tfac) (**3**). Pseudo-layered structure is observed for cesium trifluoroacetylacetonate. The layers are located into the *bc* planes with the gap between them referring to the *a* parameter. The first coordination sphere of Cs consists of seven oxygens and three fluorines belonging to five trifluoroacetylacetonates. Cs cations form zigzag distorted hexagonal grids inside the pseudo layers. Flat trifluoroacetylacetonates form the herringbone parquet pattern below and above the cationic layer. The shortest distance between Cs cations is Cs1…Cs1 ($1-x$, $-y$, $-z$) at 3.9532(2) Å.

$Cs(CF_3C(OH)_2CH_2COCH_3)(tfac)$ (**4**). Unlike the structure of **2**, this compound contains beta-diketone hydrated at only one carbonyl group ($CF_3C(OH)_2CH_2COCH_3$, H_2tfpd) as a cocrystallite. There are two crystallographically independent Cs cations in the unit cell. Both have eight oxygens and two fluorines belonging to three trifluoroacetylacetone anions and two H_2tfpd (figure 3). Despite changes in γ-carbon's hybridization, the plane is preserved through the carbons in H_2tfpd. Crystal packing gives the pseudo chain type. The

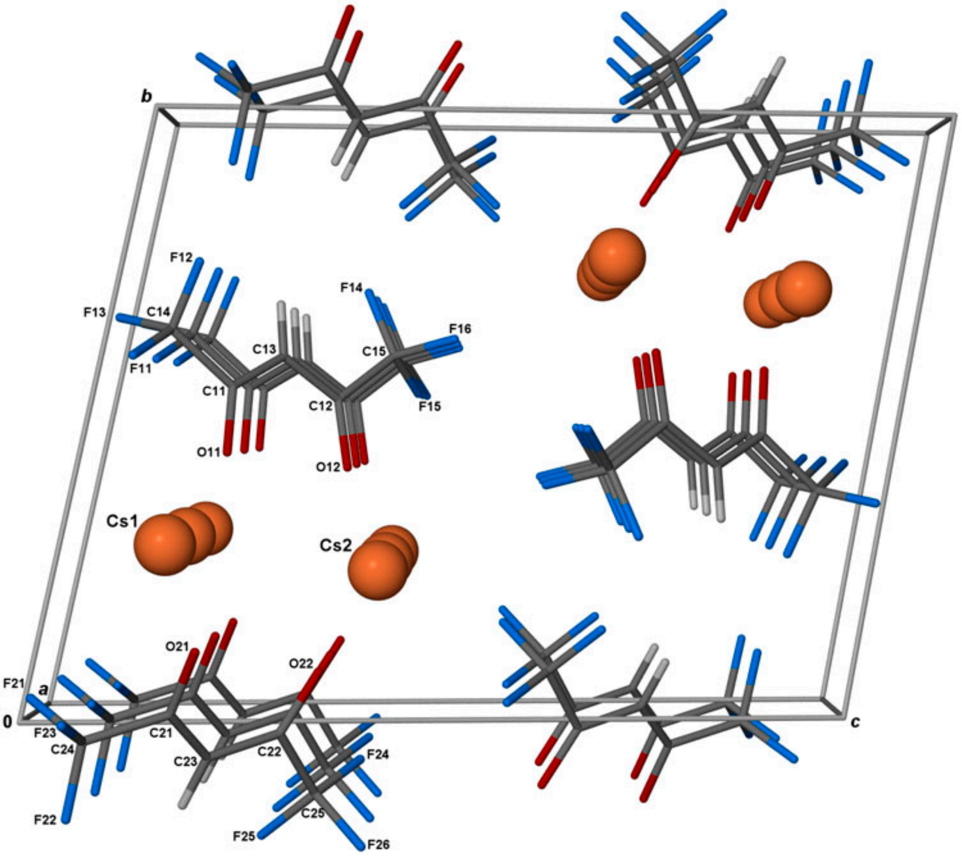

Figure 1. Example of pseudo chain structure for Cs(hfac) (**1**). Interactions between Cs cations and O or F of anions are not depicted for simplification.

anions organize such that zigzag channels with negatively charged walls consisting of carbonyl or hydroxyl groups are formed along the *b*-axis. The shortest distances between the Cs cations are Cs1…Cs1 ($1/2-x$, $y+1/2$, $1/2-z$) of 4.1402(3) Å and Cs2…Cs2 ($3/2-x$, $1/2+y$, $1/2-z$) at 4.2432(3) Å in the zigzag chains.

Table 3 presents the bond lengths for tfac, H_2tfpd, and tfpd of **3**, **4,** and Sb(p-PhCl)$_3$(tfpd) [19].

Bond length and angle values of tfac anion in **3** and **4** are practically equal. Thus, the presence of H_2tfpd in **4** reorganizing the crystal structure does not influence the geometric characteristics of tfac. For tfac structure C_γ–C_β bond is a bit shorter than C_γ–C_δ, while C_β–C_α is a bit longer than C_δ–C_ε (for atom numeration, see figure 4). This is the characteristics of unsymmetrical beta-diketonates containing CF_3 [20].

The addition of water to tfac anion causes the following structure changes as a result of ρ-π conjugation loss and redistribution of electron density; while C_β–C_α and C_δ–C_ε bond lengths remain practically the same C_γ–C_β and C_γ–C_δ bond lengths become longer and elongation of C_γ–C_β bond is increased.

Structure comparisons of protonated (**4**) and deprotonated (in Sb(p-PhCl)$_3$(tfpd) [19]) H_2tfpd show practically all geometric parameters of the gem-diol persist in both ionic and

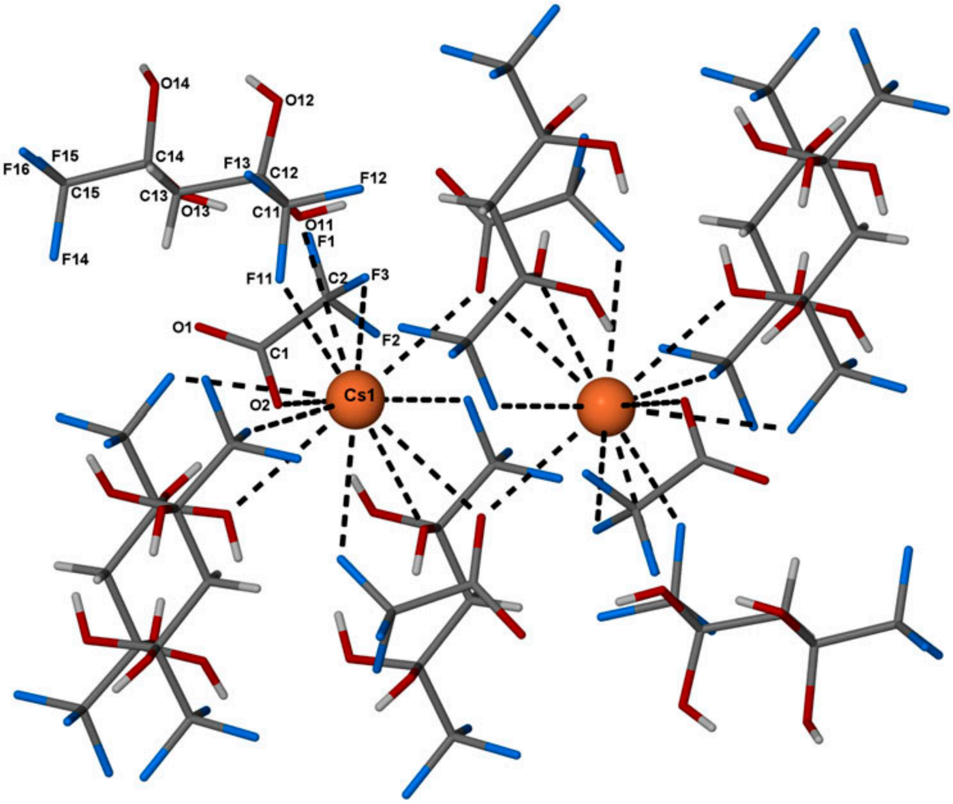

Figure 2. The nearest Cs^+ environment in the structure of **2**.

coordination compounds. Only the O–C–O angle makes an exception (112.6(2)° in **4** and 103.8° in $Sb(p\text{-}PhCl)_3(tfpd)$ [19]).

$Cs(OH_2)(ptac)$ (**5**). Cesium pivaloyltrifluoroacetonate cocrystallizes with water. There are two independent formula units in the structure. Two Cs cations have β-diketonate anionic and aqueous environment with shortest contact with the negatively charged O and F. Each cation consists of four anionic species and three water molecules such that every Cs has 10 neighboring electronegative atoms in the coordination sphere (see figure 5). The shortest distance between Cs cations is 4.2346(3) Å. There is a pseudo-layered arrangement of cationic–anionic parts inside the crystal structure. The pseudo layer directions coincide with the planes' family (101). Cs ions form distorted square network into the pseudo layer. The interlayer space is occupied with the *tert*-butyl substitutes of β-diketonate anions.

$Cs(OH_2)(btfac)$ (**6**). Compound **6** also cocrystallizes with one water molecule. There are two independent Cs cations in the structure. Cs1 has eight oxygens from four beta-diketonates in the vertices of a square antiprism and Cs2 is surrounded by four fluorines of four beta-diketonates and four water molecule (see figure 6). Crystal packing represents a pseudo-layered structure (see figure 7). The shortest distance between Cs cations is 4.2092 (2) Å. All Cs cations form nearly square frameworks.

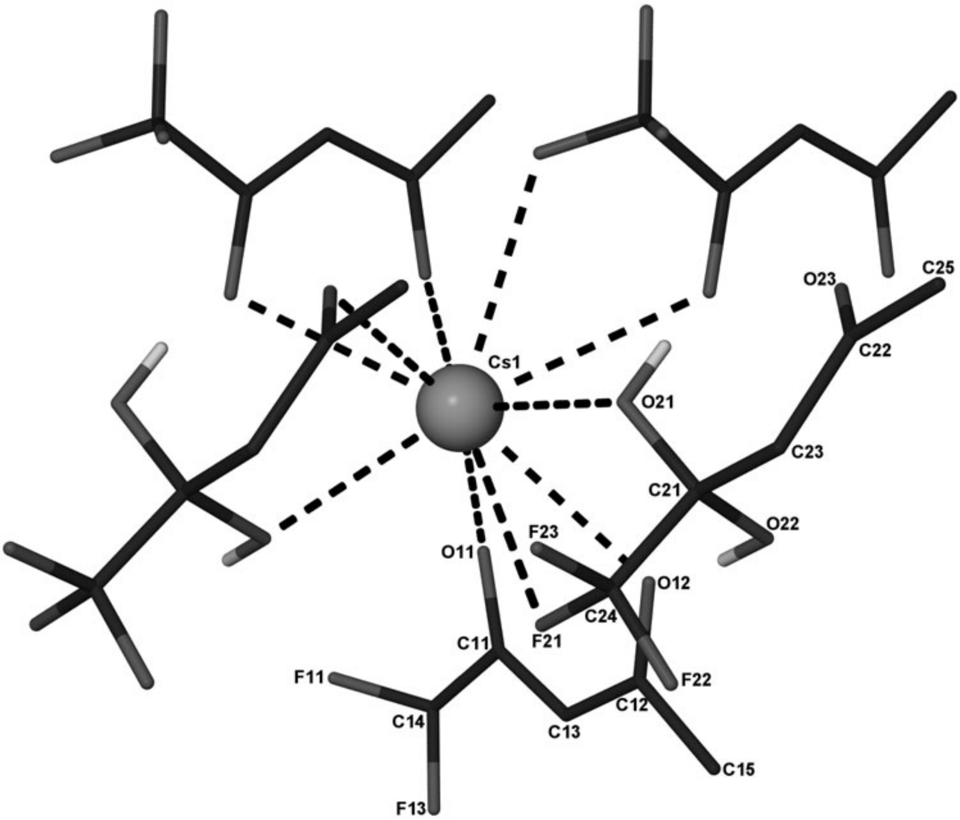

Figure 3. The nearest environment of one of the independent Cs cations in **4**.

Table 3. Bond lengths of tfac, H_2tfpd and tfpd species in **3**, **4,** and Sb(p-PhCl)$_3$(tfpd) [19]. Numeration of carbons (α, β, etc.) corresponds to figure 4.

	Bond length, Å			
		Cs(H_2tfpd)(tfac) (**4**)		
Bond	Cs(tfac) (**3**)	tfac	H_2tfpd	Sb(p-PhCl)$_3$(tfpd) [19]
C=O	1.253(2) 1.260(2)	1.252⟨4⟩	1.215⟨4⟩	1.2142(1)
C–O	–	–	1.396⟨9⟩	1.4019(1) 1.4321(1)
C_{β}–C_{α}	1.545(2)	1.551(4)	1.538⟨3⟩	1.5351(2)
C_{δ}–C_{ε}	1.512(2)	1.516⟨1⟩	1.500⟨2⟩	1.5119(1)
C_{γ}–C_{β}	1.380(2)	1.392⟨3⟩	1.528⟨1⟩	1.5300(1)
C_{γ}–C_{δ}	1.433(2)	1.416⟨4⟩	1.514⟨1⟩	1.5094(2)

3.3. *Comparison of structures presented*

The range of beta-diketonates obtained allows us to compare structures of the carbon skeleton depending on the substituent R (see figure 4). The change of R from CF_3 to Me, ^{t}Bu or Ph

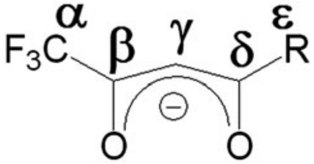

Figure 4. Numeration of carbons in beta-diketonate-anions: tfac (R = Me), ptac (R = ^{t}Bu), btfac (R = Ph). For hfac (R = CF_3), C_δ equals to C_β and C_ε to C_α are marked as C_β and C_α, respectively.

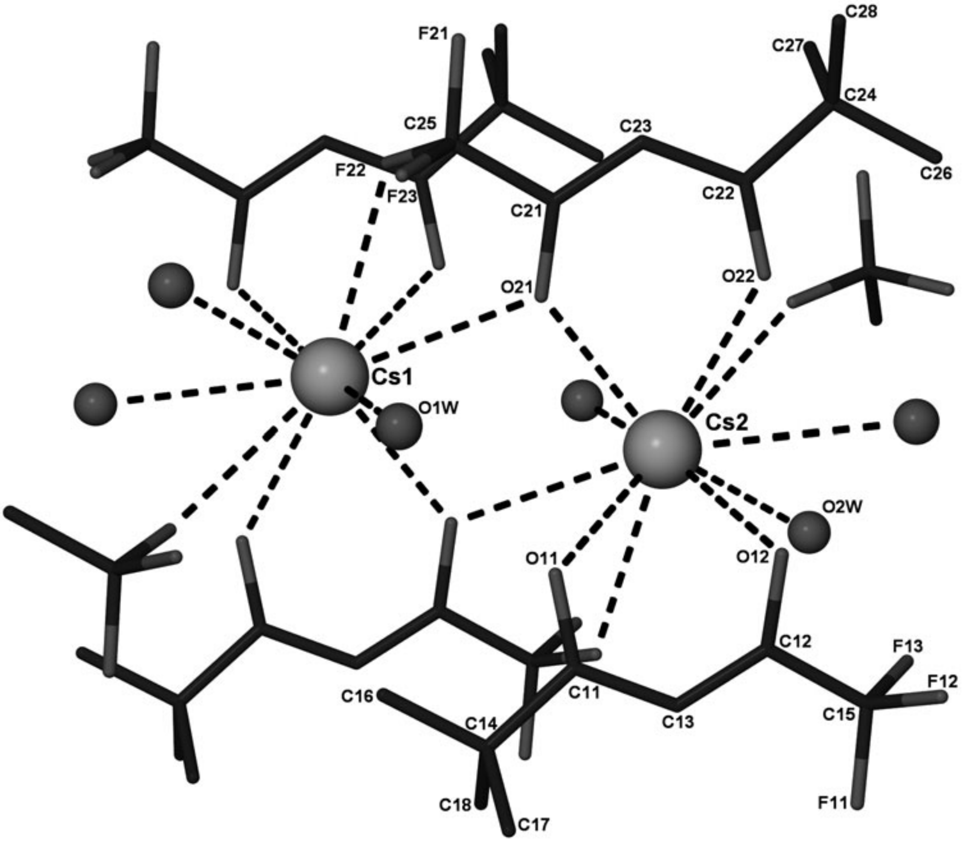

Figure 5. The nearest Cs^+ environment in **5**. All hydrogens are omitted for simplicity. Oxygens of water are depicted as balls and named Ow. Pendent CF_3-groups belong to ptac anion.

causes symmetry loss of beta-diketonate, resulting in unequal carbon–carbon bond lengths. The most striking difference is observed for R = Me and R = CF_3 (see table 4).

For all compounds C–F bond lengths are 1.30–1.36 Å; average Cs–O and Cs–F distances are almost equal (see table 2).

All hydrogens of OH of **2** and **4**–**6** are engaged in formation of hydrogen bonds (O–H…O) (see figure 8). There are either intra- or intermolecular hydrogen bonds in **2** and **4**; average distances are 2.69 < 3 > Å for **2** (figure 8) and 2.73 < 5 > Å for **4**. Every oxygen in the beta-diketonate of **5** and **6** forms hydrogen bond with water; average

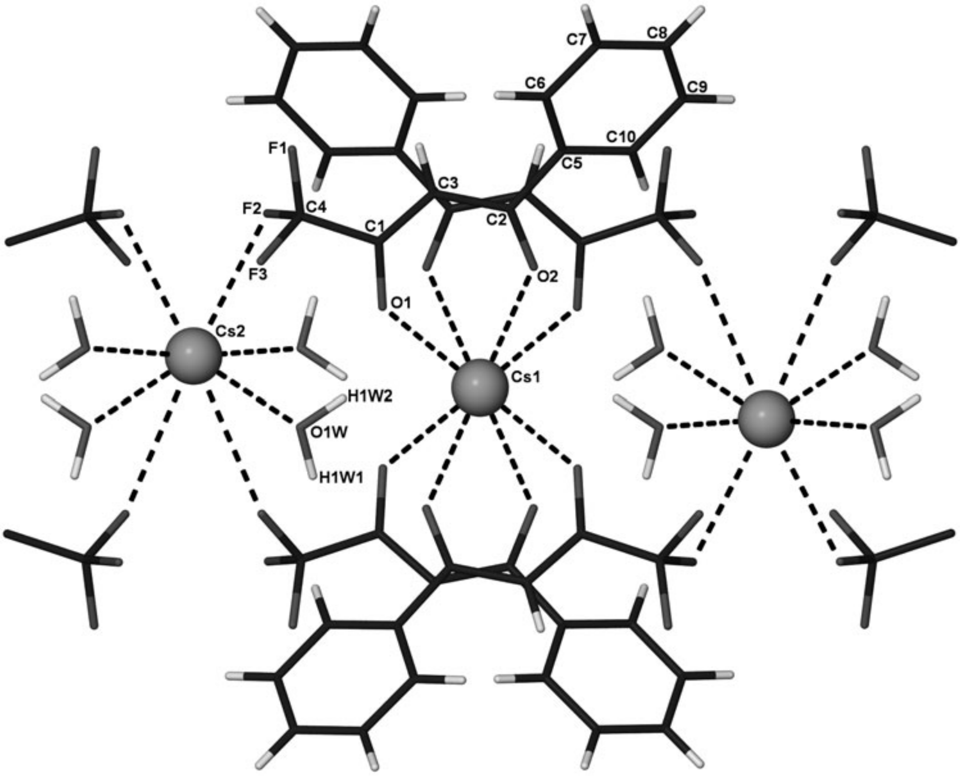

Figure 6. The nearest Cs^+ environment in **6**. All hydrogens are omitted for simplicity. Pendent CF_3-groups belong to btfac.

$O_w \ldots O$ distances are $2.79<3>$ Å for $Cs(OH_2)(ptac)$ and $2.72<6>$ Å for $Cs(OH_2)(btfac)$.

Coordination numbers of cesium are 8–12 both for cesium beta-diketonates **1**, **3**, **5**, **6,** and compounds including hydrated beta-diketones (**2** and **4)** from numerous Cs…O or Cs…F interactions. Moreover, metal in beta-diketonates having bulky substituents (**5** or **6**) add water molecules into the structure.

Comparison of cesium beta-diketonate structures with lithium and sodium ones [21] show striking difference, obviously, as a result of great inequality in atomic radius and coordination number. Nevertheless, common features can be underlined. Any alkali metal contacts to beta-diketonate by tetradentate bridge. For fluorinated beta-diketonates M–F contacts >3 Å are also typical. Geometry of ptac remains unchanged for all known structures.

3.4. *Thermogravimetric analyses*

The thermal behavior of synthesized cesium beta-diketonates was studied by TG and DTA from 25 to 600 °C. Experiments were carried out in the inert atmosphere (He) at the constant heating rate (supplementary material).

A clear endothermic peak is observed in the DTA curve for **1** at 217 °C which corresponds to melting (mp 220 °C, measured on Kofler table). At the same temperature the major mass loss on the TG curve of **1** starts, demonstrating melting with decomposition. The compound

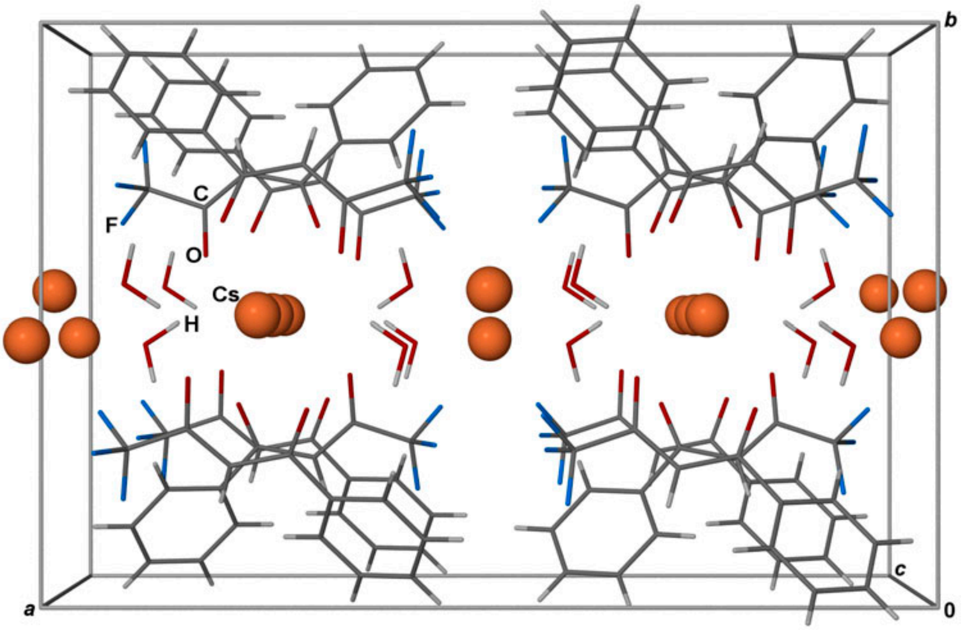

Figure 7. Pseudo-layered structure of $Cs(OH_2)(btfac)$ (**6**). Interactions between Cs and O or F of anions or water are not depicted for simplification.

Table 4. C–C bond lengths of beta-diketonate-anions.

	Bond length, Å			
Bond	Cs(hfac) (**1**)	Cs(tfac) (**3**)	$Cs(OH_2)(ptac)$ (**5**)	$Cs(OH_2)(btfac)$ (**6**)
C_β–$C\alpha$ C_δ–C_ε	1.542⟨8⟩	1.545(2) 1.512(2)	1.530⟨6⟩ 1.535⟨2⟩	1.518(8) 1.495(8)
C_γ–C_β C_γ–C_δ	1.400⟨9⟩	1.380(2) 1.433(2)	1.378⟨1⟩ 1.439⟨3⟩	1.368(8) 1.439(8)

decomposes in two stages, the mass of the residue is 48.4% of the initial mass and it corresponds to the formation of cesium carbonate (calculated for Cs_2CO_3 47.9%).

Cs(tfac) (**3**) melts with decomposition at 170 °C (mp measured is 169 °C). Decomposition proceeds in one stage and is accompanied by exoeffect. The mass of the residue is 66.8% of the initial.

Thermal decomposition of $Cs(OH_2)(ptac)$ (**5**) proceeds in two clearly separated steps. The first involves detachment of water (mass loss is 4.9%, calculated for H_2O 5.2%) which is accompanied by an endothermic peak in the DTA curve. The next exoeffect at 105 °C can be attributed to the phase transition, presumably caused by rearrangement of the structure due to water loss. The endoeffect at 170 °C corresponds to melting of Cs(ptac) (mp measured is 175 °C) proceeding with decomposition similar to the case of previously considered cesium beta-diketonates. Decomposition is over at 470 °C with formation of cesium carbonate (mass of the residue is 47.1%, the value calculated for Cs_2CO_3 is 47.1%).

Thermal decomposition of the mixture of Cs(btfac) and $Cs(OH_2)(btfac)$ (**6**) also starts from the endothermic detachment of water molecules (55–75 °C). The mass loss at the first stage is 1.8% (calculated for $Cs(OH_2)(btfac)$: 4.9%), which corresponds to the ratio of $Cs(OH_2)(btfac)$ to Cs(btfac) 37 : 63%. The results obtained are in agreement with the data

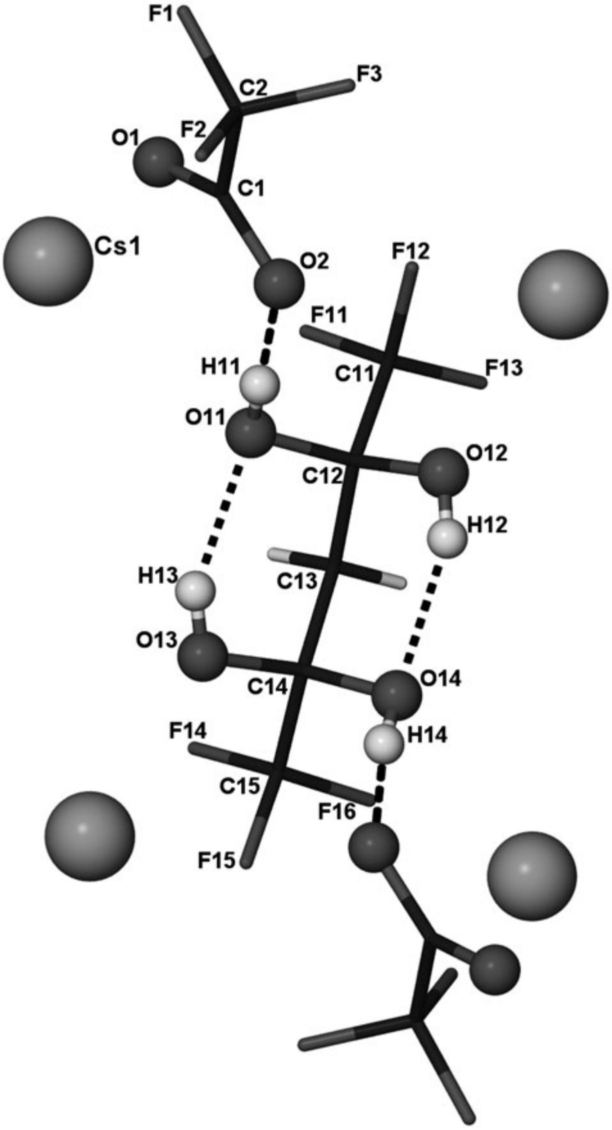

Figure 8. Example of H-bond structure for **2**. Interactions between Cs and O or F of anions or waters are not depicted for simplification.

of elemental analysis. The endo effect at 232 °C corresponds to Cs(btfac) melting (mp measured is 228 °C). The major mass loss starts at 240 °C. The decomposition of Cs(btfac) proceeds in two slightly separated stages, each accompanied by exoeffect. The mass of the residue is 67.0% of Cs(btfac) mass.

4. Conclusion

Four cesium fluorinated beta-diketonates – cesium hexaflouroacetylacetonate, trifluoroacetylacetonate, pivaloyltrifluoroacetylacetonate, and benzoyltrifluoroacetylacetonate – have been obtained by reaction of cesium carbonate and corresponding beta-diketone. The molar ratio of reagents and the presence of water molecules have an influence on the final products. Cesium salts containing hydrated beta-diketones, $Cs(CF_3C(OH)_2CH_2C(OH)_2CF_3)(CF_3COO)$ and $Cs(CF_3C(OH)_2CH_2COCH_3)$(tfac), were formed at 50% ligand molar excess of hexafluoroacetylacetone and trifluoroacetylacetone, respectively. Pure Cs(hfac) and Cs(tfac) can be obtained using stoichiometric molar amounts of reagents. For Hptac and Hbtfac, no hydration of ligands occurred; nevertheless, water molecules formed $Cs(OH_2)$(ptac) and $Cs(OH_2)$(btfac), respectively.

Single crystal XRD analysis shows that crystal packing of Cs(hfac) and $Cs(CF_3C(OH)_2CH_2COCH_3)$(tfac) can be represented by pseudo chain motifs, while the structures of other salts form pseudo-layered ones. The links of chains (layers) are connected through Cs…F and Cs…O interactions; oxygens of water in $Cs(OH_2)$(ptac) and $Cs(OH_2)$(btfac) also interact with cesium.

All the cesium beta-diketonates investigated decompose during heating in the temperature range 25–600 °C according to TG data. Destruction of $Cs(OH_2)$(ptac) and $Cs(OH_2)$(btfac) begins with loss of water.

The results presented at this paper can be used as a basis for synthesis of more complicated cesium-containing compounds.

Supplementary material

CCDC No. 888218 (**1**), 888215 (**2**), 888217 (**3**), 888216 (**4**), 888213 (**5**) and 888214 (**6**) contain the supplementary crystallographic data. These data can be obtained via the Cambridge Crystallographic Data Center (E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk/data_request/cif).

Acknowledgements

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