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Cesium Trialkylfluorometalates of Gallium and Indium: Compounds with Heterocubane Structure

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The cesium triorganofluorometalates $[Cs\{R_3MF\}]_4$ (**1**, M = Ga, R = Et; **2**, M = Ga, R = *i*-Pr; **3**, M = In, R = Et; **4**, M = In, R = *i*-Pr) have been prepared by the reaction of the corresponding group 13 metallanes $GaEt_3$, $Ga(i\text{-}Pr)_3$, $InEt_3$, and $In(i\text{-}Pr)_3$ with CsF in acetonitrile. **1**−**4** have been fully characterized by elemental analysis, and IR, NMR, and MS techniques. The crystal structures of **2** and **4** have been determined. **2** and **4** are isostructural and crystallize in the cubic space group *I*23, with $a = 1396.3(1)$ pm, $V = 2722.3(5) \times 10^6$ pm^3, $Z = 2$, and $R_1 = 0.0168$ (w$R_2 = 0.0343$) for **2** and $a = 1417.1(2)$ pm, $V = 2845.8(6) \times 10^6$ pm^3, $Z = 2$, and $R_1 = 0.0166$ (w$R_2 = 0.0354$) for **4**. The structures of **2** and **4** display strongly distorted cubes with alternating cesium and fluorine atoms and can be described as $(CsF)_4$ subunits of the CsF structure stabilized by $M(i\text{-}Pr)_3$ groups. According to the analytical and spectroscopic data, **1** and **3** also possess Cs−F heterocubane structure.

Introduction

Triorganofluoroalanates were first synthesized by Ziegler et al. in 1960.[1−3] The derivatives of the higher homologs gallium and indium, $K[Me_3GaF]$,[4] $K[Et_3GaF]$,[4−6] $[NMe_4][Et_3GaF]$,[5] $[Me_3NCH_2Ph][Et_3GaF]$,[6,7] $[Et_3NCH_2Ph][Et_3GaF]$,[7] and $[Me_3NCH_2Ph][Me_3InF]$,[8] were reported in the following years. However, very little is known about the structures of these substances. Particularly for the saltlike compounds containing alkali metal ions as counterions, the interactions of the alkali metal and fluorine ions should have an influence on the structure. This assumption was supported by the IR spectroscopic data for triorganofluoroalanates.[9] The results of the structural characterizations of $Cs[(PhCH_2)_2GaF_2]$,[10] $Cs[MesGaF_3]$,[11] and $[(i\text{-}Pr_2InF)_5(CsF\cdot 2MeCN)]$[12] confirmed the IR data. For this reason, we chose CsF as fluoridation agent for the triorganometallanes $GaEt_3$, $Ga(i\text{-}Pr)_3$, $InEt_3$, and $In(i\text{-}Pr)_3$.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon. Purification and drying of the solvents were done using standard methods.[13] $GaEt_3$ and $InEt_3$ were donated by the group of Prof. Dr. K. Dehnicke. $Ga(i\text{-}Pr)_3$ and $In(i\text{-}Pr)_3$ were prepared by literature procedures.[14,15] CsF was purchased from Merck-Schuchardt and used without further purification.

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AC-300 spectrometer (^{1}H, 300.134 MHz; ^{13}C, 75.469 MHz; ^{19}F, 282.409 MHz). The standards were TMS (external; ^{1}H, ^{13}C) and $CFCl_3$ (external; ^{19}F) with $\delta = 0.0$ ppm. The IR spectra were obtained using a Bruker IFS-88 instrument (Nujol mulls, CsI disks for the range 4000−500 cm^{-1}, polyethylene disks for the range 500−100 cm^{-1}). For the EI mass spectra a Varian CH7a mass spectrometer (70 eV) was used. The melting points were measured with a Dr. Tottoli (Büchi) melting point apparatus in sealed capillaries under argon (values not corrected). The cryoscopic measurements were performed using a Normag molecular weight determination apparatus combined with a Beckmann thermometer.

Synthesis of $[Cs\{Et_3GaF\}]_4$, 1. A 3.4 g (22.38 mmol) sample of CsF was added in one portion to a solution of 2.69 g (17.14 mmol) of $GaEt_3$ in 30 mL of acetonitrile. The mixture was stirred for 4 days at room temperature and then heated to 60 °C. The hot solution was filtered, and the solvent was removed under vacuum. The colorless solid was treated with 15 mL of *n*-pentane. The resulting solution was filtered, and the filtrate was cooled to 5 °C. Colorless crystals of **1** could be isolated (4.58 g, 87%); mp 135 °C dec. ^{1}H NMR (CD_3CN; ppm): δ −0.04 (q, 2 H, ^3J(HH) = 8.05 Hz, CH_2), 1.06 (t, 3 H, ^3J(HH) = 8.05 Hz, CH_3). ^{13}C NMR (CD_3CN; ppm): δ 4.5 (CH_2), 11.7 (CH_3). ^{19}F NMR (CD_3CN, toluene; ppm): δ −166.9, −133.7. Molecular weight determination (cryoscopic, benzene, $c = 0.0381$ mol/L): 1356; $n = 1.1$. EI-MS: *m/z* (%) 127 (100) $[GaEt_2]^+$, 98 (16) $[GaEt]^+$, 69 (33) $[Ga]^+$. IR (cm^{-1}): 2712 (m), 1420 (m), 1262 (w), 1229 (w), 1185 (w), 1104 (w), 992 (s), 951 (m), 926 (w), 804 (w), 654 (s), 519 (s), 467 (w), 388 (m), 293 (m), 238 (m), 183 (m, br). Anal. Calc for $C_6H_{15}CsFGa$ (M_r 308.81): C, 23.34; H, 4.89; Cs, 43.03; F, 6.15. Found: C, 23.21; H, 4.81; Cs 43.52; F, 6.10.

Synthesis of $[Cs\{i\text{-}Pr_3GaF\}]_4$, 2. A 3.23 g (21.23 mmol) sample of CsF was added in one portion to a solution of 3.44 g (17.26 mmol) of $Ga(i\text{-}Pr)_3$ in 40 mL of acetonitrile. The mixture was stirred for 4 days at room temperature and was then heated to 60 °C. The hot solution was filtered, and the solvent was removed under vacuum. The colorless solid was treated with 15 mL of *n*-pentane. The resulting solution was filtered, and the filtrate was cooled to 5 °C. Colorless crystals of **2** could be isolated (5.44 g, 90%); mp 128 °C. ^{1}H NMR (CD_3CN; ppm): δ 0.28 (m, 1 H, $CH(CH_3)_2$), 1.00 (d, 6 H, $CH(CH_3)_2$), AB_6 spin system. ^{13}C NMR (CD_3CN; ppm): δ 14.3 $[CH(CH_3)_2]$, 23.3 $[CH(CH_3)_3]$. ^{19}F NMR (CD_3CN, toluene; ppm): δ −181.9, −142.7. Molecular weight determination (cryoscopic, benzene, $c = 0.0292$ mol/L): 1476; $n = 1.05$. EI-MS: *m/z* (%) 305 (3) $[CsGaF(i\text{-}Pr)_3 - 3Me)$, 155 (100) $[Ga(i\text{-}Pr)_2]^+$, 133 (7) $[Cs]^+$, 112 (13) $[Ga(i\text{-}Pr)]^+$, 69 (51) $[Ga]^+$. IR (cm^{-1}): 2711 (s), 1357 (s), 1262 (s), 1065 (s), 1021 (s), 951 (s), 911 (w), 872 (s), 805 (s), 517 (s), 463 (w), 403 (m), 360 (m),

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283 (m), 221 (m), 161 (m). Anal. Calc for $C_9H_{21}CsFGa$ (M_r 350.89): C, 30.80; H, 6.03; Cs, 37.88; F, 5.41. Found: C, 30.74; H, 5.93; Cs, 37.86; F, 5.45.

Synthesis of [Cs{Et_3InF}]$_4$, 3. A 3.05 g (20.08 mmol) sample of CsF was added in one portion to a solution of 3.78 g (15.79 mmol) of $InEt_3$ in 40 mL of acetonitrile. The mixture was stirred for 4 days at room temperature and was then heated to 60 °C. The hot solution was filtered, and the solvent was removed under vacuum. The colorless solid was treated with 10 mL of Et_2O and 10 mL of *n*-pentane. The solution was cooled to 5 °C, and colorless crystals of **3** could be isolated (4.82 g, 86%); mp 192 °C. ^1H NMR (CD_3CN; ppm): δ 0.46 (q, 2 H, ^3J(HH) = 7.99 Hz, CH_2), 1.11 (t, 3 H, ^3J(HH) = 8.00 Hz, CH_3). ^{13}C NMR (CD_3CN; ppm): δ 7.1 (CH_2), 13.3 (CH_3). ^{19}F NMR (CD_3CN, toluene; ppm): δ −161.8, −123.4. EI-MS: *m/z* (%) 202 (9) $[InEt_3]^+$, 173 (25) $[InEt_2]^+$, 144 (100) $[InEt]^+$, 133 (12) $[Cs]^+$, 115 (53) $[In]^+$, 29 (89) $[Et]^+$. IR (cm^{-1}): 3765 (w), 3701 (w), 2726 (w), 1600 (w), 1414 (s), 1262 (vs), 1094 (vs), 920 (s), 801 (vs), 704 (vs), 662 (s), 633 (s), 473 (s), 457 (s), 390 (s, br), 295 (m), 270 (m), 259 (m), 239 (m), 218 (w), 188 (w), 163 (w), 144 (w), 114 (w). Anal. Calc for $C_6H_{15}CsFIn$ (M_r 353.91): C, 20.36; H, 4.28; Cs, 37.55; F, 5.37. Found: C, 19.98; H, 4.31; Cs, 37.69; F, 5.21.

Synthesis of [Cs{*i*-Pr_3In}]$_4$, 4. A 0.93 g (6.12 mmol) sample of CsF was added in one portion to a solution of 1.23 g (5.04 mmol) of In(*i*-Pr)$_3$ in 15 mL of acetonitrile. The mixture was stirred for 4 days at room temperature and was then heated to 60 °C. The hot solution was filtered, and the solvent was removed under vacuum. The colorless solid was treated with 10 mL of *n*-pentane, and the solution was filtered and cooled to 5 °C. Colorless crystals of **4** could be isolated (1.84 g, 90%); mp 143 °C. ^1H NMR (CD_3CN; ppm): δ 0.57 (m, 1 H, $HC(CH_3)_2$), 1.20 (d, 6 H, $HC(CH_3)_2$), AB_6 spin system. ^{13}C NMR (CD_3CN; ppm): δ 18.5 [$HC(CH_3)_2$], 24.9 [$HC(CH_3)_2$]. ^{19}F NMR (CD_3CN, toluene; ppm): δ −171.4, −133.2. EI-MS: *m/z* 464 (16) $[Cs_2F_2In(i\text{-}Pr)_2]^+$, 378 (12) $[Cs_2F_2In]^+$, 335 (4) $[In_2F(i\text{-}Pr)_2]^+$, 292 (11) $[In_2F(i\text{-}Pr)]^+$, 244 (6) $[In(i\text{-}Pr)_3]^+$, 201 (5) $[In(i\text{-}Pr)_2]^+$, 158 (2) $[In(i\text{-}Pr)]^+$, 115 (22) $[In]^+$, 43 (100) $[C_3H_7]^+$. IR (cm^{-1}): 2713 (w), 1304 (m), 1262 (m), 1152 (m), 1123 (m), 1069 (m), 965 (m), 942 (m), 868 (m), 828 (w), 805 (w), 648 (vw), 563 (m), 467 (m), 388 (m), 307 (w), 296 (w), 257 (m), 236 (m), 160 (w), 144 (w), 109 (w). Anal. Calc for $C_9H_{21}CsFIn$ (M_r 396.03): C, 27.30; H, 5.36; Cs, 33.56; F, 4.80. Found: C, 27.17; H, 5.42; Cs, 33.62; F, 4.68.

X-ray Structure Determinations of 2 and 4. The crystals were covered with a high-boiling paraffin oil and mounted on the top of a glass capillary under the flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections on a four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 71.073 pm; Siemens P4). The final cell parameters were determined from 25 high-angle reflections.

The intensities were corrected for Lorentz and polarization effects (for cell parameters and collection of the intensities, see Table 1). Both structures were solved by direct methods with SHELXTL-Plus[16] and refined against F^2 by full-matrix least-squares using SHELXL-93.[17] The positions of the hydrogen atoms were calculated for ideal positions and refined with a common displacement parameter. The calculation of the bond lengths, bond angles, and U_{eq} values was performed using the program PLATON.[18]

The structures of **2** and **4** were refined in the space group *I*23, and the absolute structure was determined (Table 1). A solution and refinement in the centrosymmetric space group $Im\bar{3}$ or $Im\bar{3}m$ is not possible due to the absence of mirror symmetries in the unit cells.

Atomic coordinates and equivalent isotopic displacement coefficients of **2** and **4** are given in Table 2. Selected bond lengths and angles are listed in Table 3.

Table 1. Crystallographic Data for [Cs{M(*i*-Pr)$_3$}]$_4$ (**2**, M = Ga; **4**, M = In)

	2	**4**
formula	$C_{36}H_{84}F_4Ga_4Cs_4$	$C_{36}H_{84}F_4In_4Cs_4$
fw	1403.58	1583.98
a (pm)	1396.3(1)	1417.1(2)
V ($pm^3 \times 10^6$)	2722.3(5)	2845.8(6)
Z	2	2
ρ_{calc} (g/cm^3)	1.712	1.849
temp (K)	223	223
space group	*I*23 (No. 196)[38]	*I*23
2θ range (deg)	2−50	2−50
hkl values	$-1 \le h \le 16$ $-1 \le k \le 16$ $-1 \le l \le 16$	$-16 \le h \le 1$ $-14 \le k \le 12$ $-14 \le l \le 12$
μ (cm^{-1})	46.3	41.5
no. of reflns	1744	2118
no. of unique reflns	551	842
no. of reflns with $F_o > 4\sigma(F_o)$	509	795
no. of parameters	39	39
Flack parameter	0.08(4)	0.04(4)
R_1 [$F_o > 4\sigma(F_o)$][a]	0.0168	0.0166
wR_2[b]	0.0343	0.0354
weight factor *a*[c]	0.0191	0.0193

[a] $R_1 = \sum||F_o|| - |F_c|/\sum|F_o|$. [b] $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

Results and Discussion

Addition of CsF to triorganogallanes and -indanes at room temperature in acetonitrile gives the corresponding cesium triorganofluorometalates

$$MR_3 + CsF \rightarrow Cs[R_3MF] \qquad (1)$$

$$\begin{aligned} &\mathbf{1}: M = Ga, R = Et \\ &\mathbf{2}: M = Ga, R = i\text{-}Pr \\ &\mathbf{3}: M = In, R = Et \\ &\mathbf{4}: M = In, R = i\text{-}Pr \end{aligned}$$

1−**4** are colorless solids and are sensitive to moisture and oxygen. The salts are surprisingly soluble in nonpolar solvents like *n*-pentane or toluene. We assume that this behavior results from the formation of higher aggregates in solution. These aggregates should show interionic interactions in the center of the assemblage and should be shielded by the hydrophobic organic groups. We deduced this from the structures of cesium diorganodifluorogallates and cesium organotrifluorogallates.[10,11] The cryoscopic molecular weight determinations of **1** and **2** in benzene suggest the presence of tetrameric units in solution.

The dissolved (CD_3CN) compounds **1**−**4** show the typical ^1H NMR signal groups for MR_3 fragments (M = Ga, In; R = Et, *i*-Pr), doublets and triplets for the Et ligand, and an AB_6 spin system for the *i*-Pr ligand.[14,15,19,20] Considering the results of the investigations of Cs[$(PhCH_2)_2GaF_2$][10] and Cs[$MesGaF_3$],[11] solutions of **1**−**4** in a donor solvent like acetonitrile contain complexes of the type [$Cs(MeCN)_n$][R_3MF]. Useful probes for this are the ^{19}F NMR shifts of −166.9 (**1**), −181.9 (**2**), −161.8 (**3**), and −171.4 ppm (**4**), indicating the distinct ionic character of the Ga(In)−F bonds. A downfield shift of approximatively 40 ppm has been observed, when **1**−**4** were measured in toluene, consistent with the existance of the tetrameric units [Cs{R_3MF}]$_4$ (−133.7 (**1**), −142.7 (**2**), −123.4 (**3**), −133.2 (**4**) ppm) in nonpolar solvents. The fluorine atoms are deshielded because of their bridging function with one Ga(In) atom and three Cs^+ ions.

The discrete molecules **1**−**4** allow a reliable assignment of IR bands to the corresponding vibrations. Monomeric CsF and the dimer $(CsF)_2$ investigated by matrix isolation techniques show IR bands at 313 and 251 and at 205 and 76 cm^{-1},

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Table 2. Atomic Coordinates and Isotropic Equivalent Displacement Parameters (10^{-22} m^2) of the Non-Hydrogen Atoms in **2** and **4**[a]

2					**4**				
atom	*x*	*y*	*z*	U_{eq}	atom	*x*	*y*	*z*	U_{eq}
Cs1	−0.11295(2)	0.11295(2)	0.11295(2)	4.10(1)	Cs1	−0.11126(1)	0.11126(1)	0.11126(1)	4.95(1)
Ga1	0.17634(3)	0.17634(3)	0.17634(3)	3.87(1)	In1	0.17884(2)	0.17884(2)	0.17884(2)	4.34(1)
F1	0.0949(2)	0.0949(2)	0.0949(2)	4.13(6)	F1	0.0905(1)	0.0905(1)	0.0905(1)	4.85(5)
C1	0.2030(3)	0.0886(3)	0.2862(3)	5.2(2)	C1	0.2015(3)	0.0825(3)	0.2982(3)	6.1(2)
C11	0.2556(4)	0.1213(5)	0.3483(4)	7.9(2)	C11	0.2846(4)	0.1132(5)	0.3581(3)	9.8(2)
C12	0.1147(5)	0.0723(5)	0.3474(5)	9.3(3)	C12	0.1146(6)	0.0707(5)	0.3561(5)	11.7(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (pm) and Angles (deg) in **2** and **4**

2				**4**			
Cs1−F1	292.4(2)	F1−Cs1−F1a	79.70(6)	Cs1−F1	288.9(2)	F1−Cs1−F1a	77.77(5)
Ga1−F1	197.0(4)	F1-Ga1−C1	101.3(2)	In1−F1	216.8(3)	F1-In1−C1	100.0(1)
Ga1−C1	199.8(5)	C1-Ga1−C1a	116.2(2)	In1−C1	219.9(4)	C1-In1−C1a	117.1(2)
C1−C11	151.4(7)	Cs1−F1−Ga1	118.25(9)	C1−C11	150.5(7)	Cs1−F1−In1	116.99(7)
C1−C12	151.8(8)	Cs1−F1−Cs1a	99.43(7)	C1−C12	150.1(8)	Cs1−F1−Cs1a	101.02(6)
		Ga1−C1−C11	113.3(4)			In1−C1−C11	111.9(3)
		Ga1−C1−C12	111.9(4)			In1−C1−C12	111.3(4)
		C11−C1−C12	109.9(4)			C11−C1−C12	111.4(4)

respectively.[21] Because of the low coordination numbers 3 and 4 (Cs and F atoms) in **1**−**4**, one can expect ν(CsF) values in the region 250−150 cm^{-1}. An ideal T_d symmetry gives arise to only one IR-active Cs−F cage stretching vibration.[22] According to the X-ray structure analyses, **1** and **3** have C_2 symmetry while **2** and **4** possess T symmetry [only two IR-active vibrations $\nu(Cs_4F_4)$ by theory; here accidental degeneracy]. Observable are two bands at 183 and 238 cm^{-1} for **1**, one band at 221 cm^{-1} for **2**, three bands at 188, 218, and 239 cm^{-1} for **3**, and one band at 236 cm^{-1} for **4**. The Ga(In)−F stretching vibrations of 467 (**1**), 464 (**2**), 390 (**3**), and 388 cm^{-1} (**4**) are in good agreement with the values measured for comparable compounds.[10−12] Typical values are also found for the Ga(In)−C vibrations $\nu(MC_3)$ at 519 (**1**), 517 (**2**), 473 (**3**), and 464 cm^{-1} (**4**).[23,24]

Of interest is the behavior of the tetrameric salts under EI mass spectral conditions. The spectra at 70 eV exhibit only small fragments of the heterocubanes. Only **2** and **4** generate fragments containing both metals, cesium and gallium (indium), at *m/z* 305 ([CsGaF(*i*-Pr)$_3$ − 3Me]$^+$) and *m/z* 464 ([Cs$_2$F$_2$In(*i*-Pr)$_2$]$^+$).

Crystal Structures of 2 and 4. The isostructural compounds **2** and **4** consist of heterocubane molecules with a distorted Cs$_4$F$_4$ core (Figure 1).[25] The distortion leads to butterfly-like cube faces with folding angles of 167 and 165°, respectively (folding axis F1···F1a). The Cs$_4$F$_4$ backbone has T symmetry. Threefold axes run along the space diagonals intercrossing 2-fold axes which are perpendicular to the cube faces. Interestingly, the Cs−F distance of 292.4(2) pm in **2** is significantly longer than the value of 288.9(2) pm in **4**. Two reasons can be given to explain this observation. On the one hand, the Ga−F bond of 197.0(4) pm is almost 20 pm shorter than the In−F bond of 216.8(2) pm. On the other hand, the ionic character of the M−F bond increases from gallium to indium. This leads to a stronger ionic Cs−F interaction. Both effects enable the Cs and F atoms to achieve closer contacts. The value measured for the crystalline CsF is 300.5 pm.[26]

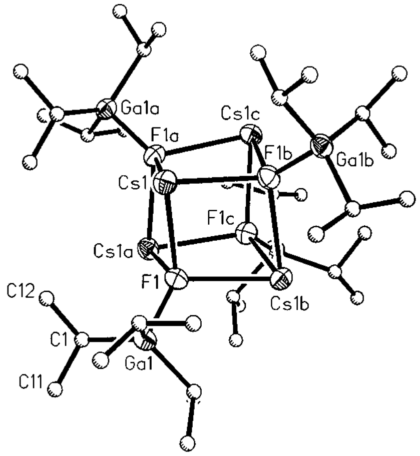

Figure 1. Molecular structure of **2** (**4** is isostructural). The thermal ellipsoids have a probability level of 50%. Carbon atoms are shown for clarity only as balls.

Comparable Ga−F and In−F distances have been observed in organometallic compounds with μ_2-bridging F functions as in [Mes$_2$GaF]$_2$ (194.7(2) pm)[27] and [Mes$_2$InF]$_3$ [212 pm (mean value)].[28] The terminal Ga−F bonds in Cs[(PhCH$_2$)$_2$GaF$_2$] (184 pm),[10] Cs[MesGaF$_3$] (180 pm),[11] and [Mes$_2$Ga(F)NH$_2$(*t*-Bu)]·2.5THF (183.8(3) pm)[28] are more than 10 pm shorter, caused by the presence of a larger number of electronegative ligands.

The Ga−C and In−C distances of 199.8(5) and 219.9(4) pm, respectively, are typical for metal centers with coordination number 4 and somewhat longer than the bond lengths in GaMe$_3$ (196.7(2) pm)[29] and InMe$_3$ (215 pm (average)).[30] The electron-pulling effect of the F atom is more distinct than the effect of

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(25) The structures of **1** and **3** have been determined. **1** and **3** are isostructural and possess a heterocubane structure like **2** and **4**; however, the Et groups are strongly disordered. This leads to an inaccurate refinement concerning the organic substituents. **1**: a = 2056.9(6) pm, b = 1082.1(5) pm, c = 2120.6(4) pm, β = 114.85(1)°, V = 4283(3) × 10^6 pm^3, $C2/c$, R_1/wR_2 = 0.0863/0.2328. **3**: a = 2076.8(4) pm, b = 1068.9(2) pm, c = 2085.0(4) pm, β = 107.68(1)°, V = 4410(1) × 10^6 pm^3, $C2/c$, R_1/wR_2 = 0.0378/0.0958. The metalate Cs[Me$_3$InF] also shows the heterocubane structure.[39]

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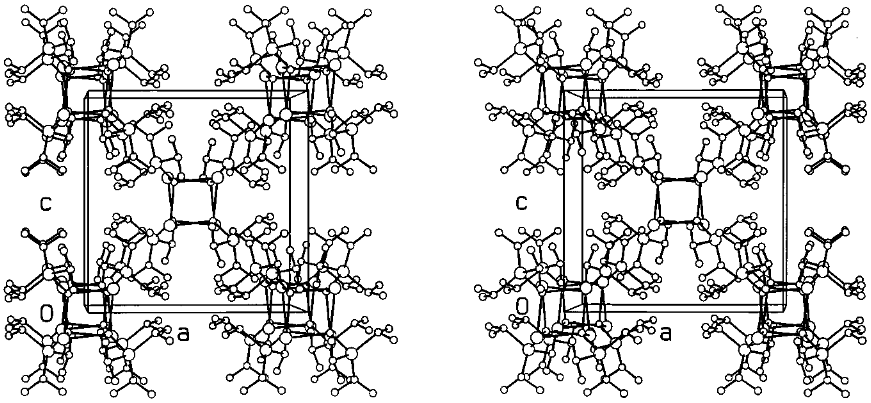

Figure 2. Stereoscopic view of the unit cell of **2** (ORTEP).[37]

a chlorine atom in triorganochlorogallates and -indates with small organic substituents. Bond lengths of 205 ([$AsMe_4$][Me_3GaCl]) and 223 pm ([$AsMe_4$][Me_3InCl])[31] have been measured. Compounds with metal centers bonded to two or three chlorine atoms show M−C distances quite similar to those of **2** and **4**: 198 pm for [$AsMe_4$][Me_2GaCl_2], 193.4(8) pm for [$AsMe_4$][$MeGaCl_3$],[32] 216 pm for [K(15-crown-5)$_2$][*i*-Pr_2InCl_2],[33] and 218(2) pm for [$AsMe_4$][$MeInCl_3$][34] have been observed.

Both compounds, **2** and **4**, exhibit no short intra- and intermolecular Cs···C contacts, as reported for Cs[$InMe_4$] (Cs···C = 347(2) pm).[35] This indicates that there are no further significant intermolecular interactions between the heterocubane units as shown in Figure 2.

The valence isoelelectronic compound $KOSiMe_3$ crystallizes also as the tetrameric aggregate [$KOSiMe_3$]$_4$.[36]

Conclusion

The reaction of CsF with triorganogallanes and -indanes in acetonitrile represents a facile route to the corresponding saltlike cesium triorganometalates in high yields. All compounds possess heterocubane structures which allow interionic interactions in the center of the molecules. In addition, the Cs_2F_2 core is shielded by a hydrophobic wrap leading to a good solubility in nonpolar organic solvents. The structures can be described in a topological way as CsF structure fragments, stabilized by organometallanes.

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Supporting Information Available: Tables of bond lengths and angles, hydrogen positional and isotropic displacement parameters, and non-hydrogen anisotropic displacement parameters for **2** and **4** (2 pages). Ordering information is given on any current masthead page.

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