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π-Electron−Cesium Interactions in Cesium Triorganofluorometalates

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The reaction of $MMes_3$ (M = Ga, In; Mes = 2,4,6-$Me_3C_6H_2$) with CsF in acetonitrile yields the trimesitylfluorometalates $[\{Cs(MeCN)_2\}\{Mes_3MF\}]_2{\cdot}2MeCN$ ($[\mathbf{1}]_2{\cdot}6MeCN$, M = Ga; $[\mathbf{2}]_2{\cdot}6MeCN$, M = In). $Ga(CH_2Ph)_3$ gives with CsF under the same conditions the salt $[Cs\{(PhCH_2)_3GaF\}]_2{\cdot}2MeCN$ ($[\mathbf{3}]_2{\cdot}2MeCN$). The treatment of 1 equiv CsF with 2 equiv of $GaMes_3$ does not lead to $Cs[Mes_3GaFGaMes_3]$ but to $[\mathbf{1}]_2{\cdot}6MeCN$ and the adduct $[Mes_3Ga(MeCN)]$ (**4**). $[\mathbf{1}]_2{\cdot}6MeCN$−**4** have been characterized by NMR, IR, and MS techniques as well as by X-ray analyses. $[\mathbf{1}]_2{\cdot}6MeCN$ and $[\mathbf{2}]_2{\cdot}6MeCN$ are solvated ion pairs in acetonitrile, while $[\mathbf{3}]_2{\cdot}2MeCN$ shows a monomer−dimer equilibrium. According to the X-ray structure determinations, $[\mathbf{1}]_2{\cdot}6MeCN$ and $[\mathbf{2}]_2{\cdot}6MeCN$ are isostructural and contain Cs−F four-membered rings. The fluorine centers at the rings are bound to the metallane groups. Each cesium cation is coordinated by two molecules of acetonitrile and by one mesityl group in a η^3-fashion. The basic structural feature of $[\mathbf{3}]_2{\cdot}2MeCN$ is also a Cs−F four-membered ring; however, the cations in $[\mathbf{3}]_2{\cdot}2MeCN$ are surrounded by three phenyl groups of the benzyl substituents. The three η^6-bound phenyl rings are contributed from two different metallane units. **4** possesses a distorted tetrahedral coordination sphere with a low pyramidalization of the Ga center (angular sum: 355°).

Although triorganofluorometalates have been known for 35 years, reports about their structures in the solid state are sparse. The aluminum derivatives[1−3] as well as the later published derivatives of the higher homologes 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] supposedly consist of linear polymer chains of $[R_3MF]^-$ units with a distorted trigonal-bipyramidal coordination sphere. In this case the cations should not be included into strong interionic interactions as it has been found for the salts $K[Et_3AlFAlEt_3]$[9] and $K[Me_3AlFAlMe_3]{\cdot}C_6H_6$.[10] This arrangement, however, does not appear likely in the case of the alkali triorganofluorometalates because of our findings during the structural studies of the metalates $Cs[(PhCH_2)_2GaF_2]$,[11] $Cs[MesGaF_3]$,[12] and $[\{Cs(MeCN)_2\}\{F(i\text{-}Pr_2InF)_5\}]$.[13] In these salts Cs−F contacts dominate the structure.

More recently, we have shown strong Cs−F interactions also in cesium triorganofluorometalates $Cs[R_3MF]$ (R = Me, M = Al, Ga, In;[14] R = Et, *i*-Pr, M = Ga, In[15]). The important structural motifs are Cs_2F_2 four-membered rings connected to puckered layers, infinite ladder-type chains, or heterocubane units.

In the present work we have investigated the influence of electronic *π*-systems on the generation of the Cs−F skeleton, particularly on the environment of the Cs^+ ions.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon using Schlenk techniques. Purification and drying of the organic solvents were performed using standard methods.[16] $GaMes_3$,[17] $InMes_3$,[18] and $Ga(CH_2Ph)_3$[11,19] were prepared following literature procedures.

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker spectrometer AC-300 (^1H, 300.134 MHz; ^{13}C, 75.469 MHz; ^{19}F, 282.409 MHz). The standards were TMS (external; ^1H, ^{13}C) and $CFCl_3$ (external; ^{19}F) with $\delta = 0.0$ ppm. The IR spectra were obtained using a Bruker instrument IFS-88 (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).

Synthesis of $[\{Cs(MeCN)_2\}\{Mes_3GaF\}]_2{\cdot}2MeCN$, $[\mathbf{1}]_2{\cdot}6MeCN$. A 1.77 g (11.65 mmol) amount of CsF was added to a solution of 3.56 g (8.32 mmol) of $GaMes_3$ in 40 mL of MeCN

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in one portion at room temperature. The colorless suspension was stirred for 4 days, heated to 60 °C and filtered at this temperature. The filtrate was cooled to 5 °C yielding colorless crystals of $[\mathbf{1}]_2\cdot$6MeCN [3.92 g, 82% yield based on GaMes$_3$, mp >270 °C (solvent-free material **1**)]. ^{1}H NMR (CD$_3$CN, ppm): 2.20 (s, 3 H, CH_3-C^4), 2.23 (s, 6 H, CH_3-C$^{2/6}$), 6.63 (s, 2 H, H-C$^{3/5}$). ^{13}C NMR (CD$_3$CN, ppm): 21.0 (CH$_3$-C^4), 24.9 (CH$_3$-C$^{2/6}$), 127.1 ($C^{3/5}$), 134.9 (C^4), 145.8 ($C^{2/6}$), 155.4 (C^1). ^{19}F NMR (CD$_3$CN, ppm): −167.8. IR (cm^{-1}): 2726 (w), 2292 (w), 2260 (w), 1735 (w), 1598 (m), 1542 (m), 1256 (m), 1169 (w), 1019 (m), 943 (w), 922 (w), 876 (s), 581 (m), 546 (vs), 496 (w), 421 (vs), 350 (s), 285 (m), 257 (s), 194 (s). EI-MS [*m/z* (rel. int.) fragment]: 503 (3) (CsFGaMes$_3$ − 5Me)$^+$, 429 (8) (CsFGaMes$_2$ − 2Me)$^+$, 415 (3) (CsFGaMes$_2$ − 3Me + H)$^+$, 401 (2) (CsFGaMes$_2$ − 4Me + 2H)$^+$, 355 (18) (CsFGaMesMe)$^+$, 341 (8) (CsFGaMes + H)$^+$, 325 (7) (FGaMes$_2$ − H)$^+$, 307 (62) (GaMes$_2$)$^+$, 281 (51) (FGaMes$_2$ − 3Me)$^+$, 267 (6) (FGaMes$_2$ − 4Me + H)$^+$, 221 (12) (FGaMesMe − H/CsFGas)$^+$, 207 (100) (FGaMes)$^+$, 191 (9) (FGaMes − Me − H)$^+$, 147 (22) (CsMe − H)$^+$, 133 (9) Cs$^+$, 119 (4) (Mes)$^+$, 69 (28) Ga$^+$. Anal. Calcd: C, 55.99; H, 5.74; Cs, 22.95; F, 3.28. Found: C, 55.76; H, 5.82; Cs, 22.68; F, 3.16 (solvent-free material **1**).

Synthesis of $[\{\mathbf{Cs(MeCN)_2}\}\{\mathbf{Mes_3InF}\}]_2\cdot$2MeCN, $[\mathbf{2}]_2\cdot$6MeCN. A 1.13 g (7.44 mmol) amount of CsF was added to a solution of 2.34 g (4.95 mmol) of InMes$_3$ in 50 mL in one portion at room temperature. The colorless suspension was stirred for 70 h, heated to 60 °C, and filtered at this temperature. The filtrate was cooled to 5 °C yielding colorless crystals of $[\mathbf{2}]_2\cdot$6MeCN [2.60 g, 84% yield based on InMes$_3$, mp 191 °C (solvent-free material **2**)]. ^{1}H NMR (CD$_3$CN, ppm): 2.10 (s, 3 H, CH_3-C^4), 2.20 (s, 6 H, CH_3-C$^{2/6}$), 6.69 (s, 2 H, H-C$^{3/5}$). ^{13}C NMR (CD$_3$CN, ppm): 21.0 (CH$_3$-C^4), 25.9 (CH$_3$-C$^{2/6}$), 126.6 ($C^{3/5}$), 135.8 (C^4), 140.7 ($C^{2/6}$), 146.4 (C^1). ^{19}F NMR (CD$_3$CN, ppm): −173.4. IR (cm^{-1}): 2728 (m), 1712 (vw), 1609 (w), 1594 (w), 1306 (m), 1225 (m), 1156 (m), 1032 (m), 969 (m), 940 (m), 890 (w), 845 (m), 836 (m), 687 (m), 604 (m), 577 (m), 538 (m), 488 (w), 462 (w), 446 (w), 402 (w), 391 (w), 297 (w), 239 (w), 190 (m), 146 (w), 135 (w), 125 (w). EI-MS [*m/z* (rel. int.) fragment]: 372 (1) (FInMes$_2$)$^+$, 353 (2) (InMes$_2$)$^+$, 253 (2) (FInMes)$^+$, 234 (3) (InMes)$^+$, 134 (3) (InF)$^+$, 133 (7) Cs$^+$, 119 (71) (Mes)$^+$, 115 (3) In$^+$, 105 (100) (MesH − Me)$^+$, 91 (9) (Mes − 2Me)$^+$, 77 (12) (C$_6$H$_5$)$^+$. Anal. Calcd: C, 51.95; H, 5.33; Cs, 21.29; F, 3.04. Found: C, 51.69; H, 5.42; Cs, 21.18; F, 3.12 (solvent-free material **2**).

Synthesis of $[\mathbf{Cs}\{\mathbf{(PhCH_2)_3GaF}\}]_2\cdot$2MeCN, $[\mathbf{3}]_2\cdot$2MeCN. A 0.75 g (4.94 mmol) amount of CsF was added to a solution of 1.14 g (3.32 mmol) of Ga(CH$_2$Ph)$_3$ in 25 mL of MeCN in one portion at room temperature. The colorless suspension was stirred for 48 h, heated to 60 °C, and filtered at this temperature. The filtrate was cooled to 5 °C yielding colorless crystals of $[\mathbf{3}]_2\cdot$2MeCN [1.49 g, 91% yield based on Ga(CH$_2$Ph)$_3$, mp 132 °C (dec, solvent-free material **3**)]. ^{1}H NMR (CD$_3$CN, ppm, rel. integral): 1.65 (s, 0.79, CH_2Ph, dimer), 1.64 (s, 1.57, CH_2Ph, dimer), 1.77 (s, 1, CH_2Ph, monomer), 6.78−7.40 (m, 8.57, H-phenyl, monomer and dimer). ^{13}C NMR (CD$_3$CN, ppm): 22.6 (br, CH$_2$Ph, monomer), 24.4 (CH$_2$Ph, dimer), 24.6 (CH$_2$Ph, dimer), 121.2 (C^4, dimer), 122.6 (C^4, monomer), 127.8 ($C^{3/5}$, dimer), 128.4 ($C^{3/5}$, monomer), 128.7 ($C^{2/6}$, dimer), 128.9 ($C^{2/6}$, monomer), 147.3 (C^1, monomer), 150.7 (C^1, dimer). ^{19}F NMR (CD$_3$CN, ppm, rel. integral): −167.7 (s, 2.2, dimer), −173.1 (s, 1.0, monomer). IR (cm^{-1}): 2717 (m), 2667 (m), 2008 (vw), 1980 (vw), 1858 (vw), 1808 (vw), 1590 (s), 1306 (m), 1267 (w), 1206 (vs), 1177 (m), 1071 (s), 1043 (s), 994 (s), 901 8m), 797 (m), 755 (vs), 699 (vs), 619 (w), 567 (w), 544 (m), 521 (m), 477 (s), 446 (s), 331 (m), 246 (s), 228 (s), 206 (s), 181 (m), 136 (vw). EI-MS [*m/z* (rel. int.) fragments]: 555 (1) [Cs$_2$F$_2$Ga(CH$_2$Ph)$_2$]$^+$, 403 (1) [CsFGa(CH$_2$Ph)$_2$]$^+$, 342 (1) [Ga(CH$_2$Ph)$_3$]$^+$, 330 (1) [CsF$_2$GaCH$_2$Ph − H]$^+$, 251 (33) [Ga(CH$_2$Ph)$_2$]$^+$, 91 (100) (CH$_2$Ph)$^+$, 69 (55) Ga$^+$. Anal. Calcd: C, 50.95; H, 4.27; Cs, 26.85; F, 3.84. Found: C, 50.79, H, 4.35; Cs, 26.59; F, 4.04 (solvent-free material **3**).

Synthesis of [Mes$_3$Ga(MeCN)], 4. A solution of 1.12 g (2.6 mmol) of GaMes$_3$ in 10 mL of MeCN was treated with 5 mL of *n*-pentane. The mixture was cooled to 5 °C yielding colorless crystals [0.96 g, 79%, mp 193 °C]. ^{1}H NMR (CD$_3$CN, ppm): 1.89 (s, 3 H, CH_3CN), 2.11 (s, 6 H, CH_3-C$^{2/6}$), 2.13 (s, 3 H, CH_3-C^4), 6.67 (s, 2 H, H-C$^{3/5}$). ^{13}C NMR (CD$_3$CN, ppm): 1.2 (CH$_3$CN), 20.9 (CH$_3$-C^4), 24.9 (CH$_3$-C$^{2/6}$), 121.2 (CH$_3$$C$N), 128.1 ($C^{3/5}$), 138.7 ($C^4$), 145.1 ($C^{2/6}$), 148.0 ($C^1$). IR (cm^{-1}): 2728 (w), 2306 (w), 2279 (w), 1600 (m), 1569 (m), 1304 (m), 1225 (m), 1169 (m), 969 (m), 932 (m), 890 (m), 847 (s), 836 (s), 687 (m), 596 (w), 581 (m), 558 (m), 544 (m), 523 (w), 490 (w), 463 (m), 447 (m), 399 (m), 345 (m), 338 (m), 327 (m), 279 (w), 247 (m), 226 (vw), 194 (m-s), 170 (vw), 151 (m), 118 (m), 105 (w). EI-MS [*m/z* (rel. int.) fragment]: 426 (10) (GaMes$_3$)$^+$, 307 (90) (GaMes$_2$)$^+$, 188 (33) (GaMes)$^+$, 119 (100) (Mes)$^+$, 105 (21) (Mes − Me)$^+$, 91 (4) (Mes − 2Me)$^+$, 69 (45) Ga$^+$, 41 (31) (MeCN)$^+$. Anal. Calcd: C, 74.36; H, 7.76; N, 2.99. Found: C, 74.18; H, 7.48; N, 2.98.

X-ray Structure Determinations of $[\mathbf{1}]_2\cdot$6MeCN−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 = 0.710 73 Å; $[\mathbf{1}]_2\cdot$6MeCN, **4**, Siemens P4; $[\mathbf{2}]_2\cdot$6MeCN, $[\mathbf{3}]_2\cdot$2MeCN, Enraf-Nonius CAD4). The final cell parameters were determined with 25 high-angle reflections.

The intensities have been corrected for Lorentz and polarization effects (cell parameters and collecting of the intensities; see Table 1). The structure of $[\mathbf{1}]_2\cdot$6MeCN has been solved by the Patterson method, and the structures of $[\mathbf{3}]_2\cdot$2MeCN and **4** have been solved by direct methods using the program SHELXTL-Plus.[20] The structure of $[\mathbf{2}]_2\cdot$6MeCN is isostructural to $[\mathbf{1}]_2\cdot$6MeCN; the coordinates of the non-hydrogen atoms of $[\mathbf{1}]_2\cdot$6MeCN have been used for the first refinement cycles. The structures were refined against F^2 by full-matrix least-squares with the program SHELXL-93.[21] 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.[22]

Selected bond lengths and angles of $[\mathbf{1}]_2\cdot$6MeCN−**4** are listed in Table 2. Table 3 shows additional metal−carbon contacts in $[\mathbf{1}]_2\cdot$6MeCN−$[\mathbf{3}]_2\cdot$2MeCN. A comparison of bond lengths for selected organogallium(indium) compounds is given in Table 4.

Results and Discussion

The cesium triorganofluorometalates [{Cs(MeCN)$_2$}{Mes$_3$MF}]$_2\cdot$2MeCN ($[\mathbf{1}]_2\cdot$6MeCN, M = Ga; $[\mathbf{2}]_2\cdot$6MeCN, M = In) have been synthesized by the reaction of the corresponding metallanes with CsF in acetonitrile at room temperature according to eq 1.

$$\begin{aligned}2\mathrm{MMes_3} + 2\mathrm{CsF} + 6\mathrm{MeCN} \rightarrow &\\ [\{\mathrm{Cs(MeCN)_2}\}\{\mathrm{Mes_3MF}\}]_2\cdot 2\mathrm{MeCN} &\quad (1)\\ [\mathbf{1}]_2\cdot 6\mathrm{MeCN},\ \mathrm{M} = \mathrm{Ga} &\\ [\mathbf{2}]_2\cdot 6\mathrm{MeCN},\ \mathrm{M} = \mathrm{In} &\end{aligned}$$

The choice of CsF as fluoridation agent is based on its highest fluoridation potential among the alkali fluorides and the highest enthalpy of complexation for the salts M′[R$_3$MF] (M′ = Li, Na, K, Rb, Cs; M = Al, Ga, In; R = alkyl groups).[1] Another reason is the possibility of obtaining crystals of high quality. Other

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Table 1. Crystallographic Data for the Compounds [1]$_2$·6MeCN−4

	compd			
	[**1**]$_2$·6MeCN	[**2**]$_2$·6MeCN	[**3**]$_2$·2MeCN	**4**
formula	$C_{66}H_{84}Cs_2F_2Ga_2N_6$	$C_{66}H_{84}Cs_2F_2In_2N_6$	$C_{46}H_{48}Cs_2F_2Ga_2N_2$	$C_{29}H_{36}GaN$
fw	1404.69	1494.89	1072.16	468.33
cryst size (mm)	0.6 × 0.3 × 0.2	0.6 × 0.5 × 0.1	0.45 × 0.4 × 0.38	0.4 × 0.08 × 0.2
a (Å)	10.359(2)	10.341(1)	12.503(2)	8.219(2)
b (Å)	13.319(3)	13.424(1)	19.755(1)	22.844(5)
c (Å)	25.498(5)	25.711(2)	9.122(1)	13.834(3)
β (deg)	101.58(1)	101.03(1)	93.05(1)	101.63(1)
V (Å^3)	3446(1)	3503.2(5)	2249.9(5)	2544(1)
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
No.[43]	14	14	14	14
Z	2	2	2	4
ρ_{calc} (g/cm^3)	1.354	1.417	1.583	1.222
temp (K)	223	213	203	223
abs corr	numerical	empirical	no	no
μ (cm^{-1})	18.7	17.3	28.3	11.0
2θ range (deg)	2−50	4.4−50	5.0−50	4−50
h,k,l values	$-1 \le h \le 12$, $-1 \le k \le 15$, $-30 \le l \le 30$	$-12 \le h \le 12$, $0 \le k \le 15$, $0 \le l \le 30$	$-14 \le h \le 14$, $-23 \le k \le 0$, $0 \le l \le 10$	$-1 \le h \le 9$, $-1 \le k \le 27$, $-16 \le l \le 16$
scan	ω-scan	ω-scan	ω-scan	ω-scan
scan width (deg)	1.4	0.58 + 0.43 tan θ	0.96 + 0.46 tan θ	1.2
no. of refls	7772	6588	4334	5939
unique refls	6050	6149	3937	4481
refls with $F_o > 4\sigma(F_o)$ for R_1	2990	5063	3103	1824
params	353	353	345	282
R_1[a]	0.0578	0.0267	0.0277	0.0501
wR_2[b]	0.1879	0.0741	0.0712	0.0967
weight fact. a, b	0.0958, 0	0.0422, 1.12	0.0346, 1.01	0.0286, 0
max/min resid electron density (e/Å^3)	1.27/−1.94	0.42/−0.49	0.63/−0.56	0.37/−0.43

[a] $R_1 = \sum||F_o - F_c||/\sum|F_c|$. [b] $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

alkali cations like K^+ give crystalline material suitable for a single-crystal X-ray structure determination only in a few cases, e.g., for the compound K[MesInBr$_3$].[12,23]

The coordination of MeCN at cesium centers can be excluded for compounds of the general formula $M'[R_{4-n}GaF_n]$ (n = 1, 2) in the case of benzyl substituents as shown in eq 2 for n = 1.

$$2Ga(CH_2Ph)_3 + 2CsF + 2MeCN \rightarrow [Cs\{(PhCH_2)_3GaF\}]_2{\cdot}2MeCN \quad (2)$$
$$[\mathbf{3}]_2{\cdot}2MeCN$$

The treatment of 1 equiv CsF with 2 equiv of MR_3 does not lead to the dimetalla fluorides Cs[R_3MFMR_3] as was observed for M[$R_3AlFAlR_3$] (M = alkali metal, R = alkyl),[1,9,10] [NMe_4][$R_3GaFGaR_3$] (R = Me,[4] Et[4,6,7]), and [NMe_4][$Me_3TlFTlMe_3$].[24] Only [**1**]$_2$·6MeCN−[**3**]$_2$·2MeCN and, in the case of GaMes$_3$, the adduct [Mes$_3$-Ga(MeCN)], **4**, could be isolated. One reason which could serve to explain this finding is the reduced Lewis acidity of gallanes and indanes compared to that of allanes on the one hand and the strong cesium−fluorine interaction on the other hand. A salt of general formula A[R_3MFMR_3] with M = Ga, In, and Tl should exist only when A^+ is a bulky nonpolarizing cation such as $[NR_4]^+$ or $[PR_4]^+$.

The title compounds are oxygen and moisture sensitive and soluble in donor solvents such as MeCN and THF. Solutions of **1** and **2** in acetonitrile contain solvated ion pairs of the type [Cs(MeCN)$_n$][Mes$_3$MF]. Earlier investigations of the saltlike compounds Cs[(PhCH$_2$)$_2$GaF$_2$],[11] Cs[MesGaF$_3$],[12] and Cs[R_3MF] (R = Me, Et, *i*-Pr; M = Al, Ga, In)[14,15] showed similar results. The ^{19}F NMR spectra of **1** and **2** exhibit one resonance at −167.8 and −173.4 ppm, respectively. The two signals at −167.7 and −173.2 ppm for **3** in acetonitrile may be caused by a monomer−dimer equilibrium. The ^{1}H and ^{13}C NMR spectra of **3** verify this assumption. The monomer gives one signal at 1.77 (^{1}H) and 22.6 ppm (^{13}C), while the dimer gives rise to two peaks at 1.64 and 1.65 ppm (^{1}H) as well as at 24.4 and 24.6 ppm (^{13}C). However, the ratio of the signals for the dimer is 1:2. This can be explained by the X-ray analysis, which shows that the three benzyl groups are coordinated to two different Cs centers. Therefore, two benzyl groups are chemically equivalent. The molar dimer−monomer ratio determined from the ^{1}H spectrum is 1.18:1 at 25 °C. A VT-^{19}F-NMR study in the range −40 to 40 °C (CD_3CN) shows only a slight temperature dependence of the dimer−monomer ratio.

The ^{1}H and ^{13}C resonances for the coordinated acetonitrile molecule in **4** at 1.89 (^{1}H) and 1.2 and 121.2 ppm (^{13}C) show typical values compared with the spectra of compounds with MeCN ligands coordinated to group 13 metal centers.[25,26] In all cases, **1**−**4**, the organic groups give ^{1}H and ^{13}C NMR signals which are characteristic for Mes and CH$_2$Ph ligands, attached to MF fragments (M = Ga, In).[11−13,25,27]

The small rings in [**1**]$_2$·6MeCN−[**3**]$_2$·2MeCN allow a reliable assignment of IR bands to the corresponding

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(23) For gallium and indium compounds, see: *Gmelin Handbook of Inorganic Chemistry, Gallium, Organogallium Compounds*; Springer: Berlin, 1987; Part 1. Weidlein, J. In *Gmelin Handbook of Inorganic Chemistry, Organoindium Compounds*; Springer: Berlin, 1991; Part 1.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) of [1]$_2$·6MeCN–4

Compound [**1**]$_2$·6MeCN			
Cs1–F1	3.207(6)	Ga1–C1	2.024(9)
Cs1–F1a	2.880(5)	Ga1–C2	2.03(1)
Cs1–N1	3.18(1)	Ga1–C3	2.02(1)
Cs1–N2	3.11(1)	N1–C4	1.13(2)
Ga1–F1	1.903(5)	N2–C5	1.10(2)
F1–Cs1–F1a	86.4(1)	C1–Ga1–C2	113.3(4)
F1–Cs1–N1	119.0(3)	C1–Ga1–C3	114.4(4)
F1–Cs1–N2	121.3(4)	C2–Ga1–C3	130.3(4)
N1–Cs1–N2	119.6(4)	Cs1–F1–Ga1	109.7(2)
N1–Cs1–F1a	105.0(3)	Cs1–F1–Cs1a	93.6(1)
N2–Cs1–F1a	82.1(3)	Ga1–F1–Cs1a	156.4(3)
F1–Ga1–C1	105.5(3)	Cs1–N1–C4	160(1)
F1–Ga1–C2	96.0(3)	Cs1–N2–C5	135(1)
F1–Ga1–C3	103.6(4)		
Compound [**2**]$_2$·6MeCN			
Cs1–F1	3.040(2)	In1–C1	2.202(3)
Cs1–F1a	2.852(2)	In1–C2	2.213(3)
Cs1–N1	3.224(4)	In1–C3	2.212(3)
Cs1–N2	3.139(4)	N1–C4	1.128(6)
In1–F1	2.113(2)	N2–C5	1.112(6)
F1–Cs1–F1a	82.26(5)	C1–In1–C2	115.1(1)
F1–Cs1–N1	121.83(9)	C1–In1–C3	116.2(1)
F1–Cs1–N2	119.5(1)	C2–In1–C3	119.3(1)
N1–Cs1–N2	118.7(1)	Cs1–F1–In1	109.41(7)
N1–Cs1–F1a	106.9(1)	Cs1–F1–Cs1a	97.74(5)
N2–Cs1–F1a	80.9(1)	In1–F1–Cs1a	152.75(9)
F1–In1–C1	103.97(9)	Cs1–N1–C4	160.0(5)
F1–In1–C2	93.9(1)	Cs1–N2–C5	137.4(4)
F1–In1–C3	103.0(1)		
Compound [**3**]$_2$·2MeCN			
Cs1–F1	2.872(2)	Ga1–C1	2.013(4)
Cs1–F1a	2.838(2)	Ga1–C2	2.007(5)
Ga1–F1	1.864(2)	Ga1–C3	2.021(5)
F1–Cs1–F1a	84.85(6)	C1–Ga1–C3	112.6(2)
F1–Ga1–C1	105.0(1)	C2–Ga1–C3	116.6(2)
F1–Ga1–C2	104.3(2)	Cs1–F1–Ga1	119.8(1)
F1–Ga1–C3	104.6(2)	Cs1–F1–Cs1a	95.15(7)
C1–Ga1–C2	112.3(2)	Ga1–F1–Cs1a	132.9(1)
Compound **4**			
Ga1–N1	2.207(5)	Ga1–C3	1.988(5)
Ga1–C1	2.014(5)	N1–C4	1.111(6)
Ga1–C2	1.999(5)		
N1–Ga1–C1	96.6(2)	C1–Ga1–C3	118.1(2)
N1–Ga1–C2	94.2(2)	C2–Ga1–C3	118.0(2)
N1–Ga1–C3	101.0(2)	Ga1–N1–C4	171.2(5)
C1–Ga1–C2	119.3(2)	N1–C4–C41	178.4(7)

Table 3. Additional Metal–Carbon Contacts in [1]$_2$·6MeCN–[3]$_2$·2MeCN (Å)

Compound [**1**]$_2$·6MeCN			
Cs1···C2	3.49(1)	Cs1···C24	4.17(1)
Cs1···C21	3.31(1)	Cs1···C25	3.94(1)
Cs1···C22	3.56(1)	Cs1···C36	3.59(1)
Cs1···C23	4.00(1)		
Compound [**2**]$_2$·6MeCN			
	3.508(3)		4.243(4)
	3.360(3)		3.988(4)
	3.761(4)		3.663(5)
	4.123(4)		
Compound [**3**]$_2$·2MeCN			
Cs1···C11a	3.700(4)	Cs1···C25	3.497(5)
Cs1···C12a	3.641(4)	Cs1···C26	3.553(5)
Cs1···C13a	3.549(5)	Cs1···C21–C26[a]	3.30
Cs1···C14a	3.477(5)	Cs1···C31	3.617(4)
Cs1···C15a	3.479(5)	Cs1···C32	3.550(5)
Cs1···C16a	3.592(4)	Cs1···C33	3.526(5)
Cs1···C11a–C16a[a]	3.29	Cs1···C34	3.545(5)
Cs1···C21	3.670(4)	Cs1···C35	3.581(5)
Cs1···C22	3.697(4)	Cs1···C36	3.614(5)
Cs1···C23	3.651(5)	Cs1···C31–C36[a]	3.29
Cs1···C24	3.556(5)		

[a] Ring centroid.

vibrations. Monomer CsF and the dimer $(CsF)_2$ investigated by matrix isolation techniques exhibit IR bands at 313 (monomer) and 251, 205, and 76 cm^{-1} (dimer), respectively.[28] The absorptions at 194 ([**1**]$_2$·6MeCN) and 190 cm^{-1} ([**2**]$_2$·6MeCN) can be attributed to the vibrations $\nu_{as}(Cs_2F_2)$. The bands at 228, 206, and 181 cm^{-1} for the ring vibrations in [**3**]$_2$·2MeCN are observed at higher wavenumbers because of the lower coordination number of the Cs$^+$ ion. The Ga(In)–F stretching vibrations have been observed at 420 ([**1**]$_2$·6MeCN), 402 ([**2**]$_2$·6MeCN), and 447 cm^{-1} ([**3**]$_2$·2MeCN); the higher value for [**3**]$_2$·2MeCN in comparison to [**1**]$_2$·6MeCN is in good agreement with the shorter Ga–F bond length in [**3**]$_2$·2MeCN compared to that in [**1**]$_2$·6MeCN. We assign the bands at 581 ([**1**]$_2$·6MeCN), 538 ([**2**]$_2$·6MeCN), 477 ([**3**]$_2$·2MeCN), and 581 cm^{-1} (**4**) to M–C vibrations. However, the M–Mes fragments lead to a mixing of M–C and aryl-ring vibrations.[29] The absorption at 338 cm^{-1} for **4** is caused by the M–N streching vibration. Interesting are the C≡N bands. A C≡N vibration for [**1**]$_2$·6MeCN and [**2**]$_2$·6MeCN has been observed only for [**1**]$_2$·6MeCN because of the weakly bound MeCN molecules. In [**1**]$_2$·6MeCN the acetonitrile molecule is attached to Cs$^+$, while **4** possesses a slightly stronger donor–acceptor Ga–N bond. Nevertheless, in both cases the resonance ν(C≡N) is split by Fermi resonance. In addition, a shift of the values to higher wavenumbers should be observable ([**1**]$_2$·6MeCN, 2292, 2260; **4**, 2306, 2279; MeCN, 2294, 2254 cm^{-1}).[30] [**1**]$_2$·6MeCN and **4** exhibit only a small splitting of the band and no significant shift of the values as it was found in $[\{B(CH_2Ph)_3\}_{0.92}\{Ga(CH_2Ph)_3\}_{0.08}(MeCN)]$ (2336, 2314, 2291 cm^{-1}).[25] The spectroscopic data and the results of the X-ray analyses confirm that [**1**]$_2$·6MeCN, [**2**]$_2$·6MeCN, and **4** are compounds with weak metal–nitrogen bonds.

The EI mass spectra exhibit only fragments for the dimers [**1**]$_2$·6MeCN–[**3**]$_2$·2MeCN. $m/z = 503$ $(CsFGaMes_3 - 5Me)^+$, $m/z = 372$ $(FInMes_2)^+$, and $m/z = 555$ $[Cs_2F_2Ga(CH_2Ph)_2]^+$ are the highest observed signals.

Centrosymmetric four-membered CsF rings are the dominating structural motif for the solid structures of [**1**]$_2$·6MeCN–[**3**]$_2$·2MeCN. In comparable derivatives such as $Cs[Me_3MF]$ and $Cs[i\text{-}Pr_3MF]$ (M = Ga, In)[14,15] the Cs_2F_2 rings are connected by additional Cs–F interactions. In [**1**]$_2$·6MeCN–[**3**]$_2$·2MeCN the π-electron systems of aryl substituents and, in part, acetonitrile molecules have to substitute the Cs–F contacts to saturate the coordination sphere of the Cs$^+$ ions. However, the interactions of π-electron systems with Cs$^+$ ions can be understood as an electrostatic one. Comparable aryl–Cs(Rb) features are known from organometallic compounds such as $[Cs(C_6H_6)_3\{C(SiMe_3)_3\}]$.[31,32] The structures of [**1**]$_2$·6MeCN and [**2**]$_2$·

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Table 4. Comparison of Bond Lengths (Å) in Selected Organogallium(indium) Compounds

compd	Cs−F	Ga(In)−F	Ga(In)−C	Ga−N	ref
$[\mathbf{1}]_2\cdot 6\mathrm{MeCN}$	2.880(5), 3.207(6)	1.903(5)	2.02[a]		*b*
$[\mathbf{3}]_2\cdot 2\mathrm{MeCN}$	2.838(2), 2.872(2)	1.864(2)	2.01[a]		*b*
$\mathrm{Cs[Me_3GaF]}$	2.96[a]	1.919(3), 1.922(3)	1.99[a]		14
$\mathrm{Cs}[i\text{-}\mathrm{Pr_3GaF}]$	2.924(2)	1.970(4)	1.998(5)		15
$\mathrm{Cs[(PhCH_2)_2GaF_2]}$	3.18[a]	1.84[a]	1.97[a]		11
$\mathrm{Cs[MesGaF_3]}$	3.11[a]	1.784(7) 1.807(4)	1.941(8)		12
$\mathrm{[Mes_2GaF]_2\cdot THF}$		1.947(2)[c]	1.949(5)		44
$\mathrm{[(PhCH_2)_3Ga(THF)]}$			1.981(6)		11
$\mathrm{GaMes_3}$			1.968(4)		17
$\mathrm{[Mes_2GaCl]_2}$			1.972(3)		45
4			2.00[a]	2.207(5)	*b*
$\mathrm{[Mes_2Ga(F)(}t\text{-}\mathrm{BuNH_2)]\cdot 2.5THF}$		1.838(3)	1.991(5)	2.049(4)	46
$\mathrm{[Mes_6Ga_6F_4O_4]\cdot THF}$		2.23[a,d]	1.93[a]		44
$\mathrm{[Me_3Ga(}t\text{-}\mathrm{BuNH_2)]}$			1.95(1), 2.01(1)	2.12(1)	36
$\mathrm{[Me_3Ga\{(C_6H_{11})_2NH\}]}$			1.97[a]	2.151(6)	38
$[t\text{-}\mathrm{Bu_3Ga(PhNH_2)]}$			2.00(1)	2.246(9)	37
$[\mathbf{2}]_2\cdot 6\mathrm{MeCN}$	2.852(2), 3.040(2)	2.113(2)	2.21[a]		*b*
$\mathrm{Cs[Me_3InF]}$	2.94[a]	2.148(9), 2.149(8)	2.18[a]		14
$\mathrm{Cs}[i\text{-}\mathrm{Pr_3InF}]$	2.889(2)	2.168(3)	2.199(4)		15
$\mathrm{[\{Cs(MeCN)_2\}\{F(}i\text{-}\mathrm{Pr_2InF)_5\}]}$	2.96[a]	2.28[a,c,d]	2.15[a]		13
$\mathrm{[(MesInF_2)_{10}MgF_2]\cdot 5tol}$		2.12[a,c,d]	2.14[a]		13
$\mathrm{[Mes_2InF]_3}$		2.12[a,c]	2.13[a]		46
$\mathrm{InMes_3}$			2.163(5), 2.170(5)		18
$\mathrm{[Mes_2InCl]_2}$			2.146(9), 2.17(1)		18

[a] Average. [b] This work. [c] Contains μ_2-bridging F atoms to two Ga(In) centers. [d] Contains μ_3-bridging F atoms to three Ga(In) centers.

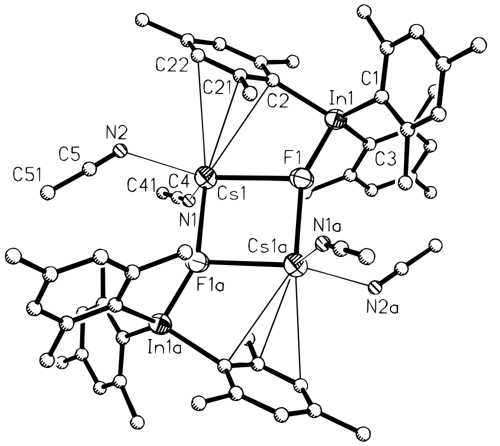

Figure 1. Molecule $[\{\mathrm{Cs(MeCN)_2}\}\{\mathrm{Me_3InF}\}]_2$ in $[\mathbf{2}]_2\cdot$6MeCN. The carbon and nitrogen atoms are drawn as balls for clarity (Cs, In, and F with 50% probability level; without H atoms).

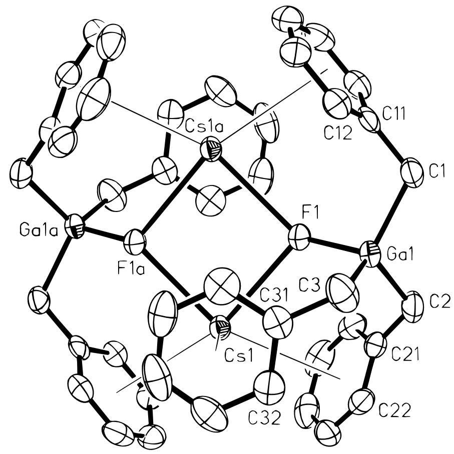

Figure 2. Molecule $[\mathrm{Cs\{(PhCH_2)_3GaF\}}]_2$ in $[\mathbf{3}]_2\cdot$2MeCN (50% probability level; without H atoms).

6MeCN are isostructural (Figure 1), but all three Cs−F four-membered rings show the same rhombic distortion [F1−Cs1−F1a, Cs1−F1−Cs1a: 86.4(1), 93.6(1)° ($[\mathbf{1}]_2\cdot$6MeCN); 82.26(5), 97.74(5)° ($[\mathbf{2}]_2\cdot$6MeCN); 84.85(6), 95.15(7)° ($[\mathbf{3}]_2\cdot$2MeCN)].

Decreasing Cs−F distances in a group of substances with the same ligand sphere but different group 13 metals have been observed recently.[14,15] We have observed an analogous effect for $[\mathbf{1}]_2\cdot$6MeCN and $[\mathbf{2}]_2\cdot$6MeCN. $[\mathbf{1}]_2\cdot$6MeCN shows Cs−F contacts of 3.207(6) and 2.880(5) Å while $[\mathbf{2}]_2\cdot$6MeCN exhibits interactions of 2.852(2) and 3.040(2) Å. This is caused by the synergetic effect of an increase of M−F(C) bond lengths (M = Ga → In) on the one hand and an increase in the ionic character of the M−F bond on the other. These combined effects cause closer Cs−F contacts with stronger electrostatic forces. A Cs−F distance of 3.005 Å has been reported for crystalline CsF.[33]

Longer Cs−C ($[\mathbf{1}]_2\cdot$6MeCN, 3.75 Å; $[\mathbf{2}]_2\cdot$6MeCN, 3.83 Å; mean values) and Cs−N distances ($[\mathbf{1}]_2\cdot$6MeCN, 3.11(1), 3.18(1) Å; $[\mathbf{2}]_2\cdot$6MeCN, 3.139(4), 3.224(4) Å) go along with the reduction of the $\mathrm{Cs_2F_2}$ ring sizes. The $\mathrm{Cs_2F_2M_2}$ cores of $[\mathbf{1}]_2\cdot$6MeCN and $[\mathbf{2}]_2\cdot$6MeCN are almost planar (angular sum at F1, 360°), while the Ga atoms in $[\mathbf{3}]_2\cdot$2MeCN have a distinct distance from the $\mathrm{Cs_2F_2}$ plane (0.88 Å; angular sum at F1, 348°; Figure 2).

The Ga−F distances depend on the number of electronegative substituents at the metal center. The observed values of 1.903(5) ($[\mathbf{1}]_2\cdot$6MeCN) and 1.864(2) Å ($[\mathbf{3}]_2\cdot$2MeCN) are between those of 1.80 Å in $\mathrm{Cs[MesGaF_3]}$ or 1.84 Å in $\mathrm{Cs[(PhCH_2)_2GaF_2]}$ and that of 1.947(2) Å in $\mathrm{[Mes_2GaF]_2\cdot THF}$ with μ_2-bridging $\mathrm{F^-}$ ions. An analogous rule cannot be developed for the softer In

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(32) For alkali metal−C interactions see e.g.: (a) Eaborn, C.; Izod, K.; Smith, J. D. *J. Organomet. Chem.* **1995**, *500*, 89. (b) Bock, H.; Hauck, T.; Näther, C. *Organometallics* **1996**, *15*, 1527. (c) Mecozzi, S.; West, A. P., Jr.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 2307. (d) Dougherty, D. A. *Science* **1996**, *271*, 163 and references therein.

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center. The In−F bond length in [**2**]$_2$·6MeCN of 2.113(2) Å is shorter than the 2.15 Å (average) in Cs[Me_3InF] or the 2.168(3) Å in Cs[*i*-Pr_3InF] but in the same region than the 2.12 Å observed in [Mes_2InF]$_3$ with μ_2-bridging F centers.

A nonlinear arrangement of the Cs−NCMe moities like in [**1**]$_2$·6MeCN and [**2**]$_2$·6MeCN with similar Cs−N bond lengths has been found in [{Cs(MeCN)$_2$}{F(*i*-Pr_2InF)$_5$}].[13,34] In all cases the acetonitrile molecules coordinated to Cs^+ ions are only loosely bound. The nonlinear CsNC sequence is probably due to packing effects. [**1**]$_2$·6MeCN−[**3**]$_2$·2MeCN contain, in addition to the coordinated solvent, MeCN molecules occupying lattice sites without any metal nitrogen interactions. Therefore, [**1**]$_2$·6MeCN−[**3**]$_2$·2MeCN lose the solvent already in a weak flow of argon under efflorescence.

As can be concluded from the Cs−C distances, only the atoms C2, C21, and C22 of the phenyl ring belong to the coordination sphere of the Cs^+ ion (sum of the van der Waals radii: 4.17 Å); the corresponding Mes ligands are rotated around the M−C2 axis (M = Ga, In) to enable this Cs−C contacts.

In contrast to [**1**]$_2$·6MeCN and [**2**]$_2$·6MeCN, the aryl rings in [**3**]$_2$·2MeCN must be described as η^6-bound, although the interaction mode is likewise an ionic one. The mean values are 3.57 (C11 → C16), 3.60 (C21 → C26), and 3.57 Å (C31 → C36). This is about 0.20 Å longer than in Cs[$InMe_4$][35] but 0.10−0.15 Å shorter than the Cs−C distances in Cs[$(PhCH_2)_2GaF_2$].[11] Cs[$(PhCH_2)_2GaF_2$] consists of a polymeric chain of Cs_2F_2 rings shielded by η^6-bound phenyl rings. The additional phenyl ring in [**3**]$_2$·2MeCN leads to a complete coverage of the Cs−F four-membered ring. The coordination geometry of the Cs center in [**3**]$_2$·2MeCN can be described as a distorted square-pyramidal environment, if one counts a phenyl ring as one ligand.

All mentioned salts Cs[$R_{4-n}MF_n$] ($n = 1-3$) possess an identical construction principle: The center of the formed structure is reserved for the interionic Cs−F interactions, while the periphery is occupied by the organic ligands, protecting the center. The number of organic ligands per group 13 metal, the steric demand of the ligands, and the M−F(C) bond lengths decide the long-range order, whether rings, strings, layers, or molecules of the heterocubane type are formed (Figure 3).

A long Ga−N distance of 2.207(5) Å and a low pyramidalization of the metal center, recognizable by the sum of the C−Ga−C angles of 355°, infer a weak donor−acceptor bond for **4** (Figure 4). An average Ga−N distance of 2.15 Å and an angular sum of 347° is typical for known adducts [$R_3Ga(NR'_3)$]. A common rule concerning the bulk of the substituents, the Ga−N bond lengths, and the rate of pyramidalization does not appear to exist.[36−42]

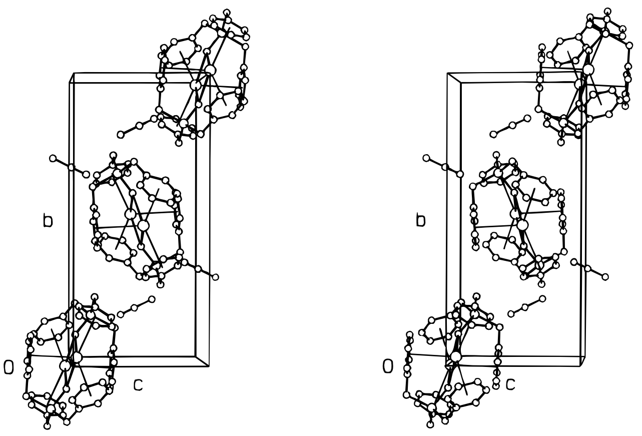

Figure 3. Stereoscopic view of the unit cell of [**3**]$_2$·2MeCN.

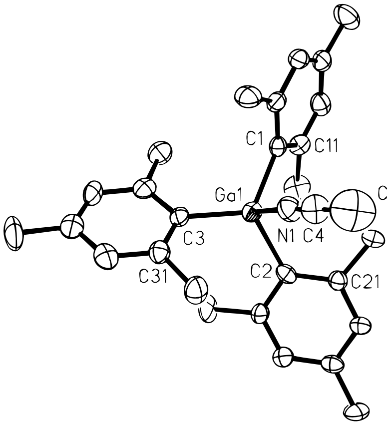

Figure 4. Computer-generated plot of **4** (50% probability level; without H atoms).

The increase of the coordination number (CN) 3 at $GaMes_3$ (Ga−C: 1.968(4) Å [17]) to CN 4 at **4** leads to a weakening of the Ga−C bonds causing longer metal−carbon distances [Ga−C: 2.00 Å]. The average values for [**1**]$_2$·6MeCN (2.02 Å), [**2**]$_2$·6MeCN (2.21 Å), and [**3**]$_2$·2MeCN (2.01 Å) can be unterstood in this context. An exception is the 1.941(8) Å observed for Cs[$MesGaF_3$],[12] which can be attributed to the cumulation of electronegative bonding partners.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and isotropic or anisotropic displacement parameters for all atoms in [**1**]$_2$·6MeCN−**4** (26 pages). Ordering information is given on any current masthead page.

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