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Stabilization of Molecular LiF and LiFHF inside Metallamacrocyclic Hosts

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Complexes of molecular LiF and LiFHF were synthesized using the metallamacrocyclic receptors [(cymene)Ru($C_5H_3NO_2$)]$_3$ (**1**), [Cp*Rh($C_5H_3NO_2$)]$_3$ (**2**), and [Cp*Ir($C_5H_3NO_2$)]$_3$ (**3**). $LiBF_4$ complexes of **1**–**3** were prepared and subsequently treated with F^- or FHF^- to give the desired products in an anion-exchange reaction. All complexes were characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{19}F, ^7Li). Strong scalar coupling between ^7Li and ^{19}F is observed for the LiF and the LiFHF complexes ($^1J_{LiF} = 91–103$ Hz). The LiFHF adduct of **1** displays fluxional behavior with fast exchange of the two fluorine atoms. The structures of the complexes **1**·$LiBF_4$, **2**·$LiBF_4$, **1**·LiF, **2**·LiF, **1**·LiFHF, and **3**·LiFHF were determined by single-crystal X-ray analysis. Li–F bond lengths between 1.77 and 1.81 Å were found. The LiFHF complexes show a hydrogen difluoride anion coordinated in a bent fashion via one fluorine atom to the lithium ion.

Introduction

The coordination chemistry of alkali metal halide complexes has been studied intensively over the past 30 years. Using crown ethers and related macrocycles, hundreds of complexes have been synthesized and structurally characterized.[1] There is one notable exception: complexes with molecular LiF are virtually unknown. Some compounds with Li···F contacts have been described,[2] but here the fluoride atom is either covalently bound to other atoms (e.g., in PF_6^- salts) or coordinatively bound to very strong Lewis acids (e.g., to Ti^{4+}).[3] The difficulty in stabilizing complexes of molecular LiF is due to the very high lattice energy of this salt.[4] Consequently, the crystalline form represents a thermodynamic trap. A similar situation is found for the less common but theoretically interesting salt LiFHF. To the best of our knowledge, structural data for complexes of LiFHF are not available. Again, a very high lattice energy was determined.[5]

In 1983, Donald J. Cram introduced the concept of molecular container compounds.[6] This proved to be a very fruitful approach to the stabilization and study of highly reactive molecules. Cyclobutadiene,[7] *o*-benzyne,[8] or cycloheptatetraene[9] are among the compounds successfully captured inside cagelike molecules. A drawback, however, is that the synthesis of these hosts (e.g., hemicarcerands) is often very demanding. In principle, an attractive alternative for the construction of macrocyclic cage compounds is the

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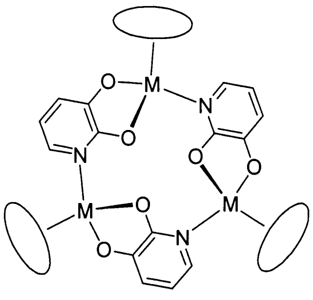

(π-ligand)M	
(cymene)Ru^{II}	**1**
Cp*Rh^{III}	**2**
Cp*Ir^{III}	**3**

utilization of transition-metal-based self-assembly processes. Such processes can give rise to complex macrocyclic structures in a single step and very good yields.[10] Complexes of this kind are increasingly being used as hosts for organic or inorganic guest molecules.[10,11] Fujita et al. reported a palladium(II)-based coordination cage that is able to stabilize labile intermediates of the polycondensation of alkoxysilanes.[12] Raymond et al. showed that the ion $[Me_2C(OH)PEt_3]^+$ can be stabilized by encapsulation in a tetrahedral Ga cluster.[13] Metallamacrocyclic receptors for alkali metal ions have been prepared by the groups of Pecoraro, Lippert, and Saalfrank, among others.[14]

In an extension of our work on half-sandwich pyridonate complexes,[15] we recently described the synthesis of trinuclear metallomacrocycles of the general formula $[(\pi\text{-ligand})M(C_5H_3NO_2)]_3$ (M = Ru, Rh, Ir; π-ligand = arene, Cp*) (**1**−**3**.[16,17] These compounds can be obtained by reaction of the corresponding chloro-bridged complexes $[(\pi\text{-ligand})MCl_2]_2$ with 2,3-dihydroxypyridine in the presence of base in good yields.

The molecular structures are very similar: the deprotonated 2,3-dihydroxypyridine acts as a tridentate ligand connecting the metal fragments. Three oxygen atoms are positioned in close proximity to each other, forming a high-affinity binding site for sodium and lithium ions. The binding constants of these organometallic analogues of [12]-crown-3 are comparable to those of cryptands. The selectivity is controlled by the nature of the π-ligand. Generally, the affinity for lithium salts is higher than that for sodium salts; in one special case (π-ligand = $C_6H_5CO_2Et$), a Li^+/Na^+ selectivity of >1000 was determined.[18] Because cations and anions are bound as ion pairs, the receptors can also be used to selectively bind anions. Using the trinuclear complex **3**, we built a chemosensor for fluoride anion.[17] During the course of this work, we were able to isolate for the first time a complex of molecular lithium fluoride (**3**·LiF). In the following, we describe the syntheses and structures of two new examples of LiF complexes using the metallomacrocycles **1** and **2** as receptors. Furthermore, we show that the organometallic hosts **1**−**3** can be used to stabilize the elusive molecular form of LiFHF. The isolated LiF and LiFHF ion pairs show unique structural and spectroscopic features, which are described in detail.

Experimental Section

General. The synthesis of all complexes was performed under an atmosphere of dry dinitrogen using standard Schlenk techniques. All solvents (analytical-grade purity) were degassed and stored under a dinitrogen atmosphere. The complexes $[(cymene)Ru(C_5H_3NO_2)]_3$ (**1**), $[Cp^*Rh(C_5H_3NO_2)]_3$ (**2**), $[Cp^*Ir(C_5H_3NO_2)]_3$ (**3**), and $[Cp^*Ir(C_5H_3NO_2)]_3 \cdot LiBF_4$ were prepared according to literature procedures.[16,17] 3-Hydroxy-2-pyridone and $Et_4NF \cdot 2(H_2O)$ were purchased from Fluka, Cs_2CO_3 and $LiBF_4$ from Aldrich, and KF from Merck, and Et_4NFHF was prepared according to a literature procedure.[19] For the synthesis of **1**·$LiBF_4$ and **2**·$LiBF_4$, stock solutions of $LiBF_4$ were employed. The ^1H, ^{13}C, ^{19}F, and ^7Li spectra were recorded on a Bruker Advance DPX 400 or a Bruker

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Advance 200 spectrometer using the residual protonated solvents (^{1}H, ^{13}C) as the internal standards and LiCl/D_2O (^{7}Li) and $CFCl_3$/benzene (^{19}F) as the external standards. The spectra were recorded at room temperature; exceptions are indicated.

[(Cymene)Ru($C_5H_3NO_2$)]$_3$·LiBF$_4$ (1·LiBF$_4$). LiBF$_4$ (4.6 mg, 48 μmol) was added to a solution of **1** (50 mg, 48 μmol) in degassed acetonitrile (50 mL). The solution was heated under reflux for 1 h. Evaporation of the solvent under reduced pressure gave an orange powder (yield: 55 mg, 100%). Red crystals were obtained by slow diffusion of pentane into a solution of **1**·LiBF$_4$ in benzene. ^{1}H NMR (400 MHz, toluene-d_8): δ (ppm) 1.15 [d, $^3J = 7$ Hz, 9H, CH(CH_3)$_2$], 1.19 [d, $^3J = 7$ Hz, 9H, CH(CH_3)$_2$], 1.52 (s, 9H, CH$_3$), 2.75 [sept, $^3J = 7$ Hz, 3H, CH(CH$_3$)$_2$], 4.48 (d, $^3J = 5$ Hz, 3H, CH, cymene), 5.47 (d, $^3J = 6$ Hz, 3H, CH, cymene), 5.79 (d, $^3J = 6$ Hz, 3H, CH, cymene), 5.85 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 3H, CH, pyridone), 6.32 (d, $^3J = 5$ Hz, 3H, CH, cymene), 6.52 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone), 6.89 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone). ^{13}C NMR (101 MHz, CD$_3$CN): δ (ppm) 18.4, 22.1, 23.9 (CH$_3$), 32.2 [CH(CH$_3$)$_2$], 75.5, 79.0, 84.0, 85.5 (CH, cymene), 98.6, 100.7 (C, cymene), 114.1, 116.9, 133.5, 157.4, 168.5 (pyridone). ^{7}Li NMR (156 MHz, toluene-d_8): δ (ppm) -0.25 (q, $J_{\text{LiF}} = 21$ Hz). ^{19}F NMR (188 MHz, toluene-d_8): δ (ppm) -149.92 (q, $J_{\text{LiF}}= 21$ Hz). Elemental anal. Calcd (%) for $C_{45}H_{51}N_3O_6Ru_3$·0.5C_6H_6·LiBF$_4$: C 49.45, H 4.69, N 3.60. Found: C 49.30, H 4.87, N 3.43.

[Cp*Rh($C_5H_3NO_2$)]$_3$·LiBF$_4$ (2·LiBF$_4$). LiBF$_4$ (3.7 mg, 38 μmol) was added to a solution of **2** (40 mg, 38 μmol) in degassed acetonitrile (50 mL). The solution was heated under reflux for 90 min. Evaporation of the solvent under reduced pressure gave an orange powder (yield: 44 mg, 100%). Red crystals were obtained by slow diffusion of pentane into a solution of **2**·LiBF$_4$ in toluene. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 1.74 (s, 45H, Cp*), 6.09 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 3H, CH, pyridone), 6.46 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone), 6.77 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone). ^{1}H NMR (400 MHz, toluene-d_8): δ (ppm) 1.53 (s, 45H, Cp*), 5.96 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 3H, CH, pyridone), 6.62 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone), 6.90 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone). ^{13}C NMR (101 MHz, toluene-d_8): δ (ppm) 8.7 (Cp*), 91.9 [d, $^1J_{\text{RhC}} = 9$ Hz, $C_5(CH_3)_5$], 114.2, 117.7, 131.0, 158.2, 169.4 (pyridone). ^{7}Li NMR (156 MHz, toluene-d_8): δ (ppm) -0.37. ^{19}F NMR (188 MHz, toluene-d_8): δ (ppm) -145.29. Elemental anal. Calcd (%) for $C_{45}H_{54}N_3O_6Rh_3$·2toluene·LiBF$_4$: C 53.70, H 5.35, N 3.18. Found: C 53.71, H 5.46, N 2.97.

[(Cymene)Ru($C_5H_3NO_2$)]$_3$·LiF (1·LiF). To a suspension of an excess of KF (52 mg, 0.9 mmol) in degassed methanol (0.8 mL) was added a yellow solution of **1**·LiBF$_4$ (20 mg, 17 μmol) in degassed benzene (20 mL). The resulting mixture was stirred vigorously for 1 h at room temperature. After filtration and evaporation of the solvent under reduced pressure, the product was extracted with degassed benzene (20 mL). Evaporation of the solvent under reduced pressure gave a yellow powder. Orange crystals were obtained by slow diffusion of pentane into a solution of **1**·LiF in benzene (yield after crystallization: 10 mg, 52%). ^{1}H NMR (400 MHz, toluene-d_8): δ (ppm) 1.18 [d, $^3J = 7$ Hz, 9H, CH(CH_3)$_2$], 1.19 [d, $^3J = 7$ Hz, 9H, CH(CH_3)$_2$], 1.67 (s, 9H, CH$_3$), 2.88 [sept, $^3J = 7$ Hz, 3H, CH(CH$_3$)$_2$], 4.92 (br, 3H, CH, cymene), 5.39 (d, $^3J = 6$ Hz, 3H, CH, cymene), 5.80 (d, $^3J = 5$ Hz, 3H, CH, cymene), 5.86 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 3H, CH, pyridone), 6.51 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone), 6.69 (br, 3H, CH, cymene), 6.91 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone). ^{13}C NMR (101 MHz, toluene-d_8): δ (ppm) 18.1, 22.0, 23.8 (CH$_3$), 31.3 [CH(CH$_3$)$_2$], 76.0, 80.4, 82.9, 83.5 (CH, cymene), 98.1, 99.1 (C, cymene), 113.1, 117.3, 131.9, 157.6, 169.0 (pyridone). ^{7}Li NMR (156 MHz, toluene-d_8): δ (ppm) 0.36 (d, $^1J_{\text{LiF}} = 95$ Hz). ^{19}F NMR (188 MHz, toluene-d_8): δ (ppm) -140.15 (q, $^1J_{\text{LiF}} = 95$ Hz). Elemental anal. Calcd (%) for $C_{45}H_{51}N_3O_6Ru_3$·2H$_2$O·LiF: C 49.36, H 5.06, N 3.84. Found: C 49.59, H 5.19, N 3.64.

[Cp*Rh($C_5H_3NO_2$)]$_3$·LiF (2·LiF). To a solution of an excess of KF (54 mg, 0.94 mmol) in degassed methanol (10 mL) was added **2**·LiBF$_4$ (20 mg, 19 μmol). The resulting mixture was stirred vigorously for 30 min at room temperature. After evaporation of the solvent under reduced pressure, the product was extracted with degassed benzene (20 mL). Evaporation of the solvent under reduced pressure gave a brown powder (yield: 17 mg, 90%). Red crystals can be obtained by slow diffusion of pentane into a solution of **2**·LiBF$_4$ in benzene or toluene. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ (ppm) 1.63 (s, 45H, Cp*), 5.99 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 3H, CH, pyridone), 6.70 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone), 7.03 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone). ^{13}C NMR (68 MHz, CDCl$_3$): δ (ppm) 9.1 (Cp*), 91.8 [d, $^1J_{\text{RhC}} = 9$ Hz, $C_5(CH_3)_5$], 112.8, 115.9, 130.8, 157.3, 169.4 (pyridone). ^{7}Li NMR (156 MHz, C$_6$D$_6$): δ (ppm) 0.43 (d, $^1J_{\text{LiF}} = 96$ Hz). ^{19}F NMR (188 MHz, C$_6$D$_6$): δ (ppm) -124.68 (q, $^1J_{\text{LiF}} = 96$ Hz). Elemental anal. Calcd (%) for $C_{45}H_{54}N_3O_6Rh_3$·1.25toluene·H$_2$O·LiF: C 53.76, H 5.54, N 3.50. Found: C 53.69, H 5.29, N 3.39.

[(Cymene)Ru($C_5H_3NO_2$)]$_3$·LiFHF (1·LiFHF). To a solution of an excess of Et$_4$NFHF (577 mg, 3.4 mmol) in degassed acetonitrile (1.5 mL) was added an orange solution of **1**·LiBF$_4$ (77 mg, 68 μmol) in degassed benzene (20 mL). The resulting mixture was stirred vigorously for 20 min at room temperature. After filtration, orange crystals were obtained by slow diffusion of pentane (yield after crystallization: 44 mg, 58%). ^{1}H NMR (400 MHz, toluene-d_8): δ (ppm) 1.15 [d, $^3J = 7$ Hz, 9H, CH(CH_3)$_2$], 1.18 [d, $^3J = 7$ Hz, 9H, CH(CH_3)$_2$], 1.62 (s, 9H, CH$_3$), 2.79 [sept, $^3J = 7$ Hz, 3H, CH(CH$_3$)$_2$], 4.74 (d, br, $^3J = 5$ Hz, 3H, CH, cymene), 5.41 (d, $^3J = 6$ Hz, 3H, CH, cymene), 5.80 (d, $^3J = 6$ Hz, 3H, CH, cymene), 5.86 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 3H, CH, pyridone), 6.45 (d, br, $^3J = 5$ Hz, 3H, CH, cymene), 6.50 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone), 6.90 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone), 16.20 (br, 1H, LiFHF). ^{1}H NMR (400 MHz, toluene-d_8, -40 °C): δ (ppm) 1.11 [d, $^3J = 7$ Hz, 9H, CH(CH_3)$_2$], 1.18 [d, $^3J = 7$ Hz, 9H, CH(CH_3)$_2$], 1.55 (s, 9H, CH$_3$), 2.77 [m, br, 3H, CH(CH$_3$)$_2$], 4.54 (br, 3H, CH, cymene), 5.39 (br, 3H, CH, cymene), 5.88 (br, 3H, CH, cymene), 5.91 (pt, $^3J = 7$ Hz, 3H, CH, pyridone), 6.49 (br, 3H, CH, cymene), 6.63 (d, $^3J = 7$ Hz, 3H, CH, pyridone), 6.95 (d, $^3J = 6$ Hz, 3H, CH, pyridone), 16.60 (d, $^1J_{\text{HF}} = 298$ Hz, 1H, LiFHF). ^{13}C NMR (101 MHz, toluene-d_8): δ (ppm) 18.1, 22.2, 23.6 (CH$_3$), 31.4 [CH(CH$_3$)$_2$], 75.6, 80.1, 83.3, 83.4 (CH, cymene), 98.4, 98.7 (C, cymene), 113.2, 117.5, 132.2, 157.4, 168.8 (pyridone). ^{7}Li NMR (156 MHz, toluene-d_8, -60 °C): δ (ppm) -0.24 (d, $^1J_{\text{LiF}} = 90$ Hz). ^{19}F NMR (188 MHz, toluene-d_8, -60 °C): δ (ppm) -154.92 (br, Li*F*HF), -165.23 (dd, $^1J_{\text{HF}} = 298$ Hz, $^2J_{\text{FF}} = 151$ Hz, LiFH*F*). Elemental anal. Calcd (%) for $C_{45}H_{51}N_3O_6Ru_3$·2H$_2$O·LiFHF: C 48.47, H 5.06, N 3.76. Found: C 48.41, H 5.12, N 3.53.

[Cp*Rh($C_5H_3NO_2$)]$_3$·LiFHF (2·LiFHF). To a solution of an excess of Et$_4$NFHF (488 mg, 2.88 mmol) in degassed acetonitrile (15 mL) was added a brown solution of **2**·LiBF$_4$ (62 mg, 58 μmol) in degassed acetonitrile (35 mL). The resulting mixture was stirred vigorously for 90 min at room temperature. After evaporation of the solvent under reduced pressure, the product was extracted with degassed benzene (50 mL). Evaporation of the solvent under reduced pressure gave a brown powder (yield: 38 mg, 64%). ^{1}H NMR (400 MHz, toluene-d_8): δ (ppm) 1.58 (s, 45H, Cp*), 5.96 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 3H, CH, pyridone), 6.60 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 3H, CH, pyridone), 6.92 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz,

Table 1. Crystallographic Data for the $LiBF_4$ Complexes of **1** and **2**

	1·$1.5C_6H_6$·$LiBF_4$	**2**·toluene·$LiBF_4$
empirical formula	$C_{54}H_{60}N_3O_6Ru_3LiBF_4$	$C_{52}H_{62}N_3O_6Rh_3LiBF_4$
molecular weight (g mol^{-1})	1244.01	1227.53
crystal size	0.26 × 0.22 × 0.18	0.25 × 0.20 × 0.15
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	*Pccn*
a (Å)	12.015(4)	36.1548(15)
b (Å)	12.5483(17)	15.5423(7)
c (Å)	17.452(5)	17.8504(8)
α (°)	85.198(15)	90
β (°)	78.62(2)	90
γ (°)	87.408(17)	90
volume (Å^3)	2569.4(11)	10 030.6(8)
Z	2	8
density (g cm^{-3})	1.608	1.626
temperature (K)	143(2)	143(2)
absorption coefficient (mm^{-1})	0.938	0.938
Θ range (°)	3.21−25.03	3.32−25.03
index ranges	−14 → 14, −13 → 13, −20 → 20	−43 → 43, −17 → 18, −21 → 21
reflections collected	15687	59019
independent reflections	8523 (R_{int} = 0.0300)	8583 (R_{int} = 0.0814)
absorption correction	empirical	semiempirical
max and min transmission	0.7630 and 0.3390	0.9215 and 0.7835
data/restraints/parameters	8523/5/610	8583/1/631
GOF on F^2	1.104	1.062
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0516, wR2 = 0.1299	R1 = 0.0476, wR2 = 0.0974
R indices (all data)	R1 = 0.0618, wR2 = 0.1414	R1 = 0.0799, wR2 = 0.1112
largest diff peak/hole (eÅ^{-3})	1.472/−0.896	1.621/−0.697

3H, CH, pyridone), 15.96 (d, $^{1}J_{\mathrm{HF}} = 317$ Hz, 1H, LiFHF). ^{13}C NMR (101 MHz, toluene-d_8): δ (ppm) 8.9 (Cp*), 91.7 [d, $^{1}J_{\mathrm{RhC}} = 9$ Hz, $C_5(CH_3)_5$], 113.7, 116.9, 130.7, 158.4, 169.9 (pyridone). ^{7}Li NMR (156 MHz, toluene-d_8): δ (ppm) 0.12 (d, $^{1}J_{\mathrm{LiF}} = 98$ Hz). ^{19}F NMR (188 MHz, toluene-d_8): δ (ppm) −142.03 (m, Li*F*HF), −168.06 (dd, br, $^{1}J_{\mathrm{HF}} = 317$ Hz, $^{2}J_{\mathrm{FF}} = 161$ Hz, LiFH*F*). Elemental anal. Calcd (%) for $C_{45}H_{54}N_3O_6Rh_3$·$3H_2O$·LiFHF: C 47.34, H 5.39, N 3.68. Found: C 47.33, H 5.86, N 3.19.

[Cp*Ir($C_5H_3NO_2$)]$_3$·LiFHF (3·LiFHF). To a suspension of an excess of KFHF (115 mg, 1.48 mmol) in degassed methanol (300 μL) was added a yellow solution of **3**·$LiBF_4$ (41 mg, 29 μmol) in degassed acetonitrile (15 mL). The resulting mixture was stirred vigorously for 1 h at room temperature. After filtration and evaporation of the solvent under reduced pressure, the product was extracted with degassed benzene (20 mL). Evaporation of the solvent under reduced pressure gave a yellow powder (yield: 38 mg, 96%). Yellow crystals were obtained by slow diffusion of pentane into a solution of **3**·LiFHF in benzene. ^{1}H NMR (400 MHz, C_6D_6): δ (ppm) 1.59 (s, 45H, Cp*), 5.90 (dd, $^{3}J = 6$ Hz, $^{3}J = 7$ Hz, 3H, CH, pyridone), 6.69 (dd, $^{3}J = 7$ Hz, $^{4}J = 2$ Hz, 3H, CH, pyridone), 7.06 (dd, $^{3}J = 6$ Hz, $^{4}J = 2$ Hz, 3H, CH, pyridone), 15.85 (d, $^{1}J_{\mathrm{HF}} = 324$ Hz, 1H, LiFHF). ^{13}C NMR (101 MHz, C_6D_6): δ (ppm) 9.2 (Cp*), 83.2 [$C_5(CH_3)_5$], 114.1, 117.9, 131.7, 158.8, 171.9 (pyridone). ^{7}Li NMR (156 MHz, C_6D_6): δ (ppm) −0.25 (d, $^{1}J_{\mathrm{LiF}} = 103$ Hz). ^{19}F NMR (188 MHz, C_6D_6): δ (ppm) −142.26 (dq, $^{1}J_{\mathrm{LiF}} = 103$ Hz, $^{2}J_{\mathrm{FF}} = 159$ Hz, Li*F*HF), −169.29 (dd, $^{1}J_{\mathrm{HF}} = 324$ Hz, $^{2}J_{\mathrm{FF}} = 159$ Hz, LiFH*F*). Elemental anal. Calcd (%) for $C_{45}H_{54}N_3O_6Ir_3$·C_6H_6·LiFHF: C 42.73, H 4.29, N 2.93. Found: C 42.47, H 4.33, N 2.80.

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement are listed in Tables 1−3. Diffraction data were collected at 143 K using Mo$_{K\alpha}$ radiation on different equipment: an Oxford Diffraction diffractometer with a kappa geometry equipped with a Sapphire CCD detector (**2**·toluene·$LiBF_4$, **1**·$1.25C_6H_6$·H_2O·LiF), and a mar345 imaging plate detector (all of the remaining structures). Data reduction was performed with CrysAlis RED 1.6.9β[20] and marHKL 1.9.1[21] (**2**·$1.5C_6H_6$·H_2O·LiF). Absorption correction was applied to all data sets but one (**2**·$1.5C_6H_6$·H_2O·LiF). For **2**·toluene·$LiBF_4$ and **1**·$1.25C_6H_6$·H_2O·LiF, a semiempirical method (MULTI−SCAN)[22] was employed, whereas an empirical method (DIFABS)[23] was used for the remaining structures. Structure solutions were determined with ab initio direct methods.[24] All structures were refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with $U_{\mathrm{iso}} = aU_{\mathrm{eq}}(\mathrm{C})$ (where *a* is 1.5 for methyl hydrogen atoms and 1.2 for other atoms and C is the parent carbon atom). Some disorder problems were encountered during the refinement of **1**·$1.5C_6H_6$·$LiBF_4$ and **1**·$1.25C_6H_6$·H_2O·LiF (disordered BF_4^- anion and C_6H_6 solvent molecules). Particular attention was paid to H_2O and HF molecules, for which hydrogen atoms are isotropic and free. In such cases, constraints deal with the X−H and H···H distances for water molecules, whereas, in the case of HF, they concern the F···H and H−F distances. Space group determination, structure refinement, and geometrical calculations were carried out on all structures with the SHELXTL software package, release 5.1.[25] Graphical representations of the molecular structures in the crystal were generated with the program ORTEP.[26]

Results and Discussion

$LiBF_4$ Complexes. Because of the low solubility of LiF and LiFHF in organic solvents, complexes of these salts are best prepared in situ. For this purpose, we have first synthesized the adducts **1**·$LiBF_4$, **2**·$LiBF_4$, and **3**·$LiBF_4$.[17] The weekly bonded tetrafluoro borate anion is then exchanged with F^- or FHF^- in a salt metathesis reaction. The

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Table 2. Crystallographic Data for the LiF Complexes of **1** and **2**

	1·$1.25C_6H_6 \cdot H_2O \cdot LiF$	**2**·$1.5C_6H_6 \cdot H_2O \cdot LiF$
empirical formula	$C_{52.5}H_{60.5}N_3O_7Ru_3LiF_2$	$C_{54}H_{65}N_3O_7Rh_3LiF$
molecular weight (g mol^{-1})	1174.69	1202.76
crystal size	0.26 × 0.21 × 0.17	0.30 × 0.26 × 0.21
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a (Å)	14.8439(11)	44.177(9)
b (Å)	18.8894(13)	12.390(3)
c (Å)	20.9897(12)	20.164(4)
α (°)	115.783(6)	90
β (°)	103.291(5)	112.44(3)
γ (°)	97.565(6)	90
volume (Å^3)	4974.1(6)	10 201(4)
Z	4	8
density (g cm^{-3})	1.569	1.566
temperature (K)	143(2)	143(2)
absorption coefficient (mm^{-1})	0.957	1.017
Θ range (°)	3.51−25.03	1.00−27.59
index ranges	−17 → 17, −22 → 22, −22 → 24	−57 → 57, −15 → 15, −25 → 26
reflections collected	29 404	29 489
independent reflections	15 404 (R_{int} = 0.0399)	10 389 (R_{int} = 0.0317)
absorption correction	Semiempirical	none
max and min transmission	0.9941 and 0.7595	−
data/restraints/parameters	15 404/33/1118	10 389/3/630
GOF on F^2	1.055	1.041
final R indices [$I > 2\sigma(I)$]	R1 = 0.0779, wR2 = 0.1928	R1 = 0.0469, wR2 = 0.1256
R indices (all data)	R1 = 0.1011, wR2 = 0.2128	R1 = 0.0512, wR2 = 0.1284
largest diff peak/hole (eÅ^{-3})	2.211/−2.267	1.562/−1.165

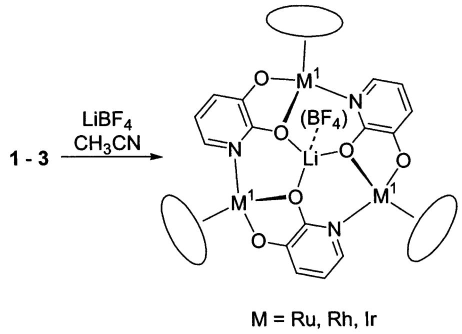
Table 3. Crystallographic Data for the LiFHF Complexes of **1** and **3**

	1·$1.75C_6H_6 \cdot LiFHF$	**3**·$C_6H_6 \cdot LiFHF$
empirical formula	$C_{55.5}H_{62.5}N_3O_6Ru_3LiF_2$	$C_{51}H_{61}N_3O_6Ir_3LiF_2$
molecular weight (g mol^{-1})	1215.73	1433.57
crystal size	0.23 × 0.20 × 0.16	0.18 × 0.15 × 0.12
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	$Pccn$
a (Å)	9.880(2)	36.438(2)
b (Å)	22.193(4)	15.100(3)
c (Å)	23.801(4)	17.742(4)
α (°)	92.737(14)	90
β (°)	94.985(15)	90
γ (°)	99.633(17)	90
volume (Å^3)	5115.2(17)	9762(3)
Z	4	8
density (g cm^{-3})	1.579	1.951
temperature (K)	143(2)	143(2)
absorption coefficient (mm^{-1})	0.935	8.218
Θ range (°)	3.13−25.03	3.38−25.03
index ranges	−11 → 11, −26 → 26, −28 → 28	−41 → 42, −17 → 17, −19 → 21
reflections collected	31 029	56 251
independent reflections	16 913 (R_{int} = 0.0360)	8511 (R_{int} = 0.0667)
absorption correction	empirical	empirical
max and min transmission	0.6510 and 0.1800	0.6070 and 0.1360
data/restraints/parameters	16 913/5/1278	8511/2/599
GOF on F^2	1.094	1.113
final R indices [$I > 2\sigma(I)$]	R1 = 0.0560, wR2 = 0.1310	R1 = 0.0425, wR2 = 0.0963
R indices (all data)	R1 = 0.0684, wR2 = 0.1407	R1 = 0.0589, wR2 = 0.1055
largest diff peak/hole (eÅ^{-3})	1.253/−0.802	1.844/−1.279

$LiBF_4$ adducts were obtained by reaction of the metallomacrocycles **1**−**3** with $NaBF_4$ in acetonitrile (Scheme 1). All complexes were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, ^{7}Li), elemental analysis, and single-crystal X-ray crystallography.

The presence of $LiBF_4$ guest molecules results in significant changes in the ^{1}H NMR spectra of the macrocyclic receptors: the signals of the π-ligands as well as the signals of the pyridone ligands are shifted toward lower field. In all cases, the exchange of the guest is slow compared to the NMR time scale. Previous studies with LiCl guests have shown that there is a strong preference for binding of the guest as an ion pair.[16] For **1**·$LiBF_4$, a similar coordination mode is confirmed by NMR spectroscopy because the spectra display coupling between the ^{7}Li and ^{19}F atoms (toluene-d_8). In the ^{7}Li NMR spectrum of **1**·$LiBF_4$, a quintet is observed. This points to a BF_4^- anion directly bound to the Li^+ ion with fast exchange between bridging and terminal fluoride atoms. Contrary to what is found for **1**·$LiBF_4$, the ^{7}Li and the ^{19}F spectra of the complexes **2**·$LiBF_4$ and **3**·$LiBF_4$ show simple singlets, indicating solvent-separated BF_4^- ions. Apparently, the sterically demanding Cp* ligands disfavor

Scheme 1. Synthesis of the LiBF$_4$ Complexes of **1**−**3**



the simultaneous binding of Li$^+$ and BF$_4$$^-$ to the metallamacrocyclic receptor in solution.

The structures of **1**·LiBF$_4$ and **2**·LiBF$_4$ were determined by single-crystal X-ray crystallography (Figure 1). In both cases, the lithium ion is coordinated to the three adjacent oxygen atoms of the metallamacrocyclic receptors with the remaining coordination site being occupied by the BF$_4$$^-$ anion, which is connected by one bridging fluorine atom.

Although the overall structures of the lithium complexes **1**·LiBF$_4$ and **2**·LiBF$_4$ are similar [pseudo-C_3-symmetric structures with a Li(μ-F)BF$_3$ guest molecule], the bond lengths around the lithium ion show pronounced differences. The Li−F bond distance of the Cp*Rh complex **2**·LiBF$_4$ [1.968(11) Å] is significantly longer than what is found for the (cymene)Ru complex **1**·LiBF$_4$ [1.836(9) Å]. The complex [(PPh$_3$)$_2$Pt(μ-O)]$_2$·Li(μ-F)$_2$BF$_2$, for comparison, shows a Li−F bond distance of 1.89(2) Å.[27] These structural data suggest a very weak interaction between the Li$^+$ and BF$_4$$^-$ ions for complex **2**·LiBF$_4$, in agreement with the results of the NMR study described above.

LiF and LiFHF Complexes. LiF complexes of the receptors **1** and **2** were obtained in a metathesis reaction of the LiBF$_4$ adducts with KF and subsequent extraction with benzene. Clear evidence for successful anion exchange was provided by the ^{7}Li and ^{19}F NMR spectra. In the ^{7}Li NMR spectra, doublets were observed instead of the quintet for **1**·LiBF$_4$ or the singlet for **2**·LiBF$_4$. The $^1J_{\mathrm{LiF}}$ coupling constants of 95 Hz (**1**·LiF) or 96 Hz (**2**·LiF) are large compared to what is found for other compounds with Li···F contacts.[2] The ^{19}F NMR spectra show the corresponding quartets at $\delta = -140.15$ ppm (**1**·LiF, toluene-d_6) and $\delta = -124.68$ ppm (**2**·LiF, C$_6$D$_6$).

Hydrogen difluoride is a unique anion because it is the simplest example of a molecule with a strong hydrogen bond.[28] In FHF salts, a typical F···F distance between 2.24 and 2.28 Å is found, with the proton being located in the center between the two fluoride atoms.[29] The experimentally determined value for the hydrogen bond energy is 45.8 ± 1.6 kcal/mol.[30] Numerous theoretical[31] and NMR spectroscopic studies[32] on the FHF$^-$ anion have been carried out to unravel the peculiar bonding situation in FHF$^-$. It is only recently that hydrogen difluoride has been recognized as a ligand for transition metal complexes. Although still rare, FHF complexes of the metals Mo, W, Ru, Ni, Pd, and Pt have been synthesized and characterized.[33] To the best of our knowledge, structural data for complexes containing *molecular* MFHF (M = alkali metal ion) are not available.

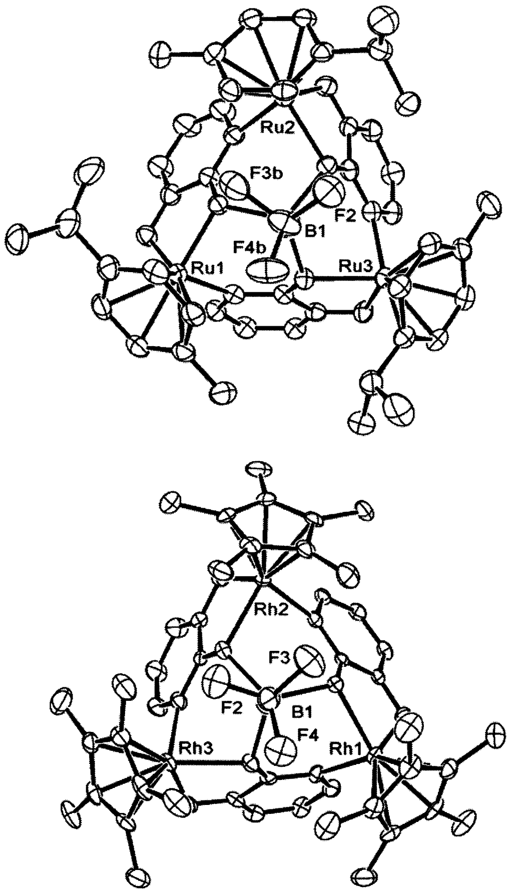


Figure 1. ORTEP drawings of the molecular structures of **1**·LiBF$_4$ (top) and **2**·LiBF$_4$ (bottom) in the crystal. Displacement ellipsoids are drawn at the 40% probability level. The hydrogen atoms are not shown for clarity. The lithium atoms are hidden by the boron atoms.

The complexes **1**·LiFHF, **2**·LiFHF, and **3**·LiFHF were obtained by reaction of the corresponding LiBF$_4$ adducts with KFHF or Et$_4$NFHF. The ^{1}H NMR spectrum of **3**·LiFHF

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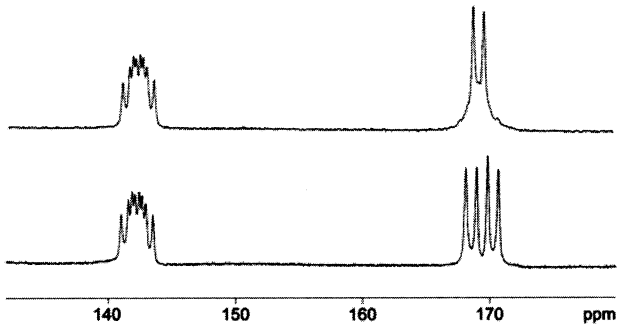

Figure 2. ^{19}F NMR spectrum of **3**·LiFHF in C_6D_6 with (bottom) and without (top) coupling to ^1H.

Table 4. NMR Data for the LiF and the LiFHF Complexes of **1**−**3** (ppm, Hz)

complex	δ (^7Li)	$^1J_{LiF}$	δ (^{19}F)	$^1J_{HF}$	$^2J_{FF}$
1·LiF^a	0.36	95	−140.15	−	−
2·LiF^b	0.43	96	−124.68	−	−
3·LiF^{b,c}	0.00	101	−124.65	−	−
1·LiFHF^{a,d}	−0.24	90	−154.92, − 165.23	298	151
2·LiFHF^b	0.12	98	−142.03, − 168.06	317	161
3·LiFHF^b	−0.25	103	−142.26, − 169.29	324	159

^{a} Toluene-d_8. ^{b} C_6D_6. ^{c} Reference 17. ^{d} −60 °C.

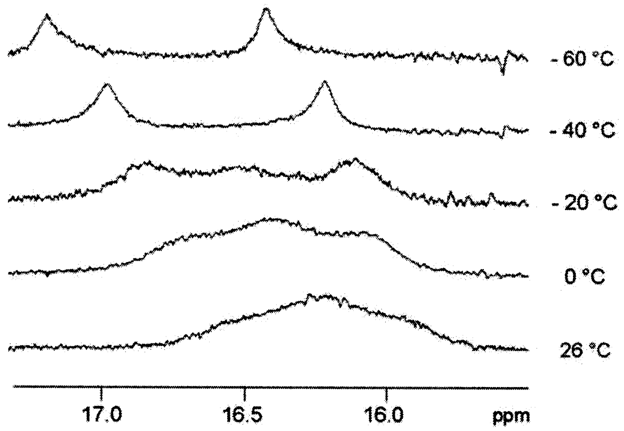

Figure 3. ^1H NMR spectra of **1**·$LiBF_4$ in toluene-d_8 in the region of the acidic hydrogen at various temperatures.

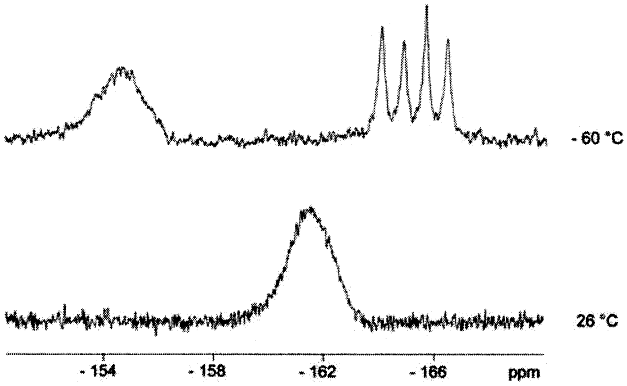

Figure 4. ^{19}F NMR spectra of **1**·LiFHF in toluene-d_8 at different temperatures.

(C_6D_6) exhibits a doublet at δ = 15.85 ppm with a $^1J_{HF}$ coupling constant of 324 Hz. This coupling is associated with the distal fluorine as determined by ^{19}F NMR spectroscopy (see below).[34] Coupling between the acidic hydrogen and the proximal fluorine is not observed. For comparison, the ^1H NMR spectrum of the free FHF^- anion is a triplet with a $^1J_{HF}$ coupling constant of 121 Hz.[32e] The value of $^1J_{HF}$ for HF is strongly solvent-dependent and ranges from 410 to 529 Hz.[32d] Thus, the value of $^1J_{HF}$ found for **3**·LiFHF lies between those for the hydrogen difluoride anion and HF. A similar behavior is found for transition metal complexes with FHF^- ligands: the value of $^1J_{HF}$ of the distal fluorine atom is large compared to that of the free FHF^- anion, and coupling to the proximal fluorine atom is small or not observed.[33] An adequate description of MFHF complexes is therefore a metal fluoride complex hydrogen bonded to a HF molecule (MF···HF). The ^7Li NMR spectrum of **3**·LiFHF (C_6D_6) shows a doublet at δ = −0.25 ppm resulting from coupling to the proximal fluorine. The $^1J_{LiF}$ coupling constant of 103 Hz is even larger than what was found for the LiF complexes of **1**−**3**. In the ^{19}F NMR spectrum of **3**·LiFHF (C_6D_6), two resonances are observed. One signal appears as a doublet of a quartet at δ = −142.26 ppm. This resonance is assigned to the proximal fluorine atom with coupling to the lithium and to the distal fluorine ($^2J_{FF}$ = 159 Hz). The second signal, assigned to the distal fluorine, is observed at δ = −169.29 ppm and appears as a doublet of a doublet. In the ^{19}F NMR spectrum of **3**·LiFHF, recorded with decoupling to ^1H, the latter signal is a simple doublet, whereas the former signal is not affected, in agreement with the assignments made (Figure 2).

The NMR spectra of the Cp*Rh complex **2**·LiFHF are similar to those for the Cp*Ir complex **3**·LiFHF (Table 4). The spectra of **1**·LiFHF, on the other hand, show pronounced differences. At room temperature, the acidic proton gives rise to a very broad signal at $\delta \approx$ 16.4 ppm (toluene-d_8). Upon cooling to −60 °C, the resonance sharpens into a doublet (Figure 3).

The ^{19}F NMR spectrum of **1**·LiFHF shows a broad singlet at room temperature, whereas at −60 °C, a spectrum comparable to that of **3**·LiFHF with two chemically distinct fluoride atoms is observed (Figure 4). The underlying dynamic process is most likely an intramolecular exchange between the proximal and distal fluorines via a pentacoordinated lithium ion (Scheme 2). A similar dynamic process has been observed for the palladium complex $[(Ph_3P)_2Pd(Ph)(FHF)]$.[33c] The fact that this exchange is only observed for the LiFHF complex of receptor **1** can be explained by the reduced steric bulk of the cymene ligands as compared

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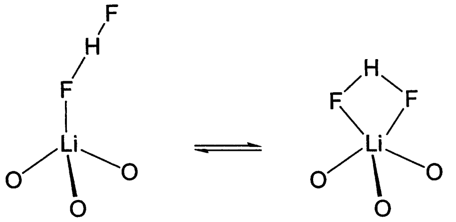
(34) The fluorine bound directly to the lithium is referred to as proximal, and the fluorine bound via the hydrogen bond as distal.

Scheme 2. Dynamic Equilibrium between Tetra- and Pentacoordinated Lithium Cations for Complex **1**·LiFHF[a]



[a] Only the oxygen atoms of the receptor are shown for clarity.

to the Cp* ligands, allowing for a Li(μ-F)$_2$H coordination mode. It is interesting to note that the energy-minimized structure for isolated NaFHF molecules in the gas phase also shows a cyclic Na(μ-F)$_2$H geometry (B3LYP/6-31+G**).[35]

Single-crystal X-ray structural analyses were carried out for the complexes **1**·LiF, **2**·LiF, **1**·LiFHF, and **3**·LiFHF. As for the LiBF$_4$ complexes, the lithium cation is coordinated to the three oxygen atoms of the receptors. The fourth coordination site is occupied by either the fluoride or the hydrogen difluoride anion. For complex **1**·LiF, two chemically similar but crystallographically independent molecules are found in the crystal with Li−F bond distances of 1.771(14) and 1.810(14) Å. A similar value is observed for **2**·LiF [Li−F = 1.782(6) Å]. These values are among the smallest Li···F distances reported so far,[2] highlighting the unique situation of monomolecular LiF inside these macrocyclic hosts. In crystalline LiF, for comparison, a Li···F distance of 2.009 Å is observed.[36] For both LiF complexes, a hydrogen-bonded water molecule is found in close proximity to the fluorine atom with F···O distances of 2.644(4) Å (**2**·LiF), 2.632(8) Å (**1**·LiF, molecule A), and 2.622(9) Å (**1**·LiF, molecule B) (Figure 5). The water molecules create a more complicated hydrogen-bond network (infinite one-dimensional chain) linking external oxygen atoms of a symmetry-related complex [O···O = 2.861(9)−3.135(4) Å].

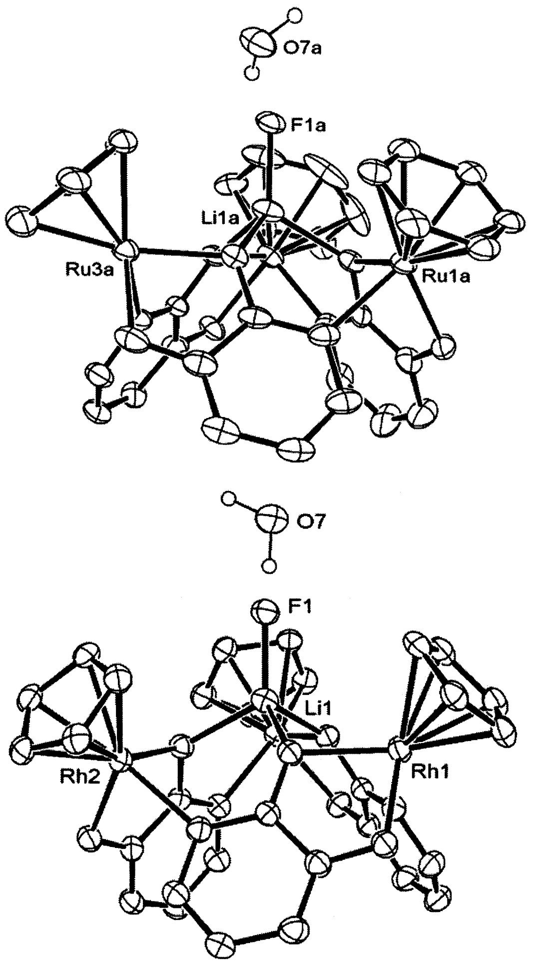


Figure 5. ORTEP drawings of the molecular structures of **1**·LiF·H$_2$O (top) and **2**·LiF·H$_2$O (bottom) in the crystal. Displacement ellipsoids are drawn at the 40% probability level. The hydrogen atoms and the side chains of the π-ligands are not shown for clarity.

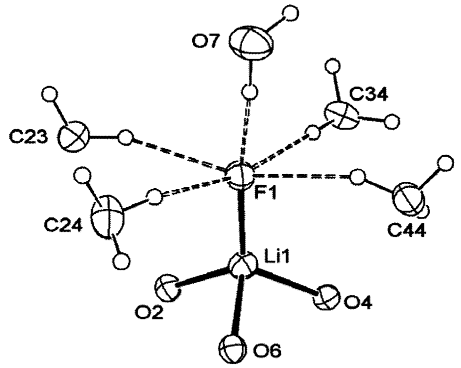


Figure 6. ORTEP drawing of the first coordination sphere of the guest molecule in **2**·LiF highlighting the close CH···F contacts. Displacement ellipsoids are drawn at the 40% probability level.

In **2**·LiF, the guest molecule is tightly encapsulated by the host compound: four short CH···F contacts between the methyl groups of the Cp* ligands and the fluorine atom are observed (CH···F = 2.14−2.27 Å). These distances are significantly smaller than the sum of the van der Waals radii of H and F (2.54 Å).[37] Contacts of this kind are thought to be of an attractive nature[38] and to contribute to the overall stability of the host−guest complex. Together with the hydrogen atom of the water molecule a distorted octahedral geometry around the fluorine atom is observed (Figure 6). For the (cymene)Ru complex **1**·LiF, on the other hand, a more open binding site is observed with three aromatic protons pointing toward the fluorine atom (CH···F = 2.38−2.61 Å).

In accordance with the NMR studies, the LiFHF complexes display a Li(μ-F)HF coordination mode with only one bridging fluorine atom (Figure 7). As expected, the acidic hydrogen atoms are difficult to locate, and therefore, we restrict the discussion to the lithium and fluorine atoms. For **3**·LiFHF, a slightly bent geometry is observed [Li−F−F =

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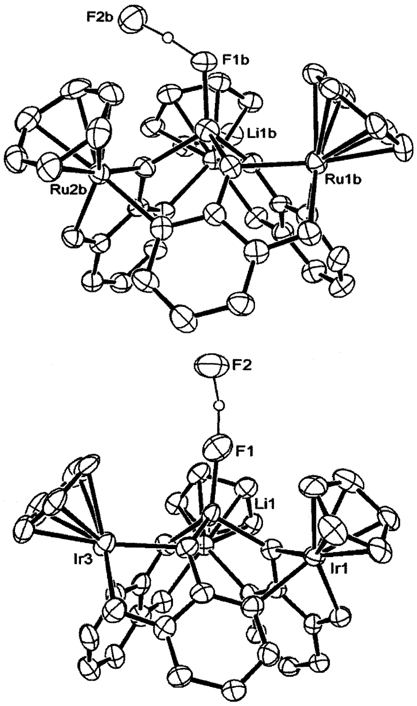

Figure 7. ORTEP drawings of the molecular structures of **1**·LiFHF (top) and **3**·LiFHF (bottom) in the crystal. Displacement ellipsoids are drawn at the 40% probability level. The hydrogen atoms and the side chains of the π-ligands are not shown for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (°) for the LiFHF Complexes of **1** and **3**

complex	Li−F	Li−O[a]	F−F	Li−F−F
1·LiFHF (A)	1.810(10)	1.93	2.319(5)	126.9(4)
1·LiFHF (B)	1.769(11)	1.95	2.300(6)	123.2(4)
3·LiFHF	1.814(18)	1.96	2.247(11)	159.4(6)

[a] Average values are given.

159.4(6)°]. The F···F distance of 2.247(11) Å is similar to that found for simple hydrogen difluoride salts in the crystal (2.24−2.28 Å).[29] The proximal fluorine atom in **3**·LiFHF is not as closely encapsulated by the Cp* ligands as it was in **2**·LiF: six methyl groups are pointed toward the fluorine atom with CH···F distances between 2.29 and 2.73 Å.

For the two independent molecules of **1**·LiFHF, the Li−F−F angles [123.2(4) and 126.9(4)°] are much smaller than those found for **3**·LiFHF [159.4(6)°]. As a result, the distal fluorine atom in **1**·LiFHF approaches the cymene ligands, and CH···F contacts between 2.24 and 2.34 Å are observed. The F···F distances [2.319(5) and 2.300(6) Å] are in the range of what is found for transition metal FHF complexes (2.28−2.40 Å)[33] but larger than what is found for **3**·LiFHF. The main structural features of the LiFHF complexes are summarized in Table 5.

Figure 8 shows space-filling representations of the molecular structures of **1**·LiF, **2**·LiF, **1**·LiFHF, and **3**·LiFHF in the crystal (view along the pseudo-C_3-symmetric axis). It is evident that the binding site of the cymene complexes (a and c) is more open and accessible than those of the Cp* complexes (b and d). As a result, a dynamic behavior for the LiFHF complex of **1** can be observed. For the Cp*Ir complex **3**·LiFHF, on the other hand, a dynamic behavior is disfavored because of the steric bulk of the Cp* ligands. The space-filling representation of **1**·LiFHF (Figure 8c) shows nicely how the FHF^- anion is bent toward the cymene ligands to maximize the interaction with the CH hydrogen atoms.

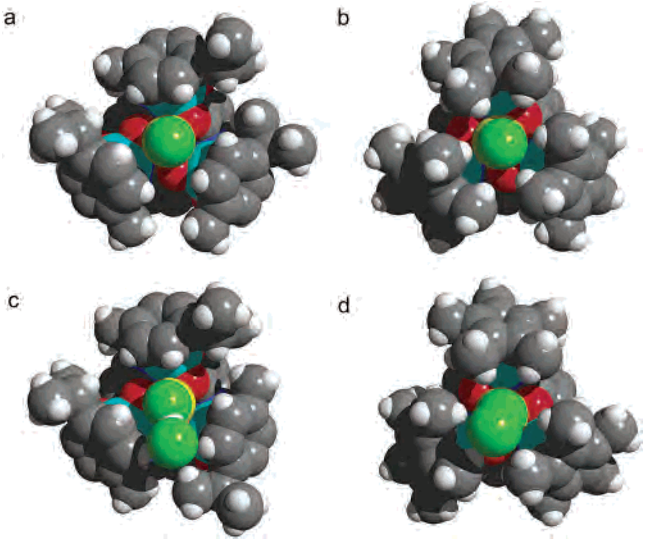

Figure 8. Space-filling representation of the molecular structures of (a) **1**·LiF, (b) **2**·LiF, (c) **1**·LiFHF, and (d) **3**·LiFHF in the crystal.

Conclusions

Metallamacrocyclic complexes of (cymene)Ru^{II}, Cp*Rh^{III}, and Cp*Ir^{III} have been used to stabilize the molecular forms of LiF and LiFHF. This provided the opportunity to study the structural and spectroscopic features of the isolated ion pair. Two interesting characteristics observed are the very short Li−F bond distances and the strong scalar coupling between ^{7}Li and ^{19}F. The geometry of the host molecule was shown to influence not only the structure but also the dynamics of the encapsulated guest molecule.

The results presented in this paper underline the potential of self-assembled coordination compounds to act as stabilizing hosts for unusual guest molecules. In view of the fact that the ability to construct complex inorganic host compounds has increased dramatically,[10] it is conceivable that many more examples will be presented soon.

Acknowledgment. This work was supported by the Swiss National Science Foundation and by OMG.

Supporting Information Available: Crystallographic data in CIF format of the complexes **1**·$LiBF_4$, **2**·$LiBF_4$ **1**·LiF, **2**·LiF, **1**·LiFHF, and **3**·LiFHF. This material is available free of charge on the Internet at http://pubs.acs.org.

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