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Novel fluorenyl alkali metal DIGLYME complexes: synthesis and solid state structures

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Dedicated to Professor Rüdiger Mews, on the occasion of his 60th birthday

Abstract

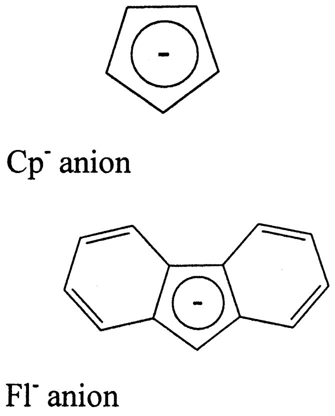
The reaction of the fluorenyl alkali metals with the tridentate Lewis base diethyleneglycol–dimethylether (DIGLYME) yielded the compounds $[Li(DIGLYME)_2]Fl$ (**1**, Fl = fluorenide anion), $[Na(DIGLYME)_2]Fl$ (**2**), $[KFl(DIGLYME)]_3$ (**3**), $[RbFl(DIGLYME)]_9$ (**4**), $[CsFl(DIGLYME)]_9$ (**5**), $[NaFl(DIGLYME)]_2$ (**6**), and $[(KFl)_2DIGLYME]_n$ (**7**). The solid state structures of all complexes were determined by X-ray single crystal structure analysis. According to the X-ray analyses, the compounds **1** and **2** crystallize as solvent separated ion pairs, the complexes **3**, **4**, **5**, and **6** as aggregates built up by two, three, or nine MFl(DIGLYME) units, and compound **7** as a polymeric band. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkali metals; Diethyleneglycol–dimethylether; Fluorenyl

1. Introduction

The fluorenide anion (Fl^-, Scheme 1), the dibenzo analog of the cyclopentadienide anion (Cp^-), has become an important ligand in synthetic organometallic chemistry within the last decade. Ansa metallocene complexes of Group 4 elements, containing the fluorenyl group, are in wide use as catalysts in poly-olefine productions (i.e. the complex $ZrCl_2(CpCMe_2Fl)$) [1–4].

For the preparation of these catalysts, fluorenyl alkali metal complexes are of high importance as precursors. While the fluorenyl alkali metal complexes have been well characterized in solution, the solid state structures are known only for few compounds. Recently, the solid state structures of base-free LiFl [5] and basefree NaFl [6] have been described. Some Lewis base adducts were characterized by X-ray single structure analysis as well (i.e. $LiFl(Et_2O)$ [7], NaFl(TMEDA) [8], MFl(18-crown-6) [9,10] (M = K–Cs), or MFl(PMDTA) (M = Na, Rb, Cs) [8,11], for the heavier alkali metals see also Ref. [12]). From the reported examples, it is obvious that there is a distinct influence of the cation size and of the neutral Lewis base ligand to the degree of association and the connectivity of the fluorenyl system to the metal ions. To discuss and understand these interesting effects a more detailed investigation of the solid state structures of these compounds is needed. In literature reported examples use a widely spread variety of Lewis bases



Scheme 1.

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which makes the discussion of the bonding effects quite difficult.

In this article for the first time a more systematic approach is used: it describes the solid state structures of complexes obtained by the reactions between all homoleptic fluorenyl alkali metal compounds (MFl; M = Li–Cs) and only one additional neutral ligand (here diethyleneglycol–dimethylether; DIGLYME). All obtained complexes were characterized by X-ray single crystal structure analysis.

2. Results and discussion

2.1. Synthesis

The fluorenyl alkali metals react with an excess of the tridentate oxygen containing Lewis base DIGLYME in a solution of DIGLYME–toluene–*n*-hexane to complexes of the general formula MFl(DIGLYME)$_2$ (M = Li (**1**), Na (**2**)) and MFl(DIGLYME) (M = K (**3**), Rb (**4**), Cs (**5**)) in yields between 25 and 70%. In the case that the ligand DIGLYME is used in an equimolar ratio instead of an excess, complexes of a different composition have been obtained. Fluorenyl sodium reacts with one equivalent DIGLYME to the complex NaFl(DIGLYME) (**6**, 5% yield) while fluorenyl potassium forms in similar reaction conditions the compound (KFl)$_2$(DIGLYME) (**7**, 64% yield). All obtained complexes are very air and moisture sensitive. They can, however, be stored under argon for months at room temperature. The lithium and sodium derivatives are yellow while the complexes of the heavier alkali metals are orange or red. The compounds are very soluble in THF or DIGLYME, less soluble in toluene, and insoluble in *n*-hexane.

2.2. ^{1}H-NMR spectroscopy

^{1}H-NMR spectroscopy of the complexes was carried out in THF-d_8. The resonance signals of the methylene protons of the DIGLYME ligands were shifted upfield for the compounds **1**, **2**, **6**, and **7** compared to the free DIGLYME molecule (CH$_2$ DIGLYME: free: 3.44 ppm; in **1**: 3.30 ppm; in **2**: 3.28 ppm; in **6**: 3.28 ppm; in **7**: 3.37 ppm). It is obvious that the DIGLYME ligand is coordinated to the different cations. In contrast to this, we observed CH$_2$ resonance signals at 3.44 ppm for the complexes **3**–**5**. This could indicate that in the complexes **3**–**5** the DIGLYME ligand is replaced by THF in this solvent. A similar tendancy was observed for the methyl protons of the DIGLYME ligand (data see Section 4). For the proton signals of the fluorenyl ligands we observed chemical shifts similar to those found for related compounds [9–12].

2.3. X-ray crystal structures

The solid state structures of the compounds [Li(DIGLYME)$_2$]Fl (**1**), [Na(DIGLYME)$_2$]Fl (**2**) [14], [KFl(DIGLYME)]$_3$ (**3**), [RbFl(DIGLYME)]$_9$ (**4**), [CsFl(DIGLYME)]$_9$ (**5**), [NaFl(DIGLYME)]$_2$ (**6**), and [(KFl)$_2$DIGLYME]$_n$ (**7**) have been determined by single crystal structure analysis. Crystallographic data are given in Table 1.

The lithium and sodium compounds **1** and **2** crystallize in an isostructural salt like fashion as solvent separated ion pairs (Fig. 1). Both metal ions (Li$^+$ or Na$^+$) are coordinated by six oxygen atoms of two DIGLYME molecules in a distorted octahedral environment. The fluorenide anions are not connected to the metal cations and can be described as ‘naked’ anions. They are located close to the inversion center of the space group ($P2_1/c$), and therefore they are disordered. Bond lengths and angles within the Fl$^-$ anions cannot be discussed. The [Li(DIGLYME)$_2$]$^+$ cation is only the second example of this species reported in literature; first being [Li(DIGLYME)$_2$][W(CO)$_5$I] [15]. The [Na(DIGLYME)$_2$]$^+$ cation has been isolated in a few other complexes before (i.e. [Na(DIGLYME)$_2$][C$_5$HPh$_4$] [16], [Na(DIGLYME)$_2$][C$_{10}$H$_8$] [17], or [Na(DIGLYME)$_2$][C$_{14}$H$_{10}$] [17] (C$_{10}$H$_8$ = naphthalene radical anion, C$_{14}$H$_{10}$ = anthracene radical anion). The Li–O distances of **1** are in the range 2.043(5)–2.228(5) Å, which is comparable with the values reported for [Li(DIGLYME)$_2$][W(CO)$_5$I] (1.999–2.226 Å). In this context two complexes, {[Li(en)$_2$][C$_{13}$H$_9$]}$_n$ [18] and [Na(2.2.1-cryptand)][C$_{13}$H$_9$] [19], should be mentioned, which also contain ‘naked’ fluorenide anions in the solid state.

The complexes **3**, **4**, and **5** crystallize as discreet molecules (Figs. 2 and 3). While the potassium com-

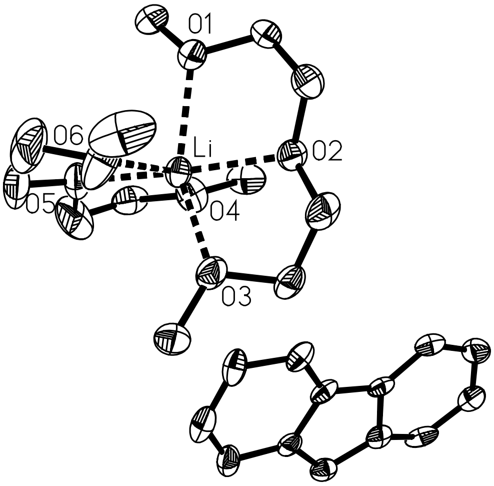

Fig. 1. Drawing of [Li(DIGLYME)$_2$]Fl (**1**; H atoms and disorder of the Fl ring are not shown). Distances (Å): Li–O 2.043(5)–2.228(5). The drawing of [Na(DIGLYME)$_2$]Fl (**2**) shows the same picture [14].

pound is an aggregate of three KFl(DIGLYME) units, the Rb and Cs derivatives form unusual solid state aggregates of nine MFl(DIGLYME) units (M = Rb, Cs).

The interactions of the metal cations (K^+, Rb^+, and Cs^+) to the ligands (Fl^- anion and neutral DIGLYME molecule) are comparable within all three complexes **3**–**5**. All cations are located above the five-membered ring of one fluorenide anion and bound in a fashion between η^2 to η^5 (i.e. Figs. 4 and 5 for complex **3**). Because of this different M–C bonding mode the M–C distances are within a widely spread range for the complexes **3**–**5**: K–C 3.041(2)–3.384(2); Rb–C 3.116(6)–3.403(6); Cs–C 3.14(2)–3.50(3) Å.

Besides the interactions described above, the cations K^+, Rb^+, and Cs^+ are coordinated by three oxygen atoms of the DIGLYME ligand, and, to complete the coordination sphere of the metal ions, interact with the fluorenyl ring of a neighboring MFl(DIGLYME) unit in an η^1 to η^3 M–C bonding mode.

Only a small number of solid state structures for fluorenyl alkali metal complexes of the heavier alkali metals potassium to cesium have been reported in literature [20]. The distances for the K–C interaction in the compounds $[KFl(TMEDA)]_n$ [13] (parallel zigzag chains; K–C(η^3) 3.043(2)–3.350(2) Å; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) or $[KFl(TMEDA)_2]$ [21] (monomeric complex; K–C(η^5) 3.071(5)–3.320(4) Å) are in the same range as found for complex **3**. For the single example of rubidium compounds $[RbFl(PMDTA)]_n$ [11] (PMDTA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) which shows a comparable environment of the ligands at the Rb^+ ion, Rb–C distances of 3.16(1)–3.41(2) Å were observed.

Very recently, three further complexes within the class of fluorenyl alkali metal complexes were published: MFl(18-crown-6) (M = K–Cs) [9,10]. In these compounds the M^+ ions are located above one six-membered ring of the fluorenyl ligand with M–C bonding modes between η^2 to η^6.

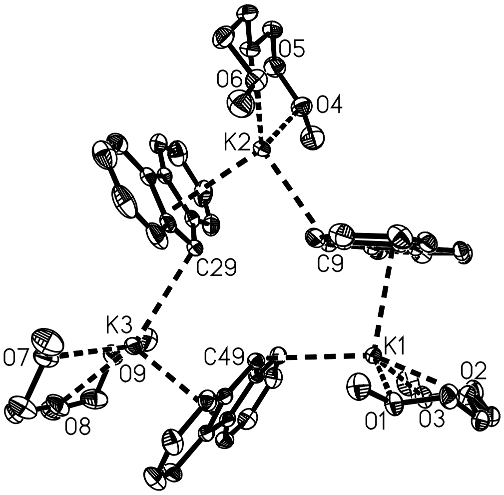

Fig. 2. Drawing of $[KFl(DIGLYME)]_3$ (**3**, no H atoms). Distances (Å): K–O 2.708(2)–2.817(2), K–C 3.041(2)–3.384(2).

The compound $[NaFl(DIGLYME)]_2$ (**6**) crystallizes as an unusual binuclear dimeric complex (Fig. 6). The central unit of **6** is built up by a planar Na_2O_2 four-membered ring (crystallographic inversion center in the ring). The Na^+ ions are coordinated in a square pyramidal environment by four oxygen atoms of the DIGLYME ligands and the central carbon atom (C9) of the five-membered ring of one Fl^- anion. It is remarkable that the Fl^- anions in this binuclear complex **6** are bound in an end-on fashion instead as bridging ligands. Bridging fluorenyl ligands were found in all but very special cases (i.e. 'naked' Fl^- anions or monomeric compounds) for fluorenyl alkali metal complexes. The Na–O distances are in the range 2.316(1)–2.564(1) Å, which is significantly longer than in the $[Na(DIGLYME)_2]^+$ cation [15,16]. The Na^+ ion is

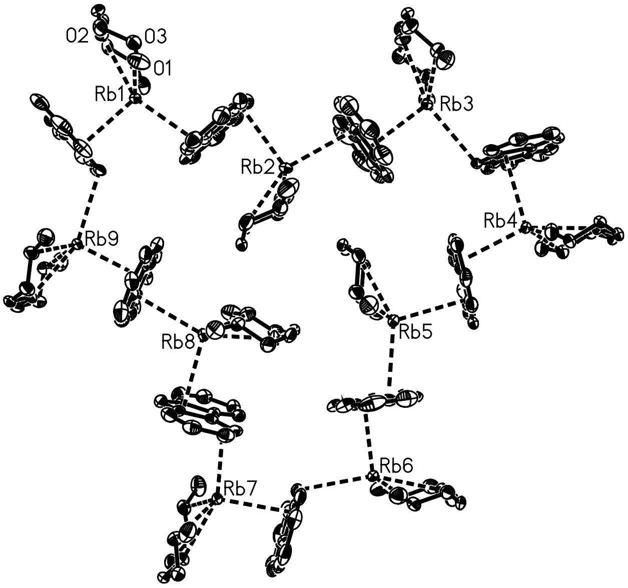

Fig. 3. Drawing of $[RbFl(DIGLYME)]_9$ (**4**, no H atoms). Distances (Å): Rb–O 2.842(4)–3.007(5), Rb–C 3.116(6)–3.403(6). The drawing of $[CsFl(DIGLYME)]_9$ (**5**) shows the same picture. Distances (Å): Cs–

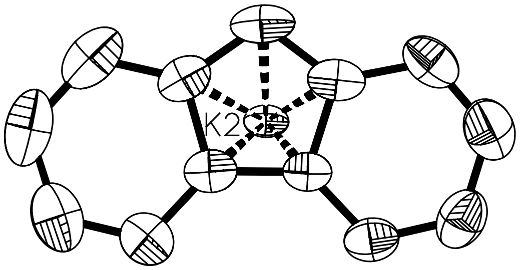

Fig. 4. η^5 Coordination mode of K2 to the five-membered ring of the fluorenide anion in **3**.

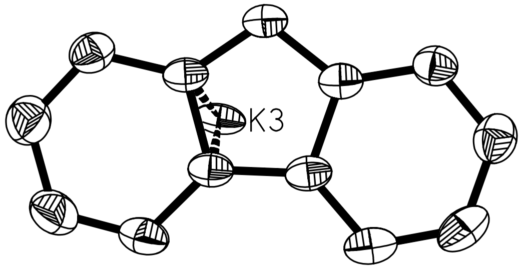

Fig. 5. η^2 Coordination mode of K3 to the five-membered ring of the fluorenide anion in **3**.

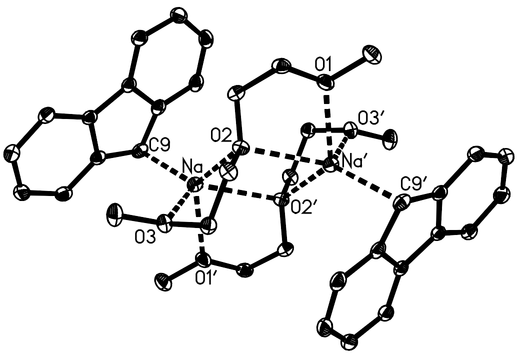

Fig. 6. Drawing of [NaFl(DIGLYME)]$_2$ (**6**, no H atoms). Distances (Å): Na–O 2.316(1)–2.564(1), Na–C9 2.589(1).

localized nearly perpendicular above the carbon atom C9 of the fluorenyl ring (angle Na–C9–C10 92.5(1)°, Na–C9–C13 84.9(1)°) with a Na–C9 bond length of 2.589(1) Å. Much longer are the distances to the adjacent carbon atoms C10 (3.006(1) Å) or C13 (2.838(1) Å). Therefore, the Na–C interaction in **6** can be interpreted as η^1 bonding. A similar bond length of a Na–C(η^1) interaction was observed in the compound [NaFl(TMEDA)]$_n$ (2.634(3) Å) [8], but the Na–C(η^1) distances in the base free salt fluorenyl sodium are significantly shorter (2.483(3) Å) [6]. The higher coordination number of five in [NaFl(DIGLYME)]$_2$ compared to the coordination number of three in base-free NaFl causes the longer Na–C(η^1) bond length found in **6**. The solid state structures of two further fluorenyl sodium compounds are described in literature, [NaFl(PMDTA)] and [NaFl(TMPDA)]$_4$ [TMPDA = *N*,*N*,*N′*,*N′*-tetramethylpropylenediamine) [8]. While [NaFl(PMDTA)] crystallizes as a monomeric complex with an unsymmetric Na–C(η^5) interaction, [NaFl(TMPDA)]$_4$ is an aggregate built up by four NaFl(TMPDA) units.

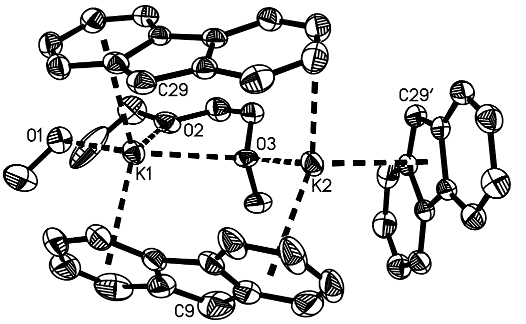

Fig. 7. Drawing of the binuclear unit of [(KFl)$_2$DIGLYME]$_n$ (**7**) with one additional symmetry related fluorenyl ligand (H atoms and disorder of the DIGLYME ligand are not shown). Distances (Å): K1–C(η^6) 3.092(3)–3.414(4), K2–C(η^2) 3.219, K2–C(η^5) 3.143(3)–3.370(3), K2–C(η^6) 3.206(4)–3.385(3).

Another new and unusual type of structure within this group of compounds was observed in the complex [(KFl)$_2$DIGLYME]$_n$ (**7**; Figs. 7 and 8). The compound crystallizes as a polymeric band, which is formed by binuclear (KFl)$_2$DIGLYME units. While one potassium ion (K1$^+$) is coordinated by two six-membered rings of two fluorenide anions (in both cases asymmetric η^6 bonding mode) and the three oxygen atoms of the DIGLYME ligand within this binuclear unit, the second potassium ion (K2$^+$) also interacts with the six-membered rings of the two mentioned Fl$^-$ anions (η^2 and η^6 bonding) but only with one oxygen atom of the DIGLYME molecule. Therefore, the ion K2$^+$ is open to one side, and can interact with a neighboring (KFl)$_2$DIGLYME unit in a K2–C(η^5) fashion to the five-membered ring of one symmetry related fluorenyl ligand. As a result of this bonding mode the binulear units are connected to form a polymeric band (Fig. 8). Because of a disorder of the DIGLYME molecule, K–O distances can not be discussed. The fluorenide anions can be described as μ^2-η^6:η^6- and μ^3-η^2:η^5:η^6-ligands. The K–C bond lengths are longer in complex **7** than in other fluorenyl potassium derivatives. In comparison: the K–C(η^2) bond lengths in **7** are 3.189(4) and 3.249(4) Å, while they are only 3.041(2) and 3.048(2) Å in the complex [KFl(DIGLYME)]$_3$ (**3**). For the K–C(η^5) distances in **7** values between 3.143(3) and 3.370(3) Å were observed, while this kind of interaction in **3** lies in the range of 3.086(2) to 3.260(3) Å. Finally, for the third connecting mode, K–C(η^6), values between 3.092(3) and 3.414(4) Å were found in **7** whereas 3.239(2)–3.371(2) Å were found in [KFl(18-crown-6)] [9].

3. Conclusion

For the first time a comparative study of Lewis base complexes of all fluorenyl alkali metals using a single Lewis base, namely DIGLYME, was performed. The smaller alkali metal cations, Li$^+$ and Na$^+$, can be surrounded by two neutral DIGLYME ligands. In this way these cations are coordinatively satisfied and form solvent separated ion pairs with the fluorenide anion. The bigger cations, K$^+$, Rb$^+$, and Cs$^+$, are coordinated by only one DIGLYME ligand. In these compounds the coordination sphere is completed by

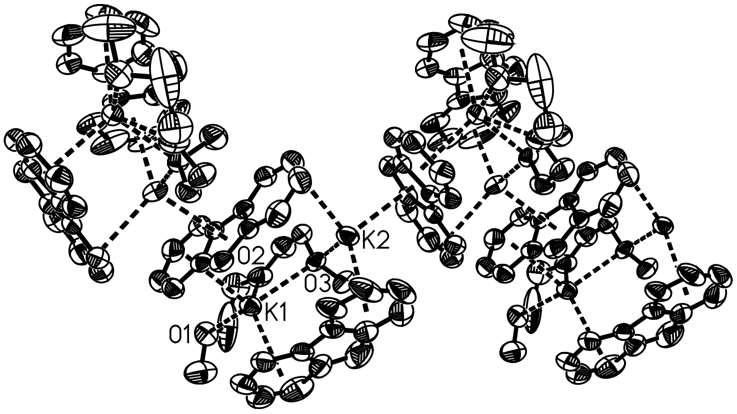

Fig. 8. Drawing of the polymeric band of $[(KFl)_2DIGLYME]_n$ (**7**). Four binuclear units are shown.

Table 1
Crystallographic data for $[Li(DIGLYME)_2]Fl$ (**1**), $[KFl(DIGLYME)]_3$ (**3**), $[RbFl(DIGLYME)]_9$ (**4**), $[CsFl(DIGLYME)]_9$ (**5**), $[NaFl(DIGLYME)]_2$ (**6**), and $[(KFl)_2DIGLYME]_n$ (**7**)

	1	**3**	**4**	**5**	**6**	**7**
Formula	$C_{25}H_{37}LiO_6$	$C_{57}H_{69}K_3O_9$	$C_{171}H_{207}O_{27}Rb_9$	$C_{171}H_{207}Cs_9O_{27}$	$C_{38}H_{46}Na_2O_6$	$C_{32}H_{32}K_2O_3$
Formula weight	440.49	1015.42	3463.60	3890.56	644.72	542.78
Temperature (K)	173	173	173	173	173	173
Radiation (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	P-1	Cc	Cc	$Pbcn$	$P2_1/n$
a (Å)	12.672(1)	12.751(1)	22.542(1)	22.821(5)	16.060(1)	9.053(1)
b (Å)	14.420(1)	12.812(1)	38.943(1)	39.688(8)	11.659(1)	13.202(1)
c (Å)	14.468(1)	20.376(1)	19.987(1)	19.714(4)	18.457(1)	23.551(1)
α (°)		72.99(1)				
β (°)	107.20(1)	75.92(1)	105.68(1)	105.99(3)		93.04(1)
γ (°)		60.36(1)				
V (Å^3)	2525.51(4)	2746.77(3)	16893.0(3)	17165(6)	3455.7(3)	2810.64(6)
Z	4	2	4	4	4	4
D_{calc} (Mg m^{-3})	1.158	1.228	1.362	1.506	1.239	1.283
μ (cm^{-1})	0.8	3.0	26.5	19.5	1.0	3.7
Crystal size (mm)	0.5 × 0.5 × 0.5	0.7 × 0.5 × 0.4	0.5 × 0.4 × 0.4	0.4 × 0.4 × 0.4	0.5 × 0.5 × 0.5	0.5 × 0.5 × 0.4
2θ max (°)	50.0	57.3	55.0	55.2	55.0	50.0
Index ranges	$-13 \leq h \leq 15$, $-17 \leq k \leq 17$, $-17 \leq l \leq 9$	$-16 \leq h \leq 16$, $-17 \leq k \leq 13$, $-27 \leq l \leq 27$	$-24 \leq h \leq 29$, $-50 \leq k \leq 48$, $-25 \leq l \leq 23$	$0 \leq h \leq 29$, $0 \leq k \leq 51$, $-25 \leq l \leq 24$	$-20 \leq h \leq 20$, $-15 \leq k \leq 7$, $-23 \leq l \leq 23$	$-10 \leq h \leq$, $-15 \leq k \leq 15$, $-27 \leq l \leq 23$
Observational data [$I > 2\sigma_I$]	3158	8527	17114	14165	3182	3208
Independent reflections	4430	12990	27367	17685	3969	4944
Parameters	415	632	1885	1886	213	422
R_1 ($I > 2\sigma(I)$, all data)	0.070, 0.096	0.055, 0.091	0.053, 0.105	0.081, 0.103	0.037, 0.050	0.052, 0.093
wR_2 ($I > 2\sigma(I)$, all data)	0.180, 0.200	0.135, 0.156	0.088, 0.104	0.213, 0.232	0.086, 0.094	0.118, 0.140
Goodness-of-fit	1.031	1.019	0.986	1.040	1.047	1.070
Largest difference peak (e Å^{-3})	0.571, −0.454	0.753, −0.409	0.590, −0.413	1.540, −1.921	0.209, −0.205	0.443, −0.219

additional interactions of these cations with two Fl^- anions. A comparison of the known alkali metal fluorenyl complexes of the heavier metals potasium, rubidium, and cesium show, that the bonding mode is similar between the cations and the Fl^- anions (cations located above the five-membered ring with a bonding mode between η^2 and η^5). On the other hand, it is remarkable that small differences between the neutral ligands (i.e. the tridentate ligands DIGLYME versus PMDTA) cause a completely different aggregation of the [MFl(L)] (L = DIGLYME, PMDTA) units. At this point of research, it is not possible to make reliable predictions about what type of aggregation will be formed by the alkali metal fluorenyl complexes, which are prepared under different conditions. For that, the investigation of many more examples of solid state structures within this group of complexes is required.

4. Experimental

4.1. General procedures

All reactions were carried out under an atmosphere of dry Ar using conventional Schlenk techniques. Solvents were freshly distilled from Na ($C_6H_5CH_3$), K (DIGLYME) or a Na–K alloy (cyclopentane, n-C_6H_{14}, THF and Et_2O). LiFl, RbFl, and CsFl were prepared as described in previous literature [5,10] IR spectra: Perkin–Elmer FT-IR 1720 spectrometer, Nujol suspension. NMR spectra: Varian Gemini 200 BB spectrometer, 200 MHz (^1H), 50.3 MHz (^{13}C), THF-d_8.

4.2. Synthesis of [Li(DIGLYME)$_2$]Fl (**1**)

DIGLYME (2.2 ml, 2.07 g 15.5 mmol) was added to a suspension of LiFl (1.22 g, 7.1 mmol) in $C_6H_5CH_3$ (10 ml) at room temperature (r.t.). The mixture was stirred for 1 h. The solution was filtered, carefully overlayered with n-C_6H_{14} (15 ml) and stored at r.t. After 1 day the product started to crystallize as big yellow needles. The crystals were separated, washed twice with n-C_6H_{14} (2×20 ml) and dried at 10^{-2} torr. Yield: 1.85 g (59%) of yellow, air-sensitive crystalline product. Dec. > 78 °C. Solubility: very good in DIGLYME, good in THF, weak in hot $C_6H_5CH_3$, and insoluble in cyclopentane or n-C_6H_{14}. Anal. Calc. for $C_{25}H_{37}LiO_6$: C, 68.2; H, 8.5; O, 21.8. Found: C, 67.8; H, 8.5; O, 23.1%. ^1H-NMR: δ 7.82 (d, 2H, 4-, 5-H), 7.22 (d, 2 H, 1-, 8-H), 6.72 (t, 2H, 2-, 7-H), 6.34 (t, 2 H, 3-, 6-H), 5.87 (s, 1H, 9-H), 3.30 (m, 16H, OCH_2), 3.18 (s, 12H, OCH_3) ppm. $^{13}C\{^1H\}$-NMR: δ 138.1 (C10, C13), 123.4 (C11, C12), 119.3 (C2, C7), 119.0 (C4, C5), 116.5 (C1, C8), 108.2 (C3, C6), 82.1 (C9), 72.5 (OCH_2), 70.9 (OCH_2), 58.8 (OCH_3) ppm. IR: v 1569 (w), 1351 (w), 1321 (w), 1245 (w), 1221 (w), 1200 (w), 1113 (s), 1015 (w), 982 (w), 949 (w), 870 (w), 840 (w), 741 (s), and 717 (m) cm^{-1}.

4.3. Synthesis of [Na(DIGLYME)$_2$]Fl (**2**)

A mixture of NaH (0.13 g, 5.9 mmol), fluorene (1.03 g, 6.2 mmol), DIGLYME (5.0 ml, 4.72 g, 35.1 mmol) and $C_6H_5CH_3$ (10 ml) was stirred at 80 °C for 1 h until the gas evolution stopped. The dark brown solution was cooled to r.t. and then filtered. The obtained solution was carefully overlayered with n-C_6H_{14} (5 ml) and stored at -20 °C. After 1 day, the product started to crystallize as big orange blocks. The crystals were separated, washed twice with n-C_6H_{14} (2×10 ml) and dried at 10^{-2} torr. Yield: 1.62 g (60%) of orange, air-sensitive crystals. Dec. > 76 °C. Solubility: very good in DIGLYME, good in THF, weak in hot $C_6H_5CH_3$, and insoluble in cyclopentane or n-C_6H_{14}. Anal. Calc. for $C_{25}H_{37}NaO_6$: C, 65.8; H, 8.2; O, 21.0. Found: C, 65.1; H, 8.1; O, 21.3%. ^1H-NMR: δ 7.79 (d, 2H, 4-, 5-H), 7.21 (d, 2H, 1-, 8-H), 6.68 (t, 2H, 2-, 7-H), 6.32 (t, 2H, 3-, 6-H), 5.82 (s, 1H, 9-H), 3.28 (m, 16 H, OCH_2), 3.22 (s, 12H, OCH_3) ppm. $^{13}C\{^1H\}$-NMR: δ 136.5 (C10, C13), 125.6 (C11, C12), 120.4 (C2, C7), 119.6 (C4, C5), 116.8 (C1, C8), 109.8 (C3, C6), 80.5 (C9), 72.8 (OCH_2), 71.2 (OCH_2), 58.8 (OCH_3) ppm. IR: v 3044 (m), 3024 (m), 1569 (m), 1529 (vw), 1351 (m), 1321 (vs), 1221 (vs), 1135 (s), 1106 (vs), 1084 (vs), 983 (m), 743 (s), 734 (w), and 713 (s) cm^{-1}.

4.4. Synthesis of [KFl(DIGLYME)]$_3$ (**3**)

A mixture of KH (0.27 g, 6.8 mmol), fluorene (1.24 g, 7.5 mmol), DIGLYME (2.9 ml, 2.73 g, 20.4 mmol), and $C_6H_5CH_3$ (29 ml) were stirred at 80 °C for 1 h until the gas evolution stopped. The dark brown solution was cooled to r.t. and then filtered. The obtained solution was carefully overlayered with n-C_6H_{14} (35 ml) and stored at r.t. After 3 days, the product started to crystallize as big orange blocks. The crystals were separated, washed twice with n-C_6H_{14} (2×15 ml), and dried at 10^{-2} torr. Yield: 1.91 g (82%) of red, air-sensitive crystals. Dec. > 68 °C. Solubility: very good in DIGLYME, good in THF, weak in hot $C_6H_5CH_3$, and insoluble in cyclopentane or n-C_6H_{14}. Anal. Calc. for $C_{19}H_{23}KO_3$: C, 67.4; H, 6.9; O, 14.2. Found: C, 67.0; H, 6.9; O, 16.6%. ^1H-NMR: δ 7.96 (d, 2H, 4-, 5-H), 7.36 (d, 2H, 1-, 8-H), 6.85 (t, 2H, 2-, 7-H), 6.48 (t, 2H, 3-, 6-H), 6.04 (s, 1H, 9-H), 3.44 (m, 8H, OCH_2), 3.24 (s, 6H, OCH_3) ppm. $^{13}C\{^1H\}$-NMR: δ 137.0 (C10, C13), 127.3 (C11, C12), 120.1 (C2, C7), 119.4 (C4, C5), 116.8 (C1, C8), 109.3 (C3, C6), 83.0 (C9), 72.7 (OCH_2), 71.2 (OCH_2), 58.8 (OCH_3) ppm. IR: v 3047 (m), 1600 (m), 1575 (w), 1376 (m), 1352 (m), 1323 (s), 1244 (w), 1203, 1141 (s), 1113 (vs), 868 (m), 749 (vs), and 727 (s) cm^{-1}.

4.5. Synthesis of [RbFl(DIGLYME)]$_9$ (**4**)

DIGLYME (3.0 ml, 2.83 g, 21.1 mmol) was added to a suspension of RbFl (0.24 g, 1.0 mmol) in $C_6H_5CH_3$ (10 ml). The mixture was stirred for 1 h at 70 °C. The clear solution was cooled to r.t., filtered, carefully overlayered with n-C_6H_{14} (20 ml), and stored at r.t. After 1 day, the product started to crystallize as big red blocks. The crystals were separated, washed twice with n-C_6H_{14} (2×5 ml), and dried at 10^{-2} torr. Yield: 0.26 g (71%) of red, air-sensitive crystals. Dec. > 76 °C. Solubility: very good in DIGLYME, good in THF, weak in hot $C_6H_5CH_3$, and insoluble in cyclopentane or n-C_6H_{14}. Anal. Calc. for $C_{19}H_{23}O_3Rb$: C, 59.3; H, 6.0; O, 12.5. Found: C, 58.5; H, 6.0; O, 13.1%. ^{1}H-NMR: δ 7.89 (d, 2H, 4-, 5-H), 7.30 (d, 2H, 1-, 8-H), 6.84 (t, 2H, 2-, 7-H), 6.51 (t, 2H, 3-, 6-H), 6.01 (s, 1H, 9-H), 3.46 (m, 8H, OCH_2), 3.25 (s, 6H, OCH_3) ppm. $^{13}C\{^1H\}$-NMR: δ 137.5 (C10, C13), 127.3 (C11, C12), 120.3 (C2, C7), 119.6 (C4, C5), 117.2 (C1, C8), 109.6 (C3, C6), 84.2 (C9), 72.8 (OCH_2), 71.2 (OCH_2), 58.8 (OCH_3) ppm. IR: ν 3049 (m), 1600 (w), 1573 (m), 1352 (m), 1323 (s), 1246 (w), 1223 (s), 1132 (m), 1112 (vs), 1087 (s), 983 (m), 751 (vs), and 724 (vs) cm^{-1}.

4.6. Synthesis of [CsFl(DIGLYME)]$_9$ (**5**)

DIGLYME (1.8 ml, 1.70 g, 12.7 mmol) was added to a suspension of CsFl (0.26 g, 0.9 mmol) in $C_6H_5CH_3$ (5 ml). The mixture was stirred for 2 h at 70 °C. The clear solution was cooled to r.t., filtered, carefully overlayered with n-C_6H_{14} (5 ml), and stored at r.t. After 2 days the product started to crystallize as big red blocks. The crystals were separated, washed twice with n-C_6H_{14} (2×5 ml), and dried at 10^{-2} torr. Yield: 0.10 g (26%) of red, air-sensitive crystals. Dec. > 80 °C. Solubility: very good in DIGLYME, good in THF, weak in hot $C_6H_5CH_3$, and insoluble in cyclopentane or n-C_6H_{14}. Anal. Calc. for $C_{19}H_{23}CsO_3$: C, 52.8; H, 5.4; O, 11.1. Found: C, 52.0; H, 5.2; O, 10.3%. ^{1}H-NMR: δ 7.88 (d, 2H, 4-, 5-H), 7.29 (d, 2H, 1-, 8-H), 6.87 (t, 2H, 2-, 7-H), 6.47 (t, 2H, 3-, 6-H), 6.01 (s, 1H, 9-H), 3.44 (m, 8H, OCH_2), 3.25 (s, 6H, OCH_3) ppm. $^{13}C\{^1H\}$-NMR: δ 137.5 (C10, C13), 127.4 (C11, C12), 120.4 (C2, C7), 119.7 (C4, C5), 117.3 (C1, C8), 109.7 (C3, C6), 84.2 (C9), 72.9 (OCH_2), 71.3 (OCH_2), 58.8 (OCH_3) ppm. IR: ν 3049 (w), 1599 (vw), 1573 (w), 1351 (w), 1323 (s), 1245 (vw), 1223 (m), 1133 (w), 1110 (m), 1087 (m), 984 (m), 751 (s), and 724 (s) cm^{-1}.

4.7. Synthesis of [NaFl(DIGLYME)]$_2$ (**6**)

$NaN(SiMe_3)_2$ (1.11 g, 6.1 mmol), fluorene (1.00 g, 6.0 mmol), DIGLYME (0.9 ml, 0.85 g, 6.3 mmol), and 35 ml $C_6H_5CH_3$ were heated under reflux for 15 min to give an orange emulsion. The upper layer were separated and carefully overlayered with n-C_6H_{14} (20 ml). The product precipitated as yellow crystals, suitable for X-ray structure analysis. The crystals were washed with n-C_6H_{14} and dried at 10^{-2} torr. Yield: 0.05 g (5%) of yellow crystals. Dec. > 82 °C. Solubility: very good in DIGLYME, good in THF, weak in hot $C_6H_5CH_3$, and insoluble in cyclopentane or n-C_6H_{14}. Anal. Calc. for $C_{19}H_{23}NaO_3$: C, 70.8; H, 7.2; O, 14.9. Found: C, 70.3; H, 7.1; O, 14.9%. ^{1}H-NMR: δ 7.94 (d, 2H, 4-, 5-H), 7.36 (d, 2H, 1-, 8-H), 6.85 (t, 2H, 2-, 7-H), 6.48 (t, 2H, 3-, 6-H), 5.98 (s, 1H, 9-H), 3.28 (m, 8H, OCH_2), 3.16 (s, 6H, OCH_3) ppm. $^{13}C\{^1H\}$-NMR: δ 135.9 (C10, C13), 126.5 (C11, C12), 119.3 (C2, C7), 118.7 (C4, C5), 115.9 (C1, C8), 108.7 (C3, C6), 80.0 (C9), 71.6 (OCH_2), 70.0 (OCH_2), 58.1 (OCH_3) ppm. IR: ν 3043 (m), 1569 (m), 1518 (w), 1351 (m), 1321 (s), 1243 (s), 1221 (vs), 1106 (vs), 1083 (vs), 983 (m), 743 (s), and 713 (s) cm^{-1}.

4.8. Synthesis of [(KFl)$_2$(DIGLYME)]$_n$ (**7**)

Potassium hydride (0.55 g, 13.7 mmol), DIGLYME (2.2 ml, 2.07 g, 15.5 mmol), and fluorene (2.51 g, 15.1 mmol) were stirred in $C_6H_5CH_3$ (24 ml) for 2 h at r.t. and refluxed for 15 min. After filtration of the red suspension at r.t., 47 ml $C_6H_5CH_3$ and 35 ml n-C_6H_{14} were added to the solution to precipitate the product. The precipitate was separated, washed twice with 16 ml $C_6H_5CH_3$, and dried at 10^{-2} torr. Yield: 2.38 g (64%) of orange, air-sensitive powder. Dec. > 95 °C. Solubility: very good in DIGLYME, good in THF, weak in hot $C_6H_5CH_3$, and insoluble in cyclopentane or n-C_6H_{14}. Crystals of good quality for X-ray structure analysis could be obtained by carefully overlayering the mother liquid with n-C_6H_{14}. Anal. Calc. for $C_{32}H_{32}K_2O_3$: C, 70.8; H, 5.9; O, 8.8. Found: C, 70.3; H, 6.0; O, 8.6%. ^{1}H-NMR: δ 7.94 (d, 4H, 4-, 5-H), 7.35 (d, 4H, 1-, 8-H), 6.84 (t, 4H, 2-, 7-H), 6.47 (t, 4H, 3-, 6-H), 6.02 (s, 2H, 9-H), 3.37 (m, 8H, OCH_2), 3.20 (s, 6H, OCH_3) ppm. $^{13}C\{^1H\}$-NMR: δ 136.1 (C10, C13), 126.5 (C11, C12), 119.3 (C2, C7), 118.6 (C4, C5), 116.0 (C1, C8), 108.5 (C3, C6), 82.2 (C9), 71.8 (OCH_2), 70.2 (OCH_2), 58.0 (OCH_3) ppm. IR: ν 3050 (w), 3025(w), 1569 (m), 1322 (vs), 1223 (s), 1195(w), 1108 (m), 984 (m), 776 (w), 761(s), 755 (s), 738 (s), and 724 (s) cm^{-1}.

4.9. X-ray data collection, structure determination, and refinement

The data sets for the complexes **1**, **2** [14], **3**, **4**, **6**, and **7** were collected on a Siemens axs SMART CCD system (Mo–K$_\alpha$ radiation, graphite monochromator, ω-scans). A full hemisphere of the reciprocal space was scanned with 1271 frames in three sets, each frame covered 0.3° in ω. An empirical absorption correction was carried out with the program SADABS [22]. The data set for compound **5** was collected on a Hilger&Watts four-circle diffractometer (Mo–K$_\alpha$ radiation, graphite monochromator). An absorption correction was carried out using the program DIFABS [23]. All structures were solved with direct methods (SHELXS-97) [24] and refined with full-matrix least-squares on F_o^2, using the program SHELXL-7 [25]. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were calculated in idealized positions using a riding model with isotropic temperature factors combined in different logical groups. For molecular graphics and publication materials, the program package SHELXTL

(PC v5.03) [26] was used. For special refinement procedures see supporting information.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 124984 for **1**, 124985 for **2** [14], 124986 for **3**, 124987 for **4**, 124988 for **5**, 124990 for **6**, and 124989 for **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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