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Cyclopentadienyl, indenyl, fluorenyl, and pentamethylcyclopentadienyl complexes of potassium with 18-crown-6[☆]

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Abstract

The first 18-crown-6 Lewis base adducts of potassium organometallic compounds are described. The mononuclear complexes [KCp(18-crown-6)] (**1**), [KCp*(18-crown-6)]·0.5THF (**2a**), [KInd(18-crown-6)] (**3**), [KFl(18-crown-6)]·0.5toluene (**4**), and [{KFl(18-crown-6)}{KFl(18-crown-6)(THF)}] (**5**) and the binuclear complex [{KFl(18-crown-6)}$_2$(DME)] (**6**) were synthesised and single-crystal X-ray diffraction analyses were carried out (Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl, Ind = Indenyl, Fl = Fluorenyl). The influence of the neutral ligand on the potassium–anion-interaction is discussed in a comparative study. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Potassium; 18-Crown-6; Cyclopentadienyl; Indenyl; Fluorenyl; Pentamethylcyclopentadienyl

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1. Introduction

Interest in cyclopentadienylpotassium (KCp) and its benzocondensed homologous indenylpotassium (KInd) and fluorenylpotassium (KFl) as well as pentamethylcyclopentadienylpotassium (KCp*) in organometallic synthesis has increased during the past decade. Usually these compounds were prepared in THF or similar solvents and reacted without further separation and characterisation with main group, transition or rare earth metal halides [1–4]. Crystallographic studies were only rarely done although knowledge of the solid state structure gives us important information about the bond type of the anions Cp^-, Ind^-, Fl^- and Cp^{*-} in the potassium complexes [5]. Very often the investigation of the solid state structures of these basefree potassium compounds has proven very difficult because single crystals could not be obtained in sufficient size. Recently, the solid state structure of basefree KCp was solved by synchrotron powder diffraction methods [6]. Additional methods of gathering information about the bonding modes of the potassium complexes have been provided by studies of their Lewis base adducts as $[KCp(Et_2O)]_n$ [7], $[(KInd)_2THF]_n$ [8], $[(KFl)_2THF]_n$ [8], $[KFl(TMEDA)]_n$ [9], $[KFl(TMEDA)_2]$ [10] or $[KCp^*(py)_2]$ [11].

In this work we report on the first examples of organometallic potassium complexes with the Lewis basic 18-crown-6 macrocycle. X-ray crystallographic studies were carried out on all the isolated complexes.

2. Results and discussion

2.1. Synthesis

The reaction of KCp with 18-crown-6 in diethyl ether gave the complex [KCp(18-crown-6] (**1**) as a white

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[☆] Dedicated to Professor Alan H. Cowley, on the occasion of his 65th birthday.

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precipitate. A similar reaction of a white suspension of KCp* in THF (KCp* is barely soluble in THF) with 18-crown-6 yielded the colorless complex [KCp*(18-crown-6)] (**2**). To prepare the analogous indenyl and fluorenyl derivatives, potassium hydride was treated with indene or fluorene in the presence of 18-crown-6 in THF (for indene) or toluene (for fluorene) to give the slightly green complex [KInd(18-crown-6)] (**3**) and the orange compound [KFl(18-crown-6)] · 0.5toluene (**4**). Treatment of **4** with THF or dimethoxyethane (DME) formed the red compounds [{KFl(18-crown-6)}{KFl(18-crown-6)(THF)}] (**5**) and [{KFl(18-crown-6)}$_2$(DME)] (**6**), respectively. All compounds obtained are highly sensitive to air and moisture and decompose when in contact with air after a short time. These compounds are very soluble in pyridine, DME, diglyme or warm THF. Analogous reactions were carried out with 12-crown-4 as a Lewis base. Unfortunately, these reactions yielded no analytically pure products.

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 18-crown-6 ligands were shifted up field for the compounds **3**–**6**, compared to the free 18-crown-6 molecule (CH$_2$ 18-crown-6 (free): 3.56 ppm; in **3**: 3.43 ppm; in **4**: 3.39 ppm; in **5**: 3.39 ppm; in **6**: 3.26 ppm). It is obvious that the 18-crown-6 ligand is connected to the potassium cation. In contrast to this, we observed CH$_2$ resonance signals at 3.55 ppm for complexes **1** and **2**. This could indicate that the ligand 18-crown-6 is substituted by THF molecules in complexes **1** and **2**. For the proton signals of the carbanionic ligands Cp, Ind, Fl, and Cp*, we observed chemical shifts similar to those found for related compounds [11–13].

2.3. Crystal structures

The solid state structures of compounds **1**–**6** were investigated by single crystal structure analysis. Tables 1–3 provide the crystallographic results. The compounds [KCp(18-crown-6] (**1**), [KCp*(18-crown-6] · 0.5THF (**2a**), [KInd(18-crown-6)] (**3**), [KFl(18-crown-6)] · 0.5toluene (**4**), and [{KFl(18-crown-6)}{KFl(18-crown-6)(THF)}] (**5**) form mononuclear complexes, whereas [{KFl(18-crown-6)}$_2$(DME)] (**6**) crystallizes in a binuclear fashion.

Compound **2** crystallizes with THF as crystal solvent. Half a molecule of THF per formula is found to give the compound [KCp*(18-crown-6] · 0.5THF (**2a**). The THF molecule in **2a** is not connected to the K$^+$ cation (K–O(THF) distance 3.965(15) Å). In all three compounds with the fluorenyl ligands (**4**, **5**, and **6**), we observed a solvent molecule also. This solvent molecule is always located close to the inversion center of the space group between two [KFl(18-crown-6)] units. The toluene molecule in **5** is not connected to the K$^+$ cations (shortest K–C(toluene) distance 3.634(6) Å). In complex **6** each O atom of the DME molecule is bonded to one K$^+$ cation. As a result this compound is binuclear (see Fig. 6). Surprisingly, the THF molecule in [{KFl(18-crown-6)}{KFl(18-crown-6)(THF)}] (**5**) is not a bridging ligand. The crystal structure shows us that, in the solid state, this compound is a mixture of [KFl(18-crown-6)] (**5a**) and [KFl(18-crown-6)(THF)] (**5b**) (see Fig. 5). We found four molecules of [KFl(18-crown-6)] and two molecules of THF in the unit cell of **5,** wherein the two THF molecules are connected to only one K$^+$ cation each.

For all complexes we observed [KR(18-crown-6)] (R = Cp, Ind, Fl, and Cp*) units to be the fundamental

Table 1
Crystallographic data for [KCp(18-crown-6)] (**1**), [KCp*(18-crown-6)] · 0.5THF (**2a**), and [KInd(18-crown-6)] (**3**)

	1	**2a**	**3**
Formula	$C_{17}H_{29}KO_6$	$C_{24}H_{43}KO_{6.5}$	$C_{21}H_{31}KO_6$
Formula weight	368.50	474.68	418.56
T (K)	173	163	173
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$	Cu–K$_\alpha$
Crystal size (mm)	$0.4 \times 0.3 \times 0.2$	$0.4 \times 0.2 \times 0.2$	$1.0 \times 0.6 \times 0.6$
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pna2_1$ (no. 33)	$P2_1/n$ (no. 14)	$Pna2_1$ (no. 33)
Unit cell dimensions			
a (Å)	18.190(1)	9.767(1)	19.612(3)
b (Å)	12.364(1)	15.767(1)	11.345(2)
c (Å)	8.791(1)	17.640(1)	9.853(2)
β (°)		97.54(1)	
V (Å^3)	1977.0(1)	2693.0(2)	2192.3(7)
Z	4	4	4
$D_{\text{calc.}}$ (Mg m^{-3})	1.238	1.171	1.268
μ (cm^{-1})	2.95	2.32	23.96
Index ranges	$-21 \le h \le 20$ $-13 \le k \le 14$ $-10 \le l \le 10$	$-11 \le h \le 8$ $-18 \le k \le 18$ $-20 \le l \le 20$	$-9 \le h \le 24$ $-3 \le k \le 14$ $-12 \le l \le 0$
2Θ max (°)	50.0	48.0	153.0
Independent reflections	3461	4222	2444
Observed data ($I > 2\sigma_I$)	2514	2622	2422
No. of parameters	219	315	256
R_1 ($I > 2\sigma_I$, all data)	0.081, 0.107	0.048, 0.096	0.043, 0.043
wR_2 ($I > 2\sigma_I$, all data)	0.188, 0.203	0.101, 0.119	0.114, 0.114
GOF	1.043	0.997	1.049
Largest diff. peak (e Å^{-3})	1.055/−0.913	0.231/−0.317	0.553/−0.712

Table 2
Crystallographic data for [KFl(18-crown-6)] · 0.5toluene (**4**), [{KFl(18-crown-6)}{KFl(18-crown-6)(THF)}] (**5**), and [{KFl(18-crown-6)}$_2$(DME)] (**6**)

	4	**5**	**6**
Formula	$C_{28.5}H_{37}KO_6$	$C_{27}H_{37}KO_{6.5}$	$C_{54}H_{76}K_2O_{14}$
Formula weight	514.68	504.67	1027.34
T (K)	173	173	173
Radiation	Cu–K_α	Cu–K_α	Cu–K_α
Crystal size (mm)	$0.8\times0.4\times0.4$	$0.6\times0.3\times0.2$	$0.8\times0.4\times0.4$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
Unit cell dimensions			
a (Å)	9.831(4)	9.556(3)	9.692(4)
b (Å)	21.215(4)	15.364(4)	21.260(7)
c (Å)	13.080(3)	18.086(3)	13.131(4)
β (°)	99.95(3)	91.43(2)	99.90(3)
V (Å^3)	2687.0(14)	2654.5(12)	2665.4(16)
Z	4	4	2
$D_{\text{calc.}}$ (Mg m^{-3})	1.272	1.263	1.280
μ (cm^{-1})	20.56	20.84	20.98
Index ranges	$0\leq h\leq 12$ $-26\leq k\leq 8$ $-16\leq l\leq 16$	$-11\leq h\leq 11$ $0\leq k\leq 18$ $0\leq l\leq 22$	$-2\leq h\leq 12$ $-2\leq k\leq 26$ $-16\leq l\leq 16$
2Θ max (°)	152.7	140.0	152.4
Independent reflections	5645	5031	5350
Observed data ($I>2\sigma_I$)	5110	3053	4741
No. of parameters	346	391	331
R_1 ($I>2\sigma_I$, all data)	0.050, 0.055	0.067, 0.137	0.077, 0.085
wR_2 ($I>2\sigma_I$, all data)	0.127, 0.132	0.150, 0.193	0.202, 0.212
GOF	1.059	1.076	1.025
Largest diff. peak (e Å^{-3})	0.891/−0.513	0.434/−0.450	1.493/0.556

units. The coordination sphere of the potassium cation is made up of one 18-crown-6 ligand and one organic anion. The angle between the center of the six O atoms of the 18-crown-6 ligand (center(O_6)), the K^+ cation, the center of the five or six C atoms of the carbanionic ligands (center(C_5) for **1**, **2a** and **3**, and the center(C_6) for **4**, **5** and **6**) are all within a range of 171.6–177.9°. The K^+ cations are always connected to the six O atoms of the 18-crown-6 ligands. In **5** and **6** an additional ligand is bonded to the K^+ cations (THF ligand in **5a**; DME ligand in **6**). It is interesting that **1**, **2a** and **3** do not show any tendency to react with further O-containing ligands, provided by the solvent molecules, as was observed in **4**. The organic anions are always π-bonded to the K^+ cations. Herein the Cp-, Cp*- and Ind-ligands are η^5 connected to the K^+ cations, whereas we found η^6 interactions of one six-membered ring of the fluorenyl ligands in complexes **4**, **5** and **6**; this finding is completely new for non polymeric fluorenyl potassium compounds [14,19]. This is notable because calculations have shown that the highest electron density is located above the center(C_5) (exactly at C9) [10]. The unusual η^6 coordination of the potassium ion to the center(C_6) of one six-membered ring of the fluorenyl system may be explained by repulsive interactions between the benzo rings and the 18-crown-6 ligand if η^5 coordination occurred. The two fluorenyl potassium complexes (unsubstituted fluorenyl rings), which were described earlier in the literature, only show interactions between the metal and the central five-membered ring ([KFl(TMEDA)]$_n$ [9] and [KFl(TMEDA)$_2$] [10]).

The distances of the potassium cations to the four anions are different (Table 3). We found the order Cp < Cp* < Ind < Fl (distances (Å) K-center(C_5) = **1**: 2.82, **2a**: 2.85, **3**: 2.86; K-center(C_6) = **4**: 3.00). This order stands in agreement with our expectations and with distances reported in the literature (Table 4). According to this result, an opposite order was expected for the interaction of the potassium cation with the 18-crown-6 ligand. Instead of this, the following sequence for the K–O distances was observed: Cp* > Cp > Ind > Fl. The K–O bond lengths in the complex with the Cp* ligand (**2a**) are significantly longer than those of the Cp complex (**1**). We found the following K-center(O_6) distances (Å): **2a**: 1.02, **1**: 0.77, **3**: 0.75, **4**: 0.58. The reason is the steric influence of the methyl groups of the Cp* anion to the 18-crown-6 ligand. Four out of the five CH_3-groups are bent away from the crown ether (0.014(5)–0.100(5) (Å) out of the best plane through the five-membered ring of the Cp*). Except for **2a**, all complexes show the expected order. In complex **1** the negative charge is resonance-stabilized over only five atoms. Therefore cyclopentadienyl is the strongest ligand and the K–O distances are longer when compared to the indenyl or fluorenyl complexes. A weaker ligand is the indenyl anion. In addition, repulsive interaction in complex **3** was found also. The indenyl ring is bent away from the crown ether at the side of the six-membered ring. The two planes of the ligands (best plane through the six O atoms of the crown ether; best plane through the nine C atoms of the indenyl ring) show an angle of 8.9(1)° (the indenyl ring itself is not bent!). The fluorenyl ligand in **4** could not bend away from the crown ether in case of a η^5 interaction with the K^+ cation. Therefore the ligand switched position and preferred η^6 bonding to the potassium cation. Because of this, the interaction of the K^+ cation is weaker (compared to η^5 bonding), the K–C distances are longer, and the K–O bond lengths are shorter in **4**.

A few comparable X-ray crystal structures of potassium organometallic compounds with the unsubstituted

Table 3
Selected distances (Å) for [KCp(18-crown-6)] (**1**), [KCp*(18-crown-6)] · 0.5THF (**2a**), [KInd(18-crown-6)] (**3**), [KFl(18-crown-6)] · 0.5 toluene (**4**), [{KFl(18-crown-6)}{KFl(18-crown-6)(THF)}] (**5**), and [{KFl(18-crown-6)}**2**(DME)] (**6**)

	1	**2a**	**3**	**4**	**5**	**6**
K–O(1)	2.946(4)	2.963(2)	2.792(2)	2.7846(17)	2.887(3)	2.760(2)
K–O(2)	2.787(4)	2.966(2)	2.8856(19)	2.8155(14)	2.814(3)	2.805(2)
K–O(3)	2.929(4)	2.853(2)	2.878(2)	2.8735(14)	2.924(3)	2.846(2)
K–O(4)	2.898(4)	3.022(2)	2.914(2)	2.9594(16)	2.824(3)	2.922(2)
K–O(5)	2.983(4)	3.056(2)	2.8518(19)	2.8096(14)	2.797(3)	2.802(2)
K–O(6)	2.861(4)	2.942(2)	2.957(2)	2.8368(15)	2.878(3)	2.813(2)
K–O(40)	–	–	–	–	3.020(7)	2.889(4)
K–C(1)	3.049(6)	3.124(3)	3.114(3)	3.239(2)	–[a]	3.264(4)
K–C(2)	2.969(6)	3.105(3)	3.065(3)	3.239(2)	–	3.234(4)
K–C(3)	3.027(7)	3.072(3)	3.065(2)	3.311(3)	–	3.382(4)
K–C(4)	3.118(6)	3.066(3)	–	3.371(2)	–	3.530(4)
K–C(5)	3.131(7)	3.099(3)	–	–	–	
K–C(8)	–	–	3.154(2)	–	–	–
K–C(9)	–	–	3.122(2)	–	–	–
K–C(10)	–	–	–	3.311(2)	–	3.442(3)
K–C(11)	–	–	–	3.365(2)	–	3.566(3)

[a] No distances given because of the disorder of the fluorenyl ring.

carbanions Cp, Ind, Fl, and Cp* are described in the literature, with the Lewis bases diethyl ether, pyridine, TMEDA or PMDTA (Table 4; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; PMDTA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine). Except for the monomeric complex [KFl(TMEDA)$_2$] [10], all known compounds crystallize as polymeric zig-zag chains with interactions of the potassium cation to two anions. The anions are always η^2–η^5 connected with the five-membered ring to the K^+ cations. In these compounds the K–C bond lengths are usually longer than those found for the complexes containing 18-crown-6 as a Lewis base. Although oxygen containing Lewis bases are weaker ligands than nitrogen containing Lewis bases to potassium cations, this is understandable because the crown ether is a hexadentate ligand. Therefore, the electron density at the metal is higher than for the known examples (Table 4) and a weaker bonding to the carbanions is the result. Two exceptions are shown: basefree [KCp]$_n$ and [KInd(PMDTA)]$_n$. In basefree [KCp]$_n$ the potassium cation is interacting with four cyclopentadienyl rings (η^5, η^5, η^2, η^2 see [6]), which lengthens the K–C bond lengths. For the complex [KInd(PMDTA)]$_n$ it may be possible that the tridentate N-Lewis base is a stronger ligand for potassium ions than the hexadentate O-Lewis base.

3. Experimental

3.1. General comments

All manipulations were carried out under purified argon using standard Schlenk techniques. Solvents were distilled under nitrogen from Na (toluene), K (THF), or from Na/K alloy (cyclopentane and diethyl ether). KH was washed carefully with *n*-hexane. 18-crown-6 was stored for 2 weeks in a Schlenk tube, which was connected by a U-tube to a flask containing phosphorpentoxid. KCp [6] and KCp* [11] were prepared as described in the literature. IR spectra: Perkin–Elmer FT-IR 1720. ^{1}H- and ^{13}C-NMR spectra: Varian Gemini 200 BB.

3.2. Synthesis of [KCp(18-crown-6)] (1)

A sample of KCp (1.00 g, 9.6 mmol) was dissolved in diethyl ether (50 ml) and filtered. A solution of 18-crown-6 (3.00 g, 11.3 mmol) in diethyl ether (10 ml) was added at room temperature (r.t.). A white solid precipitated during this process. The mixture was filtered and the white powder was washed twice with diethyl ether and dried at 10^{-2} Torr. Yield: 3.04 g (82%). **1** is soluble in acetonitrile, warm THF, diglyme or DME, is slightly soluble in diethyl ether and toluene, but not soluble in cyclopentane. M.p.: 214°C (dec.; beginning of slight decomposition at 120°C). Anal. Calc. (found) for $C_{17}H_{29}KO_6$: C, 55.4 (54.6); H, 7.9 (7.7)%. IR (nujol suspension): ν 3051 (m), 1619 (vw), 1351 (s), 1285 (m), 1251 (m), 1112 (vs), 1004 (m), 962 (s), 836 (m) and 691 (s) cm^{-1}. ^{1}H-NMR (200 MHz, TMS, THF-d_8): δ 5.61 (s, 5H, C_5H_5); 3.55 (s, 24H, OCH_2) ppm.^{13}C{^{1}H}-NMR (50.3 MHz, TMS, THF-d_8): δ 104.0 ($\underline{C}_5H_5$); 70.8 ($O\underline{C}H_2$) ppm. X-ray quality crystals were obtained by recrystallisation from warm DME.

3.3. Synthesis of [KCp*(18-crown-6)] (2)

A sample of KCp* (0.18 g, 1.0 mmol) was suspended in THF (20 ml). A solution of 18-crown-6 (0.32 g, 1.2

Table 4
Comparison of potassium cation distances for the anions Cp, Cp*, Ind and Fl

Compound	Aggregation	Connectivity	K–C distance (Å)	Mean value	Reference
$[KCp]_n$	Polymer	η^5	3.033(7)–3.080(7)	3.056	[6]
		η^5	2.955(5)–3.140(6)	3.055	
$[KCp(Et_2O)]_n$	Polymer	η^5	2.992(2)–3.104(2)	3.011	[7]
		η^5	2.991(2)–3.032(2)	3.011	
$[KCp^*(py)_2]_n$	Polymer	η^5	2.962(2)–3.104(2)	3.030	[11]
		η^5	2.959(2)–3.104(2)	3.040	
$[KInd(TMEDA)]_n$	Polymer	η^5	2.952(2)–3.192(2)	3.077	[7]
		η^5	3.046(2)–3.113(2)	3.076	
$[KInd(PMDTA)]_n$	Polymer	η^5	3.074(7)–3.155(9)	3.120	[7]
		η^3	3.195(9)–3.305(7)	3.253	
$[KFl(TMEDA)]_n$	Polymer	η^3	3.074(2)–3.350(2)	3.224	[9]
		η^2	3.043(2)–3.176(2)	3.110	
$[KFl(TMEDA)_2]$	Monomer	η^5	3.071(5)–3.320(4)	3.208	[10]

mmol) in THF (5 ml) was added at r.t. and produced a slightly yellow solution. After filtration cyclopentane (60 ml) was added, whereupon a light yellow powder precipitated. The product was separated and washed twice with cyclopentane and dried at 10^{-2} Torr. Yield: 0.31 g (66%). **2** is soluble in THF, but not soluble in cyclopentane. Decomposition above 150°C. Anal. Calc. (found) for $C_{22}H_{39}KO_6$: C, 60.2 (59.8); H, 9.0 (9.2)%. IR (nujol suspension): ν 1600 (w), 1366 (m), 1351 (s), 1284 (m), 1249 (m), 1114 (vs), 963 (s) and 837 (m) cm^{-1}. ^1H-NMR (200 MHz, TMS, THF-d_8): δ 3.55 (s, 24H, OCH_2); 2.01 (s, 15H, $C_5(CH_3)_5$) ppm. $^{13}C\{^1H\}$-NMR (50.3 MHz, TMS, THF-d_8): δ 105.3 ($\underline{C}_5(CH_3)_5$); 71.0 ($O\underline{C}H_2$); 12.9 ($C_5(\underline{C}H_3)_5$) ppm. X-ray quality crystals were obtained by cooling down a solution of **2** in THF to −25°C. The crystals contain half a molecule of THF per formula unit as a solvent molecule, giving $[KCp^*(18\text{-crown-}6)]\cdot 0.5THF$ (**2a**).

*3.4. Synthesis of [KInd(18-crown-6)] (**3**)*

A sample of KH (0.10 g, 2.5 mmol) reacted in THF (5 ml) with indene (0.35 ml, 3.0 mmol) to give a green solution after filtration. A solution of 18-crown-6 (2.61 g, 2.7 mmol) in THF (4 ml) was added after which a slightly green powder precipitated. The mixture was heated at 50°C for 1 h and filtered while it was still warm. The precipitate was washed twice with cyclopentane and dried at 10^{-2} Torr. The combined solutions were kept at r.t. to deliver X-ray quality crystals. Yield: 0.88 g (84%). Complex **3** is soluble in acetonitrile, pyridine and hot THF, but not soluble in cyclopentane. Decomposition above 85°C. Anal. Calc. (found) for $C_{21}H_{31}KO_6$: C, 60.3 (60.1); H, 7.5 (7.5); O, 22.9 (23.8)%. IR (nujol suspension): ν 3068 (m), 3029 (m), 1583 (m), 1352 (m), 1319 (s), 1132 (vs), 1109 (vs), 965 (s) and 734 (s) cm^{-1}. ^1H-NMR (200 MHz, TMS, THF-d_8): δ 7.27 (m, 2H, 4-,7-H); 6.54 (t, 1H, 2-H); 6.33 (m, 2H, 5-, 6-H); 5.91 (d, 2H, 1-, 3-H); 3.43 (s, 24H, OCH_2) ppm. $^{13}C\{^1H\}$-NMR (50.3 MHz, TMS, THF-d_8): δ 130.5 (C8, C9); 119.2 (C4, C7); 118.2 (C2); 111.9 (C5, C6); 93.5 (C1, C3); 70.8 ($O\underline{C}H_2$) ppm.

*3.5. Synthesis of [KFl(18-crown-6)] · 0.5toluene (**4**)*

A sample of KH (0.22 g, 5.5 mmol) and fluorene (0.67 g, 4.0 mmol) were stirred in toluene (100 ml). A solution of 18-crown-6 (1.20 g, 4.5 mmol) in toluene (60 ml) was added, immediately producing an orange mixture. After heating for 5 h under reflux, the mixture was filtered while it was still hot. An orange product (1.40 g) precipitated after cooling to r.t. The volume of the separated mother liquid was reduced to half of its original size. The remaining solution was kept for 3 days at −20°C to give X-ray quality crystals (0.20 g). The crystals were separated, washed three times with cyclopentane, and dried at 10^{-2} Torr. Yield: 1.60 g (78%). Complex **4** is very soluble in THF and DME, less soluble in hot toluene, and not soluble in cyclopentane. Decomposition above 150°C. Anal. Calc. (found) for $C_{28.5}H_{37}KO_6$: C, 66.5 (66.3); H, 7.3 (7.4)%. IR (nujol suspension): ν 3043 (m), 1569 (s), 1350 (vs), 1321 (m), 1222 (vs), 1111 (vs), 983 (s), 970 (s), 963 (s), 747 (vs), 721 (vs) cm^{-1}. ^1H-NMR (200 MHz, TMS, THF-d_8): δ 7.93 (d, 2H, 4-, 5-H); 7.35–7.06 (m, 2H, 1-, 8-H and 2.5H, CH(toluene)); 6.79 (t, 2H, 2-, 7-H); 6.42 (t, 2H, 3-, 6-H); 6.02 (s, 1H, 9-H); 3.39 (s, 24H, OCH_2); 2.30 (s, 1.5H, CH_3(toluene)) ppm.

*3.6. Synthesis of [{KFl(18-crown-6)}{KFl(18-crown-6)(THF)}] (**5**)*

A sample of KH (0.18 g, 4.5 mmol) and fluorene (0.75 g, 4.5 mmol) were stirred in toluene/THF (30 ml, 2:1) at 70°C for 2.5 h to give an orange solution. The solution was filtered and 18-crown-6 (1.31 g, 5.0 mmol), dissolved in toluene (8 ml), was added to deliver an orange precipitate (1.79 g). The precipitate was separated and washed twice with cyclopentane. A total of 20% of the volume of the mother liquid was distilled off and the mixture was kept at −20°C for 2 days to give X-ray quality crystals (0.20 g). Yield: 1.99 g (88%). Decomposition above 160°C. Anal. Calc. (found) for $C_{27}H_{37}KO_{6.5}$: C, 64.5 (64.7); H, 7.0 (7.6); O, 20.7 (19.7)%. IR (nujol suspension): exactly the same was found for **4**. ^{1}H-NMR (200 MHz, TMS, THF-d_8): δ 7.93 (d, 2H, 4-, 5-H); 7.35 (d, 2H, 1-, 8-H); 6.79 (t, 2H, 2-, 7-H); 6.41 (t, 2H, 3-, 6-H); 6.02 (s, 1H, 9-H); 3.39 (s, 24H, OCH_2) ppm.

*3.7. Synthesis of [{KFl(18-crown-6)}$_2$(DME)] (**6**)*

A mixture of KH (0.19 g, 4.7 mmol), fluorene (0.67 g, 4.0 mmol), 18-crown-6 (1.13 g, 4.3 mmol), toluene (25 ml), and dimethoxyethane (40 ml) was stirred at 65°C for 1 h. The dark orange solution was then filtered and stored at r.t. After 12 h orange red crystals were obtained (1.68 g). The mother liquid was removed, 80% of its solvent was distilled off and 15 ml of cyclopentane was added to give additional microcystalline powder (0.20 g). The crystals and the powder were washed three times with cyclopentane and dried at 10^{-2} Torr. Yield: 1.88 g (94%). Decomposition above 50°C. Anal. Calc. (found) for $C_{54}H_{76}K_2O_{14}$: C, 63.1 (63.1); H, 7.5 (7.7)%. IR (nujol suspension): 3046 (m), 1599 (w), 1568 (m), 1350 (s), 1322 (vs), 1222 (s), 1110 (vs), 983 (s), 965 (s), 747 (s), 722 (s) cm^{-1}. ^{1}H-NMR (200 MHz, TMS, THF-d_8): δ 7.93 (d, 4H, 4-, 5-H); 7.33 (d, 4H, 1-, 8-H); 6.79 (t, 4H, 2-, 7-H); 6.42 (t, 4H, 3-, 6-H); 6.02 (s, 2H, 9-H); 3.57 (s, 4H, OCH_2 (DME)); 3.42 (s, 6H, OCH_3); 3.26 (s, 48H, OCH_2 (18-crown-6)) ppm.

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

Crystallographic results are given in Tables 1–3 and Figs. 1–6. All crystallographic data have been deposited at the Cambridge Structural Database (**1**: CSD-102855, **2a**: CSD-102856, **3**: CSD-102857, **4**: CSD-102858, **5**: CSD-102859, **6**: CSD-102860). The crystals of complexes **1** and **2a** were measured on a SIEMENS axs SMART CCD system (parallel graphite monochromator). 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 [15] (**1**: T_{min} 0.891, T_{max} 0.943; **2a**: T_{min} 0.913, T_{max} 0.955). The data sets for complexes **3**–**6** were collected on an Enraf–Nonius CAD4 diffractometer (graphite monochromator, $\omega/2\theta$ scans). No absorption corrections were carried out. The structures were solved with direct methods (SHELXS-86) [16] and refined with full-matrix least-squares against F_o^2, using the program SHELXL-97 [17]. All non hydrogen atoms were refined with anisotropic temperature factors. H atoms were calculated in idealized positions using a riding model (isotropic temperature factors combined in different groups). For molecular graphics and publication materials, the program package SHELXTL (PC v5.03) [18] was used. Special refinement procedures included: **1**, the structure was refined using a model of a racemic twin crystal (TWIN option of SHELXL-97); **2a**, the THF molecule was calculated with a side occupation factor of 50% for all atoms and restrained bond lengths (DFIX option of SHELXL-97); **3**, the absolute structure was determined with a Flack parameter of 0.015(12); **4**, the toluene molecule was refined with a side occupation factor of 50% for all atoms and the bond lengths were refined with restrained distances (AFIX and DFIX op-

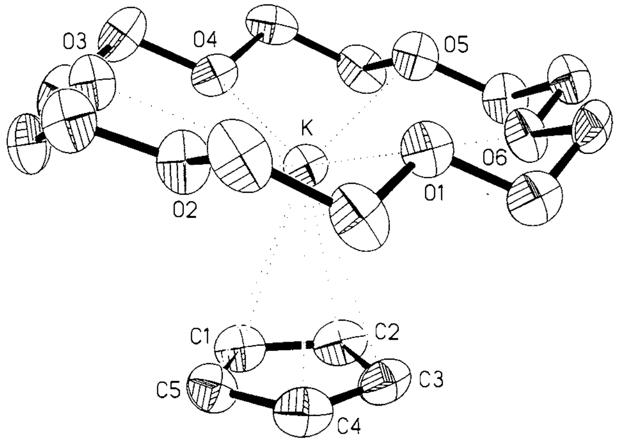

Fig. 1. Molecular structure of [KCp(18-crown-6)] (**1**). No H atoms are shown. Distances (Å): O–C: 1.399(7)–1.463(7), mean value 1.420; C–C(18-crown-6): 1.469(10)–1.523(10), mean value 1.495; C⋯C(Cp): 1.371(10)–1.411(9), mean value 1.396.

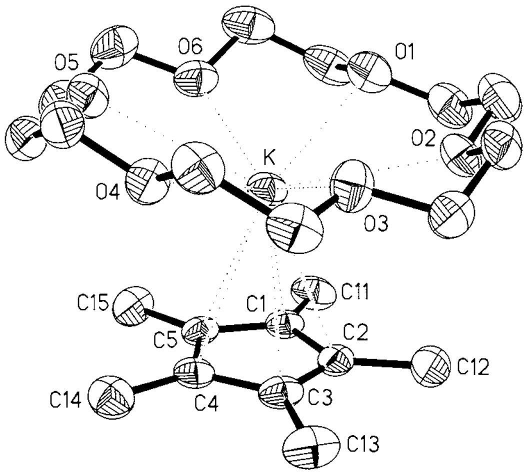

Fig. 2. Molecular structure of [KCp*(18-crown-6)] · 0.5THF (**2a**). The THF molecule and the H atoms are not shown. Distances (Å): O–C: 1.412(4)–1.435(3), mean value 1.422; C–C(18-crown-6): 1.482(4)–1.498(4), mean value 1.490; C⋯C(Cp*): 1.408(4)–1.415(4), mean value 1.411.

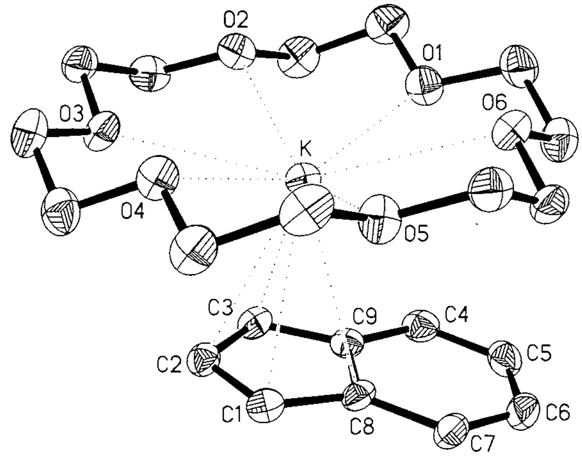

Fig. 3. Molecular structure of [KInd(18-crown-6)] (**3**). No H atoms are shown. Distances (Å): O–C: 1.413(4)–1.426(4), mean value 1.420; C–C(18-crown-6): 1.488(5)–1.505(4), mean value 1.495; C⋯C(Ind): C(1)–C(2) 1.408(3), C(2)–C(3) 1.404(4), C(3)–C(9) 1.417(4), C(4)–C(5) 1.380(4), C(5)–C(6) 1.408(5), C(6)–C(7) 1.370(5), C(7)–C(8) 1.409(3), C(8)–C(1) 1.421(4), C(8)–C(9) 1.455(3).

tions of SHELXL-97); **5**: the THF molecule was modelled with half occupancy and the distances therein were restrained (DFIX option of SHELXL-97). The fluorenyl anion was disordered and needed to be refined with two positions for each atom (side occupation factors 67 and 33%) and with restrained distances also (SADI option of SHELXL-97); **6**: the ethylen bridge in the DME molecule is disordered and therefore refined with two positions for each C atom and with restrained distance (DFIX option of SHELXL-97).

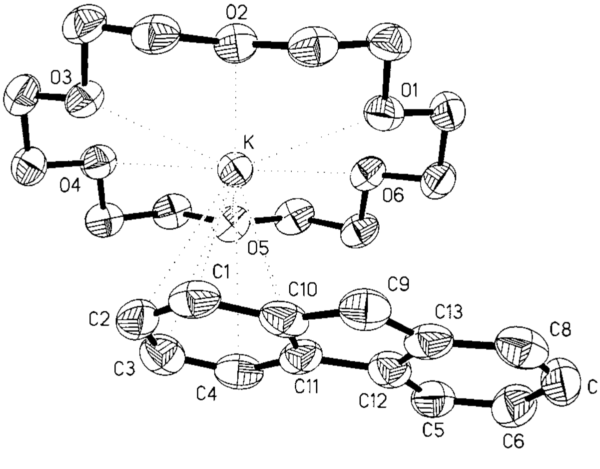

Fig. 4. Molecular structure of [KFl(18-crown-6)] · 0.5toluene (**4**). Solvent molecule and H atoms are not shown. Distances (Å): O–C: 1.416(2)–1.428(2), mean value 1.422; C–C(18-crown-6): 1.493(3)–1.495(3), mean value 1.494; C⋯C(Fl): C(1)–C(2) 1.369(3), C(1)–C(10) 1.429(3), C(2)–C(3) 1.386(3), C(3)–C(4) 1.352(3), C(4)–C(11) 1.380(3), C(5)–C(12) 1.363(3), C(5)–C(6) 1.373(3), C(6)–C(7) 1.407(3), C(7)–C(8) 1.386(4), C(8)–C(13) 1.441(3), C(9)–C(10) 1.410(3), C(9)–C(13) 1.414(3), C(10)–C(11) 1.465(3), C(11)–C(12) 1.458(3), C(12)–C(13) 1.420(3).

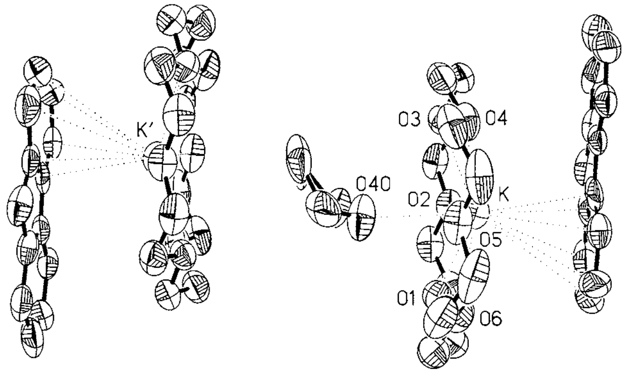

Fig. 5. Molecular structure of [{KFl(18-crown-6)}{KFl(18-crown-6)(THF)}] (**5**). Half of the unit cell is shown with one molecule of [KFl(18-crown-6)] (**5a**, left) and one molecule of [KFl(18-crown-6)(THF)] (**5b**, right). The disorder of the fluorenyl and THF ligands was omitted for clarity. H atoms are not shown. Distances (Å): O–C: 1.412(5)–1.432(6), mean value 1.425; C–C(18-crown-6): 1.474(7)–1.492(6), mean value 1.482.

4. Conclusions

The Lewis base 18-crown-6 is a useful ligand for potassium organic compounds containing π-bonding anions. Normally complexes of the type [(L)KR] (L = Lewis base; R = cyclopentadienyl, indenyl, fluorenyl, and pentamethylcyclopentadienyl) build polymeric zigzag chains. We obtained, for the first time, monomeric compounds with the hexadentade ligand 18-crown-6. The anions Cp, Cp* and Ind are η^5 bonded to the K$^+$ cations, whereas the interactions of the K$^+$ cations with the Fl$^-$ anions in the complexes containing 18-crown-6 are always η^6. Interestingly, the compound [KFl(18-crown-6)] · 0.5toluene shows a ten-

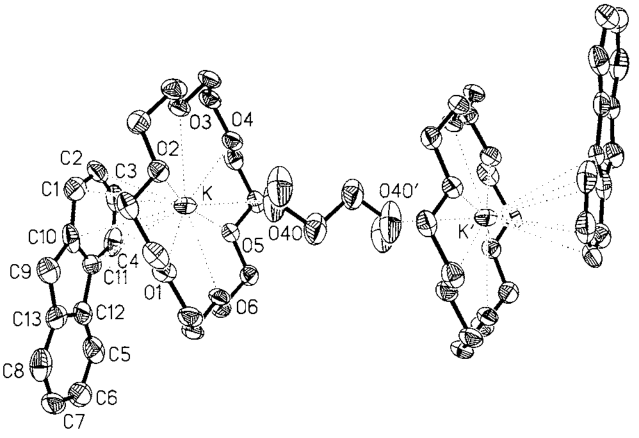

Fig. 6. Molecular structure of [{KFl(18-crown-6)}$_2$(DME)] (**6**). No H atoms are shown. Distances (Å): O–C: 1.413(4)–1.427(4), mean value 1.421; C–C(18-crown-6): 1.488(5)–1.499(5), mean value 1.496; C⋯C(Fl): C(1)–C(2) 1.369(6), C(1)–C(10) 1.431(5), C(2)–C(3) 1.367(6), C(3)–C(4) 1.330(6), C(4)–C(11) 1.388(6), C(5)–C12) 1.341(6), C(5)–C(6) 1.370(6), C(6)–C(7) 1.411(6), C(7)–C(8) 1.392(6), C(8)–C(13) 1.429(6), C(9)–C(10) 1.410(5), C(9)–C(13) 1.423(5), C(10)–C(11) 1.447(6), C(11)–C(12) 1.468(5), C(12)–C(13) 1.395(6).

dency to react with further Lewis bases (i.e. THF or DME). In our opinion the crown ether 18-crown-6 deserves more attention as a complex ligand in potassium organometallic chemistry.

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