## **Supporting Information**

# Thermodynamic Study of Crown Ether–Lithium/Magnesium Complexes based on Benz-1,4-Dioxane and its Homologues

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#### Benzo-7-crown-2



Fig. S1: <sup>1</sup>H NMR spectrum of the crude B7C2 and purified B7C2 after column chromatography treatment.



Fig. S2: <sup>13</sup>C NMR spectrum of the purified B7C2.



Fig. S3: IR spectrum of the purified B7C2.



Fig. S4: DSC measurement of the purified B7C2.

#### Benzo-8-crown-2



Fig. S5: <sup>1</sup>H NMR spectrum of the crude B8C2 and purified B7C2 after column chromatography treatment.



**Fig. S6:** <sup>13</sup>C NMR spectrum of the purified B8C2.



Fig. S7: IR spectrum of the purified B8C2.



Fig. S8: DSC measurement of the purified B8C2.

#### UV-vis Data

#### Lithium



Fig. S9: Absorbance maxima of LIS  $\lambda_{max}$  = 323 nm as linear regression against concentration [mol·L<sup>-1</sup>].



Fig. S10: UV-vis spectrum of LIS at different concentrations  $[\mu mol \cdot L^{-1}]$ .

#### Magnesium



**Fig. S11:** Absorbance maxima of MgA  $\lambda_{max}$  = 267 nm as linear regression against concentration [mol·L<sup>-1</sup>].



Fig. S12: UV-vis spectrum of MgA at different concentrations  $[\mu mol \cdot L^{-1}]$ .

### CE solubility measurements in the aqueous phase



**Fig. S13:** UV-vis spectroscopy of the aqueous LiCl phase after extraction and formation of the CE–cation complex.

#### **Thermodynamic Evaluation**



**Fig. S14:** logarithmic complexation stability *K* of a) B6C2 assuming single complexes, b) B6C2 assuming sandwich-type complexes, c) B7C2 assuming single complexes, d) B7C2 assuming sandwich-type complexes, e) B8C2 assuming single complexes, f) B8C2 assuming sandwich-type complexes. The green line shows the lithium, and the blue line the magnesium complexes with the CEs.

#### Van't Hoff Plot



**Fig. S15:** Van't Hoff plot of the a) B6C2-Li complex b) B6C2-Mg complex, c) B7C2-Li complex, d) B7C2-Mg complex, e) B8C2-Li complex, and f) B8C2-Mg complex with a constant molar ratio of CE:salt = 14:1.

B6C2-Li <sup>+</sup>	Single		Sandwich	
CE:metal	$\log K$	$\Delta G$ [kJmol <sup>-1</sup> ]	log K	$\Delta G$ [kJmol <sup>-1</sup> ]
1:25	4.9	-28	7.06	-40
1:20	4.6	-26	6.71	-38
1:17	5.0	-28	7.07	-40
1:14	4.8	-27	6.89	-40
1:13	4.9	-28	7.05	-40
1:11	4.8	-27	6.98	-40
B6C2-Mg <sup>2+</sup>	Single		Sandwich	
CE:metal	log K	$\Delta G$ [kJmol <sup>-1</sup> ]	log K	$\Delta G$ [kJmol <sup>-1</sup> ]
1:25	7.8	-44	9.9	-57
1:20	7.5	-43	9.6	-55
1:17	7.6	-44	9.8	-56
1:14	7.5	-43	9.7	-55
1:13	7.3	-42	9.5	-54
1:11	7.1	-41	9.3	-53
B7C2-Li <sup>+</sup>	Single		Sandwich	
CE:metal	log K	$\Delta G$ [kJmol <sup>-1</sup> ]	log K	$\Delta G$ [kJmol <sup>-1</sup> ]
1:25	5.1	-29	7.3	-42
1:20	5.1	-29	7.3	-42
1:17	4.9	-28	7.1	-40
1:14	4.7	-27	6.9	-39
1:13	4.6	-25	6.7	-39
1:11	4.5	-25	6.7	-38
$B7C2-Mg^{2+}$	Single		Sandwich	
B7C2-Mg <sup>2+</sup> CE:metal	Single log K	$\Delta G$ [kJmol <sup>-1</sup> ]	Sandwich log K	$\Delta G$ [kJmol <sup>-1</sup> ]
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25	Single           log K           9.0	Δ <i>G</i> [kJmol <sup>-1</sup> ] -51	Sandwich log K 11	Δ <i>G</i> [kJmol <sup>-1</sup> ] -64
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20	Single           log K           9.0           8.8	$\Delta G  [kJmol^{-1}]$ -51 -50	Sandwich           log K           11           11	Δ <i>G</i> [kJmol <sup>-1</sup> ] -64 -63
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17	Single           log K           9.0           8.8           8.4	Δ <i>G</i> [kJmol <sup>-1</sup> ] -51 -50 -48	Sandwich           log K           11           11           11	Δ <i>G</i> [kJmol <sup>-1</sup> ] -64 -63 -61
B7C2-Mg <sup>2+</sup> CE:metal           1:25           1:20           1:17           1:14	Single           log K           9.0           8.8           8.4           8.2	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47	Sandwich           log K           11           11           11           10	Δ <i>G</i> [kJmol <sup>-1</sup> ] -64 -63 -61 -60
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13	Single           log K           9.0           8.8           8.4           8.2           7.9	Δ <i>G</i> [kJmol <sup>-1</sup> ] -51 -50 -48 -47 -45	Sandwich           log K           11           11           11           10           10	Δ <i>G</i> [kJmol <sup>-1</sup> ] -64 -63 -61 -60 -59
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6	Δ <i>G</i> [kJmol <sup>-1</sup> ] -51 -50 -48 -47 -45 -43	Sandwich           log K           11           11           11           10           10           10	$\Delta G \text{ [kJmol^{-1}]} -64 -63 -61 -60 -59 -58$
B7C2-Mg <sup>2+</sup> CE:metal         1:25         1:20         1:17         1:14         1:13         1:11         B8C2-Li <sup>+</sup>	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single	$\Delta G [kJmol-1] -51 -50 -48 -47 -45 -43 -43$	Sandwich           log K           11           11           11           10           10           Sandwich	$\Delta G \text{ [kJmol-1]} -64 -63 -61 -60 -59 -58 -58 -58 -58 -58 -58 -58 -58 -58 -58$
B7C2-Mg <sup>2+</sup> CE:metal         1:25         1:20         1:17         1:14         1:13         1:11         B8C2-Li <sup>+</sup> CE:metal	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K	$\Delta G  [kJmol^{-1}] \\ -51 \\ -50 \\ -48 \\ -47 \\ -45 \\ -43 \\ \\ \Delta G  [kJmol^{-1}] \\ $	Sandwich           log K           11           11           11           10           10           10           log K	$\Delta G [kJmol^{-1}]  -64  -63  -61  -60  -59  -58  \Delta G [kJmol^{-1}]$
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 <b>B8C2-Li</b> <sup>+</sup> CE:metal 1:25	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7	$\Delta G [kJmol^{-1}]  -51  -50  -48  -47  -45  -43  \Delta G [kJmol^{-1}]  -27  -$	Sandwich           log K           11           11           11           10           10           10           10           6.9	$\Delta G [kJmol^{-1}] -64 -63 -61 -60 -59 -58 -58 -58 -58 -58 -58 -58 -59 -58 -59 -58 -59 -58 -58 -59 -58 -58 -58 -58 -58 -58 -58 -58 -58 -58$
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 <b>B8C2-Li</b> <sup>+</sup> CE:metal 1:25 1:20	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.7	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47 -45 -43 $\Delta G [kJmol^{-1}]$ -27 -27	Sandwich           log K           11           11           11           10           10           10           10           6.9           6.9           6.9	$\Delta G [kJmol^{-1}] -64 -63 -61 -60 -59 -58 -58 -58 -58 -58 -59 -58 -59 -39 -39 -39 -39 -39 -39 -39 -39 -39 -3$
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 <b>B8C2-Li</b> <sup>+</sup> CE:metal 1:25 1:20 1:17	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.7           4.3	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47 -45 -43 $\Delta G [kJmol^{-1}]$ -27 -27 -27 -25	Sandwich           log K           11           11           11           10           10           10           10           6.9           6.6	$\Delta G [kJmol^{-1}] -64 -63 -61 -60 -59 -58 -58 -58 -58 -58 -58 -59 -39 -39 -39 -37 -37 -56 -56 -56 -56 -56 -56 -56 -56 -56 -56$
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 <b>B8C2-Li</b> <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.3           4.0	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47 -45 -43 $\Delta G [kJmol^{-1}]$ -27 -27 -25 -23	Sandwich           log K           11           11           11           10           10           10           10           6.9           6.9           6.6           6.2	$\Delta G [kJmol-1] -64 -63 -61 -60 -59 -58 \Delta G [kJmol-1] -39 -39 -37 -36 -50 -30 -30 -30 -30 -30 -30 -30 -3$
B7C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Li <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.7           4.3           4.0           3.6	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47 -45 -43 $\Delta G [kJmol^{-1}]$ -27 -27 -27 -25 -23 -21	Sandwich           log K           11           11           11           10           10           10           10           6.9           6.6           6.2           5.8	$\Delta G [kJmol-1] -64 -63 -61 -60 -59 -58 \Delta G [kJmol-1] -39 -39 -39 -37 -36 -33 24$
B7C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Li <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.3           4.0           3.6           4.0	$\Delta G [kJmol-1]  -51  -50  -48  -47  -45  -43  \Delta G [kJmol-1]  -27  -27  -27  -25  -23  -21  -20  -20  -20  -21  -20  -51  -50  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -51  -50  -48  -47  -45  -45  -43  -27  -27  -25  -23  -21  -20  -21  -20  -21  -22  -22  -23  -21  -20  -20  -20  -20  -21  -20  -21  -22$	Sandwich           log K           11           11           11           10           10           10           6.9           6.9           6.6           6.2           5.8           6.3	$\Delta G [kJmol-1] -64 -63 -61 -60 -59 -58 \Delta G [kJmol-1] -39 -39 -39 -37 -36 -33 -36$
B7C2-Mg <sup>2+</sup> CE:metal         1:25         1:20         1:17         1:14         1:13         1:11         B8C2-Li <sup>+</sup> CE:metal         1:25         1:20         1:17         1:25         1:20         1:17         1:14         1:17         1:14         1:13         1:11         B8C2-Mg <sup>2+</sup>	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.7           4.3           4.0           3.6           4.0           Single	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47 -45 -43 $\Delta G [kJmol^{-1}]$ -27 -27 -25 -23 -21 -20	Sandwich           log K           11           11           11           10           10           10           10           6.9           6.9           6.6           6.2           5.8           6.3           Sandwich	$\Delta G [kJmol-1] -64 -63 -61 -60 -59 -58 \Delta G [kJmol-1] -39 -39 -37 -36 -33 -36 -33 -36$
B7C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Li <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Mg <sup>2+</sup> CE:metal 1:25	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.3           4.0           3.6           4.0           Single           log K	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47 -45 -43 $\Delta G [kJmol^{-1}]$ -27 -27 -27 -25 -23 -21 -20 $\Delta G [kJmol^{-1}]$	Sandwich           log K           11           11           11           10           10           10           6.9           6.6           6.2           5.8           6.3           Sandwich           log K           10	$\Delta G [kJmol^{-1}] -64 -63 -61 -60 -59 -58 -61 -60 -59 -58 -61 -60 -59 -58 -61 -60 -59 -58 -60 -59 -58 -58 -58 -58 -58 -58 -58 -58 -58 -58$
B7C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Li <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Mg <sup>2+</sup> CE:metal 1:25	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.3           4.0           3.6           4.0           Single           log K           8.7	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47 -45 -43 $\Delta G [kJmol^{-1}]$ -27 -27 -25 -23 -21 -20 $\Delta G [kJmol^{-1}]$ -50	Sandwich           log K           11           11           11           10           10           10           10           6.9           6.9           6.6           6.2           5.8           6.3           Sandwich           log K           11	$\Delta G [kJmol-1] -64 -63 -61 -60 -59 -58 \Delta G [kJmol-1] -39 -39 -37 -36 -33 -36 \Delta G [kJmol-1] -63 (1)$
B7C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Li <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:25 1:20	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.3           4.0           3.6           4.0           Single           log K           8.7           8.4           7.9	$\Delta G [kJmol^{-1}]$ -51 -50 -48 -47 -45 -43 $\Delta G [kJmol^{-1}]$ -27 -27 -27 -25 -23 -21 -20 $\Delta G [kJmol^{-1}]$ -50 -48 45	Sandwich           log K           11           11           11           10           10           10           10           6.9           6.6           6.2           5.8           6.3           Sandwich           log K           11           11	$\Delta G [kJmol^{-1}] -64 -63 -61 -60 -59 -58 -58 -58 -58 -58 -58 -58 -58 -58 -58$
<b>B7C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 <b>B8C2-Li</b> <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 <b>B8C2-Mg</b> <sup>2+</sup> CE:metal 1:25 1:20 1:17	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.3           4.0           3.6           4.0           Single           log K           8.7           8.4           7.9	$\begin{array}{c} \Delta G  [\rm kJmol^{-1}] \\ -51 \\ -50 \\ -48 \\ -47 \\ -45 \\ -43 \\ \hline \\ \Delta G  [\rm kJmol^{-1}] \\ -27 \\ -27 \\ -27 \\ -27 \\ -27 \\ -25 \\ -23 \\ -21 \\ -20 \\ \hline \\ \Delta G  [\rm kJmol^{-1}] \\ -50 \\ -48 \\ -45 \\ \hline \end{array}$	Sandwich           log K           11           11           11           10           10           10           10           6.9           6.9           6.6           6.2           5.8           6.3           Sandwich           log K           11           11           11           11           11           12	$\Delta G [kJmol^{-1}] -64 -63 -61 -60 -59 -58 -58 -58 -58 -58 -58 -58 -58 -58 -58$
B7C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Li <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:25	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.7           4.3           4.0           3.6           4.0           Single           log K           8.7           8.4           7.9           8.2           7.9	$\begin{array}{c} \Delta G  [\rm kJmol^{-1}] \\ -51 \\ -51 \\ -50 \\ -48 \\ -47 \\ -45 \\ -43 \\ \hline \\ \Delta G  [\rm kJmol^{-1}] \\ -27 \\ -27 \\ -27 \\ -27 \\ -25 \\ -23 \\ -21 \\ -20 \\ \hline \\ \Delta G  [\rm kJmol^{-1}] \\ -50 \\ -48 \\ -45 \\ -47 \\ \hline \end{array}$	Sandwich           log K           11           11           11           10           10           10           10           10           6.9           6.9           6.6           6.2           5.8           6.3           Sandwich           log K           11           11           10           10	$\Delta G [kJmol^{-1}]$ -64 -63 -61 -60 -59 -58
B7C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Li <sup>+</sup> CE:metal 1:25 1:20 1:17 1:14 1:13 1:11 B8C2-Mg <sup>2+</sup> CE:metal 1:25 1:20 1:17 1:25 1:20 1:17	Single           log K           9.0           8.8           8.4           8.2           7.9           7.6           Single           log K           4.7           4.3           4.0           3.6           4.0           Single           log K           8.7           8.4           7.9           8.2           7.8	$\begin{array}{c} \Delta G  [\rm kJmol^{-1}] \\ -51 \\ -51 \\ -50 \\ -48 \\ -47 \\ -45 \\ -43 \\ \hline \\ \Delta G  [\rm kJmol^{-1}] \\ -27 \\ -27 \\ -27 \\ -27 \\ -27 \\ -25 \\ -23 \\ -21 \\ -20 \\ \hline \\ \Delta G  [\rm kJmol^{-1}] \\ -50 \\ -48 \\ -45 \\ -47 \\ -45 \\ \hline \\ -47 \\ -45 \\ \hline \end{array}$	Sandwich           log K           11           11           11           11           10           10           10           10           10           10           10           10           10           10           10           10           10           6.9           6.6           6.2           5.8           6.3           Sandwich           log K           11           11           10           10           10	$\Delta G [kJmol^{-1}] -64 -63 -61 -60 -59 -58 -39 -39 -39 -39 -37 -36 -33 -36 -33 -36 -33 -36 -33 -36 -33 -61 -58 -60 -57 -57 -57 -57 -57 -57 -57 -57 -57 -57$

**Tab. S1:** Log K and Gibbs energy  $\Delta G$  at 25 °C of the extraction of B6C2, B7C2 and B8C2 with Li<sup>+</sup> and Mg<sup>2+</sup>.

**Tab. S2:** Slope and intercept values of the Van't Hoff plot and the determined data of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  (at 25 °C).

Li <sup>+</sup>	<b>R</b> <sup>2</sup>	Slope	$(\Delta S)$	$\Delta H$ [Jmol <sup>-1</sup> ]	$\Delta S [Jmol^{-1}K^{-1}]$	$\Delta G \operatorname{VH} [kJmol^{-1}]$
		$\left(\frac{-\Delta H}{R}\right)$	Intercept $(\overline{R})$			
B6C2	0.997	-46.6	14.3	387	119	-35
<b>B7C2</b>	0.998	20.1	15.0	-167	125	-37
<b>B8C2</b>	0.999	13.7	14.9	-114	124	-37
Mg <sup>2+</sup>	<b>R</b> <sup>2</sup>	Slope	$(\Delta S)$	$\Delta H$ [Jmol <sup>-1</sup> ]	$\Delta S$ [Jmol <sup>-1</sup> K <sup>-1</sup> ]	$\Delta G \operatorname{VH} [kJmol^{-1}]$
		$\left(\frac{-\Delta H}{R}\right)$	Intercept $(\overline{R})$			
B6C2	0.993	-8.70	22.6	72.3	188	-56
<b>B7C2</b>	0.997	-31.7	23.9	263	199	-59
<b>B8C2</b>	0.995	-28.0	25.0	233	208	-62