

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

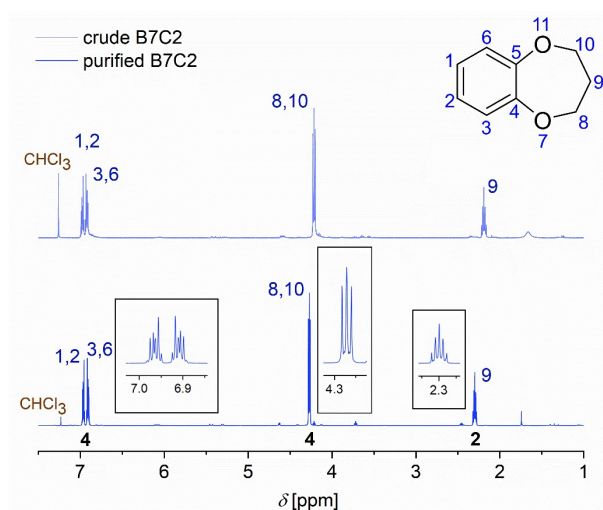


Fig. S1: ^1H NMR spectrum of the crude B7C2 and purified B7C2 after column chromatography treatment.

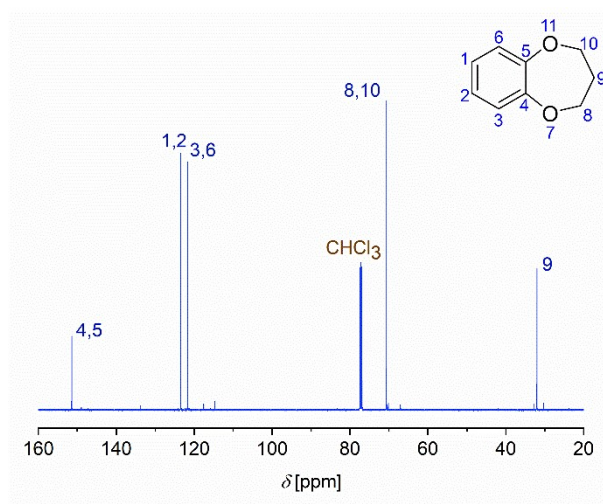


Fig. S2: ^{13}C NMR spectrum of the purified B7C2.

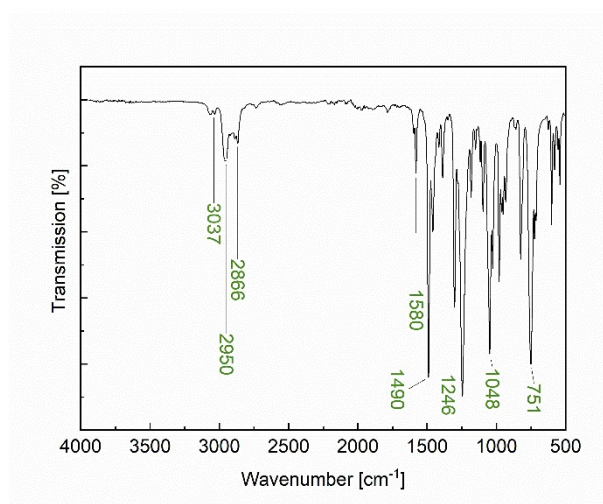


Fig. S3: IR spectrum of the purified B7C2.

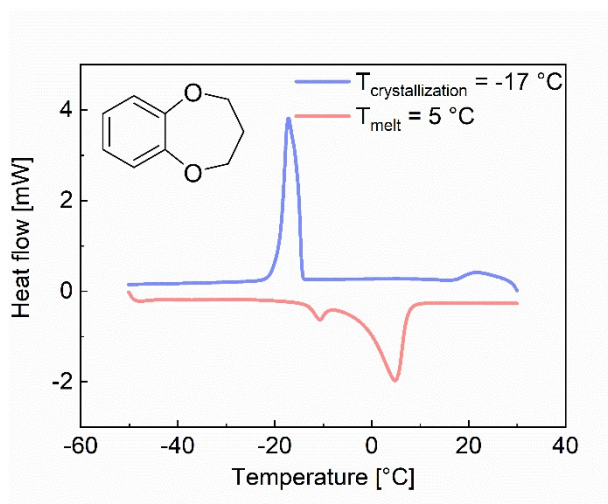


Fig. S4: DSC measurement of the purified B7C2.

Benzo-8-crown-2

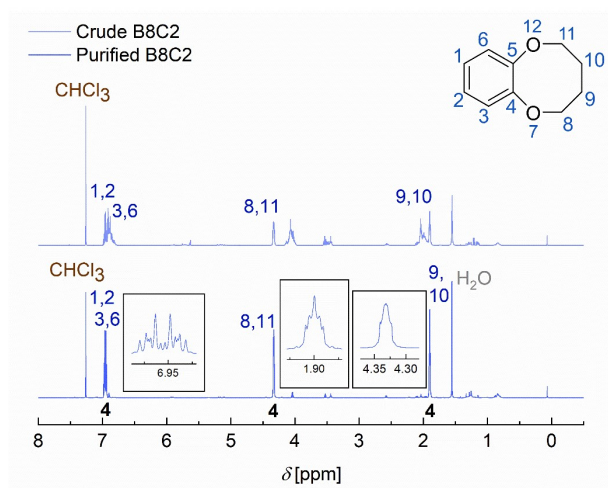


Fig. S5: ^1H NMR spectrum of the crude B8C2 and purified B7C2 after column chromatography treatment.

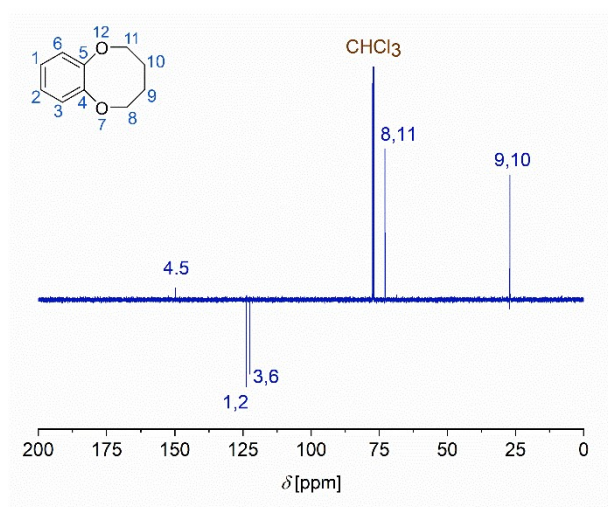


Fig. S6: ^{13}C NMR spectrum of the purified B8C2.

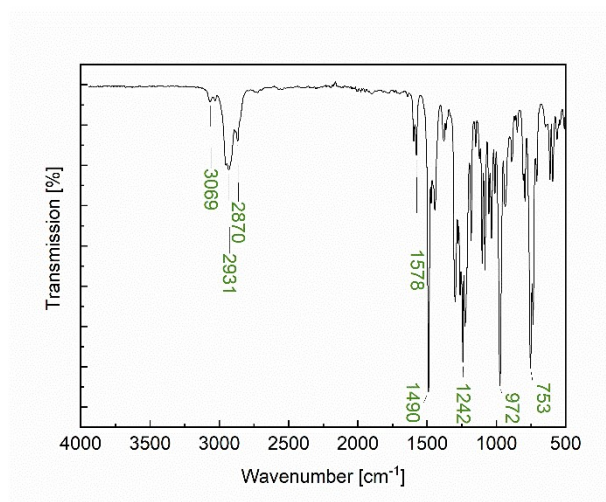


Fig. S7: IR spectrum of the purified B8C2.

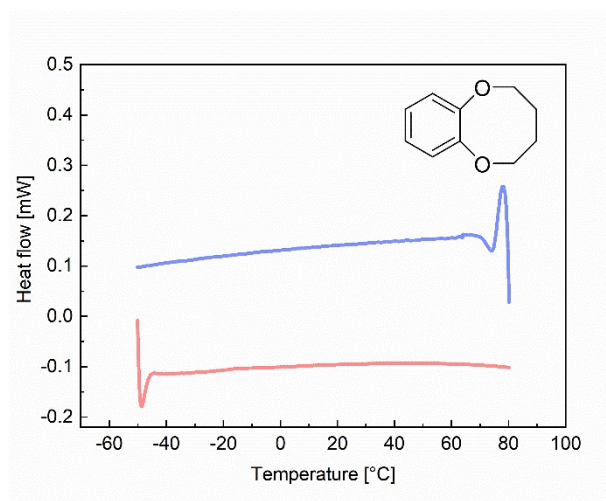


Fig. S8: DSC measurement of the purified B8C2.

UV-vis Data

Lithium

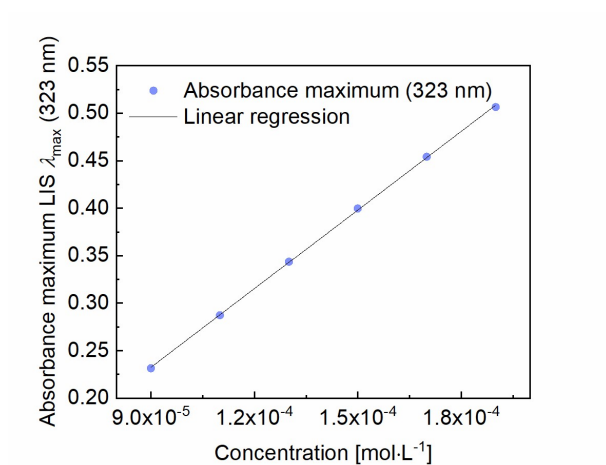


Fig. S9: Absorbance maxima of LIS $\lambda_{\text{max}} = 323 \text{ nm}$ as linear regression against concentration $[\text{mol} \cdot \text{L}^{-1}]$.

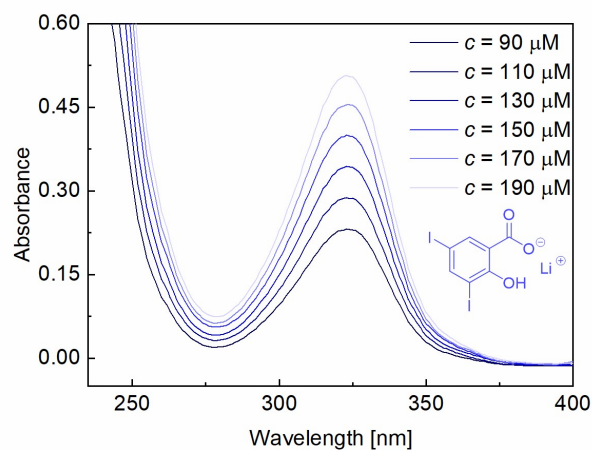


Fig. S10: UV-vis spectrum of LIS at different concentrations [$\mu\text{mol}\cdot\text{L}^{-1}$].

Magnesium

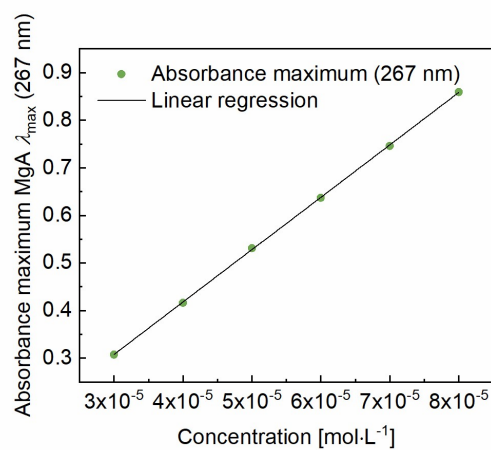


Fig. S11: Absorbance maxima of MgA $\lambda_{\text{max}} = 267 \text{ nm}$ as linear regression against concentration [$\text{mol}\cdot\text{L}^{-1}$].

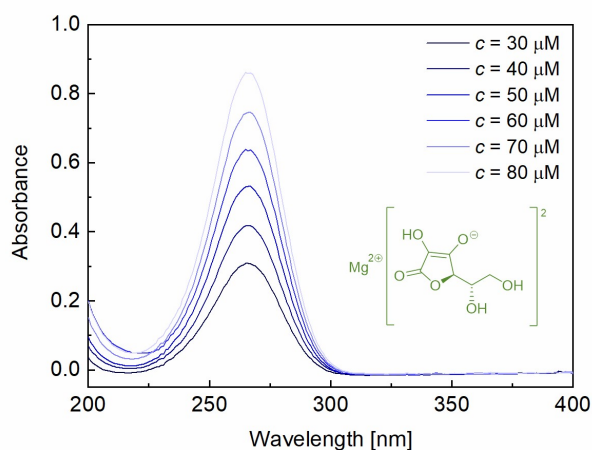


Fig. S12: UV-vis spectrum of MgA at different concentrations [$\mu\text{mol}\cdot\text{L}^{-1}$].

CE solubility measurements in the aqueous phase

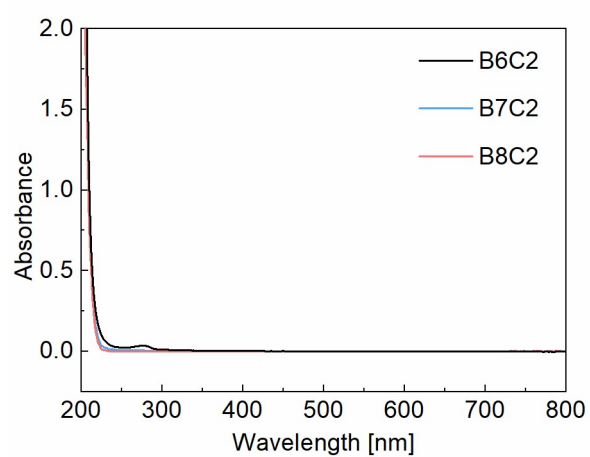


Fig. S13: UV-vis spectroscopy of the aqueous LiCl phase after extraction and formation of the CE–cation complex.

Thermodynamic Evaluation

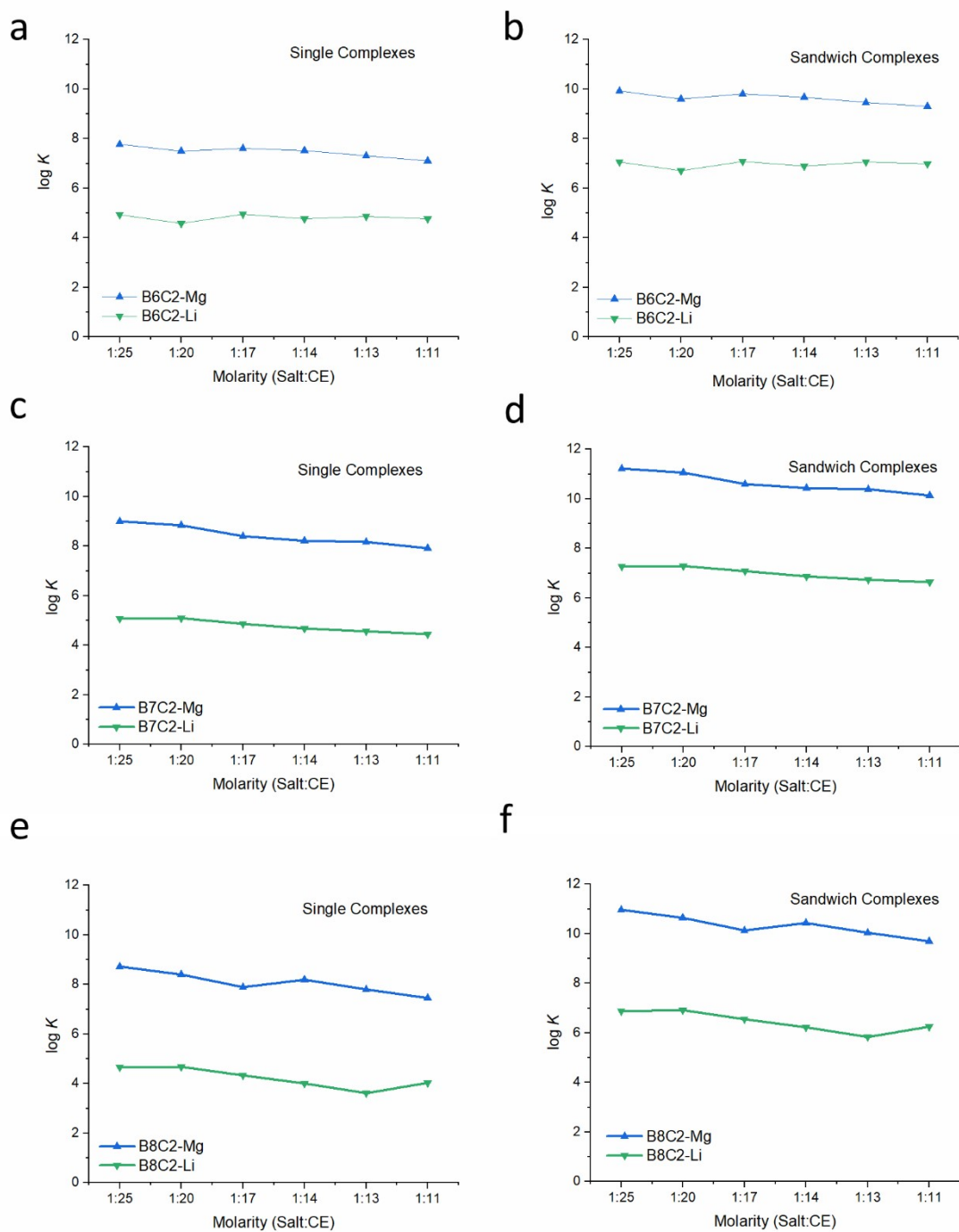


Fig. S14: logarithmic complexation stability K of a) B6C2 assuming single complexes, b) B6C2 assuming sandwich-type complexes, c) B7C2 assuming single complexes, d) B7C2 assuming sandwich-type complexes, e) B8C2 assuming single complexes, f) B8C2 assuming sandwich-type complexes. The green line shows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

Van't Hoff Plot

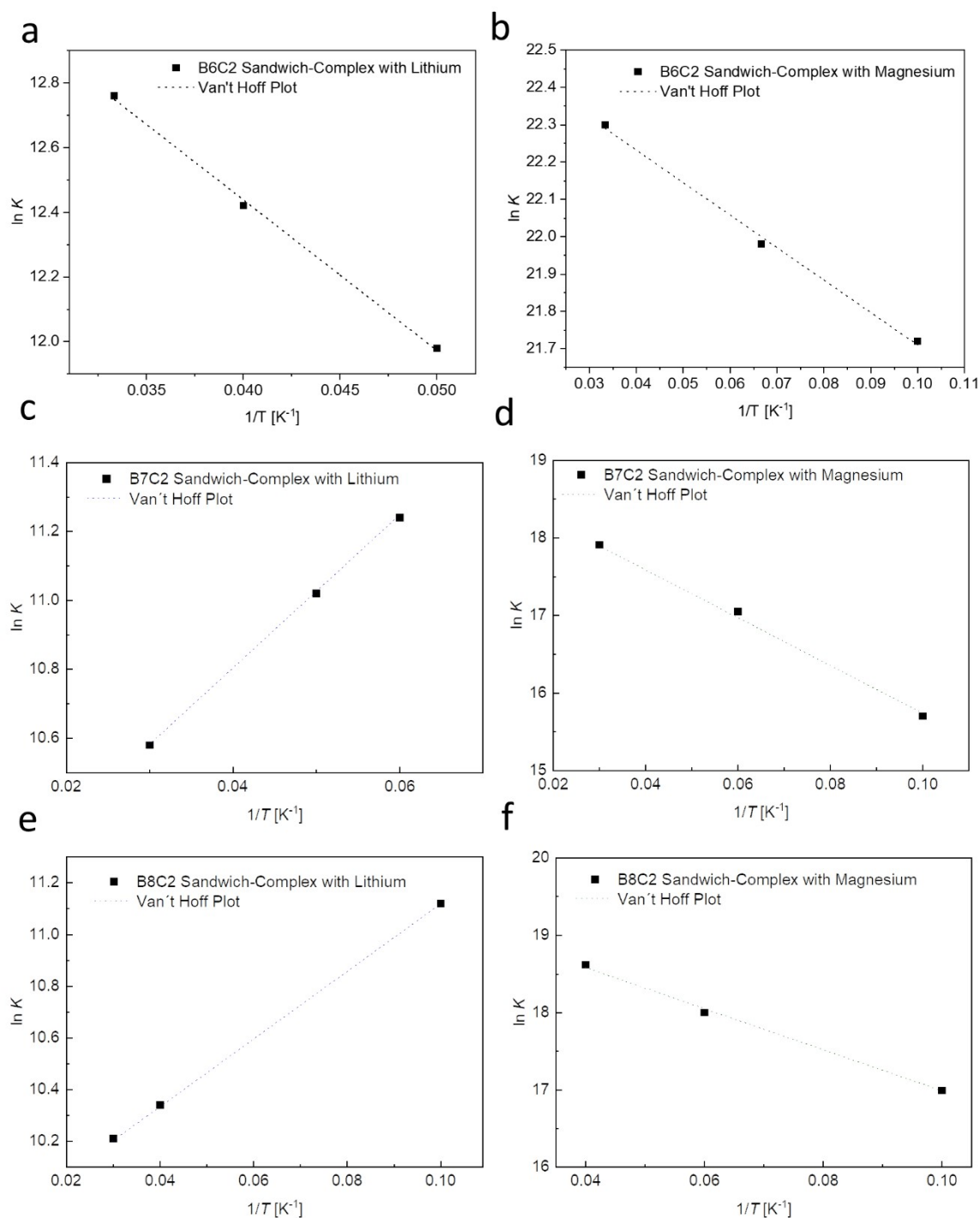


Fig. S15: Van't Hoff plot of the a) B6C2-Li complex b) B6C2-Mg complex, c) B7C2-Li complex, d) B7C2-Mg complex, e) B8C2-Li complex, and f) B8C2-Mg complex with a constant molar ratio of CE:salt = 14:1.

Tab. S1: Log K and Gibbs energy ΔG at 25 °C of the extraction of B6C2, B7C2 and B8C2 with Li^+ and Mg^{2+} .

B6C2-Li⁺	Single		Sandwich	
CE:metal	log K	ΔG [kJmol ⁻¹]	log K	ΔG [kJmol ⁻¹]
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-Mg²⁺	Single		Sandwich	
CE:metal	log K	ΔG [kJmol ⁻¹]	log K	ΔG [kJmol ⁻¹]
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⁺	Single		Sandwich	
CE:metal	log K	ΔG [kJmol ⁻¹]	log K	ΔG [kJmol ⁻¹]
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-Mg²⁺	Single		Sandwich	
CE:metal	log K	ΔG [kJmol ⁻¹]	log K	ΔG [kJmol ⁻¹]
1:25	9.0	-51	11	-64
1:20	8.8	-50	11	-63
1:17	8.4	-48	11	-61
1:14	8.2	-47	10	-60
1:13	7.9	-45	10	-59
1:11	7.6	-43	10	-58
B8C2-Li⁺	Single		Sandwich	
CE:metal	log K	ΔG [kJmol ⁻¹]	log K	ΔG [kJmol ⁻¹]
1:25	4.7	-27	6.9	-39
1:20	4.7	-27	6.9	-39
1:17	4.3	-25	6.6	-37
1:14	4.0	-23	6.2	-36
1:13	3.6	-21	5.8	-33
1:11	4.0	-20	6.3	-36
B8C2-Mg²⁺	Single		Sandwich	
CE:metal	log K	ΔG [kJmol ⁻¹]	log K	ΔG [kJmol ⁻¹]
1:25	8.7	-50	11	-63
1:20	8.4	-48	11	-61
1:17	7.9	-45	10	-58
1:14	8.2	-47	10	-60
1:13	7.8	-45	10	-57
1:11	7.5	-43	9.1	-55

Tab. S2: Slope and intercept values of the Van't Hoff plot and the determined data of ΔH , ΔS and ΔG (at 25 °C).

Li⁺	R²	Slope $\left(\frac{-\Delta H}{R}\right)$	Intercept $\left(\frac{\Delta S}{R}\right)$	ΔH [Jmol⁻¹]	ΔS [Jmol⁻¹K⁻¹]	ΔG VH [kJmol⁻¹]
B6C2	0.997	-46.6	14.3	387	119	-35
B7C2	0.998	20.1	15.0	-167	125	-37
B8C2	0.999	13.7	14.9	-114	124	-37
Mg²⁺	R²	Slope $\left(\frac{-\Delta H}{R}\right)$	Intercept $\left(\frac{\Delta S}{R}\right)$	ΔH [Jmol⁻¹]	ΔS [Jmol⁻¹K⁻¹]	ΔG VH [kJmol⁻¹]
B6C2	0.993	-8.70	22.6	72.3	188	-56
B7C2	0.997	-31.7	23.9	263	199	-59
B8C2	0.995	-28.0	25.0	233	208	-62