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Supporting Information

Solid-State Dynamics and High-Pressure Studies of a Supramolecular Spiral Gear

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SOLID-STATE DYNAMICS AND HIGH-PRESSURE STUDIES OF A SUPRAMOLECULAR SPIRAL GEAR

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SUPPORTING INFORMATION

Single-crystal XRD

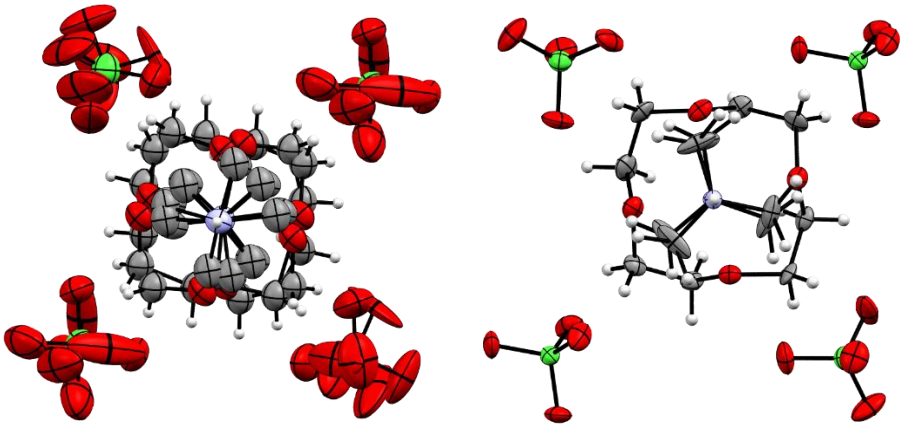

Figure SI-1. Ortep drawings (50% probability) of $[(12\text{-crown-4})_2{\cdot}DABCOH_2](ClO_4)_2$ at room temperature (left) and at 100 K (right) at ambient pressure.

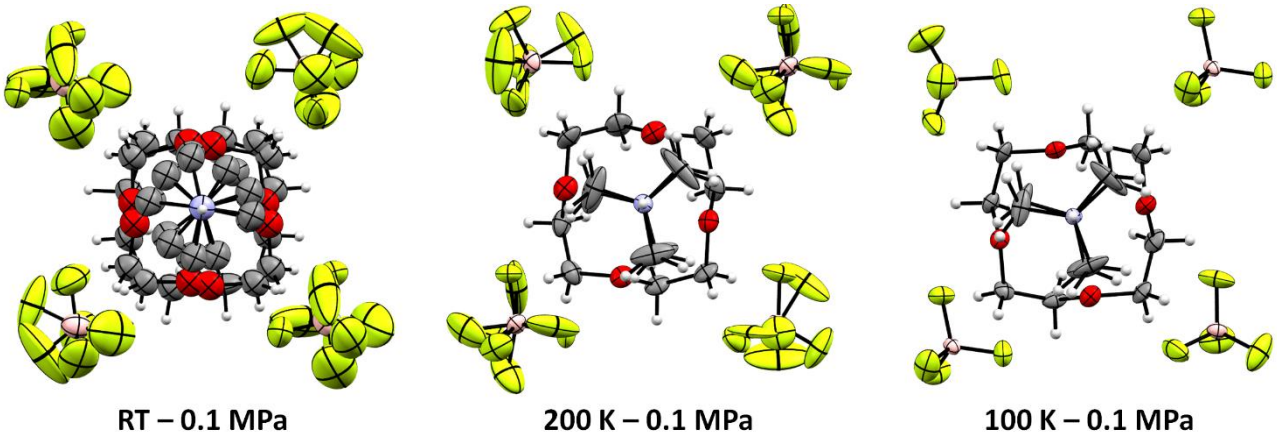

Figure SI-2. Variable-temperature Ortep drawings (50% probability) of $[(12\text{-crown-4})_2{\cdot}DABCOH_2](BF_4)_2$.

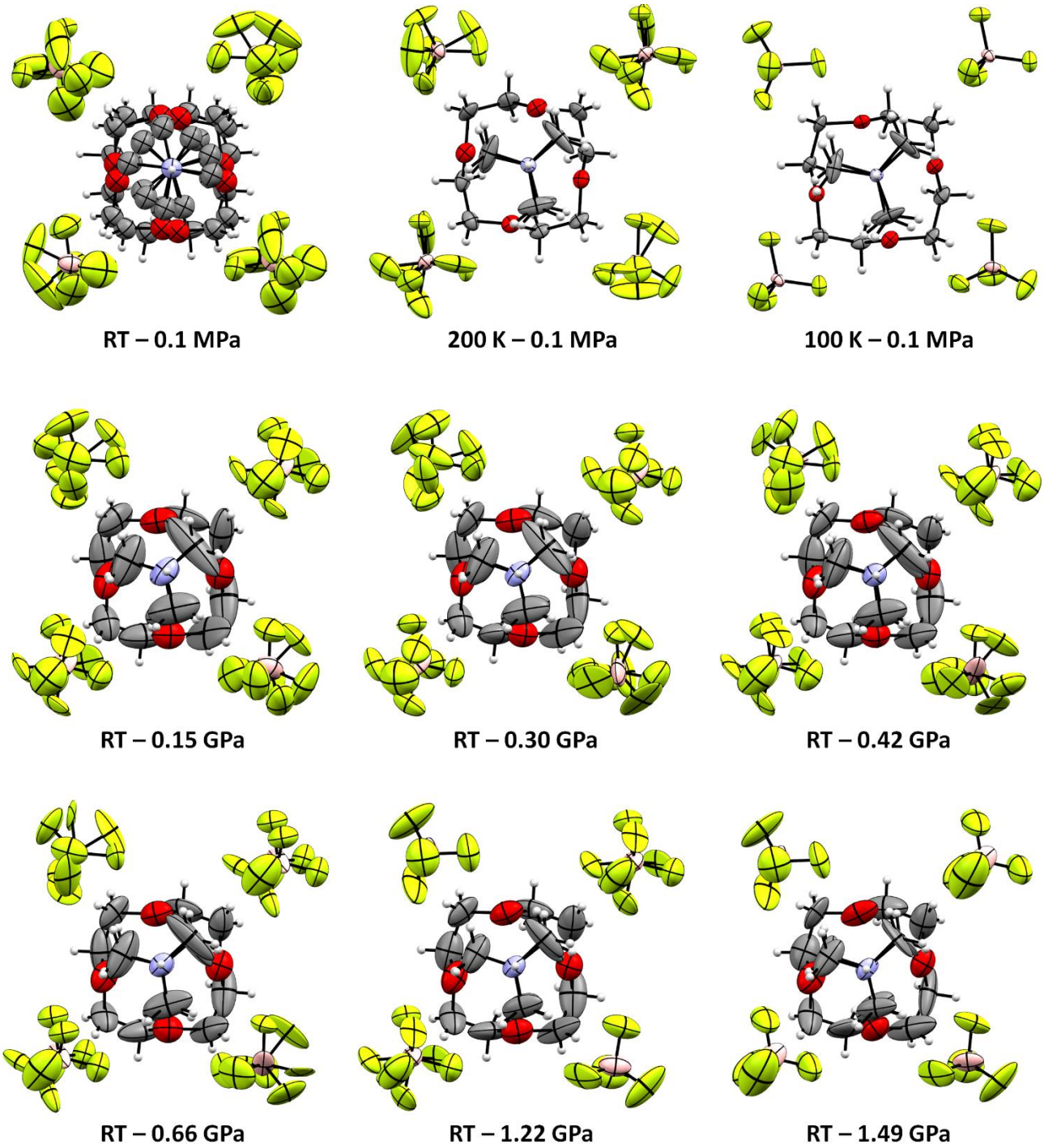

Figure SI-3. Variable-pressure Ortep drawings (50% probability) of $[(12\text{-crown-4})_2 \cdot DABCOH_2](BF_4)_2$.

Table SI-1. Crystallographic data table of the compound $[(12\text{-crown-4})_2 \cdot DABCOH_2](ClO_4)_2$.

	$[(12\text{-crown-4})_2 \cdot DABCOH_2](ClO_4)_2$	**$[(12\text{-crown-4})_2 \cdot DABCOH_2](ClO_4)_2$**
Empirical formula	$C_{22}H_{44}Cl_2N_2O_{16}$	$C_{22}H_{44}Cl_2N_2O_{16}$
Formula weight	663.49	663.49
Temperature/K	300	100
Crystal system	trigonal	trigonal
Space group	$P3_121$	$P3_121$
a/Å	10.3187(8)	10.1674(5)
b/Å	10.3187(8)	10.1674(5)
c/Å	25.2248(17)	25.0181(13)
α/°	90	90
β/°	90	90
γ/°	120	120
Volume/Å^3	2326.0(4)	2239.8(2)
Z	3	3
ρ_{calc}g/cm^3	1.399	1.476
μ/mm^{-1}	0.282	0.294
F(000)	1026.0	1056.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.654 to 58.322	6.73 to 49.962
Index ranges	$-13 \le h \le 12$, $-11 \le k \le 11$, $-33 \le l \le 29$	$-12 \le h \le 8$, $-7 \le k \le 12$, $-29 \le l \le 29$
Reflections collected	5909	9429
Independent reflections	3437 [R_{int} = 0.0213, R_{sigma} = 0.0477]	2627 [R_{int} = 0.0307, R_{sigma} = 0.0310]
Data/restraints/parameters	3437/48/209	2627/0/191
Goodness-of-fit on F^2	1.249	1.177
Final R indexes [I>=2σ (I)]	R_1 = 0.1242, wR_2 = 0.3303	R_1 = 0.0612, wR_2 = 0.1708
Final R indexes [all data]	R_1 = 0.1682, wR_2 = 0.3672	R_1 = 0.0651, wR_2 = 0.1732
Largest diff. peak/hole / e Å^{-3}	0.45/-0.35	0.62/-0.39

Table SI-2. Crystallographic data table of the variable temperature collections of compound [(12-crown-4)$_2$·DABCOH$_2$](BF$_4$)$_2$.

	[(12-crown-4)$_2$·DABCOH$_2$](BF$_4$)$_2$	**[(12-crown-4)$_2$·DABCOH$_2$](BF$_4$)$_2$**	**[(12-crown-4)$_2$·DABCOH$_2$](BF$_4$)$_2$**	**[(12-crown-4)$_2$·DABCOH$_2$](BF$_4$)$_2$**
Empirical formula	$C_{22}H_{46}B_2F_8N_2O_8$	$C_{22}H_{46}B_2F_8N_2O_8$	$C_{22}H_{46}B_2F_8N_2O_8$	$C_{22}H_{46}B_2F_8N_2O_8$
Formula weight	640.23	640.23	640.23	640.23
Temperature (K)	360	300	200	100
Crystal system	trigonal	trigonal	trigonal	trigonal
Space group	$P3_121$	$P3_121$	$P3_121$	$P3_221$
a (Å)	10.282(1)	10.2541(6)	10.1319(9)	10.0981(6)
b (Å)	10.282(1)	10.2541(6)	10.1319(9)	10.0981(6)
c (Å)	25.101(3)	25.0361(14)	24.881(2)	24.8445(15)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	120	120	120	120
Volume (Å^3)	2298.3(6)	2279.8(3)	2211.9(4)	2194.0(3)
Z	3	3	3	3
ρ_{calc} (g/cm^3)	1.337	1.359	1.435	1.454
μ (mm^{-1})	0.127	0.130	0.135	0.138
F(000)	957.0	966.0	1010.0	1014.0
Radiation	MoKα (λ =0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection (°)	6.682 to 58.898	6.7 to 59.046	6.76 to 49.976	6.776 to 51.958
Index ranges	-8 ≤ h ≤ 13, -14 ≤ k ≤ 6, -34 ≤ l ≤ 16	-13 ≤ h ≤ 12, -14 ≤ k ≤ 11, -29 ≤ l ≤ 31	-12 ≤ h ≤ 9, -10 ≤ k ≤ 6, -29 ≤ l ≤ 19	-12 ≤ h ≤ 12, -10 ≤ k ≤ 11, -30 ≤ l ≤ 18
Reflections collected	6234	10971	4452	4887
Independent reflections	3464 [R_{int} = 0.0316, R_{sigma} = 0.0926]	3567 [R_{int} = 0.0525, R_{sigma} = 0.0629]	2565 [R_{int} = 0.0229, R_{sigma} = 0.0444]	2864 [R_{int} = 0.0280, R_{sigma} = 0.0626]
Data/restraints/parameters	3464/30/307	3567/76/211	2565/24/227	2864/0/191
Goodness-of-fit on F^2	0.999	1.166	1.068	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.1178, wR_2 = 0.2660	R_1 = 0.1267, wR_2 = 0.3232	R_1 = 0.0682, wR_2 = 0.1632	R_1 = 0.0691, wR_2 = 0.1636
Final R indexes [all data]	R_1 = 0.1137, wR_2 = 0.3793	R_1 = 0.2056, wR_2 = 0.3795	R_1 = 0.0784, wR_2 = 0.1707	R_1 = 0.0910, wR_2 = 0.1758
Largest diff. peak/hole (e Å^{-3})	0.29/-0.22	0.50/-0.31	0.45/-0.22	0.58/-0.27

Table SI-3. Crystallographic data table of the high-pressure collections of compound $[(12\text{-crown-}4)_2{\cdot}DABCOH_2](BF_4)_2$.

	$[(12\text{-crown-}4)_2{\cdot}DABCOH_2](BF_4)_2$	**$[(12\text{-crown-}4)_2{\cdot}DABCOH_2](BF_4)_2$**	**$[(12\text{-crown-}4)_2{\cdot}DABCOH_2](BF_4)_2$**	**$[(12\text{-crown-}4)_2{\cdot}DABCOH_2](BF_4)_2$**	**$[(12\text{-crown-}4)_2{\cdot}DABCOH_2](BF_4)_2$**	**$[(12\text{-crown-}4)_2{\cdot}DABCOH_2](BF_4)_2$**
Empirical formula	$C_{22}H_{46}B_2F_8N_2O_8$	$C_{22}H_{46}B_2F_8N_2O_8$	$C_{22}H_{46}B_2F_8N_2O_8$	$C_{22}H_{46}B_2F_8N_2O_8$	$C_{22}H_{46}B_2F_8N_2O_8$	$C_{22}H_{46}B_2F_8N_2O_8$
Formula weight	640.23	640.23	640.23	640.23	640.23	640.23
Pressure/GPa	0.10	0.30	0.42	0.66	1.22	1.49
Crystal system	trigonal	trigonal	trigonal	trigonal	trigonal	trigonal
Space group	$P3_221$	$P3_221$	$P3_221$	$P3_221$	$P3_221$	$P3_221$
a/Å	10.186(2)	10.1310(14)	10.1069(16)	10.0564(13)	9.9543(11)	9.9117(14)
b/Å	10.186(2)	10.1310(14)	10.1069(16)	10.0564(13)	9.9543(11)	9.9117(14)
c/Å	24.934(4)	24.727(2)	24.667(3)	24.490(2)	24.1063(18)	23.924(3)
α/°	90	90	90	90	90	90
β/°	90	90	90	90	90	90
γ/°	120	120	120	120	120	120
Volume/Å^3	2240.3(10)	2197.9(6)	2182.1(7)	2144.8(6)	2068.6(5)	2035.5(6)
Z	3	3	3	3	3	3
ρ_{calc}g/cm^3	1.424	1.451	1.462	1.487	1.542	1.567
μ/mm^{-1}	0.135	0.137	0.138	0.141	0.146	0.148
F(000)	1014.0	1014.0	1014.0	1014.0	1014.0	1014.0
Crystal size/mm^3	0.274 × 0.188 × 0.051	0.274 × 0.188 × 0.051	0.274 × 0.188 × 0.051	0.274 × 0.188 × 0.051	0.274 × 0.188 × 0.051	0.274 × 0.188 × 0.051
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.006 to 54.064	8.064 to 54.578	8.084 to 54.598	8.138 to 55.112	8.252 to 54.626	8.904 to 53.23
Index ranges	-7 ≤ h ≤ 7, -7 ≤ k ≤ 7, -31 ≤ l ≤ 31	-7 ≤ h ≤ 7, -7 ≤ k ≤ 7, -30 ≤ l ≤ 31	-7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -31 ≤ l ≤ 31	-12 ≤ h ≤ 12, -6 ≤ k ≤ 6, -31 ≤ l ≤ 31	-7 ≤ h ≤ 7, -6 ≤ k ≤ 6, -30 ≤ l ≤ 31	-6 ≤ h ≤ 6, -7 ≤ k ≤ 6, -29 ≤ l ≤ 30
Reflections collected	9499	9464	8495	9469	9090	7044
Independent reflections	1670 [R_{int} = 0.1324, R_{sigma} = 0.1463]	1640 [R_{int} = 0.1246, R_{sigma} = 0.1285]	1604 [R_{int} = 0.1125, R_{sigma} = 0.1330]	1490 [R_{int} = 0.1178, R_{sigma} = 0.1135]	1431 [R_{int} = 0.1127, R_{sigma} = 0.1106]	1290 [R_{int} = 0.1014, R_{sigma} = 0.1304]
Data/restraints/ parameters	1670/48/227	1640/36/227	1604/30/227	1490/12/221	1431/12/209	1290/0/191
Goodness-of-fit on F^2	1.027	1.015	1.054	1.042	1.086	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0816, wR_2 = 0.0986	R_1 = 0.0750, wR_2 = 0.1337	R_1 = 0.0760, wR_2 = 0.1022	R_1 = 0.0681, wR_2 = 0.0893	R_1 = 0.0763, wR_2 = 0.1326	R_1 = 0.0888, wR_2 = 0.1795
Final R indexes [all data]	R_1 = 0.2363, wR_2 = 0.1352	R_1 = 0.2203, wR_2 = 0.1794	R_1 = 0.2153, wR_2 = 0.1363	R_1 = 0.1901, wR_2 = 0.1172	R_1 = 0.1873, wR_2 = 0.1696	R_1 = 0.2066, wR_2 = 0.2314
Largest diff. peak/hole / e Å^{-3}	0.14/-0.12	0.15/-0.14	0.18/-0.13	0.17/-0.14	0.17/-0.19	0.32/-0.24

Scheme SI-1. Intermolecular distances used as a reference in the crystal structure of [(12-crown-4)$_2$·DABCOH$_2$](BF$_4$)$_2$ (H-atoms omitted for clarity); a) hydrogen bonds between DABCOH$_2^{2+}$ and crown ethers, distances between the DABCO centroid and the anions; b) distances between adjacent crown ethers in parallel and crossed arrangement, note that the parallel ones are equivalent by symmetry.

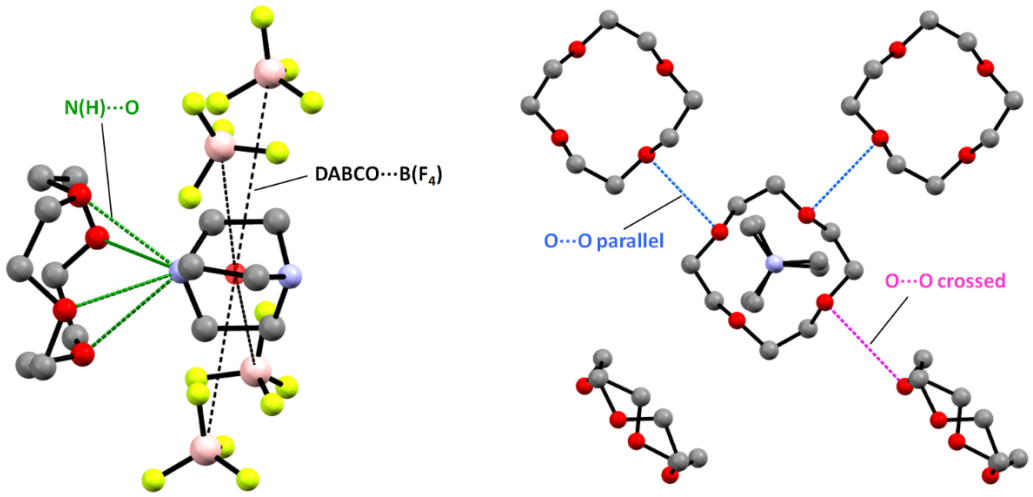

Table SI-4. List of intermolecular distances as a function of T in the crystal structure of [(12-crown-4)$_2$·DABCOH$_2$](BF$_4$)$_2$; see Scheme SI-1 for the definition of the distances.

	d(Å)			
N(H)···O	3.4(1)	3.26(3)	3.200(6)	3.198(5)
	3.20(8)	3.17(1)	3.082(7)	3.092(4)
	3.12(6)	3.081(9)	3.051(6)	3.019(6)
	3.07(4)	3.05(1)	2.935(8)	2.905(6)
	3.03(3)	3.04(2)	-	-
	3.02(2)	3.01(2)	-	-
	3.01(8)	3.00(2)	-	-
	2.8(1)	2.965(7)	-	-
DABCO···B(F$_4$)	5.35(3)	5.359(16)	5.401(7)	5.382(9)
	5.019(12)	4.982(8)	4.898(5)	4.878(5)
	5.019(12)	4.982(8)	4.898(5)	4.878(5)
	4.93(3)	4.895(16)	4.731(7)	4.716(9)
O···O par.	3.539(1)	3.51(4)	3.380(5)	3.355(7)
	3.539(3)	3.51(1)	-	-
O···O crossed	3.539(1)	3.81(3)	3.678(6)	3.664(5)
	3.735(1)	3.71(3)	-	-
T (K)	360	300	200	100

Table SI-5. List of intermolecular distances as a function of P in the crystal structure of $[(12\text{-crown-4})_2 \cdot DABCOH_2](BF_4)_2$; see Scheme SI-1 for the definition of the distances.

	d (Å)						
N(H)···O	3.26(3)	3.16(1)	3.18(1)	3.18(1)	3.19(1)	3.18(1)	3.15(2)
	3.17(1)	3.07(2)	3.06(1)	3.06(2)	3.04(2)	3.01(2)	3.01(2)
	3.081(9)	3.03(2)	3.03(1)	3.04(2)	3.03(1)	3.00(1)	3.00(3)
	3.05(1)	2.96(2)	2.96(2)	2.96(2)	2.94(2)	2.89(2)	2.90(3)
	3.04(2)	-	-	-	-	-	
	3.01(2)	-	-	-	-	-	
	3.00(2)	-	-	-	-	-	
	2.965(7)	-	-	-	-	-	
DABCO···B(F_4)	5.359(16)	5.35(4)	5.39(4)	5.33(4)	5.35(2)	5.36(2)	5.42(4)
	4.982(8)	4.94(2)	4.93(2)	4.86(2)	4.851(15)	4.776(15)	4.75(2)
	4.982(8)	4.94(2)	4.93(2)	4.86(2)	4.850(15)	4.776(15)	4.75(2)
	4.895(16)	4.84(4)	4.74(4)	4.78(4)	4.70(2)	4.60(2)	4.49(4)
O···O par.	3.51(4)	3.44(2)	3.41(2)	3.37(2)	3.34(1)	3.30(2)	3.28(2)
	3.51(1)	-	-	-	-	-	
O···O crossed	3.81(3)	3.65(2)	3.61(1)	3.56(1)	3.52(1)	3.43(1)	3.39(2)
	3.71(3)	-	-	-	-	-	
P (GPa)	0.0001*	0.10	0.30	0.42	0.66	1.22	1.49

* = ambient pressure .

Powder XRD

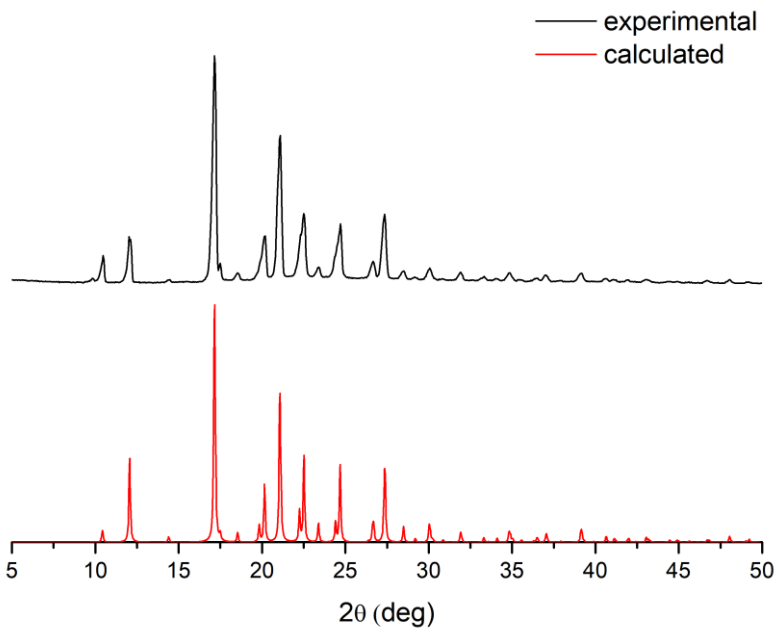

Figure SI-4. Comparison between experimental and calculated pattern of $[(12\text{-crown-4})_2{\cdot}DABCOH_2](BF_4)_2$.

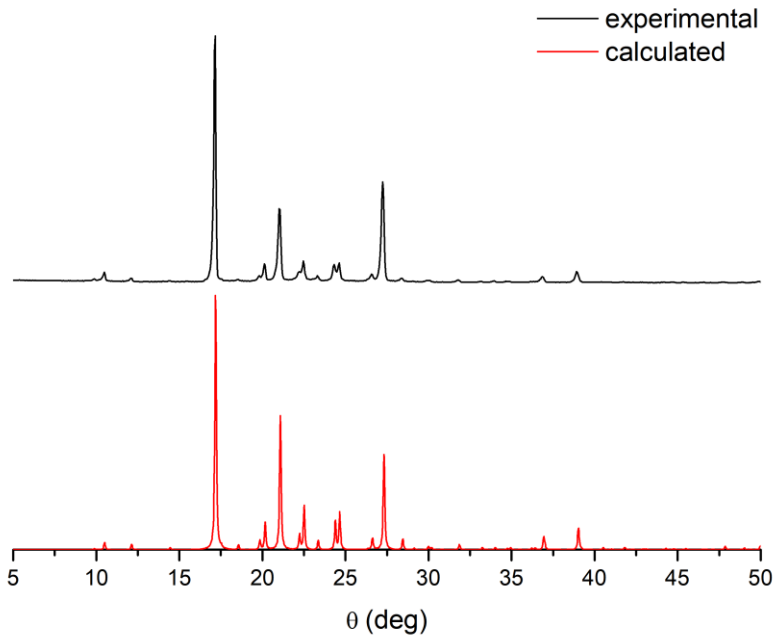

Figure SI-5. Comparison between experimental and calculated pattern of $[(12\text{-crown-4})_2{\cdot}DABCOH_2](ClO_4)_2$.

Solid-state NMR spectroscopy

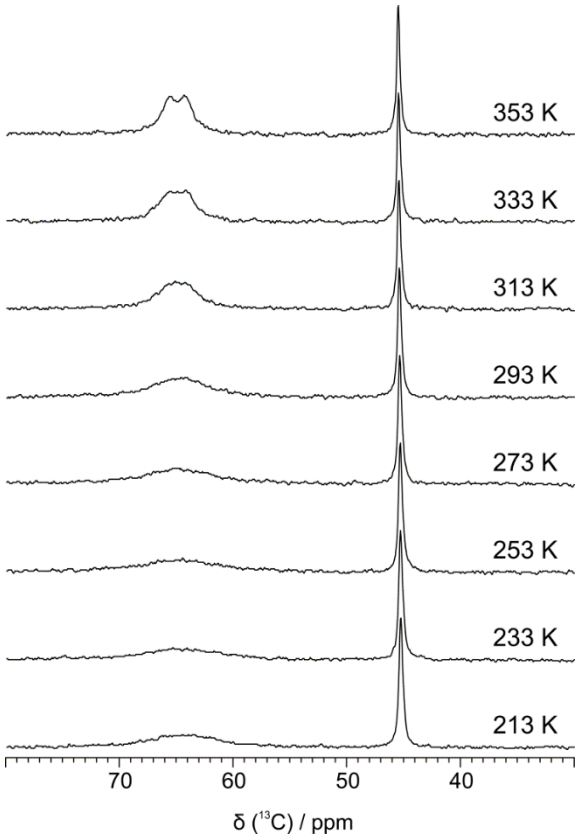

Figure SI-6. VT ^{13}C (150.9 MHz) MAS SSNMR spectra of $[(12\text{-crown-4})_2 \cdot DABCOH_2](BF_4)_2$ acquired at a spinning speed of 20 kHz.

Thermal analyses

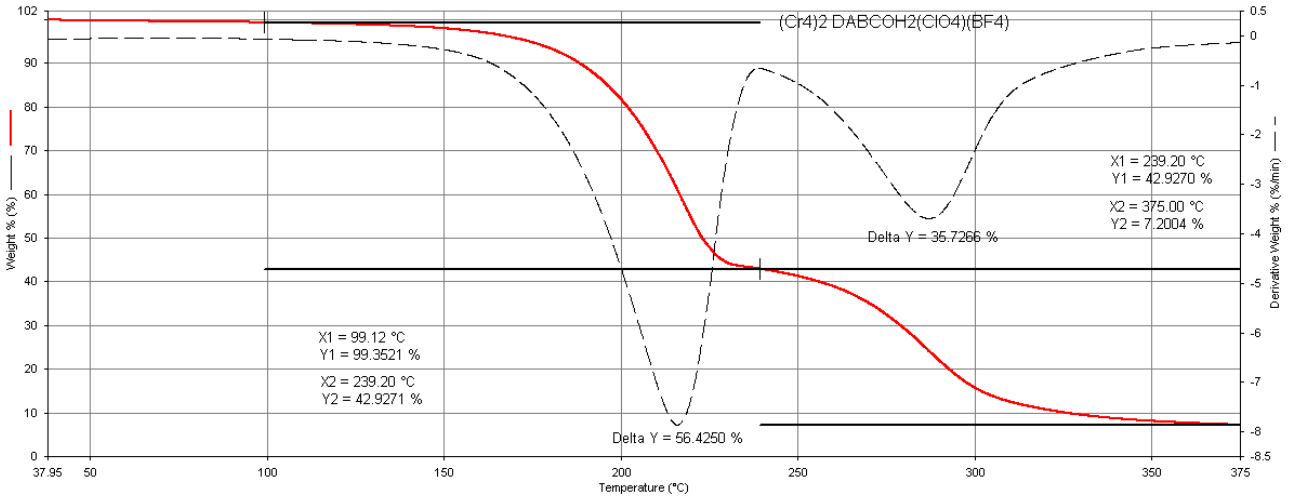

Figure SI-7. TGA track of $[(12\text{-crown-4})_2{\cdot}DABCOH_2](BF_4)_2$.

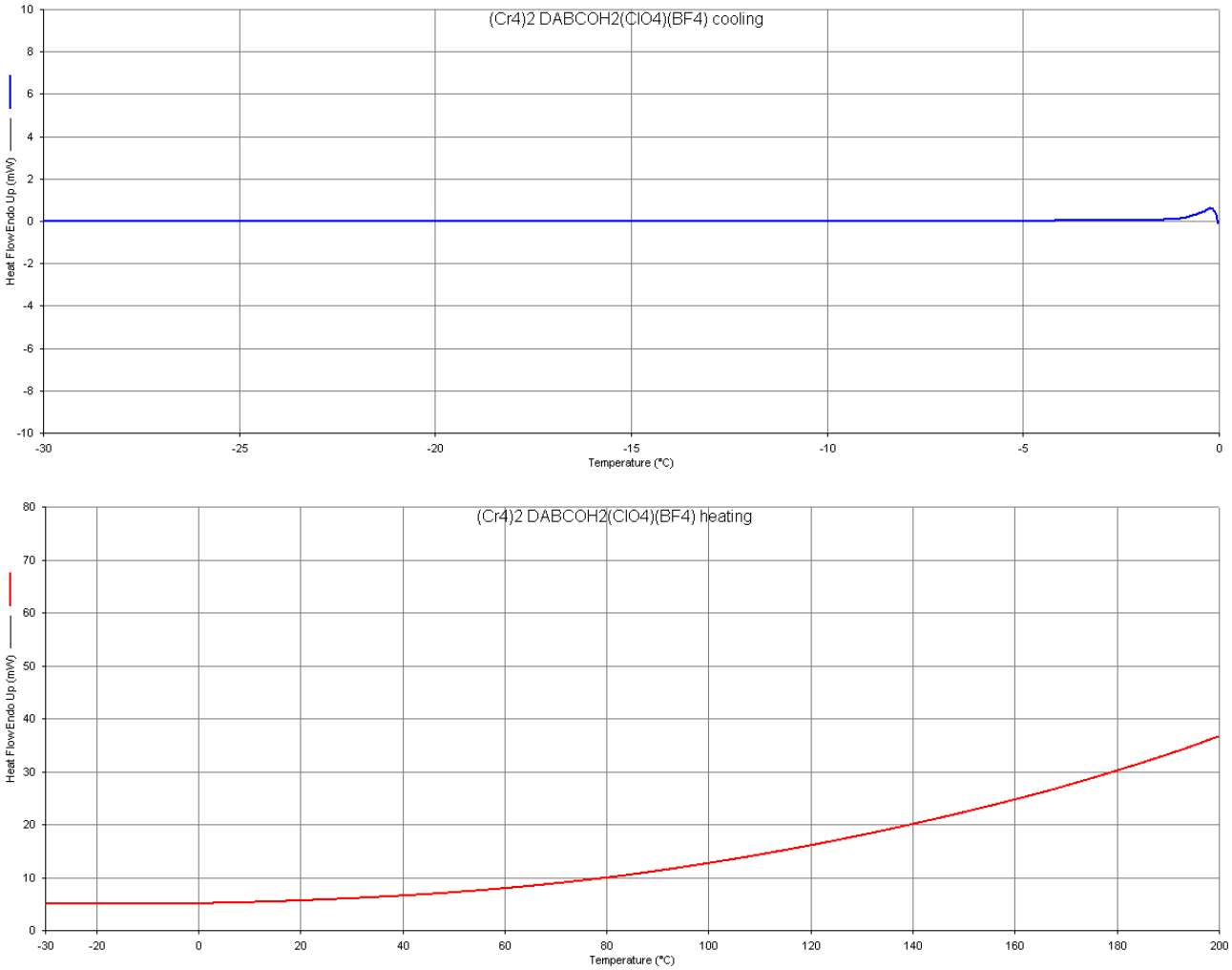

Figure SI-8. DSC track of $[(12\text{-crown-4})_2{\cdot}DABCOH_2](BF_4)_2$; cooling (top) and heating ramp(bottom).

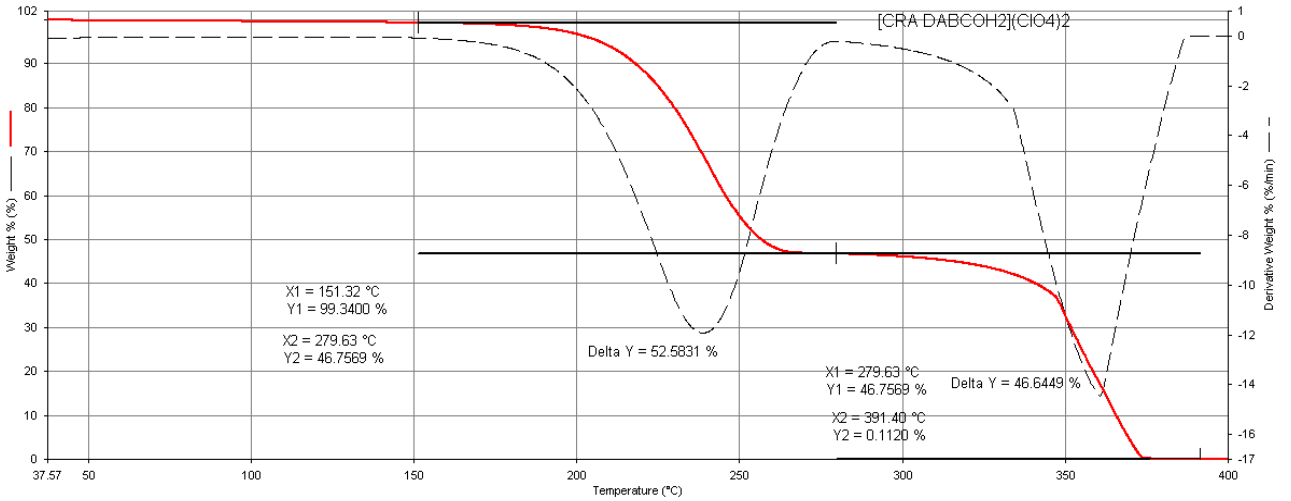

Figure SI-9. TGA track of $[(12\text{-crown-4})_2{\cdot}DABCOH_2](ClO_4)_2$.

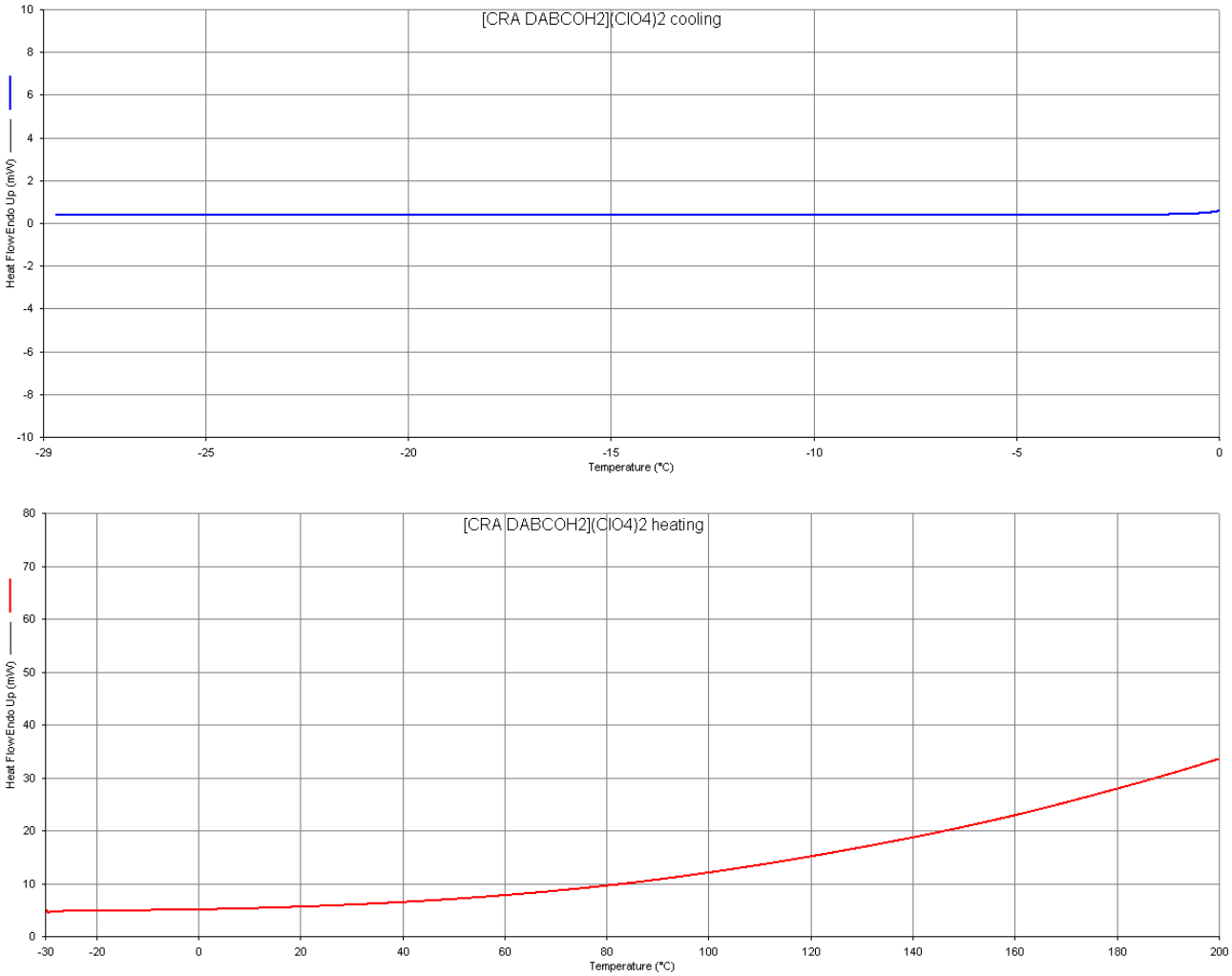

Figure SI-10. DSC track of $[(12\text{-crown-4})_2{\cdot}DABCOH_2](ClO_4)_2$; cooling (top) and heating ramp (bottom).

Isothermal Compression

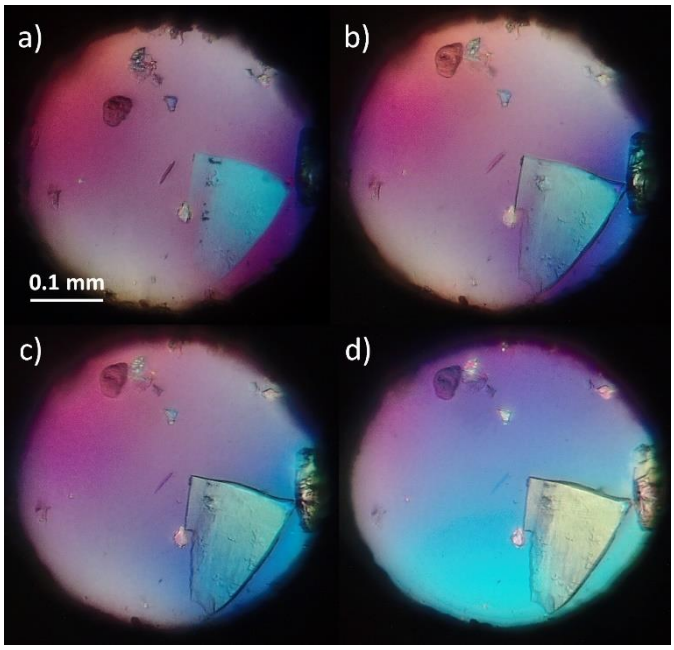

Figure SI-11. Stages of the isothermal compression of $[(12\text{-crown-4})_2(DABCOH_2)](BF_4)_2$ in daphne oil (polarized-light optical microscope images): (a) 0.3 GPa, (b) 0.66 GPa, (c) 1.22 GPa and (d) 3 GPa; all viewed in polarized light. Several ruby chips for pressure calibration lie close to the edge of the chamber and one on the left side of the crystal sample.