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SUPPLEMENTARY INFORMATION

Negative linear compressibility in nanoporous metal-organic frameworks rationalized by the empty channel structural mechanism

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Contents: Page

Appendix A. Comparison of the computed and experimental crystal structures

A.1. Zinc Squarate Tetrahydrate (ZnSqQh)

ZnSqQh is monoclinic, space group $C2/c$. Table 1 gives the computed and experimental[1] lattice parameters. As can be observed, the difference of the experimental unit cell volume and the calculated value using the PBE functional is very large, 10.5%, and is reduced to an exceedingly small value, 0.4%, when dispersion corrections are included. A comparison of the computed and experimental interatomic distances and angles is given in Table S.2 and Table S.3, respectively. The experimental C-C and C-O bond distances are reproduced within 0.01 Å. The accordance between the computed and experimental Zn-O bond lengths is better than 0.1 Å. The calculated and experimental interatomic angles, including the hydrogen bond angles, agree satisfactorily.

A.2. Titanium oxalate trioxide dihydrate (TiOxDh)

TiOxDh is orthorhombic (space group $Cmca$). For TiOxDh, as for ZnSqQh, the differences of the experimental[2] and calculated unit-cell parameters are largely reduced when dispersion corrections are introduced (see Table 1). The difference of the computed and experimental unit-cell volumes is reduced from 5.3 to 0.7%. Table S.5 and Table S.6 give the computed and experimental interatomic distances and angles in TiOxDh. The calculated and experimental C-C and C-O bond distances differ about 0.05 Å and the agreement for the calculated and experimental Ti-O bond distances is better than 0.1 Å. Since the hydrogen atom positions in TiOxDh were not provided by Boudaren *et al*.,[2] the fully optimized crystal structure obtained in this work is reported as a file with CIF (Crystallographic Information File) format.

A.4. Titanium oxalate trioxide trihydrate (TiOxTh)

The structure of TiOxTh is similar to that of TiOxDh. In this case the positions of the hydrogen atoms were given by Boudaren *et al.*[2] The accuracy of the calculated unit-cell parameters of TiOxTh, is comparable to that of TiOxDh, as expected from the similarity of their structures. The computed and experimental unit-cell volumes differ by only 0.6%. The calculated and experimental interatomic distances and angles are provided in Table S.8 and Table S.9, respectively.

Table S.1. Material data and calculation parameters for the selected metal-organic frameworks (MOF).

MOF	Acronym	Structural formula	Crystal system	Space group	ε(eV)	*k*-mesh
Zinc squarate tetrahydrate[1]	ZnOxTh	$ZnC_4O_4 \cdot 4\,H_2O$	Monoclinic	$C2/c$ (no. 15)	1000	$3 \times 2 \times 4$
Titanium oxalate trioxide dihydrate[2]	TiOxDh	$Ti_2(C_2O_4)\,O_3 \cdot 2\,H_2O$	Orthorhombic	$Cmca$ (no. 64)	1000	$1 \times 2 \times 2$
Titanium oxalate trioxide trihydrate[2]	TiOxTh	$Ti_2(C_2O_4)\,O_3 \cdot 3\,H_2O$	Orthorhombic	$Cmca$ (no. 64)	1000	$1 \times 2 \times 2$

Table S.2. Interatomic distances in zinc squarate tetrahydrate (in Å).

Distance	Exp.[1]	Calc.
Zn-O		
Zn-O1 × 2	2.076(1)	2.147
Zn-OW1 × 2	2.076(1)	2.142
Zn-OW2 × 2	2.126(1)	2.207
C-C		
C1-C2	1.464	1.470
C1-C2′	1.467	1.479
<C-C>	1.466	1.474
C-O		
C1-O1	1.250	1.258
C2-O2	1.250	1.260
<C-O>	1.250	1.259
O-H		
OW1-H11	0.965(2)	0.984
OW1-H12	0.954(3)	0.985
OW2-H21	0.984(3)	1.000
OW2-H22	0.931(4)	0.974
Hydrogen bonds Oi-H···Oj		
OW1···O2	2.787(2)	2.778
H11···O2	1.823	1.796
OW1···O1	2.806(2)	2.744
H12···O1	1.869	1.778
OW2···O2	2.716(1)	2.656
H21···O2	1.759	1.667
OW2···O2′	2.986(1)	3.051
H22···O2′	2.165	2.217

Table S.3. Interatomic angles in zinc squarate tetrahydrate (in degrees).

Angle	Exp.[1]	Calc.
O-Zn-O		
O1-Zn-O1	180	180
O1-Zn-OW1 × 2	91.14(4)	90.53
O1-Zn-OW1′ × 2	88.86(4)	89.47
O1-Zn-OW2 × 2	94.85(3)	95.88
O1-Zn-OW2′ × 2	85.15(3)	84.11
OW1-Zn-OW1′	180	180
OW1-Zn-OW2 × 2	91.48(5)	93.69
OW1-Zn-OW2′ × 2	82.52(2)	86.31
OW2-Zn-OW2′	180	180
C-C-C		
C1-C2-C1	89.66	89.61
C2-C1-C2	90.34	90.39
C-C-O		
O1-C1-C2	132.78	132.27
O1-C1-C2′	136.88	137.33
C1-C2-O2	134.42	133.92
C1′-C2-O2	135.92	136.46
O-H-O		
H11-OW1-H12	109.08	108.81
H21-OW2-H22	104.24	104.06
Hydrogen bonds Oi-H···Oj		
OW1-H11···O2	178.42(23)	175.70
OW1-H12···O1	166.39(28)	165.95
OW2-H21···O2	163.23(21)	169.04
OW2-H22···O2′	146.16(37)	142.88

Table S.4. Most intense reflections in the X-ray diffraction pattern of zinc squarate tetrahydrate: (a) X-ray pattern derived from the experimental crystal structure;[1] (b) X-ray pattern derived from the calculated crystal structure.

$[h\ k\ l]$	(a) Exp.[1]			(b) Calc.		$\Delta\ (2\theta)$
	$2\theta\ (\mathrm{deg})$	$\mathrm{d}\ (\text{Å})$	I (%)	$2\theta\ (\mathrm{deg})$	$\mathrm{d}\ (\text{Å})$	
[1 1 0]	11.952	7.399	39.63	11.928	7.414	-0.02
[0 2 0]	13.267	6.668	36.49	13.102	6.752	-0.16
[-1 1 1]	16.657	5.318	100.00	16.721	5.298	0.06
[1 1 1]	19.084	4.647	51.95	19.090	4.645	0.01
[2 0 0]	19.953	4.446	30.61	20.005	4.435	0.05
[2 2 0]	24.037	3.699	24.90	23.988	3.707	-0.05
[-1 3 1]	25.223	3.528	53.19	25.088	3.547	-0.13
[0 4 0]	26.717	3.334	10.83	26.379	3.376	-0.34
[0 0 2]	26.763	3.328	70.27	26.898	3.312	0.13
[1 3 1]	26.918	3.310	11.92	26.755	3.329	-0.16
[3 1 0]	30.877	2.894	6.44	30.937	2.888	0.06
[1 1 2]	30.885	2.893	17.49	30.962	2.886	0.08
[2 4 0]	33.570	2.667	33.89	33.328	2.686	-0.24
[-2 -4 1]	34.972	2.564	5.74	34.794	2.576	-0.18
[2 0 2]	36.211	2.479	8.53	36.288	2.474	0.08
[3 3 0]	36.400	2.466	9.76	36.325	2.471	-0.07
[1 3 2]	36.407	2.466	5.34	36.347	2.470	-0.06
[-3 -3 1]	37.098	2.422	43.17	37.090	2.422	-0.01
[0 4 2]	38.176	2.356	6.81	38.030	2.364	-0.15
[3 3 1]	40.658	2.217	9.29	40.575	2.222	-0.08
[-1 1 3]	40.818	2.209	9.37	41.057	2.197	0.24
[-2 4 2]	41.228	2.188	18.58	41.169	2.191	-0.06
[1 1 3]	44.127	2.051	14.05	44.281	2.044	0.15
[-1 3 3]	45.299	2.000	16.61	45.413	1.996	0.11
[2 4 2]	45.566	1.989	6.13	45.418	1.995	-0.15
[2 6 0]	45.592	1.988	7.30	45.139	2.007	-0.45
[-3 -5 1]	46.303	1.959	11.31	46.087	1.968	-0.22
[1 3 3]	48.363	1.881	10.37	48.405	1.879	0.04
[4 4 0]	49.221	1.850	6.95	49.116	1.853	-0.10
[-1 7 1]	50.375	1.810	8.11	49.808	1.829	-0.57
[1 7 1]	51.336	1.778	10.62	50.755	1.797	-0.58
[-5 -1 1]	51.399	1.776	10.71	51.602	1.770	0.20
[-3 3 3]	51.511	1.773	6.89	51.724	1.766	0.21
[0 0 4]	55.145	1.664	6.59	55.441	1.656	0.30
[-5 -3 1]	55.214	1.662	5.93	55.316	1.659	0.10
[3 7 1]	60.547	1.528	5.34	60.050	1.539	-0.50
[-2 4 4]	62.824	1.478	6.28	63.022	1.474	0.20

Table S.5. Interatomic distances in titanium oxalate trioxide dihydrate (in Å).

Distance	Exp.[2]	Calc.
	Ti-O	
Ti-O1	2.221(7)	2.118
Ti-O2	2.203(6)	2.227
Ti-O3	1.815(3)	1.817
Ti-O4	1.805(2)	1.807
Ti-O5	1.802(2)	1.811
Ti-OW1	2.171(7)	2.148
	C-C	
C1-C2	1.490(20)	1.533
	C-O	
C1-O1	1.264(9)	1.258
C2-O2	1.212(8)	1.259
	O-H	
OW1-H11	-	0.977
OW1-H12	-	1.001
Hydrogen bonds Oi-H···Oj		
OW1···O2	-	2.885
H12···O2	-	2.619
OW1···O3	-	3.532
H11···O2	-	2.619

Table S.6. Interatomic angles in titanium oxalate trioxide dihydrate (in degrees).

Angle	Exp.[2]	Calc.
O-Ti-O		
O1-Ti-O2	75.1(4)	74.75
O1-Ti-O3	87.3(3)	89.54
O1-Ti-O4	158.6(4)	157.46
O1-Ti-O5	96.3(4)	92.85
O1-Ti-OW1	78.0(4)	76.26
O2-Ti-O3	160.5(4)	163.90
O2-Ti-O4	90.1(3)	88.41
O2-Ti-O5	89.6(4)	85.24
O2-Ti-OW1	77.4(4)	80.05
O3-Ti-O4	104.3(3)	105.75
O3-Ti-O5	100.9(3)	99.28
O3-Ti-OW1	90.9(5)	93.01
O4-Ti-O5	98.9(2)	100.69
O4-Ti-OW1	83.8(3)	86.30
O5-Ti-OW1	166.8(4)	163.55
O-C-O		
O2-C2-O2’	123.4(9)	128.37
O1-C2-O1’	117.4(9)	127.10
C-C-O		
C1-C2-O2	117(1)	115.77
C2-C1-O1	120(1)	116.41
O-H-O		
H11-OW1-H2	-	108.42
Hydrogen bonds Oi-H···Oj		
OW1-H12···O2	-	175.40
OW1-H11···O3	-	155.66

Table S.7. Most intense reflections in the X-ray diffraction pattern of titanium oxalate trioxide dihydrate: (a) X-ray pattern derived from the experimental crystal structure;[2] (b) X-ray pattern derived from the calculated crystal structure.

$[h\ k\ l]$	(a) Exp.[2]			(b) Calc.		$\Delta\ (2\theta)$
	$2\theta\ (\mathrm{deg})$	$\mathrm{d}\ (\text{Å})$	I (%)	$2\theta\ (\mathrm{deg})$	$\mathrm{d}\ (\text{Å})$	
[2 0 0]	11.456	7.718	38.11	11.422	7.741	-0.03
[1 1 1]	13.722	6.448	100.00	13.702	6.458	-0.02
[0 2 0]	17.003	5.211	17.85	16.792	5.276	-0.21
[0 2 1]	19.325	4.589	67.44	19.176	4.625	-0.15
[1 1 2]	21.004	4.226	36.48	21.092	4.209	0.09
[3 1 1]	21.312	4.166	25.82	21.261	4.176	-0.05
[2 2 1]	22.522	3.945	5.67	22.375	3.970	-0.15
[0 2 2]	25.075	3.549	10.79	25.045	3.553	-0.03
[3 1 2]	26.656	3.342	47.14	26.697	3.337	0.04
[2 2 2]	27.646	3.224	5.98	27.604	3.229	-0.04
[1 3 1]	27.867	3.199	21.38	27.593	3.230	-0.27
[4 2 1]	30.235	2.954	9.46	30.083	2.968	-0.15
[5 1 1]	31.578	2.831	18.49	31.491	2.839	-0.09
[1 3 2]	32.206	2.777	6.20	32.035	2.792	-0.17
[0 2 3]	32.586	2.746	8.37	32.675	2.738	0.09
[0 4 0]	34.396	2.605	7.62	33.959	2.638	-0.44
[2 2 3]	34.647	2.587	14.40	34.721	2.582	0.07
[5 1 2]	35.509	2.526	17.43	35.493	2.527	-0.02
[0 4 1]	35.657	2.516	5.07	35.255	2.544	-0.40
[6 2 2]	43.410	2.083	7.37	43.302	2.088	-0.11
[0 4 3]	44.647	2.028	6.72	44.453	2.036	-0.19
[6 2 3]	48.449	1.877	22.46	48.432	1.878	-0.02
[5 1 4]	48.515	1.875	5.11	48.698	1.868	0.18
[3 5 2]	50.843	1.794	10.94	50.390	1.810	-0.45
[3 1 5]	51.067	1.787	5.17	51.419	1.776	0.35
[8 2 1]	51.325	1.779	5.27	51.122	1.785	-0.20
[6 0 4]	51.789	1.764	8.97	51.959	1.759	0.17
[1 5 3]	52.546	1.740	5.33	52.198	1.751	-0.35
[5 5 2]	56.512	1.627	5.48	56.059	1.639	-0.45
[3 3 5]	57.249	1.608	13.64	57.429	1.603	0.18

Table S.8. Interatomic distances in titanium oxalate trioxide trihydrate (in Å).

Distance	Exp.[2]	Calc.
Ti-O		
Ti-O1	2.180(9)	2.224
Ti-O2	2.271(8)	2.220
Ti-O3	1.829(4)	1.796
Ti-O4	1.801(3)	1.807
Ti-O5	1.814(3)	1.815
Ti-OW1	2.170(10)	2.110
C-C		
C1-C2	1.550(30)	1.536
C-O		
C1-O1	1.240(10)	1.261
C2-O2	1.220(10)	1.259
O-H		
OW1-H11	0.97(5)	0.992
OW1-H12	0.98(7)	0.996
OW2-H2 × 2	0.97(2)	0.989
Hydrogen bonds Oi-H···Oj		
OW1···O2	2.807(11)	2.709
H11-O2	2.04(6)	1.726
OW1···OW2	2.853(9)	2.735
H12···Ow2	1.87(7)	1.776
OW2···O1 × 2	2.909(8)	2.800
H2···O1 × 2	2.16(3)	1.922

Table S.9. Interatomic angles in titanium oxalate trioxide trihydrate (in degrees).

Angle	Exp.[2]	Calc.
O-Ti-O		
O1-Ti-O2	75.2(5)	73.61
O1-Ti-O3	88.6(4)	89.26
O1-Ti-O4	158.4(5)	156.50
O1-Ti-O5	93.2(6)	92.43
O1-Ti-OW1	79.3(5)	75.37
O2-Ti-O3	162.6(5)	162.79
O2-Ti-O4	88.7(4)	93.52
O2-Ti-O5	87.2(5)	82.66
O2-Ti-OW1	80.3(5)	78.67
O3-Ti-O4	105.3(4)	102.02
O3-Ti-O5	100.2(4)	99.97
O3-Ti-OW1	90.7(6)	95.79
O4-Ti-O5	100.3(2)	105.59
O4-Ti-OW1	84.0(4)	82.96
O5-Ti-OW1	166.7(6)	159.94
O-C-O		
O2-C2-O2’	123(1)	127.29
O1-C2-O1’	123(1)	126.47
C-C-O		
C1-C2-O2	118(2)	116.34
C2-C1-O1	118(2)	116.34
O-H-O		
H11-OW1-H12	103(9)	113.27
H2-OW2-H2’	104(3)	
Hydrogen bonds Oi-H···Oj		
OW1-H11···O2	135(3)	169.82
OW1-H12···OW2	178(4)	160.35
OW2-H2-O1 × 2	133(2)	146.50

Table S.10. Most intense reflections in the X-ray diffraction pattern of titanium oxalate trioxide trihydrate: (a) X-ray pattern derived from the experimental crystal structure;[2] (b) X-ray pattern derived from the calculated crystal structure.

$[h\ k\ l]$	(a) Exp.[2]			(b) Calc.		$\Delta\ (2\theta)$
	$2\theta\ (\mathrm{deg})$	$\mathrm{d}\ (\text{Å})$	I (%)	$2\theta\ (\mathrm{deg})$	$\mathrm{d}\ (\text{Å})$	
[1 1 1]	13.673	6.471	100.00	13.757	6.432	0.08
[2 0 0]	11.413	7.747	31.11	11.194	7.898	-0.22
[0 2 1]	19.221	4.614	21.98	18.966	4.675	-0.25
[1 1 2]	20.961	4.235	8.11	21.585	4.114	0.62
[0 2 0]	16.889	5.246	6.23	16.357	5.415	-0.53
[0 0 2]	18.277	4.850	4.30	19.135	4.635	0.86
[1 3 1]	27.699	3.218	0.96	27.081	3.290	-0.62
[4 0 0]	22.941	3.874	0.87	22.496	3.949	-0.45
[0 2 2]	24.985	3.561	0.41	25.274	3.521	0.29
[2 2 1]	22.409	3.964	0.25	22.076	4.023	-0.33
[2 2 2]	27.545	3.236	0.24	27.718	3.216	0.17
[4 2 1]	30.099	2.967	0.18	29.586	3.017	-0.51
[3 1 1]	21.233	4.181	0.12	21.050	4.217	-0.18
[5 1 1]	31.458	2.842	0.12	30.999	2.883	-0.46
[3 3 1]	32.236	2.775	0.07	31.536	2.835	-0.70
[1 3 2]	32.052	2.790	0.06	31.905	2.803	-0.15
[1 1 3]	29.453	3.030	0.05	30.592	2.920	1.14
[2 0 2]	21.600	4.111	0.05	22.222	3.997	0.62
[2 2 0]	20.430	4.344	0.04	19.864	4.466	-0.57
[4 0 2]	29.488	3.027	0.04	29.697	3.006	0.21
[4 2 2]	34.175	2.622	0.02	34.088	2.628	-0.09
[6 0 0]	34.711	2.582	0.02	34.025	2.633	-0.69
[4 2 0]	28.625	3.116	0.02	27.941	3.191	-0.68
[5 1 2]	35.395	2.534	0.02	35.340	2.538	-0.05
[0 4 0]	34.159	2.623	0.01	33.060	2.707	-1.10
[0 2 3]	32.504	2.752	0.01	33.362	2.684	0.86

Table S.11. Unit cell volume and lattice parameters of zinc squarate tetrahydrate under the effect of different external isotropic pressures.

P (GPa)	Vol. (Å^3)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ(deg)
-1.7499	938.1966	10.1639	12.9808	7.3551	90.00	104.80	90.00
-1.5001	917.3598	10.0646	13.0204	7.2287	90.00	104.44	90.00
-0.9999	871.7060	9.6916	13.1989	6.9928	90.00	102.97	90.00
-0.7504	849.6655	9.4663	13.2943	6.9002	90.00	101.92	90.00
-0.5002	824.9879	9.1171	13.4592	6.8170	90.00	99.52	90.00
-0.2500	814.4238	9.0587	13.4792	6.7597	90.00	99.35	90.00
0.0008	803.4061	8.9816	13.5039	6.7075	90.00	99.05	90.00
0.2499	794.5654	8.9333	13.5132	6.6638	90.00	98.99	90.00
0.5003	787.0704	8.8949	13.5208	6.6249	90.00	98.94	90.00
0.5600	785.4252	8.8879	13.5233	6.6151	90.00	98.95	90.00
0.6196	783.4083	8.8720	13.5266	6.6074	90.00	98.90	90.00
0.6806	780.9500	8.8369	13.5507	6.6011	90.00	98.89	90.00
0.7506	778.2663	8.7989	13.5715	6.5960	90.00	98.86	90.00
0.9999	770.5236	8.7560	13.5770	6.5599	90.00	98.87	90.00
1.5000	757.8148	8.6804	13.5904	6.5015	90.00	98.87	90.00
1.9999	746.7125	8.6121	13.6043	6.4513	90.00	98.92	90.00
2.9997	726.7429	8.4769	13.6424	6.3639	90.00	99.07	90.00
4.0002	709.8004	8.3592	13.6747	6.2918	90.00	99.28	90.00
5.0001	694.3503	8.2435	13.6937	6.2385	90.00	99.61	90.00
5.9996	678.8907	8.1154	13.7096	6.1940	90.00	99.89	90.00
8.0004	655.0801	7.9531	13.7223	6.1041	90.00	100.47	90.00
10.0002	635.5663	7.8281	13.7363	6.0267	90.00	101.26	90.00
11.9996	615.9112	7.6980	13.7110	5.9759	90.00	102.44	90.00

Table S.12. Calculated compressibilities of zinc squarate tetrahydrate along b direction ($k_b = -1/b \cdot (\partial b/\partial P)_P$) for different external isotropic pressures.

P (GPa)	$k_b(\mathrm{TPa^{-1}})$	P (GPa)	$k_b(\mathrm{TPa^{-1}})$	P (GPa)	$k_b(\mathrm{TPa^{-1}})$
-1.50	-23.80	-0.10	-5.39	1.60	-2.35
-1.40	-27.53	0.00	-6.25	1.80	-2.50
-1.30	-28.52	0.10	-5.82	2.00	-2.60
-1.20	-27.90	0.20	-4.05	3.00	-2.56
-1.10	-26.77	0.30	-1.61	4.00	-1.97
-1.00	-26.25	0.40	-0.03	5.00	-1.27
-0.90	-27.41	0.50	-1.30	6.00	-0.72
-0.80	-31.31	0.60	-8.57	7.00	-0.45
-0.70	-39.00	0.70	-33.22	8.00	-0.45
-0.60	-51.50	0.80	-1.10	9.00	-0.53
-0.50	-16.84	0.90	-1.32	10.00	-0.04
-0.40	-7.07	1.00	-1.52	11.00	0.86
-0.30	-3.85	1.20	-1.86	-	-
-0.20	-4.07	1.40	-2.13	-	-

Table S.13. Unit cell volume and lattice parameters of zinc squarate tetrahydrate under the effect of different external pressures applied along the direction of minimum compressibility, [010].

P (GPa)	Vol. (Å^3)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)
-1.0006	796.5419	8.5544	14.1555	6.6592	90.00	98.96	90.00
-0.6664	796.9636	8.6597	13.9617	6.6708	90.00	98.83	90.00
-0.4996	797.6641	8.7153	13.8649	6.6793	90.00	98.77	90.00
-0.3326	798.8661	8.7821	13.7605	6.6883	90.00	98.75	90.00
-0.2489	799.7757	8.8223	13.7037	6.6932	90.00	98.75	90.00
-0.1673	801.1386	8.8730	13.6409	6.6978	90.00	98.80	90.00
-0.0850	802.8113	8.9337	13.5711	6.7028	90.00	98.93	90.00
0.0205	804.5806	9.0035	13.4859	6.7115	90.00	99.13	90.00
0.0830	805.5518	9.0388	13.4380	6.7193	90.00	99.24	90.00
0.1661	806.6678	9.0879	13.3743	6.7268	90.00	99.38	90.00
0.2510	807.4273	9.1427	13.3056	6.7314	90.00	99.59	90.00
0.2759	807.6782	9.1624	13.2826	6.7325	90.00	99.68	90.00
0.2903	818.6625	9.4094	13.1372	6.7572	90.00	101.45	90.00
0.3338	820.7121	9.4752	13.0797	6.7643	90.00	101.76	90.00
0.3664	823.5613	9.5507	13.0227	6.7759	90.00	102.25	90.00
0.4329	828.4791	9.6955	12.9050	6.7957	90.00	103.00	90.00
0.4997	833.6776	9.8130	12.8091	6.8220	90.00	103.54	90.00
0.5826	836.0282	9.9001	12.7122	6.8419	90.00	103.85	90.00
0.6662	838.4319	9.9793	12.6097	6.8713	90.00	104.15	90.00
0.7082	840.1959	10.0108	12.5552	6.8979	90.00	104.28	90.00
0.7505	841.9666	10.0519	12.4954	6.9222	90.00	104.45	90.00

Table S.14. Calculated volumetric compressibilities ($k_V = -1/\mathrm{V} \cdot (\partial V/\partial P)_P$) of zinc squarate tetrahydrate for different external pressures applied along the direction of minimum compressibility, [010].

P (GPa)	$k_V(\mathbf{TPa^{-1}})$	P (GPa)	$k_V(\mathbf{TPa^{-1}})$
-0.50	-5.28	0.20	-11.74
-0.45	-6.75	0.25	-11.75
-0.40	-9.04	0.29	-1021.92
-0.35	-11.90	0.30	-58.34
-0.30	-15.04	0.35	-85.92
-0.25	-18.09	0.40	-103.46
-0.20	-20.71	0.45	-93.16
-0.15	-22.59	0.50	-63.10
-0.10	-23.49	0.55	-33.42
-0.05	-23.27	0.60	-23.41
0.00	-21.92	0.65	-38.80
0.05	-19.60	0.70	-58.90
0.10	-16.69	0.75	-24.00
0.15	-13.78	-	-

Fig. S.1. Views of the computed unit cell of zinc squarate tetrahydrate from [001] under the effect of two different pressures applied along the direction of minimum compressibility: (A) P = 0.276 GPa; (B) P = 0.290 GPa.

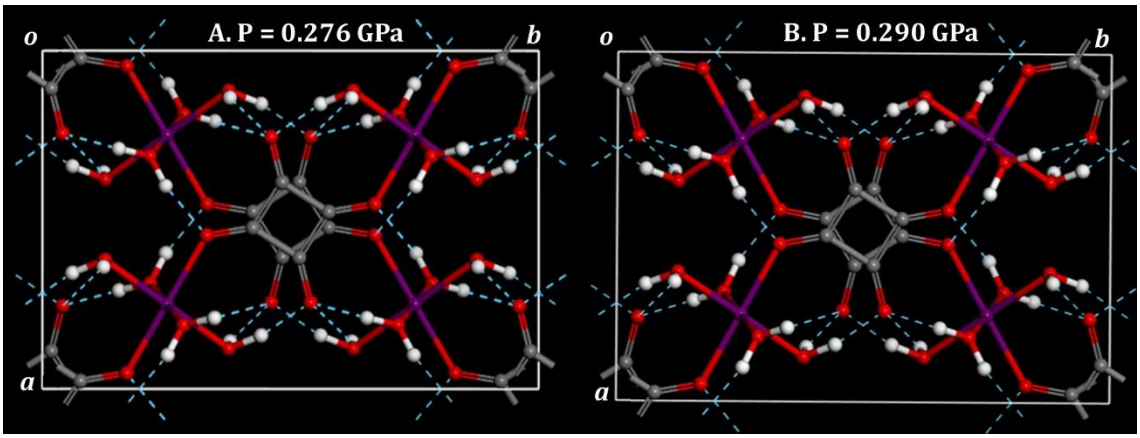

Table S.15. Unit cell volume and lattice parameters of titanium oxalate trioxide dihydrate under the effect of different external isotropic pressures.

P (GPa)	Vol. (Å^3)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ(deg)
-3.4995	1720.6618	15.3949	11.3295	9.8653	90.00	90.00	90.00
-2.9998	1699.8659	15.3913	11.2334	9.8317	90.00	90.00	90.00
-2.5001	1679.4531	15.3899	11.1354	9.8000	90.00	90.00	90.00
-1.9998	1659.1499	15.3949	11.0342	9.7672	90.00	90.00	90.00
-1.5001	1638.8068	15.4050	10.9296	9.7333	90.00	90.00	90.00
-1.0000	1618.2137	15.4200	10.8212	9.6979	90.00	90.00	90.00
-0.7503	1607.5812	15.4300	10.7644	9.6787	90.00	90.00	90.00
-0.4997	1597.0121	15.4402	10.7083	9.6590	90.00	90.00	90.00
-0.2506	1586.0487	15.4519	10.6493	9.6385	90.00	90.00	90.00
0.0001	1570.0510	15.4823	10.5510	9.6114	90.00	90.00	90.00
0.2508	1555.0545	15.5026	10.4658	9.5845	90.00	90.00	90.00
0.5002	1535.4443	15.5289	10.3522	9.5513	90.00	90.00	90.00
0.7504	1516.1407	15.5464	10.2438	9.5203	90.00	90.00	90.00
1.0000	1500.1189	15.5551	10.1585	9.4934	90.00	90.00	90.00
1.4998	1474.6533	15.5614	10.0324	9.4458	90.00	90.00	90.00
2.0001	1455.2941	15.5605	9.9454	9.4039	90.00	90.00	90.00
2.9996	1423.8666	15.5513	9.8170	9.3266	90.00	90.00	90.00
4.0000	1398.1137	15.5409	9.7192	9.2563	90.00	90.00	90.00

Table S.16. Calculated compressibilities of titanium oxalate trioxide dihydrate along a direction ($k_a = -1/a \cdot (\partial a/\partial P)_P$) for different external isotropic pressures.

P (GPa)	$k_a(\mathrm{TPa}^{-1})$	P (GPa)	$k_a(\mathrm{TPa}^{-1})$
-3.00	0.72	0.25	-6.58
-2.50	-0.30	0.50	-6.18
-2.00	-1.14	0.75	-3.91
-1.50	-1.49	1.00	-1.63
-1.00	-2.11	1.50	-0.20
-0.75	-2.77	2.00	0.35
-0.50	-3.72	2.50	0.60
-0.25	-4.85	3.00	0.78
0.00	-5.94	3.50	0.77

Table S.17. Unit cell volume and lattice parameters of titanium oxalate trioxide dihydrate under the effect of different external pressures applied along the direction of minimum compressibility, [100].

P (GPa)	Vol. ($Å^3$)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ(deg)
-1.0009	1555.0068	15.9133	10.3396	9.4508	90.00	90.00	90.00
-0.7172	1557.4324	15.7985	10.3857	9.4920	90.00	90.00	90.00
-0.5013	1560.0484	15.7084	10.4244	9.5269	90.00	90.00	90.00
-0.3331	1563.2535	15.6348	10.4677	9.5519	90.00	90.00	90.00
-0.2498	1564.7442	15.5980	10.4867	9.5661	90.00	90.00	90.00
-0.1672	1566.5938	15.5597	10.5077	9.5819	90.00	90.00	90.00
0.0006	1570.0644	15.4823	10.5510	9.6114	90.00	90.00	90.00
0.1674	1573.4620	15.4034	10.5951	9.6413	90.00	90.00	90.00
0.2500	1575.9919	15.3588	10.6232	9.6593	90.00	90.00	90.00
0.3334	1578.1013	15.3150	10.6494	9.6759	90.00	90.00	90.00
0.5005	1582.4577	15.2237	10.7093	9.7063	90.00	90.00	90.00
0.6674	1586.4240	15.1292	10.7647	9.7409	90.00	90.00	90.00
0.8328	1590.2233	15.0308	10.8271	9.7716	90.00	90.00	90.00
1.0000	1593.3192	14.9295	10.8843	9.8052	90.00	90.00	90.00
1.3337	1598.4311	14.7184	11.0069	9.8667	90.00	90.00	90.00
1.6662	1601.1461	14.5013	11.1255	9.9244	90.00	90.00	90.00
2.0009	1601.7892	14.2859	11.2359	9.9790	90.00	90.00	90.00
2.6658	1597.9674	13.8620	11.4372	10.0791	90.00	90.00	90.00
3.3335	1589.1939	13.4615	11.6111	10.1674	90.00	90.00	90.00
4.0003	1577.3757	13.0762	11.7633	10.2548	90.00	90.00	90.00

Table S.18. Calculated volumetric compressibilities ($k_V = -1/\mathrm{V} \cdot (\partial V/\partial P)_P$) of titanium oxalate trioxide dihydrate for different external pressures applied along the direction of minimum compressibility, [010].

P (GPa)	$k_V(\mathrm{TPa}^{-1})$	P (GPa)	$k_V(\mathrm{TPa}^{-1})$
-1.00	-3.50	0.50	-15.35
-0.72	-7.02	0.67	-14.53
-0.50	-9.88	0.83	-13.30
-0.33	-11.90	1.00	-11.69
-0.25	-12.78	1.33	-7.70
-0.17	-13.55	1.67	-3.30
0.00	-14.78	2.00	0.89
0.17	-15.49	2.67	6.56
0.25	-15.65	3.50	9.61
0.33	-15.68	-	-

Table S.19. Unit cell volume and lattice parameters of titanium oxalate trioxide trihydrate under the effect of different external isotropic pressures.

P (GPa)	Vol. (Å^3)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ(deg)
-0.2497	1592.8611	15.7968	10.8649	9.2808	90.00	90.00	90.00
-0.0010	1585.6488	15.7967	10.8294	9.2691	90.00	90.00	90.00
0.2498	1578.3418	15.7965	10.7940	9.2567	90.00	90.00	90.00
0.4990	1571.2949	15.7964	10.7602	9.2444	90.00	90.00	90.00
0.7499	1563.7431	15.7967	10.7224	9.2322	90.00	90.00	90.00
0.9988	1556.5141	15.7970	10.6864	9.2204	90.00	90.00	90.00
1.4989	1541.6091	15.7963	10.6116	9.1969	90.00	90.00	90.00
2.0000	1526.3997	15.7938	10.5349	9.1739	90.00	90.00	90.00
3.0000	1496.5243	15.7834	10.3843	9.1307	90.00	90.00	90.00
4.0005	1468.3155	15.7632	10.2456	9.0915	90.00	90.00	90.00
5.0004	1442.2247	15.7374	10.1192	9.0564	90.00	90.00	90.00

Table S.20. Calculated compressibilities of titanium oxalate trioxide trihydrate along a direction ($k_a = -1/a \cdot (\partial a/\partial P)_P$) for different external isotropic pressures.

P (GPa)	$k_a(\mathrm{TPa}^{-1})$	P (GPa)	$k_a(\mathrm{TPa}^{-1})$
-0.10	0.05	0.80	-0.10
0.00	0.06	0.90	-0.09
0.10	0.06	1.00	-0.07
0.20	0.05	1.10	-0.02
0.30	0.03	1.20	0.04
0.40	0.00	1.30	0.12
0.50	-0.03	1.40	0.21
0.60	-0.06	1.50	0.30
0.70	-0.08		

Table S.21. Unit cell volume and lattice parameters of titanium oxalate trioxide trihydrate under the effect of different external pressures applied along the direction of minimum compressibility, [100].

P (GPa)	Vol. (Å^3)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ(deg)
-0.9998	1588.5317	16.2824	10.6947	9.1223	90.00	90.00	90.00
-0.6674	1586.7909	16.1155	10.7363	9.1711	90.00	90.00	90.00
-0.5002	1586.2030	16.0343	10.7582	9.1954	90.00	90.00	90.00
-0.3328	1585.8963	15.9540	10.7814	9.2200	90.00	90.00	90.00
-0.2504	1585.9209	15.9140	10.7952	9.2315	90.00	90.00	90.00
-0.1662	1585.9831	15.8744	10.8085	9.2435	90.00	90.00	90.00
-0.0840	1585.9211	15.8346	10.8204	9.2561	90.00	90.00	90.00
0.0001	1585.5359	15.7967	10.8288	9.2689	90.00	90.00	90.00
0.0846	1584.9613	15.7607	10.8362	9.2804	90.00	90.00	90.00
0.2015	1584.7977	15.7066	10.8506	9.2991	90.00	90.00	90.00
0.3328	1585.0600	15.6454	10.8713	9.3191	90.00	90.00	90.00
0.5001	1585.3539	15.5692	10.8992	9.3425	90.00	90.00	90.00
0.6655	1585.7595	15.4935	10.9258	9.3677	90.00	90.00	90.00
0.9994	1586.2337	15.3462	10.9761	9.4171	90.00	90.00	90.00
1.6669	1586.7386	15.0621	11.0739	9.5131	90.00	90.00	90.00
2.3331	1587.2333	14.7890	11.1718	9.6068	90.00	90.00	90.00
2.9997	1587.6221	14.5250	11.2720	9.6969	90.00	90.00	90.00
3.6660	1587.7488	14.2714	11.3733	9.7820	90.00	90.00	90.00
3.9993	1587.6855	14.1486	11.4250	9.8218	90.00	90.00	90.00

Table S.22. Calculated volumetric compressibilities ($k_V = -1/\mathrm{V} \cdot (\partial V/\partial P)_P$) of titanium oxalate trioxide trihydrate for different external pressures applied along the direction of minimum compressibility, [010].

P (GPa)	$k_V(\mathbf{TPa^{-1}})$	P (GPa)	$k_V(\mathbf{TPa^{-1}})$
-0.80	3.30	0.20	-0.46
-0.70	2.91	0.25	-1.19
-0.60	2.37	0.30	-1.32
-0.50	1.70	0.40	-1.31
-0.40	0.94	0.50	-1.26
-0.30	0.13	0.60	-1.18
-0.25	-0.38	0.70	-1.09
-0.20	-0.52	0.80	-0.98
-0.15	-0.08	0.90	-0.87
-0.10	1.06	1.00	-0.77
-0.05	2.65	1.50	-0.42
0.00	4.11	2.00	-0.39
0.05	3.92	2.50	-0.46
0.10	2.07	3.00	-0.32
0.15	0.62	3.50	0.04

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