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Supporting information for article:

High-pressure and environment effects in selenourea and its labile crystal field around molecules

Kinga Roszak and Andrzej Katrusiak

S1. Tables

S1.1. Crystallographic details

Table S1 Crystallographic data of selenourea phase α and experimental details.

Pressure (GPa)	0.0001	0.0001	0.10	0.18	
CCDC number	2061316	2061317	2061318	2061319	
Formula	SeC(NH ₂) ₂				
Crystal form	Polymorph α	Polymorph α	Polymorph α	Polymorph α	
Formula weight	123.02	123.02	123.02	123.02	
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	
Crystal system	trigonal	trigonal	trigonal	trigonal	
Space group	<i>P</i> 3 ₂	<i>P</i> 3 ₂	<i>P</i> 3 ₂	<i>P</i> 3 ₂	
Unit cell dimensions (Å):	<i>a</i> <i>c</i>	15.2768(3)	15.2792(15)	15.2661(14)	15.3025(10)
		13.0239(3)	13.0326(9)	13.0260(8)	13.0498(7)
Volume (Å ³)	2632.31(12)	2634.9(5)	2629.0(5)	2646.4(4)	
Z/Z'	27/9	27/9	27/9	27/9	
Density (g/cm ³)	2.095	2.093	2.098	2.084	
Absorption coeff. (mm ⁻¹)	9.399	9.390	9.411	9.349	
Radiation type, λ (Å)	MoK α , 0.71073				
F(000)	1566	1566	1566	1566	
Crystal size (mm)	0.30·0.10·0.05	0.30·0.25·0.05	0.30·0.25·0.05	0.48·0.10·0.05	
Θ-range for data (°)	6.158 to 54.188	8.73 to 54.046	8.736 to 54.084	8.802 to 50.000	
Min/max indices h, k, l	-19/19, -18/19, -16/15	-13/13, -19/19, -16/16	-13/13, -19/19, -16/16	11/-11, 18/-18, 15/-15	
Reflect. collected/unique	37197/7250	13716/4059	13651/4062	10411/2981	
R _{int}	0.0630	0.0969	0.0900	0.0875	
Data/restrains/parameters	7250/0/326	4059/133/326	4062/137/326	2981/97/326	
Goodness-of-fit on F ²	1.085	1.020	1.020	1.013	
Final R ₁ /wR ₂ (I>2σ ₁)	0.0499/0.1049	0.0962/0.1721	0.0984/0.1351	0.0684/0.1545	
R ₁ /wR ₂ (all data)	0.0830/0.1189	0.1225/0.1971	0.1087/0.1878	0.1271/0.1876	

Table S1 (continued). Crystallographic data of selenourea phase α and experimental details.

Pressure (GPa)	0.20	0.23
CCDC number	2061320	2061315
Formula	SeC(NH ₂) ₂	SeC(NH ₂) ₂
Crystal form	Polymorph α	Polymorph α
Formula weight	123.02	123.02
Wavelength (Å)	0.71073	0.71073
Crystal system	trigonal	trigonal
Space group	<i>P</i> 3 ₂	<i>P</i> 3 ₂
Unit cell dimensions (Å):		
<i>a</i>	15.1445(10)	15.243(4)
<i>c</i>	12.9631(7)	13.009(3)
Volume (Å ³)	2574.8(4)	2617.7(15)
Z/Z'	27/9	27/9
Density (g/cm ³)	2.142	2.107
Absorption coeff. (mm ⁻¹)	9.609	9.451
Radiation type, λ (Å)	MoK α , 0.71073	MoK α , 0.71073
F(000)	1566	1566
Crystal size (mm)	0.35·0.20·0.05	0.30·0.25·0.05
Θ -range for data (°)	8.804 to 53.406	9.264 to 52.45
Min/max indices h, k, l	-11/11, -19/18, -16/16	-5/8, -13/12, -16/14
Reflect. collected/unique	10694/3131	2691/1795
R _{int}	0.0889	0.0563
Data/restrains/parameters	3131/103/326	1795/179/326
Goodness-of-fit on F ²	1.035	1.033
Final R ₁ /wR ₂ (I>2σ ₁)	0.0717/0.1620	0.0823/0.1874
R ₁ /wR ₂ (all data)	0.1364/0.2050	0.1568/0.2366

Table S2. Crystallographic data of selenourea phase β and experimental details.

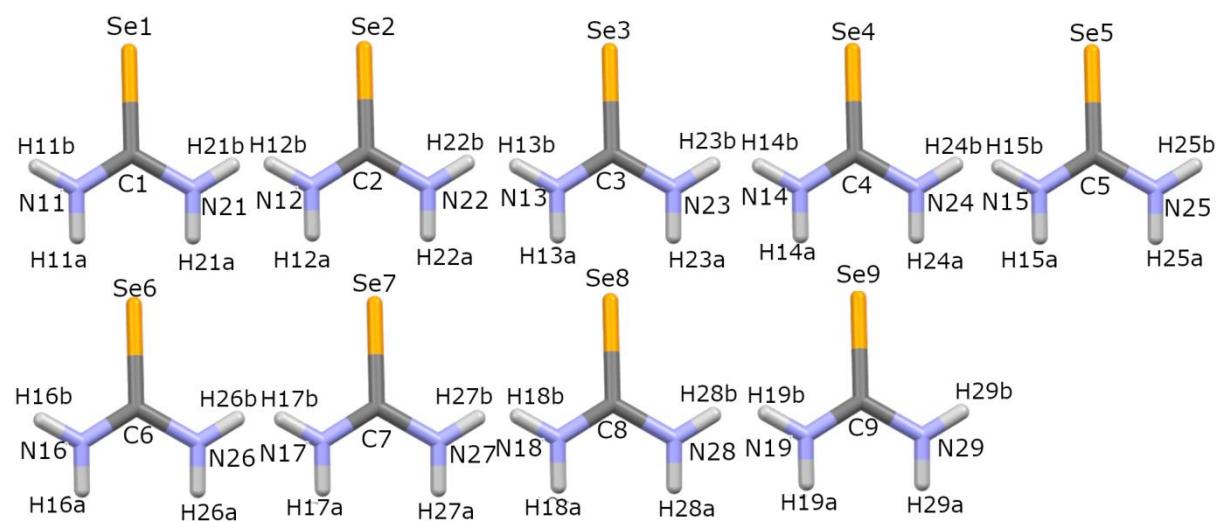
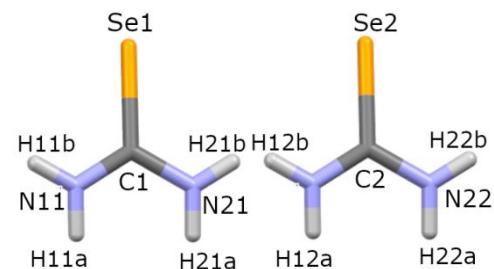
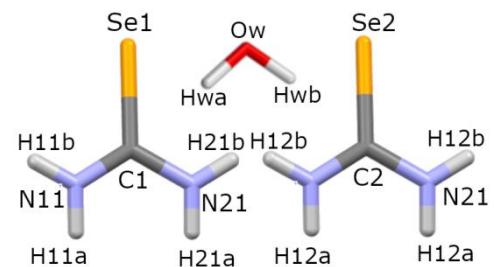
Pressure (GPa)	0.21	0.28	0.38	0.58
CCDC number	2061307	2061308	2061309	2061310
Formula	SeC(NH ₂) ₂			
Crystal form	Polymorph β	Polymorph β	Polymorph β	Polymorph β
Formula weight	123.02	123.02	123.02	123.02
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ /c			
Unit cell dimensions (Å): <i>a</i>	7.6155(13)	7.6122(13)	7.5985(3)	7.570(3)
<i>b</i>	8.4109(7)	8.4048(7)	8.3869(7)	8.3144(14)
<i>c</i>	11.709(3)	11.707(3)	11.684(2)	11.604(4)
β	100.718(16)	100.702(16)	100.609(9)	100.75(3)
Volume (Å ³)	736.9(2)	736.0(2)	731.87(14)	717.6(4)
Z/Z'	8/2	8/2	8/2	8/2
Density (g/cm ³)	2.218	2.220	2.233	2.278
Absorption coeff.(mm ⁻¹)	9.948	9.960	10.016	10.216
Radiation type, λ (Å)	MoK α , 0.71073			
F(000)	464	464	464	464
Crystal size (mm)	0.40·0.30·0.05	0.40·0.30·0.05	0.40·0.30·0.05	0.40·0.30·0.05
Θ-range for data (°)	8.538 to 53.538	8.54 to 53.99	8.552 to 54.084	8.612 to 54.048
Min/max indices h, k, l	-7/7, -10/10, -9/9	-7/7, -10/10, -9/9	-9/9, -9/9, -8/8	-7/7, -10/10, -9/9
Reflect. collected/unique	3768/570	3774/571	3681/616	3394/556
R _{int}	0.0318	0.0312	0.0281	0.0488
Data/restrains/parameters	570/0/74	571/0/74	616/0/74	556/6/73
Goodness-of-fit on F ²	1.112	1.149	1.184	1.062
Final R ₁ /wR ₂ (I>2σ ₁)	0.0240/0.0516	0.0222/0.0490	0.0241/0.0592	0.0356/0.0747
R ₁ /wR ₂ (all data)	0.0327/0.0541	0.0294/0.0520	0.0305/0.0617	0.0517/0.0826

Table S2 (continued). Crystallographic data of selenourea phase β and experimental details.

Pressure (GPa)	1.01	1.79	2.52	3.20
CCDC number	2061311	2061312	2061313	2061314
Formula	SeC(NH ₂) ₂			
Crystal form	Polymorph β	Polymorph β	Polymorph β	Polymorph β
Formula weight	123.02	123.02	123.02	123.02
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ /c			
Unit cell dimensions (Å):				
<i>a</i>	7.444(3)	7.4559(11)	7.3826(5)	7.301(6)
<i>b</i>	8.231(8)	8.117(6)	8.0113(5)	7.909(5)
<i>c</i>	11.362(3)	11.373(11)	11.135(5)	11.066(6)
β	100.46(3)	100.53(3)	100.419(16)	102.60(1)
Volume (Å ³)	684.7(15)	676.7(8)	647.7(3)	623.6(7)
Z/Z'	8/2	8/2	8/2	8/2
Density (g/cm ³)	2.387	2.415	2.523	2.621
Absorption coeff.(mm ⁻¹)	10.707	10.833	11.318	11.755
Radiation type, λ (Å)	MoK α , 0.71073			
F(000)	464	464	464	464
Crystal size (mm)	0.30·0.25·0.05	0.20·0.10·0.05	0.20·0.10·0.05	0.20·0.10·0.05
Θ-range for data (°)	9.952 to 51.526	11.128 to 53.344	10.18 to 53.282	8.762 to 50.964
Min/max indices h, k, l	-7/7, -3/3, -13/13	-9/9, -4/4, -5/5	-9/9, -10/10, -4/5	-7/7, -7/7, -4/4
Reflect. collected/unique	638/178	531/141	2838/320	458/175
R _{int}	0.2368	0.0912	0.0676	0.1169
Data/restrains/parameters	178/43/74	141/76/74	320/65/74	175/52/73
Goodness-of-fit on F ²	0.953	1.189	1.078	1.020
Final R ₁ /wR ₂ (I>2σ ₁)	0.0458/0.0464	0.0350/0.0739	0.0460/0.1033	0.0616/0.1427
R ₁ /wR ₂ (all data)	0.0750/0.0568	0.0716/0.0933	0.0682/0.1194	0.1101/0.1891

Table S3. Crystallographic data of selenourea duotrito hydrate and experimental details.

Pressure (GPa)	0.52	0.80	1.10
CCDC number	2061304	2061305	2061306
Formula	3SeC(NH ₂) ₂ ·H ₂ O	3SeC(NH ₂) ₂ ·H ₂ O	3SeC(NH ₂) ₂ ·H ₂ O
Crystal form	duotritohydrate	duotritohydrate	duotritohydrate
Formula weight	405.10	405.10	405.10
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions (Å):			
<i>a</i>	8.2698(12)	8.238(2)	8.1817(5)
<i>b</i>	8.8726(8)	8.8548(4)	8.8186(10)
<i>c</i>	16.913(3)	16.8134(11)	16.7510(10)
β	90.205(17)	90.628(14)	90.979(6)
Volume (Å ³)	1241.0(3)	1226.4(3)	1208.43(17)
Z/Z'	4/0.5	4/0.5	4/0.5
Density (g/cm ³)	2.168	2.194	2.227
Absorption coeff.(mm ⁻¹)	8.883	8.988	9.122
Radiation type, λ (Å)	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
F(000)	776	776	776
Crystal size (mm)	0.25·0.10·0.05	0.25·0.20·0.05	0.35·0.20·0.05
Θ-range for data (°)	6.736 to 52.728	9.208 to 53.36	9.916 to 53.744
Min/max indices h, k, l	-9/9, -10/10, -16/16	-5/5, -10/10, -19/20	-9/9, -7/8, -19/19
Reflect. collected/unique	3221/584	3105/473	3029/520
R _{int}	0.1610	0.0309	0.0334
Data/restrains/parameters	584/0/69	473/0/69	520/0/69
Goodness-of-fit on F ²	0.968	1.154	1.066
Final R ₁ /wR ₂ (I>2σ _I)	0.0477/0.1022	0.0225/0.0539	0.0230/0.0509
R ₁ /wR ₂ (all data)	0.0734/0.1165	0.0247/0.0549	0.0286/0.0528

S2. Figures**Figure S1** Atomic labels of symmetry-independent molecules in Selenourea phase α .**Figure S2** Atomic labels of symmetry-independent molecules in Selenourea phase β .**Figure S3** Atomic labels of symmetry-independent molecules in Selenourea duotritohydrate.

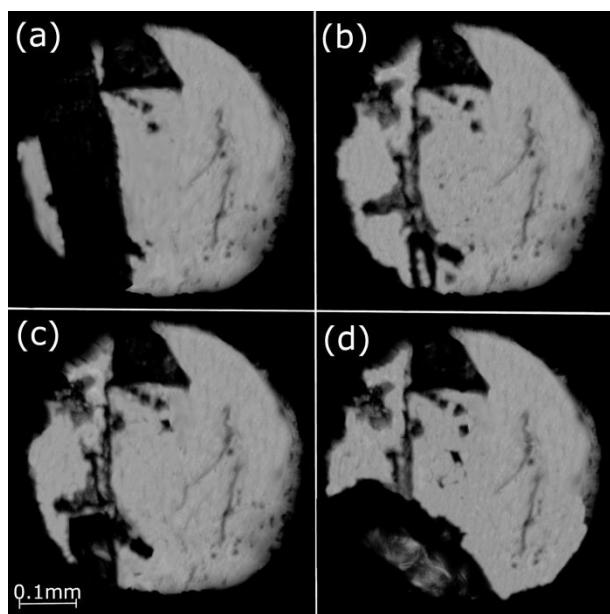


Figure S4 Stages of $3\text{SeC}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ single-crystal isochoric growth from the aqueous solution at: (a) 345 K, (b) 322 K, (c) 318 K and (d) 0.52 GPa/296 K. The ruby chip for pressure calibration is located close to the gasket upper edge.

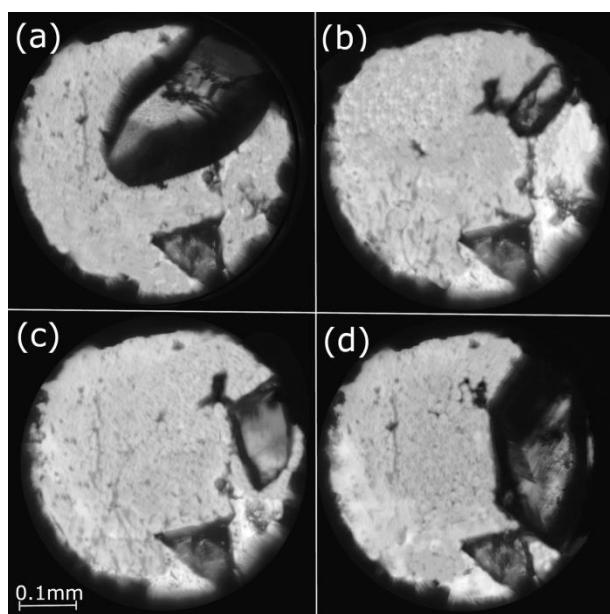


Figure S5 Stages of $3\text{SeC}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ single-crystal isochoric growth from the aqueous solution at: (a) 393 K, (b) 373 K, (c) 323 K and (d) 1.10 GPa/296 K. The ruby chip for pressure calibration is located close to the gasket upper edge.

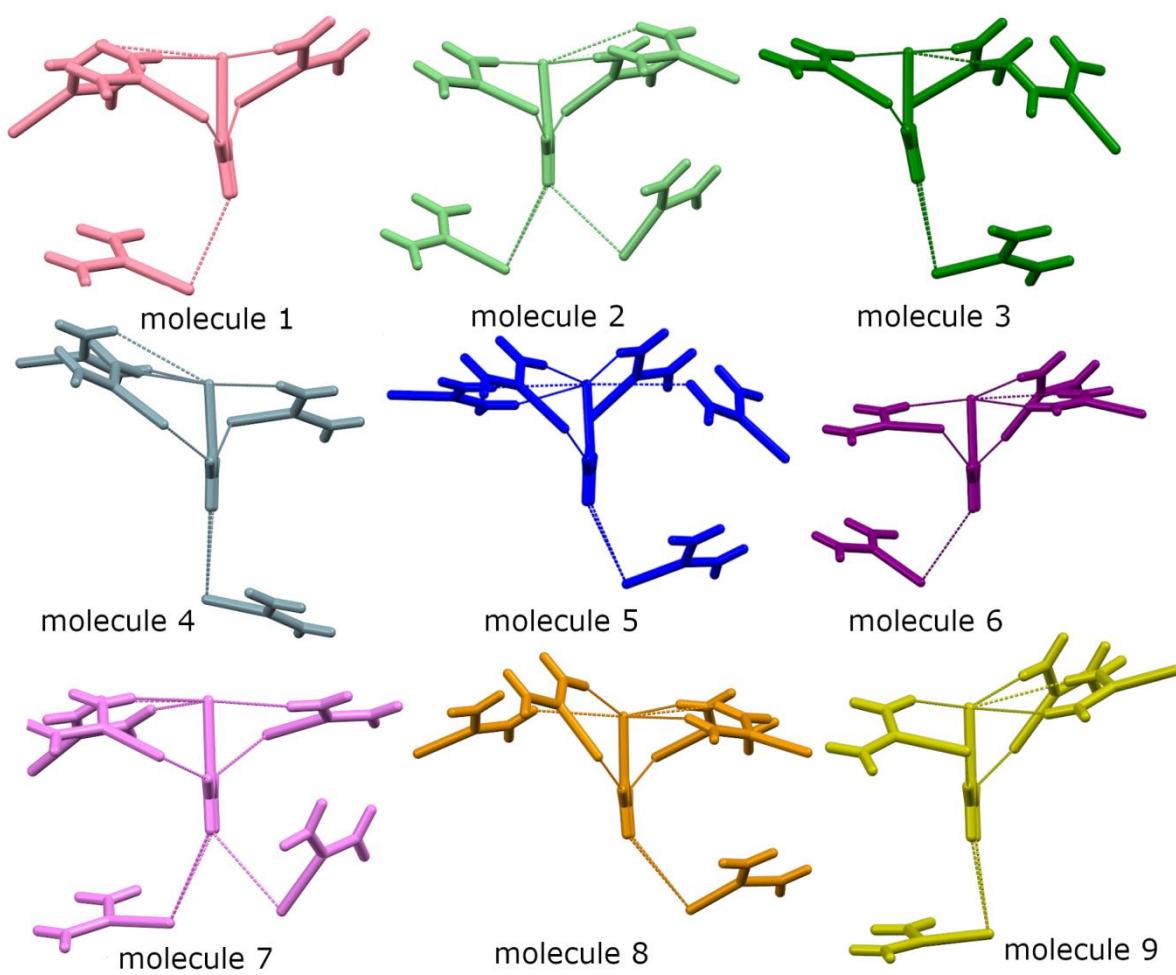


Figure S6 The components of Figure 6a shown for each of the central molecules viewed in the direction parallel to its average plane.

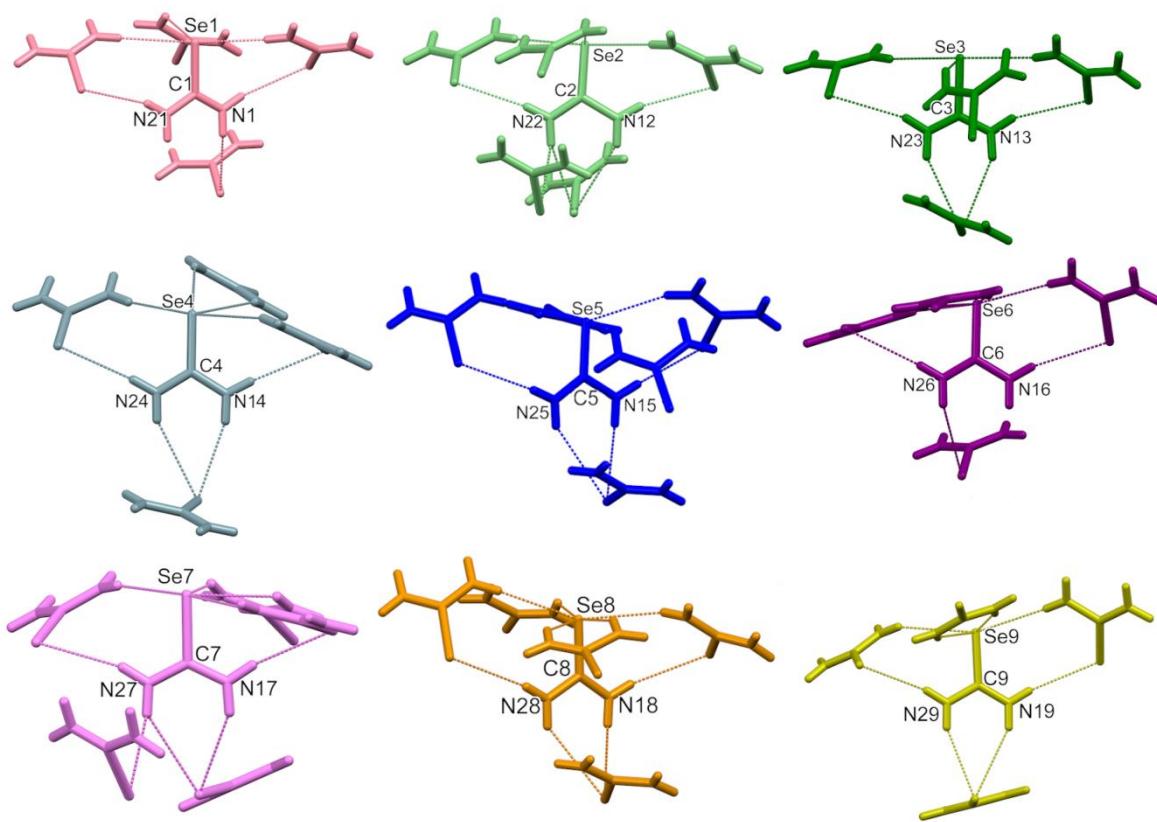


Figure S7 The components of Figure 6a shown for each of the central molecules viewed in the direction perpendicular to its average plane. The Se, C and N atoms are labelled for distinguishing the central molecules.

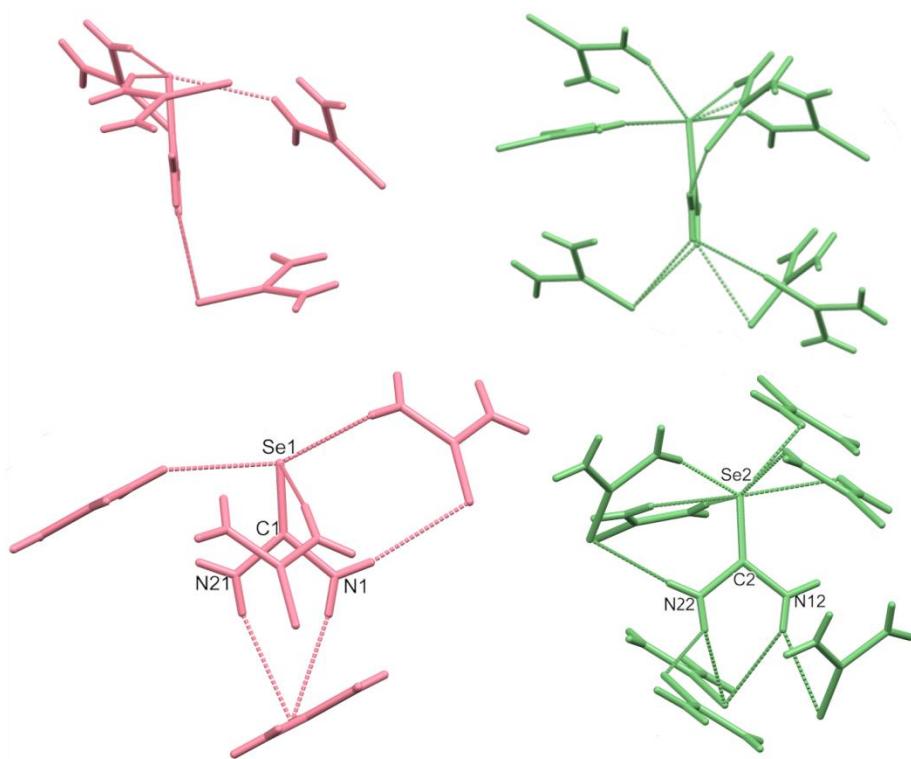


Figure S8 The components of Figure 6b shown for each of the central molecules viewed in the direction perpendicular and parallel to its average plane. The Se, C and N atoms are labelled for distinguishing the central molecules.

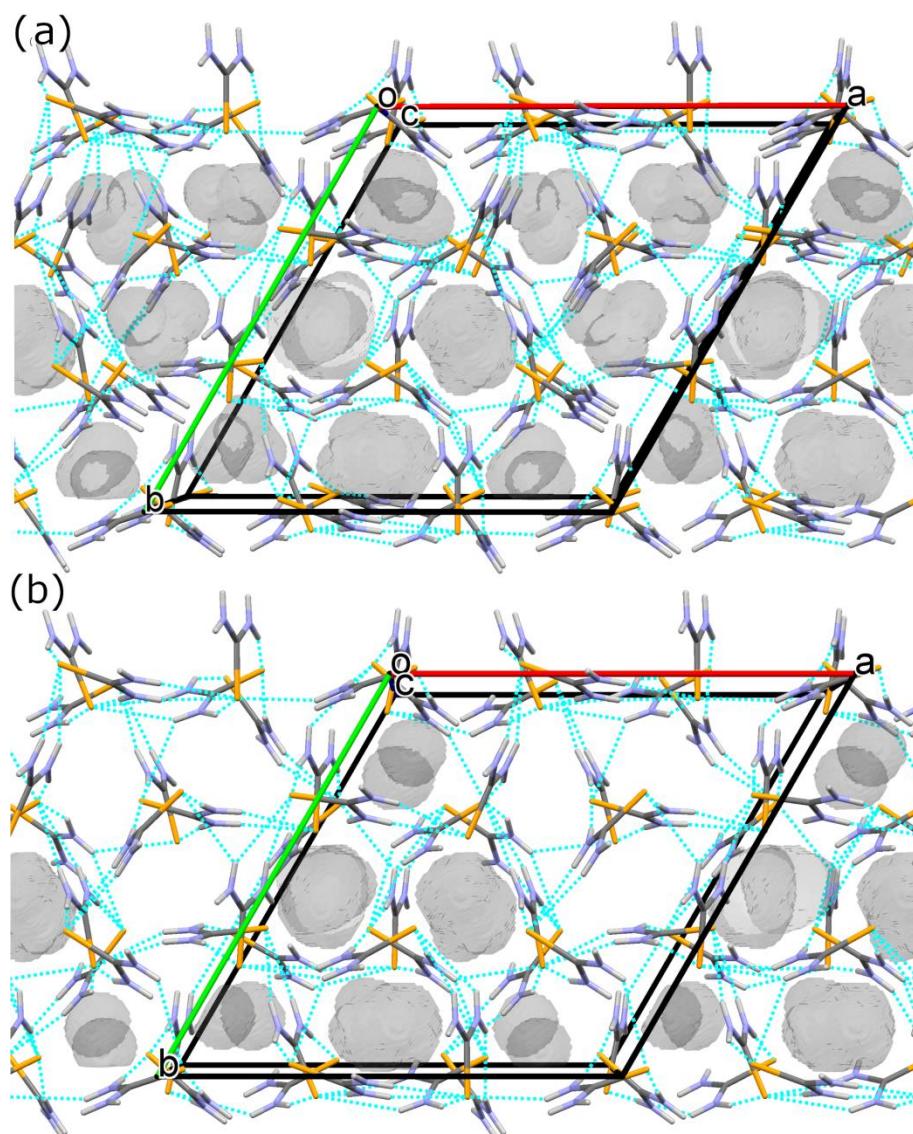


Figure S9 Crystal structure of $\text{SeC}(\text{NH}_2)_2$ phases α at: (a) 0.18 GPa and (b) 0.20 GPa. Hydrogen bonds $\text{NH}\cdots\text{Se}$ are indicated by blue dashed lines and the voids shown in yellow were calculated by Mercury (Macrae *et al.*, 2020) for the probe radius of 1.0 Å and grid step 0.1 Å.

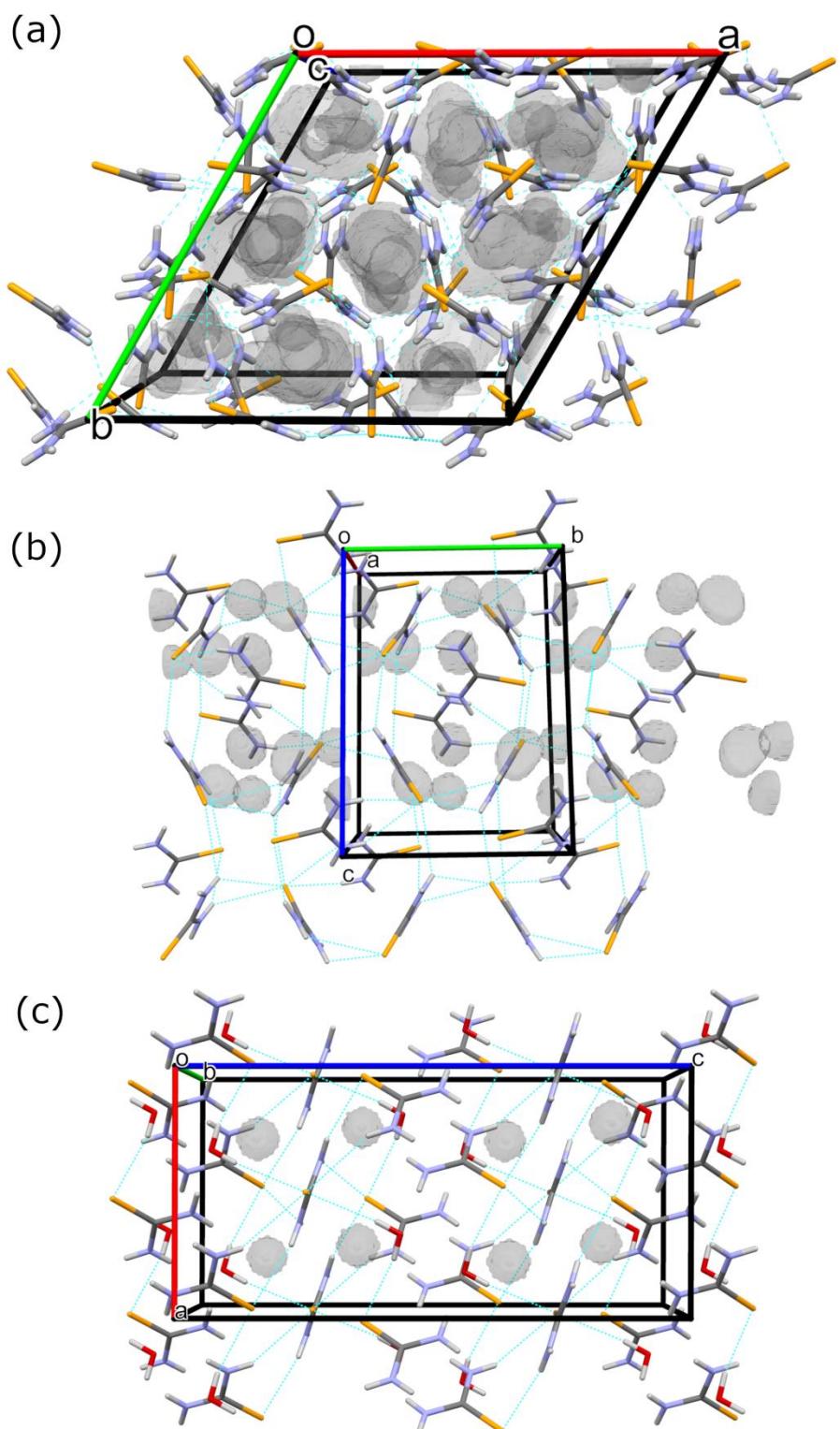


Figure S10 Crystal structure of $\text{SeC}(\text{NH}_2)_2$ phases: (a) α at 0.1 MPa, (b) β at 0.21 GPa; and (c) duotritohydrate at 0.52 GPa. Hydrogen bonds $\text{NH}\cdots\text{Se}$ and $\text{OH}\cdots\text{Se}$ in duotritohydrate are indicated by blue dashed lines and the voids shown in yellow were calculated by Mercury (Macrae *et al.*, 2020) for the probe radius of 0.7 Å and grid step 0.1 Å.

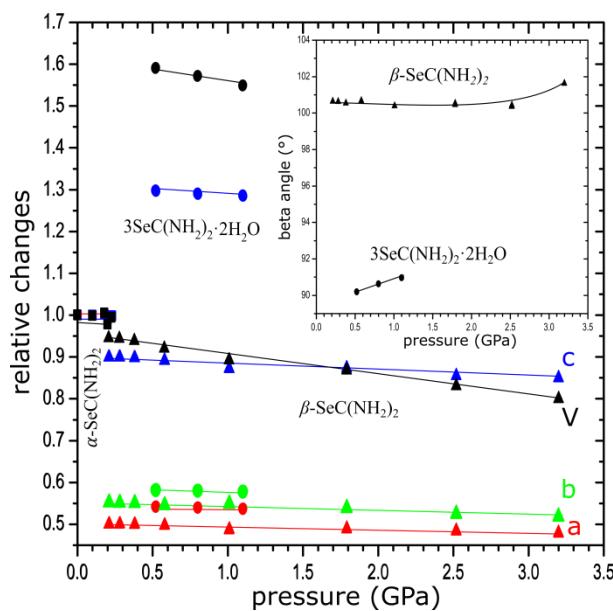


Figure S11 Compression of the unit-cell dimensions of $\text{SeC}(\text{NH}_2)_2$ polymorph α (square), polymorph β (triangle) and $3\text{SeC}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ (circle) related to the 0.1 MPa/296 K values. The lines joining the points are for guiding the eye only. Estimated standard deviations are smaller than the plotted symbols.

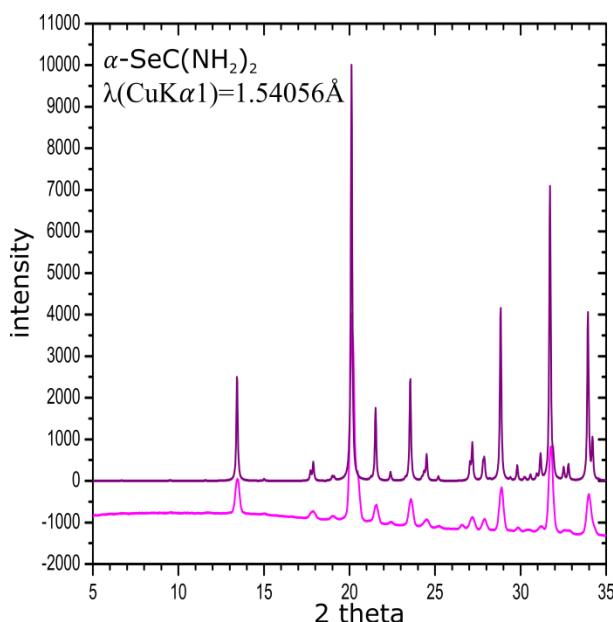


Figure S12 Calculated (top) and measurement (bottom) X-ray powder diffraction pattern for $\alpha\text{-SeC}(\text{NH}_2)_2$ at 0.1 MPa and 296 K.

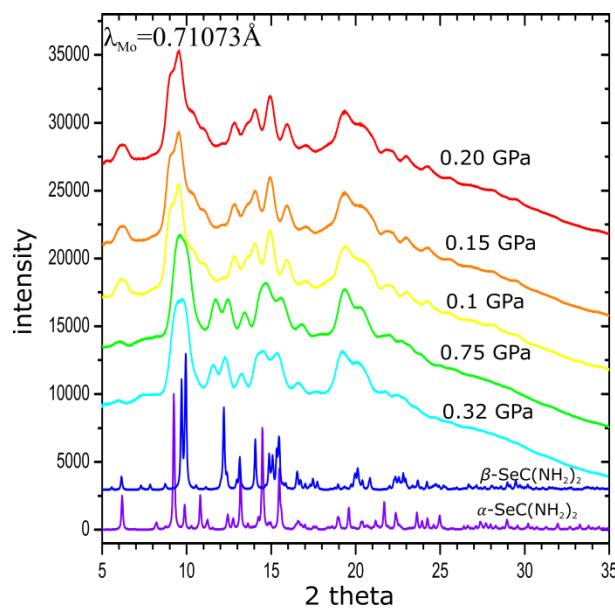


Figure S13 Calculated X-ray diffraction patterns for $\alpha\text{-SeC}(\text{NH}_2)_2$ and $\beta\text{-SeC}(\text{NH}_2)_2$ (bottom), as well as the measured powder patterns for the sample compressed in glycerin in a DAC (top).

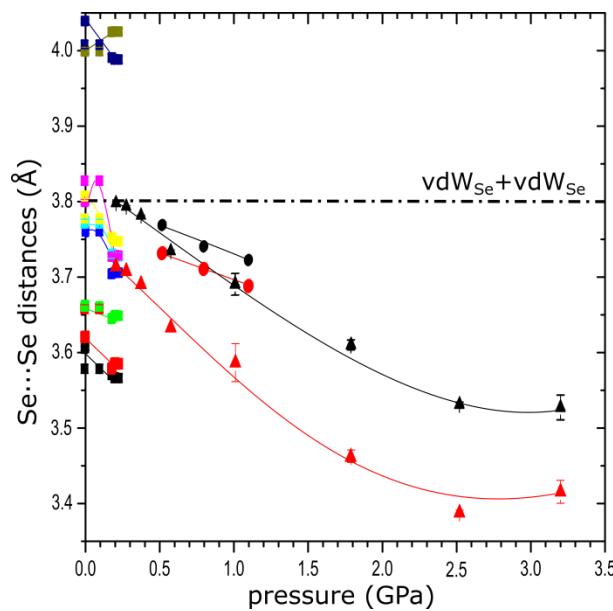


Figure S14 Distances Se...Se in the structure of $\text{SeC}(\text{NH}_2)_2$ phases α (square) and β (triangle), as well as in $3\text{SeC}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ (circle), plotted as a function of pressure.

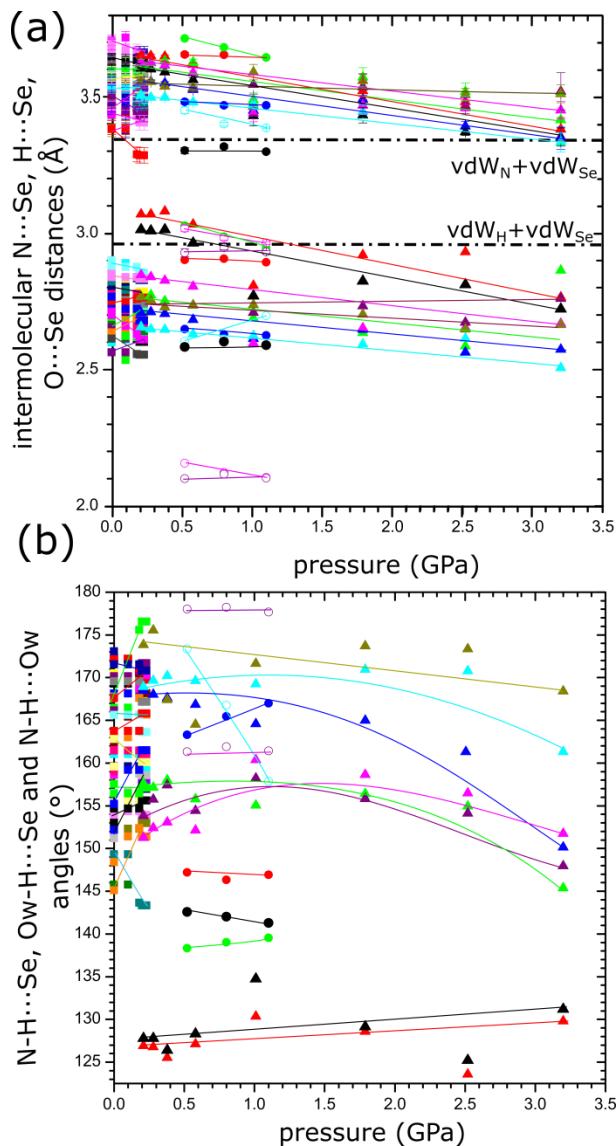
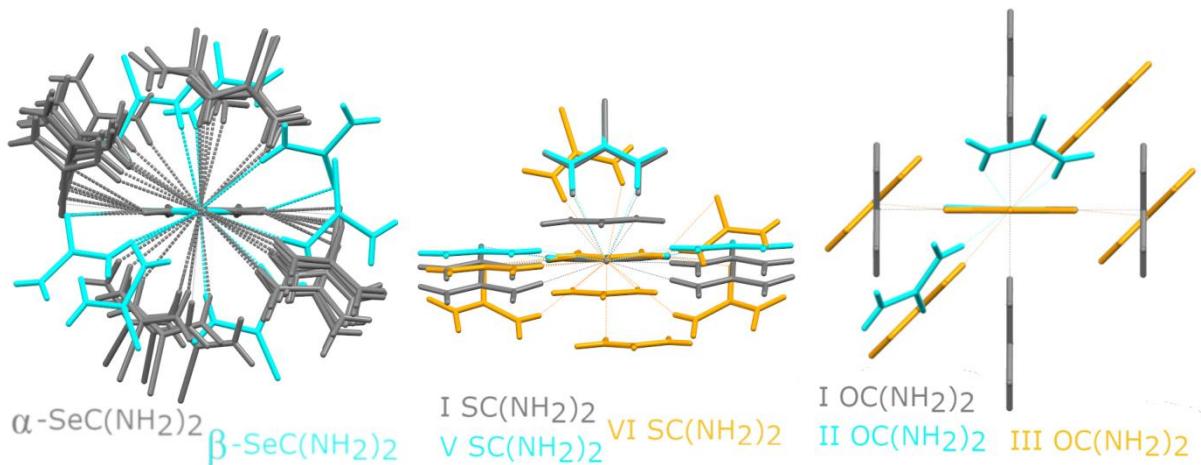


Figure S15 (a) Intermolecular distances and (b) angles Donor-H \cdots Acceptor measured as a function of pressure in α -SeC(NH₂)₂, β -SeC(NH₂)₂ and 3SeC(NH₂)₂ \cdot 2H₂O.



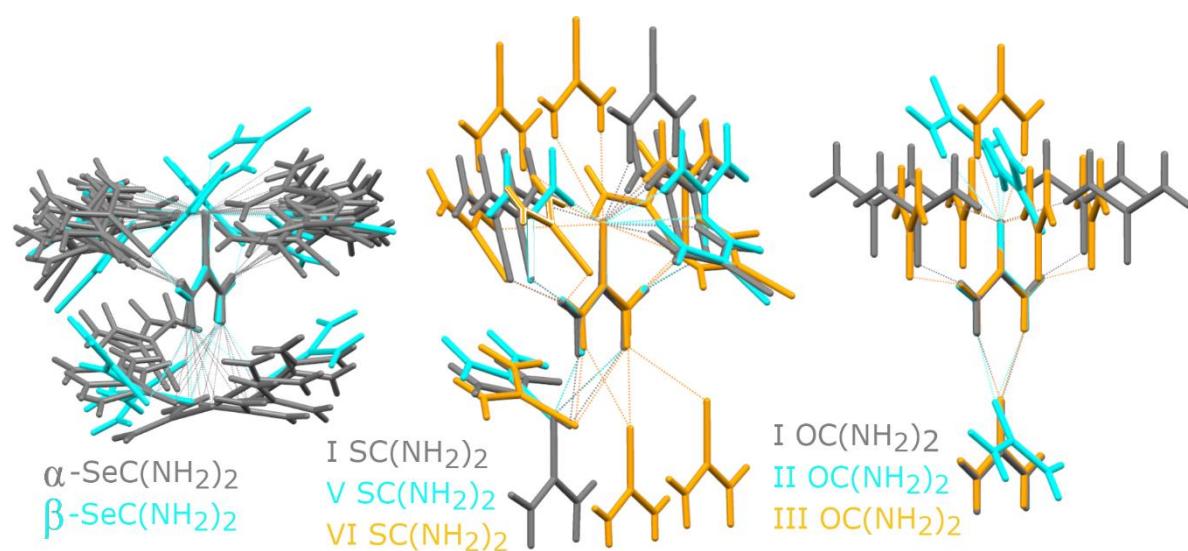


Figure S16 Exactly superimposed independent molecules and their $\text{NH}\cdots\text{X}$ ($\text{X}=\text{Se}, \text{O}, \text{S}$) bonded neighbours in Selenourea (phases α and β); urea (phases I, III and IV) and thiourea (Phase I, V and VI).