Supporting Information

1. Refinement Details

Structures were solved by Patterson methods (SHELXS–97) and were refined on F^2 as implemented in SHELXL–13. Non-H atoms were assigned anisotropic displacement parameters and hydrogen atoms connected to C were placed in idealized positions and included as riding with $U_{iso}(H) = 1.2\ U_{eq}(C)$ for CH and $U_{iso}(H) = 1.5\ U_{eq}(C)$ methyl groups. The H-atoms of the amino group were found in difference-Fourier maps and then restrained to equal distances.

1.1. Refinement Details of **1**

Hydrogen atoms related to amino groups were restrained to have similar distances to nitrogen. Water related hydrogen atoms were restrained to have similar distances towards oxygen.

1.2. Refinement Details of **2**

The hydrogen atoms of the water molecule were restrained to have similar distances to oxygen. Amino group related hydrogens were restrained to have similar distances to nitrogen. Atoms C8 and C9 were refined isotropically because the assignment of anisotropic displacement parameters led to oblate ellipsoids. Rigid bond restraints or isotropicity restraints only yielded a satisfactory model with high weighting of these pseudo observations. As the influence of those parameters on the overall structure model were low (*wR*2 anisotropic 0.0646; isotropic 0.0653) we chose isotropic refinement over the restrained refinement.

1.3. Refinement Details of **3**

Hydrogen atoms related to water and amino groups were found in difference-Fourier maps and then placed in idealized positions.

1.4. Refinement Details of **4**

The anisotropic displacement parameters of C7, C8 and C9 were refined with isotropicity restraints (ISOR s.u. 0.006). An anisotropic model led to physically unreasonable displacement parameters and unrestrained isotropic refinement effected the displacement parameters of other atoms (*wR*2 anisotropic 0.0985; isotropically restrained 0.0986). Hydrogen atoms related to water and amino groups were found in difference-Fourier maps and then placed in idealized positions.

1.5. Refinement Details of **5**

Hydrogen atoms connected to N1 and O3 were found in difference-Fourier maps and placed in idealized positions.

1.6. Refinement Details of **6**

Hydrogen atoms related to amino groups were found in difference-Fourier maps and then restrained to similar distances to nitrogen.

1.7. Refinement Details of **7**

Hydrogen atoms related to amino groups were found in difference-Fourier maps and then restrained to similar distances to nitrogen. H3W was positioned to give a reasonable water geometry and to point towards I1 (x,-1+y,z) for a reasonable hydrogen-bond network. After defining its position, H3W was treated as riding on O2W.

1.8. Refinement Details of **8** - **10**

The hydrogen atoms of the amino-group were restrained to same distances, as well as those of the coordinated and solvate water molecule. All of them were restrained as riding with $U_{iso}(H) = 1.2\ U_{eq}$(non-H). For **8** and **10** the hydrogen atoms of the coordinated water were restrained to a minimum distance of 1.3 Å to each other.

2. Asymmetric Units of all Compounds

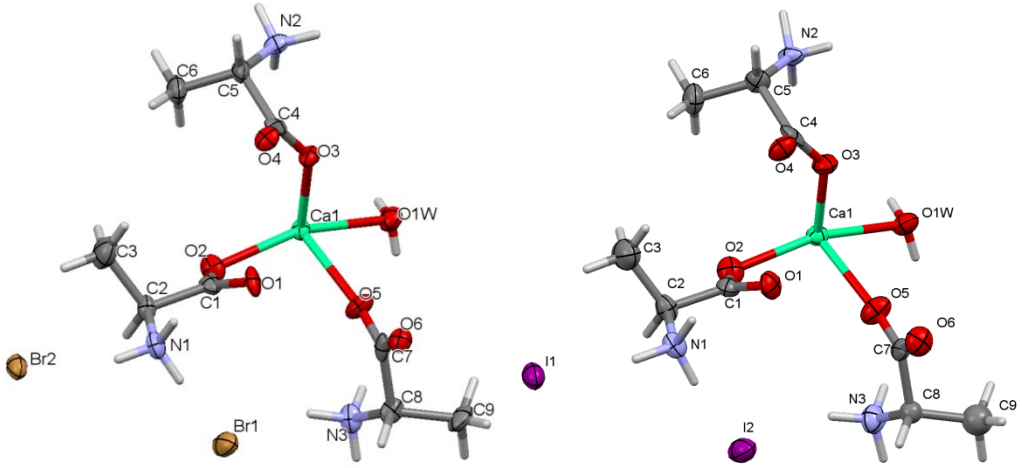

Figure 1: Asymmetric unit of structures **1** (left) and **2** (right) as displacement ellipsoid plot at 80% probability and adjacent atoms as capped sticks.

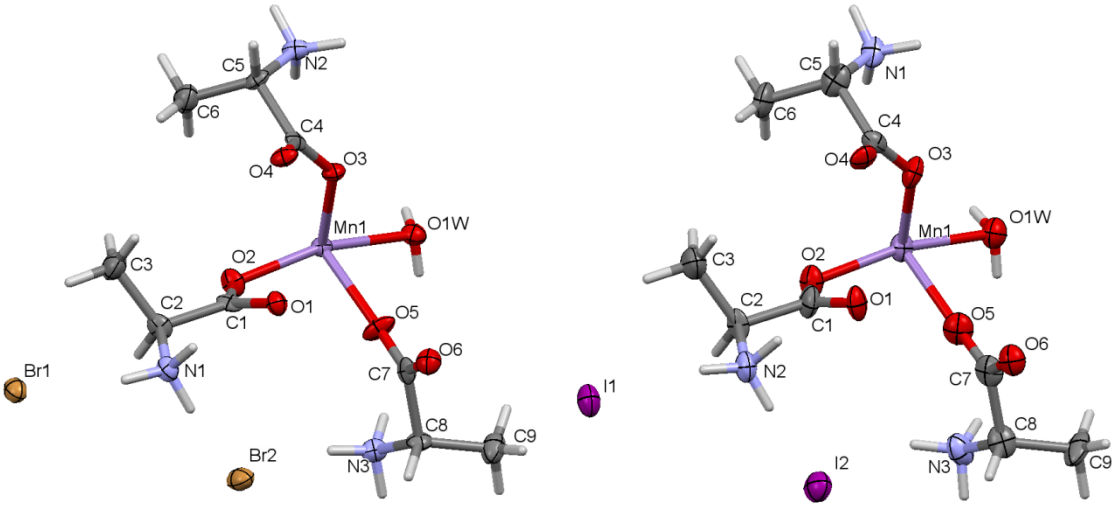

Figure 2: Asymmetric unit of structures **3** (left) and **4** (right) as displacement ellipsoid plot at 80% probability and adjacent atoms as capped sticks.

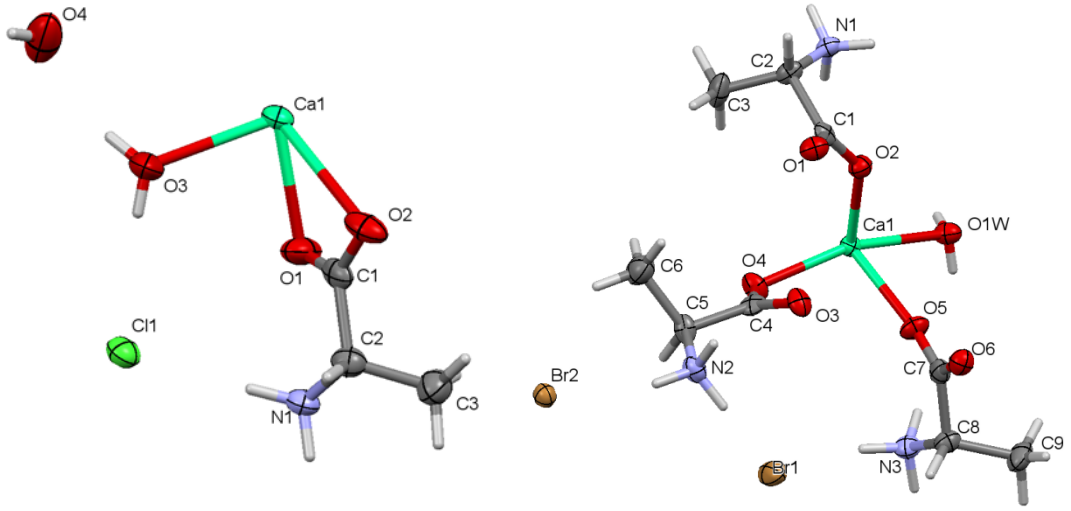

Figure 3: Asymmetric unit of structures **5** (left) and **6** (right) as displacement ellipsoid plot at 80% probability and adjacent atoms as capped sticks.

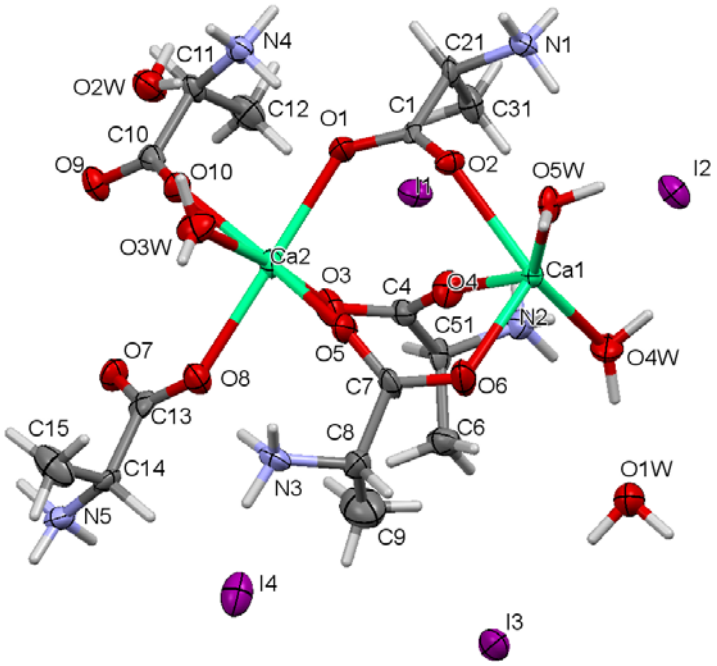

Figure 4: Asymmetric unit of structure **7** as displacement ellipsoid plot at 80% probability and adjacent atoms as capped sticks.

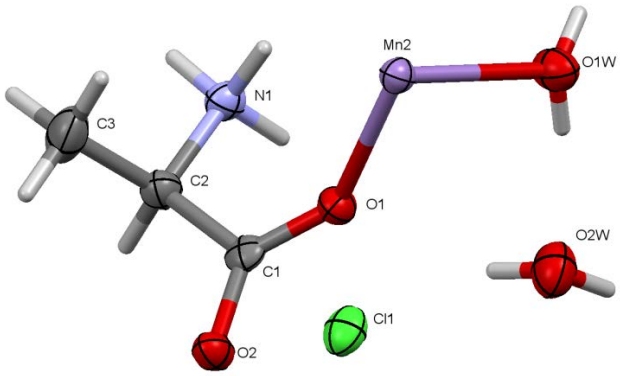

Figure 5: Asymmetric unit of structure **8** as displacement ellipsoid plot at 80% probability and adjacent atoms as capped sticks.

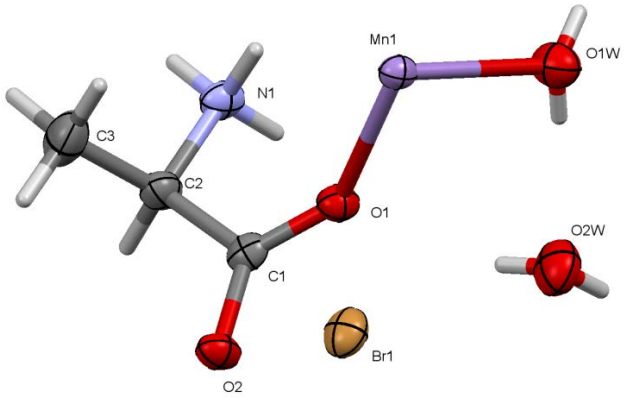

Figure 6: Asymmetric unit of structure **9** as displacement ellipsoid plot at 80% probability and adjacent atoms as capped sticks.

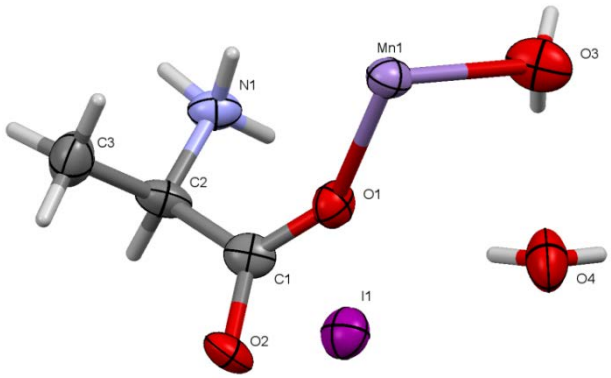

Figure 7: Asymmetric unit of structure **10** as displacement ellipsoid plot at 80% probability and adjacent atoms as capped sticks.

3. Full List of H-Bonds

Table 1: Full list of H-bonds of compound **1**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(16)···O(1)^{II}	0.89(5)	2.01(5)	2.865(6)	160(5)
N(1) – H(17)···Br(2)^{III}	0.89(4)	2.47(4)	3.317(5)	159(5)
N(1) – H(18)···Br(1)^{IV}	0.89(3)	2.63(6)	3.339(5)	137(5)
N(2) – H(5) ···Br(1)^{I}	0.90(4)	2.39(4)	3.274(5)	168(5)
N(2) – H(6) ···Br(2)	0.90(3)	2.57(5)	3.341(5)	144(5)
N(2) – H(7) ···O(4)^{II}	0.90(5)	1.88(5)	2.767(6)	168(5)
N(3) – H(19)···Br(2)	0.90(5)	2.87(6)	3.538(5)	132(5)
N(3) – H(20)···O(5)^{V}	0.90(5)	1.95(5)	2.848(6)	178(6)
N(3) – H(21)···Br(1)^{V}	0.88(4)	2.55(4)	3.392(5)	159(6)
O(1W) – H(22)···O(2)^{II}	0.75(6)	2.17(7)	2.876(5)	157(8)
O(1W) – H(23)···O(4)^{II}	0.75(5)	2.00(5)	2.737(5)	171(7)

^{I}: 2–x, 1/2+y, 1–z ^{II}: 1+x, y, z ^{III}: x, y, –1+z ^{IV}: 1–x, 1/2+y, –z ^{V}: –1+x, y, z

Table 2: Full list of H-bonds of compound **2**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1N)···O(2)^{V}	0.95(5)	1.91(5)	2.859(7)	177(6)
N(1) – H(2N)···I(2)	0.95(5)	2.83(5)	3.670(6)	149(4)
N(1) – H(3N)···I(1)^{V}	0.95(4)	2.69(4)	3.603(5)	162(5)
N(2) – H(4N)···I(1)^{IV}	0.95(4)	2.68(5)	3.559(7)	154(4)
N(2) – H(5N)···I(2)^{III}	0.95(3)	2.62(3)	3.523(6)	159(5)
N(2) – H(6N)···O(4)^{II}	0.95(5)	1.92(5)	2.842(8)	164(5)
N(3) – H(7N)···I(2)	0.95(3)	2.70(5)	3.561(7)	151(5)
N(3) – H(8N)···O(6)^{II}	0.95(6)	1.83(6)	2.768(8)	167(4)
N(3) – H(9N)···I(1)^{I}	0.96(4)	2.57(4)	3.511(6)	170(5)
O(1W) – H(1W)···O(3)^{II}	0.90(7)	2.05(7)	2.897(7)	157(6)
O(1W) – H(2W)···O(6)^{II}	0.73(8)	2.04(7)	2.750(7)	165(9)

^{I}: 2–x, 1/2+y, 1–z ^{II}: 1+x, y, z ^{III}: x, y, –1+z ^{IV}: 1–x, 1/2+y, –z ^{V}: –1+x, y, z

Table 3: Full list of H-bonds of compound **3**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1A)···Br(1)^{IV}	0.91	2.53	3.323(3)	146
N(1) – H(1B)···Br(2)^{III}	0.91	2.54	3.313(2)	143
N(1) – H(1C)···O(1)^{II}	0.91	1.99	2.870(4)	162
N(2) – H(2A)···Br(1)^{V}	0.90(2)	2.51(3)	3.395(3)	165(3)
N(2) – H(2B)···O(3)^{V}	0.91(3)	1.97(3)	2.857(4)	166(3)
N(2) – H(2C)···Br(2)	0.91(3)	2.72(3)	3.473(3)	142(3)
N(3) – H(3D)···Br(2)	0.91	2.54	3.335(3)	147
N(3) – H(3E)···Br(1)^{I}	0.91	2.41	3.290(2)	163
N(3) – H(3F)···O(6)^{II}	0.91	1.88	2.769(4)	164
O(1W) – H(1W)···O(2)^{II}	0.79(3)	2.15(4)	2.800(3)	141(4)
O(1W) – H(2W)···O(6)^{II}	0.80(3)	1.90(3)	2.700(3)	177(5)

^{I}: 2–x, 1/2+y, 1–z ^{II}: 1+x, y, z ^{III}: x, y, –1+z ^{IV}: 1–x, 1/2+y, –z ^{V}: –1+x, y, z

Table 4: Full list of H-bonds of compound **4**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1A)···O(2)^{II}	0.84(8)	2.01(8)	2.823(10)	162(7)
N(1) – H(1B)···I(1)^{IV}	0.84(7)	2.82(9)	3.535(8)	145(8)
N(1) – H(1C)···I(2)^{III}	0.84(6)	2.70(7)	3.504(8)	161(8)
N(2) – H(2A)···I(1)^{V}	0.96(6)	2.63(7)	3.585(8)	171(7)
N(2) – H(2B)···O(3)^{V}	0.95(8)	1.96(9)	2.861(11)	158(8)
N(2) – H(2B)···O(4)	0.95(8)	2.19(8)	2.671(11)	110(6)
N(2) – H(2C)···I(2)	0.96(8)	2.82(9)	3.614(9)	141(7)
N(3) – H(3A)···I(1)^{I}	0.91	2.63	3.526(8)	168
N(3) – H(3B)···O(6)^{II}	0.91	1.87	2.767(10)	170
N(3) – H(3C)···I(2)	0.91	2.77	3.539(8)	142
O(1W) – H(1W)···O(1)^{II}	0.85(9)	1.98(9)	2.823(10)	169(9)
O(1W) – H(2W)···O(6)^{II}	0.85(5)	1.89(5)	2.733(9)	174(–1)

^{I}: 2–x, 1/2+y, 1–z ^{II}: 1+x, y, z ^{III}: x, y, –1+z ^{IV}: 1–x, 1/2+y, –z ^{V}: –1+x, y, z

Table 5: Full list of H-bonds of compound **5**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1A)···Cl(1)^{I}	0.922(15)	2.292(16)	3.203(3)	169(2)
N(1) – H(1B)···Cl(1)	0.915(18)	2.296(18)	3.207(3)	174(3)
N(1) – H(1C)···Cl(1)^{II}	0.93(2)	2.25(2)	3.150(3)	165(2)
O(1W) – H(3D)···O(2W)	0.83(2)	2.05(2)	2.846(3)	161(3)
O(1W) – H(3E)···Cl(1)	0.804(19)	2.41(2)	3.212(2)	175(3)
O(2W) – H(4)···O(2)^{III}	0.84(2)	2.33(3)	3.000(3)	138(3)
O(2W) – H(4)···O(1W)^{IV}	0.84(2)	2.56(3)	3.303(3)	148(3)

^{I}: x, 1–y, 1/2+z ^{II}: 3/2–x, –1/2+y, z ^{III}: x, 1+y,z ^{IV}: 1–x, 2–y, –z

Table 6: Full list of H-bonds of compound **6**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1N)···O(2)^{V}	0.95(5)	1.91(5)	2.859(7)	177(6)
N(1) – H(2N)···I(2)	0.95(5)	2.83(5)	3.670(6)	149(4)
N(1) – H(3N)···I(1)^{V}	0.95(4)	2.69(4)	3.603(5)	162(5)
N(2) – H(4N)···I(1)^{IV}	0.95(4)	2.68(5)	3.559(7)	154(4)
N(2) – H(5N)···I(2)^{III}	0.95(3)	2.62(3)	3.523(6)	159(5)
N(2) – H(6N)···O(4)^{II}	0.95(5)	1.92(5)	2.842(8)	164(5)
N(3) – H(7N)···I(2)	0.95(3)	2.70(5)	3.561(7)	151(5)
N(3) – H(8N)···O(6)^{II}	0.95(6)	1.83(6)	2.768(8)	167(4)
N(3) – H(9N)···I(1)^{I}	0.96(4)	2.57(4)	3.511(6)	170(5)
O(1W) – H(1W)···O(3)^{II}	0.90(7)	2.05(7)	2.897(7)	157(6)
O(1W) – H(2W)···O(6)^{II}	0.73(8)	2.04(7)	2.750(7)	165(9)

^{I}: 2–x, 1/2+y, 1–z ^{II}: 1+x, y, z ^{III}: x, y, –1+z ^{IV}: 1–x, 1/2+y, –z ^{V}: –1+x, y, z

Table 7: Full list of H-bonds of compound **7**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1A)···I(1)^{I}	0.91	2.65	3.556(5)	175
N(1) – H(1B)···O(9)^{II}	0.91	1.97	2.860(7)	168
N(1) – H(1C)···I(2)^{III}	0.91	2.86	3.615(5)	142
N(2) – H(2A)···O(4)	0.91	2.34	2.723(7)	105
N(2) – H(2A)···O(4W)	0.91	2.04	2.916(7)	161
N(2) – H(2B)···I(1)	0.91	2.99	3.725(5)	139
N(2) – H(2C)···O(2)^{IV}	0.91	2.41	3.135(7)	137
N(2) – H(2C)···O(5W)^{IV}	0.91	2.18	2.998(7)	148
N(3) – H(3A)···O(8)	0.91	1.92	2.825(7)	173
N(3) – H(3B)···I(4)^{V}	0.91	3.03	3.715(6)	134
N(3) – H(3C)···I(3)^{VI}	0.91	2.65	3.524(5)	161
N(4) – H(4A)···I(2)^{V}	0.91	2.75	3.551(5)	148
N(4) – H(4B)···I(2)^{I}	0.91	2.75	3.651(5)	172
N(4) – H(4C)···O(1)	0.91	1.85	2.762(7)	175
N(5) – H(5B)···I(4)^{VII}	0.91	2.81	3.616(5)	149
N(5) – H(5C)···O(6)^{V}	0.91	1.88	2.784(7)	175
O(1W) – H(1W)···I(3)	0.92	2.50	3.415(4)	180
O(1W) – H(2W)···I(4)	0.92	2.56	3.481(4)	180
O(2W) – H(4W)···O(3)^{III}	0.92	1.84	2.764(6)	180
O(3W) – H(5W)···O(2W)	0.92	1.81	2.729(6)	179
O(3W) – H(6W)···I(4)^{V}	0.92	2.92	3.841(5)	180
O(4W) – H(7W)···O(1W)	0.92	1.83	2.752(6)	179
O(4W) – H(8W)···O(10)^{II}	0.93	1.85	2.775(6)	179
O(5W) – H(9W)···O(1W)^{III}	0.92	1.84	2.764(6)	179
O(5W) – H(10W) ..O(2W)^{VIII}	0.92	1.91	2.833(6)	179

^{I}: 1–x, –1/2+y, 3/2–z ^{II}: x, 1/2–y, 1/2+z ^{III}: x, –1+y, z ^{IV}: x, 1+y, z ^{V}: x, 1/2–y, –1/2+z
^{VI}: 2–x, –1/2+y, 3/2–z ^{VII}: x, 3/2–y, –1/2+z ^{VIII}: x, –1/2+y, 1/2+z

Table 8: Full list of H-bonds of compound **8**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1A)···Cl(1)^{I}	0.931(18)	2.277(18)	3.2044(19)	174.1(18)
N(1) – H(1B)···Cl(1)	0.943(19)	2.50(2)	3.292(2)	141.8(18)
N(1) – H(1C)···O(2)^{II}	0.923(19)	1.919(19)	2.809(2)	161.2(17)
O(1W) – H(3D)···O(2W)^{II}	0.81(2)	2.12(2)	2.926(2)	175.9(17)
O(1W) – H(3E)···O(2W)	0.81(2)	1.98(2)	2.781(2)	172(3)
O(2W) – H(4A)···Cl(1)	0.842(19)	2.41(2)	3.2210(18)	162(2)
O(2W) – H(4B)···Cl(1)^{III}	0.858(19)	2.31(2)	3.1572(17)	171.8(19)

^{I}: –1+x, y, z ^{II}: –1+x, 3/2–y, –1/2+z ^{III}: x, 3/2–y, 1/2+z

Table 9: Full list of H-bonds of compound **9**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1A)···Br(1)^{I}	0.89(2)	2.46(2)	3.3392(19)	171(2)
N(1) – H(1B)···Br(1)	0.90(2)	2.66(2)	3.4105(19)	142.3(19)
N(1) – H(1C)···O(2)^{II}	0.89(2)	1.94(2)	2.813(2)	168(2)
O(1W) – H(3D)···O(2W)^{II}	0.75(3)	2.15(2)	2.900(2)	176(2)
O(1W) – H(3E)···O(2W)	0.73(3)	2.06(2)	2.781(2)	174(3)
O(2W) – H(4A)···Br(1)	0.75(3)	2.68(3)	3.3743(18)	156(3)
O(2W) – H(4B)···Br(1)^{III}	0.74(3)	2.58(3)	3.3065(18)	168(3)

^{I}: –1+x, y, z ^{II}: –1+x, 3/2–y, –1/2+z ^{III}: x, 3/2–y, 1/2+z

Table 10: Full list of H-bonds of compound **10**.

Donor – H···Acceptor	D – H	H···A	D···A	D – H···A
N(1) – H(1A)···I(1)^{I}	0.93(6)	2.63(6)	3.561(7)	178(8)
N(1) – H(1B)···I(1)	0.93(6)	2.87(7)	3.629(7)	141(6)
N(1) – H(1C)···O(2)^{II}	0.93(6)	1.90(6)	2.796(8)	163(6)
O(3) – H(3D)···O(4)^{II}	0.81(7)	2.08(7)	2.869(9)	165(7)
O(3) – H(3E)···O(4)	0.81(7)	2.05(8)	2.785(9)	151(6)
O(4) – H(4A)···I(1)	0.82(6)	2.83(7)	3.579(6)	154(7)
O(4) – H(4B)···I(1)^{III}	0.82(6)	2.79(7)	3.518(6)	149(8)

^{I}: –1+x, y, z ^{II}: –1+x, 3/2–y, –1/2+z ^{III}: x, 3/2–y, 1/2+z

4. Crystallization Apparatus

To achieve controlled conditions and accelerated crystallization a custom build apparatus was used (see Figure 8). The lower part consists of a hollow brass block which can be heated or cooled by fluid passage. The inner part of the brass block contains cavities for snap-cap vials. The chamber containing the snap-cap vials is sealed by an acrylic glass plate which can be removed to afford access. For fast evaporation of solvents and rapid crystallization it is possible to pass dried air or inert gas throug the chamber. Additional heating possibilities an infrared lamp is placed about 15 cm above the apparaturs. Temperature controle is achieved via a sensor inside the chamber switching the lamp at a preset temperature (Figure 9).

Figure 8: Custom built crystallization apparatus (overhead heating off).

Figure 9: Custom built crystallization apparatus (overhead heating on).

5. Powder diffraction

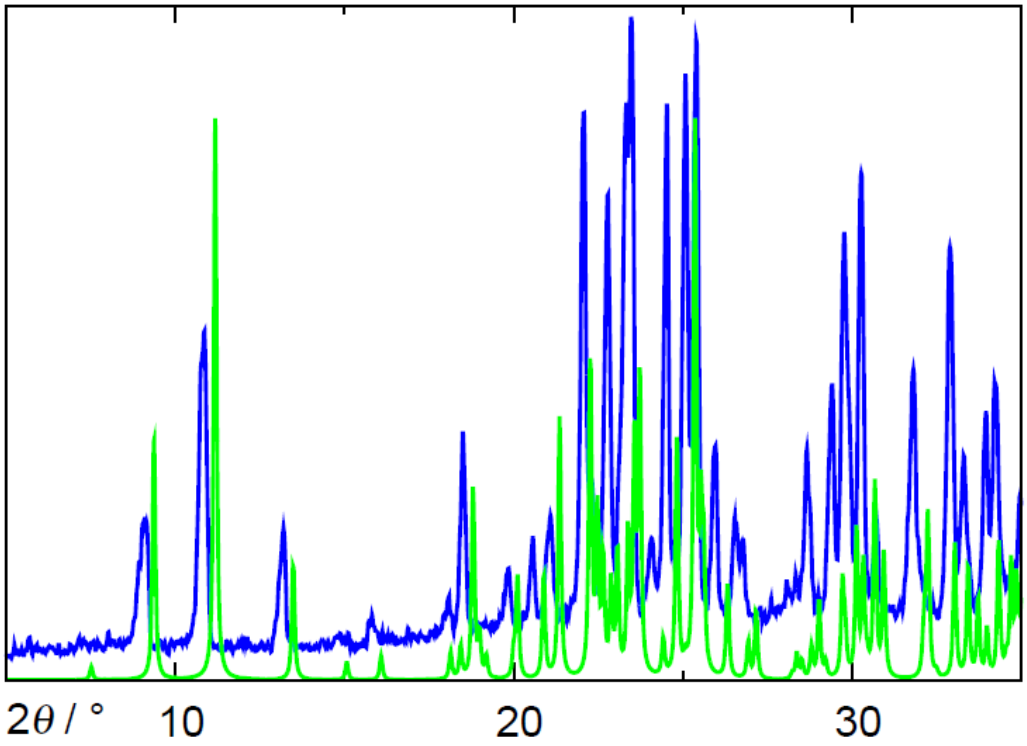

Figure 10: Measured X-ray powder diffractogram of structure **1** (blue) and calculated diffractogram (green) representative for structure type **I**.

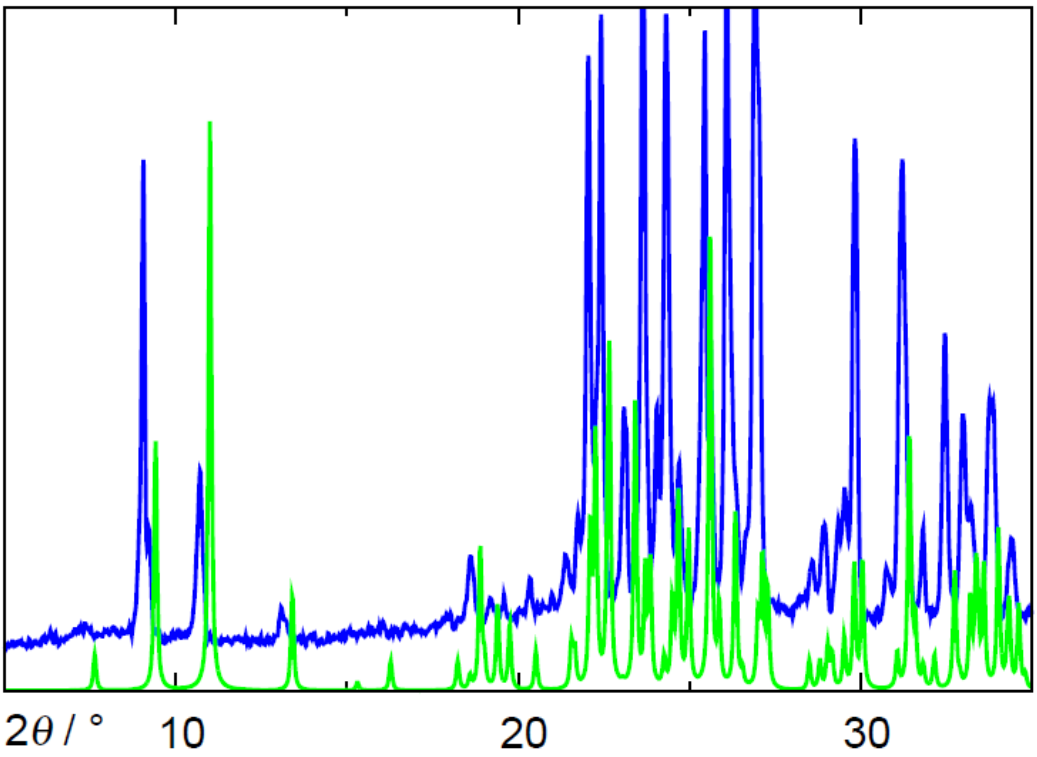

Figure 11: Measured X-ray powder diffractogram of structure **6** (blue) and calculated diffractogram (green) representative for structure type **II**.

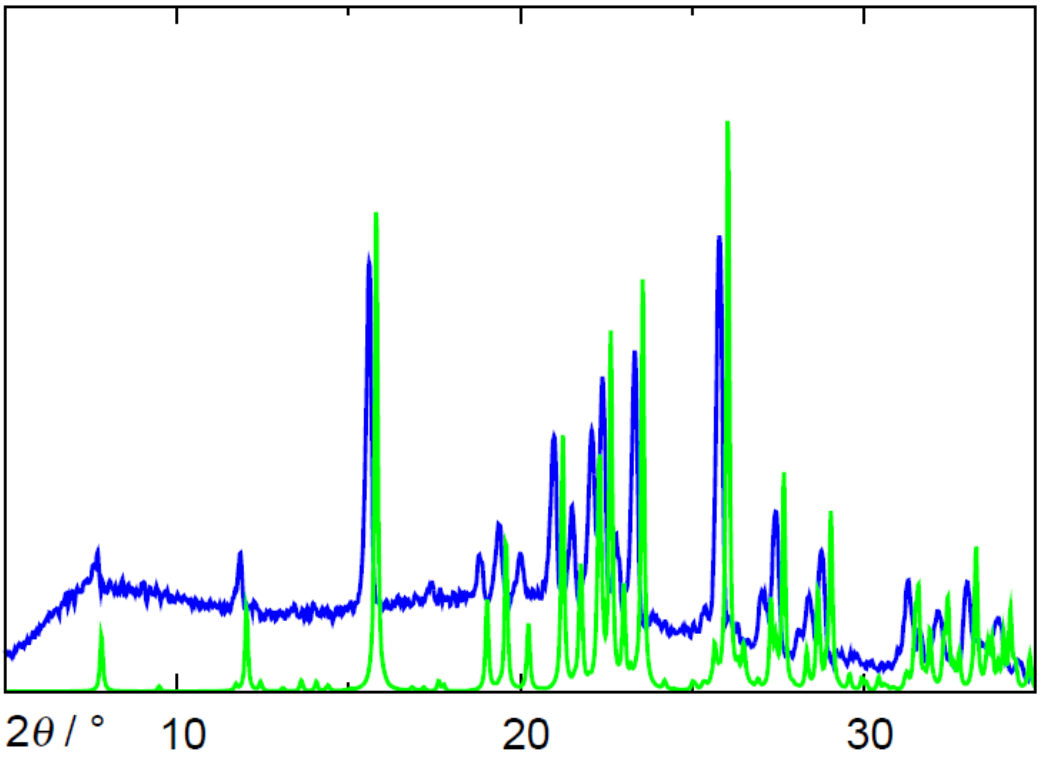

Figure 12: Measured X-ray powder diffractogram of structure **7** (blue) and calculated diffractogram (green) representative for structure type **III**.

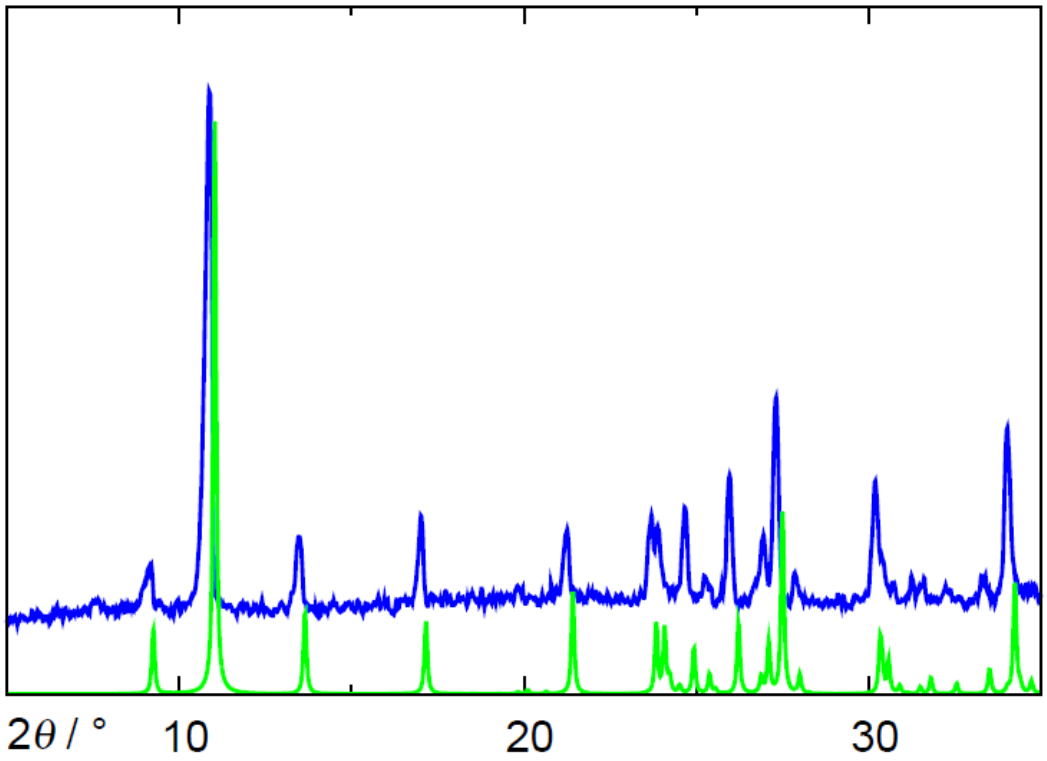

Figure 13: Measured X-ray powder diffractogram of structure **8** (blue) and calculated diffractogram (green) representative for structure type **IV**.