Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Material

Mechanochemical and Solution Reactions Between $AgCH_3COO$ and $[H_2NC_6H_{10}NH_2]$ Yield Three Isomers of the Coordination Network $\{Ag[H_2NC_6H_{10}NH_2]^+\}_\infty$

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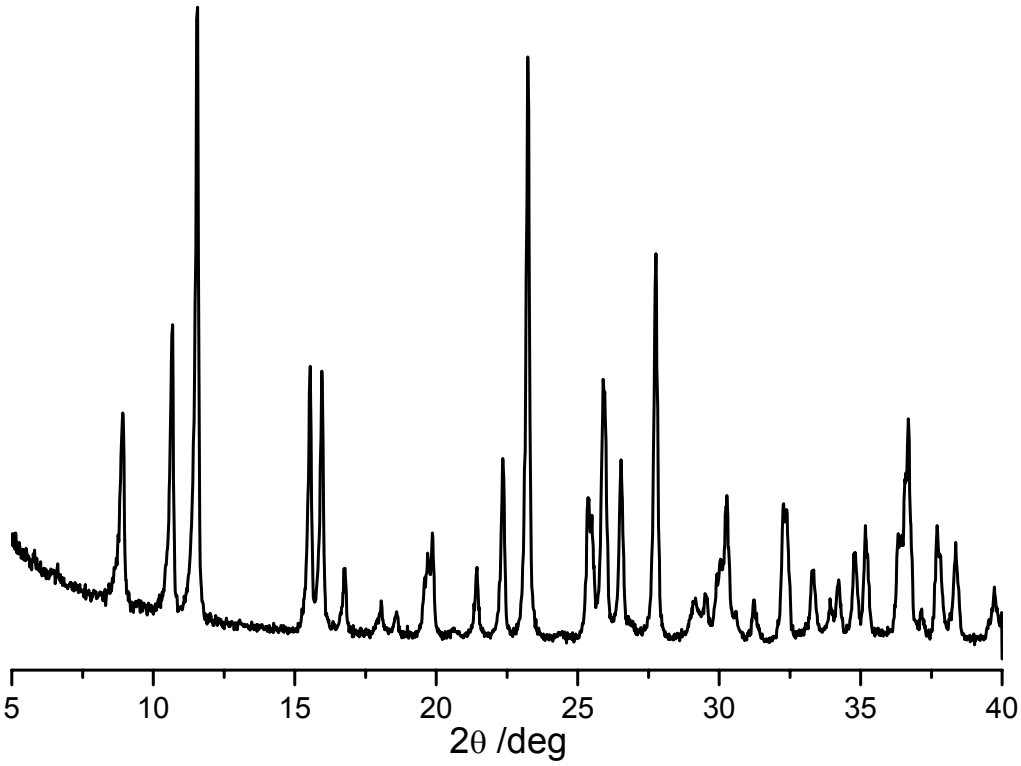


Figure 1. Observed X-ray powder pattern for **1·nH$_2$O**

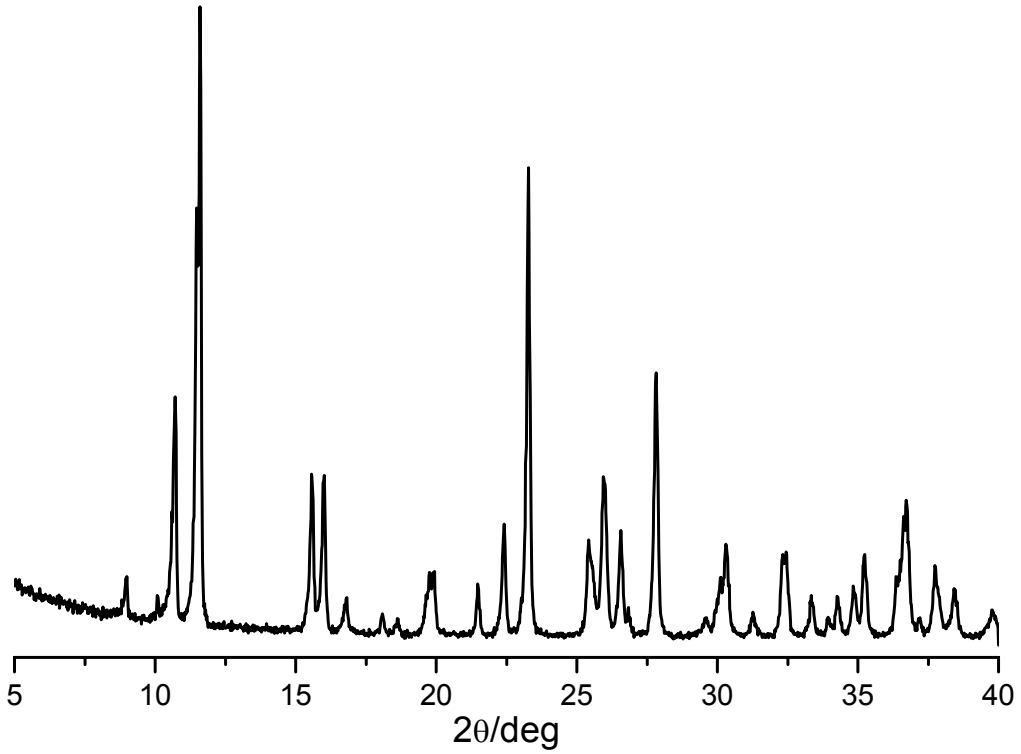


Figure 2. Observed X-ray powder pattern for **1·MeOH·0.5H$_2$O** after grinding. Note how the pattern coincides with that observed for **1·nH$_2$O**

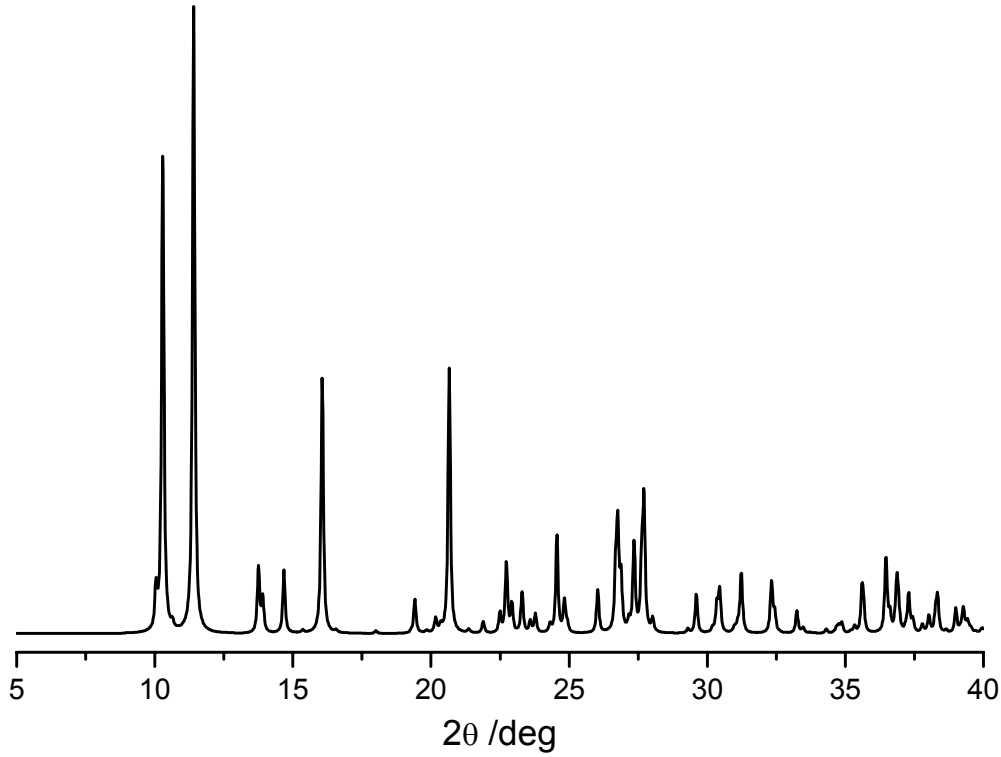


Figure 3. Calculated X-ray powder pattern for **1·MeOH·0.5H$_2$O**

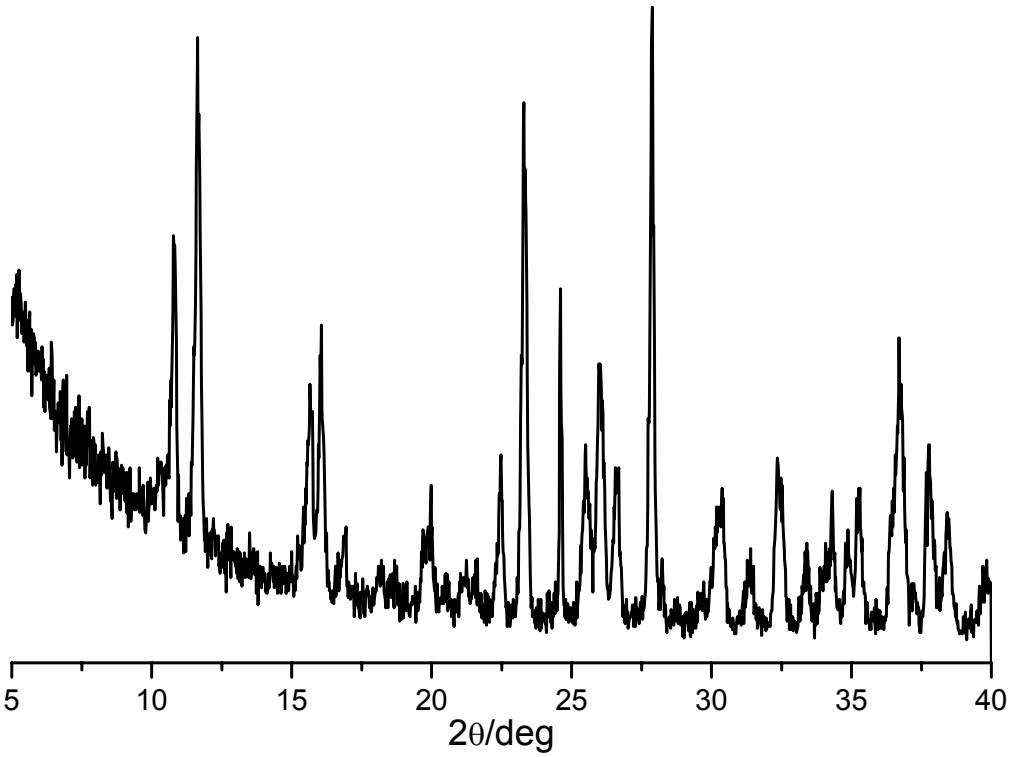


Figure 4. Observed X-ray powder pattern for **1·3H$_2$O** after grinding. Note how the pattern coincides with that observed for **1·nH$_2$O**

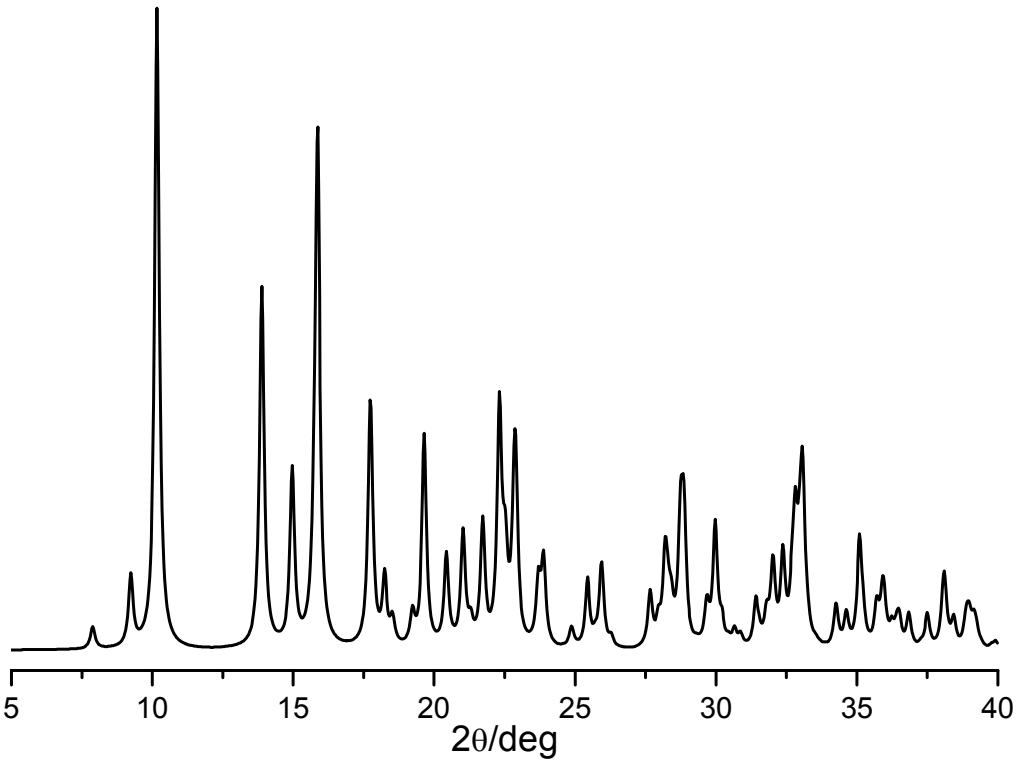


Figure 5. Calculated X-ray powder pattern for **1·nH$_2$O**

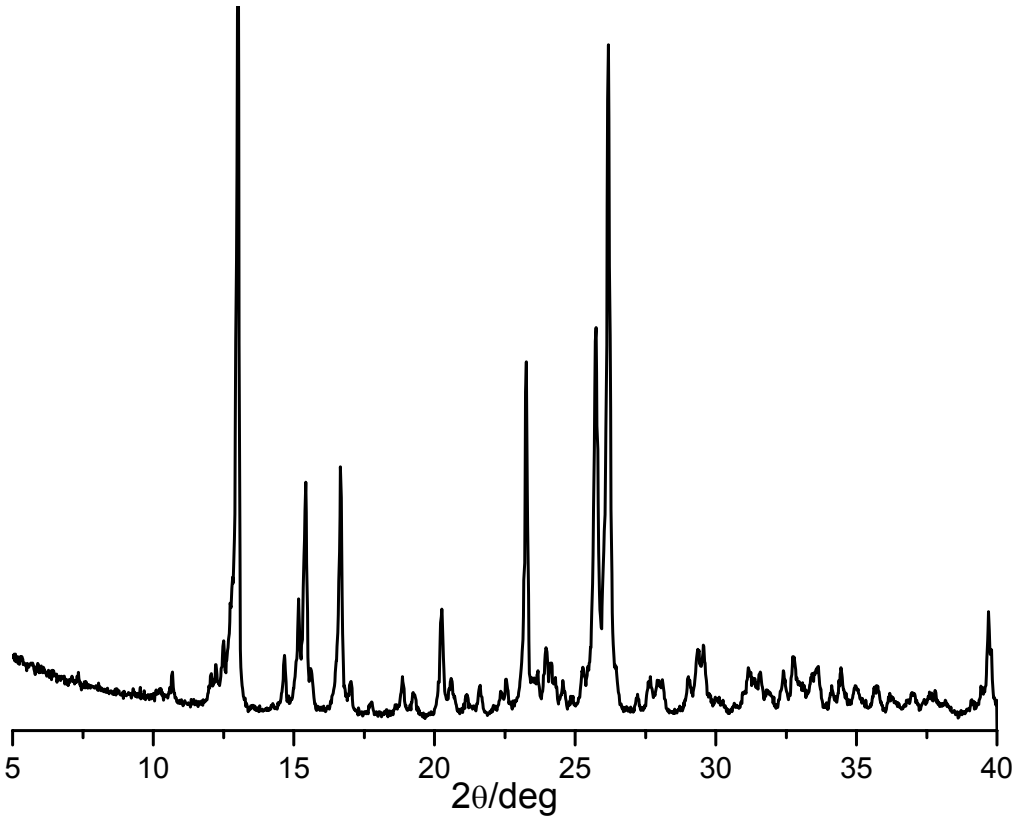


Figure 6. Observed X-ray powder pattern for **1·4H$_2$O**

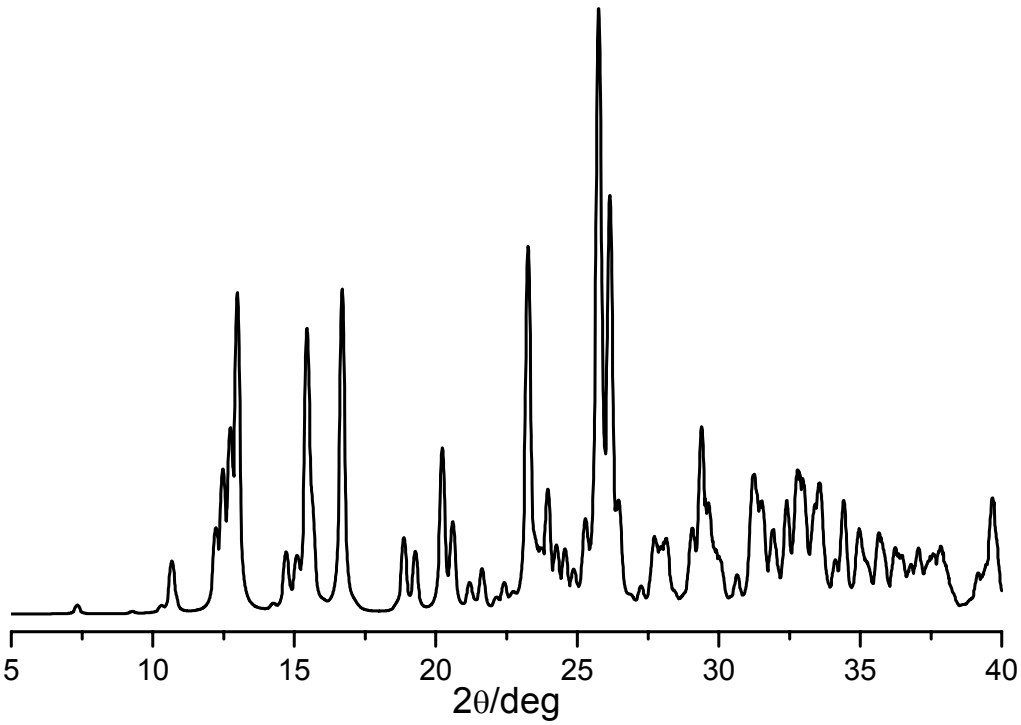


Figure 7. Calculated X-ray powder pattern for **1·4H$_2$O**

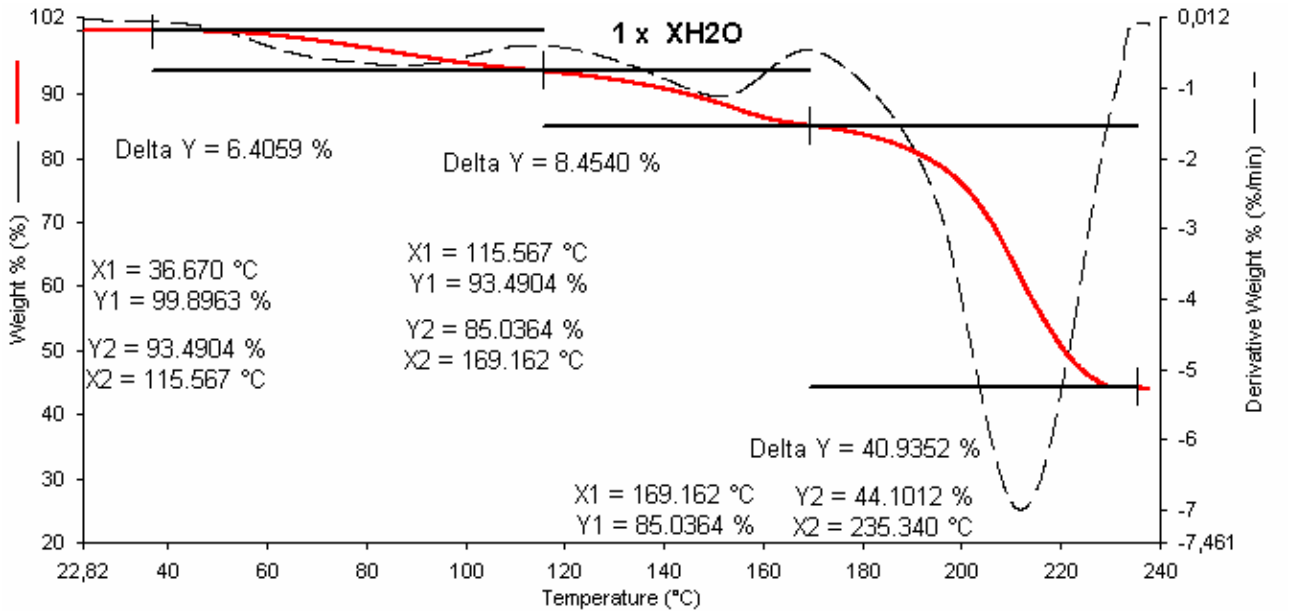
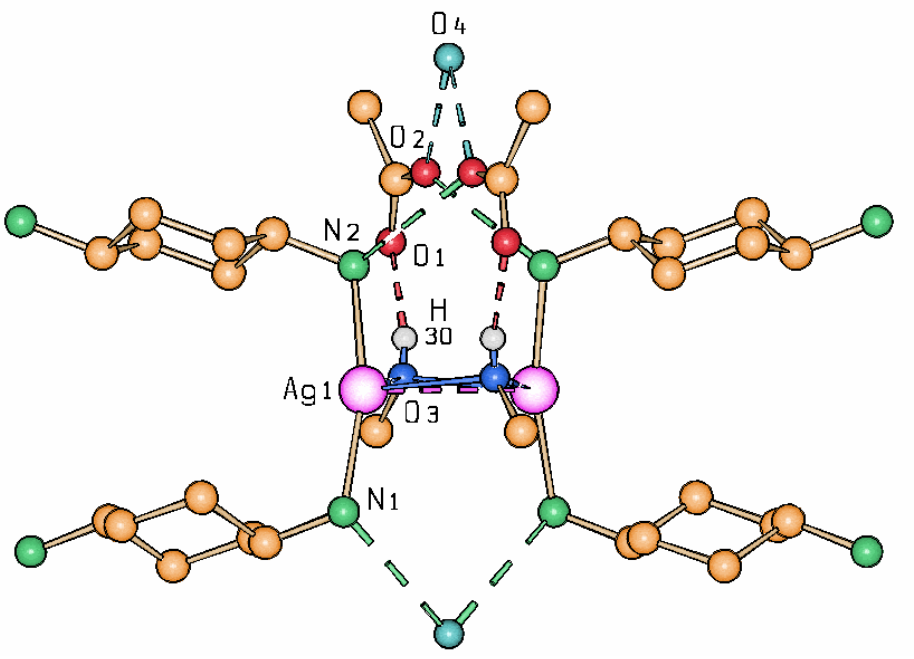
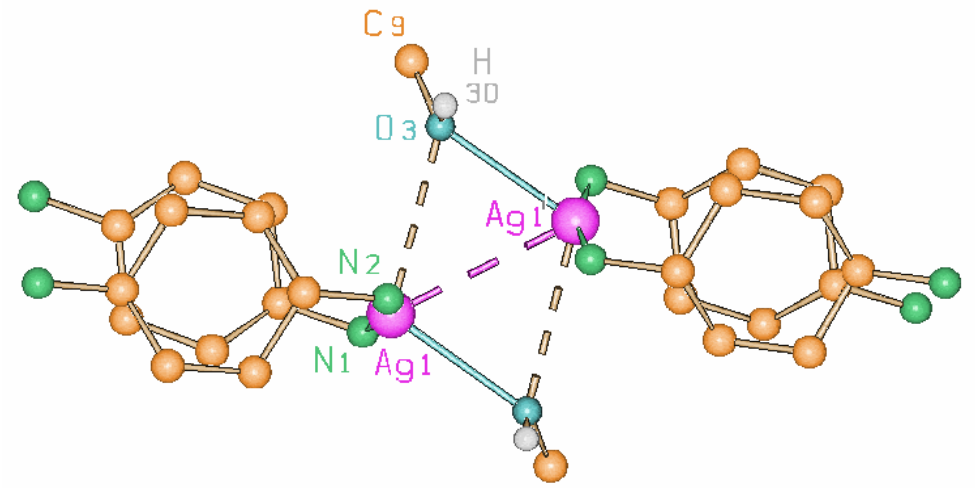


Figure 8. TGA analysis for **1·nH$_2$O**, showing that the weight loss corresponds to approximately 2.5 water molecules. At 170°C the sample starts to decompose.



(a)



(b)

Figure 9. Crystalline **1·MeOH·0.5H$_2$O**. (a) The nitrogen atoms belonging to the organic base interact via hydrogen bonding with the acetate anion and the water molecule [N(1)···O(1)$^{I}_{acetate}$ 2.972(5), N(2)···O(2)$_{acetate}$ 3.019(4), N(2)···O(2)$^{II}_{acetate}$ 2.993(5), N(1)···O(4)$_{water}$ 3.036(3)Å], and, in turn, the acetate anion interacts both with the water molecule and the methanol ligand [O(3)$_{MeOH}$···O(1)$^{II}_{acetate}$ 2.682(5); O(2)$_{acetate}$···O(4)$^{III}_{water}$ 2.740(4) Å]. (b) The methanol molecule asimmetrically bridges two silver ions belonging to adjacent chains [Ag(1)···O(3)$_{MeOH}$ 2.693(5), Ag(1)···O(3)$_{MeOH}$ 3.139(4)^{II} Å] [I: x,1-y,-1/2+z; II: 1-x,y,1/2-z; III: x,-1+y,z].

Observations:

1) The O$_{MeOH}$···Ag distance is comparable to or slightly longer than the ones observed for similar interactions in the CSD [2.394 (QEHCAH); 2.446 (QEHCIP); 2.636 Å (TIDJOF)]

2) A search has been run in the CSD for intermolecular interactions (in the range 2.5-3.5 Å) between silver atoms bound to two N atoms each. A total of 63 compounds has been found, with a mean Ag···Ag distance of 3.266 (19) Å. Therefore the Ag···Ag distance of 3.323(1) Å observed in crystalline **1·MeOH·0.5H$_2$O** is comparable to this mean value.

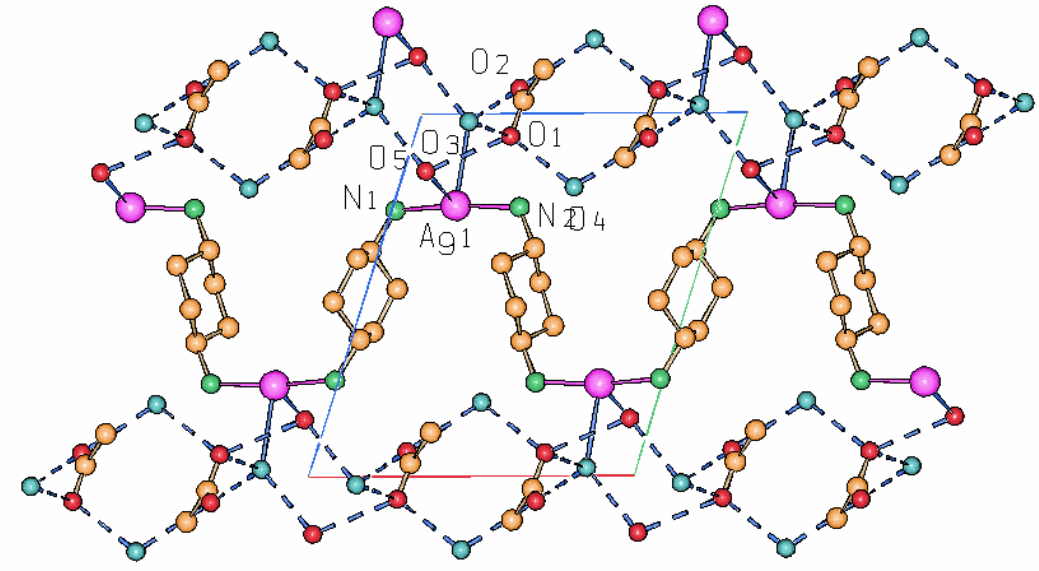
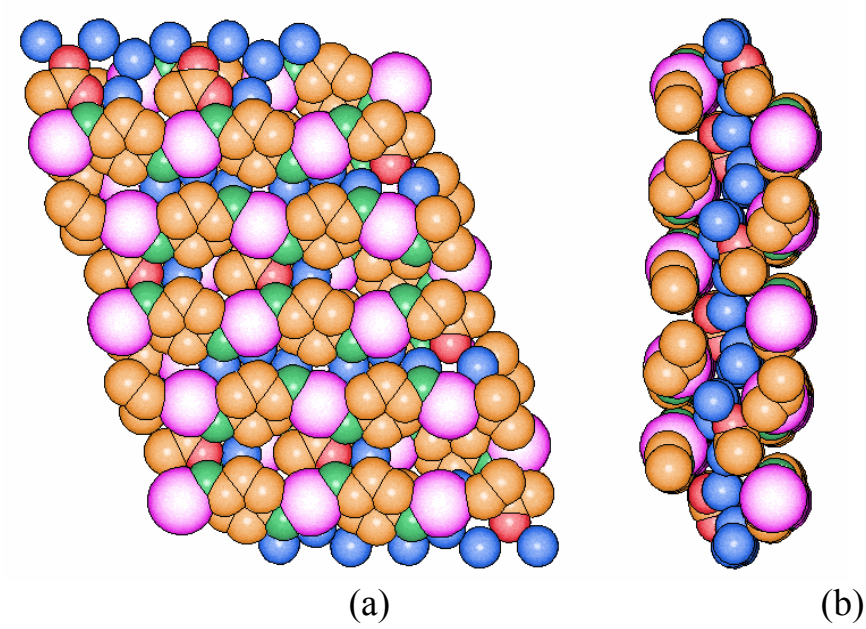


Figure 10. Crystalline **1·3H$_2$O**. The hydrogen bonded network established between the N-H donor groups on the [$H_2NC_6H_{10}NH_2$] ligand, the acetate anions [O(1) and O(2)] and the water molecules [O(3), O(4) and O(5)]. Relevant hydrogen bonding interactions (e.s.d.s. 0.005 Å): N(1)···O(2) 3.136, N(2)···O(1) 3.099, N(1)···O(5) 3.014, O(5)···O(3) 2.799, N(2)···O(4) 3.040, O(5)···O(1) 2.904, O(4)···O(2) 2.886, O(3)···O(1) 2.817, O(3)···O(2) 2.753 Å.



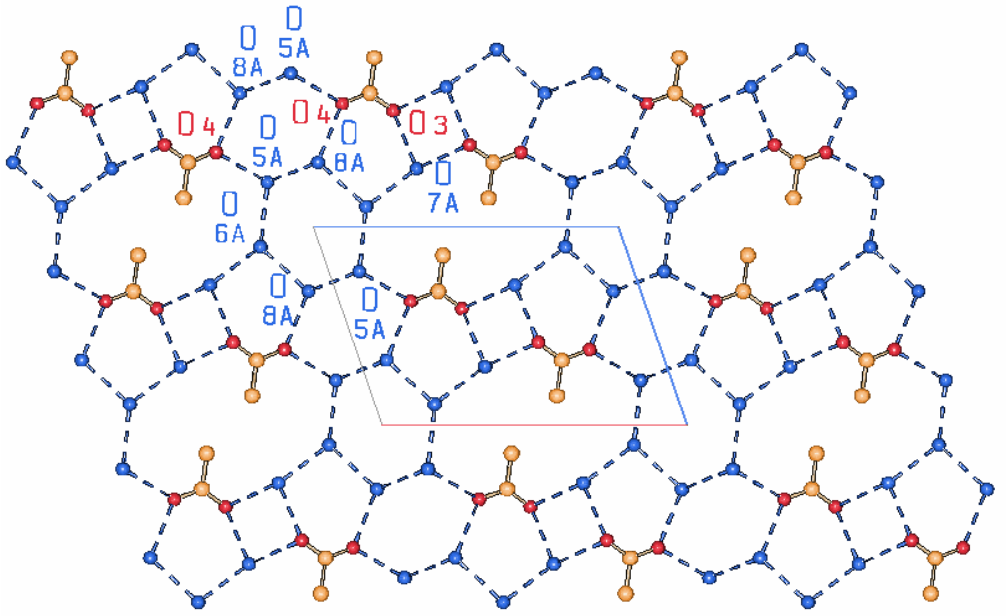


Figure 11. Crystalline **1·4H$_2$O**. (a) A view of the packing down the *c*-axis, as shown in Figure 3 (main article), together with the acetate anion and water molecules. (b) The same packing portion rotated by 90 deg around the y (vertical) axis, showing how the acetate anions and water molecules form a layer that is "sandwiched" in between layers constituted of parallel $\{Ag[H_2NC_6H_{10}NH_2]^+\}_\infty$

chains. There are two such (crystallographically independent) acetate-water layers in the structure; one of the two layers is shown in details in figure 11c. Relevant hydrogen bonding parameters are [O(1), O(2), O(3) and O(4) are the acetate oxygens]: N(1)···O(3A) 3.185(4), N(1)···O(8A) 3.144(4), N(2)···O(1) 3.209(4) 151, N(2)···O(3) 3.284(4), N(3)···O(4A) 3.113(4), N(3)···O(5A) 3.267(4), N(4)···O(1) 3.111(4), N(4)···O(3) 3.021(4), O(1A)···O(1) 2.884(4), O(1A)···O(1) 2.757(4), O(2A)··· O(1A) 2.702(4), O(2A)···O(4A) 2.779(4), O(3A)···O(2) 2.849(4), O(3A)···O(2A) 2.761(4), O(4A)···O(2) 2.757(4), O(4A)···O(3A) 2.781(3), O(5A)···O(4) 2.761(4), O(5A)···O(6A) 2.742(4), O(6A)···O(7A) 2.748(4), O(6A)···O(8A) 2.761(4), O(7A)···O(3) 2.891(4), O(7A)···O(3) 2.772(4), O(8A)···O(4) 2.797(4), O(8A)···O(5A) 2.789(4) Å.