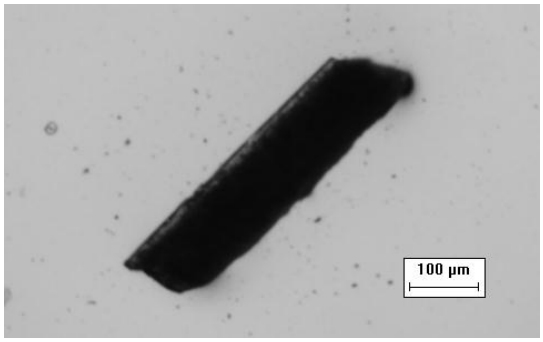
Electronic Supplementary Material (ESI) for CrystEngComm

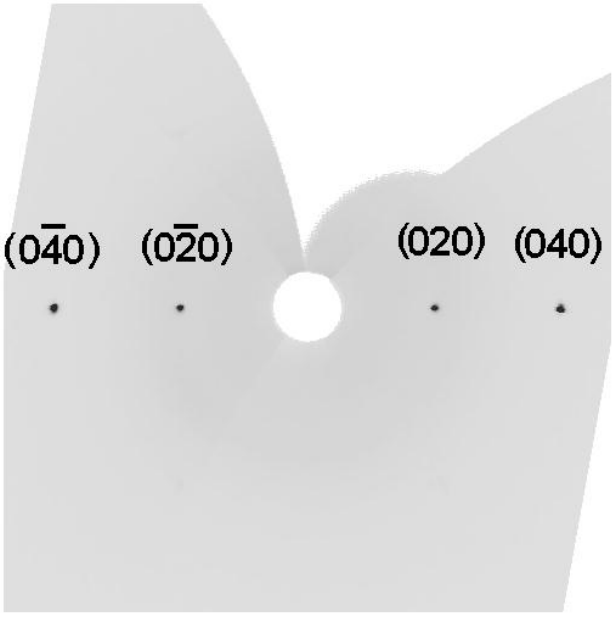

**Supplementary information to accompany "The Structure of the Melamine-Cyanuric Acid Co-Crystal"**

## 1. Photograph of the crystal employed for the X-ray diffraction study.

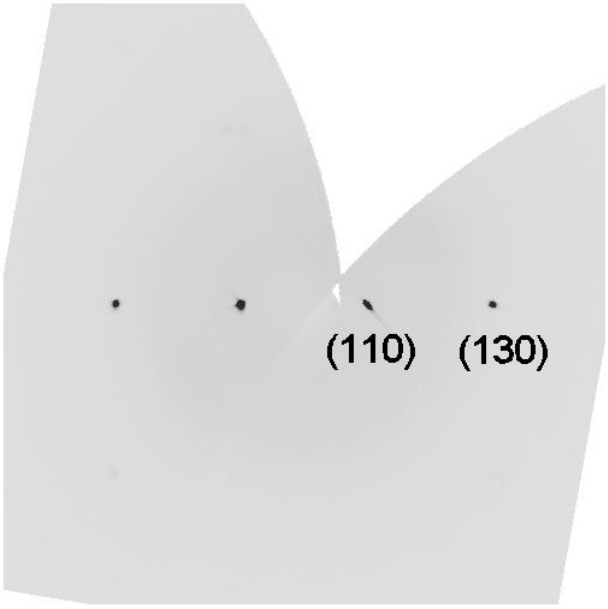



Photograph of a pale grey needle of **CA.M** lit from below, taken at 4× optical zoom.

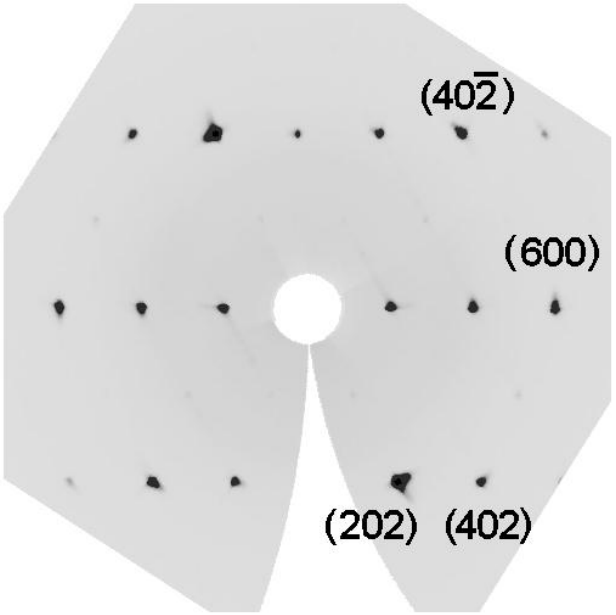
**2. Simulated precession photographs calculated using all recorded diffraction images. Selected reflections are labelled.**



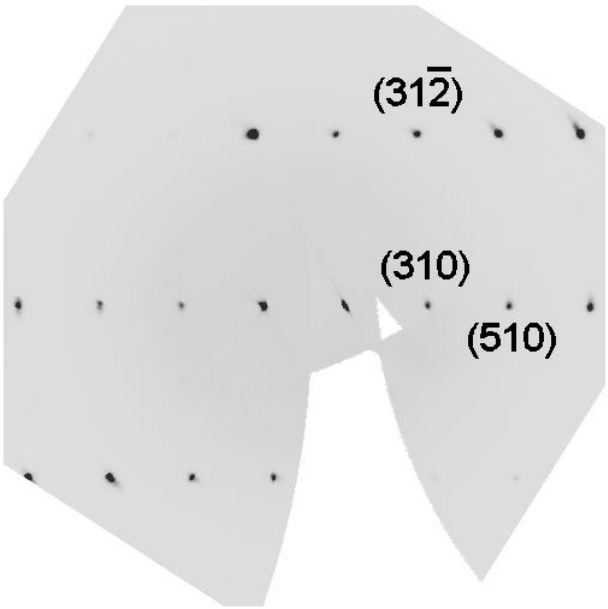

**0kl**



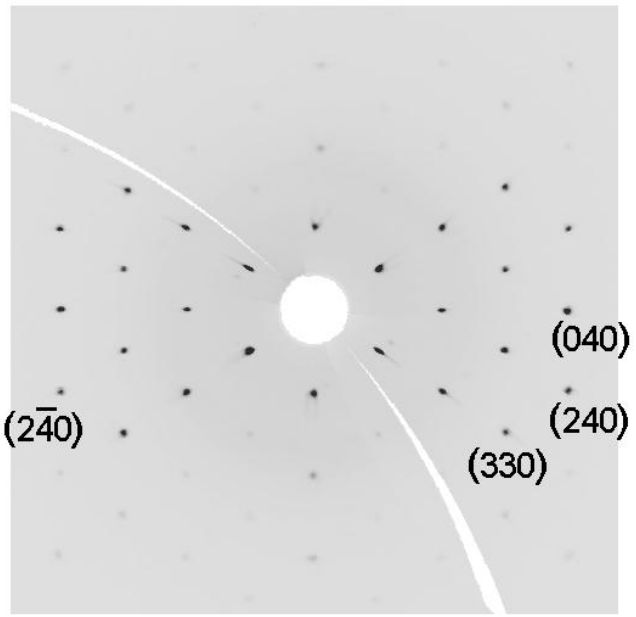

**1kl**



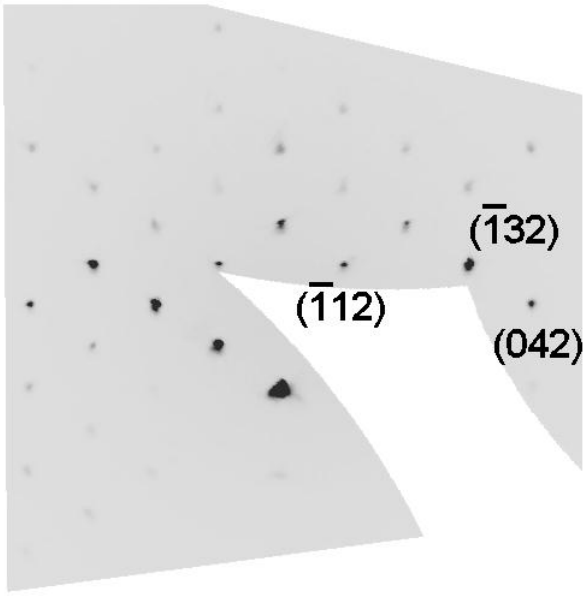

**h0l**




**h1l**

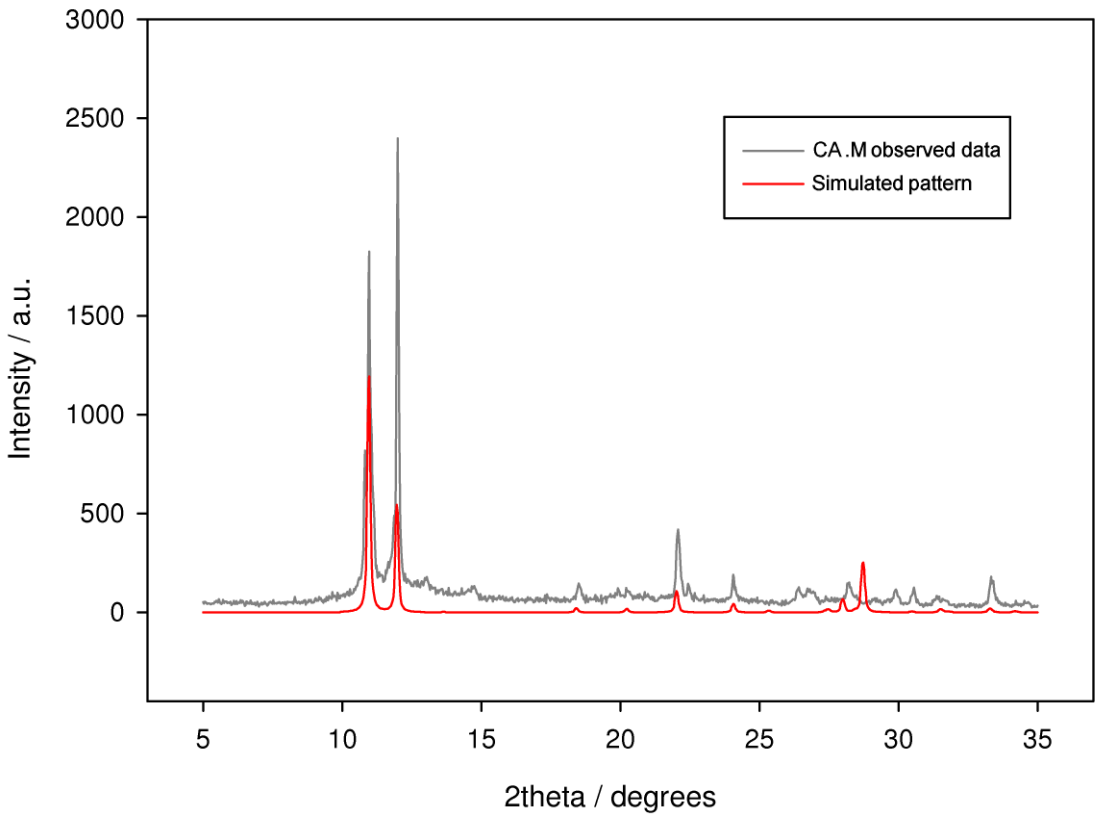



**hk0**




**hk2**

**3. X-ray powder diffraction data**




A finely ground sample was analysed by x-ray powder diffraction using a Siemens D5000 diffractometer operating with Cu Kα radiation. The diffraction pattern was recorded with a step size of 0.020° and counting time 1.0 s over the angular range $5 \leq 2\theta / ° \leq 70$. The low angle data are shown above.

**4. Quantum chemical calculations**

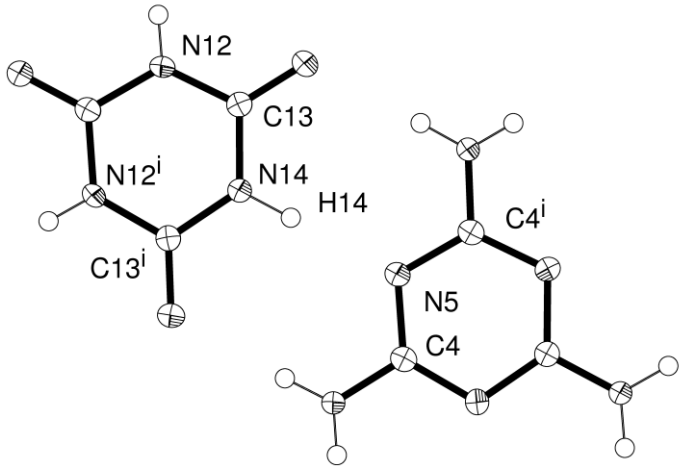
| RI-SMP3/CBS | E(RI-MP2/CBS(3,4)) [H] | E(3) correction [MP3/aug-ano-pVDZ] [H] | Etot [H] |
|---|---|---|---|
| CA – M | -951.485200269566 | 0.01790 | -951.474461 |
| CA – CA | -1011.120418533 | 0.04621 | -1011.092694 |
| M – M | -891.840486254439 | -0.00985 | -891.846398 |
| CA.M – M.CA *vs* CA.M–CA.M | -24.9 kJ/mol | -25.8 kJ/mol | |

**Table 4.1:** Total energies of the dimer stacks (CA–M, CA–CA and M–M) computed at the RI-SMP3/CBS(3,4) using a mixed basis set extrapolation. The last line provides an estimation of the relative stacking interaction energies for the CA.M–M.CA versus the CA.M–CA.M arrangement.

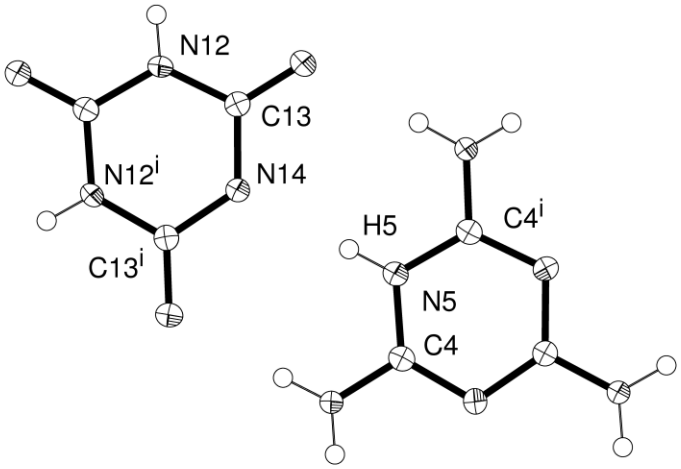
**5. Hydrogen atom location (partial protonation of melamine)**

There is evidence of some proton transfer from the cyanuric acid to melamine. Approximately 35 % of the melamine molecules are protonated at N5 and cyanuric acid deprotonated at N14. The difference Fourier map in Figure 3a (main text) shows this.

The two forms (unprotonated and protonated melamine) are shown below. Symmetry equivalent atoms are generated by the operator $i = x, -y, z$.




Major form. Fraction 0.65




Minor form. Fraction 0.35

**6. Crystal structure data tables**

Table 6.1. Crystal data and structure refinement for melamine-cyanuric acid.

| | | |
|---|---|---|
| Identification code | **CA.M** | |
| Empirical formula | C12 H18 N18 O6 | |
| Formula weight | 510.40 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | I 2/m | |
| Unit cell dimensions | a = 14.8152(19) Å | α= 90°. |
| | b = 9.6353(18) Å | β= 93.194(11)°. |
| | c = 7.0405(9) Å | γ = 90°. |
| Volume | 1003.5(3) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.689 $Mg/m^3$ | |
| Absorption coefficient | 0.139 $mm^{-1}$ | |
| F(000) | 528 | |
| Crystal size | 0.36 × 0.11 × 0.11 $mm^3$ | |
| Theta range for data collection | 2.52 to 29.19°. | |
| Index ranges | $-20 \le h \le 20$, $-13 \le k \le 13$, $-9 \le l \le 8$ | |
| Reflections collected | 7067 | |
| Independent reflections | 1434 [R(int) = 0.0462] | |
| Completeness to theta = 25.30° | 99.9 % | |
| Absorption correction | Analytical | |
| Max. and min. transmission | 0.9849 and 0.9517 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1434 / 2 / 113 | |
| Goodness-of-fit on $F^2$ | 0.957 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0353, wR2 = 0.0898 | |
| R indices (all data) | R1 = 0.0727, wR2 = 0.1047 | |
| Largest diff. peak and hole | 0.241 and -0.242 $e.Å^{-3}$ | |

Table 6.2. Atomic coordinates ( × $10^4$) and equivalent isotropic displacement parameters ($Å^2$× $10^3$) for melamine-cyanuric acid. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(1) | 1666(1) | 0 | 10461(3) | 22(1) |
| C(2) | 2481(1) | 0 | 9759(3) | 19(1) |
| N(3) | 2867(1) | 1248(1) | 9432(2) | 19(1) |
| C(4) | 3687(1) | 1193(1) | 8662(2) | 19(1) |
| N(5) | 4116(1) | 0 | 8219(3) | 20(1) |
| N(6) | 4091(1) | 2382(1) | 8297(2) | 21(1) |
| O(10) | 8286(1) | 0 | 4514(2) | 22(1) |
| C(11) | 7547(1) | 0 | 5231(3) | 19(1) |
| N(12) | 7104(1) | -1209(1) | 5636(2) | 20(1) |
| C(13) | 6268(1) | -1257(1) | 6373(2) | 19(1) |
| N(14) | 5879(1) | 0 | 6757(3) | 20(1) |
| O(15) | 5883(1) | -2366(1) | 6679(2) | 24(1) |

Table 6.3. Bond lengths [Å] and angles [°] for melamine-cyanuric acid.

| | | | |
|---|---|---|---|
| N(1)-C(2) | 1.330(2) | N(3)-C(2)-N(3)#1 | 124.82(17) |
| N(1)-H(1) | 0.88(2) | C(2)-N(3)-C(4) | 115.35(11) |
| C(2)-N(3) | 1.3562(14) | N(6)-C(4)-N(5) | 117.78(12) |
| C(2)-N(3)#1 | 1.3562(14) | N(6)-C(4)-N(3) | 117.86(11) |
| N(3)-C(4) | 1.3600(17) | N(5)-C(4)-N(3) | 124.35(12) |
| C(4)-N(6) | 1.3244(16) | C(4)#1-N(5)-C(4) | 115.69(17) |
| C(4)-N(5) | 1.3575(16) | C(4)#1-N(5)-H(5) | 122.15(12) |
| N(5)-C(4)#1 | 1.3575(16) | C(4)-N(5)-H(5) | 122.15(13) |
| N(5)-H(5) | 0.85(8) | C(4)-N(6)-H(6A) | 121.2(12) |
| N(6)-H(6A) | 0.87(2) | C(4)-N(6)-H(6B) | 117.9(13) |
| N(6)-H(6B) | 0.84(2) | H(6A)-N(6)-H(6B) | 120.9(18) |
| O(10)-C(11) | 1.232(2) | O(10)-C(11)-N(12)#1 | 122.03(8) |
| C(11)-N(12)#1 | 1.3746(15) | O(10)-C(11)-N(12) | 122.03(8) |
| C(11)-N(12) | 1.3746(15) | N(12)#1-C(11)-N(12) | 115.92(16) |
| N(12)-C(13) | 1.3708(17) | C(13)-N(12)-C(11) | 123.97(12) |
| N(12)-H(12) | 0.84(3) | C(13)-N(12)-H(12) | 120.3(14) |
| C(13)-O(15) | 1.2354(14) | C(11)-N(12)-H(12) | 115.5(15) |
| C(13)-N(14) | 1.3746(15) | O(15)-C(13)-N(12) | 122.04(11) |
| N(14)-C(13)#1 | 1.3746(15) | O(15)-C(13)-N(14) | 121.70(12) |
| N(14)-H(14) | 0.93(4) | N(12)-C(13)-N(14) | 116.26(12) |
| | | C(13)#1-N(14)-C(13) | 123.58(16) |
| C(2)-N(1)-H(1) | 122.4(13) | C(13)#1-N(14)-H(14) | 118.16(11) |
| N(1)-C(2)-N(3) | 117.59(8) | C(13)-N(14)-H(14) | 118.16(11) |
| N(1)-C(2)-N(3)#1 | 117.59(8) | | |

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,z

Table 6.4. Anisotropic displacement parameters ($Å^2 \times 10^3$)for melamine-cyanuric acid. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| N(1) | 19(1) | 14(1) | 33(1) | 0 | 11(1) | 0 |
| C(2) | 18(1) | 17(1) | 21(1) | 0 | 4(1) | 0 |
| N(3) | 18(1) | 17(1) | 24(1) | 1(1) | 5(1) | -1(1) |
| C(4) | 20(1) | 16(1) | 21(1) | -1(1) | 2(1) | 0(1) |
| N(5) | 20(1) | 15(1) | 24(1) | 0 | 5(1) | 0 |
| N(6) | 19(1) | 14(1) | 31(1) | -1(1) | 10(1) | 0(1) |
| O(10) | 21(1) | 17(1) | 28(1) | 0 | 7(1) | 0 |
| C(11) | 20(1) | 16(1) | 21(1) | 0 | 3(1) | 0 |
| N(12) | 21(1) | 12(1) | 26(1) | -2(1) | 7(1) | 1(1) |
| C(13) | 19(1) | 17(1) | 22(1) | 0(1) | 4(1) | 1(1) |
| N(14) | 19(1) | 15(1) | 26(1) | 0 | 7(1) | 0 |
| O(15) | 24(1) | 16(1) | 32(1) | 1(1) | 8(1) | -1(1) |

Table 6.5. Hydrogen coordinates ( × $10^4$) and isotropic displacement parameters ($Å^2$× $10^3$) for melamine-cyanuric acid.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 4610(50) | 0 | 7670(110) | 21(7) |
| H(1) | 1387(12) | 770(20) | 10760(30) | 36(5) |
| H(6A) | 4615(13) | 2399(19) | 7800(30) | 28(4) |
| H(6B) | 3834(13) | 3120(20) | 8590(30) | 32(4) |
| H(12) | 7357(14) | -1940(30) | 5300(30) | 50(6) |
| H(14) | 5310(30) | 0 | 7240(60) | 21(7) |