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Purported "melamine cyanuric acid trihydrochloride" $C_3H_6N_6 \cdot C_3H_3N_3O_3 \cdot 3HCl$ is actually "diprotonated-melamine cyanuric acid dichloride dihydrate" $(C_3H_8N_6)^{2+} \cdot C_3H_3N_3O_3 \cdot 2Cl^- \cdot 2H_2O$

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On the basis of the published results, melamine cyanuric acid trihydrochloride (MCA·3HCl) is shown to be better described as diprotonated melamine cyanuric acid dichloride dihydrate $(C_3H_8N_6)^{2+} \cdot C_3H_3N_3O_3 \cdot 2Cl^- \cdot 2H_2O$. Details are given of the revised hydrogen bonding scheme, which requires further elaboration.

KEY WORDS: Salt-molecule complex; revision of composition; hydrogen bonding.

The crystal structure of the salt-molecule complex "melamine-cyanuric acid trihydrochloride" ("MCA·3HCl") was reported[1] in space group $C2/c$, $Z = 4$, $a = 9.853(2)$ Å, $b = 15.305(1)$ Å, $c = 10.082(2)$ Å, $\beta = 81.28°$.[2] The composition was derived from a chemical analysis but no details were given. Six hydrogen atoms, all linked to the organic moieties, were located from difference syntheses. One chlorine (Cl(2)) had a high atomic displacement factor and was assigned an occupancy factor of 0.5.

Two different formulae have been given for "MCA·3HCl": $C_3H_6N_6 \cdot C_3H_3N_3O_3 \cdot 3HCl$ by Wang *et al.* (their table 1; formula mass 364.58) and $(C_3H_9N_6)^{3+} \cdot C_3H_3N_3O_3 \cdot 3Cl^-$ by the CSD (KEMWUU). In fact, it is clear from Fig. 2 of Wang *et al.* that the melamine moiety is doubly protonated (at N(5), N(5′)) whereas the cyanuric acid molecule is present as such. This is confirmed by the different dimensions of the diprotonated melamine and melamine itself (MELAMI02[2]; MELAMI04[3]; XRD and ND studies at room temperature), and the close resemblance of the dimensions of cyanuric acid in the complex and in the neat compound (CYURAC10[4]; CYURAC12[5]; CYURAC05[6]; XRD; and ND studies at 300 and ≈100 K). The statement by Wang *et al.* (p. 82) that "The bond lengths and angles of melamine and cyanuric acid agree with values from the literature . . . " is correct only for cyanuric acid. There is no evidence in the Wang paper for triple protonation of the melamine moiety as given by the CSD. Only one diprotonated melamine derivative was found in the CSD—*trans*-tetraaquabis(*N*,*N*′,*N*″-tricyanomelamine)cobalt(II) hexahydrate (TEZZAJ).[7] The dimensions of the six-membered rings of the two different diprotonated melamines resemble one another more than they do that of melamine itself.

The structure as reported has $d(\mathrm{N{-}H\cdots Cl}) = 2.775$ Å, which is appreciably shorter than in usual $\mathrm{N{-}H\cdots Cl}$ hydrogen bonds (lower

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[2] To avoid confusion, the nonstandard acute β angle is retained.

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limit ≈3.0 Å).[8] It seems reasonable to infer that the half-occupied Cl(2) is actually a water molecule (occupation factor = 1), the value for $d(\mathrm{N{-}H\cdots O})$ now being well within acceptable limits. Our description is based on this assumption. Although Wang *et al.* note that structure factor data were deposited with the British Library, these could be retrieved neither from the Library nor from the authors.

At the suggestion of Dr R.E. Marsh, the atomic displacement parameters (ADPs; given in Table 4 of Wang *et al.*) were used (by my colleague Dr M. Kapon) to calculate ellipsoids for the non-hydrogen atoms. The ellipsoids of O(1), O(2), and N(6) were nonpositive definite, while that for Cl(2) (now revised to W) had a cigar shape elongated nearly along [010].

The crystal data ($C2/c$, $Z = 4$) imply that the diprotonated melamine and cyanuric acid moieties are located about Wyckoff positions (e) 1/2, y, 1/4 (i.e. bisected by twofold axes; multiplicity 4), while the chloride anion and water molecule (which replaces half-occupied Cl(2)) are at general positions (multiplicity 8). The correct formula is $(C_3H_8N_6)^{2+}C_3H_3N_3O_3\cdot 2Cl^-\cdot 2H_2O$ (formula mass 364.15). The densities calculated for the two formulae are 1.611 and 1.610 mg m^{-3} and are indistinguishable. The density was not measured. There were 12 hydrogens in the original formula unit and 15 in the revised formula unit; 11 hydrogens were found by Wang *et al.*; the 2 hydrogens of the water molecule remain to be located.

The moieties lie closely in the $(10\bar{1})$ planes (Fig. 1). Within a single layer (Fig. 2), there are (horizontal) strips of cyanuric acid (CA) molecules and diprotonated melamine (H_2M^{2+}) cations hydrogen-bonded in mutually perpendicular directions. Each strip is linked to mutually bonded Cl^- anions and water molecules, which are also linked to the $CA{-}H_2M^{2+}$ strips. The rather short $Cl^-\cdots H{-}N$ distances of 2.974 and 3.113 Å suggest that these links are probably the

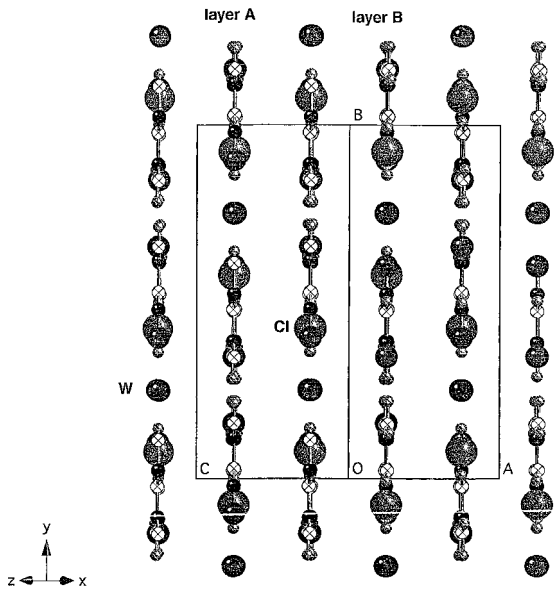

Fig. 1. KEMWUU—view down $[\bar{1}0\bar{1}]$ showing hydrogen-bonded layers seen edge-on. Coding used in these figures: large spheres are Cl^-, black C, cross-hatched N, intermediate O, small H. W denotes the previously-assigned half-occupied Cl, now designated as a fully-occupied water oxygen. Hydrogen bonding is not shown in this figure.

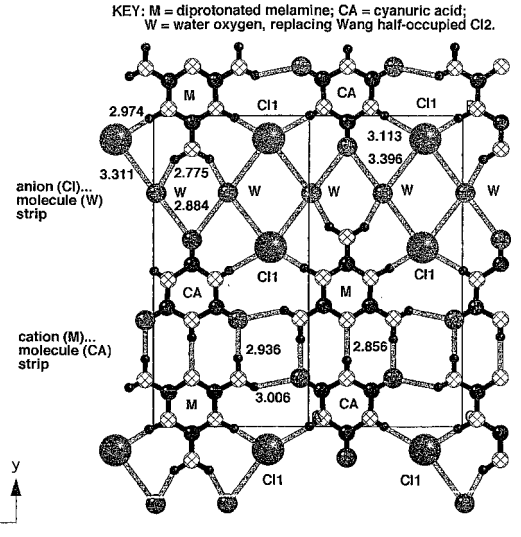

Fig. 2. KEMWUU—hydrogen bonding in layer B; view direction $[\bar{1}01]$. Note that, compared to melamine, the M moiety has two additional hydrogens. All hydrogen bonding possibilities are taken up. Distances are given between non-hydrogen atoms. Details are Cl^- to HN(CA) 3.113 Å; to HN(M) 2.974 Å; to W 3.311, 3.396 Å. W to N(M) 2.775 Å; to O(CA) 2.884 Å. N(M) to HN(CA) 2.856 Å. O(CA) to HN(M) 2.936 and 3.006 Å.

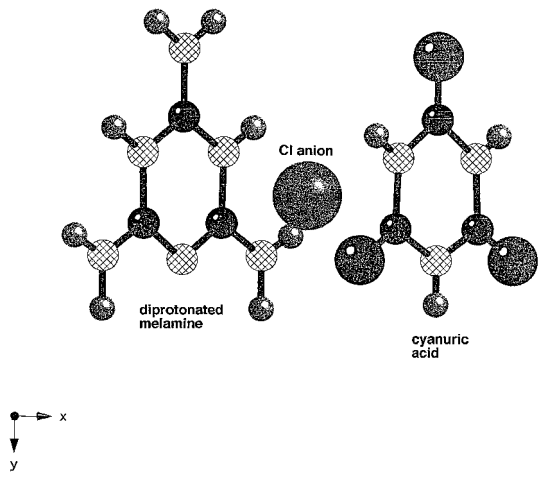

Fig. 3. KEMWUU—immediate surroundings of the Cl anion, viewed down [001]. The anion is marked by Cl in Fig. 1, between layers A and B. The more remote neighbors have been removed for clarity. Diprotonated melamine has a twofold axis but not Cl^-; thus charge balance is preserved.

most important of the individual contributions to the cohesion. The Cl^- anion is sandwiched between the C_3N_3 rings of the CA and H_2M^{2+} moieties (Fig. 3) with $d(Cl^- \cdots N(ring))$ in the range 3.45–3.55 Å. This ionic interaction must also be an important contributor to the cohesion.

Even after revision of the composition, the hydrogen bonding scheme (Fig. 2) still has unsatisfactory features. Low temperature neutron diffraction would appear to be the method of choice for checking our proposal and, in particular, for clarifying the hydrogen bonding scheme.

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