**Supramolecular N–H⋯O interactions in a new hybrid organic-inorganic decavanadate synthon**

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As part of our studies incorporating metformin with other compounds used for diabetes therapy [1,2], we have synthesized a salt of decavanadate, $V_{10}O_{28}^{6-}$, containing mixed organic cations by heating metformin and sodium metavanadate in aqueous solution at pH 4 and 60 °C in the presence of picolinic acid, followed by keeping the solution at RT overnight to give an orange crystal. The product was characterized by spectroscopic and single crystal X-ray diffraction analysis [1]. Guanylurea cation, HGU$^+$, forms from metformin in the synthesis under similar conditions to those in a previous report [2]. As often observed, the $V_{10}O_{28}^{6-}$ anion lies on an inversion center [1,2,3]. The charge of the six-minus decavanadate anion is balanced by two diprotonated metforminium(2+) dications, $H_2Met^{2+}$ and a disorder region containing single HGU$^+$ and $H_2O^{+}$ cations located about an inversion center. The salt exhibits a complex 3-D charge-assisted hydrogen bonding network involving extended chains of the eight waters of hydration, the two metforminium(2+) dications, and the $V_{10}O_{28}^{6-}$ anion through extensive $O\cdot\cdot\cdotH\cdot\cdot\cdotO$, N–H⋯O, and C–H⋯O intra- and inter-molecular interactions. The same 3-D network has also been found previously [4].

The HGU$^+$ cations, which do not appear to be structure determining, are located in cavities in the network, each connected to a single decavanadate anion through a highly concerted eight N–H⋯O interaction (Fig. 1). The HGU$^+$ cations are strongly connected to only one of the $V_{10}O_{28}^{6-}$ anions surrounding each of them and weakly connected to the inversion related $V_{10}O_{28}^{6-}$ anion (only three N–H⋯O interactions). The excess cavity space may contribute to the massive disordering of the HGU$^+$ cation and the ease of removal from the lattice with the waters (TGA results). This strong highly concerted interaction between the HGU$^+$ cation and the $V_{10}O_{28}^{6-}$ anion suggest that this interaction is a synthon, also existing in solution, may contribute to the catalytic degradation of metformin to guanylurea [1,2]. The disorder and the supramolecular environment of the multiple cations, the decavanadate anion, and the water of hydration chains will be discussed. A 100 K structure has been determined [5] and will be compared to the 296 K structure.

**Figure 1.** (left) ORTEP perspective drawing showing the HGU$^+:V_{10}O_{28}^{6-}$ synthon (50% probability ellipsoids). (right) ORTEP perspective drawing showing the four-position disordered HGU$^+$ / two-position disordered $H_2O^{+}$ (10% probability ellipsoids). The solid-bond positions are rotated relative to each other 26.4°, while the open-bond positions are inversion related to the solid-bond positions. H atoms in both drawings are represented as spheres with arbitrary radius for clarity.


