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Short communication

Face-to-face stacking of caffeinium and $[PM_{12}^{VI}O_{40}]^{3-}$ ions: A synthon for crystal engineering with purine bases

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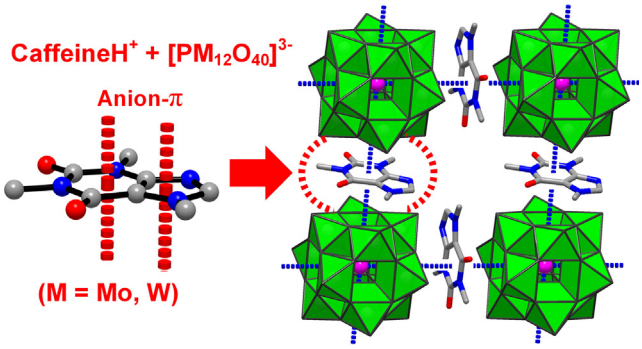
GRAPHICAL ABSTRACT

Weak anion-π bonding dominates interaction of caffeinium and $[PM_{12}O_{40}]^{3-}$ (M = Mo, W) ions and favors assembly of high-symmetry non-covalent frameworks.



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ABSTRACT

Ionic polyoxometales (H*caf*)$_3$[$PM_{12}O_{40}$]·6H_2O [M = Mo, W; *caf* = caffeine] exhibit unusual supramolecular structure dominated by multiple anion-π interactions, which occur at both axial sides of the caffeinium cations. These cations, when stacked to every of six square faces of POM cuboctahedra, afford supramolecular boxes and the resulting non-covalent cubic framework (α-Po topology) is generated by face-sharing of the boxes.

Supramolecular interactions of nucleobases, those involving multiple hydrogen bonding, π/π stacking and hydrophobic effects [1], are of primary importance for sustaining complex structure of DNA and RNA as is illustrated by a paradigmatic case of two Watson-Crick base-pairs. Selective hydrogen bonding of adenine, cytosine, guanine and related species suggests also structural models for molecular recognition and provides versatile supramolecular synthons for crystal engineering of network solids, pharmaceutical co-crystals, etc. Beyond the crucial role of hydrogen bonds, some other kinds of weaker interactions are also relevant [2]. In particular, a reliable mechanism for nucleobase stacking with water and sugar molecules [3] could be found with lone pair-π hole interactions [4], at one or two axial sides of the receptor. Such kind of weak bonding may possess even a wider significance in the case of protonated ring systems [5] and/or extended polydentate substrates supporting multiple sites for lone pair-π hole interactions. For example, fused ring system of pyridazino[4,5-*d*]pyridazine readily establishes short double contacts with polyatomic anions of appropriate geometry [6].

Supramolecular patterns sustained with protonated purine bases and polyoxometalate anions are especially interesting in this context. They may be important for understanding mechanisms of bioactivity and pharmacological action of polyoxoanions [7], while providing new insights into the structure of organic-inorganic systems. Recent studies suggest structural

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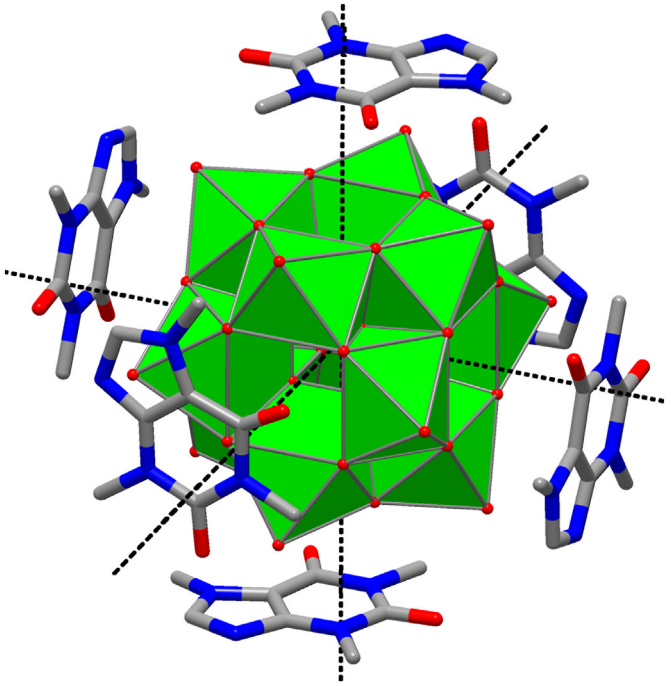

Fig. 1. The $[PW_{12}O_{40}]^{3-}$ anion in the environment of six caffeinium cations, which define a non-covalent cubic box. Dotted lines indicate mutually orthogonal four-fold axes. For every of the symmetry related $(Hcaf)^{+}$ cations, only one orientation is shown for clarity.

significance of such interactions, which may result in encapsulation of the polyoxometalates in a group of aromatic rings [8]. Indeed, in some cases the lone pair-π hole interactions (resulting in the generation of purine-anion stacks) may be recognized as local motifs of complicated hydrogen bonded networks with polyoxotungstates $[W_6O_{19}]^{2-}$, $[W_{10}O_{32}]^{4-}$, protonated guanine and closely related theobromine [9]. In the present work we demonstrate how these weak interactions may be applicable for controlling the crystal growth, as a special kind of supramolecular synthon. Such unusual self-assembly scenario was feasible with caffeine (*caf*, 1,3,7-trimethylxanthine), a close structural model of purine bases (guanine and adenine) in DNA, in a combination with triply charged anions $[PM^{VI}_{12}O_{40}]^{3-}$ (M = Mo, W). Multiple methylation at the heterocyclic backbone is essential for elimination of most competitive conventional hydrogen bonding. However, the inherent geometry and symmetry of the Keggin anions is also a beneficial factor for generation of dense stacks in three mutually orthogonal directions, as may be anticipated for $\{(Hcaf)_3[PM^{VI}_{12}O_{40}]\}_n$ compositions.

Previously, phosphomolybdic and -tungstic acids were reported as reagents for selective precipitation of caffeine and its determination in tablet mixtures and beverages [10] and the combinations of caffeine and $H_3[PM^{VI}_{12}O_{40}]$ were successfully tested for therapy of carcinoma of the intestinal tract [11]. Although the only characterized product of the reaction, in acidic media, was $(Hcaf)_2H[PW_{12}O_{40}]$ [12], the results of amperometric titration suggest that the poorly soluble ion pair formed in aqueous solutions at pH = 5.5–6.0 has the desired caffeine/$H_3[PMo_{12}O_{40}]$ ratio of 3:1. Thus two salts of the $(Hcaf)_3[PM_{12}O_{40}]\cdot 6H_2O$ [M = Mo (**1**), W (**2**)] composition were isolated [13]. TGA data reveal 4.5% (**1**) and 3.5% (**2**) mass loss in a 40-145 °C range, corresponding to elimination of solvate water molecules (calculated: 4.22% and 2.97%, respectively), followed by further decomposition above 265 °C (**1**) and 280 °C (**2**). The solutions of **1** at 25° in ethanol have a conductivity within the range of a 3:1 electrolyte (Λ_M = 120 S·cm^2·equiv.$^{-1}$) [14].

These compounds are isomorphous and crystallize in cubic space group *Pm* $\bar{3}$*m* [15]. The anion lies on Wyckoff position with octahedral point symmetry *m* $\bar{3}$*m* (O_h) and is disordered over two orientations, while the organic cation appears on a mirror plane and is equally disordered over eight orientations related by orthogonal mirror plane and four-fold axis. Interaction of these moieties reveals a number of salient features, which are clearly visible in spite of the disorder in crystal structure. The caffeinium affords stack to the anion in such a way that every of six square faces of cuboctahedron (defined by twelve terminal O-atoms of $[PM_{12}O_{40}]^{3-}$) is centered by stacked cations (Fig. 1). As a result, the anions are packed inside non-covalent cubic boxes (possessing dimensions of the single unit cell) and very simple 3D structure of

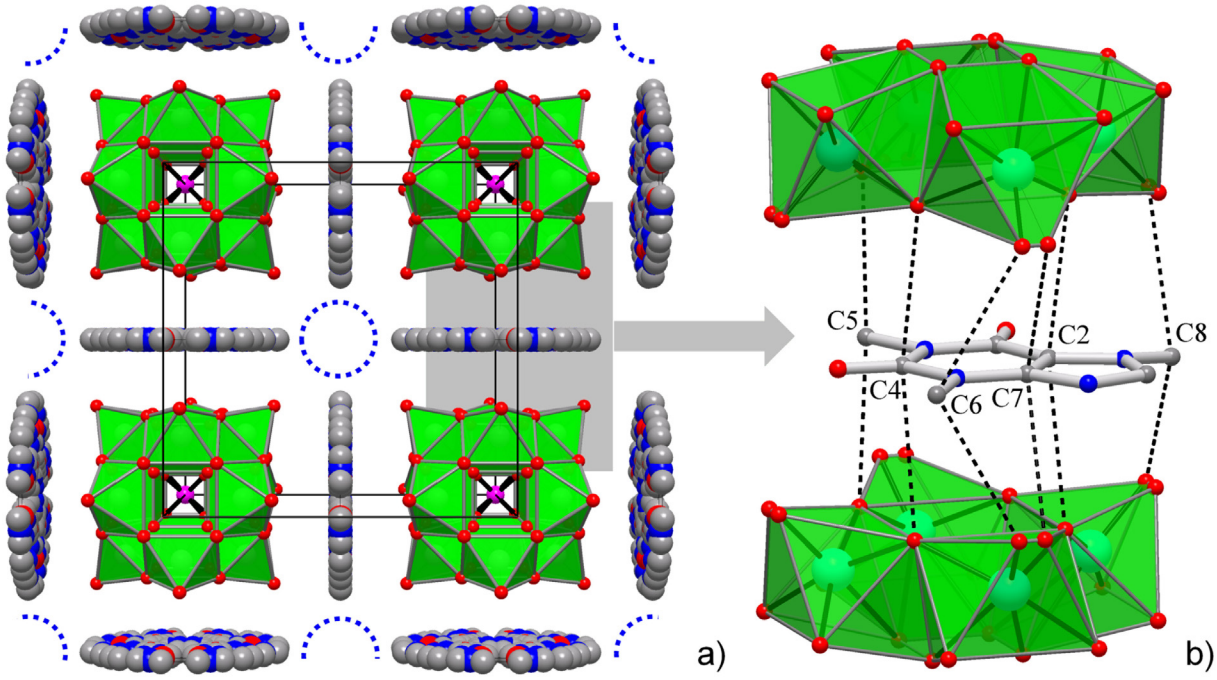

Fig. 2. a) Supramolecular structure of **2** viewed down general crystal axis. The disordered hydrate regions are marked with dotted circles. b) The caffeinium cation residing between two $[PW_{12}O_{40}]^{3-}$ anions, with the dotted lines showing short interatomic contacts. Double vertices of the polyhedra indicate equal disorder of O-atoms over two orientations; only one orientation of the cation is retained for clarity.