

Self-assembly, geometric and electronic structures, and structure-directing properties of organic–inorganic hybrid salt containing $[\text{WO}_2\text{F}_4]^{2-}$ anions and protonated 2-(2-hydroxyphenyl)benzimidazole cations



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ABSTRACT

One new organic–inorganic hybrid solid salt, $[(\text{pbmH})_2][\text{WO}_2\text{F}_4]$ (**1**) (pbm = 2-(2-hydroxyphenyl)benzimidazole), containing tungsten oxide fluoride anion $[\text{WO}_2\text{F}_4]^{2-}$, and organic cation, pbmH^+ , has been synthesized via solution-based self-assembling technique and characterized structurally. The geometric structure and electronic structure of $[\text{WO}_2\text{F}_4]^{2-}$ anion have been calculated, and discussed in detail by the density functional theory levels (DFT), the partial density of states (PDOS) and the overlap population density of states (OPDOS) analyses. The experimental results are well comparable to those of theoretical ones. The observed crystal stacking and structure-directing properties of $[\text{WO}_2\text{F}_4]^{2-}$ anion in crystalline **1** are well interpreted. Furthermore, the distortion of $[\text{WO}_2\text{F}_4]^{2-}$ octahedron, the variation trend of bonding distances of W–O/F atoms, and the structure-directing properties of $[\text{WO}_2\text{F}_4]^{2-}$ anion, together with their inter-relationships have been well discussed.

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Tungsten compounds have a variety of scientifically interesting and technologically useful properties, in particular magnetic, electronic, optical activity and catalysis features [1,2]. This has led to considerable exploratory synthesis in various tungsten-containing compounds, notably tungsten oxide fluoride system, for example $[\text{WO}_2\text{F}_4]^{2-}$ anionic compound [3–5].

Although there are many reports of solution-based self-assembling synthesis of tungsten oxide fluorides, the systematic synthetic chemistry of these systems is still relatively poorly explored and correspondingly poorly understood [3]. Especially the solution-based self-assembly of tungsten oxide fluoride anions with organic cations has been rarely looked into and systematized.

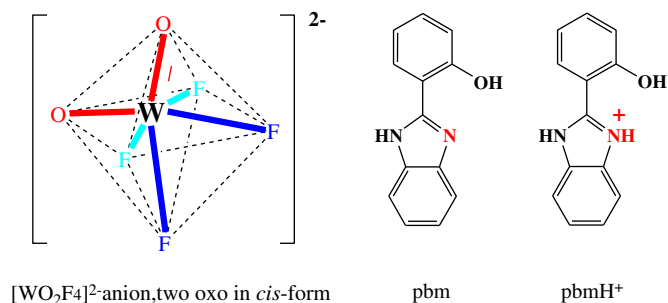
Our main motivation in this field is to expand the range of known tungsten oxide fluoride systems, in order to develop novel structural building units, in particular by using organic cations as structure-directing agents, to understand the processes of their formations and, eventually, direct towards the rational synthesis of functional tungsten oxide fluoride compounds with anticipated physical and chemical properties. We have recently reported a molybdenum analog of $[\text{MoO}_2\text{F}_4]^{2-}$ anionic compound using solution-based hydrothermal methods, and the structure-directing self-assembling of $[\text{MoO}_2\text{F}_4]^{2-}$ anion with transition metal coordination cation, which leads to the

formation of zig-zag one-dimensional (1D) chain compound [6]. Some other tungsten/molybdenum $[\text{MO}_2\text{F}_4]^{2-}$ anionic compounds with pure metal cations have been also discovered [7,8], however the assembling chemistry of $[\text{WO}_2\text{F}_4]^{2-}$ anions with organic cations was little focused on.

The aim of this paper is to focus on $[\text{WO}_2\text{F}_4]^{2-}$ anionic units, in order that we can further understand the self-assembling processes and inter-relations of these anionic units and organic cationic building units. The octahedron of $[\text{WO}_2\text{F}_4]^{2-}$ anion is usually in *cis*-arrangement (Scheme 1), thus inherently acentric and polarizable, owing to the distortion arising from the second order Jahn–Teller effect of d^0 transition metals [9]. The distortion gives rise to the difference of negative charge on the surface of octahedron, thus hydrogen bond and/or electrostatic interactions usually occur in preferred orientations so as to the easy and convenient formations of hydrogen bond between the $[\text{WO}_2\text{F}_4]^{2-}$ anion and organic cation. In this paper we discuss the self-assembly [10], geometric and electronic structures [11–13], and structure-directing properties of an organic–inorganic hybrid salt containing $[\text{WO}_2\text{F}_4]^{2-}$ anion and protonated 2-(2-hydroxyphenyl)benzimidazole cation, pbmH^+ (pbm = 2-(2-hydroxyphenyl)benzimidazole, Scheme 1), namely $[(\text{pbmH})_2][\text{WO}_2\text{F}_4]$ (**1**).

The X-ray measurement [14–16] reveals that **1** is an organic–inorganic hybrid salt containing organic cation pbmH^+ and inorganic anion $[\text{WO}_2\text{F}_4]^{2-}$ (Fig. s1, Tables s1, s2). The coordination geometry of octahedron $[\text{WO}_2\text{F}_4]^{2-}$ is acentric and two vertex O atoms are in a *cis*-form arrangement. Owing to the heavy disorder of $[\text{WO}_2\text{F}_4]^{2-}$ anions in

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Scheme 1. Structures of [WO₂F₄]²⁻ anion and pbmH⁺ cation.

crystalline solid the W–O and W–F bonds are hard to measure accurately, and just were restrained to equivalent values for those disordered vertex O/F atoms when refined. Therefore the distortion of [WO₂F₄]²⁻ octahedron cannot be readily observed by the X-ray measured geometry, but can be easily found by the calculated results (Table s2). The central tungsten is obviously shifted towards O1 and O1' atoms (Fig. s1), forms two shorter W–O bonds, and correspondingly two longer W–F bonds with the *trans* F1 and F1' atoms. Another two *cis* W–F bonds to F2 and F2' atoms are little affected by the out of center distortion.

The cation is protonated pbm, pbmH⁺, and linked to adjacent [WO₂F₄]²⁻ anions by means of intermolecular hydrogen bond interaction. The pbmH⁺ gives three hydrogen bonds via one OH and two NH groups to [WO₂F₄]²⁻ units (O4–H···F1 2.644(4) Å, N1–H···F1 2.821(4) Å and N2–H···F2 2.676(5) Å) (Fig. s2), while adjacent [WO₂F₄]²⁻ unit accepts hydrogen bonds just via F1/F1' and F2/F2' vertex atoms, and no hydrogen bonds can be observed in the O1/O1' atoms. Moreover the intramolecular hydrogen bond (N1–H···O4 2.660(5) Å) of pbmH⁺ is present, which fixes the two moieties of pbmH⁺ unit into an approximate plane.

For [WO₂F₄]²⁻ anion the F1/F1' atoms *trans* to O/O1' atoms, having the longer W–F bond length (exptl. 1.884(3)/1.884(3) Å, calcd. 2.008/2.006 Å) accept three hydrogen bonds, the F2/F2' atoms *cis* to O1/O1' atoms having the shorter W–F bond length (exptl. 1.843(4)/1.843(4) Å, calcd. 1.943/1.943 Å) accept one hydrogen bond, whereas the O1/O1' atoms having the shortest W–O bond length (exptl. 1.842(3)/1.842(3) Å, calcd. 1.759/1.759 Å) accept zero hydrogen bond. In other words, the ability of the vertex O/F atoms towards acting as hydrogen bond acceptors depends on their distances away from the central W atom. The shorter, the weaker is the ability for hydrogen bond, and the longer the stronger is the ability for hydrogen bond. In the present case, only the vertex F1 (*trans* O) and F2 (*cis* O) atoms accept hydrogen bonds from pbmH⁺, thus the crystal stacking and assembly of [WO₂F₄]²⁻ anions and pbmH⁺ cations into solid **1** is mainly governed by *cis*-directing hydrogen bonds. In other words, the assembly of [WO₂F₄]²⁻ anions with pbmH⁺ cations should be structure-directing, or hydrogen-directing.

For pbmH⁺ cation, it is approximately co-planar, thus, adjacent face-to-face pbmH⁺ units are interacted with one another via π – π stacking interactions, and such interactions further control the stacking orientation of pbmH⁺ units. This assumption has been proven by the observed fact that the head-to-tail π – π stacking interactions with a stacking distance of about 3.34 Å in an offset style are present in **1** (Fig. s3), which link adjacent pbmH⁺ units into one another. Both the hydrogen bond and π – π stacking interactions link adjacent anions and cations, which are extended into three-dimensional arrays.

The calculated electrostatic potential contour map illustrates the region of electrostatic potential population on molecule surface. The molecular electrostatic potential represents the attraction or repulsion between a molecule and a proton. Attraction is represented by negative values (blue color) and repulsion is indicated by positive values (red color). Fig. 1 shows clearly that the blue regions are mainly located on the F1/F1' atoms *trans* the O1(O1') atoms, an indicative

that the F1/F1' atoms have the strongest ability for accepting hydrogen bonds, which is in agreement with the experimental observations that F1/F1' atoms accept three hydrogen bonds, while F2/F2' atoms *cis* the O1(O1') atoms just accept one hydrogen bond, and the O/O1' atoms accept zero hydrogen bond.

The geometry optimization [11] of [WO₂F₄]²⁻ anion exhibits very short W1–O1(O1') bonds (2 × 1.759 Å, Table s2), and very long W1–F1(F1') bonds to the *trans* F1(F1') atoms (2.008/2.006 Å), while the two *cis* W1–F2(F2') bonds are 2 × 1.943 Å in length. The very short W1–O1(O1') bonds (2 × 1.759 Å), indicate that the octahedron is highly distorted with the central W shifted to the two vertex O1(O1') atoms, and as a result the two bonds to the *trans* F1(F1') atoms are correspondingly very long (2.008/2.006 Å), compared with the two *cis* W1–F2(F2') bonds (2 × 1.943 Å). The calculated distortion phenomenon of *d*⁰ W octahedron can be easily accounted for by the second order Jahn–Teller effect [9].

The calculated frontier molecular orbitals and their electron density diagrams for [WO₂F₄]²⁻ anion indicate that the frontier orbitals are primarily the W orbitals, or the vertex O/F orbitals, and the orbital mixing between them is little (Fig. 2, Table s3). The unoccupied LUMO to LUMO + 10 orbitals, in an energetic range of 8–18 eV, are composed primarily of W (5*d*, 6*s*, 6*p*) orbitals (68–100%) with minor contribution from vertex O1(O1') 2*p* orbitals (0–30%); The occupied HOMO-3 to HOMO orbitals, in an energetic range of 1.2–2.7 eV, are composed primarily of O1(O1') 2*p* orbitals (61–90%) with minor contribution from vertex F1(F1') or F2(F2') 2*p* orbitals (0–28%); The occupied HOMO-8 to HOMO-4 orbitals, in an energetic range of 0.67–1.2 eV, are composed primarily of F1(F1') 2*p* orbitals (56–80%) with minor contribution from vertex O1(O1') or F2(F2') 2*p* orbitals (13–36%); while those occupied HOMO-11 to HOMO-9 orbitals, between an energetic range of –0.9––0.3 eV, are mainly from F2(F2') 2*p* orbitals (85–93%) with minor contribution from vertex O1(O1') 2*p* orbitals (3–6%).

Density of states (DOS) or partial density of states (PDOS), in combination with the frontier molecular orbitals, gives the overall electronic structure of a molecule. The overlap population density of states (OPDOS) analysis helps in studying the detailed bonding properties between a group of atoms and the other atoms in a molecule [17–19]. The PDOS and OPDOS diagrams of [WO₂F₄]²⁻ anion are plotted in Figs. s4, s5, respectively. The bonding properties in [WO₂F₄]²⁻ anion were

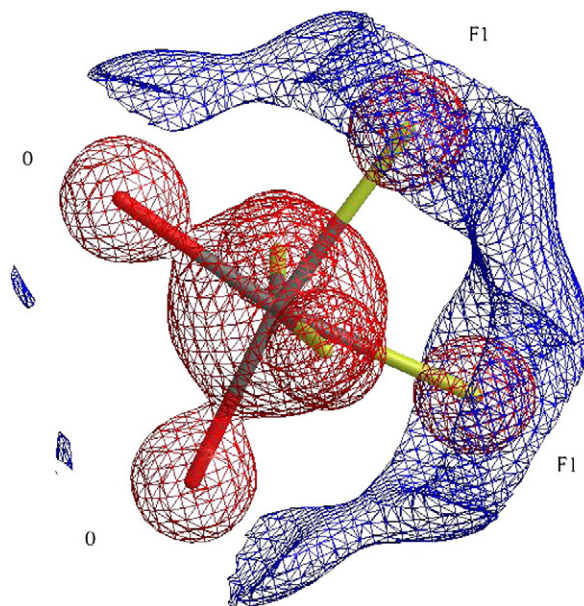


Fig. 1. The electrostatic potential contour map of [WO₂F₄]²⁻ anion. Red denotes the areas of repulsion to a proton, while blue denotes the areas of attraction to a proton.

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