The Ordered [WO₂F₄]²⁻ Anion

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Coordination to the three most charged (basic) sites on the $[WO_2F_4]^{2-}$ anion in the new compound $[HNC_6H_6OH]_2[Cu(NC_5H_5)_4$-$(WO_2F_4)_2]$, using the additional hydrogen bond from the hydroxyl group on 5-hydroxy-2-methylpyridinium, successfully distinguishes the oxide and fluoride ligands. An ordered $[WO_2F_4]^{2-}$ anion has been observed only once before in $Na_2WO_2F_4$.[1] This new compound provides insight into the group 6 oxide fluoride anions $[MoO_2F_4]^{2-}$ and $[WO_2F_4]^{2-}$ and the origins of their remarkably different solid-state structures.

The incorporation of acentric transition metal oxide fluoride anions in structures without disorder of the anion, in particular chiral or polar structures, requires that their interactions with neighboring cations be understood. Bond valence calculations, which quantify the residual negative charge on each ligand, can explain their structure-directing properties when exact bond lengths are known.[2,3] The most nucleophilic ligands on each anion have the most residual negative charge, and coordination is preferential through these ligands.

Crystallographic disorder of oxide fluoride anions is common and obscures exact bond lengths and angles.[4] Our group successfully employed two different strongly coordinating cations to discern the oxide and fluoride positions on the $[NbOF_5]^{2-}$ and $[MoO_2F_4]^{2-}$ anions.[4] However, similar efforts with the $[WO_2F_4]^{2-}$ anion ordered only one of the two oxygens in $[pyH]_2[Cu(py)_4$-$(WO_2F_4)_2]$, where py = pyridine.[5] The tungsten anion is disordered in every case with the exception of $Na_2WO_2F_4$.

An ordered structure was achieved in $[HNC_6H_6OH]_2[Cu(py)_4$-$(WO_2F_4)_2]$ by providing three different cationic contacts for the anion: two through hydrogen bonds to $[HNC_6H_6OH]^+$ and one to the $[Cu(py)_4]^{2+}$ cation. Two cis oxides and four fluorides surround a central tungsten atom constructing the octahedral $[WO_2F_4]^{2-}$ anion. The tungsten, distorted toward the cis oxides, forms short W−O bonds and longer W−F bonds to the fluorides trans to the oxides. See Table 1. One oxide ligand, O(1), coordinates to the $[Cu(py)_4]^{2+}$ cation, lengthening the W−O(1) bond. See Figure 1. F(1), the fluoride trans to O(1), accepts a hydrogen bond from the protonated amine in $[HNC_6H_6OH]^+$. The third contact to the anion is made through F(2), the fluoride trans to the uncoordinated oxide, which hydrogen bonds to a hydroxyl functional group on a second $[HNC_6H_6OH]^+$ cation.[6−9] The difference in length of the two W−O bonds is due to these coordination effects.

The octahedral d^9 Jahn−Teller $[Cu(py)_4]^{2+}$ cation is formed of four pyridine rings in equatorial positions at a distance of 2.036(2) Å. Two $[WO_2F_4]^{2-}$ anions coordinate to one $[Cu(py)_4]^{2+}$

Table 1. Bond Valence Sums for [WO₂F₄]²⁻ and [MoO₂F₄]²⁻

	R_i, Å	S_i	$V_i - S_i$
W−O(1)	1.772(2)	1.50	0.50[a]
W−O(2))	1.714(2)	1.75	0.25
W−F(1)	2.059(2)	0.54	0.46[b]
W−F(2)	2.029(2)	0.58	0.42[c]
W−F(3)	1.903(2)	0.82	0.18
W−F(4)	1.908(2)	0.81	0.19
	$\sum S_W$ 6.00		
Mo−O(1)	1.709(2)	1.71	0.29
Mo−O(2)	1.697(2)	1.76	0.24
Mo−F(1)	2.059(1)	0.51	0.49[d]
Mo−F(2)	2.114(1)	0.44	0.56[e]
Mo−F(3)	1.939(1)	0.70	0.30
Mo−F(4)	1.918(2)	0.74	0.26
	$\sum S_{Mo}$ 5.86		

$^{a-e}$ Also bonds to $^a[Cu(py)_4]^{2+}$, ^{b}H on the amine, ^{c}H on the hydroxyl group, $^d[Cu(py)_4]^{2+}$, and ^{e}H on an amine.

in the axial coordination sites at a distance of 2.321(2) Å, which leads to a dinegative 1:2 (Cu:W) cluster. A one-dimensional chain is constructed from the coordination of each cluster to two adjacent clusters through hydrogen bonds from four $[HNC_6H_6OH]^+$ cations. See Figure 1. $[HNC_6H_6OH]^+$ forms a hydrogen bond to one cluster through the protonated amine and a second hydrogen bond to a different cluster through the hydroxyl group. Every other cluster in the chain is offset slightly, creating staggered chains that run parallel to the [1 0 2] vector and form sheets in the (0 1 0) plane. Sequential anions along the chain are progressively rotated 90° around the W−O−Cu bond axis.

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(6) Single crystals of $[HNC_6H_6OH]_2[Cu(py)_4(WO_2F_4)_2]$ were synthesized by placing 0.1178 g (1.48 × 10⁻³ mol) of CuO and 0.3436 g (1.48 × 10⁻³ mol) of WO₃ in an FEP (fluoro(ethylene-propylene)) Teflon "pouch" containing 0.3908 g (1.48 × 10⁻³ mol) of (HF)ₓ·pyridine, 1.0303 g (9.44 × 10⁻³ mol) of 5-hydroxy-2-methylpyridine, and 0.0623 g (3.46 × 10⁻³ mol) of H₂O. The pouch was sealed and place in a 2000 mL autoclave (Parr) filled with 600 mL of deionized water, along with up to 30 additional pouches of different molar ratios. The autoclave was sealed, heated to 150 °C for 24 h, and then cooled to room temperature over an additional 24 h. After 3 weeks crystals formed in the pouches, which were then were opened in air. Blue block crystals were recovered by filtration in 30% yield based on copper.
(7) A Bruker Smart 1000 instrument with a CCD plate area detector was used to collect single-crystal X-ray data. Data were collected at a temperature of −120 °C using molybdenum radiation with a wavelength of $\lambda = 0.71069$. Octants collected: ±h, −14 to 14; ±k, −21 to 21; and ±l:, −28 to 27. Crystal data: monoclinic, space group C2/c (No. 15), with a = 10.900(3) Å, b = 16.099(2) Å, c = 21.424(3) Å, β = 92.57(2)°, and Z = 4. ρ_{calcd} = 2.094 g/cm³, ρ_{obsd} = 2.06(1) g/cm³ as measured by flotation pycnometry. The crystal dimensions: 0.16 × 0.15 × 0.24 mm; $2\theta_{max}$ = 56.6°; total reflections = 17352; unique reflections = 4655; $R(F_o)$ = 0.020; $R_w(F_o)$= 0.020; μ = 67.70 cm⁻¹. Mid-infrared (400−4000 cm⁻¹) spectra were collected using a Bio-Rad FTS-60 FTIR spectrometer operating at a resolution of 1 cm⁻¹. The infrared spectrum of the compound shows the ν_s(W−O) = 960 cm⁻¹ and ν_{as}(W−O) = 904 cm⁻¹.
(8) TEXSAN: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.
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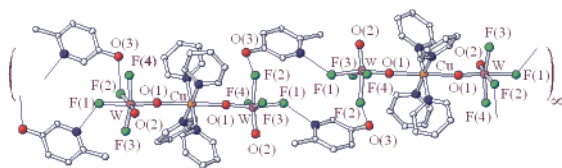
Figure 1. Two units of [HNC$_6$H$_6$OH]$_2$[Cu(py)$_4$(WO$_2$F$_4$)$_2$] create a staggered chain. Hydrogens have been removed for clarity. Lines denote hydrogen bonds.

The difficulty in ordering the [WO$_2$F$_4$]$^{2-}$ anion as compared to [MoO$_2$F$_4$]$^{2-}$, its group 6 analogue, can be understood upon an examination of the electronegativities of the two metal ions and the bond valence calculations of both. Despite similar out of center distortions of the metal, the tungsten anion has longer W−O bonds than the molybdenum anion. See Table 1. The bond lengthening occurs as a result of a decrease in electronegativity as one descends group 6 from Mo to W. The relative nucleophilicities of the ligands around the metal atom in [WO$_2$F$_4$]$^{2-}$ and [MoO$_2$F$_4$]$^{2-}$ are apparent using bond valence calculations.[10] As a result of the longer bond lengths in the tungsten case, O(1) is highly nucleophilic, closely followed by the fluorides trans to the oxides, F(1) and F(2). See Table 1. The similarly large and negative charges that remain on three ligands do not favor one orientation of the anion over another unless three contacts to each anion are made. Distinctly different, the Mo−O bonds are shorter and the remaining negative charges on the oxides are reduced. The most nucleophilic ligands in the [MoO$_2$F$_4$]$^{2-}$ anion are the cis fluorides, F(1) and F(2), which are trans to the cis oxides. With two highly nucleophilic ligands, an ordered [MoO$_2$F$_4$]$^{2-}$ anion requires two, rather than three, separate cationic contacts.[4,11]

The [WO$_2$F$_4$]$^{2-}$ anion thus directs coordination in a trans fashion.[5] The most nucleophilic ligands, O(1) and F(1), are trans to one another and bind to the electrophilic [Cu(py)$_4$]$^{2+}$ and the protonated amine. A hydrogen bond to F(2) is necessary to order the anion, for without a third contact, the anion will disorder in the O(2), F(2), F(3), and F(4) positions. The trans-directing nature of the [WO$_2$F$_4$]$^{2-}$ anions favors the formation of a one-dimensional chain.

These results and observations also explain the high-temperature solid-state structures of Cs$_2$WO$_2$F$_4$ and Na$_2$WO$_2$F$_4$, where

Figure 2. The coordination sphere around the [WO$_2$F$_4$]$^{2-}$ anion in Na$_2$WO$_2$F$_4$ (left) and Cs$_2$WO$_2$F$_4$ (right).

the [WO$_2$F$_4$]$^{2-}$ anion is disordered and ordered, respectively. Cs$_2$[WO$_2$F$_4$] is a hexagonal close packed lattice of ions in which one-third of the Cs$^+$ cations have been replaced by the similarly sized [WO$_2$F$_4$]$^{2-}$ anion.[12] Four Cs atoms, in equivalent positions, coordinate each disordered O/F ion. The coordination environment of each site is identical, leading to the random orientation of the [WO$_2$F$_4$]$^{2-}$ anion. In contrast, Na$_2$WO$_2$F$_4$ does not pack in an efficient hcp lattice because of the size disparity between the Na$^+$ cations and the [WO$_2$F$_4$]$^{2-}$ anions. Each sodium ion resides in one of two crystallographic positions, Na(1) and Na(2).[13] See Figure 2. Since two sodium ions coordinate to each fluoride and oxide ion, three combinations are possible: two Na(1), two Na(2), or one Na(1) and one Na(2). The WO$_2$F$_4$ octahedra are ordered in the solid state by the three different coordination modes, the same number as was possible with an additional hydrogen bond donor, a hydroxyl group, on 5-hydroxy-2-methylpyridinium.

(10) Valence sums calculated with the formula $S_i = \exp[(R_0 - R_i)/B]$, where S_i = bond valence of bond i, R_0 = constant dependent on the bonded elements (for Mo−O = 1.907, Mo−F = 1.81, W−O = 1.921, W−F = 1.83), R_i = bond length of bond i, and B = 0.370. V = predicted valence for a site. $V − S_i$ = residual charge on site i.
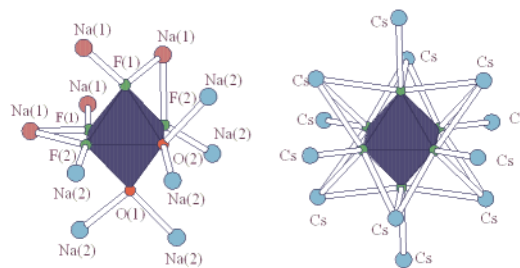(11) Grandjean, D.; Weiss, R. *Bull. Soc. Chim. Fr.* **1967**, 3049.
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