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The Structure-Directing Properties of $[VOF_5]^{2-}$

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Early transition metal oxide fluoride anions such as $[NbOF_5]^{2-}$,[1−4] $[TaOF_5]^{2-}$,[4] and $[MoO_2F_4]^{2-}$ [5] interest researchers because their inherent distortions mimic those in the $[NbO_{6/2}]^-$ octahedra in $LiNbO_3$,[6] an excellent solid state nonlinear optical material. The distortions reduce the point symmetry from octahedral, O_h, to approximately C_4 for $[NbOF_5]^{2-}$ and $[TaOF_5]^{2-}$, and C_2 for $[MoO_2F_4]^{2-}$ (see Figure 1). The focus of this work is to understand the crystallization behavior of d^0 metal oxide fluoride anions in order to form molecular nonlinear optical materials.[4] The relative nucleophilicity of the oxide and fluoride ligands of early transition metal oxide fluoride anions is the most important factor that determines their solid state structures.[7] Bond valence calculations were performed to quantify the residual negative charge on each ligand. In all cases, the ligands with greater negative charge are more nucleophilic and coordination is preferential to those sites. The difference in structure-directing properties of $[VOF_5]^{2-}$ with respect to its Group 5 analogues ($[NbOF_5]^{2-}$, $[TaOF_5]^{2-}$) is reported in this communication. Surprisingly, the solid state structure of $[VOF_5]^{2-}$ in $[pyH]_2[Cu(py)_4(VOF_5)_2]$[8,9] is identical with that of the Group 6 dioxo anion $[MoO_2F_4]^{2-}$ in $[pyH]_2[Cu(py)_4(MoO_2F_4)_2]$.[5]

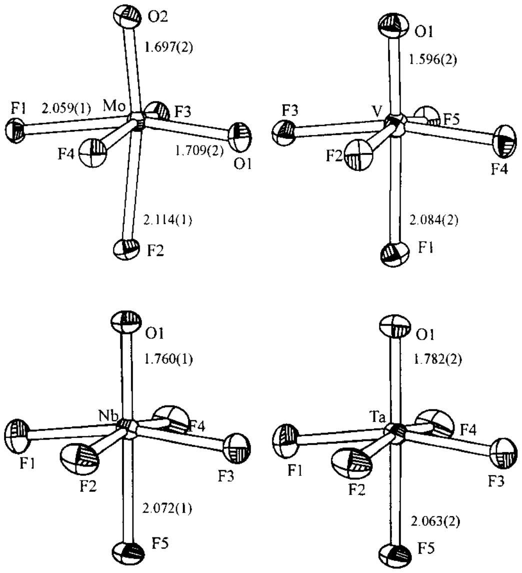

Figure 1. Thermal ellipsoid plots (50% probability) of $[MoO_2F_4]^{2-}$, $[VOF_5]^{2-}$, $[NbOF_5]^{2-}$, and $[TaOF_5]^{2-}$. Selected bond lengths are included (Å).

In the family of anions $[MOF_5]^{2-}$ (M = V, Nb, Ta) the metal cation forms a short bond to the oxygen, which leaves a long trans metal fluoride bond, resulting in a distortion of the cation from the center to a corner of the octahedron. In all cases, the long metal trans fluoride bond is weak; this ligand retains significant negative charge and is highly nucleophilic. As one descends Group 5 from V to Ta, the electronegativity decreases from 1.63 to 1.60 and 1.5 for V, Nb, and Ta, respectively. As a result the metal oxide bond lengthens, decreasing the valence of the bond, which leaves a higher negative charge on the oxide ligand. Bond lengths and bond valence calculations[10] for $[VOF_5]^{2-}$, $[NbOF_5]^{2-}$, and $[TaOF_5]^{2-}$ are listed in Table 1. In the $[VOF_5]^{2-}$ anion a strong vanadium oxide bond leaves little residual negative charge on the oxide.[11] The four equatorial fluorides, F(2)−F(5), retain equivalent or slightly greater negative charges. Coordination is then directed through the fluoride trans to the oxide, F(1), and an equatorial fluoride, F(3), the two most nucleophilic sites. The metal oxide bonds are longer in $[NbOF_5]^{2-}$ and $[TaOF_5]^{2-}$ and the oxide ligands retain much more negative charge than the four equatorial ligands on each anion. Consequently, coordination is directed through the oxide ligand and trans fluoride ligand.

Unlike the Group 5 $[MOF_5]^{2-}$ (M = V, Nb, Ta) species, $[MoO_2F_4]^{2-}$ is strongly distorted with the Mo^{6+} cation displaced from the center of the $[MoO_2F_4]^{2-}$ octahedron in the direction of the cis oxide ligands or toward an edge of the octahedron. However, as in $[VOF_5]^{2-}$, $[NbOF_5]^{2-}$, and $[TaOF_5]^{2-}$, the metal oxide bonds are short, and the bonds to the two trans fluorides are long. The oxide ligands retain little negative charge with respect to the other ligands, especially the trans fluorides, F(1) and F(2), which are highly charged (see Table 1). As a result, coordination is directed in a cis fashion through the trans fluorides. Therefore, despite

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(8) Single crystals of $[pyH]_2[Cu(py)_4(VOF_5)_2]$ were synthesized by placing 0.0635 g (7.98×10^{-4} mol) of CuO and 0.0318 g (3.50×10^{-4} mol) of V_2O_5 in an FEP Teflon (fluoro(ethylene-propylene)) "pouch" containing 0.9891 g (3.76×10^{-3} mol) of $(HF)_x$·pyridine, 1.5008 g (1.90×10^{-2} mol) of py, and 0.0471 g (2.62×10^{-3} mol) of H_2O. The pouch was sealed and placed in a 2000-mL autoclave (Parr) filled with 600 mL of deionized water. The autoclave was sealed and heated to 150 °C for 24 h and then cooled to room temperature over an additional 24 h. Pouches were opened in air, and purple prisms were recovered by filtration in 43% yield based on copper.

(9) A Bruker Smart 1000 instrument with a CCD plate area detector with a graphite monochromator was used to collect single-crystal X-ray data. An analytical absorption correction was applied. Crystal data: monoclinic, space group $C2/c$ (No. 15), with $a = 18.115(1)$ Å, $b = 11.296(1)$ Å, $c = 18.743(1)$ Å, $\beta = 107.986(1)°$, $Z = 4$, $T = -120$ K, $\lambda = 0.71069$ Å. Crystal dimensions: $0.13 \times 0.23 \times 0.02$ mm, $2\theta_{max} = 56.6°$. Reflections: total = 24620, unique = 9410, $R_{int} = 0.035$, $R = 0.037$, $R_w = 0.043$, $\mu = 11.06$ cm^{-1}; $\pm h$, −12 to 12; $\pm k$, −12 to 12; and $\pm l$, −22 to 20. Density measured by flotation pycnometry at 25 °C: $\rho_{obsd} = 1.511(2)$ g/cm^3, $\rho_{calc} = 1.491$ g/cm^3. 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 shows the V═O stretching frequency at 960 cm^{-1}.

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Table 1. Bond Valence Sums[a] for $[VOF_5]^{2-}$, $[NbOF_5]^{2-}$, $[MoO_2F_4]^{2-}$, and $[TaOF_5]^{2-}$

	R_i, Å	S_i	$V - S_i$		R_i, Å	S_i	$V - S_i$
	$[VOF_5]^{2-}$				$[MoO_2F_4]^{2-}$		
V=O(1)	1.596(2)	1.75	0.25	Mo=O(1)	1.709(2)	1.71	0.29
V−F(1)	2.084(2)	0.36	0.64[c]	Mo=O(2)	1.697(2)	1.76	0.24
V−F(2)	1.819(2)	0.74	0.26	Mo−F(1)	2.059(1)	0.51	0.49[b]
V−F(3)	1.883(2)	0.63	0.37[b]	Mo−F(2)	2.114(1)	0.44	0.56[c]
V−F(4)	1.811(2)	0.76	0.24	Mo−F(3)	1.939(1)	0.70	0.30
V−F(5)	1.836(2)	0.71	0.29	Mo−F(4)	1.918(2)	0.74	0.26
	ΣS_V	4.95			ΣS_{Mo}	5.86	
	$[NbOF_5]^{2-}$				$[TaOF_5]^{2-}$		
Nb=O(1)	1.760(1)	1.54	0.46[b]	Ta=O(1)	1.782(2)	1.45	0.55[b]
Nb−F(1)	1.953(1)	0.70	0.30	Ta−F(1)	1.946(2)	0.68	0.32
Nb−F(2)	1.923(1)	0.76	0.24	Ta−F(2)	1.923(2)	0.72	0.28
Nb−F(3)	1.928(1)	0.75	0.25	Ta−F(3)	1.920(2)	0.73	0.27
Nb−F(4)	1.928(1)	0.75	0.25	Ta−F(4)	1.925(2)	0.72	0.28
Nb−F(5)	2.072(1)	0.51	0.49[c]	Ta−F(5)	2.063(2)	0.50	0.50[c]
	ΣS_{Nb}	5.01			ΣS_{Ta}	4.80	

[a] 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, R_i = bond length of bond "*i*", and $B = 0.370$. ΣS_m = bond valence sum for the metal. V = predicted valence for a site. R_0(Mo−O) = 1.907 Å, R_0(Mo−F) = 1.808 Å, R_0(V−O) = 1.803 Å, R_0(V−F) = 1.710 Å, R_0(Nb−O) = 1.911 Å, R_0(Nb−F) = 1.822 Å, R_0(Ta−O) = 1.920 Å, R_0(Ta−F) = 1.803 Å.[13] [b] Bound to Cu^{2+}. [c] H-bond acceptor.

the structural differences between the $[MoO_2F_4]^{2-}$ and $[VOF_5]^{2-}$ anions, they both direct coordination through cis ligands.

The similar structure-directing properties of $[MoO_2F_4]^{2-}$ and $[VOF_5]^{2-}$ anions are demonstrated by the fact that two compounds $[pyH]_2[Cu(py)_4(MX_6)_2]$ (MX_6 = $[VOF_5]^{2-}$, $[MoO_2F_4]^{2-}$) composed of anionic $[Cu(py)_4(MX_6)_2]^{2-}$ clusters and pyridinium cations, are isostructural. The cluster is constructed by the coordination of two $[MX_6]^{2-}$ anions to a central $[Cu(py)_4]^{2+}$ cation. Each $[MX_6]^{2-}$ anion directs coordination through cis ligands; that is, a fluoride ligand trans to an oxide ligand accepts a hydrogen bond from pyridinium, while another fluoride ligand, cis to the hydrogen bond acceptor, coordinates to the $[Cu(py)_4]^{2+}$ cation. The oxide ligand(s) on both anions neither coordinate to the copper center nor accept a hydrogen bond. The hydrogen bond angle in $[pyH]_2[Cu(py)_4(VOF_5)_2]$, N(3)−H(16)−F(1), is 174(3)°, which is within the reported calculated range of 140−180° typical for N−H−F bonds.[12] The $[Cu(py)_4]^{2+}$ cation consists of four pyridine rings coordinated to a central Cu^{2+} cation in a square planar arrangement. The Jahn Teller Cu^{2+} (d^9) binds to the four pyridine molecules with an average Cu−N bond length of 2.035(3) Å, while the Cu−F bonds are 2.460(2) Å. The anionic clusters in each plane (−1 0 1) pack in a "herringbone" pattern with pyridinium and coordinated pyridine occupying the space between sheets (see Figure 2). Each successive sheet is shifted $(a + b)/2$, resulting in the C centering of the cell.

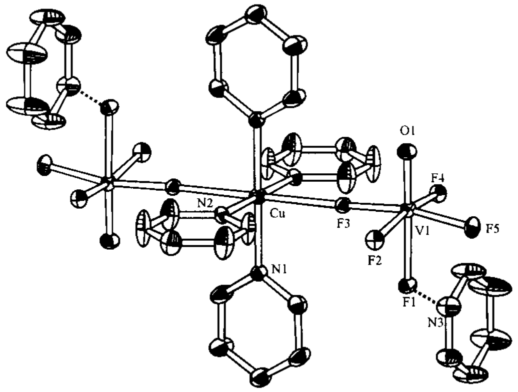

Figure 2. Thermal ellipsoid plot (50% probability) of $[pyH]_2[Cu(py)_4(VOF_5)_2]$. Hydrogen atoms have been omitted for clarity. Dashed lines represent hydrogen bonds.

The distinct difference in coordination preference between $[VOF_5]^{2-}$ and $[NbOF_5]^{2-}$ can be observed by comparing $[pyH]_2[Cu(py)_4(VOF_5)_2]$ to $[pyH]_2[Cu(py)_4(NbOF_5)_2]$,[2] both of which contain similar anionic clusters. However, the $[NbOF_5]^{2-}$ anions direct coordination in a much different fashion. As previously discussed, the most nucleophilic sites on the $[NbOF_5]^{2-}$ anion are the oxide and the trans fluoride ligands. Coordination is preferential to these ligands; accordingly, the oxide ligand coordinates to the copper center and the trans fluoride accepts a hydrogen bond from pyridinium. The trans coordination of the $[NbOF_5]^{2-}$ anion changes the three-dimensional structure of $[pyH]_2[Cu(py)_4(NbOF_5)_2]$ with respect to $[pyH]_2[Cu(py)_4(VOF_5)_2]$. $[pyH]_2[Cu(py)_4(NbOF_5)_2]$ contains planes, (0 0 1), of parallel, end to end clusters. Each layer is rotated 90° every $c/4$ creating a 4_1 screw axis.

Despite the structural differences between $[VOF_5]^{2-}$ and $[MoO_2F_4]^{2-}$, each anion directs coordination through cis ligands. In contrast, $[NbOF_5]^{2-}$ and $[TaOF_5]^{2-}$, which are structurally similar to $[VOF_5]^{2-}$, direct coordination through trans ligands. Bond valence calculations have proven valuable in explaining their varied coordination preferences and how these structure-directing properties affect the solid state structure to a greater extent than the type of out of center distortion which occurs in the anions $[MX_6]^{2-}$ (MX_6 = $[VOF_5]^{2-}$, $[NbOF_5]^{2-}$, $[TaOF_5]^{2-}$, $[MoO_2F_4]^{2-}$) of Groups 5 and 6.

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Supporting Information Available: Stereoscopic views of the crystal packing of $[pyH]_2[Cu(py)_4(VOF_5)_2]$. One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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