[pyH]$_2$[Cu(py)$_4$(MX$_6$)$_2$] (MX$_6$ = ZrF$_6$$^{2-}$, NbOF$_5$$^{2-}$, MoO$_2F_4$$^{2-}$; py = Pyridine): Rarely Observed Ordering of Metal Oxide Fluoride Anions

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Single crystals of [pyH]$_2$[Cu(py)$_4$(MX$_6$)$_2$] (MX$_6$ = ZrF$_6$$^{2-}$, MoO$_2F_4$$^{2-}$; py = pyridine), analogous to those of the previously reported [pyH]$_2$[Cu(py)$_4$(NbOF$_5$)$_2$], were synthesized by reaction of the metal oxides in (HF)$_x$·pyridine/pyridine/water solutions (150 °C, autogeneous pressure). The NbOF$_5$$^{2-}$ and MoO$_2$F$_4$$^{2-}$ anions generally crystallize with orientational disorder masking the true coordination geometry. The combination of the two different and strongly coordinating cations tetrakis(pyridine)copper(II) and pyridinium causes the anions to adopt regular and ordered orientations. Crystal data: for [pyH]$_2$[Cu(py)$_4$(ZrF$_6$)$_2$], tetragonal, space group *I*4/*mmm* (No. 139), with *a* = 11.047(1) Å, *c* = 16.763(3) Å, and *Z* = 2; for [pyH]$_2$[Cu(py)$_4$(MoO$_2$F$_4$)$_2$], monoclinic, space group *C*2/*c* (No. 15), with *a* = 19.195(4) Å, *b* = 11.316(3) Å, *c* = 18.920(5) Å, β = 107.68(2)°, and *Z* = 4.

Introduction

Materials which crystallize in acentric space groups often display important physical properties. Piezoelectricity, ferroelectricity, and second-order nonlinear optical behavior are all possible with acentric materials. Unfortunately, serendipity often determines whether a crystal adopts an acentric structure. Therefore, any systematic and rational chemical advances leading to new functional materials with acentric crystal structures would be of technological interest. An obvious strategy is to begin with discrete acentric subunits. For example, the oxide fluoride anions NbOF$_5$$^{2-}$ and (*cis*-) MoO$_2$F$_4$$^{2-}$ are each inherently acentric (Figure 1). A survey of the literature (see Table 1) revealed 14 crystal structures containing NbOF$_5$$^{2-}$ [1−13] and 3 containing MoO$_2$F$_4$$^{2-}$.[14−16] All are reported centrosymmetric. Only two contain ordered NbOF$_5$$^{2-}$ octahedra,[6,12] while one contains ordered MoO$_2$F$_4$$^{2-}$.[14] In most cases,

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Figure 1. Thermal ellipsoid plots (50% probability) of the complex anions (a) ZrF$_6$$^{2-}$, (b) NbOF$_5$$^{2-}$, and (c) MoO$_2F_4$$^{2-}$.

Table 1. Crystal Structures Containing NbOF$_5$$^{2-}$ or MoO$_2$F$_4$$^{2-}$ anions

compound	ref	compound	ref
NbOF$_5$$^{2-}$			
K$_2$NbOF$_5$·KHF$_2$	1	BaNbOF$_5$	9
CuNbOF$_5$·4H$_2$O	2	[Sn$_6$F$_{10}$][NbOF$_5$]	10
K$_2$NbOF$_5$	3	CuNbOF$_5$·4py	11
Li$_2$NbOF$_5$	4	[pyH]$_2$[Cu(py)$_4$(NbOF$_5$)$_2$]	11
Cs$_2$NbOF$_5$	5	Cu(pyz)$_2$NbOF$_5$·(pyz)(H$_2$O)^a	12
N$_2$H$_6$[NbOF$_5$]·H$_2$O^a	6	CdNbOF$_5$·4py	13
[C$_9$H$_8$NO]$_2$[NbOF$_5$]·2H$_2$O	7	[Cd(4,4′-bpy)$_2$(H$_2$O)$_2$][NbOF$_5$]	13
Na$_2$NbOF$_5$	8		
MoO$_2$F$_4$$^{2-}$			
K$_2$MoO$_2$F$_4$·H$_2$O^a	14	Rb$_2$MoO$_2$F$_4$	16
K$_2$MoO$_2$F$_4$	15		

^{a} Crystallographically ordered anion.

the desired properties of the crystal are lost when the anions conform to the centricity of the crystal lattice because of disorder.

Therefore, in order to produce an acentric crystal structure from acentric octahedra, two goals must be met. First, the octahedra must crystallize with no disorder (no internal center of symmetry). Second, the octahedra must order in a noncentrosymmetric arrangement with respect to each other (no center of symmetry between the octahedra). The first of these goals has been met in the current work by crystallizing the complex anions with two different cations: tetrakis(pyridine)copper(II) $(Cu(py)_4^{2+})$ and pyridinium (pyH^+). Each cation coordinates to a specific site on the anion avoiding orientational disorder. Thus, accurate determination of bond lengths and angles by single-crystal X-ray diffraction is possible and the differences and similarities in the coordination of the isoelectronic series $[MO_xF_{6-x}]^{2-}$ (M = Zr(IV), Nb(V), Mo(VI)) may be examined.

Experimental Section

Caution! $(HF)_x \cdot$pyridine is toxic and corrosive.

Materials. CuO (99%, Aldrich), MoO_3 (99.5%, Aldrich), ZrO_2 (99%, Aldrich), pyridine (99.8%, anhydrous, Aldrich), and $(HF)_x \cdot$ pyridine (pyridinium poly(hydrogen fluoride), 70% by weight, Aldrich) were used as received. Reagent amounts of deionized H_2O were used in the syntheses.

Synthesis. The synthesis and structure of $[pyH]_2[Cu(py)_4(NbOF_5)_2]$ have been previously reported.[11] $[pyH]_2[Cu(py)_4(ZrF_6)_2]$ was synthesized by adding 2.98×10^{-2} g (3.75×10^{-4} mol) of CuO, 4.62×10^{-2} g (3.75×10^{-4} mol) of ZrO_2, 9.99×10^{-2} g (5.55×10^{-3} mol) of deionized water, 1.0157 g (1.28×10^{-2} mol) of pyridine, and 0.8272 g (3.14×10^{-3} mol) of $(HF)_x \cdot$pyridine to a FEP Teflon "pouch."[17] $[pyH]_2[Cu(py)_4(MoO_2F_4)_2]$ was synthesized by adding 1.1×10^{-1} g (1.4×10^{-3} mol) of CuO, 1.8×10^{-2} g (1.4×10^{-3} mol) of MoO_3, 1.3×10^{-2} g (7.2×10^{-4} mol) of deionized water, 1.0 g (1.26×10^{-2} mol) of pyridine, and 5.8×10^{-1} g (2.2×10^{-3} mol) of $(HF)_x \times$ pyridine to a FEP Teflon "pouch."

The pouches were sealed and placed into a 2000 mL autoclave (Parr) filled with 600 mL of deionized water. The autoclave was sealed and heated at 150 °C for 24 h and then cooled to room temperature over an additional 24 h. The pouches were removed from the autoclave and opened in air. Products were recovered by filtration. $[pyH]_2[Cu(py)_4(ZrF_6)_2]$ was recovered as pale blue crystals in approximately 70% yield (based on zirconium), and large dark blue crystals of $[pyH]_2[Cu(py)_4(MoO_2F_4)_2]$ were recovered in approximately 60% yield (based on molybdenum).

Crystallographic Determination. Relevant crystallographic data and selected atomic coordinates and isotropic thermal parameters are listed in Tables 2 and 3. Principal bond distances and angles are listed in Table 4. All calculations were performed using the TEXSAN crystallographic software package from Molecular Structure Corp.[18] The structures were solved by direct methods[19] and expanded using Fourier techniques.[20]

Crystal Structure of $[pyH]_2[Cu(py)_4(ZrF_6)_2]$. On the basis of systematic absences and successful solution and refinement of the structure, the space group was determined to be $I4/mmm$ (No. 139). Disorder in the pyridinium cation results from imposing 4-fold symmetry on the six-membered rings. Two unique sites in the asymmetric unit generate 12 sites over which each pyridinium is disordered (two sets of six positions). Potential hydrogen-bonding interactions were used to constrain N(2) and C(5) over the same position. N(2) and C(5) were refined isotropically, while all other non-

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Table 2. Crystallographic Data for $[pyH]_2[Cu(py)_4(ZrF_6)_2]$ and $[pyH]_2[Cu(py)_4(MoO_2F_4)_2]$

$[pyH]_2[Cu(py)_4(ZrF_6)_2]$	$[pyH]2[Cu(py)_4(MoO_2F_4)_2]$
empirical formula: $C_{30}H_{32}CuF_{12}N_6Zr_2$	empirical formula: $C_{30}H_{32}CuF_8N_6Mo_2O_4$
fw 950.59	fw 948.04
space group: $I4/mmm$ (No. 139)	space group: $C2/c$ (No. 15)
$a = 11.047(1)$ Å	$a = 19.195(4)$ Å
$c = 16.763(3)$ Å	$b = 11.316(3)$ Å
$V = 2045.6(4)$ Å^3	$c = 18.920(5)$ Å
$Z = 2$	$\beta = 107.68(2)$
$T = -120(1)$ °C	$V = 3915(1)$ Å^3
$\lambda = 0.71069$ Å	$Z = 4$
$\rho_{calcd} = 1.543$ g/cm^3	$T = -120(1)$ °C
$\rho_{obsd}{}^a = 1.55(1)$ g/cm^3	$\lambda = 0.71069$ Å
$\mu = 10.97$ cm^{-1}	$\rho_{calcd} = 1.608$ g/cm^3
$R^b = 0.031$	$\rho_{obsd}{}^a = 1.62(2)$ g/cm^3
$R_w{}^c = 0.034$	$\mu = 12.46$ cm^{-1}
	$R^b = 0.024$
	$R_w{}^c = 0.027$

^{a} Density measurements by flotation pycnometry at 25 °C. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table 3. Selected Atomic Coordinates for $[pyH]_2[Cu(py)_4(ZrF_6)_2]$ and $[pyH]_2[Cu(py)_4(MoO_2F_4)_2]$

atom	site	x	y	z	$B_{eq},{}^a$ Å^2
			$[pyH]_2[Cu(py)_4(ZrF_6)_2]$		
Zr	4e	0	0	0.26849(4)	1.186(6)
Cu	2a	0	0	0	1.27(1)
F(1)	4e	0	0	0.1463(2)	1.50(4)
F(2)	16m	0.1278(1)	0.1278(1)	0.2623(1)	2.55(2)
F(3)	4e	0	0	0.3856(2)	2.55(2)
N(1)	8h	0.1307(2)	0.1307(2)	0	1.55(3)
N(2)^b	32o	0.3809(5)	0.0315(4)	0.2514(3)	3.7(1)^c
C(4)^d	16k	0.4099(4)	0.0901(4)	0.25	4.2(1)
C(5)^b	32o	0.3809(5)	0.315(4)	0.2514(3)	3.7(1)^c
			$[pyH]_2[Cu(py)_4(MoO_2F_4)_2]$		
Mo	8f	0.85619(1)	0.21973(2)	0.36093(1)	0.883(5)
Cu	4b	0.5	0	0.5	1.04(1)
F(1)	8f	0.92402(7)	0.3438(1)	0.42691(8)	1.16(3)
F(2)	8f	0.92620(7)	0.1140(1)	0.44499(8)	1.18(3)
F(3)	8f	0.80540(7)	0.2399(1)	0.43443(8)	1.34(3)
F(4)	8f	0.93354(8)	0.2025(1)	0.31712(8)	1.44(3)
O(1)	8f	0.80991(9)	0.0940(2)	0.3243(1)	1.45(4)
O(2)	8f	0.80951(9)	0.3250(2)	0.3013(1)	1.42(4)
N(1)	8f	0.5638(1)	−0.0093(2)	0.4313(1)	1.19(5)
N(2)	8f	0.4347(1)	0.1218(2)	0.4322(1)	1.16(5)
N(3)	8f	0.8912(1)	0.0567(3)	0.5602(1)	2.51(6)
H(16)	8f	0.901(2)	0.080(3)	0.515(2)	4.0(9)^c

^{a} $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$. ^{b} Site occupancies: 0.125, N(2); 0.375, C(5). ^{c} Isotropic refinement. ^{d} Site occupancy: 0.5.

hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions.

Crystal Structure of $[pyH]_2[Cu(py)_4(MoO_2F_4)_2]$. On the basis of systematic absences and a successful solution and refinement of the structure, the space group was determined to be $C2/c$ (No. 15). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions, except for H(16) (pyridinium proton), which was refined isotropically.

Spectroscopic Measurements. Mid-infrared (400−4000 cm^{-1}) spectra were collected using a Bio-Rad FTS-60 FTIR spectrometer operating at a resolution of 2 cm^{-1}.

Results

All three $[pyH]_2[Cu(py)_4(MO_xF_{6-x})_2]$ compounds (M = Zr-(IV), Nb(V), Mo(VI)) are built from anionic $[Cu(py)_4(MO_x-F_{6-x})_2]^{2-}$ clusters hydrogen bonded to pyridinium (pyH^+) cations. These clusters comprise two smaller complex anions

Table 4. Principal Bond Distances (Å) and Angles (deg) in
[pyH]$_2$[Cu(py)$_4$(ZrF$_6$)$_2$], [pyH]$_2$[Cu(py)$_4$(NbOF$_5$)$_2$],[1] and
[pyH]$_2$[Cu(py)$_4$(MoO$_2$F$_4$)$_2$]

	[pyH]$_2$[Cu(py)$_4$(ZrF$_6$)$_2$]		
	Bond Distances		
Zr−F(1)	2.053(7)	Cu−N(1) × 4	2.038(7)
Zr−F(2) × 4	2.002(4)	Cu−F(1) × 2	2.446(7)
Zr−F(3)	1.966(9)		
	Bond Angles		
F(1)−Zr−F(2)	87.0(1)	F(2)−Zr−F(2)*	174.1(6)
F(1)−Zr−F(3)	180	F(2)−Zr−F(2)*	89.84(1)
N(1)−Cu−N(1)*	180	N(1)−Cu−N(1)*	90

	[pyH]$_2$[Cu(py)$_4$(NbOF$_5$)$_2$]		
	Bond Distances		
Nb−F(1) × 2	1.937(6)	Cu−N(1) × 2	2.06(1)
Nb−F(2) × 2	1.927(5)	Cu−N(2) × 2	2.06(1)
Nb−F(3)	2.099(8)	Cu−O × 2	2.417(9)
Nb−O	1.728(8)		
	Bond Angles		
O(1)−Nb−F(1)	95.7(2)	F(1)−Nb−F(1)*	168.7(2)
O(1)−Nb−F(2)	96.0(1)	F(2)−Nb−F(2)*	167.9(3)
O(1)−Nb−F(3)	180.0	F(1)−Nb−F(2)	89.5(1)
		N(1)−Cu−N(2)	90.0

	[pyH]$_2$[Cu(py)$_4$(MoO$_2$F$_4$)$_2$]		
	Bond Distances		
Mo−O(1)	1.709(2)	Cu−N(1)	2.040(2)
Mo−O(2)	1.697(2)	Cu−N(2)	2.034(2)
Mo−F(1)	2.059(1)	Cu−F(1)	2.437(1)
Mo−F(2)	2.114(1)	N(3)−H(16)	0.96(3)
Mo−F(3)	1.939(1)	N(3)···F(2)	2.551(3)
Mo−F(4)	1.918(2)	F(2)···H(16)	1.59(3)
	Bond Angles		
F(1)−Mo−O(1)	165.70(7)	F(3)−Mo−O(1)	94.35(8)
F(1)−Mo−O(2)	91.90(7)	F(3)−Mo−O(2)	96.61(8)
F(1)−Mo−F(2)	77.84(6)	F(3)−Mo−F(4)	161.07(6)
F(1)−Mo−F(3)	81.26(6)	F(4)−Mo−O(1)	96.63(8)
F(1)−Mo−F(4)	84.34(6)	F(4)−Mo−O(2)	96.08(8)
F(2)−Mo−O(1)	88.12(7)	O(1)−Mo−O(2)	102.16(9)
F(2)−Mo−O(2)	169.72(7)	N(1)−Cu−N(2)	90.43(9)
F(2)−Mo−F(3)	82.55(6)	N(2)−Cu−N(1)*	89.57(9)
F(2)−Mo−F(4)	82.46(6)	N(3)−H(16)···F(3)	174(3)

Figure 2. Thermal ellipsoid plots (50% probability) of the anionic [Cu(py)$_4$(MX$_6$)$_2$]$^{2-}$ clusters where MX$_6$ = (a) ZrF$_6^{2-}$, (b) NbOF$_5^{2-}$, and (c) MoO$_2$F$_4^{2-}$.

([MO$_x$F$_{6-x}$]$^{2-}$) coordinated to a central [Cu(py)$_4$]$^{2+}$ cation (Figure 2). The coordination environment around the d^9 Jahn−Teller copper ion is nearly identical in all three compounds, consisting of four equatorial pyridine ligands and two longer axial bonds to the respective complex anions. The infrared spectrum of each compound confirms the presence of both coordinated pyridine (1610 and 640 cm^{-1}) and pyridinium (1630, 1530, 1335, and 1255 cm^{-1}).[21] The crystal packing, however, differs in each compound as a result of the hydrogen bonding of the pyridinium to different nucleophilic sites on each octahedral anion (stereoscopic views of the crystal packing of each title compound are available in the Supporting Information).

[pyH]$_2$[Cu(py)$_4$(ZrF$_6$)$_2$]. Zr(IV) is slightly distorted from the center of the F$^-$ octahedron away from the Cu. This results in the long axial Zr−F(1) distance, trans to the short Zr−F(3) distance. The infrared spectrum contains three strong, broad, overlapping peaks in the region expected for Zr−F stretching frequencies[22] at 506, 481, and 454 cm^{-1}. The pyH$^+$ cations are disordered, allowing hydrogen bonding to any of the four equatorial fluorides. The crystal packing is related to the *anti-*

fluorite structure. The anionic clusters can be thought of as closest packed, while the disordered pyH$^+$ cations occupy "tetrahedral holes". The fact that the anions in this structure are not spheres but instead have only 4-fold symmetry explains the reduction of the crystal system from cubic to tetragonal. Alternatively, the structure may be viewed as (110) planes of parallel, end to end clusters, with each plane shifted c/2 from the one above and below it and pyH$^+$ cations occupying the spaces between the anions.

[pyH]$_2$[Cu(py)$_4$(NbOF$_5$)$_2$]. The structure and infrared spectrum of [pyH]$_2$[Cu(py)$_4$(NbOF$_5$)$_2$] have been previously reported.[11] Nb(V) is strongly distorted from the center of the octahedron toward the oxide ligand in NbOF$_5^{2-}$. Despite this distortion, the ligands themselves remain in a nearly perfect octahedral arrangement. This results in a short Nb=O bond and a long Nb−F(3) bond in the trans position. The NbOF$_5^{2-}$ anion is bound to Cu through the oxide ligand, and pyridinium

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cations hydrogen-bond to the trans F(3) site. The structure contains planes ((001)) of parallel, end to end clusters, just as in the zirconium compound. However, each layer is rotated 90° with respect to the one beneath it. This creates a 4_1 screw axis in the structure.

[pyH]$_2$[Cu(py)$_4$(MoO$_2$F$_4$)$_2$]. Mo(VI) is strongly distorted away from the center of the MoO$_2$F$_4$$^{2-}$ octahedron toward the (cis) oxide ligands. As in NbOF$_5$$^{2-}$, the metal–oxide bonds are short and the bonds to the trans fluorides are long. One of these trans fluorides bonds to the copper, while the other hydrogen-bonds with the pyH$^+$ cation. The infrared spectrum of the compound shows two Mo=O stretching frequencies at 950 and 906 cm^{-1} for the symmetric and asymmetric stretches, respectively, confirming the cis nature of the oxides.[23] The Mo–F stretching region contains one strong, broad peak at 549 cm^{-1} and two weaker peaks at 455 and 425 cm^{-1}. The structure is built up from planes of clusters as in the Zr and Nb compounds. However, in the [pyH]$_2$[Cu(py)$_4$(MoO$_2$F$_4$)$_2$] structure, the clusters in each (001) plane pack in a "herringbone" pattern, in contrast to the end to end pattern in the others. Each successive plane is shifted by $(a + b)/2$, resulting in the *C*-centering of the unit cell.

Discussion

An interesting characteristic of this family of compounds is that the crystal packing is determined largely by which complex anion is present. Substituting different cations for copper in [pyH]$_2$[Cu(py)$_4$(NbOF$_5$)$_2$] has little effect, resulting in the isostructural compounds [pyH]$_2$[Zn(py)$_4$(NbOF$_5$)$_2$][24] and [pyH]$_2$-[Cd(py)$_4$(NbOF$_5$)$_2$].[25] By contrast, substituting the isoelectronic series of anions ZrF$_6$$^{2-}$, NbOF$_5$$^{2-}$, and MoO$_2F_4$$^{2-}$ into the formula results in three different crystal packing arrangements. The distribution of the negative charge among the six O/F ligands on each anion is the key difference. Bond valence calculations[26] help quantify this charge distribution, and the results are summarized in Table 5. There is a consistency between the observed bond lengths and the configuration the cations and anions adopt; that is, the ligands with the highest partial negative charges ($V - S_i$) are the most nucleophilic and either coordinate to copper or become H-bond acceptors for pyH$^+$. The positions of these ligands change for each anion, and the Cu(py)$_4$$^{2+}$ and pyH$^+$ cations must pack differently in each case to accommodate them.

In [pyH]$_2$[Cu(py)$_4$(ZrF$_6$)$_2$], coordination of ZrF$_6$$^{2-}$ to Cu^{2+} weakens the Zr–F(1) bond. Zr compensates for this loss of valence by distorting slightly toward trans F(3), thereby strengthening the Zr–F(3) bond and lowering the effective negative charge at that site. The four equivalent equatorial F(2) ligands are left as the most negative available sites, and all four become possible H-bond acceptors. The pyH$^+$ cations reside in the equatorial plane of the anions, in close contact with all four F(2) sites.

Substituting Nb(V) for Zr(IV) requires the substitution of one of the fluorides in the octahedron with an oxide to maintain the overall 2$-$ charge. O^{2-} is a good π-donating ligand and forms a strong bond with the d^0 Nb(V). This results in a weak trans Nb–F(3) bond and a net distortion from the center of the octahedron toward the O^{2-}. Despite its highly covalent bond

Table 5. Bond Valence Sums^{a,b} for ZrF$_6$$^{2-}$, NbOF$_5$$^{2-}$, and MoO$_2F_4$$^{2-}$

	R_i, Å	S_i	$\sum S_M$	$V - S_i$
	ZrF$_6$$^{2-}$			
			3.93	
Zr–F(1)	2.053(7)	0.57		0.43^c
Zr–F(2) × 4	2.002(4)	0.66		0.34^d
Zr–F(3)	1.966(9)	0.72		0.28
	NbOF$_5$$^{2-}$			
			5.08	
Nb=O	1.728(8)	1.64		0.36^c
Nb–F(1) × 2	1.937(6)	0.73		0.27
Nb–F(2) × 2	1.927(5)	0.75		0.25
Nb–F(3)	2.099(8)	0.47		0.53^d
	MoO$_2$F$_4$$^{2-}$			
			5.86	
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^c
Mo–F(2)	2.114(1)	0.44		0.56^d
Mo–F(3)	1.939(1)	0.70		0.30
Mo–F(4)	1.918(2)	0.74		0.26

^{a} Bond valence calculated with the program Bond Valence Calculator v. 2.00, by C. Hormillosa, S. Healy, and T. Stephen, McMaster University (1993). ^{b} 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 $B = 0.370$. $\sum S_M$ = bond valence sum for the metal. V = predicted valence for a site. R_0(Zr–F) = 1.846, R_0(Nb–O) = 1.911, R_0(Nb–F) = 1.822, R_0(Mo–O) = 1.907, R_0(Mo–F) = 1.808 Å. ^{c} Bound to Cu^{2+}. ^{d} H-bond acceptor.

to niobium, the O^{2-} site retains enough negative charge to coordinate to copper. The weakly bound F(3) is by far the most negative of the remaining sites available and becomes the H-bond acceptor. In order to hydrogen-bond at this position, the pyH$^+$ cations must lie in an axial plane instead of the equatorial plane, and a different structure is produced.

Replacing Nb(V) with Mo(VI) requires another substitution of an oxide for a fluoride in the octahedron. As in NbOF$_5$$^{2-}$, short Mo=O bonds and long trans Mo–F bonds result in a distortion of the Mo toward the oxides. The tightly bound oxides retain little negative charge, but the trans Mo–F bonds are weak and these fluorides remain highly nucleophilic. As a result, one of these trans fluorides coordinates to Cu^{2+}, while the other acts as the H-bond acceptor. These two F$^-$ sites are cis to each other, so the hydrogen-bonding pyridinium resides in the equatorial plane, similar to the ZrF$_6$$^{2-}$ case, and in contrast to NbOF$_5$$^{2-}$. However, instead of adopting the [pyH]$_2$[Cu(py)$_4$-(ZrF$_6$)$_2$] structure, it crystallizes in a third structure, with the clusters in a herringbone arrangement in each plane. This structure puts the pyH$^+$ cations in close contact with only the unique H-bond acceptor and not the other three equatorial ligands. It also allows the smaller Mo octahedra to pack more closely together.

Another unusual feature of this family of compounds is that the complex anions always crystallize in an ordered fashion. Static orientational disorder is common with these anions, as they often have an equal probability of orienting in two or more directions. In some cases, these orientations may be ordered in a larger "supercell." However, the difference between O^{2-} and F$^-$ in the acentric anions is generally not sufficient to break up the symmetry of the rest of the lattice and a smaller, disordered unit cell is observed. Consequently, the bond lengths and angles are averaged and the true geometry of the anion is obscured.

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The $[pyH]_2[Cu(py)_4(MO_xF_{6-x})_2]$ compounds avoid disorder by coordinating two different cations ($Cu(py)_4^{2+}$ and pyH^+) to specific sites on different corners of each MX_6^{2-} anion. As a result, no higher symmetry can be imposed on the anions by the lattice and they need not disorder to accommodate it. In addition, the strongly directional coordination and the packing requirements of the bulky cations hold the anions in specific orientations which are consistent with the translational symmetry. In this way, orientational disorder between unit cells is prevented. The few other examples of ordered $NbOF_5^{2-}$ and $MoO_2F_4^{2-}$ compounds include $[N_2H_6][NbOF_5] \cdot H_2O$,[6] $Cu(pyz)_2$-$NbOF_5 \cdot (pyz)(H_2O)$,[12] and $K_2MoO_2F_4 \cdot H_2O$.[14]

Conclusion

The first step in producing acentric crystal structures from the ZrF_6^{2-}, $NbOF_5^{2-}$, and $MoO_2F_4^{2-}$ anions is to crystallize them without disorder. Providing an acentric coordination sphere around the MX_6^{2-} anion allows it to occupy a crystal-lographic position of relatively low symmetry, as illustrated in the few reported examples of ordered $NbOF_5^{2-}$ and $MoO_2F_4^{2-}$ anions. For example, the site symmetries of ZrF_6^{2-}, $NbOF_5^{2-}$, and $MoO_2F_4^{2-}$ in the $[pyH]_2[Cu(py)_4(MX_6)_2]$ crystal structures are C_{4v}, C_2, and C_1, respectively.

Supporting Information Available: Stereoscopic views of the crystal packing of each title compound (3 pages). Two X-ray crystallographic files, in CIF format, are available on the Internet. Ordering and access information is given on any current masthead page.

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