



Orientalional order of $[\text{VOF}_5]^{2-}$ and $[\text{NbOF}_5]^{2-}$ polar units in chains

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ABSTRACT

The generation of polarity in the solid state necessitates ordered, polar basic-building units (BBUs). This paper examines the evolution of ordered BBUs of 1D chains constructed of early transition metals (ETMs) and late transition metals. The cause of polar distortion orientation is illustrated with subtle alterations in the heterotypic structures of one previously reported compound ($\text{CuNbOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$) and three new hybrid materials, presented here: $\text{CuNbOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ (**1**), $\text{CuVOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ (**2**) and $\text{CuVOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ (**3**) ($\text{pyz} = \text{pyrazine}$). In contrast to the $[\text{NbOF}_5]^{2-}$ octahedra of $\text{CuNbOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ and compound (**1**) that have oxide ligands within the 1D BBUs, the $[\text{VOF}_5]^{2-}$ octahedra of compounds (**2**) and (**3**) contain disordered oxide ligands perpendicular to the chains. To create polar 1D BBUs in the solid state, one must have an understanding of how to direct distortions. We demonstrate that the choice of specific polar BBUs within a distinct environment is necessary for orientational order of the ETM anions.

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1. Introduction

Noncentrosymmetric (NCS) compounds have been extensively studied for their potential physical properties including piezoelectric, nonlinear optic (NLO), and/or ferroelectric activity [1,2]. To synthesize new NCS materials, researchers often employ polar basic-building units (BBUs) as these can result in permanent dipole moments. The use of asymmetric BBUs such as d^0 early transition metals (ETM) polyhedra or lone pair cations has shown success in the synthesis of new polar materials with NLO activity [3–7]. These asymmetric BBUs display strong individual polar moments and are able to create a strong net dipole moment in the overall structure if the antialignment of polar moments is minimized [8,9]. However, the net dipole moment of these materials is rarely maximized and control of the alignment needs to be addressed to engineer highly polar materials. This phenomenon is achieved in the technologically useful compounds LiNbO_3 and KTiOPO_4 . An initial step towards directional control of BBUs in a 3D crystal structure is an understanding of this order in 1D BBUs to create long-range coordination environments that exhibit a polar moment.

In oxyfluoride chemistry, chains (or 1D BBUs) composed of both polar $[\text{MO}_x\text{F}_{6-x}]^{2-}$ anions and late-transition metal cations have been previously reported [10,11]. These 1D-chain BBUs are linear

($\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$ [12]), zigzag ($\text{CuWO}_2\text{F}_4(\text{H}_2\text{O})_2(\text{py})_2$ [13]), or helical ($\text{AMoO}_2\text{F}_4(\text{H}_2\text{O})_2(\text{pyz})$ with $A = \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}$ [14]). While helical chains are ordered and zigzag chains are disordered, linear chains have interesting $[\text{MO}_x\text{F}_{6-x}]^{2-}$ octahedra that present either orientational order or disorder. The compounds $\text{CuNbOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ (**1**), $\text{CuVOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ (**2**) and $\text{CuVOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ (**3**) consist of 1D linear BBUs and were targeted to study the evolution of the order in these chains. The order of the oxide(s) in the 1D BBU determines the direction of the distortion (orientational order). These crystal structures are discussed in relationship to the previously reported $\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$ compound which exhibits complete orientational order [12].

A trend of these BBUs is immediately apparent: $[\text{NbOF}_5]^{2-}$ BBUs have oxide ligands within the linear chains while $[\text{VOF}_5]^{2-}$ anions have oxide ligands perpendicular to the linear chains. New insights for eliminating orientational disorder are suggested and the relationships between complete order and NCS properties in the helical compounds $\text{AMoO}_2\text{F}_4(\text{H}_2\text{O})_2(\text{pyz})$ (with $A = \text{Zn}, \text{Cd}$) [14] are discussed.

2. Experimental details

2.1. Synthesis

Hydrofluoric acid is toxic and corrosive! It must be handled with extreme caution and the appropriate protective gear [15–17]. V_2O_5 (99.6%, Aldrich), Nb_2O_5 (99.9%, Aldrich), CuO (99%, Aldrich), pyrazine (99%, Aldrich) and aqueous hydrofluoric acid (48% HF by weight, Aldrich) were used as received. Reagent

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amounts of deionized water were used in the synthesis. All reagents were sealed in Teflon pouches [18] and placed into a 125 mL Parr autoclave with a backfill of 45 mL distilled water. The autoclave was heated to 150 °C for 24 h and slowly cooled to room temperature at 6 °C/h. The single-crystals were recovered by vacuum filtration in air.

CuNbOF₅(H₂O)₄(pyz)₂ single-crystals (**1**) were synthesized as described above with 0.85 × 10⁻³ mol (0.225 g) of Nb₂O₅, 1.690 × 10⁻³ mol (0.134 g) of CuO, 2.5 × 10⁻³ mol (0.200 g) of pyrazine, 5.5 × 10⁻³ mol (0.10 mL) of deionized water and 2.780 × 10⁻⁴ mol (1.00 mL) of 48% aqueous HF.

CuVOF₅(H₂O)₄(pyz)₂ single-crystals (**2**) were synthesized as described above with 0.75 × 10⁻³ mol (0.136 g) of V₂O₅, 1.690 × 10⁻³ mol (0.134 g) of CuO, 2.5 × 10⁻³ mol (0.200 g) of pyrazine, 5.5 × 10⁻³ mol (0.10 mL) of deionized water and 27.8 × 10⁻³ mol (1.00 mL) of 48% aqueous HF.

CuVOF₅(H₂O)₂(pyz)₃ single-crystals (**3**) were synthesized as described above with 0.750 × 10⁻³ mol (0.136 g) of V₂O₅, 1.690 × 10⁻³ mol (0.134 mg) of CuO, 1.00 × 10⁻² mol (1.00 g) of pyrazine and 2.78 × 10⁻² mol (1.00 mL) of 48% aqueous HF.

2.2. X-ray diffraction.

Single crystal X-ray diffraction experiments were conducted at 100 K using a Bruker-APEX II CCD diffractometer with monochromatic Mo K_α radiation (λ=0.71073 Å). The crystal-to-detector distance was 60 mm and data integrations were made using SAINT-PLUS [19]. Absorption corrections were applied with SADABS [20]. The structures were determined by direct methods, completed by Fourier difference syntheses with SIR97 [21], and refined with SHELXL-97 [22]. No higher symmetry or unit cells were found by examination with PLATON [23]. Hydrogen atoms of pyrazine molecules were included in the refinement model as riding atoms in idealized positions (C–H=1.93 Å and U_{iso}(H)=1.5U_{eq}(C)). Crystallographic data are reported in Table 1.

3. Results

The three structures reported here have infinite chain-like 1D BBUs with alternating *trans* corner sharing Cu²⁺ centered octahedra and ETM anions [MOF₅]²⁻ (M=V⁵⁺ or Nb⁵⁺). The coordination of Cu²⁺ cations by pyrazine ligands leads to the connection of adjacent inorganic BBUs. The Jahn–Teller distortion of Cu²⁺ runs parallel to the propagation of the 1D BBUs. The crystallization of the metal units into linear BBUs is consistent with previously reported structures [24,25].

This crystallization arises from *trans*-directing anions [VOF₅]²⁻ or [NbOF₅]²⁻ and the absence of inter- and intrachain hydrogen bonding [14]. The crystal structures reported here exhibit partial orientational order of the anionic groups. The previously reported CuNbOF₅(H₂O)(pyz)₃ structure [12] is completely ordered.

3.1. Category (I) compounds

CuNbOF₅(H₂O)₄(pyz)₂. The compound CuNbOF₅(H₂O)₄(pyz)₂ (**1**) crystallizes in the space-group *I4/mcm*. Fig. 1(a) shows two crystallographically-distinct water molecules O_w1 and O_w2 occupying the cavities of the 3D framework. Four pyrazine molecules are coordinated to each Cu²⁺ cation and each pyrazine ligand connects two adjacent 1D BBUs and forms the cavities. The tilting angle between Cu²⁺ centered octahedra and Nb⁵⁺ centered octahedra is 32.608 (42)° and the Cu1–X1 and Cu1–N1 bond lengths are 2.2288(18) Å and 2.0503(15) Å, respectively (X=F⁻/O²⁻) (Table 2). The Nb1–X1 and Nb1–F2 internuclear distances are 1.9152(18) Å and 1.9304(12) Å, respectively (X=F⁻/O²⁻).

CuVOF₅(H₂O)₄(pyz)₂. The structure CuVOF₅(H₂O)₄(pyz)₂ (**2**) crystallizes in the space-group *P4/nbm*. The coordination of the infinite inorganic 1D BBUs with pyrazine creates a 3D framework with one crystallographically independent water molecule O_w1 occupying the cavities (Fig. 1(c)). Four pyrazine molecules are coordinated to each Cu²⁺ cation and each pyrazine ligand connects adjacent 1D BBUs to form cavities between the BBUs. The tilting angle between Cu²⁺ centered octahedra and V⁵⁺ centered octahedra along the chain is 45°. The Cu1–F2 and Cu1–N1 internuclear distances are 2.191(2) Å and 2.045(2) Å, respectively (Table 2). The V1 atom connects to Cu1 through the F2 ligand. The V1–X1 (X=F⁻/O²⁻) and V1–F2 bond lengths are 1.9416(19) Å and 1.910(2) Å, respectively.

3.2. Category (II) compounds

CuNbOF₅(H₂O)₂(pyz)₃. Our group has previously reported the structure of CuNbOF₅(H₂O)₂(pyz)₃ (Fig. 1 (b)) [12]. The compound was synthesized in water with (HF)_x · pyridine as source of fluorine. For this study, the compound was made with analogous synthetic conditions as compound (**3**), but with alternation of equimolar amounts of Nb₂O₅ for V₂O₅.

CuVOF₅(H₂O)₂(pyz)₃. The structure CuVOF₅(H₂O)₂(pyz)₃ (**3**) crystallizes in the space-group *P4/nbm*. The coordination of the infinite inorganic 1D BBUs and pyrazine creates a 2D framework with two free water molecules O_w1 and O_w2 occupying the interlayer space (Fig. 1(d)). Similarly to compounds (**1**) and (**2**),

Table 1
Crystal data, structure solutions and refinements for CuNbOF₅(H₂O)₄(pyz)₂ (**1**), CuVOF₅(H₂O)₄(pyz)₂ (**2**) and CuVOF₅(H₂O)₂(pyz)₃ (**3**). Category I and II refer to distinct M:pyz ratios of the compounds.

Category	I	I	II
compound	1	2	3
formula	CuNbOF ₅ (H ₂ O) ₄ (pyz) ₂	CuVOF ₅ (H ₂ O) ₄ (pyz) ₂	CuVOF ₅ (H ₂ O) ₂ (pyz) ₃
space group	<i>I4/mcm</i> (1 4 0)	<i>P4/nbm</i> (1 2 5)	<i>Cmca</i> (64)
<i>a</i> (Å)	9.7196(6)	9.7153(4)	16.7484(6)
<i>b</i> (Å)	9.7196(6)	9.7153(4)	13.7450(5)
<i>c</i> (Å)	16.5761(14)	8.2024(4)	15.5695(6)
<i>V</i> (Å ³)	1565.95(19)	774.20(6)	3584.2(2)
<i>T</i> (°K)	100(2)	100(2)	100(2)
<i>Z</i>	4	2	8
Maximum θ	36.3°	30.0°	32.4°
λ (Mo K _α) (Å)	0.71073	0.71073	0.71073
ρ _{calc.} (g cm ⁻³)	2.085	1.929	1.845
<i>R</i> _{int}	0.020	0.019	0.101
<i>R</i> ₁	0.030	0.031	0.044
<i>wR</i> ₂	0.098	0.102	0.119
Goodness-of-fit	1.11	1.04	0.92

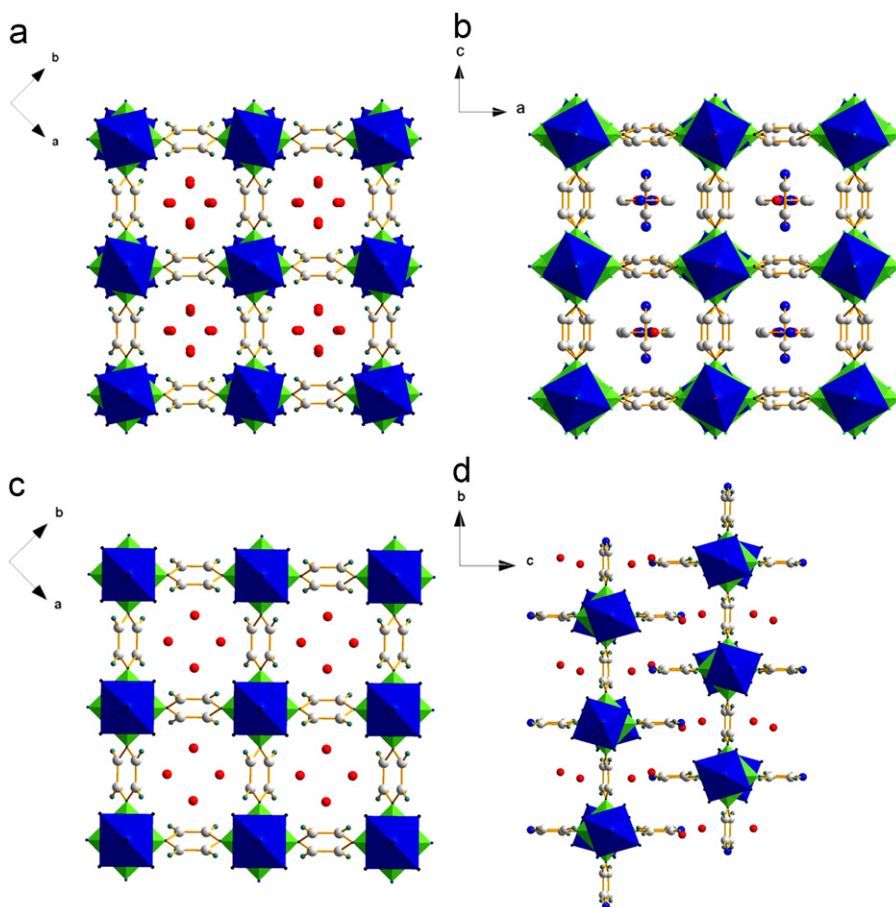


Fig. 1. View along the infinite inorganic 1D BBUs of (a) $\text{CuNbOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ crystal structure (1), (b) $\text{CuNbOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ crystal structure [12], (c) $\text{CuVOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ crystal structure (2) and (d) $\text{CuVOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ crystal structure (3).

compound (3) has four pyrazine molecules coordinated to each Cu^{2+} cation but only two pyrazine ligands connect adjacent BBUs, which results in layers. The tilting angle between Cu^{2+} centered octahedra and V^{5+} centered octahedra is $25.663(85)^\circ$. The Cu1-N bond lengths vary from $2.025(2)$ Å to $2.047(3)$ Å (Table 2). The Cu1-F1 bond distance is $2.2783(14)$ Å. The V1-X ($\text{X}=\text{F}^-/\text{O}^{2-}$) internuclear distances vary from $1.890(2)$ Å to $2.125(3)$ Å.

4. Discussion

4.1. Distortions and nucleophilicity of $[\text{MOF}_5]^{2-}$ anions

In oxyfluoride chemistry, the individual dipole moment of $[\text{MOF}_5]^{2-}$ anions is induced by the off-center distortion of the ETM “M” in its octahedral environment. The primary distortion arises from electronic effects of the d^0 ETM and is characterized by $d\pi-p\pi$ metal-oxide orbital interactions [26]. The weaker secondary distortions arise from the interactions of the anion and the extended structure [6,24]. The interactions between the bond network and the anions $[\text{NbOF}_5]^{2-}$ and $[\text{VOF}_5]^{2-}$ have been previously reported [24,27]. The oxide and its *trans* fluoride ligands are the most nucleophilic sites in the $[\text{NbOF}_5]^{2-}$ anion; however, despite its structural similarities with $[\text{NbOF}_5]^{2-}$, the ordered $[\text{VOF}_5]^{2-}$ directs coordination through *cis* F^- ligands (the F^- ligand in *trans* position of O^{2-} and one of the F^- ligand in equatorial position). This occurs as a result of the low nucleophilicity of the oxide ligand owing to significant π -bonding between vanadium and the oxide ligand.

4.2. Dipole alignment in linear basic building units

In infinite mixed-metal 1D BBUs, the alignment of polar anions can be identified by the successive positions of the O^{2-}/F^- ligands along the BBUs. The identity of the ligand – either oxide or fluoride – is distinguished by the comparison of metal-ligand bond lengths. X-ray crystallography is unable to definitively distinguish an oxide from a fluoride ligand owing to their similar electron density. The $\text{M}=\text{O}$ bond lengths are typically ~ 1.60 Å for $\text{M}=\text{V}^{5+}$ and ~ 1.80 Å for $\text{M}=\text{Nb}^{5+}$ while $\text{M}-\text{F}_{\text{trans}}$ length is ~ 2.10 Å. The $\text{M}-\text{F}_{\text{eq}}$ are typically ~ 1.80 Å for $\text{M}=\text{V}^{5+}$ and ~ 1.90 Å for $\text{M}=\text{Nb}^{5+}$ [27]. The dipole moments of $[\text{MOF}_5]^{2-}$ anions with C_{4v} symmetry are parallel to the $\text{F}-\text{M}=\text{O}$ axis. Four different configurations of linear BBUs are possible: (a) nonpolar, disordered chains with disorder perpendicular to the chain, (b) nonpolar, disordered chains with disorder collinear to the chain, (c) polar, ordered chains, and (d) nonpolar, ordered chains (Fig. 2). Configuration (c) consists of successive anions oriented in similar directions: The individual dipole moments combine in an additive manner. Configuration (d) consists of polar anions with opposing polar moments. This results in cancellation of the individual dipole moments. Although orientational order of $[\text{MO}_x\text{F}_{6-x}]^{2-}$ anions is not a common occurrence, ordered anions within linear chains have been described before. The structure of $\text{CuNbOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ exhibits nonpolar alignment of $[\text{NbOF}_5]^{2-}$ anions [12]; a polar alignment along the chains has been reported in the structure of $\text{CdNbOF}_5(3\text{-apy})_4$ [24]. Nonpolar alignment of linear chains (configuration a, b, and d) cannot lead to polar, NCS spacegroups owing to the presence of an inversion center within

Table 2
Selected bond distances for $\text{CuNbOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ (**1**), $\text{CuVOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ (**2**) and $\text{CuVOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ (**3**).

Bond	Length (Å)
$\text{CuNbOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ (1)	
Nb1–O1/F1 ($\times 2$)	1.9152(18)
Nb1–F2 ($\times 4$)	1.9304(12)
Cu1–N1 ($\times 4$)	2.0503(15)
Cu1–O1/F1 ($\times 2$)	2.2288(18)
$\text{CuVOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ (2)	
V1–O1/F1 ($\times 4$)	1.9416(19)
V1–F2 ($\times 2$)	1.910(2)
Cu–N1 ($\times 4$)	2.045(2)
Cu1–F2 ($\times 2$)	2.191(2)
$\text{CuVOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ (3)	
V1–F1 ($\times 2$)	1.9213(14)
V1–O2/F2	1.911(2)
V1–O3/F3	2.125(3)
V1–O4/F4	1.941(2)
V1–O5/F5	1.890(2)
Cu1–N2 ($\times 2$)	2.025(2)
Cu1–N3	2.047(3)
Cu1–N4	2.042(3)

the linear chains. Noncentrosymmetry could be engineered by combining the net dipole of polar chains in an additive manner. The alignment of anions in the infinite chains can be modified with different organic ligands, but the cause of local ordering is not fully understood [25].

For the compounds (**1**) and $(\text{CuNbOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3)$, the $[\text{NbOF}_5]^{2-}$ anions with C_{4v} symmetry align in the Cu–O/F–Nb–O/F–Cu pattern because the oxide is sufficiently nucleophilic to bind to the extended structure; however, the $[\text{VOF}_5]^{2-}$ anions are not aligned along the chains owing to the poor nucleophilicity of the oxide ligand. These nucleophilicity concerns mean that $[\text{NbOF}_5]^{2-}$ will crystallize in configurations (b), (c), or (d) of figure 2 as the oxide is sufficiently nucleophilic to be located within the chains of ETMs; however, unless additional considerations of electronics alter binding to the ETM, the $[\text{VOF}_5]^{2-}$ OD BBU is not sufficiently nucleophilic to bind with metallic units of 1D-linear BBUs. Therefore, compounds (**2**) and (**3**) exhibit nonpolar, disordered 1D BBUs in which the disorder is perpendicular to the chain (Fig. 2(a)).

4.3. From partial to complete orientational order in linear chains

Various methodologies to prevent orientational disorder have been previously reported [25,28,29]; Anisotropy around a metal center within an octahedra can result in ordered structures; this has been achieved by different ligand environments of the polar anions to limit the possible orientations of the anionic group relative to its environment. Anisotropy of the anionic group can be achieved in various ways: the use of a late transition metal cation to crystallize the anion into mixed-metal infinite chains [25], the matching of hard/soft cations and anions [28], and hydrogen bonding [29]. Instead of subtle modifications of the crystal structure to generate complete ordering, these strategies focus on the frustration of orientational disorder and only lead to partial orientational order in most instances.

Two categories of structures with different M:pyz ratios ($M=\text{V}^{5+}$ or Nb^{5+}) are discussed in this article: (I) a 1:2 ratio and (II) a 1:3 ratio. The M:pyz ratios of these structures are controlled with different initial reagent quantities of pyrazine. The category (II) compounds result from an excess of pyrazine in solution. Category (I) exhibits partial orientational order of the

$[\text{MOF}_5]^{2-}$ anions. The cavities within the structure are occupied by water molecules (Compounds (**1**) and (**2**)). Category (II) exhibits complete orientational order for $M=\text{Nb}^{5+}$ ($\text{CuNbOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ compound [12]) and partial orientational order for $M=\text{V}^{5+}$ (Compound (**3**)) with different coordination of inorganic chains with organic ligands (Fig. 1).

In the niobium system, both compound (**1**) and $\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$ consist of infinite inorganic 1D BBUs connected by pyrazine ligands (Fig. 1). The water molecules in the cavities of framework (**1**) do not noticeably sterically affect the configuration of these chains. Fig. 3(a) shows that in compound (**1**), the Jahn–Teller distortion of Cu^{2+} propagates along the linear BBU. Every O^{2-}/F^- ligands bridging early and late transition metals are crystallographically equivalent, which indicates the presence of orientational disorder. Synthesis of the compound with an increased amount of pyrazine results the compound of category (II). This compound has a structure with free, neutral pyrazine molecules within the cavities of $\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$; these pyrazine molecules replace the water molecules of compound (**1**) (Fig. 3(b)). Owing to the size of pyrazine molecule, the distance between two adjacent chains increases to accommodate the organic molecule. The increase in cavity size is achieved by direction of the Cu^{2+} Jahn–Teller distortions into alternating parallel and perpendicular distortions along the linear chains. This specific orientation causes differentiation of every O^{2-}/F^- crystallographic site that bridges early and late transition metals. The oxide ligand in $[\text{NbOF}_5]^{2-}$ anion has been previously reported to exhibit a higher electrostatic potential than the fluoride ligand in its *trans* position [10]. In the $\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$ structure, the $[\text{NbOF}_5]^{2-}$ anion strongly bond to the copper through the oxide ligand (the most nucleophilic ligand) and weakly bond to the copper through the *trans* fluoride (the second most nucleophilic ligand). The resulting orientational order of $[\text{NbOF}_5]^{2-}$ anions creates a nonpolar alignment configuration with individual dipole moments canceling each other.

The cavity size (as estimated from Cu–Cu distances) vary from $6.873 \text{ \AA} \times 6.873 \text{ \AA} \times 8.288 \text{ \AA}$ in $\text{CuNbOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ to $6.901 \text{ \AA} \times 7.273 \text{ \AA} \times 8.067 \text{ \AA}$ in $\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$ owing to the free pyrazine molecule occupying the cavities. The specific order of Cu^{2+} Jahn–Teller distortions in $\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$ structure leads to the increase of distances between adjacent chains along one direction and the decrease of Cu–Cu distances along the chains (Fig. 3).

The structure of (**2**) exhibits infinite inorganic 1D BBUs connected by pyrazine ligands where steric effects do not noticeably influence the alignment of $[\text{VOF}_5]^{2-}$ anions within these BBUs. Similarly to (**1**), the Jahn–Teller distortion of Cu^{2+} runs along the BBU, and the F^- crystallographic sites coordinated to copper are equivalent. In contrast to the compounds (**1**) and $\text{CuNbOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ [12], the excess of pyrazine in structure (**3**) leads to a different coordination of organic ligands with the inorganic chains (Fig. 1). Owing to the strong coordinate–covalent bonds of the 2D framework, the alignment within infinite 1D BBUs is not influenced by water molecules or steric effects. The environment of the anion in the chain is not a sufficient source of anisotropy and partial orientational order results; specifically, the oxide ligand of the anion is disordered between four ligand sites (perpendicularly to the chain) and not amongst all six ligand sites. The difference of V–O/F bond lengths showed an unequal (and unknown) distribution of the oxide on these four sites and can be attributed to the asymmetric hydrogen-bonding network around the $[\text{VOF}_5]^{2-}$ anion (Table 2).

Despite structural similarities, the O^{2-} ligand was previously reported to be nucleophilic in $[\text{NbOF}_5]^{2-}$ and non-nucleophilic in $[\text{VOF}_5]^{2-}$ [27]. This difference of nucleophilicity determines the alignment of $[\text{NbOF}_5]^{2-}$ along the BBUs – Cu–F–Nb=O–Cu – in the structure of $\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$ and non-alignment of

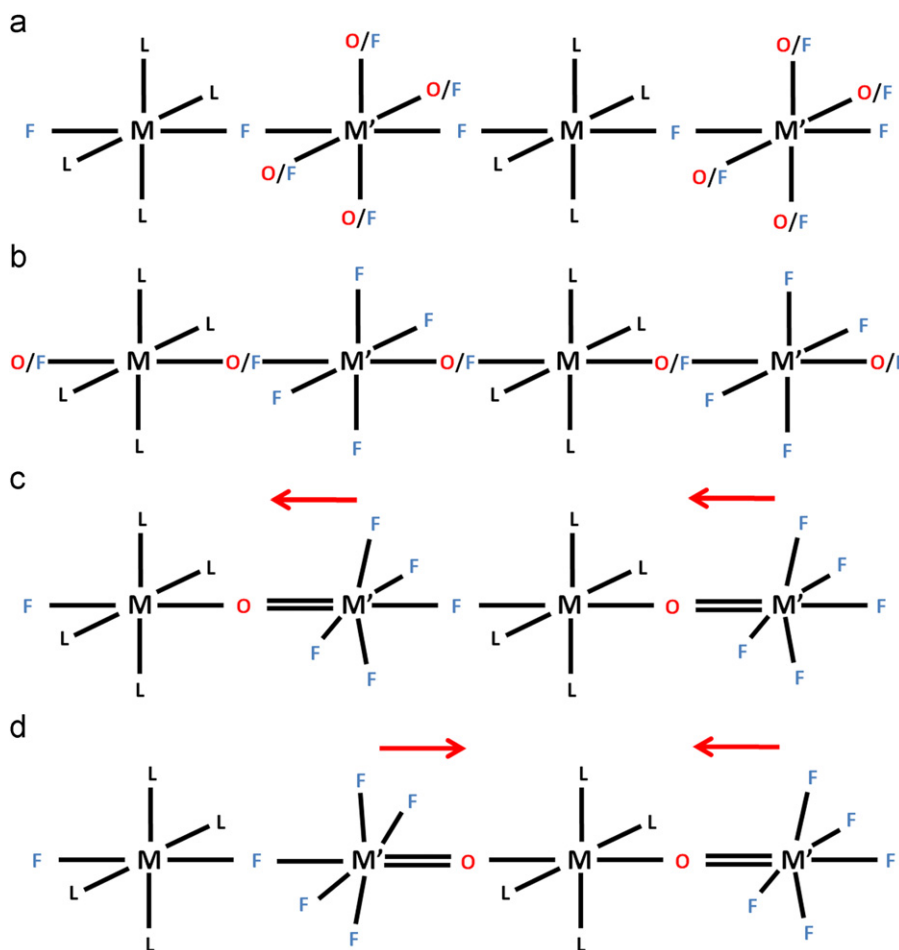


Fig. 2. Representation of dipole alignment in (a) nonpolar disordered chain with disorder perpendicular to the chain, (b) nonpolar disordered chain with disorder collinear to the chain, (c) polar ordered chain and (d) nonpolar ordered chain. Red arrows represent distortions exhibited by the anionic groups. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

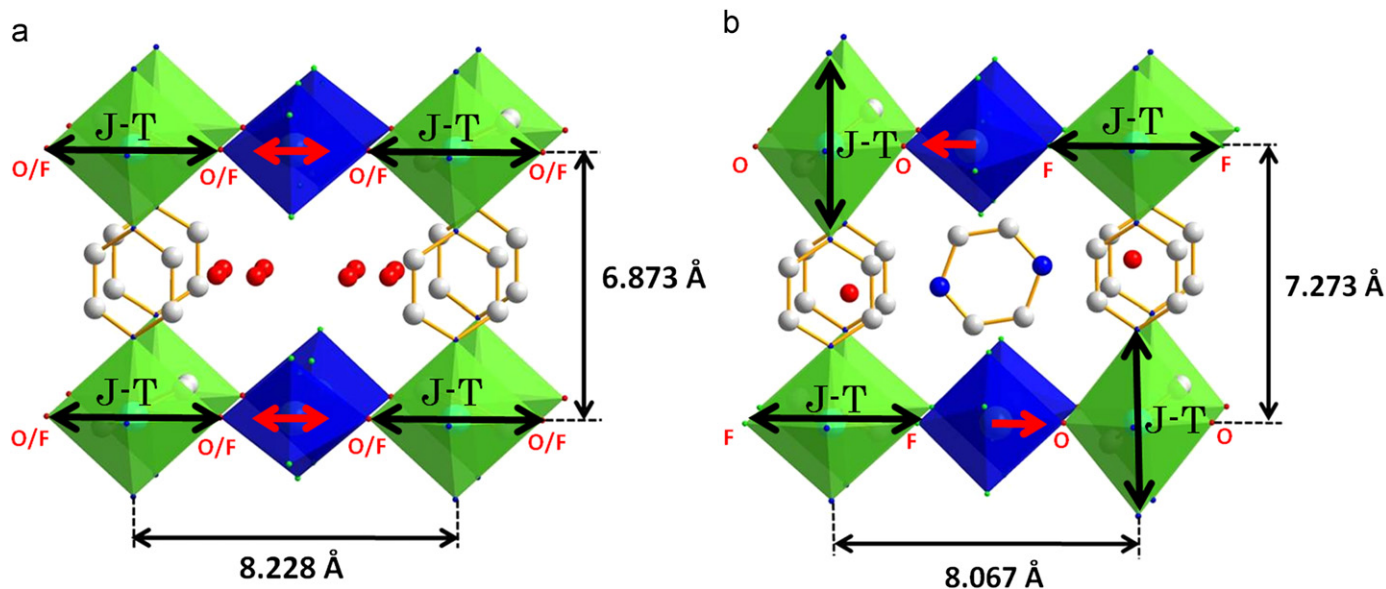


Fig. 3. Representation of the cavities in (a) structure (1) with orientational disorder and (b) $\text{CuNbOF}_5(\text{H}_2\text{O})(\text{pyz})_3$ structure with orientational order. Red arrows represent distortions exhibited by the anionic groups. The Jahn-Teller (J-T) distortions of copper centered octahedra have been highlighted for clarity.

$[\text{VOF}_5]^{2-}$ anions in the structure (3). A directional ordering of the Jahn-Teller distortion of Cu^{2+} is not possible because the O^{2-} ligand of $[\text{VOF}_5]^{2-}$ anions cannot bond to the extended chains

owing to the poor nucleophilicity of the $\text{V}=\text{O}$ moiety. The modification of cavity volume to accommodate the extra organic molecule with complete orientational ordering along the chains

would also not be possible in vanadium compounds owing to the low O^{2-} nucleophilicity.

The *trans*- or *cis*-directing properties of the ETM-centered anions are not sufficient to predict the bonding of the anion to the network: the nucleophilicity of the ligands is integral to order the anions. In the instance of compounds of category (I) and (II), the orientational order of anions is also achieved by introduction of a specific anion into a specific environment (Fig. 4). For example, the $[VOF_5]^{2-}$ anion is reported to be *cis*-directing in $[pyH_2][Cu(py)_4(VOF_5)_2]$ [27], but it exists in a *trans* configuration in compounds (2) and (3). This occurs because every fluoride ligand is nucleophilic while the oxide ligand is less nucleophilic within this anion. The coordination through *trans* equatorial fluoride ligands to the extended chains is also possible, but only *cis*-directing $[VOF_5]^{2-}$ can be ordered owing to possible V=O bond rotation about the chain propagation axis in the *trans* configuration (Fig. 4(a) and (c)).

As confirmed here with compounds (2) and (3), $[VOF_5]^{2-}$ is unable to be successfully order along the linear BBUs owing to the inability of the oxide ligands to bond to the chain. The anion is coordinated through *trans* equatorial fluoride ligands to the extended chains with dipole moments perpendicular to the chains. An orientational disorder of the ligands not bonded to the extended chain is also observed for both compounds (2) and (3). Conversely, the individual dipole of the *trans*-directing $[NbOF_5]^{2-}$ anion can align along the chain because the oxide and *trans* fluoride ligands are the most nucleophilic; however, the anisotropic environment of these anions into chains is not sufficient to consider an ordered alignment and a specific environment must be considered. The bonding of the oxide must also be different from the bonding of the *trans* fluoride. If the bonding

of these two ligands are not differentiated, orientational disorder along the chain will result (Fig. 4(b)). In the instance of $CuNbOF_5(H_2O)(pyz)_3$, the ligands are differentiated by ordering the directions of the Cu^{2+} Jahn–Teller distortion. This directional ordering of the Jahn–Teller distortion occurs as a result of the cavity volume between BBUs – modified by inclusion of an organic molecule (pyrazine). Orientational order is not inherent to ETM octahedra and can be controlled by environmental considerations; in this case, alternation of the cavity volume creates the necessary anisotropy to order the ligands of the BBUs of $CuNbOF_5(H_2O)(pyz)_3$.

4.4. Complete orientational order and noncentrosymmetry in helical chains

The $[MoO_2F_4]^{2-}$ anion has been reported to be a *cis*-director. This property has been exploited to synthesize helical 1D BBUs (Fig. 5) [10,11,14]. These helices are chiral and lead to an NCS environment. Owing to its C_{2v} symmetry, the $[MoO_2F_4]^{2-}$ anion bonds to the extended chain through the two equivalent F^- ligands located *trans* to the two *cis* O^{2-} ligands. In contrast to the $[MOF_5]^{2-}$ anions, the interaction of $[MoO_2F_4]^{2-}$ anion with the extended chains is also sufficient to order the orientation of the anionic groups (Fig. 5). Consequently, it is rare to order the $[MOF_5]^{2-}$ anions in linear or zigzag BBUs but helical chains with $[MO_2F_4]^{2-}$ anions are always ordered. The nucleophilicity of fluoride ligands coordinated to the extended chain are equivalent in the $[MoO_2F_4]^{2-}$ anion but different in the $[VOF_5]^{2-}$ anion (Fig. 4 (c) and Fig. 5). Contrary to the $[MoO_2F_4]^{2-}$ anion, the $[VOF_5]^{2-}$ anion cannot create two equivalent bonds with the

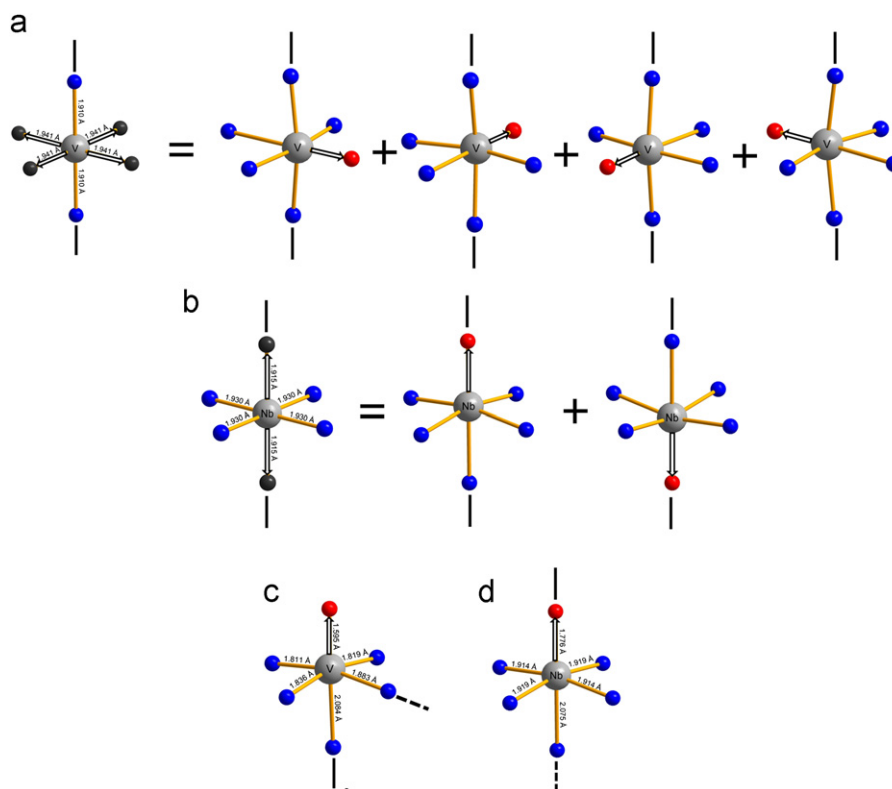


Fig. 4. Early transition metals centered anion (a) disordered $[VOF_5]^{2-}$ in compound (2), (b) disordered $[NbOF_5]^{2-}$ in compound (1), (c) ordered $[VOF_5]^{2-}$ in compound [12], and (d) ordered $[NbOF_5]^{2-}$ in $[pyH_2][Cu(py)_4(VOF_5)_2]$ compound [27]. Black solid lines indicate the strongest interactions between the anions ligands and the extended structure. Black dashed lines indicate the second strongest interactions between the anions ligands and the extended structure. Red, blue and black spheres represent O sites, F sites and disordered O/F sites, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

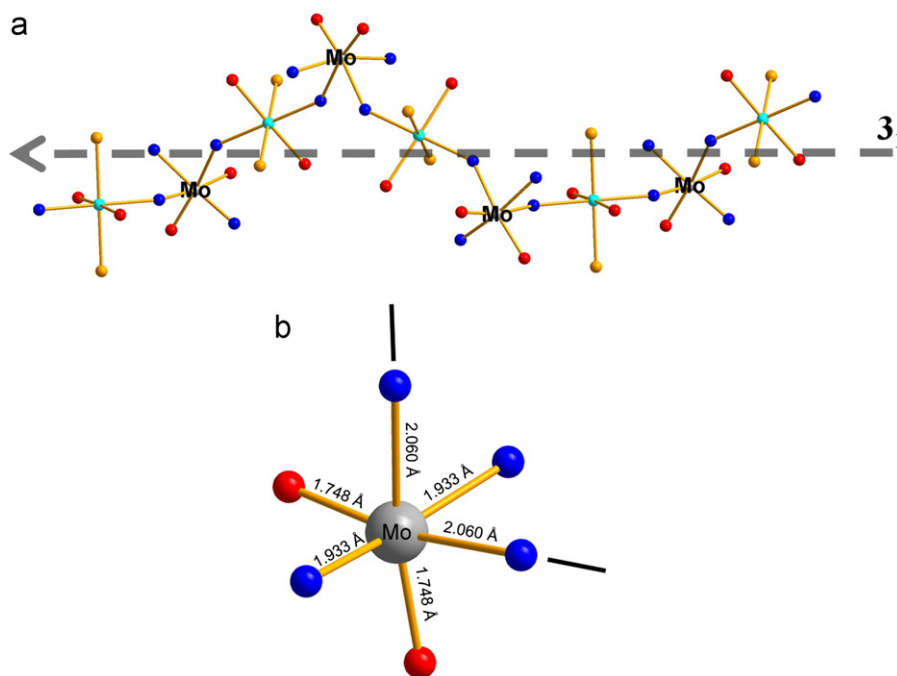


Fig. 5. Representations of (a) helical chains and (b) ordered $[\text{MoO}_2\text{F}_4]^{2-}$ anion in $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$ compound. Black solid lines represent the strongest interactions between the anions ligands and the extended structure. Strong interactions between the two fluorides in *trans* position of the oxide ligands and the extended structure is necessary to order the orientation of $[\text{MoO}_2\text{F}_4]^{2-}$ anion.

chains. This results in an inability of the $[\text{VOF}_5]^{2-}$ to crystallize in helical structures.

5. Conclusion

For group V transition metal anions with *trans*-directing properties, the crystallization into infinite BBUs induces partial orientational order of $[\text{MOF}_5]^{2-}$ owing to the creation of an axial anisotropic environment for polar anionic groups. Complete ordering can be achieved by increase of this anisotropy. We have demonstrated a new strategy to achieve this anisotropy: modification of the free volume within a crystal structure. In the $\text{CuNb}(\text{pyz})_2\text{OF}_5(\text{H}_2\text{O})(\text{pyz})_3$ structure, the cavities accommodate pyrazine molecules. A specific orientational order is accomplished by modification of the cavity's size and subsequent anisotropy of ligand environments. In $\text{CuMOF}_5(\text{H}_2\text{O})_4(\text{pyz})_2$ structures with $\text{M}=\text{V}^{5+}$ and Nb^{5+} , no modification of the volume to accommodate an included pyrazine molecule is required for the cavities and this results in partial orientational order of $[\text{MOF}_5]^{2-}$ anions. In the $\text{CuVOF}_5(\text{H}_2\text{O})_2(\text{pyz})_3$ structure, the cavity volume cannot be altered because of the ligands' nucleophilicities: a different coordination of pyrazine ligands results. This study shows the importance of placing a polar unit in an anisotropic environment to order a 1D BBU and that subtle modification of the environment – in this case, the occupied volume – can differentiate an ordered structure from a disordered structure. The use of different polar units and/or the subtle increase of the anisotropy in its environment could be a valuable analysis and method to induce polarity along 1D BBUs and create a noncentrosymmetric structure.

Supplementary materials

Crystallographic data of compounds (1), (2) and (3) have been deposited at the Cambridge Crystallographic Data Centre (CCDC

853534, CCDC 853535 and CCDC 853536, respectively). These data can be requested free of charge at www.ccdc.cam.ac.uk/data_request/cif.

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