INTRODUCTION

Chiral basic building units (BBUs) are of interest owing to their role in the synthesis of noncentrosymmetric chiral materials. Thus, the ability of BBUs with a unique handedness to crystallize into chiral materials is extensively used in organic and inorganic chemistry.\(^1\)\(^2\) Similarly, polar BBUs have been used to synthesize polar materials, but their arrangement remains difficult to predict.\(^3\)\(^4\) To improve control over the alignment of polar BBUs, several authors have recently reported the addition of chiral BBUs as a means of preventing the antiparallel alignment of polar BBUs.\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\)\(^13\) The polarity, however, cannot be guaranteed, as chiral, nonpolar structures can result (Figure 1).

The crystallization of racemates into chiral space groups is extremely rare. Two cases can be distinguished: (i) the resolution of the two chiral structures into distinct enantiomorphs (chiral resolution) or into twin domains (racemic twins) and (ii) the observation of both racemates as enantiomorphs (chiral resolution) or into twin domains (racemic twins) and (ii) the observation of both racemates as enantiomorphs (chiral resolution) or into twin domains (racemic twins). Therefore, the role of racemic BBUs in polarity in the solid state has not been investigated. Here, we present a study of a racemic mixture of the same chiral cations that can crystallize into either a centrosymmetric structure or a polar, achiral structure.

EXPERIMENTAL SECTION

Synthesis. \([\text{HfF}_6]_2[\text{Cu(H}_2\text{O})(\text{bpy})_2]_2 \cdot 3\text{H}_2\text{O}\) crystals were synthesized by hydrothermal synthesis. A mixture of \(\text{HFO}_2\) (1.69 mmol), \(\text{CuO}\) (1.69 mmol), \(22\)-bipyridine (2.56 mmol), 48% HF (27.8 mmol), and deionized \(\text{H}_2\text{O}\) (5.5 mmol) was added to a Teflon pouch. The heat-sealed pouches were placed in a 125 mL Parr autoclave with 40 mL of distilled water, heated to 150 °C for 24 h, and cooled to room temperature at the rate of 6 °C/h. Blue crystals were recovered by filtration under vacuum.

Single-Crystal X-ray Diffraction. Single-crystal X-ray diffraction analyses were performed in a Bruker-AXIS II CCD diffractometer at 100(2) K. The crystal-to-detector distance was 60 mm, and data integration was achieved using the SAINT-PLUS program.\(^16\) Absorption corrections were applied with SADABS.\(^17\) The structures were determined by direct methods, completed by Fourier difference syntheses with SIR97.\(^18\) and refined using SHELXL-97.\(^19\) No higher-symmetry or unit cells were found upon examination with the program PLATON.\(^20\) The \([\text{HfF}_6]_2[\text{Cu(H}_2\text{O})(\text{bpy})_2]_2 \cdot 3\text{H}_2\text{O}\) structure crystallizes in the space group \(\text{Pna}_2_1\) (No. 33) with the unit-cell parameters \(a = 20.5420(8)\) Å, \(b = 14.8692(5)\) Å, and \(c = 15.0844(6)\) Å. The final agreement factors are \(R_1 = 0.052\), \(wR_2 = 0.14\), and \(GoF = 1.09\).

RESULTS AND DISCUSSION

\([\text{Cu(H}_2\text{O})(\text{bpy})_2]_2[\text{HfF}_6]_2 \cdot 3\text{H}_2\text{O}\) was synthesized under mild hydrothermal conditions, single-crystal X-ray diffraction data were collected, and a noncentrosymmetric polar structure was
determined (space group Pna2₁, crystal class mm2) (Figure 2a). To our knowledge, [Cu(bpy)₂(H₂O)][BF₄]₂ is the only reported structure with [Cu(H₂O)(bpy)₂]²⁺ cations and fluoride anions in the CSD. This structure crystallizes in the centrosymmetric space group P2₁/c (Figure 2b). Owing to π–π interactions between the bipyridine ligands, the [Cu-(H₂O)(bpy)₂]²⁺ cations create layers that stack along the a axis in both structures. The stereochemistry of the [Cu(H₂O)-(bpy)₂]²⁺ cations is described by the Δ and Λ enantiomers, which are related by symmetry (Figure 3).²²

The two structures differ in the nature of the anions and the geometries of the layers. The [BF₄]⁻ anions are both smaller (B–F bond lengths ranging between 1.307(7) to 1.397(7) Å) and more numerous (two [BF₄]⁻ per [Cu(H₂O)(bpy)₂]²⁺) than the [HfF₆]⁻ anions. The Hf–F bonds range between 1.929(6) and 2.010(5) Å, and a 1:1 ratio is observed between [HfF₆]⁻ and [Cu(H₂O)(bpy)₂]²⁺ in [Cu(H₂O)-(bpy)₂][HfF₆]·3H₂O. This difference directly affects the distance between copper centers in these compounds and the orientations of the [Cu(H₂O)(bpy)₂]²⁺ cations. The nearest Cu–Cu distance in [Cu(H₂O)(bpy)₂][HfF₆]·3H₂O is 5.707(13) Å, versus 8.203(11) Å in [Cu(H₂O)(bpy)₂][BF₄]₂. The short Cu–Cu distances in [Cu(H₂O)-(bpy)₂][HfF₆]·3H₂O are found in Δ–Δ and Λ–Λ dimers, in which two distinct π–π interactions are observed. Layers are built from chains of −Δd−Δu−Δd−Δu− enantiomers (u = up and d = down describe the orientation of the cation along the b axis) in [Cu(H₂O)(bpy)₂][BF₄]₂, whereas both −Δu−Δd−Δu−Δd− and −Δd−Δu−Δd−Δu− chains are present in [Cu(H₂O)(bpy)₂][HfF₆]·3H₂O (Figure 4).

The presence of similar chains in both structures can be explained by the optimization of π–π interactions between bpy ligands. To stabilize these interactions, the planes of bpy ligands of successive aligned cations must be parallel or perpendicular, which is achieved through an alternation of the Δ and Λ enantiomers.²³ Moreover, the angle between the copper cation and the two bpy ligands is 150.6° because of the repulsion with the water ligand (Figure 3). For this reason, the alternation of both the handedness (Δ and Λ) and the direction (u = up and d = down) such as −Δd−Δu−Δd−Δu− or −Δu−Δd−Δu−Δd− allows for the optimization of the π–π interactions (Figure S1, Supporting Information).

Two different stacking sequences of these layers are observed in [Cu(H₂O)(bpy)₂][BF₄]₂ and [Cu(H₂O)(bpy)₂][HfF₆]·3H₂O (Figure 5). In [Cu(H₂O)(bpy)₂][BF₄]₂, the layers of [Cu(H₂O)(bpy)₂]²⁺ align along the a axis, creating centers of inversion between adjacent layers that reverse the handedness of the racemic building units. In contrast, layer translations are observed in [Cu(H₂O)(bpy)₂][HfF₆]·3H₂O that preclude inversion symmetry between enantiomers (Figure 5). These translations are derived from the hydrogen-bonding interactions within this compound. The fluoride anions in [Cu(H₂O)(bpy)₂][HfF₆]·3H₂O are more nucleophilic than those in [Cu(H₂O)(bpy)₂][BF₄]₂, the result of a decreased Hf–F bond strength compared to the strength of B–F bonds in [BF₄]⁻. This increase in fluoride-

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**Figure 1.** Polar and chiral crystal classes targeted in the solid state from polar BBUs, chiral BBUs, or a combination of polar BBUs and chiral BBUs. Chiral BBUs must crystallize in a chiral space group (solid arrows). Polar BBUs might crystallize in a polar space group (dashed arrows).

**Figure 2.** Views of (a) [Cu(H₂O)(bpy)₂][HfF₆]·3H₂O and (b) [Cu(H₂O)(bpy)₂][BF₄]₂ along layers built from [Cu(H₂O)(bpy)₂]²⁺ cations. Blue and green octahedra represent [HfF₆]⁻ or [BF₄]⁻ anions and [Cu(H₂O)(bpy)₂]²⁺ cations, respectively. The water molecules in structure [Cu(H₂O)(bpy)₂][HfF₆]·3H₂O have been removed for clarity. Red arrows represent the distortion of the anions.
anion nucleophilicity promotes the inclusion of water molecules in \([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\cdot3\text{H}_2\text{O}\), in order to stabilize the underbonded fluoride anions. Three water molecules are required per formula unit to bridge between successive \([\text{HfF}_6]^{-}\) groups, owing to the distance between Hf centers \([14.8692(6)\ \text{Å}]\). An extensive two-dimensional hydrogen-bonding network is observed between the bound and occluded water molecules and \([\text{HfF}_6]^{-}\) anions. The occluded water molecules “bridge” between adjacent \([\text{HfF}_6]^{-}\) anions, which adopt a staggered geometry that precludes inversion symmetry that would reverse the handedness of \([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\) cations of different layers. Secondary distortions are present in both the \([\text{HfF}_6]^{-}\) and \([\text{BF}_4]^{-}\) ions, as a result of hydrogen-bonding interactions. The distortions within the \([\text{HfF}_6]^{-}\) anions roughly align along the \(c\) axis in \([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\cdot3\text{H}_2\text{O}\), whereas complete cancellation is observed in the \([\text{BF}_4]^{-}\) anions in \([\text{Cu(bpy)}_2\text{H}_2\text{O}])[[\text{BF}_4]^{-}](\text{Figure 2}).

To relate symmetrically left- and right-handed enantiomers, improper symmetry operations must be considered. Three improper symmetry operations exist: the mirror plane \((S_h)\), the inversion center \((S_2)\), and the rotoinversion \((S_n)\) with \(n > 2\). As mentioned above, kryptoracemates, which are materials exhibiting crystallographically independent racemates, are extremely rare. For this reason, at least one improper operation is usually generated by the packing in the solid state to relate symmetrically both left- and right-handed enantiomers. If the structure is centrosymmetric, the inversion center relates the left- and right-handed enantiomers. If the structure is noncentrosymmetric but nonpolar, rotoinversions relate the enantiomers \([\text{five crystal classes: } 6 (C_{6v}), 4 (S_4), 42m (D_{2h}), 43m (T_d), \text{ and } 62m (D_{4h})]\). If the structure is polar, the mirror (or glide) plane is the unique improper operation relating the left- and right-handed enantiomers (Figure 6). Only five crystal classes, among the 10 polar crystal classes, are achiral: \(m (C_m), mm2 (C_{2mm}), 3m (C_{3m}), 4mm (C_{4mm})\), and \(6mm (C_{6mm})\). Moreover, these five classes are also the only ones.

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**Figure 3.** Representation of the \(\Delta\)- and \(\Lambda\)-\([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\) enantiomers with \(C_2\) symmetry.

**Figure 4.** Layers of \(\Delta\)-/\(\Lambda\)-\([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\) enantiomers in \([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\cdot3\text{H}_2\text{O}\) and \([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\cdot\text{HfF}_6\cdot3\text{H}_2\text{O}\). The cation complexes pack through \(\pi\)-\(\pi\) stacking of the \(2,2^\prime\)-bipyridine ligands. \([\text{HfF}_6]^{-}\) or \([\text{BF}_4]^{-}\) anions occupy the cavities formed by the \(\Delta\)-/\(\Lambda\)-\([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\) units. The letters \(d\) and \(u\) within \(\Delta d\), \(\Delta u\), \(\Lambda d\), and \(\Lambda u\) indicate the orientation of the \([\text{Cu(H}_2\text{O})(\text{bpy})_2]^{2+}\) cation: \(u\) for up \([\text{Cu(H}_2\text{O})\text{ bond along the } +b \text{ axis}]\) and \(d\) for down \([\text{Cu(H}_2\text{O})\text{ bond along the } -b \text{ axis}]\).
containing a mirror plane as the unique improper operation. For this reason, relating the left- and right-handed enantiomers with only mirror planes (or glide planes) is a sufficient condition to have polarity in the solid state.

The two structures discussed in this article also show that racemic layered compounds are of interest in the design of polar materials. The layers of right- and left-handed enantiomers can be symmetrically related by only glide planes according to the specific arrangement or/and translation of layers. The charge and size of \([\text{HfF}_6]^{2-}\) and \([\text{BF}_4]^-\) anions play an important role in the rearrangement and translation of the layers in \([\text{Cu(H}_2\text{O})(\text{bpy})_2]\_2[\text{HfF}_6]_2\_3\text{H}_2\text{O}\) and \([\text{Cu(H}_2\text{O})(\text{bpy})_2]\_2[\text{BF}_4]_2\_3\text{H}_2\text{O}\) structure and contribute to the absence of inversion centers.

**CONCLUSIONS**

This article describes the relation between the improper symmetry operations relating left- and right-handed enantiomers and the centrosymmetry or noncentrosymmetry in the solid state. In the \([\text{Cu(H}_2\text{O})(\text{bpy})_2]\_2[\text{BF}_4]_2\) centrosymmetric structure, \(\Delta\) and \(\Lambda\) \(\text{Cu(H}_2\text{O})(\text{bpy})_2\) enantiomers of adjacent layers are related by an inversion center. In the \([\text{Cu(H}_2\text{O})(\text{bpy})_2]\_2[\text{HfF}_6]_2\) noncentrosymmetric structure, translations and new arrangement of the layers allow glide planes (instead of an inversion center) to relate \(\text{Cu(H}_2\text{O})(\text{bpy})_2\) enantiomers of different handedness and lead to polar symmetry. The driving force of translations and the new arrangement of layers is the use of different anions (charge and/or size) and could also be imitated in other lamellar racemic compounds to create polarity. Relating enantiomers of left- and right-handedness with only mirror or glide planes is also a promising alternative route for engineering polarity in the solid state.

**ASSOCIATED CONTENT**

**Supporting Information**

X-ray crystallographic file in CIF format for compound \([\text{Cu(H}_2\text{O})(\text{bpy})_2]\_2[\text{HfF}_6]_2\_3\text{H}_2\text{O}\) structure description, Figure S1. This material is available free of charge via the Internet at pub.acs.org.
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