Homochiral Helical Metal−Organic Frameworks of Potassium

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Ⓢ *Supporting Information*

ABSTRACT: Two trifunctional ligands built from enantiopure amino acids and containing a 1,8-naphthalimide group have been used to prepare two new complexes of potassium that have extended structures based on homochiral-rod secondary building units. One structure is a three-dimensional metal−organic framework (MOF), while the other is a two-dimensional solid that is organized into a supramolecular MOF by strong $\pi\cdots\pi$-stacking interactions of the naphthalimide groups in the third dimension.

The syntheses, structures, and properties of metal−organic frameworks (MOFs) represent a diverse and exciting area of chemistry because these solids have a wide range of potential applications.[1] We have recently synthesized a series of ligands designed for the preparation of related solids with specific properties. These ligands, two of which are pictured in Scheme 1, contain three functional groups: a carboxylate anion designed

Scheme 1
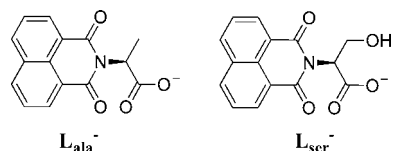
as the donor group to bond metal cations forming the "joints", the secondary building units (SBUs), of the structures,[2] an enantiopure amino acid linking "strut" so as to prepare enantiopure extended structures[3] and a 1,8-naphthalimide group to block the amine end of the acid from coordination[4] and to act as an organizing group in the molecular/ supramolecular structure through strong $\pi\cdots\pi$-stacking or other interactions.[3d,5] Using these ligands with transition metals, we have reported a copper(II) carboxylate "dimer" that undergoes the first enantioselective gas/solid single-crystal to single-crystal exchange at a metal[5] center and complexes with homochiral, helical, three-dimensional structures organized by noncovalent $\pi\cdots\pi$ stacking that undergo reversible single-crystal transformations of the interstitial waters, despite the absence of "channels" in the solid-state structures.[3d]

Given this success with transition-metal complexes, we wished to develop the chemistry of these ligands with group 1 and 2 metals for two main reasons. First, the MOF chemistry of these metals is not well developed,[6] with limited chemistry using enantiopure ligands, mainly the important work with tartaric acid derivatives.[7] Second, we anticipated the oxophilicity of these metals would produce extended structures very different from those observed in our earlier work with transition metals. In that research, the overall structures were partially or completely dominated by noncovalent, but relatively strong $\pi\cdots\pi$-stacking interactions of the naphthalimide groups,[5,8] forming what we have termed supramolecular MOFs (SMOFs), three-dimensional MOF-type architectures that combine the robustness of SBU cores with strong supramolecular organization in at least one dimension.[8b] With transition metals, the naphthalimide carbonyl groups do not act as ligands, but we anticipated different results with group 1 and 2 metals.

Reported here are two new complexes of potassium, $K(L_{ala})(MeOH)$ (**1**) and KL_{ser} (**2**). The structures of these complexes are unique in that the backbones of both are *homochiral-"rod" SBUs*.[2] In **1**, the other two dimensions of the structure are dominated by additional strong interactions (highly polar covalent bonds) of the naphthalimide carbonyl groups acting as ligands to the potassium cations, whereas in **2**, only the second dimension is organized in this way and strong $\pi\cdots\pi$-stacking interactions of the naphthalimide groups organize the third dimension, thus forming an SMOF-type structure.

Single crystals of **1** and **2** were grown under solvothermal conditions using methanol (see the Supporting Information, SI). The irregular six-coordinate geometry of the potassium cations and part of the extended structure in compound **1** is shown in Figure 1. Methanol (O5) and μ^2-carboxylate (O3) oxygen atoms dibridge potassium cations, forming a homochiral-"rod" SBU structure, thus filling four coordination sites of each metal. The other two coordination sites are filled by carbonyl oxygen atoms of the naphthalimide groups, one (O2)
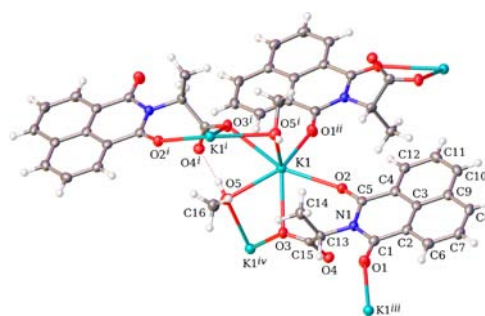

Figure 1. Coordination environment for the potassium cation and part of the extended structure in **1**. Superscripts denote symmetry-equivalent atoms.

from the naphthalimide of the μ^2-carboxylate ligand also linked to this potassium, forming a seven-membered ring, and the other (O1) from a naphthalimide of a neighboring rod. This coordination of naphthalimide carbonyl oxygen atoms to the potassium cation is a major difference in this structure compared with those reported earlier with transition metals.[3d,5,8]

Figure 2a shows the edge-sharing, irregular potassium polyhedra that form the one-dimensional homochiral-rod
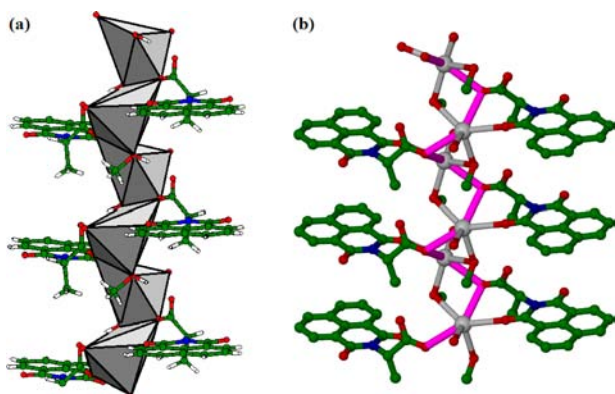

Figure 2. (a) Homochiral helical rods in **1** composed of edge-sharing irregular potassium polyhedra. (b) Rods are *P*-handed helices, where the K1–O3–K1–O3 chain is highlighted in purple.

SBU. All of the rods are *P*-handed helices following the K1–O3–K1–O3 chain, where O3 is the μ^2-carboxylate oxygen atom (Figure 2b) with a pitch of 6.90 Å. Each helical-rod SBU is linked to four adjacent *P*-handed helical rods, forming "squares" by coordination of the oxygen atom (O1) from the rod-bridging naphthalimide ring interaction, generating a three-dimensional structure with a uninodal 4*c* net (Figure 3). As is
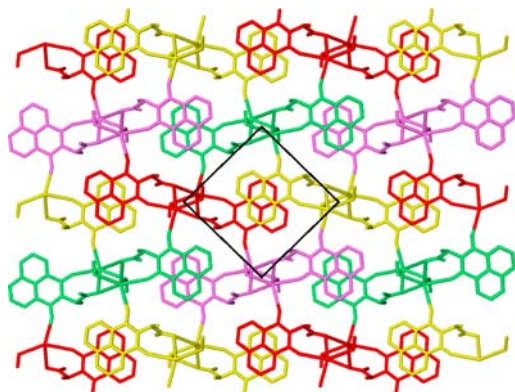

Figure 3. View down the crystallographic *a* axis of **1** showing the overall connectivity of the helical rods. Neighboring helical rods are distinguished by different colors and are bridged by the naphthalimide carbonyls. The square overlay shows one of the connections between four different helical rods. The naphthalimide stacking occupies the centers of the squares.

also shown, the structure is supported by $\pi\cdots\pi$-stacking interactions (middle of squares) of the naphthalimide rings between the rods, forming an interdigitated arrangement. In these interactions, the perpendicular distance between the parallel rings is 3.45 Å and the dipole vectors of the naphthalimide rings are at 180°, a head-to-tail arrangement.

The slippage parameter χ, the third side of the right triangle formed with the average perpendicular distance between the rings and the line joining the central carbon atoms of the two rings, is 1.34 Å, in the range of 0.43−2.40 Å that is considered a strong interaction.[8]

The distorted trigonal-prismatic coordination environment of the potassium cation and part of the extended structure of compound **2** is shown in Figure 4. The O_6 coordination of the
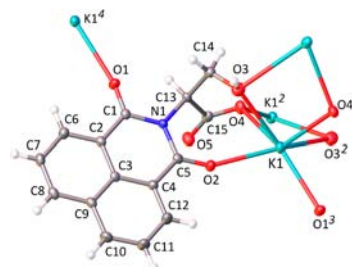

Figure 4. Coordination environment for the potassium cation and part of the extended structure in **2**. Superscripts denote symmetry equivalent atoms.

potassium cations in this compound is the same as that in **1**, but in this structure, the bridging methanol molecules are replaced by a bridging alcohol (O3) originating from the side chain of the amino acid, demonstrating an interesting application of *designed ligand modification* on the structure. This additional interaction from the functional group in the carboxylate ligand leads to the formation of a bicyclic [3.2.2] ring with each potassium.

As shown in Figure 5, the bridging alcohol and carboxylate ligands again support a homochiral-rod SBU structure. All of
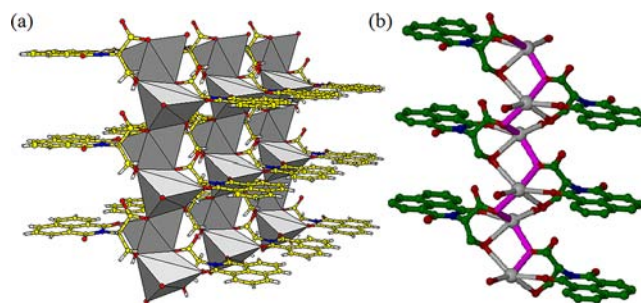

Figure 5. (a) Homochiral helical rods in **2** composed of edge-sharing trigonal-prismatic potassium polyhedra bridged by the naphthalimide groups to form a two-dimensional sheet structure. (b) Rods are *P*-handed helices, where the K1–O4–K1–O4 chain is highlighted in purple.

the rods are *P*-handed helices following the K1–O4–K1–O4 chain, where O4 is the μ^2-carboxylate oxygen atom, with the pitch being 6.61 Å. In contrast to **1**, the helical rods are bridged in a linear array to only two adjacent rods by the carbonyls of the rod-bridging naphthalimide rings to form extended sheets. All of the naphthalimide rings point away from the sheets and are in parallel ribbons. These naphthalimide rings form an interdigitated $\pi\cdots\pi$-stacking "zipperlike" structure in the third dimension (Figure 6). The average distance between the planes of the naphthalimide rings is 3.30 Å; the dipole vectors between ligands are again 180°; the slippage parameter χ is fairly large at 2.56 Å, as can be seen in the drawing on the right side of Figure 6. Thus, in this SMOF structure, two of the dimensions are
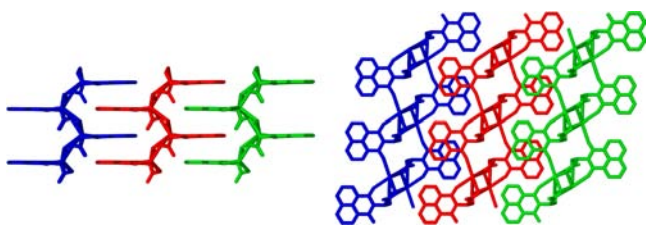
Figure 6. Structure of **2** seen from the crystallographic *a* (left) and *c* (right) axes. These two views show $\pi\cdots\pi$ interactions joining the sheets to generate a three-dimensional supramolecular structure.

defined by strong interactions, while the third is dominated by supramolecular interactions.

Thermogravimetric analysis (TGA; Figure S1 in the SI) of crystals of **1** shows a weight loss of 9.81% occurring at 128 °C and a color change from transparent light brown to opaque white, indicative of a loss of methanol within the structure. The crystals retained their shape when heated to 200 °C, but single crystallinity was lost. Powder X-ray diffraction (PXRD) analysis indicated a polycrystalline solid, although the pattern did not match that predicted from the single-crystal structure of **1** (Figures S3−S5 in the SI). The compound then undergoes complete decomposition at 318 °C, and a remaining weight of 19% at 700 °C correlates with potassium hydroxide. Interestingly, if this solid that has been heated to 200 °C is redissolved in methanol, single crystals of 1 reform (as shown by X−ray crystallography) TGA of K(L_{ser}) (Figure S2 in the SI) shows no weight loss until decomposition at 280 °C. The stability of this solid is highlighted by the fact that, even after heating to 250 °C, single crystals *still diffract*, showing sharp diffraction maxima and lattice parameters identical with those of the unheated crystals.

The fluorescence excitation and emission spectra for the protonated forms of the two ligands, their complexes with potassium, and the solid formed by heating **1** to 200 °C were recorded (Figures S6 and S7 in the SI). HL_{ala} and HL_{ser} have spectra similar with fluorescence emission maxima ($\lambda_{max,Fl}$) at 450 and 470 nm, respectively. The spectrum for compound **1** is red-shifted with $\lambda_{max,Fl}$ = 469 nm, the heated solid is broad in this same region, and the spectrum for **2** is blue-shifted with a $\lambda_{max,Fl}$ = 438 nm.

In conclusion, we have used the trifunctional ligands pictured in Scheme 1 to form two new complexes of potassium with a number of interesting physical and structural properties. Both structures are built on homochiral-rod SBUs, only a few of which have been reported previously.[7] In **1**, the naphthalimides connect to potassium through both carbonyl groups, an interaction that we have not previously observed with transition metals, to build the homochiral-rod SBUs into a three-dimensional MOF structure. These interactions are clearly a result of the oxophilicity of the potassium ions, demonstrating that with the same ligands extended structures of main-group metals can be very different from those of transition metals. Although this type of interaction is also present in **2**, it only supports a second dimension of the structure. The third dimension is supported by $\pi\cdots\pi$-stacking interactions of the naphthalimide groups, forming an SMOF structure. This type of interaction is also present in **1**, although it only supports the three-dimensional MOF structure, showing the importance of the naphthalimide supramolecular synthon. This importance is highlighted by the fact that the $\pi\cdots\pi$-stacking interactions are observed for naphthalimide groups that are also connected to

potassium through the carbonyl oxygen atoms. TGA indicates that both the MOF structure of **1** and the SMOF structure of **2** are robust, especially with **2**, where the crystals can be heated to 250 °C without loss of crystallinity. The presence of the small-molecule methanol in **1** leads to a lower mass loss onset temperature than that in **2**, even though it has a three-dimensional structure, whereas in **2**, designed ligand modification avoids the small molecule and leads to greater stability in this SMOF.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

X-ray crystallographic files in CIF format for the structural determinations, a detailed description of the X-ray structural analyses, tables of bond lengths and angles, TGA plots for compounds 1 and 2, and PXRD plots for 1 before (predicted) and after (the loss of methanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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