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The Dimeric $[V_2O_4F_6]^{4-}$ Vanadium Oxide-Fluoride Anion in $Na_2(M(H_2O)_2)(V_2O_4F_6)$ (M = Co^{2+}, Ni^{2+}, and Cu^{2+})

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Dedicated to Professor Rudolf Hoppe on the Occasion of His 90th Birthday

Keywords: Crystal structures; Dioxo vanadium fluoride anion; Hydrothermal synthesis; Oxide-fluorides; Vanadates

Abstract. Three new vanadium oxide-fluoride phases, $Na_2(M(H_2O)_2)(V_2O_4F_6)$ (M = Co^{2+}, Ni^{2+}, and Cu^{2+}), were prepared by hydrothermal techniques in hydrofluoric acid. The compounds contain the dioxo vanadium fluoride dimeric anion: $[V_2O_4F_6]^{4-}$. The harder (Na^+) and softer (M = Co^{2+}, Ni^{2+}, and Cu^{2+}) cations coordinate to the harder fluoride and softer oxide anions, respectively. In contrast to monoxo vanadium fluorides, the dioxo vanadium fluoride exhibits an increased nucleophilicity of the oxide anions. This increased nucleophilicity allows the anion to bond covalently with late transition metals to form 2D layers that contain both an early transition metal (V^{5+}) and a late transition metal (Co^{2+}, Ni^{2+}, or Cu^{2+}).

Introduction

Vanadium oxides have been used in catalytic and battery materials owing to their diverse oxidation states and/or common, layered geometries.[1–3] More recently, various vanadium oxide-fluorides (VOFs) have been proposed for use as battery, piezoelectric, and nonlinear optical (NLO) materials.[4–11] These VOF materials can be described in terms of basic-building units (BBUs) as 0D, 1D, or 2D moieties which can be synthesized reproducibly in the solid state.[12] In isolation, the BBUs found in these compounds can be analyzed for their structure-directing properties to predict their orientation in materials.[13–17]

The syntheses of new, ordered VOF BBUs can greatly expand the current library of VOF materials. Oxide-fluoride compounds are frequently disordered owing to the similar sizes and electronegativities of the oxide and fluoride anions. Methodologies to create ordered oxide-fluoride materials create anisotropic environments around early transition metals (ETMs); these environments induce anions of the ETM to be either an oxide or a fluoride. To generate this anisotropy, various authors employ void space optimization,[18] polarizability matching,[19–23] and/or multiple cations.[22–24]

In the context of this paper, owing to the relative difference in their free ion polarizabilities as derived by *Shannon* and *Fischer*,[25] we will refer to alkali metals and fluoride anions as "harder" ions and late transition metals (LTMs) and oxide anions as "softer" ions. We have previously discussed the role of polarizability to order oxide and fluoride anions;[19,21] more recently, the structures of $Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo^{6+}, W^{6+}) were ordered with combinatorial use of two cations.[23] The harder (Na^+) and softer (Ag^+) cations of $Na_{1.5}Ag_{1.5}MO_3F_3$ (M = Mo^{6+} and W^{6+}) decidedly coordinate to the harder fluoride and softer oxide anions, respectively. These strategies create anisotropy and induce order in the solid state.

In solution, the dioxo vanadium fluoride anion $[VO_2F_4]^{3-}$ BBU has been observed by ^{51}V and ^{19}F NMR. The anion was speculated to have a *trans* octahedral geometry in 48% aqueous hydrofluoric acid.[26] Despite this observation and the existence of many vanadium oxide-fluoride materials,[20,27–30] the dioxo vanadium fluoride anion has not often been observed as an ordered species in a solid state structure. Disordered monomeric $[VO_2F_4]^{3-}$ have been previously observed,[10] but, to our knowledge, the only observation of a fully ordered dioxo vanadium fluoride material is the compound $K_2VO_2F_3$.[31] The compound consists of infinite chains of corner-sharing $[VO_2F_2F_{2/2}]^{3-}$ BBUs.

Herein, we describe the syntheses of the $[V_2O_4F_6]^{4-}$ anion in the solid state with the use of combinatorial cations. Specifically, we present hydrothermal syntheses of $Na_2M(H_2O)_2(V_2O_4F_6)$ (M = Co^{2+}, Ni^{2+}, and Cu^{2+}), and describe the structural and electronic properties of the dimeric $[V_2O_4F_6]^{4-}$ BBUs.

Results and Discussion

Structural Descriptions

The crystallographic and acquisition parameters of the materials $Na_2(M(H_2O)_2)(V_2O_4F_6)$ (M = Co^{2+}, Ni^{2+}, and Cu^{2+}) are

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Table 1. Crystallographic and acquisition parameters for $Na_2(M(H_2O)_2)(V_2O_4F_6)$, Compounds **1**–**3**.

Compound	M = Co^{2+} **1**	M = Ni^{2+} **2**	M=Cu^{2+} **3**
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a /Å	8.2450 (5)	8.1669 (4)	8.1190 (6)
b /Å	5.2440 (3)	5.2403 (3)	5.3362 (4)
c /Å	10.2286	10.2450 (6)	10.1166 (7)
β /°	90.844 (3)	90.094 (3)	90.684 (2)
V /Å^3	442.20 (4)	438.45 (4)	438.27 (6)
Z	2	2	2
Temperature /K	100	100	100
θ-range /°	4.0 to 30.0	2.5 to 30.0	2.51 to 30.07
Index Range	$-11 \le h \le 11$ $-7 \le k \le 7$ $-14 \le l \le 13$	$-11 \le h \le 11$ $-7 \le k \le 4$ $-14 \le l \le 11$	$-11 \le h \le 11$ $-7 \le k \le 7$ $-14 \le l \le 12$
Measured Reflections	13254	5825	12417
Unique Reflections	1295	1261	1290
Ind. Reflns $> 2\sigma(I)$	1072	1187	1287
ρ_{calc} /g·cm^{-3}	3.160	3.186	3.224
Absorption Coefficient /mm^{-1}	4.138	4.429	4.709
R_1 [$I > 2\sigma(I)$]	0.0228	0.0243	0.0182
wR_2 [$I > 2\sigma(I)$]	0.0514	0.065	0.0506
R_1 (all data)	0.0290	0.0253	0.0183
wR_2 (all data)	0.0531	0.0658	0.0507
GooF	1.016	1.127	1.200
Min/max e-density /e·Å^{-3}	–0.56/0.534	–0.99/0.665	–0.431/0.385

provided in Table 1; the compounds are isostructural and crystallize within space group $P2_1/c$.

The ordered VOF BBU of $[V_2O_4F_6]^{4-}$ is shown in Figure 1. This is the first instance to our knowledge of this anion. Similar monoxo vanadium(IV) fluoride dimers exist within the structures of $Na_4V_2O_2F_8$, $[C_6N_4H_{22}][V_2O_2F_8]$, and $[C_{10}N_2H_{10}][V_2O_2F_6(H_2O)_2]$.[20,32] Fluoride anions bridge the two vanadium(IV) atoms. The vanadium atoms are distorted away from each other to generate a centrosymmetric BBU. As *Brock* and *Dunitz* have described, centrosymmetric molecules typically lie on inversion centers;[33] similarly, the centrosymmetric BBU $[V_2O_4F_6]^{4-}$ lies on an inversion center. The two vanadium atoms and four oxide anions all lie on one plane.

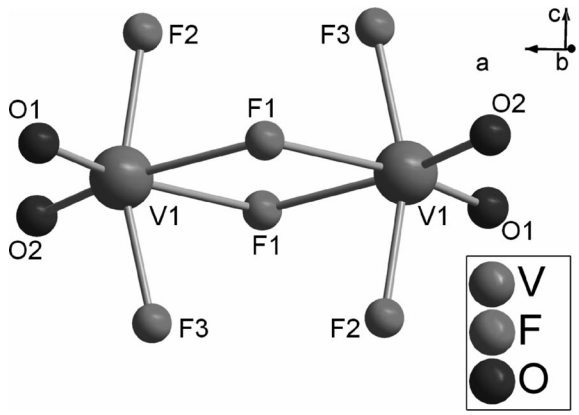

Figure 1. The ordered $[V_2O_4F_6]^{4-}$ dimer present within $Na_2(M(H_2O)_2)(V_2O_4F_6$ (M = Co^{2+}, Ni^{2+}, and Cu^{2+}).

Figure 2A and Figure 2B show the transition metal oxide-fluoride layers within compounds **1**–**3**. The softer oxide anions preferentially bind to softer LTM cations. The oxide anions of each individual dimer lie on one plane and planar connections are made to the LTMs. This results in layers of covalently bonded early (V^{5+}) and late (M = Co^{2+}, Ni^{2+}, and Cu^{2+}) transition metals. Owing to the short distance between the oxide anions of the VCs (2.616(2) for compound **1** and 2.625(2) Å for both compounds **2** and **3**), the vanadium dimers are unable to bind in an *edge*-sharing manner with the octahedral LTMs. The LTMs have distances of the *cis* O–M–O components of 2.871(2), 2.897(1), and 3.040(2) Å for compounds **1**, **2**, and **3**, respectively; consequently, the LTMs bind in a *corner*-sharing manner. The Jahn–Teller distortion within compound **3** associated with Cu^{2+} lies within the layer of the transition metals. This slightly alters bond lengths and unit cell parameters of the structure but does not have significant structural changes for compound **3**.

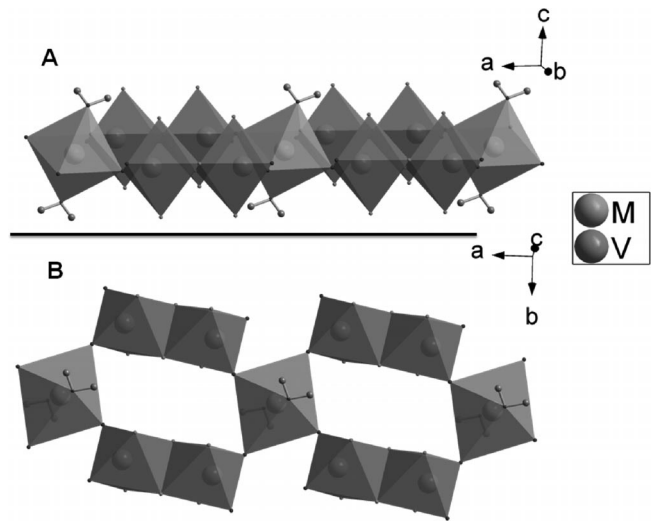

Figure 2. A The 2D layers of the transition metals within compounds **1**–**3**. B The 2D layers consists of $[V_2O_4F_6]^{4-}$ anionic BBUs that bond through their four oxide anions to four different LTMs (Co^{2+}, Ni^{2+} , or Cu^{2+}). Water and fluoride anions lie above and below the layers of transition metals.

The layers of transition metals are connected along the c axis with ionic bonds of fluoride anions to sodium cations and hydrogen bonds of the water ligands of the LTM octahedra. This is shown in Figure 3, distinct regions of electrostatic attractions (Na–F bonds) and hydrogen bonding attractions (O–H···X) alternate along the a axis; the hydrogen bond geometry for compounds **1**–**3** is provided in the Supporting Information, Tables S10–S12.

Compounds 1–3 Necessitate a Low pH to Crystallize from Solution

Despite the lack of any nitrate anions within compounds **1**–**3**, nitric acid was required for their crystallization. We reason

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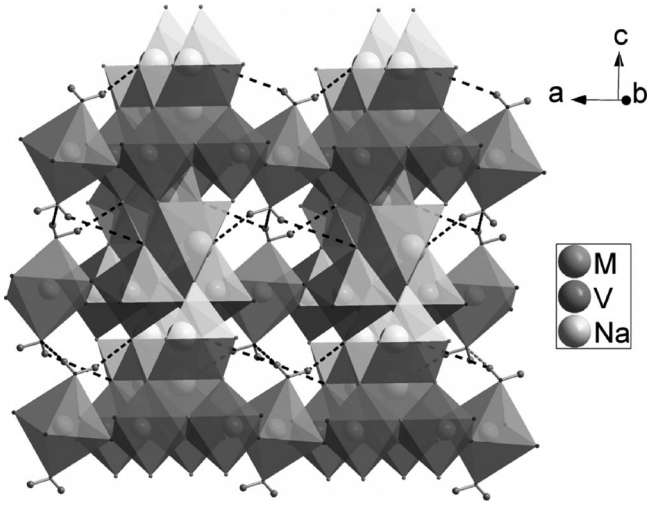

Figure 3. The 3D structure of Compounds **1–3** wherein the individual layers of transition metals are connected along the *c* axis via electrostatic (Na–F) bonds and hydrogen bonds between water ligands and fluoride anions. Hydrogen bonds are marked with black, dashed lines.

the role of nitric acid is to lower the pH of the reaction (pH = 1 before and after the reactions). Omission of a strong acid resulted in the syntheses of $CoVOF_4(H_2O)_7$ instead of compound **1** and $AF_2{\cdot}4(H_2O)$ (A = Ni^{2+} and Cu^{2+}) in place of compounds **2** and **3**.[11] To confirm this, we successfully synthesized compounds **1–3** with an equal volume of aqueous hydrochloric acid in place of nitric acid. *Gillespie* and *Rao* first described observation of the *trans*-dioxo $[VO_2F_4]^{3-}$ anion in solution.[26] They additionally noted they may observe a square pyramidal structure of $[VOF_4]^-$ that could undergo structural changes to $[VO_2F_4]^{3-}$ based upon pH; this square pyramidal anion of $[VOF_4]^-$ was speculated in an earlier study by *Hatton* et al.[34] In contrast to solution studies of *trans*-dioxo $[VO_2F_4]^{3-}$, we note that the solid state structures of compounds **1–3** and $K_2VO_2F_3$ contain *cis*-dioxo vanadium fluorides.

Compounds **1–3** contain dimerized dioxo vanadium fluoride anions and were only obtainable in solutions where the pH was lowered to approximately 1 by using a mineral acid (an "acidifed" hydrofluoric acid). We therefore speculate that the dioxo vanadium fluoride anion is stable in "acidified" solutions of hydrofluoric acid and/or monoxo vanadium fluoride anions are stable in "acidified" solutions of hydrofluoric acid and can precipitate to the solid state with the formation of a dioxo vanadium fluoride anion.

Previous studies have reported multiple ETM anions within the polar compounds $A_5Nb_3OF_{18}$ (A = K^+, Rb^+, Cs^+, $[NH_4]^+$) and $(Ag_3MoO_3F_3)(Ag_3MoO_4)Cl$.[35–38] Such materials form in reaction equilibria where multiple, different oxide-fluoride anions are stable. Future work will be directed towards in-situ examination of oxide-fluoride ETMs and implementation of synthetic conditions (pH, fluoride and reagent concentrations, and/or temperature) to isolate new BBUs and new oxide-fluoride materials.

The VOF Dimeric BBU Shows Strong Distortion Effects

Table 2 shows selected bonding parameters of the dimeric BBU. These BBUs show distorted octahedral environments of the vanadium oxide-fluoride as a result of two factors: 1) The Second Order Jahn–Teller distortion of V^{5+},[39,40] and 2) a second distortion on account of the specific ions in the terminal (oxide) and bridging (fluoride) positions. Distortions from factor (1) occur on account of orbital states that are nondegenerate but close in energy – this is the case for d^0 early transition metals such as vanadium(V).

It is important to note, however, that effects of factor (2) additionally influence in the geometry of the dimeric VOF units. We have previously described the placement of fluoride anions within bridging positions of two ETMs within the ordered $[Mo_2O_6F_3]^{3-}$ dimeric BBU. The position of oxide anions in terminal (non-bridging) positions of the VOF BBU allows greater stability owing to greater π-overlap between V^{5+} and O^{2-}.[16] Additionally, the two vanadium(V) cations, shown in Figure 1, repel each other to result in elongated, bridging V–F bonds. As the fluoride bonds bridge *two* vanadium cations the fluoride anions have less valence to contribute to each V–F bond and subsequently, the bonds are elongated further.

The short bonds of V=O contribute additional distortion effects to the VOF BBU. The bond angles of the O=V=O moieties are relatively large; these values are much closer to the angle of a tetrahedral species than an octahedral species. In a purely octahedral geometry, the short V=O bond lengths would bring the oxide anions closer together; subsequently the oxide anions would repel each other and widen the angle of the O=V=O moiety. A similar geometry is observed in the compound $K_2VO_2F_3$ which consists of $[VO_2F_2F_{2/2}]^{3-}$ BBUs.[31] It can be difficult to isolate distortions of type (1) and type (2) but it is apparent that both play significant roles in the geometry of bimetallic BBUs of ETMs.

The VOF BBUs Are Ordered Owing to the Use of Two Cations with Different Polarizabilities

In Table 3 we demonstrate the VOFs are ordered by use of Bond-Valence Sum (BVS) calculations.[41,42] The use of differing cations (with variations in size and/or polarizability) generates the necessary anisotropy around the environment of the VOF BBUs to achieve ordered F^- or O^{2-} sites.[22–24] Within compounds **1–3**, the harder and softer cations decidedly coordinate to the harder (fluoride) and softer (oxide) anions.

The use of LTMs as softer cations can result in new, ordered oxide-fluoride compounds, but VOF compounds rarely bind through oxide anions to LTMs.

The Dimeric VOF BBUs are Able to Bind to the LTMs Owing to an Increased Nucleophilicity of the Oxide Anions

The VOF anion $[VOF_5]^{2-}$ has a weakly nucleophilic oxide anion; the strong V=O bond leaves little negative charge on the oxide anion to coordinate to other metals.[13] For this reason, and in contrast to $[NbOF_5]^{2-}$, the $[VOF_5]^{2-}$ anion was

Table 2. Selected bonding parameters of the $[V_2O_4F_6]^{4-}$ basic-building unit for $Na_2(M(H_2O)_2(V_2O_4F_6)$, compounds **1**–**3** /Å,°.

Bond	Compound **1** M = Co^{2+}	Compound **2** M = Ni^{2+}	Compound **3** M = Cu^{2+}
V1=O1	1.627 (1)	1.629 (1)	1.606 (1)
V1=O2	1.664 (1)	1.667 (1)	1.702 (1)
V1–F1	2.056 (1)	2.055 (1)	2.078 (1)
V1–F1*	2.173 (1)	2.177 (1)	2.160 (1)
V1–F2	1.872 (1)	1.887 (1)	1.887 (1)
V1–F3	1.911 (1)	1.900 (1)	1.896 (1)
O1=V1=O2	105.24 (7)	105.60 (5)	104.99 (5)

* generated by symmetry operator (–1–*x*, 1–*y*, –*z*)

Table 3. Bond valence sum (BVS) calculations for $Na_2(M(H_2O)_2(V_2O_4F_6)$, compounds **1**–**3** in valence units.

Compound **1** M = Co^{2+}		Compound **2** M = Ni^{2+}		Compound **3** M = Cu^{2+}	
Cation	BVS*	Cation	BVS*	Cation	BVS*
Na^+	1.12	Na^+	1.09	Na^+	1.06
Co^{2+}	2.19	Ni^{2+}	2.27	Cu^{2+}	2.19
V^{5+}	4.82	V^{5+}	4.79	V^{5+}	4.76

unable to bind to LTMs within the compounds $CuMOF_5(H_2O)_4(pyz)_2$ and $CuMOF_5(H_2O)(pyz)_3$ (M = V^{5+} and Nb^{5+}).[18] In order for the oxide anion of a VOF to form a bond to an LTM, the electronic distribution on the vanadium oxide anion must be situated so that less valence is present within the V=O bond and significant electron density exists on the oxide anion.[11] Within the anionic BBUs $[VO_2F_2F_{2/2}]^{3-}$ and $[V_2O_4F_6]^{4-}$ the π-bonding of the vanadium cation is divided amongst *two* V=O bonds; consequently, as compared to the $[VOF_5]^{2-}$ anion, the $[V_2O_4F_6]^{4-}$ has less valence within each V=O bond. Additionally, the VOFs have O=V=O bond angles that are more characteristic of tetrahedral species (see Table 2). Therefore, the π orbitals of V^{5+} are less able to contribute to the V=O bonds. This results in an increased electron density on the oxide anions and the oxide anions more readily form bonds with LTMs than the monomeric BBU $[VOF_5]^{2-}$.

Conclusions

We have successfully isolated the ordered dioxo vanadium fluoride anion as part of the dimeric $[V_2O_4F_6]^{4-}$ BBU in the solid state by use of harder sodium cations and softer late transition metals and a low pH in the hydrothermal synthetic conditions. We attribute the anionic order to the combinatorial use of harder and softer ions. In contrast to monoxo vanadium fluorides, the dioxo vanadium fluoride anions have an increased nucleophilicity of the oxide anions. The layered structure arises from this greater nucleophilicity of the oxide anions which allows the VOF dimers to coordinate to LTMs.

Experimental Section

Caution. Hydrofluoric acid is toxic and corrosive! It must be handled with extreme caution and the appropriate protective gear and training.[43–45]

Materials

Copper oxide (99.99+%), nickel oxide (99.99 %), were obtained from Sigma-Aldrich. Cobalt carbonate (99.5 % metals basis), sodium chloride (99 %), and zinc oxide (99.99 %), were obtained from Alfa-Aesar. Hydrofluoric acid (48–51 % in water) was obtained from Aristair. Nitric acid (69 % in water) and hydrochloric acid (38 % in water) was obtained from Macron Chemicals. All materials were used as received. Deionized water was used as backfill in the pressure vessels.

Synthesis

The compounds $Na_2(M(H_2O)_2)(V_2O_4F_6)$ (M = Ni^{2+} and Cu^{2+}; compounds **2** and **3**, respectively) were synthesized by sealing MO (6.21 mmol), V_2O_5 (0.305 g, 1.68 mmol), NaCl (0.24 g, 4.11 mmol), HNO_3 (69 % in water, 0.05 mL), and hydrofluoric acid (49 % in water, 1.0 mL) in a Teflon (fluoroethylenepropylene) pouch, that was made as described previously.[46] Compound **1**, $Na_2(Co(H_2O)_2)(V_2O_4F_6)$ was synthesized by an equimolar replacement of $CoCO_3$ for MO and use of an additional 0.6 mL hydrofluoric acid in water. The reaction of $CoCO_3$ with hydrofluoric acid caused gaseous CO_2 to evolve – this gas was allowed to leave the pouch before the pouch was sealed. The pouches were each placed, alone, in a 250 mL Teflon-Lined Parr autoclave vessel. The vessel was filled with 42 mL deionized H_2O as backfill, sealed, heated for 24 hours at 150 °C, cooled to 25 °C at a rate of 0.1 K min^{-1}, allowed to sit – undisturbed – for 48 hours, opened in air, and the crystals were recovered by vacuum filtration. Compound **1** was separated from side products of $CoVOF_4(H_2O)_7$ while Compounds **2** and **3** were separated from side products of $AF_2{\cdot}(H_2O)_4$ (A = Co^{2+}, Ni^{2+}) with tweezers.

Crystallographic Determination

Single crystal XRD data were obtained at 100K with a Bruker Kappa APEX 2 CCD diffractometer with monochromated Mo-K_α radiation (λ= 0.71073 Å). The crystal-to-detector distance was 60 mm. The data were integrated with the program SAINT-V7.23A.[47] The structures have β angles that are nearly 90°, but use of an orthorhombic space group gave unreasonable fitness values. Face-indexed absorption corrections were applied to the data in the program XPREP.[48] The structures were determined by direct methods with Fourier Difference syntheses in the program OLEX2 with the XS solution algorithm.[48,49] After the position and identity of the metallic atoms were determined, the anion sites were found with Fourier techniques within OLEX2 and use of SHELXL-97.[48,49] The final structures were examined with PLATON and no higher symmetry was found.[50] Further details of the crystal-structure investigations may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-424344 (compound **1**),

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CSD-424345 (compound **2**), CSD-424346 (compound **3**) (http://www.fiz-karlsruhe.de/)

Supporting Information (see footnote on the first page of this article): Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters, atomic displacement parameters, geometric parameters, and hydrogen bond geometry for compounds **1**–**3**.

Acknowledgment

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