

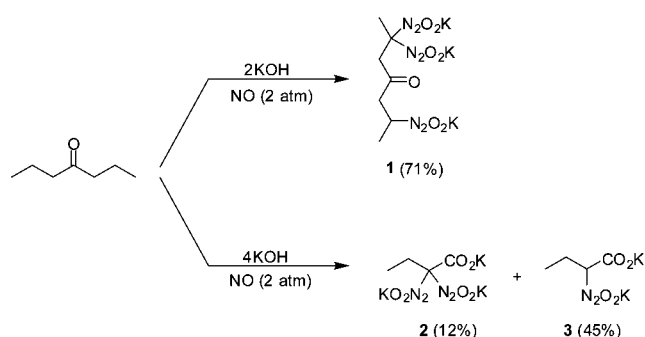
## Base Controlled Polydiazeniumdiolation of 4-Heptanone and a New Water Layer Structure

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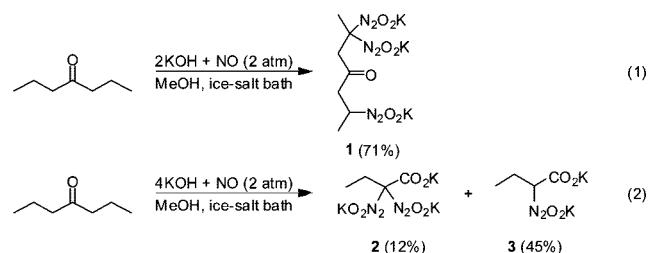


In a stoichiometry-controlled reaction, nitric oxide adds to the enolate of 4-heptanone at ca.  $-23\text{ }^{\circ}\text{C}$  to give mono-, bis-, or tris-diazeniumdiolate ( $-\text{N}_2\text{O}_2^-$ ) products: potassium 4-heptanone-3,3,5-tris(diazeniumdiolate) (**1**), potassium butanoate 2,2-bis(diazeniumdiolate) (**2**), and potassium butanoate 2-diazeniumdiolate (**3**). The diazeniumdiolate products are stable crystalline solids under ambient conditions and as solids exothermally decompose at high temperatures. Single-crystal X-ray data measured for the dihydrate **3** reveal a new layer aggregation, L4(4)8(8), as octameric water aggregates in a stair conformation which interacts minimally with the cation of the salt.

The chemical reactivity of nitric oxide manifests a number of patterns, including (a) the addition of a single NO to electrophilic centers such as ligand bound metal ions<sup>1–3</sup> and (b) its pairwise addition to nucleophilic centers such as secondary amines and carbanions to give diazeniumdiolates.<sup>4–7</sup> The latter type of reactions have yielded a wide variety of diazeniumdiolated products. While the reactions exemplify the intricacy of its potential biological reactivity, some of the products have also proven useful as synthetic nitric oxide donors in biomedical research.<sup>6</sup> Derivatives of organic compounds with  $-\text{N}_2\text{O}_2^-$  substituents are thermally unstable at elevated tem-

peratures and are possible high energy dense materials.<sup>7,8</sup> As part of our research toward the synthesis of such materials, we have prepared a diverse group of diazeniumdiolates from 4-heptanone. The underlying chemical reaction between nitric oxide and 4-heptanone reveals the dependence of the amount of base used in the formation of polydiazeniumdiolates.

When a degassed solution of 4-heptanone in methanol with 2 equiv of KOH is pressurized with nitric oxide gas (2 atm) under strictly anaerobic conditions in an ice–salt bath, potassium 4-heptanone-3,3,5-tris(diazeniumdiolate), **1**, is formed in 71% yield based on the amount of KOH (eq 1). With 1 equiv of base only the trisdiazeniumdiolate **1** is isolated in low yield. Attempts to synthesize the tetrakis(diazeniumdiolate) derivative of 4-heptanone have proven unsuccessful. For example, when 4 equiv of KOH was used in the above reaction, the product underwent hydrolytic cleavage of a carbonyl C–C bond to form potassium butanoate 2,2-bis(diazeniumdiolate), **2**, together with potassium butanoate 2-diazeniumdiolate, **3**.



The reaction is related to that of nitric oxide and acetone which give the potassium salts of methylenebis(diazeniumdiolate) and acetate.<sup>7</sup> Greater yields of the two products are obtained when 4 equiv of the base is used in the reaction (eq 2). In general, these reactions with aliphatic ketones are faster than with methanol itself,<sup>9</sup> but enolate formation is required before the addition of  $\text{N}_2\text{O}_2$  occurs. The products are purified by careful recrystallization from aq KOH (0.1 N) as described in the Experimental Section. Depending upon the crystallization conditions, monodiazeniumdiolate **3** crystallizes either as the dihydrate or the ethanol solvate crystals, both of which have been characterized by single-crystal X-ray diffraction. When dried in a vacuum oven at room temperature, the dihydrate crystals lose one of the water solvates, whereas the ethanol-solvated crystals lose the ethanol solvates completely.

**Structures of  $3 \cdot 2\text{H}_2\text{O}$  and  $3 \cdot \text{EtOH}$ .** As expected, the structure of the anions in the two crystals share similar structural features. A view of the anion in  $3 \cdot 2\text{H}_2\text{O}$  is shown in Figure 1. Pertinent metric parameters for the anion in the hydrate- and ethanol-solvated crystals are collected in Table 1. The anion contains an asymmetric tertiary C atom (C2) which is substituted with carboxylate, diazeniumdiolate, and ethyl groups. The diazeniumdiolate group is planar with comparable N–N and

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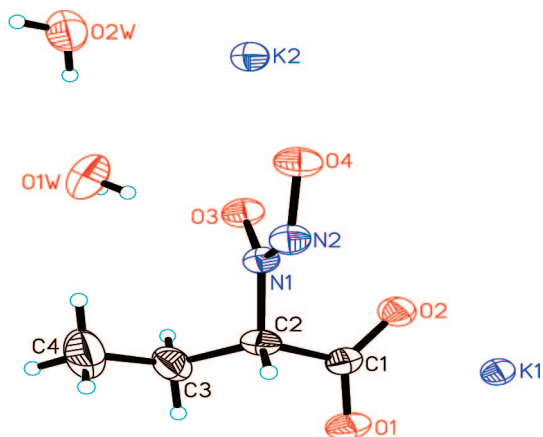
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**FIGURE 1.** Drawing of the asymmetric unit in  $3 \cdot 2\text{H}_2\text{O}$ . Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres with arbitrary radii.

**TABLE 1.** Selected Bond Distances (Å) and Angles (deg) for  $3 \cdot 2\text{H}_2\text{O}$  and  $3 \cdot \text{EtOH}$

	$3 \cdot 2\text{H}_2\text{O}$	$3 \cdot \text{EtOH}$
C2–N1	1.476(2)	1.475(3)
N1–N2	1.287(2)	1.281(3)
N1–O3	1.317(1)	1.298(3)
N2–O4	1.289(1)	1.211(3)
N2–N1–O3	124.2(1)	124.6(2)
N2–N1–C2	116.2(1)	115.9(2)
O3–N1–C2	119.4(1)	119.5(2)
N1–N2–O4	114.7(1)	114.0(2)

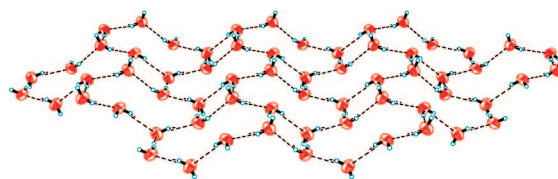
**TABLE 2.** Hydrogen Bonds (Å) and Angles (deg) in  $3 \cdot 2\text{H}_2\text{O}$

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
O1W–H1A···O3	0.80(3)	1.91(3)	2.696(2)	165(2)
O1W–H1B···O2W <sup>a</sup>	0.79(2)	2.04(2)	2.811(2)	166(2)
O2W–H2A···O1W <sup>b</sup>	0.82(3)	2.05(3)	2.831(2)	159(2)
O2W–H2B···O1W	0.86(3)	1.96(3)	2.805(2)	169(3)

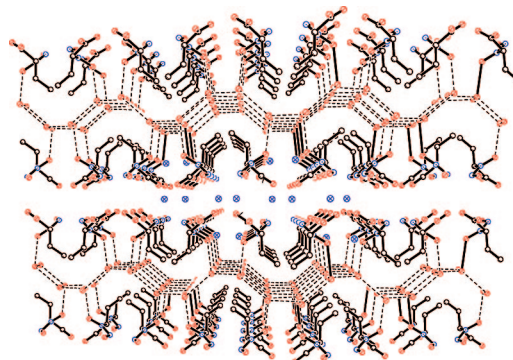
<sup>a</sup> *x*, –*y* + 1/2, *z* + 1/2. <sup>b</sup> –*x* + 2, –*y*, –*z*.

N–O distances as found for other C-bound diazeniumdiolates.<sup>10–16</sup> The water solvates in  $3 \cdot 2\text{H}_2\text{O}$  are involved in novel H-bond interactions, whereas the ethanol solvates in  $3 \cdot \text{EtOH}$  are associated with a straightforward intramolecular H-bonding with a neighboring anion (Table 2).

**Water clusters in  $3 \cdot 2\text{H}_2\text{O}$ .** One of the two solvated water molecules is not coordinated to any of the  $\text{K}^+$  ions. However, the other water molecule is coordinated to a cation with the associated K–O distance of 2.831(1) Å. The absence of strong interaction between the cations and the solvated water molecules



**FIGURE 2.** Octomeric clusters of solvated water molecules in  $3 \cdot 2\text{H}_2\text{O}$ .



**FIGURE 3.** Layers of water clusters (bottom) and stacking (top) in the structure of  $3 \cdot \text{H}_2\text{O}$ .

is offset by strong hydrogen bonding interaction between the water solvates. The hydrogen-bonding interaction leads to a two-dimensional network of supramolecular  $(\text{H}_2\text{O})_8$  clusters with eight oxygen atoms belonging to four pairs of the two water solvates (Figure 2). At the center of the  $(\text{H}_2\text{O})_8$  cluster is a 2-fold screw axis, and the clusters are arranged with their four- and eight-membered rings disposed around the inversion centers on the *bc* face.

The structure of the  $(\text{H}_2\text{O})_8$  cluster found in  $3 \cdot 2\text{H}_2\text{O}$  assumes a stairlike geometry (Figure 3) and is similar to a cluster present in the structure of a hydrated calix{4}resorcinarene.<sup>17</sup> In the latter structure an isolated  $(\text{H}_2\text{O})_8$  unit is surrounded by four adjacent calix{4}resorcinarene molecules. Two other structures also contain hydrogen bonded  $(\text{H}_2\text{O})_8$  units,<sup>18,19</sup> which are present as blocks surrounded by the rest of the molecules. In  $1 \cdot 2\text{H}_2\text{O}$ , however, the  $(\text{H}_2\text{O})_8$  clusters form extended two-dimensional network of layers. Specifically, the  $(\text{H}_2\text{O})_8$  clusters in  $3 \cdot 2\text{H}_2\text{O}$  are connected to four neighboring  $(\text{H}_2\text{O})_8$  clusters through hydrogen-bonding interactions forming wavelike layers as shown in Figure 3 with mutually shared rectangular  $(\text{H}_2\text{O})_4$

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units. The water network fits layer motif L4(4)8(8) as defined by Mascall et al.<sup>20</sup>

One of the solvated water molecules is also hydrogen bonded to the anion. The hydrogen bond between O3 and O1W is the strongest in the structure, and it serves to tether the anion to the (H<sub>2</sub>O)<sub>8</sub> cluster (Figure 2). The anions are oriented above and below the (H<sub>2</sub>O)<sub>8</sub> clusters. The anions are stacked between two successive layers of the water clusters. The cations are located in the central area between the layers.

When dried overnight at reduced pressure the crystals of 3·2H<sub>2</sub>O lose one of their water solvates as revealed by the analytical data.

**Thermochemistry.** DSC data collected for 1·2H<sub>2</sub>O, 2·3H<sub>2</sub>O, and 3·H<sub>2</sub>O reveal that the three diazeniumdiolate salts undergo exothermic decomposition at 186, 192, and 278 °C with −79, −48, and −63 kcal/mol, respectively. Significantly, although all of the salts contain solvated water molecules, only minor endothermic transitions associated with their removal from the solids are observed. The anhydrous sample of 3 obtained from drying the crystals of 3·EtOH decomposes at 271 °C with an enthalpy of −41 kcal/mol; both values are slightly less than for 3·H<sub>2</sub>O. Regardless of its solvation, the carboxylate/diazeniumdiolate 3 decomposes ca. 100 °C higher in temperature than do most diazeniumdiolates. This process is almost invariant with respect to the presence of the water layer and illustrates the relatively minor stabilization offered by the latter to the lattice.

## Conclusions

The reaction of nitric oxide with 4-heptanone, a symmetric ketone with two activated  $\alpha$ -methylene groups and KOH, either provides a tris(diazeniumdiolate) or a mixture of bis- and mono(diazeniumdiolates). When 4 equiv of KOH is used in the reaction, the tris(diazeniumdiolated) product formed undergoes hydrolytic cleavage of the C–C bond adjacent to the carbonyl group precluding further diazeniumdiolation. This observation extends the known reactions of ketones with nitric oxide in that a net trisdiazeniumdiolation is possible. Finally, we have also observed the presence of a novel water cluster in one of the products.

## Experimental Section

The reactions with nitric oxide were carried out using the nitric oxide reactor described previously.<sup>7</sup> UV–vis spectra were measured in water or in 0.1 N aq KOH solutions. The NMR spectra were measured in either D<sub>2</sub>O or 0.1 N KOD/D<sub>2</sub>O solvent containing DSS-*d*<sub>6</sub> (0.1% w/v) as internal standard on a 400 MHz NMR spectrometer. Infrared spectra were obtained as KBr disks with an FTIR spectrophotometer. Thermograms were obtained using a differential scanning calorimeter under a steady flow of argon gas and at the heating rate of 10 °C per min in the temperature range 25–500 °C. Approximately 2 mg of the sample was placed in aluminum sample cups and crimped with a cover.

**Potassium 4-Heptanone-3,3,5-tris(diazeniumdiolate) Dihydrate (1·2H<sub>2</sub>O).** To a solution of KOH (5.71 g, 0.100 mol) in methanol (100 mL) in a glass pressure bottle was added 4-heptanone (5.71 g, 0.050 mol). The mixture was cooled in an ice–salt bath and degassed by applying reduced pressure and pressurizing with N<sub>2</sub> gas to 2 atm repeatedly 6 times. Subsequently, the reaction mixture was pressurized with nitric oxide to 2 atm. As the reaction

ensued, significant absorption of the gas was observed in the first 6 h, and the reaction mixture was repeatedly pressurized with nitric oxide and then allowed to warm to room temperature. The nitric oxide pressurization was continued for 2 d when the absorption of the gas stopped. The reaction mixture was flushed with N<sub>2</sub> for 30 min to remove the residual gases, and the white precipitate of potassium 4-heptanone-3,3,5-tris(diazeniumdiolate) dihydrate formed was filtered, washed with hot methanol (2 × 10 mL), and dried in a vacuum oven at room temperature overnight. Yield: 10.52 g (71.0% based on KOH). IR (KBr, cm<sup>−1</sup>): 3342 b, 2976 m, 2941 m, 2883 w, 1724 s, 1463 m, 1397 s, 1353 s, 1330 s, 1301 s, 1275 s, 1244 s, 1189 s, 1126 m, 1086 m, 1041 m, 959 s, 904 s, 887 s, 826 s, 798 s, 735 w, 697 m, 588 w, 569 m, 517 m, 484 w, 450 w, 431 w. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  5.26 (1H, dd, *J* = 11.2, 3.3 Hz), 2.77 (1H, m), 2.41 (1H, m), 2.22 (1H, m), 1.80 (1H, m), 0.923 (3H, t, *J* = 7.3 Hz), 0.811 (3H, t, *J* = 7.3 Hz). <sup>13</sup>C NMR (400 MHz, D<sub>2</sub>O)  $\delta$  192.4, 99.3, 73.3 (d, *J* = 145.0 Hz), 26.1 (t, *J* = 133.7 Hz), 23.2 (t, *J* = 132.0 Hz), 9.88 (q, *J* = 127.2 Hz), 8.25 (t, *J* = 128.0 Hz). Anal. Calcd for C<sub>7</sub>H<sub>15</sub>N<sub>6</sub>O<sub>9</sub>K<sub>3</sub> (444.52): C, 18.91; H, 3.40; N, 18.91. Found: C, 19.09; H, 3.12; N, 18.95.  $\lambda_{\max}$  ( $\epsilon$ ) in 0.1 N aq KOH: 256 nm (19990 M<sup>−1</sup>cm<sup>−1</sup>). DSC:  $\Delta H$  = −79 kcal/mol. *T*<sub>onset</sub> = 186 °C.

**Potassium Butanoate 2,2-Bis(diazeniumdiolate) Trihydrate (2·3H<sub>2</sub>O).** To a solution of KOH (5.71 g, 0.100 mol) in methanol (100 mL) in a glass pressure bottle was added 4-heptanone (2.86 g, 0.025 mol). The reaction was carried out as described above over 2 d, and the small amount of white precipitate formed was filtered. The crude product was recrystallized by diffusing methanol into a saturated solution of the product in 0.1 N aq KOH. Fluffy microcrystals of potassium butanoate 2,2-bis(diazeniumdiolate) trihydrate formed were filtered, washed with methanol and dried in a vacuum oven at room temperature overnight. Yield: 1.12 g (11.9% assuming 1 equiv of the product will be formed from 1 equiv of the heptanone). IR (KBr, cm<sup>−1</sup>): 3369 b, 2981 m, 2952 m, 2892 w, 1721 s, 1700 m, 1652 s, 1626 s, 1605 s, 1561 m, 1543 w, 1522 w, 1509 w, 1458 m, 1372 m, 1343 s, 1309 s, 1280 s, 1205 s, 1118 m, 1095 w, 1048 w, 958 m, 927 m, 864 s, 849 m, 763 s, 725 s, 611 m, 526 m, 421 w. <sup>1</sup>H NMR (400 MHz, 0.1 M KOD/D<sub>2</sub>O)  $\delta$  2.60 (q, 2H, *J* = 7.1 Hz), 1.07 (t, 3H, *J* = 7.1 Hz). <sup>13</sup>C NMR (400 MHz, 0.1 M KOD/D<sub>2</sub>O)  $\delta$  190.6, 102.7, 29.1 (t, *J* = 134.1 Hz), 11.7 (q, *J* = 128.1 Hz). Anal. Calcd for C<sub>4</sub>H<sub>11</sub>N<sub>4</sub>O<sub>9</sub>K<sub>3</sub> (376.45): C, 12.76; H, 2.94; N, 14.88. Found: C, 12.66; H, 2.57; N, 14.69.  $\lambda_{\max}$  ( $\epsilon$ ) in 0.1 N aq KOH: 256 nm (13495 M<sup>−1</sup>cm<sup>−1</sup>). DSC:  $\Delta H$  = −48 kcal/mol. *T*<sub>onset</sub> = 192 °C.

**Potassium Butanoate 2-Diazeniumdiolate (3).** The filtrate from the synthesis above was allowed to evaporate in a fume hood, and the syrupy residue was dissolved in 50 mL of 0.1 N aq KOH. Potassium butanoate 2-diazeniumdiolate was crystallized out from the solution by two methods either as the dihydrate or as the ethanol solvate.

**Method 1 (3·2H<sub>2</sub>O).** On slow evaporation of the solution under ambient conditions crystals of 3 crystallized out as its dihydrate (as characterized by the X-ray data). The crystals were filtered, washed with methanol, and dried in a vacuum oven at room temperature. Anal. Calcd for C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>5</sub>K<sub>2</sub> (242.3): C, 19.83; H, 3.33; N, 11.56. Found: C, 19.77; H, 3.24; N, 11.51. The elemental analysis data obtained for the dried crystals are consistent with the salt with one solvated water molecule indicating the loss one of the solvated water molecules on drying. Yield: 2.74 g (45% assuming one equiv of the product will be formed from 1 equiv of the heptanone). IR (KBr, cm<sup>−1</sup>): 3330 b, 2974 w, 1625 s, 1406 s, 1370 s, 1335 w, 1314 m, 1268 s, 1241 s, 1210 m, 1109 w, 1088 m, 1038 m, 939 s, 906 m, 846 m, 775 m, 704 m, 665 m, 584 w, 489 w. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta$  4.59 (dd, 1H, *J* = 10.5, 5.5), 2.02 (m, 2H), 0.85 (t, 3H, *J* = 7.4). <sup>13</sup>C NMR (400 MHz, D<sub>2</sub>O):  $\delta$  177.9, 78.3 (d, *J* = 140.3), 25.2 (t, *J* = 130.1), 12.9 (q, *J* = 124.1).  $\lambda_{\max}$  ( $\epsilon$ ) in 0.1 N aq KOH: 250 nm (8270 M<sup>−1</sup>cm<sup>−1</sup>). DSC:  $\Delta H$  = −63 kcal/mol, *T*<sub>onset</sub> = 278 °C.

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**Method 2 (3•EtOH).** Ethanol was slowly diffused over a period of 3 d into the solution in a crystallization flask, when potassium butanoate 2-diazeniumdiolate crystallized out as its di(ethanol) solvate. The crystals were filtered and dried in a vacuum oven at room temperature. NMR spectral data and combustion data reveal that the crystals lose the solvated ethanol on drying. Yield: 0.90 g (16.0% assuming one equiv of the product will be formed from 1 equiv of the heptanone). On further diffusion of ethanol into the filtrate more crystals were formed. NMR characterization of the crystals reveals that the crystals are a mixture of potassium butanoate 2-diazeniumdiolate and potassium propane-1,1-bis(diazeniumdiolate).<sup>7</sup>

Single crystal X-ray diffraction data for **3**•2H<sub>2</sub>O were collected on a Bruker P4 diffractometer. Absorption effects were corrected by the  $\psi$ -scans method. The asymmetric unit contains two potassium cations, one butanoate 2-diazeniumdiolate anion, and two solvated water molecules. All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The hydrogen atoms of the methyl groups of the anion were placed in calculated positions and refined isotropically. The rest of the hydrogen atoms were located in the Fourier maps and refined isotropically. The data for **3**•EtOH were collected on a Bruker SMART APEX II CCD area detector system. The asymmetric unit contains two potassium cations, one butanoate 2-diazeniumdiolate anion, and one solvated ethanol molecule. All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The hydrogen atoms of the anion and the ethanolic O–H group were located in the Fourier maps and refined isotropically. The hydrogen atoms of the ethanolic ethyl group were placed in calculated positions and refined isotropically. Both structures were solved by direct methods using the Bruker SHELXTL (V. 6.14)

**TABLE 3.** Crystallographic Data for **3**•2H<sub>2</sub>O and **3**•EtOH

formula	C <sub>4</sub> H <sub>10</sub> K <sub>2</sub> N <sub>2</sub> O <sub>6</sub>	C <sub>6</sub> H <sub>12</sub> K <sub>2</sub> N <sub>2</sub> O <sub>5</sub>
fw	260.34	270.38
crystal system	monoclinic	orthorhombic
space group, Z	<i>P</i> 2 <sub>1</sub> / <i>c</i> , 4	<i>Pbca</i> , 8
<i>T</i> , K	295	150
<i>a</i> , Å	13.6188(11)	13.5648(3)
<i>b</i> , Å	8.9743(7)	7.2039(2)
<i>c</i> , Å	8.6284(6)	24.3207(5)
$\beta$ , deg	90.192(11)	90
<i>V</i> , Å <sup>3</sup>	1054.55(14)	2376.61(10)
$\rho_{\text{calc}}$ , g•cm <sup>-3</sup>	1.640	1.511
$\mu$ , mm <sup>-1</sup>	0.905	0.801
$R_1[I > 2\sigma(I)]^a$	0.0217	0.0567
$wR_2(\text{all data})^b$	0.0583	0.1349

$$^a R_1 = \sum |F_o - |F_c|| / |F_o|. \quad ^b wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}.$$

software package.<sup>1</sup> Crystallographic data for the two salts are collected in Table 3.

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**Supporting Information Available:** Crystallographic data (CIF files, Tables S1–S10) for both the hydrate and ethanol solvate. Views of **3**•EtOH (Figures S1 and S2), and the IR and NMR spectra (Figures S3–S9). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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