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The Oxamate Anion: A Flexible Building Block of Hydrogen-Bonded Architectures for Crystal Engineering

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Abstract: In order to examine the possibilities of using the oxamate anion, $[OOCCONH_2]^-$, as a versatile building block of low-dimensional, hydrogen-bonded scaffolding, the preferential assembly patterns displayed by this anion were identified using X-ray single-crystal data for a sequence of simple oxamate salts. Several new compounds were synthesized, and the crystal structures of six materials are presented: piperidinium oxamate (**1**), 2-amino-5-nitropyridine 2-amino-5-nitropyridinium oxamate (**2**), imidazolium oxamate (**3**), (4-chlorobenzyl)ammonium oxamate (**4**), (3-chlorobenzyl)ammonium oxamate (**5**), and potassium oxamate monohydrate (**6**). The oxamate anion acts as a building block of either 1-D (ribbons or ladders) or 2-D (layers) motifs. These architectures (generated by NH···O hydrogen bonds) are the result of the selectivity of complimentary hydrogen-bond sites of the anion. However, the type of network adopted is also influenced by cation−anion interactions, and the role of the physical−chemical characteristics of the cation in inducing a specific anionic motif, is discussed. The oxamate anion, as well as other deprotonated carboxylic amides, may represent useful additions to the existing collection of building blocks capable of generating extended hydrogen-bonded motifs for crystal engineering.

Introduction

One of the many intriguing and demanding facets of crystal engineering is the continuous need to develop new tools and strategies for intermolecular, synthetic solid-state chemistry.[1] The underlying targets for research in this area range from an improved understanding of the very nature of, and structural effects of, intermolecular forces to the development of new materials with specific electrical, optical, or magnetic properties.[2]

So far, most efforts in crystal engineering have typically been concerned with limiting, or controlling, the positional freedom and inherent spatial flexibility of individual molecules, "building blocks", as they assemble into a 3-D crystal. One way of solving this central problem may be through the design of chemical systems with preferred (and therefore predictable), structural assembly patterns where individual components are "locked" into specific positions. In this way, the positional freedom of each building block can be severely restricted which, in turn, improves our chances of determining *a priori* the main structural features of new materials. Intermolecular synthesis, as distinct from intramolecular (covalent) synthesis, must obviously rely on a variety of weaker intermolecular forces, *e.g.* halogen−halogen attractions, hydrogen-bonding, and ring−ring interactions,[3] and the delicate balance between these forces will ultimately determine the structure (and properties) of a new compound.

Recent years have seen considerable progress in this field, and several elegant examples of reliable aggregates, assembled through a perceptive use of complimentary hydrogen bonds, have been presented. These efforts have illustrated that the selectivity and directionality of such interactions can be employed in the deliberate design of new, and reproducible, structural motifs. So far, most of this work has been carried out on organic molecular solids,[4] but recently, ionic scaffolding[5,6] and metal-containing networks[7] have also been conceived and characterized.

Despite these advancements, we are still a considerable distance away from a complete understanding of the way in which the balance between a multitude of intermolecular forces influences and determines the 3-D arrangement of molecules and ions in new materials.

Rationale. As part of an extensive study of recognition patterns of specific hydrogen-bond functionalities, and of their role in determining the structure of ionic solids, we have

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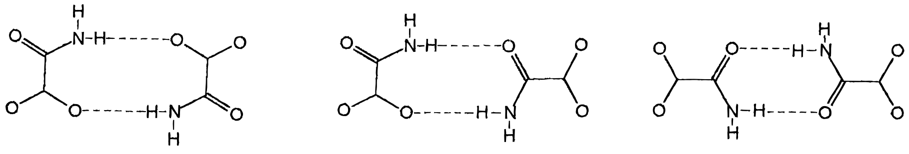
Chart 1



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examined the structural behavior of the oxamate anion, $[OOCCONH_2]^-$, in several simple salts. The oxamate anion was selected because it has inherent possibilities of generating infinite anionic aggregates through the complimentary hydrogen-bond functionalities $-COO^-$ and $-CONH_2$. Analogous to the anionic motifs observed in most hydrogen dicarboxylate salts where head-to-tail OH···O hydrogen bonds (from the carboxylic head to the carboxylate tail) give rise to infinite chains, oxamate ions can be expected to aggregate into 1-D patterns built around a central hydrogen-bonded dimeric unit (where the dimer is held together by two hydrogen bonds). The remaining hydrogen-bond sites are then available for providing a cross-link between neighboring 1-D motifs (chains or ladders), thereby creating a 2-D scaffolding, unless the cations can compete successfully with the existing sites. The oxamate anion also offers the opportunity to examine competition between different hydrogen-bond donors and acceptors since, if neighboring anions are linked into pairs by two hydrogen bonds, there are (hypothetically) three different ways in which such an arrangement can be achieved. These three dimeric motifs will be labeled as acid−acid (I), acid−amide (II), or amide−amide (III), depending upon which pairs of oxygen atoms act as acceptor sites in the dimer (Chart 1).

A search of the Cambridge Structural Database[8] revealed that only one simple oxamate salt, ammonium oxamate, had previously been characterized by X-ray single-crystal structure determination[9] (transition-metal complexes were not included). Consequently, in order to gather the necessary structural information, a range of oxamates (predominantly with an organic cation) were synthesized and the most suitable crystals were subjected to X-ray single-crystal structure determinations. In order not to unnecessarily bias the structural data, a wide variety of cations were included which would explore the influence of several factors (*e.g.,* size, shape, number of hydrogen-bond donors/acceptors, *etc.*). All of these components can be expected to be of some importance for determining the final crystal structure. The subsequent results and discussion are based upon the crystal structures of the following six compounds: piperidinium oxamate (**1**), 2-amino-5-nitropyridine 2-amino-5-nitropyridinium oxamate (**2**), imidazolium oxamate (**3**), (4-chlorobenzyl)ammonium oxamate (**4**), (3-chlorobenzyl)ammonium oxamate (**5**), and potassium oxamate monohydrate (**6**). The aim of the discussion is to describe and highlight some salient structural features, notably the oxamate aggregation patterns, in this family of compounds, and in addition, some possible explanations for the observed structural behavior are put forward.

Results

The syntheses of **1**−**6** are described in detail in the Experimental Section and the relevant X-ray crystallographic information is displayed in Table 1.

The X-ray structure determinations of **1**−**6** showed that the oxamate anion is, as intended, capable of creating infinite low-dimensional architectures, held together by complimentary NH···O hydrogen bonds. The geometry of the anion itself shows little conformational variation (Table 2), despite the fact that rotation can, in theory, take place around the central C−C bond. This planarity of the anion, despite considerable variations in the cation characteristics, can partly be attributed to the presence of an intramolecular hydrogen bond N(1)···O(22) (the oxygen atom *cis* to the nitrogen atom is consistently labeled as O(22), Chart 2). Due to the geometry of the anion, the NH···O angle is invariably very steep, 97−115°. Variations in bond lengths involving the carboxylate oxygens are also observed, and this can be ascribed to the diversity of hydrogen-bond interactions (intra and inter) that these oxygen atoms participate in.

The crystal structure of **1** contains infinite anionic ribbons held together by two NH···O hydrogen bonds involving a carboxylate oxygen atom and the amide oxygen atom (hence a Type II dimer) (Table 3). These ribbons (Figure 1), built around an acid−amide linkage, are oriented in a zig-zag fashion, parallel with *b*. There are no hydrogen bonds between neighboring ribbons. However, adjacent ribbons are cross-linked by cations so that each cation is hydrogen bonded to two different ribbons simultaneously *via* one bifurcated and one simple NH···O interaction (Figure 2). This leads to a structure where all hydrogen bond donors/acceptors are confined to a narrow layer, separated by the hydrophobic moieties of the cations.

The structure determination of **2** revealed that, in addition to the expected ion pair, a neutral molecule of the original amine, 2-amino-5-nitropyridine, had been incorporated into the lattice. The anionic motif in **2** is identical to the ribbon which appeared in **1**. Again, the acid−amide linkage (created by NH···O hydrogen bonds) gives rise to a ribbon-like zig-zag arrangement (Table 4). Similarly to **1**, there are no hydrogen bonds between neighboring ribbons. Instead of viewing the cation and the neutral amine as separate structural entities, it is possible to treat them as one building block since they appear as tetramers, held together by NH···N and CH···O interactions (Figure 3). The function of the amine groups of the cations, which are now positioned at opposite ends of the tetrameric unit, is to cross-link adjacent anionic ribbons *via* two NH···O hydrogen bonds (Figure 4). There is a total of four CH···O interactions in this structure, and this is in accordance with several studies of hydrogen-bond patterns of heterocyclic cations.

The crystal structure of **3** also contains a 1-D anionic motif, but in this case, the central anionic dimer (where a "dimer" is delineated as being held together by two hydrogen bonds) is of the acid−acid type (both acceptors site in the dimer reside on the carboxylate moiety) and adjacent dimers are linked into an infinite motif, a ladder, parallel with *a* (Figure 5). The cation, with strong hydrogen-bond donors on opposite sides of a rigid spacer, is positioned between neighboring anionic ladders and acts as a bridge *via* three NH···O and two CH···O interactions (Figure 6, Table 5). The overall packing is essentially 2-D, with anionic ribbons parallel with *a*, cross-linked, along *c*, by

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[8] Cambridge Structural Database version 5.11 (April 1996). Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 46.

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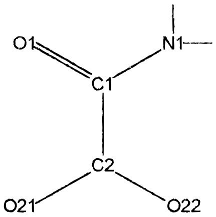
Table 1. Data Collection and Refinement for **1**−**6**

crystal data	**1**	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_7H_{14}N_2O_3$	$C_{12}H_{13}N_7O_7$	$C_5H_7N_3O_3$	$C_9H_{11}ClN_2O_3$	$C_9H_{11}ClN_2O_3$	$C_2H_4KNO_4$
MW	174.20	367.29	157.14	230.65	230.65	145.16
crystal size (mm)	0.51 × 0.34 × 0.25	0.56 × 0.35 × 0.19	0.68 × 0.18 × 0.12	0.44 × 0.28 × 0.18	0.3 × 0.45 × 0.2	0.8 × 0.52 × 0.36
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	9.5230(10)	10.206(6)	6.162(3)	15.6740(10)	8.800(2)	3.8160(10)
b (Å)	7.0500(10)	7.598(5)	12.801(2)	12.1290(10)	11.727(2)	13.553(3)
c (Å)	13.747(2)	19.78(2)	8.7770(10)	11.429(2)	11.115(2)	10.506(2)
α (deg)	90	90	90	90	90	90
β (deg)	96.730(10)	94.86(5)	96.61(4)	92.820(10)	99.14(3)	90.18(3)
γ (deg)	90	90	90	90	90	90
volume (Å^3)	919.6(2)	1592(2)	687.7(4)	2170.1(4)	1132.5(4)	543.3(2)
Z	4	4	4	8	4	4
D_{calcd} (g cm^{-3})	1.262	1.596	1.518	1.412	1.353	1.775
F(000)	376	760	328	960	480	296
μ(Mo Kα) (mm^{-1})	0.099	0.134	0.127	0.341	0.327	0.902
temp (K)	123	123	123	293	293	293
ω scans; θ range (deg)	2.47−25.00	2.00−25.00	2.83−24.99	2.12−22.50	2.34−19.99	2.45−25.0
range h	−11 to 1	0 to 12	0 to 7	-16 to 16	−1 to 8	0 to 4
range k	0 to 8	0 to 9	0 to 15	-13 to 0	-1 to 11	0 to 16
range l	−16 to 16	−23 to 23	−10 to 10	0 to 12	−10 to 10	−12 to 12
no. of reflns colld	1734	2847	1332	3002	1506	1114
unique reflns	1622	2686	1215	2830	1062	963
data:parameter ratio	14.9	11.4	12.15	10.4	7.81	13.19
refinement	full-matrix least squares	full-matrix least squares	full-matrix least squares	full-matrix least squares	full-matrix least squares	full-matrix least squares
$R/R_w{}^2$ (obs data)	0.0347/0.0863	0.0420/0.0994	0.0770/0.1717	0.0471/0.0972	0.0438/0.1003	0.0347/0.0854
$R/R_w{}^2$ (all data)	0.0434/0.0925	0.0646/0.1117	0.1483/0.2162	0.0903/0.1171	0.0598/0.1100	0.0409/0.0897
$\Delta\rho_{max/min}$ (e Å^{-3})	0.199/−0.206	0.211/−0.263	0.408/−0.483	0.261/−0.244	0.224/−0.220	0.331/−0.781
S	1.050	1.057	1.035	1.051	1.046	1.167

Table 2. Selected Geometric Parameters of the Oxamate Anion in **1**−**6**

compd	C(2)−O(21)/ Å	C(2)−O(22)/ Å	O(1)−C(1)−C(2)−O(21)/ deg
1	1.254(2)	1.247(2)	−9.87(19)
2	1.240(3)	1.263(3)	−4.81(30)
3	1.244(6)	1.259(6)	14.26(72)
4	1.249(4)	1.249(4)	−3.98(51)
	1.251(4)	1.249(4)	5.21(50)
5	1.244(4)	1.250(4)	12.96(47)
6	1.239(2)	1.248(3)	14.29(30)

Chart 2



the planar cations. There are seemingly no attractive cation−cation interactions.

Table 3. Geometry of the Hydrogen Bonds in **1**[a]

D−H···A	r(H···A)/Å	r(D···A)/Å	∠(D−H···A)/deg
N(1)−H(11)···O(22)′	1.947(2)	2.864(2)	170.05(5)
N(1)−H(12)···O(22)	2.287(2)	2.728(2)	115.58(4)
N(1)−H(12)···O(1)″	2.315(2)	2.930(2)	134.47(4)
N(3)−H(31)···O(21)‴	1.952(2)	2.790(2)	163.95(4)
N(3)−H(32)···O(1)	2.149(2)	2.873(2)	135.88(4)
N(3)−H(32)···O(21)	2.095(2)	2.880(2)	143.80(4)

[a] Symmetry code: (′) $-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2$; (″) $-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_2$; (‴) $-x - {}^1/_2, y + {}^1/_2, -z + {}^1/_2$.

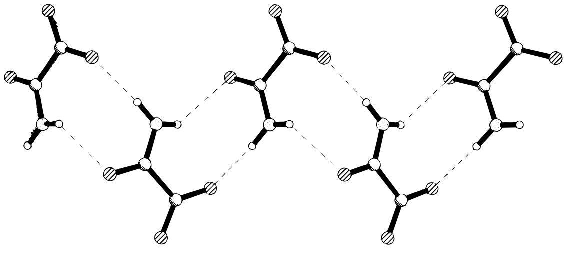


Figure 1. Ribbon of oxamate anions (parallel with b) in **1** generated by complimentary NH···O hydrogen bonds (indicated by dashed lines).

The X-ray structure determination of **4** revealed the presence of two unique ion pairs. The central anionic unit is an acid−acid dimer (held together by two hydrogen bonds involving carboxylate oxygen atoms), and the dimers are held together in such a way as to generate an infinite 2-D layer (Figure 7). Due to the fact that there are four crystallographically different ions in **4**, the hydrogen-bond interactions are particularly numerous (Table 6). Within the anionic layer, there are two "holes"; a 10-membered dimeric ring and a larger 22-membered cavity. This cavity provides the attachment point for two cations, each of which uses three hydrogen bonds to link to the same side of the anionic cavity (Figure 8). The overall packing consists of alternating bilayers of cations and bilayers of anions (Figure 9). An examination of the environment around each chlorine atom did not uncover any unusually short Cl···Cl distances. Neighboring rings are tilted with respect to each other and there is no suggestion of attractive $\pi-\pi$ interactions within the cationic layer.

The anions in **5** are also arranged in infinite layers, comparable to the anionic motif in **4**. The infinite 2-D sheet (identical to the anionic motif in **4**) is built around an acid−acid dimeric unit and contains the 10-membered and a 22-membered ring. This motif is the result of two unique NH···O hydrogen bonds

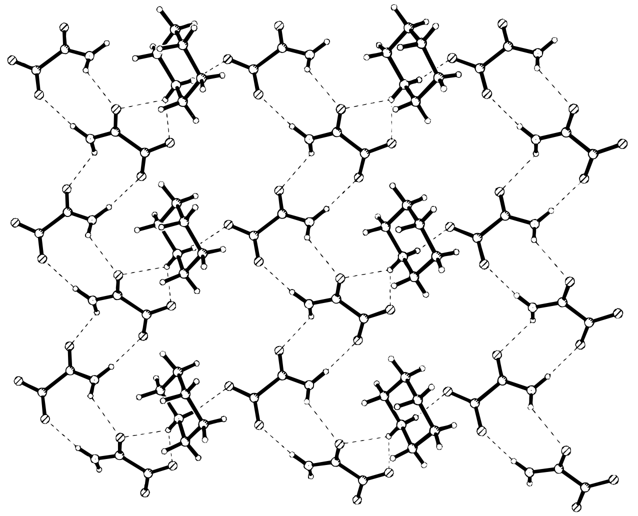


Figure 2. Crystal packing in **1**, with neighboring ribbons of anions cross-linked via NH···O hydrogen bonds to the cation. Some cations removed for clarity.

Table 4. Geometry of the Hydrogen Bonds in **2**[a]

D−H···A	*r*(H···A)/ Å	*r*(D···A)/ Å	∠(D−H···A)/ deg
N(1)−H(11)···O(21)′	1.956(3)	2.889(3)	168.07(7)
N(1)−H(12)···O(21)	2.357(3)	2.727(3)	103.03(7)
N(1)−H(12)···O(1)″	2.068(3)	2.904(3)	147.55(7)
N(3A)−H(3A)···O(21)′	1.727(3)	2.694(3)	166.01(8)
N(4A)−H(41A)···O(1)‴	1.872(3)	2.847(3)	170.85(7)
N(4A)−H(42A)···O(22)′	1.861(3)	2.790(3)	169.18(8)
N(4B)−H(41B)···O(71A)′′′′	2.570(3)	3.060(3)	109.31(8)
N(4B)−H(41B)···O(72B)′′′′′	2.642(3)	3.325(3)	124.50(7)
C(6A)−H(6A)···O(72B)′′′′′′′	2.475(3)	3.336(4)	145.82(7)
C(8A)−H(8A)···O(71B)	2.227(3)	3.092(4)	141.00(8)
C(6B)−H(6B)···O(72A)′′′′′	2.564(3)	3.366(4)	138.23(7)
C(8B)−H(8B)···O(71A)′′′′′′′′	2.617(3)	3.352(4)	149.38(7)

[a] Symmetry code: (′) $-x + 1, y - {}^{3}/_{2}, -z + {}^{3}/_{2}$; (″) $-x + 1, y + {}^{1}/_{2}, -z + {}^{3}/_{2}$; (‴) $x, -y - {}^{1}/_{2}, z + {}^{1}/_{2}$; (′′′′) $-x, y - {}^{3}/_{2}, -z + {}^{3}/_{2}$; (′′′′′) $x, y - 1, z$. (′′′′′′) $-x, -y - 1, -z + 1$; (′′′′′′′) $x, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; (′′′′′′′′) $x, -y + {}^{1}/_{2}, z - {}^{1}/_{2}$.

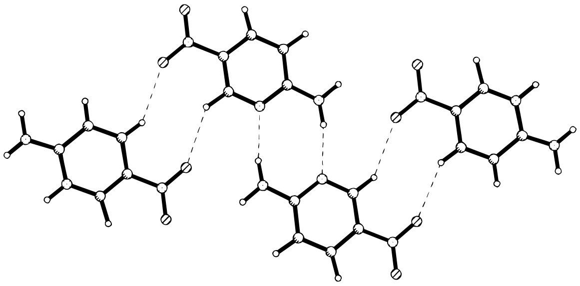


Figure 3. Tetrameric unit (held together by NH···N and CH···O hydrogen bonds) in **2**, containing two cations and two 2-amino-5-nitropyridine molecules.

(Table 7). The larger cavity acts as an attachment site for two cations but, in this case, the two cations approach the cavity from opposite sides (Figure 10), which consequently gives rise to an overall packing with alternating single cationic and anionic layers. Neighboring cations are arranged in an antiparallel fashion with their aromatic moieties face-to-face. The chlorine substituent does not seem to participate in any distinctive attractive intermolecular interactions, which was also the case in the structure of **4**.

Even though the syntheses of **1**−**6** took place in an aqueous environment, only one salt, potassium oxamate hydrate (**6**), incorporated a solvent molecule into its lattice as revealed by the X-ray single-crystal structure determination. Furthermore, this is the first example of a simple oxamate salt where the central dimeric unit (held together by two hydrogen bonds) utilizes the two amide oxygen atoms as acceptor sites. Again, similar to **4** and **5**, the central dimer forms the basis for a buckled, 2-D infinite layer (Figure 11) held together by two NH···O interactions (Table 8). The water molecule is positioned between layers and acts as a bridge *via* two OH···O hydrogen bonds (Figure 12). Each potassium ion is surrounded by seven oxygen atoms (*ca.* 2.74−2.84 Å), creating a distorted capped octahedral arrangement.

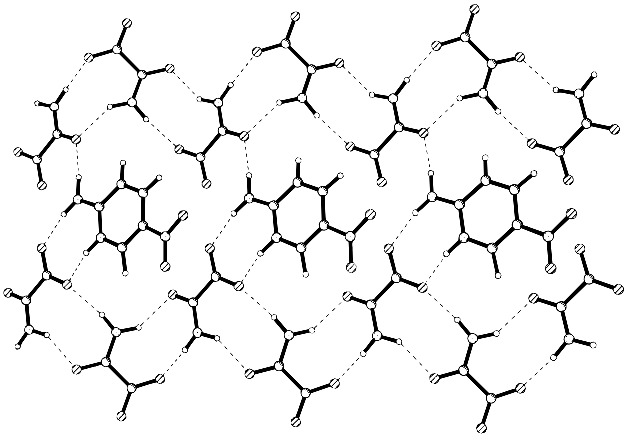


Figure 4. Packing in **2**, with neighboring anionic ribbons cross-linked by 2-amino-5-nitropyridinium cations.

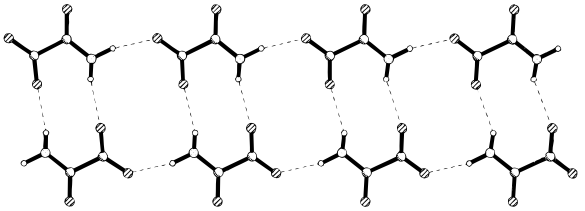


Figure 5. Ladder of anions, parallel with *a*, in **3**, generated by two unique NH···O hydrogen bonds.

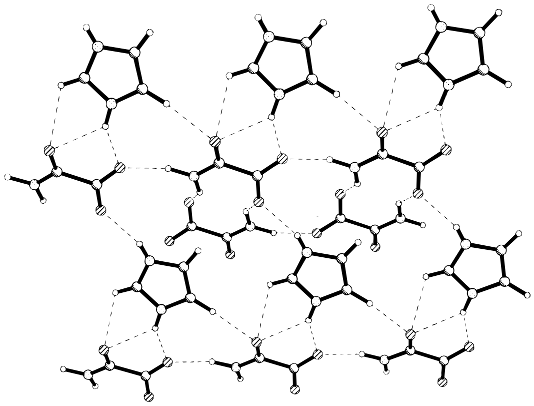


Figure 6. Cations in **3** provide cross-links between neighboring anionic ladders through bond NH···O and CH···O interactions.

An amide−amide dimeric unit is somewhat unexpected, but the presence of this motif may be due to the fact that the potassium ion is strongly coordinated to the carboxylate moiety, leaving only the amide oxygen as an acceptor site for hydrogen bonding between neighboring anions.[10]

Discussion

An examination of six crystal structures of simple salts of oxamic acid has demonstrated that the oxamate anion has a

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[10] Our thanks to one reviewer for drawing our attention to this.

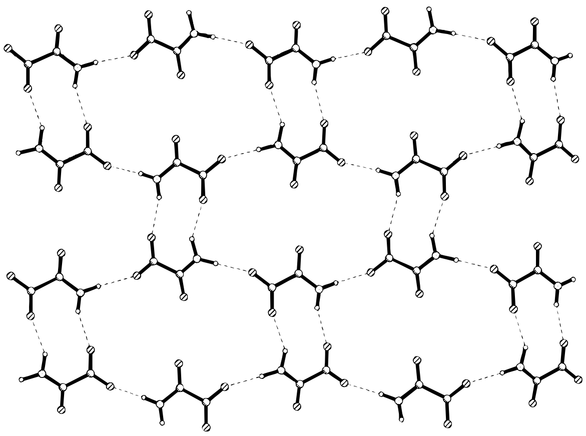

Figure 7. Infinite of anions, in the *b*−*c* plane, in **4**, held together by NH···O interactions.

Table 5. Geometry of the Hydrogen Bonds in **3**[a]

D−H···A	*r*(H···A)/Å	*r*(D···A)/Å	∠(D−H···A)/deg
N(1)−H(11)···O(21)′	1.902(6)	2.863(6)	165.76(17)
N(1)−H(12)···O(22)	2.386(6)	2.716(6)	103.13(13)
N(1)−H(12)···O(22)″	2.262(6)	2.957(6)	137.31(13)
N(3)−H(3)···O(22)‴	1.903(6)	2.729(5)	152.88(17)
N(6)−H(6)···O(1)⁗	2.302(6)	2.962(6)	124.58(13)
N(6)−H(6)···O(21)⁗	1.870(5)	2.705(5)	142.58(18)
C(5)−H(5)···O(1)⁗′	2.367(6)	3.299(6)	156.96(16)
C(7)−H(7)···O(1)⁗″	2.488(6)	3.058(6)	119.67(14)

[a] Symmetry code: (′) $x - 1, y, z$; (″) $-x + 1, -y + 1, -z$; (‴) $-x + 2, -y + 1, -z$; (⁗) $-x + 2, -y + 1, -z + 1$.

Table 6. Geometry of the hydrogen bonds in **4**[a]

D−H···A	*r*(H···A)/Å	*r*(D···A)/Å	∠(D−H···A)/deg
N(1A)−H(11A)···O(22B)′	2.061(4)	3.007(4)	173.43(10)
N(1A)−H(12A)···O(21A)	2.327(4)	2.692(4)	102.47(13)
N(1A)−H(12A)···O(21B)″	2.180(4)	3.030(4)	149.64(10)
N(1B)−H(11B)···O(22A)	1.930(4)	2.973(4)	171.20(11)
N(1B)−H(12B)···O(21B)	2.287(4)	2.668(4)	99.04(9)
N(1B)−H(12B)···O(21A)‴	2.083(3)	3.050(3)	150.08(10)
N(3A)−H(31A)···O(21A)	1.775(4)	2.758(4)	168.08(12)
N(3A)−H(32A)···O(1A)″	2.220(4)	2.892(4)	132.08(10)
N(3A)−H(32A)···O(22A)″	2.109(3)	2.868(4)	142.84(10)
N(3A)−H(33A)···O(1B)	1.955(4)	2.789(4)	174.61(10)
N(3B)−H(31B)···O(21B)	1.848(4)	2.774(4)	173.06(12)
N(3B)−H(32B)···O(1B)⁗	2.302(4)	2.887(4)	120.27(9)
N(3B)−H(32B)···O(22B)⁗	1.941(3)	2.836(3)	160.38(11)
N(3B)−H(33B)···O(1A)⁗′	1.934(4)	2.822(4)	156.04(12)

[a] Symmetry code: (′) $x, y - 1, z$; (″) $x, -y + {}^1/_2, z - {}^1/_2$; (‴) $x, -y + {}^1/_2, z + {}^1/_2$; (⁗) $x, -y + {}^3/_2, z + {}^1/_2$; (⁗′) $x, y + 1, z$.

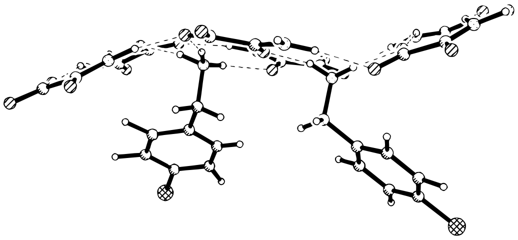

Figure 8. Positioning of cations with respect to the infinite buckled layer of anions in **4** (edge-on view). Cations are only attached to one side of the layer.

pronounced tendency to engage in infinite anionic structural assemblies, irrespective of the character of the cation. These networks are typically held together by two, or more, NH···O hydrogen bonds, and at the center of each motif is a dimeric anionic unit. The networks can be broadly classified into two groups, one-dimensional (ribbons or ladders) and two-dimensional (sheets) assemblies. In addition to the crystal structures discussed here, the structure of ammonium oxamate[9] also contains a 2-D anionic network with a connectivity identical to that found in the anionic motifs of **4** and **5**.

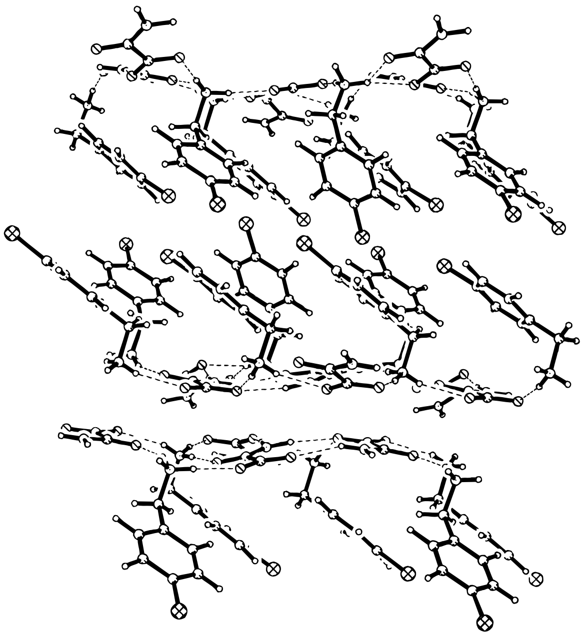

Figure 9. Alternating bilayers of anions and cations in the crystal structure of **4**.

Table 7. Geometry of the Hydrogen Bonds in **5**[a]

D−H···A	*r*(H···A)/Å	*r*(D···A)/Å	∠(D−H···A)/deg
N(1)−H(1A)···O(22)′	2.037(4)	2.916(4)	153.52(10)
N(1)−H(1B)···O(21)″	2.010(4)	2.939(4)	175.50(10)
N(17)−H(17A)···O(1)‴	1.818(3)	2.792(4)	163.43(11)
N(17)−H(17B)···O(22)⁗	1.840(3)	2.788(3)	166.04(11)
N(17)−H(17C)···O(21)⁗′	1.959(3)	2.844(3)	172.50(10)
N(1)−H(1A)···O(22)⁗	2.403(3)	2.694(4)	97.38(9)

[a] Symmetry code: (′) $3 - x, -y, -z + 1$; (″) $3 - x, -{}^1/_2 + y, 1{}^1/_2 - z$; (‴) $3 - x, {}^1/_2 + y, 1{}^1/_2 - z$; (⁗) x, y, z; (⁗′) $x, {}^1/_2 - y, -{}^1/_2 + z$.

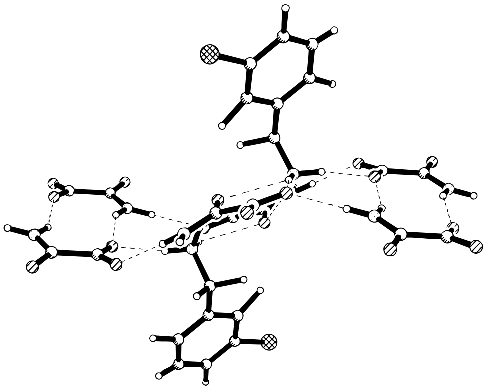

Figure 10. Positioning of cations with respect to the 2-D anionic layer (viewed edge-on). Cations are attached to both sides of the anionic layer in **5**.

Upon the basis of extant data, there is little doubt that the oxamate anion can be used as a building block of specific hydrogen-bonded architectures. However, is it possible to rationalize (and thus, to predict) which of the two main anionic motifs is going to form with any given cation? Furthermore, is there an obvious reason why a water molecule is incorporated into **6**, but not in any of the other compounds?

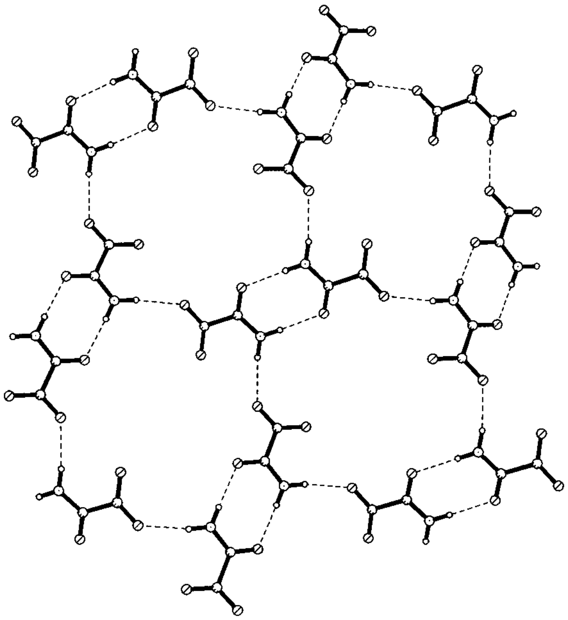

Figure 11. Infinite anionic layer in **6**, with a central amide−amide (Type III) dimeric motif.

Table 8. Geometry of the Hydrogen Bonds in **6**[a]

D−H···A	r(H···A)/Å	r(D···A)/Å	∠(D−H···A)/deg
N(1)−H(1A)···O(21)′	2.081(2)	3.001(2)	167.42(7)
N(1)−H(1B)···O(1)″	2.065(2)	2.930(2)	171.64(7)
O(1W)−H(1W)···O(22)‴	1.864(2)	2.734(2)	153.11(7)
O(1W)−H(2W)···O(1)⁗	2.022(2)	2.809(2)	146.02(7)
N(1)−H(1A)···O(22)‴	2.409(2)	2.693(2)	97.31(6)

[a] Symmetry code: (′) x, $1^1/_2 - y$, $z - {}^1/_2$; (″) $2 - x$, $2 - y$, $2 - z$; (‴) x, y, z; (⁗) $1 - x$, $-{}^1/_2 + y$, $2^1/_2 - z$.

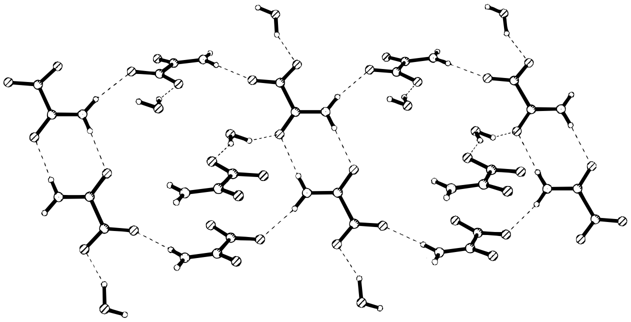

Figure 12. Bridging water molecules between neighboring anionic layers in **6**. Some ions removed for clarity and the four "isolated" anions belong to the layer above.

In order to elucidate, or rationalize, why a certain cation induces the formation of a specific anionic motif, we need to be able to identify some common features within groups of cations, *i.e.* 1-D motifs in **1**−**3** and 2-D motifs in **4**−**6** (as well as in ammonium oxamate). At this stage, it would seem as if primary ammonium cations, with three hydrogen-bond donors attached to the same point, are capable of bringing three adjacent anions close enough together (*via* NH···O interactions), which enables them to form the infinite layer. This behavior is observed with the (4-chlorobenzyl)ammonium, (3-chlorobenzyl)-ammonium, and ammonium[9] cations. In contrast, secondary or tertiary amines (present in **1**−**3**) are only able to, at best, form a bridge between two anions which seems to be insufficient to bring about the formation of the infinite 2-D sheet. In those cases, the anions arrange themselves in 1-D motifs (as in **1**−**3**). Another factor that may be of importance is the size of the cation. Obviously, a very large cation is likely to increase the spacing between anionic regions which may inhibit sheet formation. In contrast, if the cation is rather small, *e.g.* the potassium ion, the anions will be closer together which, in turn, will facilitate the formation of an infinite anionic layer (as in the crystal structure of **6**).

Other factors like shape and hydrogen-bond donor/acceptor ratio can clearly be equally (or more) important for the outcome of the aggregation in three dimensions, but until more structural data becomes available, it is impossible to make guaranteed predictions.

The presence of water in **6** may be explained in terms of the hydrogen-bond donor/acceptor ratio. A crystal structure of potassium oxamate would have a surplus of hydrogen-bond acceptors (three acceptor atoms, two donor atoms), which is in contrast to all the compounds **1**−**5** (as well as ammonium oxamate[9]) which carry a surplus of hydrogen-bond donors. One way in which potassium oxamate could achieve a more desirable ratio would be to include a water molecule (potassium oxamate monohydrate is well balanced with four acceptor atoms and four donor atoms). This, in combination with the fact that the small metal ion is very capable of coordinating water molecules, is the likely explanation for the appearance of one solvent molecule in **6**.

Given our current appreciation of the strength and selectivity of the hydrogen bond, it is not surprising that the oxamate ion so readily forms infinite hydrogen-bonded architectures as demonstrated in **1**−**6**. However, there is some variation in the type of motifs that are being formed, especially in comparison with the more predictable structural assemblies formed by hydrogen malate and hydrogen tartrate ions. This diversity is probably related to the fact that the oxamate ion has the ability to form three different dimeric aggregates (I, II, and III), all of which have considerable stability. It is interesting to note that all three dimers were present in the series of materials presented here: type I in **3**−**5**, type II in **1**−**2**, and type III in **6**. This observation would also suggest that there is, energetically, little to choose between the three possible dimeric assemblies. Our preliminary geometry optimizations at the 3-21G* level of these three dimers also support this notion with calculated energies of −707.905 28, −707.912 98, −707.921 81 hartree, for Types I, II, and III, respectively. The relatively small inherent energy differences between the three dimers indicate that it may be quite easy to influence the final structure with the aid of external hydrogen-bond interactions. Consequently, this system may allow us to probe the relative donor/acceptor ability of the hydrogen-bond sites of the anion. Comparatively subtle changes to the cation may encourage, or control, the formation of one dimeric type relative to the other two which may provide us with additional information regarding the selectivity and directionality among competitive hydrogen-bond sites.

Summary

This study has established that the oxamate anions have a proclivity to generate extended, low-dimensional motifs, held together by two, or more, NH···O hydrogen bonds. These motifs also appear irrespective of the characteristics of the cation, although the precise topology of the anionic scaffolding is determined by the nature of the cation. The fact that these anionic assemblies display limited, but significant, diversity can be an advantage, since it will allow us to incorporate either 1-D or 2-D infinite networks (depending upon the choice of cation) which, in turn, will affect structural rigidity and overall anisotropy (1-D *vs* 2-D) of a given material. The oxamate anion, apart from acting as a synthetic/structural building block, may also be useful as a testbed for theoretical investigations which aim to explore the energetic balance between the three dimeric structures observed in this series of compounds.

Experimental Section

Piperidinium Oxamate (1). A solution of oxamic acid (0.50 g, 5.6 mmol) in methanol was added to piperidine (0.55 g, 5.6 mmol). The mixture was heated until approximately one-half the solvent had evaporated and was then left at ambient temperature. After a few days, a white crystalline solid appeared. The product was filtered off and recrystallized from water to produce colorless crystals, mp 173−174 °C. Calcd for $C_7H_{14}N_2O_6$: C, 48.26; H, 8.10; N, 16.08%. Found: C, 48.3; H, 8.4; N, 16.2%.

2-Amino-5-nitropyridine 2-Amino-5-nitropyridinium Oxamate (2). 2-Amino-5-nitropyridine (0.78 g, 5.6 mmol) was added to a methanolic solution of oxamic acid (0.50 g, 5.6 mmol). The mixture was heated until approximately one-half the solvent had evaporated and was then left at ambient temperature. After a few days, a yellow crystalline solid appeared. The product was filtered off and recrystallized from water to produce yellow needle-like crystals, mp 192−193 °C. Calcd for $C_{12}H_{13}N_7O_7$: C, 39.24; H, 3.57; N, 26.10%. Found: C, 37.8; H, 3.5; N, 25.4%.

Imidazolium Oxamate (3). Imidazole (0.38 g, 5.6 mmol) was added to an aqueous solution of oxamic acid (0.50 g, 5.6 mmol). The mixture was heated until approximately one-half the solvent had evaporated and was then left at ambient temperature. After a few days, a white solid appeared. The product was filtered off and recrystallized from water to produce colorless, transparent, rodlike crystals, mp 150−151 °C. Calcd for $C_5H_7N_3O_3$: C, 38.21; H, 4.50; N, 26.75%. Found: C, 38.9; H, 4.2; N, 25.4%.

(4-Chlorobenzyl)ammonium Oxamate (4). A solution of oxamic acid (0.50 g, 5.6 mmol) in methanol was added to 4-chlorobenzylamine (0.5 g, 5.6 mmol). The mixture was heated until approximately one-half the solvent had evaporated and was then left at ambient temperature. After a few days, a white crystalline solid appeared. The product was filtered off and recrystallized from water to produce colorless grainlike crystals, mp 210−211 °C. Calcd for $C_9H_{11}ClN_2O_3$: C, 46.87; H, 4.82; N, 12.15%. Found: C, 46.6; H, 4.9; N, 11.9%.

(3-Chlorobenzyl)ammonium Oxamate (5). A methanolic solution of oxamic acid (0.50 g, 5.6 mmol) was added to 3-chlorobenzylamine (0.68 cm^{-3}, 5.6 mmol). The mixture was left at ambient temperature until approximately one-half the solvent had evaporated. This resulted in the precipitation of a white crystalline solid. The product was filtered off and recrystallized from methanol to produce colorless, transparent, diamond-shaped crystals, mp 203−204 °C. Calcd for $C_9H_{11}N_2O_3$: C, 46.87; H, 4.82; N, 12.15%. Found: C, 45.5; H, 5.0; N, 11.3%.

Potassium Oxamate Monohydrate (6). An aqueous solution of oxamic acid (0.5 g, 5.6 mmol) was added to an aqueous solution of $KHCO_3$ (0.56 g, 5.6 mmol). Slight effervescence was observed, and the mixture was then gently heated until one-half the solvent had evaporated. The mixture was then left at ambient temperature. After a few days, a white crystalline solid appeared. The product was filtered off and recrystallized from water to produce colourless, rod-shaped crystals, mp 273−274 °C. Calcd for $C_2H_4KNO_4$: C, 16.53; H, 2.78; N, 9.65%. Found: C, 17.4; H, 2.1; N, 9.7%.

X-ray Crystallography. Crystal data were collected using a Siemens P4 four-circle diffractometer with graphite monochromated Mo Kα radiation. Crystal stabilities were monitored by measuring standard reflections every 100 reflections, and there were no significant variations ($<\pm 1\%$). Cell parameters were obtained from 35 accurately centered reflections in the 2θ range 10°−28°. $\acute{\omega}$ scans were employed for data collection, and Lorentz and polarization corrections were applied.

The structures were solved by direct methods, and the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were located from difference Fourier maps and a riding model with fixed thermal parameters ($u_{ij} = 1.2U_{ij}(\mathrm{eq})$) for the atom to which they are bonded) was used for subsequent refinements. The function minimized was $\sum[\omega(|F_o|^2 - |F_c|^2)]$ with reflection weights $\omega^{-1} = [\sigma^2||F_o|^2 + (g_1P)^2 + (g_2P)]$, where $P = [\max |F_o|^2 + 2|F_c|^2]/3$. The SHELXTL PC and SHELXL-93 packages were used for data reduction and structure solution and refinement.[11]

Acknowledgment. We would like to thank NIDevR for a research studentship (D.P.H.).

Supporting Information Available: Crystallographic details for **1**−**6**, including descriptions of structure determinations, tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles and anisotropic thermal parameters (42 pages). See any current masthead page for ordering and Internet access instructions.

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[11] Sheldrick, G. M. SHELXL-93, University of Göttingen.