Water Superstructures within Organic Arrays; Hydrogen-Bonded Water Sheets, Chains and Clusters

Neil S. Oxtoby, Alexander J. Blake, Neil R. Champness,* and Claire Wilson[a]

Abstract: A strategy for encouraging the formation of extended water arrays is presented, in which molecules that contain a 1,4-dihydroquinoxaline-2,3-dione core are used as supramolecular hosts for the accommodation of guest water molecules and arrays. These molecules were selected as they contain a hydrophilic oxalamide-based "terminus" that allows water molecules to hydrogen-bond to the host organic molecules as well as to each other. The host molecules also contain a hydrophobic "end" based upon an aromatic ring, which serves to encourage the formation of discrete water clusters in preference to three-dimensional networks, as the water molecules cannot form strong hydrogen bonds with this part of the molecule. A systematic study of several hydrated structures of four organic molecules based on 1,4-dihydroquinoxaline-2,3-dione (qd) is discussed. The organic molecules, qd, 6-methyl-1,4-dihydroquinoxaline-2,3-dione (mqd), 6,7-dimethyl-1,4-dihydroquinoxaline-2,3-dione (dmqd) and 1,4-dihydrobenzo[*g*]quinoxaline-2,3-dione (Phqd), act as supramolecular crystal hosts for the clusters of water, with zero-, one- and two-dimensional arrays of water being observed. The hydrogen bonding in the structures, both within the water clusters and between the clusters and organic molecules, is examined. In particular, the structure of dmqd·6H_2O contains a two-dimensional water sheet composed of pentagonal and octagonal units. Phqd·3H_2O forms a hydrophilic extended structure encouraging the formation of one-dimensional chains consisting entirely of water. Both qd·2H_2O and dmqd·2H_2O can be considered to form one-dimensional chains, but only by utilising bridging carbonyl groups of the oxalamide moieties to form the extended array; if only the water is considered, zero-dimensional water tetramers are observed. The remaining hydrated structures, [Na^+ dmqd$^-$]dmqd·H_2O, dmqd·$^1/_3H_2O$ and mqd·$^1/_2H_2O$, all contain discrete water molecules but do not form extended water structures.

Keywords: clathrates · crystal engineering · crystal structures · host–guest systems · water

Introduction

Water clusters and networks are often found in the crystal structures of molecules, ranging from clathrate hydrates to biological macromolecules.[1] Although clathrate hydrates were discovered nearly 200 years ago by Davy and Faraday,[2,3] the study of extended water structures in the solid state is perhaps more topical than ever. One particularly successful way of investigating hydrogen-bonded clusters and networks of water is by studying hydrated crystal structures of small molecules, and there have been several recent reports of clusters, sheets and chains of water molecules contained within crystal structures of "small" molecules.[1,4–15] Three-dimensional networks of water clathrates have been particularly well studied over many years,[2,16] and now smaller clusters of lower dimensionality are receiving significantly more attention[1,4–15] owing to their relevance to biological structures and processes. Indeed, it has been found that water has a very important role in determining the three-dimensional structure of biological macromolecules.[17]

A survey of water clusters in the crystal structures of organic molecular arrays has recently been published,[18] classifying the structures based upon the pattern of the water molecules. Of the 1424 structures surveyed, most contained discrete acyclic chains of water molecules (61.1 % of the total structures) with extended acyclic structures being the next most common pattern (19.9 % of the total structures). Of the structures involving cyclic water clusters, those with four water molecules were the most common. Of all the

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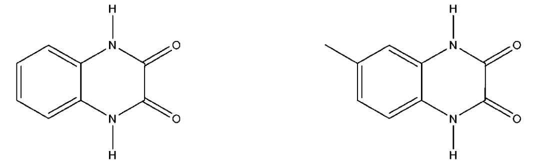
structures there were very few examples of two- or three-dimensional water aggregation (<4% of the total structures).

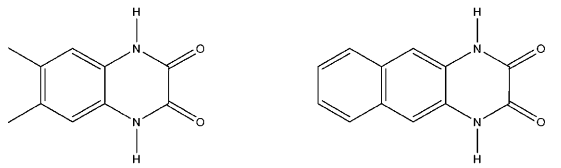
The key to understanding interactions between water molecules is to understand the precise structural arrangement of hydrogen-bonded arrays of water molecules.[13] Water clusters and networks are seen as the perfect way of investigating and characterising the structural changes and intermolecular interactions on moving from isolated molecules to the bulk state.[3] Attempts to model the behaviour of water often involve the use of clusters, whose structures are either found experimentally or theoretically.[19]

However, no systematic study has been undertaken of water clusters formed within organic host crystals formed from a series of closely related organic molecules. Therefore, we designed a series of organic molecules to act as crystal hosts based upon the 1,4-dihydroquinoxaline-2,3-dione (qd) core (Scheme 1), which incorporates several design features. Firstly, all of the molecules contain a hydrophilic oxalamide-based "terminus", which serves both to increase the water solubility of the organic molecules and allows water molecules to hydrogen-bond to the organic molecules as well as to each other. Secondly, the molecules all contain a hydrophobic "end" based upon an aromatic ring, which serves to encourage the formation of discrete water clusters in preference to three-dimensional water networks, as the water molecules cannot form strong hydrogen bonds with this part of the molecule. In addition, the planar aromatic rings will encourage the formation of single crystals by forming stacks of organic molecules through π–π interactions. Derivatives of such dihydroquinoxalinedione molecules are known to act in a variety of biological roles.[20]



1,4-Dihydroquinoxaline-2,3-dione (qd)

6-Methyl-1,4-dihydroquinoxaline-2,3-dione (mqd)

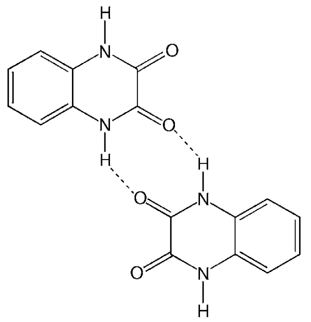


6,7-Dimethyl-1,4-dihydroquinoxaline-2,3-dione (dmqd)

1,4-Dihydrobenzo[*g*]quinoxaline-2,3-dione (Phqd)

Scheme 1. The structures of the four molecules, based upon 1,4-dihydroquinoxaline-2,3-dione, designed to interact with water to form clusters and networks of water molecules.

Finally, the number of hydrogen-bond donors and acceptors is not equal in the molecules, as there are two N–H donor groups capable of acting as donors in two hydrogen bonds and two C=O acceptor groups capable of accepting a total of four hydrogen bonds (Scheme 2). This lack of parity of donors and acceptors has been shown to encourage the inclusion of water in crystal structures.[21] In a recent survey of 311 structures of hydrated small organic molecules, it was found that most of the structures (77%) contained water molecules that donated more hydrogen bonds than they accepted;[22] hence, an acceptor excess in the organic molecules used in this study may thus be "compensated" by water molecules.



Scheme 2. The commonly observed $R_2^2(8)$ inter-dihydroquinoxalinedione hydrogen-bonding arrangement.

The family of compounds described below shows the successful application of our strategy, which includes rare examples of water sheets, chains and clusters.

Results and Discussion

Four molecules, 1,4-dihydroquinoxaline-2,3-dione (qd), 6-methyl-1,4-dihydroquinoxaline-2,3-dione (mqd), 6,7-dimethyl-1,4-dihydroquinoxaline-2,3-dione (dmqd) and 1,4-dihydrobenzo[*g*]quinoxaline-2,3-dione (Phqd), were used in this study to create the organic arrays, or matrices, which act as hosts for the water-based superstructures (Scheme 1). As discussed above, the molecules were specifically designed to offer both hydrophilic and hydrophobic parts to allow the utilisation of both hydrogen-bonding and π–π interactions in the generation of an extended organic array that could act as a host for water molecules. The mismatch between the number of strong hydrogen-bond donors and acceptors in each molecule provides a useful supramolecular tool for the inclusion of guest water molecules. All of the molecules were synthesised in an analogous manner from the appropriate diamine, such as *o*-phenylenediamine, and refluxed with oxalic acid in 4 M HCl. The products were obtained as precipitates from the cooled reaction mixtures.

Single crystals of the hydrate crystals were obtained by three different crystallisation methods. Attempts were made to obtain single crystals suitable for X-ray diffraction for each of the four compounds from water, water containing Na_2CO_3 and a 1:1 solution of DMF and water. It is unclear as to the precise effect of Na_2CO_3 in the crystallisation process, although the formation of $[Na^+dmqd^-]dmqd \cdot H_2O$ in one instance indicates that the pH alteration of the solution may affect the crystallisation. However, no other examples of deprotonated sodium salts were observed for the other species studied and the effect on crystallisation under the Na_2CO_3/water conditions may be due to other subtle nucleation effects. In some instances, no single crystals were obtained for a given compound under one, or more, of the crystallisation conditions.

Structural studies: The numbering schemes used for the dihydroquinoxalinedione species are shown with representative examples in Figure 1. All of the structures reveal that qd and its analogues are involved in π–π stacking interactions and intermolecular hydrogen-bonding interactions. In those cases in which hydrates are observed, the oxalamide moieties are involved in hydrogen-bonding interactions with the included water molecules, which are in some instances part of a much larger hydrogen-bonded water array. In summary, the π–π interactions between individual aromatic molecules serve to form extended stacks, and reliably form an extended scaffold in which the oxalamide moieties are oriented perpendicular to the direction of the stack so that they may participate in hydrogen-bonding interactions. The details of the π–π interactions are given in Table 1.

In all cases, the dihydroquinoxalinedione species are also involved in homomolecular hydrogen-bonding interactions. Most commonly, the inter-dihydroquinoxalinedione interactions involve the formation of intermolecular N–H···O hydrogen bonds, forming $R_2^2(8)$ rings (Scheme 2). The only exceptions to the formation of the $R_2^2(8)$ rings are $[Na^+dmqd^-]dmqd{\cdot}H_2O$, in which the carbonyl moieties of the dmqd molecules participate in coordinative bonds with the Na^+ cations, and $dmqd{\cdot}6\,H_2O$. The hydrogen-bonding parameters are summarised in Tables 3–7, using the numbering scheme shown in Figure 1, accompanied by a more detailed description of the extended hydrogen-bonded structure formed by these hydrogen-bonding interactions.

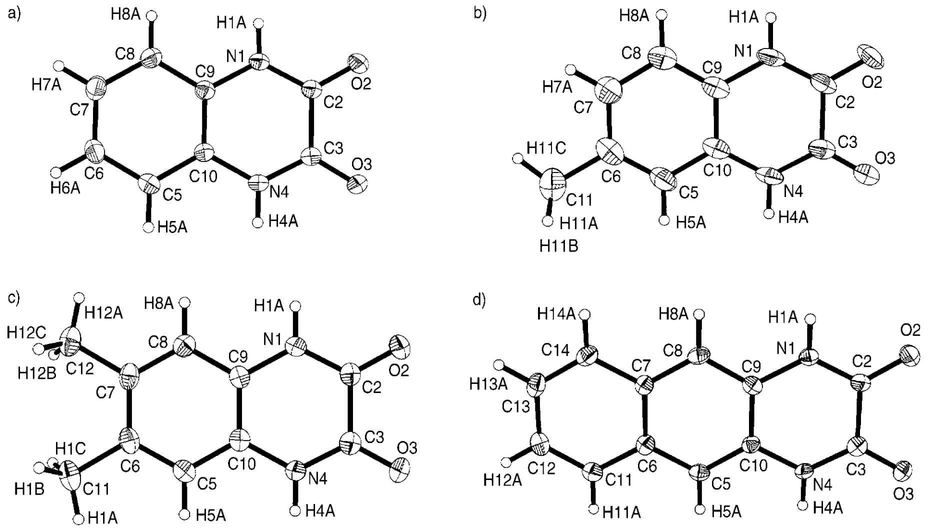


Figure 1. Atomic displacement ellipsoid plots (50% probability level) of a) 1,4-dihydroquinoxaline-2,3-dione (qd), b) 6-methyl-1,4-dihydroquinoxaline-2,3-dione (mqd) in $mqd{\cdot}{}^1\!/_2H_2O$, c) 6,7-dimethyl-1,4-dihydroquinoxaline-2,3-dione (dmqd) and d) 1,4-dihydrobenzo[*g*]quinoxaline-2,3-dione (Phqd).

Structures of qd hydrates: From the three crystallisation condi-

Table 1. The π–π interactions in novel structures.

Compound	π–π Stacked motif/description	Centroid···centroid separations [Å]	Plane···plane separations [Å]	Offset angles [°]
$qd{\cdot}2\,H_2O$	Infinite arrays containing two different alternating π–π interactions; head-to-tail molecular orientation.	3.583 3.468	3.329 3.392	21.7 12.0
$mqd{\cdot}{}^1\!/_2H_2O$	Aromatic interactions between symmetry related, coplanar mqd molecules generating infinite stacks; head-to-head molecular orientation.	3.44 3.55	3.30 3.25	16.4 23.7
$dmqd{\cdot}6\,H_2O$	Stacks of dmqd molecules consisting of two distinct aromatic interactions, both between coplanar dmqd molecules related by an inversion centre; head-to-tail molecular orientation.	3.393 3.450	3.33 3.27	11.1 18.6
$dmqd{\cdot}{}^1\!/_3H_2O$	Two dmqd tetramers form aromatic interactions with each other, with one pair of dmqd molecules forming two long interactions; head-to-head molecular orientation. Edge-to-face aromatic interactions are also observed.	3.8701 2.746[a]	3.9081 3.664[b]	2.50 15.05[c]
$[Na^+dmqd^-]dmqd{\cdot}H_2O$	Pairs of chains form a strong aromatic interaction between two coplanar $dmqd^-$ molecules; head-to-tail molecular orientation.	3.35 3.573	3.653	23.5 20.3
dmqd	Pair of dmqd molecules from aromatic interactions related by an inversion centre.	3.47	3.36	14.5
$Phqd{\cdot}3\,H_2O$	Infinite arrays containing two different alternating π–π interactions parallel to the crystallographic *a* axis: the stacks are orthogonal to the chains of water molecules and held together by $R_2^2(8)$ hydrogen-bonding interactions; head-to-tail molecular orientation.	3.503[d] 3.673[d]	3.26[d] 3.37[d]	21.4[d] 23.4[d]

[a] C–H···centroid. [b] C···centroid. [c] C–H-centroid angle. [d] Average for three aromatic rings of the Phqd molecule.

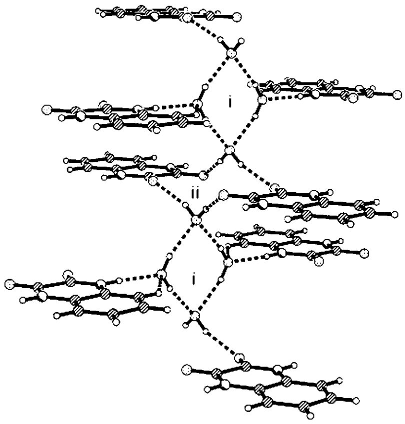


Figure 2. The hydrogen bonding (---) of the $R_4^2(8)$ water tetramers (i) into one-dimensional chains by hydrogen bonding to qd molecules ($R_4^4(14)$ rings, ii) in the crystal structure of qd•2 H_2O. (Nitrogen atoms: large open circles, oxygen: dotted, carbon: hashed, hydrogen atoms: small open circles).

Table 2. The hydrogen-bond parameters for qd•2 H_2O and mqd•$^1/_2H_2O$.[a]

	D–H···A [Å]	D–H···A [°]	D···A [Å]
qd•2 H_2O			
O2W–H2WB···O2	1.87(2)	164(2)	2.7195(13)
N1–H1A···O1W	1.87	168	2.7372(13)
O1W–H1WA···O2W$^{\text{i}}$	1.95(2)	170(2)	2.7502(14)
O2W–H2WA···O3$^{\text{ii}}$	1.98(2)	162(2)	2.7796(13)
O1W–H1WB···O2W$^{\text{iii}}$	1.99(2)	167(2)	2.7906(13)
N4–H4A···O3$^{\text{iv}}$	2.00	171	2.8723(13)
C7–H7A···O1W$^{\text{v}}$	2.61	172	3.5579(16)
C8–H8A···O1W	2.65	130	3.3468(16)
C6–H6C···O1W$^{\text{vi}}$	2.72	159	3.6242(16)
mqd•$^1/_2H_2O$			
N4A–H4AA···O1W$^{\text{vii}}$	1.87	172.5	2.748(4)
O1W–H1WA···O2$^{\text{viii}}$	1.91(4)	172(5)	2.761(4)
N4–H4A···O3$^{\text{ix}}$	1.93	169	2.794(4)
N1A–H1AA···O2A$^{\text{x}}$	1.96	172	2.830(4)
N1–H1A···O3A$^{\text{x}}$	1.97	168	2.839(4)
O1W–H1WB···O3A$^{\text{x}}$	2.02(4)	163(5)	2.809(4)
C5A–H5AA···O$^{\text{xi}}$	2.47	166	3.396(5)
C11A–H11F···O2$^{\text{vi}}$	2.62	177	3.600(6)

[a] Symmetry codes: i: $(x, y+1, z)$; ii: $(-x+1, -y, -z+1)$; iii: $(-x, -y+1, -z+1)$; iv: $(-x+1, -y, -z+2)$; v: $(-x, -y+2, -z+2)$; vi: $(x, y, z+1)$; vii: $(x-1, y-1, z)$; viii: $(x+1, y, z)$; ix: $(-x, -y+2, -z)$; x: $(-x, -y+1, -z+1)$; xi: $(x, y-1, z)$.

tions used in this study, (water, water/Na_2CO_3 and DMF/water 1:1), crystals of qd•2 H_2O were obtained from both pure water and aqueous Na_2CO_3 solutions; crystals of non-hydrated qd were grown from DMF/water (1:1 solution) and also from water. In the latter case, crystals of qd were grown simultaneously with qd•2 H_2O.

Hydrate qd•2 H_2O: Only one hydrate of qd was prepared during our investigations, namely qd•2 H_2O, the crystals of which were grown from an aqueous Na_2CO_3 solution. The structure of qd•2 H_2O shows the qd molecules involved in π–π stacking interactions, inter-qd hydrogen-bonding and water–qd hydrogen-bonding interactions, thus confirming the success of the design strategy employed in targeting hydrates of qd and its analogues. Each qd molecule adopts intermolecular (inter-qd) N–H···O hydrogen bonds forming $R_2^2(8)$ rings, with two qd molecules forming the hydrogen-bonded dimer that is related by an inversion centre; this allows the formation of cavities between qd stacks, which accommodate water tetramers (see Table 2 for hydrogen-bonding parameters).

The discrete water tetramers are formed by inter-water hydrogen bonding to form a $R_4^2(8)$ ring (Figure 2i). One of the water molecules, O1W, is further involved in forming N–H···O and C–H···O hydrogen bonds with qd molecules, which have a $R_2^1(6)$ hydrogen-bonding arrangement. The other water molecule, O2W, forms two O–H···O hydrogen bonds with qd molecules, in turn forming further hydrogen-bonding rings, with a $R_4^4(14)$ hydrogen-bonding arrangement (Figure 2ii), linking the water tetramers into extended hydrogen-bonded chains by "bridging" qd molecules.

Crystal qd: The nonhydrated structure of qd has been reported previously,[23] and during the course of this work crystals with the same unit cell were obtained from the recrystallisation of qd in a 1:1 solution of DMF/H_2O and also from pure H_2O. This structure reveals that the qd molecules participate in both π–π stacking interactions and intermolecular N–H···O hydrogen bonding. Although all N–H hydrogen-bond donors are utilised in generating the extended structure, the carbonyl acceptors of qd remain capable of accepting further hydrogen bonds, due to the incompatibility between the number of donors and acceptors offered by the oxalamide moieties. In the absence of water molecules, two longer C–H···O hydrogen bonds are formed per qd molecule. It is perhaps surprising that no water is included in the structure when the crystals are grown from pure H_2O or DMF/H_2O (1:1), but this illustrates the influence of Na_2CO_3 on the formation of dihydroquinoxalinedione hydrates.

Structure of an mqd hydrate: Unlike qd, crystals suitable for single-crystal X-ray diffraction studies were only grown from DMF/H_2O (1:1), those of mqd•$^1/_2H_2O$, despite attempts at crystal growth under all three crystallisation conditions. The use of alternative crystallisation solvents, aqueous Na_2CO_3 or pure water, resulted in the formation of microcrystalline material.

Hydrate mqd•$^1/_2H_2O$: As with qd, only a single hydrate of mqd was found, namely mqd•$^1/_2H_2O$, the crystal structure of which comprises two crystallographically independent mqd molecules, with very similar bond lengths and angles, and one water molecule. Three O–H···O hydrogen bonds between the water and mqd molecules are observed, in addition to five N–H···O and C–H···O hydrogen bonds between the mqd molecules (Table 2).

The water molecules involved in the three hydrogen bonds act twice as a donor and once as an acceptor. As no hydrogen bonds are formed solely between water molecules, no extended water structure is observed. However, the water molecule and the two crystallographically independent mqd molecules form chains of hydrogen bonds with a $C_3^3(8)$ hydrogen-bonding arrangement (Figure 3i). They also form hydrogen-bonding rings which have an $R_3^2(8)$ hydrogen-bonding arrangement (Figure 3iii). The water molecules form what can be considered "expanded dimers" of symmetry related mqd molecules (Figure 3ii): In these rings two water molecules sit between the two mqd molecules, expanding the dimer and creating a $R_4^4(12)$ hydrogen-bonding arrangement.

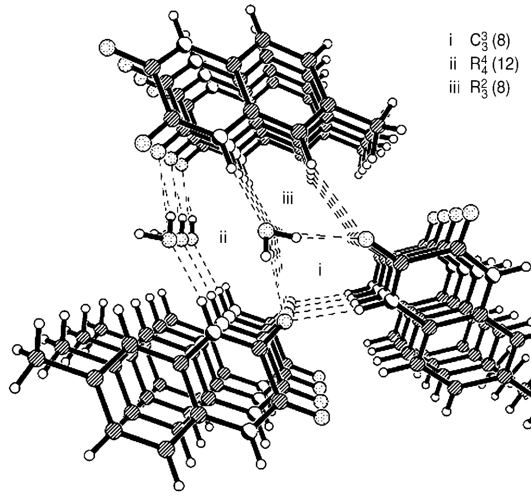


Figure 3. The rings and chains of hydrogen bonds formed by water and mqd molecules in mqd·$^{1}/_{2}H_2O$, viewed approximately along the crystallographic *a* axis. (Nitrogen atoms: large open circles, oxygen: dotted, carbon: hashed, hydrogen atoms: small open circles).

Structures of dmqd hydrates: Dmqd forms the most extensive series of hydrate structures, the particular product being highly dependent upon crystallisation conditions. Three hydrates have been identified, namely dmqd·6H_2O, dmqd·2H_2O[33] and dmqd·$^{1}/_{3}H_2O$, in addition to a Na salt of dmqd, [Na^+dmqd$^-$]dmqd·H_2O, which forms an extended coordination polymer structure. Crystals of dmqd·6H_2O and [Na^+dmqd$^-$]dmqd·H_2O were grown from aqueous Na_2CO_3 solutions but from different reaction attempts. Crystallisation attempts from DMF/H_2O (1:1) gave crystals of two distinct morphologies from each crystallisation attempt: needles of dmqd·$^{1}/_{3}H_2O$ and hexagonal blocks of dmqd.

Hydrate dmqd·6H_2O: Crystals of dmqd·6H_2O were grown from an aqueous Na_2CO_3 solution, which had been heated to boiling, followed by cooling to room temperature. The crystal structure of dmqd·6H_2O has been determined at both 90 and 150 K to obtain a more precise location of hydrogen-bonding interactions. However, no significant difference between the two structures was observed and, unless otherwise stated, all bond lengths and angles relate to the 150 K structure for consistency of comparison.

The structure of dmqd·6H_2O, composed of one crystallographically unique dmqd molecule and six crystallographically distinct water molecules, is quite different from the others discussed in this study in that two-dimensional sheets composed entirely of water molecules are observed sandwiched between stacks of dmqd molecules. The hydrogen-bond parameters for dmqd hexahydrate are shown in Table 3. Five of the six water molecules form at least four hydrogen bonds, the remaining water molecule (O4W) forms only three hydrogen bonds, accepting only one hydrogen bond. The water molecules form sheets, which further hydrogen-bond to stacks of dmqd molecules by O1W, O2W, O5W and O6W. The sheets of water molecules are composed of pentagons and octagons (Figure 4). There are two crystallographically distinct pentagons and a single octagon, with the chains of pentagons running along the *a* axis.

One type of pentagon, formed by O1W to O5W (Figure 5 top left), has a $R_5^5(10)$ arrangement with homodromic hydrogen bonding. The other crystallographically distinct pentagon is formed by O2W to O6W (Figure 5 top right); this has a $R_5^3(10)$ arrangement with heterodromic hydrogen bonding. The octamers are formed from six crystallographically distinct water molecules and have a $R_8^6(16)$ arrangement with hetetrodromic hydrogen bonding (Figure 5 bottom). If a C=O group of a dmqd molecule is considered, the octamer can be thought of as being composed of a pentamer and a hep-

Table 3. The hydrogen-bond parameters for dmqd·6H_2O.[a]

	D-H···A [Å]		D-H···A [°]		D···A [Å]	
	150 K	90 K	150 K	90 K	150 K	90 K
O5W−H5WB···O4W	1.867(10)	1.879(9)	177(3)	177.4(16)	2.721(3)	2.7245(15)
O1W−H1WA···O3W^{i}	1.901(10)	1.895(9)	175(2)	174.8(17)	2.738(3)	2.7298(14)
O3W−H3WB···O2W	1.931(10)	1.935(9)	169(3)	166.4(17)	2.759(3)	2.7483(15)
O3W−H3WA···O6W^{ii}	1.904(10)	1.926(9)	175(3)	173.5(18)	2.747(2)	2.7508(14)
O2W−H2WA···O3	1.923(10)	1.929(9)	177(3)	177.2(18)	2.775(2)	2.7682(13)
O2W−H2WB···O1W	1.945(10)	1.940(9)	169(2)	171.3(17)	2.779(2)	2.7769(14)
N1−H1A···O5W^{iii}	1.95	1.94	170.1	171.2	2.824(2)	2.8177(14)
O1W−H1WB···O5W	1.957(10)	1.942(9)	171(2)	173.3(15)	2.787(3)	2.7766(14)
O6W−H6WB···O2	1.990(11)	1.949(9)	168(3)	171.5(16)	2.792(2)	2.7829(13)
O5W−H5WA···O2W^{iv}	1.949(13)	1.947(10)	164(3)	164.5(17)	2.768(2)	2.7635(14)
O4W−H4WB···O3W	2.021(13)	1.974(9)	156(3)	160.4(17)	2.798(3)	2.7829(16)
O4W−H4WA···O6W^{v}	1.999(14)	2.005(10)	158(3)	160.4(18)	2.799(3)	2.8046(15)
N4−H4A···O1W^{vi}	2.00	2.01	158.5	157.3	2.840(2)	2.8389(14)
O6W−H6WA···O2^{vii}	2.214(18)	2.120(12)	143(2)	152.6(15)	2.908(2)	2.8864(13)
O6W−H6WA···O3^{v}	2.297(15)	2.359(12)	143(2)	133.1(14)	2.991(2)	2.9921(14)

[a] Symmetry codes: i ($x+{}^{1}/_{2}, -y+{}^{1}/_{2}, z+{}^{1}/_{2}$); ii ($-x+{}^{3}/_{2}, y+{}^{1}/_{2}, -z+{}^{3}/_{2}$); iii ($-x+{}^{5}/_{2}, y+{}^{1}/_{2}, -z+{}^{3}/_{2}$); iv ($x+1, y, z$); v ($-x+{}^{5}/_{2}, y+{}^{1}/_{2}, -z+{}^{3}/_{2}$); vi ($x-{}^{1}/_{2}, -y+{}^{1}/_{2}, z-{}^{1}/_{2}$); vii ($-x+2, -y, -z+2$).

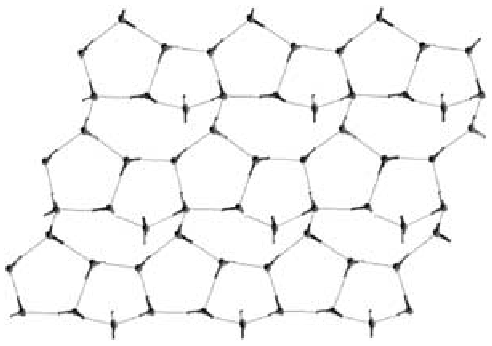


Figure 4. A view of the hydrogen bonding within the water sheets of dmqd$\cdot$6 H_2O, viewed down the *b* axis.

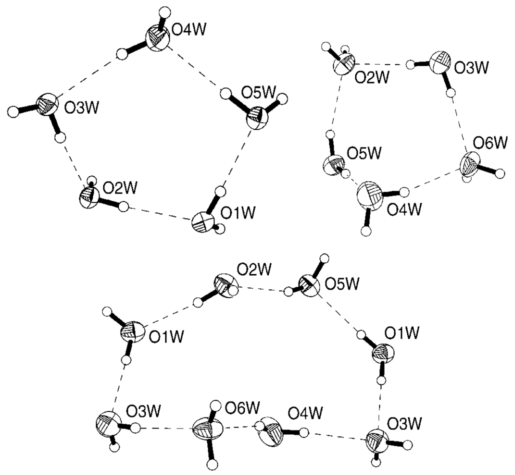


Figure 5. Top left: The homodromic hydrogen bonding in one of the "water pentagons" within the crystal structure of dmqd$\cdot$6 H_2O. Top right: The heterodromic hydrogen bonding in one the "water pentagons" within the crystal structure of dmqd$\cdot$6 H_2O. Bottom: The heterodromic hydrogen bonding in the "water octagons" within the crystal structure of dmqd$\cdot$6 H_2O.

tamer, with $R_5^4(10)$ and $R_7^5(14)$ hydrogen-bonding arrangements, respectively. In this way the sheet of "water" molecules is composed of pentagons and heptagons, both of which are seen in ice structures,[24] and pentagons are the main ring size observed in clathrates.[3] Two-dimensional sheets consisting of "buckled" pentagons have also previously been reported within organic crystal hosts.[25–27]

Hydrate dmqd$\cdot$2 H_2O: The crystal structure of dmqd dihydrate has been previously reported by Codding et al.[33] and was determined from crystals grown by recrystallisation from DMF. For the sake of completeness the structure is briefly described here. As with other dihydroquinoxalinedione hydrates, extensive O−H···O and N−H···O hydrogen bonding is observed between the dmqd molecule and water molecules. The water molecules in dmqd dihydrate hydrogen-bond to each other forming discrete water tetramers with a $R_4^2(8)$ hydrogen-bonding arrangement. These water tetramers are linked by tetramers formed between two water molecules and two C=O groups from two dmqd molecules, this second type of tetramer also having a $R_4^2(8)$ hydrogen-bonding arrangement. This arrangement of chains of water-molecule tetramers is very similar to chains consisting of only water molecules within a organic host crystal that have been recently described in the literature.[13] The tetramers themselves are very similar to those seen in the crystal structure of qd$\cdot$2 H_2O, however, the way that the tetramers link differs.

Hydrate dmqd$\cdot{}^1\!/_3H_2O$: Crystals of dmqd$\cdot{}^1\!/_3H_2O$ were grown by slowly cooling, from boiling to room temperature, a solution of dmqd in DMF/H_2O (1:1). The crystal structure of dmqd$\cdot{}^1\!/_3H_2O$ comprises three crystallographically independent dmqd molecules and one crystallographically independent water molecule.

Extensive π–π stacking interactions are observed throughout the structure (summarised in Table 1), but the structure is dominated by intricate hydrogen-bonding interactions (Table 4). Three O−H···O hydrogen bonds are observed between the water molecules and dmqd molecules, and thirteen O−H···O, N−H···O and C−H···O hydrogen bonds between dmqd molecules. The water molecule is involved in three hydrogen bonds, in only one of which does it act as an acceptor. Two crystallographically independent dmqd molecules form a dimer, which adopts a $R_2^2(8)$ hydrogen-bonding arrangement through N−H···O interactions. Pairs of these dimers are related by an inversion centre and these hydrogen bonds form another distinct "dimer" also with a $R_2^2(8)$ hydrogen-bonding arrangement, leading to a tetramer of dmqd molecules (Figure 6a). The third crystallographically independent dmqd molecule also forms a dimer through N−H···O interactions with a $R_2^2(8)$ hydrogen-bonding arrangement between two molecules related by an inversion centre. These dimers are "capped" by water molecules and so do not form longer arrangements (Figure 6b). This third type of dimer is hydrogen-bonded to the tetramer discussed above through water molecules (Figure 6c). As the water molecules do not directly interact with each other, no extended water cluster structure is observed.

Hydrate [Na^+dmqd$^-$]dmqd$\cdot H_2O$: Crystals of [Na^+dmqd$^-$]dmqd$\cdot H_2O$ were grown by slow cooling of a boiling solution of dmqd and Na_2CO_3 in H_2O. The crystal structure of [Na^+dmqd$^-$]dmqd$\cdot H_2O$ has been determined at both 150 and 298 K in an attempt to investigate any possible structural variations, but no significant difference between the two structures was observed, and for consistency, unless otherwise stated, all bond lengths and angles relate to the 150 K structure. The asymmetric unit of [Na^+dmqd$^-$]dmqd$\cdot H_2O$ consists of one (crystallographically distinct) water molecule, one molecule of dmqd and the one molecule of the sodium salt of dmqd.

The hydrogen bonds observed for [Na^+dmqd$^-$]dmqd$\cdot H_2O$ are shown in Table 4. There are two short O−H···O and O−H···N hydrogen bonds between the water and dmqd molecules, and three short N−H···O and three longer N−H···O and C−H···O hydrogen bonds between the dmqd and dmqd$^-$

Table 4. The hydrogen-bond parameters for dmqd·2 H_2O, dmqd·$^1/_3H_2O$ and dmqd.[a]

	D−H···A [Å]	D−H···A [°]	D···A [Å]
dmqd·2 H_2O[33]			
N1−H1A···O2$^{\text{i}}$	1.88(1)	165(2)	2.825(1)
N4−H4A···O2W$^{\text{ii}}$	1.88(2)	170(2)	2.800(1)
O1W−H1WA···O3$^{\text{iii}}$	1.98(2)	173(3)	2.828(1)
O1W−H1WB···O2	2.02(2)	162(2)	2.866(2)
O2W−H2WA···O1W$^{\text{iv}}$	2.00(3)	178(2)	2.828(2)
O2W−H2WB···O1W$^{\text{v}}$	2.10(4)	149(3)	2.886(2)
O1W−H1WB···O3	2.55(2)	124(2)	3.112(2)
dmqd·$^1/_3H_2O$			
N1′−H1′A···O3	1.91	175	2.792(3)
N1″−H1A···O2″$^{\text{vi}}$	1.92	174	2.792(3)
N4′-H4′A···O1W$^{\text{vii}}$	1.94	172	2.817(3)
O1W−H1WB···O3″	1.945(10)	174(3)	2.783(3)
N4−H4A···O2′	1.94	174	2.822(3)
N1−H1A···O2$^{\text{viii}}$	1.95	174	2.830(3)
O1W−H1WA···O3′$^{\text{ix}}$	2.104(18)	152(3)	2.874(3)
N4″−H4A···O3	2.30	136	2.997(3)
N4″−H4A···O2	2.32	152	3.120(3)
C5″−H5A···O2′$^{\text{x}}$	2.48	141	3.271(3)
C12−H12A···O2″$^{\text{xi}}$	2.49	163	3.437(4)
C12″−H12H···O2″$^{\text{xii}}$	2.56	175	3.541(4)
C5′−H5′A···O3″$^{\text{vii}}$	2.57	169	3.509(4)
C11″−H11G···O2′$^{\text{x}}$	2.66	141	3.477(4)
C11″−H11I···O3″$^{\text{xii}}$	2.67	151	3.561(4)
C11″−H11G···O3′$^{\text{x}}$	2.68	152	3.570(4)
dmqd[28]			
N4−H4A···O3$^{\text{xiii}}$	1.92	170	2.835
N1−H1A···O3$^{\text{xiv}}$	2.11	146	2.931
N1−H1A···O2$^{\text{xiv}}$	2.40	140	3.179
C8−H8A···O2$^{\text{xiv}}$	2.52	137	3.283

[a] Symmetry codes: i ($-x+1$, $-y+1$, $-z+2$); ii ($-x$, $-y$, $-z+2$); iii ($-x$, $-y$, $-z+1$); iv (x, y, $z+1$); v ($-x$, $-y+1$, $z+2$); vi ($-x$, $-y$, $-z-1$); vii (x, $y-1$, z); viii ($-x$, $-y+1$, $-z$); ix ($-x+1$, $-y$, $-z$); x ($-x$, $-y$, $-z$); xi ($-x+1$, $-y+1$, $-z$); xii ($x-1$, y, z); xiii ($-x+1$, $-y+2$, $-z+1$); xiv ($-x+1$, $+y-0.5$, $-z+1.5$).

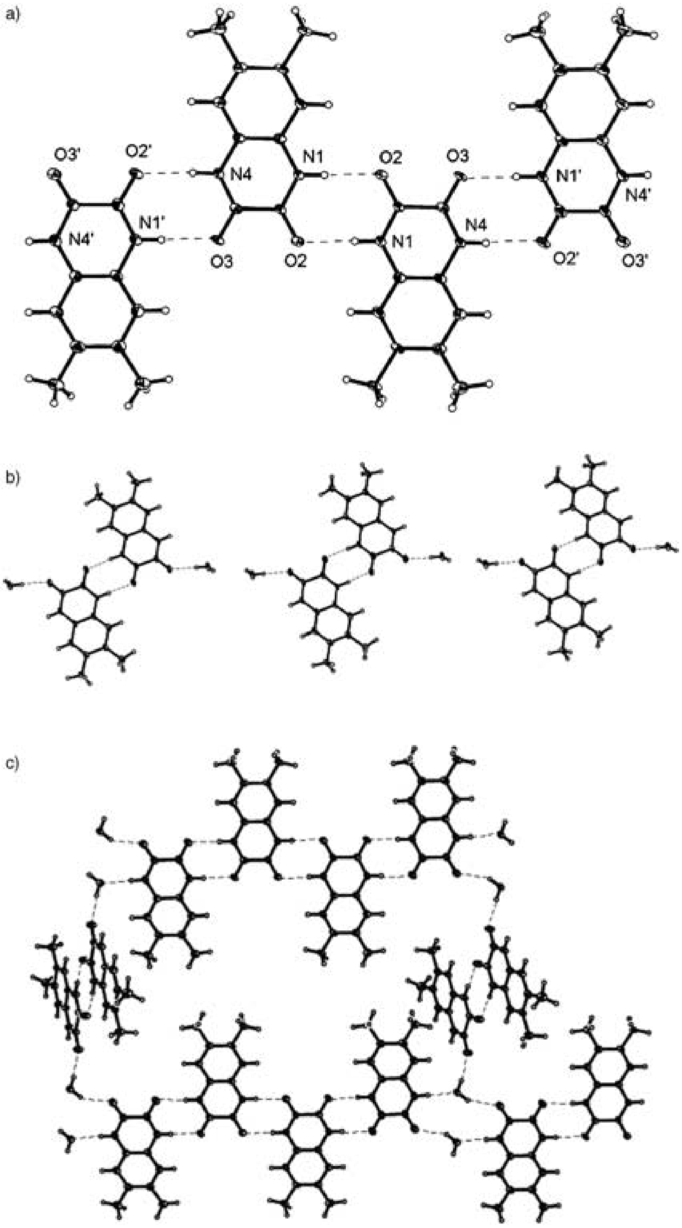


Figure 6. View of a) the tetramer of hydrogen-bonded dmqd molecules in dmqd·$^1/_3H_2O$, with an inversion centre in the middle and consisting of two crystallographically distinct dmqd molecules, b) the hydrogen bonding between the crystallographically independent dmqd in dmqd·$^1/_3H_2O$ to form the third type of dimer which is "capped" by water molecules and c) the hydrogen-bonding network of dmqd molecules within the crystal structure of dmqd·$^1/_3H_2O$ containing both the dmqd tetramers and dimers shown in more detail in (a) and (b).

molecules. The structure of [Na^+dmqd$^-$]dmqd·H_2O consists of one-dimensional coordination polymer chains running parallel to the c axis (Figure 7) that are constructed from Na^+ ions bridged by coordination bonds from dmqd and water ligands (see Table 5 for selected bond lengths and angles). The coordination bonds are supplemented by a range of O−H···O and N−H···O intrachain hydrogen bonds (Table 5). The environment around each Na^+ consists of six Na−O interactions (2.318–2.680 Å). This coordination sphere consists of one bidentate dmqd ligand (Na−O = 2.3460(10), 2.3742(11) Å), one monodentate dmqd ligand (Na−O = 2.3180(10) Å), one monodentate dmqd$^-$ ligand (Na−O = 2.6800(12) Å) and two water molecules (Na−O = 2.4246(12), 2.2873(11) Å). Along the chains, the Na···Na separation is 3.5036(10) Å, with both a water molecule and a dmqd ligand bridging Na centres. The chains interact strongly to generate a three-dimensional structure through extensive π–π stacking interactions (see Table 1), notably between dmqd and dmqd$^-$ anions but also between dmqd molecules forming extended stacks.

Crystal dmqd: The crystal structure of the nonhydrated form of dmqd has been previously deposited in the Cambridge Structural Database (CSD) as a private communication.[28] During the course of this work, crystals with the same unit cell were obtained from the recrystallisation of a solution of dmqd in DMF/H_2O (1:1). For the sake of completeness the important structural features of this compound are reported here. Analysis of the hydrogen-bond parameters for dmqd (Table 4) reveal that pairs of dmqd molecules

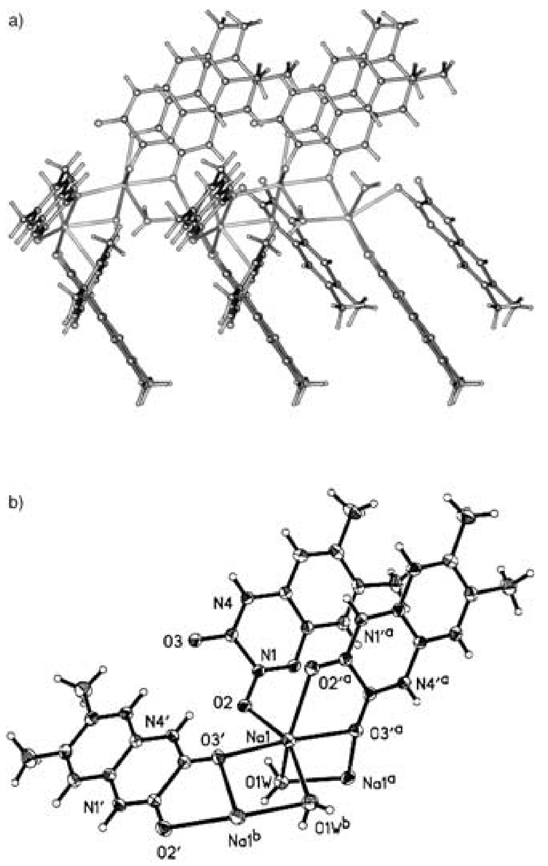


Figure 7. View of a) a chain of [Na^+dmqd$^-$]dmqd·H_2O and b) the Na^+ coordination sphere observed in [Na^+dmqd$^-$]dmqd·H_2O. Displacement ellipsoids drawn at the 50% probability level. Symmetry codes: a) ($^2/_3-y$, $-^2/_3+x-y$, $^1/_3+z$); b) ($^4/_3-x+y$, $^2/_3-x$, $-^1/_3+z$).

form $R_2^2(8)$ hydrogen-bonded dimers in which the molecules are related by an inversion centre and linked by N−H···O interactions. The N−H group not involved in the dimer forms two hydrogen bonds to the C=O groups of a molecule related by a 2_1 screw axis.

Structure of a Phqd hydrate: Crystals containing Phqd could not be grown from water or aqueous Na_2CO_3 solutions due to the insolubility of Phqd in these solvents; however, crystals of Phqd·3H_2O were grown from DMF/H_2O(1:1).

Hydrate Phqd·3H₂O: Only one hydrate of Phqd was isolated during our studies reflecting the low solubility of Phqd in aqueous media. Crystals of Phqd·3H_2O were successfully grown by slowly cooling a solution of Phqd in DMF/H_2O (1:1 mixture) from boiling to room temperature.

The crystal structure of Phqd·3H_2O consists of one Phqd molecule and three crystallographically independent water molecules. The extended structure is dominated by π–π stacking interactions (see Table 1) and by hydrogen bonding between Phqd and water molecules (Table 6). Both water–water, Phqd–Phqd and water–Phqd hydrogen-bonding interactions are observed, ultimately allowing the formation of decorated one-dimensional water chains (Figure 8a), with a $C_2^2(4)$ hydrogen-bonding arrangement. The chains consist of alternating molecules of O1W and O2W, with the appended O3W molecules hydrogen-bonded to O2W molecules. These chains further interact with the C=O groups of the Phqd molecules by O3W to form a honeycomb arrangement of six-membered rings (Figure 8b). Two distinct 12-membered rings are observed, with rings A and B having $R_6^5(12)$ and $R_6^4(12)$ hydrogen-bonding arrangements, respectively.

Discussion of structures: It is clear that the strategy of using dihydroquinoxalinediones as a matrix for the generation of extended water structures is successful. In all instances, the extended aromatic moieties of the organic molecules allow the formation of π–π stacked arrays that serve to group these hydrophobic moieties together within the extended three-dimensional structure. This allows the orientation of the hydrophilic oxalamide moieties, often in a head-to-tail fashion, and presents these hydrogen-bonding moieties to included guest molecules. Although the oxalamide groups are commonly involved in inter-oxalamide hydrogen-bonding interactions, such as the commonly observed $R_2^2(8)$ arrangement, the excess of hydrogen-bond accepting sites provided by the carbonyl groups always generates the possibility of interactions with guest molecules. In those examples of nonhydrated structures reported here and elsewhere,[23,28] the additional hydrogen-bonding sites are commonly satisfied by intermolecular C−H···O interactions. These relatively weak bonds can readily be replaced by stronger interactions, such as the inter-dihydroquinoxalinedione N−H···O interactions, or O−H···O interactions generated by water-molecule inclusion. Thus, although dihydroquinoxalinedione molecules are well suited to the formation of hydrate species, control over the precise nature of the extended water structure remains a significant challenge.

Of the observed extended water structures only one (dmqd·6H_2O) contains a two-dimensional sheet. Such sheets are uncommon, although related examples have been reported previously and are observed as subsections of ice structures and clathrates.[3,24] The formation of this sheet structure is supported by the particular arrangement of the dmqd molecules which form head-to-tail stacks thus presenting two-dimensional hydrophilic surfaces to the guest molecules, thereby encouraging the formation of a two-dimensional water structure.

As with the dmqd molecules in dmqd·6H_2O, the Phqd molecules in Phqd·3H_2O form a hydrophilic extended structure encouraging the formation of one-dimensional chains consisting entirely of water. Both qd·2H_2O and dmqd·2H_2O also form one-dimensional chains but only by using bridging carbonyl moieties to form the extended array; if only the water is considered, zero-dimensional water tetramers are observed. Such tetramers are the most common of the smaller discrete water structures.[18] The remaining hydrated structures, [Na^+dmqd$^-$]dmqd·H_2O, dmqd·$^1/_3H_2O$, and mqd·$^1/_2H_2O$ all contain water molecules that do not form extended water structures.

Table 5. Selected bond lengths (Å), angles (°) and hydrogen-bond parameters for [Na$^+$dmqd$^-$]dmqd$\cdot$H$_2$O.[a]

	150 K	298 K		150 K	298 K
Na1–O1W^{i}	2.2873(11)	2.2936(12)	O1W-Na1-O3′^{i}	84.51(4)	84.40(4)
Na1–O3′	2.3180(10)	2.3265(10)	O1W^{i}-Na1-O3′^{ii}	93.09(4)	93.29(4)
Na1–O3′^{ii}	2.3460(10)	2.3531(10)	O3′-Na1-O3′^{ii}	174.31(4)	173.83(4)
Na1–O2′^{ii}	2.3742(11)	2.3850(11)	O1W^{i}-Na1-O2′^{ii}	124.82(4)	125.29(5)
Na1–O1W	2.4246(12)	2.4393(13)	O3′-Na1-O2′^{ii}	115.01(4)	115.76(4)
Na1–O2	2.6800(12)	2.7047(13)	O3′^{ii}-Na1-O2′^{ii}	70.57(3)	70.20(3)
Na1–Na1^{ii}	3.5036(10)	3.5200(6)	O1W-Na1-O1W^{i}	90.05(2)	89.86(2)
Na1–Na1^{i}	3.5037(10)	3.5201(6)	O3′-Na1-O1W	93.89(4)	93.56(4)
O3′^{ii}-Na1-O1W	80.93(4)	80.69(4)	O3′^{ii}-Na1-O2	98.31(4)	98.03(4)
O2′^{ii}-Na1-O1W	134.87(4)	134.30(4)	O2′^{ii}-Na1-O2	85.04(3)	85.06(4)
O1W^{i}-Na1-O2	150.14(4)	149.64(4)	O1W-Na1-O2	64.89(3)	64.56(4)
O3′-Na1-O2	81.48(4)	81.37(3)	Na1-O1W-Na1^{ii}	96.03(4)	96.06(4)

	D–H$\cdots$A [Å]		D–H$\cdots$A [°]		D$\cdots$A [Å]	
	150 K	298 K	150 K	298 K	150 K	298 K
N1′–H1′A$\cdots$O3^{iii}	1.93	1.95	163	163	2.7647(13)	2.7880(13)
O1W–H1WA$\cdots$N1^{i}	1.936(9)	1.942(9)	179(2)	180(2)	2.7764(14)	2.7822(15)
O1W–H1WB$\cdots$O2	1.979(13)	2.012(16)	152(2)	148(2)	2.7470(13)	2.7565(14)
N4′–H4′A$\cdots$O2	2.01	2.01	140	140	2.7240(14)	2.7325(13)
N4–H4A$\cdots$O2′^{iv}	2.10	2.13	168	167	2.9467(14)	2.9741(13)
N4′–H4′A$\cdots$O3	2.48	2.50	146	146	3.2303(14)	3.2480(13)
C12–H12F$\cdots$O3^{v}	2.55	2.56	163	163	3.4768(18)	3.4888(18)
C5′–H5′A$\cdots$O3	2.68	2.69	138	139	3.4331(16)	3.4454(16)

[a] Symmetry codes: i ($-x+y+{}^4\!/_3$, $-x+{}^2\!/_3$, $z-{}^1\!/_3$); ii ($-y+{}^2\!/_3$, $x-y-{}^2\!/_3$, $z+{}^1\!/_3$); iii ($x-y+{}^1\!/_3$, $x-{}^1\!/_3$, $-z-{}^1\!/_3$); iv ($y+{}^1\!/_3$, $-x+y+{}^2\!/_3$, $-z-{}^1\!/_3$); v ($-x+1$, $-y$, $-z+1$).

Table 6. The hydrogen-bond parameters for Phqd$\cdot$3H$_2$O.[a]

	D–H$\cdots$A [Å]	D–H$\cdots$A [°]	D$\cdots$A [Å]
O1W–H1WB$\cdots$O2^{i}	1.78(3)	172(3)	2.726(3)
O1W–H1WA$\cdots$O2W^{ii}	1.82(3)	172(3)	2.722(3)
O2W–H2WB$\cdots$O3W	1.86(4)	177(3)	2.770(3)
N1–H1A$\cdots$O1W	1.93	172	2.787(3)
O2W–H2WA$\cdots$O1W	1.96(3)	170(4)	2.817(3)
N4–H4A$\cdots$O3^{iii}	1.99	169	2.838(2)
O3W–H3WA$\cdots$O2^{iv}	2.01(4)	164(3)	2.909(3)
O3W–H3WB$\cdots$O3^{v}	2.04(4)	143(3)	2.837(3)
O3W–H3WB$\cdots$O2^{v}	2.57(4)	143(3)	3.357(3)
C5–H5A$\cdots$O3W^{vi}	2.62	175	3.549(3)
C13–H13A$\cdots$O2W^{vii}	2.67	137	3.408(3)

[a] Symmetry codes: i (x, $-y+{}^1\!/_2$, $z-{}^1\!/_2$); ii (x, $-y+{}^1\!/_2$, $z+{}^1\!/_2$); iii ($-x+2$, $-y$, $-z+2$); iv ($x-1$, $-y+{}^1\!/_2$, $z-{}^1\!/_2$); v ($x-1$, y, $z-1$); vi ($-x+1$, $-y$, $-z+1$); vii ($-x+1$, $-y$, $-z$).

In most of the crystal structures containing water molecules, the water molecules participate in more hydrogen bonds as donors than as acceptors. There are two exceptions, however. The first is dmqd$\cdot$6H$_2$O, in which the water molecules are involved in as many hydrogen bonds as acceptors as they are as donors, but in this structure all of the hydrogen bonds involve water molecules and many are water$\cdots$water hydrogen bonds. The other exception is qd$\cdot$2H$_2$O, where water molecules accept six hydrogen bonds and donate only four, but in three of the cases in which the water molecules accept hydrogen bonds these are very long ($\geq$2.61 Å). Hence, this study supports recent findings that in the structure of hydrated small organic molecules, the water molecules tend to behave more as hydrogen-bond donors than acceptors.[22]

As found in a recent study of water clusters in organic molecular crystals, the structures in which $Z'=1$ (Z' = number of molecules per asymmetric unit) for the organic molecules (qd$\cdot$2H$_2$O, dqmd$\cdot$2H$_2$O,[29] dmqd$\cdot$6H$_2$O and Phqd$\cdot$3H$_2$O) have stacks of organic molecules parallel to the shortest crystallographic axis. The same study found that the water molecules often lie in channels parallel to the shortest crystallographic axis, as was found for qd$\cdot$2H$_2$O, and in dmqd$\cdot$6H$_2$O the water sheets lie in the plane of the two shortest crystallographic axes. However, for dmqd$\cdot$2H$_2$O and Phqd$\cdot$3H$_2$O this was not found to be the case, with the water molecules extending in a direction parallel to the second-shortest crystallographic axis.

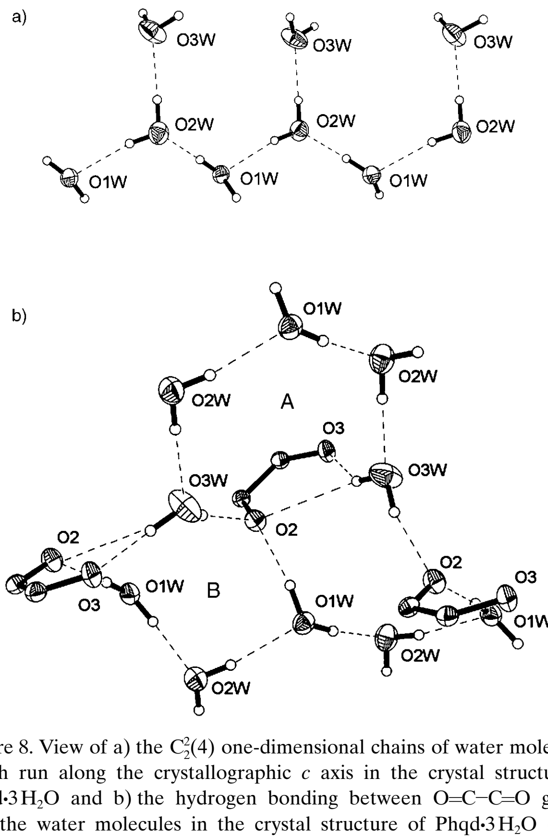


Figure 8. View of a) the $C_2^2(4)$ one-dimensional chains of water molecules, which run along the crystallographic c axis in the crystal structure of Phqd$\cdot$3H$_2$O and b) the hydrogen bonding between O=C–C=O groups and the water molecules in the crystal structure of Phqd$\cdot$3H$_2$O (apart from the carbonyl moieties, the Phqd molecules have been omitted for clarity).

Conclusion

It is clear that the dihydroquinoxalinedione molecules encourage water inclusion but the precise arrangement of those included water molecules is controlled by a number of factors. Indeed, a number of competing, relatively weak, interactions combine to allow the formation of a particular arrangement that ultimately produces the given extended water structure. It could be considered that the dihydroquinoxalinedione molecules arrange through hydrogen-bonding interactions, such as the intermolecular $R_2^2(8)$ arrangement, and π–π stacking to form a host with included cavities that can then accommodate water molecules in confined space. However, this view is highly simplistic as the water–carbonyl O−H···O hydrogen-bonding interactions are at least of comparable energy to the other inter-dihydroquinoxalinedione interactions that are observed. Thus, it would be invalid to conclude that the dihydroquinoxalinedione molecules control the water structure in any dominant fashion, but rather the plethora of observed interactions must act in unison to form the observed structures. The number of different hydrated and nonhydrated structures observed for the systems further supports the observation that the organic oxalamide moiety only serves as a supporting, but not controlling, factor in the formation of the observed water arrays.

The design strategy used in this work has been successful, with a series of molecules based upon qd being synthesised and utilised as organic arrays for water clusters. The hydrophilic oxalamide part of the molecules, with an unequal number of hydrogen-bonding donors and acceptors, becomes involved in hydrogen bonding in all of the hydrated crystal structures. The aromatic parts of the molecules have been involved in offset face-to-face aromatic interactions forming extended chains of organic molecules. By using a series of closely related molecules it has been possible to survey a much greater number of water clusters and arrays than would have been possible with any single small molecule. It has also been possible to investigate how these water structures interact with a specific hydrophilic group, in this case an oxalamide group. It is also clear that this design strategy should be more widely applicable to investigate a range of water structures and we are currently pursuing such studies.

Experimental Section

All chemicals were purchased from Aldrich or Acros Chemicals and used without further purification except *o*-phenylenediamine which was recrystallised by adding *n*-hexane to the filtrate of a hot solution of crude *o*-phenylenediamine in CH_2Cl_2 and charcoal. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained by using a Bruker DPX 300 spectrometer. Infrared spectra were measured as KBr disks by using a Nicolet Avatar 380 FT-IR spectrometer over the range 400–4000 cm^{-1}. Microanalyses were performed by using the University of Nottingham Chemistry Department microanalytical service on a Perkin–Elmer 240B analyser.

X-ray crystallography: All single-crystal X-ray experiments were performed by using either a Bruker AXS SMART 1000 CCD area detector diffractometer (dmqd·6 H_2O, qd·2 H_2O and Phqd·3 H_2O) or a Bruker AXS SMART APEX CCD area detector diffractometer ([Na^+ $dmqd^-$]dmqd·H_2O, dmqd·$^1/_3H_2O$ and mqd·$^1/_2H_2O$) (graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); ω scans), both equipped with an Oxford Cryosystems open-flow cryostat.[31] Other details of crystal data, data collection and processing are given in Table 7. CCDC-261616 (qd·2 H_2O), CCDC-261617 (mqd·$^1/_2H_2O$), CCDC-261618 (dmqd·6 H_2O at 150 K), CCDC-261619 (dmqd·6 H_2O at 90 K), CCDC-261620 (dmqd·$^1/_3H_2O$), CCDC-261621 ([$Na^+$$dmqd^-$]dmqd·$H_2O$ at 150 K), CCDC-261622 ([$Na^+$$dmqd^-$]dmqd·$H_2O$ at 298 K) and CCDC-261623 (Phqd·3 H_2O) contain the supplementary crystallographic data for this

Table 7. Crystallographic data for all compounds.

	dmqd·6 H_2O	dmqd·6 H_2O[a]	dmqd·$^1/_3H_2O$	qd·2 H_2O	Phqd·3 H_2O	mqd·$^1/_2H_2O$	[$Na^+$$dmqd^-$]dmqd·$H_2O$	[$Na^+$$dmqd^-$]dmqd·$H_2O$[b]
formula	$C_{10}H_{22}N_2O_8$	$C_{10}H_{22}N_2O_8$	$C_{30}H_{32}N_6O_7$	$C_8H_{10}N_2O_4$	$C_{12}H_{14}N_2O_5$	$C_9H_9N_2O_{2.5}$	$C_{20}H_{21}N_4O_5Na$	$C_{20}H_{21}N_4O_5Na$
M_r	298.30	298.30	588.62	198.18	266.25	185.18	420.40	420.40
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic	trigonal	trigonal
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)	$R\bar{3}$ (No. 148)
a [Å]	6.8102(8)	6.7893(6)	9.359(2)	7.0236(6)	7.1636(10)	4.362(3)	34.530(12)	34.631(3)
b [Å]	19.604(2)	19.617(2)	10.049(2)	7.7282(7)	20.084(3)	12.833(10)	34.530(12)	34.631(3)
c [Å]	11.761(14)	11.7387(11)	16.360(3)	8.8047(8)	8.5157(11)	16.034(12)	8.600(3)	8.6287(8)
α [°]	90	90	99.270(3)	85.617(1)	90	70.392(12)	90	90
β [°]	104.471(2)	104.301(2)	98.167(3)	78.443(1)	92.335(3)	88.895(12)	90	90
γ [°]	90	90	110.009(3)	76.035(1)	90	87.696(13)	120	120
V [Å^3]	1520.3(5)	1515.0(4)	1394.2(8)	454.19(7)	1224.2(5)	845(2)	8880(9)	8962(2)
Z	4	4	2	2	4	4	18	18
ρ_{calcd} [g cm^{-3}]	1.303	1.308	1.402	1.449	1.445	1.456	1.415	1.402
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.113	0.113	0.102	0.118	0.114	0.109	0.122	0.121
T [K]	150(2)	90(2)	150(2)	150(2)	150(2)	150(2)	150(2)	298(2)
total reflns	9519	12444	12519	4080	7690	7702	27025	30428
unique reflns	3647	3644	6546	2081	2870	4046	5082	5138
R_{int}	0.034	0.037	0.15	0.10	0.073	0.118	0.074	0.076
reflns with $[I > 2\sigma(I)]$	2123	2684	4077	1924	205	1786	4400	4216
final R_1	0.0419	0.0356	0.0853	0.0476	0.0434	0.0831	0.0421	0.0427
wR_2 (all data)	0.1063	0.1045	0.2197	0.1455	0.1316	0.2030	0.1209	0.1305

[a] 90 K data set. [b] 298 K data set.

paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All of the single-crystal structures were solved by direct methods using SHELXS-97,[32] except for Phqd·$3H_2O$ which was solved using SIR92,[33] and all non-hydrogen atoms were located using subsequent difference-Fourier methods.[34] In all cases, hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms, except for water hydrogen atoms which were located from the difference Fourier map. The water hydrogen atoms were refined with suitable O–H and H···H distance restraints. Analysis of extended hydrogen-bonded structures was performed and several of the figures were produced using OLEX.[35]

Synthesis

1,4-Dihydroquinoxaline-2,3-dione (qd): 1,4-Dihydroquinoxaline-2,3-dione (qd) was prepared as previously described.[36] A solution of *o*-phenylenediamine (1.204 g, 0.011 mol) and oxalic acid (1.480 g, 0.016 mol) in HCl (4 M, 40 cm^3) was refluxed for 8 h. The resulting solution was cooled to room temperature, filtered and the filtrate washed with cold water (50 cm^3). Yield: 1.602 g, 88 %; ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.09$ (m, 2H; H5A, H8A), 7.09 (m, 2H; H6A, H7A), 11.92 ppm (s, 2H; H1A, H4A); ^{13}C NMR ([D$_6$]DMSO): $\delta = 115.5$ (C5, C8), 123.3 (C6, C7), 125.9 (C9, C10), 155.5 ppm (C2, C3); IR (KBr): $\tilde{\nu} = 3048$ (m), 2969 (m), 2882 (m), 1681 (vs), 1629 (m), 1614 (m), 1392 (m), 855 (m), 753 cm^{-1} (m); elemental analysis calcd (%) for $C_8H_6N_2O_2$: C 59.26, H 3.73, N 17.28; found: C 58.95, H 3.77, N 17.30; MS (EI+) *m*/*z*: 162.0 ($C_8H_6N_2O_2$).

6-Methyl-1,4-dihydroquinoxaline-2,3-dione (mqd): 6-Methyl-1,4-dihydroquinoxaline-2,3-dione (mqd) was prepared in an analogous way to that described for qd. A solution of 3,4-diaminotoluene (3.446 g, 0.028 mol) and oxalic acid (4.876 g, 0.054 mol) in HCl (4 M, 50 cm^3) was refluxed for 8 h. The resulting solution was cooled to room temperature, filtered and the filtrate washed with cold water (50 cm^3). Yield: 4.822 g, 97 %; ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.16$ (s, 3H; H11A, H11B, H11C), 6.76 (d, $^3J_{H,H} = 8.15$ Hz, 1H; H8A), 6.82 (s, 1H; H5A), 6.91 (d, $^3J_{H,H} = 8.15$ Hz, 1H; H7A) 11.86 (s, 1H; H1A/H4A), 11.88 ppm (s, 1H; H4A/H1A); ^{13}C NMR ([D$_6$]DMSO): $\delta = 20.8$ (C11), 115.3 (C7), 115.5 (C5), 123.5 (C8), 124.1 (C9), 125.7 (C10), 132.6 (C6), 155.3, (C2/C3), 155.6 ppm (C3/C2); IR (KBr): $\tilde{\nu} = 3468$ (m), 3060 (m), 2918 (m), 2854 (m), 1697 (vs), 1533 (m), 1393 (m), 872 (m), 807 (m), 690 cm^{-1} (m); elemental analysis calcd (%) for $C_9H_8N_2O_2$: C 61.36, H 4.58, N 15.90; C 61.32, H 4.49, N 16.04; MS (EI+) *m*/*z*: 176.3 ($C_9H_8N_2O_2$).

6,7-Dimethyl-1,4-dihydroquinoxaline-2,3-dione (dmqd): 6,7-Dimethyl-1,4-dihydroquinoxaline-2,3-dione (dmqd) was prepared in an analogous way to that described for qd. A solution of 4,5-dimethyl,-1,2-phenylenediamine (1.352 g, 4.75 mmol) and oxalic acid (1.352 g, 15.0 mmol) in HCl (4 M, 50 cm^3) was refluxed for 8 h. The resulting solution was cooled to room temperature, filtered and the filtrate washed with cold water (50 cm^3). Yield 0.656 g, 72 %; ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.14$ (s, 6H; H11A, H11B, H11C, H12A, H12B, H12C), 6.84 (s, 2H; H5A, H8A) 11.79 ppm (s, 2H; H1A, H4A); ^{13}C NMR ([D$_6$]DMSO): $\delta = 19.3$ (C11, C12), 116.0 (C5, C8), 123.7 (C9, C10), 131.4 (C6, C7), 155.5 ppm (C2,C3); IR (KBr): $\tilde{\nu} = 3156$ (m), 2945 (m), 2920 (m), 1689 (vs), 1628 (m), 1397 (m), 687 cm^{-1} (m); elemental analysis calcd (%) for $C_{10}H_{10}N_2O_2$: C 63.15, H 5.30, N 14.73; C 63.22, H 5.34, N 14.60; MS (EI+) *m*/*z*: 190.2 ($C_{10}H_{10}N_2O_2$).

1,4-Dihydrobenzo[g]quinoxaline-2,3-dione (Phqd): 1,4-Dihydrobenzo[*g*]quinoxaline-2,3-dione (Phqd) was prepared in an analogous way to that described for qd. A solution of 2,3-diaminonaphthalene (0.120 g, 0.76 mmol) and oxalic acid (0.125 g, 1.39 mmol) in 4 M HCl (20 cm^3) was refluxed for 8 h. The resulting solution was cooled to room temperature, filtered and the filtrate washed with cold water (50 cm^3). Yield 0.132 g, 82 %; ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.37$ (m, 2H; H12A, H13A), 7.52 (s, 2H; H5A, H8A), 7.81 (m, 2H; H11A, H14A), 12.11 ppm (s, 2H; H1A, H4A); ^{13}C NMR ([D$_6$]DMSO): $\delta = 111.2$ (C5, C8), 125.4 (C12, C13), 126.6 (C11, C14/C6, C7), 127.1 (C6, C7/C11, C14), 129.6 (C9, C10) 155.5 ppm (C2, C3); IR (KBr): $\tilde{\nu} = 3241$ (m), 3048 (m), 2944 (m), 2909 (m), 2862 (w), 1691 (vs), 1641 (m), 1399 (m), 866 (m), 737 (m), 560 cm^{-1} (m); elemental analysis calcd (%) for $C_{12}H_8N_2O_2$: C 67.92, H 3.80, N 13.20; found: C 67.82, H 3.70, N 12.91; MS (EI+) *m*/*z*: 212.0 ($C_{12}H_8N_2O_2$).

Hydrate qd·$2H_2O$: A solution of 1,4-dihydroquinoxaline-2,3-dione (qd) (0.311 g, 1.92 mmol) and Na_2CO_3 (0.755 g, 7.13 mmol) in H_2O (60 cm^3) was heated to boiling and the solution was allowed to slowly cool to room temperature. After being left at room temperature for 24 h, the solution was filtered, producing a white microcrystalline solid, qd·$2H_2O$ (213 mg, 56 %). Single crystals were prepared by heating to boiling a solution of qd (0.151 g, 0.93 mmol) and Na_2CO_3 (0.301 g, 2.84 mmol) in H_2O (40 cm^3) and allowing the solution to slowly cool to room temperature. IR (KBr): $\tilde{\nu} = 3436$ (w), 3157 (m), 3049 (m), 2967 (m), 2883 (m), 2778 (m), 1695 (vs), 1392 (m), 1248 (m), 865 (m), 855 (m), 760 (m), 705 cm^{-1} (m). We were unable to obtain accurate CHN elemental analysis due to the concomitant precipitation/crystallisation of nonhydrated qd.

Hydrate mqd·$\frac{1}{2}H_2O$: A solution of 6-methyl-1,4-dihydroquinoxaline-2,3-dione (mqd) (0.852 g, 4.83 mmol) in DMF/H_2O (1:1, 50 cm^3) was heated to boiling and the solution was allowed to slowly cool to room temperature. After being left at room temperature for 24 h, the solution was filtered, producing a brown microcrystalline solid, mqd·$\frac{1}{2}H_2O$ (752 mg, 84 %). Single crystals were prepared by slowly cooling a solution of mqd (13.6 mg, 0.077 mmol) in DMF/H_2O (1:1, 15 cm^3). IR (KBr): $\tilde{\nu} = 3470$ (w), 3171 (m), 3061 (m), 2950 (m), 2849 (m), 2770 (m), 1693 (vs), 1626 (s), 1387 (m), 808 (m), 689 cm^{-1} (m); elemental analysis calcd (%) for $C_9H_9N_2O_{2.5}$: C 58.37, H 4.90, N 15.13; found: C 59.56, H 4.75, N 15.43.

Hydrate dmqd·$\frac{1}{3}H_2O$: A solution of 6,7-dimethyl-1,4-dihydroquinoxaline-2,3-dione (dmqd) (0.385 g, 2.02 mmol) in DMF/H_2O (1:1, 50 cm^3) was heated to boiling and the solution was allowed to slowly cool to room temperature. After being left at room temperature for 24 h, the solution was filtered, producing a white microcrystalline solid, dmqd·$\frac{1}{3}H_2O$ (320 mg, 80 %). Single crystals were prepared by slowly cooling a solution of dmqd (14.8 mg, 0.078 mmol) in DMF/H_2O (1:1, 15 cm^3). IR (KBr): $\tilde{\nu} = 3436$ (w), 3160 (m), 3073 (m), 2946 (m), 2920 (m), 1686 (vs), 1628 (s), 1397 (m), 687 cm^{-1} (m). We were unable to obtain accurate CHN elemental analysis due to the concomitant precipitation/crystallisation of nonhydrated dmqd and other hydrates of dmqd.

Hydrates dmqd·$6H_2O$ and [Na$^+$dmqd$^-$]dmqd·H_2O: A solution of 6,7-dimethyl-1,4-dihydroquinoxaline-2,3-dione (dmqd) (0.334 g, 1.76 mmol) and Na_2CO_3 (1.169 g, 11.03 mmol) in H_2O (50 cm^3) was heated to boiling and the solution was allowed to slowly cool to room temperature. After being left at room temperature for 24 h, the solution was filtered, producing a white microcrystalline solid (344 mg, 66 %). Single crystals of dmqd·$6H_2O$ were prepared by heating a solution of dmqd (0.151 g, 0.79 mmol) and Na_2CO_3 (0.248 g, 2.36 mmol) in water (30 cm^3) to boiling and allowing the solution to slowly cool to room temperature. Single crystals of [Na$^+$dmqd$^-$]dmqd·H_2O were prepared by heating to boiling a solution of dmqd (0.124 g, 0.59 mmol) and Na_2CO_3 (0.227 g, 2.13 mmol) in water (30 cm^3) and allowing the solution to slowly cool to room temperature. IR (KBr): $\tilde{\nu} = 3527$ (w), 3436 (m br), 3166 (m), 3067 (m), 2929 (m), 1678 (vs), 1387 (m), 688 cm^{-1} (m). We were unable to obtain accurate CHN elemental analysis due to the concomitant precipitation/crystallisation of dmqd·$6H_2O$, [Na$^+$dmqd$^-$]dmqd·H_2O and nonhydrated dmqd.

Hydrate Phqd·$3H_2O$: A solution of 1,4-dihydrobenzo[*g*]quinoxaline-2,3-dione (Phqd) (0.206 g, 0.97 mmol) in DMF/H_2O (1:1, 50 cm^3) was heated to boiling and then allowed to slowly cool to room temperature. After being left at room temperature for 24 h, the solution was filtered, producing a brown microcrystalline solid, Phqd·$3H_2O$ (0.170 g, 62 %). Single crystals were prepared by heating to boiling a solution of Phqd (4.0 mg, 0.002 mmol) in DMF/H_2O (1:1, 10 cm^3) and allowing the solution to slowly cool to room temperature. IR (KBr): $\tilde{\nu} = 3515$ (s), 3455 (m), 3223 (w), 3055 (w), 2946 (w), 1690 (vs), 1643 (s), 1398 (s), 879 cm^{-1} (s). We were unable to obtain accurate CHN elemental analysis due to the concomitant precipitation/crystallisation of nonhydrated Phqd.

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