Amide-water hydrogen-bond motifs in alkali-metal/crown ether complexes of carbamoyldicyanomethanide, $C(CONH_2)(CN)_2^-$

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A series of complexes have been obtained from the crystallisation of M(cdm) (M = Na, K; cdm = carbamoyldicyanomethanide) with crown ethers from aqueous solution. The structures of these complexes display a range of hydrogen-bonding tape and sheet motifs incorporating both coordinated and lattice water molecules. Identical syntheses result in differing degrees of hydration, and consequently different packing, despite only minor changes in the nature of counter-cation. Complexes with 12-crown[4], $[Na(12c4)_2](cdm)\cdot 2H_2O$ **1** and $[K(12c4)_2](cdm)\cdot H_2O$ **2**, both contain metal/crown sandwich complexes between hydrogen-bonded sheets of composition $\{cdm\cdot xH_2O\}_n$ (x = 1 or 2, respectively). The incorporation of a slightly larger crown ether in the complex $[K(15c5)_2](cdm)\cdot H_2O$ **3** incorporates isolated hydrogen-bonded tapes of $\{cdm\cdot H_2O\}$ rather than sheets and has been obtained as two polymorphs. A serendipitous water-free structure, $[K(15c5)_2](cdm)(cdmH)$ **4**, contains a protonated cdm ligand incorporated into 2D sheets with the anionic cdm. The use of 18-crown[6] yields a complex in which the cdm ligand is coordinated to potassium through a nitrile arm, $[K(18c6)(cdm)(H_2O)]$ **5**. The individual complexes in the structure of **5** join together through a hydrogen-bonded tape that incorporates all available donor and acceptor groups of both the cdm and aqua ligands.

Introduction

Hydrogen bonding within crystalline systems is an essential tool for the rational design of organised solids.[1–4] A large amount of research has been conducted into the elucidation of strong and reproducible interactions between molecules or 'supramolecular synthons', both by experimental studies or through statistical analysis of the Cambridge structural database.[5–7] The directionality offered by hydrogen bonds, due to rigidly orientated dipoles and predictable lone-pair acceptors, lends itself to the synthon-based approach of crystal engineering.[8–13] Common motifs that are utilised involve self-complementary species such as carboxylic acids, amides and urea or combinations of such species.[14–17] In such systems there is generally a predominance of a single supramolecular synthon that determines the structure, albeit often supported by secondary interactions. Few systems show multiple, strong interactions that define a single motif.[18,19] Recently there has been significant interest by a number of researchers in amide/water interactions [20–22] and in small, isolated water clusters in crystalline materials.[23–29]

Our recent work has involved small, functionalised dicyanomethanide anions and their derivatives as ligands in both rare-earth and transition-metal chemistry.[30–34] A significant part of this work has focussed on the use of carbamoyldicyanomethanide (cdm), $C(CONH_2)(CN)_2^-$, Scheme 1.[32–34] In addition to the dicyanomethanide group, intended to coordinate to, or bridge between, metals the ligand incorporates an amide group to enable hydrogen bonding between or within complexes. We have previously identified two strong hydrogen-bonding motifs using the cdm ligand; a recurring 'heterotape'[32] and a guest templated (6,3)-sheet.[33] As a part of this work we have previously reported the compound $[K(15c5)_2](cdm)\cdot H_2O$, **3a**.[32] The structure of this separated ion-pair compound contains isolated 1D hydrogen-bonded chains with the composition $cdm\cdot H_2O$. The chains contain the 'heterotape' motif—a hydrogen-bond chain containing both $R_2^2(8)$ and $R_2^2(12)$ rings, Scheme 1. We now report a series of hydrated alkali-metal/crown ether/cdm structures that incorporate new and interesting hydrogen-bonding motifs of the cdm ligand in conjunction with water.

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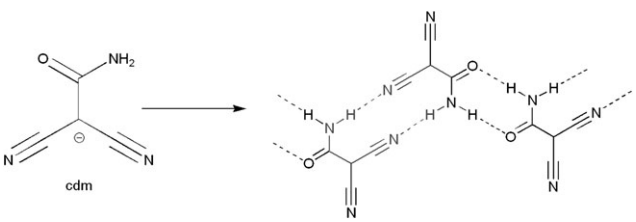
Results and discussion

The ion-pair complex $[K(15c5)_2](cdm)\cdot H_2O$ **3a** was previously reported by ourselves and contains 1D ribbons of composition $\{cdm\cdot H_2O\}_n$.[32] The water molecules exist at the side of the



Scheme 1 The anionic, dinitrile ligand carbamoyldicyanomethanide, cdm, has previously been observed to form a hydrogen-bonded amide/nitrile 'heterotape' motif in $[K(15c5)_2](cdm)\cdot H_2O$, **3a**, and between coordination complexes. The tape contains both an $R_2^2(8)$ amide dimer and an $R_2^2(12)$ amide–nitrile ring.

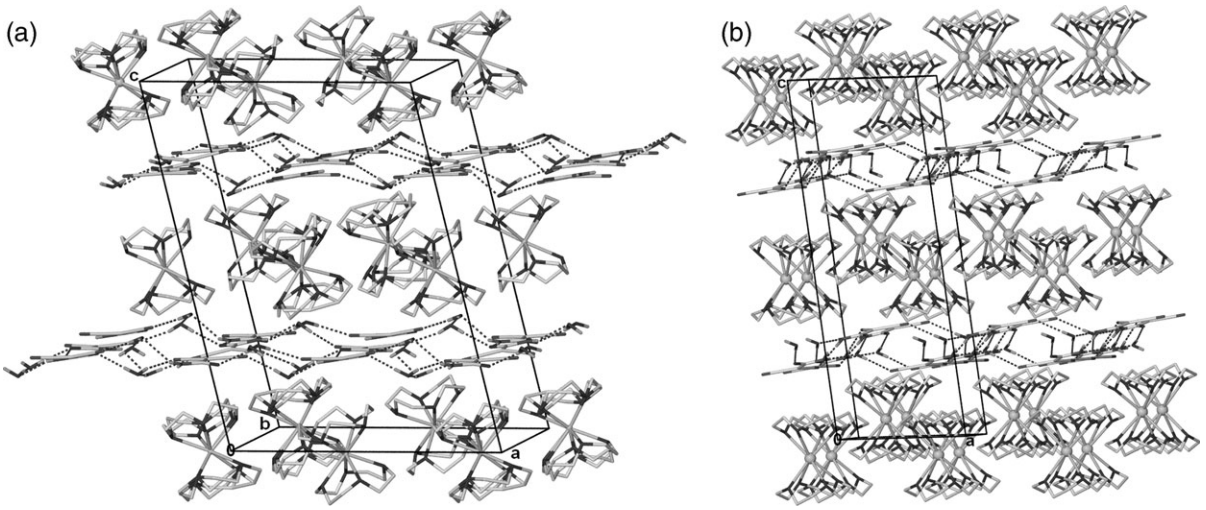


Fig. 1 The complexes (a) $[Na(12c4)_2](cdm)\cdot 2H_2O$ **1** and (b) $[K(12c4)_2](cdm)\cdot H_2O$ **2** both contain hydrogen-bonded sheets between layers of metal/crown sandwich counter-cations.

ribbon, with the tape held together by amide/nitrile hydrogen bonds, Scheme 1. The hydrogen-bonding motif exhibited by the ligand persists into transition metal complexes resulting in the formation of 2D sheets held together by the 1D ribbon. These results posed the question of whether the 'heterotape' motif would remain in other ion-pair structures or, if not, what other hydrogen-bond motifs could be displayed by the uncoordinated ligand. Our approach was the use of crown ethers to form alkali-metal sandwich complexes, thereby leaving the anion free to self-associate although other metal/crown motifs remained a possibility.[35]

Slow evaporation of aqueous solutions containing M(cdm) (M = Na, K) and crown ethers readily yielded crystalline products that contain a variety of water/cdm hydrogen-bonding motifs. 12-crown[4] (12c4) forms sandwich complexes with both Na^+ and K^+, **1** and **2**, although the subtle change in size of the resulting sandwich complex alters the structures observed in the anion/water sheets. Crystallisation of K(cdm) in the presence of 15-crown[5] (15c5) yields a potassium/crown sandwich complex, **3a**, with cdm/H_2O chains that we have previously reported,[32] rather than the sheets observed with the 12c4 sandwich counter-cations (a product could not be obtained with an Na^+/15c5 combination). A second polymorph of this compound, **3b**, has also been obtained, with the same tape motif occurring despite a significant difference in the unit cells of the two polymorphs. A serendipitous, anhydrous product was also obtained that contains the protonated version of cdm, $[K(15c5)_2](cdm)(cdmH)$, **4**, when $GdCl_3$ was present in the reaction mixture. Reactions were also carried out using 18-crown[6] (18c6) with the expectation of a cdm coordination complex rather than a separated ion pair. Reaction of K(cdm) with 18c6 yields a product containing the cdm ligand bound to the metal *via* a single nitrile arm, in addition to a bound aqua ligand, resulting in hydrogen-bonded chains of the complex $[K(18c6)(cdm)(H_2O)]$, **5**. Complexes are discussed below according to the size of the crown ether that they contain. Throughout the discussion we adopt Graph Set nomenclature to describe the hydrogen-bonded ring systems that are present.[36]

12-Crown[4] structures

Complexes were obtained from reaction of both Na(cdm) and K(cdm) with 12-crown[4], $[Na(12c4)_2](cdm)\cdot 2H_2O$ **1** and $[K(12c4)_2](cdm)\cdot H_2O$ **2**, respectively. Both structures contain hydrogen-bonded layers of cdm/xH_2O (x = 1 or 2 for complexes **2** and **1**, respectively) between layers of $[M(12c4)_2]$ cations, Fig. 1. However, the small change in the size of the counter-cation appears responsible for altering the degree of hydration of the structures and consequently changing the intermolecular interactions within the cdm/water sheets. The dihydrated sodium structure **1** contains corrugated sheets with the $[Na(12c4)_2]^+$ cations residing between the peaks and troughs of the sheets above and below, Fig. 1(a). The compound crystallises in the space group $P2_1/c$ and contains two unique $[Na(12c4)_2](cdm)\cdot 2H_2O$ formula units in the asymmetric unit (Z' = 2) (Table 1). Indeed, several of the structures herein have multiple crystallographically unique formula units ($Z' > 1$).[37] The $[Na(12c4)_2]^+$ cations in the structure of **1** contain no significant structural features themselves (average Na–O bond length = 2.475 Å) and do not interact significantly with the hydrogen-bonded sheets.

The hydrogen-bonded sheets in **1** contain several different motifs that incorporate all of the strong hydrogen-bond donors and acceptors available, Fig. 2. The hydrogen-bond distances in the structure are spread over a very narrow range, despite the variety of donors (NH_2 and H_2O) and acceptors (nitrile, carbonyl and water) present, with D···A distances in the range 2.80–2.91 Å, Table 2. The sheet is comprised of four distinct hydrogen-bonded rings of various sizes; $R_2^2(8)$, $R_4^4(8)$, $R_4^4(16)$ and $R_6^6(20)$. The two smallest ring systems are associated with the amide functionalities, one of which also incorporates the water molecules. Amide $R_2^2(8)$ dimers, a common supramolecular motif,[16] connect two ligands together in a co-planar manner such that the dinitrile groups are orientated in opposing directions. At either side of the amide dimers are $R_4^4(8)$ rings incorporating two water molecules in addition to the two amide groups. The NH···OH_2 interactions deviate significantly from linearity, Table 2,

Table 1 Crystal and refinement data for structures **1–5**. **3a** and **3b** are polymorphs of which **3a** has previously been reported (crystal data is included below for comparison)

	1	**2**	**3a**	**3b**	**4**	**5**
Compound	$[Na(12c4)_2](cdm)\cdot 2H_2O$	$[K(12c4)_2](cdm)\cdot H_2O$	$[K(15c5)_2](cdm)\cdot H_2O$		$[K(15c5)_2](cdm)(cdmH)$	$[K(18c6)(cdm)(H_2O)]$
Formula	$C_{20}H_{38}N_3NaO_{11}$	$C_{20}H_{36}KN_3O_{10}$	$C_{24}H_{44}KN_3O_{12}$		$C_{28}H_{45}KN_6O_{12}$	$C_{16}H_{28}KN_3O_8$
M	519.52	517.62	605.72		696.80	429.51
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal size/mm	0.17 × 0.12 × 0.12	0.24 × 0.26 × 0.12	—	0.24 × 0.20 × 0.20	0.22 × 0.18 × 0.18	0.18 × 0.18 × 0.05
a/Å	16.7758(3)	9.1376(25)	9.2366(8)	16.1381(3)	10.4626(2)	13.4619(2)
b/Å	14.1320(3)	11.0086(29)	16.125(3)	18.4737(4)	11.7836(3)	17.6252(3)
c/Å	23.1203(4)	25.6293(66)	20.820(3)	22.6934(5)	14.8886(3)	18.4777(3)
α/°	90	90	81.064(6)	113.547(1)	106.085(2)	90.386(1)
β/°	103.193(1)	96.335(12)	89.502(6)	96.583(1)	90.672(1)	90.441(1)
γ/°	90	90	86.172(6)	93.778(1)	91.569(1)	103.642(1)
V/Å^3	5336.59(17)	2562.4(12)	3056.5(7)	6119.2(2)	1762.69(7)	4260.20(12)
Z	8	4	4	8	2	8
μ/mm^{-1}	0.118	0.263	—	0.236	0.216	0.295
No. unique	12218	5827	—	26518	7914	19367
No. obs [$I \geq 2\sigma I$]	6328	5638	—	16950	5598	14899
Parameters	795	323	—	1505	445	1236
R_{int}	0.0937	0.0654	—	0.0319	0.0814	0.0221
GooF	0.967	1.105	—	1.023	1.037	1.011
$\Delta\rho_{max/min}$/e Å^{-3}	0.312/−0.385	1.388/−0.638	—	1.036/−0.384	0.575/−0.764	0.363/−0.310
wR_2 (all data/[$I \geq 2\sigma I$])	0.1800/0.1458	0.3254/0.3251	—	0.1211/0.1020	0.1749/0.1561	0.0855/0.773
$R1$ (all data/[$I \geq 2\sigma I$])	0.1450/0.0649	0.1276/0.1261	—	0.0846/0.0458	0.0947/0.0648	0.0491/0.0329

however, there are no other hydrogen-bond acceptors in the vicinity of the NH group. The distortion of the interaction appears to be due to weaker, yet more directional, interactions between crown ether CH_2 groups and the water molecules (H···O = 2.88 Å, C–H···O = 169° for O21; the crown ether close to O20 is disordered).

The remaining two ring motifs in **1** both involve the nitrile groups as hydrogen-bond acceptors, all of which interact with water molecules as the hydrogen-bond donor species. The large $R_6^6(20)$ ring contains only two dinitrile groups and four water molecules whereas the slightly smaller $R_4^4(16)$ ring additionally incorporates two NH···OH_2 interactions. The water···nitrile distances are all within a very narrow range of 2.873(3) to 2.898(3) Å, shorter than those observed for the NH···nitrile interactions (*vide infra*). The nitrile groups appear to show a distinct preference for near linear interactions with an average CN···O angle of 160°.

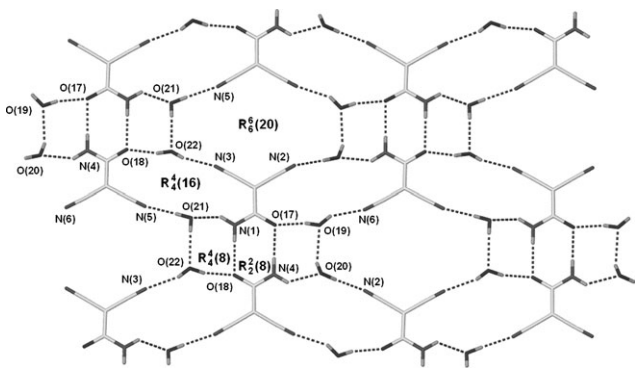


Fig. 2 The hydrogen-bonded sheet, $\{cdm\cdot 2H_2O\}_n$, in the structure of $[Na(12c4)_2](cdm)\cdot 2H_2O$, **1**. Hydrogen-bond data is supplied in Table 2. Symmetry equivalents used; †, 3/2 − x, y − 1/2, 1/2 − z; ‡, 3/2 − x, 1/2 + y, 1/2 − z; §, x − 1, y, z; #, 1/2 − x, y − 1/2, 1/2 − z.

An identical synthesis carried out using K^+ rather than Na^+ yielded the expected compound but with a lower degree of hydration, $[K(12c4)_2](cdm)\cdot H_2O$, **2**. As with **1** the anions and water molecules assemble into a 2D sheet between layers of the sandwich cations, Fig. 1(b), with all hydrogen-bond donors and acceptors involved. However, the different anion : water ratio results in a differently assembled network featuring none of the ring motifs observed in the structure of **1**, Fig. 3. Only two distinct hydrogen-bond ring motifs are observed in **2**, $R_3^3(12)$ and $R_5^5(18)$, both of which are asymmetric. The amide group of the cdm anion forms part of the smaller $R_3^3(12)$ ring with the carbonyl oxygen atom interacting with a water molecule. It is interesting that the oxygen atom accepts only a single significant hydrogen bond rather than two as is more commonly seen and is observed in all other examples in this paper. The 'free site' of the oxygen atom is interacting weakly with a CH_2 hydrogen atom from an adjacent $[K(12c4)_2]^+$ cation (H···O = 2.60 Å). The water molecule bridges between

Table 2 Hydrogen-bonding parameters for complex **1**[a]

	H···A[b]/Å	D···A/Å	D–H···A/°
N(1)···O(21)	2.28	2.889(2)	126
N(1)···O(18)†	1.98	2.857(3)	175
N(4)···O(17)‡	2.05	2.909(3)	164
N(4)···O(20)‡	2.19	2.887(3)	136
O(19)···O(17)	1.93	2.800(2)	168
O(19)···N(6)§	2.09	2.875(3)	153
O(20)···O(19)	2.19	2.800(3)	146
O(20)···N(2)#	1.93	2.886(4)	176
O(21)···N(5)	1.97	2.899(3)	177
O(21)···O(22)	2.11	2.840(3)	176
O(22)···O(18)†	1.93	2.798(2)	167
O(22)···N(3)†	2.07	2.897(3)	162

[a] Symmetry equivalents as per Fig. 2. [b] Hydrogen atoms refined using riding model.

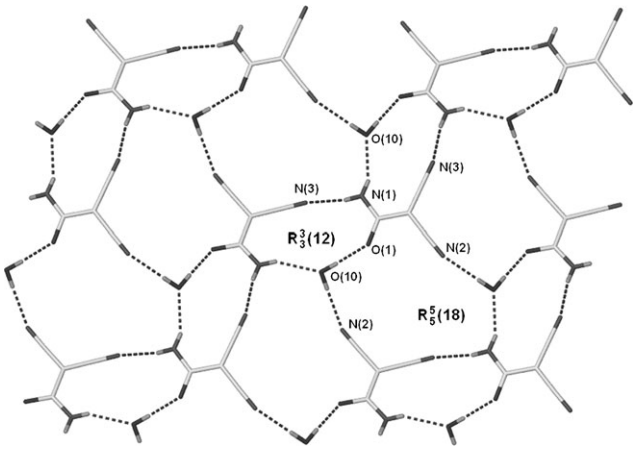


Fig. 3 The hydrogen-bonded sheet, $\{cdm{\cdot}H_2O\}_n$, in the structure of $[K(12c4)_2](cdm){\cdot}H_2O$, **2**. Hydrogen-bond data is supplied in Table 3. Symmetry equivalents used; †, $-x$, $1/2 + y$, $1/2 - z$; ‡, $-x$, $y - 1/2$, $1/2 - z$; §, $1 - x$, $y - 1/2$, $1/2 - z$.

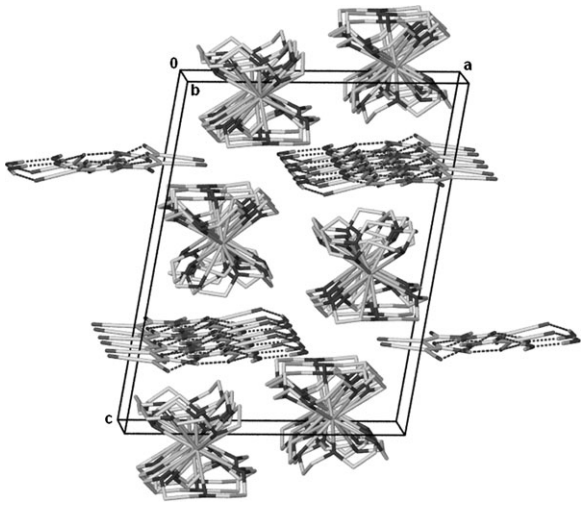


Fig. 4 Packing of the second polymorph of $[K(15c5)_2](cdm){\cdot}H_2O$, **3b**. The structure contains 1D chains of $\{cdm{\cdot}H_2O\}_n$ that propagate parallel to the *b*-axis.

the amide oxygen atom and a nitrile group in a similar arrangement to that of two of the unique water molecules in **1** and with similar distances, Table 3. The larger $R_5^5(18)$ rings comprise three cdm anions and two water molecules, with the majority of hydrogen-bond acceptors being nitrile groups.

15-Crown[5] structures

We recently reported the structure of the compound $[K(15c5)_2](cdm){\cdot}H_2O$, **3a**.[32] This structure contains a 1D hydrogen-bonded anion/water tape, Scheme 1, the anionic component of which was seen to persist in 2D sheets assemblies of metal complexes. During the course of further investigations into rare-earth/crown ether complexes of the cdm ligand,[38] we serendipitously obtained a second polymorph of this compound, **3b** (see Table 1). The previously reported structure, **3a**, contains two unique formula units in the asymmetric unit ($Z' = 2$) whereas in the second phase $Z' = 4$. The structures of the two polymorphs are extremely similar, with **3b** also containing hydrogen-bonded chains running between layers of counter-cations, Fig. 4.

The chemical content of the 1D chain is the same composition as that of the sheet in **2** (*i.e.*, cdm : water in a 1 : 1 ratio), however, the arrangement of the species is radically different, despite the only change between the **2** and **3** being the difference in the size of the crown ethers used. The major synthons within the chain are the $R_2^2(8)$ amide dimer, the $R_2^2(12)$ amide/nitrile dimer and an $R_4^4(8)$ ring incorporating a water molecule, Fig. 5. Although the amide dimer is the more 'predictable' of these two motifs we increasingly observe the presence of the nitrile-containing dimer in complexes of the cdm ligand (such as **4**) and in those of related ligands such as $C(CONH_2)(COMeNH)(CN)^-$.[32,34] The water molecules are associated only with one side of the chain, despite both sides being near identical. The manner in which the water molecules bridge between a nitrile and an amide oxygen atom in an $R_4^4(8)$ ring (water molecules O(6) and O(8) in Fig. 5) is particularly interesting as a similar motif is observed in the complex $[K(18c6)(cdm)(H_2O)]$, **5** (*vide infra*). The water molecules and nitrile groups at the periphery of the chain are weakly interacting with CH_2 groups from adjacent crown ethers, Fig. 4. It is curious that in **3**, with the same cdm : water ratio as in **2**, there are weak CH···O/N interactions rather than adoption of the sheet structure that incorporates more strong donor/acceptor pairs (Fig. 6).

A serendipitous anhydrous structure was also obtained that incorporates the $[K(15c5)_2]^+$ cation from a reaction mixture that incorporated $GdCl_3$ whilst attempting to synthesise rare-earth/cdm complexes.[33] The structure is unique for containing a protonated cdm ligand, cdmH, giving the compound an

Table 3 Hydrogen-bonding parameters for complex **2**[a]

	H···A/Å	D···A/Å	D–H···A/°
N(1)···O(10)†	2.17(6)	2.847(6)	154(5)
N(1)···N(3)‡	2.38(6)	3.227(6)	169(5)
O(10)···O(1)	1.97(6)	2.768(5)	170(5)
O(10)···N(2)§	2.14(8)	2.977(6)	178(7)

[a] Symmetry equivalents as per Fig. 3.

Table 4 Hydrogen-bonding parameters for complex **3b**[a]

	H···A/Å	D···A/Å	D–H···A/°
N(1)···O(4)†	1.99(2)	2.884(2)	175(2)
N(1)···N(5)	2.34(2)	3.190(2)	156(2)
N(4)···O(3)	1.99(2)	2.887(2)	178(2)
N(4)···N(2)	2.28(2)	3.060(2)	154(2)
N(7)···O(2)	1.97(2)	2.889(2)	176(2)
N(7)···N(11)	2.34(2)	3.187(2)	150(2)
N(10)···N(8)	2.33(2)	3.093(2)	150(2)
N(10)···O(1)‡	1.96(2)	2.870(2)	178(2)
O(5)···O(2)	1.87(2)	2.778(2)	170(2)
O(5)···N(11)	2.28(3)	3.069(2)	175(3)
O(6)···O(5)	1.73(4)	2.822(2)	160(3)
O(6)···N(6)	2.27(3)	3.040(2)	164(3)
O(7)···O(4)	1.86(3)	2.793(2)	171(3)
O(7)···N(5)‡	2.29(3)	3.082(2)	173(2)
O(8)···O(7)	1.81(4)	2.835(2)	166(3)
O(8)···N(12)	2.17(3)	3.002(2)	163(3)

[a] Symmetry equivalents as per Fig. 5.

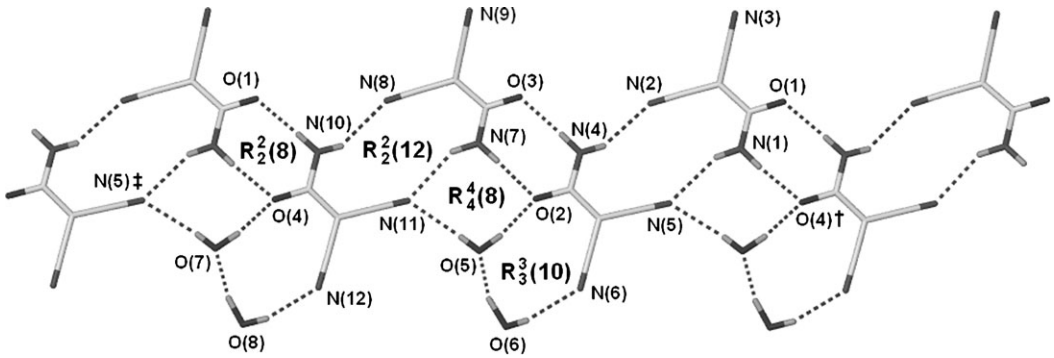


Fig. 5 The hydrogen-bonded chain, $\{cdm{\cdot}H_2O\}_n$, in the structure of the second polymorph of $[K(15c5)_2](cdm){\cdot}H_2O$, **3b**. Hydrogen-bond data is supplied in Table 4. Symmetry equivalents used; †, x, $y-1$, z; ‡, x, $1+y$, z.

overall formula of $[K(15c5)_2](cdm)(cdmH)$, **4** (Fig. 7). The asymmetric unit contains a single formula unit with the proton of the cdmH molecule apparently residing almost equidistant between the carbonyl groups of the two cdm groups, suggesting that a better description of the speciation may be $(cdm)H(cdm)^-$. Bond lengths and angles within the two cdm groups present in **4** (and those within the other structures) are all comparable within experimental error and provide no distinction between the cdm^- anion and cdmH.

The carbonyl groups within the structure of **4** are directed towards each other with the H^+ situated in between, effectively removing them from further intermolecular interactions. The OH···O interactions form part of large $R_4^4(16)$ rings. The remaining hydrogen bonds within the sheet, in the absence of water, are therefore between the NH_2 groups and the nitrile arms of the cdm^- anions. Whilst the four unique NH···N interactions are of comparable distance, Table 5, the closest to linearity are those contained within the $R_2^2(12)$ amide/nitrile dimer which is once again observed. Compared to the $R_2^2(12)$ rings in the chains of **3**, those in **4** are stronger (*i.e.*, shorter N···N distances) and more directional. This can be rationalised by the absence of other stronger interactions involving NH_2 as a hydrogen-bond donor, such as those utilising carbonyls or waters as acceptors seen in **1–3**. The amide/nitrile dimer therefore becomes the predominant interaction (ignoring the hydrogen bridge between cdm groups) and can adopt an orientation closer to its preferred geometry. The remaining NH···nitrile interactions in **4** are less directional although there is little difference in the N···N distances compared to those in the dimer synthon, Table 5.

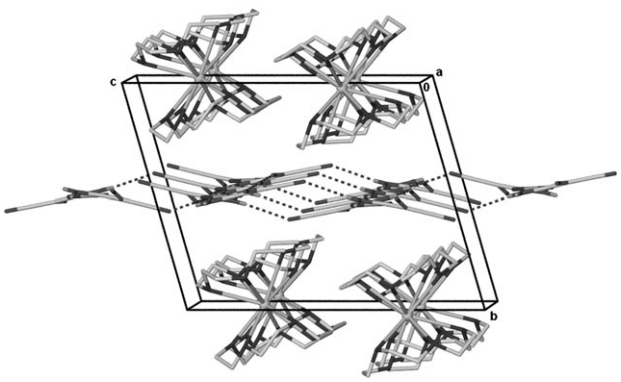


Fig. 6 Packing in the structure of $[K(15c5)_2](cdm)(cdmH)$, **4**, containing sheets of $\{(cdm)(cdmH)\}_n$ between layers of counter cations.

[K(18-Crown-6)(cdm)(H_2O)] 5

Attempts were made to obtain products from solutions of both Na(cdm) and K(cdm) with 18-crown[6] although a crystalline product was only obtained from the K^+ mixture, $[K(18c6)(cdm)(H_2O)]$, **5** (presumably due to the poorer size fit for the Na^+/18c6 combination). The complex crystallises in $P\bar{1}$ with four unique $[K(18c6)(cdm)(H_2O)]$ units in the asymmetric unit, Table 1. Structurally there is negligible difference between the unique complexes except for a disordered crown ether in one of them. Each complex contains the K^+ ions positioned above the mean plane of the ether oxygen atoms (average distance of 0.85 Å) with a cdm ligand coordinated through a single nitrile arm, in addition to a coordinated water molecule, Fig. 8. Within the complexes there is an intramolecular hydrogen bond between the aqua ligand and the oxygen atom of the cdm ligand, Table 6. The cdm ligands and water molecules interact with those on adjacent complexes resulting in the formation of 1D tapes, Fig. 8. The chains pack such that

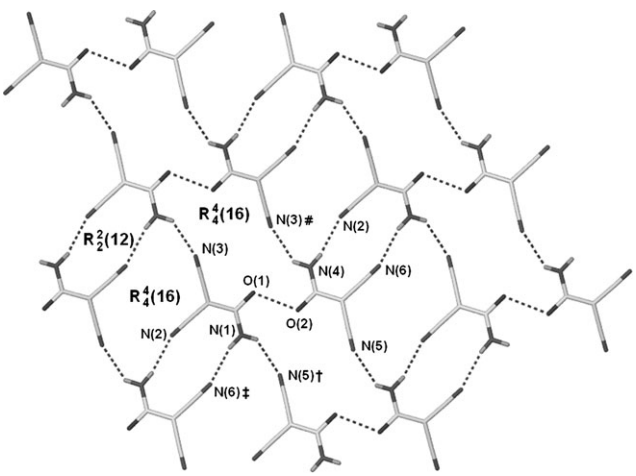


Fig. 7 The hydrogen-bonded sheets in the structure of [K(15c5)2](cdm)(cdmH), **4**. The hydrogen atoms in the O–H–O bridge between cdm groups are not shown for clarity. Symmetry equivalents used; †, $1-x$, $1-y$, $1-z$; ‡, $x-1$, y, z; §, $1+x$, y, z; #, $1-x$, $1-y$, $-z$.

Table 5 Hydrogen-bonding parameters for complex **4**[a]

	H···A/Å	D···A/Å	D–H···A/°
N(1)···N(5)†	2.35(3)	2.978(3)	139(3)
N(1)···N(6)‡	2.17(3)	3.010(3)	165(2)
N(4)···N(2)§	2.19(3)	2.981(3)	167(2)
N(4)···N(3)#	2.24(2)	2.976(3)	143(2)
O(1)···O(2)[b]	1.62	2.435(2)	174
O(2)···O(1)[b]	1.62	2.435(2)	173

[a] Symmetry equivalents as per Fig. 7. [b] Proton disordered between oxygen atoms and refined in fixed positions.

the crown ethers are 'back-to-back' and interweave with adjacent chains (Fig. 9).

Within the hydrogen-bonded chains, each complex is involved in intermolecular interactions with four others with all of the strong donor and acceptor groups incorporated. Both the amide oxygen atoms and uncoordinated nitrile groups act as acceptors for two hydrogen bonds each. The water molecules and NH_2 groups form hydrogen-bond bridges between carbonyl and nitrile acceptors in a manner very similar to that observed in **3b** (Fig. 5) in the smallest of the ring motifs present, $R_2^4(8)$. The other ring motif is $R_2^2(10)$ in which the non-coordinating nitrile arm and amide oxygen atom act as acceptors for hydrogen bonds from NH_2 groups.

Conclusions

A series of compounds have been presented that display a variety of amide/water hydrogen-bonding motifs. Subtle changes in the size of the counter-cation have a surprisingly significant effect on the nature of the cdm/water assemblies with changes in the degree of hydration and a transition from 2D to 1D arrays. In all cases the nitrile groups are incorporated into the hydrogen-bonding motifs with distances comparable to interactions in which the amide is the acceptor species. The previously observed 'heterotape' motif, as seen in **3b**, is not present in other structures, presumably due to competition from water.

Table 6 Hydrogen-bonding parameters for **5**[a]

	H···A/Å	D···A/Å	D–H···A/°
N(1)···N(12)‡	2.16(2)	3.030(2)	178(1)
N(1)···O(23)	2.18(2)	2.973(2)	155(1)
N(4)···N(9)	2.18(2)	3.033(2)	178(2)
N(4)···O(31)	2.15(2)	2.920(2)	151(1)
N(7)···N(3)	2.22(2)	3.058(2)	176(1)
N(7)···O(15)	2.20(2)	2.981(2)	151(1)
N(10)···N(6)	2.18(2)	3.040(2)	179(1)
N(10)···O(7)†	2.18(2)	2.967(2)	152(1)
O(8)···N(6)‡	2.25(2)	3.130(2)	166(2)
O(8)···O(7)	1.99(2)	2.894(1)	170(2)
O(16)···N(3)	2.38(2)	3.143(2)	164(2)
O(16)···O(15)	1.98(2)	2.835(1)	175(2)
O(24)···N(12)‡	2.17(2)	3.018(2)	174(2)
O(24)···O(23)	2.01(2)	2.844(1)	171(2)
O(32)···N(9)	2.17(2)	3.017(2)	176(2)
O(32)···O(31)	2.04(2)	2.858(1)	170(2)

[a] Symmetry equivalents as per Fig. 8.

Experimental

Synthesis

All reagents were purchased from standard commercial sources and used without further purification. K(cdm) was synthesised according to literature.[39] The synthesis of **3** has previously been reported. IR spectra were collected as Nujol mulls using a Perkin Elmer 1600 series spectrophotometer. Elemental analyses were conducted at the Campbell Analytical Laboratories, University of Otago, New Zealand. Compounds **3b** and **4** were obtained as serendipitous products from reactions incorporating rare-earth chlorides in addition to 15-crown-5 and K(cdm) (1/3 equivalent of $LaCl_3$ and $GdCl_3$, respectively) and were obtained only in sufficient quantity for characterisation by X-ray crystallography.

$[Na(12c4)_2](cdm)\cdot 2H_2O$, 1. Na(cdm) (0.05 g, 0.38 mmol) and 12-crown[4] (0.11 g, 0.63 mmol) were dissolved in water (5 ml). The resulting solution was left to slowly evaporate at room temperature for two months, yielding large (~5 mm)

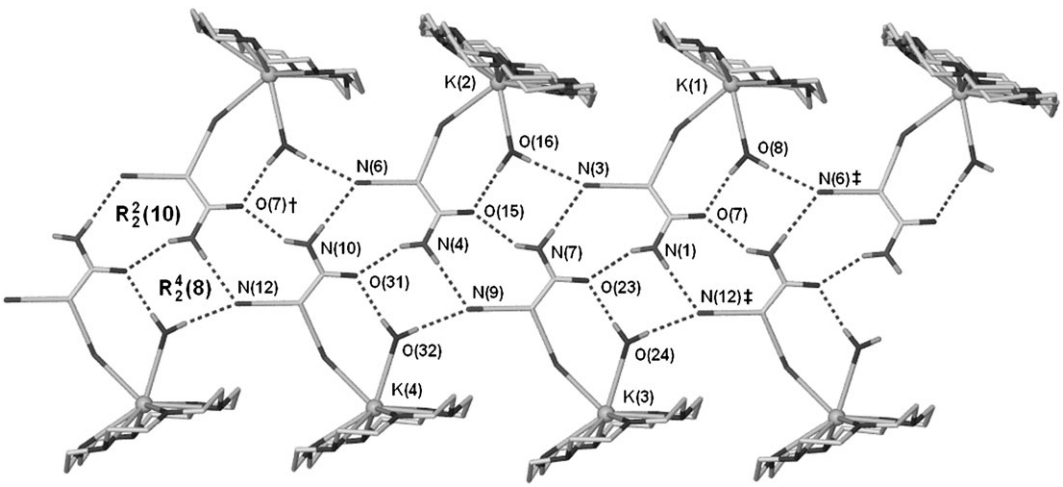


Fig. 8 The hydrogen-bonded chain in the structure of [K(18c6)(cdm)(H_2O)], **5**. Symmetry equivalents used; †, x, $1 + y$, z; ‡, x, $y - 1$, z.

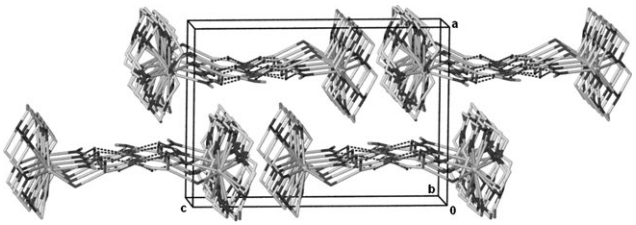


Fig. 9 The packing of **5**, viewed along the hydrogen-bonded chains.

colourless crystals in approximately 2 ml of remaining solvent (yield = 60%). Anal. Calc. for $C_{20}H_{34}N_3O_9Na$ (dehydrated sample): C, 49.68; H, 7.09; N, 8.69%. Found: C, 49.56; H, 7.10; N, 8.72%. ATR-IR (ν/cm^{-1}): 3392w, 3167w, 2728w, 2198m, 2165m, 1652w, 1568w, 1305w, 1247w, 1136w, 1093w, 1023w, 965w, 917w, 851w, 722w.

[K(12c4)$_2$](cdm)·H$_2$O, 2. K(cdm) (0.06 g, 0.41 mmol) and 12-crown[4] (0.11 g, 0.63 mmol) were dissolved in water (5 ml). The resulting solution was left to slowly evaporate at room temperature for one month, yielding colourless, plate-like crystals in approximately 1 ml of remaining solvent (yield = 50%). Anal. Calc. for $C_{20}H_{36}N_3O_{10}K$: C, 46.41; H, 7.01; N, 8.12%. Found: C, 46.30; H, 6.89; N, 8.14%. ATR-IR (ν/cm^{-1}): 3506m, 3405m, 3313w, 3187w, 2730m, 2186s, 2151s, 1922w, 1645m, 1573m, 1301w, 1288w, 1248w, 1135m, 1094m, 1020m, 911m, 845m, 722m.

[K(18c6)(cdm)(H$_2$O)], 5. K(cdm) (0.06 g, 0.41 mmol) and 18-crown[6] (0.14 g, 0.53 mmol) were dissolved in water (5 ml). The resulting solution was left to slowly evaporate at room temperature for three months to almost complete dryness, yielding colourless, plate-like crystals (yield = 60%). Anal. Calc. for $C_{16}H_{28}N_3O_8K_1$: C, 44.74; H, 6.57; N, 9.78%. Found: C, 44.73; H, 5.90; N, 9.85%. ATR-IR (ν/cm^{-1}): 3540w, 3396w, 3182w, 2728m, 2192s, 2150s, 1974w, 1630m, 1555m, 1286w, 1251w, 1076w, 959m, 834w, 760w, 721m.

Crystallography

Crystal and refinement data for structures **1–5**. **3a** and **3b** are provided in Table 1. Single crystals were mounted on fine glass fibres using viscous hydrocarbon oil. Data were collected using either a Bruker X8 Apex II CCD (**2**, **3b** and **5**) or Nonius Kappa-CCD (**1** and **4**) diffractometer, both equipped with monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collections were maintained at 123 K using an open-flow N_2 cryostream. Data were initially processed using DENZO[40] or the Apex II program suite[41] for the respective instruments. Structures were solved by direct methods using SHELXS-97.[42] Refinement was carried out by conventional alternating least squares cycles against F^2 using SHELXL-97[42] and the program X-Seed as a graphical interface.[43] Where possible hydrogen atoms attached to oxygen or nitrogen were experimentally located from the Fourier difference map. Hydrogen atoms attached to carbon were placed in idealised positions and refined using a riding model to the atom to which they are attached. Several of the structures have $Z' > 1$. Whilst it appears that there may be a translational relationship between molecules, no higher crystallographic symmetry could be found for these structures, with no systematically weak data indicating the presence of a supercell. No significant correlation matrix elements were observed for these structures. The observation of the polymorphs **3a** and **3b**, which are not related by a simple doubling of a cell axis, is further evidence that high Z' values exist with no higher cell symmetry.

Special refinement details

1: Hydrogen atoms attached to nitrogen were placed in idealised positions and refined using a riding model. Hydrogen atoms attached to oxygen were located from the Fourier difference map but did not refine satisfactorily and were therefore held in position using AFIX commands.[42] One of the unique $[Na(12c4)_2]^+$ cations contains both crown ethers disordered over two positions, with occupancies of the two components refined freely against each other (63 : 37 and 85 : 15 for the two crowns). The minor component was fixed using AFIX and ISOR restraints.

2: Crystals of [K(12c4)$_2$](cdm)·H$_2$O were small and weakly diffracting, leading to a high $R1$ value. However, the structure refines without restraints and connectivity is unambiguous. The largest residual peak (1.39 e$^-$) lies close (0.76 Å) to the potassium. Microanalysis confirms the refined formulation. Despite the low data quality the hydrogen atoms were experimentally located ans allowed to refine freely.

3: Hydrogen atoms attached to oxygen and nitrogen were located experimentally and allowed to refine freely.

4: The hydrogen atom of the protonated cdmH is refined as disordered between the two cdm species (each with a half occupancy hydrogen atom refined using DFIX restraints).

5: The 18-crown[6] in one of the unique complexes is disordered over two positions, the occupancies of which were refined freely against each other (78 : 22). Some elongated ADPs remain within the disordered component.

CCDC reference numbers 669556–669560.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716191c

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