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Heterotapes: A Persistent, Dual-Synthon Hydrogen-Bonding Motif

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Abstract: The small dinitrile anion carbamoyldicyanomethanide, $[C(CN)_2(CONH_2)]^-$ (cdm), reproducibly forms a hydrogen-bonded tape containing two different supramolecular synthons: a "heterotape". The tape incorporates both an amide dimer and a nitrile-containing ring. The robustness of the motif is confirmed by its persistence from an isolated tape in a separated ion-pair structure, $[K(15c5)_2](cdm)\cdot H_2O$, to its incorporation into coordination complexes of octahedral metals, thus facilitating the formation of 2D sheets. Complexes containing coligands that occupy the equatorial coordination sites, $[Cu(2,2'\text{-}py_2NH)_2(cdm)_2]\cdot 2MeOH$, $[Ni(cyclam)(cdm)_2]$, and $[Cu(cyclam)(cdm)_2]\cdot 2MeOH$ (cyclam = 1,4,8,11-tetraazacyclotetradecane, 2,2'-py_2NH = di(2-pyridyl)amine), show retention of the heterotape motif, whilst the ethylene diamine complex $[Cu(en)_2(cdm)_2]$ (en = ethylene diamine) displays an alternative hydrogen-bonding motif due to interference from the diamine ligands.

Keywords: crystal engineering · hydrogen bonds · self-assembly · supramolecular synthons · tape structures

Introduction

The growth in importance of the fields of crystal engineering and supramolecular chemistry has provided the impetus for large amounts of research over the past decade.[1,2] A large portion of this research is dedicated to elucidating new structural motifs, whether from an experimental approach or database analysis, and to studying the reproducibility of these supramolecular synthons.[3] It is this reproducibility that lies at the heart of the "engineering" aspect of the discipline: unless a supramolecular motif can be reproduced in a predictable manner, the products that are obtained cannot truly be said to have been engineered; rather, they remain a product of serendipity.[4]

Since the inception of crystal engineering, the use of hydrogen bonds to assemble complex structures has been recognized as one of the more predictable approaches to self-assembly, owing largely to the directionality of the dipolar interaction.[5] Such is their "predictability" that many of the commonly observed trends were summarized as a set of "rules" in a seminal paper by Etter.[6] Some commonly observed motifs are those of tapes or ribbons in which hydrogen bonds form a chain of synthons in a "zipperlike" pattern that joins molecular species.[7] Recognized tape and ribbon motifs almost exclusively contain a single synthon between complementary groups such as urea,[8] amides,[7b,9] carboxylic acids,[10] and NH–metal chlorides[11] as well as other less common motifs.[12] The incorporation of more than one synthon into tape motifs is rare, and examples are isolated.[13]

As part of our work with small polynitrile anions,[14] we have investigated the carbamoyldicyanomethanide anion (cdm, $C(CONH_2)(CN)_2^-$), which contains a potential hydrogen-bonding functionality (an amide) as well as sites for metal coordination (nitriles). We now report a series of compounds of the cdm anion that contain a hydrogen-bonded tape that incorporates two different synthons: a "heterotape".

Results and Discussion

The hydrogen-bonded heterotape involves the amide group of the ligand and one of the nitrile arms and contains two hydrogen-bond rings: the ubiquitous amide $R_2^2(8)$ ring and an $R_2^2(12)$ ring that incorporates the nitrile group (Scheme 1).[15] The persistence of this dual-synthon motif is observed in the transition from a structure containing the noncoordinated anion in an anionic ribbon, $[K(15c5)_2](cdm)\cdot H_2O$ (**1**; 15c5 = [15]crown-5), to those containing neutral metal complexes of cdm. The metal complexes all con-

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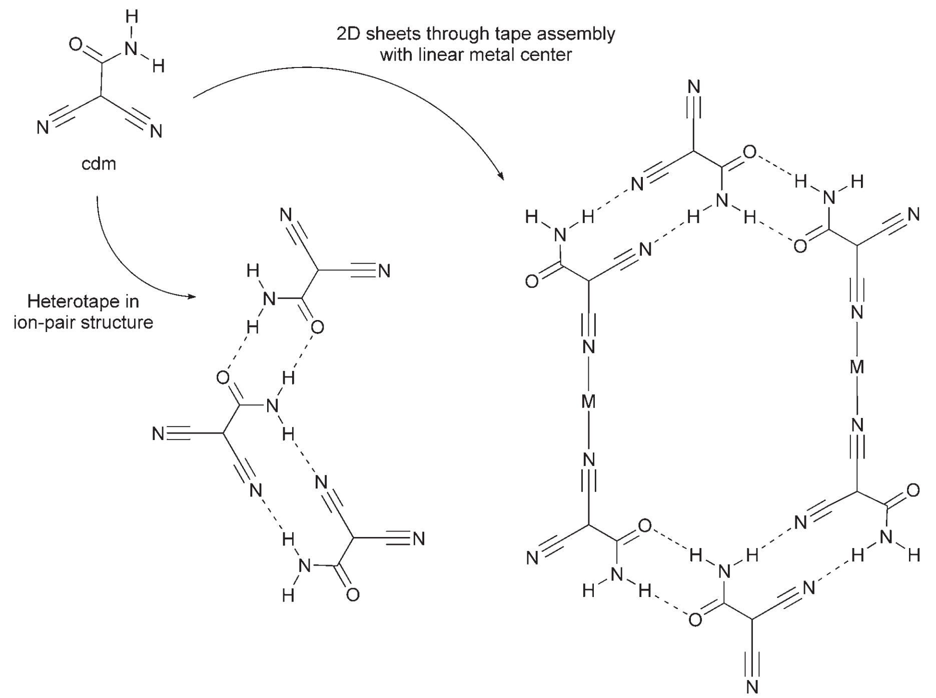

Scheme 1. The amide–nitrile heterotape motif of the free anion in the structure of $[K(15c5)_2](cdm)\cdot H_2O$ (**1**) contains two different synthons (left); thus, 2D sheets (right) can assemble by using a linearly connecting metal ion (i.e., an equatorially protected octahedral metal center).

tain an octahedrally coordinated metal center (Cu or Ni) with four equatorial nitrogen donor atoms from coligands, thus allowing monodentate binding of cdm to the axial positions through a single nitrile arm, thereby facilitating the formation of 2D hydrogen-bonded sheets (Scheme 1).

The hydrated separated ion-pair complex $[K(15c5)_2]$-$(cdm)\cdot H_2O$ (**1**) was isolated by crystallization from an aqueous solution of K(cdm) in the presence of 2 equivalents of [15]crown-5. The $[K(15c5)_2]^+$ sandwich complex isolates the metal ions from the anions, thus allowing the anionic heterotape to form (Figure 1 a). The anions assemble into a hydrogen-bonded zigzag 1D chain in which the amide NH_2 group acts as a donor to both the amide oxygen atom and one of the nitrile arms of the ligand (Figure 1 b). The encapsulated water molecules in the structure are involved in hydrogen bonding with only one side of the anionic tape and with each other (Table 1).

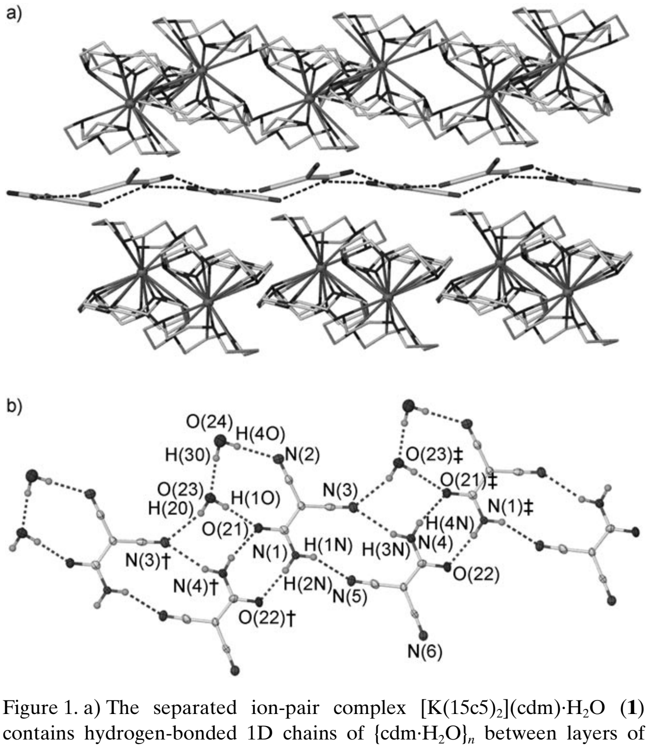

Figure 1. a) The separated ion-pair complex $[K(15c5)_2](cdm)\cdot H_2O$ (**1**) contains hydrogen-bonded 1D chains of $\{cdm\cdot H_2O\}_n$ between layers of $[K(15c5)_2]^+$ countercations. b) The zigzag chains consist of cdm anions forming the "heterotape" motif with water molecules hydrogen-bonded to one side. Symmetry equivalents used: $\dagger = x-1, y, z$; $\ddagger = x+1, y, z$. Hydrogen-bonding parameters are listed in Table 1.

Table 1. Hydrogen-bonding parameters for $[K(15c5)_2]cdm\cdot H_2O$ (**1**).[a]

	D···A [Å]	H···A [Å]	D–H···A [°]
N(1)···O(22)†	2.871(4)	2.00(1)	171(4)
N(1)···N(5)	3.077(5)	2.27(1)	153(3)
N(4)···N(3)	3.180(5)	2.34(1)	159(3)
N(4)···O(21)‡	2.890(5)	2.03(1)	166(4)
O(23)···O(21)	2.786(4)	1.93(1)	175(5)
O(23)···N(3)†	3.083(4)	2.26(1)	161(3)
O(24)···O(23)	2.813(5)	1.96(1)	175(7)
O(24)···N(2)	2.997(4)	2.15(2)	171(11)

[a] Symmetry equivalents used as in Figure 1.

The vast majority of examples of ribbon or tape motifs in crystal engineering result from self-assembly with a single synthon between one or more complementary species.[7–12] The amide–nitrile ribbon is an example of self-assembly through two different synthons between a single self-complementary species. It is perhaps surprising that the encapsulated water molecules do not interfere with the ribbon motif; rather, they are involved in hydrogen bonding with the "free" nitrile arms and with the remaining lone-pair electrons of the amide oxygen atom. Within the ribbon, hydrogen-bond distances are similar, with the average N···N distance being slightly longer than the average N···O distance (3.13 vs. 2.88 Å). The relative positions of the NH_2, carbonyl, and nitrile groups are such as to allow the two hydrogen-bond rings to form with the preferred hydrogen-bond orientations (nonlinear for C=O and near linear for CN).[16]

The free nitrile arms within the heterotape in **1** raises the possibility of metal coordination to these positions, thus allowing the tape to assemble metal complexes (Scheme 1). Towards this end, four metal complexes that contain the cdm ligand were synthesised: two contain Cu^{II} with N,N′-chelating ligands, $[Cu(cdm)_2(2,2'\text{-}py_2NH)_2]$ (**2**; 2,2′-py_2NH = di(2-pyridyl)amine) and $[Cu(cdm)_2(H_2N(CH_2)_2NH_2)_2]$ (**3**), and two with cyclam (1,4,8,11-tetraazacyclotetradecane) as a coligand, $[Ni(cdm)_2(cyclam)]$ (**4**) and $[Cu(cdm)_2(cyclam)]\cdot 2MeOH$ (**5**).

The discrete complex within the structure of $[Cu(cdm)_2(2,2'\text{-}py_2NH)_2]\cdot 2MeOH$ (**2**) contains two equatorial 2,2′-dipyridylamine ligands, which chelate through the pyridyl groups, and two cdm ligands in the Jahn–Teller distorted axial positions (Figure 2a). The cdm ligands are bound through a single nitrile group, thus leaving the amide group and the second nitrile free to form the heterotape motif (Figure 2b). The tape displays a remarkable robustness in the change from an isolated anion to its incorporation into a metal complex. The axial binding of the ligands to the metal allows for a 2D sheet to form; the ribbons are used to link the discrete complexes. The 2D sheets are connected into an overall 3D net by hydrogen bonding that involves the methanol in the lattice: NH of the 2,2′-dipyridylamine ligand donates a hydrogen bond to methanol, which in turn undergoes hydrogen bonding with a carbonyl oxygen atom. The persistence of the hydrogen-bonded tape is also remarkable in that the encapsulated methanol, both a strong donor and acceptor, does not disrupt the motif. Previous work by others using the cdm ligand mostly incorporated water molecules that participate in hydrogen bonding[17] or nonprotected metals that result in coordination of both nitriles;[18] hence, this motif has not been observed.

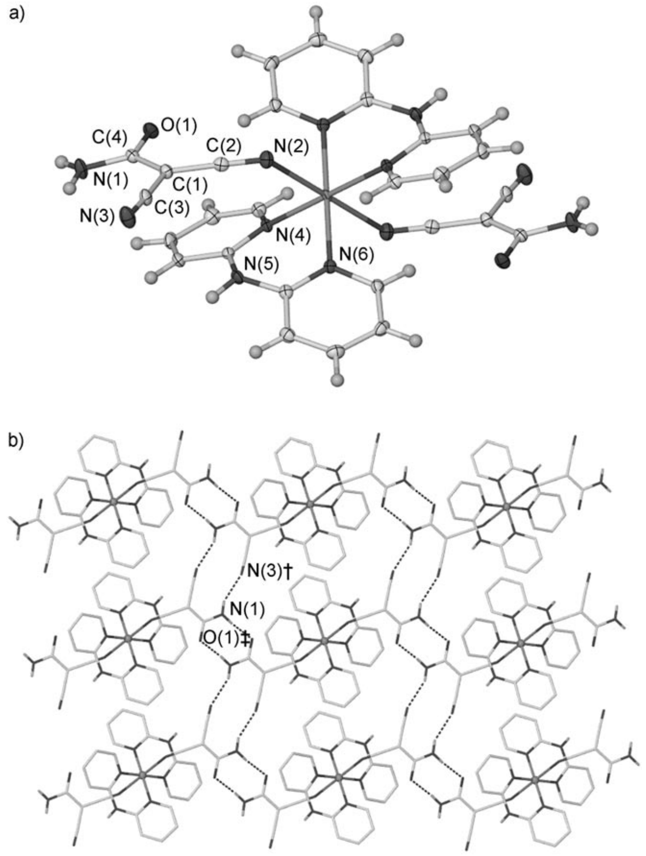

Figure 2. a) The discrete complex $[Cu(2,2'\text{-}py_2NH)_2(cdm)_2]$ (**2**) shows b) the persistence of the heterotape motif that joins the complexes into 2D sheets. Ellipsoids are shown at 50% probability. Symmetry equivalents used: † = 1−*x*, 1−*y*, 1−*z*; ‡ = −*x*, −*y*, 1−*z*. Hydrogen-bonding parameters are listed in Table 2.

The use of ethylene diamine as a coligand disrupts the heterotape motif seen in **1** and **2**, although it gives rise to an alternative 1D tape that contains only hydrogen-bonded amide dimers. The structure of $[Cu(cdm)_2(H_2N(CH_2)_2NH_2)_2]$ (**3**) contains a similar metal-coordination environment to that in **2**; however, the orientation of the ligand is different with respect to the bonding nitrile. The NH_2 group, rather than being orientated between the free nitrile arm and the carbonyl group, is situated adjacent to the coordinating nitrile arm, thus removing the possibility of forming the R_2^2 (12) ring. The predominant hydrogen-bond pattern in the structure of **3** is the R_2^2 (8) amide dimer with the complexes arranged as zigzag 1D chains (Figure 3 and Table 2). The hydrogen-bonded chains are stacked parallel to each other and joined by several interactions that involve the NH protons of the ethylene diamine ligands. Two of the unique NH protons form hydrogen bonds to amide oxygen atoms of adjacent complexes (H···A = 2.18(2) and 2.32(2) Å), whilst a third forms a short interaction to a neighboring nitrile group (H···A = 2.32(2) Å). The remaining proton of the NH_2 group is only involved in an interaction with a nitrile group that is much weaker and less directional than those observed in **1** and **2** (H···A = 2.81(2) Å). The absence of the heterotape motif can most likely be attributed to competition from the ability of the ethylene diamine ligands for hydrogen-bond donation. The multiple interactions between the amine protons and the amide groups of the cdm ligands are presumably stronger and more favorable than the interactions within the tape.

To minimize unfavorable NH···X interactions from the equatorial coligands, reactions were carried out with cyclam instead of ethylene diamine to yield the products $[Ni(cdm)_2(cyclam)]$ (**4**) and $[Cu(cdm)_2(cyclam)]\cdot 2MeOH$ (**5**), both of which contain 2D sheets that comprise complexes connected by the heterotape motif. Within both of these complexes, the orientation of the cdm ligands with respect to the metal is fixed in place by an intramolecular hydrogen bond from one of the cyclam NH groups to the amide oxygen atom (Figure 4). This serves to lock the ligand in the correct conformation to form the heterotape motif (Figure 5a), unlike in **3**. In the Ni complex, the ligands within the tape are offset from coplanarity with their neighbors by around 0.7 Å (Figure 5b). This arrangement allows for an NH···N interac-

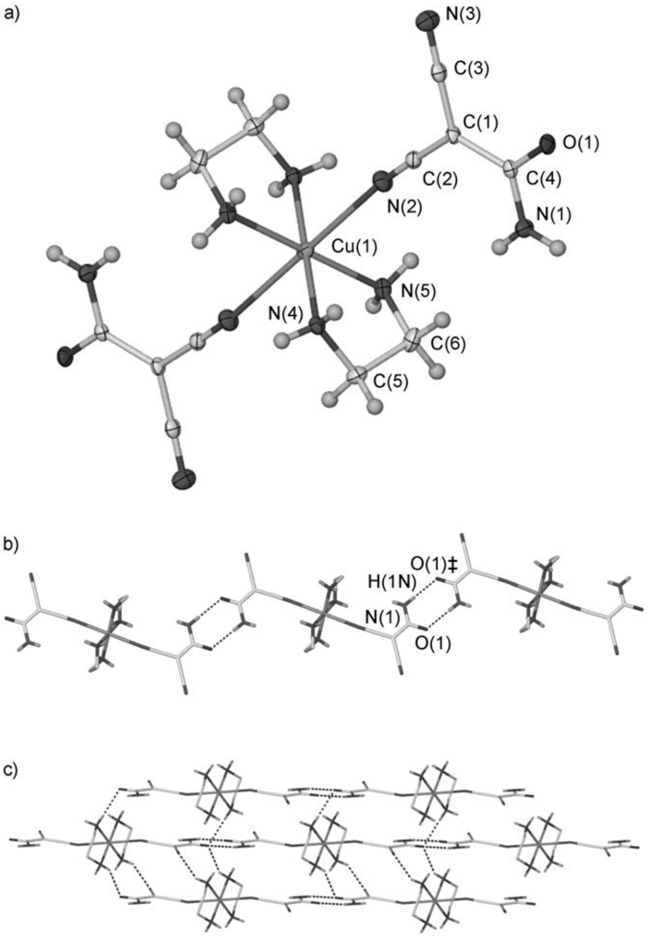

Figure 3. a) The discrete complex $[Cu(NH_2(CH_2)_2NH_2)_2(cdm)_2]$ (**3**), with ellipsoids shown at 50 % probability. b) Hydrogen-bonded amide dimers join the complexes together into zigzag 1D chains, which then c) pack through interactions that involve the ethylene diamine NH_2 groups. Hydrogen-bonding parameters are listed in Table 2.

Table 2. Hydrogen-bonding parameters for amide-containing interactions in complexes **2**–**5**.[a,b]

	D···A [Å]	H···A [Å]	D-H···A [°]
2			
N(1)···O(1)‡	2.896(3)	2.03(4)	167(3)
N(1)···N(3)†	3.028(4)	2.26(5)	151(4)
3			
N(1)···O(1)‡	3.016(2)	2.17(2)	174(2)
4			
N(1)···O(1)‡	2.851(2)	1.98(2)	177(2)
N(1)···N(3)†	3.059(3)	2.35(2)	143(2)
5			
N(1)···O(1)‡	2.965(3)	2.13(3)	168(3)
N(1)···N(3)†	3.030(4)	2.22(3)	169(3)

[a] Symmetry equivalents for **2** and **3** as in the respective figures. [b] Further hydrogen-bonding data on non-amide interactions are supplied in the Supporting Information.

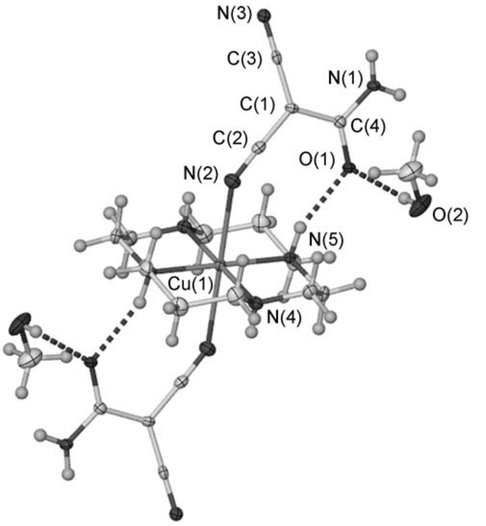

Figure 4. The discrete complexes [M(cyclam)(cdm)$_2$] (M = Ni, Cu) both have the same coordination environment and intramolecular hydrogen bonds that fix the orientation of the cdm ligands.

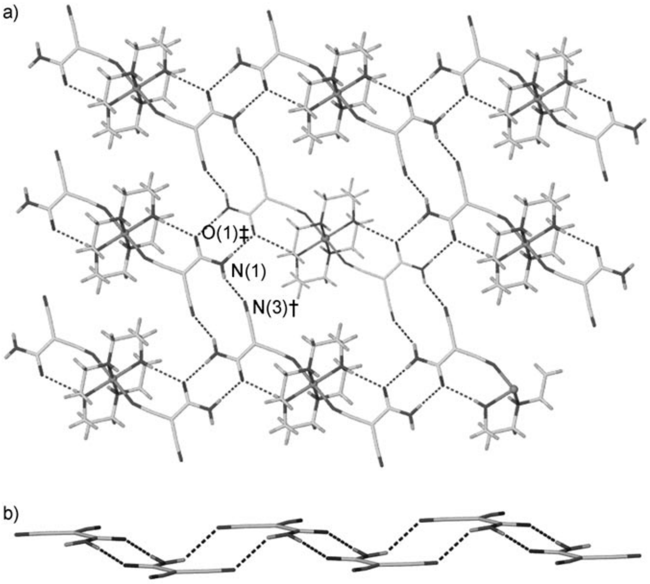

Figure 5. a) The heterotape in [Ni(cyclam)(cdm)$_2$] (**4**) with the orientation of the ligand fixed by an intramolecular NH···O hydrogen bond. b) The ligands are offset from each other by about 0.7 Å, thus allowing intersheet interactions that involve the nitrile arm. Symmetry equivalents used: † = $-x, 2-y, 2-z$; ‡ = $-x, 2-y, 1-z$.

tion between a cyclam NH group and a nitrile arm from an adjacent sheet to generate an overall 3D network.

The copper analogue, [Cu(cdm)$_2$(cyclam)]·2MeOH (**5**), contains two encapsulated methanol molecules per metal complex, although, as with **2**, this solvent does not interfere with the amide–nitrile hydrogen-bonding motif (Figure 6a). The intramolecular cyclam···cdm hydrogen bond is present, despite the cdm ligand now being bound in a Jahn–Teller distorted position on the metal. The ligating nitrile arm is less perpendicular to the equatorial plane to accommodate this hydrogen bond (Cu−N−C = 164 and 128° for **3** and **5**, respectively). The methanol molecules undergo hydrogen bonding with the amide oxygen atoms and reside above and below the 2D sheet (Figure 6b). These solvent molecules

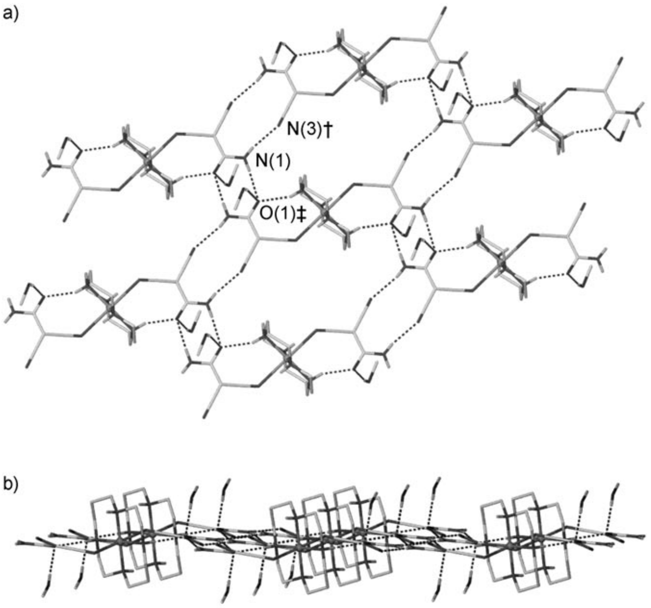

Figure 6. The heterotape motif (a) persists in the structure of $[Cu(cdm)_2(cyclam)]\cdot 2MeOH$ (**5**) despite the presence of methanol, the molecules of which are situated above and below the 2D sheets (b). Symmetry equivalents used: † = −x−1, 1−y, 1−z; ‡ = −x, 1−y, 1−z.

form a bridge between the layers by accepting hydrogen bonds from the remaining cyclam NH groups to generate an overall 3D network. Unlike the structure of **4**, the noncoordinating nitrile arm accepts only a single hydrogen bond from the NH_2 group of a cdm ligand.

Conclusions

The highly unusual dual-synthon heterotape motif of the cdm anion is both persistent and robust. The tape forms in a separated ion-pair structure and can be incorporated into transition-metal complexes to produce 2D sheets. The motif can withstand the presence of competitive hydrogen-bond-donor/acceptor species such as methanol, although the incorporation of ethylene diamine as a coligand results in the formation of an alternative motif. It is anticipated that this motif may be further utilized to generate solid-state arrays of metal clusters.

Experimental Section

General

All starting materials were purchased from standard commercial sources and used without further purification. Potassium carbamoyldicyanomethanide, K(cdm), was prepared according to the literature.[19] Attenuated total reflection (ATR) IR spectra were collected on a Bruker Equinox 55 series FTIR spectrometer. Microanalysis was conducted at Campbell Analytical Laboratories, University of Otago, New Zealand. All products were obtained in approximately 60–80% yield. Powder XRD confirmed the bulk polymorphic purity for **1**, **3**, and **4**; however, loss of methanol occurred rapidly for **2** and **5** (evidenced by microanalysis for **5**), which did not allow for accurate bulk analysis (see Supporting Information for details), although the crystals appeared homogenous by inspection.

Syntheses

1: K(cdm) (0.050 g, 0.318 mmol) and [15]crown-5 (0.140 g, 0.636 mmol) were dissolved in water (5 mL). The solution was left to evaporate slowly for several weeks. ATR-IR: $\tilde{\nu}$ = 3542 (w), 3361 (w), 3173 (w), 2868 (m), 2189 (s), 2151 (s), 1623 (m), 1575 (s), 1398 (m), 1355 (m), 1305 (m), 1246 (m), 1116 (s), 1090 (s), 1029 (m), 938 (m), 856 (m), 829 cm^{-1} (m); elemental analysis: calcd (%) for $C_{24}H_{44}N_3O_{12}K$: C 47.59, H 7.32, N 6.94; found, C 47.79, H 7.32, N 6.98.

2: A solution of K(cdm) (0.025 g, 0.159 mmol) and 2,2′-dipyridylamine (0.055 g, 0.320 mmol) in methanol (5 mL) was added to a solution of $CuCl_2$ (0.014 g, 0.104 mmol) in methanol (2 mL). The solution immediately turned deep green. The solution was left at room temperature for one week, which resulted in the formation of green crystals of **2**. ATR-IR: $\tilde{\nu}$ = 3628 (w), 3374 (m), 3165 (w), 3077 (w), 3019 (w), 2188 (s), 2150 (s), 1643 (s), 1584 (m), 1554 (m), 1528 (m), 1472 (m), 1403 (m), 1367 (m), 1239 (m), 1161 (w), 1062 (m), 1018 (m), 883 cm^{-1} (w); elemental analysis: calcd (%) for $C_{30}H_{30}N_{12}O_4Cu$: C 52.51, H 4.41, N 24.50; found: C 52.15, H 4.34, N 24.67.

3: A solution of K(cdm) (0.025 g, 0.159 mmol) and ethylene diamine (0.020 g, 0.333 mmol) in methanol (5 mL) was added to a solution of $CuCl_2$ (0.014 g, 0.104 mmol) in methanol (2 mL). The solution immediately turned violet. The solution was left at room temperature overnight, which resulted in the formation of violet crystals of **3**. ATR-IR: $\tilde{\nu}$ = 3650 (w), 3475 (m), 3260 (m), 3161 (m), 2968 (w), 2889 (w), 2427 (w), 2191 (s), 2159 (s), 1625 (m), 1595 (m), 1542 (m), 1402 (m), 1161 (w), 1093 (m), 1040 cm^{-1} (w); elemental analysis: calcd (%) for $C_{12}H_{20}N_{10}O_2Cu$: C 36.04, H 5.04, N 35.03; found: C 36.25, H 4.96, N 35.11.

4: A solution of K(cdm) (0.025 g, 0.159 mmol) and cyclam (0.017 g, 0.085 mmol) in methanol (5 mL) was added to a solution of $NiCl_2$ (0.020 g, 0.154 mmol) in methanol (2 mL) to give a colorless solution. The solution was left at room temperature for two weeks to yield colorless crystals of **4**. ATR-IR: $\tilde{\nu}$ = 3643 (w), 3400 (m), 3321 (m), 3231 (m), 3197 (m), 3123 (m), 2902 (w), 2862 (w), 2368 (w), 2200 (s), 2161 (s), 1650 (s), 1577 (s), 1462 (w), 1388 (m), 1155 (w), 1093 (w), 1035 (w), 993 (w), 881 cm^{-1} (w); elemental analysis: calcd (%) for $C_{18}H_{28}N_{10}O_2Ni$: C 45.50, H 5.94, N 29.48; found: C 45.24, H 5.99, N 28.91.

5: A solution of K(cdm) (0.025 g, 0.159 mmol) and cyclam (0.024 g, 0.122 mmol) in methanol (5 mL) was added to a solution of $CuCl_2$ (0.014 g, 0.104 mmol) in methanol (2 mL) to give an orange solution. The solution was left at room temperature for two weeks with a gradual color change, which resulted in the formation of purple crystals of **5**. ATR-IR: $\tilde{\nu}$ = 3384 (m), 3328 (m), 3127 (m), 2869 (w), 2193 (s), 2156 (s), 1653 (s), 1572 (s), 1458 (w), 1395 (m), 1300 (w), 1160 (w), 1094 (m), 1069 (w), 1009 (w), 886 cm^{-1} (w); elemental analysis: calcd (%) for $C_{20}H_{36}N_{10}O_4Cu$: C 44.15, H 6.67, N 25.74; found: C 44.42, H 5.79, N 28.88 (partial loss of methanol).

Crystallography

Crystals were mounted on fine glass fibers with viscous hydrocarbon oil. Data were collected on a Bruker X8 Apex II diffractometer equipped with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Collection temperatures were maintained at 123 K under an open-flow N_2 cryostream. Data were processed with the Bruker Apex II program suite.[20] Structures were solved by direct methods with SHELXS-97[21] and refined by conventional alternating least-squares cycles against F^2 with SHELXL-97[21] and X-Seed as a graphical interface.[22] Hydrogen atoms attached to the oxygen or nitrogen atoms were located from the Fourier difference map and refined freely (except for **1**).

Crystal data for **1**: $C_{24}H_{44}KN_3O_{12}$, $M = 605.72$, colorless block, $0.24 \times 0.12 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.2366(8)$, $b = 16.125(3)$, $c = 20.820(3)$ Å, $\alpha = 81.064(6)$, $\beta = 89.502(6)$, $\gamma = 86.172(6)°$, $V = 3056.5(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.316$ $g\,cm^{-3}$, $F_{000} = 1296$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 123(1)$ K, $2\theta_{max} = 50.0°$, 22487 reflections collected, 10709 unique ($R_{int} = 0.0757$). Final GOF = 0.939, $R1 = 0.0587$, $wR2 = 0.0995$, R indices based on 5233 reflections with $I>2\sigma(I)$ (refinement on F^2), 1026 parameters, 104 restraints, $\mu=0.236\ \text{mm}^{-1}$.

Crystal data for **2**: $C_{30}H_{30}CuN_{12}O_4$, $M=686.20$, green-brown plate, $0.24\times0.16\times0.08\ \text{mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a=8.1034(5)$, $b=8.1670(5)$, $c=12.7451(16)$ Å, $\alpha=90.577(4)$, $\beta=97.015(3)$, $\gamma=112.569(3)°$, $V=771.56(12)$ Å^3, $Z=1$, $\rho_{\text{calcd}}=1.477\ \text{g cm}^{-3}$, $F_{000}=355$, $\text{Mo}_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $T=123(2)$ K, $2\theta_{\max}=55.0°$, 6317 reflections collected, 3506 unique ($R_{\text{int}}=0.0220$). Final GOF $=1.125$, $R1=0.0486$, $wR2=0.1095$, R indices based on 3198 reflections with $I>2\sigma(I)$ (refinement on F^2), 231 parameters, 0 restraints, $\mu=0.766\ \text{mm}^{-1}$.

Crystal data for **3**: $C_{12}H_{20}CuN_{10}O_2$, $M=399.92$, violet block, $0.20\times0.14\times0.10\ \text{mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a=7.5726(3)$, $b=7.7247(3)$, $c=8.6669(5)$ Å, $\alpha=106.794(2)$, $\beta=110.563(2)$, $\gamma=103.191(1)°$, $V=422.58(3)$ Å^3, $Z=1$, $\rho_{\text{calcd}}=1.572\ \text{g cm}^{-3}$, $F_{000}=207$, $\text{Mo}_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $T=123(1)$ K, $2\theta_{\max}=55.0°$, 3003 reflections collected, 1926 unique ($R_{\text{int}}=0.0131$). Final GOF $=1.059$, $R1=0.0247$, $wR2=0.0607$, R indices based on 1870 reflections with $I>2\sigma(I)$ (refinement on F^2), 139 parameters, 0 restraints, $\mu=1.323\ \text{mm}^{-1}$.

Crystal data for **4**: $C_{18}H_{28}N_{10}NiO_2$, $M=475.21$, colorless prism, $0.32\times0.12\times0.12\ \text{mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a=8.7204(4)$, $b=8.7535(3)$, $c=8.8248(5)$ Å, $\alpha=67.883(2)$, $\beta=62.863(2)$, $\gamma=88.120(2)°$, $V=547.43(4)$ Å^3, $Z=1$, $\rho_{\text{calcd}}=1.441\ \text{g cm}^{-3}$, $F_{000}=250$, $\text{Mo}_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $T=123(1)$ K, $2\theta_{\max}=55.0°$, 3922 reflections collected, 2506 unique ($R_{\text{int}}=0.0235$). Final GOF $=1.086$, $R1=0.0375$, $wR2=0.0784$, R indices based on 2244 reflections with $I>2\sigma(I)$ (refinement on F^2), 158 parameters, 0 restraints, $\mu=0.923\ \text{mm}^{-1}$.

Crystal data for **5**: $C_{20}H_{36}CuN_{10}O_4$, $M=544.13$, pink block, $0.24\times0.12\times0.10\ \text{mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), $a=9.586(3)$, $b=11.882(4)$, $c=12.044(4)$ Å, $\beta=101.315(15)°$, $V=1345.2(7)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=1.343\ \text{g cm}^{-3}$, $F_{000}=574$, $\text{Mo}_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $T=123(1)$ K, $2\theta_{\max}=52.0°$, 7576 reflections collected, 2569 unique ($R_{\text{int}}=0.0631$). Final GOF $=1.050$, $R1=0.0492$, $wR2=0.1099$, R indices based on 1983 reflections with $I>2\sigma(I)$ (refinement on F^2), 181 parameters, 0 restraints, $\mu=0.856\ \text{mm}^{-1}$.

CCDC-649271–649275 (**1**–**5**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif (e-mail: deposit@ccdc.cam.ac.uk).

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