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$KCd_2[N(CN)_2]_5(H_2O)_4$: an enmeshed honeycomb grid

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The title compound, poly[potassium [diaquapenta-μ_2-dicyanamido-dicadmium(II)] dihydrate], $\{K[Cd_2(C_2N_3)_5(H_2O)_2]\cdot 2H_2O\}_n$, contains two-dimensional anionic sheets of $\{[Cd_2\{N(CN)_2\}(H_2O)_2]^-\}_n$ with a modified (6,3)-net (layer group *cm*2*m*, No. 35). Two sets of equivalent sheets interpenetrate orthogonally to form a tetragonal enmeshed grid.

Comment

A growing number of coordination polymers have utilized the dicyanamide pseudohalide anion [$N(CN)_2^-$, hereafter abbreviated dca], because its large variety of bonding modes enables the formation of a wide range of structural types (Miller & Manson, 2001; Batten & Murray, 2003; Manson, 2005). The majority of these materials utilize divalent first-row transition elements as the structural nodes that link the dca anion into polymeric motifs. The neutral binary $M(dca)_2$ complexes of the first-row elements form rutile-like structures in which dca is coordinated in a $\mu_{1,3,5}$ fashion. Long-range ferromagnetic order is observed in the cobalt, nickel and copper complexes, with antiferromagnetic ordering in the vanadium, chromium, manganese and iron analogs (Manson, 2005).

Among the second-row transition metals, cadmium is the most studied in the area of network polymers. Two polymorphs of the $Cd(dca)_2$ structure are known: the ambient-temperature β-$Cd(dca)_2$ structure transforms into α-$Cd(dca)_2$ at temperatures above 328 K. This α form is isotypic with the rutile-like structures of the first-row transition elements (Jürgens *et al.*, 2004). Novel structural motifs can be achieved through the incorporation of ancillary ligands. For example, $Cd(dca)_2$(2-aminobenzimidazole) is characterized as a one-dimensional tube-like structure which contains dca anions coordinated in both $\mu_{1,3,5}$ and $\mu_{1,5}$ modes (Ding *et al.*, 2007). Such cadmium-containing compounds have potential applications as luminescent materials (Ding *et al.*, 2006, 2007).

More recently, increased emphasis has been placed on the characterization of anionic dca complexes where cation templation enables the assembly of a diverse set of topologies (Schlueter & Geiser, 2007). Through the appropriate choice of cation, one-dimensional chain and ladder-type structures can be assembled. Similarly, square, honeycomb and triangular two-dimensional motifs have been reported. Three-dimensional motifs, including cube, triple rutile and lithium antimonate types, have been identified. For each of these motifs, the dicyanamide anion is coordinated in a $\mu_{1,5}$ fashion, with the various structural types achieved by varying the ratio and arrangement of single and double dca bridges. Surprisingly, there are no previous structurally characterized examples of anionic dicyanamide coordination polymers that contain alkali metal cations as the charge-compensating and structure-directing entities.

Only two examples of cadmium-based anionic dca structures are known. In the $(Et_4N)[Cd(dca)_3]\cdot 0.75H_2O$ structure, two-dimensional sheets with (4,4)-topology are formed. These sheets possess single $\mu_{1,5}$ bridges in one direction and double $\mu_{1,5}$ bridges in the other (Biswas *et al.*, 2006). The $[Fe(Cp^*)_2][Cd(dca)_3]$ (Cp* is pentamethylcyclopentadienyl) salt contains a three-dimensional cube-type anionic structure with single $\mu_{1,5}$ dca bridges (Van der Werff *et al.*, 2005).

There are no previous examples of published crystal structures that contain both K and dca. Furthermore, although interpenetration is a common phenomenon among coordination polymers (Batten & Robson, 1998), there are also no previous examples of interpenetrated anionic dca lattices. We report that the title compound, $KCd_2(dca)_5(H_2O)_4$, (I), contains orthogonally interpenetrated two-dimensional anionic sheets with a modified (6,3)-net. This new structural motif for anionic dca coordination polymers is perhaps enabled by the templating effects of the octahedrally coordinated potassium cation. The anionic component in the title

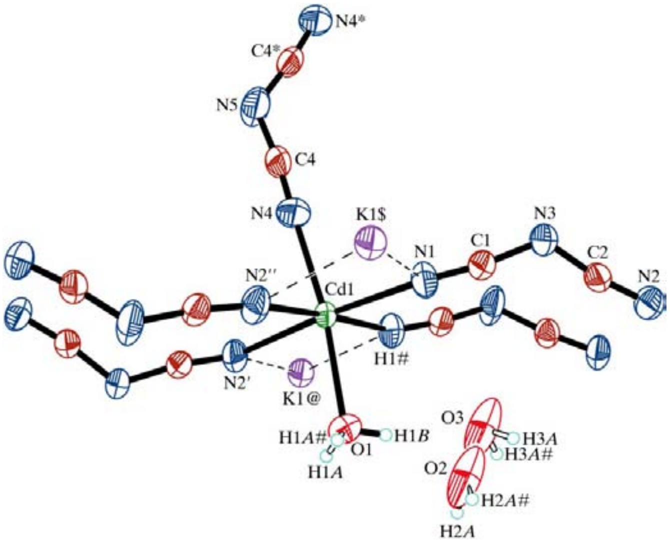

Figure 1
The atom-numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (*) $1 - x, 1 - y, z$; (#) y, x, z; (′) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (″) $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} + z$; ($) $\frac{1}{2} - y, -\frac{1}{2} + x, \frac{1}{2} - z$; (@) $-\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$.]

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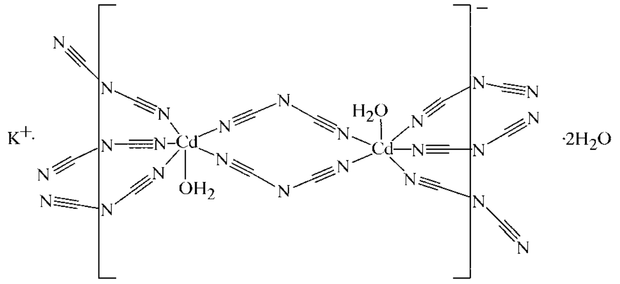
compound is isotypic with the cationic component of $Cu^I_2(pyrazine)_3(SiF_6)$ (MacGillivray *et al.*, 1994).



(I)

The atom-numbering scheme of (I) is illustrated in Fig. 1. The geometry of the dca anions is typical. The nitrile C≡N bond lengths range from 1.127 (4) to 1.145 (2) Å, the amide N—C bond lengths range from 1.277 (3) to 1.298 (2) Å, the C—N—C angles are 123.9 (2) and 124.4 (4)°, and the N≡C—N angles range from 171.7 (2) to 174.3 (3)°. The displacement ellipsoids of the amide N atoms are elongated, indicating a rocking thermal motion of the dca anions. The coordination geometry about the Cd^{II} center is distorted octahedral (site symmetry *m*). Within the equatorial plane, the Cd—N bond lengths are 2.339 (2) and 2.355 (2) Å, and the N—Cd—N angles range from 89.06 (9) to 91.08 (9)° (Table 1). A dca anion is also coordinated to the apical position with a slightly shorter Cd—N bond length of 2.221 (2) Å. The sixth coordination site is occupied by a water molecule, with a Cd—O distance of 2.327 (2) Å. This Cd^{II} coordination geometry is similar to that observed in $Cd(dca)_2(bpno)_2(H_2O)$ (bpno is 4,4′-bipyridine *N*,*N*′-dioxide; Xu *et al.*, 2004). The K^+ cation is coordinated by eight dca nitrile N atoms with four K—N1 contacts of 2.978 (2) Å and four K—N2 contacts of 3.077 (2) Å, forming a twisted cube configuration (site symmetry 222).

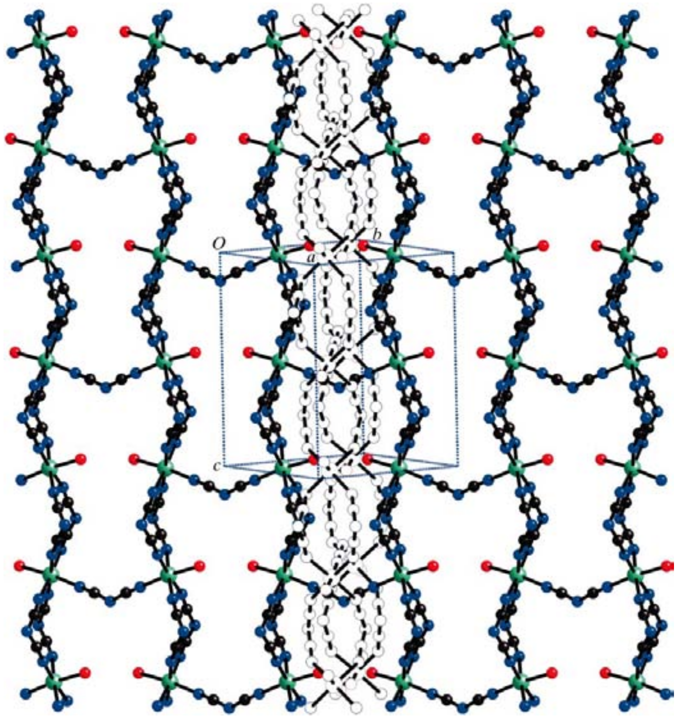


Figure 2
Ball-and-stick representation of the orthogonally interpenetrated (6,3)-nets formed by the $[Cd_2(dca)_5(H_2O)_2]^-$ anions. Two sheets, one parallel to each of the (110) and ($1\bar{1}0$) planes, are illustrated. H atoms have been omitted for clarity.

The Cd^{II} cations are joined into polymeric chains through double $\mu_{1,5}$ bridges that lie along the *c* axis. Along these chains, the Cd···Cd separation is 7.5856 (3) Å. These bibridged chains are linked into layers through single $\mu_{1,5}$ bridges with Cd···Cd separations of 8.4391 (3) Å. The coordinated water molecule is a terminal ligand and hence, the Cd^{II} node is three-connecting. The $[Cd_2(dca)_5(H_2O)_2]^-$ layers form a (6,3) brick-wall motif (Moulton & Zaworotko, 2001). The Cd···Cd separation through the terminal water molecules is 8.3250 (3) Å, slightly shorter than that through the single dca bridges, resulting in a slight constriction in the center of the bricks. Parallel two-dimensional layers are separated by 8.3822 (1) Å. As illustrated in Fig. 2, equivalent sets of anionic layers lie parallel to both the (110) and the ($1\bar{1}0$) planes, resulting in orthogonal interpenetration. The shortest Cd···Cd separations, *viz*. 5.8922 (2) and 5.9729 (2) Å, occur between the interpenetrated sheets.

In addition to the water molecule that is coordinated to Cd, an uncoordinated water molecule resides in cavities formed by the interpenetrated structure. Perhaps as a result of a lack of strong hydrogen-bond acceptor sites within this cavity, the uncoordinated water molecule is disordered between two sites. Refinement of the occupancy of these two sites results in an approximately 2:1 preference of the O2 site over O3. Intermolecular hydrogen bonding between water molecules is apparent in the structure. The H1*B* atomic position on the coordinated water molecule is fully occupied. This H atom forms hydrogen bonds with the O atoms of both locations of the uncoordinated water molecule. By symmetry, atom H1*A* on the coordinated water molecule is disordered over two sites. This H atom forms a hydrogen bond with the O atom of a structurally equivalent water molecule. The H atoms of the uncoordinated water molecules form additional hydrogen bonds, as detailed in Table 2. Impossibly short intermolecular contacts between some of the partially occupied atomic sites imply at least local correlation between disordered components at adjacent sites.

We conclude that alkali metal cations provide a different templating effect for the crystallization of dca-based coordination polymers than has previously been described with organic cations. If similar structures can be crystallized with paramagnetic nodes, a new family of magnetic dca structures may be achieved.

Experimental

$KCd_2(dca)_5(H_2O)_4$ was unexpectedly prepared while following the literature procedure for the synthesis of $K_4Cd(dca)_6$ (Keler *et al.*, 1974). Potassium dicyanamide, K(dca), prepared according to a literature procedure (Van der Werff *et al.*, 2001), was dissolved (315 mg, 3 mmol) in methanol (10 ml) and combined with 10 ml of a methanol solution of cadmium nitrate tetrahydrate (154 mg, 0.5 mmol, Acros). The white precipitate of potassium nitrate was removed by filtration and the remaining solution allowed to evaporate slowly until small colorless crystals formed.

Crystal data

$K[Cd_2(C_2N_3)_5(H_2O)_2]\cdot 2H_2O$
$M_r = 666.21$
Tetragonal, $I\bar{4}2m$
$a = 11.8540$ (2) Å
$c = 15.1708$ (5) Å
$V = 2131.76$ (9) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.24$ mm^{-1}
$T = 298$ (2) K
0.42 × 0.40 × 0.22 mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: integration (*SHELXTL*; Sheldrick, 2001) $T_{\min} = 0.417$, $T_{\max} = 0.624$
10190 measured reflections
1385 independent reflections
1354 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.013$
$wR(F^2) = 0.034$
$S = 1.12$
1385 reflections
99 parameters
26 restraints
Only H-atom coordinates refined
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Absolute structure: Flack (1983), 597 Friedel pairs
Flack parameter: 0.58 (3)

Table 1
Selected geometric parameters (Å, °).

Cd1—N4	2.221 (2)	Cd1—N1	2.3390 (16)
Cd1—O1	2.3270 (19)	Cd1—N2$^{\rm i}$	2.3552 (16)
N4—Cd1—O1	172.29 (8)	N1—Cd1—N2$^{\rm iii}$	89.79 (6)
N4—Cd1—N1	95.65 (7)	N2$^{\rm iii}$—Cd1—N2$^{\rm i}$	91.08 (9)
O1—Cd1—N1	89.84 (6)	N4—Cd1—N2$^{\rm i}$	88.36 (6)
O1—Cd1—N2$^{\rm i}$	86.24 (6)	C1—N1—Cd1	143.21 (16)
N1—Cd1—N1$^{\rm ii}$	89.06 (9)	C2—N2—Cd1$^{\rm iv}$	141.31 (16)
N1—Cd1—N2$^{\rm i}$	175.92 (6)	C4—N4—Cd1	179.2 (3)

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) y, x, z; (iii) $-y+\frac{1}{2}, -x+\frac{1}{2}, z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O1$^{\rm v}$	0.810 (18)	2.10 (2)	2.877 (3)	162 (5)
O1—H1*B*···O2	0.805 (17)	1.76 (2)	2.526 (10)	160 (4)
O1—H1*B*···O3	0.805 (17)	1.948 (19)	2.740 (6)	168 (4)
O2—H2*A*···O2$^{\rm vi}$	0.85 (2)	2.12 (5)	2.59 (4)	115 (3)
O3—H3*A*···N3$^{\rm vii}$	0.848 (18)	2.139 (17)	2.875 (2)	145 (3)

Symmetry codes: (v) $-x, y, -z+1$; (vi) $-x, -y, z$; (vii) $-y+\frac{1}{2}, x-\frac{1}{2}, -z+\frac{1}{2}$.

The positions of the water H atoms were obtained from a difference map and were refined subject to both an O—H DFIX restraint of 0.82 (3) Å and a H···H DANG restraint of 1.30 Å (*SHELXTL*; Sheldrick, 2001). All the H-atom $U_{\rm iso}$ values were constrained to be 1.5 times the $U_{\rm eq}$ value of the carrier atom. The structure was refined as an inversion twin, where the Flack (1983) parameter corresponds to the volume fraction of one of the twin components.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3182). Services for accessing these data are described at the back of the journal.

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