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Synthesis and Rutilelike Structure of [Cd(tcm)(hmt)(H$_2$O)](tcm) (tcm$^-$ = Tricyanomethanide, C(CN)$_3^-$; hmt = Hexamethylenetetramine)

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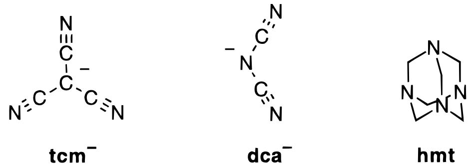
Introduction

We[1] and others[2] have been studying the assembly and the detailed structures of a range of coordination polymers. By the combination of metal centers of known preference regarding coordination geometry with bridging ligands containing various geometrical arrays of metal binding sites, such as linear 2-connectors, trigonal 3-connectors, and tetrahedral or square planar 4-connectors, the ultimate aim is to be able to control the structure of the coordination polymer formed. An alternative means of linking building blocks together, in a manner that, in principle, is controllable, is provided by hydrogen bonding, an approach to constructing 2D and 3D networks that has been actively pursued in recent years.[3]

Of the readily accessible 3-connecting ligands, one of the simplest is the tricyanomethanide anion, tcm$^-$, C(CN)$_3^-$ (see Chart 1). We have been studying the coordination polymers formed by this and the related ligand dicyanamide anion, dca$^-$, N(CN)$_2^-$. The structures of M(tcm)$_2$ (M = Cr^{II}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Hg^{II}) are all isomorphous and contain two independent and equivalent 3D networks each having a connectivity, or topology, identical to that seen in the prototype rutile, that are entangled with each other.[1b,4,5] They display weak antiferromagnetic coupling.[6] The structures of M(dca)$_2$ (M = Co^{II}, Ni^{II}, Cu$^{II)}$ are also isomorphous and contain a single network with the rutilelike topology.[7] The Co^{II} and Ni^{II} derivatives display ferromagnetic coupling, while the Cu^{II} derivative is a near-paramagnet.

Chart 1



tcm$^-$ **dca$^-$** **hmt**

Although a number of compounds containing metal centers coordinated by both tcm$^-$ and *monodentate* coligands have been structurally characterized,[8] few that involve *bridging* coligands have been studied. Ag(tcm), which contains layers of two interpenetrating hexagonal sheets, upon reaction with linear 2-connecting bridging ligands such as pyrazine, 4,4′-bipyridine, dabco, phenazine, 1,4-bis(4-pyridyl)ethene, and tetramethylpyrazine, gives new types of 3D framework structures.[5,9] The structure of Cd(tcm)(B(OMe)$_4$)·*x*MeOH contains 3-connecting tcm$^-$ anions and bridging, chelating B(OMe)$_4^-$ anions.[10] We report here the synthesis and structure of [Cd(tcm)(hmt)(H$_2$O)](tcm) (**1**), hmt = hexamethylenetetramine, which curiously displays the same rutilelike topology seen in the parent M(tcm)$_2$ compounds and their M(dca)$_2$ relatives, but now one-sixth of the linkages between 3-connecting and 6-connecting centers involve hydrogen bonding, the others being of the coordinative type.

Experimental Section

Materials. Cd(NO$_3$)$_2$·4H$_2$O and hexamethylenetetramine were purchased from BDH and Ajax, respectively, and used without further purification. (Me$_4$N)(tcm) was obtained by combining concentrated aqueous solutions of (Me$_4$N)Cl (BDH) and K(tcm).[11]

Preparation of [Cd(tcm)(hmt)(H$_2$O)](tcm) (1). A solution obtained by adding Cd(NO$_3$)$_2$·4H$_2$O (200 mg, 0.65 mmol) in 3 mL of H$_2$O and hexamethylenetetramine (91 mg, 0.65 mmol) in 2 mL of H$_2$O to (Me$_4$N)(tcm) (213 mg, 1.30 mmol) in 5 mL of H$_2$O deposited large colorless crystals of **1** after 5 h (195 mg, 0.43 mmol, 66% yield). IR data (Biorad FTS 165 spectrophotometer, KBr disk): ν (cm^{-1}) 3232 (br), 2582 (w), 2542 (w), 2489 (w), 2456 (w), 2205 (s), 2172 (s), 2159 (s), 1688 (m), 1492 (w), 1464 (m), 1396 (w), 1384 (m), 1339 (w), 1326 (w), 1294 (w), 1241 (s), 1227 (s), 1060 (w), 1056 (w), 1025 (s), 1014 (s), 1002 (s), 986 (s), 928 (m), 835 (w), 812 (m), 792 (w), 773 (w), 702 (m), 692 (m), 663 (m), 560 (m), 514 (m), 499 (w). Anal. Calcd for C$_{14}$H$_{14}$N$_{10}$OCd: C, 37.30; H, 3.14; N, 31.08. Found: C, 37.06; H, 2.87; N, 30.91.

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Table 1. Crystallographic Data for **1**

chem formula: $CdC_{14}H_{14}N_{10}O$	space group $P2_1/c$ (No. 14)
$a = 11.994(2)$ Å	$T = 22$ °C
$b = 12.367(2)$ Å	$\lambda = 0.710\,69$ Å
$c = 12.552(3)$ Å	$\rho_{calcd} = 1.794$ g cm^{-3}
$\beta = 116.36(1)°$	$\mu = 13.01$ cm^{-1}
$V = 1668.3$ Å^3	$R(F_o)^a = 0.0416$
$Z = 4$	$R_w(F_o)^b = 0.0441$
fw = 450.78	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|]$.

Table 2. Fractional Atomic Coordinates and Equivalent Displacement Parameters for Non-Hydrogen Atoms in **1**

atom	x/a	y/b	z/c	U_{eq}, Å^2
Cd1	$^1/_2$	0	$^1/_2$	0.0168(3)
Cd2	0	0	0	0.0184(3)
C1	0.2539(6)	−0.1538(5)	0.0745(5)	0.025(2)
N1	0.1534(6)	−0.1230(5)	0.0305(5)	0.033(2)
C2	0.4464(6)	−0.1343(5)	0.2494(5)	0.021(2)
N2	0.4952(6)	−0.0877(5)	0.3372(5)	0.033(2)
C3	0.4312(6)	−0.2689(5)	0.1021(5)	0.021(2)
N3	0.4751(5)	−0.3377(5)	0.0718(5)	0.033(2)
C4	0.3786(6)	−0.1852(5)	0.1386(5)	0.022(2)
C5	0.4962(7)	0.0866(6)	0.1297(7)	0.039(2)
N5	0.3912(6)	0.1007(6)	0.0964(6)	0.054(2)
C6	0.7020(6)	0.1566(6)	0.1796(6)	0.033(2)
N6	0.7673(6)	0.2279(5)	0.1880(6)	0.049(2)
C7	0.6758(7)	−0.0354(7)	0.2046(7)	0.041(2)
N7	0.7209(6)	−0.1176(6)	0.2341(7)	0.060(2)
C8	0.6245(6)	0.0693(6)	0.1709(6)	0.033(2)
N11	0.0877(5)	0.0399(4)	0.2134(5)	0.019(2)
C10	0.2224(6)	0.0167(5)	0.2753(5)	0.020(1)
C11	0.0254(6)	−0.0308(5)	0.2692(6)	0.024(2)
C12	0.0694(6)	0.1555(5)	0.2382(5)	0.022(2)
N12	0.2781(5)	0.0362(4)	0.4059(4)	0.017(1)
C13	0.2087(6)	−0.0347(6)	0.4543(5)	0.023(2)
C14	0.2517(5)	0.1511(5)	0.4240(6)	0.025(2)
N13	0.0747(5)	−0.0106(4)	0.3975(5)	0.026(1)
N14	0.1178(5)	0.1757(4)	0.3664(5)	0.023(1)
C15	0.0556(6)	0.1031(6)	0.4164(6)	0.028(2)
O1	0.1320(4)	0.1287(4)	−0.0096(4)	0.031(2)

X-ray Structure Determination of 1. Crystal parameters and details of the data collection and refinement are given in Table 1 (for full details see the Supporting Information). A clear, colorless crystal was mounted on a glass fiber on an Enraf-Nonius CAD-4F diffractometer with graphite-monochromated Mo Kα radiation, and the unit cell parameters were determined by least-squares refinement of 25 reflections. A total of 5184 reflection data (3929 unique, $R_{int} = 0.0411$) were collected using the $\omega-2\theta$ scan method ($2 \leq 2\theta \leq 60°$). Corrections for absorption effects were applied to the data. The structure was solved using direct methods (SHELX-86),[12] and refinement was achieved using SHELX-76.[13] All hydrogen atoms were found in subsequent difference maps, and all hmt hydrogens were assigned to calculated positions (C−H = 1.08 Å) and refined with a common isotropic thermal parameter. The water hydrogens were fixed such that the H···H distance was 1.63 times the O−H distance. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Atomic positions and equivalent displacement parameters for all non-hydrogen atoms are given in Table 2, and selected bond distances and angles are given in Table 3.

Results and Discussion

The structure is most simply described by focusing initially on chains that can be discerned and then seeing how these chains are linked to produce the overall rutilelike 3D topology. Each chain contains two types of octahedral cadmium atoms which alternate along its length. The atom numbering and the detailed coordination spheres for Cd1 and Cd2 are shown in Figure 1. Cd1 is coordinated to two trans hmt ligands and to four tcm$^-$ ions. Cd2 is coordinated to two trans tcm$^-$ ions, to two trans hmt ligands, and to two trans water ligands. Both metals are located on centers of symmetry.

As can be seen from Figure 1a,b taken together, chains consisting of alternating Cd1 and Cd2 are formed. The links between adjacent metals in the chain consist of one bridging tcm$^-$ and one bridging hmt.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Cd1−N2	2.292(6)	Cd1−N3^{III}	2.274(6)
Cd1−N12	2.426(5)	Cd2−N1	2.285(6)
Cd2−O1	2.286(5)	Cd2−N11	2.454(6)
N14···O1^{I}	2.840(7)	N5···O1	2.808(8)
N2−Cd1−N12	93.8(2)	N2−Cd1−N3^{IV}	88.9(2)
N12−Cd1−N3^{IV}	92.7(2)	N1−Cd2−O1	87.0(2)
N1−Cd2−N11	91.6(2)	O1−Cd2−N11	86.9(2)
C3^{III}−N3^{III}−Cd1	160.7(7)	C2−N2−Cd1	153.4(6)
C1−N1−Cd2	154.1(6)	N5···O1−Cd2	122.4(2)
N14···O1−Cd2	138.4(2)		

[a] Symmetry operations: (I): $x, {}^1/_2 - y, {}^1/_2 + z$; (II) $1 - x, -y, 1 - z$; (III) $1 - x, {}^1/_2 + y, {}^1/_2 - z$; (IV) $x, -{}^1/_2 - y, {}^1/_2 + z$; (V) $-x, -y, -z$; (VI) $x, {}^1/_2 - y, z - {}^1/_2$; (VII) $-x, y - {}^1/_2, {}^1/_2 - z$.

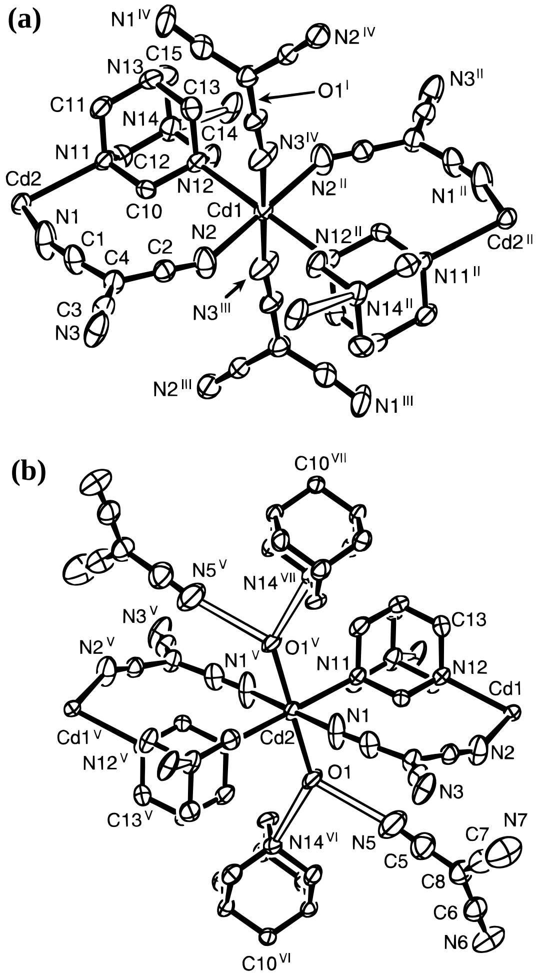

Figure 1. Metal ion geometry and atom-numbering scheme for **1** (thermal ellipsoids at 50% probability levels) for the two types of cadmium. Open bonds represent hydrogen-bonding interactions.

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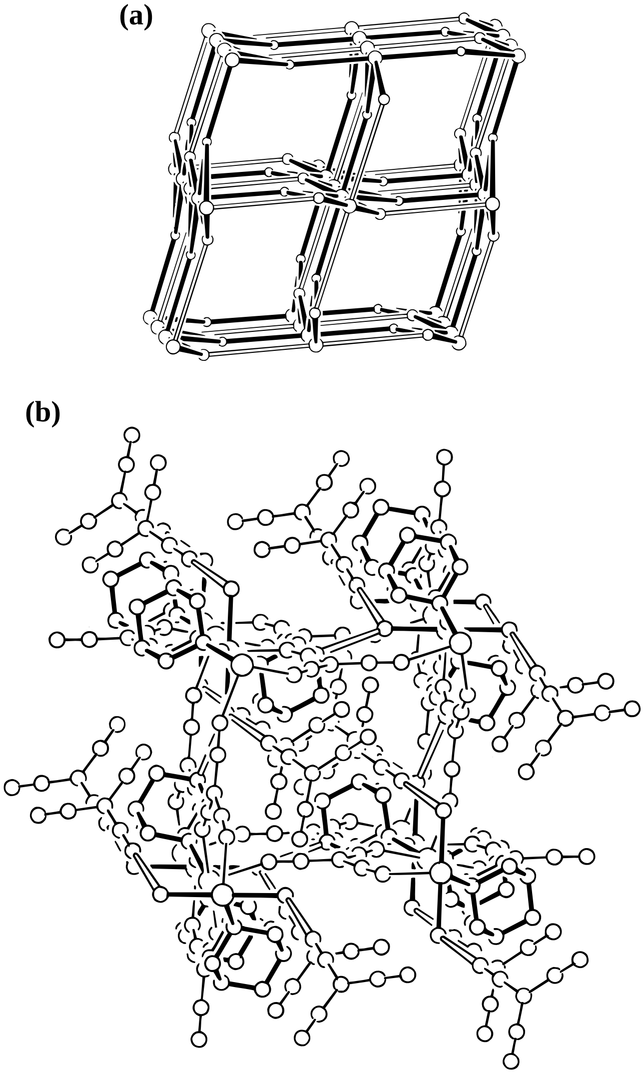

Figure 2. (a) Schematic representation of the rutilelike network topology in **1**. Large circles represent the cadmium atoms. The smallest circles represent the trigonal carbons of the tcm1 anion. Circles of intermediate size represent the 3-connecting nodes located at the midpoint of the three nitrogen atoms of the hmt ligands that are involved in the network connectivity. Coordinative bonding connections are represented by solid lines, and hydrogen bonding connections by open bonds. (b) One of the four channels seen in (a) with all non-hydrogen atoms included, seen from the same angle. For clarity, the tcm anions are shown with thin connections, hmt ligands with thick connections, and hydrogen-bonding interactions with open bonds.

Two unique tcm^- ions are present. The first, tcm1 (containing N1, N2, and N3), provides the bridging via N2−Cd1 and N1−Cd2 coordinate bonds to generate the chains. The third nitrogen of tcm1, N3, coordinates to a Cd1 of an adjacent chain (see Figure 1) and because the metals are located at centers of symmetry each Cd1 is linked in this way to two adjacent chains, establishing a 3D connectivity.

The second type of tcm^-, tcm 2 (containing N5, N6, and N7 in Figure 1), is essentially ionic and is hydrogen bonded to a water molecule coordinated to Cd2 but does not contribute to the connectivity of the 3D net.

All hmt ligands are equivalent. They participate in the chains, as can be seen in Figure 1a,b, by N12−Cd1 and N11−Cd2 coordinate bonds but, in addition, are involved in hydrogen bonding via N14 to a water molecule coordinated to Cd2 of an adjacent chain. In this way both hmt and tcm1 can be seen to act as 3-connectors in the 3D net.

Figure 2a shows the rutilelike connectivity of the 3D net in which 3-connecting tcm1 nodes are represented by the smallest circles, 3-connecting hmt nodes by circles of intermediate diameter, and 6-connecting Cd centers of both types by the largest circles. In Figure 2a the “open” connections between 6-connecting Cd nodes and 3-connecting hmt nodes represent the Cd2−O1−H14···N14 hydrogen-bonded linkages whereas the heavy bold connections represent coordinative linkages. The linear chains containing alternating Cd1···Cd2···Cd1···Cd2··· chains are seen in Figure 2 almost perpendicular to the page. Figure 2b shows all the non-hydrogen atoms in the structure seen from the same angle as the simplified schematic representation in Figure 2a. Comparison of Figure 2b, which at first sight appears complicated, with Figure 2a affords a simple appreciation of the rutilelike connectivity and the geometry.

The rutile topology has now been seen not only in the “binary” $M(tcm)_2$ and $M(dca)_2$ series of compounds as mentioned in the Introduction but also in $[Cd\{Cd(CN)_3(Him)\}_2]\cdot$ p-$C_6H_4Me_2$ (Him = imidazole)[14] and is beginning to emerge as an important and increasingly prevalent motif for coordination polymers containing 3-connecting and 6-connecting centers in the ratio 2:1. An alternative possible topology, however, is seen in the structure of $Hg(tpt)_2(ClO_4)_2(C_2H_2Cl_4)_6$ (tpt = 2,4,6-tri-(4-pyridyl)-1,3,5-triazine.[15]

Supporting Information Available: Text describing X-ray procedures and listings of crystallographic data and refinement details, atomic positions and thermal parameters, bond lengths and angles, and equations of mean planes (11 pages). Ordering information is given on any current masthead page.

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