Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

A novel two-dimensional network cadmium(II) coordination polymer containing one 1,4-bis(1,2,4-triazol-1-yl)butane and double dicyanamide bridges

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Received 11 October 2005
Accepted 18 November 2005
Online 10 December 2005

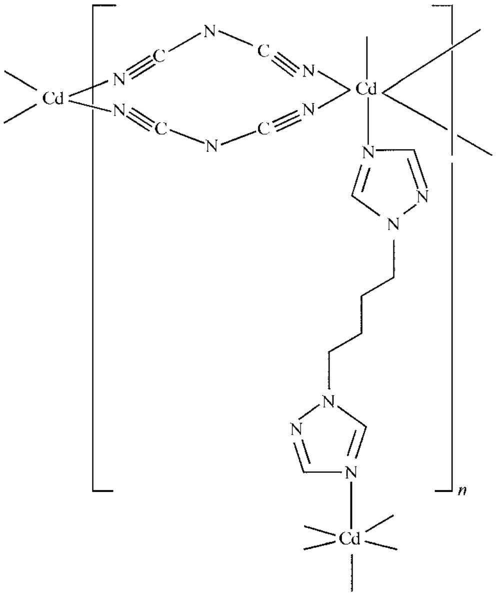
In the crystal structure of the title complex, poly[μ-1,4-bis(1,2,4-triazol-1-yl)butane-di-μ-1,5-dicyanamido-cadmium(II)], $[Cd(C_2N_3)_2(C_8H_{12}N_6)]_n$ or $[Cd(dca)_2(btb)]_n$, where dca is dicyanamide and btb is 1,4-bis(1,2,4-triazol-1-yl)butane, each Cd^{II} atom occupies a center of symmetry and is in a six-coordinated distorted octahedral environment. Four N atoms from four dca ligands fill the equatorial positions, and two N atoms from two btb ligands occupy the axial positions. The dca ligands adopt an end-to-end coordination mode and link the Cd^{II} atoms to form a 12-membered $Cd(dca)_2Cd$ ring, and neighboring rings extend along the *b* axis to form a $[Cd(dca)_2]_n$ chain. The btb ligands, acting as bridging bidentate ligands, link the Cd^{II} atoms of adjacent one-dimensional $[Cd(dca)_2]_n$ chains, forming a rhombic two-dimensional network.

Comment

Metal coordination polymers with multidimensionality have attracted much interest in coordination chemistry because of their intriguing structural topologies and their interesting applications as functional materials (Batten & Robson, 1998; Blake *et al.*, 1999).

The structural motifs of coordination polymers depend on several factors, such as the central atom, the performance of the ligands, the counter-ions, the solvent systems and the reaction conditions. The ligand is no doubt the key factor for manipulating the topologies of coordination polymers. A flexible ligand, which can adopt various conformations, may induce coordination polymers with novel topologies or supramolecular isomers (Carlucci *et al.*, 2004; Li *et al.*, 2005).

The dicyanamide ligand, $[N(CN)_2]^-$, is a remarkably versatile building block for the construction of coordination polymers (Riggio *et al.*, 2001; Li *et al.*, 2003). However, there are relatively few structurally characterized cadmium(II) dicyanamide complexes (Luo, Hong, Cao *et al.*, 2002; Luo, Hong, Weng *et al.*, 2002; Luo *et al.*, 2003; Gao *et al.*, 2002). The combination of the flexible ligand 1,4-bis(1,2,4-triazol-1-yl)butane (btb) and dicyanamide (dca) can give rise to novel motifs. In the present work, we report the crystal structure of a novel two-dimensional network polymer, *viz.* $[Cd(dca)_2(btb)]_n$, (I).



(I)

The structure of (I) consists of uniform neutral chains in which neighboring Cd^{II} atoms are connected through two end-to-end dca bridges, and btb ligands link the chains forming a two-dimensional network (Fig. 1). Each Cd^{II} atom occupies a center of symmetry. The Cd^{II} atom has a distorted octahedral coordination geometry, being coordinated by four N atoms of four dca ligands in the equatorial plane and two N atoms of the triazole rings of two btb ligands in the axial positions. This coordination environment is similar to those observed in $[Cd(dca)_2(bpp)]_n$, (II) [bpp is 1,3-bis(4-pyridyl)propane; Gao *et al.*, 2002], and $[Cd(dca)_2(dadpm)]_n$ (dadpm is 4,4′-methylenedianiline; Luo *et al.*, 2003). The N—Cd—N

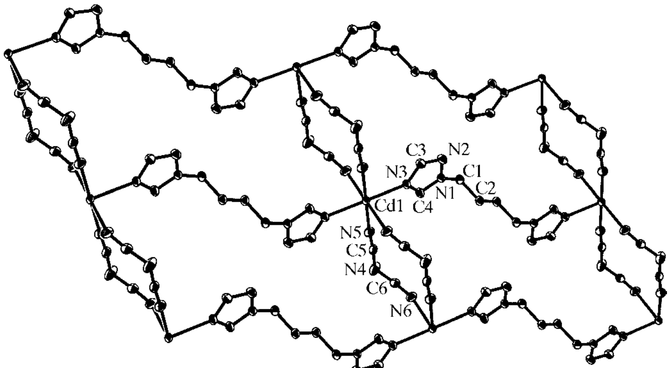


Figure 1
The two-dimensional network of (I), with displacement ellipsoids drawn at the 50% probability level and all atoms of the asymmetric unit labeled. H atoms have been omitted for clarity.

DOI: 10.1107/S0108270105038102

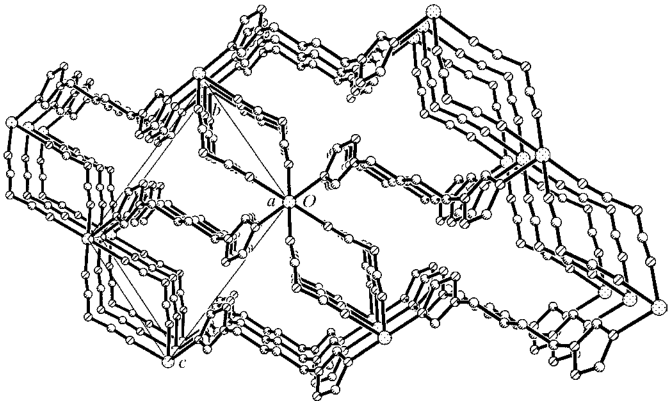


Figure 2
A view of the stacked sheets along the *a* axis in (I).

bond angles are in the range 88.71 (6)–91.29 (6)°, close to 90°. The Cd—N_{dca} and Cd—N_{btb} bond lengths (Table 1) in (I) are similar to corresponding values reported in $[Cd(dca)_2(bpp)]_n$ and $[Cd(dca)_2(dadpm)]_n$.

The dca ligand adopts an end-to-end coordination mode. Two dca ions link two Cd^{II} atoms to form a 12-membered $Cd(dca)_2Cd$ ring, and neighboring rings share Cd^{II} atoms to form a $[Cd(dca)_2]_n$ chain along the *b* axis. The shortest Cd···Cd distance in these chains is 7.627 (2) Å, corresponding to the *b*-axis translation, and is similar to the corresponding distances in $[Cd(dca)_2(dadpm)]_n$ (7.597 Å; Luo *et al.*, 2003) and $[Cd(dca)_2(pyridine)_2]_n$ (7.67 Å; Luo, Hong, Weng *et al.*, 2002).

Free dca possesses C_{2v} symmetry, while the dca ligand in (I) possesses pseudo-C_{2v} symmetry, with nitrile C—N bond lengths of 1.146 (3) (for N5—C5) and 1.152 (3) Å (for N6—C6). The C5—N4—C6 bond angle is 121.75 (19)°, corresponding to an amide N atom with sp^2-hybrid orbitals; the N5—C5—N4 and N6—C6—N4 angles are 173.1 (2) and 172.8 (2)°, respectively, corresponding to atoms N5, C5, C6 and N6 having *sp* hybridization.

Each btb ligand has an extended geometry in which the $N(CH_2)_4N$ chain has an all-*anti* geometry and has its plane steeply inclined, by 80.0 (2)°, to the triazole ring planes. The r.m.s. deviation of the triazole ring atoms from the mean plane is 0.0031 (11) Å.

The btb ligands, acting as bridging bidentate ligands, link the Cd^{II} atoms of adjacent one-dimensional $[Cd(dca)_2]_n$ chains, resulting in a rhombic two-dimensional network. The shortest Cd···Cd distance between Cd atoms separated by a btb ligand is 14.304 (3) Å. The two-dimensional sheets are stacked in parallel along the *a* axis (Fig. 2). The shortest Cd···Cd distance between adjacent sheets is 6.424 (2) Å, corresponding to the *a*-axis translation.

Although some interesting Cd^{II}–dca complexes have been reported, a Cd^{II}–dca complex forming such a two-dimensional network has not been observed previously. For example, the structure of (II) consists of uniform sinusoidal chains in which adjacent Cd atoms are triply linked by two dca and one bpp bridge. The intrachain cadmium–cadmium separation in (II) is 7.26 Å, shorter than the value of 7.627 (2) Å in (I).

Experimental

A water–methanol solution (20 ml, 1:1 *v*/*v*) of btb (0.096 g, 0.50 mmol) and Na(dca) (0.089 g, 1.0 mmol) was added to one leg of a H-shaped tube, and a water–methanol solution (20 ml, 1:1 *v*/*v*) of $Cd(NO_3)_2\cdot 4H_2O$ (0.155 g, 0.5 mmol) was added to the other leg of the tube. Colorless crystals suitable for X-ray analysis were obtained after about two months. The product is stable in an ambient atmosphere and insoluble in most common inorganic and organic solvents. Analysis found: C 32.95, H 2.73, N 38.42%; calculated for $C_{12}H_{12}CdN_{12}$: C 33.00, H 2.77, N 38.49%.

Crystal data

$[Cd(C_2N_3)_2(C_8H_{12}N_6)]$
M_r = 436.75
Triclinic, $P\bar{1}$
a = 6.4236 (17) Å
b = 7.627 (2) Å
c = 9.814 (3) Å
α = 104.424 (6)°
β = 96.634 (2)°
γ = 108.810 (5)°
V = 430.6 (2) Å^3

Z = 1
D_x = 1.684 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 2027 reflections
θ = 3.1–25.4°
μ = 1.29 mm^{-1}
T = 193 (2) K
Block, colorless
0.34 × 0.22 × 0.16 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.668, T_{max} = 0.820
4239 measured reflections

1565 independent reflections
1561 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 25.4°
h = −7 → 7
k = −9 → 8
l = −11 → 11

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.045
S = 1.04
1565 reflections
116 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 0.1146P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N3	2.2985 (16)	N5—C5	1.146 (3)
Cd1—N5	2.3210 (17)	N6—C6	1.152 (3)
Cd1—N6^i	2.3867 (18)		
N3—Cd1—N5	89.50 (6)	N1—C1—C2	113.45 (15)
N3—Cd1—N6^i	89.74 (6)	N5—C5—N4	173.1 (2)
N5—Cd1—N6^i	91.29 (6)	N6—C6—N4	172.8 (2)
C6—N4—C5	121.75 (19)		

Symmetry code: (i) *x*, *y* − 1, *z*.

H atoms were placed in idealized positions and refined as riding, with C—H distances of 0.95 (triazole) and 0.99 Å (butane), and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Fund of the Key Laboratory of Organic Synthesis of Jiangsu Province, People's Republic of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1270). Services for accessing these data are described at the back of the journal.

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