

**Yong Zhang, Zhao-Hui Wang,
 Yu-Ping Zhang and Bao-Long Li***

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, People's Republic of China

Correspondence e-mail:
 bli1965@pub.sz.jsinfo.net

Key indicators

Single-crystal X-ray study
 T = 193 K
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 Disorder in main residue
 R factor = 0.020
 wR factor = 0.054
 Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

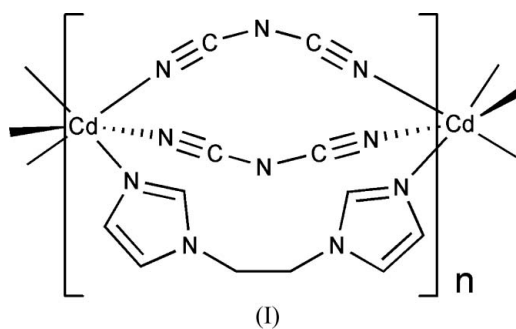
A novel triple-stranded cadmium(II) polymer chain: catena-poly[cadmium(II)- μ -1,2-bis(imidazol-1-yl)ethane- $\kappa^2\text{N}^3:\text{N}^{3'}$ -di- μ -1,5-dicyanamido- $\kappa^4\text{N}^1:\text{N}^5$]

In the crystal structure of the title complex, $[\text{Cd}(\text{C}_2\text{N}_3)_2(\text{C}_8\text{H}_{10}\text{N}_4)]_n$ or $[\text{Cd}(\text{dca})_2(\text{bim})]_n$, where dca is dicyanamide and bim is 1,2-bis(imidazol-1-yl)ethane, each Cd^{II} atom is in a distorted octahedral environment. Four N atoms from four dca ligands occupy the equatorial positions, and two N atoms from two bim ligands occupy the axial positions. Each Cd^{II} atom is situated at a center of symmetry, and a twofold axis runs through the mid-points of the bim exocyclic C—C bond and the $\text{Cd}\cdots\text{Cd}$ vector. The structure consists of chains in which neighboring Cd^{II} atoms are connected through one bim and two end-to-end dca bridges.

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Comment

Recently, the design and synthesis of coordination polymers have been an area of rapid growth, because of their intriguing structural topologies and their interesting applications in the areas of magnetic, optical and electronic properties (Batten & Robson, 1998; Blake *et al.*, 1999). When rigid bifunctional ligands are used as a spacer to connect metal centers, the topology of the network is usually determined by the coordination geometry of the central metal. In contrast to a rigid spacer, a flexible ligand, which can adopt various conformations, may yield coordination polymers with novel topologies. However, the flexible ligand 1,2-bis(imidazol-1-yl)ethane (bim) has not been well studied to date (Wu *et al.*, 1997; Li *et al.*, 2004).



The dicyanamide ligand, $[\text{N}(\text{CN})_2]^-$, is also a remarkably versatile building block for the construction of coordination polymers, since it can act in mono-, bi- or tridentate coordination modes (Riggio *et al.*, 2001; Li *et al.*, 2002). However, the structurally characterized cadmium(II) dicyanamide complexes are relatively few (Luo, Hong, Cao *et al.*, 2002; Luo, Hong, Weng *et al.*, 2002; Luo *et al.*, 2003; Gao *et al.*, 2002). The combination of bim and dicyanamide (dca) can give rise to novel motifs. In the present work, we report the crystal structure of a triple-stranded chain polymer, *viz.* $[\text{Cd}(\text{dca})_2-$

(bim)]_n, (I), which has been synthesized with a combination of bim and dca ligands.

Fig. 1 shows the coordination about the cadmium(II) center in (I). The structure of (I) consists of chains in which neighboring Cd^{II} atoms are connected through one bim and two end-to-end dca bridges (Fig. 2). Each Cd^{II} atom is situated at a center of symmetry, and a twofold axis runs through the mid-points of the bim exocyclic C—C bond and the Cd···Cd vector. The coordination geometry of the Cd^{II} atom is distorted octahedral, being coordinated by four N atoms of four symmetry-related dca ligands in the equatorial plane and two N atoms of the imidazole rings of two symmetry-related bim ligands at the axial positions. This coordination environment is similar to those observed in [Cd(dca)₂(bpp)]_n [bpp is 1,3-bis(4-pyridyl)propane; Gao *et al.*, 2002] and [Cd(dca)₂(dadpm)]_n (dadpm is 4,4'-diaminodiphenylmethane; Luo *et al.*, 2003). The N—Cd—N bond angles are in the range 88.39 (7)–91.61 (7)°. The Cd—N_{dca} and Cd—N_{bim} bond lengths (Table 1) in (I) are similar to corresponding values reported in [Cd(dca)₂(bpp)]_n [Cd—N_{dca} = 2.325 (3) and 2.331 (3) Å; Cd—N_{bpp} = 2.317 (3) Å] and [Cd(dca)₂(dadpm)]_n [Cd—N_{dca} = 2.31 (1) and 2.33 (1) Å; Cd—N_{dadpm} = 2.39 (1) Å].

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 the neighboring rings share Cd^{II} atoms to form a [Cd(dca)₂]_n chain. Similar one-dimensional chains with double dca bridges have been reported. The chains are usually linear, with the *M*(dca)₂*M* rings being flat or in a slight chair conformation. In (I), the Cd(dca)₂Cd rings are bent into an unusual boat conformation and result a sinusoidal chain. As a consequence of the bend, the Cd···Cd distances separated by dca are 7.284 (2) Å; this is shorter than the corresponding distances of 7.597 Å in [Cd(dca)₂(dadpm)]_n (Luo *et al.*, 2003) and 7.67 Å in [Cd(dca)₂(pyridine)₂]_n (Luo, Hong, Weng *et al.*, 2002).

The bim ligand acts as an additional intra-chain bridge connecting neighboring Cd^{II} atoms, without increasing the dimensionality. This behavior of bim is different from that of the rigid ligand 4,4'-bipyridine, which would act as inter-chain bridges to increase the dimensionality (Jensen *et al.*, 2002; Martin *et al.*, 2002). The r.m.s. deviation of the imidazole ring atoms from the mean plane is 0.0002 Å. The bridging bim molecule exhibits a *gauche* conformation. The dihedral angle between the two imidazole ring planes of bim is 48.3 (1)° and the torsion angle N1—C4—C4ⁱ—N1ⁱ is –79.1 (3)°. The C—C and C—N bond distances within the bim ligand are in agreement with those of the ligand in its metal complexes (Wu *et al.*, 1997; Li *et al.*, 2004).

The free dca ligand possesses C_{2v} symmetry, while dca in (I) is disordered. Occupancy factors of 0.50 were assigned to the disordered amide atoms N4A and N4B. The nitrile C—N bond lengths and the angles within the dca ligand (Table 1) are consistent with the expected hybridization of the atoms.

The chains extend along the crystallographic *c* axis and the intra-chain cadmium–cadmium separation is 7.284 (2) Å, corresponding to half of the *c* axis translation. Parallel chains stack along the *b* axis such that the convex bim bow of one

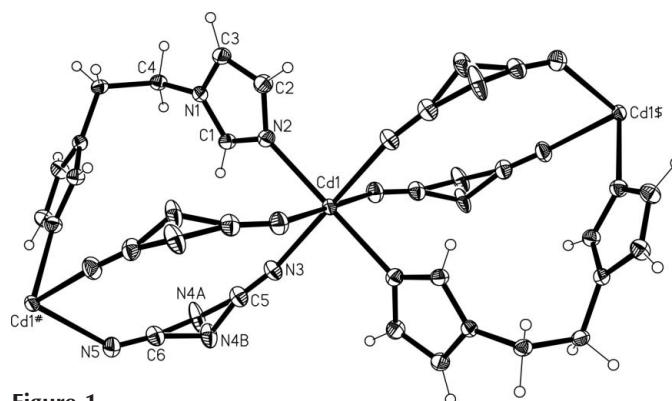


Figure 1
A view of (I), showing the coordination of the Cd^{II} atom, with displacement ellipsoids drawn at the 50% probability level. Both disorder components of the dca ligands are shown. [Symmetry codes: (\$) 1 – *x*, *y*, $\frac{1}{2}$ – *z*; (#) 1 – *x*, *y*, $\frac{3}{2}$ – *z*.]

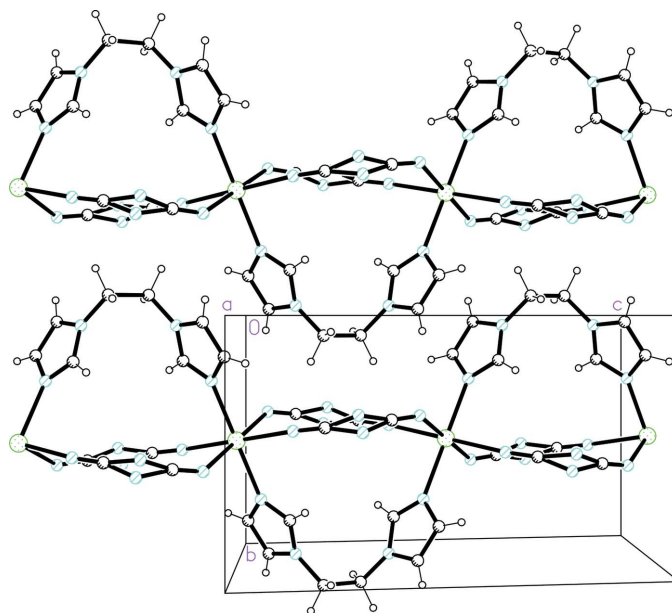


Figure 2
View, along the *a* axis, of the triple-stranded chains in (I). Both disorder components of the dca ligands are shown.

chain extends into the concave bay of the neighboring chain (Fig. 2). The shortest interchain metal–metal distance along the *b* direction is 8.499 (2) Å, corresponding to the *b* axis translation. Parallel chains also stack along the *a* direction through weak hydrogen-bond interactions between the uncoordinated amide N atom of dca and the H atom of the ethane group of a neighboring chain [C4—H4A···N4A($\frac{3}{2}$ – *x*, $-\frac{1}{2}$ + *y*, $\frac{3}{2}$ – *z*; Table 2 and Fig. 3)]. The shortest inter-chain metal–metal distance along the *a* axis is 7.670 (2) Å. Although a number of the chain complexes were synthesized, such uniform triple-stranded chain complexes containing double bridging dca are relatively few. One example is [Cd(dca)₂(bpp)]_n, (II) [bpp is 1,3-bis(4-pyridyl)propane; Gao, *et al.*, 2002]. The structure of (II) consists of uniform sinusoidal chains in which adjacent Cd atoms are triply linked by two dca and one bpp bridges. The intra-chain cadmium–cadmium separation of (II) is 7.26 Å, corresponding to a value of

7.284 (2) Å in (I). Two other examples are [Zn(dca)₂(bpp)]_n (Gao *et al.*, 2003) and [Cu(dca)₂(bpa)]_n (bpa is 1,2-bis(4-pyridyl)ethane; Carranza *et al.*, 2002).

Experimental

An H₂O/CH₃OH solution (20 ml, 1:1 v/v) of bim (0.081 g, 0.50 mmol) and Na(dca) (0.089 g, 1.0 mmol) was added to one leg of an H-shaped tube and an H₂O/CH₃OH solution (20 ml, 1:1 v/v) of Cd(NO₃)₂·4H₂O (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 the ambient atmosphere and insoluble in most common inorganic and organic solvents. Analysis found: C 35.41, H 2.42, N 34.32%; calculated for C₁₂H₁₀CdN₁₀: C 35.44, H 2.48, N 34.45%.

Crystal data

[Cd(C₂N₃)₂(C₈H₁₀N₄)]
M_r = 406.71
 Monoclinic, *C2/c*
a = 12.770 (3) Å
b = 8.4986 (17) Å
c = 14.568 (3) Å
 β = 100.162 (6)°
V = 1556.2 (6) Å³
Z = 4

D_x = 1.736 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 3014 reflections
 θ = 3.1–25.4°
 μ = 1.42 mm⁻¹
T = 193 (2) K
 Block, colorless
 0.40 × 0.30 × 0.11 mm

Data collection

Rigaku Mercury CCD diffractometer
 ω scans
 Absorption correction: multi-scan (North *et al.*, 1968)
T_{min} = 0.601, *T_{max}* = 0.860
 7367 measured reflections

1424 independent reflections
 1339 reflections with *I* > 2σ(*I*)
R_{int} = 0.019
 θ_{max} = 25.3°
h = -15 → 15
k = -9 → 10
l = -17 → 17

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.020
wR(*F*²) = 0.054
S = 1.06
 1424 reflections
 116 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0312*P*)² + 1.6119*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.37 e Å⁻³
 Δρ_{min} = -0.36 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cd1—N2	2.2769 (17)	N3—C5	1.133 (3)
Cd1—N3	2.331 (2)	N5—C6	1.139 (3)
Cd1—N5 ⁱ	2.3900 (19)		
N2—Cd1—N3	89.26 (7)	N3—C5—N4 <i>B</i>	165.7 (4)
N2—Cd1—N5 ⁱⁱ	91.26 (6)	N3—C5—N4 <i>A</i>	167.1 (5)
N3—Cd1—N5 ⁱⁱ	88.39 (7)	N5—C6—N4 <i>A</i>	167.2 (5)
C6—N4 <i>A</i> —C5	116.0 (7)	N5—C6—N4 <i>B</i>	165.8 (5)
C5—N4 <i>B</i> —C6	115.3 (7)		

Symmetry codes: (i) -*x* + 1, *y*, -*z* + 3/2; (ii) *x*, -*y* + 1, *z* - 1/2.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4 <i>A</i> ...N4 <i>A</i> ⁱⁱⁱ	0.99	2.50	3.414 (10)	154

Symmetry code: (iii) -*x* + 3/2, *y* - 1/2, -*z* + 3/2.

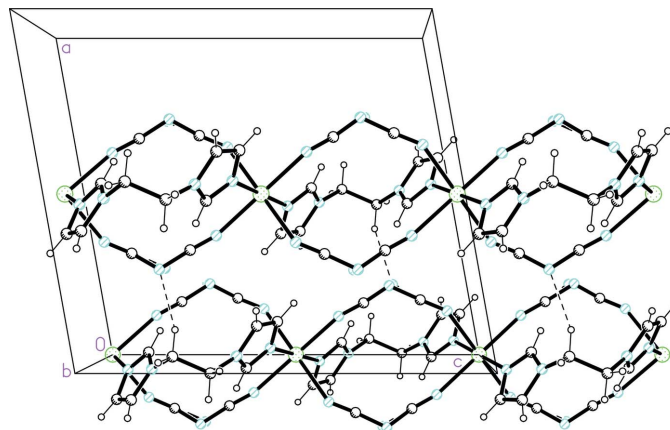


Figure 3

View, along the *b* axis, of the triple-stranded chains in (I), showing the weak C—H...N hydrogen bond (dashed lines) between amide N atom of dca and the H atom of the ethane group. Both disorder components of the dca ligands are shown.

H atoms were placed in idealized positions and refined as riding, with C—H distances of 0.95 (imidazole) and 0.99 Å (ethane), and with *U*_{iso}(H) = 1.2*U*_{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*.

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