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A novel two-dimensional framework based on unprecedented cadmium(II) chains

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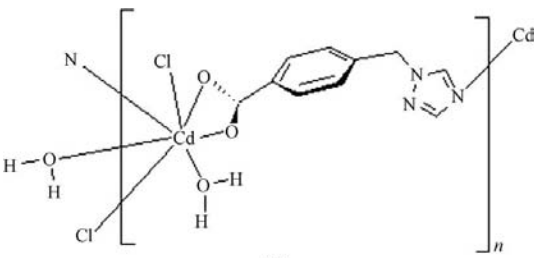
The bent ligand 4-[(1*H*-1,2,4-triazol-1-yl)methyl]benzoic acid (H*L*) has been used to create the novel two-dimensional coordination polymer poly[μ_2-aqua-μ_2-chlorido-{μ_2-4-[(1*H*-1,2,4-triazol-1-yl)methyl]benzoato}cadmium(II)], $[Cd(C_{10}H_8N_3O_2)Cl(H_2O)]_n$, under hydrothermal reaction of H*L* with cadmium chloride. The crystallographically unique Cd atom is seven-coordinated in an approximately pentagonal–bipyramidal environment of two carboxylate O atoms, two water O atoms, two Cl atoms and one triazole N atom. A notable feature is the presence of zigzag $\cdots$Cd$\cdots$Cd$\cdots$ inorganic chains, in which neighboring Cd^{II} ions are doubly bridged by pairs of μ_2-Cl atoms and μ_2-H_2O ligands in an alternating fashion. To the authors' knowledge, this is the first example containing this bridging mode in a cadmium(II) framework. The chains are connected to one another through the bridging L^- ligand into a two-dimensional undulating network. All of the two-dimensional nets stack exactly together in an $\ldots AA \ldots$ stacking sequence along the crystallographic *b* axis. Neighboring layers are further linked into a three-dimensional framework *via* interlayer hydrogen-bonding interactions.

Comment

The rational design and synthesis of supramolecular complexes are of great interest not only because of their potential applications in heterogenous catalysis (Wu & Lin, 2007), magnetism (Maspoch *et al.*, 2004), gas adsorption and separation (Rowsell & Yaghi, 2005), and luminescent materials (Dong *et al.*, 2007), but also owing to their intriguing structures (Wan *et al.*, 2008). In principle, some control over the type and topology of the product generated from the self-assembly of organic ligands and inorganic metal ions can be achieved by consideration of the functionality of the ligand (Munakata *et al.*, 1997). It is well known that 1,2,4-triazole and its derivatives are useful building blocks for the construction of metal–organic frameworks because they unite the coordination modes of pyrazole and imidazole. They exhibit the particularly useful property of acting as bridging ligands between two metal centers, which can afford diverse supramolecular complexes (Haasnoot, 2000).

Although derivatives of the 1,2,4-triazole ligand, especially the amino-substituted (Keij *et al.*, 1984; Shakir *et al.*, 2003), aryl-substituted (Klingele & Brooker, 2003; Wang *et al.*, 2007) and alkyl-substituted (Bradford *et al.*, 2004; Yi *et al.*, 2004) derivatives, have been well studied, very little attention has been paid to carboxylate-substituted 1,2,4-triazole ligands (Ding *et al.*, 2008). Previously, we reported a study of the M^{II} (M = Co and Zn) coordination chemistry of the carboxylate-substituted 1,2,4-triazole 4-[(1*H*-1,2,4-triazol-1-yl)methyl]benzoic acid (H*L*; Zhao *et al.*, 2007). As an extension of this study, we investigated the self-assembly reaction of L^- with cadmium chloride under hydrothermal conditions, and the novel supramolecular complex $[CdLCl(H_2O)]_n$, (I), was isolated.



(I)

Compound (I) crystallizes in the triclinic space group $P\overline{1}$ with only one unique seven-coordinated Cd^{II} center. Each Cd^{II} ion lies in a pseudo-pentagonal–bipyramidal coordination environment, with two O atoms (O1 and O2) from the carboxylate group, two O atoms [O3 and O3^{iii}; symmetry code: (iii) $-x + 2, -y, -z$] from water molecules and one Cl atom (Cl1) in the equatorial plane, and with one N atom [N1^{i}; symmetry code: (i) $-x + 2, -y + 1, -z + 1$] and one Cl atom [Cl1^{ii}; symmetry code: (ii) $-x + 1, -y, -z$] in the axial posi-

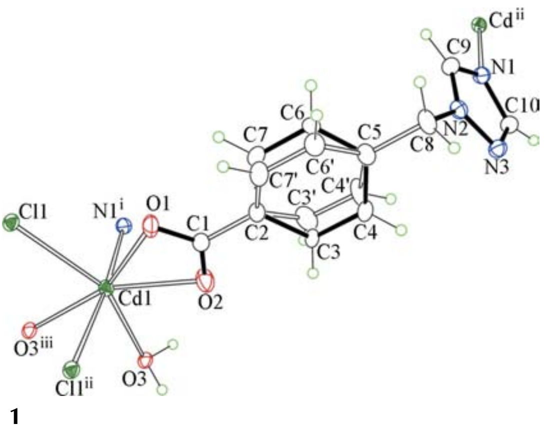


Figure 1
The molecular structure of (I) (displacement ellipsoids are shown at the 30% probability level). [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z$; (iii) $-x + 2, -y, -z$.]

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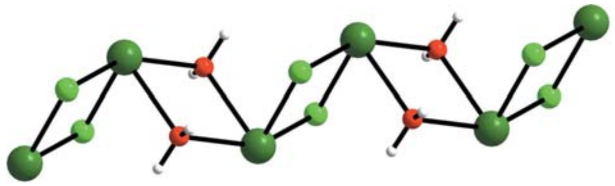


Figure 2
The zigzag chain in (I), showing the alternating Cl and H_2O bridging of the Cd^{II} centers.

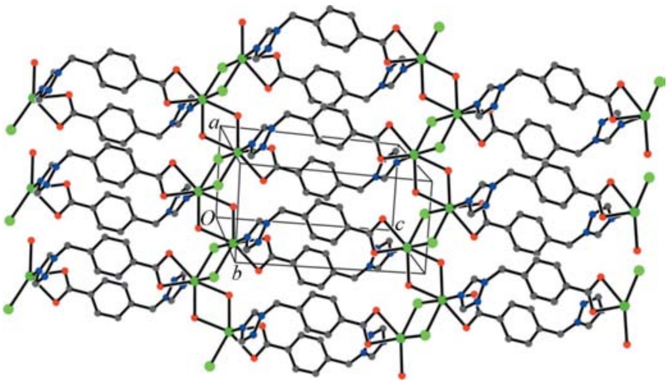


Figure 3
A view of the two-dimensional supramolecular framework of (I) approximately in the *ac* plane.

tions (Fig. 1 and Table 1). All the Cd—O, Cd—Cl and Cd—N bonds are consistent with values reported for Cd–carboxylate, $[Cd_2(\mu_2\text{-}H_2O)_2]$, $[Cd_2(\mu_2\text{-}Cl)_2]$ and Cd–triazole complexes (Yong *et al.*, 2005; Liu *et al.*, 2006; Yi *et al.*, 2004).

In the extended structure, neighboring Cd^{II} centers are doubly bridged by μ_2-Cl atoms and μ_2-H_2O molecules, alternately, to form a square $[Cd_2(\mu_2\text{-}Cl)_2]$ core with a Cd···Cd contact distance of 3.703 (15) Å and a rhomboidal $[Cd_2(\mu_2\text{-}H_2O)_2]$ core with a Cd···Cd contact distance of 4.028 (12) Å. These adjacent units are almost perpendicular [the dihedral angle is 82.09 (7)°] and are arranged alternately to form a zigzag chain extending along the crystallographic *a* axis (Fig. 2). In previously reported Cd coordination polymers, adjacent $[Cd_2(\mu_2\text{-}Cl)_2]$ units are mostly doubly bridged by μ_2-Cl atoms (Huang *et al.*, 1998; Yi *et al.*, 2004; Barros-Garcia *et al.*, 2004). In those cases, no bridging water molecules were observed, whereas in this study, adjacent $[Cd_2(\mu_2\text{-}Cl)_2]$ units are doubly bridged by μ_2-H_2O molecules. As far as we know, (I) is the first complex containing both μ_2-Cl and μ_2-H_2O bridges between two Cd^{II} ions.

These inorganic chains are doubly bridged by the chelating carboxylate group and terminal triazole N atom of the L^- ligand into a novel two-dimensional network (Fig. 3). When viewed down the crystallographic *a* axis, parallelogram-like cavities are found, which are composed of two Cd^{II} centers and two bent L^- ligands; the distance between two diagonal Cd^{II} centers is 12.40 (4) Å (Fig. 4). The two-dimensional network is strengthened by intralayer hydrogen bonds (O—H···O) consisting of a water H atom and an O atom of the carboxylate group. These two-dimensional layers are arranged in an ...*AA*... fashion and are further linked into a three-dimensional framework *via* interlayer hydrogen-bonding interactions along the crystallographic *b* axis (Fig. 4 and Table 2). The hydrogen-bonding system involves an uncoordinated N atom of the triazole ring and a water H atom of a neighboring layer.

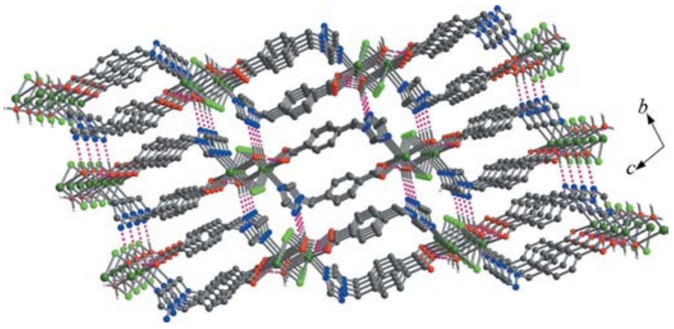
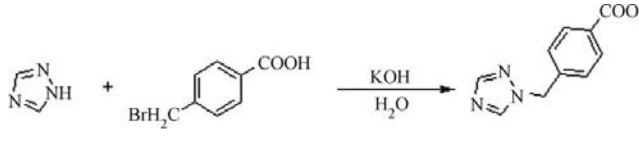


Figure 4
A perspective view along the *a* axis of the three-dimensional hydrogen-bonded network in (I) (hydrogen-bonding interactions are shown as dashed lines).

In summary, the most interesting feature in (I) is the presence of zigzag Cd^{II} chains formed by μ_2-Cl and μ_2-H_2O bridges. This behavior may offer a route to new types of Cl-bridged structures.

Experimental

All the solvents and reagents for synthesis were commercially available and were used as received. A mixture of 4-methylbenzoic acid (2.72 g, 20.0 mmol), succinbromimide (3.56 g, 20.0 mmol), benzoyl peroxide (0.050 g, 206.0 mmol) and tetrachloromethane (40 ml) was refluxed for 5 h. After cooling to room temperature, a pink precipitate was obtained by filtration and subsequently washed with tetrachloromethane and water. Recrystallization from dichloromethane provided a white solid, namely 4-bromomethylbenzoic acid, in 88.3% yield. KOH (3.02 g, 5.0 mmol) was added with stirring to a solution of 4-bromomethylbenzoic acid (2.15 g, 1 mmol) and 1*H*-1,2,4-triazole (0.70 g, 1 mmol) in water (60 ml). The mixture was stirred for 12 h, then acidified with hydrochloric acid to adjust the pH value to 2; the white precipitate which formed was filtered off and recrystallized from methanol to give the product H*L* (yield 89.2%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.99 (*s*, 1H, COOH), 8.68 (*s*, 1H, CH), 8.02 (*s*, 1H, CH), 7.92–7.32 (*m*, 4H, *p*-C_6H_4), 5.50 (*s*, 2H, CH_2). IR (KBr, cm^{-1}): 3455, 3119, 2950, 2362, 1913, 1694, 1516, 1432, 1275, 1142, 1013, 917, 731, 675.



A mixture of H*L* (20.3 mg, 0.10 mmol), $CdCl_2$ (23.8 mg, 0.10 mmol) and deionized water (2 ml) was sealed in a 5 ml test tube, heated at 453 K for 40 h and cooled slowly to room temperature over a period of 50 h. Colorless crystals were isolated in 80% yield (based on H*L*). IR (KBr, cm^{-1}): 3446, 3119, 1590, 1541, 1393, 1281, 1216, 1117, 1132, 997, 785, 761, 677, 639. Elemental analysis calculated for

$C_{10}H_{10}CdClN_3O_3$: C 32.60, H 2.71, N 11.41%; found: C 32.64, H 2.68, N 11.43%.

Crystal data

$[Cd(C_{10}H_8N_3O_2)Cl(H_2O)]$
$M_r = 368.06$
Triclinic, $P\overline{1}$
$a = 5.977$ (3) Å
$b = 8.052$ (4) Å
$c = 13.091$ (6) Å
$\alpha = 101.516$ (6)°
$\beta = 96.291$ (6)°
$\gamma = 96.612$ (6)°
$V = 607.6$ (5) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.02$ mm^{-1}
$T = 298$ (2) K
0.45 × 0.11 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.463$, $T_{max} = 0.906$
2928 measured reflections
2089 independent reflections
1993 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.105$
$S = 1.03$
2089 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.29$ e Å^{-3}
$\Delta\rho_{min} = -1.05$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N1^{i}	2.284 (4)	Cd1—Cl1^{ii}	2.5364 (15)
Cd1—O2	2.358 (4)	Cd1—O3^{iii}	2.546 (3)
Cd1—O3	2.414 (3)	Cd1—Cl1	2.7075 (14)
Cd1—O1	2.507 (4)		
N1^{i}—Cd1—O3	91.10 (13)	N1^{i}—Cd1—Cl1^{ii}	172.00 (10)
O2—Cd1—O3	78.83 (12)	O2—Cd1—Cl1^{ii}	100.50 (12)
O2—Cd1—O1	53.35 (13)	O3—Cd1—Cl1^{ii}	87.38 (9)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y, -z$; (iii) $-x+2, -y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···N3^{iv}	0.97	1.89	2.854 (5)	177
O3—H3B···O1^{v}	0.97	1.87	2.824 (5)	167

Symmetry codes: (iv) $-x+2, -y, -z+1$; (v) $x+1, y, z$.

H atoms were placed in geometrically idealized positions and included as riding atoms, with C—H distances of 0.97 (CH_2) or 0.93 Å (CH), O—H distances of 0.97 Å, and U_{iso}(H) values of $1.2U_{eq}$(C,O). The benzene ring was disordered over two positions that refined to a ratio of 0.48 (4):0.52 (4).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3183). Services for accessing these data are described at the back of the journal.

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