

# A new cadmium coordination polymer based on 4-amino-4*H*-1,2,4-triazole

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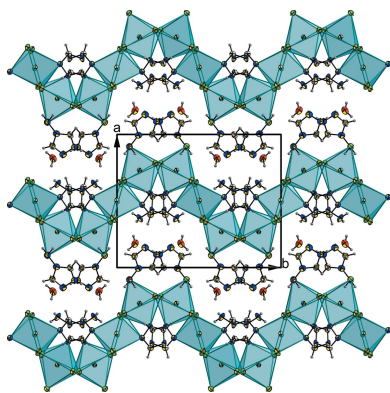
A new cadmium coordination polymer, poly[bis(4-amino-4*H*-1,2,4-triazolium) [bis( $\mu_2$ -4-amino-4*H*-1,2,4-triazole- $\kappa^2$ N<sup>1</sup>:N<sup>2</sup>)tetra- $\mu_2$ -chlorido-tetrachloridotricadmium(II)] dihydrate],  $\{(C_2H_5N_4)_2[Cd_3Cl_8(C_2H_4N_4)_2 \cdot 2H_2O]\}_n$ , was synthesized by the reaction of 4-amino-4*H*-1,2,4 triazole with cadmium(II) chloride in aqueous solution. With an unusual architecture, the crystal structure exhibits two distorted octahedral coordinations of Cd<sup>II</sup> joined by edge sharing. The first is composed by four chlorine and two N atoms from the triazole ligands. The second is formed by five Cl atoms and by one N atom from the triazole ligand. The charge of the resulting two-dimensional anionic framework is balanced by the organic triazole cations. The lattice water molecules form a network of hydrogen bonding. N–H...Cl and  $\pi$ – $\pi$  stacking interactions are also involved in the supramolecular network stability.

## 1. Chemical context

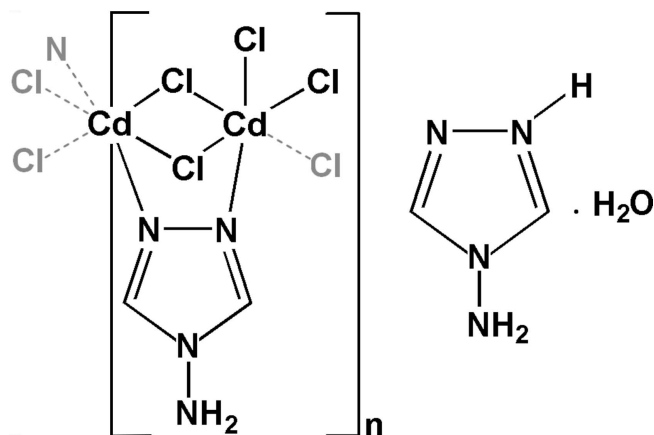
The last decade has seen a large number of investigations of Cd<sup>II</sup> hybrid coordination polymers (HCPs). Indeed, these materials exhibit a wide variety of polymeric frameworks with attractive properties. The coordination sphere of Cd<sup>II</sup> is variable, with coordination numbers ranging from four to eight, corresponding to different geometries (tetrahedral, square planar, square pyramidal, trigonal bipyramidal, octahedral, pentagonal bipyramidal, bicapped triangular prismatic and dodecahedral; Li & Du, 2011). Many factors should be considered in the self-assembly processes of HCPs, such as the nature of the organic ligands, temperature, pH values, solvents, and so on (Guo *et al.*, 2013). The choice of the organic ligands is an important factor that greatly influences the structure and stabilization of the coordination architecture formed (Tao *et al.*, 2000; Choi & Jeon, 2003). In this regard, organic building units that are based on five-membered N-heterocycles such as 1,2,4 triazole exhibit a strong and typical property of acting as bridging ligands between two metal centres. These bridges can adopt various different geometries, depending on the donor atoms of the ligand and the properties of the metal (Haasnoot *et al.*, 2000). The reaction of 4-amino-4*H*-1,2,4 triazole (NH<sub>2</sub>trz) with cadmium dichloride leads to the formation of the title two-dimensional coordination polymer.

## 2. Structural commentary

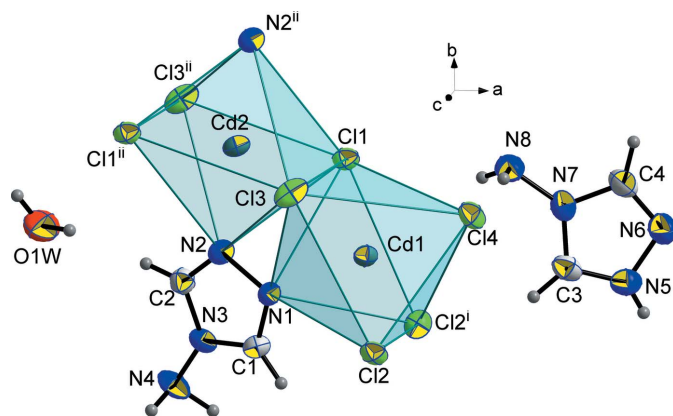
The asymmetric unit of the studied compound, completed by the atoms necessary to achieve the coordination around the Cd ions, is represented in Fig. 1. It comprises one and a half



Cd<sup>II</sup> cations [with Cd2 occupying the special position ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ )], one triazole molecule (NH<sub>2</sub>trz), one triazolium cation (NH<sub>2</sub>trzH)<sup>+</sup>, four chloride anions and one lattice water molecule. Cd1 and Cd2 are bridged by the coordinated triazole molecule (NH<sub>2</sub>trz) through atoms N1 and N2, and by the two chlorine atoms Cl1 and Cl3.



Both metals show an octahedral coordination geometry. Cd1 is surrounded by the five chloride anions Cl1, Cl2, Cl3, Cl4, Cl2<sup>i</sup> [symmetry code: (i)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ ] and the nitrogen N1 of the coordinated triazole ring (NH<sub>2</sub>trz). On the other hand, Cd2 is bonded to four equatorial chloride anions (Cl1, Cl3, Cl1<sup>ii</sup> and Cl3<sup>ii</sup>) and two axial nitrogen atoms, N2 and N2<sup>ii</sup>, belonging to the coordinated triazole (NH<sub>2</sub>trz) and to its symmetry-related analogue, respectively [symmetry code: (ii)  $1 - x, 1 - y, 1 - z$ ]. As a result of the bridge formed by atoms N1 and N2 of the triazole ligand, the Cd1...Cd2 distance is 3.6145 (7) Å. Selected geometrical parameters are summarized in Table 1, showing that the octahedron around Cd1 is more distorted than the one around Cd2.



**Figure 1**  
ORTEP of the asymmetric unit of the studied compound plus the atoms necessary to complete the coordination around the Cd ions. Cd2 is on the special position ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ). Displacement ellipsoids are drawn at the at the 50% probability level. [Symmetry codes: (i)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (ii)  $1 - x, 1 - y, 1 - z$ .]

**Table 1**  
Selected geometric parameters (Å, °).

|                      |             |             |             |
|----------------------|-------------|-------------|-------------|
| Cd1—N1               | 2.365 (4)   | Cd1—Cl1     | 2.6769 (14) |
| Cd1—Cl4              | 2.5120 (14) | Cd2—N2      | 2.393 (5)   |
| Cd1—Cl2              | 2.6148 (13) | Cd2—Cl3     | 2.5874 (16) |
| Cd1—Cl3              | 2.6418 (14) | Cd2—Cl1     | 2.6332 (14) |
| Cd1—Cl2 <sup>i</sup> | 2.6754 (13) |             |             |
| N1—Cd1—Cl4           | 174.37 (11) | Cl3—Cd1—Cl1 | 84.86 (4)   |
| Cl2—Cd1—Cl1          | 174.60 (4)  | Cl3—Cd2—Cl1 | 86.85 (5)   |

Symmetry code: (i)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ .

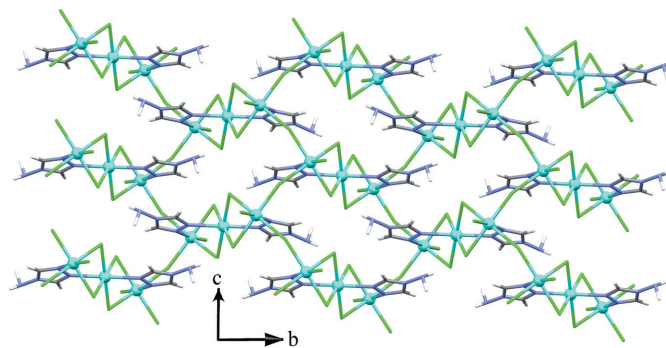
When symmetry is applied, a Cd<sub>3</sub>Cl<sub>8</sub>(NH<sub>2</sub>trz)<sub>2</sub> building block is formed. These trinuclear units are connected *via* the chloride ions Cl2 to build up infinite inorganic corrugated sheets in the *bc* plane, stacked along the *a*-axis direction (Fig. 2). The triazolium cations (NH<sub>2</sub>trzH)<sup>+</sup> and the water molecules are located in the interlayer space (Fig. 3), interacting with the anionic framework by hydrogen bonds. Thus, the overall three-dimensional network consists of alternate organic–inorganic hybrid layers, responsible for the interesting behaviour of this class of materials.

### 3. Supramolecular features

The crystal structure of the title compound is mainly stabilized by hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions. In particular, a number of O—H...Cl, O—H...N, N—H...O and N—H...Cl hydrogen bonds is present (Table 2), involving the lattice water molecules, the triazolium cations, the organic ligands and the chlorine anions. These hydrogen bonds connect the organic and inorganic moieties, leading to a self-organized, hydrated hybrid structure.

The chloride anions around Cd1 and Cd2 form hydrogen bonds both with the amine H atoms of the (NH<sub>2</sub>trz) ligands and with the H atoms of the water molecules (Figs. 4 and 5; Table 2): Cl1...HW2<sup>ii</sup>—O1W<sup>ii</sup>, Cl3...H4B<sup>iii</sup>—N4<sup>iii</sup>, Cl4...HW1<sup>ii</sup>—O1W<sup>ii</sup>, Cl4...H8B—N8, and Cl2...H8A<sup>iv</sup>—N8<sup>iv</sup> [symmetry codes: (iii)  $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (iv)  $x, y, 1 + z$ ].

Besides forming hydrogen bonds with the chloride anions Cl1 and Cl4, the water molecules also interact with the triazole ligands and with the lattice triazolium cations, acting as



**Figure 2**  
Crystal packing showing the two-dimensional anionic framework of the title compound.

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

| $D-H\cdots A$                  | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------|----------|-------------|-------------|---------------|
| $O1W^{ii}-HW2^{ii}\cdots Cl1$  | 0.86 (6) | 2.68 (7)    | 3.239 (6)   | 124 (6)       |
| $N4^{iii}-H4B^{iii}\cdots Cl3$ | 1.00 (8) | 2.60 (7)    | 3.399 (5)   | 136 (5)       |
| $N8^{iv}-H8A^{iv}\cdots Cl2$   | 0.85     | 2.64        | 3.370 (5)   | 144           |
| $O1W^{ii}-HW1^{ii}\cdots Cl4$  | 0.86 (7) | 2.67 (8)    | 3.319 (6)   | 134 (8)       |
| $N8-H8B\cdots Cl4$             | 0.90     | 2.53        | 3.423 (5)   | 172           |
| $N5^v-H5^v\cdots O1W$          | 0.75 (8) | 1.97 (8)    | 2.649 (8)   | 151 (8)       |
| $O1W-HW2\cdots N4^{vi}$        | 0.86 (6) | 2.44 (6)    | 3.247 (9)   | 157 (6)       |

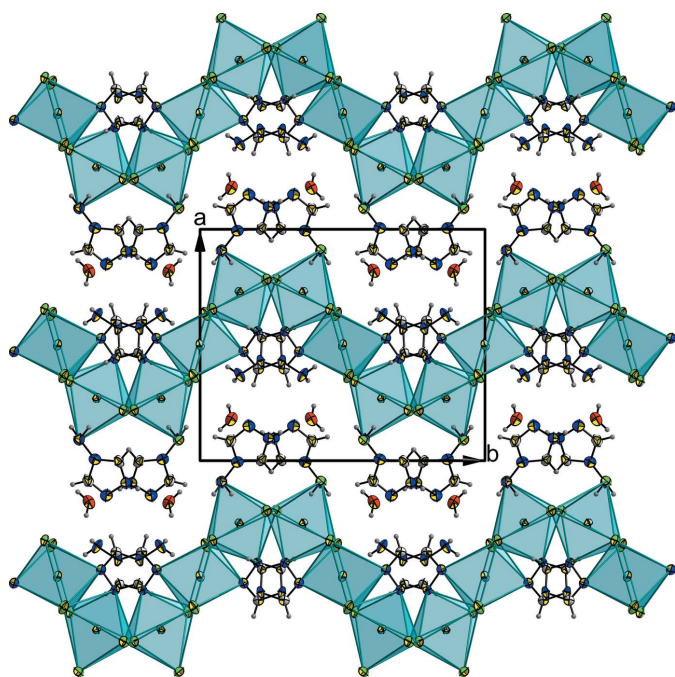
Symmetry codes: (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$ ; (iv)  $x, y, z+1$ ; (v)  $x-1, -y+\frac{1}{2}, z+\frac{1}{2}$ ; (vi)  $x, -y+\frac{1}{2}, z+\frac{1}{2}$ .

acceptor and donor, respectively (Fig. 6 and Table 2):  $O1W\cdots H5^v-N5^v$  and  $N4^{vi}\cdots HW2-O1W$  [symmetry codes: (v)  $x-1, \frac{1}{2}-y, \frac{1}{2}+z$ ; (vi)  $x, \frac{1}{2}-y, z+\frac{1}{2}$ ].

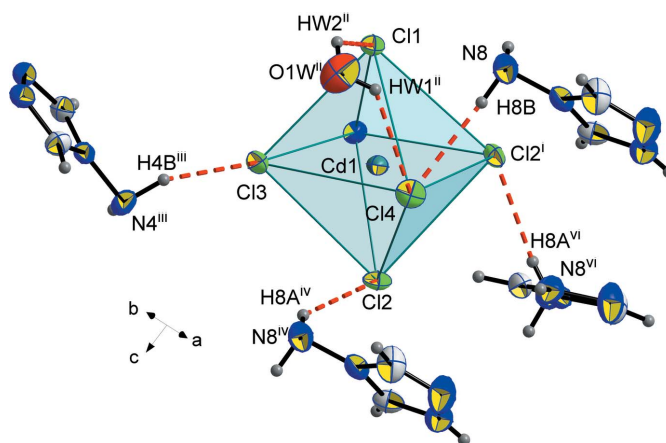
Finally, the coordinated triazole rings ( $NH_2trz$ ) are connected along the  $c$ -axis direction through  $\pi$ - $\pi$  stacking interactions, with a centroid-centroid distance of 3.761 (7) Å.

#### 4. Database survey

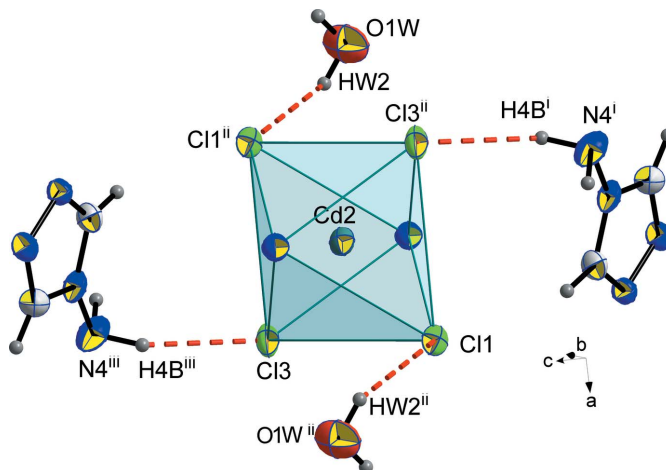
Recently, a great deal of attention has been paid to the rational design and synthesis of new hybrid coordination polymers (HCPs) composed of metal ions and bridging ligands due to their fascinating structural diversity and their potential application as functional materials (Xiong *et al.*, 2001; Liao *et al.*, 2004; Gao *et al.*, 2008). These coordination polymers exhibit a wide range of infinite zero- to three-dimensional frameworks with interesting structural features, which result



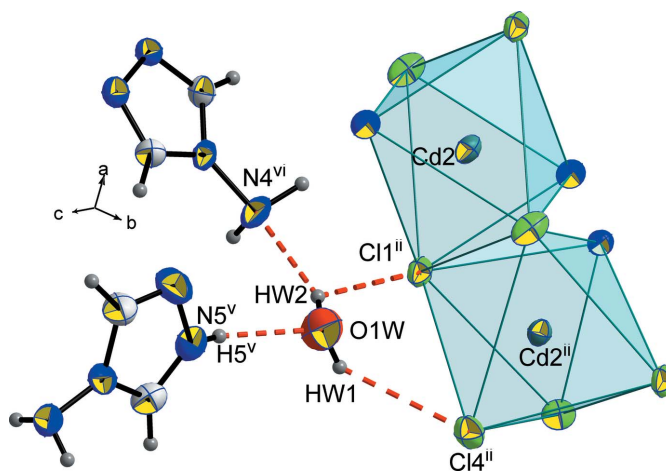
**Figure 3**  
Corrugated anionic sheets with the non-coordinating triazolium cations and water molecules located in the interlayer space. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 4**  
Hydrogen bonds (red dashed lines) involving the chloride anions around Cd1. Displacement ellipsoids are displayed at the 50% probability level. [Symmetry codes: (i)  $x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (ii)  $1-x, 1-y, 1-z$ ; (iii)  $1-x, \frac{1}{2}+y, \frac{3}{2}-z$ ; (iv)  $x, y, 1+z$ ; (vi)  $x, \frac{1}{2}-y, \frac{1}{2}+z$ .]



**Figure 5**  
Hydrogen bonds (red dashed lines) involving the chloride anions around Cd2. Displacement ellipsoids are displayed at the 50% probability level. [Symmetry codes: (i)  $x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (ii)  $1-x, 1-y, 1-z$ ; (iii)  $1-x, \frac{1}{2}+y, \frac{3}{2}-z$ .]



**Figure 6**  
The hydrogen-bonding interactions around a single water molecule involving the chlorine atoms, the ( $NH_2trz$ ) ligand and the ( $NH_2trzH$ )<sup>+</sup> cation. Displacement ellipsoids are displayed at the 50% probability level. [Symmetry codes: (ii)  $1-x, 1-y, 1-z$ ; (v)  $-1+x, \frac{1}{2}-y, \frac{1}{2}+z$ ; (vi)  $x, \frac{1}{2}-y, \frac{1}{2}+z$ .]

**Table 3**  
Experimental details.

|   |  |
|---|--|
| Crystal data  |  |
| Chemical formula  | (C <sub>2</sub> H <sub>5</sub> N <sub>4</sub> ) <sub>2</sub> [Cd <sub>3</sub> Cl <sub>8</sub> (C <sub>2</sub> H <sub>4</sub> N <sub>4</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O |
| <i>M<sub>r</sub></i>  | 995.21   |
| Crystal system, space group   | Monoclinic, <i>P2<sub>1</sub>/c</i>  |
| Temperature (K)   | 298  |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)  | 12.685 (3), 15.498 (3), 7.375 (2)  |
| $\beta$ (°)   | 97.12 (3)  |
| <i>V</i> (Å <sup>3</sup> )  | 1438.6 (6)   |
| <i>Z</i>  | 2  |
| Radiation type  | Mo <i>K</i> $\alpha$   |
| $\mu$ (mm <sup>-1</sup> )   | 2.98   |
| Crystal size (mm)   | 0.71 × 0.21 × 0.21   |
| Data collection   |  |
| Diffractometer  | Enraf–Nonius CAD-4   |
| Absorption correction   | $\psi$ scan (North <i>et al.</i> , 1968)   |
| <i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>   | 0.799, 1.000   |
| No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections                             | 3670, 3136, 2654   |
| <i>R<sub>int</sub></i>  | 0.032  |
| ( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )   | 0.638  |
| Refinement  |  |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.040, 0.123, 1.06   |
| No. of reflections  | 3136   |
| No. of parameters   | 190  |
| No. of restraints   | 5  |
| H-atom treatment  | H atoms treated by a mixture of independent and constrained refinement   |
| $\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )  | 1.58, -1.99  |

from coordination bonding, hydrogen-bonding and aromatic  $\pi$ – $\pi$  stacking interactions as well as van der Waals forces (Su *et al.*, 2003).

A search of the latest version of the Cambridge Structural Database (Version 5.38; Groom *et al.*, 2016) based on the organic fragment ‘4-amino-4*H*-1,2,4-triazole’ of the studied compound yielded 70 hits. The structure of the chloro-cadmate PEPWIR (Zhai *et al.*, 2006) is probably the nearest to that of the title compound, even if it lacks the water molecules of crystallization and the protonated triazole cations. This is probably due to the difference in the stoichiometry of the initial reagents and to the solvent used in the chemical synthesis. Two other related compounds comprising 4-amino-4*H*-1,2,4-triazole in combination with chloride ligands are the coordination polymer ROFJED (Wang *et al.*, 2014) and the discrete complex GAVFEP (Xuan-Wen, 2005).

## 5. Synthesis and crystallization

The compound was prepared by the reaction of 4-amino-4*H*-1,2,4-triazole and CdCl<sub>2</sub>·H<sub>2</sub>O (molar ratio 1:1) in an equal volume of water and ethanol (10 ml) mixed with 2 ml of hydrochloric acid (37%). The solution was stirred for 1 h.

Colourless crystals suitable for X-ray diffraction were grown in two weeks by slow evaporation at room temperature.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Atoms H1, H2 and H3 were placed in calculated positions and refined using a riding model: C–H = 0.93 Å with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The other hydrogen atoms were found in the difference-Fourier map. The coordinates of H8A, H8B and H4A of the amine terminal groups were kept fixed, with *U*<sub>iso</sub>(H) = 0.05.

## Acknowledgements

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## supporting information

*Acta Cryst.* (2018). E74, 147-150 [https://doi.org/10.1107/S2056989018000464]

## A new cadmium coordination polymer based on 4-amino-4*H*-1,2,4-triazole

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### Computing details

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Poly[bis(4-amino-4*H*-1,2,4-triazolium) [bis( $\mu_2$ -4-amino-4*H*-1,2,4-triazole- $\kappa^2 N^1:N^2$ )tetra- $\mu_2$ -chlorido-tetrachloridotricadmium(II)] dihydrate]

### Crystal data

$(C_2H_5N_4)_2[Cd_3Cl_8(C_2H_4N_4)_2] \cdot 2H_2O$

$M_r = 995.21$

Monoclinic,  $P2_1/c$

$a = 12.685$  (3) Å

$b = 15.498$  (3) Å

$c = 7.375$  (2) Å

$\beta = 97.12$  (3)°

$V = 1438.6$  (6) Å<sup>3</sup>

$Z = 2$

$F(000) = 956$

$D_x = 2.298$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 10$ – $15^\circ$

$\mu = 2.98$  mm<sup>-1</sup>

$T = 298$  K

Prism, colourless

$0.71 \times 0.21 \times 0.21$  mm

### Data collection

Enraf–Nonius CAD-4  
diffractometer

Radiation source: Enraf Nonius FR590  
non-profiled  $\omega/2\tau$  scans

Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)

$T_{\min} = 0.799$ ,  $T_{\max} = 1.000$

3670 measured reflections

3136 independent reflections

2654 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 27.0^\circ$ ,  $\theta_{\min} = 2.1^\circ$

$h = -16$ → $16$

$k = -19$ → $1$

$l = -9$ → $1$

2 standard reflections every 120 min

intensity decay: 8%

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.123$

$S = 1.06$

3136 reflections

190 parameters

5 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2 + 1.0345P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.58$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.99$  e Å<sup>-3</sup>

Extinction correction: SHELXL2014  
 (Sheldrick, 2015),  
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0041 (7)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and goodness of fit S are based on  $F^2$ , conventional R-factors R are based on F, with F set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|     | x            | y           | z            | $U_{iso}^*/U_{eq}$ |
|-----|--------------|-------------|--------------|--------------------|
| Cd1 | 0.72922 (3)  | 0.36225 (2) | 0.60671 (4)  | 0.02384 (16)       |
| Cd2 | 0.5000       | 0.5000      | 0.5000       | 0.02726 (18)       |
| Cl1 | 0.65520 (10) | 0.45547 (8) | 0.31268 (16) | 0.0291 (3)         |
| Cl2 | 0.78296 (10) | 0.26723 (9) | 0.89644 (16) | 0.0307 (3)         |
| Cl3 | 0.63396 (12) | 0.47886 (9) | 0.79095 (17) | 0.0379 (3)         |
| Cl4 | 0.91217 (11) | 0.42626 (9) | 0.6250 (2)   | 0.0369 (3)         |
| N1  | 0.5591 (3)   | 0.2978 (3)  | 0.5599 (6)   | 0.0271 (9)         |
| N2  | 0.4709 (4)   | 0.3474 (3)  | 0.5015 (6)   | 0.0300 (9)         |
| N3  | 0.4303 (4)   | 0.2130 (3)  | 0.4573 (6)   | 0.0284 (9)         |
| N4  | 0.3704 (5)   | 0.1390 (3)  | 0.3952 (8)   | 0.0427 (12)        |
| N5  | 1.0964 (5)   | 0.2603 (4)  | 0.1439 (8)   | 0.0406 (11)        |
| N6  | 1.1503 (5)   | 0.3284 (4)  | 0.0808 (9)   | 0.0552 (15)        |
| N7  | 0.9940 (4)   | 0.3688 (3)  | 0.1463 (6)   | 0.0341 (10)        |
| N8  | 0.9074 (4)   | 0.4233 (3)  | 0.1599 (6)   | 0.0388 (11)        |
| C1  | 0.5314 (4)   | 0.2172 (3)  | 0.5326 (7)   | 0.0301 (10)        |
| H1  | 0.5755       | 0.1699      | 0.5613       | 0.036*             |
| C2  | 0.3953 (4)   | 0.2949 (4)  | 0.4392 (8)   | 0.0326 (11)        |
| H2  | 0.3273       | 0.3114      | 0.3895       | 0.039*             |
| C3  | 1.0035 (5)   | 0.2844 (4)  | 0.1816 (8)   | 0.0371 (12)        |
| H3  | 0.9528       | 0.2493      | 0.2253       | 0.044*             |
| C4  | 1.0865 (6)   | 0.3931 (4)  | 0.0848 (11)  | 0.0481 (16)        |
| O1W | 0.1792 (5)   | 0.3900 (4)  | 0.5653 (10)  | 0.0663 (15)        |
| H4  | 1.103 (5)    | 0.450 (4)   | 0.066 (9)    | 0.038 (17)*        |
| H5  | 1.127 (6)    | 0.219 (5)   | 0.158 (11)   | 0.05 (2)*          |
| H8A | 0.8524       | 0.4002      | 0.1015       | 0.050*             |
| H8B | 0.9153       | 0.4271      | 0.2827       | 0.050*             |
| H4A | 0.4298       | 0.0977      | 0.3612       | 0.050*             |
| H4B | 0.350 (6)    | 0.120 (4)   | 0.516 (11)   | 0.045 (19)*        |
| HW2 | 0.237 (4)    | 0.396 (5)   | 0.638 (9)    | 0.07 (3)*          |
| HW1 | 0.142 (6)    | 0.435 (4)   | 0.580 (14)   | 0.11 (4)*          |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|------------|------------|------------|--------------|--------------|--------------|
| Cd1 | 0.0255 (2) | 0.0249 (2) | 0.0204 (2) | 0.00043 (12) | 0.00023 (14) | 0.00166 (12) |
| Cd2 | 0.0335 (3) | 0.0216 (3) | 0.0261 (3) | 0.00527 (19) | 0.0016 (2)   | 0.00027 (18) |
| C11 | 0.0363 (6) | 0.0285 (6) | 0.0229 (5) | 0.0036 (5)   | 0.0046 (5)   | 0.0044 (4)   |
| C12 | 0.0347 (6) | 0.0341 (7) | 0.0227 (6) | -0.0022 (5)  | 0.0013 (5)   | 0.0100 (5)   |
| C13 | 0.0507 (8) | 0.0372 (7) | 0.0235 (6) | 0.0143 (6)   | -0.0041 (5)  | -0.0085 (5)  |
| C14 | 0.0327 (7) | 0.0366 (7) | 0.0410 (7) | -0.0101 (5)  | 0.0027 (5)   | -0.0007 (6)  |
| N1  | 0.026 (2)  | 0.026 (2)  | 0.029 (2)  | 0.0019 (16)  | 0.0020 (16)  | 0.0019 (16)  |
| N2  | 0.032 (2)  | 0.029 (2)  | 0.028 (2)  | 0.0029 (18)  | 0.0022 (17)  | -0.0003 (17) |
| N3  | 0.040 (2)  | 0.025 (2)  | 0.022 (2)  | -0.0059 (18) | 0.0095 (17)  | -0.0032 (15) |
| N4  | 0.054 (3)  | 0.034 (3)  | 0.042 (3)  | -0.020 (2)   | 0.011 (2)    | -0.009 (2)   |
| N5  | 0.046 (3)  | 0.034 (3)  | 0.041 (3)  | -0.001 (2)   | 0.003 (2)    | 0.000 (2)    |
| N6  | 0.054 (3)  | 0.047 (3)  | 0.071 (4)  | 0.002 (3)    | 0.031 (3)    | 0.005 (3)    |
| N7  | 0.035 (2)  | 0.043 (3)  | 0.025 (2)  | -0.0025 (19) | 0.0072 (18)  | -0.0042 (18) |
| N8  | 0.044 (3)  | 0.034 (2)  | 0.040 (3)  | -0.002 (2)   | 0.009 (2)    | -0.006 (2)   |
| C1  | 0.034 (3)  | 0.025 (2)  | 0.031 (3)  | 0.003 (2)    | 0.002 (2)    | 0.002 (2)    |
| C2  | 0.030 (3)  | 0.034 (3)  | 0.034 (3)  | -0.001 (2)   | 0.003 (2)    | -0.001 (2)   |
| C3  | 0.042 (3)  | 0.037 (3)  | 0.031 (3)  | -0.007 (2)   | 0.001 (2)    | 0.007 (2)    |
| C4  | 0.051 (4)  | 0.037 (3)  | 0.061 (4)  | -0.007 (3)   | 0.023 (3)    | 0.000 (3)    |
| O1W | 0.057 (3)  | 0.043 (3)  | 0.095 (5)  | -0.011 (3)   | -0.002 (3)   | -0.002 (3)   |

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|                         |             |           |            |
|-------------------------|-------------|-----------|------------|
| Cd1—N1                  | 2.365 (4)   | N4—H4A    | 1.0400     |
| Cd1—C14                 | 2.5120 (14) | N4—H4B    | 1.01 (8)   |
| Cd1—C12                 | 2.6148 (13) | N5—C3     | 1.299 (9)  |
| Cd1—C13                 | 2.6418 (14) | N5—N6     | 1.369 (8)  |
| Cd1—C12 <sup>i</sup>    | 2.6754 (13) | N5—H5     | 0.75 (8)   |
| Cd1—C11                 | 2.6769 (14) | N6—C4     | 1.292 (9)  |
| Cd2—N2 <sup>ii</sup>    | 2.393 (5)   | N7—C3     | 1.336 (7)  |
| Cd2—N2                  | 2.393 (5)   | N7—C4     | 1.362 (8)  |
| Cd2—C13                 | 2.5874 (16) | N7—N8     | 1.399 (7)  |
| Cd2—C13 <sup>iii</sup>  | 2.5875 (16) | N8—H8A    | 0.850      |
| Cd2—C11                 | 2.6332 (14) | N8—H8B    | 0.900      |
| Cd2—C11 <sup>ii</sup>   | 2.6333 (14) | C1—H1     | 0.9300     |
| N1—C1                   | 1.306 (7)   | C2—H2     | 0.9300     |
| N1—N2                   | 1.382 (6)   | C3—H3     | 0.9300     |
| N2—C2                   | 1.297 (7)   | C4—H4     | 0.92 (6)   |
| N3—C1                   | 1.335 (7)   | O1W—HW2   | 0.862 (10) |
| N3—C2                   | 1.346 (7)   | O1W—HW1   | 0.857 (10) |
| N3—N4                   | 1.419 (6)   |           |            |
| N1—Cd1—C14              | 174.37 (11) | N1—N2—Cd2 | 115.6 (3)  |
| C14—Cd1—C13             | 100.40 (5)  | C1—N3—C2  | 106.4 (4)  |
| C12—Cd1—C13             | 93.13 (5)   | C1—N3—N4  | 128.4 (5)  |
| N1—Cd1—C12 <sup>i</sup> | 83.80 (11)  | C2—N3—N4  | 125.0 (5)  |

|  |            |             |           |
|--|------------|-------------|-----------|
| C14—Cd1—C12 <sup>i</sup>                 | 91.57 (5)  | N3—N4—H4A   | 102.00    |
| C12—Cd1—C12 <sup>i</sup>                 | 89.53 (3)  | N3—N4—H4B   | 98 (4)    |
| N1—Cd1—C11                               | 83.54 (11) | H4A—N4—H4B  | 108.00    |
| C14—Cd1—C11                              | 93.40 (5)  | C3—N5—N6    | 110.8 (5) |
| C12—Cd1—C11                              | 174.60 (4) | C3—N5—H5    | 133 (6)   |
| C13—Cd1—C11                              | 84.86 (4)  | N6—N5—H5    | 116 (6)   |
| C12 <sup>i</sup> —Cd1—C11                | 91.39 (4)  | C4—N6—N5    | 104.5 (6) |
| N2 <sup>ii</sup> —Cd2—C13                | 92.46 (11) | C3—N7—C4    | 106.0 (5) |
| N2—Cd2—C13                               | 87.54 (12) | C3—N7—N8    | 129.0 (5) |
| N2 <sup>ii</sup> —Cd2—C13 <sup>ii</sup>  | 87.54 (11) | C4—N7—N8    | 125.0 (5) |
| N2—Cd2—C13 <sup>ii</sup>                 | 92.46 (12) | N7—N8—H8A   | 108.00    |
| N2 <sup>ii</sup> —Cd2—C11                | 97.50 (11) | N7—N8—H8B   | 97.00     |
| N2—Cd2—C11                               | 82.50 (11) | H8A—N8—H8B  | 121.00    |
| C13—Cd2—C11                              | 86.85 (5)  | N1—C1—N3    | 109.7 (5) |
| C13 <sup>ii</sup> —Cd2—C11               | 93.15 (5)  | N1—C1—H1    | 125.2     |
| N2 <sup>ii</sup> —Cd2—C11 <sup>ii</sup>  | 82.50 (11) | N3—C1—H1    | 125.2     |
| N2—Cd2—C11 <sup>ii</sup>                 | 97.50 (11) | N2—C2—N3    | 109.7 (5) |
| C13—Cd2—C11 <sup>ii</sup>                | 93.15 (5)  | N2—C2—H2    | 125.1     |
| C13 <sup>ii</sup> —Cd2—C11 <sup>ii</sup> | 86.85 (5)  | N3—C2—H2    | 125.1     |
| Cd2—C11—Cd1                              | 85.79 (4)  | N5—C3—N7    | 107.6 (5) |
| Cd1—C12—Cd1 <sup>iii</sup>               | 146.79 (5) | N5—C3—H3    | 126.2     |
| Cd2—C13—Cd1                              | 87.44 (4)  | N7—C3—H3    | 126.2     |
| C1—N1—N2                                 | 107.0 (4)  | N6—C4—N7    | 111.1 (6) |
| C1—N1—Cd1                                | 130.5 (3)  | N6—C4—H4    | 126 (4)   |
| N2—N1—Cd1                                | 120.0 (3)  | N7—C4—H4    | 122 (4)   |
| C2—N2—N1                                 | 107.2 (4)  | HW2—O1W—HW1 | 106 (3)   |
| C2—N2—Cd2                                | 136.6 (4)  |             |           |

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

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

| $D-H\cdots A$                               | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| O1W <sup>ii</sup> —HW2 <sup>ii</sup> ...C11 | 0.86 (6) | 2.68 (7)    | 3.239 (6)   | 124 (6)       |
| N4 <sup>iv</sup> —H4B <sup>iv</sup> ...C13  | 1.00 (8) | 2.60 (7)    | 3.399 (5)   | 136 (5)       |
| N8 <sup>v</sup> —H8A <sup>v</sup> ...C12    | 0.85     | 2.64        | 3.370 (5)   | 144           |
| O1W <sup>ii</sup> —HW1 <sup>ii</sup> ...C14 | 0.86 (7) | 2.67 (8)    | 3.319 (6)   | 134 (8)       |
| N8—H8B...C14                                | 0.90     | 2.53        | 3.423 (5)   | 172           |
| N5 <sup>vi</sup> —H5 <sup>vi</sup> ...O1W   | 0.75 (8) | 1.97 (8)    | 2.649 (8)   | 151 (8)       |
| O1W—HW2...N4 <sup>iii</sup>                 | 0.86 (6) | 2.44 (6)    | 3.247 (9)   | 157 (6)       |

Symmetry codes: (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $x, -y+1/2, z+1/2$ ; (iv)  $-x+1, y+1/2, -z+3/2$ ; (v)  $x, y, z+1$ ; (vi)  $x-1, -y+1/2, z+1/2$ .