

Di- μ_3 -chlorido-tetra- μ_2 -chlorido-dichloridobis(dimethylformamide- κO)-hexakis(1*H*-imidazole- κN^3)tetracadmium

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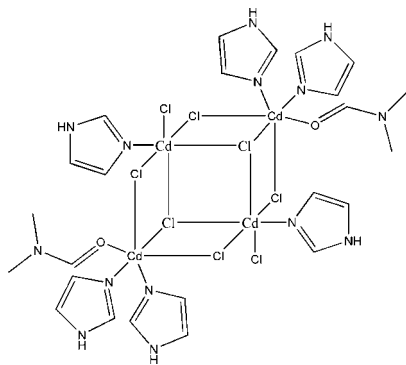
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.028; wR factor = 0.069; data-to-parameter ratio = 20.4.

The centrosymmetric molecule of the title complex, $[Cd_4Cl_8(C_3H_4N_2)_6(C_3H_7NO)_2]$, contains four Cd^{II} atoms, six imidazole, two dimethylformamide and eight chloride ligands. The structure shows a novel chloride-bridged tetranuclear cadmium quasi-cubane cluster. The coordination geometry of all Cd^{II} atoms is distorted octahedral, with the two metal atoms in the asymmetric unit in different coordination environments. One of the Cd^{2+} ions is coordinated by five Cl^- ions and by one N atom from an imidazole ligand, while the second is coordinated by three chloride ligands, two N atoms from two imidazole ligands and one O atom from a dimethylformamide molecule. Intermolecular $N-H \cdots Cl$ hydrogen bonds link the molecules into a two-dimensional polymeric structure parallel to the ab plane.

Related literature

For general background to ferroelectric compounds with metal-organic frameworks, see: Ye *et al.* (2009); Zhang *et al.* (2009).



Experimental

Crystal data

$[Cd_4Cl_8(C_3H_4N_2)_6(C_3H_7NO)_2]$
 $M_r = 1287.92$
Monoclinic, $P2_1/c$
 $a = 8.2540$ (17) Å
 $b = 12.290$ (3) Å
 $c = 21.119$ (4) Å
 $\beta = 99.23$ (3)°
 $V = 2114.6$ (8) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 2.53$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{min} = 0.472$, $T_{max} = 0.603$
21502 measured reflections
4833 independent reflections
4241 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.069$
 $S = 1.05$
4833 reflections
237 parameters
H-atom parameters constrained
 $\Delta\rho_{max} = 0.34$ e Å⁻³
 $\Delta\rho_{min} = -0.66$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---------------------------|-------|--------------|--------------|----------------|
| $N2-H2A \cdots Cl2^i$ | 0.86 | 2.44 | 3.226 (3) | 152 |
| $N4-H4A \cdots Cl1^{ii}$ | 0.86 | 2.45 | 3.212 (3) | 148 |
| $N6-H6A \cdots Cl2^{iii}$ | 0.86 | 2.63 | 3.314 (3) | 137 |

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

The author is are grateful to the starter fund of Southeast University for financial support to buy the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2402).

References

Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Ye, H. Y., Fu, D. W., Zhang, Y., Zhang, W., Xiong, R. G. & Huang, S. P. (2009). *J. Am. Chem. Soc.* **131**, 42–43.
Zhang, W., Cheng, L. Z., Xiong, R. G., Nakamura, T. & Huang, S. P. (2009). *J. Am. Chem. Soc.* **131**, 12544–12545.

supplementary materials

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Di- μ_3 -chlorido-tetra- μ_2 -chlorido-dichloridobis(dimethylformamide- κO)hexakis(1*H*-imidazole- κN^3)tetracadmium

R.-Q. Zhu

Comment

The title compound (I) was prepared from imidazole and cadmium(II) chloride in DMF. The solid state structure of (I) at 298 K shows a novel centrosymmetric tetranuclear cadmium quasi-cubane cluster with a $Cd_4(Cl)_2(\mu-Cl)_4(\mu_3-Cl)_2$ core structure surrounded by six imidazole and two DMF molecules (Fig. 1). There are two different coordination environments about the Cd centers: Cd(1) is coordinated by one imidazole ligand, four bridging and one terminal Cl ions, and Cd(2) is coordinated by one O atom from DMF, two N atoms from two imidazole ligands and three bridging Cl ions. The shortest intra-molecular Cd(1)—Cd(1 A) separation is 4.103 (5) Å.

In the tetranuclear cluster, the cadmium atoms are connected by six Cl atoms among which the Cl1 and Cl3 atoms act as bridges between Cd(1) and Cd(2) centers, and the Cl(4) atom is a node to connect two Cd1 and one Cd2 together. The bond length Cd1—Cl2 to the terminal Cl ligand of 2.5475 (10) Å is shorter than the mean values of Cd—Cl(μ) [2.654 (2) Å] and Cd—Cl(μ_3) [2.729 (2) Å] bond lengths.

In order to check a possibility of a structural phase transitions in compound (I), we measured its temperature-dependent dielectric constant. Large dielectric anomalies usually indicate structural changes such as paraelectric-to-ferroelectric phase transitions. Unfortunately, the dielectric constant of compound (I) goes smoothly in the temperature range 93–273 K, suggesting no distinct phase transitions occurring in this temperature range (Ye *et al.*, 2009; Zhang *et al.*, 2009).

Experimental

The mixture of $CdCl_2$ (2.27 g, 10 mmol) and imidazole (2.76 g, 40 mmol) in DMF was stirred for several days at room temperature. Colourless needle-like crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solution at room temperature over 2 weeks.

Refinement

Positional parameters of all H atoms were calculated geometrically and the H atoms were set to ride on the C atoms and N atoms to which they were bonded, with $U_{iso}(H) = 1.2 U_{iso}(C, N)$ and $1.5 U_{iso}(C)$ for methyl H atoms. C—H atoms were included with bond distances ranging from 0.98 to 1.00 Å and N—H hydrogen atoms were included with the N—H distance set to 0.84 Å.

Figures

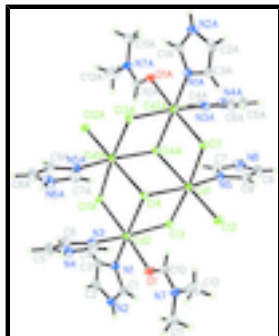


Fig. 1. The molecular structure of the title complex with displacement ellipsoids shown at the 50% probability level. Symmetry codes for the atoms with the A label: $-x, 1 - y, 1 - z$.

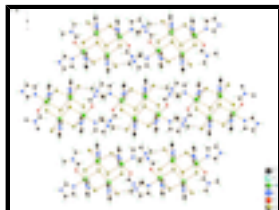


Fig. 2. Packing diagram of the title compound projected along the a axis. Hydrogen bonds are shown as dashed lines.

Di- μ_3 -chlorido-tetra- μ_2 -chlorido-dichloridobis(dimethylformamide- κO)hexakis(1*H*-imidazole- κN^3)tetracadmium

Crystal data

$[\text{Cd}_4\text{Cl}_8(\text{C}_3\text{H}_4\text{N}_2)_6(\text{C}_3\text{H}_7\text{NO})_2]$

$M_r = 1287.92$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 8.2540\ (17)\ \text{\AA}$

$b = 12.290\ (3)\ \text{\AA}$

$c = 21.119\ (4)\ \text{\AA}$

$\beta = 99.23\ (3)^\circ$

$V = 2114.6\ (8)\ \text{\AA}^3$

$Z = 2$

$F(000) = 1248$

$D_x = 2.023\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4835 reflections

$\theta = 2.5\text{--}27.5^\circ$

$\mu = 2.53\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, colourless

$0.30 \times 0.25 \times 0.20\ \text{mm}$

Data collection

Rigaku SCXmini
diffractometer

Radiation source: fine-focus sealed tube
graphite

CCD_Profile_fitting scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)

$T_{\min} = 0.472, T_{\max} = 0.603$

21502 measured reflections

4833 independent reflections

4241 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 27.5^\circ, \theta_{\min} = 3.0^\circ$

$h = -10 \rightarrow 10$

$k = -15 \rightarrow 15$

$l = -27 \rightarrow 27$

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.028$ | H-atom parameters constrained |
| $wR(F^2) = 0.069$ | $w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 1.0319P]$ |
| $S = 1.05$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 4833 reflections | $(\Delta/\sigma)_{\max} = 0.002$ |
| 237 parameters | $\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$ |
| 0 restraints | $\Delta\rho_{\min} = -0.66 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008) |
| | Extinction coefficient: 0 |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|-------------|-------------|--------------|----------------------------------|
| C1 | 0.1022 (4) | 0.0007 (3) | 0.59318 (17) | 0.0415 (8) |
| H1 | 0.1309 | -0.0205 | 0.5542 | 0.050* |
| C2 | 0.0277 (4) | -0.0083 (3) | 0.68722 (18) | 0.0457 (9) |
| H2 | -0.0036 | -0.0348 | 0.7247 | 0.055* |
| C3 | 0.0450 (4) | 0.0970 (3) | 0.67154 (16) | 0.0380 (8) |
| H3 | 0.0275 | 0.1563 | 0.6969 | 0.046* |
| C4 | 0.5413 (4) | 0.2881 (3) | 0.57582 (18) | 0.0416 (8) |
| H4 | 0.5389 | 0.2891 | 0.5316 | 0.050* |
| C5 | 0.6345 (5) | 0.2923 (4) | 0.6781 (2) | 0.0559 (10) |
| H5 | 0.7043 | 0.2964 | 0.7172 | 0.067* |
| C6 | 0.4692 (4) | 0.2792 (3) | 0.66852 (18) | 0.0484 (9) |
| H6 | 0.4053 | 0.2730 | 0.7008 | 0.058* |
| C7 | -0.5008 (4) | 0.4395 (3) | 0.38982 (19) | 0.0429 (8) |
| H7 | -0.5052 | 0.4478 | 0.4333 | 0.051* |
| C8 | -0.5764 (5) | 0.4230 (3) | 0.2874 (2) | 0.0582 (11) |
| H8 | -0.6402 | 0.4178 | 0.2470 | 0.070* |
| C9 | -0.4130 (5) | 0.4196 (3) | 0.30070 (17) | 0.0457 (9) |

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|------|--------------|---------------|---------------|--------------|
| H9 | -0.3428 | 0.4114 | 0.2707 | 0.055* |
| C10 | 0.3020 (4) | 0.1635 (3) | 0.43669 (16) | 0.0384 (8) |
| H10 | 0.2958 | 0.2363 | 0.4245 | 0.046* |
| C11 | 0.3797 (6) | -0.0201 (3) | 0.4151 (2) | 0.0638 (12) |
| H11A | 0.3284 | -0.0347 | 0.4519 | 0.096* |
| H11B | 0.4930 | -0.0415 | 0.4239 | 0.096* |
| H11C | 0.3249 | -0.0605 | 0.3790 | 0.096* |
| C12 | 0.4289 (8) | 0.1321 (5) | 0.3439 (3) | 0.096 (2) |
| H12A | 0.3740 | 0.0932 | 0.3072 | 0.144* |
| H12B | 0.5449 | 0.1192 | 0.3485 | 0.144* |
| H12C | 0.4078 | 0.2086 | 0.3382 | 0.144* |
| Cd1 | -0.10174 (3) | 0.428101 (17) | 0.415237 (10) | 0.02728 (7) |
| Cd2 | 0.14449 (3) | 0.254846 (17) | 0.557490 (11) | 0.02742 (7) |
| N1 | 0.0926 (3) | 0.1030 (2) | 0.61219 (12) | 0.0322 (6) |
| N2 | 0.0649 (4) | -0.0674 (2) | 0.63767 (16) | 0.0480 (8) |
| H2A | 0.0647 | -0.1373 | 0.6353 | 0.058* |
| N3 | 0.4108 (3) | 0.2763 (2) | 0.60408 (13) | 0.0319 (6) |
| N4 | 0.6769 (4) | 0.2984 (3) | 0.61908 (17) | 0.0502 (8) |
| H4A | 0.7747 | 0.3073 | 0.6108 | 0.060* |
| N5 | -0.3653 (3) | 0.4301 (2) | 0.36550 (13) | 0.0318 (6) |
| N6 | -0.6315 (4) | 0.4356 (3) | 0.34380 (19) | 0.0549 (9) |
| H6A | -0.7325 | 0.4402 | 0.3490 | 0.066* |
| N7 | 0.3690 (4) | 0.0952 (2) | 0.40063 (15) | 0.0433 (7) |
| O1 | 0.2472 (3) | 0.13812 (19) | 0.48519 (11) | 0.0423 (6) |
| Cl1 | -0.04823 (9) | 0.61386 (6) | 0.35684 (4) | 0.02980 (16) |
| Cl2 | 0.00339 (10) | 0.31740 (6) | 0.32819 (4) | 0.03436 (17) |
| Cl3 | -0.14308 (9) | 0.25405 (6) | 0.48437 (4) | 0.03149 (17) |
| Cl4 | 0.19278 (8) | 0.44090 (6) | 0.48833 (3) | 0.02730 (15) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| C1 | 0.053 (2) | 0.0290 (17) | 0.042 (2) | -0.0073 (16) | 0.0058 (16) | -0.0043 (15) |
| C2 | 0.045 (2) | 0.052 (2) | 0.038 (2) | -0.0087 (17) | 0.0011 (16) | 0.0146 (17) |
| C3 | 0.0392 (18) | 0.0418 (19) | 0.0326 (18) | -0.0001 (15) | 0.0045 (14) | 0.0006 (15) |
| C4 | 0.0326 (18) | 0.046 (2) | 0.048 (2) | 0.0014 (16) | 0.0132 (15) | 0.0057 (17) |
| C5 | 0.043 (2) | 0.066 (3) | 0.054 (3) | -0.002 (2) | -0.0067 (18) | -0.003 (2) |
| C6 | 0.041 (2) | 0.065 (3) | 0.040 (2) | -0.0048 (18) | 0.0077 (16) | -0.0007 (18) |
| C7 | 0.0342 (18) | 0.044 (2) | 0.052 (2) | -0.0048 (15) | 0.0136 (16) | 0.0018 (16) |
| C8 | 0.040 (2) | 0.067 (3) | 0.059 (3) | 0.001 (2) | -0.0162 (19) | -0.002 (2) |
| C9 | 0.042 (2) | 0.062 (2) | 0.0334 (19) | -0.0014 (18) | 0.0045 (15) | -0.0018 (17) |
| C10 | 0.047 (2) | 0.0311 (17) | 0.0377 (19) | 0.0053 (15) | 0.0091 (15) | -0.0054 (14) |
| C11 | 0.078 (3) | 0.042 (2) | 0.072 (3) | 0.019 (2) | 0.014 (2) | -0.007 (2) |
| C12 | 0.143 (5) | 0.082 (4) | 0.080 (4) | 0.007 (4) | 0.071 (4) | 0.001 (3) |
| Cd1 | 0.02655 (12) | 0.02762 (12) | 0.02745 (13) | -0.00098 (9) | 0.00362 (9) | -0.00129 (9) |
| Cd2 | 0.02759 (12) | 0.02543 (12) | 0.03022 (13) | 0.00193 (9) | 0.00767 (9) | 0.00044 (9) |
| N1 | 0.0365 (14) | 0.0279 (13) | 0.0323 (15) | -0.0019 (11) | 0.0058 (11) | 0.0029 (11) |
| N2 | 0.0547 (19) | 0.0268 (15) | 0.060 (2) | -0.0064 (14) | 0.0004 (16) | 0.0056 (14) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| N3 | 0.0283 (13) | 0.0317 (14) | 0.0369 (15) | 0.0022 (11) | 0.0090 (11) | 0.0024 (11) |
| N4 | 0.0294 (16) | 0.0476 (19) | 0.074 (2) | -0.0023 (14) | 0.0098 (15) | 0.0005 (17) |
| N5 | 0.0266 (13) | 0.0353 (14) | 0.0334 (15) | -0.0027 (11) | 0.0047 (11) | -0.0015 (11) |
| N6 | 0.0235 (15) | 0.053 (2) | 0.088 (3) | -0.0017 (14) | 0.0089 (16) | 0.0052 (18) |
| N7 | 0.0524 (18) | 0.0368 (16) | 0.0440 (17) | 0.0076 (14) | 0.0178 (14) | -0.0062 (13) |
| O1 | 0.0542 (15) | 0.0369 (13) | 0.0385 (14) | 0.0081 (11) | 0.0156 (11) | -0.0038 (10) |
| Cl1 | 0.0327 (4) | 0.0265 (4) | 0.0323 (4) | -0.0034 (3) | 0.0117 (3) | -0.0020 (3) |
| Cl2 | 0.0418 (4) | 0.0305 (4) | 0.0335 (4) | -0.0011 (3) | 0.0144 (3) | -0.0021 (3) |
| Cl3 | 0.0327 (4) | 0.0306 (4) | 0.0313 (4) | -0.0037 (3) | 0.0057 (3) | 0.0020 (3) |
| Cl4 | 0.0249 (3) | 0.0298 (4) | 0.0277 (4) | 0.0005 (3) | 0.0058 (3) | -0.0008 (3) |

Geometric parameters (Å, °)

| | | | |
|----------|-----------|--------------------------|-------------|
| C1—N1 | 1.326 (4) | C10—H10 | 0.9300 |
| C1—N2 | 1.330 (5) | C11—N7 | 1.450 (5) |
| C1—H1 | 0.9300 | C11—H11A | 0.9600 |
| C2—C3 | 1.349 (5) | C11—H11B | 0.9600 |
| C2—N2 | 1.350 (5) | C11—H11C | 0.9600 |
| C2—H2 | 0.9300 | C12—N7 | 1.440 (5) |
| C3—N1 | 1.374 (4) | C12—H12A | 0.9600 |
| C3—H3 | 0.9300 | C12—H12B | 0.9600 |
| C4—N3 | 1.320 (4) | C12—H12C | 0.9600 |
| C4—N4 | 1.332 (5) | Cd1—N5 | 2.259 (3) |
| C4—H4 | 0.9300 | Cd1—Cl2 | 2.5486 (9) |
| C5—N4 | 1.349 (5) | Cd1—Cl3 | 2.6426 (9) |
| C5—C6 | 1.357 (5) | Cd1—Cl1 | 2.6651 (9) |
| C5—H5 | 0.9300 | Cd1—Cl4 | 2.6671 (11) |
| C6—N3 | 1.369 (4) | Cd1—Cl4 ⁱ | 2.7920 (9) |
| C6—H6 | 0.9300 | Cd2—N1 | 2.272 (3) |
| C7—N5 | 1.308 (4) | Cd2—N3 | 2.275 (3) |
| C7—N6 | 1.332 (5) | Cd2—O1 | 2.350 (2) |
| C7—H7 | 0.9300 | Cd2—Cl3 | 2.6158 (12) |
| C8—C9 | 1.333 (5) | Cd2—Cl1 ⁱ | 2.6400 (9) |
| C8—N6 | 1.350 (6) | Cd2—Cl4 | 2.7762 (9) |
| C8—H8 | 0.9300 | N2—H2A | 0.8600 |
| C9—N5 | 1.368 (4) | N4—H4A | 0.8600 |
| C9—H9 | 0.9300 | N6—H6A | 0.8600 |
| C10—O1 | 1.225 (4) | Cl1—Cd2 ⁱ | 2.6400 (9) |
| C10—N7 | 1.313 (4) | Cl4—Cd1 ⁱ | 2.7920 (9) |
| N1—C1—N2 | 110.5 (3) | Cl3—Cd1—Cl4 | 85.09 (3) |
| N1—C1—H1 | 124.7 | Cl1—Cd1—Cl4 | 90.80 (3) |
| N2—C1—H1 | 124.7 | N5—Cd1—Cl4 ⁱ | 88.92 (7) |
| C3—C2—N2 | 106.3 (3) | Cl2—Cd1—Cl4 ⁱ | 175.27 (2) |
| C3—C2—H2 | 126.9 | Cl3—Cd1—Cl4 ⁱ | 89.43 (3) |
| N2—C2—H2 | 126.9 | Cl1—Cd1—Cl4 ⁱ | 85.84 (3) |
| C2—C3—N1 | 109.4 (3) | Cl4—Cd1—Cl4 ⁱ | 82.58 (3) |
| C2—C3—H3 | 125.3 | N1—Cd2—N3 | 97.08 (9) |

supplementary materials

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|---------------|------------|---------------------------|------------|
| N1—C3—H3 | 125.3 | N1—Cd2—O1 | 86.90 (9) |
| N3—C4—N4 | 110.9 (3) | N3—Cd2—O1 | 85.85 (9) |
| N3—C4—H4 | 124.6 | N1—Cd2—Cl3 | 94.01 (7) |
| N4—C4—H4 | 124.6 | N3—Cd2—Cl3 | 167.97 (7) |
| N4—C5—C6 | 105.8 (3) | O1—Cd2—Cl3 | 90.10 (7) |
| N4—C5—H5 | 127.1 | N1—Cd2—Cl1 ⁱ | 92.97 (7) |
| C6—C5—H5 | 127.1 | N3—Cd2—Cl1 ⁱ | 90.51 (7) |
| C5—C6—N3 | 109.6 (3) | O1—Cd2—Cl1 ⁱ | 176.31 (6) |
| C5—C6—H6 | 125.2 | Cl3—Cd2—Cl1 ⁱ | 93.58 (3) |
| N3—C6—H6 | 125.2 | N1—Cd2—Cl4 | 177.38 (7) |
| N5—C7—N6 | 110.7 (3) | N3—Cd2—Cl4 | 85.51 (7) |
| N5—C7—H7 | 124.6 | O1—Cd2—Cl4 | 93.66 (6) |
| N6—C7—H7 | 124.6 | Cl3—Cd2—Cl4 | 83.44 (3) |
| C9—C8—N6 | 106.9 (4) | Cl1 ⁱ —Cd2—Cl4 | 86.65 (3) |
| C9—C8—H8 | 126.5 | C1—N1—C3 | 105.4 (3) |
| N6—C8—H8 | 126.5 | C1—N1—Cd2 | 126.9 (2) |
| C8—C9—N5 | 109.0 (4) | C3—N1—Cd2 | 127.7 (2) |
| C8—C9—H9 | 125.5 | C1—N2—C2 | 108.4 (3) |
| N5—C9—H9 | 125.5 | C1—N2—H2A | 125.8 |
| O1—C10—N7 | 124.7 (3) | C2—N2—H2A | 125.8 |
| O1—C10—H10 | 117.7 | C4—N3—C6 | 105.3 (3) |
| N7—C10—H10 | 117.7 | C4—N3—Cd2 | 128.2 (2) |
| N7—C11—H11A | 109.5 | C6—N3—Cd2 | 126.5 (2) |
| N7—C11—H11B | 109.5 | C4—N4—C5 | 108.3 (3) |
| H11A—C11—H11B | 109.5 | C4—N4—H4A | 125.8 |
| N7—C11—H11C | 109.5 | C5—N4—H4A | 125.8 |
| H11A—C11—H11C | 109.5 | C7—N5—C9 | 105.9 (3) |
| H11B—C11—H11C | 109.5 | C7—N5—Cd1 | 129.7 (2) |
| N7—C12—H12A | 109.5 | C9—N5—Cd1 | 124.4 (2) |
| N7—C12—H12B | 109.5 | C7—N6—C8 | 107.4 (3) |
| H12A—C12—H12B | 109.5 | C7—N6—H6A | 126.3 |
| N7—C12—H12C | 109.5 | C8—N6—H6A | 126.3 |
| H12A—C12—H12C | 109.5 | C10—N7—C12 | 120.9 (4) |
| H12B—C12—H12C | 109.5 | C10—N7—C11 | 121.3 (3) |
| N5—Cd1—Cl2 | 94.83 (7) | C12—N7—C11 | 117.7 (3) |
| N5—Cd1—Cl3 | 93.76 (7) | C10—O1—Cd2 | 127.5 (2) |
| Cl2—Cd1—Cl3 | 93.18 (3) | Cd2 ⁱ —Cl1—Cd1 | 96.66 (3) |
| N5—Cd1—Cl1 | 89.68 (7) | Cd2—Cl3—Cd1 | 97.92 (3) |
| Cl2—Cd1—Cl1 | 91.30 (3) | Cd1—Cl4—Cd2 | 93.53 (3) |
| Cl3—Cd1—Cl1 | 174.11 (2) | Cd1—Cl4—Cd1 ⁱ | 97.42 (3) |
| N5—Cd1—Cl4 | 171.43 (7) | Cd2—Cl4—Cd1 ⁱ | 90.75 (3) |
| Cl2—Cd1—Cl4 | 93.71 (3) | | |

Symmetry codes: (i) $-x, -y+1, -z+1$.

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------|-------|-------------|-------------|---------------|
|---------------|-------|-------------|-------------|---------------|

| | | | | |
|-----------------------------|------|------|-----------|------|
| N2—H2A···C12 ⁱⁱ | 0.86 | 2.44 | 3.226 (3) | 152. |
| N4—H4A···C11 ⁱⁱⁱ | 0.86 | 2.45 | 3.212 (3) | 148. |
| N6—H6A···C12 ^{iv} | 0.86 | 2.63 | 3.314 (3) | 137. |

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

Fig. 1

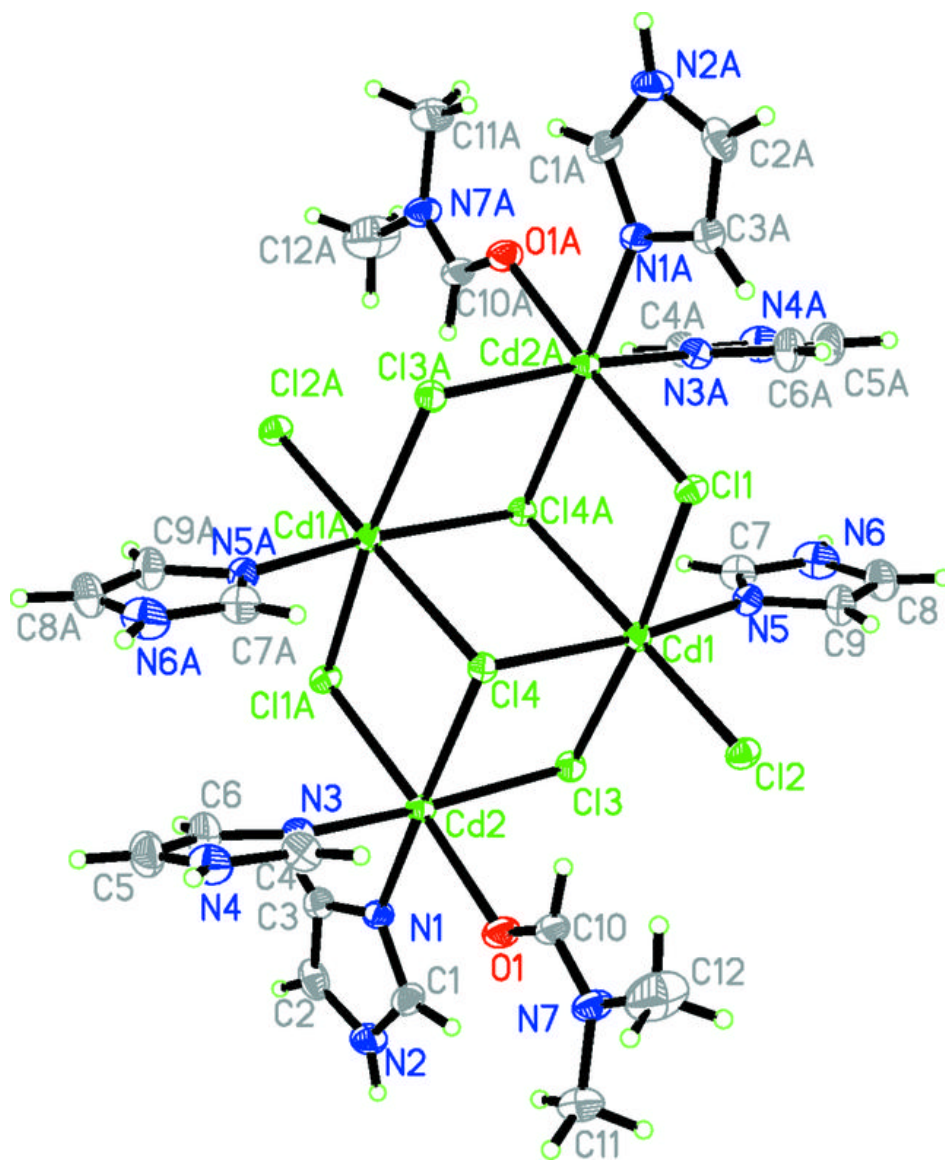


Fig. 2

