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Crystal structure of di-μ-chlorido-bis[dichlorido-(L-histidinium-κO)cadmium(II)]

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In the title compound, $[Cd_2(C_6H_9N_3O_2)_2Cl_6]$, the coordination polyhedra around the Cd^{II} cations are distorted trigonal bipyramids. Two of the chloride ions (one axial and one equatorial) are bridging to the other metal atom, leading to a Cd···Cd separation of 3.9162 (4) Å. The O atom of the L-histidinium cation lies in an axial site. In the crystal, numerous N-H···Cl, N-H···O, C-H···O and C-H···Cl hydrogen bonds link the molecules into a three-dimensional network. Theoretical calculations and spectroscopic data are available as supporting information.

1. Chemical context

As a natural amino acid, L-histidine occurs in all organisms. It is a metal chelator in plants accumulating nickel from the soil (Krämer et al., 1996) and a part of the copper-transport system in human blood (Deschamps et al., 2005). Considerable efforts have been made to combine amino acids with organic and inorganic matrices to produce materials having a noncentrosymmetric cell, large polarizabilities and a strong nonlinear optical coefficient (Ben Ahmed et al., 2008). As a chelating ligand, L-histidine provides up to three potential binding sites, as has been shown in complexes with nickel(II) (Sakurai et al., 1978), chromium(III) (Pennington et al., 1984), cobalt(III) (Herak et al., 1981), molybdenum(V) (Wu et al., 2005), vanadium(IV) (Islam et al., 2007) and copper(II) (Deschamps et al., 2005). In this work, we report the synthesis and structure of the title cadmium complex with L-histidine, (I). Cadmium is structurally interesting as it exhibits a number of coordination numbers and geometries such as those in [CdCl₄] (Boufas et al., 2009), [Cd₃Cl₁₁] (Kurawa et al., 2008), $[CdCl_6]_n$ (Jarboui *et al.*, 2011) and $[CdCl_4]_n$ (Loseva *et al.*, 2010).



2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The asymmetric unit contains a $[Cd_2Cl_6]^{2-}$ anionic core bridging a pair of histidinium cations *via* Cd–O bonds. Each

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The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level.

cadmium atom is five-coordinated within a CdCl₄O environment, where atoms Cl3, Cl4 and Cl5 define the equatorial plane for Cd1, and Cl2 and O1 are in axial positions [O1–Cd1–Cl2 = 166.2 (1)°]. A similar coordination is observed for Cd2, and in this case the equatorial plane is formed by atoms Cl1, Cl2 and Cl6, while O3 and Cl5 are in equatorial positions [O3–Cd2–Cl5 = 165.2 (1)°]. Two μ -Cl atoms lead to a Cd₂Cl₂ square with a Cd1···Cd2 distance of 3.9162 (4) Å. The Cd–Cl distances lie in the range 2.4662 (12) to 2.7244 (14) Å for Cd1 and 2.4812 (11) to 2.7344 (14) Å for Cd2. The Cl–Cd–Cl angles are in the range of 82.61 (4) to 121.93 (3)°.

In the histidinium cation, the α -amino and imidazole groups are protonated and positively charged, while the carboxyl group is deprotonated and negatively charged, which confirms that cations occur in their zwitterionic forms and carry a net positive charge. As expected, the imidazol rings are almost planar with r.m.s deviations for the non-H atoms of 0.003 Å in each molecule. The imidazol group is *trans* to the carboxyl group and *gauche* to the amino N atom.

The conformation of the histidine side chain can be described by the two torsion angles, χ_1 and χ_{21} (IUPAC–IUB Commission on Biochemical Nomenclature, 1970). Angle χ_1 , which defines the disposition of the side chain with respect to the main chain, can take values in the neighbourhood of -60, +60 or 180° , corresponding to the open conformation I (g^{-}), closed conformation (g^{+}) and open conformation II (t), respectively (Krause *et al.*, 1991). The χ_{21} values lie near -90 or $+90^{\circ}$ but the angle often deviates from these ideal values, as a result of interactions between the imidazole ring and other groups in the structure. In the title compound, the following values are seen: $\chi_1 = -52.9$ (6); $\chi_{1'} = -52.3$ (5); $\chi_{21} = -72.2$ (7); $\chi_{21'} = -82.5$ (7)°. Hence, both histidinium cations adopt the sterically favourable open conformation in (I).



Figure 2 Packing diagram for (I). Red dashed lines indicate hydrogen bonds.

rjurogen bond geometry (ri,).				
$D - H \cdot \cdot \cdot A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
$N1-H1A\cdots O3^{i}$	0.89	2.01	2.881 (5)	167
$N1-H1C\cdots Cl6^{i}$	0.89	2.44	3.070 (4)	128
$N2-H2\cdots Cl4^{i}$	0.86	2.37	3.215 (5)	167
N3-H3···O4 ⁱⁱ	0.86	1.99	2.751 (6)	146
$N4-H11A\cdots Cl1^{iii}$	0.89	2.38	3.229 (4)	160
N4-H11 B ···Cl3 ^{iv}	0.89	2.70	3.426 (5)	140
$N4-H11C\cdotsO1^{v}$	0.89	1.96	2.846 (6)	171
$N5-H22A\cdots O2^{iv}$	0.86	1.94	2.699 (6)	147
$N6-H33\cdots Cl6^{v}$	0.86	2.28	3.137 (5)	174
$C2-H2A\cdots O4^{ii}$	0.98	2.56	3.252 (7)	128
$C5-H5\cdots Cl2^{i}$	0.93	2.79	3.424 (6)	126
$C9-H33B\cdots Cl3^{vi}$	0.97	2.81	3.686 (6)	151
$C11-H55\cdots Cl5^{v}$	0.93	2.71	3.405 (6)	132
$C11-H55\cdots O1^{v}$	0.93	2.53	3.245 (7)	134
$C12-H66\cdots Cl1^{iv}$	0.93	2.78	3.618 (6)	151

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

3. Supramolecular features

The extended structure of (I) is consolidated by a number of hydrogen-bonding $(N-H\cdots Cl \text{ and } N-H\cdots O)$ interactions (Table 1). The chloride anions and oxygen atoms play an important role in accepting hydrogen bonds from the amine N atom and the N atoms of the imidazolium ring. These interactions, together with weak $C-H\cdots Cl$ and $C-H\cdots O$ interactions, generate a three-dimensional network (Fig. 2).

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update May 2017; Groom *et al.*, 2016) revealed that the geometric parameters of the title compound are similar to those found in bis(creatininium) tetrachloridocadmate(II) (Boufas *et al.*, 2009). The imidazol group conformation of the title compound is in contrast to the bent *gauche* conformation found in the structure of L-HisH⁺·Cl⁻·H₂O (Donohue *et al.*, 1956, 1964), but similar to the *trans* conformation observed in DL-HisH⁺·Cl⁻·2H₂O (Steiner, 1996)

5. Synthesis and crystallization

The title compound was prepared by dissolving 1 mmol (155.16 mg) of L-histidine in 50.0 ml of water with a mixture of $CdCl_2 \cdot 2H_2O$ (1 mmol) and HCl (8 mmol). The resulting mixture was capped and then heated at 353 K in a water bath for 1 h under continuous stirring and then left to slowly evaporate at room temperature. After two weeks, colourless crystals were obtained, which appear to be indefinitely stable when stored in air. Theoretical calculations and spectroscopic data are available as supporting information.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in difference-Fourier maps and subsequently treated as riding
 Table 2

 Experimental details.

Crystal data Chemical formula [Cd₂(C₆H₉N₃O₂)₂Cl₆] 749.87 M_r Crystal system, space group Triclinic, P1 Temperature (K) 100 7.1540 (6), 8.2591 (6), 10.4459 (8) a, b, c (Å) α, β, γ (°) V (Å³) 108.502 (2), 97.499 (2), 94.512 (2) 575.54 (8) Ζ 1 Radiation type Μο Κα $\mu \ (\mathrm{mm}^{-1})$ 2 58 Crystal size (mm) $0.08 \times 0.03 \times 0.02$ Data collection Diffractometer Bruker Nonius KappaCCD Absorption correction Multi-scan (SADABS; Sheldrick, 2003) 0.820, 0.950 T_{\min}, T_{\max} No. of measured, independent and 7735, 4856, 4799 observed $[I > 2\sigma(I)]$ reflections 0.025 R_{int} $(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$ 0.651 Refinement $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ 0.024, 0.057, 1.08 No. of reflections 4856 No. of parameters 274 No. of restraints 3 H-atom treatment H-atom parameters constrained $\Delta \rho_{\rm max}, \, \Delta \rho_{\rm min} \ ({\rm e} \ {\rm \AA}^{-3})$ 1.33, -0.44 Flack & Bernardinelli (2000) Absolute structure Absolute structure parameter 0.02(2)

Computer programs: COLLECT(Nonius, 2002), DENZO and SCALEPACK (Otwinowski & Minor, 1997), SIR2014 (Burla et al., 2015), SHELXL2018 (Sheldrick, 2015), Mercury (Macrae et al., 2006), WinGX (Farrugia, 2012) and PARST (Nardelli, 1995).

atoms in geometrically idealized positions: N-H = 0.86 (NH) or 0.89 (NH₃) Å, C-H = 0.93 (cyclic), 0.97 (CH₂) or 0.98 (aliphatic C-H) Å with $U_{iso}(H) = kU_{eq}(N,C)$, where k = 1.5for the NH₃ and methyl groups (which were permitted to rotate but not to tilt) and 1.2 for all other H atoms.

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Crystal structure of di-μ-chlorido-bis[dichlorido(L-histidinium-κO)cadmium(II)]

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Computing details

Data collection: *COLLECT*(Nonius, 2002); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR2014* (Burla *et al.*, 2015); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PARST* (Nardelli, 1995).

Z = 1

Di-µ-chlorido-bis[dichlorido(L-histidinium- κO)cadmium(II)]

Crystal data

 $\begin{bmatrix} Cd_{2}(C_{6}H_{9}N_{3}O_{2})_{2}Cl_{6} \end{bmatrix}$ $M_{r} = 749.87$ Triclinic, P1 Hall symbol: P 1 a = 7.1540 (6) Å b = 8.2591 (6) Å c = 10.4459 (8) Å $a = 108.502 (2)^{\circ}$ $\beta = 97.499 (2)^{\circ}$ $\gamma = 94.512 (2)^{\circ}$ $V = 575.54 (8) Å^{3}$

Data collection

Bruker Nonius KappaCCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.2632 pixels mm ⁻¹
ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 2003)
$T_{\min} = 0.820, \ T_{\max} = 0.950$

Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.024$ $wR(F^2) = 0.057$ S = 1.084856 reflections 274 parameters 3 restraints F(000) = 364 $D_x = 2.163 \text{ Mg m}^{-3}$ Mo Ka radiation, $\lambda = 0.71073 \text{ Å}$ Cell parameters from 6833 reflections $\theta = 2.6-27.6^{\circ}$ $\mu = 2.58 \text{ mm}^{-1}$ T = 100 KBlock, colourless $0.08 \times 0.03 \times 0.02 \text{ mm}$ 7735 measured reflections
4856 independent reflections
4799 reflections with $I > 2\sigma(I)$

 $R_{int} = 0.025$ $\theta_{max} = 27.6^{\circ}, \ \theta_{min} = 2.6^{\circ}$ $h = -9 \rightarrow 9$ $k = -10 \rightarrow 10$ $l = -13 \rightarrow 13$

Hydrogen site location: inferred from neighbouring sites H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0263P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 1.33$ e Å⁻³ $\Delta\rho_{min} = -0.43$ e Å⁻³

Absolute structure: Flack & Bernardinelli (2000)

Absolute structure parameter: 0.02 (2)

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.

	x	у	Ζ	$U_{ m iso}$ */ $U_{ m eq}$	
Cd2	0.32732 (4)	0.13067 (3)	0.53489 (3)	0.00958 (10)	
Cd1	0.21319 (4)	-0.04006 (3)	0.13444 (3)	0.00944 (10)	
C12	0.5118 (2)	0.10427 (15)	0.34159 (13)	0.0111 (3)	
Cl4	0.38809 (19)	-0.29705 (15)	0.05541 (13)	0.0118 (2)	
C15	0.0240 (2)	0.02992 (15)	0.32637 (13)	0.0107 (3)	
C11	0.25293 (19)	0.42775 (14)	0.63993 (13)	0.0131 (3)	
C16	0.18541 (19)	-0.11633 (15)	0.59302 (13)	0.0138 (3)	
C13	0.2694 (2)	0.17319 (16)	0.01896 (15)	0.0161 (3)	
03	0.5872 (5)	0.1400 (4)	0.6964 (4)	0.0117 (7)	
C4	-0.3126 (9)	-0.3001 (7)	-0.4445 (6)	0.0096 (12)	
O4	0.7438 (5)	0.3680 (4)	0.6649 (4)	0.0133 (8)	
01	-0.0490 (5)	-0.2181 (4)	-0.0211 (4)	0.0115 (7)	
N1	-0.4829 (6)	-0.1360 (5)	-0.1962 (4)	0.0126 (9)	
H1A	-0.447402	-0.043754	-0.218017	0.019*	
H1B	-0.522967	-0.102932	-0.115773	0.019*	
H1C	-0.576801	-0.202840	-0.260150	0.019*	
O2	-0.2172 (6)	0.0068 (4)	0.0144 (4)	0.0133 (8)	
C8	0.8474 (9)	0.3019 (6)	0.8662 (6)	0.0101 (11)	
H22	0.891581	0.194267	0.870762	0.012*	
N5	0.8879 (7)	0.3255 (6)	1.1983 (5)	0.0115 (10)	
H22A	0.860404	0.215366	1.170454	0.014*	
N2	-0.4575 (7)	-0.3273 (6)	-0.6510 (5)	0.0124 (10)	
H2	-0.502332	-0.302327	-0.721887	0.015*	
N3	-0.3875 (7)	-0.4694 (6)	-0.5153 (5)	0.0130 (10)	
H3	-0.378659	-0.553255	-0.483665	0.016*	
N4	1.0146 (6)	0.4309 (5)	0.8826 (4)	0.0107 (9)	
H11A	1.054037	0.413115	0.802492	0.013*	
H11B	1.108038	0.420170	0.943384	0.013*	
H11C	0.981433	0.536510	0.911830	0.013*	
C3	-0.2016 (8)	-0.2381 (6)	-0.3028 (5)	0.0097 (11)	
H3A	-0.138831	-0.122866	-0.284998	0.012*	
H3B	-0.103314	-0.311671	-0.298755	0.012*	
C6	-0.4754 (9)	-0.4837 (7)	-0.6399 (6)	0.0135 (12)	
H6	-0.537559	-0.584164	-0.706536	0.016*	
C9	0.7299 (8)	0.3710 (6)	0.9811 (6)	0.0097 (11)	
H33A	0.669343	0.465858	0.966065	0.012*	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters $(Å^2)$

H33B	0.630052	0.280691	0.974320	0.012*
C1	-0.1857 (10)	-0.1393 (7)	-0.0503 (6)	0.0117 (13)
C5	-0.3564 (9)	-0.2120 (7)	-0.5316 (6)	0.0147 (13)
Н5	-0.323972	-0.094758	-0.513781	0.018*
C2	-0.3185 (8)	-0.2340 (6)	-0.1874 (6)	0.0090 (11)
H2A	-0.362841	-0.351433	-0.192256	0.011*
C10	0.8396 (9)	0.4311 (7)	1.1223 (6)	0.0095 (12)
N6	0.9961 (7)	0.5842 (6)	1.3260 (5)	0.0129 (10)
H33	1.051801	0.670205	1.395165	0.015*
C12	0.9823 (9)	0.4198 (7)	1.3198 (6)	0.0137 (12)
H66	1.030715	0.378824	1.388932	0.016*
C7	0.7185 (9)	0.2673 (7)	0.7288 (6)	0.0086 (12)
C11	0.9078 (9)	0.5944 (6)	1.2053 (6)	0.0136 (12)
H55	0.896359	0.694526	1.183723	0.016*

Atomic displacement parameters $(Å^2)$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd2	0.0101 (2)	0.00984 (15)	0.0073 (2)	-0.00029 (13)	-0.00021 (15)	0.00184 (13)
Cd1	0.0105 (2)	0.00944 (15)	0.0071 (2)	0.00022 (13)	-0.00009 (15)	0.00171 (13)
Cl2	0.0106 (7)	0.0129 (5)	0.0080 (6)	-0.0004 (5)	-0.0004 (5)	0.0020 (5)
Cl4	0.0112 (7)	0.0124 (5)	0.0097 (6)	0.0026 (5)	0.0001 (5)	0.0013 (4)
C15	0.0106 (7)	0.0127 (5)	0.0071 (6)	0.0004 (5)	0.0007 (5)	0.0016 (5)
Cl1	0.0155 (7)	0.0120 (5)	0.0111 (6)	0.0024 (5)	0.0040 (6)	0.0021 (5)
Cl6	0.0123 (7)	0.0171 (5)	0.0111 (6)	-0.0051 (5)	-0.0026 (5)	0.0069 (5)
C13	0.0145 (7)	0.0195 (5)	0.0185 (7)	0.0018 (5)	0.0022 (6)	0.0123 (5)
O3	0.012 (2)	0.0110 (14)	0.0090 (18)	-0.0013 (13)	-0.0035 (15)	0.0016 (13)
C4	0.008 (3)	0.013 (2)	0.007 (3)	0.001 (2)	0.002 (2)	0.001 (2)
O4	0.015 (2)	0.0168 (16)	0.0083 (19)	0.0010 (15)	-0.0007 (16)	0.0057 (14)
O1	0.012 (2)	0.0102 (14)	0.0091 (18)	0.0019 (14)	-0.0026 (15)	0.0000 (13)
N1	0.012 (2)	0.0147 (18)	0.011 (2)	0.0012 (17)	0.0015 (19)	0.0044 (17)
02	0.016 (2)	0.0105 (14)	0.0098 (19)	0.0018 (13)	-0.0032 (16)	0.0005 (13)
C8	0.012 (3)	0.009 (2)	0.009 (3)	-0.003(2)	-0.002 (2)	0.004 (2)
N5	0.011 (3)	0.0110 (18)	0.010 (3)	0.0024 (17)	0.003 (2)	0.0005 (17)
N2	0.014 (3)	0.019 (2)	0.006 (2)	0.0066 (19)	0.004 (2)	0.0040 (19)
N3	0.011 (3)	0.017 (2)	0.012 (2)	0.0009 (17)	0.001 (2)	0.0072 (18)
N4	0.014 (2)	0.0109 (16)	0.007 (2)	0.0009 (16)	0.0019 (18)	0.0030 (15)
С3	0.010 (3)	0.012 (2)	0.006 (3)	0.0005 (19)	0.001 (2)	0.0022 (19)
C6	0.010 (3)	0.016 (2)	0.012 (3)	-0.002(2)	0.001 (2)	0.003 (2)
С9	0.009 (3)	0.009 (2)	0.010 (3)	0.0004 (18)	0.003 (2)	0.0012 (19)
C1	0.013 (3)	0.010 (2)	0.012 (3)	-0.001 (2)	0.001 (2)	0.005 (2)
C5	0.017 (3)	0.014 (2)	0.013 (3)	0.004 (2)	0.002 (3)	0.004 (2)
C2	0.009 (3)	0.012 (2)	0.006 (3)	0.003 (2)	0.002 (2)	0.002 (2)
C10	0.009 (3)	0.010 (2)	0.009 (3)	0.001 (2)	0.003 (2)	0.003 (2)
N6	0.012 (3)	0.015 (2)	0.008 (3)	-0.0009 (19)	0.001 (2)	-0.0014 (19)
C12	0.014 (3)	0.016 (3)	0.009 (3)	0.002 (2)	0.001 (2)	0.002 (2)
C7	0.010 (3)	0.008 (2)	0.006 (3)	0.001 (2)	0.002 (2)	-0.001 (2)
C11	0.017 (3)	0.012(2)	0.012 (3)	0.000(2)	0.003 (2)	0.004(2)

Geometric parameters (Å, °)

Cd1—01	2.361 (4)	N5—C10	1.388 (6)	
Cd1—Cl3	2.4662 (12)	N5—H22A	0.8600	
Cd1—Cl5	2.5061 (14)	N2—C6	1.331 (7)	
Cd1—Cl4	2.5155 (12)	N2—C5	1.374 (8)	
Cd1—Cl2	2.7244 (14)	N2—H2	0.8600	
Cd2—O3	2.320 (3)	N3—C6	1.335 (7)	
Cd2—C11	2.4812 (11)	N3—H3	0.8600	
Cd2—C16	2.4864 (12)	N4—H11A	0.8900	
Cd2—Cl2	2.5155 (14)	N4—H11B	0.8900	
Cd2—C15	2.7344 (14)	N4—H11C	0.8900	
Cd2—Cd1	3.9162 (5)	C3—C2	1.548 (8)	
O3—C7	1.280 (7)	C3—H3A	0.9700	
C4—C5	1.355 (7)	C3—H3B	0.9700	
C4—N3	1.383 (7)	С6—Н6	0.9300	
C4—C3	1.494 (8)	C9—C10	1.486 (8)	
O4—C7	1.236 (6)	C9—H33A	0.9700	
O1—C1	1.274 (7)	C9—H33B	0.9700	
N1—C2	1.489 (6)	C1—C2	1.543 (9)	
N1—H1A	0.8900	C5—H5	0.9300	
N1—H1B	0.8900	C2—H2A	0.9800	
N1—H1C	0.8900	C10—C11	1.362 (8)	
O2—C1	1.236 (7)	N6—C12	1.334 (7)	
C8—N4	1.492 (7)	N6—C11	1.366 (7)	
C8—C7	1.531 (8)	N6—H33	0.8600	
C8—C9	1.542 (8)	С12—Н66	0.9300	
C8—H22	0.9800	C11—H55	0.9300	
N5—C12	1.319 (8)			
O1—Cd1—Cl3	99.31 (8)	C8—N4—H11A	109.5	
O1—Cd1—Cl5	91.97 (9)	C8—N4—H11B	109.5	
Cl3—Cd1—Cl5	118.96 (4)	H11A—N4—H11B	109.5	
O1—Cd1—Cl4	84.88 (8)	C8—N4—H11C	109.5	
Cl3—Cd1—Cl4	113.33 (4)	H11A—N4—H11C	109.5	
Cl5—Cd1—Cl4	127.41 (4)	H11B—N4—H11C	109.5	
O1—Cd1—Cl2	166.16 (8)	C4—C3—C2	115.5 (5)	
Cl3—Cd1—Cl2	94.41 (4)	C4—C3—H3A	108.4	
Cl5—Cd1—Cl2	82.99 (4)	C2—C3—H3A	108.4	
Cl4—Cd1—Cl2	87.97 (4)	C4—C3—H3B	108.4	
O3—Cd2—Cl1	97.93 (9)	C2—C3—H3B	108.4	
O3—Cd2—Cl6	85.65 (9)	НЗА—СЗ—НЗВ	107.5	
Cl1—Cd2—Cl6	121.93 (4)	N2—C6—N3	107.2 (5)	
O3—Cd2—Cl2	95.70 (10)	N2—C6—H6	126.4	
Cl1—Cd2—Cl2	112.59 (4)	N3—C6—H6	126.4	
Cl6—Cd2—Cl2	124.74 (4)	C10—C9—C8	115.2 (5)	
O3—Cd2—Cl5	165.13 (8)	С10—С9—Н33А	108.5	
Cl1—Cd2—Cl5	96.33 (4)	C8—C9—H33A	108.5	

Cl6—Cd2—Cl5	83.27 (4)	C10—C9—H33B	108.5
Cl2—Cd2—Cl5	82.61 (4)	С8—С9—Н33В	108.5
Cd2—Cl2—Cd1	96.64 (5)	H33A—C9—H33B	107.5
Cd1— $Cl5$ — $Cd2$	96.62 (5)	02-C1-01	127.5 (6)
C7-O3-Cd2	117.6(3)	0^{2} -C1 -C2	1169(5)
$C_{5}-C_{4}-N_{3}$	105.7(5)	01 - C1 - C2	115.5(5)
$C_{5} - C_{4} - C_{3}$	129.8 (5)	C4-C5-N2	107.6(5)
$N_3 - C_4 - C_3$	129.0(3) 124 5 (4)	C4-C5-H5	126.2
C1 = O1 = Cd1	124.9(4) 1149(3)	N2-C5-H5	126.2
C_2 _N1_H1A	109.5	$N_{1} - C_{2} - C_{1}$	120.2 108 2 (4)
C_2 N1 H1R	109.5	N1 C2 C3	100.2(4)
H14 $N1$ $H1B$	109.5	C1 - C2 - C3	110.9(4)
$C_2 N1 H1C$	109.5	N1 C2 H2A	110.2
HIA NI HIC	109.5	N1 - C2 - H2A	110.2
HIA-NI-HIC	109.5	C1 - C2 - H2A	110.2
$\mathbf{M} = \mathbf{M} = \mathbf{M} = \mathbf{M} = \mathbf{M}$	109.5	C_{3} C_{2} $H_{2}A$	110.2 105.7(5)
N4 = C8 = C7	110.0(4)	$C_{11} = C_{10} = N_3$	103.7(3)
N4-C8-C9	109.8 (4)	CII—CI0—C9	129.2 (4)
C = C = C = C = C = C = C = C = C = C =	108.1 (5)	N5 - C10 - C9	125.1 (5)
N4-C8-H22	109.4	C12—N6— $C11$	109.2 (5)
C/-C8-H22	109.4	C12—N6—H33	125.4
C9—C8—H22	109.4	C11—N6—H33	125.4
C12—N5—C10	109.6 (5)	N5-C12-N6	108.0 (5)
C12—N5—H22A	125.2	N5—C12—H66	126.0
C10—N5—H22A	125.2	N6—C12—H66	126.0
C6—N2—C5	109.5 (5)	O4—C7—O3	126.8 (6)
C6—N2—H2	125.3	O4—C7—C8	118.0 (5)
C5—N2—H2	125.3	O3—C7—C8	115.0 (4)
C6—N3—C4	110.1 (4)	C10—C11—N6	107.4 (4)
C6—N3—H3	125.0	C10—C11—H55	126.3
C4—N3—H3	125.0	N6-C11-H55	126.3
C5—C4—N3—C6	-0.7 (7)	C4—C3—C2—N1	-52.9 (6)
C3—C4—N3—C6	-178.8 (5)	C4—C3—C2—C1	-170.8(4)
C5—C4—C3—C2	110.2 (7)	C12—N5—C10—C11	-0.8 (7)
N3—C4—C3—C2	-72.2 (7)	C12—N5—C10—C9	-179.0(6)
C5—N2—C6—N3	0.1 (7)	C8—C9—C10—C11	99.8 (7)
C4—N3—C6—N2	0.4 (7)	C8—C9—C10—N5	-82.5 (7)
N4—C8—C9—C10	-52.3 (5)	C10—N5—C12—N6	0.5 (7)
C7—C8—C9—C10	-173.0(4)	C11—N6—C12—N5	0.1 (7)
Cd1-01-C1-02	-18.4 (8)	Cd2—O3—C7—O4	-16.1(8)
Cd1-01-C1-C2	157.2 (3)	Cd2—O3—C7—C8	159.6 (4)
N3-C4-C5-N2	0.7 (7)	N4—C8—C7—O4	-13.9(7)
$C_{3}-C_{4}-C_{5}-N_{2}$	178.7 (6)	C9—C8—C7—O4	106.4 (6)
C6—N2—C5—C4	-0.5(7)	N4—C8—C7—O3	169.9 (4)
02-C1-C2-N1	-11.4 (7)	C9—C8—C7—O3	-69.8(5)
01-C1-C2-N1	172.5 (5)	N5-C10-C11-N6	0.9 (7)
02-C1-C2-C3	108.2 (6)	C9-C10-C11-N6	178.9 (6)
01-C1-C2-C3	-67.8 (6)	C_{12} N6 C_{11} C10	-0.6(7)
			··· (/)

supporting information

D—H···A	<i>D</i> —Н	$H \cdots A$	$D \cdots A$	D—H···A
N1—H1A···O3 ⁱ	0.89	2.01	2.881 (5)	167
N1—H1 <i>C</i> ···Cl6 ⁱ	0.89	2.44	3.070 (4)	128
N2—H2···Cl4 ⁱ	0.86	2.37	3.215 (5)	167
N3—H3…O4 ⁱⁱ	0.86	1.99	2.751 (6)	146
N4—H11A…C11 ⁱⁱⁱ	0.89	2.38	3.229 (4)	160
N4—H11 <i>B</i> ····Cl3 ^{iv}	0.89	2.70	3.426 (5)	140
N4—H11 <i>C</i> …O1 ^v	0.89	1.96	2.846 (6)	171
N5—H22 <i>A</i> …O2 ^{iv}	0.86	1.94	2.699 (6)	147
N6—H33····Cl6 ^v	0.86	2.28	3.137 (5)	174
C2—H2A····O4 ⁱⁱ	0.98	2.56	3.252 (7)	128
C5—H5····Cl2 ⁱ	0.93	2.79	3.424 (6)	126
C9—H33 <i>B</i> ····Cl3 ^{vi}	0.97	2.81	3.686 (6)	151
C11—H55····Cl5 ^v	0.93	2.71	3.405 (6)	132
C11—H55…O1 ^v	0.93	2.53	3.245 (7)	134
C12—H66…C11 ^{iv}	0.93	2.78	3.618 (6)	151

Hydrogen-bond geometry (Å, °)

Symmetry codes: (i) *x*-1, *y*, *z*-1; (ii) *x*-1, *y*-1, *z*-1; (iii) *x*+1, *y*, *z*; (iv) *x*+1, *y*, *z*+1; (v) *x*+1, *y*+1, *z*+1; (vi) *x*, *y*, *z*+1.