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Bis[3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato]cadmium(II) tetrahydrate

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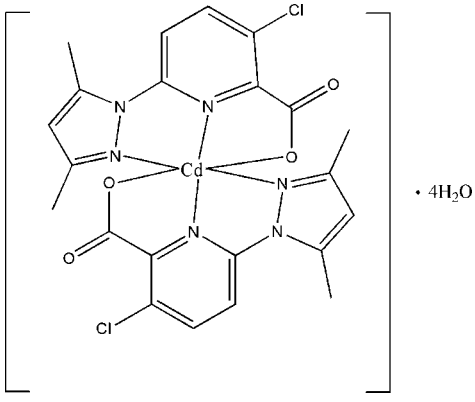
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.007 Å; R factor = 0.037; wR factor = 0.101; data-to-parameter ratio = 13.2.

In the title compound, $[Cd(C_{11}H_9ClN_3O_2)_2]\cdot 4H_2O$, the Cd^{II} atom is coordinated by four N atoms and two O atoms from two picolinate ligands in a distorted octahedral geometry. In the crystal structure, molecules are linked together by intermolecular O—H···O hydrogen bonds.

Related literature

For related literature, see: Bhatia *et al.* (1981); Costamagna *et al.* (1992).



Experimental

Crystal data

$[Cd(C_{11}H_9ClN_3O_2)_2]\cdot 4H_2O$
M_r = 685.79
Triclinic, $P\overline{1}$
a = 10.1790 (10) Å
b = 11.4140 (14) Å
c = 13.4240 (18) Å
α = 114.745 (3)°
β = 102.249 (2)°
γ = 96.4280 (10)°
V = 1348.3 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.07 mm^{-1}
T = 298 (2) K
0.51 × 0.50 × 0.48 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.613, T_{max} = 0.629
6989 measured reflections
4645 independent reflections
3752 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.101
S = 1.05
4645 reflections
352 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.60 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O2^{i}	0.85	2.31	3.155 (6)	176
O5—H5B···O4^{ii}	0.85	2.03	2.883 (6)	176
O6—H6A···O2^{iii}	0.85	1.96	2.804 (10)	176
O6—H6B···O2^{iv}	0.85	2.29	3.135 (10)	176
O7—H7D···O5^{v}	0.85	1.91	2.757 (9)	176
O7—H7E···O8^{v}	0.85	2.02	2.866 (13)	176
O8—H8A···O6^{v}	0.85	1.82	2.664 (13)	177
O8—H8B···O7^{vi}	0.85	1.82	2.670 (15)	177

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2342).

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supplementary materials

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Bis[3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato]cadmium(II) tetrahydrate

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Comment

In recent years, there has been an increasing interest in the coordination chemistry due to the increased recognition of it's role in catalysis enzymatic reactions, magnetism and molecular architectures (Costamagna *et al.*, 1992; Bhatia *et al.*, 1981). We report here the crystal structure of a new zinc(II) complex with the ligand 6-(3-chloro- (3,5-dimethyl-1*H*-pyrazol-1-yl)) picolinic acid(CDPA)·(I) (Fig.1).

The title compound, (I), consists of a cadmium(II) complex cation and four uncoordinated water molecules. In the cation (Fig. 1), the Cd atom is six-coordinated by four N atoms and two O atomsfrom two CDPA ligands. The Cd(II) atom is a slightly distorted octahedral environment. The Cd–O bond lengths are 2.243 (3) and 2.266 (3) Å,The Cd—N distances range from 2.320 (3) to 2.350 (3) Å. The C1–C2 bond length is 1.533 (6) Å, being in the normal C–C ranges in cadmium carboxylate complexes. The angles around Cd(II) atom are from 68.54 (11) to 139.29 (11)°. The CDPA molecule acts as a bidentate ligand.

In the title compound, the oxygen atoms contribute to the formation of intermolecular hydrogen bonds involving water O atoms. (Table 1).

Experimental

6-(3-chloro-(3,5-dimethyl-1*H*-pyrazol-1-yl))picolinic acid, and $CdCl_2$. $6H_2O$ were available commercially and were used without further purification. Equimolar 6-(3-chloro-(3,5-dimethyl-1*H*-pyrazol-1-yl))picolinic acid (1 mmol, 250 mg) was dissolved in anhydrous alcohol (15 ml). The mixture was stirred to give a clear solution, To this solution was added $CdCl_2·6H_2O$ (0.5 mmol, 142 mg) in anhydrous alcohol (10 ml). After keeping the resulting solution in air to evaporate about half of the solvents, dark red prisms of the title compound were formed. The crystals were isolated, washed with alcohol three times and dried in a vacuum desiccator using silica gel (Yield 75%). Elemental analysis: found: C, 38.43; H, 3.92; N, 12.15; O, 18.76; calc. for $C_{22}H_{26}CdCl_2N_6O_8$: C, 38.53; H, 3.82; N, 12.25; O, 18.66%.

Refinement

All the H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with N—H and C—H distances of 0.90 Å and 0.96 Å, respectively. They were treated as riding atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$, $U_{iso}(H) = 1.2U_{eq}(N)$ and $U_{iso}(H) = 1.5U_{eq}(O)$.

Figures

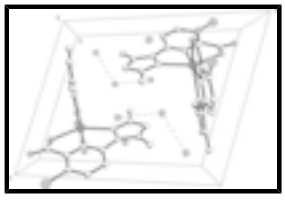


Fig. 1. The structure of the title compound (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

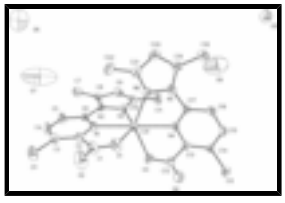


Fig. 2. Crystal packing of (I) showing the hydrogen bonded interactions as dashed lines.

Bis[3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato]cadmium(II) tetrahydrate

Crystal data

$[Cd(C_{11}H_9ClN_3O_2)_2]\cdot 4H_2O$	$Z = 2$
$M_r = 685.79$	$F_{000} = 692$
Triclinic, $P\overline{1}$	$D_x = 1.689$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 10.1790$ (10) Å	Cell parameters from 3835 reflections
$b = 11.4140$ (14) Å	$\theta = 2.6$–27.6º
$c = 13.4240$ (18) Å	$\mu = 1.07$ mm^{-1}
$\alpha = 114.745$ (3)º	$T = 298$ (2) K
$\beta = 102.249$ (2)º	Block, colorless
$\gamma = 96.4280$ (10)º	0.51 × 0.50 × 0.48 mm
$V = 1348.3$ (3) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	4645 independent reflections
Radiation source: fine-focus sealed tube	3752 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.020$
$T = 298$(2) K	$\theta_{max} = 25.0$º
phi and ω scans	$\theta_{min} = 1.7$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -12\rightarrow11$
$T_{min} = 0.613$, $T_{max} = 0.629$	$k = -6\rightarrow13$
6989 measured reflections	$l = -15\rightarrow13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 1.4843P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
4645 reflections	$\Delta\rho_{max} = 0.68$ e Å^{-3}
352 parameters	$\Delta\rho_{min} = -0.60$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2$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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.28358 (3)	0.52895 (3)	0.75795 (3)	0.04744 (13)
Cl1	0.28940 (15)	0.04201 (12)	0.81008 (14)	0.0788 (4)
Cl2	−0.05630 (14)	0.92388 (12)	0.82716 (12)	0.0679 (4)
N1	0.3954 (3)	0.3897 (3)	0.8128 (2)	0.0354 (7)
N2	0.5982 (3)	0.5488 (3)	0.8803 (3)	0.0366 (7)
N3	0.5202 (3)	0.6247 (3)	0.8477 (3)	0.0429 (8)
N4	0.1674 (3)	0.6646 (3)	0.6998 (3)	0.0363 (7)
N5	0.2145 (3)	0.5588 (3)	0.5272 (3)	0.0412 (7)
N6	0.2745 (3)	0.4811 (3)	0.5704 (3)	0.0461 (8)
O1	0.1292 (3)	0.3403 (4)	0.7077 (3)	0.0696 (10)
O2	0.0848 (4)	0.1492 (4)	0.7108 (5)	0.1164 (18)
O3	0.2019 (4)	0.6588 (4)	0.8981 (3)	0.0711 (10)
O4	0.1175 (5)	0.8337 (4)	0.9710 (3)	0.0928 (13)
O5	0.1574 (4)	0.7985 (4)	0.1750 (3)	0.0868 (11)
H5A	0.0902	0.8134	0.2033	0.104*
H5B	0.1419	0.8098	0.1152	0.104*
O6	0.8516 (7)	0.0186 (7)	0.5197 (7)	0.194 (3)
H6A	0.9247	0.0565	0.5755	0.232*
H6B	0.8737	−0.0257	0.4593	0.232*
O7	0.5992 (8)	0.1002 (12)	0.6502 (7)	0.320 (7)
H7D	0.6761	0.1315	0.7021	0.384*
H7E	0.6127	0.0984	0.5893	0.384*

O8	0.3705 (9)	0.9082 (10)	0.5599 (7)	0.252 (5)
H8A	0.3011	0.9345	0.5363	0.303*
H8B	0.4417	0.9709	0.5876	0.303*
C1	0.1637 (5)	0.2515 (5)	0.7311 (4)	0.0619 (13)
C2	0.3166 (4)	0.2746 (4)	0.7924 (3)	0.0411 (9)
C3	0.3773 (4)	0.1916 (4)	0.8290 (4)	0.0471 (10)
C4	0.5165 (5)	0.2285 (4)	0.8846 (4)	0.0583 (12)
H4	0.5579	0.1730	0.9091	0.070*
C5	0.5943 (4)	0.3456 (4)	0.9043 (4)	0.0520 (11)
H5	0.6880	0.3714	0.9428	0.062*
C6	0.5290 (4)	0.4244 (4)	0.8650 (3)	0.0348 (8)
C7	0.8520 (4)	0.5611 (5)	0.9700 (4)	0.0592 (12)
H7A	0.9379	0.6213	0.9900	0.089*
H7B	0.8509	0.4762	0.9107	0.089*
H7C	0.8418	0.5523	1.0362	0.089*
C8	0.7345 (4)	0.6139 (4)	0.9277 (3)	0.0425 (9)
C9	0.7415 (5)	0.7315 (4)	0.9249 (4)	0.0526 (11)
H9	0.8208	0.7975	0.9509	0.063*
C10	0.6079 (4)	0.7357 (4)	0.8756 (4)	0.0479 (10)
C11	0.5576 (6)	0.8428 (5)	0.8524 (5)	0.0756 (15)
H11A	0.4841	0.8036	0.7821	0.113*
H11B	0.6321	0.8962	0.8460	0.113*
H11C	0.5243	0.8971	0.9141	0.113*
C12	0.1458 (4)	0.7485 (4)	0.8925 (4)	0.0494 (10)
C13	0.1089 (4)	0.7461 (4)	0.7743 (3)	0.0379 (8)
C14	0.0228 (4)	0.8155 (4)	0.7387 (4)	0.0433 (9)
C15	−0.0012 (4)	0.7982 (4)	0.6274 (4)	0.0498 (10)
H15	−0.0588	0.8445	0.6030	0.060*
C16	0.0583 (4)	0.7141 (4)	0.5526 (4)	0.0458 (10)
H16	0.0411	0.7011	0.4775	0.055*
C17	0.1456 (4)	0.6489 (4)	0.5942 (3)	0.0371 (8)
C18	0.1855 (6)	0.5966 (7)	0.3503 (5)	0.0856 (18)
H18A	0.2302	0.5746	0.2907	0.128*
H18B	0.2100	0.6907	0.3978	0.128*
H18C	0.0873	0.5682	0.3168	0.128*
C19	0.2308 (4)	0.5284 (5)	0.4213 (4)	0.0521 (11)
C20	0.3009 (5)	0.4300 (5)	0.3984 (4)	0.0618 (13)
H20	0.3274	0.3884	0.3322	0.074*
C21	0.3260 (4)	0.4027 (4)	0.4918 (4)	0.0520 (11)
C22	0.3962 (6)	0.3021 (5)	0.5088 (5)	0.0752 (15)
H22A	0.4616	0.3425	0.5834	0.113*
H22B	0.4434	0.2675	0.4516	0.113*
H22C	0.3288	0.2313	0.5023	0.113*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.04307 (19)	0.0611 (2)	0.0546 (2)	0.02603 (15)	0.01381 (14)	0.03812 (16)

Cl1	0.0807 (9)	0.0469 (7)	0.1047 (11)	0.0000 (6)	0.0116 (8)	0.0413 (7)
Cl2	0.0791 (8)	0.0659 (7)	0.0984 (10)	0.0460 (7)	0.0555 (8)	0.0525 (7)
N1	0.0331 (16)	0.0381 (17)	0.0355 (16)	0.0099 (13)	0.0052 (13)	0.0188 (14)
N2	0.0322 (16)	0.0397 (17)	0.0433 (18)	0.0124 (14)	0.0090 (14)	0.0235 (15)
N3	0.0434 (19)	0.0458 (19)	0.050 (2)	0.0178 (16)	0.0146 (16)	0.0289 (16)
N4	0.0327 (16)	0.0420 (17)	0.0405 (18)	0.0120 (14)	0.0097 (14)	0.0242 (14)
N5	0.0399 (18)	0.0475 (19)	0.0367 (18)	0.0136 (15)	0.0072 (14)	0.0204 (15)
N6	0.050 (2)	0.0453 (19)	0.048 (2)	0.0194 (16)	0.0143 (16)	0.0230 (16)
O1	0.0348 (16)	0.094 (3)	0.089 (2)	0.0062 (16)	−0.0037 (16)	0.063 (2)
O2	0.059 (2)	0.095 (3)	0.180 (5)	−0.020 (2)	−0.024 (3)	0.085 (3)
O3	0.086 (2)	0.108 (3)	0.0575 (19)	0.066 (2)	0.0353 (18)	0.056 (2)
O4	0.154 (4)	0.099 (3)	0.058 (2)	0.078 (3)	0.054 (2)	0.042 (2)
O5	0.092 (3)	0.102 (3)	0.079 (3)	0.045 (2)	0.029 (2)	0.044 (2)
O6	0.153 (6)	0.172 (6)	0.193 (7)	0.002 (5)	−0.010 (5)	0.061 (5)
O7	0.161 (7)	0.516 (18)	0.122 (6)	−0.095 (9)	0.018 (5)	0.049 (8)
O8	0.207 (8)	0.286 (11)	0.192 (8)	0.021 (8)	0.069 (7)	0.045 (8)
C1	0.043 (2)	0.066 (3)	0.074 (3)	0.000 (2)	0.000 (2)	0.039 (3)
C2	0.040 (2)	0.041 (2)	0.039 (2)	0.0070 (18)	0.0069 (17)	0.0176 (17)
C3	0.054 (3)	0.037 (2)	0.051 (2)	0.0104 (19)	0.011 (2)	0.0229 (19)
C4	0.058 (3)	0.045 (3)	0.076 (3)	0.016 (2)	0.006 (2)	0.037 (2)
C5	0.040 (2)	0.052 (3)	0.069 (3)	0.012 (2)	0.004 (2)	0.037 (2)
C6	0.0330 (19)	0.038 (2)	0.0331 (19)	0.0126 (16)	0.0072 (16)	0.0166 (16)
C7	0.035 (2)	0.077 (3)	0.068 (3)	0.008 (2)	0.004 (2)	0.042 (3)
C8	0.039 (2)	0.050 (2)	0.042 (2)	0.0084 (18)	0.0131 (18)	0.0239 (19)
C9	0.049 (3)	0.052 (3)	0.054 (3)	−0.001 (2)	0.014 (2)	0.025 (2)
C10	0.056 (3)	0.046 (2)	0.055 (3)	0.016 (2)	0.023 (2)	0.031 (2)
C11	0.086 (4)	0.058 (3)	0.104 (4)	0.022 (3)	0.031 (3)	0.053 (3)
C12	0.048 (2)	0.062 (3)	0.050 (3)	0.023 (2)	0.022 (2)	0.030 (2)
C13	0.035 (2)	0.040 (2)	0.047 (2)	0.0115 (17)	0.0160 (17)	0.0248 (18)
C14	0.040 (2)	0.041 (2)	0.064 (3)	0.0161 (18)	0.024 (2)	0.033 (2)
C15	0.042 (2)	0.056 (3)	0.073 (3)	0.022 (2)	0.016 (2)	0.046 (2)
C16	0.043 (2)	0.054 (2)	0.048 (2)	0.0135 (19)	0.0087 (19)	0.033 (2)
C17	0.0321 (19)	0.042 (2)	0.041 (2)	0.0068 (16)	0.0073 (16)	0.0236 (17)
C18	0.092 (4)	0.137 (5)	0.063 (3)	0.055 (4)	0.038 (3)	0.063 (4)
C19	0.048 (2)	0.070 (3)	0.040 (2)	0.017 (2)	0.0142 (19)	0.025 (2)
C20	0.061 (3)	0.076 (3)	0.045 (3)	0.025 (3)	0.023 (2)	0.018 (2)
C21	0.046 (2)	0.054 (3)	0.053 (3)	0.018 (2)	0.016 (2)	0.019 (2)
C22	0.079 (4)	0.068 (3)	0.088 (4)	0.043 (3)	0.032 (3)	0.033 (3)

Geometric parameters (Å, °)

Cd1—O3	2.243 (3)	C3—C4	1.377 (6)
Cd1—O1	2.266 (3)	C4—C5	1.364 (6)
Cd1—N6	2.320 (3)	C4—H4	0.9300
Cd1—N1	2.322 (3)	C5—C6	1.383 (5)
Cd1—N4	2.331 (3)	C5—H5	0.9300
Cd1—N3	2.350 (3)	C7—C8	1.508 (6)
Cl1—C3	1.726 (4)	C7—H7A	0.9600
Cl2—C14	1.728 (4)	C7—H7B	0.9600

N1—C6	1.319 (4)	C7—H7C	0.9600
N1—C2	1.346 (5)	C8—C9	1.353 (6)
N2—C8	1.371 (5)	C9—C10	1.396 (6)
N2—N3	1.378 (4)	C9—H9	0.9300
N2—C6	1.423 (5)	C10—C11	1.498 (6)
N3—C10	1.323 (5)	C11—H11A	0.9600
N4—C17	1.317 (5)	C11—H11B	0.9600
N4—C13	1.348 (5)	C11—H11C	0.9600
N5—C19	1.368 (5)	C12—C13	1.539 (6)
N5—N6	1.378 (4)	C13—C14	1.385 (5)
N5—C17	1.419 (5)	C14—C15	1.385 (6)
N6—C21	1.318 (5)	C15—C16	1.370 (6)
O1—C1	1.245 (5)	C15—H15	0.9300
O2—C1	1.230 (6)	C16—C17	1.393 (5)
O3—C12	1.248 (5)	C16—H16	0.9300
O4—C12	1.213 (5)	C18—C19	1.498 (7)
O5—H5A	0.8500	C18—H18A	0.9600
O5—H5B	0.8501	C18—H18B	0.9600
O6—H6A	0.8500	C18—H18C	0.9600
O6—H6B	0.8500	C19—C20	1.359 (6)
O7—H7D	0.8500	C20—C21	1.394 (7)
O7—H7E	0.8501	C20—H20	0.9300
O8—H8A	0.8500	C21—C22	1.489 (6)
O8—H8B	0.8501	C22—H22A	0.9600
C1—C2	1.533 (6)	C22—H22B	0.9600
C2—C3	1.384 (5)	C22—H22C	0.9600
O3—Cd1—O1	95.33 (14)	H7A—C7—H7B	109.5
O3—Cd1—N6	138.84 (11)	C8—C7—H7C	109.5
O1—Cd1—N6	94.09 (13)	H7A—C7—H7C	109.5
O3—Cd1—N1	110.04 (11)	H7B—C7—H7C	109.5
O1—Cd1—N1	70.52 (11)	C9—C8—N2	106.1 (4)
N6—Cd1—N1	110.88 (11)	C9—C8—C7	127.7 (4)
O3—Cd1—N4	70.45 (11)	N2—C8—C7	126.2 (4)
O1—Cd1—N4	108.27 (11)	C8—C9—C10	107.5 (4)
N6—Cd1—N4	68.54 (11)	C8—C9—H9	126.3
N1—Cd1—N4	178.70 (11)	C10—C9—H9	126.3
O3—Cd1—N3	98.39 (13)	N3—C10—C9	110.2 (4)
O1—Cd1—N3	139.29 (11)	N3—C10—C11	120.3 (4)
N6—Cd1—N3	100.11 (12)	C9—C10—C11	129.6 (4)
N1—Cd1—N3	68.76 (11)	C10—C11—H11A	109.5
N4—Cd1—N3	112.44 (11)	C10—C11—H11B	109.5
C6—N1—C2	121.9 (3)	H11A—C11—H11B	109.5
C6—N1—Cd1	121.2 (2)	C10—C11—H11C	109.5
C2—N1—Cd1	116.8 (2)	H11A—C11—H11C	109.5
C8—N2—N3	110.5 (3)	H11B—C11—H11C	109.5
C8—N2—C6	131.3 (3)	O4—C12—O3	125.4 (4)
N3—N2—C6	118.1 (3)	O4—C12—C13	119.1 (4)
C10—N3—N2	105.7 (3)	O3—C12—C13	115.5 (4)
C10—N3—Cd1	137.9 (3)	N4—C13—C14	119.0 (4)

N2—N3—Cd1	116.4 (2)	N4—C13—C12	114.0 (3)
C17—N4—C13	122.1 (3)	C14—C13—C12	127.0 (3)
C17—N4—Cd1	120.9 (2)	C13—C14—C15	118.9 (4)
C13—N4—Cd1	116.4 (2)	C13—C14—Cl2	123.1 (3)
C19—N5—N6	110.3 (3)	C15—C14—Cl2	118.1 (3)
C19—N5—C17	132.0 (3)	C16—C15—C14	121.3 (4)
N6—N5—C17	117.6 (3)	C16—C15—H15	119.4
C21—N6—N5	106.4 (3)	C14—C15—H15	119.4
C21—N6—Cd1	135.9 (3)	C15—C16—C17	117.0 (4)
N5—N6—Cd1	117.3 (2)	C15—C16—H16	121.5
C1—O1—Cd1	121.6 (3)	C17—C16—H16	121.5
C12—O3—Cd1	122.4 (3)	N4—C17—C16	121.6 (3)
H5A—O5—H5B	108.5	N4—C17—N5	114.7 (3)
H6A—O6—H6B	108.5	C16—C17—N5	123.6 (3)
H7D—O7—H7E	108.5	C19—C18—H18A	109.5
H8A—O8—H8B	108.5	C19—C18—H18B	109.5
O2—C1—O1	125.3 (4)	H18A—C18—H18B	109.5
O2—C1—C2	118.2 (4)	C19—C18—H18C	109.5
O1—C1—C2	116.5 (4)	H18A—C18—H18C	109.5
N1—C2—C3	118.9 (3)	H18B—C18—H18C	109.5
N1—C2—C1	114.5 (4)	C20—C19—N5	105.8 (4)
C3—C2—C1	126.6 (4)	C20—C19—C18	128.4 (4)
C4—C3—C2	119.2 (4)	N5—C19—C18	125.7 (4)
C4—C3—Cl1	116.7 (3)	C19—C20—C21	107.8 (4)
C2—C3—Cl1	124.1 (3)	C19—C20—H20	126.1
C5—C4—C3	120.9 (4)	C21—C20—H20	126.1
C5—C4—H4	119.6	N6—C21—C20	109.6 (4)
C3—C4—H4	119.6	N6—C21—C22	121.1 (4)
C4—C5—C6	117.7 (4)	C20—C21—C22	129.3 (4)
C4—C5—H5	121.1	C21—C22—H22A	109.5
C6—C5—H5	121.1	C21—C22—H22B	109.5
N1—C6—C5	121.4 (3)	H22A—C22—H22B	109.5
N1—C6—N2	115.3 (3)	C21—C22—H22C	109.5
C5—C6—N2	123.3 (3)	H22A—C22—H22C	109.5
C8—C7—H7A	109.5	H22B—C22—H22C	109.5
C8—C7—H7B	109.5		
O3—Cd1—N1—C6	−91.2 (3)	N1—C2—C3—C4	−0.3 (6)
O1—Cd1—N1—C6	−179.9 (3)	C1—C2—C3—C4	−178.9 (4)
N6—Cd1—N1—C6	93.2 (3)	N1—C2—C3—Cl1	179.4 (3)
N4—Cd1—N1—C6	157 (5)	C1—C2—C3—Cl1	0.8 (6)
N3—Cd1—N1—C6	0.2 (3)	C2—C3—C4—C5	0.3 (7)
O3—Cd1—N1—C2	86.4 (3)	Cl1—C3—C4—C5	−179.5 (4)
O1—Cd1—N1—C2	−2.2 (3)	C3—C4—C5—C6	−0.9 (7)
N6—Cd1—N1—C2	−89.1 (3)	C2—N1—C6—C5	−1.7 (6)
N4—Cd1—N1—C2	−26 (5)	Cd1—N1—C6—C5	175.8 (3)
N3—Cd1—N1—C2	177.8 (3)	C2—N1—C6—N2	180.0 (3)
C8—N2—N3—C10	−0.3 (4)	Cd1—N1—C6—N2	−2.5 (4)
C6—N2—N3—C10	177.2 (3)	C4—C5—C6—N1	1.6 (6)
C8—N2—N3—Cd1	177.9 (2)	C4—C5—C6—N2	179.8 (4)

C6—N2—N3—Cd1	−4.6 (4)	C8—N2—C6—N1	−178.4 (4)
O3—Cd1—N3—C10	−71.9 (4)	N3—N2—C6—N1	4.7 (5)
O1—Cd1—N3—C10	179.7 (4)	C8—N2—C6—C5	3.3 (6)
N6—Cd1—N3—C10	71.1 (4)	N3—N2—C6—C5	−173.7 (4)
N1—Cd1—N3—C10	179.7 (4)	N3—N2—C8—C9	0.0 (4)
N4—Cd1—N3—C10	0.3 (4)	C6—N2—C8—C9	−177.1 (4)
O3—Cd1—N3—N2	110.6 (2)	N3—N2—C8—C7	−177.9 (4)
O1—Cd1—N3—N2	2.2 (3)	C6—N2—C8—C7	5.0 (7)
N6—Cd1—N3—N2	−106.3 (2)	N2—C8—C9—C10	0.2 (5)
N1—Cd1—N3—N2	2.3 (2)	C7—C8—C9—C10	178.1 (4)
N4—Cd1—N3—N2	−177.1 (2)	N2—N3—C10—C9	0.5 (4)
O3—Cd1—N4—C17	−173.3 (3)	Cd1—N3—C10—C9	−177.2 (3)
O1—Cd1—N4—C17	−84.0 (3)	N2—N3—C10—C11	−179.8 (4)
N6—Cd1—N4—C17	3.1 (3)	Cd1—N3—C10—C11	2.5 (7)
N1—Cd1—N4—C17	−61 (5)	C8—C9—C10—N3	−0.4 (5)
N3—Cd1—N4—C17	95.5 (3)	C8—C9—C10—C11	179.9 (5)
O3—Cd1—N4—C13	−1.8 (3)	Cd1—O3—C12—O4	−168.9 (4)
O1—Cd1—N4—C13	87.5 (3)	Cd1—O3—C12—C13	12.2 (5)
N6—Cd1—N4—C13	174.6 (3)	C17—N4—C13—C14	0.2 (5)
N1—Cd1—N4—C13	111 (5)	Cd1—N4—C13—C14	−171.2 (3)
N3—Cd1—N4—C13	−93.0 (3)	C17—N4—C13—C12	179.1 (3)
C19—N5—N6—C21	−0.7 (4)	Cd1—N4—C13—C12	7.7 (4)
C17—N5—N6—C21	177.3 (3)	O4—C12—C13—N4	168.1 (4)
C19—N5—N6—Cd1	173.2 (3)	O3—C12—C13—N4	−12.9 (5)
C17—N5—N6—Cd1	−8.8 (4)	O4—C12—C13—C14	−13.1 (7)
O3—Cd1—N6—C21	179.8 (4)	O3—C12—C13—C14	165.9 (4)
O1—Cd1—N6—C21	−77.3 (4)	N4—C13—C14—C15	0.4 (6)
N1—Cd1—N6—C21	−6.6 (4)	C12—C13—C14—C15	−178.3 (4)
N4—Cd1—N6—C21	174.6 (4)	N4—C13—C14—Cl2	−179.3 (3)
N3—Cd1—N6—C21	64.4 (4)	C12—C13—C14—Cl2	1.9 (6)
O3—Cd1—N6—N5	8.3 (4)	C13—C14—C15—C16	0.1 (6)
O1—Cd1—N6—N5	111.2 (3)	Cl2—C14—C15—C16	179.8 (3)
N1—Cd1—N6—N5	−178.1 (2)	C14—C15—C16—C17	−1.1 (6)
N4—Cd1—N6—N5	3.2 (2)	C13—N4—C17—C16	−1.3 (6)
N3—Cd1—N6—N5	−107.1 (3)	Cd1—N4—C17—C16	169.7 (3)
O3—Cd1—O1—C1	−107.2 (4)	C13—N4—C17—N5	−179.6 (3)
N6—Cd1—O1—C1	112.9 (4)	Cd1—N4—C17—N5	−8.6 (4)
N1—Cd1—O1—C1	2.2 (4)	C15—C16—C17—N4	1.7 (6)
N4—Cd1—O1—C1	−178.4 (4)	C15—C16—C17—N5	179.9 (4)
N3—Cd1—O1—C1	2.2 (5)	C19—N5—C17—N4	−171.2 (4)
O1—Cd1—O3—C12	−113.7 (4)	N6—N5—C17—N4	11.3 (5)
N6—Cd1—O3—C12	−11.3 (5)	C19—N5—C17—C16	10.5 (6)
N1—Cd1—O3—C12	175.1 (4)	N6—N5—C17—C16	−167.0 (3)
N4—Cd1—O3—C12	−6.2 (4)	N6—N5—C19—C20	0.5 (5)
N3—Cd1—O3—C12	104.7 (4)	C17—N5—C19—C20	−177.1 (4)
Cd1—O1—C1—O2	176.9 (5)	N6—N5—C19—C18	−176.8 (5)
Cd1—O1—C1—C2	−1.8 (6)	C17—N5—C19—C18	5.6 (8)
C6—N1—C2—C3	1.0 (5)	N5—C19—C20—C21	−0.1 (5)
Cd1—N1—C2—C3	−176.6 (3)	C18—C19—C20—C21	177.1 (5)

C6—N1—C2—C1	179.8 (4)	N5—N6—C21—C20	0.6 (5)
Cd1—N1—C2—C1	2.2 (4)	Cd1—N6—C21—C20	−171.5 (3)
O2—C1—C2—N1	−179.1 (5)	N5—N6—C21—C22	−178.5 (4)
O1—C1—C2—N1	−0.4 (6)	Cd1—N6—C21—C22	9.4 (7)
O2—C1—C2—C3	−0.4 (8)	C19—C20—C21—N6	−0.3 (6)
O1—C1—C2—C3	178.3 (4)	C19—C20—C21—C22	178.6 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5A···O2^{i}	0.85	2.31	3.155 (6)	176
O5—H5B···O4^{ii}	0.85	2.03	2.883 (6)	176
O6—H6A···O2^{iii}	0.85	1.96	2.804 (10)	176
O6—H6B···O2^{iv}	0.85	2.29	3.135 (10)	176
O7—H7D···O5^{v}	0.85	1.91	2.757 (9)	176
O7—H7E···O8^{v}	0.85	2.02	2.866 (13)	176
O8—H8A···O6^{v}	0.85	1.82	2.664 (13)	177
O8—H8B···O7^{vi}	0.85	1.82	2.670 (15)	177

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

Fig. 1

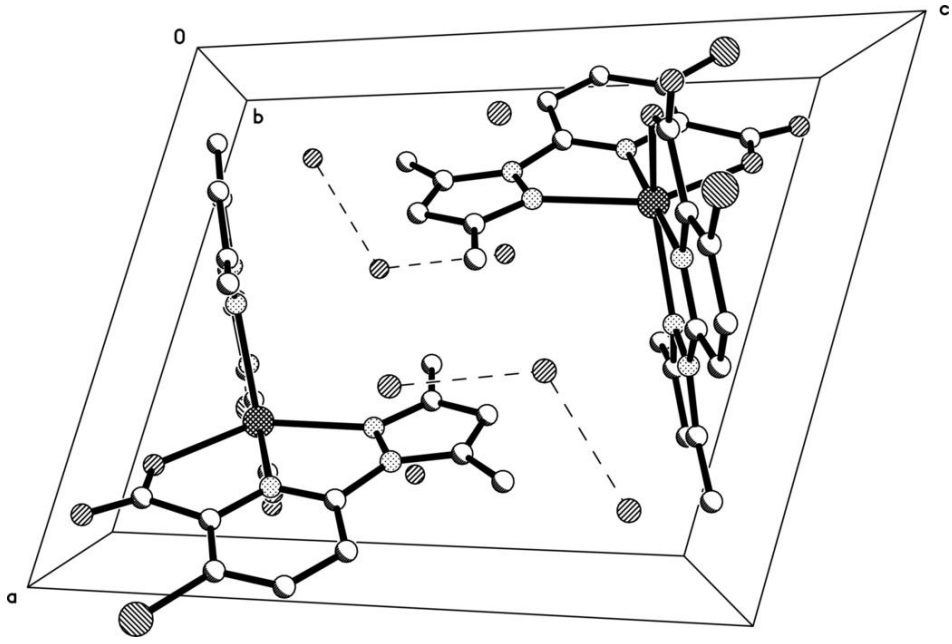
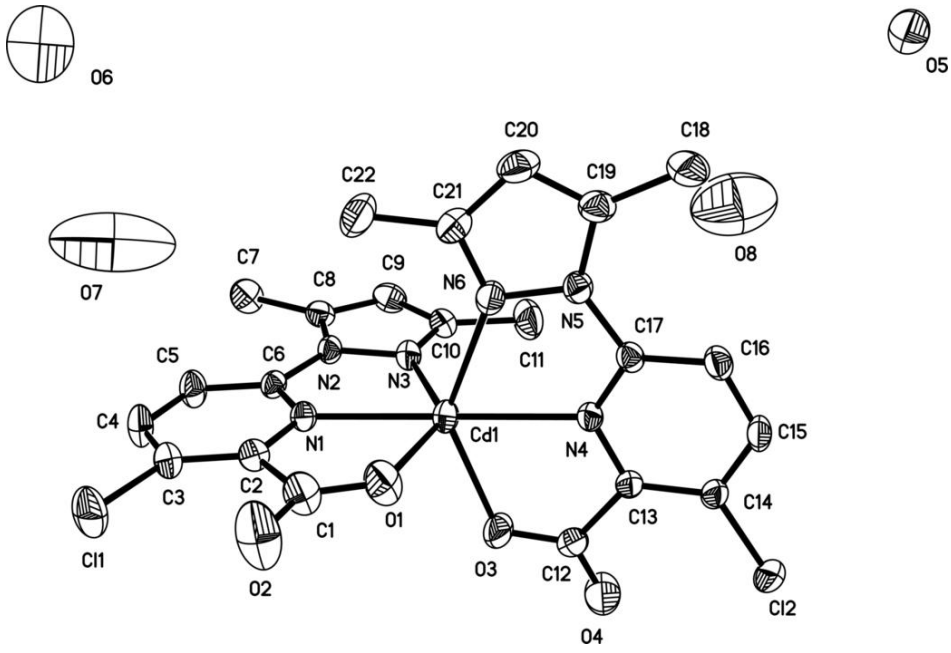


Fig. 2


O6
O5
C20
C18
C22
C21
C19
O8
O7
C7
C8
C9
N6
N5
C17
C16
C5
C6
N2
N3
C10
C11
C4
N1
Cd1
N4
C15
C3
C2
C1
O1
C13
C14
Cl1
O2
O3
C12
Cl2
O4