

# Dichlorido(4-methoxy-2-[[2-(piperazin-4-ium-1-yl)ethyl]iminomethyl]phenolate)cadmium

Muhammad Saleh Salga, Hamid Khaleedi\* and Hapipah Mohd Ali

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia  
Correspondence e-mail: khaleedi@siswa.um.edu.my

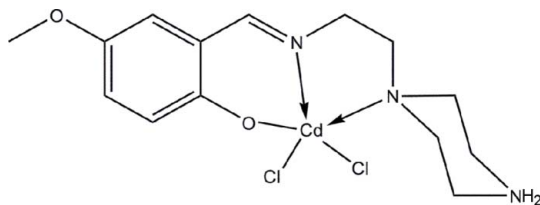
Received 29 May 2011; accepted 7 June 2011

Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å; disorder in main residue;  $R$  factor = 0.031;  $wR$  factor = 0.061; data-to-parameter ratio = 16.1.

In the title compound,  $[\text{CdCl}_2(\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_2)]$ , the Schiff base ligand chelates the  $\text{Cd}^{\text{II}}$  ion in an  $N,N,O$ -tridentate fashion. Two Cl atoms complete a distorted square-pyramidal coordination environment around the metal atom. In the crystal, adjacent molecules are linked through  $\text{C}-\text{H}\cdots\pi$  interactions into infinite chains along the  $a$  axis. The molecules are further connected into a three-dimensional network *via*  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{Cl}$  and  $\text{C}-\text{H}\cdots\text{Cl}$  interactions. The ethylene group is disordered over two sets of sites in a 0.520 (10):0.480 (10) ratio.

## Related literature

For similar structures, see: Mukhopadhyay *et al.* (2003); Xu *et al.* (2008); Saleh Salga *et al.* (2010). For a description of the geometry of complexes with five-coordinated metal ions, see: Addison *et al.* (1984).



## Experimental

### Crystal data

$[\text{CdCl}_2(\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_2)]$   
 $M_r = 446.64$

Monoclinic,  $P2_1/c$   
 $a = 10.1173$  (9) Å  
 $b = 16.2686$  (15) Å  
 $c = 10.3486$  (10) Å  
 $\beta = 103.069$  (1)°

$V = 1659.2$  (3) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 1.65$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.25 \times 0.18 \times 0.04$  mm

### Data collection

Bruker APEXII CCD diffractometer  
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.684$ ,  $T_{\text{max}} = 0.937$

14540 measured reflections  
3624 independent reflections  
3138 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.061$   
 $S = 1.07$   
3624 reflections  
225 parameters  
5 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.65$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.78$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

Cd1—O1	2.241 (2)	Cd1—Cl1	2.4584 (8)
Cd1—N1	2.245 (3)	Cd1—Cl2	2.4797 (8)
Cd1—N2	2.475 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

$\text{Cg1}$  is the centroid of the C1–C6 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H3A}\cdots\text{O1}^{\text{i}}$	0.92 (2)	1.80 (2)	2.705 (3)	166 (4)
$\text{N3}-\text{H3B}\cdots\text{Cl2}^{\text{ii}}$	0.90 (2)	2.33 (2)	3.222 (3)	174 (4)
$\text{C9}-\text{H9A}\cdots\text{Cl1}^{\text{iii}}$	0.99	2.64	3.454 (8)	139
$\text{C8}-\text{H8A}\cdots\text{Cl2}^{\text{iv}}$	0.98	2.82	3.777 (3)	167
$\text{C8}-\text{H8B}\cdots\text{Cl1}^{\text{v}}$	0.98	2.76	3.514 (3)	134
$\text{C13}-\text{H13A}\cdots\text{Cl1}^{\text{i}}$	0.99	2.71	3.542 (4)	142
$\text{C12}-\text{H12A}\cdots\text{Cg1}^{\text{vi}}$	0.99	2.48	3.408 (4)	156
$\text{C9}'-\text{H9D}\cdots\text{Cg1}^{\text{iv}}$	0.99	2.72	3.620 (8)	151

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97* and *PUBLICIF* (Westrip, 2010).

The authors thank the University of Malaya for funding this study (FRGS grant No. FP004/2010B).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5230).

## References

- Addison, A. W., Rao, T. N., Reedijk, J., Rijn, V. J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.  
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.  
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Mukhopadhyay, S., Mandal, D., Ghosh, D., Goldberg, I. & Chaudhury, M. (2003). *Inorg. Chem.* **42**, 8439–8445.  
Saleh Salga, M., Khaleedi, H. & Mohd Ali, H. (2010). *Acta Cryst. E66*, m1131.  
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
Sheldrick, G. M. (2008). *Acta Cryst. A64*, 112–122.  
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.  
Xu, R.-B., Xu, X.-Y., Wang, M.-Y., Wang, D.-Q., Yin, T., Xu, G.-X., Yang, X.-J., Lu, L.-D., Wang, X. & Lei, Y.-J. (2008). *J. Coord. Chem.* **61**, 3306–3313.

**supplementary materials**

*Acta Cryst.* (2011). E67, m927 [ doi:10.1107/S1600536811022100 ]

## Dichlorido(4-methoxy-2-[[2-(piperazin-4-ium-1-yl)ethyl]iminomethyl]phenolate)cadmium

M. Saleh Salga, H. Khaledi and H. Mohd Ali

### Comment

The ligands containing a piperazine ring have been reported to possess ambidentate character, capable of binding metal centers through one or both piperazine N atoms (Mukhopadhyay *et al.*, 2003; Xu *et al.*, 2008; Saleh Salga *et al.*, 2010). The coordination mode depends largely on the conformation (chair or boat) adopted by the ring which, in turn, depends on the metal salt entity and remote substitutions in the ligand. In the present structure, the piperazine ring assumes a chair conformation and employs only one of the ring N atoms to bind to the metal center. The Schiff base ligand chelates the metal atom in an *N,N,O*-mode, along with two Cl atoms makes a distorted square-pyramidal cadmium(II) complex. The distortion from the ideal geometry is evident from the  $\tau$  index of 0.30 ( $\tau$  is 0 for an ideal square-pyramid and is 1 for a perfect trigonal-bipyramid, Addison *et al.*, 1984). The other ring N atom stays away from the chelation, and is protonated to keep the electroneutrality of the molecule, thus the complex can be described as a zwitterion. In the crystal, C—H $\cdots$  $\pi$  interactions link the molecules into infinite chains along the *a* axis and these are connected into a three-dimensional network *via* N—H $\cdots$ O, N—H $\cdots$ Cl and C—H $\cdots$ Cl hydrogen bonds (Table 1).

### Experimental

A mixture of 5-methoxysalicylaldehyde (0.35 g, 2.3 mmol) and aminoethylpiperazine (0.3 g, 2.3 mmol) in ethanol (20 ml) was refluxed for 2 h, followed by addition of a solution of cadmium(II) chloride (0.42 g, 2.3 mmol) in a minimum amount of ethanol. The resulting solution was refluxed for 1 h and then left at room temperature for one day to give the X-ray quality crystals of the title compound.

### Refinement

The C-bound hydrogen atoms were placed at calculated positions and refined as riding atoms with C—H distances of 0.95 (aryl), 0.98 (methyl) and 0.99 Å (methylene). The N-bound hydrogen atoms were located in a difference Fourier map and refined with distance restraint of N—H 0.91 (2) Å. For all hydrogen atoms  $U_{iso}(H)$  were set to 1.2 (1.5 for methyl) $U_{eq}(\text{carrier atom})$ . C9 and C10 were found to be disordered with two positions being resolved for each of the atoms. From anisotropic refinement, the site occupancy factor of the major component refined is 0.52 (1). The corresponding bond distances involving the disordered atoms were restrained to be equal with the SADI command in *SHELXL97* (Sheldrick, 2008).

### Figures

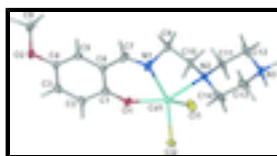


Fig. 1. Thermal ellipsoid plot of the title compound at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. Only the major disordered component is shown.

## Dichlorido(4-methoxy-2-[[2-(piperazin-4-ium-1-yl)ethyl]iminomethyl]phenolate)cadmium

### Crystal data

[CdCl<sub>2</sub>(C<sub>14</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>)]

$M_r = 446.64$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.1173$  (9) Å

$b = 16.2686$  (15) Å

$c = 10.3486$  (10) Å

$\beta = 103.069$  (1)°

$V = 1659.2$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 896$

$D_x = 1.788$  Mg m<sup>-3</sup>

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

Cell parameters from 4675 reflections

$\theta = 2.4$ – $30.3$ °

$\mu = 1.65$  mm<sup>-1</sup>

$T = 100$  K

Plate, yellow

$0.25 \times 0.18 \times 0.04$  mm

### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.684$ ,  $T_{\max} = 0.937$

14540 measured reflections

3624 independent reflections

3138 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 27.0$ °,  $\theta_{\min} = 2.1$ °

$h = -12 \rightarrow 12$

$k = -20 \rightarrow 20$

$l = -12 \rightarrow 13$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.061$

$S = 1.07$

3624 reflections

225 parameters

5 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0115P)^2 + 3.0473P]$

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

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

$\Delta\rho_{\max} = 0.65$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.78$  e Å<sup>-3</sup>

### 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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cd1	0.34107 (2)	-0.052048 (13)	0.68131 (2)	0.01663 (7)	
Cl1	0.56656 (8)	-0.11579 (5)	0.74780 (10)	0.0354 (2)	
Cl2	0.23070 (8)	-0.07175 (5)	0.87000 (8)	0.02395 (17)	
O1	0.2602 (2)	-0.15436 (13)	0.5407 (2)	0.0251 (5)	
O2	-0.1051 (2)	-0.17553 (14)	0.0579 (2)	0.0268 (5)	
N1	0.2318 (3)	0.02551 (17)	0.5110 (3)	0.0360 (8)	
N2	0.4238 (3)	0.08960 (15)	0.7371 (3)	0.0201 (6)	
N3	0.6073 (3)	0.20036 (17)	0.9144 (3)	0.0282 (7)	
H3A	0.644 (3)	0.2509 (14)	0.941 (4)	0.034*	
H3B	0.647 (3)	0.1620 (18)	0.972 (3)	0.034*	
C1	0.1647 (3)	-0.15272 (19)	0.4325 (3)	0.0213 (7)	
C2	0.1038 (3)	-0.22708 (19)	0.3799 (4)	0.0250 (7)	
H2	0.1240	-0.2756	0.4316	0.030*	
C3	0.0166 (3)	-0.2327 (2)	0.2574 (4)	0.0259 (7)	
H3	-0.0201	-0.2846	0.2257	0.031*	
C4	-0.0181 (3)	-0.16303 (19)	0.1797 (3)	0.0199 (6)	
C5	0.0301 (3)	-0.08803 (19)	0.2301 (3)	0.0221 (7)	
H5	0.0028	-0.0398	0.1792	0.027*	
C6	0.1199 (3)	-0.08094 (18)	0.3567 (3)	0.0198 (6)	
C7	0.1562 (4)	0.0024 (2)	0.3998 (4)	0.0336 (9)	
H7	0.1201	0.0448	0.3390	0.040*	
C8	-0.1108 (3)	-0.1114 (2)	-0.0365 (3)	0.0277 (7)	
H8A	-0.1539	-0.0629	-0.0077	0.042*	
H8B	-0.1639	-0.1297	-0.1230	0.042*	
H8C	-0.0186	-0.0974	-0.0440	0.042*	
C9	0.2794 (9)	0.1146 (3)	0.5179 (6)	0.027 (2)	0.520 (10)
H9A	0.3623	0.1195	0.4828	0.033*	0.520 (10)
H9B	0.2081	0.1500	0.4639	0.033*	0.520 (10)
C10	0.3083 (6)	0.1410 (3)	0.6602 (6)	0.0207 (17)	0.520 (10)
H10A	0.2267	0.1333	0.6965	0.025*	0.520 (10)
H10B	0.3334	0.1999	0.6674	0.025*	0.520 (10)
C9'	0.2199 (7)	0.1130 (4)	0.5540 (8)	0.0213 (18)	0.480 (10)
H9C	0.1786	0.1483	0.4775	0.026*	0.480 (10)
H9D	0.1646	0.1166	0.6215	0.026*	0.480 (10)
C10'	0.3645 (7)	0.1373 (4)	0.6114 (7)	0.0227 (19)	0.480 (10)
H10C	0.3686	0.1969	0.6314	0.027*	0.480 (10)
H10D	0.4195	0.1270	0.5452	0.027*	0.480 (10)
C11	0.5665 (4)	0.0977 (2)	0.7352 (4)	0.0374 (10)	

## supplementary materials

---

H11A	0.5772	0.0875	0.6438	0.045*
H11B	0.6185	0.0549	0.7932	0.045*
C12	0.6273 (4)	0.1815 (2)	0.7807 (4)	0.0363 (9)
H12A	0.7255	0.1814	0.7821	0.044*
H12B	0.5833	0.2244	0.7175	0.044*
C13	0.4637 (4)	0.1933 (2)	0.9208 (4)	0.0407 (10)
H13A	0.4098	0.2365	0.8652	0.049*
H13B	0.4550	0.2012	1.0134	0.049*
C14	0.4095 (4)	0.1085 (2)	0.8714 (4)	0.0441 (11)
H14A	0.4583	0.0662	0.9329	0.053*
H14B	0.3123	0.1054	0.8735	0.053*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cd1	0.01874 (11)	0.01363 (11)	0.01584 (12)	-0.00060 (9)	0.00039 (8)	0.00174 (9)
Cl1	0.0207 (4)	0.0231 (4)	0.0576 (6)	0.0037 (3)	-0.0014 (4)	0.0042 (4)
Cl2	0.0276 (4)	0.0202 (4)	0.0259 (4)	-0.0011 (3)	0.0097 (3)	0.0048 (3)
O1	0.0382 (13)	0.0120 (10)	0.0204 (12)	0.0043 (9)	-0.0033 (10)	0.0012 (9)
O2	0.0250 (12)	0.0280 (13)	0.0245 (13)	-0.0034 (10)	-0.0007 (10)	-0.0050 (10)
N1	0.060 (2)	0.0154 (14)	0.0215 (16)	0.0037 (14)	-0.0132 (15)	-0.0005 (12)
N2	0.0188 (13)	0.0163 (12)	0.0217 (15)	-0.0021 (10)	-0.0028 (11)	0.0021 (11)
N3	0.0386 (17)	0.0143 (13)	0.0228 (17)	-0.0021 (12)	-0.0119 (13)	-0.0002 (11)
C1	0.0189 (15)	0.0175 (15)	0.0274 (18)	0.0022 (12)	0.0050 (13)	0.0013 (13)
C2	0.0249 (17)	0.0140 (15)	0.033 (2)	0.0000 (13)	0.0008 (14)	0.0041 (14)
C3	0.0233 (16)	0.0178 (15)	0.035 (2)	-0.0022 (13)	0.0036 (15)	-0.0054 (14)
C4	0.0135 (14)	0.0259 (16)	0.0187 (16)	0.0003 (12)	0.0004 (12)	-0.0044 (13)
C5	0.0251 (16)	0.0184 (15)	0.0226 (18)	0.0016 (13)	0.0049 (13)	0.0031 (13)
C6	0.0256 (16)	0.0150 (14)	0.0179 (17)	0.0009 (12)	0.0032 (13)	-0.0023 (12)
C7	0.053 (2)	0.0176 (16)	0.0223 (19)	0.0073 (16)	-0.0088 (17)	0.0040 (14)
C8	0.0235 (17)	0.0355 (19)	0.0224 (19)	0.0033 (14)	0.0015 (14)	-0.0050 (15)
C9	0.040 (5)	0.012 (3)	0.021 (4)	0.003 (3)	-0.010 (3)	-0.004 (3)
C10	0.020 (3)	0.012 (3)	0.027 (4)	-0.003 (2)	-0.002 (3)	-0.004 (3)
C9'	0.023 (4)	0.020 (4)	0.020 (4)	0.007 (3)	0.002 (3)	0.000 (3)
C10'	0.031 (4)	0.014 (3)	0.021 (4)	-0.005 (3)	0.004 (3)	0.001 (3)
C11	0.034 (2)	0.034 (2)	0.053 (3)	-0.0217 (16)	0.0285 (19)	-0.0279 (18)
C12	0.0297 (19)	0.0302 (19)	0.057 (3)	-0.0137 (15)	0.0255 (18)	-0.0224 (18)
C13	0.060 (3)	0.0272 (19)	0.046 (3)	-0.0171 (18)	0.035 (2)	-0.0180 (17)
C14	0.062 (3)	0.0273 (19)	0.058 (3)	-0.0221 (18)	0.044 (2)	-0.0194 (19)

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

Cd1—O1	2.241 (2)	C5—H5	0.9500
Cd1—N1	2.245 (3)	C6—C7	1.448 (4)
Cd1—N2	2.475 (2)	C7—H7	0.9500
Cd1—Cl1	2.4584 (8)	C8—H8A	0.9800
Cd1—Cl2	2.4797 (8)	C8—H8B	0.9800
O1—C1	1.303 (4)	C8—H8C	0.9800
O2—C4	1.380 (4)	C9—C10	1.498 (7)

O2—C8	1.421 (4)	C9—H9A	0.9900
N1—C7	1.285 (4)	C9—H9B	0.9900
N1—C9'	1.505 (6)	C10—H10A	0.9900
N1—C9	1.524 (6)	C10—H10B	0.9900
N2—C11	1.455 (4)	C9'—C10'	1.503 (7)
N2—C14	1.462 (4)	C9'—H9C	0.9900
N2—C10	1.509 (6)	C9'—H9D	0.9900
N2—C10'	1.518 (6)	C10'—H10C	0.9900
N3—C13	1.474 (5)	C10'—H10D	0.9900
N3—C12	1.476 (5)	C11—C12	1.525 (4)
N3—H3A	0.918 (18)	C11—H11A	0.9900
N3—H3B	0.897 (18)	C11—H11B	0.9900
C1—C2	1.410 (4)	C12—H12A	0.9900
C1—C6	1.423 (4)	C12—H12B	0.9900
C2—C3	1.373 (5)	C13—C14	1.529 (5)
C2—H2	0.9500	C13—H13A	0.9900
C3—C4	1.388 (5)	C13—H13B	0.9900
C3—H3	0.9500	C14—H14A	0.9900
C4—C5	1.372 (4)	C14—H14B	0.9900
C5—C6	1.420 (4)		
O1—Cd1—N1	82.23 (9)	O2—C8—H8A	109.5
O1—Cd1—C11	92.75 (6)	O2—C8—H8B	109.5
N1—Cd1—C11	135.90 (10)	H8A—C8—H8B	109.5
O1—Cd1—N2	153.88 (8)	O2—C8—H8C	109.5
N1—Cd1—N2	74.96 (9)	H8A—C8—H8C	109.5
C11—Cd1—N2	94.82 (6)	H8B—C8—H8C	109.5
O1—Cd1—C12	104.60 (6)	C10—C9—N1	107.9 (5)
N1—Cd1—C12	117.46 (9)	C10—C9—H9A	110.1
C11—Cd1—C12	106.24 (3)	N1—C9—H9A	110.1
N2—Cd1—C12	97.20 (7)	C10—C9—H9B	110.1
C1—O1—Cd1	129.33 (19)	N1—C9—H9B	110.1
C4—O2—C8	116.0 (2)	H9A—C9—H9B	108.4
C7—N1—C9'	118.1 (4)	C9—C10—N2	108.4 (5)
C7—N1—C9	116.0 (4)	C9—C10—H10A	110.0
C9'—N1—C9	29.7 (3)	N2—C10—H10A	110.0
C7—N1—Cd1	128.7 (2)	C9—C10—H10B	110.0
C9'—N1—Cd1	111.0 (3)	N2—C10—H10B	110.0
C9—N1—Cd1	113.8 (3)	H10A—C10—H10B	108.4
C11—N2—C14	107.8 (3)	C10'—C9'—N1	103.3 (5)
C11—N2—C10	126.5 (4)	C10'—C9'—H9C	111.1
C14—N2—C10	98.8 (4)	N1—C9'—H9C	111.1
C11—N2—C10'	98.2 (4)	C10'—C9'—H9D	111.1
C14—N2—C10'	127.0 (4)	N1—C9'—H9D	111.1
C10—N2—C10'	32.4 (3)	H9C—C9'—H9D	109.1
C11—N2—Cd1	111.46 (19)	C9'—C10'—N2	111.4 (6)
C14—N2—Cd1	108.48 (19)	C9'—C10'—H10C	109.3
C10—N2—Cd1	102.3 (3)	N2—C10'—H10C	109.3
C10'—N2—Cd1	103.2 (3)	C9'—C10'—H10D	109.3
C13—N3—C12	111.8 (3)	N2—C10'—H10D	109.3

## supplementary materials

C13—N3—H3A	113 (2)	H10C—C10'—H10D	108.0
C12—N3—H3A	110 (2)	N2—C11—C12	114.2 (3)
C13—N3—H3B	103 (2)	N2—C11—H11A	108.7
C12—N3—H3B	110 (2)	C12—C11—H11A	108.7
H3A—N3—H3B	109 (3)	N2—C11—H11B	108.7
O1—C1—C2	119.3 (3)	C12—C11—H11B	108.7
O1—C1—C6	124.9 (3)	H11A—C11—H11B	107.6
C2—C1—C6	115.7 (3)	N3—C12—C11	110.1 (3)
C3—C2—C1	123.2 (3)	N3—C12—H12A	109.6
C3—C2—H2	118.4	C11—C12—H12A	109.6
C1—C2—H2	118.4	N3—C12—H12B	109.6
C2—C3—C4	120.4 (3)	C11—C12—H12B	109.6
C2—C3—H3	119.8	H12A—C12—H12B	108.2
C4—C3—H3	119.8	N3—C13—C14	109.8 (3)
C5—C4—O2	125.2 (3)	N3—C13—H13A	109.7
C5—C4—C3	119.0 (3)	C14—C13—H13A	109.7
O2—C4—C3	115.8 (3)	N3—C13—H13B	109.7
C4—C5—C6	121.4 (3)	C14—C13—H13B	109.7
C4—C5—H5	119.3	H13A—C13—H13B	108.2
C6—C5—H5	119.3	N2—C14—C13	113.8 (3)
C5—C6—C1	120.0 (3)	N2—C14—H14A	108.8
C5—C6—C7	115.2 (3)	C13—C14—H14A	108.8
C1—C6—C7	124.8 (3)	N2—C14—H14B	108.8
N1—C7—C6	127.5 (3)	C13—C14—H14B	108.8
N1—C7—H7	116.3	H14A—C14—H14B	107.7
C6—C7—H7	116.3		

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

Cg1 is the centroid of the C1—C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3A $\cdots$ O1 <sup>i</sup>	0.92 (2)	1.80 (2)	2.705 (3)	166 (4)
N3—H3B $\cdots$ Cl2 <sup>ii</sup>	0.90 (2)	2.33 (2)	3.222 (3)	174 (4)
C9—H9A $\cdots$ Cl1 <sup>iii</sup>	0.99	2.64	3.454 (8)	139
C8—H8A $\cdots$ Cl2 <sup>iv</sup>	0.98	2.82	3.777 (3)	167
C8—H8B $\cdots$ Cl1 <sup>v</sup>	0.98	2.76	3.514 (3)	134
C13—H13A $\cdots$ Cl1 <sup>i</sup>	0.99	2.71	3.542 (4)	142
C12—H12A $\cdots$ Cg1 <sup>vi</sup>	0.99	2.48	3.408 (4)	156
C9'—H9D $\cdots$ Cg1 <sup>iv</sup>	0.99	2.72	3.620 (8)	151

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

Fig. 1

