Crystal structure of di-μ_2-chlorido-bis[(1-aza-4-azoniabicyclo[2.2.2]octane-κN^1)-dichloridodicadmium]

Jing-Jing Yan, Qi-Jian Pan and Li-Zhuang Chen*

School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, People's Republic of China. *Correspondence e-mail: clz1977@sina.com

In the structure of the binuclear title compound, [Cd$_2$(C$_6$H$_{13}$N$_2$)$_2$Cl$_6$], two Cd^{II} atoms are bridged by two Cl$^-$ ligands, defining a centrosymmetric Cd$_2$Cl$_2$ motif. Each metal cation is additionally coordinated by two Cl$^-$ ligands and the N atom of a protonated 1,4-diazabicyclo[2.2.2]octane (H-DABCO)$^+$ ligand, leading to an overall trigonal–bipyramidal coordination environment with one of the bridging Cl$^-$ ligands and the N atom at the apical sites. In the crystal, the neutral dimers are linked via N—H···Cl hydrogen bonds, forming a two-dimensional network expanding parallel to (100).

1. Related literature

For a study on phase transition of related Cd$_2$(DABCO-CH$_2$Cl)$_2$(μ-Cl$_2$), see: Chen et al. (2014). Mononuclear and dinuclear bromide-nitrite cadmium complexes with DABCO derivatives were reported by Cai (2011).
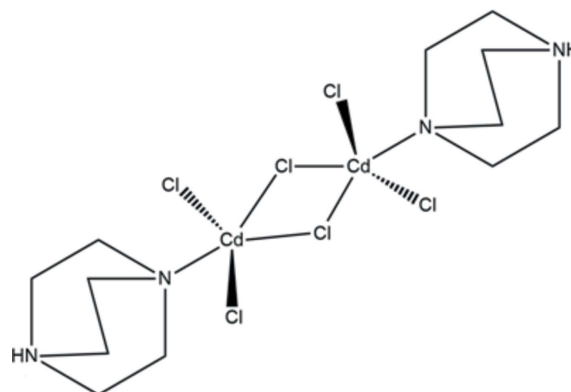
2. Experimental

2.1. Crystal data

[Cd$_2$(C$_6$H$_{13}$N$_2$)$_2$Cl$_6$]	$V = 2185.7$ (6) Å^3
$M_r = 663.86$	$Z = 4$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 12.317$ (2) Å	$\mu = 2.68$ mm^{-1}
$b = 12.289$ (2) Å	$T = 296$ K
$c = 14.440$ (2) Å	$0.3 \times 0.2 \times 0.2$ mm

2.2. Data collection

Bruker APEXII CCD diffractometer	14939 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	1924 independent reflections
$T_{min} = 0.500$, $T_{max} = 0.616$	1752 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.025$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	30 restraints
$wR(F^2) = 0.183$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{max} = 1.98$ e Å^{-3}
1924 reflections	$\Delta\rho_{min} = -1.65$ e Å^{-3}
109 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Cl3^i	0.91	2.33	3.205 (3)	162

Symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Acknowledgements

Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5244).

References

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2004). *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cai, Y. (2011). *Acta Cryst.* C**67**, m13–m16.

Chen, L. Z., Huang, D. D., Pan, Q. J. & Zhang, L. (2014). *J. Mol. Struct.* **1078**, 68–73.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Crystal structure of di-μ_2-chlorido-bis[(1-aza-4-azoniabicyclo[2.2.2]octane-κN^1)dichloridodicadmium]

Jing-Jing Yan, Qi-Jian Pan and Li-Zhuang Chen

S1. Synthesis and crystallization

$CdCl_2 \cdot 2.5H_2O$ (2.28 g, 10 mmol) and 1,4-diazabicyclo [2.2.2]octan (1.12 g, 10 mmol) were mixed in water (20 ml). After being stirred for 30 min, the reaction mixture was filtered and evaporated slowly at room temperature for 3 days. Colourless block-like crystals were obtained.

S2. Refinement

C-bound H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). The H atom of the protonated N2 atom was discernible from a difference map. It was modelled with N—H = 0.91 Å and U_{iso}(H) = 1.2U_{eq}(N). The maximum and minimum electron density peaks are found 0.20 Å from atom Cl3 and 0.27 Å from atom Cd1, respectively.
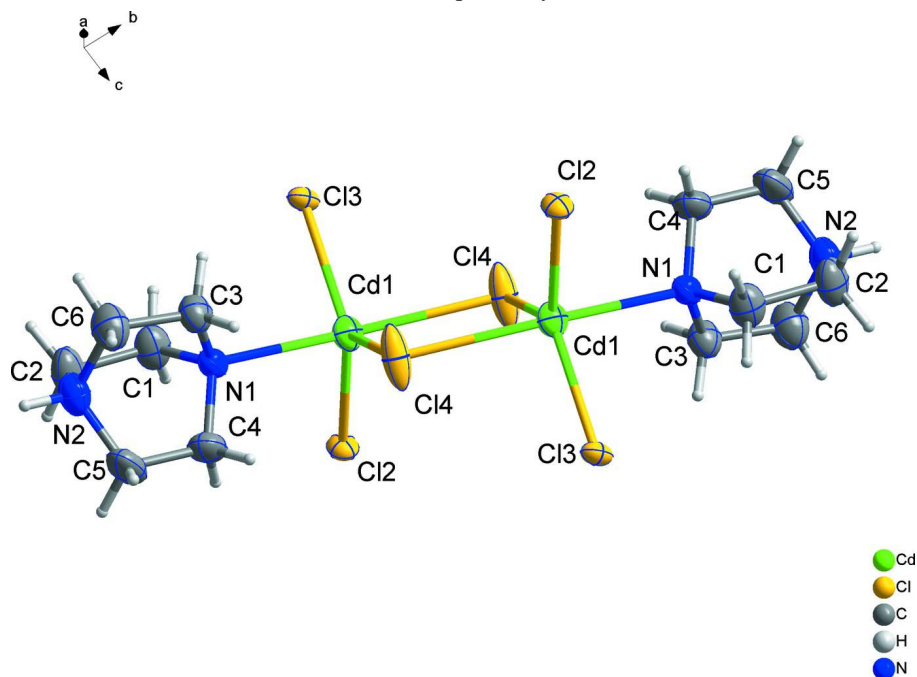

Figure 1

The molecular structure of the dinuclear complex in the title compound. Displacement ellipsoids are drawn at the 30% probability level. The left part of the binuclear complex is generated by symmetry code -*x* + 1, -*y*, -*z* + 1.
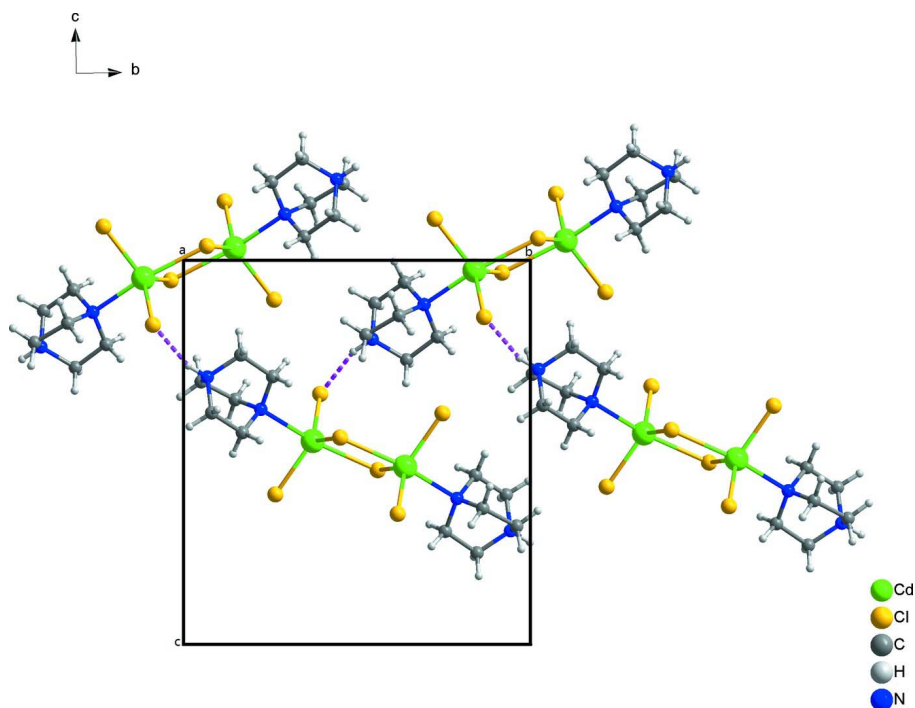
Figure 2
View onto a layer of complexes in the title compound with N—H···Cl hydrogen bonds drawn as dashed lines.

Di-μ_2-chlorido-bis[(1-aza-4-azoniabicyclo[2.2.2]octane-κN^1)dichloridodicadmium]

Crystal data

[Cd$_2$(C$_6$H$_{13}$N$_2$)$_2$Cl$_6$]	$D_x = 2.017$ Mg m^{-3}
$M_r = 663.86$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 6044 reflections
$a = 12.317$ (2) Å	$\theta = 2.7$–27.4°
$b = 12.289$ (2) Å	$\mu = 2.68$ mm^{-1}
$c = 14.440$ (2) Å	$T = 296$ K
$V = 2185.7$ (6) Å^3	Block, colorless
$Z = 4$	$0.3 \times 0.2 \times 0.2$ mm
$F(000) = 1296$	

Data collection

Bruker APEXII CCD diffractometer	14939 measured reflections
Radiation source: fine-focus sealed tube	1924 independent reflections
Graphite monochromator	1752 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$, $\theta_{min} = 2.7°$
(*SADABS*; Bruker, 2004)	$h = -13 \rightarrow 14$
$T_{min} = 0.500$, $T_{max} = 0.616$	$k = -14 \rightarrow 14$
	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.183$	
$S = 1.12$	H-atom parameters constrained
1924 reflections	$w = 1/[\sigma^2(F_o^2) + (0.1089P)^2 + 19.3777P]$
109 parameters	where $P = (F_o^2 + 2F_c^2)/3$
30 restraints	$(\Delta/\sigma)_{max} = 0.006$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.98$ e Å^{-3}
	$\Delta\rho_{min} = -1.65$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.42960 (2)	0.138551 (19)	0.535783 (17)	0.03153 (7)
Cl2	0.37788 (6)	0.25484 (6)	0.40100 (5)	0.02553 (17)
Cl3	0.28196 (6)	0.11273 (6)	0.65621 (5)	0.02369 (17)
Cl4	0.61656 (7)	0.05552 (8)	0.54294 (8)	0.0606 (3)
C1	0.4234 (3)	0.3697 (3)	0.6469 (3)	0.0453 (12)
H1A	0.3732	0.3344	0.6890	0.054*
H1B	0.3833	0.3921	0.5923	0.054*
C3	0.5670 (3)	0.2551 (3)	0.7038 (2)	0.0401 (9)
H3A	0.6263	0.2078	0.6853	0.048*
H3B	0.5177	0.2128	0.7418	0.048*
N1	0.5090 (2)	0.2930 (2)	0.62028 (18)	0.0284 (7)
C4	0.5890 (3)	0.3502 (3)	0.5617 (3)	0.0418 (10)
H4A	0.5526	0.3799	0.5078	0.050*
H4B	0.6432	0.2987	0.5404	0.050*
C2	0.4742 (3)	0.4710 (3)	0.6946 (3)	0.0512 (12)
H2A	0.4624	0.5352	0.6568	0.061*
H2B	0.4403	0.4829	0.7544	0.061*
N2	0.5912 (3)	0.4521 (3)	0.7064 (2)	0.0429 (8)
H2	0.6208	0.5096	0.7370	0.051*
C5	0.6446 (4)	0.4414 (3)	0.6140 (3)	0.0553 (12)
H5A	0.7211	0.4251	0.6218	0.066*
H5B	0.6381	0.5091	0.5799	0.066*
C6	0.6123 (4)	0.3495 (3)	0.7611 (3)	0.0537 (10)
H6A	0.5763	0.3531	0.8208	0.064*
H6B	0.6895	0.3400	0.7713	0.064*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.03132 (14)	0.02795 (13)	0.03533 (14)	0.00383 (9)	−0.00315 (9)	−0.00071 (9)
Cl2	0.0293 (3)	0.0249 (3)	0.0224 (3)	0.0010 (3)	−0.0047 (3)	0.0066 (3)
Cl3	0.0201 (3)	0.0231 (3)	0.0278 (3)	0.0002 (3)	0.0055 (3)	0.0068 (3)
Cl4	0.0362 (4)	0.0375 (4)	0.1082 (7)	0.0139 (4)	−0.0311 (4)	−0.0347 (4)
C1	0.0315 (19)	0.042 (2)	0.062 (2)	0.0035 (15)	0.0005 (17)	−0.0087 (17)
C3	0.0468 (17)	0.0325 (15)	0.0408 (16)	0.0022 (13)	−0.0054 (14)	0.0003 (14)
N1	0.0269 (12)	0.0237 (12)	0.0346 (13)	−0.0007 (10)	0.0030 (11)	0.0011 (11)
C4	0.0393 (18)	0.0414 (19)	0.0448 (19)	−0.0063 (16)	0.0128 (17)	0.0046 (16)
C2	0.041 (2)	0.0406 (19)	0.072 (2)	0.0050 (17)	0.003 (2)	−0.0175 (19)
N2	0.0411 (14)	0.0361 (14)	0.0515 (15)	−0.0060 (12)	−0.0063 (13)	−0.0092 (12)
C5	0.054 (2)	0.0381 (19)	0.074 (3)	−0.0152 (17)	0.024 (2)	0.0006 (19)
C6	0.0584 (17)	0.0475 (16)	0.0551 (17)	−0.0017 (15)	−0.0138 (16)	−0.0050 (15)

Geometric parameters (Å, º)

Cd1—Cl2	2.4972 (8)	N1—C4	1.477 (5)
Cd1—Cl3	2.5361 (8)	C4—H4A	0.9700
Cd1—Cl4^i	2.7025 (11)	C4—H4B	0.9700
Cd1—Cl4	2.5207 (10)	C4—C5	1.515 (6)
Cd1—N1	2.460 (3)	C2—H2A	0.9700
Cl4—Cd1^i	2.7025 (11)	C2—H2B	0.9700
C1—H1A	0.9700	C2—N2	1.470 (5)
C1—H1B	0.9700	N2—H2	0.9100
C1—N1	1.465 (5)	N2—C5	1.493 (5)
C1—C2	1.555 (6)	N2—C6	1.510 (5)
C3—H3A	0.9700	C5—H5A	0.9700
C3—H3B	0.9700	C5—H5B	0.9700
C3—N1	1.477 (4)	C6—H6A	0.9700
C3—C6	1.530 (6)	C6—H6B	0.9700
Cl2—Cd1—Cl3	115.03 (3)	N1—C4—H4B	109.3
Cl2—Cd1—Cl4	119.78 (3)	N1—C4—C5	111.6 (3)
Cl2—Cd1—Cl4^i	97.09 (3)	H4A—C4—H4B	108.0
Cl3—Cd1—Cl4^i	91.56 (3)	C5—C4—H4A	109.3
Cl4—Cd1—Cl3	125.19 (3)	C5—C4—H4B	109.3
Cl4—Cd1—Cl4^i	81.50 (3)	C1—C2—H2A	110.0
N1—Cd1—Cl2	92.66 (6)	C1—C2—H2B	110.0
N1—Cd1—Cl3	92.39 (6)	H2A—C2—H2B	108.3
N1—Cd1—Cl4	85.91 (7)	N2—C2—C1	108.6 (3)
N1—Cd1—Cl4^i	166.77 (6)	N2—C2—H2A	110.0
Cd1—Cl4—Cd1^i	98.50 (3)	N2—C2—H2B	110.0
H1A—C1—H1B	108.2	C2—N2—H2	109.0
N1—C1—H1A	109.7	C2—N2—C5	110.0 (3)
N1—C1—H1B	109.7	C2—N2—C6	111.2 (3)
N1—C1—C2	110.0 (3)	C5—N2—H2	109.0

C2—C1—H1A	109.7	C5—N2—C6	108.5 (3)
C2—C1—H1B	109.7	C6—N2—H2	109.0
H3A—C3—H3B	107.9	C4—C5—H5A	110.1
N1—C3—H3A	109.2	C4—C5—H5B	110.1
N1—C3—H3B	109.2	N2—C5—C4	108.2 (3)
N1—C3—C6	112.2 (3)	N2—C5—H5A	110.1
C6—C3—H3A	109.2	N2—C5—H5B	110.1
C6—C3—H3B	109.2	H5A—C5—H5B	108.4
C1—N1—Cd1	109.9 (2)	C3—C6—H6A	110.4
C1—N1—C3	109.7 (3)	C3—C6—H6B	110.4
C1—N1—C4	108.9 (3)	N2—C6—C3	106.7 (3)
C3—N1—Cd1	110.70 (19)	N2—C6—H6A	110.4
C4—N1—Cd1	110.4 (2)	N2—C6—H6B	110.4
C4—N1—C3	107.2 (3)	H6A—C6—H6B	108.6
N1—C4—H4A	109.3		

Cd1—N1—C4—C5	−176.4 (2)	C1—C2—N2—C5	63.5 (4)
Cl2—Cd1—Cl4—Cd1ⁱ	−93.35 (4)	C1—C2—N2—C6	−56.8 (4)
Cl2—Cd1—N1—C1	67.3 (2)	C3—N1—C4—C5	−55.7 (4)
Cl2—Cd1—N1—C3	−171.4 (2)	N1—Cd1—Cl4—Cd1ⁱ	175.92 (7)
Cl2—Cd1—N1—C4	−52.9 (2)	N1—C1—C2—N2	−5.9 (5)
Cl3—Cd1—Cl4—Cd1ⁱ	85.88 (4)	N1—C3—C6—N2	−5.6 (4)
Cl3—Cd1—N1—C1	−47.9 (2)	N1—C4—C5—N2	−6.1 (4)
Cl3—Cd1—N1—C3	73.4 (2)	C2—C1—N1—Cd1	−176.3 (3)
Cl3—Cd1—N1—C4	−168.1 (2)	C2—C1—N1—C3	61.8 (4)
Cl4ⁱ—Cd1—Cl4—Cd1ⁱ	0.0	C2—C1—N1—C4	−55.2 (4)
Cl4—Cd1—N1—C1	−173.0 (2)	C2—N2—C5—C4	−56.7 (4)
Cl4ⁱ—Cd1—N1—C1	−155.2 (3)	C2—N2—C6—C3	63.1 (4)
Cl4—Cd1—N1—C3	−51.7 (2)	C5—N2—C6—C3	−58.0 (4)
Cl4ⁱ—Cd1—N1—C3	−33.9 (4)	C6—C3—N1—Cd1	−176.8 (3)
Cl4—Cd1—N1—C4	66.8 (2)	C6—C3—N1—C1	−55.5 (4)
Cl4ⁱ—Cd1—N1—C4	84.7 (4)	C6—C3—N1—C4	62.7 (4)
C1—N1—C4—C5	62.9 (4)	C6—N2—C5—C4	65.1 (4)

Symmetry code: (i) −x+1, −y, −z+1.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2⋯Cl3ⁱⁱ	0.91	2.33	3.205 (3)	162

Symmetry code: (ii) −x+1, y+1/2, −z+3/2.