

catena-Poly[[diaquacadmium(II)]- μ -(methyl morpholino dichloromethylene-diphosphonato)- κ^3 O,O':O''-[tetraqua-cadmium(II)]- μ -(methyl morpholino dichloromethylenediphosphonato)- κ^3 O:O',O'']

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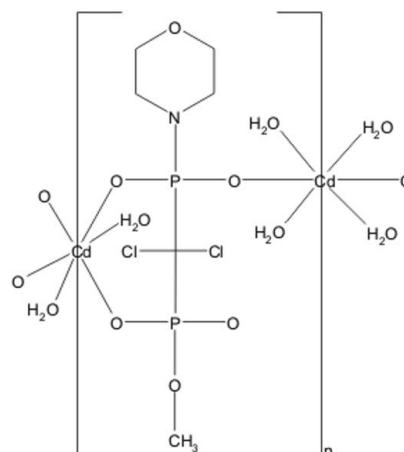
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.027; wR factor = 0.068; data-to-parameter ratio = 20.8.

The asymmetric unit of the title compound, $[\text{Cd}(\text{C}_6\text{H}_{11}\text{Cl}_2\text{N}-\text{O}_6\text{P}_2)(\text{H}_2\text{O})_3]_n$, contains two octahedrally coordinated Cd atoms located in special positions, one on a twofold rotation axis and the other on a centre of symmetry. The metal atoms are connected by methyl morpholino dichloromethylenediphosphonate ligands into chains in the c -axis direction. These chains are further connected by O—H...O hydrogen bonds into a layer-like construction along (100).

Related literature

For applications of metal complexes of bisphosphonates, see: Clearfield (1998); Clearfield *et al.* (2001); Fu *et al.* (2007). For cadmium bisphosphonate complexes, see: Ying & Mao (2006); Man *et al.* (2006). For metal complexes of bisphosphonate ester derivatives, see: Jokiniemi *et al.* (2007, 2008). For Mg, Zn and Cd complexes of the symmetrical diethyl ester derivative of (dichloromethylene)bisphosphonate, see: Kontturi *et al.* (2002, 2005a,b).



Experimental

Crystal data

$[\text{Cd}(\text{C}_6\text{H}_{11}\text{Cl}_2\text{NO}_6\text{P}_2)(\text{H}_2\text{O})_3]$
 $M_r = 492.45$
Monoclinic, $C2/c$
 $a = 26.2488$ (8) Å
 $b = 7.6578$ (3) Å
 $c = 17.5445$ (7) Å
 $\beta = 116.002$ (3)°

$V = 3169.6$ (2) Å³
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 1.96$ mm⁻¹
 $T = 120$ K
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*XPRED* in *SHELXTL*;
Sheldrick, 2008)
 $T_{\min} = 0.565$, $T_{\max} = 0.676$

21828 measured reflections
4053 independent reflections
3370 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.068$
 $S = 1.06$
4053 reflections

195 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 1.04$ e Å⁻³
 $\Delta\rho_{\min} = -1.12$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---------|-------------|---------|-------------|
| Cd1—O11 | 2.2256 (17) | Cd2—O12 | 2.1884 (17) |
| Cd1—O21 | 2.3173 (16) | Cd2—O3 | 2.2795 (16) |
| Cd1—O1 | 2.3409 (17) | Cd2—O2 | 2.3486 (16) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------|-------|-------------|-------------|---------------|
| O1—H1A...O2 ⁱ | 0.84 | 2.06 | 2.849 (2) | 156 |
| O1—H1B...O22 ⁱⁱ | 0.88 | 2.12 | 2.990 (2) | 170 |
| O2—H2A...O21 ⁱⁱⁱ | 0.86 | 2.04 | 2.844 (2) | 155 |
| O2—H2B...O22 | 0.86 | 1.84 | 2.662 (2) | 159 |
| O3—H3A...O22 | 0.83 | 2.03 | 2.773 (2) | 149 |
| O3—H3B...O13 ^{iv} | 0.90 | 1.87 | 2.745 (2) | 163 |

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

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ER2063).

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supplementary materials

Acta Cryst. (2009). E65, m600-m601 [doi:10.1107/S160053680901527X]

***catena*-Poly[[diaquacadmium(II)]- μ -(methyl morpholino dichloromethylenediphosphonato)- κ^3 O,O',O''-[tetraaquacadmium(II)]- μ -(methyl morpholino dichloromethylenediphosphonato)- κ^3 O:O',O'']**

J. Jokiniemi, J. Vepsäläinen and M. Ahlgrén

Comment

Metal complexes with bisphosphonic acids have interesting structures with various coordination architectures, and properties that offer practical applications in catalysis, ion-exchange and sorption (Clearfield *et al.*, 2001, Clearfield, 1998, Fu *et al.*, 2007). In our recent investigations, we studied the complexing properties of amide ester derivatives of (dichloromethylene)bisphosphonate, Cl₂MBP (Jokiniemi *et al.*, 2007, 2008). Introduction of these ester substituents to phosphorus groups can result in novel structures of metal bisphosphonates and lead to interesting functionalities. We now present the crystal structure of the Cd(II) complex of the *P*-morpholinyl-*P'*-methyl ester derivative of Cl₂MBP obtained by gel crystallization.

The title compound is isomorphous with the earlier reported Mg complexes of (dichloromethylene)bisphosphonic acid methyl esters of piperidinyll and morpholinyl derivatives (Jokiniemi *et al.*, 2007, 2008). The title compound is polymeric, consisting of chains in the direction of the *c*-axis. There are two crystallographically independent six-coordinated Cd²⁺ cations in the asymmetric unit, located in special positions: Cd1 on the twofold rotation axis and Cd2 on the centre of symmetry (Fig. 1). Two symmetrically related *L*₁ ligands, *L*₁ = (Cl₂CP₂O₅MeNC₄H₈O), around the Cd1 atom form six-membered chelate rings. The *L*₁ ligand is further connected to Cd2 through one O atom, and thus acts as a triatomic bridge between the adjacent Cd atoms. The fourth phosphonate O atom remains non-coordinated but is involved in hydrogen bonding. The remaining coordination sites around the Cd1 atoms are occupied by aqua ligands in *cis* position; the geometry is a significantly distorted octahedron having Cd1–O bond distances 2.226 (2)–2.341 (2) Å (Table 1). The three *trans* angles are O11–Cd1–O11A 166.14 (9), O21–Cd1–O1A 174.23 (5) and O21A–Cd1–O1 174.23 (5)°. The Cd2 atom has a distorted octahedral geometry, and the binding sites around the metal atom are occupied by two phosphonate O atoms in axial positions and four aqua ligands having Cd2–O bond lengths 2.188 (2)–2.349 (2) Å. The three *trans* bond angles are 180°, while the *cis* bond angles around the Cd2 atom range from 82.50 (6) to 97.50 (6)°. In addition to isomorphous Mg complexes of monomethyl ester of morpholinyl and piperidinyll derivatives of Cl₂MBP (Jokiniemi *et al.*, 2007 and 2008), the same kind of chain construction is found in Mg, Zn and Cd complexes of the symmetrical diethyl ester derivative of Cl₂MBP (Kontturi *et al.*, 2002, 2005a and 2005b).

The polymeric chains are connected, in a layer-like structure parallel to the (100) plane, by hydrogen bonds [O⋯O 2.745 (2)–2.990 (2) Å, 149–170°, Table 2]. The morpholinyl rings and chlorine atoms of the *L*₁ ligands point out from the layers (Fig. 2), which are held together solely by weak Van der Waals interactions, with an interlayer distance of 11.7959 Å.

Experimental

(H₂N[(CH₂)₂]₂O)₂CH₃PO₃CCl₂PO₂NC₄H₈O (19.8 mg, 0.039 mmol) and Cd(NO₃)₂×4H₂O (12.1 mg, 0.039 mmol) were dissolved separately in water (0.45 ml), the solutions were mixed, and tetramethoxysilane (TMOS 0.1 ml) was added. The two-phase system was shaken until homogeneous. After gel formation, a precipitant, acetone (1.0 ml), was added above the gel to induce crystallization. After about three weeks, large, colourless plank-shaped crystals suitable for X-ray analysis formed at the gel-liquid boundary. Anal. Found: C, 14.63; H, 3.48; N, 2.84; Cd, 22.83%. Calc. for C₆H₁₇Cl₂CdNO₉P₂: C, 14.74; H, 3.48; N, 2.86; Cd, 22.45%. Main IR absorptions (KBr pellet, cm⁻¹): 3432 (*s*), 2961 (*m*), 2926 (*m*), 2854 (*m*), 1627 (*m*), 1204 (*versus*), 1145 (*m*), 1101 (*versus*), 1072 (*s*), 1056 (*s*), 981 (*s*), 869 (*m*), 843 (*m*). ³¹P CP/MAS NMR: δ_p 8.4 and 4.3 p.p.m.. TGA (25–900 °C under a synthetic air): 30–110 °C 12.6% (calculated 11.0% for the loss of three aqua ligands). The second step (190–900 °C) is attributed to the release of organic groups, chlorine atoms and a methylene carbon atom. The observed total weight loss is 47.0% (calculated 45.1% if the final product is assumed to be Cd(PO₃)₂).

Refinement

H atoms of the methyl and morpholinyl groups were placed at calculated positions in the riding-model approximation with C–H = 0.99 Å (morpholinyl) [*U*_{ISO}(H) = 1.2*U*_{eq}(C)] and C–H = 0.98 Å (methyl) [*U*_{ISO}(H) = 1.5*U*_{eq}(C)]. H atoms of the aqua ligands were located in a difference map and treated as riding, with O–H bond lengths constrained to 0.83–0.90 Å and with *U*_{ISO}(H) = 1.5*U*_{eq}(O).

Figures

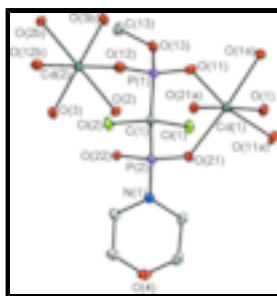


Fig. 1. Structure of the title compound showing the atomic numbering scheme and 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Atoms labelled with suffixes A and B are at the symmetry positions (1 - *x*, *y*, 1/2 - *z*) and (1 - *x*, 1 - *y*, - *z*) respectively.

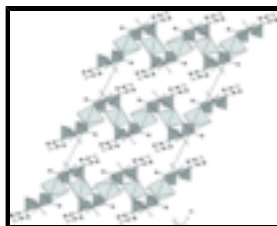


Fig. 2. Packing of the title compound viewed along the *b*-axis. CdO₆ octahedra are presented in medium grey and PO₃C and NPO₂C tetrahedra in dark grey. Hydrogen atoms are omitted for clarity.

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[tetraaquacadmium(II)]- μ -(methyl morpholino dichloromethylenediphosphonato)- $\kappa^3 O, O', O''$]**

Crystal data

| | |
|--|---|
| [Cd(C ₆ H ₁₁ Cl ₂ NO ₆ P ₂)(H ₂ O) ₃] | $F_{000} = 1952$ |
| $M_r = 492.45$ | $D_x = 2.064 \text{ Mg m}^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| Hall symbol: $-C 2yc$ | $\lambda = 0.71073 \text{ \AA}$ |
| $a = 26.2488 (8) \text{ \AA}$ | Cell parameters from 21828 reflections |
| $b = 7.6578 (3) \text{ \AA}$ | $\theta = 2.8\text{--}28.7^\circ$ |
| $c = 17.5445 (7) \text{ \AA}$ | $\mu = 1.96 \text{ mm}^{-1}$ |
| $\beta = 116.002 (3)^\circ$ | $T = 120 \text{ K}$ |
| $V = 3169.6 (2) \text{ \AA}^3$ | Plank, colourless |
| $Z = 8$ | $0.30 \times 0.25 \times 0.20 \text{ mm}$ |

Data collection

| | |
|---|--|
| Nonius KappaCCD diffractometer | 4053 independent reflections |
| Radiation source: fine-focus sealed tube | 3370 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.038$ |
| $T = 120 \text{ K}$ | $\theta_{\text{max}} = 28.7^\circ$ |
| multi-scan | $\theta_{\text{min}} = 2.8^\circ$ |
| Absorption correction: multi-scan (XPREP in SHELXTL; Sheldrick, 2008) | $h = -35 \rightarrow 35$ |
| $T_{\text{min}} = 0.565$, $T_{\text{max}} = 0.676$ | $k = -10 \rightarrow 10$ |
| 21828 measured reflections | $l = -23 \rightarrow 21$ |

Refinement

| | |
|--|---|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.027$ | $w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ |
| $wR(F^2) = 0.068$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.06$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 4053 reflections | $\Delta\rho_{\text{max}} = 1.04 \text{ e \AA}^{-3}$ |
| 195 parameters | $\Delta\rho_{\text{min}} = -1.12 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ |
| Secondary atom site location: difference Fourier map | Extinction coefficient: 0.00053 (7) |

supplementary materials

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> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|---------------|----------------------------------|
| C11 | 0.33755 (3) | 0.03444 (8) | 0.08713 (4) | 0.01735 (14) |
| C12 | 0.31951 (3) | 0.31865 (8) | -0.03219 (3) | 0.01910 (14) |
| P1 | 0.42845 (3) | 0.12553 (8) | 0.03696 (4) | 0.01308 (14) |
| P2 | 0.39459 (2) | 0.37248 (8) | 0.15068 (4) | 0.01129 (13) |
| Cd1 | 0.5000 | 0.05298 (3) | 0.2500 | 0.01210 (8) |
| Cd2 | 0.5000 | 0.5000 | 0.0000 | 0.01366 (8) |
| O1 | 0.43819 (7) | -0.1737 (2) | 0.24266 (10) | 0.0170 (4) |
| H1A | 0.4474 | -0.2385 | 0.2856 | 0.025* |
| H1B | 0.4298 | -0.2517 | 0.2023 | 0.025* |
| O2 | 0.52362 (7) | 0.5362 (2) | 0.14457 (10) | 0.0149 (4) |
| H2A | 0.5420 | 0.4483 | 0.1748 | 0.022* |
| H2B | 0.4929 | 0.5313 | 0.1507 | 0.022* |
| O3 | 0.41722 (7) | 0.6409 (2) | -0.02767 (10) | 0.0182 (4) |
| H3A | 0.4041 | 0.6034 | 0.0045 | 0.027* |
| H3B | 0.4177 | 0.7579 | -0.0243 | 0.042 (9)* |
| O4 | 0.26897 (8) | 0.6093 (3) | 0.22336 (12) | 0.0281 (4) |
| O11 | 0.46611 (8) | 0.0179 (2) | 0.11038 (11) | 0.0182 (4) |
| O12 | 0.45203 (8) | 0.2725 (2) | 0.00769 (11) | 0.0220 (4) |
| O13 | 0.39645 (7) | -0.0065 (2) | -0.03937 (10) | 0.0172 (4) |
| O21 | 0.43465 (7) | 0.2737 (2) | 0.22805 (9) | 0.0138 (3) |
| O22 | 0.41655 (7) | 0.5285 (2) | 0.12215 (10) | 0.0142 (4) |
| N1 | 0.33955 (8) | 0.4329 (3) | 0.16396 (12) | 0.0147 (4) |
| C1 | 0.37131 (10) | 0.2129 (3) | 0.06118 (14) | 0.0130 (5) |
| C2 | 0.29966 (10) | 0.5686 (3) | 0.11230 (15) | 0.0187 (5) |
| H2E | 0.2634 | 0.5141 | 0.0731 | 0.022* |
| H2F | 0.3155 | 0.6307 | 0.0781 | 0.022* |
| C3 | 0.28936 (12) | 0.6969 (4) | 0.16995 (17) | 0.0246 (6) |
| H3E | 0.3251 | 0.7585 | 0.2056 | 0.029* |
| H3F | 0.2612 | 0.7851 | 0.1351 | 0.029* |
| C5 | 0.30950 (12) | 0.4819 (4) | 0.27479 (17) | 0.0240 (6) |
| H5E | 0.2955 | 0.4245 | 0.3125 | 0.029* |
| H5F | 0.3457 | 0.5408 | 0.3109 | 0.029* |
| C6 | 0.31968 (11) | 0.3450 (3) | 0.22048 (15) | 0.0188 (5) |

| | | | | |
|------|--------------|------------|---------------|------------|
| H6E | 0.3485 | 0.2601 | 0.2570 | 0.023* |
| H6F | 0.2841 | 0.2808 | 0.1865 | 0.023* |
| C13 | 0.37843 (13) | 0.0444 (4) | -0.12767 (15) | 0.0267 (6) |
| H13A | 0.3832 | 0.1707 | -0.1308 | 0.040* |
| H13B | 0.3384 | 0.0137 | -0.1610 | 0.040* |
| H13C | 0.4015 | -0.0171 | -0.1504 | 0.040* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Cl1 | 0.0178 (3) | 0.0143 (3) | 0.0189 (3) | -0.0048 (2) | 0.0070 (2) | 0.0009 (2) |
| Cl2 | 0.0207 (3) | 0.0164 (3) | 0.0133 (3) | 0.0014 (2) | 0.0010 (2) | 0.0018 (2) |
| P1 | 0.0172 (3) | 0.0098 (3) | 0.0123 (3) | -0.0019 (2) | 0.0065 (2) | -0.0020 (2) |
| P2 | 0.0116 (3) | 0.0097 (3) | 0.0117 (3) | -0.0005 (2) | 0.0042 (2) | -0.0006 (2) |
| Cd1 | 0.01370 (13) | 0.00967 (13) | 0.01166 (13) | 0.000 | 0.00440 (9) | 0.000 |
| Cd2 | 0.01748 (14) | 0.01108 (14) | 0.01369 (14) | -0.00167 (9) | 0.00800 (10) | -0.00030 (9) |
| O1 | 0.0202 (9) | 0.0148 (9) | 0.0144 (8) | -0.0028 (7) | 0.0062 (7) | 0.0010 (7) |
| O2 | 0.0155 (9) | 0.0161 (9) | 0.0129 (9) | 0.0000 (7) | 0.0060 (7) | 0.0004 (7) |
| O3 | 0.0229 (10) | 0.0124 (9) | 0.0210 (9) | 0.0016 (7) | 0.0112 (7) | 0.0029 (7) |
| O4 | 0.0294 (11) | 0.0286 (11) | 0.0380 (11) | 0.0081 (9) | 0.0254 (9) | 0.0052 (9) |
| O11 | 0.0201 (9) | 0.0220 (10) | 0.0104 (9) | 0.0041 (7) | 0.0047 (7) | -0.0021 (7) |
| O12 | 0.0316 (11) | 0.0129 (9) | 0.0309 (10) | -0.0063 (8) | 0.0225 (9) | -0.0042 (7) |
| O13 | 0.0257 (10) | 0.0107 (9) | 0.0117 (9) | -0.0015 (7) | 0.0050 (7) | -0.0020 (6) |
| O21 | 0.0137 (8) | 0.0132 (9) | 0.0123 (8) | 0.0013 (6) | 0.0036 (6) | -0.0002 (6) |
| O22 | 0.0165 (9) | 0.0120 (9) | 0.0165 (9) | -0.0007 (7) | 0.0094 (7) | 0.0003 (6) |
| N1 | 0.0172 (11) | 0.0143 (11) | 0.0150 (10) | 0.0018 (8) | 0.0092 (8) | 0.0031 (8) |
| C1 | 0.0142 (11) | 0.0108 (12) | 0.0111 (11) | -0.0021 (9) | 0.0030 (9) | 0.0015 (9) |
| C2 | 0.0159 (12) | 0.0208 (14) | 0.0187 (13) | 0.0049 (10) | 0.0071 (10) | 0.0043 (10) |
| C3 | 0.0276 (15) | 0.0210 (14) | 0.0301 (15) | 0.0069 (11) | 0.0173 (12) | 0.0027 (11) |
| C5 | 0.0303 (16) | 0.0247 (15) | 0.0247 (15) | -0.0005 (11) | 0.0192 (12) | 0.0025 (11) |
| C6 | 0.0202 (13) | 0.0185 (13) | 0.0212 (13) | -0.0030 (10) | 0.0124 (10) | 0.0025 (10) |
| C13 | 0.0457 (18) | 0.0198 (14) | 0.0107 (13) | 0.0026 (12) | 0.0088 (12) | -0.0007 (10) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|----------------------|-------------|---------|-----------|
| Cl1—C1 | 1.792 (2) | O1—H1B | 0.8775 |
| Cl2—C1 | 1.799 (2) | O2—H2A | 0.8617 |
| P1—O12 | 1.4803 (18) | O2—H2B | 0.8598 |
| P1—O11 | 1.4829 (18) | O3—H3A | 0.8298 |
| P1—O13 | 1.5922 (17) | O3—H3B | 0.8982 |
| P1—C1 | 1.854 (2) | O4—C3 | 1.433 (3) |
| P2—O22 | 1.5044 (17) | O4—C5 | 1.434 (3) |
| P2—O21 | 1.5062 (16) | O13—C13 | 1.460 (3) |
| P2—N1 | 1.628 (2) | N1—C6 | 1.470 (3) |
| P2—C1 | 1.869 (2) | N1—C2 | 1.472 (3) |
| Cd1—O11 | 2.2256 (17) | C2—C3 | 1.517 (3) |
| Cd1—O11 ⁱ | 2.2256 (17) | C2—H2E | 0.9900 |
| Cd1—O21 ⁱ | 2.3173 (16) | C2—H2F | 0.9900 |

supplementary materials

| | | | |
|---|-------------|------------|-------------|
| Cd1—O21 | 2.3173 (16) | C3—H3E | 0.9900 |
| Cd1—O1 | 2.3409 (17) | C3—H3F | 0.9900 |
| Cd1—O1 ⁱ | 2.3409 (17) | C5—C6 | 1.517 (4) |
| Cd2—O12 ⁱⁱ | 2.1884 (17) | C5—H5E | 0.9900 |
| Cd2—O12 | 2.1884 (17) | C5—H5F | 0.9900 |
| Cd2—O3 ⁱⁱ | 2.2795 (16) | C6—H6E | 0.9900 |
| Cd2—O3 | 2.2795 (16) | C6—H6F | 0.9900 |
| Cd2—O2 | 2.3486 (16) | C13—H13A | 0.9800 |
| Cd2—O2 ⁱⁱ | 2.3486 (16) | C13—H13B | 0.9800 |
| O1—H1A | 0.8439 | C13—H13C | 0.9800 |
| O12—P1—O11 | 120.19 (11) | Cd2—O3—H3A | 109.4 |
| O12—P1—O13 | 109.73 (10) | Cd2—O3—H3B | 118.2 |
| O11—P1—O13 | 106.42 (10) | H3A—O3—H3B | 107.4 |
| O12—P1—C1 | 107.98 (10) | C3—O4—C5 | 110.07 (19) |
| O11—P1—C1 | 107.43 (10) | P1—O11—Cd1 | 132.97 (10) |
| O13—P1—C1 | 103.90 (10) | P1—O12—Cd2 | 165.00 (12) |
| O22—P2—O21 | 118.72 (10) | C13—O13—P1 | 121.93 (16) |
| O22—P2—N1 | 108.40 (10) | P2—O21—Cd1 | 133.58 (9) |
| O21—P2—N1 | 109.04 (10) | C6—N1—C2 | 111.82 (19) |
| O22—P2—C1 | 105.77 (10) | C6—N1—P2 | 124.48 (17) |
| O21—P2—C1 | 105.72 (10) | C2—N1—P2 | 123.28 (16) |
| N1—P2—C1 | 108.80 (11) | Cl1—C1—Cl2 | 108.31 (12) |
| O11—Cd1—O11 ⁱ | 166.14 (9) | Cl1—C1—P1 | 108.85 (12) |
| O11—Cd1—O21 ⁱ | 100.40 (6) | Cl2—C1—P1 | 108.55 (12) |
| O11 ⁱ —Cd1—O21 ⁱ | 89.75 (6) | Cl1—C1—P2 | 107.53 (11) |
| O11—Cd1—O21 | 89.75 (6) | Cl2—C1—P2 | 107.98 (12) |
| O11 ⁱ —Cd1—O21 | 100.40 (6) | P1—C1—P2 | 115.42 (12) |
| O21 ⁱ —Cd1—O21 | 86.31 (8) | N1—C2—C3 | 109.5 (2) |
| O11—Cd1—O1 | 85.24 (6) | N1—C2—H2E | 109.8 |
| O11 ⁱ —Cd1—O1 | 84.49 (6) | C3—C2—H2E | 109.8 |
| O21 ⁱ —Cd1—O1 | 174.23 (5) | N1—C2—H2F | 109.8 |
| O21—Cd1—O1 | 95.00 (6) | C3—C2—H2F | 109.8 |
| O11—Cd1—O1 ⁱ | 84.49 (6) | H2E—C2—H2F | 108.2 |
| O11 ⁱ —Cd1—O1 ⁱ | 85.24 (6) | O4—C3—C2 | 111.1 (2) |
| O21 ⁱ —Cd1—O1 ⁱ | 95.00 (6) | O4—C3—H3E | 109.4 |
| O21—Cd1—O1 ⁱ | 174.23 (5) | C2—C3—H3E | 109.4 |
| O1—Cd1—O1 ⁱ | 84.25 (8) | O4—C3—H3F | 109.4 |
| O12 ⁱⁱ —Cd2—O12 | 180.00 (9) | C2—C3—H3F | 109.4 |
| O12 ⁱⁱ —Cd2—O3 ⁱⁱ | 82.50 (6) | H3E—C3—H3F | 108.0 |
| O12—Cd2—O3 ⁱⁱ | 97.50 (6) | O4—C5—C6 | 111.2 (2) |
| O12 ⁱⁱ —Cd2—O3 | 97.50 (6) | O4—C5—H5E | 109.4 |
| O12—Cd2—O3 | 82.50 (6) | C6—C5—H5E | 109.4 |
| O3 ⁱⁱ —Cd2—O3 | 180.00 (8) | O4—C5—H5F | 109.4 |
| O12 ⁱⁱ —Cd2—O2 | 94.94 (6) | C6—C5—H5F | 109.4 |

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|---|--------------|---------------|--------------|
| O12—Cd2—O2 | 85.06 (6) | H5E—C5—H5F | 108.0 |
| O3 ⁱⁱ —Cd2—O2 | 92.88 (6) | N1—C6—C5 | 108.6 (2) |
| O3—Cd2—O2 | 87.12 (6) | N1—C6—H6E | 110.0 |
| O12 ⁱⁱ —Cd2—O2 ⁱⁱ | 85.06 (6) | C5—C6—H6E | 110.0 |
| O12—Cd2—O2 ⁱⁱ | 94.94 (6) | N1—C6—H6F | 110.0 |
| O3 ⁱⁱ —Cd2—O2 ⁱⁱ | 87.12 (6) | C5—C6—H6F | 110.0 |
| O3—Cd2—O2 ⁱⁱ | 92.88 (6) | H6E—C6—H6F | 108.3 |
| O2—Cd2—O2 ⁱⁱ | 180.0 | O13—C13—H13A | 109.5 |
| Cd1—O1—H1A | 117.7 | O13—C13—H13B | 109.5 |
| Cd1—O1—H1B | 118.1 | H13A—C13—H13B | 109.5 |
| H1A—O1—H1B | 101.1 | O13—C13—H13C | 109.5 |
| Cd2—O2—H2A | 112.6 | H13A—C13—H13C | 109.5 |
| Cd2—O2—H2B | 108.2 | H13B—C13—H13C | 109.5 |
| H2A—O2—H2B | 101.1 | | |
| O12—P1—O11—Cd1 | 82.84 (17) | O21—P2—N1—C2 | 163.49 (18) |
| O13—P1—O11—Cd1 | -151.80 (14) | C1—P2—N1—C2 | -81.7 (2) |
| C1—P1—O11—Cd1 | -41.01 (18) | O12—P1—C1—C11 | 174.59 (11) |
| O11 ⁱ —Cd1—O11—P1 | 151.44 (15) | O11—P1—C1—C11 | -54.41 (14) |
| O21 ⁱ —Cd1—O11—P1 | -72.10 (16) | O13—P1—C1—C11 | 58.11 (13) |
| O21—Cd1—O11—P1 | 14.09 (16) | O12—P1—C1—C12 | 56.89 (14) |
| O1—Cd1—O11—P1 | 109.13 (16) | O11—P1—C1—C12 | -172.11 (11) |
| O1 ⁱ —Cd1—O11—P1 | -166.20 (16) | O13—P1—C1—C12 | -59.59 (13) |
| O11—P1—O12—Cd2 | -39.7 (5) | O12—P1—C1—P2 | -64.44 (15) |
| O13—P1—O12—Cd2 | -163.4 (4) | O11—P1—C1—P2 | 66.56 (15) |
| C1—P1—O12—Cd2 | 83.9 (5) | O13—P1—C1—P2 | 179.07 (11) |
| O3 ⁱⁱ —Cd2—O12—P1 | 77.6 (4) | O22—P2—C1—C11 | -173.74 (11) |
| O3—Cd2—O12—P1 | -102.4 (4) | O21—P2—C1—C11 | 59.52 (13) |
| O2—Cd2—O12—P1 | -14.7 (4) | N1—P2—C1—C11 | -57.47 (14) |
| O2 ⁱⁱ —Cd2—O12—P1 | 165.3 (4) | O22—P2—C1—C12 | -57.06 (14) |
| O12—P1—O13—C13 | -18.2 (2) | O21—P2—C1—C12 | 176.19 (10) |
| O11—P1—O13—C13 | -149.7 (2) | N1—P2—C1—C12 | 59.21 (14) |
| C1—P1—O13—C13 | 97.1 (2) | O22—P2—C1—P1 | 64.58 (14) |
| O22—P2—O21—Cd1 | -84.54 (15) | O21—P2—C1—P1 | -62.16 (14) |
| N1—P2—O21—Cd1 | 150.72 (12) | N1—P2—C1—P1 | -179.15 (11) |
| C1—P2—O21—Cd1 | 33.90 (15) | C6—N1—C2—C3 | 55.4 (3) |
| O11—Cd1—O21—P2 | -10.33 (14) | P2—N1—C2—C3 | -131.8 (2) |
| O11 ⁱ —Cd1—O21—P2 | 179.17 (13) | C5—O4—C3—C2 | 59.5 (3) |
| O21 ⁱ —Cd1—O21—P2 | 90.11 (13) | N1—C2—C3—O4 | -56.6 (3) |
| O1—Cd1—O21—P2 | -95.53 (13) | C3—O4—C5—C6 | -60.6 (3) |
| O22—P2—N1—C6 | -155.22 (19) | C2—N1—C6—C5 | -55.9 (3) |
| O21—P2—N1—C6 | -24.6 (2) | P2—N1—C6—C5 | 131.4 (2) |
| C1—P2—N1—C6 | 90.2 (2) | O4—C5—C6—N1 | 58.1 (3) |
| O22—P2—N1—C2 | 32.9 (2) | | |

Symmetry codes: (i) $-x+1, y, -z+1/2$; (ii) $-x+1, -y+1, -z$.

supplementary materials

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1A···O2 ⁱⁱⁱ | 0.84 | 2.06 | 2.849 (2) | 156 |
| O1—H1B···O22 ^{iv} | 0.88 | 2.12 | 2.990 (2) | 170 |
| O2—H2A···O21 ⁱ | 0.86 | 2.04 | 2.844 (2) | 155 |
| O2—H2B···O22 | 0.86 | 1.84 | 2.662 (2) | 159 |
| O3—H3A···O22 | 0.83 | 2.03 | 2.773 (2) | 149 |
| O3—H3B···O13 ^v | 0.90 | 1.87 | 2.745 (2) | 163 |

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

Fig. 1

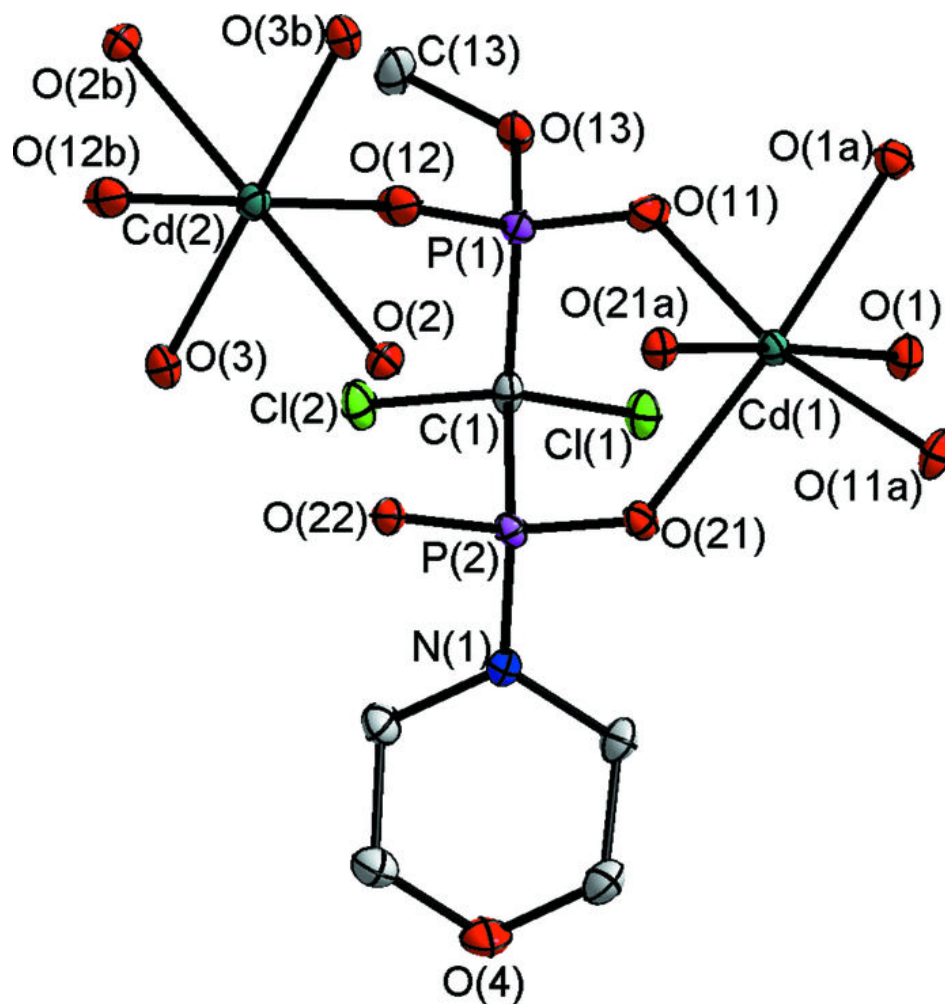


Fig. 2

