CRYSTALLOGRAPHIC COMMUNICATIONS

Acta Cryst E

ISSN 2056-9890

Synthesis, crystal structure and Hirshfeld surface analysis of diacetatobis[4-(2-aminoethyl)morpholine]cadmium tetrahydrate

B. Chidambaranathan, S. Sivaraj, P. Vijayamathubalan and S. Selvakumar*

PG and Research Department of Physics, Government Arts College for Men, (Autonomous), Chennai 600 035, Tamil Nadu, India. *Correspondence e-mail: drsskphy@gmail.com

Received 17 July 2023
Accepted 5 October 2023

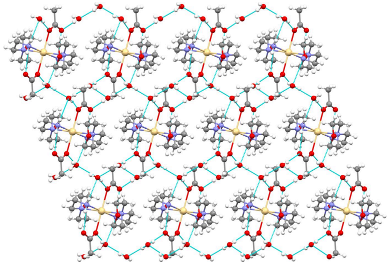
Edited by V. Jancik, Universidad Nacional Autónoma de México, México

Keywords: crystal structure; coordination compound; morpholine ligand; crystal structure.

CCDC reference: 2299387

Supporting information: this article has supporting information at journals.iucr.org/e

The title coordination compound, $[Cd(C_2H_3O_2)_2(C_6H_{14}N_2O)_2]\cdot 4H_2O$, was synthesized by mixing 2 moles of 4-(2-aminoethyl)morpholine and 1 mole of cadmium acetate in double-distilled water. The Cd atom is octahedrally coordinated by two *N*,*N*′-bidentate ligands [4-(2-aminoethyl)morpholine] and two *trans*-located acetate molecules. The Cd atom is located on a center of inversion, whereas the 4-(2-aminoethyl)morpholine and four water molecules are adjacent to the acetate molecules. The chair conformation of the morpholine molecules is confirmed. In the crystal, adjacent metal complexes and uncoordinated water molecules are linked *via* N—H⋯O and O—H⋯O hydrogen-bonding interactions, generating $R_2^2(6)$, $R_6^6(16)$, $R_6^6(20)$ and $S_1^1(6)$ motifs and forming a three-dimensional network. A Hirshfeld surface analysis indicated the contributions of various contacts: H⋯H (71.8%), O⋯H/H⋯O (27.1%), and C⋯H/H⋯C (1.0%).



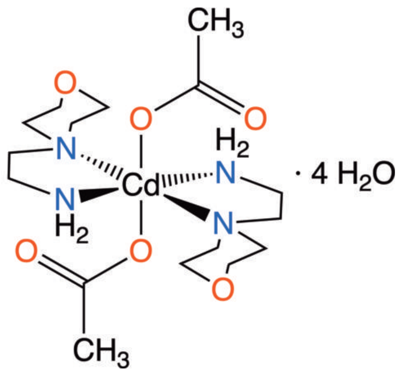
1. Chemical context

Morpholine is generally recognized as a convenient ligand for the synthesis of a wide range of organometallic compounds (Beller *et al.*, 1999*a*,*b*) including discrete complexes (Stilinovic *et al.*, 2012) and metal–organic polymers (Sil Moon *et al.*, 2000). Although a morpholine molecule is potentially an ambidentate N- and O- donor ligand, binding of morpholine to a metal centre is most commonly accomplished through the nitrogen atom (Cvrtila *et al.*, 2012; Cindric *et al.*, 2013), except in cases where the nitrogen atom is protonated (Li *et al.*, 2010; Willett *et al.*, 2005). Therefore, the oxygen atom can act as a halogen-bond acceptor (Lapadula *et al.*, 2010) or participate in hydrogen bonding (Weinberger *et al.*, 1998), among others, resulting in many different supramolecular architectures. In the O⋯halogen bond, the O atom acts as an acceptor and the halogen (except F) acts as a donor.

The hydrogen atom of the secondary amino group can be easily substituted by an electrophilic species, allowing for the derivatization of morpholine to corresponding hydrazines (Johnson *et al.*, 2009), carbonyl compounds (Cheadle *et al.*, 2017; Tazi *et al.*, 2017) or Schiff bases (Hellmann *et al.*, 2019). A potentially interesting way of derivatizing the morpholine molecule is carboxylation of the nitrogen atom, resulting in morpholine-*N*-carboxylic acid, or the respective morpholine-*N*-carboxylate (Morph COO^-) anion (Brown & Gray, 1981). This should act as an anionic ligand in coordinating metal ions through the carboxylate group (Rao *et al.*, 2004). In a continuation of our recent work on compounds belonging to the morpholine family, we report here another compound in which morpholine is a ligand for a coordination complex. In

https://doi.org/10.1107/S2056989023008782

the present study, a metal-coordinated compound of diacetatobis[4-(2-aminoethyl)morpholine]cadmium tetrahydrate was synthesized and its structure was analysed by single crystal XRD.



2. Structural commentary

The title compound (Fig. 1) crystallizes in the triclinic crystal system, space group $P\overline{1}$. The asymmetric unit comprises one-half of the Cd cation, which is located on an inversion centre, one [4-(2-aminoethyl)morpholine] ligand, one coordinated acetate anion and two water molecules outside the metal coordination sphere. The structure consists of $[CdL_2(OOCCH_3)_2]\cdot4H_2O$ units [where L= 4-(2-aminoethyl)-morpholine]. The coordination polyhedron around the metal atom may be best described as a distorted octahedron. The four nitrogen atoms of the diamine ligands define the equatorial plane, and two oxygen atoms from the acetate anions coordinate in the *trans*-axial positions. The coordination of the morpholine ligands creates two five-membered chelate rings (Fig. 2). Upon coordination and formation of the five-membered chelate rings, these ligands are able to adapt themselves to the requirements of different metals (M) by varying the $M—N$ distances and $N—M—N$ angles. Many articles and reviews have reported that an important factor for metal-ion selection is the chelate ring size, in which five-membered chelate rings promote selectivity for large metal ions with an ionic radius (r^+) close to 1.0 Å. Theoretical calculations show that for five-membered N–C–C–N–M chelate rings, the ideal values for the $N—M$ distance and $N—M—N$ angle are 2.5 Å and 69°, respectively (Hancock 1992; Hancock *et al.*, 2007; Dean *et al.*, 2008). An inverse relationship exists between the $M—N$ bond length and the $N—M—N$ bond angle in the five-membered chelate rings, meaning that the variation of the $N—M—N$ angle is directly related to the $M—N$ bond length (Bazargan *et al.*, 2019). In the present study, the Cd—N (amine) distances are 2.5239 (13) Å (Cd—N1 and Cd—N1^i) and 2.2788 (15) Å (Cd—N2 and Cd—N2^i), are in good agreement with the values reported in the literature (Chiumia *et al.*, 1999; Chattopadhyay *et al.*, 2005). The substantial difference in their values is a consequence of the steric constraints imposed by the bulky morpholine group. As a result of symmetry, the N2—Cd1—N2^i, N1—Cd1—N1^i and O2—Cd1—O2^i angles are 180° [symmetry code: (i) $-x + 1, -y, -z + 1$] and the *cis*-angles of the octahedron involving O2 and O2^i are close to the ideal value of 90°. The morpholine rings adopt a chair conformation. The acetate group is disordered over two positions of equal occupancy and in both of the crystallographically independent water molecules, one of the protons is equally disordered over two positions. Finally, water atom O5 from the water molecules is disordered over two positions in a 75 (3):25 (3) ratio.

3. Supramolecular features

Hydrogen bonding is the most dominant mechanism for molecular recognition. Graph-set analysis potentially provides the tools for a systematic analysis of the patterns of hydrogen-bonded networks. Hydrogen-bond pattern functionality might

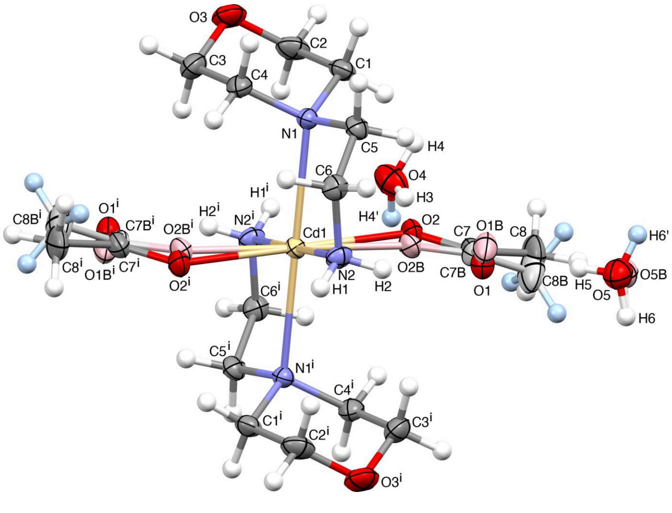


Figure 1
ORTEP diagram of the title compound with the atom-numbering scheme. Ellipsoids are drawn at 30% probability. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]

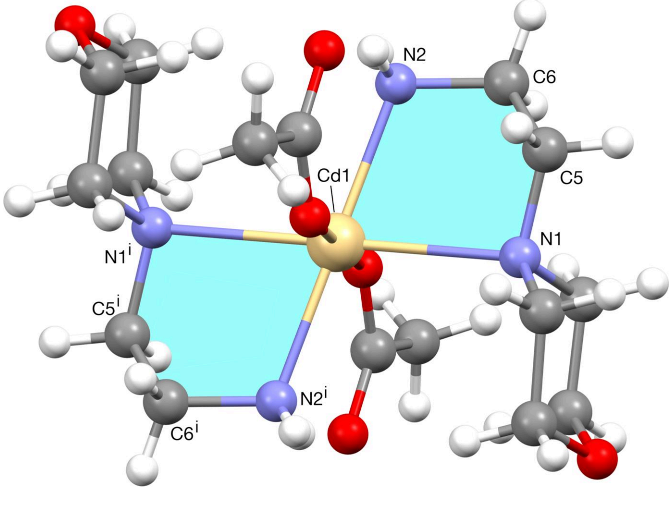


Figure 2
Five-membered chelate ring with metal as a centre. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···O2*B*$^{\rm i}$	0.97	2.66	3.264 (19)	121
C5—H5*B*···O1*B*	0.97	2.63	3.425 (16)	139
N2—H1···O4$^{\rm i}$	0.84 (2)	2.44 (2)	3.096 (3)	136 (2)
N2—H2···O1	0.84 (2)	2.26 (2)	3.009 (16)	147 (2)
N2—H2···O1*B*	0.84 (2)	2.26 (3)	2.993 (17)	145 (2)
O4—H3···O2	0.83 (2)	1.84 (3)	2.661 (17)	167 (4)
O4—H3···O2*B*	0.83 (2)	2.02 (3)	2.837 (17)	165 (3)
O4—H4···O5$^{\rm ii}$	0.82 (5)	2.06 (5)	2.879 (7)	178 (7)
O4—H4···O5*B*$^{\rm ii}$	0.82 (5)	2.05 (5)	2.847 (18)	165 (5)
O4—H4′···O4$^{\rm iii}$	0.83 (2)	2.11 (3)	2.917 (4)	164 (6)
O5—H5···O1	0.84 (2)	1.99 (2)	2.828 (16)	173 (3)
O5*B*—H5···O1*B*	0.83 (2)	1.93 (2)	2.70 (2)	155 (3)
O5—H6···O5$^{\rm iv}$	0.82 (2)	2.09 (3)	2.895 (13)	166 (5)
O5—H6···O5*B*$^{\rm iv}$	0.82 (4)	1.93 (5)	2.75 (2)	173 (5)
O5—H6′···O4$^{\rm ii}$	0.83 (2)	2.07 (2)	2.878 (5)	168 (5)
O5*B*—H6′···O4$^{\rm ii}$	0.84 (2)	2.07 (2)	2.846 (17)	154 (5)

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

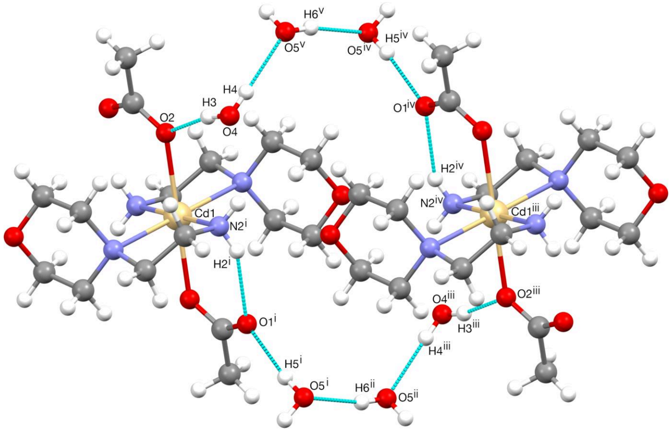


Figure 5
Intermolecular interactions forming the $R_6^6(20)$ ring motif. [Symmetry codes: (i) $-x+1, -y, -z+1$, (ii) $-x+1, -y+1, z+1$, (iii) $-x, -y, -z+1$, (iv) $x-1, y, z$, (v) $1-x, 1-y, -z$.]

then be employed to predict the three-dimensional structure of a compound or to design substances with a desired and predetermined structure (Bernstein *et al.*, 1995; Motherwell *et al.*, 2000). The crystal packing of the title compound is shown in Fig. 3, illustrating the infinite chain structure formed through a hydrogen-bonding network along the *a*-axis direction indicated by cyan dashed lines. In the crystal, the molecules are linked by numerous N—H···O and O—H···O interactions (Table 1), enclosing $R_2^2(6)$, $R_6^6(16)$ and $R_6^6(20)$ ring motifs. Fig. 4 shows the $R_6^6(16)$ ring motif formed by O4—H3···O2, O4—H4···O5 and O5—H5···O1 hydrogen bonds while the N2—H2···O1, O5—H5···O1, O4—H4···O5 and O4—H3···O2 interactions form an $R_6^6(20)$ ring motif (Fig. 5). Fig. 6 illustrates the $R_2^2(6)$ ring formed between the complex and the O4-containing water molecule *via* O4—H3···O2 and N2—H1···O4$^{\rm i}$ hydroge bonds. Finally, the molecular structure is stabilized by an intramolecular N2—H2···O1 hydrogen bond, which forms an $S_1^1(6)$ motif (Fig. 6). These interactions link the molecules into a three-dimensional network. For the sake of clarity, the figures show only one position of the disordered moieties. While the

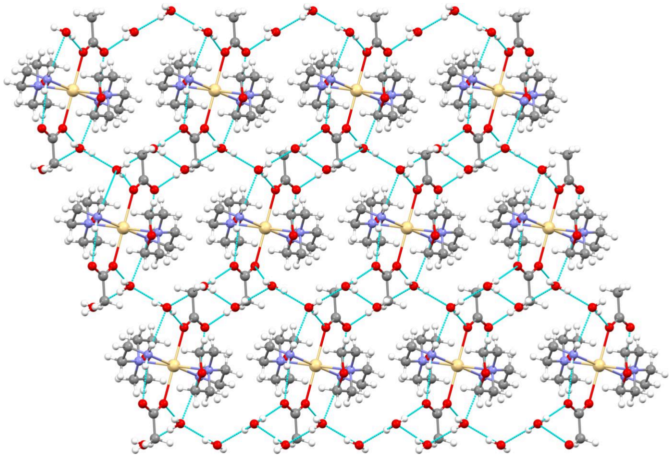


Figure 3
Crystal packing diagram of the title compound along the *a* axis.

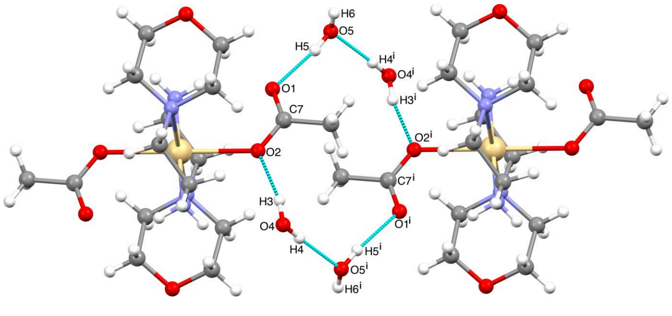


Figure 4
Intermolecular interactions forming the $R_6^6(16)$ ring motif. [Symmetry code: (i) $1-x, 1-y, -z$.]

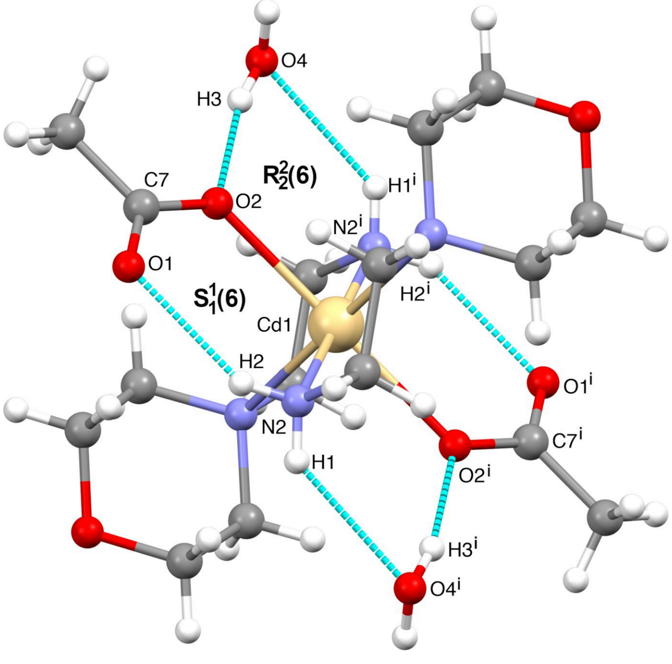


Figure 6
The N—H···O intramolecular interaction forming an $S_1^1(6)$ motif.

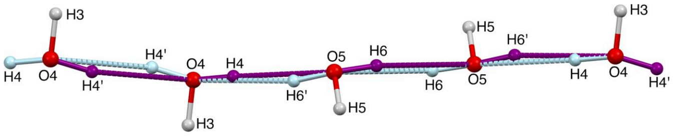


Figure 7
Two different orientations of the hydrogen bonds connecting the water molecules into infinite chains running in opposite directions.

disorder of the acetate group or O5 does not change significantly the hydrogen-bond pattern, the disorder of the water protons H4 and H6 creates two different orientations of the hydrogen bonds connecting the water molecules into infinite chains running in opposite directions, as depicted in Fig. 7.

A Hirshfeld surface analysis was performed for the complex alone (excluding the water molecules) and the two-dimensional (2D) fingerprint plots were created with *Crystal Explorer 21.5* (Spackman *et al.*, 2021; McKinnon *et al.*, 2007). The Hirshfeld surface mapped over $d_{\rm norm}$, in the range −0.5934 to 1.4137 a.u is shown in Fig. 8 where red spots on the Hirshfeld surface indicate hydrogen bonds. The two-dimensional fingerprint plots illustrate the distribution of the different interactions (Fig. 9). H⋯H interactions (Fig. 9*b*) are the most significant, contributing 71.8% to the total crystal packing. This major contribution may be due to van der Waals interactions (Hathwar *et al.*, 2015). The next most frequent interaction is O⋯H/H⋯O (27.1%) (Fig. 9*c*). Fig. 9*d* shows the C⋯H/H⋯C interactions, which contribute 1.0% to the Hirshfeld surface.

4. Database survey

A search in the Cambridge Structural Database (CSD, version 5.40; Groom *et al.*, 2016) for 4-(2-aminoethyl)morpholine yielded eleven hits for coordination compounds of 4-(2-aminoethyl)morpholine with metals, including *catena*-[bis(μ_2-dicyanamide-*N*,*N*′)-[4-(2-aminoethyl)morpholine]]nickel(II) (FIJROG; Konar *et al.*, 2005), bis[2-(morpholin-4-yl)ethanamine)(5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato]-iron(II) (NABXEW; Ben Haj Hassen *et al.*, 2016; NABXEW01; Khelifa *et al.*, 2016), *trans*-bis[4-(2-aminoethyl)morpholine]bis(nitrito)nickel(II) (NAVNAA; Chattopadhyay *et al.*, 2005; RANVEJ and NAVNAA01; Brayshaw *et al.*,2012), *trans*-bis(isothiocyanato-*N*)bis[4-(2-aminoethyl)morpholine-*N*,*N*′]nickel(II) (NENSUU; Laskar *et al.*, 2001), 4-[(2-aminoethyl)morpholine-*N*,*N*′]aqua(oxalato-*O*,*O*′)copper(II) monohydrate (XAZRUM; Koćwin-Giełzak & Marciniak *et al.*, 2006), (μ_2-oxalato)bis[4-(2-aminoethyl)morpholine]dicopper(II) (YIKQAK; Mukherjee *et al.*, 2001), dichloro-bis(2-morpholine-4-yl)ethanaminecadmium(II) (ULAJEX; Suleiman Gwaram *et al.*, 2011) and *trans*-diaquabis[4-(2-aminoethyl)morpholine-κ^2-*N*,*N*′]nickel(II) dichloride (VEPHIL; Chidambaranathan *et al.*, 2023). It is found that all of these structures are stabilized by hydrogen bonds. The morpholine ring adopts a chair conformation, and the amine functions as an *N*,*N*′-bidentate ligand to form a five-membered chelate ring with the metal centre, as observed with the other metal complexes of 4-(2-aminoethyl)morpholine.

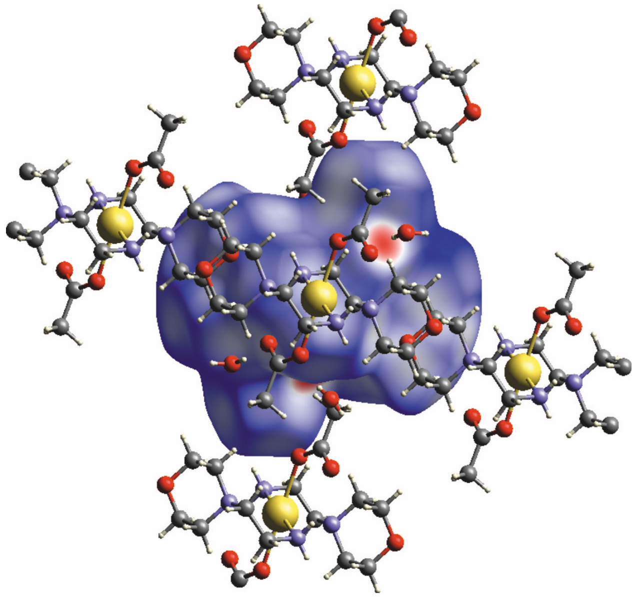


Figure 8
The Hirshfeld surface of the title compound mapped over $d_{\rm norm}$, showing the relevant close contacts.

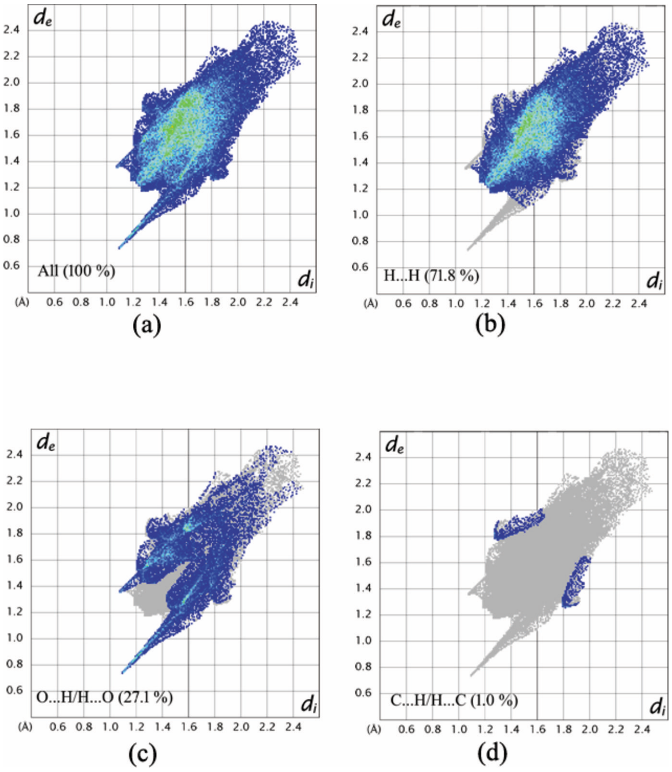


Figure 9
Two-dimensional fingerprint plots for the title compound, showing (*a*) all interactions, and delineated into (*b*) H⋯H, (*c*) O⋯H/H⋯O and (*d*) C⋯H/H⋯C interactions.

5. Synthesis and crystallization

As shown in the reaction scheme (Fig. 10), the title compound was synthesized by mixing two moles of 4-(2-aminoethyl)

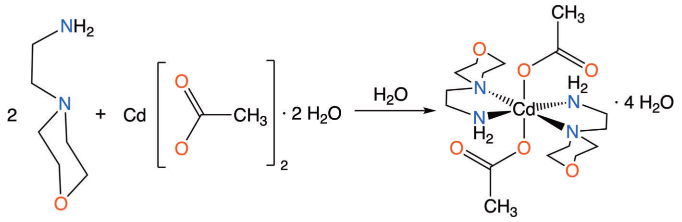


Figure 10
Synthesis of the title compound.

morpholine (2.40 g) and one mole of cadmium acetate (2.67 g) in 150 ml of double-distilled water at 303 K. The solution was allowed to evaporate at room temperature and needle-like crystals of the title compound were obtained. The FT–IR spectrum of the compound was recorded on a Bruker FT–IR spectrometer. FT–IR (KBr, cm^{-1}): 3301 (*w*, OH), 2887 (*w*, CH_2), 1549 (*s*, NH), 1411 (*s*, C—C), 1342 (*s*, C—N), 1192 (*w*, C—N), 960 (*w*, C—O), 653 (*s*, OH_2) and 594 (*s*, *M*—N).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C—H atoms were positioned geometrically (C—H = 0.96–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$, while the N—H and O—H protons were located in residual electron-density maps and refined with distance restraints (DFIX and SADI) and with $U_{iso}(H) = 1.2U_{eq}(N)$ and $1.5U_{eq}(O)$. The acetate group was refined as disordered over two positions (ratio 50:50%) with distance, geometry and U_{ij} restraints (SADI, FLAT, SIMU and RIGU). H4 and H6 are disordered over two positions in a 50:50 ratio due to symmetry-related hydrogen bonds. O5 is disordered over two positions in a 75 (3):25 (3) ratio. As both positions have the same distance to H5, H6 and H6′, only one set of the hydrogen atoms was refined for both O5 and O5*B*.

Acknowledgements

The authors gratefully acknowledge Dr Shobhana Krishnaswamy, SAIF, IITM, Chennai, for undertaking the single-crystal X-ray diffraction data collection and structure solution.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cd(C_2H_3O_2)_2(C_6H_{14}N_2O)_2]·4H_2O$
M_r	562.93
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, *b*, *c* (Å)	8.8639 (4), 9.1035 (5), 9.2106 (5)
α, β, γ (°)	66.004 (2), 73.603 (2), 70.161 (2)
V ($Å^3$)	629.63 (6)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	0.92
Crystal size (mm)	0.42 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.603, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19482, 3034, 3024
R_{int}	0.065
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.022, 0.056, 1.03
No. of reflections	3034
No. of parameters	209
No. of restraints	156
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.35, −0.41

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*) and *Mercury* (Macrae *et al.*, 2020).

References

Bazargan, M., Mirzaei, M., Franconetti, A. & Frontera, A. (2019). *Dalton Trans.* **45**, 1–39.

Beller, M., Trauthwein, H., Eichberger, M., Breindl, C., Herwig, J., Muller, T. E. & Thiel, O. R. (1999*b*). *Eur. J. Inorg. Chem.* **5**, 1306–1319.

Beller, M., Trauthwein, H., Eichberger, M., Breindl, C. & Müller, T. E. (1999*a*). *Eur. J. Inorg. Chem.* pp. 1121–1132.

Ben Haj Hassen, L., Ezzayani, K., Rousselin, Y., Stern, C., Nasri, H. & Schulz, C. E. (2016). *J. Mol. Struct.* **1110**, 138–142.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Brayshaw, S. K., Easun, T. L., George, M. W., Griffin, A. M. E., Johnson, A. L., Raithby, P. R., Savarese, T. L., Schiffers, S., Warren, J. E., Warren, M. R. & Teat, S. J. (2012). *Dalton Trans.* **41**, 90–97.

Brown, C. J. & Gray, L. R. (1981). *Acta Cryst.* A**37**, C202.

Bruker, (2004). *APEX2*, *SAINT* and *XPREP*. Bruker AXS Inc., Madison, WI, USA.

Chattopadhyay, T., Ghosh, M., Majee, A., Nethaji, M. & Das, D. (2005). *Polyhedron*, **24**, 1677–1681.

Cheadle, C., Ratcliff, J., Berezin, M., Pal'shin, V., Nemykin, V. N. & Gerasimchuk, N. N. (2017). *Dalton Trans.* **46**, 13562–13581.

Chidambaranathan, B., Sivaraj, S., Vijayamathubalan, P. & Selvakumar, S. (2023). *Acta Cryst.* E**79**, 226–230.

Chiumia, G. C., Craig, D. C., Phillips, D. J., Rae, A. D. & Kaifi, F. M. Z. (1999). *Inorg. Chim. Acta*, **285**, 297–300.

Cindric, M., Pavlovic, G., Hrenar, T., Uzelac, M. & Curic, M. (2013). *Eur. J. Inorg. Chem.* **4**, 63–571.

Cvrtila, I., Stilinović, V. & Kaitner, B. (2012). *Struct. Chem.* **23**, 587–594.

Dean, N. E., Hancock, R. D., Cahill, C. L. & Frisch, M. (2008). *Inorg. Chem.* **47**, 2000–2010.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hancock, R. D. (1992). *J. Chem. Educ.* **69**, 615–620.

Hancock, R. D., Melton, D. L., Harrington, J. M., McDonald, F. C., Gephart, R. T., Boone, L. L., Jones, S. B., Dean, N. E., Whitehead, J. R. & Cockrell, G. M. (2007). *Coord. Chem. Rev.* **251**, 1678–1689.

Hathwar, V. R., Sist, M., Jørgensen, M. R. V., Mamakhel, A. H., Wang, X., Hoffmann, C. M., Sugimoto, K., Overgaard, J. & Iversen, B. B. (2015). *IUCrJ*, **2**, 563–574.

Hellmann, J., Rhotert, I., Westenberg, H., Frohlich, R., Wibbeling, B., Uhl, W. & Wurthwein, E. U. (2019). *Eur. J. Org. Chem.* **16**, 3356–3368.

Johnson, A. L., Hollingsworth, N., Kingsley, A., Kociok-Köhn, G. & Molloy, C. (2009). *Organometallics*, **28**, 2650–2653.

Khélifa, A. B., Ezzayani, K. & Belkhiria, M. S. (2016). *J. Mol. Struct.* **1122**, 18–23.

Koćwin-Giełzak, K. & Marciniak, B. (2006). *Acta Cryst.* E**62**, m155–m157.

Konar, S., Dalai, S., Mukherjee, P. S., Drew, M. G. B., Ribas, J. & Ray Chaudhuri, N. (2005). *Inorg. Chim. Acta*, **358**, 957–963.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Lapadula, G., Judaš, N., Friščić, T. & Jones, W. (2010). *Chem. Eur. J.* **16**, 7400–7403.

Laskar, I. R., Maji, T. K., Das, D., Lu, T.-H., Wong, W.-T., Okamoto, K. I. & Ray Chaudhuri, N. (2001). *Polyhedron*, **20**, 2073–2082.

Li, H. H., Chen, Z. R., Cheng, L. C., Wang, Y. J., Feng, M. & Wang, M. (2010). *Dalton Trans.* **39**, 11000–11007.

Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (2000). *Acta Cryst.* B**56**, 857–871.

Mukherjee, P. S., Maji, T. K., Koner, S., Rosair, G. & Chaudhuri, N. R. (2001). *Ind. J. Chem. A* **40**, 451–455.

Rao, C. N. R., Natarajan, S. & Vaidhyanathan, R. (2004). *Angew. Chem. Int. Ed.* **43**, 466–496.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Sil Moon, H., Kim, C. H. & Lee, S. G. (2000). *Bull. Korean Chem. Soc.* **21**, 339–341.

Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.

Stilinović, V., Užarević, K., Cvrtila, I. & Kaitner, B. (2012). *CrystEngComm*, **14**, 7493–7501.

Suleiman Gwaram, N., Khaledi, H. & Mohd Ali, H. (2011). *Acta Cryst.* E**67**, m298.

Tazi, M., Erb, W., Halauko, Y. S., Ivashkevich, O. A., Matulis, V. E., Roisnel, T., Dorcet, V. & Mongin, F. (2017). *Organometallics*, **36**, 4770–4778.

Weinberger, P., Schamschule, R., Mereiter, K., Dlhán, L., Boca, R. & Linert, W. (1998). *J. Mol. Struct.* **446**, 115–126.

Willett, R. D., Butcher, R., Landee, C. P. & Twamley, B. (2005). *Polyhedron*, **24**, 2222–2231.

supporting information

Acta Cryst. (2023). E**79**, 1049-1054 [https://doi.org/10.1107/S2056989023008782]

Synthesis, crystal structure and Hirshfeld surface analysis of diacetatobis[4-(2-aminoethyl)morpholine]cadmium tetrahydrate

B. Chidambaranathan, S. Sivaraj, P. Vijayamathubalan and S. Selvakumar

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2019/2* (Sheldrick, 2015b).

Diacetatobis[4-(2-aminoethyl)morpholine]cadmium tetrahydrate

Crystal data

$[Cd(C_2H_3O_2)_2(C_6H_{14}N_2O)_2]\cdot 4H_2O$	$Z = 1$
$M_r = 562.93$	$F(000) = 294$
Triclinic, $P\overline{1}$	$D_x = 1.485$ Mg m^{-3}
$a = 8.8639$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.1035$ (5) Å	Cell parameters from 8460 reflections
$c = 9.2106$ (5) Å	$\theta = 2.5–27.7°$
$\alpha = 66.004$ (2)°	$\mu = 0.92$ mm^{-1}
$\beta = 73.603$ (2)°	$T = 296$ K
$\gamma = 70.161$ (2)°	BLOCK, yellow
$V = 629.63$ (6) Å^3	0.42 × 0.25 × 0.20 mm

Data collection

Bruker APEXII diffractometer	19482 measured reflections
Radiation source: fine-focus sealed tube	3034 independent reflections
Graphite monochromator	3024 reflections with $I > 2\sigma(I)$
Detector resolution: 8.333 pixels mm^{-1}	$R_{int} = 0.065$
ω and φ scan	$\theta_{max} = 28.0°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$h = -11 \rightarrow 11$
$T_{min} = 0.603$, $T_{max} = 0.746$	$k = -12 \rightarrow 12$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.022$	Hydrogen site location: mixed
$wR(F^2) = 0.056$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.03$	
3034 reflections	
209 parameters	
156 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 0.0883P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Extinction correction: *SHELXL2019/2* (Sheldrick 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.070 (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. Acetate moiety is disordered over two positions with an occupancy ratio of 1:1. SADI restraint was used to fix similar distances to be equal for the disordered atoms. The anisotropic displacement parameters of atoms in the disordered groups were restrained to be equal with an effective standard deviation of 0.02A2 using SIMU restraint. Hydrogen, H6, on O5 water molecules is having two possible locations labelled as H6 and H6′. The refined occupancy ratio of H6 and H6′ was found to be 47:53

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cd1	0.500000	0.000000	0.500000	0.02834 (8)	
C1	0.1597 (2)	0.3173 (2)	0.3992 (2)	0.0414 (4)	
H1A	0.234102	0.335992	0.297375	0.050*	
H1B	0.092779	0.424930	0.404315	0.050*	
C2	0.0527 (3)	0.2171 (3)	0.4051 (3)	0.0526 (5)	
H2A	−0.011008	0.279160	0.318855	0.063*	
H2B	0.120004	0.114484	0.388209	0.063*	
C3	0.0405 (3)	0.0877 (3)	0.6807 (3)	0.0525 (5)	
H3A	0.110930	−0.013930	0.663716	0.063*	
H3B	−0.031524	0.057256	0.783056	0.063*	
C4	0.1428 (2)	0.1877 (2)	0.6869 (2)	0.0410 (4)	
H4A	0.072480	0.287436	0.707912	0.049*	
H4B	0.204906	0.122555	0.774156	0.049*	
C5	0.3357 (2)	0.3536 (2)	0.5304 (2)	0.0378 (4)	
H5A	0.254126	0.441193	0.564346	0.045*	
H5B	0.386251	0.404292	0.420633	0.045*	
C6	0.4629 (2)	0.2741 (2)	0.6376 (2)	0.0371 (4)	
H6A	0.504495	0.359169	0.639032	0.044*	
H6B	0.414465	0.218855	0.746809	0.044*	
N1	0.25477 (17)	0.23413 (17)	0.53308 (17)	0.0309 (3)	
N2	0.59686 (19)	0.1529 (2)	0.5791 (2)	0.0373 (3)	
H1	0.657 (3)	0.101 (3)	0.649 (3)	0.045*	
H2	0.654 (3)	0.202 (3)	0.495 (2)	0.045*	
C7	0.6344 (19)	0.2664 (19)	0.1517 (17)	0.046 (2)	0.5
C8	0.667 (2)	0.321 (2)	−0.0301 (15)	0.072 (3)	0.5
H8A	0.565533	0.368190	−0.069697	0.108*	0.5
H8B	0.727822	0.226857	−0.062787	0.108*	0.5
H8C	0.728342	0.402997	−0.073442	0.108*	0.5
O1	0.6956 (18)	0.3179 (17)	0.2228 (18)	0.0498 (19)	0.5

O2	0.539 (2)	0.171 (2)	0.223 (2)	0.045 (3)	0.5
C7B	0.6416 (18)	0.2682 (19)	0.1635 (16)	0.046 (2)	0.5
C8B	0.707 (2)	0.297 (2)	−0.0148 (15)	0.079 (4)	0.5
H8B1	0.647320	0.403671	−0.077770	0.119*	0.5
H8B2	0.694369	0.211533	−0.042399	0.119*	0.5
H8B3	0.819967	0.295000	−0.036825	0.119*	0.5
O1B	0.6664 (19)	0.3510 (17)	0.228 (2)	0.055 (3)	0.5
O2B	0.566 (2)	0.154 (2)	0.233 (2)	0.0407 (19)	0.5
O3	−0.05347 (18)	0.1793 (2)	0.5549 (2)	0.0623 (4)	
O4	0.3639 (3)	0.1019 (2)	0.0781 (2)	0.0653 (5)	
H3	0.424 (4)	0.133 (4)	0.109 (4)	0.098*	
H4	0.302 (6)	0.190 (4)	0.034 (8)	0.098*	0.5
H4′	0.431 (5)	0.030 (7)	0.044 (8)	0.098*	0.5
O5	0.8474 (6)	0.5833 (6)	0.0761 (12)	0.0584 (13)	0.75 (3)
H5	0.796 (3)	0.510 (3)	0.115 (3)	0.088*	
H6	0.939 (2)	0.529 (6)	0.049 (6)	0.088*	0.5
H6′	0.778 (5)	0.665 (3)	0.032 (6)	0.088*	0.5
O5B	0.842 (2)	0.572 (2)	0.034 (2)	0.0584 (13)	0.25 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02855 (11)	0.02433 (10)	0.03058 (10)	−0.00663 (6)	−0.00444 (6)	−0.00839 (6)
C1	0.0356 (9)	0.0330 (9)	0.0487 (10)	0.0015 (7)	−0.0159 (8)	−0.0100 (8)
C2	0.0369 (11)	0.0521 (12)	0.0715 (14)	−0.0020 (9)	−0.0257 (10)	−0.0205 (11)
C3	0.0335 (10)	0.0498 (12)	0.0665 (14)	−0.0143 (9)	0.0022 (9)	−0.0167 (10)
C4	0.0337 (9)	0.0371 (9)	0.0456 (10)	−0.0056 (7)	0.0011 (7)	−0.0159 (8)
C5	0.0391 (10)	0.0241 (8)	0.0487 (10)	−0.0070 (7)	−0.0070 (8)	−0.0123 (7)
C6	0.0383 (9)	0.0358 (9)	0.0452 (9)	−0.0120 (7)	−0.0064 (7)	−0.0203 (8)
N1	0.0266 (7)	0.0260 (6)	0.0375 (7)	−0.0052 (5)	−0.0057 (5)	−0.0094 (5)
N2	0.0286 (8)	0.0410 (8)	0.0470 (9)	−0.0105 (6)	−0.0073 (6)	−0.0179 (7)
C7	0.049 (5)	0.034 (4)	0.038 (4)	−0.006 (3)	−0.006 (3)	−0.002 (3)
C8	0.084 (7)	0.069 (5)	0.033 (3)	−0.022 (5)	0.004 (3)	0.005 (3)
O1	0.050 (4)	0.043 (5)	0.045 (3)	−0.017 (4)	−0.001 (3)	−0.005 (3)
O2	0.044 (5)	0.045 (4)	0.032 (3)	−0.014 (4)	−0.007 (3)	0.002 (2)
C7B	0.042 (4)	0.042 (4)	0.028 (3)	−0.005 (3)	0.009 (3)	−0.002 (3)
C8B	0.106 (10)	0.079 (8)	0.041 (4)	−0.040 (8)	0.020 (5)	−0.019 (5)
O1B	0.063 (6)	0.041 (5)	0.049 (3)	−0.018 (4)	0.013 (3)	−0.014 (3)
O2B	0.041 (4)	0.040 (3)	0.030 (3)	−0.006 (3)	−0.010 (3)	−0.002 (2)
O3	0.0278 (7)	0.0637 (10)	0.0934 (13)	−0.0077 (7)	−0.0151 (8)	−0.0249 (9)
O4	0.0829 (13)	0.0561 (10)	0.0529 (9)	−0.0055 (9)	−0.0237 (9)	−0.0168 (8)
O5	0.0560 (11)	0.0528 (12)	0.065 (3)	−0.0172 (9)	−0.0029 (15)	−0.0208 (15)
O5B	0.0560 (11)	0.0528 (12)	0.065 (3)	−0.0172 (9)	−0.0029 (15)	−0.0208 (15)

Geometric parameters (Å, º)

Cd1—N2	2.2788 (15)	C6—N2	1.467 (2)
Cd1—N2$^{\rm i}$	2.2788 (15)	C6—H6A	0.9700

Cd1—O2B^{i}	2.301 (16)	C6—H6B	0.9700
Cd1—O2B	2.301 (16)	N2—H1	0.838 (18)
Cd1—O2^{i}	2.386 (16)	N2—H2	0.844 (18)
Cd1—O2	2.386 (16)	C7—O1	1.252 (9)
Cd1—N1	2.5239 (13)	C7—O2	1.276 (9)
Cd1—N1^{i}	2.5239 (13)	C7—C8	1.511 (10)
C1—N1	1.482 (2)	C8—H8A	0.9600
C1—C2	1.501 (3)	C8—H8B	0.9600
C1—H1A	0.9700	C8—H8C	0.9600
C1—H1B	0.9700	C7B—O1B	1.236 (10)
C2—O3	1.417 (3)	C7B—O2B	1.275 (9)
C2—H2A	0.9700	C7B—C8B	1.522 (9)
C2—H2B	0.9700	C8B—H8B1	0.9600
C3—O3	1.421 (3)	C8B—H8B2	0.9600
C3—C4	1.512 (3)	C8B—H8B3	0.9600
C3—H3A	0.9700	O4—H3	0.834 (17)
C3—H3B	0.9700	O4—H4	0.820 (19)
C4—N1	1.475 (2)	O4—H4′	0.827 (19)
C4—H4A	0.9700	O5—H5	0.838 (16)
C4—H4B	0.9700	O5—H6	0.823 (18)
C5—N1	1.481 (2)	O5—H6′	0.827 (19)
C5—C6	1.504 (3)	O5B—H5	0.825 (17)
C5—H5A	0.9700	O5B—H6	0.838 (19)
C5—H5B	0.9700	O5B—H6′	0.842 (19)

N2—Cd1—N2^{i}	180.0	N1—C5—H5B	109.0
N2—Cd1—O2B^{i}	88.9 (4)	C6—C5—H5B	109.0
N2^{i}—Cd1—O2B^{i}	91.1 (4)	H5A—C5—H5B	107.8
N2—Cd1—O2B	91.1 (4)	N2—C6—C5	110.33 (14)
N2^{i}—Cd1—O2B	88.9 (4)	N2—C6—H6A	109.6
O2B^{i}—Cd1—O2B	180.0	C5—C6—H6A	109.6
N2—Cd1—O2^{i}	86.6 (4)	N2—C6—H6B	109.6
N2^{i}—Cd1—O2^{i}	93.4 (4)	C5—C6—H6B	109.6
O2B^{i}—Cd1—O2^{i}	5.9 (8)	H6A—C6—H6B	108.1
O2B—Cd1—O2^{i}	174.1 (8)	C4—N1—C5	110.11 (14)
N2—Cd1—O2	93.4 (4)	C4—N1—C1	108.91 (14)
N2^{i}—Cd1—O2	86.6 (4)	C5—N1—C1	107.85 (14)
O2^{i}—Cd1—O2	180.0	C4—N1—Cd1	113.82 (10)
N2—Cd1—N1	76.46 (5)	C5—N1—Cd1	100.13 (10)
N2^{i}—Cd1—N1	103.54 (5)	C1—N1—Cd1	115.51 (11)
O2B^{i}—Cd1—N1	89.6 (5)	C6—N2—Cd1	110.81 (11)
O2B—Cd1—N1	90.4 (5)	C6—N2—H1	107.4 (16)
O2^{i}—Cd1—N1	94.4 (5)	Cd1—N2—H1	117.5 (16)
O2—Cd1—N1	85.6 (5)	C6—N2—H2	110.1 (16)
N2—Cd1—N1^{i}	103.54 (5)	Cd1—N2—H2	104.7 (15)
N2^{i}—Cd1—N1^{i}	76.46 (5)	H1—N2—H2	106 (2)
O2^{i}—Cd1—N1^{i}	85.6 (5)	O1—C7—O2	124.2 (10)
O2—Cd1—N1^{i}	94.4 (5)	O1—C7—C8	120.4 (9)

N1—Cd1—N1^{i}	180.0	O2—C7—C8	115.3 (9)
N1—C1—C2	112.45 (16)	C7—C8—H8A	109.5
N1—C1—H1A	109.1	C7—C8—H8B	109.5
C2—C1—H1A	109.1	H8A—C8—H8B	109.5
N1—C1—H1B	109.1	C7—C8—H8C	109.5
C2—C1—H1B	109.1	H8A—C8—H8C	109.5
H1A—C1—H1B	107.8	H8B—C8—H8C	109.5
O3—C2—C1	111.52 (19)	C7—O2—Cd1	128.0 (11)
O3—C2—H2A	109.3	O1B—C7B—O2B	126.0 (10)
C1—C2—H2A	109.3	O1B—C7B—C8B	119.6 (9)
O3—C2—H2B	109.3	O2B—C7B—C8B	114.4 (9)
C1—C2—H2B	109.3	C7B—C8B—H8B1	109.5
H2A—C2—H2B	108.0	C7B—C8B—H8B2	109.5
O3—C3—C4	111.37 (18)	H8B1—C8B—H8B2	109.5
O3—C3—H3A	109.4	C7B—C8B—H8B3	109.5
C4—C3—H3A	109.4	H8B1—C8B—H8B3	109.5
O3—C3—H3B	109.4	H8B2—C8B—H8B3	109.5
C4—C3—H3B	109.4	C7B—O2B—Cd1	132.3 (10)
H3A—C3—H3B	108.0	C2—O3—C3	109.06 (16)
N1—C4—C3	110.44 (16)	H3—O4—H4	103 (3)
N1—C4—H4A	109.6	H3—O4—H4′	102 (3)
C3—C4—H4A	109.6	H4—O4—H4′	132 (7)
N1—C4—H4B	109.6	H5—O5—H6	101 (3)
C3—C4—H4B	109.6	H5—O5—H6′	101 (3)
H4A—C4—H4B	108.1	H6—O5—H6′	137 (5)
N1—C5—C6	113.08 (14)	H5—O5B—H6	101 (3)
N1—C5—H5A	109.0	H5—O5B—H6′	100 (3)
C6—C5—H5A	109.0	H6—O5B—H6′	132 (5)

N1—C1—C2—O3	56.0 (2)	C2—C1—N1—C5	−171.48 (16)
O3—C3—C4—N1	−59.6 (2)	C2—C1—N1—Cd1	77.53 (18)
N1—C5—C6—N2	64.5 (2)	C5—C6—N2—Cd1	−41.77 (17)
C3—C4—N1—C5	171.13 (15)	O1—C7—O2—Cd1	−18 (2)
C3—C4—N1—C1	53.06 (19)	C8—C7—O2—Cd1	163.7 (13)
C3—C4—N1—Cd1	−77.39 (17)	O1B—C7B—O2B—Cd1	−18 (2)
C6—C5—N1—C4	73.18 (18)	C8B—C7B—O2B—Cd1	160.8 (14)
C6—C5—N1—C1	−168.10 (15)	C1—C2—O3—C3	−59.3 (2)
C6—C5—N1—Cd1	−46.96 (16)	C4—C3—O3—C2	61.5 (2)
C2—C1—N1—C4	−52.0 (2)		

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*
C4—H4*B*···O2*B*^{i}	0.97	2.66	3.264 (19)	121
C5—H5*B*···O1*B*	0.97	2.63	3.425 (16)	139
N2—H1···O4^{i}	0.84 (2)	2.44 (2)	3.096 (3)	136 (2)

N2—H2···O1	0.84 (2)	2.26 (2)	3.009 (16)	147 (2)
N2—H2···O1*B*	0.84 (2)	2.26 (3)	2.993 (17)	145 (2)
O4—H3···O2	0.83 (2)	1.84 (3)	2.661 (17)	167 (4)
O4—H3···O2*B*	0.83 (2)	2.02 (3)	2.837 (17)	165 (3)
O4—H4···O5^{ii}	0.82 (5)	2.06 (5)	2.879 (7)	178 (7)
O4—H4···O5*B*^{ii}	0.82 (5)	2.05 (5)	2.847 (18)	165 (5)
O4—H4′···O4^{iii}	0.83 (2)	2.11 (3)	2.917 (4)	164 (6)
O5—H5···O1	0.84 (2)	1.99 (2)	2.828 (16)	173 (3)
O5*B*—H5···O1*B*	0.83 (2)	1.93 (2)	2.70 (2)	155 (3)
O5—H6···O5^{iv}	0.82 (2)	2.09 (3)	2.895 (13)	166 (5)
O5—H6···O5*B*^{iv}	0.82 (4)	1.93 (5)	2.75 (2)	173 (5)
O5—H6′···O4^{ii}	0.83 (2)	2.07 (2)	2.878 (5)	168 (5)
O5*B*—H6′···O4^{ii}	0.84 (2)	2.07 (2)	2.846 (17)	154 (5)

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