Crystal structure of hexakis(N,N-dimethylformamide-κO)iron(III) μ-chlorido-bis(trichlorido-cadmium)

Olga Yu. Vassilyeva,a* Vladimir N. Kokozay,a Svitlana Petrusenkoa and Alexandre N. Sobolevb

a Department of Chemistry, Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska Street, Kyiv 01601, Ukraine, and b School of Molecular Sciences, M310, University of Western Australia, 35 Stirling Highway, Perth, 6009, W.A., Australia. *Correspondence e-mail: vassilyeva@univ.kiev.ua

The title compound, [Fe(C3H7NO)6][Cd2Cl7], crystallizes in the trigonal space group R3 and is assembled from discrete [Fe(DMF)6]3+ cations (DMF = N,N-dimethylformamide) and [Cd2Cl7]3− anions. In the cation, the iron(III) atom, located on a special position of 3 site symmetry, is coordinated by six oxygen atoms from DMF ligands with all Fe−O distances being equal [2.0072 (16) Å]. A slight distortion of the octahedral environment of the metal comes from the cis O−Fe−O angles deviating from the ideal value of 90° [86.85 (7) and 93.16 (7)] whilst all the trans angles are strictly 180°. The central Cl atom of the [Cd2Cl7]3− anion is also located on a special position of 3 site symmetry and bridges two corner sharing, tetrahedrally coordinated CdII atoms. The two Cd atoms and the central Cl atom are collinear. The two sets of terminal chloride ligands on either side of the dumbbell-like anion are rotated relative to each other by 30°. In the crystal, the cations and anions, stacked one above the other along the c-axis direction, are held in place principally by electrostatic interactions. There are also C−H···Cl and C−H···O interactions, but these are rather weak. Of the six crystal structures reported to date for ionic salts of [Fe(DMF)6]n+ cations (n = 2, 3), five contain FeII ions. The title compound is the second example of a stable compound containing the [Fe(DMF)6]3+ cation. The existence of both [Fe(DMF)6]2+ and [Fe(DMF)6]3+ cations shows that the DMF ligand coordination sphere can accommodate changes in the charge and spin states of the metal centre.

1. Chemical context

In our ongoing research into the new functions and applications of coordination compounds with Schiff-base ligands, we have utilized a synthetic scheme involving a zerovalent metal as the source of metal ions, together with another metal salt, in order to prepare new heterometallic complexes (Kokozay et al., 2018; Vassilyeva et al., 2018, 2021). In a typical procedure, the metal powder undergoes oxidative dissolution in air to generate metal ions that then interact with the second metal salt and pre-formed ligand. The condensation reaction between the Schiff-base precursors occurs in situ without isolation of the imine. Dioxygen from the air is reduced to form a water molecule with participation of protons donated by the imine, which is capable of deprotonation.

By using the above scheme, new homo- and heterometallic CoIII, CoII/ZnII and CoIII/CdII complexes with a Schiff-base ligand derived from 2-hydroxy-3-methoxybenzaldehyde (o-vanillin) and the simple amine methylamine have been prepared (Nesterova et al., 2018, 2019). Comparative studies...
of their catalytic behaviours in oxidation reactions of alkanes with \( \text{H}_2\text{O}_2 \) and \( \text{m}-\)chloroperoxybenzoic acid were undertaken to elucidate the role of the second (inactive) metal centre (Cd) in the catalytic performance of the heterometallic compounds. Given the remarkable catalytic activity of the Schiff base Fe\( ^{\text{III}} \) metal complexes mimicking the Fe-containing enzymes that oxidize alkanes in nature (Nesterov et al., 2015), we decided to extend our work and replace the cobalt centre with iron in a heterometallic core supported by the above Schiff-base ligand.

To facilitate formation of the desired compound, an additional basic agent, \( \text{N} \)-phenyldiethanolamine, was introduced in the formation of a mixed-ligand Schiff base Ni\( ^{\text{II}} \)/Zn\( ^{\text{II}} \), followed by the previous successful participation of diethano-\( \text{N} \)-phenyldiethanolamine, was introduced alkoxo-bridges between the metal centres. The use of alkoxo-deprotonation in reactions employing zero-valent metals in the synthesis of heterometallics was established by a number of us several years ago (Vassilyeva et al., 1997; Buvaylo et al., 2005, 2012).

In the present work, the treatment of cadmium powder and \( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \) with a solution of the \( \text{in situ} \)-formed Schiff base in open air worked a different way than expected and led to the isolation of the title compound, the mixed-metal ionic salt \( \text{Fe}^{\text{III}}(\text{DMF})_6\)\( \text{[Cd}_2\text{Cl}_7\)\( ] \), the identity of which was established by X-ray crystallography and confirmed by chemical analysis.

### 2. Structural Commentary

Compound (I), \( \text{[Fe(C}_3\text{H}_7\text{NO})_6\)\( ]\text{[Cd}_2\text{Cl}_7\)\( ] \), crystallizes in the trigonal space group \( \text{R}3 \) and is assembled from discrete \( \text{Fe(DMF)}_6^{3+} \) cations (DMF = \( \text{N},\text{N-dimethylformamide} \) and \( \text{[Cd}_2\text{Cl}_7\)\( ]^{3-} \) anions. In the cation, the iron(III) atom sits on a special position of \( \text{3} \) site symmetry and is coordinated by six oxygen atoms from the DMF ligands with all the \( \text{Fe}–\text{O} \) bond lengths being equal at 2.0072 (16) \( \text{Å} \) (Fig. 1, Table 1). The octahedral environment of the metal is slightly distorted as a result of the \( \text{cis} \) \( \text{O}1–\text{Fe}1–\text{O}1 \) angles deviating from the ideal value of 90° [86.85 (7) and 93.16 (7)]° while all the \( \text{trans} \) angles are strictly 180°. The central Cd atom of the \( \text{[Cd}_2\text{Cl}_7\)\( ]^{3-} \) anion, \( \text{C}1 \), is also located on a special position of \( \text{3} \) site symmetry and bridges two corner-sharing, tetrahedrally coordinated Cd\( ^{\text{II}} \) atoms. The two Cd atoms and the central Cd atom are colinear (Cd1–Cd1–Cd1\( ^{\text{IV}} \) angle = 180°) and the bridging Cd1·Cd1\( ^{\text{IV}} \) distance is 5.0752 (3) \( \text{Å} \) (Fig. 1). The two sets of terminal chloride ligands, C12, on either side of the dumbbell–like anion are rotated relative to each other by 30°. Around each Cd atom, the bridging Cd–C1 distance at 2.5377 (3) \( \text{Å} \) is 0.1 \( \text{Å} \) longer than that of the terminal Cd–C12 distance (2.4358 (5) \( \text{Å} \)) and the \( \text{C}12–\text{Cd}–\text{C}1 \) and \( \text{C}12–\text{Cd}–\text{C}12\( ^{\text{IV}} \) angles are 107.547 (14) and 111.325 (13), respectively, which are very close to the ideal value of 109°. The bond lengths and angles of the DMF ligands are similar to those found in \( \text{Fe(DMF)}_6\)\( \text{[ClO}_4\)\( ] \) (Houlton et al., 2015).

### 3. Supramolecular Features

In the crystal, the cations and anions are stacked one above the other along the \( \text{c} \)-axis direction (Fig. 2). Although classical

### Table 1

Selected geometric parameters (\( \text{Å}, ^\circ \)).

| Bond/Angle | Value |
|------------|-------|
| Cd1–Cd2   | 2.4358 (5) |
| Cd1–Cl1   | 2.3577 (3) |
| Cl2–Cd1–Cl2 | 111.325 (13) |
| Fe1–O1    | 2.0072 (16) |

| Symmetry codes: | (i) \(-y+1, x-y+1, z\); (ii) \(-x+y, -x+1, z\); (iii) \(y+\frac{1}{2}, -x+y+\frac{1}{2}, -z+\frac{1}{4}\); (iv) \(-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{3}{4}\); (v) \(x-y+\frac{3}{2}, x+\frac{1}{2}, -z+\frac{1}{4}\); (vi) \(-x+\frac{3}{2}, -y+x+\frac{1}{2}, z+\frac{3}{4}\); (vii) \(y+\frac{3}{2}, -x+y+\frac{1}{2}, -z+\frac{1}{4}\); (viii) \(-y+\frac{1}{2}, -x+y+\frac{1}{2}, z+\frac{3}{4}\) | |

### Table 2

Hydrogen-bond geometry (\( \text{Å}, ^\circ \)).

| Bond/Angle | Value |
|------------|-------|
| C12–H123···Cl2vi | 0.98 |
| C1–H1···Cl2vii | 0.97 (3) |
| C1–H1···O1ii | 0.97 (3) |
| C12–H122···Cl2viii | 0.98 |

| Symmetry codes: | (i) \(-y+1, x-y+1, z\); (ii) \(-x+y, -x+1, z\); (iii) \(y+\frac{1}{2}, -x+y+\frac{1}{2}, -z+\frac{1}{4}\) | |

Figure 1

Molecular structure and labelling of \( \text{[Fe}^{\text{III}}(\text{DMF})_6\)\( ]\text{[Cd}_2\text{Cl}_7\)\( ] \) with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) \(-y+1, x-y+1, z\); (ii) \(-x+y, -x+1, z\); (iii) \(y+\frac{1}{2}, -x+y+\frac{1}{2}, -z+\frac{1}{4}\); (iv) \(-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{3}{4}\); (v) \(x-y+\frac{3}{2}, x+\frac{1}{2}, -z+\frac{1}{4}\); (vi) \(-x+\frac{3}{2}, -y+x+\frac{1}{2}, z+\frac{3}{4}\); (vii) \(y+\frac{3}{2}, -x+y+\frac{1}{2}, -z+\frac{1}{4}\); (viii) \(-y+\frac{1}{2}, -x+y+\frac{1}{2}, z+\frac{3}{4}\); (ix) \(x-y+\frac{3}{2}, x+\frac{1}{2}, -z+\frac{1}{4}\)]
hydrogen bonds are absent, several weak C—H···O and C—H···Cl interactions are detected in the structure [Cl—H1···Cl2], 3.772 (3) Å; C12—H123···Cl12(IVI), 3.783 (3) Å and Cl—H1···O1I, 3.097 (3) Å]. The minimum H···O distance (H1—O1I) between DMF molecules within the same cation is 2.62 (3) Å and the shortest distance between Cl atoms of the anions and adjacent H atoms of DMF methyl groups (H123···Cl12(IVI)) is 2.82 Å (Table 2), implying that the halide ions act as weak hydrogen-bond acceptors.

4. Database survey
A survey of the Cambridge Structural Database (CSD, Version 5.42, update May 2021; Groom et al., 2016) reveals six ionic salts containing octahedral [Fe(DMF)6]3+ (n = 2, 3) cations. Five of the structures contain FeII ions, which crystallize in the presence of the counter-ions [FeCl4]2− (CALMOS01; Cheaib et al., 2013), [FeCl5S4W]2− (CUSNOT; Coucouvanis et al., 1984), [Mo2S6]2− (DEZMIF; Li et al., 2007), [Fe2Cl5S4]2− (VAMFI; Müller et al., 1989) and ClO4− (GAZGET; Baumgartner, 1986). The only example to date containing the FeIII cation, [Fe(DMF)6]3+, is found as the perchlorate salt (DMFAFE01; Houlton et al., 2015).

In the pair of perchlorate salts, the FeII and FeIII ions are easily distinguishable by their dissimilar Fe—O bond distances (H1—O= 0.95 Å, Cl—O = 1.77 Å) and Cl—Fe—Cl angles in the ranges 86.3–93.7° (GAZGET) and 88.57 (6)–91.43 (6)° (DMFAFE01), while all the trans angles are equal to the ideal value of 180°. The geometric parameters of the [Fe(DMF)6]3+ cation in the title compound, (I), are very close to those found in [Fe(DMF)6](ClO4)3 (DMFAFE01) with slight differences arising due to the different counter-ions present. The existence of both [Fe(DMF)6]2+ and [Fe(DMF)6]3+ cations shows that the DMF ligand coordina-

5. Synthesis and crystallization
2-Hydroxy-3-methoxy-benzaldehyde (0.3 g, 2 mmol) was stirred magnetically with CH3NH2 (0.82 g, 10 mmol) and Na-phenyl-diethanolamine (0.36 g, 2 mmol) in methanol (20 mL) in a 50 mL conical flask at 303 K for 20 min. A fine Cd powder (0.11 g, 1 mmol) and dry FeCl3·6H2O (0.27 g, 1 mmol) were introduced to the flask, and the mixture was kept stirring at 333 K to achieve dissolution of the zerovalent metal (1 h). The resulting dark blue–green solution was then filtered and allowed to evaporate at room temperature. After a week, the solution was diluted with DMF (7 mL) since it was thickening and filtered again. Dark-green octahedral crystals of (I) formed over two months after successive addition of Pr iOH (4 mL) and diethyl ether (4 mL) in several portions. The crystals were filtered off, washed with diethyl ether and finally dried in air. Yield (based on Fe): 0.13 g (64%). Analysis calculated for C18H42FeN6O6Cd2Cl7 (967.37): C 22.35, H 4.38, N 8.69%. Found: C 22.86, H 4.30, C 8.36%.

6. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 3. Anisotropic displacement parameters were refined for all non-hydrogen atoms. All the carbon-bound hydrogen atoms were placed in calculated positions and refined using a riding model with isotropic displacement parameters based on those of the parent atom [C—H = 0.95 Å, Ueq(H) = 1.2Ueq(C) for CH and C—H = 0.98 Å, Ueq(H) = 1.5Ueq(C) for CH3].

Acknowledgements
The authors acknowledge use of the facilities and the scientific and technical assistance at the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterization & Analysis, The University of Western Australia. This facility is funded by the University, State and Commonwealth Governments.
Table 3
Experimental details

| Parameter                      | Value                        |
|--------------------------------|------------------------------|
| Crystal data                   |                              |
| Chemical formula               | [Fe(C3H7NO)6][Cd2Cl7]        |
| M1                             | 967.37                       |
| Crystal system, space group    | Trigonal, R3                 |
| Temperature (K)                | 100                          |
| a, c (Å)                       | 13.7143 (2), 16.1312 (2)     |
| V (Å³)                         | 2627.51 (5)                  |
| Z                              | 3                            |
| Radiation type                 | Cu K                         |
| μ (mm⁻¹)                       | 18.18                        |
| Crystal size (mm)              | 0.06 × 0.05 × 0.05           |
| Data collection                | Oxford Diffraction Gemini-R  |
| Absorption correction         | Multi-scan (CrysAlis PRO; Rigaku OD, 2015) |
| Tmin, Tmax                     | 0.760, 1.0                   |
| No. of measured, independent and observed | 16143, 1051, 980 |
| Rint                          | 0.038                        |
| (sin θ/λ)max (Å⁻¹)             | 0.598                        |
| Refinement                     |                              |
| R[F² > 2σ(F²)], wR(F²), S     | 0.020, 0.057, 1.00           |
| No. of reflections             | 1051                         |
| No. of parameters              | 67                           |
| H-atom treatment              | H atoms treated by a mixture of independent and constrained refinement |
| ∆ρmax, ∆ρmin (e Å⁻³)          | 0.79, −0.33                  |

Computer programs: CrysAlis PRO (Rigaku OD, 2015), SHELXT (Sheldrick, 2015a), SHELXL2014/7 (Sheldrick, 2015b) and Mercury (Macrae et al., 2020).

Funding information

Funding for this research was provided by: Ministry of Education and Science of Ukraine (contract No. BF/30-2021).

References

Baumgartner, O. (1986). Z. Kristallogr. 174, 253–263.
Buvaylo, E. A., Kokozay, V. N., Vassilyeva, O. Y., Skelton, B. W., Jezierska, J., Brunel, L. C. & Ozarowski, A. (2005). Chem. Commun., pp. 4976–4978.
Buvaylo, E. A., Nesterova, O. V., Kokozay, V. N., Vassilyeva, O. Y., Skelton, B. W., Boha, R. & Nesterov, D. S. (2012). Crystal Growth Des. 12, 3200–3208.
Cheaib, K., Martel, D., Clément, N., Ecker, F., Kouaho, S., Rogez, G., Dagorne, S., Kurmoo, M., Choua, S. & Welter, R. (2013). Dalton Trans. 42, 1406–1416.

Chen, W. T., Hu, R. H., Luo, Z. G., Chen, H. L., Zhang, X. & Liu, J. (2014). Indian J. Chem. A53, 294–298.
Coucouvanis, D., Simhon, E. D., Stremple, P., Ryan, M., Swenson, D., Baenziger, N. C., Simopoulos, A., Papanthiymiou, V., Kostikas, A. & Petroules, V. (1984). Inorg. Chem. 23, 741–749.
Cui, X., Zhao, W., Chen, K., Ni, X. L., Zhang, Y. Q. & Tao, Z. (2017). Chem. Eur. J. 23, 2759–2763.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Houlton, A., Lamming, G. & Waddell, P. G. (2015). CSD Communication (deposit code CCDC 1422466). CCDC, Cambridge, England.
Kokozay, V. N., Vassilyeva, O. Y. & Makankova, V. G. (2018). Direct Synthesis of Metal Complexes, edited by B. Kharisov, pp. 183–237. Amsterdam: Elsevier.
Li, Y., Zhang, Z. X., Li, K. C., Xu, J. Q., Song, W. D. & Pan, L. Y. (2007). J. Mol. Struct. 833, 8–12.
Macrè, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. J., Towler, M. & Wood, P. A. (2020). J. Appl. Cryst. 53, 226–235.
Müller, A., Schlenderbeck, N. H., Krickemeyer, E., Böge, H., Schmitz, K., Bill, E. & Trautwein, A. X. (1989). Z. Anorg. Allg. Chem. 570, 7–36.
Nesterova, O. V., Kasyanova, K. V., Buvaylo, E. A., Vassilyeva, O. Yu., Skelton, B. W., Nesterov, D. S. & Pompeiro, A. J. L. (2019). Catalysts, 9, 209.
Nesterova, O. V., Kasyanova, K. V., Makankova, V. G., Kokozay, V. N., Vassilyeva, O. Yu., Skelton, B. W., Nesterov, D. S. & Pompeiro, A. J. L. (2018). Appl. Catal. Gen. 560, 171–184.
Nesterov, D. S., Nesterova, O. V., da Silva, M. F. C. G. & Pompeiro, A. J. L. (2015). Catal. Sci. Technol. 5, 1801–1812.
Rigaku OD (2015). CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, England.
Sharma, R. P., Singh, A., Venugopalan, P., Yanan, G., Yu, J., Angeli, C. & Ferretti, V. (2012). Eur. J. Inorg. Chem. pp. 1195–1203.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Shen, F. F., Zhao, J. L., Chen, K., Hua, Z. Y., Chen, M. D., Zhang, Y. Q., Zhu, Q. J. & Tao, Z. (2017). CrystEngComm, 19, 2464–2474.
Vassilyeva, O. Y., Kasyanova, K. V., Kokozay, V. N. & Skelton, B. W. (2018). Acta Cryst. E74, 1532–1535.
Vassilyeva, O. Y., Buvaylo, E. A., Kokozay, V. N., Skelton, B. W., Sobolev, A. N., Biečko, A. & Ozarowski, A. (2021). Dalton Trans. 50, 2841–2853.
Vassilyeva, O. Y., Kokozay, V. N., Zhukova, N. A. & Kovbasyuk, L. A. (1997). Polyhedron, 16, 263–266.
Zhou, J. J., Yu, X., Zhao, Y. C., Xiao, X., Zhang, Y. Q., Zhu, Q. J., Xue, S. F., Zhang, Q. J., Liu, J. X. & Tao, Z. (2014). Tetrahedron, 70, 800–804.
Crystal structure of hexakis(N,N-dimethylformamide-κO)iron(III) µ-chlorido-bis(trichloridocadmium)

Olga Yu. Vassilyeva, Vladimir N. Kokozay, Svitlana Petrusenko and Alexandre N. Sobolev

Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2015); cell refinement: CrysAlis PRO (Rigaku OD, 2015); data reduction: CrysAlis PRO (Rigaku OD, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2014/7 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: SHELXL2014/7 (Sheldrick, 2015b).

Hexakis(N,N-dimethylformamide-κO)iron(III) µ-chlorido-bis(trichloridocadmium)

Crystal data

\[\text{[Fe(C}_3\text{H}_7\text{NO})_6]\text{[Cd}_2\text{Cl}_7]\]

Mr = 967.37
Trigonal, \text{R}3
\(a = 13.7143 (2) \text{ Å}\)
\(c = 16.1312 (2) \text{ Å}\)
\(V = 2627.51 (5) \text{ Å}^3\)
\(Z = 3\)
\(F(000) = 1443\)

\(D_\lambda = 1.834 \text{ Mg m}^{-3}\)
\(\text{Cu K} \alpha \text{ radiation, } \lambda = 1.54178 \text{ Å}\)

Cell parameters from 9616 reflections

\(\theta = 4.6–67.0^\circ\)
\(\mu = 18.18 \text{ mm}^{-1}\)
\(T = 100 \text{ K}\)

Octahedral, dark green

0.06 × 0.05 × 0.05 mm

Data collection

Oxford Diffraction Gemini-R Ultra, Ruby CCD diffractometer

Radiation source: Enhance (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.4738 pixels mm\(^{-1}\)

\(\omega\) scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

\(T_{\text{min}} = 0.760, T_{\text{max}} = 1.0\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.020\)

\(wR(F^2) = 0.057\)

\(S = 1.00\)

16143 measured reflections

1051 independent reflections

980 reflections with \(I > 2\sigma(I)\)

\(\theta_{\text{max}} = 67.2^\circ, \theta_{\text{min}} = 4.6^\circ\)

\(h = -16→15\)

\(k = -16→16\)

\(l = -19→19\)

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

\(\Delta/\sigma)_{\text{max}} = 0.001\)

\(\Delta r_{\text{max}} = 0.79 \text{ e Å}^{-3}\)

\(\Delta r_{\text{min}} = -0.33 \text{ e Å}^{-3}\)
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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x      | y      | z       | Uiso*/Ueq |
|---|--------|--------|---------|-----------|
| Cd1| 0.3333 | 0.6667 | 0.32398 (2) | 0.01664 (12) |
| Fe1| 0.3333 | 0.6667 | 0.6667 | 0.0139 (2) |
| O1 | 0.47367 (14) | 0.75401 (14) | 0.59890 (10) | 0.0200 (4) |
| N1 | 0.59569 (16) | 0.90250 (17) | 0.52091 (12) | 0.0187 (4) |
| C1 | 0.4941 (2) | 0.8248 (2) | 0.54225 (15) | 0.0191 (5) |
| H1 | 0.431 (2) | 0.819 (2) | 0.5111 (17) | 0.023* |
| C11| 0.6967 (2) | 0.9151 (2) | 0.56042 (17) | 0.0257 (6) |
| H113| 0.7392 | 0.9902 | 0.5852 | 0.039* |
| Cl1| 0.3333 | 0.9055 | 0.5189 | 0.039* |
| Cl2| 0.6754 | 0.8579 | 0.6038 | 0.039* |
| Cl1| 0.6127 (2) | 0.9772 (2) | 0.45107 (16) | 0.0244 (5) |
| Cl2| 0.6547 | 0.9645 | 0.4073 | 0.037* |
| Cl1| 0.6553 | 1.0557 | 0.4696 | 0.037* |
| Cl2| 0.5394 | 0.9614 | 0.4295 | 0.037* |
| Cl1| 0.3333 | 0.6667 | 0.1667 | 0.0233 (3) |
| Cl2| 0.51428 (4) | 0.69293 (5) | 0.36951 (3) | 0.02102 (16) |

Atomic displacement parameters (Å²)

|   | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|---|-------|-------|-------|-------|-------|-------|
| Cd1| 0.01759 (14) | 0.01759 (14) | 0.01476 (17) | 0.00879 (7) | 0.000 | 0.000 |
| Fe1| 0.0141 (3) | 0.0141 (3) | 0.0136 (4) | 0.00706 (14) | 0.000 | 0.000 |
| O1 | 0.0207 (8) | 0.0213 (8) | 0.0183 (8) | 0.0107 (7) | 0.0051 (6) | 0.0042 (7) |
| N1 | 0.0201 (10) | 0.0195 (10) | 0.0164 (10) | 0.0097 (8) | 0.0014 (8) | −0.0016 (8) |
| C1 | 0.0214 (12) | 0.0210 (12) | 0.0159 (11) | 0.0114 (10) | −0.0012 (9) | −0.0029 (10) |
| C11| 0.0225 (13) | 0.0261 (13) | 0.0290 (14) | 0.0126 (11) | −0.0022 (10) | −0.0020 (11) |
| C12| 0.0248 (13) | 0.0267 (13) | 0.0217 (13) | 0.0129 (11) | 0.0041 (10) | 0.0036 (10) |
| C11| 0.0300 (5) | 0.0300 (5) | 0.0100 (6) | 0.0150 (2) | 0.000 | 0.000 |
| Cl2| 0.0191 (3) | 0.0249 (3) | 0.0201 (3) | 0.0119 (2) | −0.0019 (2) | −0.0020 (2) |

Geometric parameters (Å, °)

|   |      |      |      |      |      |      |
|---|------|------|------|------|------|------|
| Cd1—Cl2i | 2.4358 (5) | N1—C11 | 1.455 (3) |
| Cd1—Cl2ii | 2.4358 (5) | N1—C12 | 1.461 (3) |
| Cd1—Cl2 | 2.4358 (5) | C1—H1 | 0.97 (3) |
| Cd1—Cl1 | 2.5377 (3) | C11—H113 | 0.9800 |
| Fe1—O1iii | 2.0071 (16) | C11—H111 | 0.9800 |
| Fe1—O1ii | 2.0072 (16) | C11—H112 | 0.9800 |
| Fe1—O1i | 2.0072 (16) | C12—H123 | 0.9800 |
Fe1—O1          2.0072 (16)      C12—H121      0.9800
Fe1—O1^iv       2.0072 (16)      C12—H122      0.9800
Fe1—O1^v        2.0072 (16)      Cl1—Cd1^vi     2.5376 (3)
O1—C1           1.258 (3)        Cd1—Cd1^vi     5.0752 (3)
N1—C1           1.307 (3)

Cl2—Cd1—Cl2^ii  111.323 (13)     C1—O1—Fe1      129.31 (16)
Cl2—Cd1—Cl2     111.325 (13)     C1—N1—C11      120.4 (2)
Cl2^ii—Cd1—Cl2  111.324 (13)     C11—N1—C12     116.51 (19)
Cl2—Cd1—Cl1     107.547 (14)     O1—C1—N1       123.8 (2)
Cl2^ii—Cd1—Cl1  107.549 (14)     C1—N1—C12      120.4 (2)
Cl2—Cd1—Cl1     107.547 (14)     C11—N1—C12     116.51 (19)
O1^ii—Fe1—O1^i  86.85 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^i  93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1    93.15 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1    86.84 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1    93.15 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^iv 93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^iv 93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^iv 86.84 (7)        N1—Cl1—Cd1     118.4 (17)
O1—Fe1—O1^iv    180.0           N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  86.84 (7)        N1—Cl1—Cd1     118.4 (17)
O1—Fe1—O1^v     180.0           N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  86.84 (7)        N1—Cl1—Cd1     118.4 (17)
O1—Fe1—O1^v     180.0           N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  93.16 (7)        N1—Cl1—Cd1     118.4 (17)
O1^ii—Fe1—O1^v  86.84 (7)        N1—Cl1—Cd1     118.4 (17)

Fe1—O1—C1—N1    156.61 (17)     C12—N1—C1—O1   176.2 (2)
C11—N1—C1—O1    0.4 (4)

Hydrogen-bond geometry (Å, °)

\begin{tabular}{lllll}
   \multicolumn{2}{c}{D—H···A} & D—H & H···A & D···A & D—H···A \\
   \hline
   C12—H123···Cl2^vii & 0.98 & 2.82 & 3.783 (3) & 167 \\
   C1—H1···Cl2^i & 0.97 (3) & 2.86 (3) & 3.772 (3) & 158 (2) \\
   C1—H1···O1^i & 0.97 (3) & 2.62 (3) & 3.097 (3) & 111 (2) \\
   C12—H122···Cl2^i & 0.98 & 2.94 & 3.861 (3) & 157 \\
\end{tabular}

Symmetry codes: (i) \(\bar{y}+1, x-y+1, z\); (ii) \(-x+y, -x+1, z\); (iii) \(y-1/3, -x+y+1/3, -z+4/3\); (iv) \(-x+2/3, -y+4/3, -z+4/3\); (v) \(x-y+2/3, x+1/3, -z+4/3\); (vi) \(-x+2/3, -y+4/3, -z+1/3\).