Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of poly[tetrakis(4-methylanilinium) [octa-μ-chlorido-dichloridotricadmium(II)]]: a two-dimensional organic–inorganic hybrid perovskite

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Received 1 November 2022
Accepted 11 November 2022

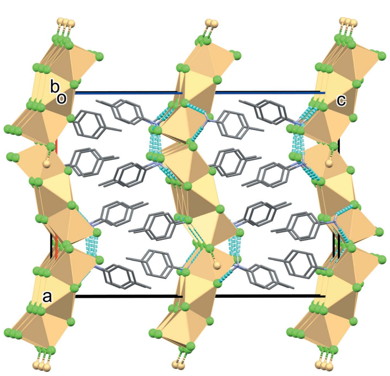
Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

Keywords: crystal structure; cadmium; two-dimensional perovskite; hydrogen bonding.

CCDC reference: 922195

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

The title polymeric compound, $(C_7H_{10}N)_4[Cd_3Cl_{10}]$, involves a centrosymmetric $[Cd_3Cl_{10}]^{4-}$ tetra-anion, which is made up of three face-sharing $CdCl_6$ octahedra, linked by four corner Cl atoms, forming layers propagating in the *ab* plane. The *p*-methylanilinium cations, situated between the layers, form N—H···Cl hydrogen bonds to the layers, which stack up the *c*-axis direction. There are no π–π or C—H···π interactions involving the aromatic rings, which are inclined to each other by 42.3 (1) ° in the asymmetric unit.



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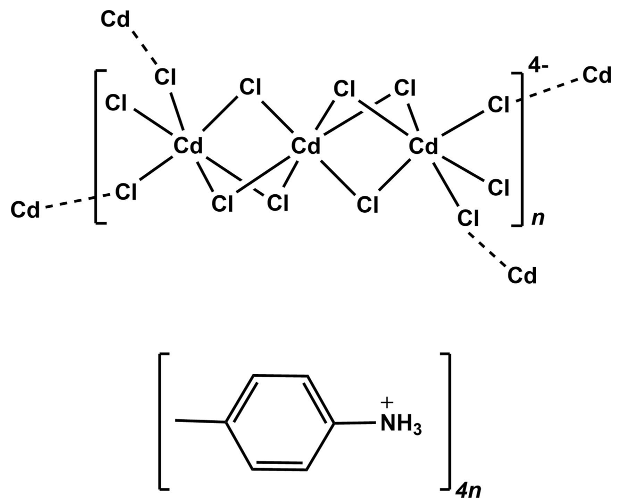
1. Chemical context

There are numerous reports of the structures of polymeric structures involving transition metal halide networks with organic cations to provide charge compensation [Cambridge Structural Database (CSD), Version 5.43, last update September 2022; Groom *et al.*, 2016]. They include a number of layer-like structures that have been described as organic–inorganic two-dimensional hybrid perovskites. The structure, properties and applications, especially optoelectronic applications, of such compounds have been reviewed recently by Zhu and collaborators (Zhang *et al.*, 2020).

Beatty and collaborators (Costin-Hogan *et al.*, 2008) reported on a number of complexes formed by the reaction of *ortho*-substituted phenylamines with cadmium halide salts. They showed, for example, that the reaction of an acidified solution in methanol of $CdCl_2$ with aniline led to the formation of the $[Cd_3Cl_{10}]^{4-}$ linear tetra-anion in the compound poly[tetrakis(anilinium) [decachlorotricadmium(II)]] (CSD refcode EGUFUI). In the present work an analogous reaction has been studied using a *para*-substituted derivative of aniline, 4-methylaniline. The resulting structure of the title compound, (**I**), is isostructural with that of EGUFUI.

A search of the CSD for polymeric compounds involving the title cation, 4-methylanilinium, gave only four hits. One in particular is of interest, namely bis(4-methylanilinium) pentamolybdate (YIKLIP; Oszajca *et al.*, 2013), whose structure was determined by powder X-ray diffraction analysis. It is composed of layers of inorganic $\{[Mo_5O_{16}]^{2-}\}_n$ polyanions alternating with layers of 4-methylanilinium cations. The latter are linked to the inorganic polyanions by N—H···O hydrogen bonds, involving both terminal and shared O atoms.



2. Structural commentary

The asymmetric unit of the title compound, $\{[Cd_3Cl_{10}]^{4-}\cdot 4[(C_7H_{10}N)^+]\}_n$ (**I**), is composed of half of a centrosymmetric $[Cd_3Cl_{10}]^{4-}$ tetra-anion, with the central Cd2 atom being situated on a crystallographic inversion centre, and two 4-methylanilinium cations (Fig. 1). The complete $[Cd_3Cl_{10}]^{4-}$ unit is made up of three face sharing $CdCl_6$ octahedra. They are linked by four corner Cl^- ions (Cl2, Cl2^{i}, Cl2^{iv} and Cl2^{v}; Fig. 1) to form a layer-like structure lying parallel to the *ab* plane (Figs. 2 and 3). The octahedral environment of atom Cd1 is slightly distorted with one short contact to a terminal Cl atom (Cl1) of 2.5051 (5) Å, while the other five Cd—Cl bond lengths vary from 2.6329 (5) to 2.7220 (5) Å. The Cd2—Cl bond lengths vary from 2.5764 (5) to 2.6750 (4) Å (Table 1). The cadmium atoms are separated by 3.4082 (2) Å. These bond lengths and the metal···metal distance are very similar to those observed for the three compounds involving cadmium chloride mentioned below in § *6. Database survey*.

Table 1
Selected bond lengths (Å).

Cd1—Cl1	2.5051 (5)	Cd1—Cl5	2.6511 (5)
Cd1—Cl2	2.6560 (5)	Cd2—Cl3	2.6750 (4)
Cd1—Cl2^{i}	2.6329 (5)	Cd2—Cl4	2.6551 (4)
Cd1—Cl3	2.6462 (5)	Cd2—Cl5	2.5764 (5)
Cd1—Cl4	2.7220 (5)		

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

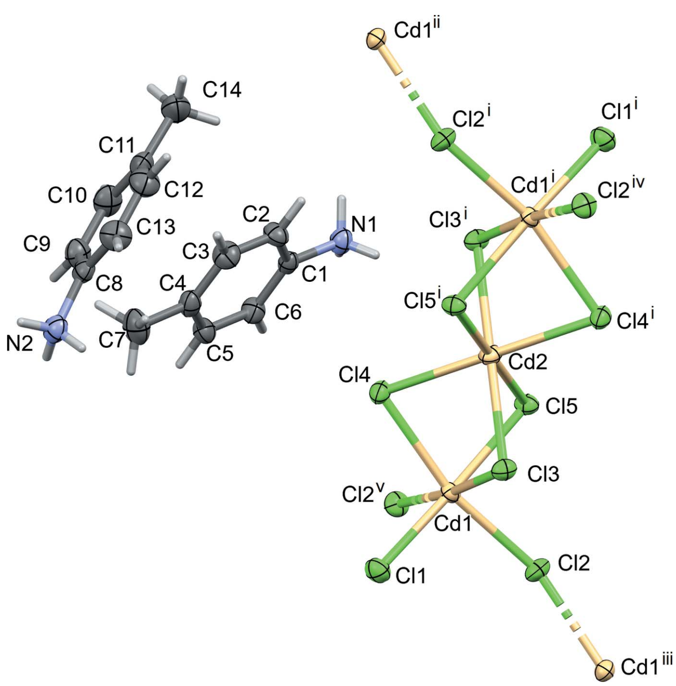


Figure 1
A view of the structure of the polymeric unit of compound **I**. The displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (iv) $x-\frac{1}{2}, -y+\frac{5}{2}, -z$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, z$.]

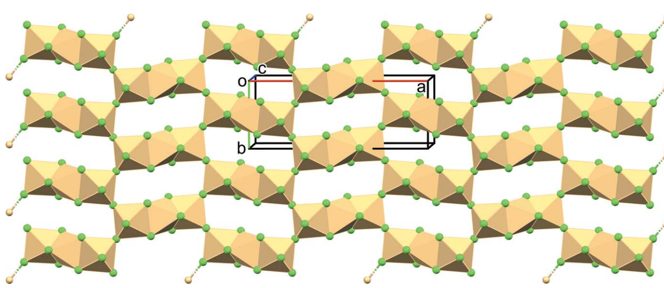


Figure 2
A view along the *c*-axis of the layer-like structure of the $[Cd_3Cl_{10}]^{4-}$ polymeric arrangement in **I**. Colour code: Cd yellow, Cl green.

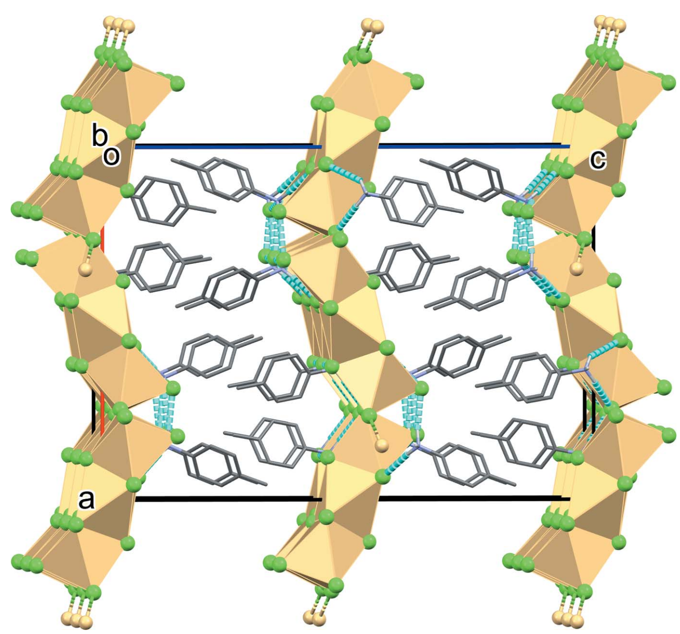


Figure 3
A view along the *b*-axis of the crystal packing of compound **I**. The N—H···Cl hydrogen bonds (see Table 2) are shown as dashed lines. For clarity, the C-bound H atoms have been omitted. Colour code as in Fig. 2.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1AN···Cl5^{ii}	0.86 (3)	2.42 (3)	3.258 (2)	166 (2)
N1—H1BN···Cl2^{iii}	0.91 (3)	2.38 (3)	3.236 (2)	158 (3)
N1—H1CN···Cl4^{iv}	0.80 (3)	2.70 (3)	3.360 (2)	141 (3)
N2—H2AN···Cl3^{v}	0.87 (3)	2.34 (3)	3.198 (2)	170 (3)
N2—H2BN···Cl1^{vi}	0.85 (3)	2.48 (3)	3.273 (2)	156 (2)
N2—H2CN···Cl1^{vii}	0.93 (4)	2.29 (4)	3.194 (2)	164 (3)

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

The two *p*-methylanilinium cations lie in the interstitial space between the layers (Fig. 3). They have normal geometry, with the heteroatoms of each cation being almost coplanar with their attached rings: cation N1/C1–C7 is almost planar (r.m.s. deviation = 0.009 Å) with atoms N1 and C7 both being displaced from the mean plane by 0.011 (2) Å; cation N2/C8–C14 is slightly less planar (r.m.s. deviation = 0.047 Å) with N2 and C14 being displaced from the mean plane by 0.064 (2) and 0.060 (3) Å, respectively.

3. Supramolecular features

In the crystal of **I**, the *p*-methylanilinium cations that are situated between the layers are N—H···Cl hydrogen bonded to the front and back of the layers that stack up the *c*-axis (Fig. 3). All six ammonium H atoms are involved in hydrogen bonding with all five chloride ions (Table 2). However, there are no identified π–π or C—H···π interactions involving the aromatic rings (C1–C6 and C8–C13) of the *p*-methylanilinium cations. The rings are inclined to each other by 42.3 (1) ° in the asymmetric unit and by *ca* 71.8 and 73.8°, respectively, to the *ab* plane in which lies the anionic $\{[Cd_3Cl_{10}]^{4-}\}_n$ layer-like structure.

4. Thermal analyses

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were recorded in the temperature range 25–650°C, at a heating rate of 10°C min^{-1} under a nitrogen atmosphere, using an SDT Q600 simultaneous thermo analytical system. The alumina crucible was loaded with 6.191 mg of compound **I**. It can be seen in the TGA and DTA curves for **I** (Fig. 4), that the sample begins to decompose before reaching the melting point. In the TGA curve, the first weight loss (198–216°C) is due to the loss of two methylanilinium cations and two chloride anions: calculated 25.5%, observed 24.8%. The second weight loss (216–250°C) is due to the loss of the two remaining methylanilinium cations: calculated 19.2%, observed 18.2%. The third weight loss (553–559°C) involves the loss of two equivalents of HCl: calculated 6.3%, experimental 6.3%. The residual cadmium chloride ($CdCl_2$) begins to evaporate at 559°C as observed from the DTA curve (Fig. 4), and it continues slowly up to 650°C. There is a small residue (0.83%) remaining at 650°C.

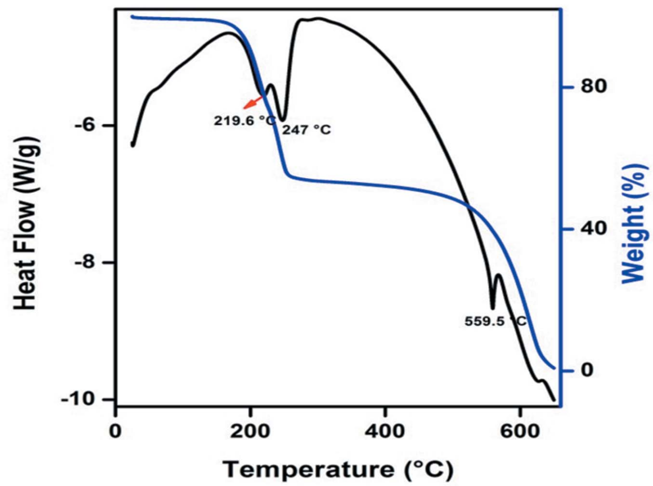


Figure 4
The TGA (blue) and DTA (black) curves for **I**.

5. FT–IR and FT–Raman spectroscopy

A Perkin Elmer-paragon-500 Fourier transform infrared (FT–IR) was used to record the FT–IR spectrum (KBr pellet) in the wavelength range of 450–4000 cm^{-1}. A Varian FT–Raman spectrometer was used to record the FT–Raman spectrum in the wavelength range 400–4000 cm^{-1}.

The FT–IR and FT–Raman spectra of **I** are illustrated in Fig. 5, and the assignment of the vibrational frequencies are presented in Table 3. The intermolecular N—H···Cl stretching vibration is observed at 3129 cm^{-1} (FT–IR) and 3126 cm^{-1} (FT–Raman) (Haigh *et al.*, 1967). The band at 637 cm^{-1} in the FT–IR and 638 cm^{-1} in the FT–Raman corresponds to the NH_2 twisting frequency. The asymmetric NH stretching frequency is observed at 3510 cm^{-1} in the FT–IR spectrum. The peak at 1243 cm^{-1} in the FT–IR spectrum is due to the C—N vibration. The frequencies of the FT–IR spectrum agree well with the corresponding values of the FT–Raman spectrum and also when compared with those of *p*-methylaniline (Altun *et al.*, 2003).

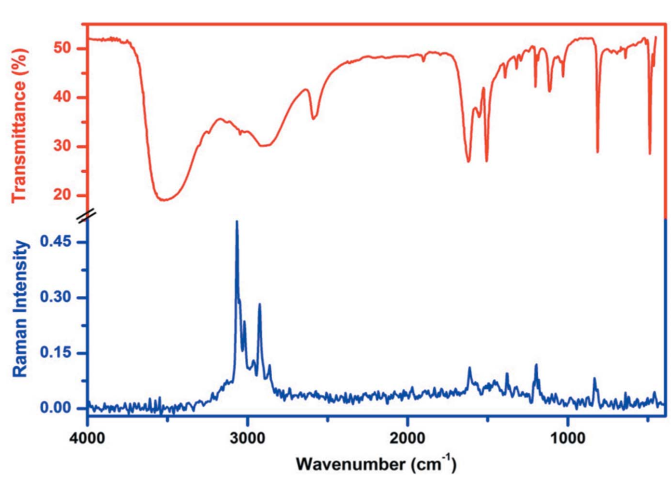


Figure 5
FT–IR and FT–Raman spectra for **I**.

Table 3
Assignment of FT–IR and FT–Raman vibrational frequencies (cm^{-1}) for **I** and *p*-methylaniline.

	FT–IR		FT–Raman	
Assignment of vibrational frequencies	**I**	*p*-methylaniline[a]	**I**	*p*-methylaniline[b]
ν (NH) asymmetric	3510	3416	-	3418
γ NH_2 (twisting)	637	-	638	-
β NH_2 (scis.)	1616	1621	1608	1617
β CH_3 *sym*	1391	-	1380	1380
γ CH_3 *sym*	2881	2912	2922	2917
ν (C═C) aromatic	1560, 1503, 1291	1582, 1514, 1441	-	1581, 1281
β (C—H) 1,4-disubstituted	1190, 1114	1176, 1120	1196	1179
ν (C—N)	1243	1267	-	1271
ν (N—H···Cl) intermolecular	3129	-	3126	-

Notes: (*a*) Haigh *et al.* (1967);(*b*) Altun *et al.* (2003).

Table 4
A comparison of selected geometrical parameters (Å) for **I**, EGUFUI[a], IPEMAS01[b] and QOHGU*R*[c].

Distances	**I**	EGUFUI[a]	IPEMAS01[b]	QOHGU*R*[c]
Cd1—Cl1	2.5051 (5)	2.4962 (9)	2.4880 (7)	2.496 (2)
Cd1—Cl(2,3,4,5)	2.6329 (5)–2.7220 (5)	2.5882 (9)–2.8926 (9)	2.6218 (7)–2.7404 (6)	2.660 (2)–2.763 (2)
Cd2[d]—Cl(3,4,5)	2.5764 (5)–2.6750 (4)	2.5632 (9)–2.7391 (9)	2.5795 (6)–2.6903 (6)	2.577 (2)–2.697 (2)
Cd1···Cd2[d]	3.4082 (2)	3.4714 (6)	3.4493 (3)	3.4396 (9)

Notes: (*a*) Costin-Hogan *et al.* (2008); (*b*) Gagor *et al.* (2011); (*c*) Liao *et al.* (2014); (*d*) Atom Cd2 is located on an inversion centre

6. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, last update September 2022; Groom *et al.*, 2016) for polymeric-type structures involving transition-metal halide salts with organic cations gave over 150 hits. The large majority involve cadmium halide salts forming zero-dimensional (molecular) salts or one-dimensional polymer chains.

There are only four reports of two-dimensional layered perovskite-type compounds involving the same $[Cd_3X_{10}]^{4-}$ (where X = Br, Cl) linear tetra-anion as in the title compound **I**. They include: *catena*-[tetrakis(anilinium) [octakis(μ_2-bromo)dibromotricadmium]] (CSD refcode POPHAD; Ishihara *et al.*, 1994), *catena*-[tetrakis(anilinium) [octakis(μ_2-chloro)dichlorotricadmium(II)]] (EGUFUI; Costin-Hogan *et al.*, 2008), *catena*-[tetrakis(isopropylammonium) [decachlorotricadmium(II)]] (IPEMAS01; Gagor *et al.*, 2011) and *catena*-[tetrakis(cyclopentanaminium) [octakis(μ-chloro)dichlorotricadmium(II)]] (QOHGUR; Liao *et al.*, 2014). The various Cd—Cl bond lengths, involving atoms Cd1 and Cd2, for the three compounds are similar to those observed for **I**, as seen in Table 4. The Cd1···Cd2 interatomic distance for **I** [3.4082 (2) Å] however, is shorter than that observed in the other three compounds; see Table 4.

All four compounds crystallize at room temperature in the orthorhombic space group *Pbca*, as does the title compound (**I**). Hence, all five compounds are isostructural. As noted by Gagor *et al.* (2011) and Liao *et al.* (2014), some layered organic–inorganic hybrids have been shown to show reversible structural phase transitions because cooling and heating can induce reorientation of the organic cations and deformation of the anionic framework. Such changes were observed for compounds IPEMASS01 and QOHGUR, which undergo two phase transitions. At low temperature they transform into the non-centrosymmetric orthorhombic space group $P2_12_12_1$ [structures IPEMAS02 (275 K) and QOHGUR01 (93 K)], while at high temperature they transform to the centrosymmetric orthorhombic space group *Cmca* [structures IPEMAS (320 K) and QOHGUR02 (343 K)]. As reported by Gagor *et al.* (2011), the transition from *Pbca* to $P2_12_12_1$ is type I: *translationengleiche*; the crystal class changes from *mmm* to *222*. The change from *Cmca* to *Pbca* is type IIA: *klassengleiche*; the crystal class does not change (*mmm* to *mmm*). For further details concerning subgroups and supergroups of space groups, see Müller (2013).

7. Synthesis and crystallization

Concentrated HCl (1 ml) was added dropwise to a mixture of cadmium chloride dihydrate (1 g, 0.009 mol) and *p*-methylaniline (1.71 g, 0.009 mol) in methanol (30 ml) until the solution was clear. The solution was then stirred and heated under reflux at 353 K for 6 h and filtered. The solution was allowed to evaporate slowly at room temperature, yielding small, orange block-like crystals of **I** after *ca* 21 days.

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. The ammonium H atoms were located in difference-Fourier maps and freely refined. The C-bound H atoms were included in calculated positions (C—H = 0.95 Å) and treated as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. The average hkl measurement multiplicity was low, hence an empirical absorption correction was applied.

Table 5
Experimental details.

Crystal data	
Chemical formula	$(C_7H_{10}N)_4[Cd_3Cl_{10}]$
M_r	1124.34
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	200
a, *b*, *c* (Å)	19.4883 (7), 7.3754 (3), 27.1557 (10)
V (Å^3)	3903.2 (3)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	2.33
Crystal size (mm)	0.12 × 0.10 × 0.08
Data collection	
Diffractometer	STOE IPDS 2T
Absorption correction	Empirical (using intensity measurements) (*ShxAbs*; Spek, 2020)
T_{min}, T_{max}	0.495, 0.839
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	49498, 3681, 3072
R_{int}	0.040
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.609
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.015, 0.031, 0.95
No. of reflections	3681
No. of parameters	231
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.35

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

Acknowledgements

The authors thank the Central Instrumentation Facility, Pondicherry University, and the Advanced Instrumentation Research Facility, Jawaharlal Nehru University, New Delhi, for access to their analytical facilities. HSE is grateful to the University of Neuchâtel for their support over the years.

Funding information

AS thanks the University Grants Commission, New Delhi, for the award of a UGC Meritorious Fellowship [File No. 4-1/2008 (BSR)].

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supporting information

Acta Cryst. (2022). E**78**, 1223-1227 [https://doi.org/10.1107/S2056989022010830]

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A. Subashini, Aurelien Crochet, K. Ramamurthi, R. Ramesh Babu and Helen Stoeckli-Evans

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2020) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

Poly[tetrakis(4-methylanilinium) [octa-μ-chlorido-dichloridotricadmium(II)]]

Crystal data

$(C_7H_{10}N)_4[Cd_3Cl_{10}]$
M_r = 1124.34
Orthorhombic, *Pbca*
a = 19.4883 (7) Å
b = 7.3754 (3) Å
c = 27.1557 (10) Å
V = 3903.2 (3) Å^3
Z = 4
$F(000)$ = 2200
D_x = 1.913 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 42237 reflections
θ = 1.5–26.1°
μ = 2.33 mm^{-1}
T = 200 K
Block, orange
0.12 × 0.10 × 0.08 mm

Data collection

STOE IPDS 2T diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: empirical (using intensity measurements) (*ShxAbs*; Spek, 2020)
T_{min} = 0.495, T_{max} = 0.839
49498 measured reflections
3681 independent reflections
3072 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 25.7°, θ_{min} = 1.5°
$h = -23 \rightarrow 23$
$k = -8 \rightarrow 9$
$l = -32 \rightarrow 33$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.015
$wR(F^2)$ = 0.031
S = 0.95
3681 reflections
231 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.019P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.65796 (2)	0.94295 (2)	0.05158 (2)	0.02163 (4)
Cd2	0.500000	1.000000	0.000000	0.02469 (5)
Cl1	0.68348 (3)	0.90247 (7)	0.14132 (2)	0.03240 (11)
Cl2	0.75872 (2)	1.17278 (6)	0.03058 (2)	0.02941 (11)
Cl3	0.56591 (2)	1.20044 (6)	0.06710 (2)	0.02527 (10)
Cl4	0.54771 (2)	0.71648 (6)	0.04958 (2)	0.02671 (10)
Cl5	0.61915 (2)	0.99188 (6)	−0.04104 (2)	0.02448 (10)
N1	0.37129 (12)	0.5701 (3)	0.02703 (7)	0.0315 (4)
H1AN	0.3750 (13)	0.686 (4)	0.0249 (9)	0.053 (8)*
H1BN	0.3360 (18)	0.533 (4)	0.0078 (13)	0.083 (11)*
H1CN	0.4063 (17)	0.527 (4)	0.0167 (11)	0.062 (10)*
C1	0.35738 (10)	0.5140 (2)	0.07793 (7)	0.0244 (4)
C2	0.29246 (10)	0.5348 (3)	0.09622 (8)	0.0311 (5)
H2	0.256915	0.583871	0.076329	0.037*
C3	0.27966 (11)	0.4828 (3)	0.14427 (8)	0.0361 (5)
H3	0.234749	0.495974	0.157397	0.043*
C4	0.33130 (11)	0.4116 (3)	0.17363 (7)	0.0316 (5)
C5	0.39604 (11)	0.3939 (3)	0.15362 (8)	0.0327 (5)
H5	0.432061	0.346507	0.173362	0.039*
C6	0.40968 (10)	0.4435 (3)	0.10564 (8)	0.0304 (4)
H6	0.454307	0.429046	0.092124	0.036*
C7	0.31785 (14)	0.3573 (3)	0.22625 (8)	0.0495 (6)
H7A	0.304491	0.229302	0.227434	0.074*
H7B	0.280746	0.432013	0.239740	0.074*
H7C	0.359564	0.375359	0.245799	0.074*
N2	0.15463 (12)	0.4659 (3)	0.36493 (7)	0.0346 (4)
H2AN	0.1309 (15)	0.405 (4)	0.3864 (11)	0.061 (9)*
H2BN	0.1564 (14)	0.578 (4)	0.3724 (10)	0.055 (8)*
H2CN	0.1999 (19)	0.426 (4)	0.3665 (12)	0.082 (11)*
C8	0.12388 (11)	0.4504 (3)	0.31563 (7)	0.0290 (4)
C9	0.15310 (12)	0.3358 (3)	0.28179 (8)	0.0375 (5)
H9	0.191036	0.261630	0.290563	0.045*
C10	0.12627 (13)	0.3304 (3)	0.23464 (8)	0.0417 (5)
H10	0.146815	0.252891	0.210894	0.050*

C11	0.07051 (12)	0.4343 (3)	0.22117 (8)	0.0370 (5)
C12	0.04108 (12)	0.5428 (3)	0.25683 (9)	0.0442 (6)
H12	0.001676	0.612632	0.248775	0.053*
C13	0.06764 (12)	0.5523 (3)	0.30399 (9)	0.0413 (5)
H13	0.047045	0.628683	0.327979	0.050*
C14	0.04386 (15)	0.4313 (4)	0.16891 (9)	0.0542 (7)
H14A	−0.004455	0.468112	0.168625	0.081*
H14B	0.048053	0.308410	0.155525	0.081*
H14C	0.070716	0.515440	0.148688	0.081*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02012 (7)	0.02084 (7)	0.02392 (7)	0.00165 (5)	−0.00197 (6)	0.00028 (5)
Cd2	0.01681 (9)	0.02408 (9)	0.03317 (11)	−0.00019 (7)	−0.00311 (8)	−0.00007 (8)
Cl1	0.0366 (3)	0.0388 (3)	0.0218 (2)	−0.0015 (2)	−0.0016 (2)	−0.00037 (19)
Cl2	0.0259 (2)	0.0242 (2)	0.0381 (3)	−0.00793 (18)	0.0008 (2)	−0.00288 (19)
Cl3	0.0229 (2)	0.0237 (2)	0.0293 (2)	0.00188 (18)	−0.00075 (19)	−0.00623 (17)
Cl4	0.0243 (2)	0.0212 (2)	0.0346 (3)	−0.00105 (17)	−0.0002 (2)	0.00392 (19)
Cl5	0.0211 (2)	0.0293 (2)	0.0231 (2)	0.00007 (18)	−0.00004 (18)	−0.00205 (17)
N1	0.0376 (11)	0.0297 (10)	0.0273 (10)	−0.0036 (9)	0.0048 (9)	0.0014 (8)
C1	0.0298 (10)	0.0194 (9)	0.0241 (10)	−0.0036 (7)	0.0017 (8)	−0.0018 (7)
C2	0.0259 (10)	0.0363 (11)	0.0311 (11)	0.0036 (9)	−0.0029 (8)	0.0026 (9)
C3	0.0289 (11)	0.0432 (12)	0.0361 (12)	0.0019 (9)	0.0072 (9)	0.0010 (10)
C4	0.0423 (13)	0.0242 (10)	0.0281 (11)	−0.0018 (9)	0.0022 (9)	0.0001 (8)
C5	0.0344 (12)	0.0283 (11)	0.0352 (12)	0.0038 (9)	−0.0062 (9)	0.0046 (9)
C6	0.0257 (10)	0.0274 (10)	0.0380 (12)	0.0034 (8)	0.0040 (9)	0.0022 (9)
C7	0.0652 (17)	0.0510 (14)	0.0324 (13)	0.0030 (12)	0.0088 (12)	0.0075 (11)
N2	0.0383 (11)	0.0352 (11)	0.0303 (10)	−0.0064 (9)	0.0065 (9)	0.0023 (8)
C8	0.0297 (11)	0.0280 (10)	0.0292 (10)	−0.0063 (8)	0.0047 (8)	0.0023 (8)
C9	0.0423 (12)	0.0307 (11)	0.0394 (12)	0.0068 (10)	0.0016 (11)	0.0003 (9)
C10	0.0557 (15)	0.0316 (11)	0.0377 (13)	0.0018 (11)	0.0052 (11)	−0.0071 (9)
C11	0.0453 (13)	0.0280 (10)	0.0377 (12)	−0.0103 (10)	−0.0019 (10)	0.0027 (9)
C12	0.0350 (13)	0.0466 (14)	0.0511 (15)	0.0062 (10)	−0.0015 (11)	0.0019 (11)
C13	0.0374 (13)	0.0451 (13)	0.0414 (13)	0.0070 (11)	0.0061 (10)	−0.0069 (10)
C14	0.0718 (19)	0.0462 (13)	0.0447 (15)	−0.0153 (13)	−0.0137 (13)	0.0041 (12)

Geometric parameters (Å, º)

Cd1—Cd2	3.4082 (2)	C5—C6	1.379 (3)
Cd1—Cl1	2.5051 (5)	C5—H5	0.9500
Cd1—Cl2	2.6560 (5)	C6—H6	0.9500
Cd1—Cl2^{i}	2.6329 (5)	C7—H7A	0.9800
Cd1—Cl3	2.6462 (5)	C7—H7B	0.9800
Cd1—Cl4	2.7220 (5)	C7—H7C	0.9800
Cd1—Cl5	2.6511 (5)	N2—C8	1.471 (3)
Cd2—Cl3	2.6750 (4)	N2—H2AN	0.87 (3)
Cd2—Cl3^{ii}	2.6750 (4)	N2—H2BN	0.85 (3)

Cd2—Cl4	2.6551 (4)	N2—H2CN	0.93 (4)
Cd2—Cl4^{ii}	2.6551 (4)	C8—C13	1.366 (3)
Cd2—Cl5	2.5764 (5)	C8—C9	1.372 (3)
Cd2—Cl5^{ii}	2.5764 (5)	C9—C10	1.384 (3)
N1—C1	1.468 (3)	C9—H9	0.9500
N1—H1AN	0.86 (3)	C10—C11	1.380 (3)
N1—H1BN	0.90 (4)	C10—H10	0.9500
N1—H1CN	0.80 (3)	C11—C12	1.381 (3)
C1—C2	1.368 (3)	C11—C14	1.511 (3)
C1—C6	1.370 (3)	C12—C13	1.383 (3)
C2—C3	1.383 (3)	C12—H12	0.9500
C2—H2	0.9500	C13—H13	0.9500
C3—C4	1.387 (3)	C14—H14A	0.9800
C3—H3	0.9500	C14—H14B	0.9800
C4—C5	1.380 (3)	C14—H14C	0.9800
C4—C7	1.507 (3)		

Cl1—Cd1—Cl2^{i}	89.894 (17)	H1AN—N1—H1CN	107 (3)
Cl1—Cd1—Cl3	93.735 (16)	H1BN—N1—H1CN	109 (3)
Cl2^{i}—Cd1—Cl3	174.692 (15)	C2—C1—C6	122.10 (18)
Cl1—Cd1—Cl5	174.745 (17)	C2—C1—N1	118.77 (18)
Cl2^{i}—Cd1—Cl5	94.211 (15)	C6—C1—N1	119.14 (18)
Cl3—Cd1—Cl5	81.953 (15)	C1—C2—C3	118.58 (19)
Cl1—Cd1—Cl2	97.945 (17)	C1—C2—H2	120.7
Cl2^{i}—Cd1—Cl2	88.887 (7)	C3—C2—H2	120.7
Cl3—Cd1—Cl2	94.439 (15)	C2—C3—C4	121.1 (2)
Cl5—Cd1—Cl2	85.430 (15)	C2—C3—H3	119.5
Cl1—Cd1—Cl4	95.911 (16)	C4—C3—H3	119.5
Cl2^{i}—Cd1—Cl4	91.033 (15)	C5—C4—C3	118.23 (19)
Cl3—Cd1—Cl4	84.747 (15)	C5—C4—C7	120.5 (2)
Cl5—Cd1—Cl4	80.755 (15)	C3—C4—C7	121.3 (2)
Cl2—Cd1—Cl4	166.143 (16)	C6—C5—C4	121.54 (19)
Cl1—Cd1—Cd2	126.427 (13)	C6—C5—H5	119.2
Cl2^{i}—Cd1—Cd2	124.153 (12)	C4—C5—H5	119.2
Cl3—Cd1—Cd2	50.545 (10)	C1—C6—C5	118.45 (19)
Cl5—Cd1—Cd2	48.363 (10)	C1—C6—H6	120.8
Cl2—Cd1—Cd2	120.049 (12)	C5—C6—H6	120.8
Cl4—Cd1—Cd2	49.802 (10)	C4—C7—H7A	109.5
Cl5^{ii}—Cd2—Cl5	180.0	C4—C7—H7B	109.5
Cl5^{ii}—Cd2—Cl4	96.582 (14)	H7A—C7—H7B	109.5
Cl5—Cd2—Cl4	83.419 (14)	C4—C7—H7C	109.5
Cl5^{ii}—Cd2—Cl4^{ii}	83.418 (14)	H7A—C7—H7C	109.5
Cl5—Cd2—Cl4^{ii}	96.580 (14)	H7B—C7—H7C	109.5
Cl4—Cd2—Cl4^{ii}	180.0	C8—N2—H2AN	110.7 (19)
Cl5^{ii}—Cd2—Cl3^{ii}	82.800 (14)	C8—N2—H2BN	108.1 (19)
Cl5—Cd2—Cl3^{ii}	97.198 (14)	H2AN—N2—H2BN	111 (3)
Cl4—Cd2—Cl3^{ii}	94.491 (14)	C8—N2—H2CN	114 (2)
Cl4^{ii}—Cd2—Cl3^{ii}	85.509 (14)	H2AN—N2—H2CN	108 (3)

Cl5^{ii}—Cd2—Cl3	97.198 (14)	H2BN—N2—H2CN	105 (3)
Cl5—Cd2—Cl3	82.804 (14)	C13—C8—C9	121.1 (2)
Cl4—Cd2—Cl3	85.508 (14)	C13—C8—N2	119.6 (2)
Cl4^{ii}—Cd2—Cl3	94.492 (14)	C9—C8—N2	119.2 (2)
Cl3^{ii}—Cd2—Cl3	180.0	C8—C9—C10	118.7 (2)
Cl5^{ii}—Cd2—Cd1	129.733 (10)	C8—C9—H9	120.6
Cl5—Cd2—Cd1	50.270 (10)	C10—C9—H9	120.6
Cl4—Cd2—Cd1	51.542 (10)	C11—C10—C9	121.8 (2)
Cl4^{ii}—Cd2—Cd1	128.458 (10)	C11—C10—H10	119.1
Cl3^{ii}—Cd2—Cd1	130.200 (10)	C9—C10—H10	119.1
Cl3—Cd2—Cd1	49.800 (10)	C10—C11—C12	117.6 (2)
Cl5^{ii}—Cd2—Cd1^{ii}	50.268 (10)	C10—C11—C14	120.8 (2)
Cl5—Cd2—Cd1^{ii}	129.730 (10)	C12—C11—C14	121.6 (2)
Cl4—Cd2—Cd1^{ii}	128.458 (10)	C11—C12—C13	121.5 (2)
Cl4^{ii}—Cd2—Cd1^{ii}	51.542 (10)	C11—C12—H12	119.2
Cl3^{ii}—Cd2—Cd1^{ii}	49.799 (10)	C13—C12—H12	119.2
Cl3—Cd2—Cd1^{ii}	130.200 (10)	C8—C13—C12	119.1 (2)
Cd1—Cd2—Cd1^{ii}	180.0	C8—C13—H13	120.4
Cd1^{iii}—Cl2—Cd1	153.18 (2)	C12—C13—H13	120.4
Cd1—Cl3—Cd2	79.655 (12)	C11—C14—H14A	109.5
Cd2—Cl4—Cd1	78.656 (12)	C11—C14—H14B	109.5
Cd2—Cl5—Cd1	81.367 (13)	H14A—C14—H14B	109.5
C1—N1—H1AN	111.0 (18)	C11—C14—H14C	109.5
C1—N1—H1BN	109 (2)	H14A—C14—H14C	109.5
H1AN—N1—H1BN	109 (3)	H14B—C14—H14C	109.5
C1—N1—H1CN	112 (2)		

C6—C1—C2—C3	0.1 (3)	C13—C8—C9—C10	2.6 (3)
N1—C1—C2—C3	−179.64 (19)	N2—C8—C9—C10	−176.2 (2)
C1—C2—C3—C4	0.3 (3)	C8—C9—C10—C11	−1.1 (3)
C2—C3—C4—C5	0.0 (3)	C9—C10—C11—C12	−1.2 (3)
C2—C3—C4—C7	179.1 (2)	C9—C10—C11—C14	177.6 (2)
C3—C4—C5—C6	−0.6 (3)	C10—C11—C12—C13	2.1 (3)
C7—C4—C5—C6	−179.7 (2)	C14—C11—C12—C13	−176.7 (2)
C2—C1—C6—C5	−0.7 (3)	C9—C8—C13—C12	−1.7 (3)
N1—C1—C6—C5	179.06 (18)	N2—C8—C13—C12	177.0 (2)
C4—C5—C6—C1	0.9 (3)	C11—C12—C13—C8	−0.7 (4)

Symmetry codes: (i) −*x*+3/2, *y*−1/2, *z*; (ii) −*x*+1, −*y*+2, −*z*; (iii) −*x*+3/2, *y*+1/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*AN*···Cl5^{ii}	0.86 (3)	2.42 (3)	3.258 (2)	166 (2)
N1—H1*BN*···Cl2^{iv}	0.91 (3)	2.38 (3)	3.236 (2)	158 (3)
N1—H1*CN*···Cl4^{v}	0.80 (3)	2.70 (3)	3.360 (2)	141 (3)
N2—H2*AN*···Cl3^{vi}	0.87 (3)	2.34 (3)	3.198 (2)	170 (3)

N2—H2*BN*···Cl1[vii]	0.85 (3)	2.48 (3)	3.273 (2)	156 (2)
N2—H2*CN*···Cl1[viii]	0.93 (4)	2.29 (4)	3.194 (2)	164 (3)

Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*; (iv) *x*−1/2, −*y*+3/2, −*z*; (v) −*x*+1, −*y*+1, −*z*; (vi) *x*−1/2, *y*−1, −*z*+1/2; (vii) *x*−1/2, *y*, −*z*+1/2; (viii) −*x*+1, *y*−1/2, −*z*+1/2.