



# Synthesis and characterization of a new noncentrosymmetric organic–inorganic hybrid material $(C_5N_2ClH_6)_2[CdCl_{3.57}(H_2O)_{0.43}].Cl_{0.43}.H_2O_{1.57}$

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## ABSTRACT

The title organic–inorganic hybrid material,  $(C_5N_2ClH_6)_2[CdCl_{3.57}(H_2O)_{0.43}].Cl_{0.43}.H_2O_{1.57}$ , crystallizes in the non-centrosymmetric setting in the chiral space group  $P2_12_12_1$ . Its simplified structure consists of edge sharing  $[CdCl_4]^{2-}$  units that are connected with each other to form infinite  $\{[CdCl_2Cl_{4/2}]^{2-}\}_n$  anionic chains; of 2-amino-5-chloropyridinium cations (two for every cadmium ion); and of one localized water molecule. Areas with additional electron density, adding up to 12 electrons each, are found in the form of narrow tubes that stretch along the direction of the *a*-axis, but no meaningful model for these regions could be devised and the electron density in there was instead corrected for by back-Fourier transformation methods. In the solid state structure one of the chlorine atoms of the tetrachlorocadmium units is partially replaced by a water molecule in a 0.568 (7) to 0.432 (7) ratio, with charge balance achieved through partial replacement of an interstitial water molecule by a chlorine ion. This leads to an actual formula for the compound of  $(C_5N_2ClH_6)_2[CdCl_{3.57}(H_2O)_{0.43}].Cl_{0.43}.H_2O_{1.57}$  rather than the simplified  $(C_5N_2ClH_6)_2[CdCl_4].2H_2O$ . In the more prevalent cadmium units the metal centers have a distorted octahedral  $CdCl_6$  coordination sphere. In the remainder of the sites with one of the chlorines replaced by water, the coordination geometry is  $CdCl_5(OH_2)$  instead. The anionic and cationic units and the water molecules are connected through intricate  $O—H \cdots Cl$ ,  $N—H \cdots Cl$  and  $N—H \cdots O$  hydrogen bonding interactions, with three of these being three-center interactions. The exocyclic N atom is an electron receiving center, which is consistent with features of imino resonance evidenced by bond lengths and angles. Results from solid state <sup>13</sup>C and <sup>15</sup>N CP-MAS NMR spectroscopy are in good agreement with the X-ray structure. Density functional theory calculations allowed for the assignment of the carbon peaks to the independent crystallographic sites.

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## Introduction

Organic-inorganic hybrid materials with noncentrosymmetric structures are interesting for their application in various fields such as e.g. quadratic non-linear optical materials research [1]. Their abilities to combine the properties of organic and inorganic compounds within one single molecular scale leads to interesting crystal structures [2]. In these materials, the crystal packing is ensured by hydrogen bonds and coulombic interactions [3]. Polynuclear d<sup>10</sup>-metal complexes have been found to exhibit important structural and photoluminescent properties [4, 5]. Moreover, chloride-bridged cadmium(II) polymeric complexes are of considerable interest, because they may act as photoactive materials. As a contribution to the investigation of the above materials, we report here the crystal structure of one such compound,  $(C_5N_2ClH_6)_2[CdCl_{3.57}(H_2O)_{0.43}].Cl_{0.43}.H_2O_{1.57}$ , formed from the reaction of 2-amino-5-chloropyridine and cadmium chloride.

## Experimental

### Chemical preparation

A mixture of an aqueous solution of 2-amino-5-chloropyridine (3 mmol, 0.385 g), cadmium chloride (1.5 mmol, 0.275 g) and HCl (10 mL, 0.3 M) in a Petri dish was

slowly evaporated at room temperature. Colorless single crystals of the title compound were isolated after several days (yield 52 %). Elemental analysis calculated: C 21.84, H 2.91, N 10.19 %; found: C 21.67, H 2.65, N 10.05 %.

### Investigation techniques

#### X-ray diffraction

A single crystal was carefully selected under a microscope in order to perform its structural analysis by X-ray diffraction. The intensity data were collected on a Bruker AXS SMART APEX CCD diffractometer using the omega scan technique with MoK $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Data were collected, unit cell determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs [6]. The structure was solved with direct methods of SHELXS-97 [7] and refined with full-matrix least-squares techniques using the SHELXL-97 program [8] within WINGX [9]. All non hydrogen atoms were refined anisotropically. C-H hydrogen atoms were placed in calculated positions riding on their respective carrier atom with C—H in the range 0.93–0.98 and N—H in the range 0.86–0.89  $\text{\AA}$ .  $U_{iso}(H)$  values were constrained to be in the range of 1.2–1.5 times  $U_{eq}$  of that of the

parent atom. Water H atoms were located in difference density Fourier maps and their positions were refined with  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ . H atom H1D, coordinated to the partially occupied water molecule O1, was restrained to be at a distance of  $2.50(2) \text{ \AA}$  from Cl4. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1. The drawings were made with Diamond [10].

Reflection 0 1 1 was obstructed by the beam stop and was omitted from the refinement. One of the chlorine atoms is disordered over two positions in a ratio of  $0.568(7)$  to  $0.432(7)$ . In the major position, Cl4, the chlorine atom is located in bonding distance to the cadmium ion and completes the metal sphere to  $\text{CdCl}_6$ . The alternative location of the chloride anion, Cl4B, is an interstitial position far removed from the metal center. At both alternative positions the chlorine ions are disordered with water molecules that complete the site occupancies to one, O1 and O1B. The ADPs of the Cl and O sharing the Cd coordinated site, Cl4 and O1B, were constrained to be identical.

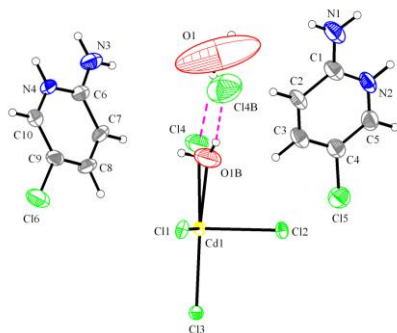
Areas filled with highly disordered solvate molecules stretch along the direction of the *a*-axis parallel to chains formed by the interstitial disordered chlorine ions and water molecules. No meaningful model for these regions could be devised and the electron density in there was instead corrected for using the Squeeze algorithm as implemented in Platon. Individual volumes were found to be  $29 \text{ \AA}^3$  in size and to contain each 12 electrons, thus indicating the presence of each one disordered water molecules per void.

#### NMR Spectroscopy and *ab initio* calculations

All NMR spectra were recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz for  $^{13}\text{C}$  and 30.30 MHz for  $^{15}\text{N}$ , with a classical 4 mm probehead allowing spinning rates up to 10 kHz. The chemical shifts are given relative to tetramethylsilane and glycine, respectively (external references, precision 0.5 p.p.m). The spectra were recorded by use of cross-polarization (CP) from protons (contact times 0.1 ms and 5 ms) and MAS. It was checked that there was a sufficient delay between the scans allowing a full relaxation of the nuclei.

#### IR Spectroscopy

The spectrum was recorded in the range  $4000 - 400 \text{ cm}^{-1}$  with a "Perkin-Elmer FTIR" spectrophotometer 1000 using a sample dispersed in spectroscopically pure KBr pressed into a pellet.



**Fig 1. View of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability level. H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are denoted as dashed lines.**

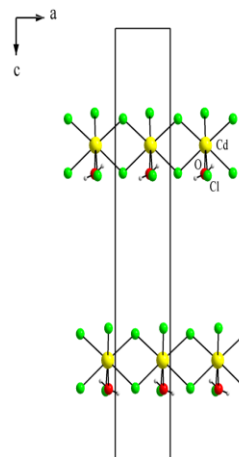
#### Thermal analysis

Thermal analysis was performed using the "multimodule 92 Setaram" analyzer operated between room temperature and  $420 \text{ }^\circ\text{C}$  with an average heating rate of  $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .

#### Results and discussion

##### Structure description

The title organic-inorganic hybrid material crystallizes in a non-centrosymmetric setting in the chiral space group  $P2_12_12_1$ . The structure is complicated by substantial disorder of chlorine ions with water molecules (Fig.1). If one ignores this disorder the structure can be described in more simple terms. In this basic structure three moieties can be found in the asymmetric unit: Edge sharing  $[\text{CdCl}_4]^{2-}$  anions combine with each other to form infinite  $\{[\text{CdCl}_2\text{Cl}_{4/2}]^{2-}\}_n$  anionic chains that stretch along the *a*-axis of the unit cell (Fig. 2). Two such chains cross the unit cell at  $z = (2n + 1)/4$  and  $y = 0.5$ . Between these chains 2-amino-5-chloropyridinium cations (two for every cadmium ion) are located, and one localized water molecule is found per building unit. Areas with additional electron density, adding up to 12 electrons each, are found in the form of narrow tubes that stretch along the direction of the *a*-axis. No meaningful structural model for these regions could be devised and the electron density in there was instead corrected for by back-Fourier transformation methods (the SQUEEZE method as implemented in Platon, [11]).

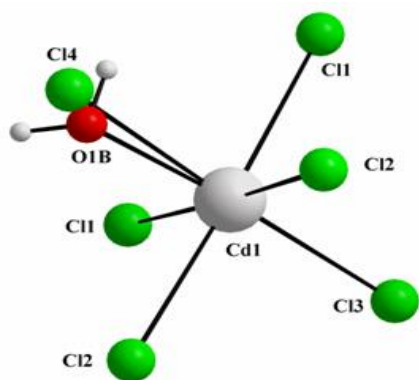


**Fig 2. A projection, along the b axis, of a part of the crystal structure showing the formation of anionic chains**

This basic structure is complicated by partial disorder of the chlorine and the water molecules. In the solid state structure one of the chlorine atoms of the tetrachlorocadmium units is partially replaced by a water molecule in a  $0.568(7)$  to  $0.432(7)$  ratio, with charge balance achieved through partial replacement of an interstitial water molecule by a chlorine ion. The chlorine ion thus disordered is not edge sharing between neighboring tetrachlorocadmium ions.

The disorder thus leads to an actual formula for the compound of  $(\text{C}_5\text{N}_2\text{ClH}_6)_2 [\text{CdCl}_{3.57}(\text{H}_2\text{O})_{0.43}] \cdot \text{Cl}_{0.43} \cdot \text{H}_2\text{O}_{1.57}$ , rather than the simplified  $(\text{C}_5\text{N}_2\text{ClH}_6)_2 [\text{CdCl}_4] \cdot 2\text{H}_2\text{O}$ . In the more prevalent cadmate units the metal centers have a distorted octahedral  $\text{CdCl}_6$  coordination sphere.

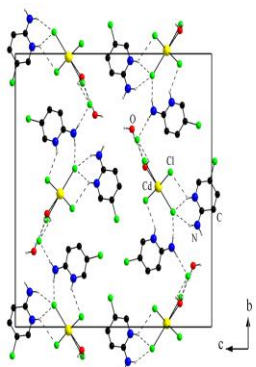
In the remainder of the sites with one of the chlorines replaced by water, the coordination geometry is  $\text{CdCl}_5(\text{OH}_2)$  instead (Fig. 3).



**Fig. 3** Coordination geometry around the Cd(II) cation in the studied compound

Cd—Cl distances in the octahedra are quite regular and range between 2.602(1) and 2.629(1) Å. Cd—Cl distances of edge sharing chlorine atoms are 2.6249 (8) (Cd1—Cl1), 2.6289 (8) (Cd1—Cl11), 2.6274 (8) (Cd1—Cl1<sup>1</sup>) and 2.6186 (8) (Cd1—Cl2<sup>1</sup>) Å (symmetry operator (i):  $x+1, y, z$ ). The Cd—Cl—Cd bridges can thus be regarded as symmetric. The shortest Cd···Cd distance within the chain is 3.809 (1) Å. The Cd—Cl distances of terminal chlorines are 2.6019(8) Å for the not disordered chlorine atom, and 2.608(3) Å for the chlorine atom partially replaced by water, and thus - as expected - a bit shorter than those of the bridging chlorine atoms. The Cl—Cd—Cl bond angles average exactly 90.0° and range between 86.80 (3)° (for Cl1—Cd1—Cl2) and 91.71(11)° (for Cl4—Cd1—Cl2), again confirming the close to symmetric octahedral nature of the CdCl<sub>6</sub> building units. The bond length of Cd1—O1B towards the partially occupied water molecule is 2.191(12) Å. A Mogul geometry check of these parameters against the entries of the Cambridge Crystallographic database (updates until Nov 2011) indicates the Cd—Cl/O bonds and Cl—Cd—Cl/O angles to be not unusual. All other bond distances and angles in the structure are also within their respective ranges.

The anionic and organic entities and the water molecules are connected through intricate O—H···Cl, N—H···Cl, N—H···O hydrogen bonding interactions, with three of these being three-center interactions, *viz.* N4—H4···(Cl2, Cl3), N3—H3B···(O1, Cl4B) and N2—H2A···(Cl1, Cl3) (Fig. 4, details and symmetry codes in Table 3). Weak intermolecular  $\pi$ - $\pi$  stacking interactions between neighbouring organic rings are observed with a face-to-face distance of 3.809 (1) Å.



**Fig. 4** A projection of the structure of  $(C_5N_2ClH_6)_2[CdCl_{3.57}(H_2O)_{0.43}].Cl_{0.43}.H_2O_{1.57}$  along the a axis direction. Hydrogen bonds are denoted as dashed lines

Examination of the organic moiety geometrical features shows that the N2—C1 and N3—C6 bond lengths of 1.334(6) and 1.318(5) Å, respectively, are approximately equal to a typical C=N double bond indicating that the nitrogen atoms N1 and N3 of the imino groups must be sp<sup>2</sup> hybridized. This is well supported by the angle values around N1 (C1—N1—H1A = C1—N1—H1B = H1A—N1—H1B = 120.0°) and N3 (C6—N3—H3A = C6—N3—H3B = H3A—N1—H3B = 120.0°).

All these features of the bond lengths and angles are consistent with an imino resonance form and suggest a substantial contribution from this resonance form to the title compound [12]. Furthermore, The C—N—C angles of pyridine are very sensitive to protonation. A pyridinium cation always possesses an expanded angle of C—N—C in comparison with parent pyridine.

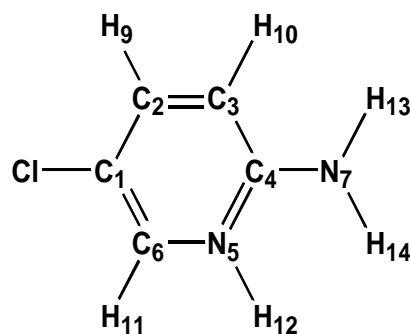
The angles of C1—N2—C5 [123.1(3)°] and C6—N4—C10 [123.2(3)°] are consistent with that of a pyridinium cation [13, 14]. The hydrogen atom H(N2) and H(N4), which are removed from their parent atoms, attach instead the pyridine nitrogen atoms. It is worth noticing that all these geometrical characteristics are in good agreement with those of the related tetrachlorozincate structure of the same cation, (C<sub>5</sub>H<sub>6</sub>ClN<sub>2</sub>)<sub>2</sub>[ZnCl<sub>4</sub>] [15].

#### NMR results

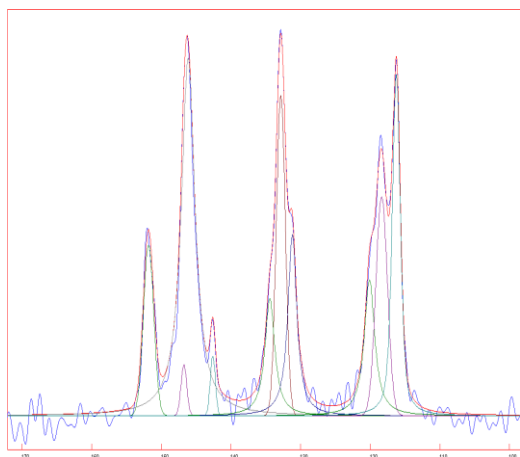
The <sup>13</sup>C CP—MAS—NMR spectrum of crystalline title compound is shown in Fig. 5 and 6. The spectrum displays seven resonances corresponding to the ten carbon atoms of the asymmetric unit.

This result is consistent with the presence of two organic moieties in the asymmetric unit of the compound, in agreement with the X-ray diffraction data.

Density functional theory (DFT) calculations were undertaken in order to assign the NMR resonances to the different crystallographically non-equivalent C atoms of the unit cell. These calculations were made at the B3LYP/6-31+G\* level using the GAUSSIAN98 program [16]. The different atoms were labeled as depicted below:



Three different calculations were made on the two non-equivalent organic cations in the unit cell and in all cases the theoretical chemical shifts were subtracted from those of the reference (tetramethylsilane) calculated at the same level of theory. Firstly, calculation of the NMR chemical shifts [with the Gauge-Independent Atomic Orbital (GIAO) method] by taking the geometry obtained from the X-ray diffraction data. Secondly, optimization of the positions of the H atoms in the molecule and calculation of the NMR chemical shifts in this semi-optimized geometry (X-ray diffraction always leads to underestimated X—H bond lengths, due to the fact that it is sensitive to the electron cloud and does not see the nuclei).

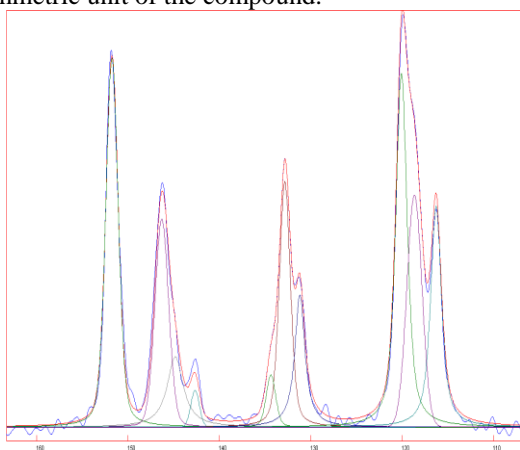


**Fig. 5 Experimental and simulated  $^{13}\text{C}$  CP-MAS NMR spectra of the studied compound for a contact time of 0.1 ms**

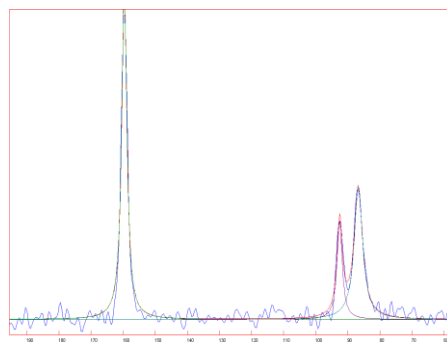
Thirdly, full optimization of all atoms and calculation of NMR chemical shifts. This calculation, compared with that above, will give indications of the steric hindrance around the organic cation and the positions where it is the strongest. The results are listed in Table 2.

There is a good agreement between the experimental and theoretical values calculated after optimization of the H-atom positions, allowing the unambiguous assignment of the different NMR signals to the various C atoms of the structure. The increase of the intensities of the peaks at about 120 and 152 p.p.m. with contact time from 0.1 ms (Fig. 5) to 5 ms (Fig. 6) proves that they correspond to two carbon atoms not bonded to H atoms.

It is worth noticing that the resonances at 134.4 and 142.7 p.p.m. are probably related to impurities. Fig. 7 shows the solid-state  $^{15}\text{N}$  CP-MAS-NMR spectrum of the title compound. The spectrum is also in good agreement with the X-ray structure. Indeed, the observation of three resonances (i.e. more than two signals) proves the presence of at least two organic moieties in the asymmetric unit of the compound.



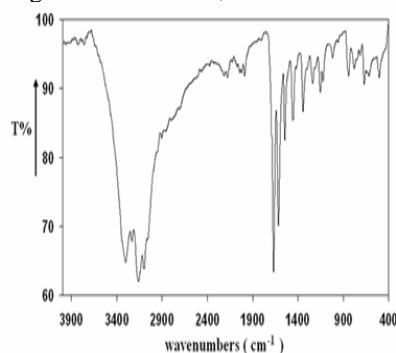
**Fig. 6 Experimental and simulated  $^{13}\text{C}$  CP-MAS NMR spectra of  $(\text{C}_5\text{N}_2\text{ClH}_6)_2[\text{CdCl}_{3.57}(\text{H}_2\text{O})_{0.43}]\cdot\text{Cl}_{0.43}\cdot\text{H}_2\text{O}_{1.57}$  for a contact time of 5 ms**



**Fig. 7 Experimental and simulated  $^{15}\text{N}$  CP-MAS NMR spectra of  $(\text{C}_5\text{N}_2\text{ClH}_6)_2[\text{CdCl}_{3.57}(\text{H}_2\text{O})_{0.43}]\cdot\text{Cl}_{0.43}\cdot\text{H}_2\text{O}_{1.57}$ .**

#### IR spectroscopy investigations

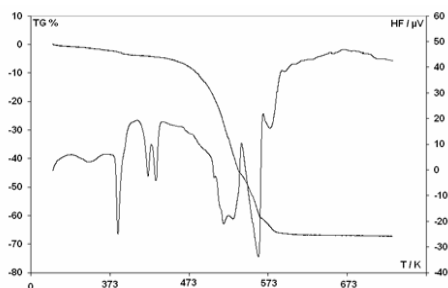
The IR spectrum of crystalline title compound is shown in Fig. 8. The most representative and characteristic vibrational modes of this compound can be compared to those of similar complexes [17]. The high-frequency region, between 3600 and 2800  $\text{cm}^{-1}$ , corresponds to the valence vibrations of C—H and N—H groups interconnected by a system of hydrogen bonds in the crystal [18]. Bands in the 1650 - 1100  $\text{cm}^{-1}$  region correspond to the N—H bending vibrations and to the valence vibrations of C—C, C—O and C—N groups [19]. The observed bands in the range 1000 - 600  $\text{cm}^{-1}$  can be attributed to the out of plane bending modes of C—H, C—C and C—N groups [20].



**Fig. 8 IR absorption spectrum of  $(\text{C}_5\text{N}_2\text{ClH}_6)_2[\text{CdCl}_{3.57}(\text{H}_2\text{O})_{0.43}]\cdot\text{Cl}_{0.43}\cdot\text{H}_2\text{O}_{1.57}$ .**

#### Thermal analysis

The simultaneous TGA-DTA curves of the title compound are given in Fig. 9. The DTA curve shows that this compound undertakes a series of endothermic peaks in a wide temperature range (323-460 K) corresponding to the complete dehydration of the compound. It is accompanied with a weight loss obviously observed on the TGA curve. From this latter, we deduced a departure of between one and two water molecules (% water: experimental 5.7 %, calculated for two water molecules 6.5 %). This agrees well with the assumption that water molecules not coordinated to the cadmium metal (1.57 per formula unit) are readily driven off, while the coordinated water molecule (0.43 per formula unit) is more tightly bound and only partially or not at all displaced during the TGA-DTA experiment. At 460 K the organic groups start to decompose over a wide temperature range (460-600K). This is also confirmed by the significant weight loss observed in the TGA. The mass of the black residue obtained at the end of the experiment, ca. 35%, agrees well with all organic moieties and HCl being driven off and  $\text{CdCl}_2$  being left behind (ca.33%).



**Fig. 9 DTA and TGA curves of  $(C_5N_2ClH_6)_2[CdCl_{3.57}(H_2O)_{0.43}].Cl_{0.43}.H_2O_{1.57}$  at rising temperature.**

#### Supplementary material

Crystallographic data for the title compound has been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC 850225). These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; mailto: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

#### Conclusion

The title compound was prepared as single crystals at room temperature and characterized by physicochemical methods. On the structural level, the atomic arrangement of this material consists of a network of  $[CdCl_4]^{2-}$  anions, 2-amino-5-chloropyridinium cations and water molecules connected by O—H...Cl, N—H...Cl, N—H...O hydrogen bonding interactions. The number of  $^{13}C$  and  $^{15}C$  CP-MAS-NMR components is in full agreement with the ones of crystallographically independent sites. Upon heating this salt loses its interstitial lattice water molecules. By heating at higher temperatures, the organic entities degrade and  $CdCl_2$  is left behind.

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**Table 1. Crystallographic data and refinement details of the title compound**

$C_{10}H_{16}CdCl_6N_4O_2$	$D_x = 1.904 \text{ g.cm}^{-3}$
Mr = 549.35	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Triclinic, $P2_12_12_1$	Cell parameters from 5404 reflections
$a = 3.8095 (6) \text{ \AA}$	$\theta = 3.0\text{--}30.8^\circ$
$b = 21.767 (4) \text{ \AA}$	$\mu = 2.05 \text{ cm}^{-1}$
$c = 22.356(4) \text{ \AA}$	$T = 100 \text{ K}$
$V = 1853.8(5) \text{ \AA}^3$	Crystal size: $0.4 \times 0.19 \times 0.17 \text{ mm}$
$Z = 4$	5509 independent reflections
$\varphi$ and $\omega$ scans	5395 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.586, T_{\max} = 0.746$	$R_{\text{int}} = 0.042$
Color : colourless	$\theta_{\max} = 30.8^\circ, \theta_{\min} = 3.0^\circ$
Goodness-of-fit on $F^2$ : 1.11	$-5 < h < 5$
16471 measured reflections	$-31 < k < 31$
Refinement on $F^2$	$-31 < l < 31$
$R[F^2 > 2\sigma(F^2)] = 3.3$	$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 0.2678P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.074$	$(\Delta/\sigma)_{\max} = 0.001$
212 parameters	$\Delta\rho_{\max} = 0.77 \text{ e \AA}^{-3}$
$F(000) = 1040.00$	$\Delta\rho_{\min} = -0.89 \text{ e \AA}^{-3}$

**Table 2. Selected bond lengths (Å) and angle (°) for the studied compound**

Cd1—Cl3	2.6019 (8)	C3—C4	1.385 (6)
Cd1—Cl4	2.608 (3)	C4—C5	1.355 (5)
Cd1—Cl2 <sup>i</sup>	2.6186 (8)	C4—Cl5	1.737 (4)
Cd1—Cl1	2.6249 (8)	N1—H1A	0.8800
Cd1—Cl1 <sup>i</sup>	2.6274 (8)	N1—H1B	0.8800
Cd1—Cl2	2.6289 (8)	N2—H2A	0.8800
Cl1—Cd1 <sup>ii</sup>	2.6274 (8)	N3—H3A	0.8800
Cl2—Cd1 <sup>ii</sup>	2.6185 (8)	N3—H3B	0.8800
Cd1—O1B	2.191 (12)	N4—H4	0.8800
C5—N2	1.347 (6)	O1—H1C	0.8476
C6—N3	1.318 (5)	O1—H1D	0.8562
C6—N4	1.367 (5)	Cl4B—H1C	1.7869
C6—C7	1.406 (5)	Cl4B—H1D	0.9595
C7—C8	1.376 (6)	O1B—H1E	0.8318
C8—C9	1.382 (6)	O1B—H1F	0.8364
C9—C10	1.370 (6)	C2—H2	0.9500
C9—Cl6	1.732 (4)	C3—H3	0.9500
C10—N4	1.357 (5)	C10—H10	0.9500
C1—N2	1.329 (6)	C7—H7	0.9500
C1—N1	1.334 (6)	C8—H8	0.9500
C1—C2	1.419 (5)	C5—H5	0.9500
C2—C3	1.358 (6)		

**Table 3. Hydrogen-bond geometry (Å, °) in (C<sub>5</sub>N<sub>2</sub>ClH<sub>6</sub>)<sub>2</sub>[CdCl<sub>3.57</sub>(H<sub>2</sub>O)<sub>0.43</sub>].Cl<sub>0.43</sub>.H<sub>2</sub>O<sub>1.57</sub>.**

<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>
O1B—H1F...Cl4B	0.84	2.20	3.013 (18)	164
O1B—H1E...Cl4B <sup>i</sup>	0.83	2.55	3.038 (18)	118
O1—H1D...Cl4	0.86	2.53	3.376 (14)	170
N4—H4...Cl3 <sup>iii</sup>	0.88	2.89	3.380 (3)	117
N4—H4...Cl2 <sup>iii</sup>	0.88	2.50	3.219 (3)	139
N3—H3B...O1 <sup>i</sup>	0.88	2.21	3.03 (3)	155
N3—H3B...Cl4B <sup>i</sup>	0.88	2.14	3.021 (6)	175
N3—H3A...Cl3 <sup>iv</sup>	0.88	2.40	3.230 (4)	157
N2—H2A...Cl1 <sup>v</sup>	0.88	2.85	3.438 (4)	125
N2—H2A...Cl3 <sup>v</sup>	0.88	2.61	3.379 (4)	147
N1—H1A...Cl3 <sup>v</sup>	0.88	2.49	3.279 (4)	150

**Table 4. Calculated and experimental carbon-13 and nitrogen-15 chemical shift in  $(C_5N_2ClH_6)_2[CdCl_{3.57}(H_2O)_{0.43}] \cdot Cl_{0.43} \cdot H_2O_{1.57}$ .**

Atom	No optimization		Optimization of all atoms	Optimization of protons		Experimental
	Ligand-1	Ligand-2		Ligand-1	Ligand-2	
C1	142.2	142.6	142.6	138.8	139.1	120.0
C2	148.3	150.1	157.7	152.1	154.2	146.3 144.8
C3	114.1	113.7	119.2	118.6	118.4	118.6 116.3
C4	151.1	152.9	154.9	151.5	153.1	151.8
C6	130.0	135.2	139.6	134.7	139.6	132.8 131.2
N5	110.8	105.1	88.7	94.9	89.1	92.6 86.7
N7	196.4	196.5	170.3	172.0	172.4	159.7