NMR, STRUCTURE AND SPECTROSCOPIC INVESTIGATIONS ON A CESIUM-AMMONIUM CADMIUM TRICHLORIDE

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Abstract

The structure of cesium-ammonium cadmium trichloride $Cs_{0.99}(NH_4)_{0.01}CdCl_3$, has been determined by X-ray single crystal analysis at room temperature. This material crystallizes in Ia-3 space group with $Z = 8$, and unit cell dimension $a = 10.4487(4)$Å. Several cycles of least squares refinement reduced the disagreement R(F) factor for 342 reflections to a final value of 0.01 and W_{R2} for 0.05. The compound structure consists of Cs^+(or NH_4^+) ions and $CdCl_6$ octahedra ensuring the stability of the structure by ionic and hydrogen bonding contacts N–H…Cl. The NH_4^+ substitution gives more orientation disorder in the structure at room temperatures. IR and Raman spectroscopy studied at room temperature were performed to confirm results of the X-ray diffraction.

1. Introduction

Compounds based on cadmium have attracted much attention because of their applications in optics and acoustics. These materials are also of special interest because they undergo structural transitions [1-5]. Crystals of $ABCl_3$ family (A being alkali and B = Cd, Mn), undergo phase transitions to structures that are slightly distorted from ideal Perovskite-type structures [6, 7]. The phase transition temperatures and the structures of the $ABCl_3$ (A = Cs and B = Cd, Mn) crystals are different from one another, but their phase transition mechanisms are distinguished as the quadruple and magnetic origin. The differences between the chemical properties of Cd and Mn are attributed to the nature of the phase transitions of these crystals. Therefore, the relaxation mechanisms of these different types of $ABCl_3$ crystals (quadruple and magnetic) are completely different NMR behaviour [7].

Mixed metal halides of the ABX_3 type [A = alkali metal, B = divalent metal Pb^{2+}, Cd^{2+} …, and X a halogen] belong to the Perovskite like structure, slightly distorted by cation displacements or by tilts of BX_6-octahedra as compared with the ideal cubic structure. The nature of the distortions is connected with the instability of lattice with respect to one or several vibration modes [8].

In this paper, we report the structure of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ at room temperature in order to examine the effect of the cationic substitution on symmetry related to the ammonium dynamics.

2. Experimental

2.1. Synthesis

$Cs_{0.99}(NH_4)_{0.01}CdCl_3$ was synthesized by dissolving a mixture of $CsCl$, NH_4Cl, and $CdCl_2$ in hot water, the chemical reaction is

$$(1-x)CsCl + xNH_4Cl + CdCl_2 \xrightarrow{\text{H}_2\text{O}} Cs_{0.99}(NH_4)_{0.01}CdCl_3.$$

Colourless thin rectangular parallelepiped crystals were grown after vapourizing in air for 18 days approximately.

2.2. X-ray structure determination

The crystal structure of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ was studied using an APEX II diffractometer with graphite-crystal monochromatic MoK_α radiation (0.71073Å). A total of 342 reflections were collected, among which only 114 reflections, namely those for which $Fo > 4\sigma(Fo)$, were used to determine and refine the structure. Corrections were made for Lorentz–polarization and absorption effects.

Data collection procedure and structure refinement at room temperature, are given in Table 1.

Table 1. Crystal structure data and experimental conditions of structure determination for $Cs_{0.99}(NH_4)_{0.01}CdCl_3$

Summary of crystallographic data T = 296(2) K	
Formula	$Cs_{0.99}(NH_4)_{0.01}CdCl_3$
Formula weight	350.367
Space group	Ia-3
a (Å)	10.4487(4)
Z	8
$V(Å^3)$	1140.74(8)
$\rho_{calc}(g/cm^3)$	4.306
$\mu(mm^{-1})$	13.025
Crystal size (mm^3)	$0.25 \times 0.16 \times 0.07$
Crystal shape	Parallelepipedic
F(000)	1280
Data collection instrument	Kappa-APEX II
Radiation. graphite monochromator	$\lambda_{K\alpha\,Mo}(0.71073Å)$
θ range for data collection $(°)$	4.78-33.11
Index ranges	$-10 \leq h \leq 11. -15 \leq k \leq 4. -6 \leq 1 \leq 15$
Total reflections	342
Reflection with $(F > 4\sigma(F))$	114
R(F) [a](%)	0.01
WR_2[b](%)	0.05
R_{int}-R_σ	0.018-0.020

$$^a R = \sum \|F_o|-|F_C\| / \sum |F_o|. \qquad ^b WR_2 = \left[\frac{\sum\left[w\left(|F_o|^2 - |F_C|^2\right)\right]^2}{\sum\left[w\left(|F_o|^2\right)\right]^2}\right]^{1/2}.$$

The cadmium atoms positions were determined by using a three dimensional Patterson synthesis. Chlorine, nitrogen, and cesium atoms were located by a three-dimensional Fourier function. The H atoms were located geometrically, and attributed isotropic thermal factors equal to those of the atoms on which they are linked. Structure solution and refinement were carried out by using (SHELX) programs [9, 10]. The non-hydrogen atoms were refined anisotropically. The atomic coordinates at room temperature are given in Table 2, the anisotropic displacement parameters in Table 3, the bond lengths and angles in Table 4.

Table 2. Fractional atomic and equivalent thermal parameters

Atoms	x	y	z	U_{eq}	Occupation	Sites
Cs	¼	¼	¼	0.0239(3)	0.992(2)	8b
N	¼	¼	¼	0.0239(3)	0.008(2)	8b
H1	0.20027(5)	0.20027(5)	0.20027(5)	0.029	0.008(2)	16c
H2	0.331(2)	0.221(8)	0.246(10)	0.029	0.001(0)	48e
Cd	0	0	0	0.0117(3)	1	8a
Cl	0.0004(2)	0	¼	0.0242(3)	1	24d

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a^*_i a^*_j a_i a_j.$

Table 3. Anisotropic displacement parameters (in 10^{-3}Å^2)

Atoms	U11	U22	U33	U23	U13	U12
Cs	0.0239(3)	0.0239(3)	0.0239(3)	0.00029(2)	0.0003(2)	0.0003(2)
N	0.0239(3)	0.0239(3)	0.0239(3)	0.0003(2)	0.0003(2)	0.0003(2)
Cd	0.0117(3)	0.0117(3)	0.0117(3)	0.00002(1)	0.00002(1)	0.00002(1)
Cl	0.0307(4)	0.0310(4)	0.0108(3)	– 0.0013(7)	0	0

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Table 4. Principal interatomic distances (Å) and bond angles (°) in $Cs_{0.99}(NH_4)_{0.01}CdCl_3$

Cs — Cl^i	3.691(2)	(i) y + 1/2. – z. x
Cs — Cl^{ii}	3.691(2)	(ii) – y. z + 1/2. – x + 1/2
Cs — Cl^{iii}	3.691(2)	(iii) – z. x. y + 1/2
Cs — Cl^{iv}	3.691(2)	(iv) z + 1/2. – x + /2. – y
Cs — Cl^v	3.691(2)	(v) x. y + 1/2. – z
Cs — Cl^{vi}	3.697(2)	(vi) – y– 1/2. z– 1/2. x
Cs — Cl^{vii}	3.697(2)	(vii) y + 1. – z. – x– 1/2
Cs — Cl^{viii}	3.697(2)	(viii) z + 1/2. x + 1. – y– 1/2
Cs — Cl^{ix}	3.697(2)	(ix) – z. – x– 1/2. y + 1
Cs — Cl^x	3.697(2)	(x) x + 1/2. – y – 1/2. z + 1/2
Cs — Cl^{xi}	3.697(2)	(xi) – x– 1/2. y + 1. – z
Cs — H1	0.9(1)	–
Cs — H2	0.9(1)	–
Cd — Cl^{xiv}	2.612(1)	(xiv) y. – z– 1/2. x– 1/2
Cd — Cl^{ii}	2.612(1)	(ii) – y. z + 1/2. – x + 1/2
Cd — C1	2.612(1)	–
Cd — Cl^{xii}	2.612(1)	(xii) – z – 1/2. x – 1/2. y
Cd — Cl^{iv}	2.612(1)	(iv) z + 1/2. – x + /2. – y
Cd — Cl^{xiii}	2.612(1)	(xiii) x – 1/2. y. – z– 1/2
Cd — Cs^{xiv}	4.524(2)	(xiv) – x. – y– 1/2. z
Cd — Cs^{xv}	4.524(2)	(xv) x + 1. – y. – z– 1/2
Cd — Cs^{xvi}	4.524(2)	(xvi) z– 1/2. x + 1/2. y + 1/2
Cd — Cs^{xvii}	4.524(2)	(xvii) x + 1/2. – y– 1/2. – z
Cd — Cs^{xi}	4.524(2)	(xi) – x– 1/2. y + 1. – z
Cl — Cd	2.612(2)	–
Cl — Cs^{xvi}	3.697(2)	(xvi) z– 1/2. x – 1/2. y + 1/2

Table 4. (continued)

Cl — Cs^{xvii}		3.697(2)	(xvii) x + 1/2. – y – 1/2. – z
Cl^i —	Cs — Cl^{ii}	180	(i) y + 1/2. – z. x
Cl^i —	Cs — Cl^{iii}	60	(ii) – y. z + 1/2. – x + 1/2
Cl^{ii} —	Cs — Cl^{iii}	120	(iii) – z. x. y + 1/2
Cl^i —	Cs — Cl^{iv}	90	(iv) – y– 1/2. z + 1/2. x + 1
Cl^{iv} —	Cs — Cl^{v}	180	(v) – y– 1/2. – z. – x– 1/2
Cl^i —	Cs — $H1$	144.7(2)	(vi) z + 1/2. x + 1. – y– 1/2
Cl^{ii} —	Cs — $H1$	35.3(1)	(vii) – z. – x– 1/2. y + 1
Cl^{iv} —	Cs — $H1$	90.04(2)	(viii) – z– 1/2. x– 1/2. y
Cl^{v} —	Cs — $H1$	89.96(2)	(ix) z + 1/2. – x + 1/2. y– ½
Cl^i —	Cs — $H2$	51(5)	(x) y. – z– 1/2.y– 1/2
Cl^{iii} —	Cs — $H2^{iii}$	105.4(11)	(xi) – x. – y– 1/2. z
Cl^{iv} —	Cs — $H2$	134(8)	(xiv) x + 1. – y. – z– 1/2
Cl^{vi} —	Cs — $H2$	102(8)	(xii) x + 1/2. – y– 1/2. – z
Cl^{vii} —	Cs — $H2$	78(8)	(xiii) z– 1/2. x– 1/2. y + 1/2
Cl^{ii} —	Cd — Cl^{viii}	90.10(5)	
Cl^{viii} —	Cd — Cl^{ix}	180	
Cl —	Cd — Cl^{x}	90.10(5)	
Cl^{xi} —	Cd — Cs^{xi}	54.67(4)	
Cl^{ii} —	Cd — Cs^{xi}	125.33(4)	
Cl —	Cd — Cs^{xiv}	125.19(4)	
Cs^{xi} —	Cd — Cs^{xiv}	109.5	
Cl^{x} —	Cd — Cs^{xii}	54.81(4)	
Cl^{xi} —	Cd — Cs^{xii}	125.33(4)	
Cd^{xiii} —	Cl — Cs^{xiii}	90.07(4)	

2.3. Spectroscopic analysis

The infrared absorption spectrum was carried out on a Perkin-Elmer 1750 spectrophotometer in the $4000\text{-}400\text{cm}^{-1}$ range on a pellet on powdered sample dispersed in KBr.

The Raman spectrum of polycrystalline samples sealed in glass tube was recorded on a Horiba Jobin yvon Raman spectrometer T64000 equipped with CCD detector. The spectrum was recorded in the region $400\text{-}10\text{cm}^{-1}$ with a resolution of 2cm^{-1}.

^{113}Cd MAS NMR spectra were measured on powdered crystals and glasses at 63, 637MHz with a Varian UNITY INOVA 400 MAS FT-NMR spectrometer. A single pulse sequence was used; for the crystals a pulse length of 2μs, the accumulation of 5343 and a pulse delay of 3s. A cylindrical zirconia rotor in which a sample was put, was rotated at a speed of about 8000Hz. A 1M of $Cd(ClO_4)_2$ aqueous solution was used as a standard.

3. Results and Discussion

3.1. Structure of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ description

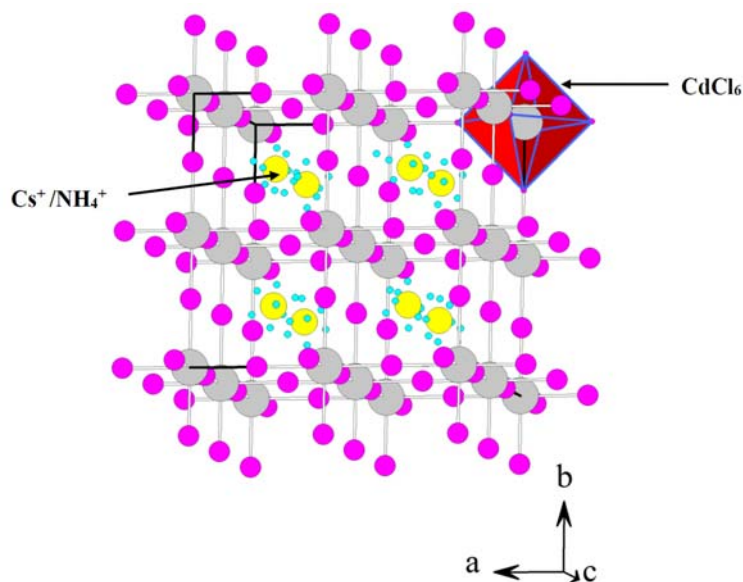The crystal structure of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ is presented in Figure 1.

Figure 1. Projection of the $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ structure.

At room temperature, $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ single crystals have an cubic structure with eight molecules per unit cell, and belong to the Ia-3 space group. The lattice parameters is a = 10.4487(4)Å at 293K. In this cubic phase, each Cd atom is surrounded by six Cl atoms, which form a nearly regular octahedron.

Cadmium atoms are located in the 8(a) sites (0, 0, 0) of the Ia-3 space group, surrounded by an octahedron chlorine atom in the 24(d) positions (0, 0, ¼). The Cs or N atoms occupy also the 8(b) sites (¼, ¼, ¼). The Cs^+ or NH_4^+ tetrahedra, reside in between the octahedra with Cs/N–H...Cl distances about 3.697(2) Å and Cl–Cs/N–Cl angles varying from 60º to 180º. The presence of NH_4^+ cations induces the coexistence of

H bonding contacts N–H...Cl, which providing a linkage between NH_4^+ cationic entities and $[CdCl_6]^{4-}$ anionic complexes. Nitrogen or cesium atoms are nine fold coordinated by Cl atom neighbors (Figure 3).

The nitrogen N occupies the (8b) (¼, ¼, ¼) Wyckoff position. Therefore to determine the hydrogen positions, there are three probable cases:

● Four special positions (8b or 8a).

● Two special positions (16a).

● One position of multiplicity of 32, is impossible because there is no Wyckoff position with this multiplicity in the Ia-3 space group.

We deduced that it is impossible to apply one of these cases, while taking into account a 0.9Å distance for the N–H bond.

For this reason, it was thought that in this structure the ammonium groups probably have an orientation disorder.

Therefore, two hydrogen atoms were placed in both (48e) general and (16c) special positions selected from the three-dimensional Fourier function, leading to a two-fold disorder model of the ammonium groups.

3.2. Influence of ammonium-substituting on the $CsCdCl_3$ structure

To understand the NH_4^+ substituted effect on halogenocadmate, the structures of $CsCdCl_3$, $Cs_{0.99}(NH_4)_{0.01}CdCl_3$, and NH_4CdCl_3 materials are compared.

Comparison with $CsCdCl_3$ [11] compound, we can deduce that the title compound crystallizes in the same structure but with a relative increase of the maximal cation-chlorine distances and a decrease of the minimal cation-chlorine distances. This variation is accompanied by a relative contraction of Cd–Cl bonds. The Cd–Cl distance values in $CsCdCl_3(2.64Å)$ [11] are relatively higher than those in $Cs_{0.99}(NH_4)_{0.01}CdCl_3(2, 612(1)Å)$ (Figure 2).
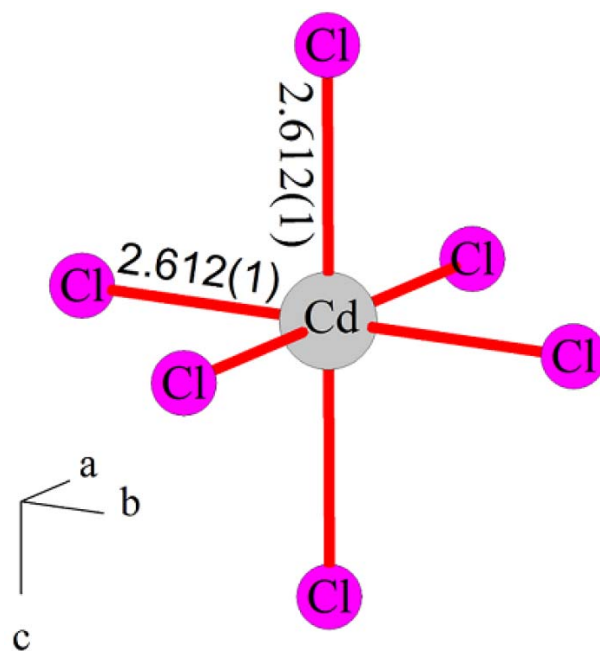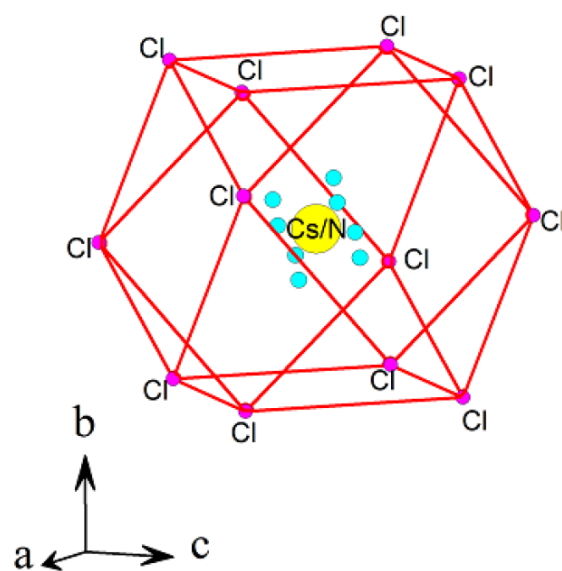
Figure 2. Cadmium environment.

Figure 3. Cs^+/NH_4^+ environment.

However, in the NH_4CdCl_3 material [12], these distances are slightly shorter than those observed in $CsCdCl_3$ and $Cs_{0.99}(NH_4)_{0.01}$ $CdCl_3$: $2.513(2) - 2.660(2)Å$. This fact suggests that the $CdCl_6$ octahedron adopts a rather geometry with shorter Cd–Cl distances in the pure ammonium compound.

Details of lattice parameters and the cell volume of $CsCdCl_3$, NH_4CdCl_3 and $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ materials are given in Table 5.

The net behaviour is a decrease of the unit cell volume as well as the "b" and "c" parameters with partial substituting cesium by ammonium.

Table 5. Lattice parameters, unit cell volume, and interatomic distances for $CsCdCl_3$, $Cs_{0.99}(NH_4)_{0.01}CdCl_3$, and NH_4CdCl_3 samples

Compounds	a(Å)	b(Å)	c(Å)	V(Å^3)	Cd–Cl(Å)	Cs/N–Cl(Å)
NH_4CdCl_3 [11]	9.026(3)	3.994(1)	14.938(4)	538.51	2.513(2) – 2.660(2)	3.278(6) – 3.818(8)
$Cs_{0.99}(NH_4)_{0.01}CdCl_3$	10.4487(4)	10.4487(4)	10.4487(4)	1140.74	2.612(1)	3.691(2) – 3.697(2)
$CsCdCl_3$ [12]	5.22	5.22	5.22	1131.366	2.64	3.82(1) – 3.84(3)

3.3. Vibrational studies

To have more information on the crystal structure, we have undertaken a vibrational study by using infrared spectroscopy and Raman scattering. The tentative assignments of the vibrations are based on a comparison of the infrared and Raman spectra of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ with other compounds based on cadmium [13].

The Raman and infrared peaks frequencies are quoted in Table 6.

Table 6. Wavenumbers (cm^{-1}) of the bands observed in the IR and Raman spectra at 298K of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ and their tentative assignments (ν: stretching; δ: deformation)

Wavenumbers (cm^{-1})	Raman	IR
500	—	$\delta(H_2O)$
2934	—	$\delta_s(NH_4{}^+)$
1640	—	$\delta_s(NH_4{}^+)$
1374	—	$\delta_{as}(NH_4{}^+)$
50	Lattice mode translation	—
76	Cs^+ translation	—
95	Cl^- translation	—
110	$CdCl_2$ libration	—
147	$NH_4{}^+$ translation	—
208	$NH_4{}^+$ libration	
232	$\nu(Cd-Cl)$	

The IR spectra of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ (Figure 4) were recorded for the wave number region between 4000 and $400cm^{-1}$. The IR spectra show, at high wave numbers, a band at $3500cm^{-1}$ may be assigned to the deformation H_2O vibration, and a band observed at $2934cm^{-1}$ relative

to the $\delta(NH_4^+)$ stretching modes. The symmetric and asymmetric bending vibration of (NH_4^+) appears in two bands at 1640 and $1374cm^{-1}$.
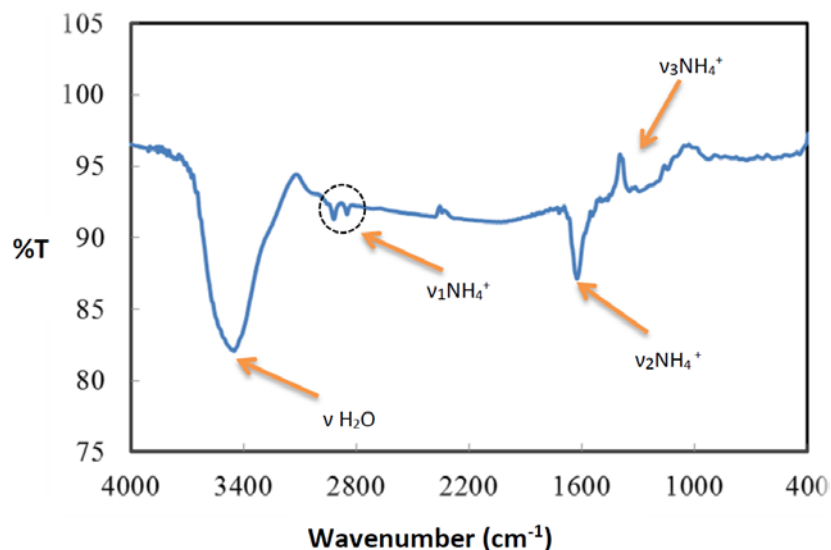

Figure 4. Infrared absorption spectrum of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$.

The Raman spectrum of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ was recorded in the external region of the sub-lattice vibrations, $400\text{-}50cm^{-1}$ (Figure 5).

Compared with mercury compounds [13], the observed Raman lines at $50cm^{-1}$ is associated to the lattice mode translation. The bands at 147 and $208cm^{-1}$ correspond to the NH_4^+ libration. The band at $110cm^{-1}$ corresponds to the $CdCl_2$ libration of the layers and the chains. We have assigned the band at $95cm^{-1}$ and the shoulder at $76cm^{-1}$ to the translation mode of Cl^- anion and to the translation mode of Cs^+ cation, respectively.

From these vibrational studies, we can confirm the presence of the ammonium groups in the structure.
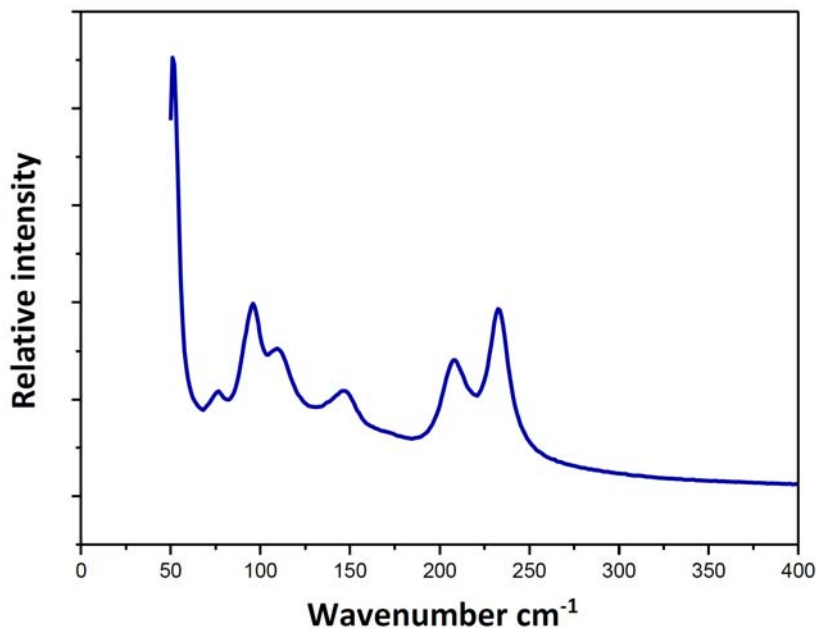

Figure 5. Low-frequency Raman spectra of $Cs_{0.99}(NH_4)_{0.01}CdCl_3$.

3.4. NMR spectroscopy

$Cs_{0.99}(NH_4)_{0.01}CdCl_3$ with a cubic structure is expected to have a seven-line NMR spectrum due to the quadruple interactions of $^{113}Cd(I = 7/2)$. Instead of seven resonance lines, the ^{113}Cd nuclei in $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ produce only one resonance line in the temperature range 160-400K, as shown in Figure 6. This result indicates that we have only one local structure around the Cd atoms. The same behaviour was detected in cadmium thiocyanate compounds [14]. According to this result provided by the NMR measurements at room temperature, we can confirm the octahedral coordination for cadmium atoms, which confirms the results of the single crystal measurements.
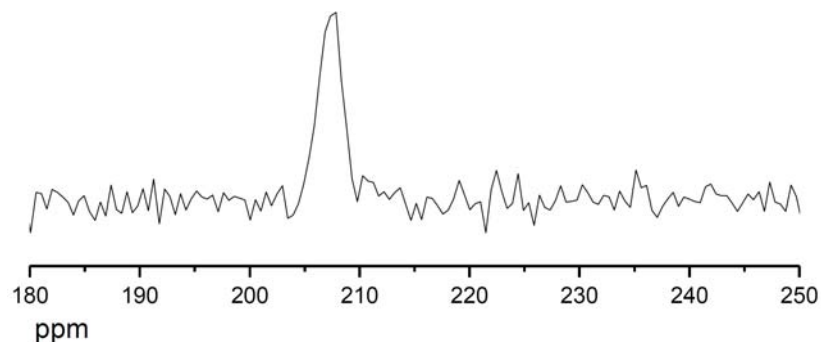
Figure 6. NMR spectrum for ^{113}Cd in $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ at room temperature.

4. Conclusion

In conclusion, we have successfully prepared a novel substituted halogenocadmate $Cs_{0.99}(NH_4)_{0.01}CdCl_3$ via slow evaporation method. The crystal structure of the title compound is characterized by $CdCl_6$ octahedra. The cesium or ammonium cations are inserted between these octahedra ensuring the stability of the structure by ionic and hydrogen bonding contacts N–H...Cl.

The ammonium substitution in $CsCdCl_3$ material gives more disorder of the ammonium groups in the structure and leads to a decrease of the unit cell volume as well as the "b" and "c" parameters. However, we noted an increase of the "a" parameter. This finding appears to reflect the difference of between the ionic radii of Cs^+ and NH_4^+ cations.

In addition, analysis by IR spectroscopy and Raman scattering confirms the presence of ammonium group and $CdCl_6$ octahedra in our compound.

MAS-NMR spectrum of ^{113}Cd confirms the octahedral coordination of cadmium in the structure.

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