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Synthesis, infra-red, MAS-NMR characterization, structural study and electrical properties of the new compound $[C_5H_6ClN_2]_2Cd_3Cl_8$

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ABSTRACT

A new organic inorganic compound, octachlorocadmate of bis (4-amino-2-chlorinopyridinium) $[CAP]_2Cd_3Cl_8$, has been synthesized and is characterized by a single-crystal X-ray diffraction. It crystallizes in monoclinic space group $P2_1/C$ (N°: 14) with the parameters $\underline{a}$ = 3.8039 (2) Å, $\underline{b}$ = 23.26510 (10) Å, $\underline{c}$ = 12.8800 (2) Å, $\underline{\beta}$ = 95.7100 (10)°, V = 1134.20 (6) Å^3, Z = 2. This compound shows the presence of the organic cations as spacers between the inorganic layers that can be visualized as triple chains of edge-shared $CdCl_6$ extending in the *ac* plane and are combined by static attracting forces in the crystal and π–π interactions which reinforce the association between cations. The studies by FT-IR and TGA show the presence of the surface water molecule. The MAS-NMR spectra showed two and five isotropic resonances, ^{111}Cd and ^{13}C, respectively. The dielectric conductivity of this compound has been measured in the temperature range 303–418 K and the frequency range 209 Hz–5 MHz. The Cole–Cole (Z' versus Z'') plots are well fitted to an equivalent circuit model. The analysis of the experimental data based on the jump relaxation model, showed that translation motion of the charge carrier and reorientation hopping between equivalent sites of the metal chloride anion and the cation groups are responsible for the observed conductivity in the temperature regions (I) (303–348 K) and (II) (373–413 K).

1. Introduction

The octachlorocadmate of bis (4-amino-2-chlorinopyridinium) has been synthesized as part of a major research area in order to study the interesting properties of organic–inorganic complexes. These salts offer, scientifically and technologically significant opportunities in different areas of catalysis, optical properties, biology, magnetic functional materials, and electronic [1–9]. The general formula in this family is $A_2[MX_4]$ where M = metal, transition metal, X = Cl, Br, I and A is an organic cation. A wide variety of these complexes is known where the A-group is a protonated alkyl amine [10–12], or heterocyclic such as pyridine [13,14]. In this case the Cd(II) ion has been chose, because it adopts a variety of coordination numbers and geometries [15–20], depending on crystal packing, hydrogen bonding and halide dimensions and the use of pyridine as templating agents in supramolecular chemistry [21,22] has led to some success in the preparation of materials with interesting physical properties. For this purpose 4-amino-2-chloropyridine is chosen.

In this paper, a detailed single-crystal structure refinement is presented, the FT-IR spectroscopy, the MAS-NMR ^{111}Cd and ^{13}C, the differential scanning calorimetry are reported and discussed. The results of the simulation of the complex impedance are also reported by an equivalent circuit and conductivity measurements as related to the conduction mechanism in the temperature range 303–418 K and the frequency range 209 Hz–5 MHz for $[CAP]_2Cd_3Cl_8$ compound.

2. Experimental

2.1. Synthesis of $[CAP]_2Cd_3Cl_8$ compound

The 4-amino-2-chloropyridine (52.25 mg) was dissolved in concentrated acid of HCl 38%. Then stoichiometric quantities of cadmium chloride (molar ratio 2:3) were added and were stirred for a few minutes. Colorless single crystals suitable for X-ray structure determination were obtained from the mother liquor by slow evaporation at room temperature over several days.

2.2. Characterization

The FT-IR spectra were obtained using a Nicole Impact 410 FT-IR spectrophotometer with a sample depressed in KBr pellet in the 400–4000 cm^{-1} region. The thermal behavior was studied under an air flow in Mettler Toledo DSC 822^e calorimeter and Perkin Elmer Pyris 6 TGA equipment, at a heating rate of 5 K min^{-1}.

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The MAS NMR of ^{13}C (75.47 MHz with acquisition number 12540) and of ^{111}Cd (63.64 MHz with acquisition number 11456) were registered at room temperature by means of a spectrometer Brucker DSX-300 with a classical 4 mm probe head allowing spinning rates up to 8 kHz. The chemical shifts were referenced relatively to tetramethylsilane and to 0.1 M Cd(ClO4)2 aqueous solution, respectively. In all cases, it was checked that there was a sufficient delay (5.000 s) between the scans allowing a full relaxation of the nuclei.

2.3. Electrical measurements

The compound fine powder was cold pressed into a cylindrical pellet of an 8 mm diameter and 1.2 mm thickness at a pressure of $4 \times 104\ Nm^2$ using a hydraulic press. In order to study the electrical/impedance properties of the compound, the pellet was undertaken using the impedance method on a TEGAM 3550 ALF, automatic bridge monitored by a microcomputer, between 303 and 413 K (with the rate of $5\ K\ min^{-1}$) with the signal frequency ranging from 209 Hz to 5 MHz.

2.4. Crystal data and structure determination

A single crystal was selected in order to perform its structural analysis by an X-ray diffraction. The intensity data were collected on a Bruker AXS CCD area detector system equipped with graphite monochromatic MoKα radiation (0.71073 Å) at 292(2) K. Lattice parameters were refined from setting angles of 446 reflections in the $3.1 < \theta < 29.6°$. The empirical absorption corrections were based on a multi-scan. A total of 8198 reflections were collected using the ω–2θ scan technique of which 1975 have $I > 2\sigma(I)$ and were used for the structure determination. Then the structure was solved by the automated Patterson method using SHELXS 86 [23] and SHELXL 97 [24] programs, which readily established the heavy atom position and facilitated the identification of the light atoms from difference Fourier maps. The pertinent experimental details of the structure determination for the new compounds are presented in Table 1. All the hydrogen atoms were placed geometrically and refined isotropically. The last cycle of refinement included the atomic coordinates for all the atoms, anisotropic thermal parameters and isotropic thermal whose values are listed in Table 2 and Table 3.

3. Results and discussion

3.1. Structure description

The asymmetric unit of $[C_5H_6Cl\ N_2]_2Cd_3Cl_8$ is shown in Fig. 1, it consists of two atoms of cadmium Cd1 and Cd2. The Cd2 is located in a special position, which is the center of inversion and gives in both sides the Cd1 forming infinite triple chains with edge-shared $[Cd_3Cl_8]^{2-}$. The $[CdCl_6]$ octahedra are slightly distorted octahedral geometry, the bond angles of Cl—Cd—Cl are in the range of 80.92–168° and deviate slightly from the ideal octahedral values (90° and 180°). The bond lengths and angles are listed in Table 4.

The packing of $[CAP]_2Cd_3Cl_8$ viewed along *a* axis created with DIAMOND [25] (Fig. 2a) shows an alternation of organic and inorganic layers. The Fig. 2b shows that the inorganic part is formed by an infinite layer of $[Cd_3Cl_8]^{2-}$ extending the *ac* plane. The infinite anions chains were formed, by sharing on the one hand the chlorides of the square plan, and on the second hand they were linked by the axial chlorides (Fig. 2c). Both types of bonds formed the tetrahedral empty sites between the octahedral environments in the same layer.

Table 1
Crystal data and structure refinement for $[CAP]_2Cd_3Cl_8$ crystal.

Crystal data	
Empirical formula	$[(C_5H_6ClN_2)_2]Cd_3Cl_8$
Formula weight	879.94
Crystal system	Monoclinic
Space group:	P 21/c (N°14)
Hall symbol:	−P 2ybc
Unit cell dimensions	
a (Å)	3.8039(2)
b (Å)	23.26510(10)
c (Å)	12.8800(2)
α (°)	90.00
β (°)	95.7100(10)
γ (°)	90.00
Volume (Å^3)	1134.20(6)
Z	2
D_{calc} (g cm^{-3})	2.577
Absorption coefficient (mm^{-1})	3.971
F(000)	826.25
Crystal dimensions (mm)	0.32 × 0.25 × 0.22
Crystal color	Plate, colorless
θ Range for data collection (°)	$\theta_{max} = 29.6°$, $\theta_{min} = 3.1$
Data collection	
Reflections collected	8198
Independent reflections	2723
Reflections with $I > 2\sigma(I)$	1975
Limiting indices	$h = -4 \rightarrow 4$ $k = -30 \rightarrow 31$ $l = -15 \rightarrow 16$
CCD area detector diffractometer Radiation source: fine-focus sealed tube graphite φ and ω scans absorption correction: multi-scan	$T_{min} = 0.348$, $T_{max} = 0.470$
Refinement	
$R[F^2 > 2\sigma(F^2)]$	0.0247
$wR(F^2)$	0.0342
Goodness-of-fit on F^2	$S = 1.112$
Data/restraints/parameters	2723/0/125
Extinction coefficient	0.0000
$\Delta\rho_{max}$ (e Å^{-3})	0.757
$\Delta\rho_{min}$ (e Å^{-3})	−0.642

$w = 1/[\sigma^2(Fo^2) + (0.0000P)^2 + 0.0000P]$ where $P = (Fo^2 + 2Fc^2)/3$.
$(\Delta/\sigma)_{max} < 0.001$. Extinction correction: SHELXL.

Table 2
Atomic coordinates and equivalent thermal factors of agitation U_{eq} (Å^2) and isotropic U_{iso} (Å^2)* in $[CAP]_2Cd_3Cl_8$ crystal.

	X	*Y*	*Z*	*Uiso*/Ueq*
Cd1	0.59972(6)	0.06098(1)	0.75023(2)	0.0113(1)
Cd2	1.00000	0.00000	0.50000	0.0116(1)
Cl1	0.6105(2)	0.15636(4)	0.84081(8)	0.0138(3)
Cl2	1.1356(2)	0.01303(4)	0.85497(7)	0.0124(3)
Cl3	1.0417(2)	0.09400(4)	0.61305(7)	0.0113(3)
Cl4	0.5443(2)	−0.03617(4)	0.62435(7)	0.0113(3)
Cl5	−0.1758(2)	0.18388(4)	0.38807(8)	0.0206(3)
N1	0.2121(7)	0.10709(13)	0.0493(3)	0.0170(10)
N2	0.0322(7)	0.24377(13)	0.2350(3)	0.0161(10)
C1	−0.0305(8)	0.18961(17)	0.2670(3)	0.0131(11)
C2	0.0226(8)	0.14324(16)	0.2067(3)	0.0127(11)
C3	0.1487(8)	0.15115(16)	0.1090(3)	0.0126(11)
C4	0.2121(9)	0.20825(16)	0.0781(3)	0.0138(11)
C5	0.1541(8)	0.25259(17)	0.1409(3)	0.0166(14)
H1A	0.17626	0.07264	0.07006	0.0203*
H1B	0.28929	0.11278	−0.01037	0.0203*
H2	−0.02424	0.10645	0.22992	0.0152*
H2A	−0.00537	0.27256	0.27426	0.0192*
H4	0.29490	0.21515	0.01369	0.0164*
H5	0.19816	0.28987	0.11953	0.0200*

The protonated 4-amino-2-chloropyridinium molecules are located in the cavities formed by the infinite triple chains of edge-