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Synthesis and Characterization of Poly[bis 4-methoxybenzylammonium] tetra-μ-chlorido-cadmate (II)

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ABSTRACT

The crystal structure of the new inorganic-organic hybrid compound $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ has been determined by single crystal X-ray diffraction The compound crystallizes in the triclinic space group $P\bar{1}$ with lattice parameters a = 19.007(2), b = 7.3410(8), c = 7.4451(8) Å, , β =97.222(1)°, V = 1030.59(19) Å^3, and Z = 2. The framework of the title compound is built upon layers parallel to (100) made up from corner-sharing $[CdCl_6]$ octahedra. 4-methoxybenzylammonium cations are situated between the layers and connect them via an N-H…Cl hydrogen-bonding network. The Cd atom is located on an inversion centre and the coordination environment is described as distorted octahedra. Solid state ^{13}C CP-MAS NMR spectroscopy is in agreement with the X – ray structure. DFT calculations allow the attribution of the carbon peaks to the independent crystallographic sites. Thermal analysis and Infrared spectroscopy were also used to characterize the complex.

Introduction

Organic-inorganic hybrid materials have received extensive attention in recent years owing to their great specific properties, such as electronic, optical, thermal and catalytic [1,2]. Among halometallates (II), chlorocadmates (II) have been of special interest for their structural flexibility. They can occur as simple tetrahedral anions CdX_4^{2-} or form the backbone of chain polymers. This is due to the fact that the Cd^{2+} ion, being a d^{10} transition metal ion, exhibits a great variety of coordination numbers and geometries, depending on crystal packing and hydrogen bonding, as well as halide dimensions [3-8]. A wide variety of stoichiometries belonging to this class of compounds makes the crystal chemistry of chlorocadmates extremely diverse and complex. Common features of all these compounds are the invariable presence of octahedral ($CdCl_6$) units in the anhydrous species. A network of hydrogen bonding, involving organic cations generally connects the inorganic anions together and stabilizes the whole crystal structure [9-11].

As a part of our ongoing investigations in molecular salts containing meta-chlorido complexes [12, 13], we present here the crystal structure of one such compound, $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$.

Experimental

Chemical preparation

4-methoxybenzylamine (2 mmol, 0.274 g) and $CdCl_2$ (1 mmol, 0.183 g), were dissolved in dilute HCl (10 mL, 1 M) and the resultant solution was slowly evaporated at room temperature. A crystal of the title compound, which remained stable under normal conditions of temperature and humidity, was isolated after several days and subjected to X-ray diffraction analysis (yield 42%). Elemental analysis calculated: C 36.18, H 4.52, N 5.27 %; found: C 36.37, H 4.65, N 5.05 %.

Investigation techniques

The characterization of these salts was carried out using X-ray diffraction, solid state NMR spectroscopy, DFT calculations, Infrared spectroscopy, and thermal analysis (differential thermal analysis, DTA, and thermal gravimetric analysis, TGA).

X-ray diffraction

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 omega scan technique with MoKα radiation (λ = 0.7107 Å). The structure was solved with direct methods using SHELXS-97 [14] and refined with full-matrix least-squares techniques using SHELXTL-6.14 [15]. The drawings were made with Diamond [16]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

NMR spectroscopy

The ^{13}C NMR spectrum was recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ^{13}C NMR chemical shifts are given relative to tetramethylsilane (external references, precision 0.5 ppm). The spectrum was recorded by use of cross-polarization (CP) from protons (contact time 5 ms) and MAS. Before recording the spectrum it was checked that there was a sufficient delay between the scans allowing a full relaxation of the protons.

IR Spectroscopy

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

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Thermal analysis

Thermal analysis was performed using the "multimodule 92 Setaram" analyzer operated between room temperature and 250°C with an average heating rate of 5 °C.min^{-1}.

Results and discussion

X-ray diffraction study

The main geometrical features of the different chemical entities of the coordination compound [4-$OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ are reported in Tables 2 and 3.

The asymmetric unit of the title compound (Fig. 1) contains one 4-methoxybenzylammonium and a half of $CdCl_4^{2-}$ fragment. Packing of [4-$OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ viewed along *a*-axis (Fig. 2) shows a layer of corner sharing $[CdCl_6]$ octahedra. The shortest Cd-Cd distance within a layer is 5.228 (5) Å. In the structure, two symmetric independent chlorine atoms are observed (Cl1, Cl2) and only Cl1 forms a bridge between two cadmium centers. In this way, the chlorine atoms form a distorted octahedron around each cadmium atom (Fig. 3), giving the overall stoichiometry for the anions of $[CdCl_2(Cl_{1/2})_4]^{2-}$.

The Cd atom is located on an inversion centre. The two symmetric bridging Cd-Cl distances are long [2.6586(5) and 2.6613(5) Å] while the terminal Cd-Cl distances are close to 2.5571(5) Å, which is typical of six coordinated Cd(II) [17]. The Cl—Cd—Cl bond angles average exactly 90.0° and range between 87.20 (2)° for $Cl2^{i}$—Cd1—$Cl1^{iii}$ and 92.50 (2)° for $Cl2^{i}$—Cd1—$Cl1^{ii}$ (details and symmetry codes in Table 2), again confirming the close to symmetric octahedral nature of the $CdCl_6$ building units.

In this structure, the 4-methoxybenzylammonium cationic group compensates the negative charge of half $CdCl_4^{2-}$ anion leading to neutrality for the structure as a whole. $CdCl_6$ octahedra and the 4-methoxybenzylammonium cations connected via hydrogen bonds N1—H1D···Cl1, N1—H1C···Cl2 and N1—H1E···Cl2 (Fig. 4, details and symmetry codes in Table 3). All the chlorine atoms of the $CdCl_6$ octahedron participate in hydrogen bonding, as well as all hydrogens that are attached to N1.

Intermolecular π-π stacking interactions between neighboring aromatic rings are also observed with a face-to-face distance of 3.723(5) Å, less than 3.8 Å, the maximum value regarded as relevant for π-π stacking interactions [18]. The interlayer space is large enough to allow only minimal distortions of 4-methoxybenzylamonium cation. The angles and atom the cation have their usual values as reported for the related compound with the same cation, 4-Methoxyphenyl) methanaminium chloride [19].

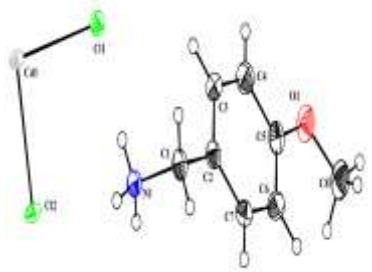

Fig. 1
Asymmetric unit of [4-$OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ with atom labels and 50% probability displacement ellipsoids for non- H atoms

Fig. 2
Projection of [4-$OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ structure in the plane (b, c). The dotted lines indicate hydrogen bonds. A polyhedral representation is given for $[CdCl_6]$.

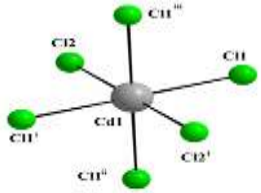

Fig. 3
Coordination geometry of Cd(II) ions in [4-$OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$. Symmetry codes: (i) −*x*, −*y*+1, −*z*+2; (ii) *x*, −*y*+1/2, *z*+1/2; (iii) −*x*, *y*+1/2,

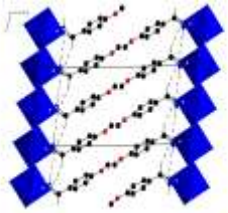

Fig. 4
Projection of [4-$OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ structure along the b-axis. The dotted lines indicate hydrogen bonds. A polyhedral representation is given for $[CdCl_6]$.

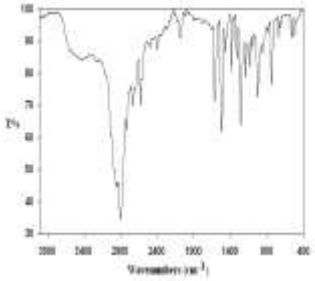

Fig. 5
IR absorption spectrum of [4-$OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$

An examination of the bond length data in Table 2 shows that C5-O1 [1.367(3) Å] is shorter than C8-O1 [1.428(3) Å] which is probably due the mesomeric effect of the methoxy group. These distances are in good agreement with those of Bis(5-chloro-2,4-dimethoxyanininium) tetrachlorozincate trihydrate [20].

IR Spectroscopy

The IR spectrum of crystalline [4-$OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ is shown in Figure 5. The most representative and characteristic vibrational modes of this compound can be compared to those of similar complexes [21]. Some aspects of the performed assignments are briefly commented as follows:

- In the high-frequency region, the broad band between 3600 and 2700 cm^{-1} corresponds to the valence vibrations of C-H and N-H groups [22].
- The observed bands in the 1620-1200 cm^{-1} region can be attributed to the bending vibrations of N-H groups and to the valence vibrations of C=C, C-O and C-N groups [23].
- The bands between 1000 and 700 cm^{-1} are assigned to out of plane bending modes $\gamma(C_{ary}\text{-H})$ and $\gamma(C_{ary}\text{-C})$ [24].

Thermal analysis

Two curves corresponding to DTA and TGA analysis of $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ in open air are given in Figure 6. The DTA curve shows that this compound undergoes a succession of endothermic phenomena. It is worth noting that the most important peak, observed at 493 K, corresponds to the melting point of the complex, which is in good agreement with the result obtained by the capillarity tube method. Then, the product undergoes a degradation of the organic group over a wide temperature range (500-773 K). This is also confirmed by the significant weight loss observed in the TGA curve. A black deposit of carbon is obtained at the end of the experiment.

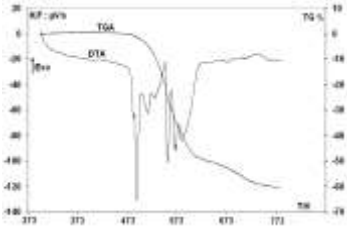

Fig. 6

DTA and TGA curves of $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$ at rising temperature.

NMR spectroscopy

The ^{13}C CP-MAS NMR spectrum of the title compound is shown on Figure 7. It displays 7 well-defined resonances, showing that the asymmetric unit cell should contain only one organic molecule. Theoretical calculations were then undertaken in order to assign the NMR resonances to the different crystallographically inequivalent carbon atoms of the unit cell. These calculations were made at the B3LYP/6-31+G* level. Three different calculations were made on the organic cation and in all cases the theoretical chemical shifts were subtracted from those of the reference (tetramethylsilane) calculated at the same level of theory:

(1) Calculation of the NMR chemical shifts (with the GIAO method) by taking the positions of atoms obtained by X-ray diffraction;

(2) Optimization of the positions of the protons in the above molecule and calculation of the NMR chemical shifts in this semi-optimized geometry. Indeed X-ray diffraction leads always to underestimated X-H bond lengths, due to the fact that it is sensitive to the electronic cloud and does not see the nuclei;

(3) Full optimization of all atoms and calculation of NMR chemical shifts. This calculation, compared to the above one will give indications on the steric hindrance around the organic cation and on the positions where it is the strongest.

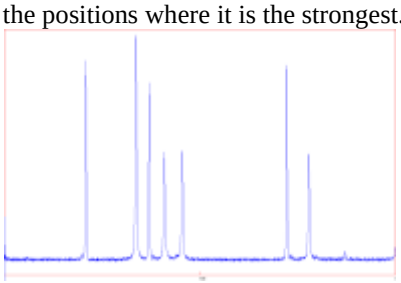

Fig. 7

^{13}C CP-MAS NMR spectrum of $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$.

The results are listed in Table 4 while Figure 8 shows the correlation between experimental and calculated values (after optimization of the protons positions). Clearly, there is a good agreement between the experimental and theoretical values calculated after optimization of the position of the protons, allowing unambiguously the attribution of the different NMR signals to some carbon atoms of the structure. The fact that the slope of the correlation curve is not 1 is probably related to the calculation method used.

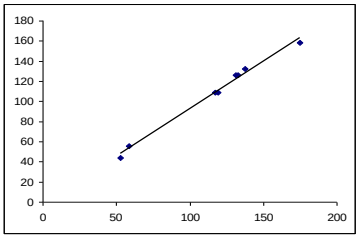

Fig.8

Comparison between experimental and calculated carbon-13 chemical shifts in $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$.

Supplementary material

Crystallographic data for the title compound have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC 851463). These data can be obtained free of charge at 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).*

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 and 4-methoxybenzyl-ammonium cations connected by N—H···Cl hydrogen bonding interactions. The number of ^{13}C CP-MAS-NMR components is in full agreement with the ones of crystallographically independent sites. Upon heating this salt is stable until 473 K and then the organic entities degrade.

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Table 1. Cristallographic data and refinement details of the title compound

$C_{16}H_{24}CdCl_4N_2O_2$	$F(000) = 532$
$M_r = 530.57$	$D_x = 1.710$ Mg m^{-3}
Triclinic, $P_{2_1/C}$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 19.007$ (2) Å	Cell parameters from 5404 reflections
$b = 7.341$ (8) Å	$\theta = 3.2–30.9°$
$c = 7.4451(8)$ Å	$\mu = 2.471$ cm^{-1}
$\beta = 97.222$ (1)°	$T = 100$ K
$V = 1030.59(19)$ Å^3	Crystal size:0.39 × 0.28 × 0.10 mm
$Z = 2$	3075 independent reflections
φ and ω scans	2835 reflections with $I > 2\sigma(I)$
$T_{min} = 0.608$, $T_{max} = 0.746$	$R_{int} = 0.027$
Color : colourless	$\theta_{max} = 28.6°$, $\theta_{min} = 3.2°$
Goodness-of-fit on F ^{2}: 1.04	$-27<h<27$
9441measured reflections	$-10<k<10$
Refinement on F^2	$-10<l<10$
$R[F^2> 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 0.2678P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{max} = 0.001$
11674 reflections	$\Delta\rho_{max} = 3.70$ e Å^{-3}
117 parameters	$\Delta\rho_{min} = -1.13$ e Å^{-3}

Table 2. Geometric parameters (Å, °) of $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$

Cd1—Cl2^{i}	2.5571 (5)	C6—C7	1.399 (3)
Cd1—Cl2	2.5571 (6)	C4—C5	1.403 (3)
Cd1—Cl1	2.6586 (5)	N1—H1C	0.9100
Cd1—Cl1^{i}	2.6586 (5)	N1—H1D	0.9100
Cd1—Cl1^{ii}	2.6613 (5)	N1—H1E	0.9100
Cd1—Cl1^{iii}	2.6613 (5)	C8—H8A	0.9800
Cl1—Cd1^{iv}	2.6613 (5)	C8—H8B	0.9800
C1—C2	1.499 (3)	C8—H8C	0.9800
C1—N1	1.503 (3)	C1—H1A	0.9900
C2—C7	1.385 (3)	C1—H1B	0.9900
C2—C3	1.398 (3)	C3—H3	0.9500
C3—C4	1.386 (3)	C4—H4	0.9500
C8—O1	1.428 (3)	C6—H6	0.9500
C5—O1	1.367 (3)	C7—H7	0.9500
C5—C6	1.386 (3)		
Cl2^{i}—Cd1—Cl2	180.0	C7—C2—C3	118.6 (2)
Cl2^{i}—Cd1—Cl1	89.61 (2)	C7—C2—C1	120.2 (2)
Cl2—Cd1—Cl1	90.39 (2)	C3—C2—C1	121.2 (2)
Cl2^{i}—Cd1—Cl1^{i}	90.39 (2)	C4—C3—C2	120.8 (2)
Cl2—Cd1—Cl1^{i}	89.61 (2)	C4—C3—H3	119.6
Cl1—Cd1—Cl1^{i}	180.00 (2)	C2—C3—H3	119.6
Cl2^{i}—Cd1—Cl1^{ii}	92.50 (2)	C3—C4—C5	119.8 (2)
Cl2—Cd1—Cl1^{ii}	87.50 (2)	C3—C4—H4	120.1
Cl1—Cd1—Cl1^{ii}	89.95 (1)	C5—C4—H4	120.1
Cl1^{i}—Cd1—Cl1^{ii}	90.05 (1)	O1—C5—C6	124.7 (2)
Cl2^{i}—Cd1—Cl1^{iii}	87.50 (2)	O1—C5—C4	115.3 (2)
Cl2—Cd1—Cl1^{iii}	92.50 (2)	C6—C5—C4	120.1 (2)

Cl1—Cd1—Cl1^{iii}	90.045 (9)	C5—C6—C7	119.2 (2)
Cl1^{i}—Cd1—Cl1^{iii}	89.955 (9)	C5—C6—H6	120.4
Cl1^{ii}—Cd1—Cl1^{iii}	180.0	C7—C6—H6	120.4
Cd1—Cl1—Cd1^{iv}	158.65 (2)	C2—C7—C6	121.5 (2)
C2—C1—N1	112.34 (17)	C5—O1—C8	116.8 (2)
C2—C1—H1A	109.1	C1—N1—H1C	109.5
N1—C1—H1A	109.1	C1—N1—H1D	109.5
C2—C1—H1B	109.1	C1—N1—H1E	109.5
N1—C1—H1B	109.1	H8A—C8—H8C	109.5
C2—C7—H7	119.2	H8B—C8—H8C	109.5
C6—C7—H7	119.2	H8A—C8—H8B	109.5
O1—C8—H8A	109.5	H1A—C1—H1B	107.9
O1—C8—H8B	109.5	H1C—N1—H1D	109.5
O1—C8—H8C	109.5	H1C—N1—H1E	109.5
		H1D—N1—H1E	109.5

Symmetry codes: (i) $-x$, $-y+1$, $-z+2$; (ii) x, $-y+1/2$, $z+1/2$; (iii) $-x$, $y+1/2$, $-z+3/2$; (iv) $-x$, $y-1/2$, $-z+3/2$.

Table 3. Hydrogen-bond geometry (Å, °) of $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1C···Cl2^{v}	0.91	2.29	3.1962 (19)	175
N1—H1D···Cl1	0.91	2.42	3.252 (2)	153
N1—H1E···Cl2^{vi}	0.91	2.42	3.279 (2)	156

Symmetry codes: (v) x, $-y+3/2$, $z-1/2$; (vi) x, y, $z-1$.

Table 4. Calculated and experimental carbon-13 chemical shifts for $[4\text{-}OCH_3C_6H_4CH_2NH_3]_2[CdCl_4]$

Atom	X-rays (ppm)	full optimization (ppm)	optimization of protons positions(ppm)	Experimental (ppm)
C1	176.6	174.7	174.8	158.2
C2	112.3	118	117.4	109.0
C3	131.5	137.9	137.4	132.6
C4	118.3	119.9	119.3	109.0
C5	128.8	136.2	132.7	125.9
C6	126	130	131.2	125.9
C8	41.6	58.6	58.4	55.5
C9	38.8	60.7	52.8	44.2