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[Cd(O₂C(CH₂)₂CO₂)] an unprecedented 3D Hybrid**Organic-Inorganic Topology**

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Abstract

The $[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$ has been hydrothermally prepared and structurally characterized using single - crystal X - Ray diffraction. It crystallizes in the monoclinic system, S.G.: $I 2/a$, $a = 6.515(2) \text{ \AA}$, $b = 4.889(3) \text{ \AA}$, $c = 30.769(3) \text{ \AA}$, $\beta = 94.34(8)^\circ$. The structure exhibited alternating infinite chains of edge-sharing CdO_6 octahedra which progress parallel to the a axis and four corner-sharing CdO_6 octahedra layers which progress in the (a,b) plane, pillared by succinate anion. The topology leads to intersecting hydrophobic channels along $[110]$ and $[\bar{1}10]$ directions. The preparation, structural, thermal and infrared spectroscopic characterizations and ^{113}Cd NMR are presented.

Keywords: A. microporous materials, D. crystal structure, C. thermogravimetric analysis (TGA), C. infrared spectroscopy, D. nuclear magnetic resonance (NMR).

Introduction

There is intense interest today in open-framework materials due to the numerous high-performance properties that these materials may present. One can find two main classes of open-frameworks materials. The first class corresponds to the inorganic compounds in which MO_6 octahedra and/or tetrahedral $\text{M}'\text{O}_4$ share edges or apexes to form a three dimensional framework which delimits tunnels and/or cavities where ions and/or solvent molecules can be intercalated [1]. The second class corresponds to layered compounds such as smectite clays [2], α -ZrP phases [3], titanium-niobium oxide [4], Layered Double Hydroxides [5] and layered hydroxysalts [6]. Recently attention has been drawn to a novel class of open-framework materials namely organic-inorganic materials [7, 8]. In this context, numerous chemical synthesis routes mainly ionic exchange reaction and hydrothermal treatment have been developed [7-9]. We present here the structure features of a new (3D) Layered organic-inorganic metal succinate elaborated by the hydrothermal method. This compound presents a new hybrid topology in which 1D and 2D inorganic moiety exist and are pillared by succinate anions.

Experimental:

Infrared spectroscopy, thermal analyses and syntheses were carried out in the same condition as in our previous work [10]. Plate-like colorless crystals of the title compound are prepared starting from $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ / $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H}$ / KOH / H_2O (in

the molar ratio 1/1/2/330 for 3 days at 180 °C). ^{113}Cd MAS-NMR spectra were measured on powdered samples with a Bruker AVANCE 500 MHz spectrometer.

Characterization

Infrared spectrum of $[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$ (I) (Fig. 1), show peaks in three characteristic spectral regions: 1385- 1532 cm^{-1} , should be assigned to $\nu_s(\text{C}-\text{O})$ and $\nu_{as}(\text{C}-\text{O})$ of the carboxyl groups. The band at 1385 is split into three components due to the existence of two independent carboxyl groups. 2912 - 2986 cm^{-1} , is characteristic of the $\nu(\text{C}-\text{H})$ vibrational modes. Low number waves correspond to $\nu(\text{C}-\text{C})$ modes [11, 12]. The decomposition of (I) is exothermic and occurs at 700 K in one stage involving the combustion of the organic moiety and the formation of CdO (Theoretical and Experimental weight loss: 43.78% and 43.80%) (Fig. 2). ^{113}Cd NMR-MAS chemical shifts (table 1) relative to cadmium chlorate show a displacement towards negative δ depending on the cadmium coordinated oxygen type.

Structure description and discussion

The asymmetric unit of (I) consists of one succinate anion and two cadmium atoms which are crystallography independent (Fig.3). Both of the cadmium atoms (Cd1 and Cd2) are octahedrally coordinated by the succinate oxygens, with Cd-O distances ranging from 2.228 Å to 2.334 Å and from 2.184 Å to 2.449 Å for Cd1 and Cd2 respectively. The Cd1O_6 octahedra share two edges to form infinite chains (1D) parallel

to the *c* axis. The Cd₂O₆ octahedra share four corners to form layers (2D) which develop parallel to (*a*, *b*) plane. Both of these parts are alternately pillared by the carbon atoms of the organic moiety (Fig. 4). Succinate carbon and carboxyl function atoms lay in the same medium plane. In addition to its lamellar character, the framework exhibited intersecting channels along [110] and $[\bar{1}10]$ directions with almost the same dimension which is about 7.7 x 3.6 Å² (Fig. 4). In recent work we have reported on the structures of [Cd(OH)₂][O₂C(CH₂)₂CO₂] (II) and [Cd₃(OH)₂][O₂C(CH₂)₂CO₂]₂ (III) showing 2-D structural topology [10] with open frameworks. They are built up of (2D) inorganic moieties pillared by succinate anions and present channels, the dimensions of which are about 7.48 x 3.61 Å² and 8.08 x 4.85 Å² respectively for (II) and (III). In addition to their modulated channels, which can be suitable for selective non-polar species adsorption [9, 13], the three compounds can be regarded as structural models to synthesize magnetic materials presenting synergy between inorganic layers and organic molecules, Cd can be replaced by Mn, Co, Fe, Ni or Cu and succinate molecules can be substituted by other carboxylate so as to the control of magnetic interactions through extended polyatomic ligands and, particularly ligands with conjugated molecules [14]. The investigation of such hybrid systems are under progress. Moreover, cadmium is applied as a metallic probe of Ca(II) and Zn(II) sites, indeed ¹¹³Cd NMR spectroscopy has been widely used in the study of biological systems

because of its chemical shift sensibility [15, 16].

Supplementary material: Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre N°. CCDC (252286).

Accepted manuscript

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Figure captions

Figure 1. Infrared spectrum of $[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$

Figure 2. Thermal analyses of $[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$

Figure 3. Asymmetric unit of $[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$

Figure 4. $[\bar{1}10]$ view showing channels in $[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$

Tables

Table 1. Cadmium environment and ^{113}Cd MAS-NMR chemical shifts

Compound	Cadmium environment	δ (ppm)
$[\text{Cd}(\text{OH})]_2[\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2]$	$\text{Cd}(\text{OH}-\mu_3)_3(\text{O}-\mu_3)_2(\text{O}-\mu_2)$ one edge shared	60
$[\text{Cd}_3(\text{OH})_2][\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2]_2$	$\text{Cd}2(\text{OH}-\mu_3)_2(\text{O}-\mu_3)_3(\text{O}-\mu_2)$ two edges shared	8,5
	$\text{Cd}1(\text{OH}-\mu_3)_2(\text{O}-\mu_3)_2(\text{O}-\mu_2)_2$ two edges shared	-19,1
$[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$	$\text{Cd}1(\text{O}-\mu_3)_4(\text{O}-\mu_2)_2$ two edges shared	-71,2
	$\text{Cd}2(\text{O}-\mu_3)_4(\text{O}-\mu_2)_2$ four corner shared	-84,5

Figure 1

Figure 2

Figure 3

Fig. 4