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Journal of Solid State Chemistry 177 (2004) 1852–1857

JOURNAL OF SOLID STATE CHEMISTRY

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Organically pillared layered zinc hydroxides

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Received 29 October 2003; received in revised form 12 January 2004; accepted 16 January 2004

Abstract

The two organically pillared layered zinc hydroxides [$Zn_2(OH)_2$(ndc)], CPO-6, and [$Zn_3(OH)_4$(bpdc)], CPO-7, were obtained in hydrothermal reactions between 2,6-naphthalenedicarboxylic acid (ndc) and zinc nitrate (CPO-6) and 4,4′biphenyldicarboxylate (bpdc) and zinc nitrate (CPO-7), respectively. In CPO-6, the tetrahedral zinc atoms are connected by two μ_2-OH groups and two carboxylate oxygen atoms, forming infinite layers extending parallel to the *bc*-plane. These layers are pillared by ndc to form a three-dimensional structure. In CPO-7, the zinc hydroxide layers are containing four-, five- and six coordinated zinc atoms, and the layers are built like stairways running along the [001] direction. Each step is composed of three infinite chains running in the [010] direction. Both crystal structures were solved from conventional single crystal data. Crystal data for CPO-6: Monoclinic space group $P2_1/c$ (No. 14), $a = 11.9703(7)$, $b = 7.8154(5)$, $c = 6.2428(4)$ Å, $\beta = 90.816(2)^\circ$, $V = 583.97(6)$ Å^3 and $Z = 4$. Crystal data for CPO-7: Monoclinic space group $C2/c$ (No. 15), $a = 35.220(4)$, $b = 6.2658(8)$, $c = 14.8888(17)$ Å, $\beta = 112.580(4)^\circ$, $V = 3033.8(6)$ Å^3 and $Z = 8$. The compounds were further characterized by thermogravimetric- and chemical analysis.

Keywords: Pillared layered; Zinc hydroxide

1. Introduction

Pillared layered materials like clays, layered double hydroxides and metal phosphonates are an important class of materials because of their potential applications in catalysis [1–3], separation [4,5], ion exchange [6] and photochemistry [7]. Recently, there has been considerable interest in using multifunctional ligands and metal centers to construct infinite frameworks. Many of the most interesting coordination polymers are based on anionic, polycarboxylate ligands. A large number of rigid ligands have successfully been used to create 3D frameworks with enormous porosity [8]. These materials also have potential applications in catalysis, gas storage, magnetism and molecular recognition [9–12].

Carboxylate ligands have also been used to create a new class of pillared layered materials [13–19] in which transition metal hydroxide layers are pillared by carboxylate ligands. In the present study we introduces two new phases into this class of materials. Both compounds, denoted CPO-6 and -7, are based on zinc hydroxide layers that are, respectively, pillared by 2,6-naphthalenedicarboxylate (ndc) and 4,4′biphenyldicarboxylate (bpdc). These structures represent the first well-characterized derivatives of layered zinc hydroxides containing dicarboxylate anions.

2. Experimental

2.1. [$Zn_2(OH)_2$(ndc)] CPO-6

A mixture of $Zn(NO_3)_2 \cdot 4H_2O$, ndc, pyridine and water in a molar ratio of 2:1:175:750 was heated to 180°C in a Teflon-lined steel autoclave. The crystallization time was 24 h, and the product was washed with water and dried at 60°C. The yield based on Zn was 43%. Chemical analysis calculated for $C_6H_4O_3Zn$: C, 38.03; H, 2.13; found: C, 38.54; H, 2.15.

2.2. [$Zn_3(OH)_4$(bpdc)] CPO-7

The compound was synthesized hydrothermally from a mixture of $Zn(NO_3)_2 \cdot 4H_2O$, bpdc, pyridine and water in a molar ratio of 2:1:175:750. The crystallization took place in a Teflon-lined steel autoclave at 180°C for 24 h.

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0022-4596/$ - see front matter © 2004 Published by Elsevier Inc.
doi:10.1016/j.jssc.2004.01.017

The product was washed with water and dried in air at 60°C. The yield based on Zn was 31%. Chemical analysis calculated for $C_{14}H_{12}O_8Zn_3$:C, 33.34; H, 2.40; found: C, 33.48; H, 2.55.

Thermogravimetric analysis was performed with a Rheometric Scientific STA 1500. The samples (ca. 20 mg) of CPO-6 and -7 were heated to 600°C in flowing nitrogen at a rate of 5°C min^{-1}. Both compounds show similar thermal behavior with a single weight loss starting at about 350°C due to decomposition of the organic components.

Single crystal X-ray diffraction data for CPO-6 and -7 were collected at 150 K on a Siemens Smart CCD diffractometer. A total of 1525 frames were collected, thereby covering one hemisphere of reciprocal space ($\Delta\theta = 0.3°$, 30 s per frame). Data reduction and empirical absorption correction were carried out using the programs SAINT [20] and SADABS [21], respectively. The crystal structures were solved by direct methods and refined using the SHELXTL program package [22]. Non-hydrogen atoms were refined anisotropically. In both cases the organic hydrogen atoms were generated geometrically and refined in the riding mode. In case of CPO-6, the single hydrogen atom belonging to the hydroxide group was refined without restraints and with a constant isotropic displacement parameter of 0.02 Å^2. In case of CPO-7, the hydrogen atoms belonging to the hydroxide groups were refined with a distance restraint d(O–H) = 0.95(2) Å and constant isotropic displacement parameters of 0.02 Å^2. The crystallographic data and details on the refinements for both compounds are listed in Table 1. Atomic coordinates and displacement parameter are listed in Tables 2 and 3, and selected bond distances and angles are given in Table 4.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 222544 and 222545. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Crystal structures

CPO-6, $Zn_2(OH)_2$(ndc), crystallizes in the monoclinic space group $P2_1/c$ with one crystallographically independent zinc atom. Zn adopts a distorted tetrahedral coordination being coordinated by two μ_2-OH groups and two carboxylate oxygen atoms of two different ndc ligands (Fig. 1). In addition there is a long interaction between Zn and O(1) of 2.695 Å. Bond valence analyses give a calculated valence close to the expected value of two for Zn. There is a hydrogen bonding interaction

Table 1
Crystal data and structure refinement data for CPO-6 and -7

Identification code	CPO-6	CPO-7
Empirical formula	$C_6H_3O_3Zn$	$C_{14}H_{12}O_8Zn_3$
Formula weight	188.45	504.35
Temperature (K)	150	150
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	11.9703(7)	35.220(4)
b (Å)	7.8154(5)	6.2658(8)
c (Å)	6.2428(4)	14.8888(17)
β (deg)	90.816(2)	112.580(4)
Volume (Å^3)	583.97(6)	3033.8(6)
Z	4	8
Density (g cm^{-3})	2.143	2.208
Absorption coefficient (mm^{-1})	4.129	4.749
F(000)	372	2000
Theta range for data collection	1.70–25.01°.	2.51–26.42°.
Miller index ranges	$-14 \leqslant h \leqslant 14$; $-9 \leqslant k \leqslant 9$; $-7 \leqslant l \leqslant 7$	$-44 \leqslant h \leqslant 44$; $-7 \leqslant k \leqslant 7$; $-18 \leqslant l \leqslant 18$
Reflections collected	5286	16070
Independent reflections	1030 [R(int) = 0.0223]	3111 [R(int) = 0.0425]
Reflections observed (>2s)	1003	2918
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1030/0/94	3111/2/239
Goodness-of-fit on F^2	1.382	1.623
Final R indices [$I > 2s(I)$]	$R_1 = 0.0177 \mathrm{w}R_2 = 0.0590$	$R_1 = 0.0433 \mathrm{w}R_2 = 0.1801$
R indices (all data)	$R_1 = 0.0228 \mathrm{w}R_2 = 0.0832$	$R_1 = 0.0457 \mathrm{w}R_2 = 0.1818$
Largest diff. peak and hole	0.625 and -0.899 e Å^{-3}	0.857 and -2.144 e Å^{-3}

Calculated standard deviations in parentheses.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^3) for CPO-6

Atom	x	y	z	U(eq)
Zn(1)	0.4818(1)	0.3346(1)	0.2346(1)	0.013(1)
O(1)	0.3999(1)	0.5582(2)	0.1387(3)	0.014(1)
O(2)	0.6398(1)	0.4053(2)	0.2086(3)	0.014(1)
O(3)	0.4234(2)	0.1860(2)	0.0166(3)	0.014(1)
C(1)	0.1320(2)	0.5674(3)	−0.1337(4)	0.015(1)
C(2)	0.2105(2)	0.5244(3)	0.0197(4)	0.015(1)
C(3)	0.1773(2)	0.4487(4)	0.2154(4)	0.019(1)
C(4)	−0.0669(2)	0.5823(3)	−0.2527(4)	0.019(1)
C(5)	0.0167(2)	0.5382(3)	−0.0982(4)	0.015(1)
C(6)	0.3318(2)	0.5603(3)	−0.0185(4)	0.013(1)

Calculated standard deviations in parentheses.

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (Å^3) for CPO-7

Atom	x	y	z	U(eq)
Zn(1)	0.2020(1)	0.1385(1)	0.3919(1)	0.010(1)
Zn(2)	0.2118(1)	0.6487(1)	0.4213(1)	0.011(1)
Zn(3)	0.2501(1)	0.9337(1)	0.2479(1)	0.010(1)
O(1)	0.1936(1)	0.3861(5)	0.4631(3)	0.012(1)
O(2)	0.2457(1)	0.1781(5)	0.3438(3)	0.010(1)
O(3)	0.2252(1)	0.9222(6)	0.4966(3)	0.011(1)
O(4)	0.2221(1)	0.6895(5)	0.2999(3)	0.012(1)
O(5)	0.1925(1)	0.0147(5)	0.1418(3)	0.013(1)
O(6)	0.3110(1)	0.8696(6)	0.3375(3)	0.016(1)
O(7)	0.1468(1)	0.0613(6)	0.3013(3)	0.018(1)
O(8)	0.1481(1)	0.7170(6)	0.3420(3)	0.020(1)
C(1)	0.0444(2)	0.1808(8)	−0.0622(4)	0.018(1)
C(2)	0.0696(2)	0.0002(9)	−0.0528(4)	0.019(1)
C(3)	0.1111(2)	0.0063(9)	0.0092(4)	0.015(1)
C(4)	0.1286(2)	0.1911(8)	0.0609(4)	0.015(1)
C(5)	0.1037(2)	0.3705(8)	0.0495(4)	0.016(1)
C(6)	0.0624(2)	0.3658(8)	−0.0099(4)	0.017(1)
C(7)	−0.0007(2)	0.1678(8)	−0.1224(4)	0.018(1)
C(8)	−0.0224(2)	0.3473(8)	−0.1696(4)	0.016(1)
C(9)	0.0647(2)	0.6683(8)	0.2274(5)	0.018(1)
C(10)	0.0852(2)	0.8627(8)	0.2364(4)	0.013(1)
C(11)	0.0632(2)	0.0417(8)	0.1887(4)	0.018(1)
C(12)	−0.0216(2)	0.9739(8)	−0.1326(4)	0.016(1)
C(13)	0.3266(2)	0.6917(8)	0.3721(4)	0.010(1)
C(14)	0.1304(2)	0.8790(8)	0.2983(4)	0.014(1)

Calculated standard deviations in parentheses.

between the OH groups and the carboxylate O(2) atoms [d(O(3)$\cdots$O(2)) = 2.893 Å].

Each Zn atom is connected to two adjacent Zn atoms through two OH bridges forming infinite tetrahedral chains running along [001]. These chains are crosslinked by double carboxylate bridges involving two Zn atoms. The bridges have syn-anti-conformations. The result is infinite layers extending parallel to the *bc*-plane (Fig. 2a). These layers are pillared by ndc ligands to form a three-dimensional structure (Fig. 2b).

Table 4
Selected bond lengths [Å] and angles [°] for CPO-6 and -7

CPO-6			
Zn(1)–O(3)	1.9104(19)	O(3)–Zn(1)–O(3)	118.01(8)
Zn(1)–O(2)	1.9798(17)	O(3)–Zn(1)–O(2)	116.81(8)
Zn(1)–O(3)	1.9132(19)	O(3)–Zn(1)–O(1)	97.97(7)
Zn(1)–O(1)	2.0879(18)	O(3)–Zn(1)–O(2)	117.51(8)
O(2)–C(6)	1.268(3)	O(3)–Zn(1)–O(1)	99.10(8)
O(1)–C(6)	1.267(3)	O(2)–Zn(1)–O(1)	100.84(7)
CPO-7			
Zn(1)–O(2)	1.947(4)	O(2)–Zn(1)–O(7)	119.64(16)
Zn(1)–O(1)	1.964(3)	O(7)–Zn(1)–O(1)	104.63(16)
Zn(1)–O(7)	1.954(4)	O(7)–Zn(1)–O(3)	111.91(15)
Zn(1)–O(3)	1.989(4)	O(2)–Zn(1)–O(1)	113.66(14)
Zn(2)–O(4)	1.992(4)	O(2)–Zn(1)–O(3)	103.30(15)
Zn(2)–O(3)	2.129(4)	O(1)–Zn(1)–O(3)	102.56(15)
Zn(2)–O(1)	1.952(3)	O(1)–Zn(2)–O(4)	126.42(15)
Zn(2)–O(3)	2.003(4)	O(4)–Zn(2)–O(3)	108.17(15)
Zn(2)–O(8)	2.139(4)	O(4)–Zn(2)–O(3)	91.97(15)
Zn(3)–O(5)	2.101(4)	O(1)–Zn(2)–O(8)	86.66(15)
Zn(3)–O(4)	2.137(3)	O(3)–Zn(2)–O(8)	96.30(15)
Zn(3) –O(2)	2.146(3)	O(1)–Zn(2)–O(3)	125.38(15)
Zn(3)-O(6)	2.083(4)	O(1)–Zn(2)–O(3)	92.18(14)
Zn(3) –O(4)	2.122(3)	O(3)–Zn(2)–O(3)	83.52(15)
Zn(3)-O(2)	2.140(3)	O(4)–Zn(2)–O(8)	89.56(16)
O(6)-C(13)	1.263(6)	O(3)–Zn(2)–O(8)	178.44(15)
O(8)-C(14)	1.237(7)	O(6)–Zn(3)–O(4)	97.77(15)
O(5) –C(13)	1.272(6)	O(6)–Zn(3)–O(4)	82.42(15)
O(7) –C(14)	1.274(6)	O(4)–Zn(3)–O(4)	177.40(12)
		O(5)–Zn(3)–O(2)	91.84(14)
		O(4)–Zn(3)–O(2)	81.12(14)
		O(5)–Zn(3)–O(2)	89.10(14)
		O(4)–Zn(3)–O(2)	101.28(13)
		O(6)–Zn(3)–O(5)	171.10(15)
		O(5)–Zn(3)–O(4)	89.90(14)
		O(5)–Zn(3)–O(4)	90.12(14)
		O(6)–Zn(3)–O(2)	91.79(15)
		O(4)–Zn(3)–O(2)	96.28(13)
		O(6)–Zn(3)–O(2)	87.62(15)
		O(4)–Zn(3)–O(2)	81.32(14)
		O(2)–Zn(3)–O(2)	177.42(12)

Calculated standard deviations in parentheses.

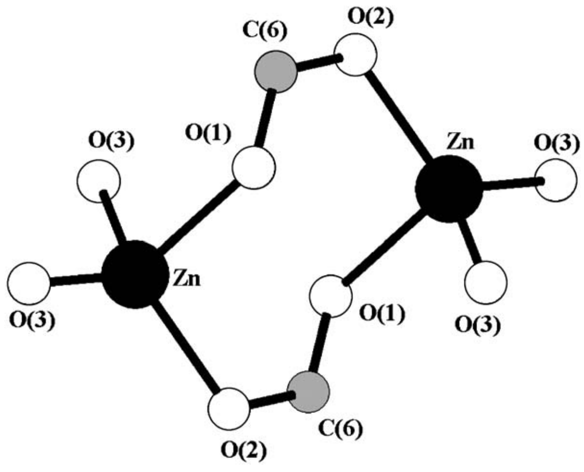

Fig. 1. Coordination environment for Zn in CPO-6.

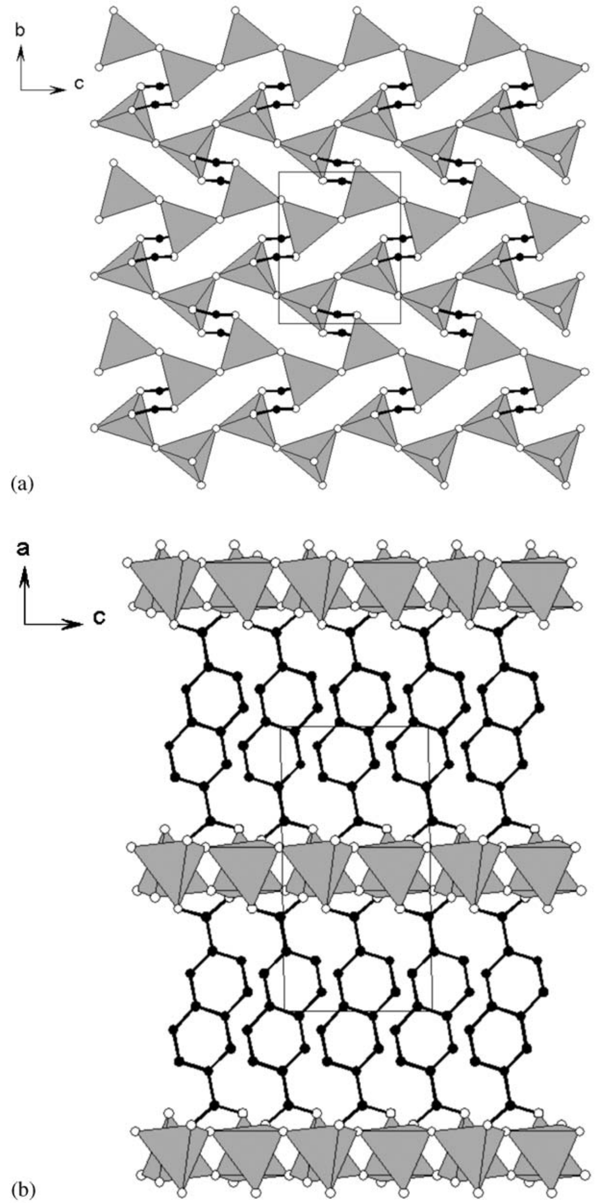

Fig. 2. Polyhedral representation of CPO-6 seen along (a) [100] and (b) [010]. C atoms with filled circles and O atoms with open circles.

A terephthlate-based cobalt hydroxide, $Co_2(OH)_2(tp)$, has the same $[M_2(OH)_2(dicarboxylate)]$ stoichiometry as CPO-6 [14]. However, the two crystal structures are different. $Co_2(OH)_2(tp)$ is also a layered compound, but the cobalt hydroxide layers have a brucite like structure [23] with octahedral Co and μ_3-OH groups. Compared with the brucite structure, one μ_3-OH is substituted with a RCO_2 fragment leading to increased Co⋯Co distances in $Co_2(OH)_2(tp)$.

$Zn(OH)_2$ itself is a polymorphic compound, and β-$Zn(OH)_2$ [24] belongs to the brucite structural type, but CPO-6 has no similarity with this structure. The difference in crystal structure between CPO-6 and $Co_2(OH)_2(tp)$ is an illustration of the well-known tendency of Zn to attain a tetrahedral coordination environment as opposed to other first-row divalent transition metals. Tetrahedral coordination environment for Zn is also the case in two other known zinc hydroxide polymorphs, γ-$Zn(OH)_2$ [25] and ε-$Zn(OH)_2$ [26]. None of these polymorphs have, however, layered crystal structures.

CPO-7, $Zn_3(OH)_4(bpdc)$, crystallizes in the monoclinic space group $C2/c$, and represents a pillared layered structure with three crystallographically independent zinc atoms (Fig. 3). Zn(1) adopts a slightly distorted tetrahedral geometry, being coordinated by one μ_2-OH group, two μ_3-OH groups and one carboxylate oxygen atom. Zn(2) resides in a distorted trigonal-bipyramidal environment, being coordinated by one μ_2-OH group, three μ_3-OH groups and one carboxylate oxygen atom. The octahedral environment around Zn(3) is composed of four μ_3-OH groups in the equatorial plane and two carboxylate oxygen atoms in the axial positions.

The inorganic zinc hydroxide layers are built like stairways running along the [001] direction (Fig. 4a). Each step is composed of three infinite chains extending in the [010] direction (Fig. 4b). In the middle there is a chain of edge-sharing octahedra, which are linked by μ_3-OH groups and carboxylate bridges with syn–syn conformation. The octahedal chain is crosslinked on both sides to two other chains both composed of alternating tetrahedra and trigonal-bipyramids. These are shifted in proportion to each other along [010] so that the position of the trigonal-bipyramid in one chain is corresponding to the position of the tetrahedra in the other chain. The linkages within the chains are ensured by μ_2-OH and μ_3-OH groups and by carboxylate bridges with syn–syn conformation.

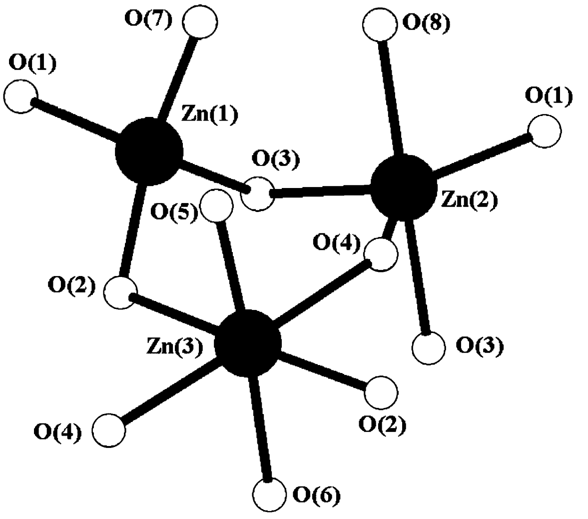

Fig. 3. Coordination environment for Zn in CPO-7.

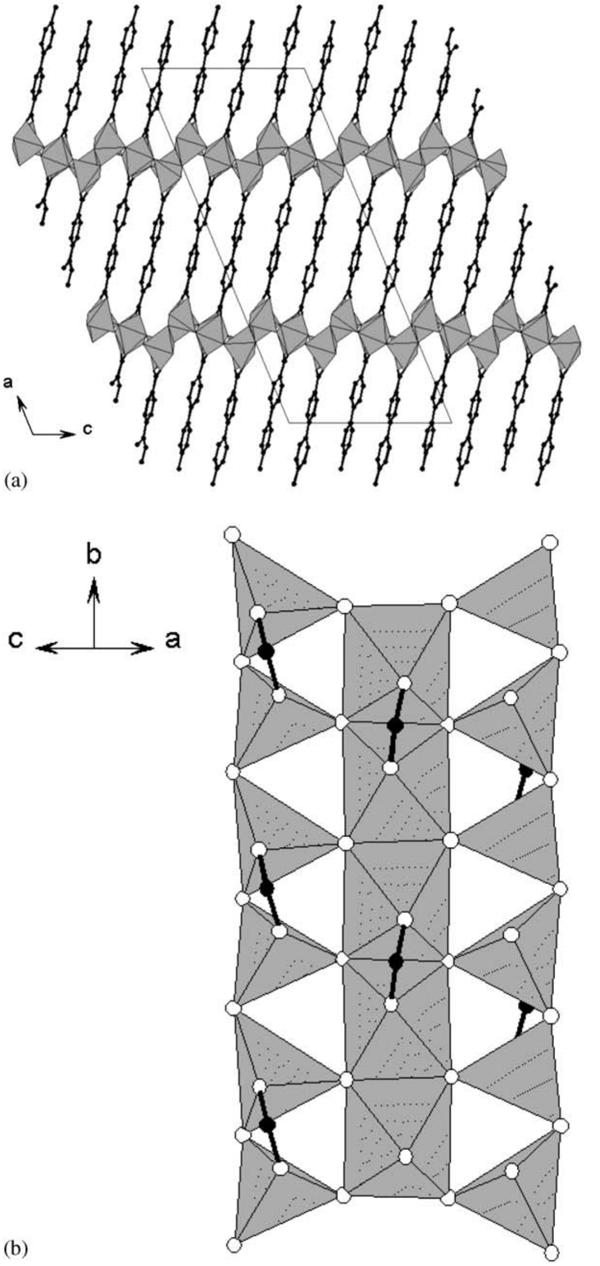

Fig. 4. Polyhedral representation of CPO-7 seen along (a) [010] and (b) [101]. C atoms with filled circles and O atoms with open circles.

The $[M_3(OH)_4(\text{dicarboxylate})]$ stoichiometry of CPO-7 is unique. To the best of our knowledge no other compound with this stoichiometry is known in literature. The presence of four-, five- and six coordinated zinc atoms in the same compound is also quite rare. Searching the Cambridge Structural Database [27], just six such compounds could be identified [28–33].

CPO-6 and -7 presents the first well-characterized organically pillared layered zinc hydroxides. Several compounds of this type have been reported in literature [15,16], however, owing to very bad crystallinity, no exact crystal structure solutions are at hand for those materials. There exist speculations of crystal structures possibly based on brucite [23] or hydrozincite [34] layers and pillared by organic components. The present structure solutions of CPO-6 and -7 illustrate how novel structures with unexpected construction of the hydroxide layers can be formed when organic and inorganic components are reacted.

The improved crystallinity of CPO-6 and -7 compared to other organically pillared layered zinc hydroxides is believed to be due differences in the synthesis conditions. The hydrothermal method can give well-crystalline products containing crystals large enough for single crystal analysis as is the case for CPO-6 and -7. The other organically pillared layered zinc hydroxides reported in the literature [15,16] have been prepared by precipitation reactions in different organic solvents at atmospheric pressure and at temperatures up to 100°C. Under these conditions the products tend to be poorly crystalline containing crystals of submicron size.

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