Structure of zinc hydroxy-terephthalate: Zn₃(OH)₄(C₈H₄O₄)

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Abstract
The new lamellar hydroxide teraphthalate Zn₃(OH)₄(C₈H₄O₄) was synthesised by the hydrothermal method and was characterized by single crystal X-ray diffraction, IR and UV spectroscopy and thermogravimetric analysis. The compound crystallises in the monoclinic space group C2/c with: a = 28.1000(5) Å, b = 6.3101(1) Å, c = 14.8359(3) Å, β = 121.564(1)°, V = 2241.43 Å³, D_x = 2.538 g/cm³ and Z = 4. The zinc(II) atoms present four, five and six fold O-coordination. Due to the peculiar coordination of the zinc atoms, the inorganic layers form stairways running along [001]. These stairways-like layers are bridged by terephthalate (tp) groups leading to a 3D framework.

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1. Introduction

Particular interest was marked to hybrid compounds for obtaining functional or multi-property materials. In the case of multi-property materials, the mineral and organic components of the structure, closely connected, would allow to obtain the synergy of their individual properties [1,2]. Currently, intensive research is performed in the domain of layered single hydroxides or layered double hydroxide, for their magnetic [2–4], catalytic [5], adsorption [6], conductivity [7] and optical [1] properties.

Despite the fact that numerous such hybrid hydroxide compounds have been discovered, only few of them have a well characterised crystallographic structure. They were obtained more or less well crystallised, depending on the nature of the organic anions (e.g., carboxylate and dicarboxylate) and on the synthesis routes. In the case of the dicarboxylate anions, the bridging effect of the two COO⁰ carboxylate functions allows to obtain coherent three dimensional framework due to the fact that the carboxylate groups can be grafted to the hydroxide layers by covalent bonding [8]. More generally, in the field of coordination chemistry, and more particularly, in the domain of porous materials, accurate crystallographic structures have been determined for hydroxy-terephthalates containing zinc [9], vanadium [10] and chrome [11,12], and terephthalates containing zinc and solvated molecules [13–16]. Moreover, the hydrothermal synthesis favouring more condensed coordination networks around the transition metal centres, it usually leads to better crystallised materials compared to other methods. Intercalation or insertion methods by ‘chimie douce’ lead to different compounds even when using similar dicarboxylate anions [17]. In that case, the carboxylates are linked by weak hydrogen bonding to the hydroxide layers. Hydration of dehydrated zinc hydroxide with a water solution containing a carboxylate anion results in a non-crystallised powder [18].

One of our goals in the area of hybrid materials is the resolution of the crystallographic structures of hydroxy-dicarboxylates (mainly terephthalate) of the first transition metal raw, since, to the best of our knowledge, only few structures of layered transition metal hydroxy-carboxylates have been accurately solved up to now [10–12,19–24]. Recently, some of us published the structure of the low-temperature ferromagnet Cu₂(OH)₂–(C₈H₄O₄) from high resolution powder diffraction data [25].
The present work concerns the crystallographic structure of the zinc hydroxy-terephthalate for which single crystals have been obtained.

2. Experimental

2.1. Synthesis and chemical analysis

The compound was obtained by hydrothermal synthesis from a mixture (1:2) of 3.5 g of Zn(NO$_3$)$_2$, 4H$_2$O (Aldrich, 98%) and terephthalic acid disodium salt Na$_2$C$_8$H$_4$O$_4$ (Aldrich, 98%), in 15 ml of distilled water and adjusted with a NaOH, 1 M solution to pH = 8 resulting in a volume of 20 ml. This mixture was poured into a Teflon container (capacity 22 ml) closed in an autoclave at 150°C under autogenous pressure during five days.

The product obtained was washed 3 times with a distilled water : ethanol (1:1 in volume) solution and then dried under vacuum at room temperature. It consisted of numerous needle-like crystals of approximately 100 to 150 micrometers, as shown by the SEM photography in Fig. 1.

The product was controlled by XRPD at several steps during the synthesis, using a Xpert Pro Philips diffractometer (filtered copper K$_\alpha$ radiation $\lambda = 1.5418$ Å, Bragg–Brentano geometry). An interesting feature was observed concerning the evolution of the patterns as a function of the heating time as shown in Fig. 2. Actually, an intermediate layered phase with a stacking parameter $d_0 = 10.74$ Å (phase 1) was identified in the first three days and transformed progressively to the final product (phase 2, $d_0 = 11.87$ Å) after five days.

Thermogravimetric (TG) measurements were performed with a ‘TG/ATD 92-16.18’ SETARAM instrument between 20–1000°C in air and using a heating rate of 1°C/min. The weight loss due to the combustion of the compounds was of 53 and 43% for phase 1 and 2 respectively, and the final product was zinc oxide. For the phase 2, it corresponds to the formula unit (Zn$_3$(OH)$_4$(C$_8$H$_4$O$_4$) determined by single crystal X-ray diffraction analysis (see hereafter). The deduced formula for the unknown phase 1, taken into account the electro neutrality of the compound, is Zn(OH)$_{0.84}$(C$_8$H$_4$O$_4$)$_{0.58}$.

2.2. IR and UV spectroscopies

The IR spectrum of the title compound was recorded with a “Spectrum one FT-IR” spectrometer in the ATR mode by using the “Universal ATR Sampling” accessory. The spectrum is reported in Fig. 3. The band at 3621 cm$^{-1}$ corresponds to the elongation of the hydroxide groups, bands at 1560 and 1380 cm$^{-1}$ are assigned to $\nu_{as}$($–$COO$–$) and $\nu_{s}$(–COO$–$) respectively. The difference between these two bands agrees with a bridging character of the –COO$–$ groups with two oxygen atoms linked to Zn$^{II}$. The peak at 1502 cm$^{-1}$ identifies the aro-
matic cycle. A band appearing at 3564 cm$^{-1}$ may be due to OH– vibration belonging to an impurity which could be amorphous Zn(OH)$_2$ present in the sample.

The UV spectroscopy of the solid product was carried out on a suspension of the powder into a water:ethanol (3 : 1 in volume) mixture, the addition of ethanol facilitating the dispersion of the powder. The UV-visible spectrum (not shown) recorded with a Hitachi U3000 spectrophotometer indicated a somewhat wide absorption band around 300 nm. This band is clearly assignable to the absorption by the terephthalate ligand, the spectrum of which in solution shows two bands at 215 nm (strong, wide) and 315 nm (medium, narrow). Thus the photoluminescence of the present zinc hydroxy-terephthalate was investigated with a PTI Quantum Master fluorescence system on the suspension and by reflection on solid powder deposited on a silica lamella. The two sample preparation lead to very similar excitation and emission spectra, as shown in Fig. 4. No luminescence was observed with excitation at 215 nm. Emission spectra under $\lambda_{\text{ex}} = 325$ nm exhibit only a very weak and wide luminescence peak around 380 nm in accordance with the corresponding excitation spectra ($\lambda_{\text{em}} = 380$ nm). By comparison with the spectrum observed for terephthalic acid solution ($\lambda_{\text{ex max}} = 315$ nm, $\lambda_{\text{em max}} = 350$ nm), one notices a significant blue shift of both the excitation and emission spectra. However, the luminescence is extremely weaken in the zinc derivative, which suggests a quasi quenching of the luminescence of the ligand by the inorganic sub-network.

2.3. Structural analysis

A needle like crystal with dimension ($\approx 0.04 \times 0.04 \times 0.15$ mm$^3$) was chosen for diffraction measurements and mounted on a goniometric head for structural analysis. Full data sets were collected on a “Nonius Kappa CCD area Detector” at room temperature. 689 images were collected ($\phi$ and $\omega$ scans) with a 40 seconds exposition time per image. The data collection and cell refinement were respectively performed by COLLECT [26] and SCALEPACK in HKL2000 program package [27]. Data reduction was realised by SCALEPACK and DENZO in HKL2000. The reliability factor of the mean equivalent reflections, $R_{\text{int}}$, is of 0.06. The experimental data and data collection parameters are reported in Table 1.

To solve the structure, the SIR2000 program was used [28]. The refinement was realised using the WINGX software [29]. H atoms of tp molecules were first geometrically placed and then their coordinates were refined. H atoms of hydroxyl groups could not be determined by Fourier synthesis. Atomic positions of non-hydrogen atoms and selected bond can be found in supplementary material deposited at CCDC.
3. Results and discussion

3.1. Structural description

Zn₃(OH)₄(tp) crystallises in the C2/c space group, with \(a = 28.1000(5)\) Å, \(b = 6.3101(1)\) Å, \(c = 14.8359(3)\) Å, \(\beta = 121.564(1)^\circ\) and \(V = 2241.43 A^3\). The structure is very similar to that reported for Zn₃(OH)₄(bpdc) (bpdc = biphenyldicarboxylate) during our investigation [22], with the same space group and the lattice parameters \(a = 35.220(4)\) Å, \(b = 6.2658(8)\) Å, \(c = 14.8888(17)\) Å, \(\beta = 112.580(4)^\circ\). Thus, the two unit cells differ mainly by the \(a\) parameter which represents in both cases the periodicity along the stacking slabs direction, the \(a\) value depending on the molecule length, i.e., the distance between the two carboxylate groups.

The structure of Zn₃(OH)₄(tp) is presented in Fig. 5 and can be described similarly to that of Zn₃(OH)₄(bpdc) in [22]. Both structures are pillared by dicarboxylate anions, making a three dimensional framework. The structure consists of parallel layers of zinc O-polyhedra separated by terephthalate molecules grafted more or less orthogonally to these layers. The Zinc atoms are situated on three crystallographic independent sites, namely the 4 and 6 coordination types, usually encountered for Zn(II), and the less regularly observed 5 coordination mode, are present in the same structure as shown in Fig. 6.

The Zn1 atoms are located in a triangular based bi-pyramid. The base is formed by three \(\mu_3\)-OH groups (\(\mu_3\)-OH6, \(2 \times \mu_3\)-OH8) and the two apexes being one \(\mu_2\)-OH7 and one oxygen O4 of carboxylate group. The five-fold coordination is relatively rare for the zinc atom but has already been reported in the case of polymer [31]. Metal–oxygen distances range between 1.952(2) and 2.155(2) Å.

The Zn2 atoms lie at the centre of a distorted O-tetrahedron (distances between 1.946(2)–1.986(2) Å) made up of two \(\mu_2\)-OH7 and one oxygen O4 of carboxylate anion. The Zn3 atoms are at the centre of an octahedron formed by two oxygen atoms (O1 and O2) from two carboxylate groups and by four \(\mu_3\)-OH equatorial (2 \(\times \mu_3\)-OH6 and 2 \(\times \mu_3\)-OH5). The distances are ranging between 2.082(3) and 2.151(2) Å.

The hydroxide layers (see Figs. 7 and 8) form stairways running along the [001] direction. Each step is built from three infinite chains extending along the [010] direction. The middle...
of the step is formed by edge-sharing octahedra (OH5–OH6).
On both sides the octahedra are linked to chains of alternat-
ing bi-pyramids and tetrahedra. The difference of elevation
between two edge-sharing pyramids (OH8–OH8) creates the
appearance of a step as shown on the Fig. 7. The lower and
upper bi-pyramid units share vertex (atom μ3-OH6) with lower
and upper octahedra respectively. The tetrahedra around Zn2
are linked to pyramids around Zn1 by the vertexes OH7, OH8,
and to the octahedra around Zn3 by the vertex OH5. The tetra-
hedra are not connected together.

The distances and angles values concerning the tp molecules
in the structure are those expected for this ligand.

For the Rietveld analysis, the intensity dependent parama-
ters (atomic coordinates, temperature factors . . . ) were let fixed.
The number of global and profile refined parameters were 5 and
13 respectively and the $R_{\text{Bragg}}$ factor converged to 11% thus
showing that the single crystal model is available for the whole
polycrystalline sample. The observed, calculated and difference
pattern are presented in Fig. 9.

4. Conclusion

With the zinc hydroxybiphenyldicarboxylate Zn$_3$(OH)$_4$-
(C$_{14}$H$_8$O$_4$) [22] the present zinc hydroxylterephthalate Zn$_3$
(OH)$_4$(C$_8$H$_4$O$_4$) provides a second example of an uncommon
structure containing zinc atoms with 4, 5 and 6-fold coordina-
tions. Hence, dicarboxylate anions, (tp and bpdc) with
comparable geometries have been grafted by hydrothermal syn-
thesis route on zinc hydroxide layers leading to very similar
structures, the main difference being the spacing between the
hydroxide layers. Photofluorescence measurements suggest the
possibility of inducing a blue shift of the luminescence of the
terephthalate ligand in such Zn(II) hydroxide compounds, al-
though a quasi quenching of luminescence is observed in the
present compound.

It has also been shown that an intermediate compound is
formed during the synthesis of Zn$_3$(OH)$_4$(C$_8$H$_4$O$_4$) with a $d_0$
spacing of 10.74 Å, which is significantly lower than that of the
final product ($d_0 = 11.87$ Å). Single crystal for this phase was
not obtained but powder diffraction diagram could allow an ab
initio structural determination.
Supplementary material

CCDC 295966 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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