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Synthesis, structure and thermal behaviour of a barium-glutarate framework

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Abstract

A hybrid framework material has been synthesized via a gel diffusive technique. Its X-ray single crystal structure has been determined at 120 K, in the tetragonal space group $P4_2/mbc$. The ligand is partially deprotonated giving interesting supramolecular bonding formed by hydrogenoglutarate anion, which can act as a building synthon. The layer-type polymeric structure is built up from isolated polyhedra linked via conventional carboxylate bridges and forming inorganic layers in the plane (001). Along [001], layers consisting of the methylene spacers of the ligands, complete the three-dimensional framework. The thermal analysis performed by TGA and DSC in air and under N_2, respectively, revealed the high stability of the non-templated framework (up to 210 °C) and showed several phase transitions and one solid-state reaction detected by an exothermic peak at 500 °C.

Keywords: Glutarate; Extended framework; Coordination polymer; Thermal behaviour

1. Introduction

New generations of metal-organic coordination polymers have emerged in last years, enhancing the field of supramolecular chemistry from both theoretical and practical point of view. These compounds, often porous, known as metal-organic framework materials (MOFs) are based on building unit concept, which is used in computational (simulation/prediction of crystals structures) as well as synthetic (crystal engineering) design of new materials [1–3].

Metal-organic framework materials present multidimensional extended networks, assembled from various combinations of the metals and the linkers, leading to unusual architectures. A wide fields of applications have emerged, exploiting the various properties induced through these molecular-based materials [4–7]. One approach to evaluate the controlled assembly in the resulting coordination polymers is to choose metals assuming a variable coordination number and ligands offering several coordination modes, and involving linking sites with different binding strength and orientation. With this purpose, we have undertaken a systematic investigation focused on flexible polycarboxylic ligands, and monometallic or heterometallic connectors using mainly rare-earth or transition metals [8–16].

In order to understand the significance of specific interactions inducing the expected properties, we have extended the study to the alkaline-earth metals which, like p-block cations have received much less attention in the literature despite their potential application as precursors materials for obtaining oxides or nitrides with particular conductivity [17]. The linkers remain the anions stemming from α, ω aliphatic dicarboxylic acids. These laters are known to be an essential feature in designing multi-dimensional hybrid framework, with porous architectures or other physical properties [18].

We report on this paper, the synthesis, structure and thermal behaviour of an extended non-templated barium-

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glutarate polymer consisting of isolated polyhedra bridged in layers, obtained by a soft chemical process and distinguished by its open framework, and high thermal stability.

2. Experimental

2.1. Synthesis and thermal behaviour

All chemical were purchased from MERCK and used without any further purification. Elemental analysis were carried out in order to determine C, and H contents. Infrared (IR) spectra was recorded in 4000–400 cm^{-1} range on Perkin-Elmer FTIR spectrophotometer, with samples prepared as KBr pellets. Thermogravimetric analysis (TGA and DTA) were conducted on SETARAM 92-16 equipment with a heating of 5 °C mn^{-1} in air from ambient to 800 °C. Differential scanning calorimetry (DSC) was performed on SETARAM DSC 111 apparatus from ambient to 450 °C with 5 °C mn^{-1} flow rate and under N_2 [19].

Single crystals were obtained by gel method. The experiments were performed with an aqueous silicate gel prepared in a test tube by mixing sodium metasilicate pentahydrate of density 1.10 g cm^{-3}, and glutaric acid. The pH is adjusted to 5.6. After the gel was set, a mixture of barium nitrate and glutaric acid in a 1:2 molar ratio, was carefully added on top and crystals allowed to grow by diffusion at room temperature. After 10 days, colourless needles suitable for X-ray analysis appeared in the gel. Anal. Calcd for $C_{10}H_{14}O_8Ba$ (399.55): C, 30.06; H, 3.53. Found: C, 30.48; H, 3.91%. IR (KBr pellet): 3450(s), 2950(vw), 1750(vs), 1620(vs), 1420(m), 1230(w), 1100(w), 850(vw), 720(vw).

Significant differences appeared in TGA and DSC curves. In air, TGA curve evidenced three sharp endothermic peaks at 229, 280 and 419 °C, followed by a weak exothermic one at 500 °C. Under N_2, DSC curve showed five endothermic peaks, three strong, occurring at 226.10, 270.48 and 410.77 °C and two weaker observed at 65.91 and 248.77 °C. Only one distinct mass loss region was seen in TGA, conducted in air.

2.2. X-ray crystallography

For crystal structure determination, the single crystal removed from the gel, washed and dried at room temperature, had dimensions$0.3 \times 0.2 \times 0.2$ mm^3. The reflection intensities were collected on a Kappa-CCD diffractometer at 120 K. Empirical absorption corrections were applied by using MULABS in PLATON program [20]. The structure was solved by direct method and subsequent Fourier analysis. All the hydrogen atoms were located in the Fourier difference map. Then the structure was refined by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for all non-hydrogen atoms, and for hydrogen atoms with geometrical con-

Table 1
Crystallographic data

CCDC deposit no	613557	
Empirical formula	C_{10} H_{14} Ba O_8	
F_w	399.55	
Temperature	120(2), K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_2/mbc$	
Unit cell dimensions	$a = 8.3463(12)$ Å	$\alpha = 90°$.
	$b = 8.3463(12)$ Å	$\beta = 90°$.
	$c = 18.533(4)$ Å	$\gamma = 90°$.
Volume	1291.0(4) $Å^3$	
Z	4	
Density (calculated)	2.056 Mg/m^3	
Absorption coefficient	3.109 mm^{-1}	
$F(000)$	776	
Crystal size	$0.30 \times 0.20 \times 0.20$ mm^3	
Theta range for data collection	3.45 to 35.64°.	
Index ranges	$0 \leq h \leq 12$, $-13 \leq k \leq 13$, $-30 \leq l \leq 30$	
Reflections collected	8685	
Independent reflections	1529 [R(int) = 0.0427]	
Completeness to theta = 35.64°	99.7 %	
Absorption correction	Multi-scan	
T_{min}/T_{max}	0.48/0.54	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1529/0/49	
Goodness-of-fit on F^2	0.966	
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0199$, $wR_2 = 0.0500$	
R indices (all data)	$R_1 = 0.0435$, $wR_2 = 0.0547$	
Extinction coefficient	0.0069(4)	
Largest diff. peak and hole	1.607 and −0.815 e $Å^{-3}$	