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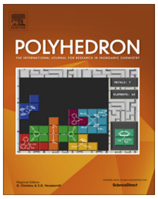

MgTi(cat)$_3$, a promising precursor for the preparation of Ti–MOFs?

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ABSTRACT

A new Ti(IV) triscatecholate complex was prepared in aqueous conditions. Its crystal structure was solved, and the complex was fully characterized by multiple techniques, including thermogravimetric analysis, temperature dependent powder X-ray diffraction (XRD), as well as NMR and UV–Vis spectroscopies. Thanks to liquid-state NMR, it is shown that such a complex is simultaneously stable enough in water to avoid the hydrolysis of the Ti(IV) ion, while still being able to undergo ligand exchange. Eventually, preliminary experiments suggest that this precursor is suitable for the preparation of new MOFs built up from polycatecholate ligands in aqueous media.

1. Introduction

There is a strong interest in the development of titanium Metal Organic Frameworks (MOFs), with the final aim of combining the unique optoelectronic and photocatalytic properties of titanium oxide with microporosity. While the number of MOFs based of divalent cations (as well Zr(IV)) have risen exponentially, the examples of Ti–MOFs remain scarce [1,2]. This mainly relates to the challenging crystallization of such polymeric compounds: Ti (IV) ions are both prone to spontaneous hydrolysis and fast coordination reaction, favoring the formation of TiO_2 and amorphous solids, respectively. As a consequence, whereas other MOFs are typically prepared from metal salts, the formation of crystalline Ti–MOFs frequently relies on the presence of species competing with the polytopic ligand for Ti coordination in the reaction medium. This could be done either using strongly complexing reactions media (carboxylic acid used as a solvent [3,4]) or tailored inorganic precursors (such as Ti–carboxylate [5] or –oxalate [6] oxoclusters, as well as titanocene [7]).

In this prospect, we focused our attention on titanium pyrocatecholate (cat^{2-}) complexes, as these compounds might present the following advantages: (i) strongly complexing anions limiting the rate of polymerization, (ii) a decent solubility in water and (ii) a good stability even in the presence of base, with the final aim of using this medium for the preparation of MOFs. The green synthesis, crystal structure and full characterization (thermogravimetric analyses, temperature dependent XRD, UV–Vis spectroscopy, solid-state and liquid-state NMR) of a new Ti pyrocatecholate precursor formulated $[Mg(H_2O)_6][Ti(cat)_3]$ are reported. Finally, preliminary experiments evidencing that this precursor could be suitable for the preparation of new MOFs built up from polycatecholate ligands in aqueous medium are presented.

2. Experimental

2.1. Synthesis

$[Mg(H_2O)_6][Ti(cat)_3]$ was first prepared under hydrothermal conditions in a form suitable for single crystal XRD analysis. In a 25 mL Teflon lined Parr autoclave, pyrocatechol (3.3 g, 30 mmol) was introduced with 10 mL of distilled water and stirred at room temperature. $TiO(acac)_2$ (1.3 g, 5 mmol) was then added, followed by $Mg(OH)_2$ (0.2 g, 5 mmol). The reactor was then sealed, placed into an oven and heated at 120 °C for 72 h. The resulting dark brown solid was recovered by filtration, washed with water and dried in air. Yield *ca.* 80%. Alternatively, $[Mg(H_2O)_6][Ti(cat)_3]$ was prepared under reflux in a microcrystalline form. In a 50 mL round bottom flask, pyrocatechol (3.3 g, 30 mmol) was introduced with 20 mL of distilled water and stirred at room temperature. TiO (acac)$_2$ (1.3 g, 5 mmol) was then added, followed by $Mg(OH)_2$ (0.2 g, 5 mmol). The mixture was then heated under reflux, and a

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dark precipitate started to form after *ca.* 5 min. The resulting dark brown solid was recovered by filtration, washed with water and dried in air. Yield 89%.

Ti–TzBC was prepared under hydrothermal conditions. In a 25 mL Teflon lined Parr autoclave, H_4-TzBC or 5,5′-(1,2,4,5-tetrazine-3,6-diyl)bis(benzene-1,2-diol) (25 mg, 0.08 mmol), which was synthesized according to a procedure derived from the one of 5,5′-(1,2,4,5-tetrazine-3,6-diyl)bis(benzene-1,2, 3-triol) [8], was introduced with 5 mL of distilled water and stirred at room temperature. $[Mg(H_2O)_6][Ti(cat)_3]$ (21 mg, 0.04 mmol) was then added. The reactor was then sealed, placed into an oven and heated at 130 °C for 24 h. The resulting dark brown solid was recovered by filtration, washed with water and dried in air. The solid was then washed with DMF at room temperature to remove all traces of the free organic ligand, placed in ethanol under stirring and finally recovered by filtration.

Ti–BC was prepared under identical conditions in a 1.5 mL Teflon lined autoclave, starting from H_4-BC or 4,4′-bis(benzene-1,2-diol) (5 mg, 0.02 mmol), $[Mg(H_2O)_6][Ti(cat)_3]$ (5.8 mg, 0.01 mmol) and 1 mL of water.

2.2. Characterizations

Thermogravimetric analysis was carried out under oxygen with a heating rate of 3 °C/min up to 800 °C on a Mettler Toledo TGA/DSC 1, Star® System analyzer. The UV–Vis absorption spectrum was recorded between 200 and 800 nm on a Perkin Elmer UV/VIS/NIR Lambda 900 spectrophotometer. Routine powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 Advance diffractometer working on transmission mode and equipped with a focusing Göbel mirror producing Cu Kα radiation (λ = 1.5418 Å) and a LynxEye detector. High resolution PXRD data were measured on a Bruker D8 Advance diffractometer with a Debye–Scherrer geometry, this system being equipped with a Ge(1 1 1) monochromator producing Cu Kα1 radiation (λ = 1.540598 Å) and a LynxEye detector. Extractions from the peak positions, pattern indexing and Lebail refinement were carried out with the TOPAS program [9]. Temperature dependent powder XRD measurement was performed on a θ–θ Bruker-D8 Advance diffractometer equipped with a HTK-1200N (Anton Parr) high-temperature chamber furnace and a LynxEye detector. A step of 10 °C was applied. Single crystal XRD analysis was carried out at room temperature using a Bruker Nonius X8 APEX diffractometer equipped with a CCD area detector. SAINT software was used to integrate and scale intensities and a semi-empirical absorption correction (SADABS) was applied on the basis of multiple scans of equivalent reflections. The structure of $[Mg(H_2O)_6][Ti(cat)_3]$ was solved by direct methods using SHELXS-97 and refined with the full matrix least squares routine SHELXL-2016/6 [10]. Non H-atoms were refined anisotropically. The aromatic protons were attached in geometrically idealized positions and constrained to ride on their parent atoms whilst hydrogen atoms bound to the water molecules were localized using difference Fourier maps. CCDC 1849183 contains the supplementary crystallographic data for $[Mg(H_2O)_6][Ti(cat)_3]$. Liquid ^1H NMR experiments were carried out at room temperature (27 °C) on a Bruker Avance 400 spectrometer operating at 400 MHz. For each measurement, 500 µL of solution were used using standard 5 mm NMR tubes. The spectra were processed using NMRNoteBook and chemical shifts are referenced to the signal of TMS. Solid-state ^{13}C cross-polarization under magic-angle spinning (CPMAS) NMR spectra were recorded on a Bruker Avance 500 spectrometer (B_0 = 11.7 T), using a 4 mm double-resonance probehead. The contact time was 4 ms. ^1H SPINAL-64 decoupling (~70 kHz radio-frequency field) was applied during signal acquisition. The recycle time is 4 s and between 512 and 1024 transients were accumulated for each sample. The spectra were analyzed using DMFIT software [11], and ^{13}C chemical shifts are referenced to the signal of TMS. EDX analysis was performed on a JEOL JSM-7001F microscope using gold-coated samples equipped with an energy-dispersive X-ray (EDX) spectrometer and a X-Max SDD (Silicon Drift Detector) by Oxford. The N_2 sorption measurement was performed at 77 K on BEL Japan Belsorp Mini apparatus. Prior to measurement, the solid powder was soaked in absolute ethanol to fully exchange guest molecules. Then, the sample was activated using supercritical CO_2 (5 successive cycles) at room temperature using a Tousimis critical point dryer.

3. Results and discussion

$[Mg(H_2O)_6][Ti(cat)_3]$ was initially prepared from the reaction of pyrocatechol (H_2cat), titanyl acetylacetonate ($TiO(acac)_2$) and magnesium hydroxide ($Mg(OH)_2$) under hydrothermal conditions at 120 °C. This synthesis afforded dark-red single crystals suitable for structure determination by X-ray diffraction (XRD), as detailed later. When replacing $Mg(OH)_2$ by $MgCl_2$, only amorphous products were recovered, although the color of the precipitate (brown-red) confirmed the formation of Ti–cat coordination bonds (see discussion later). Alternatively, the title compound could also be prepared in a polycrystalline form under ambient pressure in refluxing water with a yield of *ca.* 90%. In that case, it was also possible to follow the kinetics of crystallization by powder XRD, as shown in Fig. 1. To a suspension of H_2cat (6 eq.) and $TiO(acac)_2$ (1 eq.) in water at room temperature, $Mg(OH)_2$ (1 eq.) was added. After 5 min of reaction, the intensity of the Bragg peaks associated with the precursors decreases, while new peaks attributed to the title complex appear. This suspension was then heated at 100 °C, and after 5 min, only the peaks belonging to $[Mg(H_2O)_6][Ti(cat)_3]$ are visible. Upon increasing the reaction time, these peaks become narrower, and the compound finally reaches its optimal crystallinity after less than one hour. This experiment clearly indicates that the formation of $[Mg(H_2O)_6][Ti(cat)_3]$ is almost immediate, and does not request high temperature.

The structure of $[Mg(H_2O)_6][Ti(cat)_3]$ was determined by single-crystal XRD. The solid crystallizes in the *R*-3*c* space group, and the molecular structure consists of anionic $Ti(cat)_3^{2-}$ and cationic $Mg(OH_2)_6^{2+}$ entities, both lying on the 3 fold axis. The Ti(IV) ion is chelated by three catecholates, and adopts a distorted octahedral environment, with Ti—O distances equal to 1.9705(9) Å, as expected for a Ti(IV) compound (Fig. 2, top left). The strong distortion of the TiO_6 octahedron is associated to the chelation by the ligand, imposing a O—Ti—O angle equal to 78.53(4)°. On the other side, the Mg(II) ions adopts a nearly perfect octahedral coordination (angles O—Mg—O equal to 89.58(4) and 90.42(4)°), with Mg—O distances equal to 2.058(1) Å. Both species interact through strong hydrogen bonds involving the bound water molecules and the negatively charged O atoms of the catecholate ligands (distance $H_{H2O}\cdots O_{cat}$ = 1.83(2) Å, $O_{H2O}\cdots O_{cat}$ = 2.683(2) Å, angle $O—H_{H2O}\cdots O_{cat}$ = 178(2)°, see Fig. 2, top right), giving rise to 1-D chain running along the 1 1 1 direction (Fig. 2, bottom).

Such $Ti(cat)_3^{2-}$ complexes were already identified in several alkylammonium salts prepared in aqueous media [12,13]. One should note the absence of any inorganic oxo or hydroxo co-ligands even if the synthesis was carried out in water, under basic conditions. This is a major difference with carboxylate and alkoxide ligands [1,14,15], and could be related both to the high charge and chelating ability of the catecholate moieties. A similar behavior was observed previously by some of us through the use of carboxyphenolate ligands which led to 2D or 3D coordination networks [6] constructed from monomeric or dimeric Ti species against trimeric to dodecameric for MOFs bearing carboxylate type ligands [1].