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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-visible 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.

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 TiO₂ 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 (cat²⁻) 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(H₂O)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.

Experimental section

Synthesis

[Mg(H₂O)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 hours. The resulting dark brown solid was recovered by filtration, washed with water and dried in air. Yield ca 80%. Alternatively, [Mg(H₂O)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 dark precipitate started to form after ca 5 minutes. 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, H₄-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(H₂O)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 hours. 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 H₄-BC or 4,4'-bis(benzene-1,2-diol) (5 mg, 0.02 mmol), [Mg(H₂O)₆][Ti(cat)₃] (5.8 mg, 0.01 mmol) and 1 mL of water.

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-visible absorption spectrum was recorded between 200 and 800 nm on a Perkin Elmer UV /VIS/NIR Lambda 900 spectrophotometer. Powder X-ray diffraction patterns were measured on a Bruker D8 Advance diffractometer working on transmission mode and equipped with a focusing Göbel mirror producing CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) and a LynxEye detector. 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) were applied on the basis of multiple scans of equivalent reflections. The structure of [Mg(H₂O)₆][Ti(cat)₃] was solved by direct methods using SHELXS-97 and refined with the full matrix least squares routine SHELXL-2016/6.^[9] 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(H₂O)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 μ L 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 ($B_0 = 11.7\text{ T}$), using a 4 mm double-resonance probehead. The contact time was 4 ms. ^1H SPINAL-64 decoupling ($\sim 70\text{ kHz}$ 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,^[10] 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.

Results and discussion

$[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$ was initially prepared from the reaction of pyrocatechol (H_2cat), titanyl acetylacetonate ($\text{TiO}(\text{acac})_2$) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) 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 $\text{Mg}(\text{OH})_2$ 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 Figure 1. To a suspension of H_2cat (6 eq.) and $\text{TiO}(\text{acac})_2$ (1 eq.) in water at room temperature, $\text{Mg}(\text{OH})_2$ (1 eq.) was added. After 5 minutes 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 minutes, only the peaks belonging to $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$ 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 $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$ is almost immediate, and does not request high temperature.

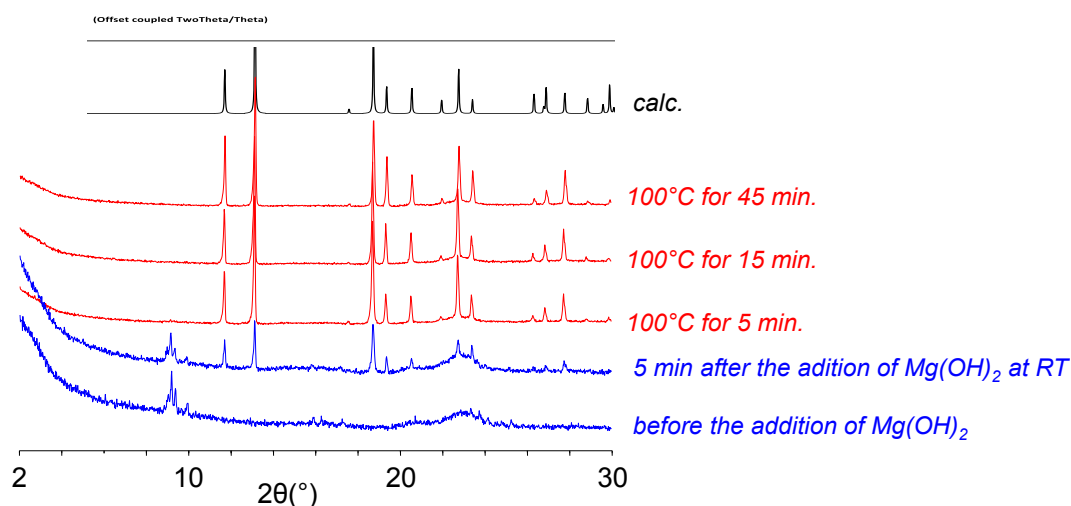


Figure 1. Kinetics of crystallization of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$: powder XRD patterns ($\lambda = 1.5406 \text{ \AA}$) of the precipitate obtained from a suspension of $\text{TiO}(\text{acac})_2$ and H_2cat . From bottom to top: before the addition of $\text{Mg}(\text{OH})_2$, 5 minutes after the addition of $\text{Mg}(\text{OH})_2$ at room temperature (RT), and after 5, 15 and 45 minutes under reflux. For comparison, the theoretical pattern issued from the single crystal structure determination is also shown in black.

The structure of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$ was determined by single-crystal XRD. The solid crystallizes in the $R\text{-}3c$ space group, and the molecular structure consists of anionic $\text{Ti}(\text{cat})_3^{2-}$ and cationic $\text{Mg}(\text{OH}_2)_6^{2+}$ 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 $1.9705(9) \text{ \AA}$, as expected for a Ti(IV) compound (Figure 2, top left). The strong distortion

of the TiO_6 octahedron is associated to the chelation by the ligand, while imposes of O-Ti-O angle equal to $78.53(4)^\circ$. On the other side, the Mg(II) ions adopts a nearly perfect octahedral coordination (angles O-Mg-O equal to $89.58(4)$ and $90.42(4)^\circ$), with again 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 $\text{H}_{\text{H}_2\text{O}}\cdots\text{O}_{\text{cat}} = 1.83(2)$ Å, $\text{O}_{\text{H}_2\text{O}}\cdots\text{O}_{\text{cat}} = 2.683(2)$ Å, angle $\text{O}-\text{H}_{\text{H}_2\text{O}}\cdots\text{O}_{\text{cat}} = 178(2)^\circ$, see Figure 2, top right), giving rise to 1-D chain running along the 111 direction (Figure 2, bottom).

Such $\text{Ti}(\text{cat})_3^{2-}$ complexes were already identified in several alkylammonium salts prepared in aqueous media.^[11,12] 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,^[1,13,14] 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]

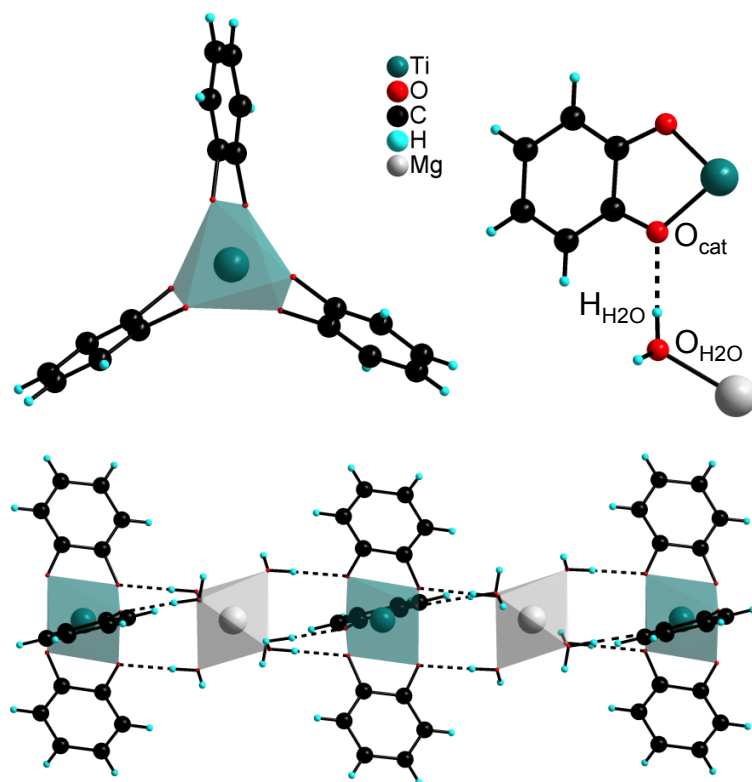


Figure 2. Crystal structure of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$. Top: the $\text{Ti}(\text{cat})_3^{2-}$ complex; bottom: the hydrogen bond network (dotted line) linking the $\text{Ti}(\text{cat})_3^{2-}$ and $\text{Mg}(\text{OH}_2)_6^{2+}$ ions.

Powder XRD further confirmed that the title compound was obtained in a pure crystalline form (see Figure 1). On the thermogravimetric (TG) curve (Figure 3), two weight loss are clearly distinguishable : a first one at low temperature (120-140°C) and a second one above 200°C, associated with the water departure and the ligand combustion respectively. The experimental weights associated with the resulting formation of $\text{MgTi}(\text{cat})_3$ and $\text{TiO}_2 + \text{MgO}$ matched well with the calculated values (see Figure 3), confirming that the title compound was produced in a pure form. Eventually, temperature dependent XRD indicated that water departure is accompanied by a complete loss of crystallinity (Figure 3).

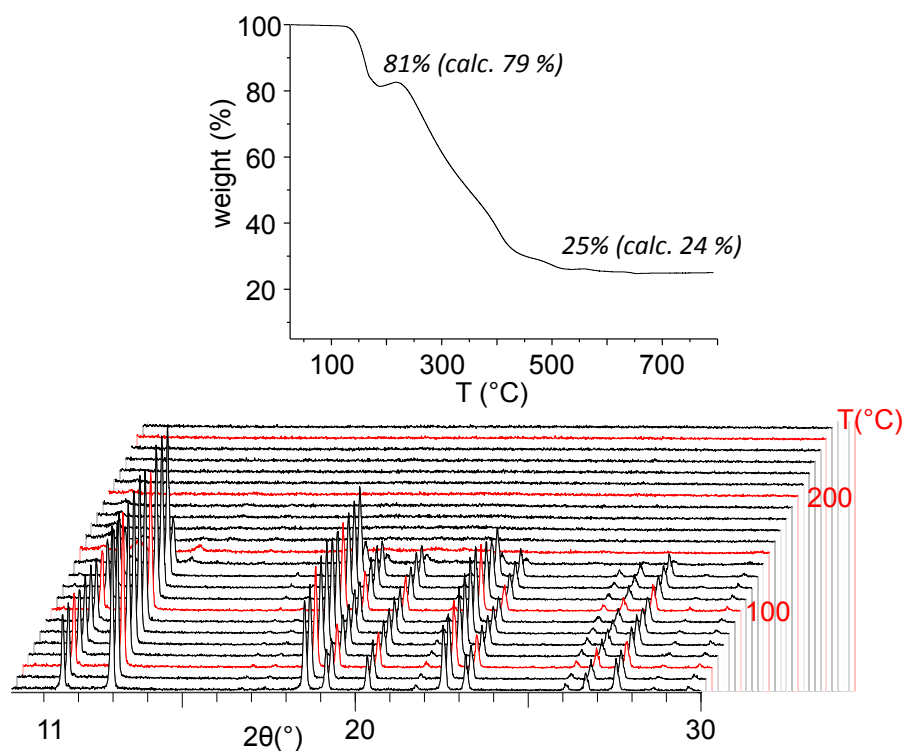


Figure 3. Thermal behavior of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$. Top: thermogravimetric analysis carried out under O_2 flow (experimental and calculated weight losses are also given, considering the formation of $\text{Mg}[\text{Ti}(\text{cat})_3]$ and $\text{MgO}+\text{TiO}_2$ for the first and second plateaus, respectively); bottom: temperature dependent powder XRD diffraction performed under air ($\lambda = 1.5418 \text{ \AA}$).

The solid state ^{13}C CPMAS NMR spectrum of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$ is shown in Figure 4 (top), together with the one of the pristine pyrocatechol. In both cases, three signals are discernible, corresponding to the non-equivalent C atoms of the catechol(ate) fragment. As expected, coordination of the ligand to the Ti(IV) cation is accompanied, compared to the pristine pyrocatechol, by a shift of the ^{13}C resonances,^[6] which is more strongly marked for the C atom bearing the O atom.

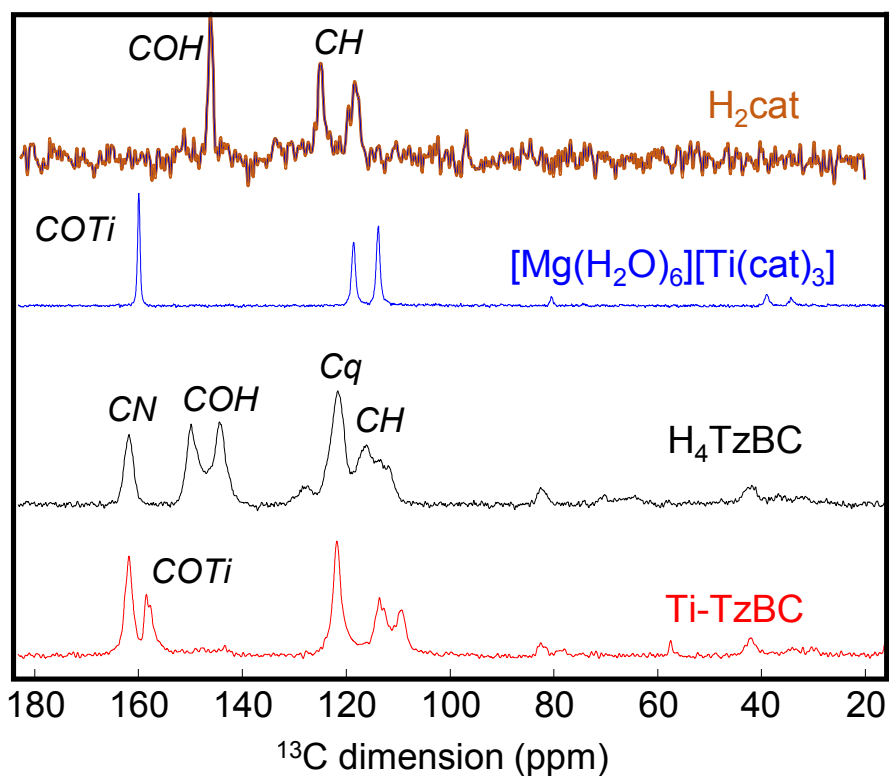


Figure 4. ^{13}C CPMAS NMR spectra of $\text{H}_2(\text{cat})$, $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$, H_4TzBC and Ti-TzBC .

Finally, the solid state UV-vis absorption spectrum of the complex, derived from the diffuse reflection measurement by means of the Kubelka-Munk model, is shown in Figure 5. At least two bands are clearly discernible: a thin one centered at *ca.* 260 nm and attributed to ligand-ligand transitions, and a broad band (maybe structured) covering the 350-500 nm region characteristic of phenolate-Ti(IV) ligand to metal charge transfer (LMCT),^[6,15,16] and responsible for the deep brown color.

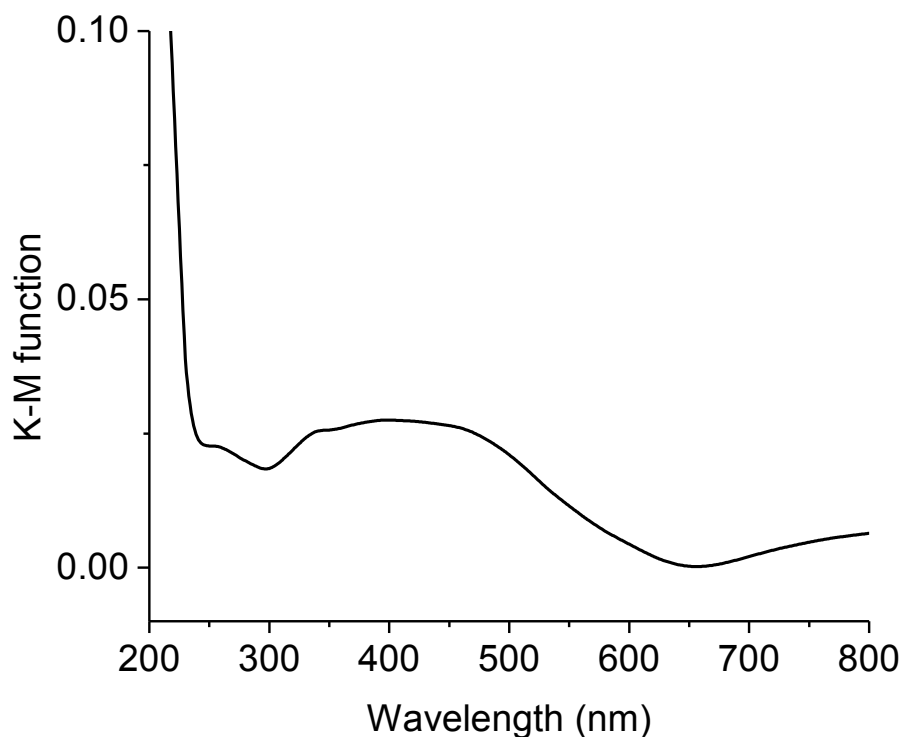


Figure 5. Solid state UV-visible absorption spectrum of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$.

In order to evaluate the possibility of exchanging the catecholates by competitive ligands, a first set of experiments were carried out by liquid ^1H NMR. Millimolar solutions of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$ in D_2O were first prepared, and their pD adjusted to 2, 4 and 9 by the addition of either DCl or NaOD . The resulting ^1H NMR spectra are shown Figure 6, and the aromatic H atoms were specially scrutinized. Whereas in basic medium, only a couple of signals centered at $\delta = 6.4$ and 6.6 ppm associated to Ti-bound catecholate is visible, the acidification of the medium leads to a progressive protonation and de-coordination of the catechol molecule, which appears complete at $\text{pH} = 2$ (signals centered at $\delta = 6.8$ and 6.9 ppm). This was confirmed by a visual examination: while the solutions at $\text{pH} = 4$ and 9 are brownish, in line with the LMCT associated with the Ti-catecholate bonds, the solution becomes colorless at $\text{pH} = 2$. Then, a second set of experiments was carried out, in the presence of a competitive ligand, namely oxalic acid. This molecule was chosen based on our previous studies, which evidenced that -2 oxygenated ligands (hydroxycarboxylate and

oxalate in ref^[6]) could be exchanged in aqueous solution under specific conditions. We thus anticipated that catecholate, which holds the same charge, might behave in a similar way. Again, millimolar solutions of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$ were prepared, in which oxalic acid was added (either 2 or 4 equivalent per Ti) prior to the adjustment of the pH. With two equivalents of oxalic acid, the initial complex remains intact at high pH. Nevertheless, the vast majority of catecholate is readily displaced at $\text{pH} = 4$. When the amount of oxalic acid is increased to 4 equivalents, the displacement is complete at $\text{pH} = 4$, but also visible at $\text{pH} = 9$. This is again further confirmed by a visual examination: not only the very acidic ($\text{pH} = 2$) solutions are colorless, but also the one at $\text{pH} = 4$ when 4 equivalents of oxalic acid are introduced.

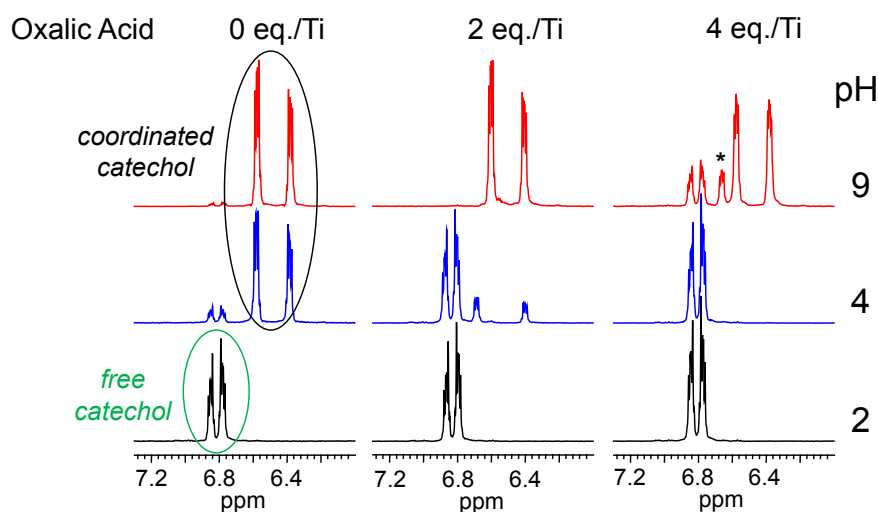


Figure 6. ^1H liquid NMR spectra of a 10^{-3} M $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ti}(\text{cat})_3]$ aqueous solution at various pH and in the presence of 0 (left), 2 (middle) and 4 (right) equivalents of oxalic acid. The signals centered at $\delta = 6.4/6.6$ and $6.8/6.9$ ppm are attributed to $[\text{Ti}(\text{cat})_3]^{2-}$ and H_2cat respectively. A third product (signal marked with an asterisk) was observed at $\text{pH} = 4.4$ eq. oxalic acid ($\delta = 6.7$ ppm), which might be a mixed oxalate-catecholate complex.

This study indicates that the pH and the relative stoichiometry of both ligands are key factors governing the ligand displacement, and thus suggests that, once extended to polytopic ligands,

subtle variations of these parameters should modulate the kinetics of polymerization and hence the crystallization of Ti coordination polymers. First attempts were carried out with two bis-catecholate ligands shown in Figure 7 and labelled H₄BC and H₄TzBC. Their reactivity with [Mg(H₂O)₆][Ti(cat)₃] under hydrothermal conditions was investigated.

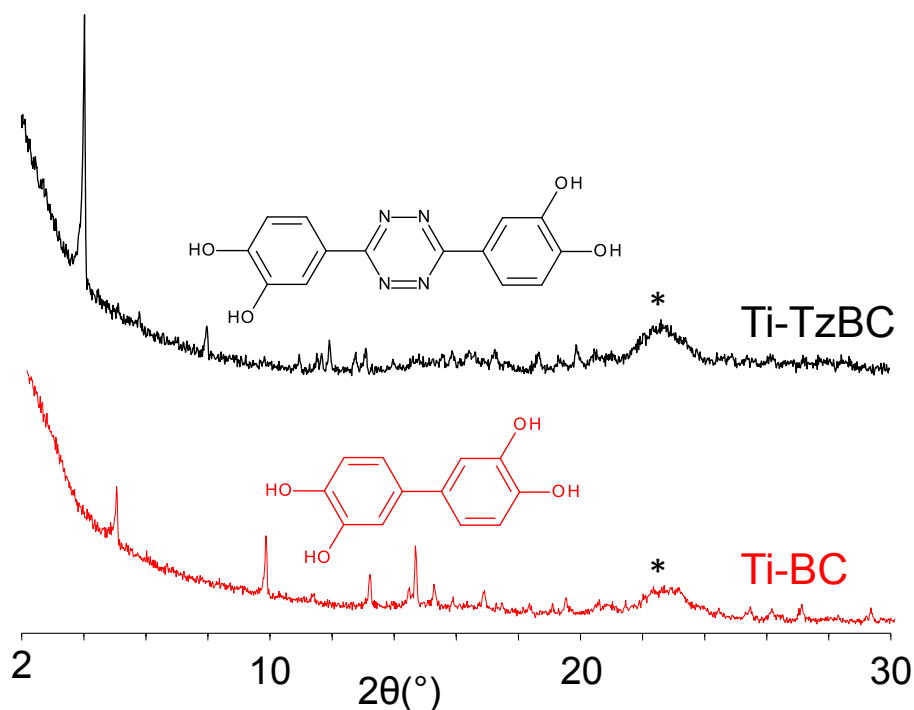


Figure 7. Powder XRD patterns of Ti-TzBC and Ti-BC ($\lambda = 1.5418 \text{ \AA}$). * = sample holder.

It was found that for a ligand to complex ratio equal to 2 and a temperature of 130°C, polycrystalline phases were obtained with both ligands. When compared to typical exploratory syntheses carried out with titanium, the **crystallinity** appeared rather encouraging (see the width of the Bragg's peaks). Issues with the reproducibility of the synthesis precluded the analysis of the H₄BC-based solid. **On the contrary, for the longer ligand (solid labelled Ti-TzBC), crystalline powders were reproducibly obtained. Preliminary attempts** to index the powder XRD pattern suggested a trigonal unit cell, with $a = 31.0 \text{ \AA}$ and $c = 40.6 \text{ \AA}$, with $R3$ as a plausible space group. Although it was not possible to solve the structure, the strong shift of the C-O resonances in the ¹³C CPMAS NMR spectrum of Ti-TzBC (Figure 4, bottom) clearly

proved the **connection** of the TzBC⁴⁻ ligand to the **Ti⁴⁺ cation**. This spectrum also showed the absence of remaining pyrocatechol(ate). This thus confirmed that the ligand exchange was effective, in line with the formation of a polymeric compound. EDX analyses indicated a Ti to Mg ratio equal to 2, suggesting the presence of an anionic framework, as commonly observed in catecholate coordination polymers.^[17-20] Finally, nitrogen sorption experiment revealed a microporous character, with a BET surface area equal to 200(20) m² g⁻¹ after activation with supercritical CO₂ (Figure 8).

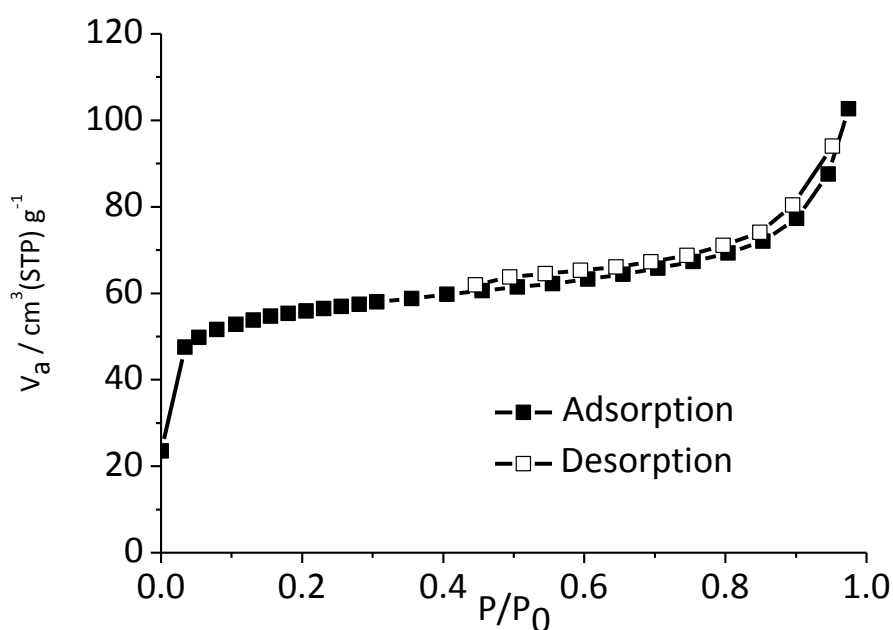


Figure 8. Nitrogen sorption isotherm of Ti-TzBC carried out at 77 K after activation with supercritical CO₂.

Conclusion

A new salt of the complex [Ti(cat)₃]²⁻ was reported, and thoroughly characterized by a wide range of techniques. It was shown that such a complex is simultaneously stable enough in water to avoid the hydrolysis of the Ti(IV) ion, while still able to undergo ligand exchange. In

this prospect, and as suggested by preliminary experiments, it appears suitable for the preparation of new Ti-MOFs in aqueous media.

Acknowledgements

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