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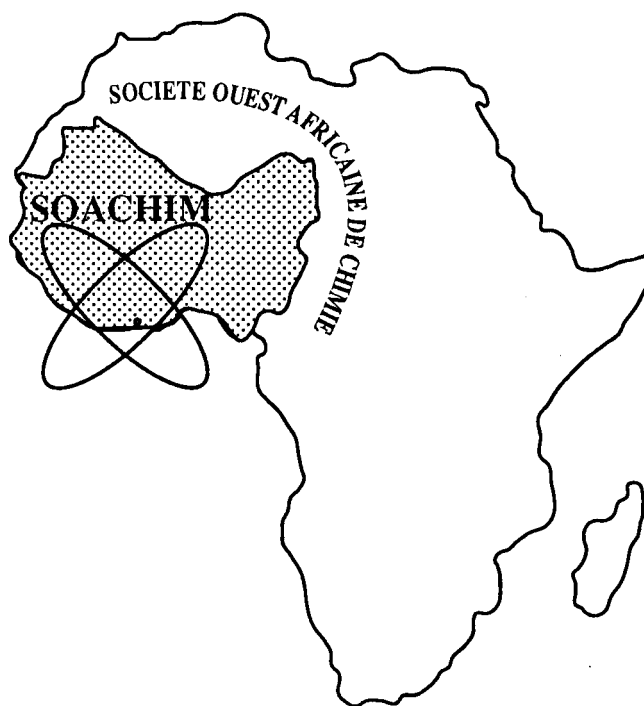
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## **Synthesis and crystal structure of a new calcium-containing trimesate coordination polymer: $[\text{Ca}_3(\text{btc})_2(\text{H}_2\text{O})_{12}]_\infty$ .**

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**Abstract :** Reaction in gel between the sodium salt of 1,3,5-benzenetricarboxylic acid or trimesic ( $\text{Na}_3[\text{C}_6\text{H}_3(\text{COO})_3]$  hereafter referenced as  $\text{Na}_3\text{btc}$ ) and calcium chloride has afforded single crystals of a bidimensional coordination polymer with chemical formula  $[\text{Ca}_3(\text{btc})_2(\text{H}_2\text{O})_{12}]_\infty$ . This compound crystallizes in the monoclinic system, space group  $\text{C2/c}$  (n° 15) with  $a = 19.3028$  (16) Å,  $b = 11.4850$  (9) Å,  $c = 13.0435$  (12) Å,  $\beta = 106.394$  (10)° and  $Z = 4$ . The crystal structure consists of a superposition of molecular planes that spread parallel to the  $(\vec{a}, \vec{b})$  plane.

**Keywords :** Ca(II); Crystal structure; Trimesate coordination polymers.

## **Synthèse et caractérisation structurale d'un nouveau polymère de coordination à base de calcium et du ligand trimésate: $[\text{Ca}_3(\text{btc})_2(\text{H}_2\text{O})_{12}]_\infty$ .**

**Résumé :** La réaction en milieu gel entre le sel de sodium de l'acide 1,3,5-benzènetricarboxylique ou trimésique ( $\text{Na}_3[\text{C}_6\text{H}_3(\text{COO})_3]$  noté par la suite  $\text{Na}_3\text{btc}$ ) et le chlorure de calcium a donné des monocristaux d'un polymère de coordination bidimensionnel de formule chimique  $[\text{Ca}_3(\text{btc})_2(\text{H}_2\text{O})_{12}]_\infty$ . Ce composé cristallise dans le système monoclinique, groupe d'espace  $\text{C2/c}$  (n°15) avec  $a = 19,3028$  (16) Å,  $b = 11,4850$  (9) Å,  $c = 13,0435$  (12) Å,  $\beta = 106,394$  (10) ° et  $Z = 4$ . La structure cristalline consiste en une superposition de plans moléculaires se propageant parallèlement au plan  $(\vec{a}, \vec{b})$ .

**Mots-clés :** Ca(II); Structure cristalline; Polymères de coordination à base de l'acide trimésique.

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## 1. Introduction.

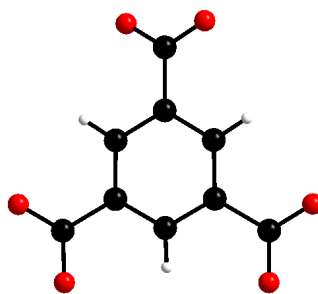
Over the past few decades, a number of coordination polymers have been published for their fascinating topologies coupled with their potential application in gas storage<sup>[1-3]</sup>, catalysis<sup>[4]</sup>, separation<sup>[5]</sup>, luminescent devices<sup>[6,7]</sup> or magnetism<sup>[8]</sup>. For more than a decade some of us are engaged in that research field with the objective of designing new lanthanide-based coordination polymers exhibiting interesting luminescent properties<sup>[9,10]</sup> and/or porosity<sup>[11-13]</sup>. As far as this second objective is targeted lanthanide ions are mainly used because of their ability to adopt various coordination modes. Actually, it is generally admitted that, due to the innerness of their 4f valence orbitals, lanthanide ions, in contrast with 3d metal ions, present only little preference in bond direction<sup>[14]</sup>. However, shortage of these metals is a global concern<sup>[15,16]</sup> and rationalization of their use is mandatory. Therefore, we have undertaken a study in which alkaline earth metal ions would replace lanthanide ions in coordination polymers. Indeed, alkaline earth metal ions as well as lanthanide ions present little preference in bond direction and their coordination mode is essentially governed by steric hindrance and intermolecular interaction between ligands. Moreover, alkaline earth ionic radii vary from 0.72 Å (Mg<sup>2+</sup>) to 1.35 Å (Ba<sup>2+</sup>) while lanthanide ionic radii vary from 0.86 Å (Lu<sup>3+</sup>) to 1.03 Å (La<sup>3+</sup>)<sup>[17]</sup>. Therefore, it must be

possible to obtain different crystal structure by replacing an alkaline earth metal ion by another.

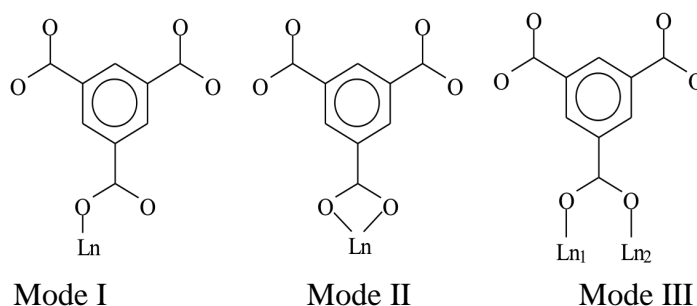
In order to initiate this study, we have chosen to use Ca<sup>2+</sup> as metal ions because it is non-toxic and abundant in earth crust and because its ionic radius (1.00 Å) is similar to the one of the lightest lanthanide ions. Trimesate or 1,3,5-benzenetricarboxylate ligand (hereafter symbolized by btc<sup>2-</sup>) has been chosen because it is a non-toxic and commercially available ligand (See Scheme 1). Moreover, this ligand presents a great ability to form infinite connections with lanthanide metal ions<sup>[18-21]</sup> and a remarkable versatility in adopting several different coordination modes ranging from unidentate to chelating and bridging. At last, to the best of our knowledge, there are only few reported trimesate coordination polymers that involve this metallic cation<sup>[22,23]</sup>.

In lanthanide coordination polymers three bonding modes have been observed according to the coordination environment of the COO<sup>-</sup> group<sup>[18,24]</sup> as shown in Scheme 2: Mode I, acting as a unidentate ligand to bind one metal ion; Mode II, acting as a bidentate ligand to chelate one metal ion; Mode III, acting as a bridging group between two metal ions.

In this paper we wish to report the synthesis and the crystal structure of a new coordination polymer, [Ca<sub>3</sub>(btc)<sub>2</sub>(H<sub>2</sub>O)<sub>12</sub>]<sub>∞</sub>, that constitutes our first result in this project.



**Scheme 1.** 1,3,5-benzenetricarboxylate (or trimesate) ligand (btc<sup>3-</sup>).



**Scheme 2.** Bonding modes in lanthanide-containing trimesate coordination polymers.

## 2. Experimental section

### 2.1 Synthesis

Trimesic acid was purchased from Acros Organics and used without further purification. Calcium chloride was purchased from STREM Chemicals and used without further purification. Its sodium salt was prepared by addition of three equivalents of sodium hydroxide to a suspension of trimesic acid in de-ionized water until complete dissolution. Then, the solution was evaporated to dryness. The solid phase was then put in suspension in ethanol, stirred and refluxed during 1 h. After filtration and drying in a desiccator, a white powder of tri-sodium trimesate was obtained. The yield of this synthesis is 90%. Anal. Calc.(found) for  $C_9H_3O_6Na_3$  (MW = 276 g mol<sup>-1</sup>) : C : 39.1%(39.0%) ; H : 1.1%(1.1%) ; O : 34.8%(34.5%) ; Na : 25.0%(25.4%).

Single crystals of the coordination polymer were obtained by slow diffusions of dilute aqueous solutions of Ca(II) chloride (0.25 mmol in 20mL) and of sodium salt of trimesate (0.25 mmol in 20mL) through an agar-agar gel bridge in a U-shaped tube. The gel was purchased from Acros Organics and jellified according to established procedure [25-27]. After several weeks, colorless single crystals were obtained.

Anal. Calc.(found) for  $[Ca_3(btc)_2(H_2O)_{12}]_{\infty}$  (MW = 750.66 g mol<sup>-1</sup>) : Ca : 16,0% (16,2%); C : 28.8%(28.79%) ; H : 4.0%(4.0%) ; O : 51.2%(51.0%).

IR spectrum clearly shows vibration bands characteristic of the – (O– C – O) – groups around 1560 cm<sup>-1</sup> and 1490 cm<sup>-1</sup> confirming the presence of carboxylate groups. It does not show any absorption band of any protonated carboxylic group (1715-1680 cm<sup>-1</sup>).

### 2.2 X-ray crystallographic studies

Single crystal has been sealed in a glass capillary for X-ray single crystal data collection in order to avoid potential dehydration. It was mounted on a Nonius Kappa CCD with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal data collection was performed at room temperature. A crystal-to-detector distance of 25.0 mm was used, and data collection strategy (determination and optimization of the detector and goniometer positions) was performed with the help of the COLLECT program [28], to measure Bragg reflections of the unique volume in reciprocal space. Structure determination was performed with the solving program SIR97 [29] that revealed all the non-

hydrogen atoms. All non-hydrogen atoms were refined anisotropically using the SHELXL program [30]. Hydrogen atoms bound to the organic ligands were localized at ideal positions. Hydrogen atoms of water molecules have not been localized. Absorption corrections were performed using the facilities [29,31,32] included in the WINGX program suite [31]. Crystal and final structure refinement data are listed in **Table I**. Positional parameters, selected bond lengths and angles are listed in **Tables II to IV**.

**Table I.** Crystal and final structure refinement data for  $[Ca_3(btc)_2(H_2O)_{12}]_{\infty}$ .

Molecular formula	Ca <sub>3</sub> C <sub>18</sub> O <sub>24</sub> H <sub>30</sub>
Formula weight	750.66
System	monoclinic
Space-group	C2/c (n° 15)
a/Å	19.3028(16)
b/Å	11.4850(9)
c/Å	13.0435(12)
$\alpha/^\circ$	90
$\beta/^\circ$	106.394(10)
$\gamma/^\circ$	90
V/Å <sup>3</sup>	2774.1(4)
Z	4
D <sub>calcd</sub> /g·cm <sup>-3</sup>	1.797
F(000)	1560
$\mu$ /mm <sup>-1</sup>	0,703
Radiation	Monochromated Mo K $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )
hkl Range	-23 ≤ h ≤ 22; 0 ≤ k ≤ 14; 0 ≤ l ≤ 15
$\theta$ Range (°)	2.09 ≤ $\theta$ ≤ 25.92
Data Collected	2547
Observed data (F <sub>obs</sub> ≥ 2 $\sigma$ (F <sub>obs</sub> <sup>2</sup> ))	1895
Parameters refined	205
R (%)	4.14
R <sub>w</sub> (%)	8.53
Goodness-of-fit	0.901
Final shift/error	0
$^aR_1 = \Sigma[ F_o  -  F_c ] / \Sigma F_o $ ; $^bR_w = [\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o ^2]^{1/2}$ $w = 1 / [\sigma^2(F_o^2) + (0.0650 \times P)^2 + 42.0485 \times P]$ where $P = (F_o^2 + 2 \times F_c^2) / 3$ .	

## 3. Results and discussion

### 3.1 Description of the structure of $[Ca_3(btc)_2(H_2O)_{12}]_{\infty}$

Extended asymmetric unit along with the atomic numbering scheme is depicted in **Figure 1**. There are two crystallographically independent Ca(II) ions in this crystal structure. Ca1 is seven-coordinated by five oxygen atoms from coordination water molecules as well as by two oxygen atoms from two different carboxylate groups that form a capped trigonal prism. Ca2 is eight-coordinated by four oxygen atoms from coordination water molecules as well as by four oxygen atoms from four carboxylate groups that form a dodecahedron. One coordination water molecule (O20) belongs to both coordination spheres. It coordinates Ca1 and Ca2 in a  $\mu_2$ -fashion and leads to trinuclear species Ca1-Ca2-Ca1 with short Ca1-Ca2 distances (**Figure 2**). Apart by these

$\mu_2$  water molecules, the three  $\text{Ca}^{2+}$  ions that form these trinuclear entities are held together by strong

hydrogen bonds O6---H10A and O5---H20A (See **Figure 2**).

**Table II.** Atomic positional and isotropic displacement parameters

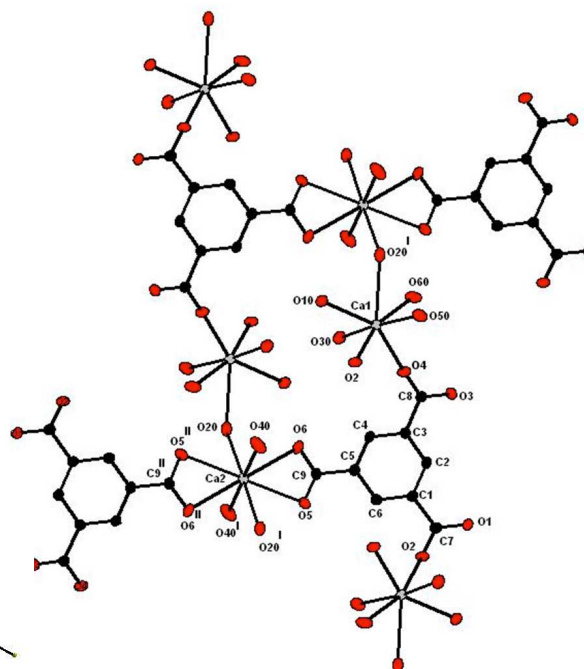
Atom 1	Atom 2	Distance
Ca1	O4	2.300(2)
Ca1	O10	2.344(2)
Ca1	O2	2.3810(19)
Ca1	O60	2.401(2)
Ca1	O30	2.4195(19)
Ca1	O50	2.457(2)
Ca1	O20	2.726(2)
Ca2	O40	2.373(2)
Ca2	O20	2.5076(18)
Ca2	O6	2.526(2)
Ca2	O5	2.580(2)

**Table III.** Selected bond distances (Å)

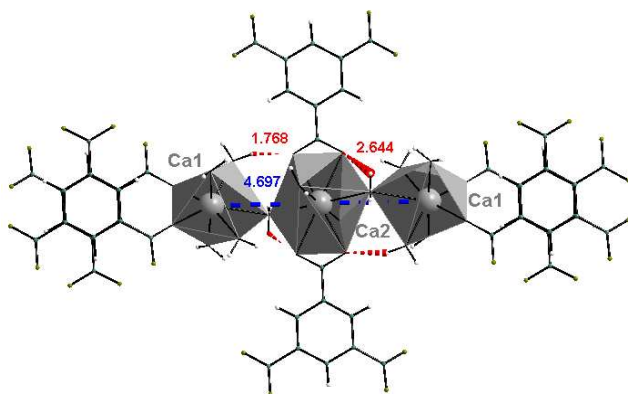
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i>
Ca1	0.13375(3)	0.10390(4)	0.02446(4)	0.01818(18)
Ca2	1/4	3/4	0	0.0173(2)
O1	-0.21825(10)	0.57436(15)	-0.19397(16)	0.0220(4)
O2	-0.15564(11)	0.73655(15)	-0.14595(16)	0.0252(5)
O3	-0.08123(10)	0.19625(15)	-0.17253(16)	0.0227(4)
O4	0.03321(11)	0.20240(16)	-0.07400(17)	0.0273(5)
O5	0.11099(12)	0.73670(17)	-0.0653(2)	0.0417(6)
O6	0.16894(11)	0.57545(18)	-0.0591(2)	0.0376(6)
C1	-0.09034(14)	0.5637(2)	-0.15386(19)	0.0155(5)
C2	-0.08998(13)	0.4424(2)	-0.15893(19)	0.0155(5)
C3	-0.02507(14)	0.3814(2)	-0.13454(19)	0.0148(5)
C4	0.03987(13)	0.4433(2)	0.1090(2)	0.0157(5)
C5	0.04028(13)	0.5643(2)	-0.1090(2)	0.0159(5)
C6	-0.02501(14)	0.6240(2)	-0.1309(2)	0.0176(5)
C7	-0.15957(14)	0.6295(2)	-0.16580(19)	0.0168(5)
C8	-0.02370(14)	0.2511(2)	-0.1267(2)	0.0172(5)
C9	0.11076(14)	0.6295(2)	-0.0772(2)	0.0186(5)
O10	0.25976(11)	0.10899(16)	0.0931(2)	0.0339(5)
O20	0.19156(10)	0.10780(16)	0.59559(16)	0.0244(4)
O30	0.17200(11)	0.17408(16)	0.87418(16)	0.0261(4)
O40	0.23082(13)	0.14657(18)	0.33690(17)	0.0355(5)
O50	0.07871(12)	0.03455(17)	0.16159(18)	0.0325(5)
O60	0.07401(13)	-0.04442(18)	-0.0986(2)	0.0448(6)

**Table IV.** Selected bond angles (°)

Atom 1	Atom 2	Atom 3	Angle
O4	Ca1	O10	145.33(7)
O4	Ca1	O2	87.50(7)
O4	Ca1	O60	78.77(7)
O4	Ca1	O30	77.65(7)
O4	Ca1	O50	95.50(7)
O4	Ca1	O20	145.95(7)
O10	Ca1	O60	121.61(8)
O10	Ca1	O30	77.30(8)
O10	Ca1	O20	67.12(6)
O10	Ca1	O50	110.20(8)
O10	Ca1	O2	75.90(7)
O2	Ca1	O60	162.29(8)
O2	Ca1	O50	78.28(7)
O2	Ca1	O20	118.76(7)
O2	Ca1	O30	104.21(7)
O60	Ca1	O30	83.88(8)
O60	Ca1	O20	70.61(7)
O60	Ca1	O50	91.83(8)
O30	Ca1	O20	112.55(6)
O30	Ca1	O50	172.50(8)
O50	Ca1	O20	71.50(6)
O40	Ca2	O20	98.13(7)
O40	Ca2	O6	101.36(8)
O40	Ca2	O5	98.69(8)
O20	Ca2	O6	109.99(6)
O20	Ca2	O5	111.66(7)
O6	Ca2	O5	130.13(6)



**Figure 1.** Extended asymmetric unit of  $[\text{Ca}_3(\text{btc})_2(\text{H}_2\text{O})_{12}]_x$ . Indexed atoms are obtained by one of the following operations: <sup>I</sup>  $(1/2 - x, 1/2 - y, 1 - z)$ ; <sup>II</sup>  $(x, 2 - y, 1/2 - z)$ .



**Figure 2.** Projection view of a trinuclear entity Ca1-Ca2-Ca1. Intermetallic distance is reported in blue. Hydrogen bonds are drawn in red.

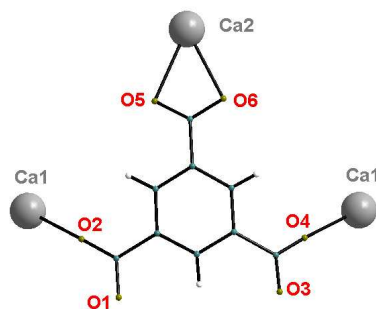
There is only one crystallographically independent  $\text{btc}^{2-}$  ligand in the crystal structure (See **Figure 3**). One carboxylato group binds in a bidentate way (mode II) the Ca2 ion while the two others adopt a unidentate coordination mode (mode I) for binding Ca1 ions.

Pairs of ligands  $\text{btc}^{2-}$  orientated at  $180^\circ$  from each other are connected by strong  $\pi$ -stacking interactions along the  $\vec{c}$  axis (See **Figure 4**).

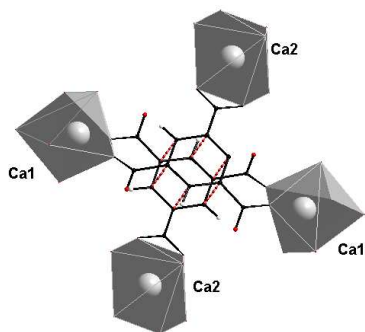
Expanded this motif leads to thick stair-like molecular planes that spread parallel to the  $(\vec{a}, \vec{c})$

plane (See **Figure 5**). These molecular layers stack along the c-axis direction (See **Figure 6**). The molecular packing is ensured by a complex hydrogen bonds network.

Despite the fact that there is no crystallization water molecule in the crystal structure, the water content of this compound is very important (27.4%). This could be of interest as far as highly hydrated compounds are targeted.

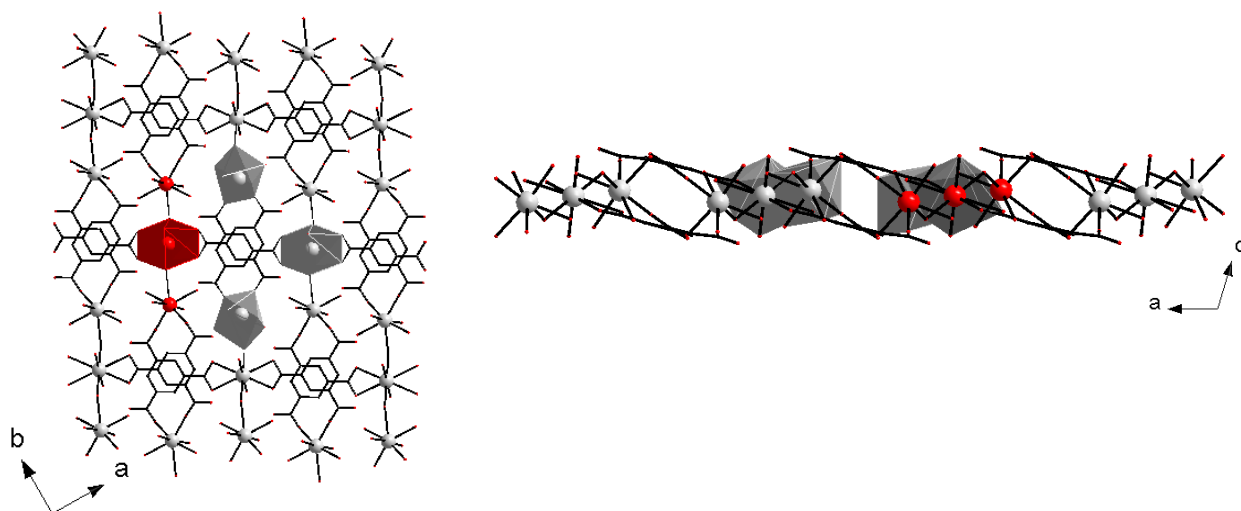


**Figure 3.** Coordination modes of the  $\text{btc}^{2-}$  ligand.



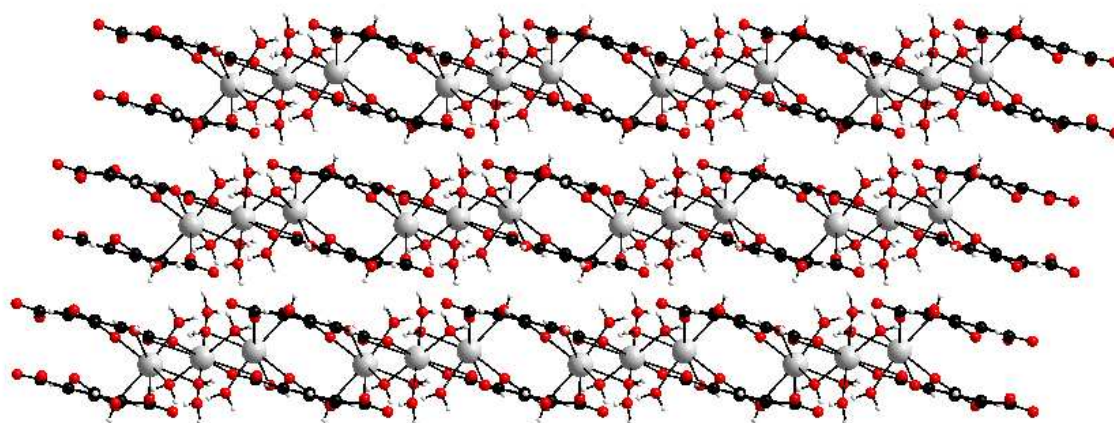
Atom 1	Symmetry	Atom 2	Symmetry	distance(Å)
C3	x, y, z	C6	-x, 1-y, -z	3.3225(3)
C2	x, y, z	C5	-x, 1-y, -z	3.3532(4)
C1	x, y, z	C4	-x, 1-y, -z	3.2908(3)

**Figure 4.** Left : Projection view of a pair of ligands  $\text{btc}^{2-}$ .  $\pi$ -stacking interactions are symbolized by dotted red lines. Right : distances between the two ligands.



**Figure 5.** Projection views along the c-axis (top) and b-axis (bottom) of a molecular layer. A trinuclear entity described above has been drawn in red. Polyhedron that belong to the molecular motif described above have been drawn.





**Figure 6.** Projection view along the b-axis of the crystal packing.

#### 4. Conclusion and outlooks

This single crystal structure represents our first published result arising from our studies of alkaline earth ions coordination polymers with trimesic acid. This compound, obtained by synthetic methods that are in agreement with the green chemistry principles<sup>[33]</sup>, confirms the validity of our approach. Actually, as expected, the use of gel medium has led to a new coordination polymer that has not been synthesized before. This had already been observed with lanthanide ions<sup>[11]</sup>. Therefore our groups have decided to pursue this research project and are currently working on the design of new potentially porous calcium-based coordination polymers.

#### SUPPORTING INFORMATION

Full details of the X-ray structure determination of compounds  $[Ca_3(TMA)_2 \cdot 12H_2O]$  have been deposited with the Cambridge Crystallographic Data Center under the depository number CCDC-151347, and can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)], on request, from the authors and the reference to this publication.

#### 5. Acknowledgments.

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