

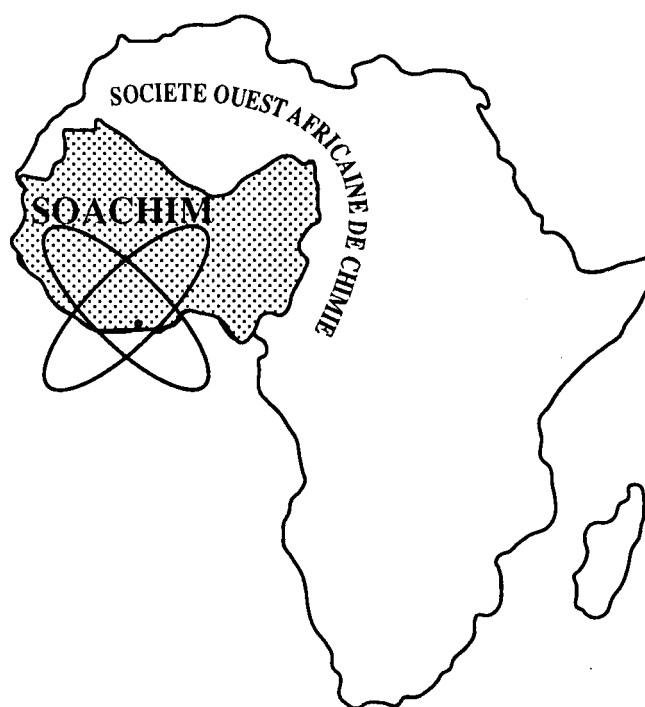
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Synthesis and crystal structure of a calcium(II)-based coordination polymer constructed from 1,2,4,5-Benzenetetracarboxylic Acid.

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Abstract : The polymeric compound, $[\text{Ca}_2(\text{btec})(\text{H}_2\text{O})_6]_\infty$ was obtained by slow diffusion of dilute aqueous solutions of calcium chloride and of the sodium salt of benzene-1,2,4,5-tetracarboxylic acid (H_4btec) through an agar-agar gel bridge in a U-shaped tube. This compound crystallizes in the triclinic system, space group P-1 ($n^\circ 2$) with $a = 5.8270$ (2) Å, $b = 7.7197$ (2) Å, $c = 9.6763$ (3) Å, $\alpha = 112.497$ (1) °, $\beta = 101.293$ (1)°, $\gamma = 97.567$ (2)° and $Z = 2$. Each Ca^{2+} ion is coordinated by three oxygen atoms from coordinated water molecules and five oxygen atoms from three btec^{4-} ligands that form a slightly distorted dodecahedron. Ligands also act as μ_6 -bridging groups between the Ca^{2+} ions. The crystal structure consists of a superimposition of 2D layers that spread parallel to the (\vec{a}, \vec{b}) plane.

Keywords : Ca(II); crystal structure; benzenetetracarboxylate; coordination polymers.

Synthèse et caractérisation structurale d'un nouveau polymère de coordination à base de calcium (II) et du ligand 1,2,4,5-Benzénététracarboxylate.

Résumé : Le polymère de coordination $[\text{Ca}_2(\text{btec})(\text{H}_2\text{O})_6]_\infty$ est obtenu par diffusion lente en milieu gel de sel de sodium de l'acide 1,2,4,5-benzénététracarboxylique (H_4btec) et du chlorure de calcium. Ce composé cristallise dans le système triclinique, groupe d'espace P-1 ($n^\circ 2$) avec $a = 5.8270$ (2) Å, $b = 7.7197$ (2) Å, $c = 9.6763$ (3) Å, $\alpha = 112.497$ (1) °, $\beta = 101.293$ (1)°, $\gamma = 97.567$ (2)° et $Z = 2$. Chaque ion Ca^{2+} est au centre d'un dodécaèdre distordu construit par trois atomes d'oxygène provenant de molécules d'eau de coordination et cinq atomes d'oxygène provenant de trois ligands btec^{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 ; acide benzénététracarboxylique.

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1. Introduction

The design of metal-organic materials with large channels and cavities has been deeply investigated, due to their intriguing structural diversity and potential functions as microporous solids for molecular adsorption, ion exchange, and heterogeneous catalysis^[1-4]. In particular, poly-benzenedicarboxylate ligands have been shown to be good building blocks in the design of metal-organic materials with desired topologies owing to their rich coordination modes. In spite of the rich coordination chemistry exhibited by 1,4-benzenedicarboxylic acid and 1,3,5-benzenetricarboxylic acids, studies on 1,2,4,5-benzenetetracarboxylic acid (H_4btec) are less numerous. However, H_4btec is also a versatile building block for the construction of metal-organic complexes through complete deprotonation of its carboxyl groups, and a series of interesting structures have been obtained^[5-9]. With the aim of understanding the coordination chemistry of H_4btec , we recently undertook a study devoted to reactions of H_4btec with metal ions in gel media. In particular, we were interested in such reactions with agar-agar gel bridge in U-shaped tubes^[10-12].

In order to initiate this study, we have chosen to use Ca^{2+} as metal ion 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. Ligand benzene-1,2,4,5-tetracarboxylate is rigid and has four carboxylate groups (See Scheme 1) that may be completely or partially deprotonated, inducing a lot of coordination modes^[13] and interesting structures with high dimensionalities.

Moreover, it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor to form new extended structures by hydrogen bonding interactions.

We report here the synthesis and the crystal structure of a new coordination polymer, with chemical formula $[Ca_2(btec)_2(H_2O)_6]_{\infty}$, that constitutes our first result in this project.

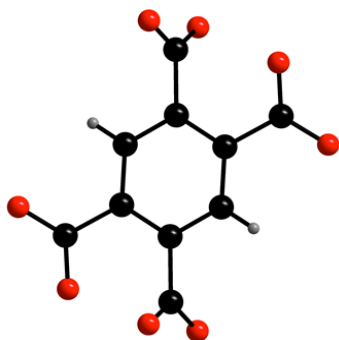


Figure 1. Benzene-1,2,4,5-tetracarboxylate ligand ($btec^{4-}$).

2. Experimental section

2.1 Synthesis

All reagents were used as obtained without further purification. Calcium chloride was purchased from STREM Chemicals. 1,2,4,5-benzenetetracarboxylic acid was purchased from Acros Organics. Its sodium salt was prepared by addition of four equivalents of sodium hydroxide to a suspension of 1,2,4,5-benzenetetracarboxylic 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 tetrasodium 1,2,4,5-benzenetetracarboxylate was obtained. The yield of this synthesis is 90%. Anal. Calc.(found) for $C_{10}H_2O_8Na_4$ (MW = 342.1 g mol⁻¹) : C : 35.1% (35.1%) ; H : 0.6% (0.7%) ; O : 37.4% (37.2%) ; Na : 26.9% (27.0%).

Single crystals of the coordination polymer were obtained by slow diffusion of dilute aqueous solutions of Ca(II) chloride (0.25 mmol in 20 mL) and of the sodium salt of benzene-1,2,4,5-tetracarboxylic acid (0.25 mmol in 20 mL) through an agar-agar gel bridge in a U-shaped tube. The gel was purchased from Acros Organics and jellified according to established procedure^[10-12]. After several weeks, colorless single crystals were obtained.

Anal. Calc.(found) for $[Ca_2(btec)(H_2O)_6]_{\infty}$ (MW = 438.4 g mol⁻¹) : Ca : 18.3% (18.3%) ; C : 27.4% (27.3%) ; H : 3.2% (3.1%) ; O : 51.1% (51.3%).

IR spectrum clearly shows vibration bands characteristic of the O–C–O groups around 1560 cm⁻¹ and 1400 cm⁻¹ confirming the presence of carboxylate groups. It does not show any absorption band of any protonated carboxylic group (1715–1680 cm⁻¹).

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 α radiation ($\lambda = 0.71073$ Å). 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^[14] to measure Bragg reflections of the unique volume in reciprocal space.

Structure determination was performed with the

solving program SIR97^[15] that revealed all the non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically using the SHELXL program^[16]. 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^[17] included in the WINGX program suite^[16]. 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 $[\text{Ca}_2(\text{btec})(\text{H}_2\text{O})_6]_{\infty}$.

Molecular formula	$\text{CaC}_5\text{O}_7\text{H}_7$
Formula weight	219.16
Crystal size (mm)	0.03 x 0.07 x 0.29
System	triclinic
Space-group	P-1 (n° 2)
a/Å	5.8270(2)
b/Å	7.7197(2)
c/Å	9.6763 (3)
$\alpha/^\circ$	112.497 (1)
$\beta/^\circ$	101.293 (2)
$\gamma/^\circ$	97.567 (2)
V/Å ³	383.96 (2)
Z	2
$D_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.870
F(000)	220
μ/mm^{-1}	0.82
Radiation	Monochromated Mo K α ($\lambda = 0.71073$ Å)
hkl Range	-10 \leq h \leq 9; -12 \leq k \leq 14; -17 \leq l \leq 18
θ Range (°)	3.7 \leq θ \leq 42.1
Data Collected	5280
Observed data ($F_{\text{obs}} \geq 2\sigma(F_{\text{obs}})$)	3147
Parameters refined	118
R (%)	5.02
R _w (%)	14.83
Goodness-of-fit	0.98
Final shift/error	0
^a R = $\Sigma(F_{\text{o}} - F_{\text{c}}) / \Sigma F_{\text{o}} $ ^b R _w = $[\Sigma w(F_{\text{o}} - F_{\text{c}})^2 / \Sigma w F_{\text{o}} ^2]^{1/2}$ $w = 1/[\sigma^2(F_{\text{o}}^2) + (0.0650 \times P)^2 + 42.0485 \times P]$ where $P = (F_{\text{o}}^2 + 2 \times F_{\text{c}}^2) / 3$.	

Table II. Atomic positional and isotropic displacement parameters

Atom	x/a	y/b	z/c	U
Ca1	0.95011 (5)	0.91241 (4)	0.15950 (3)	0.01569 (8)
C1	0.3710 (2)	0.63188 (19)	0.57345 (16)	0.0142 (2)
C2	0.5691 (2)	0.60182 (18)	0.66139 (15)	0.0132 (2)
C3	0.6961 (2)	0.4702 (2)	0.58723 (16)	0.0152 (2)
H3	0.8278	0.4502	0.6462	0.018*
C11	0.2328 (3)	0.7762 (2)	0.65095 (17)	0.0162 (2)
C22	0.6585 (2)	0.70596 (19)	0.83596 (16)	0.0140 (2)
O11	0.1000 (2)	0.83839 (19)	0.57122 (14)	0.0256 (3)
O12	0.2609 (2)	0.83086 (19)	0.79402 (13)	0.0258 (3)
O22	0.6105 (2)	0.61821 (17)	0.91598 (13)	0.0206 (2)
O23	0.7935 (2)	0.87144 (15)	0.89303 (12)	0.0181 (2)
O1	1.2835 (2)	0.9291 (2)	0.35658 (17)	0.0327 (3)
O2	1.1639 (3)	0.6872 (2)	0.01620 (18)	0.0335 (3)
O3	0.7275 (3)	0.7319 (2)	0.26705 (17)	0.0347 (3)

Table III. Selected bond distances (Å)

Ca1—O23 ⁱ	2.3587 (11)	C2—C3	1.3942 (17)
Ca1—O1	2.3922 (13)	C2—C22	1.5089 (18)
Ca1—O12 ⁱⁱ	2.4122 (11)	C3—C1 ^v	1.3908 (18)
Ca1—O3	2.4230 (14)	C11—O12	1.2519 (18)
Ca1—O2	2.4288 (12)	C11—O11	1.2537 (17)
Ca1—O23 ⁱⁱⁱ	2.4412 (11)	C11—Ca1 ⁱⁱ	2.8887 (13)
Ca1—O11 ⁱⁱ	2.6806 (12)	C22—O22	1.2542 (18)
Ca1—O22 ⁱⁱⁱ	2.7426 (12)	C22—O23	1.2576 (17)
Ca1—C11 ⁱⁱ	2.8887 (13)	C22—Ca1 ^{vi}	2.9349 (14)
Ca1—C22 ⁱⁱⁱ	2.9349 (14)	O11—Ca1 ⁱⁱ	2.6806 (12)
Ca1—Ca1 ^{iv}	3.9224 (6)	O12—Ca1 ⁱⁱ	2.4122 (11)
C1—C3 ^v	1.3908 (18)	O22—Ca1 ^{vi}	2.7426 (12)
C1—C2	1.3954 (18)	O23—Ca1 ⁱ	2.3588 (11)
C1—C11	1.5118 (17)	O23—Ca1 ^{vi}	2.4412 (11)

Symmetry codes: (i) -x+2, -y+2, -z+1; (ii) -x+1, -y+2, -z+1; (iii) x, y, z-1; (iv) -x+2, -y+2, -z; (v) -x+1, -y+1, -z+1; (vi) x, y, z+1.

Table IV. Selected bond angles (°)

O23 ⁱ —Ca1—O1	88.59 (5)	O2—Ca1—C22 ⁱⁱⁱ	71.68 (5)
O23 ⁱ —Ca1—O12 ⁱⁱ	80.22 (4)	O23 ⁱⁱⁱ —Ca1—C22 ⁱⁱⁱ	24.96 (4)
O1—Ca1—O12 ⁱⁱ	120.65 (5)	O11 ⁱⁱ —Ca1—C22 ⁱⁱⁱ	137.24 (4)
O23 ⁱ —Ca1—O3	168.58 (5)	O22 ⁱⁱⁱ —Ca1—C22 ⁱⁱⁱ	25.23 (4)
O1—Ca1—O3	82.89 (5)	C11 ⁱⁱ —Ca1—C22 ⁱⁱⁱ	114.33 (4)
O12 ⁱⁱ —Ca1—O3	97.58 (5)	O23 ⁱ —Ca1—Ca1 ^{iv}	35.90 (3)
O23 ⁱ —Ca1—O2	81.87 (4)	O1—Ca1—Ca1 ^{iv}	120.87 (4)
O1—Ca1—O2	76.31 (5)	O12 ⁱⁱ —Ca1—Ca1 ^{iv}	78.06 (3)
O12 ⁱⁱ —Ca1—O2	154.78 (5)	O3—Ca1—Ca1 ^{iv}	154.82 (4)
O3—Ca1—O2	103.34 (5)	O2—Ca1—Ca1 ^{iv}	77.01 (3)
O23 ⁱ —Ca1—O23 ⁱⁱⁱ	70.41 (4)	O23 ⁱⁱⁱ —Ca1—Ca1 ^{iv}	34.51 (3)
O1—Ca1—O23 ⁱⁱⁱ	148.03 (4)	O11 ⁱⁱ —Ca1—Ca1 ^{iv}	119.99 (3)
O12 ⁱⁱ —Ca1—O23 ⁱⁱⁱ	80.31 (4)	O22 ⁱⁱⁱ —Ca1—Ca1 ^{iv}	83.67 (3)
O3—Ca1—O23 ⁱⁱⁱ	120.47 (5)	C11 ⁱⁱ —Ca1—Ca1 ^{iv}	100.10 (3)
O2—Ca1—O23 ⁱⁱⁱ	77.04 (4)	C22 ⁱⁱⁱ —Ca1—Ca1 ^{iv}	58.52 (3)
O23 ⁱ —Ca1—O11 ⁱⁱ	98.60 (4)	C3 ^v —C1—C2	119.26 (11)
O1—Ca1—O11 ⁱⁱ	74.18 (4)	C3 ^v —C1—C11	120.08 (11)
O12 ⁱⁱ —Ca1—O11 ⁱⁱ	50.90 (4)	C2—C1—C11	120.65 (12)
O3—Ca1—O11 ⁱⁱ	71.79 (5)	C3—C2—C1	119.66 (12)
O2—Ca1—O11 ⁱⁱ	150.47 (5)	C3—C2—C22	116.73 (11)
O23 ⁱⁱⁱ —Ca1—O11 ⁱⁱ	131.20 (3)	C1—C2—C22	123.61 (11)
O23 ⁱ —Ca1—O22 ⁱⁱⁱ	118.75 (4)	C1 ^v —C3—C2	121.08 (12)
O1—Ca1—O22 ⁱⁱⁱ	134.62 (4)	O12—C11—O11	123.01 (12)
O12 ⁱⁱ —Ca1—O22 ⁱⁱⁱ	100.39 (4)	O12—C11—C1	117.71 (12)
O3—Ca1—O22 ⁱⁱⁱ	72.65 (4)	O11—C11—C1	119.27 (12)
O2—Ca1—O22 ⁱⁱⁱ	73.12 (4)	O12—C11—Ca1 ⁱⁱ	55.53 (7)
O23 ⁱⁱⁱ —Ca1—O22 ⁱⁱⁱ	50.06 (3)	O11—C11—Ca1 ⁱⁱ	67.85 (8)
O11 ⁱⁱ —Ca1—O22 ⁱⁱⁱ	129.16 (4)	C1—C11—Ca1 ⁱⁱ	169.73 (10)
O23 ⁱ —Ca1—C11 ⁱⁱ	90.82 (4)	O22—C22—O23	123.27 (13)
O1—Ca1—C11 ⁱⁱ	98.35 (5)	O22—C22—C2	118.64 (13)
O12 ⁱⁱ —Ca1—C11 ⁱⁱ	25.33 (4)	O23—C22—C2	117.85 (13)
O3—Ca1—C11 ⁱⁱ	82.95 (5)	O22—C22—Ca1 ^{vi}	68.78 (8)
O2—Ca1—C11 ⁱⁱ	170.98 (5)	O23—C22—Ca1 ^{vi}	54.98 (7)
O23 ⁱⁱⁱ —Ca1—C11 ⁱⁱ	105.54 (4)	C2—C22—Ca1 ^{vi}	165.68 (9)
O11 ⁱⁱ —Ca1—C11 ⁱⁱ	25.67 (4)	C11—O11—Ca1 ⁱⁱ	86.48 (9)
O22 ⁱⁱⁱ —Ca1—C11 ⁱⁱ	115.29 (4)	C11—O12—Ca1 ⁱⁱ	99.13 (8)
O23 ⁱ —Ca1—C22 ⁱⁱⁱ	94.01 (4)	C22—O22—Ca1 ^{vi}	85.99 (9)
O1—Ca1—C22 ⁱⁱⁱ	147.14 (4)	C22—O23—Ca1 ⁱ	144.51 (10)
O12 ⁱⁱ —Ca1—C22 ⁱⁱⁱ	92.00 (4)	C22—O23—Ca1 ^{vi}	100.06 (9)
O3—Ca1—C22 ⁱⁱⁱ	97.27 (5)	Ca1 ⁱ —O23—Ca1 ^{vi}	109.59 (4)

Symmetry codes: (i) -x+2, -y+2, -z+1; (ii) -x+1, -y+2, -z+1; (iii) x, y, z-1; (iv) -x+2, -y+2, -z;
(v) -x+1, -y+1, -z+1; (vi) x, y, z+1.

3. Results and discussion

3.1 Description of the structure of [Ca₂(btec)(H₂O)₆]_∞.

Extended asymmetric unit with the atomic numbering scheme is depicted in Figure 2.

All carboxylic groups of the organic ligand in the compounds are deprotonated, in agreement with the IR spectrum, where no absorption peak around 1700 cm⁻¹ for a protonated carboxylic group is observed. There is only one crystallographically independent Ca²⁺ ion in the asymmetric unit. The Ca²⁺ ion is eight-coordinated by five carboxylate oxygen atoms [Ca—O = 2.3587 (11) – 2.7426 (12) Å] from three btec⁴⁻ ligands, and three coordination water molecules [Ca—O = 2.3922 (13) – 2.4230 (14) Å]. The shortest Ca²⁺—Ca distance is 3.9224 (6) Å, indicating the absence of a direct metal—metal interaction. The coordination

geometry around the Ca²⁺ ion can be described as a slightly distorted dodecahedral.

There is only half-crystallographically independent btec⁴⁻ ligand in the asymmetric unit (See Figure 3). The btec⁴⁻ ligand acts as a μ₆-bridge that links six Ca²⁺ ions. Two para-carboxylate groups adopt bidentate bridging modes while the two other para-carboxylate groups act as bidentate and μ₃-bridging coordination modes.

The crystal structure can be described as the superimposition of 2D layers that spread parallel to the (ab) plane (Figure 4b). The crystal packing is ensured by aromatic π-stacking interactions (C[⋯]C inter-planar distances: 4.0102 (1) Å). Coordination water molecules and oxygen atoms from carboxylate groups are involved in a complex network of strong hydrogen bonds. It is noticeable that this crystal structure does not contain any crystallization water molecule.

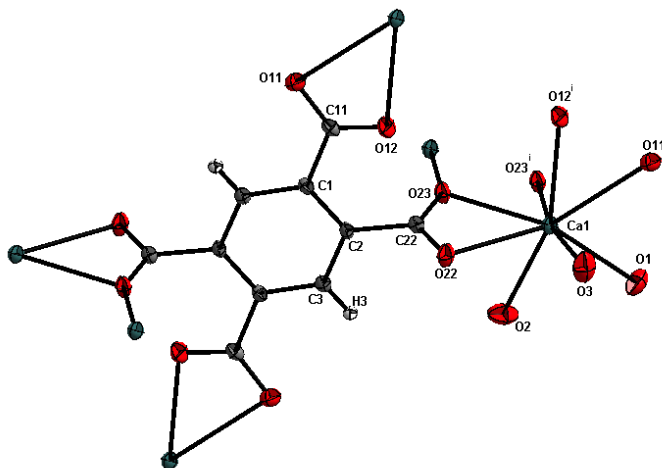


Figure 2: Extended asymmetric unit of $[\text{Ca}_2(\text{btec})(\text{H}_2\text{O})_6]_\infty$. Indexed atoms are obtained by one the following operations : (i) $-x+2, -y+2, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $x, y, z-1$; (iv) $-x+2, -y+2, -z$; (v) $-x+1, -y+1, -z+1$; (vi) $x, y, z+1$

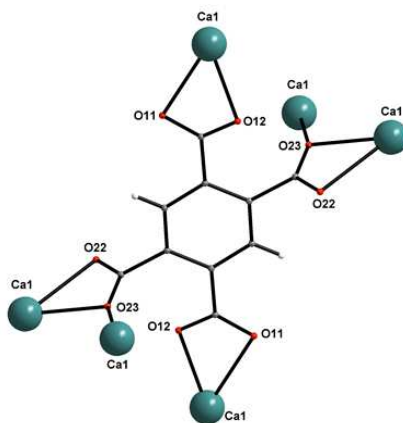


Figure 3.Coordination modes of the btec^{4-} ligand.

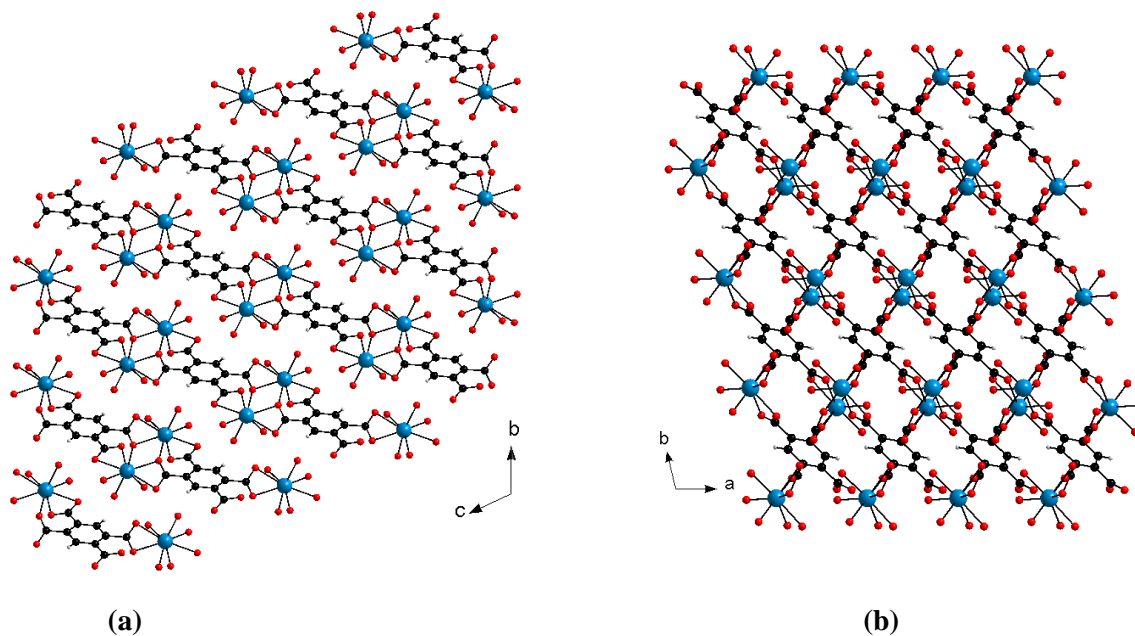


Figure 4: Projection view of the crystal packing along (a) the a-axis. (b) the c-axis.

4. Conclusion and outlooks

This single crystal structure represents our first published result arising from our studies of alkaline earth ions coordination polymers with benzene-1,2,4,5-tetracarboxylic acid. This compound, obtained by synthetic methods that are in agreement with the green chemistry principles^[18], confirms the validity of our approach. Actually, as expected, the use of gel medium has led to a new coordination polymer. This had already been observed with lanthanide ions^[9]. 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 $[\text{Ca}_2(\text{btcc})(\text{H}_2\text{O})_6]_\infty$ have been deposited with the Cambridge Crystallographic Data Center under the depository number CCDC-965873, and can be obtained free of charge at 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], on request, from the authors and the reference to this publication.

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