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Metal–organic frameworks built from alkali metal ions (Li⁺–Cs⁺) and 1,2,3,4-cyclobutanetetracarboxylic acid†

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Pierre Thuéry

Six complexes formed by alkali metal ions with 1,2,3,4-cyclobutanetetracarboxylic acid (H₄cbtc) have been synthesized and crystallographically characterized. In the complexes obtained at room temperature, the original *cis,trans,cis* form of the ligand (*c*-H₄cbtc) is retained, while in the complexes synthesized under hydrothermal conditions, isomerization occurs to give the *trans,trans,trans* form (*t*-H₄cbtc). [Li₂(*t*-H₂cbtc)(H₂O)₂] (1) crystallizes as a two-dimensional (2D) assembly, with only four oxygen atoms of the ligand being involved in the bis-chelating coordination of two Li⁺ cations. A 2D polymer is also obtained with the aliphatic analogue 1,2,3,4-butanetetracarboxylic acid (H₄btc) in the complex [Li₄(btc)(H₂O)₄]·H₂O (2), with a much larger ligand denticity of 10. All the other complexes in this series crystallize as three-dimensional (3D) frameworks, with the cation coordination number and ligand denticity increasing when going from the lighter to the heavier cations. In [Na(*t*-H₃cbtc)] (3), the cation octahedral coordination polyhedra are isolated and the {4-6⁵} framework contains only four-fold nodes. In the case of K⁺, the complexes formed with both isomers of the ligand could be isolated. The structure of [K₂(*c*-H₂cbtc)(H₂O)₄] (4) displays {[K(H₂O)₂]⁺}_∞ planar subunits which are assembled into a 3D network by the hexacoordinated *c*-H₂cbtc²⁻ ligands, while the {4¹²-6³} network built in [K(*t*-H₃cbtc)] (5) contains only six-fold nodes, K⁺ being chelated by two ligands, with four more donors resulting in a distorted square antiprismatic coordination polyhedron. Although [Rb(*c*-H₃cbtc)] (6) contains the other ligand isomer, it displays a coordination mode and an overall architecture similar to those in 5, but for the quite different cation coordination polyhedron, which is a distorted dodecahedron with triangular faces. Finally, [Cs(*t*-H₃cbtc)] (7) displays the highest coordination number and ligand denticity in the series, both equal to 10. The cation coordination polyhedron is derived from the cuboctahedron through removal of two vertices in a square face. The {4²⁴-6⁴} network formed contains chains of tightly packed Cs⁺ cations with face-sharing coordination polyhedra, thus confirming the prevalence of face-sharing subunits previously noticed in the case of the heavier alkali cations. With packing indexes larger than 0.80 in the whole series, none of these 3D frameworks exhibits appreciable porosity.

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Introduction

The use of s-block (alkali and alkaline-earth) metal cations in the design of metal–organic coordination polymers or frameworks, although less developed than that of d-block cations, has aroused much interest in the past years, and it has recently been thoroughly reviewed.¹ A large array of two- and three-dimensional assemblies involving alkali metal ions and various ligands, among which polycarboxylic acids are prominent, has thus been characterized,² with potential applications as porous materials for gas storage, separation

or catalysis.¹ In particular, the lighter alkali element, Li, as well as Mg among the alkaline-earth series, can be used to synthesize lightweight frameworks enabling the optimization of the gravimetric capacity for gas uptake, a property of much relevance for hydrogen storage;^{1,2*l,m,p*,3} Mg-based porous compounds suitable for CO₂ uptake were also described.^{3*d*,4} Besides the network-building role of these cations, it was also shown that the hydrogen, carbon dioxide or methane uptake by porous frameworks based on other metal cations could be increased upon reductive doping with Li, Na or K.⁵ From the point of view of structural chemistry, an appealing characteristic of both s block columns is that they provide a set of cations with the same charge, but differing radius and electronegativity, whose interaction with carboxylate ligands is essentially ionic (the complexes formed may thus be designated as salts). For a given ligand, the variations in coordination number

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among each column, from typically four for Li^+ up to twelve for Cs^+ in the alkali metal series, result in the formation of very different architectures, as previously illustrated in the case of two tetracarboxylic acids, pyrazinetetracarboxylic acid²⁰ and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid.²⁹ In the latter case, the assemblies formed with the whole Li^+ – Cs^+ series are either two- or three-dimensional, and the bonding mode of the ligand is different for each cation. The present work is an extension of these investigations to the alicyclic 1,2,3,4-cyclobutanetetracarboxylic acid (denoted H_4cbtc hereafter), which has not been widely used as a ligand up to now since only about a dozen metal complexes have been reported in the Cambridge Structural Database (CSD, Nov. 2013),⁶ with the cations $\text{K}^+/\text{Mg}^{2+}$,⁷ Ni^{2+} or Cu^{2+} ,⁸ Cd^{2+} ,⁹ La^{3+} ,¹⁰ and UO_2^{2+} .¹¹ This acid exists in two isomeric forms, either centrosymmetric *cis,trans,cis* (*c*- H_4cbtc) or non-centrosymmetric *trans,trans,trans* (*t*- H_4cbtc). Complexes could be obtained and crystallographically characterized for the whole Li^+ – Cs^+ series, but different experimental conditions had to be used, which resulted in one or the other isomer being present; complexes with each of them having been obtained in the case of K^+ only. For comparison, a novel complex of Li^+ with the aliphatic analogue 1,2,3,4-butanetetracarboxylic acid (H_4btc) will also be described, which is different from those recently published.^{2x}

Experimental

Synthesis

1,2,3,4-Cyclobutanetetracarboxylic and 1,2,3,4-butanetetracarboxylic acids were purchased from Aldrich. $\text{LiOH}\cdot\text{H}_2\text{O}$, NaNO_3 , KOH and RbCl were from Prolabo, KNCS from Fluka, and CsNO_3 from Acros. As reported elsewhere,¹¹ the presence of only one isomer in the commercial sample of 1,2,3,4-cyclobutanetetracarboxylic acid was checked by ^1H NMR, and recrystallization in water gave single crystals of the *cis,trans,cis* isomer only, with unit cell parameters analogous to those previously reported.¹²

[Li₂(*t*- H_2cbtc)(H_2O)₂] (1). 1,2,3,4-Cyclobutanetetracarboxylic acid (47 mg, 0.20 mmol), $\text{LiOH}\cdot\text{H}_2\text{O}$ (9 mg, 0.21 mmol), and demineralized water (3 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure, giving colourless crystals of complex 1 in low yield within one month.

[Li₄(*bc*)(H_2O)₄] $\cdot\text{H}_2\text{O}$ (2). 1,2,3,4-Butanetetracarboxylic acid (47 mg, 0.20 mmol) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (34 mg, 0.81 mmol) were dissolved in demineralized water (1.5 mL). The solution was allowed to evaporate slowly, giving colourless crystals of complex 2 in low yield within two months.

[Na(*t*- H_3cbtc)] (3). 1,2,3,4-Cyclobutanetetracarboxylic acid (23 mg, 0.10 mmol), NaNO_3 (34 mg, 0.40 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure for two weeks. The solution was then allowed to evaporate slowly at room temperature, giving colourless crystals of complex 3 in low yield within one month.

[K₂(*c*- H_2cbtc)(H_2O)₄] (4). 1,2,3,4-Cyclobutanetetracarboxylic acid (47 mg, 0.20 mmol) and KOH (23 mg, 0.41 mmol) were dissolved in demineralized water (1.5 mL). The solution was allowed to evaporate slowly, giving colourless crystals of complex 4 within one month.

[K(*t*- H_3cbtc)] (5). 1,2,3,4-Cyclobutanetetracarboxylic acid (23 mg, 0.10 mmol), KNCS (20 mg, 0.21 mmol), and demineralized water (3 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure for one week. The solution was then allowed to evaporate slowly at room temperature, giving colourless crystals of complex 5 in low yield within two months.

[Rb(*c*- H_3cbtc)] (6). 1,2,3,4-Cyclobutanetetracarboxylic acid (23 mg, 0.10 mmol) and RbCl (25 mg, 0.21 mmol) were dissolved in demineralized water (1.5 mL). The solution was allowed to evaporate slowly, giving colourless crystals of complex 6 in low yield within two months.

[Cs(*t*- H_3cbtc)] (7). 1,2,3,4-Cyclobutanetetracarboxylic acid (23 mg, 0.10 mmol), CsNO_3 (80 mg, 0.41 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure for one month. The solution was then allowed to evaporate slowly at room temperature, giving colourless crystals of complex 7 in low yield within one month.

Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer¹³ using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å). The crystals were introduced into glass capillaries with a protecting “Paratone-N” oil (Hampton Research) coating. The unit cell parameters were determined from ten frames and then refined on all data. The data (combinations of φ - and ω -scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000 .¹⁴ Absorption effects for compounds 4–7 were corrected empirically with the program SCALEPACK .¹⁴ The structures were solved by direct methods with SHELXS-97 , expanded by subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97 .¹⁵ In the absence of a suitable anomalous scatterer, the Friedel pairs were merged for compound 1. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on Fourier-difference maps in all compounds but 7, in which the three protons are likely disordered over the four possible sites. In complexes 5 and 6, the hydrogen atom bound to O1 was given an occupancy parameter of 0.5 for charge equilibrium and to account for its closeness to its image by symmetry. The carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated with a riding model, with an isotropic displacement parameter equal to 1.2 times that of the parent atom.

Crystal data and structure refinement parameters are given in Table 1 and selected bond lengths are listed in Table 2. The molecular plots were drawn with ORTEP-3 ¹⁶ and

Table 1 Crystal data and structure refinement details

	1	2	3	4	5	6	7
Chemical formula	C ₈ H ₁₀ Li ₂ O ₁₀	C ₈ H ₁₆ Li ₄ O ₁₃	C ₈ H ₇ NaO ₈	C ₈ H ₁₄ K ₂ O ₁₂	C ₈ H ₇ KO ₈	C ₈ H ₇ O ₈ Rb	C ₈ H ₇ CsO ₈
<i>M</i> /g mol ⁻¹	280.04	347.97	254.13	380.39	270.24	316.61	364.05
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Tetragonal
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2/ <i>n</i>	<i>Pccn</i>	<i>P</i> 4/ <i>n</i>
<i>a</i> /Å	4.9227(2)	21.6635(16)	5.3722(2)	8.4001(7)	8.6068(2)	8.1309(4)	9.8276(3)
<i>b</i> /Å	13.9837(3)	8.1817(4)	13.4257(11)	13.7383(11)	5.5968(2)	9.6620(5)	9.8276(3)
<i>c</i> /Å	15.7876(3)	8.1299(6)	12.4510(10)	6.4302(4)	10.7160(3)	12.7399(5)	10.2207(5)
β /°	90	98.514(4)	91.272(5)	104.284(5)	92.205(2)	90	90
<i>V</i> /Å ³	1086.78(5)	1425.10(16)	897.81(11)	719.12(10)	515.81(3)	1000.86(8)	987.13(8)
<i>Z</i>	4	4	4	2	2	4	4
<i>D</i> _{calcd} /g cm ⁻³	1.712	1.622	1.880	1.757	1.740	2.101	2.450
μ (Mo K α)/mm ⁻¹	0.157	0.150	0.210	0.721	0.545	4.978	3.783
<i>F</i> (000)	576	720	520	392	276	624	696
Reflections collected	26 925	23 295	31 005	22 296	15 997	56 474	34 426
Independent reflections	1911	1348	2734	1362	1260	1527	1497
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1803	1203	2148	1174	1217	1331	1412
<i>R</i> _{int}	0.013	0.027	0.026	0.023	0.020	0.011	0.019
Parameters refined	182	114	154	100	78	78	89
<i>R</i> ₁	0.031	0.033	0.037	0.028	0.033	0.023	0.023
w <i>R</i> ₂	0.090	0.095	0.103	0.073	0.092	0.067	0.061
<i>S</i>	1.075	1.079	1.039	1.065	1.077	1.072	1.155
$\Delta\rho_{\text{min}}$ /e Å ⁻³	-0.21	-0.27	-0.27	-0.27	-0.28	-0.60	-0.80
$\Delta\rho_{\text{max}}$ /e Å ⁻³	0.28	0.25	0.34	0.27	0.39	0.29	1.12

the views of the packings were prepared with VESTA.¹⁷ The topological analyses were performed using the program TOPOS.¹⁸

Results and discussion

Obtaining single crystals of the alkali metal salts of H₄cbtc of sufficient quality for structure determination proved more difficult than expected, and the complexes for the complete alkali metal cation series could not be crystallized under identical conditions. As indicated previously (see Experimental), H₄cbtc is originally in the *cis,trans,cis* form (*c*-H₄cbtc) and the complexes obtained at room temperature (4 and 6) retain this form. The other complexes were crystallized either under hydrothermal conditions (180 °C) or from evaporation at room temperature following a period of heating at 180 °C. In these cases, as previously noticed in the case of lanthanum¹⁰ and uranyl¹¹ complexes, H₄cbtc undergoes isomerization into the *trans,trans,trans* form (*t*-H₄cbtc), likely as a result of the formation of carbanions through acid–base equilibrium, followed by pyramidal inversion. The role of temperature in the present experiments is thus primarily to promote the ligand isomerization.

The lithium complex [Li₂(*t*-H₂cbtc)(H₂O)₂] (1) was crystallized at 180 °C, and its structure is shown in Fig. 1. The two crystallographically independent lithium atoms are in similar environments (the complex possesses a plane of pseudo-symmetry), and the cyclobutane ring is in a puckered conformation. Each of the cations is chelated by two carboxylic/ate groups adjacent to one another on the cyclobutane ring, one of them bridging the two cations, thus forming two seven-membered chelate rings. The last carboxylic group is uncoordinated, resulting in, overall, only

half the ligand being involved in complexation, in the μ_2, κ^4 mode (Scheme 1). The lithium coordination sphere is completed by two water molecules, both of them bridging, to give the usual distorted tetrahedral coordination environment. The Li–O(carboxylic/ate) and Li–O(water) bond lengths are in the ranges 1.927(3)–1.970(3) and 2.011(3)–2.035(3) Å, and their average values, 1.944(17) and 2.023(9) Å, respectively, are in agreement with the average values for comparable bonds in the CSD, 1.97(9) and 2.05(9) Å (the latter for bridging water molecules). The coordination polymer thus formed is two-dimensional (2D) and parallel to the *ab* plane, with the total point (Schläfli) symbol {12³}₂{12³}₃ (the first symbol for the cations and the second for the three ligands). A simplified view of the network is given in Scheme 2, which shows the presence of {[Li(H₂O)]_{*n*}}^{*n*+} chains comprising vertex-sharing coordination polyhedra, directed along the *a* axis, with adjacent chains along the *b* axis being linked to one another by the *t*-H₂cbtc²⁻ anions. Because these anions are located alternately above and below the mean assembly plane, the sheets have a corrugated aspect, and, due to their tight packing along the *c* axis direction, the overall structure is quite compact, with a Kitaigorodskii packing index (KPI, estimated with PLATON¹⁹) of 0.80, indicating that no significant free space is present. The two carboxylic protons bound to O4 and O6 are involved in hydrogen bonds with the carboxylate atoms O2 and O7 of an adjacent sheet, while two among the four hydrogen bonds formed by the water molecules with carboxylic/ate groups are also inter-sheet ones.

In the case of lithium, it was also possible to grow crystals of the complex with H₄btc, the aliphatic analogue of H₄cbtc, which is different from the two complexes recently reported.^{2x} The asymmetric unit in the structure of

Table 2 Environment of the alkali metal atoms in compounds 1–7: selected bond lengths (Å)^a

1	Li1–O1	1.932(3)
	Li1–O8	1.970(3)
	Li1–O9	2.011(3)
	Li1–O9 ⁱ	2.035(3)
	Li2–O2	1.927(3)
	Li2–O3	1.945(3)
	Li2–O10	2.024(3)
	Li2–O10 ^j	2.021(3)
2	Li1–O1	1.942(3)
	Li1–O3	1.990(3)
	Li1–O3 ⁱ	1.956(3)
	Li1–O4 ^j	1.911(3)
	Li2–O1	1.961(3)
	Li2–O2 ^k	1.964(3)
	Li2–O5	2.023(3)
	Li2–O6	1.980(3)
3	Na–O1	2.3866(11)
	Na–O2 ⁱ	2.3457(11)
	Na–O3	2.5416(12)
	Na–O4 ^j	2.3477(12)
	Na–O5 ^k	2.6047(11)
	Na–O7 ⁱ	2.3465(11)
4	K–O1	2.8548(13)
	K–O1 ⁱ	2.9941(13)
	K–O3 ^j	2.7359(13)
	K–O5	2.8144(14)
	K–O5 ⁱ	2.7795(14)
	K–O6 ^k	2.7219(13)
5	K–O1	3.0570(9)
	K–O2 ^j	2.8915(9)
	K–O3	2.8476(9)
	K–O4 ^m	2.8117(9)
6	Rb–O1	2.9645(10)
	Rb–O2 ^j	2.9371(10)
	Rb–O3	3.5403(10)
	Rb–O4 ^l	2.8164(11)
7	Cs1–O1	3.1498(15)
	Cs1–O3	3.4362(16)
	Cs1–O4b ^m	3.124(3)
	Cs2–O1	3.0808(15)
	Cs2–O2 ⁱ	3.2822(16)
Cs2–O4a ^u	3.111(3)	

^a Symmetry codes. 1: $i = x - 1/2, 3/2 - y, 1 - z$; $j = x - 1/2, 1/2 - y, 1 - z$. 2: $i = 3/2 - x, 3/2 - y, 2 - z$; $j = 3/2 - x, y - 1/2, 3/2 - z$; $k = x, 2 - y, z + 1/2$. 3: $i = x - 1/2, 3/2 - y, z + 1/2$; $j = x - 1, y, z$; $k = 1/2 - x, y + 1/2, 3/2 - z$. 4: $i = x, 3/2 - y, z + 1/2$; $j = x, 3/2 - y, z - 1/2$; $k = 2 - x, 1 - y, -z$. 5: $j = 2 - x, 1 - y, -z$; $m = x, y - 1, z$. 6: $j = x - 1/2; y + 1/2, 1 - z$; $l = x - 1/2, 1 - y, 1/2 - z$. 7: $i = y + 1/2, -x, 1 - z$; $m = -y, x - 1/2, 2 - z$; $u = 1 - x, -y, 1 - z$.

$[\text{Li}_4(\text{btc})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (2) contains two Li^+ cations and half the fully deprotonated ligand btc^{4-} , the other half being generated by an inversion centre (Fig. 2). The two independent lithium atoms are in different environments, with Li1 bound to four carboxylate oxygen atoms pertaining to three ligands, and Li2 bound to two carboxylate atoms from two ligands and two terminal water molecules; both are in tetrahedral environments with unexceptional bond lengths. Overall, the ligand forms two seven-membered chelate rings, as in complex 1, but each carboxylate group is tridentate, and each ligand thus connects 10 metal cations, instead of two in 1, in the μ_{10}, κ^8 mode. The same bonding mode was observed in

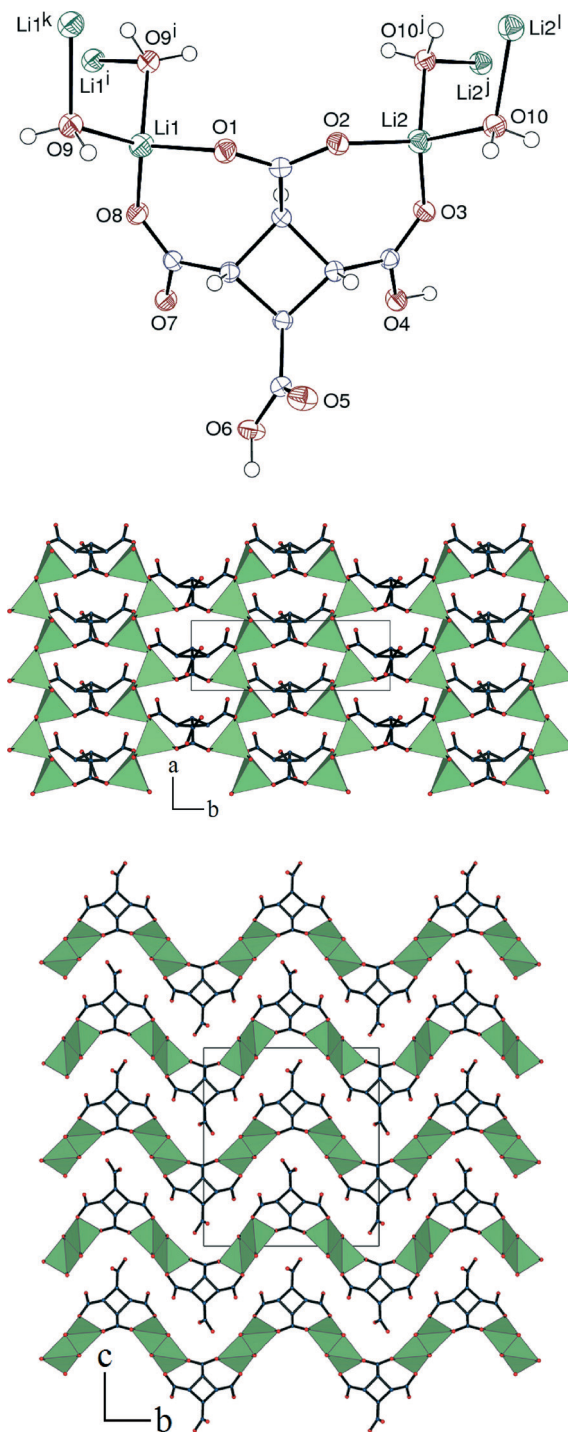
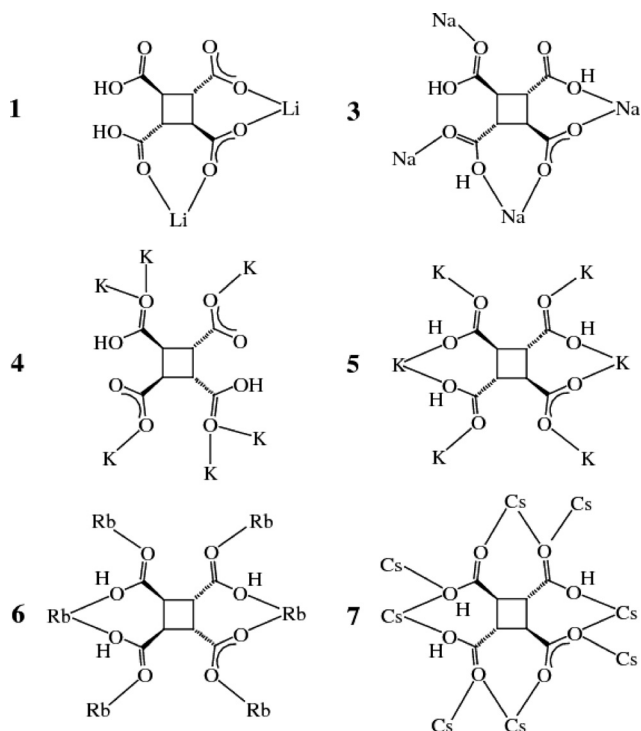
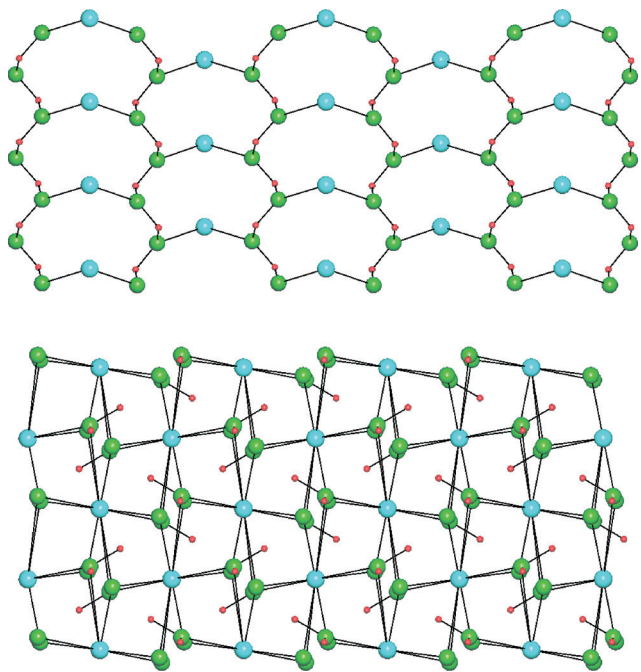


Fig. 1 Top: view of complex 1. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: $i = x - 1/2, 3/2 - y, 1 - z$; $j = x - 1/2, 1/2 - y, 1 - z$; $k = x + 1/2, 3/2 - y, 1 - z$; $l = x + 1/2, 1/2 - y, 1 - z$. Middle: view of the 2D assembly. Bottom: view of the packing with the layers viewed edge-on. Hydrogen atoms are omitted and the lithium coordination polyhedra are shown in the last two views.

$[\text{Li}_4(\text{btc})(\text{H}_2\text{O})_4]^{2x}$ as well as in $[\text{Na}_2(\text{H}_2\text{btc})]^{20}$ while each ligand connects four cations only in $(\text{H}_2\text{NMe}_2)_2[\text{Li}_2(\text{btc})(\text{H}_2\text{O})_2]^{2x}$. Complex 2 was obtained in water at room temperature, in contrast to the other two lithium complexes with the same



Scheme 1 Coordination modes of $H_{(4-x)}cbtcX^-$ in compounds 1 and 3-7.



Scheme 2 Nodal representations of the networks in the lithium complexes 1 (top) and 2 (bottom). Orientation identical to that in Fig. 1 and 2. Green, Li; red, O; light blue, centroid of the cbtc or btc ligand.

ligand, which were synthesized at 90 °C from a 1:1 mixture of water and *N,N*-dimethylformamide. This may explain the presence of one extra lattice water molecule in 2, since syntheses in water at high temperature are likely under

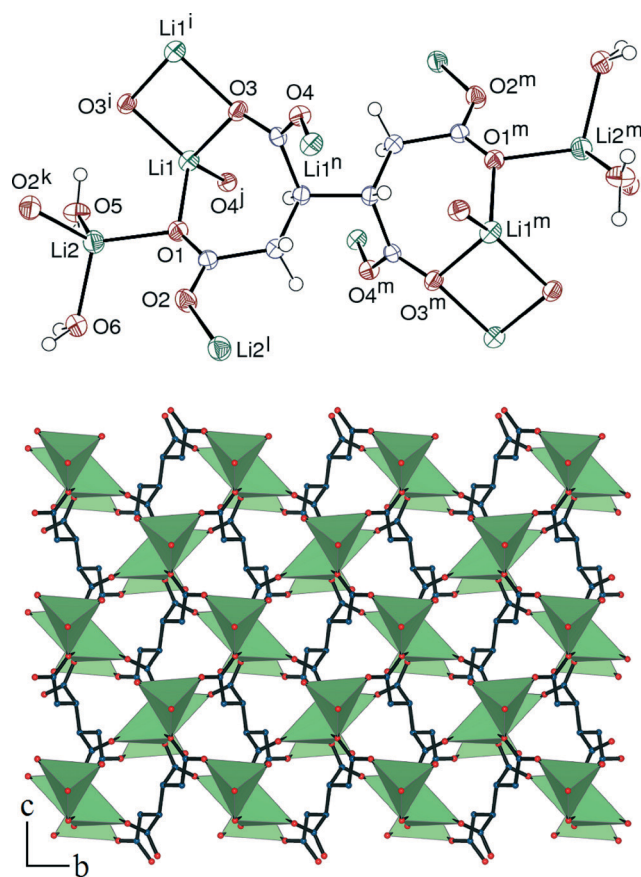


Fig. 2 Top: view of complex 2. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: $i = 3/2 - x, 3/2 - y, 2 - z$; $j = 3/2 - x, y - 1/2, 3/2 - z$; $k = x, 2 - y, z + 1/2$; $l = x, 2 - y, z - 1/2$; $m = 3/2 - x, 3/2 - y, 1 - z$; $n = 3/2 - x, y + 1/2, 3/2 - z$. Bottom: view of the 2D assembly, with solvent molecules and hydrogen atoms omitted.

thermodynamic control and entail an entropy-driven decrease in water content upon temperature increase.²¹ The main part of the ligand, including atoms O1, O2, their symmetry equivalents and the six carbon atoms in between, is nearly planar, with an rms deviation of 0.062 Å only, and the other two carboxylate groups are nearly orthogonal to this plane, with a dihedral angle of 82.00(4)°; a similar conformation was found in the uranyl ion complex of btc^{4-} .^{11a} In spite of the high connectivity displayed by the ligand in 2, the assembly formed is only 2D, with a layer thickness of about 11 Å, and it contains tetranuclear subunits with both vertex- and edge-sharing coordination polyhedra. The network, parallel to the *bc* plane and shown in simplified form in Scheme 2, has the total point symbol $\{4^{14} \cdot 6^{16} \cdot 8^{13} \cdot 10^2\}\{4^3\}_2\{4\}_2$ (the first symbol for the btc^{4-} ligand, the second for Li1 and the third for Li2). The previously reported complex $[Li_4(btc)(H_2O)_4]$ crystallizes also as a 2D assembly, with the different total point symbol $\{4^{16} \cdot 6^{14} \cdot 8^{11} \cdot 10^4\}\{4^3\}_2\{4\}_2$, while the complex including dimethylammonium counterions is 1D. The sheets in 2 display water ligands pointing outward on both sides, and they are connected to one another by hydrogen bonding interactions involving carboxylate acceptors; the KPI is 0.81

(0.77 with solvent excluded) and it indicates that no free space is present. The difference in the deprotonation degree between complexes 1 and 2 may be ascribed to the synthesis having been done with a much larger excess of LiOH in the latter case (however, the high temperature in the synthesis of 1 is likely to increase the ligand acidity); unfortunately, the conditions leading to complex 2 did not give any result with H₄cbbc.

The sodium complex [Na(*t*-H₃cbbc)] (3) crystallized upon evaporation following a period of heating and, as a consequence, it involves the isomerized ligand; it is particularly simple since it contains no water molecule. The asymmetric unit corresponds to one formula unit, with the Na⁺ cation chelated by two carboxylic/ate groups of one ligand (with the cyclobutane ring in a slightly puckered conformation), as Li⁺ in 1, and further bound to four oxygen atoms pertaining to three other ligands, one of them being chelated through two carboxylic/ate groups (Fig. 3). The Na–O bond lengths are in the range 2.3457(11)–2.6047(11) Å, and the average value of 2.43(10) Å is in perfect agreement with the average value of 2.43(14) Å for sodium to carboxylic/ate bonds from the CSD. The coordination environment is distorted octahedral,

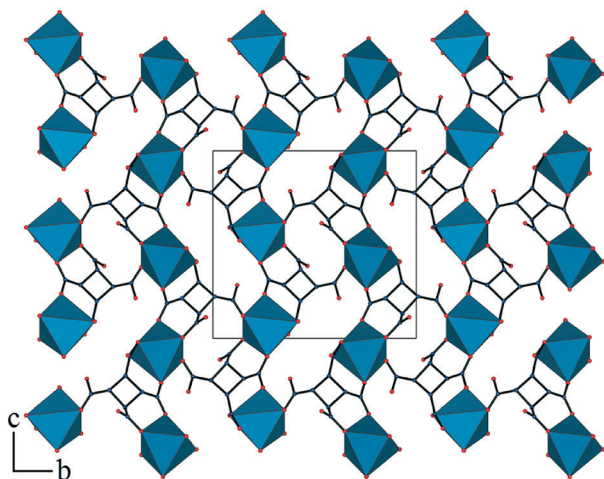
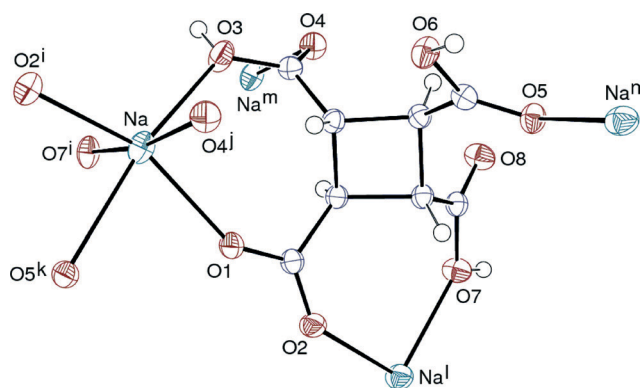
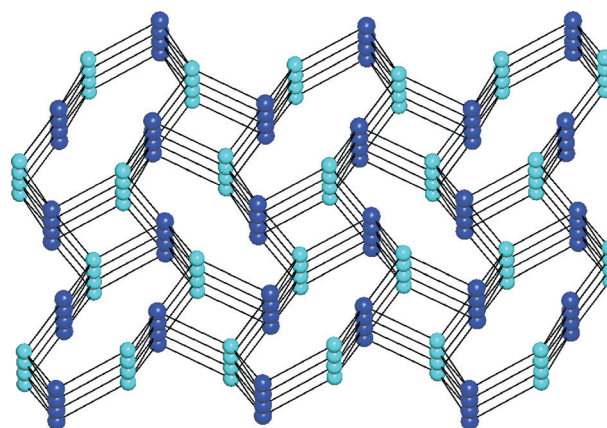


Fig. 3 Top: view of complex 3. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: $i = x - 1/2, 3/2 - y, z + 1/2$; $j = x - 1, y, z$; $k = 1/2 - x, y + 1/2, 3/2 - z$; $l = x + 1/2, 3/2 - y, z - 1/2$; $m = x + 1, y, z$; $n = 1/2 - x, y - 1/2, 3/2 - z$. Bottom: view of the 3D framework with hydrogen atoms omitted.

with some elongation along the O3–O5^k line. Each ligand is bis-chelating through three adjacent carboxylic/ate groups, as in 1, and it is bound in monodentate fashion by two more oxygen atoms, which leaves two oxygen atoms uncoordinated (μ_4, κ^6 coordination mode). It thus acts as a four-fold node in the building of the 3D framework, which has the total point symbol $\{4 \cdot 6^5\}$ (Scheme 3) and corresponds to the crb/BCT topological type in the topos&RCSR database.¹⁸ The packing is very compact, as indicated by a KPI value of 0.84.

Two potassium complexes were obtained, [K₂(*c*-H₂cbbc)(H₂O)₄] (4) and [K(*t*-H₃cbbc)] (5). The former was crystallized directly at room temperature and thus involves the *cis,trans,cis* form of the ligand, whereas the latter was crystallized after a period of heating and contains the *trans,trans,trans* isomer. The asymmetric unit in complex 4 contains one potassium cation in general position and half a *c*-H₂cbbc²⁻ ligand, the other half being generated by an inversion centre, and the butane ring being planar (Fig. 4). The cation is bound to only three carboxylic/ate oxygen atoms and to four bridging water molecules, with K–O(carboxylic/ate) and K–O(water) bond lengths in the ranges 2.7359(13)–2.9941(13) and 2.7219(13)–2.8957(13), respectively [average values of 2.86(11) and 2.80(6) Å, close to the average values of 2.80(16) and 2.84(14) Å from the CSD]. The seven-coordinate environment is very irregular and can best be viewed as pertaining to the trigonal base–tetragonal base type,²² with the former being defined by the set of atoms O1ⁱ, O5ⁱ and O6 and the latter by O1, O3^j, O5 and O6^k, with a dihedral angle of 10.40(5)° between the two bases. The ligand itself is bound to six cations through four oxygen atoms, two of them bridging (μ_6, κ^4 mode). The resulting 3D assembly contains 2D subunits parallel to the *bc* plane and corresponding to the formula [K(H₂O)₂]⁺, with edge-sharing coordination polyhedra (Fig. 4); these subunits are connected to one another along the direction of the *a* axis by the centrosymmetric *c*-H₂cbbc²⁻ ligands (KPI value of 0.89). Overall, the network has the total point symbol $\{4^6 \cdot 6^6 \cdot 8^3\} \{4^8 \cdot 6^3 \cdot 8^4 \cdot 10^6\}_2 \{4\}_4$ (the first symbol for *c*-H₂cbbc²⁻,



Scheme 3 Nodal representation of the 3D framework in the sodium complex 3. View with the *b* axis horizontal and the *c* axis vertical. Dark blue, Na; light blue, centroid of the cbbc ligand.

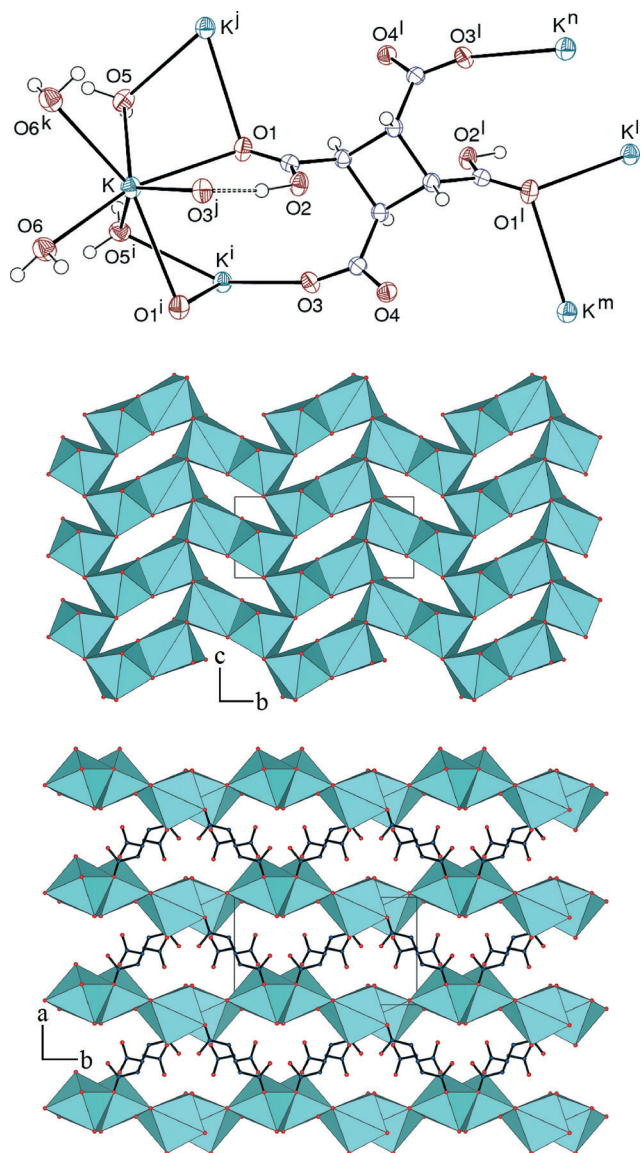
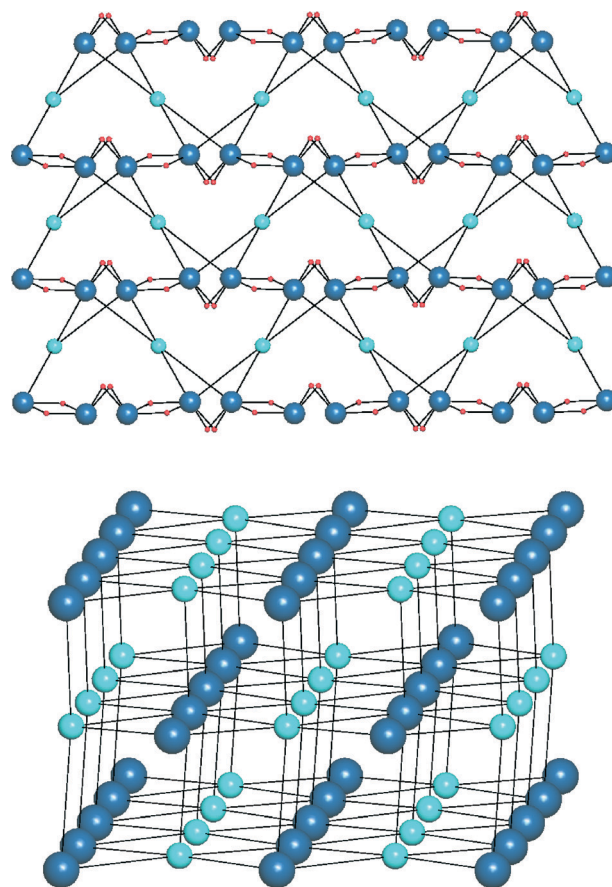


Fig. 4 Top: view of complex 4. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen bond is shown as a dashed line. Symmetry codes: $i = x, 3/2 - y, z + 1/2$; $j = x, 3/2 - y, z - 1/2$; $k = 2 - x, 1 - y, -z$; $l = 1 - x, 2 - y, -z$; $m = 1 - x, y + 1/2, 1/2 - z$; $n = 1 - x, y + 1/2, -z - 1/2$. Middle: view of the $[K(H_2O)_2]^+$ 2D subunit. Bottom: view of the 3D framework with hydrogen atoms omitted.

the second for K^+ and the third for the water molecules), and it is represented in simplified form in Scheme 4.

The asymmetric unit in complex 5 comprises one potassium ion located on a twofold rotation axis and half a $t\text{-H}_3\text{cbtc}^-$ ligand, with one carboxylic proton necessarily disordered (see Experimental). The cation is chelated by two ligands through two adjacent carboxylic/ate groups, as in 3, and it is bound to four more oxygen atoms, thus connecting six ligands, with K–O bond lengths in the range 2.8117(9)–3.0570(9) Å [average, 2.90(9) Å], and resulting in an eight-coordinate, distorted square antiprismatic environment (Fig. 5). The ligand, in a puckered conformation, is once more bis-chelating, but the groups involved are not adjacent to the



Scheme 4 Nodal representations of the 3D frameworks in the potassium complexes 4 (top) and 5 (bottom). Complex 4: orientation identical to that in Fig. 4. Complex 5: a axis horizontal, c axis vertical. Dark blue, K; red, O; light blue: centroid of the cbtc^- ligand. The network in 6 has the same topology as that in 5.

cyclobutane ring; overall, each ligand connects six cations, as in 4, in the μ_6, κ^8 mode. A 3D framework is formed, with the total point symbol of $\{4^{12}, 6^3\}$ which corresponds to the common topological type pcu alpha-Po in the topos\&RCSR database¹⁸ (Scheme 4), and a KPI value of 0.82.

The rubidium complex could be crystallized only under room temperature conditions and it thus contains the *cis, trans, cis* isomer. The asymmetric unit in $[Rb(c\text{-H}_3\text{cbtc})]$ (6) contains half a formula unit, the Rb^+ cation being located on a twofold rotation axis and the ligand admitting also twofold rotation symmetry (Fig. 6). In contrast to complex 4, the cyclobutane ring is slightly puckered, with an rms deviation of 0.073 Å. The cation is chelated by two ligands through two carboxylic/ate groups (one proton being disordered, see Experimental) in a *cis* relative position, which was not observed with potassium in 4, and it is also bound to four oxygen atoms from four different ligands. It is notable that, in contrast to the former complexes, chelation is very dissymmetrical, with the $Rb\text{-O}3$ bond being larger than $Rb\text{-O}1$ by 0.58 Å. The $Rb\text{-O}(\text{carboxylic/ate})$ bond lengths are in the range 2.8164(11)–3.5403(10) Å [average, 3.1(3) Å, or 2.91(6) Å if O3 is disregarded, close to the average value from the CSD,

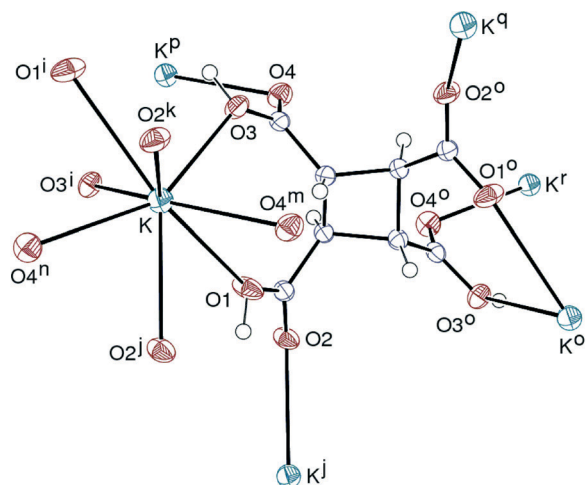


Fig. 5 Top: view of complex 5. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: $i = 3/2 - x, y, 1/2 - z$; $j = 2 - x, 1 - y, -z$; $k = x - 1/2, 1 - y, z + 1/2$; $m = x, y - 1, z$; $n = 3/2 - x, y - 1, 1/2 - z$; $o = 5/2 - x, y, 1/2 - z$; $p = x, y + 1, z$; $q = 2 - x, 1 - y, 1 - z$; $r = x + 1, y + 1, z$. Bottom: view of the 3D framework with hydrogen atoms omitted.

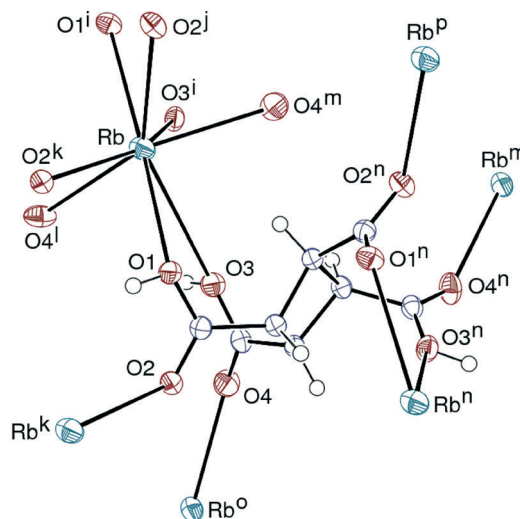


Fig. 6 Top: view of complex 6. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: $i = 3/2 - x, 3/2 - y, z$; $j = x - 1/2, y + 1/2, 1 - z$; $k = 2 - x, 1 - y, 1 - z$; $l = x - 1/2, 1 - y, 1/2 - z$; $m = 2 - x, y + 1/2, 1/2 - z$; $n = 5/2 - x, 3/2 - y, z$; $o = 2 - x, y - 1/2, 1/2 - z$; $p = 2 - x, 2 - y, 1 - z$. Bottom: view of the 3D framework with hydrogen atoms omitted.

2.99(14) Å]. The eight-coordinate environment is quite irregular but, with 18 edges and 12 triangular faces, four vertices pertaining to five faces and the other four to four faces, it can best be viewed as a very distorted dodecahedron with triangular faces as described by Moseley,²² or snub disphenoid (Johnson solid J84).²³ While the cation is thus bound to six different anions, each of the latter connects six cations (μ_6, κ^8 mode), and a 3D framework is generated, with a total point symbol and topological type identical to those of complex 5 (KPI value 0.81). In spite of different isomers of H_3cbtc being present in 5 and 6, the assemblies formed are thus very close to one another, the connectivity of the ligands being identical; in contrast, the connectivity is different in 4 and 6, although they contain the same ligand isomer.

The structure of the last complex, $[Cs(t-H_3cbtc)]$ (7), which involves the all-*trans* isomer, is plagued by disorder

effects. The asymmetric unit comprises two cesium atoms, each of them located on the fourfold rotation axis ($1/4, 1/4, z$) and twice a fourth of the ligand, the complete molecules, in puckered conformations, being generated by the fourfold rotoinversion axes, and the carboxylic protons being thus necessarily disordered (Fig. 7). Some disorder affects one carboxylic/ate group, but the two positions appeared clearly only for atom O4, and are denoted O4a and O4b; the displacement parameter of the associated carbon atom is quite anisotropic, but atom O3 does not show any sign of disorder. Atoms O4a and O4b are at bonding distances from atoms of the Cs2 and Cs1 families, respectively (while O3 is only bound to Cs1), so that, among the eight positions for atom O4 in the complete ligand, four are possibly bound to Cs1 and the other four to Cs2 (or their equivalents). Each cation has thus been assumed to be

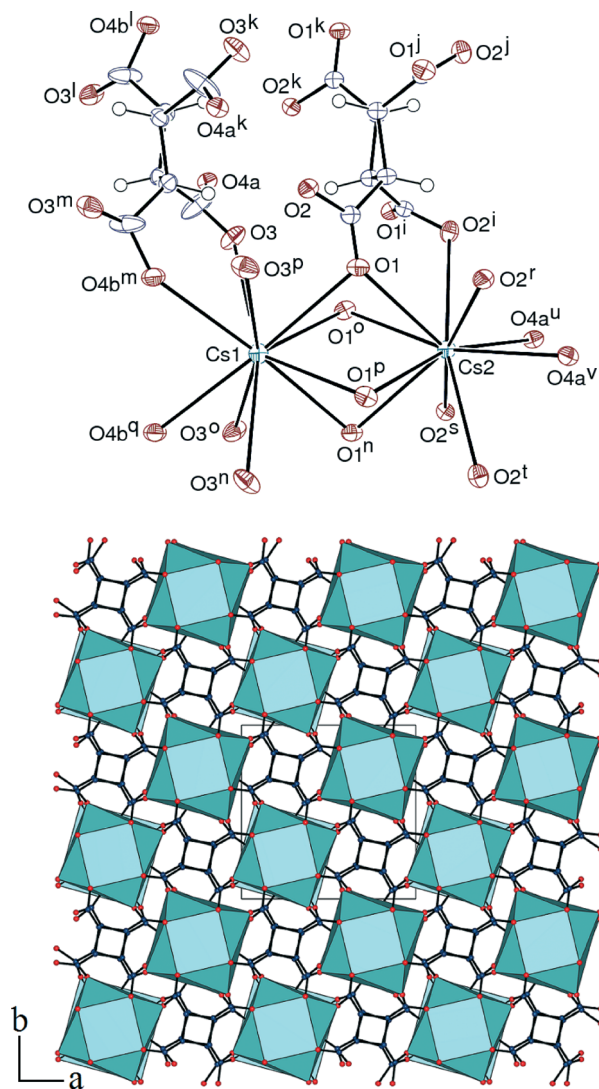
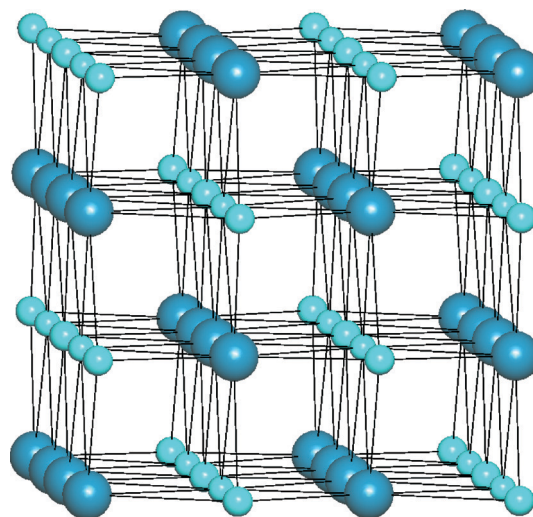


Fig. 7 Top: view of complex 7. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: $i = y + 1/2, -x, 1 - z$; $j = -y, x - 1/2, 1 - z$; $k = 1/2 - x, -y - 1/2, z$; $l = y + 1/2, -x, 2 - z$; $m = -y, x - 1/2, 2 - z$; $n = 1/2 - x, 1/2 - y, z$; $o = 1/2 - y, x, z$; $p = y, 1/2 - x, z$; $q = y + 1/2, 1 - x, 2 - z$; $r = -x, -y, 1 - z$; $s = x + 1/2, y + 1/2, 1 - z$; $t = -y, x + 1/2, 1 - z$; $u = 1 - x, -y, 1 - z$; $v = x - 1/2, y + 1/2, 1 - z$. Bottom: view of the 3D framework with hydrogen atoms omitted. Only one position of the disordered parts is represented in all views.

bound to two of these disordered atoms, and a set of possible positions for these is shown in Fig. 7. Both Cs1 and Cs2 are thus bound to ten oxygen donors, with O1 and four of its symmetry equivalents bridging. The Cs–O(carboxylic/ate) bond lengths span the range 3.0808(15)–3.4362(16) Å [average, 3.20(12) Å, in agreement with the average value from the CSD, 3.18(15) Å]. The uncertainties due to the disordered atoms prevent the precise determination of the cation coordination environment geometry. The two cations have a common square face (O1 and its symmetry equivalents) and they are close to the centre of a nearly square planar arrangement of donors (O3 and O2, respectively, and their symmetry equivalents), with the two squares for each cation

being staggered. If the four atoms of the O4 family were present, the geometry would be that of a distorted cuboctahedron; the actual geometry can thus be seen as derived from that through removal of any two vertices in a square face. Each cation is bound to either 8 (Cs1) or 6 (Cs2) ligands. The ligand containing O1 and O2 is both chelating (seven-membered ring) and bridging, but that containing O3 and O4 is chelating through O4b and only bridging through O4a; the first ligand thus connects 8 metal atoms in the μ_8, κ^8 mode (Scheme 1), while the second ligand connects six metal atoms in the μ_6, κ^8 mode. A 3D framework is generated, which is built of columns of tightly packed cesium atoms running along the c axis direction and bound to one another by columns of ligands with the cyclobutane rings parallel to the ab plane. If disordered effects were disregarded (*i.e.* if Cs2 was considered to be bound to the four atoms of the O4 family), the total point symbol would be $\{4^{24}.6^4\}$ and the topological type would be bcu from the topos&RCSR database¹⁸ (Scheme 5), with a KPI value of 0.86. Along the cesium ions column, there is an alternation of long and short Cs \cdots Cs distances, with that between cations sharing a common square face (Cs1 and Cs2 in the asymmetric unit) being 4.4483(4) Å, while that between cations separated by the disordered groups is larger, at 5.7724(4) Å. The shorter contact is comparable to those in 18-crown-6 complexes (3.84–4.66 Å),²⁴ but is much larger than the shortest Cs \cdots Cs distances known, such as 3.71 Å for metal–metal bonds in cesium suboxides of the Cs₁₁O₃ type,²⁵ 3.75 Å in a Cu²⁺/Cs⁺ 1D coordination polymer, which was noted to be shorter than the distance in three-dimensional cesium acetate and comparable to twice the 12-coordinated cesium ionic radius,²⁶ or 3.7928(4) Å between cations sharing a hexagonal face in the complex with pyrazinetetracarboxylate.²⁰



Scheme 5 Nodal representation of the 3D framework in the cesium complex 7. View with the a axis horizontal and the b axis vertical. Dark blue, Cs; light blue: centroid of the cbct ligand.

Conclusions

The seven complexes which have been described, comprising the Li^+ , Na^+ , K^+ and Cs^+ complexes with the *trans,trans,trans* isomer of $\text{H}_{(4-x)}\text{cbtc}^{x-}$, the K^+ and Rb^+ complexes with the *cis,trans,cis* isomer and also the Li^+ complex of btc^{4-} , all crystallize as polymeric species, either 2D with Li^+ or 3D in all the other cases. The packings are very tight in all the structures and none of these compounds can be considered as a candidate for applications requiring porous frameworks, such as hydrogen storage. An interesting trend in this family of compounds is the absence of water, both as a ligand and as a lattice species, in complexes 3, 5, 6, and 7, although these were crystallized at room temperature (after a period of heating for 3, 5, and 7), which generally favours a higher water content than crystallization under hydrothermal conditions. A regular increase in the denticity of the ligand is observed along the series, with the number of metal cations connected to the ligand being the smallest for Li^+ (2) and the largest for Cs^+ (8). This evolution mirrors that of the cation coordination numbers, which regularly increase from 4 for Li^+ to 10 for Cs^+ , and both influence the dimensionality of the polymeric assembly. In this respect, the present series appears as particularly well-behaved, and it is notable that such regularity in the denticity of the ligand is not always observed within the alkali metal ion series. For example, the Li^+ – Cs^+ complexes with bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid, which have been previously reported²⁹ and crystallize also as 2D or 3D architectures, display the highest denticity of 11 for Li^+ , while Rb^+ and Cs^+ correspond to values of 4 and 5, respectively; it may also be noted that the btc^{4-} ligand is bound to as many as 10 Li^+ cations in complex 2, and, albeit no complex with heavier alkali cations could be obtained for comparison in this case, this number could hardly have been much larger. As in the previous series, there is much variation in the coordination mode of the ligand in the present complexes, as evidenced in Scheme 1. Individual carboxylic/ate groups never chelate the metal cation to form a four-membered chelate ring, as they do in the complexes with Cd^{2+} ,⁹ La^{3+} ,¹⁰ and UO_2^{2+} ,¹¹ and also with K^+ in the $\text{K}^+/\text{Mg}^{2+}$ complex.⁷ Chelation through two adjacent groups is present in all but one case, the formation of seven-membered rings thus appearing favoured over four-membered ones. It is also notable that the only coordination mode which is observed twice (μ_6, κ^8), in complexes 5 and 6 (albeit for the different isomers), is also observed in the uranyl ion complex of *c*- cbtc^{4-} .^{11a} More generally, only one coordination mode is observed twice among all the complexes of $\text{H}_{(4-x)}\text{cbtc}^{x-}$ reported previously (μ_2, κ^2 in Ni^{2+} and Cu^{2+} complexes,^{8b,c} the others being μ_4, κ^4 with Cu^{2+} ; different μ_6, κ^6 modes with Cu^{2+} and La^{3+} ; μ_8, κ^6 with Cd^{2+} ; μ_{12}, κ^8 in the heterometallic $\text{K}^+/\text{Mg}^{2+}$ species; and the tetra-chelating mode μ_4, κ^8 with UO_2^{2+}). This illustrates the extreme variability and unpredictability of coordination modes with ligands displaying such a large number of donors, even when they are not highly flexible. It has

previously been noticed that, among the alkali metal cations, those with the largest ionic radius had a tendency to organize into chains of face-sharing polyhedra, while smaller units, edge- or face-sharing, are formed with the lighter cations.^{1,27} This trend appears only partly in the present series, with chains of vertex-sharing or vertex- and edge-sharing, water-bridged polyhedra in the Li^+ complexes 1 and 2, isolated cations in the Na^+ , K^+ and Rb^+ complexes 3, 5 and 6, sheets of edge-sharing, water-bridged polyhedra in the K^+ complex 4, and tightly packed chains of (partly) face-sharing polyhedra in the Cs^+ complex 7.

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