The counterion as a useful tool to obtain complexes of cytosine with alkali metal ions

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Two new sodium cytosine compounds, showing an unprecedented coordination of the nucleobase, have been synthesized from aqueous solutions containing perchlorate ions; whereas attempts to obtain similar complexes with Cl^-, Br^-, NO_3^-, SO_4^{2-}, PF_6^-, $CF_3SO_3^-$ as counterions failed, using sodium tetrafluoroborate a hemiprotonated species, without Na^+ cations, was obtained.

The interaction of metal ions with nucleic acids is of great importance for understanding their biological functions. For this purpose, many metal ion compounds of DNA or RNA fragments or constituents have been studied during the past years.[1] Particular attention was devoted to defining the structures of compounds containing ions such as Cu^{2+}, Pt^{2+} or others that exercise a destabilizing effect.[2] Structures of alkaline or alkaline-earth metal ion compounds are, on the contrary, less common because of the difficulty in obtaining suitable solid compounds, due to problems of solubility.[3]

In the studies of systems with alkaline or alkaline-earth metal ions, the adoption of neutral nucleobases is advantageous because the eventual coordination of the metal ion to the non-ionic sites of the nucleobases can be evidenced.

Limiting our attention to cytosine, only Ca^{2+} and Mg^{2+} compounds, in reference to the elements of the second group, are known.[3b,3d] From the results based on the literature it is evident that the Mg^{2+} ion shows, both with cytosine and 1-methylcytosine, a behavior similar to that of Mn^{2+} and Co^{2+}, giving rise to compounds in which the nucleobase is co-coordinated *via* O(2).[4] Ca^{2+}, on the contrary, gives rise, with cytosine, to a compound containing N(3)–O(2) and O(2) bridge coordination modes simultaneously. No compounds of Ca^{2+} with 1-methylcytosine are known, the only product being a compound containing an hemiprotonated species, obtained from aqueous solutions of $Ca(C1O_4)_2$ and 1-methylcytosine[5]

In reference to the alkali metals, several Na^+ compounds with cytidine phosphate derivatives have been studied.[3a,3c,3e] These compounds exhibit the O(2) or N(3)–O(2) coordination, but together with the coordination through O phosphate. Only two compounds, with Na^+ and K^+, exist, containing the neutral 1-methylcytosine bonded both to the alkali and the Pt^{2+} ions.[6] There are no examples of sodium(I) compounds with cytosine.

We tried to obtain compounds of Na^+ with cytosine in the presence of Cl^-, Br^-, NO_3^-, SO_4^{2-}, PF_6^-, $CF_3SO_3^-$, ClO_4^- and BF_4^- anions but, unfortunately, our attempts to obtain compounds with the first six anions failed, producing only crystals of unreacted cytosine. The use of BF_4^- affords a compound of formula $[(Hcyt)(Cyt)]BF_4$ (**1**) (Cyt = cytosine) that does not contain the metal ion but only the nucleobase protonated. On the contrary, with $C1O_4^-$ two similar coordination compounds of formula $[Na_3(Cyt)_3(H_2O)_4ClO_4](ClO_4)_2$ (**2**) and $[Na_3(Cyt)_3(H_2O)_3(ClO_4)_2]ClO_4$ (**3**), exhibiting an unprecedented coordination of Cyt towards sodium(I) ions, are formed. Our results indicate that the nature of the counterion plays an important role in obtaining coordination compounds in which the Na–cytosine bonds are present.

Compound **1** consists of cytosine molecules, cytosinium cations and tetrafluoroborate anions linked through hydrogen bonds leading to a two-dimensional supramolecular motif (Fig. 1 and Fig. 2). In particular, the pyrimidine rings interact through the formation of three hydrogen bonds in which O(2), N(4) and N(3) atoms are involved. The resulting compound could be viewed as pairs of cytosine–cytosinium, joined by further hydrogen bonds occurring between O(2) and N(1) atoms (see Table 1 and Fig. 2). Hydrogen bonds involving tetrafluoroborate anions and the $-NH_2$ nitrogen atoms of nucleobases stabilize the structure. The compound shows a supramolecular arrangement similar to that found in $[ZnCl_4][Hcyt \cdot Cyt]_2$ (**4**),[7] where cytosine molecules are joined to cytosinium cations in the same way as for **1**, the only difference being the presence of $[ZnCl_4]^{2-}$ instead of BF_4^- ions. It is noticeable that **4** precipitates from acidic solutions by addition of HCl.

Both compounds **2** and **3** contain sodium cations, perchlorate anions and cytosine molecules. The difference is due to the number of coordinated water molecules, that is four in **2** and three in **3**. In both compounds the Na^+ cations are bridged by oxygen atoms of cytosine and water molecules in such a way to form a linear stairway motif, in which four oxygen atoms and three alternating sodium atoms constitute adjacent cubes with

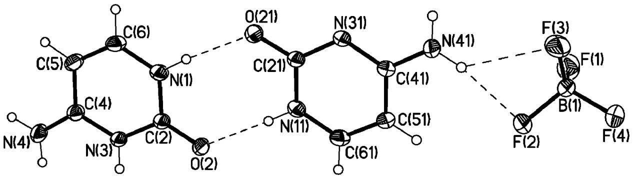

Fig. 1 Perspective drawing of the structure of compound **1**. Thermal ellipsoids are drawn at the 30% probability level.

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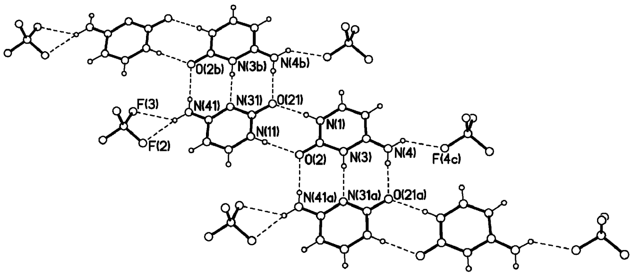


Fig. 2 View of the hydrogen bond interactions (broken lines) in **1**.

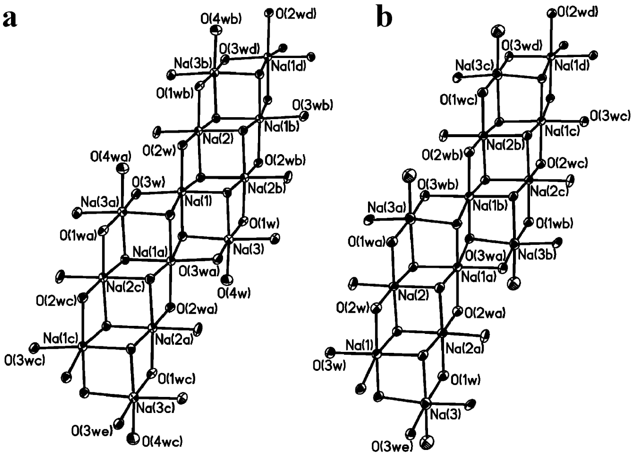
Table 1 Hydrogen bonds in **1**[a]

D–H···A	d(H···A)	d(D···A)	∠(DHA)
N(1)–H(1)···O(21)	1.95	2.804(3)	172
N(11)–H(11)···O(2)	1.98	2.840(3)	173
N(41)–H(41B)···F(2)	2.17	3.002(3)	164
N(41)–H(41B)···F(3)	2.38	3.038(4)	134
N(3)–H(3)···N(31a)	2.05(3)	2.843(3)	177(3)
N(4)–H(4A)···O(21a)	1.98	2.842(3)	174
N(41)–H(41A)···O(2b)	2.04	2.878(3)	164
N(4)–H(4B)···F(4c)	2.17	2.866(3)	138
N(4)–H(4B)···F(1d)	2.56	3.207(4)	133

[a] Symmetry code: (a) $x, y + 1, z$; (b) $x, y - 1, z$; (c) $x - 1, y + 1, z - 1$; (d) $-x, -y + 1, -z$.

a missing vertex (see Scheme 1). In these chains, the oxygen atoms of the cytosine molecules are coordinated simultaneously to three different Na^+ cations, in a μ_3-coordination mode, whereas the water molecules act as bridge.

Three Na^+ cations, three perchlorate anions and three cytosines together with three (**3**) or four (**2**) water molecules constitute the asymmetric unit of the crystallographic cell of compounds **2** and **3** (Fig. 3). Only one water molecule in **2** acts as terminal ligand [O(4w)], whereas the other three behave as bridges between sodium atoms and are responsible for the chain growing. The terminal water molecule is replaced, in **3**, by a perchlorate anion that is the only one non-coordinated instead of two in **2**.



Scheme 1 Schematic view of the quasi-cubane stairway arrangement in **2** (a) and **3** (b) showing the hexacoordination of Na atoms. Only the oxygen atoms of water molecules have been labelled for clarity. Symmetry code: (**2**) (c) $-1 + x, y, z$; (d) $1 + x, y, z$; (e) $-x, 2 - y, -z$; (**3**) (b) $1 + x, y, z$; (c) $1 - x, 1 - y, -z$, (d) $2 + x, y, z$.

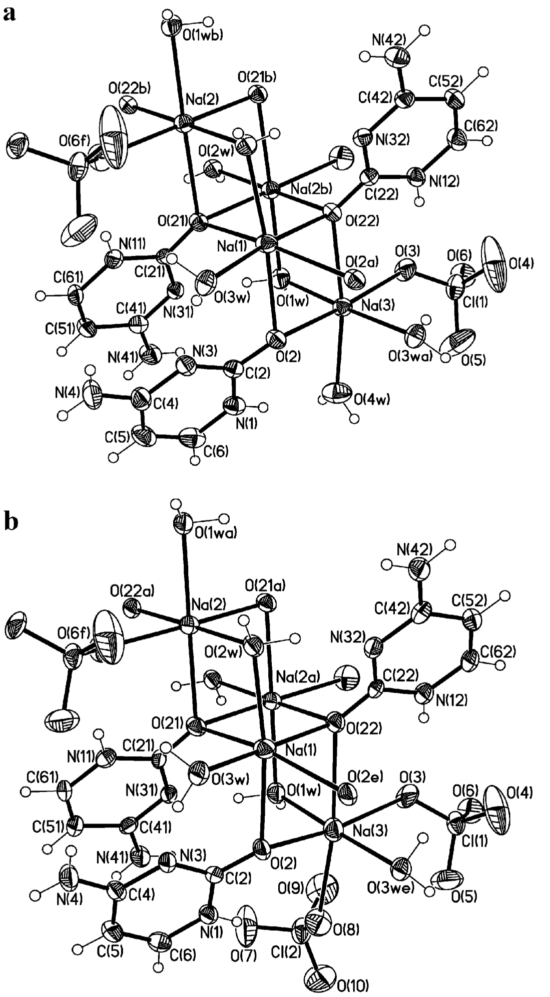


Fig. 3 Perspective drawing and atomic labelling scheme of the (a) $[Na_3(Cyt)_3(H_2O)_4(ClO_4)]^{2+}$ moiety of **2** and (b) the $[Na_3(Cyt)_3(H_2O)_3(ClO_4)_2]^+$ moiety of **3**. Thermal ellipsoids are drawn at the 30% probability level.

The sodium atoms have a slightly distorted octahedral geometry, being surrounded by six oxygen atoms. However, the three crystallographically non-equivalent Na^+ cations achieve the hexacoordination by means of different sets of ligands. By referring to Fig. 3, the Na(1) environment involves four oxygen atoms of different cytosine ligands and two oxygen atoms of water, whereas the Na(2) environment involves three oxygen atoms from cytosine ligands, two oxygen atoms from water and one from a perchlorate anion. Finally, Na(3) is coordinated by two cytosine oxygen atoms, three H_2O oxygen atoms and one perchlorate anion in **2**, two H_2O oxygen atoms and two perchlorate anions in **3**. Na–O distances for oxygen atoms of the perchlorate group and water molecules are shorter than some Na–O_{Cyt} distances (see Table 2 and Table 3).

Stacking interactions occur between adjacent cytosine molecules of the chains, the inter-planar distances being 3.35, 3.28 and 3.30 Å in **2** and 3.29, 3.28 and 3.31 Å in **3**.

In both compounds adjacent chains are linked by a bridging perchlorate anion as shown in Fig. 4.

Hydrogen bonds, involving nitrogen atoms and oxygen atoms of water molecules and perchlorate anions (see Tables

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**[a]

Na(1)–O(3w)	2.356(4)	Na(2)–O(21b)	2.422(3)
Na(1)–O(22)	2.373(3)	Na(2)–O(22b)	2.470(3)
Na(1)–O(2w)	2.373(3)	Na(2)–O(21)	2.521(3)
Na(1)–O(2)	2.401(3)	Na(3)–O(3wa)	2.343(4)
Na(1)–O(2a)	2.652(4)	Na(3)–O(4w)	2.344(4)
Na(1)–O(21)	2.672(4)	Na(3)–O(1w)	2.356(4)
Na(2)–O(1wb)	2.370(3)	Na(3)–O(3)	2.413(4)
Na(2)–O(2w)	2.374(4)	Na(3)–O(2)	2.446(3)
Na(2)–O(6f)	2.403(4)	Na(3)–O(22)	2.495(3)

[a] Symmetry code: (a) 1 − *x*, 2 − *y*, −*z*; (b) 2 − *x*, 2 − *y*, −*z*; (f) *x*, 1 + *y*, *z*.

4 and 5) contribute to stabilize the structures and give rise to an extended two-dimensional network in compound **2**, while, in compound **3**, an extended three-dimensional network is formed. It is noteworthy that the terminal water molecule (O4w), in **2**, is bonded to two different perchlorate anions [Cl(2) and Cl(3)] through oxygen atoms, O(8) and O(13), which are already interacting with two other water molecules [O(1w) and O2w(a)] (Fig. 5). In **3**, the Cl(2) perchlorate anion replaces the O(4w) water molecule, loses the link with O(1w) and binds directly the sodium atom through O(8). On the contrary, the second perchlorate maintains the link with the O(2w) water molecule through O(13) and interacts with the N(42) nitrogen atom by means of O(11) (see Table 5 and Fig. 6).

In the literature no examples of Na^+ compounds with cytosine are known and only two complexes with 1-methylcytosine or 1-methylcytosinate have been studied. These compounds contain Na^+ with Pt(II) and Cu(II)[6,8] and both show a coordination to the alkali-metal *via* O(2) different from that reported here for **2** and **3**. The cytosine derivate compounds containing phosphate groups show a metal to nucleobase coordination *via* O(2) or N(3)–O(2) and, simultaneously, as expected, to oxygen atoms of the phosphate group.

All these compounds are not easily comparable to **2** and **3**, where an unprecedented coordination mode, of μ_3 type, of the oxygen atom, O(2), of cytosine is observed. This coordination mode, even if not very usual, is found in the Na^+ cubane compounds, which are constituted by sodium and oxygen atoms alternating in a cube (one oxygen linking three Na^+ atoms).[9] Nevertheless, in this family, there exists only one compound containing a μ_3 oxygen atom of a carbonyl group, linked to three Na^+ ions.[10]

Important conclusions can be made from the analysis of the structures and syntheses of compounds **1–3**. It is noteworthy to point out that no products were obtained from solutions containing Cl^-, Br^-, NO_3^-, SO_4^{2-}, PF_6^-, $CF_3SO_3^-$ and cytosine while **1–3** are obtained with similar experimental conditions by using BF_4^- or ClO_4^- ions. In particular, **2** and **3** are, substantially, the same species, the difference being a coordinated water molecule (**2**) instead of a perchlorate anion (**3**). They were obtained together as a mixture and, assuming that the bond of an alkali-metal to a polar solvent molecule is more short-lived than that with a ClO_4^- anion, it is possible to consider **2** as a precursor of **3**, formed when the perchlorate anion replaces water solvent. Obviously, in solution the situation is different and, assuming the existence of the complexes, it is reasonable to suppose that an equilibrium exists between the two species.

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**[a]

Na(1)–O(3w)	2.329(6)	Na(2)–O(21a)	2.422(3)
Na(1)–O(22)	2.367(6)	Na(2)–O(22a)	2.470(3)
Na(1)–O(2w)	2.370(6)	Na(2)–O(21)	2.521(3)
Na(1)–O(2)	2.433(6)	Na(3)–O(3we)	2.343(4)
Na(1)–O(2e)	2.641(6)	Na(3)–O(4w)	2.344(4)
Na(1)–O(21)	2.614(6)	Na(3)–O(1w)	2.357(4)
Na(2)–O(6)	2.339(6)	Na(3)–O(3)	2.414(4)
Na(2)–O(1wa)	2.377(6)	Na(3)–O(2)	2.446(3)
Na(2)–O(6f)	2.404(4)	Na(3)–O(22)	2.495(3)

[a] Symmetry code: (a) 2 − *x*, −*y* + 1, −*z*; (e) 1 − *x*, 1 − *y*, −*z*.

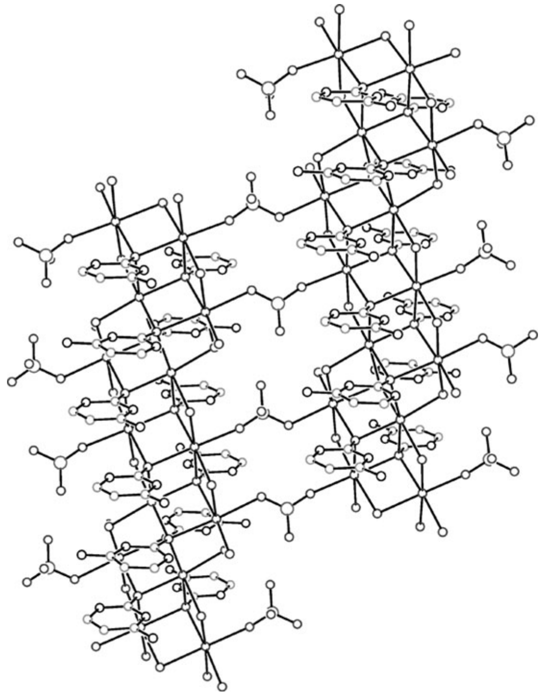


Fig. 4 View of adjacent chains linked through perchlorate anions in **2** and **3**. Hydrogen atoms have been omitted for clarity.

The tetrafluoroborate compound **1** does not contain Na^+ cations and this is the substantial difference with respect to the perchlorate compounds. On the other hand, its supramolecular motif is the same as that obtained from acidic solutions of

Table 4 Hydrogen bonds in **2**[a]

D–H···A	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1w)–H(2w)···O(8)	2.30(4)	3.041(6)	140(4)
O(1w)–H(1w)···N(31)	1.87(3)	2.777(5)	167(4)
O(2w)–H(3w)···N(32)	1.96(3)	2.825(5)	156(4)
O(2w)–H(4w)···O(13a)	2.13(3)	3.049(6)	167(4)
O(3w)–H(5w)···N(3)	1.88(3)	2.772(5)	171(5)
O(3w)–H(6w)···O(5f)	2.24(4)	3.065(6)	152(4)
O(4w)–H(7w)···O(8)	2.22(4)	2.997(7)	136(4)
O(4w)–H(8w)···O(13)	1.97(3)	2.910(7)	173(4)
N(1)–H(1)···O(4w)	2.07	2.906(6)	163
N(11)–H(11)···O(6f)	2.13	2.955(5)	159
N(12)–H(12)···O(3)	2.22	3.050(5)	161
N(41)–H(41B)···O(10)	2.26	2.996(8)	144
N(42)–H(42A)···O(10h)	2.31	3.109(7)	155

[a] Symmetry code: (a) 1 − *x*, 2 − *y*, −*z*; (f) *x*, 1 + *y*, *z*; (h) *x*, *y*, 1 + *z*.

Table 5 Hydrogen bonds in **3**[a]

D–H···A	d(H···A)	d(D···A)	∠(DHA)
O(1w)–H(1w)···N(31)	1.84(3)	2.746(8)	161(7)
O(2w)–H(3w)···N(32)	1.92(3)	2.835(8)	163(6)
O(2w)–H(4w)···O(13)	1.96(4)	2.902(8)	167(8)
O(3w)–H(6w)···N(3)	1.87(3)	2.784(9)	164(7)
N(1)–H(1)···O(8)	2.26	3.100(9)	166
N(11)–H(11)···O(6f)	2.18	2.978(9)	155
N(12)–H(12)···O(3)	2.22	3.03(1)	156
N(41)–H(41A)···O(10h)	2.05	2.90(1)	169
N(42)–H(42B)···O(11)	2.22	3.04(1)	159

[a] Symmetry code: (f) x, $y + 1$, z; (h) $-x$, $-y + 1$, $-z - 1$.

$ZnCl_2$ and Cyt (compound **4**). Similar hemiprotonated species and not complexes containing the metal atom, are formed when Ca^{2+} or Na^+, as ClO_4^- salts, react with 1-methylcytosine.[5,11] It is possible to suppose that a metal–H^+ competition exists in all sodium–cytosine solutions. In the acidic Zn-chloride case (pH *ca.* 1), this competition is, obviously, to the advantage of H^+ as in the Na-tetrafluoroborate one, even if the solution has a higher pH value (*ca.* 5.5). Nevertheless, when the counterion is perchlorate and the pH *ca.* 5.5, coordination compounds are formed. It seems to be the counterion that leads to the formation of a compound that does not contain Na^+ (**1**) or compounds with Na–Cyt bonds (**2** and **3**). This is probably due to the different interactions that the two anions can promote, giving rise to species which have different solubilities. Of course much remains to be done in order to understand the detailed relation of the counterion with alkali-metal ions and/or cytosine for the obtainment of compounds containing Na–Cyt bonds.

Furthermore it could be interesting to study similar compounds with several cytosine derivatives for a better understanding of the training force leading to a such an unusual μ_3 coordination mode of the carbonyl oxygen atom.

Experimental

Compound **1** was obtained, as a mixture of parallelepiped together with plate-shaped crystals of Cyt, by slow evaporation at room temperature of aqueous solutions containing equimolar amounts of sodium tetrafluoroborate and Cyt. The crystals were filtered, dried at room temperature and separated by hand. The yield was 60%. Anal. Calc. for $C_8H_{11}BF_4N_6O_2$: C, 30.99; H, 3.58; N, 27.11. Found: C, 30.60; H, 3.46; N, 27.25%.

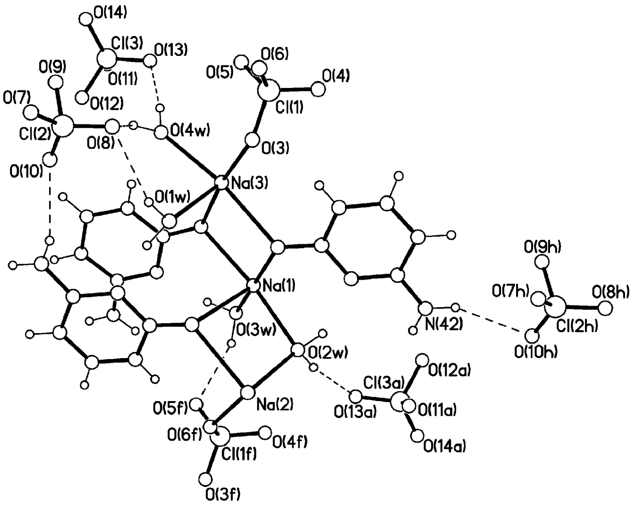


Fig. 5 View of the perchlorate hydrogen bonds in **2**.

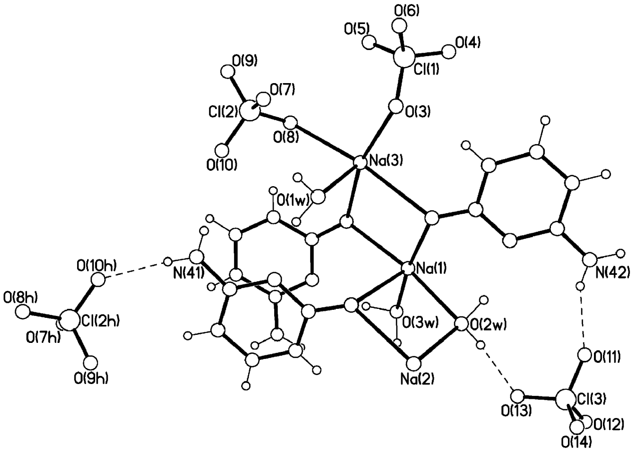


Fig. 6 View of the perchlorate hydrogen bonds in **3**.

Compounds **2** and **3** were obtained, in a similar manner, from aqueous solutions containing equimolar amounts of sodium perchlorate monohydrate and Cyt. In this case, only the cytosine ligand was primarily formed as plate-shaped crystals. The concentrated solution was covered and after four weeks the cytosine crystals disappeared to make place for needle crystals. The crystals were filtered and dried at room temperature. The yield was 48%. Anal. Calc. for $C_{12}H_{23}Cl_3N_9Na_3O_{19}$: C, 18.65; H, 3.00; N, 16.31. Found: C, 18.80; H, 2.90; N, 16.44%. Analysis by means of X-ray diffraction, performed on two crystals, revealed the coexistence of two different compounds of formulae $C_{12}H_{23}Cl_3N_9Na_3O_{19}$ and $C_{12}H_{21}Cl_3N_9Na_3O_{18}$, corresponding to **2** and **3**. It was found that the initial pH of the solution containing sodium tetrafluoroborate and Cyt (pH = 4) is lower than that of the solution with sodium perchlorate monohydrate and Cyt (pH = 5.5). Consequently, in order to work in the same conditions to obtain similar complexes with sodium cytosine tetrafluoroborate, a little amount of NaOH was added to this solution until it had an initial pH value of *ca.* 5.5. Nevertheless, the hemiprotonated species (**1**), without Na^+ cations, was the only isolated product.

Caution! Perchlorate salts in the presence of organic ligands are potentially explosive. Only small amounts of the materials should be prepared and handled with care.

X-Ray crystallography

X-Ray diffraction data were collected using a Bruker-Nonius X8 Apex CCD diffractometer for compounds **1** and **3** and integrated with the SAINT-Plus program.[12] A Bruker R3m/V automatic four-circle was used for data collection of compound **2**. Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) was used for all data collections. Lorentz-polarization and empirical absorption corrections through the Ψ-scan program[13] were applied only for compound **2**. The structures were solved by direct methods and refined by least-squares methods against F^2, using the SHELXTL software package.[14] Non-H atoms were refined anisotropically. The hydrogen atom on N(3) in **1** was located on a ΔF map and refined. The hydrogen atoms of the water molecules of **2** and **3** were located on a ΔF map and refined with three restraints for each molecule (O–H and H–H distances) with thermal factors fixed to 0.06 Å^2, whereas those of the cytosine ligand in all compounds were set in calculated positions and refined as riding atoms.

The final geometrical calculations were carried out with the PARST program.[15] The graphical manipulations were performed using the XP utility of the SHELXTL system.

Crystal data and refinement for **1**: ($C_8H_{11}BF_4N_6O_2$): triclinic, space group $P\bar{1}$, $a = 8.226(2)$, $b = 8.505(2)$, $c = 9.812(2)$ Å, $\alpha = 111.91(3)$, $\beta = 90.79(3)$, $\gamma = 102.23(2)°$, $V = 619.1(2)$ Å^3, $Z = 2$, $\rho_{calc.} = 1.663$ g cm^{-3}, $3 < 2\theta < 56°$, crystal size 0.12 × 0.10 × 0.30 mm, 4275 reflections measured, 2795 ($R_{int} = 0.015$) unique, $R_1 = 0.0586$, w$R_2 = 0.2534$, [$I > 2\sigma(I)$], $S = 1.242$. Crystal data and refinement for **2**: ($C_{12}H_{23}Cl_3N_9Na_3O_{19}$): triclinic, space group $P\bar{1}$, $a = 10.014(3)$, $b = 11.025(3)$, $c = 14.399(3)$ Å, $\alpha = 78.36(2)$, $\beta = 84.60(2)$, $\gamma = 75.62(2)°$, $V = 1506.6(7)$ Å^3, $Z = 2$, $\rho_{calc.} = 1.703$ g cm^{-3}, $3 < 2\theta < 54°$, crystal size 0.35 × 0.20 × 0.18 mm, 6988 reflections measured, 6603 ($R_{int} = 0.026$) unique, $R_1 = 0.0689$, w$R_2 = 0.1894$, [$I > 2\sigma(I)$], $S = 0.943$. Crystal data and refinement for **3**: ($C_{12}H_{21}Cl_3N_9Na_3O_{18}$): triclinic, space group $P\bar{1}$, $a = 9.943(1)$, $b = 10.986(1)$, $c = 14.691(2)$ Å, $\alpha = 75.71(1)$, $\beta = 70.49(1)$, $\gamma = 73.88(1)°$, $V = 1431.9(3)$ Å^3, $Z = 2$, $\rho_{calc.} = 1.750$ g cm^{-3}, $3 < 2\theta < 44°$, (the data collection maximum of 2θ value was 44° because of the poor diffracting power of the sample) crystal size 0.11 × 0.03 × 0.25 mm, 13832 reflections measured, 3364 ($R_{int} = 0.046$) unique, $R_1 = 0.0757$, w$R_2 = 0.2288$, [$I > 2\sigma(I)$], $S = 1.111$. CCDC reference numbers 271107–271109. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511009b.

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