ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 6, pp. 1200–1205. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © A.N. Chekhlov, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 6, pp. 972–977.

Synthesis and Crystal Structure of 4,7,13,16,21,24-Hexaoxa-1,10-diazoniabicyclo[8.8.8]hexacosane Bis(citrate) Hydrate

A. N. Chekhlov

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
ul. Semenova 1, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: anche@icp.ac.ru

Received July 31, 2007

Abstract—A crystalline salt of 2.2.2-cryptand and citric acid, 4,7,13,16,21,24-hexaoxa-1,10-diazoniabicyclo[8.8.8]hexacosane bis(citrate) hydrate $[H_2(Crypt\text{-}222)]^{2+}\cdot 2(C_6H_7O_7)^- \cdot 1.65H_2O$, was synthesized and studied by single crystal X-ray diffraction. In the crystal structure of this salt, the 2.2.2-cryptand dication is somewhat disordered, and its H atoms at two protonated N atoms are oriented inside the cryptand cavity. Two independent citrate anions are essentially different, as different COOH groups in them are deprotonated. The geometric parameters (bond lengths, bond angles, etc.) of the molecular ions and water molecules are determined with a relatively high accuracy. The structural units form a three-dimensional system of intermolecular (interionic) hydrogen bonds.
DOI: 10.1134/S1070363208060170

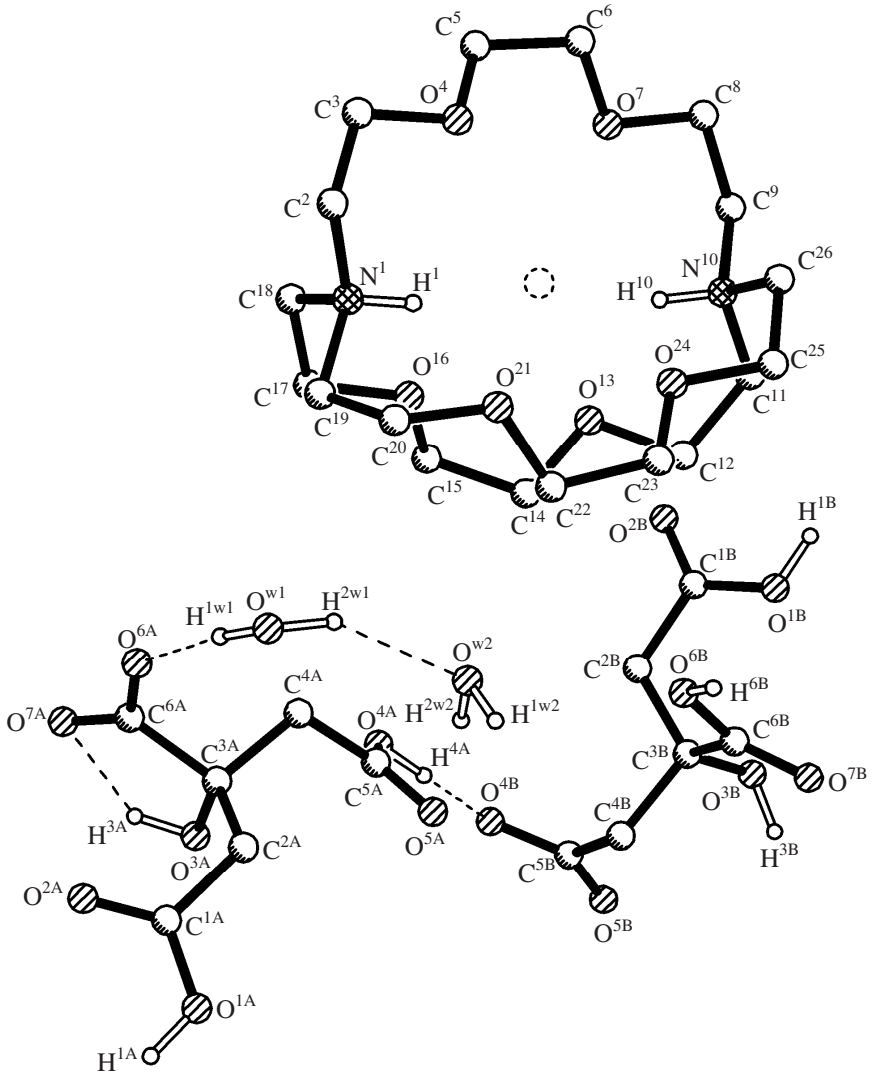
It is well known that 2.2.2-cryptand (or 4,7,13,16,21,24-hexaoxa-1,10-diazoniabicyclo[8.8.8]hexacosane) forms host–guest complexes with many metal cations [1, 2]. This cryptand is also a diacid base (as it contains two tertiary amino groups), and therefore it can form salts with various organic and inorganic acids.

The crystal structures of 2.2.2-cryptand salts with organic acids are of appreciable interest for crystal chemistry, supramolecular chemistry, and organic crystal engineering, but are studied poorly. Previously I synthesized crystalline salts of 2.2.2-cryptand with picric [3, 4], isocyanuric [5], and tartaric [6] acids and examined their crystal structures.

Here I report on the synthesis and single crystal X-ray diffraction study of a new crystalline salt of 2.2.2-cryptand with citric acid, 4,7,13,16,21,24-hexaoxa-1,10-diazoniabicyclo[8.8.8]hexacosane bis(citrate) hydrate of the composition $[H_2(Crypt\text{-}222)]^{2+}\cdot 2(C_6H_7O_7)^- \cdot 1.65H_2O$ (**I**), where $[H_2(Crypt\text{-}222)]^{2+}$ is the 2.2.2-cryptand dication (or 2.2.2-dication) with two protonated bridgehead nitrogen atoms. Note that citric (2-hydroxy-1,2,3-propanetricarboxylic) acid and its salts (citrates) are widely used in food industry and medicine.

The X-ray structural study showed (see Experimental) that the asymmetric part of the unit cell of crystals of **I** contains one 2.2.2-dication, two different citrate anions $C_6H_7O_7^-$ (A and B), and 1.65 water molecules. A fragment of their packing in the crystal structure of I is shown in the figure. The selected bond lengths, bond angles, and torsion angles are given in Tables 1–3.

The 2.2.2-dication in structure **I** is somewhat disordered: four of its nonhydrogen atoms occupy two different crystallographic positions each: C^{11} and $C^{11'}$, C^{12} and $C^{12'}$, C^{19} and $C^{19'}$, C^{20} and $C^{20'}$, with occupancies of 0.781(8) for C^{11} and C^{12}, 0.219(8) for $C^{11'}$ and $C^{12'}$, 0.700(8) for C^{19} and C^{20}, and 0.300(8) for $C^{19'}$ and $C^{20'}$. The 2.2.2-dication in the structure of **I** may be still more disoredered. However, the possible second positions of its other nonhydrogen atoms, especially of those adjacent to the above-indicated atoms, are either too close to the main position to be resolved or have very low occupancy, on the level of background peaks of the differential electron density. In what follows, when discussing the molecular geometry of the 2.2.2-dication, I will consider only the main positions of its disordered atoms, without taking into account the less occupied positions marked with a prime.



Fragment of packing of the 2.2.2-dication, two different citrate anions $C_6H_7O_7^-$ (A and B), and water molecules in the crystal structure of **I**. The H atoms at the C atoms are omitted for clarity. In the 2.2.2-dication, the second, less occupied positions of the disordered atoms C^{11}, C^{12}, C^{19}, and C^{20} are not shown either. The occupancy of the O^{w3} position of the water molecule in the 2.2.2-dication cavity is 0.074(9). Dashed lines denote some hydrogen bonds.

In the structure of **I** the mean lengths of the covalent bonds in the disordered 2.2.2-dication [N^+–C 1.503(3), O–C 1.419(8), and C–C 1.485(4) Å] are close to the mean values for the related cations. The mean lengths of the N^+–C bonds almost coincides with the average statistical value, and the mean lengths of the O–C and C–C bonds are slightly and appreciably smaller than the corresponding average statistical bond lengths: $N^+(sp^3)$–$C(sp^3)$ 1.502(15) Å for $HN^+(–C)_3$ fragments; O–$C(sp^3)$ 1.426(11) Å for C#–O–CH_2–C# fragments; $C(sp^3)$–$C(sp^3)$ 1.524(14) Å for C#–CH_2–CH_2–C# fragments [7]. The similar effective shortening of the intracyclic C–C bonds is well known for crown ethers [8]. Note that in the 2.2.2-dication in **I** some bond lengths and bond angles involving the above-mentioned four disordered nonhydrogen atoms and the adjacent atoms are appreciably distorted because of the disordering.

The major conformation of the 2.2.2-dication in **I** is characterized in detail by torsion angles τ in Table 3. It can be seen that all the angles τ of the X–C–C–Y type (X, Y = N, O) are synclinal (of the *gauche* type) and close to ±60°; and among all the angles τ of the C–N–C–C type almost half are antiperiplanar (of the *trans* type) and close to 180°, and almost half are close to –60° (of the *gauche* type); and almost all the angles τ of the C–O–C–C type are close to 180° (of the *trans*

Table 1. Selected bond lengths (*d*, Å) in the structure of **I**[a]

Bond	*d*	Bond	*d*
N^1–C^{19}	1.502(4)	C^{12}–O^{13}	1.446(4)
N^1–C^{18}	1.502(3)	O^{13}–C^{14}	1.404(4)
N^1–C^2	1.503(3)	C^{14}–C^{15}	1.488(4)
C^2–C^3	1.484(4)	C^{15}–O^{16}	1.415(3)
C^3–O^4	1.420(3)	O^{16}–C^{17}	1.419(3)
O^4–C^5	1.417(3)	C^{17}–C^{18}	1.494(4)
C^5–C^6	1.478(4)	C^{19}–C^{20}	1.484(5)
C^6–O^7	1.417(3)	C^{20}–O^{21}	1.439(4)
O^7–C^8	1.415(3)	O^{21}–C^{22}	1.401(4)
C^8–C^9	1.482(4)	C^{22}–C^{23}	1.481(4)
N^{10}–C^9	1.509(3)	C^{23}–O^{24}	1.415(3)
N^{10}–C^{11}	1.504(4)	O^{24}–C^{25}	1.419(3)
N^{10}–C^{26}	1.495(3)	C^{25}–C^{26}	1.485(4)
C^{11}–C^{12}	1.492(5)	–	–
O^{1A}–C^{1A}	1.282(3)	O^{1B}–C^{1B}	1.292(2)
O^{2A}=C^{1A}	1.208(3)	O^{2B}=C^{1B}	1.210(2)
O^{3A}–C^{3A}	1.416(3)	O^{3B}–C^{3B}	1.411(2)
O^{4A}–C^{5A}	1.280(3)	O^{4B}–C^{5B}	1.268(2)
O^{5A}=C^{5A}	1.193(3)	O^{5B}–C^{5B}	1.247(2)
O^{6A}–C^{6A}	1.261(3)	O^{6B}–C^{6B}	1.308(2)
O^{7A}–C^{6A}	1.226(3)	O^{7B}=C^{6B}	1.209(2)
C^{1A}–C^{2A}	1.497(3)	C^{1B}–C^{2B}	1.498(3)
C^{2A}–C^{3A}	1.516(3)	C^{2B}–C^{3B}	1.525(3)
C^{3A}–C^{4A}	1.544(3)	C^{3B}–C^{4B}	1.547(3)
C^{3A}–C^{6A}	1.545(3)	C^{3B}–C^{6B}	1.532(3)
C^{4A}–C^{5A}	1.494(3)	C^{4B}–C^{5B}	1.511(3)

[a] The bond lengths, bond angles, and torsion angles involving the second, less occupied positions of the disordered atoms of the 2.2.2-dication are not given for brevity. The same for Tables 2 and 3.

Table 2. Bond angles (ω, deg) in the structure of **I**

Angle	ω	Angle	ω
$C^{19}N^1C^{18}$	106.3(3)	$C^{11}C^{12}O^{13}$	107.3(3)
$C^{19}N^1C^2$	116.3(3)	$C^{12}O^{13}C^{14}$	106.9(2)
$C^{18}N^1C^2$	110.9(2)	$O^{13}C^{14}C^{15}$	110.7(2)
$N^1C^2C^3$	114.6(2)	$C^{14}C^{15}O^{16}$	110.3(2)
$C^2C^3O^4$	109.6(2)	$C^{15}O^{16}C^{17}$	110.7(2)
$C^3O^4C^5$	110.2(2)	$O^{16}C^{17}C^{18}$	108.6(2)
$O^4C^5C^6$	110.6(2)	$C^{17}C^{18}N^1$	114.6(2)
$C^5C^6O^7$	111.0(2)	$N^1C^{19}C^{20}$	111.3(4)
$C^6O^7C^8$	110.6(2)	$C^{19}C^{20}O^{21}$	113.8(4)
$O^7C^8C^9$	107.6(2)	$C^{20}O^{21}C^{22}$	120.9(3)
$C^8C^9N^{10}$	114.2(2)	$O^{21}C^{22}C^{23}$	109.3(2)
$C^9N^{10}C^{11}$	105.1(2)	$C^{22}C^{23}O^{24}$	110.4(2)
$C^9N^{10}C^{26}$	111.5(2)	$C^{23}O^{24}C^{25}$	112.5(2)
$C^{11}N^{10}C^{26}$	116.2(3)	$O^{24}C^{25}C^{26}$	108.9(2)
$N^{10}C^{11}C^{12}$	110.5(3)	$C^{25}C^{26}N^{10}$	114.0(2)
$O^{1A}C^{1A}O^{2A}$	122.7(2)	$O^{1B}C^{1B}O^{2B}$	122.7(2)
$O^{1A}C^{1A}C^{2A}$	114.6(2)	$O^{1B}C^{1B}C^{2B}$	116.3(2)
$O^{2A}C^{1A}C^{2A}$	122.7(2)	$O^{2B}C^{1B}C^{2B}$	121.0(2)
$C^{1A}C^{2A}C^{3A}$	112.8(2)	$C^{1B}C^{2B}C^{3B}$	116.1(2)
$O^{3A}C^{3A}C^{2A}$	109.0(2)	$O^{3B}C^{3B}C^{2B}$	106.8(2)
$O^{3A}C^{3A}C^{4A}$	108.6(2)	$O^{3B}C^{3B}C^{4B}$	110.7(2)
$O^{3A}C^{3A}C^{6A}$	108.3(2)	$O^{3B}C^{3B}C^{6B}$	110.4(2)
$C^{2A}C^{3A}C^{4A}$	111.5(2)	$C^{2B}C^{3B}C^{4B}$	111.7(2)
$C^{2A}C^{3A}C^{6A}$	112.7(2)	$C^{2B}C^{3B}C^{6B}$	112.4(2)
$C^{4A}C^{3A}C^{6A}$	106.7(2)	$C^{4B}C^{3B}C^{6B}$	105.0(2)
$C^{3A}C^{4A}C^{5A}$	112.6(2)	$C^{3B}C^{4B}C^{5B}$	112.2(2)
$O^{4A}C^{5A}O^{5A}$	122.4(2)	$O^{4B}C^{5B}O^{5B}$	122.7(2)
$O^{4A}C^{5A}C^{4A}$	113.7(2)	$O^{4B}C^{5B}C^{4B}$	116.9(2)
$O^{5A}C^{5A}C^{4A}$	123.8(2)	$O^{5B}C^{5B}C^{4B}$	120.4(2)
$O^{6A}C^{6A}O^{7A}$	126.5(2)	$O^{6B}C^{6B}O^{7B}$	124.7(2)
$O^{6A}C^{6A}C^{3A}$	115.7(2)	$O^{6B}C^{6B}C^{3B}$	112.9(2)
$O^{7A}C^{6A}C^{3A}$	117.8(2)	$O^{7B}C^{6B}C^{3B}$	122.2(2)
$H^{1A}O^{1A}C^{1A}$	116(3)	$H^{1B}O^{1B}C^{1B}$	118(2)
$H^{3A}O^{3A}C^{3A}$	101(2)	$H^{3B}O^{3B}C^{3B}$	108(2)
$H^{4A}O^{4A}C^{5A}$	115(2)	$H^{6B}O^{6B}C^{6B}$	111(2)
$H^{1w1}O^{w1}H^{2w1}$	109(3)	$H^{1w2}O^{w2}H^{2w2}$	109(3)

type). Only two angles τ of the C–N–C–C type ($C^9N^{10}C^{11}C^{12}$ and $C^{26}N^{10}C^{11}C^{12}$) and one angle τ of the C–O–C–C type ($C^{19}C^{20}O^{21}C^{22}$) noticeably differ from the standard angles of the gauche and trans types.

It should be noted that, in this disordered 2.2.2-dication, the gauche angles τ involving positions with low occupancy ($C^{11'}$, $C^{12'}$, $C^{19'}$, and $C^{20'}$), $N^{10}C^{11'}C^{12'}O^{13}$ –66° and $N^1C^{19'}C^{20'}O^{21}$ 85°, have signs opposite to those of the corresponding gauche angles $N^{10}C^{11}C^{12}O^{13}$ and $N^1C^{19}C^{20}O^{21}$ in the major conformers (Table 3). Note also that the 2.2.2-dication in **I** in its major conformation has no, even approximate, symmetry.

In the structure of **I**, in both conformations of the disordered 2.2.2-dication (major and minor) the hydrogen atoms H^1 and H^{10} (at the bridgehead nitrogen atoms N^1 and N^{10}) are oriented inside the cryptand cavity. Each of these hydrogen atoms has short intracationic contacts with three adjacent ether oxygen atoms: H^1 with O^4, O^{16}, and O^{21}; H^{10} with O^7, O^{13}, and O^{24}. These contacts with the H···O distances in the

Table 3. Selected torsion angles (τ, deg) in the structure of **I**

Angle	τ	Angle	τ
$C^{19}N^1C^2C^3$	–178.2(3)	$C^{14}C^{15}O^{16}C^{17}$	–162.4(2)
$C^{18}N^1C^2C^3$	–56.5(3)	$C^{15}O^{16}C^{17}C^{18}$	–166.3(2)
$N^1C^2C^3O^4$	–57.4(3)	$O^{16}C^{17}C^{18}N^1$	–51.4(3)
$C^2C^3O^4C^5$	169.3(2)	$C^{17}C^{18}N^1C^2$	175.2(2)
$C^3O^4C^5C^6$	170.8(2)	$C^{17}C^{18}N^1C^{19}$	–57.4(3)
$O^4C^5C^6O^7$	70.8(3)	$C^2N^1C^{19}C^{20}$	–73.5(5)
$C^5C^6O^7C^8$	174.7(2)	$C^{18}N^1C^{19}C^{20}$	162.4(4)
$C^6O^7C^8C^9$	172.0(2)	$N^1C^{19}C^{20}O^{21}$	–43.6(7)
$O^7C^8C^9N^{10}$	–57.3(3)	$C^{19}C^{20}O^{21}C^{22}$	–94.5(5)
$C^8C^9N^{10}C^{11}$	178.3(3)	$C^{20}O^{21}C^{22}C^{23}$	–166.0(3)
$C^8C^9N^{10}C^{26}$	–55.0(2)	$O^{21}C^{22}C^{23}O^{24}$	–66.9(3)
$C^9N^{10}C^{11}C^{12}$	–135.9(4)	$C^{22}C^{23}O^{24}C^{25}$	–172.8(2)
$C^{26}N^{10}C^{11}C^{12}$	100.3(4)	$C^{23}O^{24}C^{25}C^{26}$	–175.6(2)
$N^{10}C^{11}C^{12}O^{13}$	55.3(5)	$O^{24}C^{25}C^{26}N^{10}$	–55.2(3)
$C^{11}C^{12}O^{13}C^{14}$	–173.7(3)	$C^{25}C^{26}N^{10}C^9$	179.0(2)
$C^{12}O^{13}C^{14}C^{15}$	169.6(3)	$C^{25}C^{26}N^{10}C^{11}$	–60.6(3)
$O^{13}C^{14}C^{15}O^{16}$	–67.9(3)	–	–
$O^{1A}C^{1A}C^{2A}C^{3A}$	130.4(2)	$O^{1B}C^{1B}C^{2B}C^{3B}$	–10.0(2)
$O^{2A}C^{1A}C^{2A}C^{3A}$	–52.8(3)	$O^{2B}C^{1B}C^{2B}C^{3B}$	169.7(2)
$O^{3A}C^{3A}C^{2A}C^{1A}$	–55.8(2)	$O^{3B}C^{3B}C^{2B}C^{1B}$	–63.8(2)
$O^{3A}C^{3A}C^{4A}C^{5A}$	–47.4(3)	$O^{3B}C^{3B}C^{4B}C^{5B}$	–62.1(2)
$O^{4A}C^{5A}C^{4A}C^{3A}$	106.4(2)	$O^{4B}C^{5B}C^{4B}C^{3B}$	–97.1(2)
$O^{5A}C^{5A}C^{4A}C^{3A}$	–76.1(4)	$O^{5B}C^{5B}C^{4B}C^{3B}$	82.3(2)
$O^{6A}C^{6A}C^{3A}O^{3A}$	178.7(2)	$O^{6B}C^{6B}C^{3B}O^{3B}$	158.9(2)
$O^{7A}C^{6A}C^{3A}O^{3A}$	–3.4(3)	$O^{7B}C^{6B}C^{3B}O^{3B}$	–25.4(2)
$O^{6A}C^{6A}C^{3A}C^{2A}$	58.1(2)	$O^{6B}C^{6B}C^{3B}C^{2B}$	39.8(2)
$O^{7A}C^{6A}C^{3A}C^{2A}$	–124.1(2)	$O^{7B}C^{6B}C^{3B}C^{2B}$	–144.5(2)
$O^{6A}C^{6A}C^{3A}C^{4A}$	–64.6(2)	$O^{6B}C^{6B}C^{3B}C^{4B}$	–81.7(2)
$O^{7A}C^{6A}C^{3A}C^{4A}$	113.3(2)	$O^{7B}C^{6B}C^{3B}C^{4B}$	94.0(2)
$C^{1A}C^{2A}C^{3A}C^{4A}$	–175.7(2)	$C^{1B}C^{2B}C^{3B}C^{4B}$	175.0(2)
$C^{1A}C^{2A}C^{3A}C^{6A}$	64.4(2)	$C^{1B}C^{2B}C^{3B}C^{6B}$	57.4(2)
$C^{2A}C^{3A}C^{4A}C^{5A}$	72.8(2)	$C^{2B}C^{3B}C^{4B}C^{5B}$	56.8(2)
$C^{6A}C^{3A}C^{4A}C^{5A}$	–163.8(2)	$C^{6B}C^{3B}C^{4B}C^{5B}$	178.8(2)

range 2.29–2.58 Å can be interpreted as weak intracationic trifurcate hydrogen bonds of type N^+–H(···O)$_3$ [9].

In the crystal structure of **I**, two independent citrate anions $C_6H_7O_7^-$ (A and B) are essentially different. The deprotonation site in anion A is the COOH group at the middle carbon atom C^{3A}, and in anion B, the COOH group at the C^{4B} atom. That is why, apparently, anions A and B have different conformations (see torsion angles τ in Table 3). The lengths of the covalent bonds in the two citrate anions (A and B) are close to the average statistical values (see tables of bond lengths in [7] and the lengths of the corresponding bonds in the Cambridge Structural Database [10]).

Table 4. Geometric parameters of hydrogen bonds of the O–H···O type in the crystal structure of **I**[a, b]

H-bond O–H···O	*d*(O–H), Å	*d*(H···O), Å	*d*(O···O), Å	O–H···O angle, deg
O^{1A}–H^{1A}···O^{6A}(*i*)	0.93(2)	1.61(2)	2.526(2)	167(3)
O^{3A}–H^{3A}···O^{7A}	0.93(2)	1.89(2)	2.574(2)	129(3)
O^{4A}–H^{4A}···O^{4B}	0.93(2)	1.68(2)	2.590(2)	167(3)
O^{1B}–H^{1B}···O^{5B}(*ii*)	0.92(2)	1.61(2)	2.509(2)	165(2)
O^{3B}–H^{3B}···O^{2B}(*iii*)	0.92(2)	1.87(2)	2.777(2)	167(2)
O^{6B}–H^{6B}···O^{4B}(*iv*)	0.92(2)	1.66(2)	2.574(2)	177(3)
O^{w1}–H^{1w1}···O^{6A}	0.98(2)	1.84(2)	2.820(3)	174(3)
O^{w1}–H^{2w1}···O^{w2}	0.98(2)	2.26(2)	3.164(5)	153(3)
O^{w2}–H^{1w2}···O^{3A}(*iv*)	0.97(3)	2.14(3)	2.866(4)	131(3)
O^{w2}–H^{2w2}···O^{5A}	0.99(3)	2.18(3)	3.168(5)	173(4)

[a] The occupancy of the positions of the O^{w1}, H^{1w1}, and H^{2w1} atoms is 0.894(8), and that of the positions of the O^{w2}, H^{1w2}, and H^{2w2} atoms is 0.682(7). [b] Symmetry codes: (*i*) –*x*, 1/2+*y*, 1/2–*z*; (*ii*) 1 –*x*, *y*–1/2, 1/2–*z*; (*iii*) 1 –*x*, 1/2+*y*, 1/2–*z*; (*iv*) *x*, 3/2–*y*, *z*–1/2.

The oxygen atoms of the water molecules of hydration in the crystal structure of **I** occupy three independent positions O^{w1}, O^{w2}, and O^{w3}. The occupancies of these positions (and of the positions of H atoms bonded to these oxygen atoms), refined by the least-squares method, are 0.894(8), 0.682(7), and 0.074(9), i.e., 1.65 in total. It is seen that the positions O^{w1} and O^{w2} are occupied incompletely, and the occupancy of the O^{w3} position in the center of the 2.2.2-dication cavity is very low. The water molecule w3 occupying this minor position in the 2.2.2-dication cavity is retained in this position by strong intracation hydrogen bonds of the types N^+–H···O^{w3} and O^{w3}–H···O, where O is the atom of the 2.2.2-dication.

In the crystal structure of **I**, there are intermolecular (interionic) hydrogen bonds of the O–H···O type. Their geometric parameters are given in Table 4. All these H bonds are formed by the H atoms of all the OH groups of citrate anions A and B and by all the H atoms of two water molecules w1 and w2. The H bond acceptors are the O atoms of citrate anions A and B and the O^{w2} atom of one water molecule (w2). All these H bonds in the crystal of **I** form an infinite 3D network involving citrate anions A and B and water molecules w1 and

w2, with large cells accommodating the 2.2.2-dications. These 2.2.2-dications have with this network only van der Waals interactions of the C–H···O type, where H are the hydrogen atoms of the 2.2.2-dication and O are the oxygen atoms of citrate anions and water molecules w1 and w2.

EXPERIMENTAL

Crystalline salt **I** was prepared as follows. Crystalline 2.2.2-cryptand and citric acid, taken in 1 : 2 molar ratio, were dissolved in 70% aqueous ethanol, and the mixture was allowed to evaporate at room temperature. After the solvent evaporation, a colorless amorphous glassy substance remained on the bottom. After storage in an open vessel for 1.5 months, several colorless transparent crystals of salt **I** were isolated with difficulty.

The unit cell parameters were determined, and the 3D set of reflection intensities obtained, with an Enraf–Nonius CAD-4 autodiffractometer (MoK_α radiation, graphite monochromator). Crystals of **I** are monoclinic; $(C_{18}H_{38}N_2O_6)^{2+}\cdot 2(C_6H_7O_7)^- \cdot 1.65H_2O$, M 790.46; a 21.660(4), b 12.810(3), c 13.688(3) Å, β 93.32(2)°, V 3792(1) Å^3, Z 4, d_{calc} 1.385 g cm^{-3}, μ(MoK_α) 1.18 cm^{-1}, space group $P2_1/c$.

The intensities of 6184 reflections were measured in the reciprocal space quadrant ($2\theta \le 47°$) by the ω/2θ scanning method from a single crystal of the size 0.22×0.47×0.65 mm. When measuring the intensities, we used a special mode in which the final scanning was performed for all, including very weak, reflections. After exclusion of 301 systematically absent reflections and averaging of the intensities of 279 pairs of equivalent reflections $hk0$ and $\hbar k0$ (R_{int} 0.023), the working array of the measured $F^2(hkl)$ and $\sigma(F^2)$ included 5604 unique reflections.

The structure of **I** was solved by the direct method using the SHELXS-97 program [11] and was refined by the full-matrix least-squares method (with respect to F^2) using the SHELXL-97 program [11] in the approximation of anisotropic thermal vibrations of all nonhydrogen atoms. To refine the structure, we used almost all the reflections from the working array [including very weak reflections with $I < 2\sigma(I)$], except several reflections for which the measured and calculated F^2 values were poorly consistent.

By the direct method we obtained an ordered model of the structure of **I**, but certain bond lengths, bond angles, and torsion angles in the 2.2.2-dication were appreciably distorted. In the subsequent anisotropic refinement of the structure of I, the four highest peaks of Δρ in the differential Fourier electron density synthesis were unambiguously interpreted as the second low-occupied positions $C^{11'}$, $C^{12'}$, $C^{19'}$, and $C^{20'}$ of the four nonhydrogen atoms of the 2.2.2-dication: C^{11}, C^{12}, C^{19}, and C^{20}. Then for these disordered (double) positions, using the least-squares method, we refined the coordinates and anisotropic thermal parameters, and also their total occupancies (and the occupancies of the disordered H atoms bonded to them).

In the structure of **I**, the first two of three independent positions O^{w1}, O^{w2}, and O^{w3} of the oxygen atoms of water molecules of hydration were initially found by the direct method from the Fourier E-synthesis. The third, low-occupied position O^{w3} was revealed in the 2.2.2-dication cavity from the differential Fourier electron density synthesis in the intermediate step of the anisotropic refinement of the structure of **I**. Its parameters were refined in the isotropic approximation.

In the structure of **I**, the majority of the H atoms of the 2.2.2-dication and the H atoms of two water molecules w1 and w2 were localized objectively in the differential Fourier electron density synthesis in the intermediate step of the anisotropic refinement. Then the coordinates and isotropic thermal parameters of all the H atoms of the 2.2.2-dication (including those at disordered C atoms) were unambiguously calculated using the rider model [11] in the course of the least-squares refinement of the structure of **I**. The coordinates of the H atoms of water molecules воды w1 and w2 were refined by the least-squares method, imposing soft geometric restrictions of the DFIX type [11] on short interatomic distances involving these atoms. For the positions of the O and H atoms of water molecules w1, w2, and w3, we also refined by the least-squares method their occupancies, which for water molecules w1 and w2 appeared to be somewhat lower than unity, and for w3, considerably lower than unity (see the discussion above).

In the last cycle of the full-matrix refinement of the structure of **I**, the absolute shifts of all the 568 varied parameters were less than 0.001σ. The final coordinates and thermal parameters of the atoms in the structure of **I** will be filed in the Cambridge Structural Database [10].

REFERENCES

1. Hiraoka, M., *Crown Compounds. Their Characteristics and Applications*, Amsterdam: Elsevier, 1982.
2. *Host Guest Complex Chemistry. Macrocycles. Synthesis, Structure, Applications*, Vögtle, A. and Weber, E., Eds., Berlin: Springer, 1985.
3. Chekhlov, A.N., Z*h. Strukt. Khim*., 2005, vol. 46, no. 3, p. 521.
4. Chekhlov, A.N., *Zh. Strukt. Khim*., 2006, vol. 47, no. 3, p. 526.
5. Chekhlov, A.N., *Zh. Strukt. Khim*., 2006, vol. 47, no. 1, p. 77.
6. Chekhlov, A.N., *Zh. Strukt. Khim*., 2006, vol. 47, no. 2, p. 392.
7. Allen, F.H., Kennard, O., Watson, D.G., Brammer, L., Orpen, A.G., and Taylor, R., *J. Chem. Soc., Perkin Trans. 2*, 1987, no. 12, p. S1.
8. Van Eerden, J., Harkema, S., and Feil, D., *Acta Crystallogr., Sect. B*, 1990, vol. 46, no. 2, p. 222.
9. Chekhlov, A.N., *Zh. Obshch. Khim*., 2005, vol. 75, no. 11, p. 1883.
10. Allen, F.H., *Acta Crystallogr., Sect. B*, 2002, vol. 58, no. 3/1, p. 380.
11. Sheldrick, G.M., *The SHELX-97 Manual*, Göttingen (Germany): Univ. of Göttingen, 1997.
12. *International Tables for Crystallography*, Dordrecht (Netherlands): Kluwer Academic, 1992, vol. C.