Russian Journal of General Chemistry, Vol. 74, No. 4, 2004, pp. 574–577. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 4, 2004, pp. 628–632.
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Crystal Structure of 4,7,13,16,21,24-Hexaoxa-1,10-diazoniabicyclo[8.8.8]hexacosane Diiodide

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Received June 6, 2002

Abstract — The disordered crystal structure of 4,7,13,16,21,24-hexaoxa-1,10-diazoniabicyclo[8.8.8]hexacosane diiodide, $[H_2(2.2.2\text{-Crypt})]^{2+} \cdot 2I^-$, was studied by single crystal X-ray diffraction. The 2.2.2-cryptand dication is disordered and exists in the form of two different conformers A and B randomly occupying the same place in the unit cell with 71.5 and 28.5% probability, respectively. In both conformers A and B, the hydrogen atoms at the bridgehead nitrogen atoms are directed inside the cavity (crypta) of the conformer. The geometric parameters (bond lengths, bond angles, torsion angles) of these conformers were found, and the packing of these cations and iodide anions in the crystal were determined. The iodide anions have contacts only with the methylene hydrogen atoms of conformers A and B.

4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane (2.2.2-cryptand) forms host–guest complexes with many metal cations [1, 2]. However, this cryptand is also a diacidic base (as it contains two tertiary amino groups), and it can exist as a dication (with two protonated bridgehead nitrogen atoms) and form ionic complexes (salts) with various molecular and complex anions and halide anions. The crystal and molecular structure of these ionic complexes is of certain interest for supramolecular chemistry [3] and crystal chemistry, but it is poorly studied. The Cambridge Structural Database [4] (version 5.22 of 2001) contains data on only ten crystal structures of compounds containing the 2.2.2-cryptand dication and various anions.

In this work, we prepared a new compound of this type, 4,7,13,16,21,24-hexaoxa-1,10-diazoniabicyclo-[8.8.8]hexacosane diiodide $\{[H_2(2.2.2\text{-Crypt})]^{2+} \cdot 2I^-$, **I**} and studied it by single crystal X-ray diffraction.

We found (see Experimental) that, in the crystal structure of **I**, all the atoms of the 2.2.2-cryptand dication are disordered over two fairly similar positions A and B with the occupancies of 0.715(4) and 0.285(4), respectively. The dication in the structure of **I** exists in the form of two different conformers A and B; the corresponding positions of the disordered atoms are denoted as A and B, respectively. It should be noted that these two conformers in the unit cell of **I** randomly occupy the same place with the probabilities of 71.5 and 28.5%, respectively.

The structure of ionic complex (salt) **I** in the crystal is shown in Fig. 1. The bond lengths, bond angles, and torsion angles in these two conformers (A and B) of the disordered 2.2.2-cryptand dication are given in Tables 1–3. It should be noted also that these two conformers in the unit cell of **I** are located on a two-fold crystallographic symmetry axis passing through the middle of the C^{14A}–$C^{14A'}$ (or C^{14B}–$C^{14B'}$) bond and the middle of the $N^{1A}\cdots N^{1A'}$ (or $N^{1B}\cdots N^{1B'}$) line. For more detailed description, we give below the distances between the related symmetry-independent non-

Table 1. Bond lengths (d, Å) in the structure of **I**

Bond	d	Bond	d
N^{1A}–C^{2A}	1.499(4)	N^{1B}–C^{2B}	1.501(7)
N^{1A}–$C^{9A'}$	1.501(4)	N^{1B}–$C^{9B'}$	1.499(7)
N^{1A}–$C1^{1A}$	1.501(4)	N^{1B}–C^{11B}	1.500(7)
C^{2A}–C^{3A}	1.504(5)	C^{2B}–C^{3B}	1.502(9)
C^{3A}–O^{4A}	1.415(4)	C^{3B}–O^{4B}	1.418(7)
O^{4A}–C^{5A}	1.427(4)	O^{4B}–C^{5B}	1.422(7)
C^{5A}–C^{6A}	1.495(5)	C^{5B}–C^{6B}	1.498(9)
C^{6A}–O^{7A}	1.415(4)	C^{6B}–O^{7B}	1.417(7)
O^{7A}–C^{8A}	1.425(4)	O^{7B}–C^{8B}	1.425(7)
C^{8A}–C^{9A}	1.505(5)	C^{8B}–C^{9B}	1.504(9)
$C1^{1A}$–C^{12A}	1.497(5)	C^{11B}–C^{12B}	1.501(9)
$C1^{2A}$–O^{13A}	1.422(4)	C^{12B}–O^{13B}	1.413(7)
$O1^{3A}$–C^{14A}	1.423(4)	O^{13B}–C^{14B}	1.426(7)
$C1^{4A}$–$C^{14A'}$	1.498(5)	C^{14B}–$C^{14B'}$	1.506(9)
H^{1A}–N^{1A}	0.91	H^{1B}–N^{1B}	0.91

[a] Atoms symmetrical ($-x$, y, $1/2 - z$) to the basis atoms are marked with primes; the same for Tables 2 and 3. See also note [a] to Table 4.

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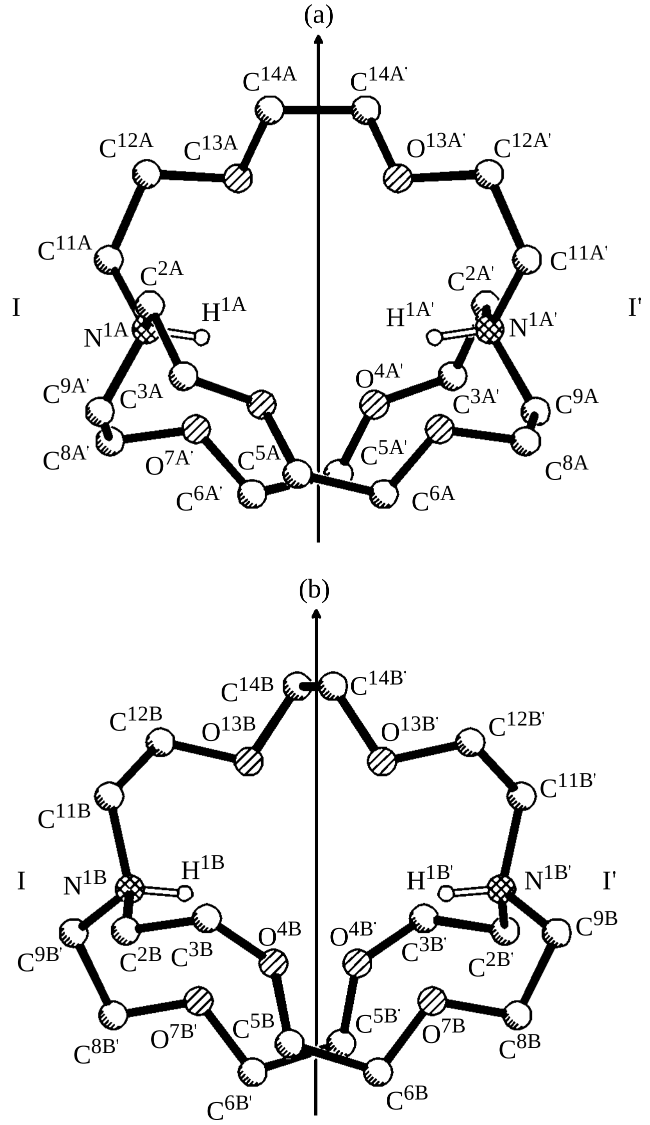

Fig. 1. Structure of ionic complex (salt) **I** in the crystal. Two conformers A and B of the disordered 2.2.2-cryptand dication randomly occupy the same place in the unit cell with 71.5 and 28.5% probability, respectively, but are shown separately for clarity [(a) A and (b) B]. The methylene hydrogen atoms are not shown. A twofold symmetry axis passes through both conformers. The atoms symmetrical to the basis atoms are marked with primes.

hydrogen atoms of conformers A and B: $N^{1A}\cdots N^{1B}$ 0.30(1), $C^{2A}\cdots C^{2B}$ 0.939(9), $C^{3A}\cdots C^{3B}$ 0.60(1), $O^{4A}\cdots O^{4B}$ 0.32(1), $C^{5A}\cdots C^{5B}$ 0.29(2), $C^{6A}\cdots C^{6B}$ 0.15(1), $O^{7A}\cdots O^{7B}$ 0.31(2), $C^{8A}\cdots C^{8B}$ 0.35(1), $C^{9A}\cdots C^{9B}$ 1.06(1), $C^{11A}\cdots C^{11B}$ 1.17(1), $C^{12A}\cdots C^{12B}$ 0.29(1), $O^{13A}\cdots O^{13B}$ 0.31(1), and $C^{14A}\cdots C^{14B}$ 0.857(7) Å.

Conformers A and B differ essentially in the torsion angles τ (Table 3). All the XCCY torsion angles (X, Y = N, O) in conformers A and B are of the *gauche* type; in conformer A, almost all of them are positive (except $O^{13A}C^{14A}C^{14A'}O^{13A'}$), and in conformer B their signs are opposite relative to the related torsion angles in conformer A. In conformer A, almost all the COCC torsion angles are *trans* (except the *gauche* angles $C^{6A}O^{7A}C^{8A}C^{9A}$ and $C^{6A'}O^{7A'}C^{8A'}C^{9A'}$), whereas in conformer B six torsion angles of this type ($C^{2B}C^{3B}O^{4B}C^{5B}$, $C^{11B}C^{12B}O^{13B}C^{14B}$, $C^{12B}O^{13B}\cdot C^{14B}C^{14B'}$, and symmetry-related angles) have unusual values of –120°±21°, i.e., are partially eclipsed (anticlinal). The CNCC torsion angles in conformers A and B have similar type (*gauche* or *trans*). Note that conformers of the 2.2.2-cryptand dication similar to A or B in **I** were observed in none of the ten previously studied crystal structures containing this dication (see above).

Conformers A and B of the 2.2.2-cryptand dication are similar in that the hydrogen atoms at the bridgehead nitrogen atoms, H^{1A} and $H^{1A'}$ or H^{1B} and $H^{1B'}$, are oriented inside the conformer cavity (crypta). These hydrogen atoms have short intracation contacts with three adjacent ether oxygen atoms: $H^{1A}\cdots O^{4A}$ 2.48, $H^{1A}\cdots O^{7A'}$ 2.32, $H^{1A}\cdots O^{13A}$ 2.58 and $H^{1B}\cdots O^{4B}$ 2.51, $H^{1B}\cdots O^{7B'}$ 2.35, $H^{1B}\cdots O^{13B}$ 2.38 Å. These contacts can be apparently interpreted as very weak intracation trifurcate hydrogen bonds of the $N^+–H(\cdots O)_3$ type.

The mean bond lengths in conformers A and B of the 2.2.2-cryptand dication [N^+–C 1.500(4), O–C 1.421(4), and C–C 1.501(5) Å] are close to the mean values for such dications. Note also that the intracation

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

Angle	ω	Angle	ω
$C^{2A}N^{1A}C^{9A'}$	112.5(3)	$C^{2B}N^{1B}C^{9B'}$	111.6(6)
$C^{2A}N^{1A}C^{11A}$	111.7(3)	$C^{2B}N^{1B}C^{11B}$	112.0(6)
$C^{9A'}N^{1A}C^{11A}$	110.9(3)	$C^{9B'}N^{1B}C^{11B}$	111.4(6)
$N^{1A}C^{2A}C^{3A}$	111.9(3)	$N^{1B}C^{2B}C^{3B}$	112.1(6)
$C^{2A}C^{3A}O^{4A}$	108.2(3)	$C^{2B}C^{3B}O^{4B}$	108.4(6)
$C^{3A}O^{4A}C^{5A}$	112.3(3)	$C^{3B}O^{4B}C^{5B}$	112.3(6)
$O^{4A}C^{5A}C^{6A}$	109.1(3)	$O^{4B}C^{5B}C^{6B}$	109.6(6)
$C^{5A}C^{6A}O^{7A}$	106.7(3)	$C^{5B}C^{6B}O^{7B}$	106.5(6)
$C^{6A}O^{7A}C^{8A}$	112.9(3)	$C^{6B}O^{7B}C^{8B}$	112.5(6)
$O^{7A}C^{8A}C^{9A}$	110.4(4)	$O^{7B}C^{8B}C^{9B}$	110.3(6)
$N^{1A'}C^{9A}C^{8A}$	110.9(3)	$N^{1B'}C^{9B}C^{8B}$	111.0(6)
$N^{1A}C^{11A}C^{12A}$	114.2(3)	$N^{1B}C^{11B}C^{12B}$	114.3(6)
$C^{11}AC^{12A}O^{13A}$	110.3(3)	$C^{11B}C^{12B}O^{13B}$	113.3(6)
$C^{12}AO^{13A}C^{14A}$	107.7(3)	$C^{12B}O^{13B}C^{14B}$	110.1(6)
$O^{13A}C^{14A}C^{14A'}$	110.2(3)	$O^{13B}C^{14B}C^{14B'}$	108.9(6)

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

Angle	τ(A)	τ(B)
$C^{11}N^{1}C^{2}C^{3}$	177.3(3)	–82(1)
$C^{9'}N^{1}C^{2}C^{3}$	51.8(4)	152.0(8)
$N^{1}C^{2}C^{3}O^{4}$	52.0(6)	–67(1)
$C^{2}C^{3}O^{4}C^{5}$	–178.5(6)	–99(1)
$C^{3}O^{4}C^{5}C^{6}$	–174.3(6)	–158(1)
$O^{4}C^{5}C^{6}O^{7}$	74.6(9)	–46(2)
$C^{5}C^{6}O^{7}C^{8}$	178.9(5)	–171(1)
$C^{6}O^{7}C^{8}C^{9}$	80.2(8)	–150(1)
$O^{7}C^{8}C^{9}N^{1'}$	42.3(4)	–53(1)
$C^{8}C^{9}N^{1'}C^{2'}$	–170.8(3)	–75(1)
$C^{8}C^{9}N^{1'}C^{11'}$	63.3(4)	–159.0(9)
$C^{9'}N^{1}C^{11}C^{12}$	175.0(4)	–90(1)
$C^{2}N^{1}C^{11}C^{12}$	48.7(5)	143.7(8)
$N^{1}C^{11}C^{12}O^{13}$	49.6(7)	–46(1)
$C^{11}C^{12}O^{13}C^{14}$	–155.4(5)	–129(1)
$C^{12}O^{13}C^{14}C^{14'}$	–178.4(5)	–106(1)
$C^{13}C^{14}C^{14'}O^{13'}$	–72.3(9)	57(1)

[a] Indices A and B at the atom numbers are omitted for brevity and are given in the column headings.

N···N distances appreciably differ in conformers A and B: $N^{1A}\cdots N^{1A'}$ 5.373(9) Å and $N^{1B}\cdots N^{1B'}$ 5.81(2) Å.

In the crystal structure of **I**, the iodide anions have contacts only with the methylene hydrogen atoms of the adjacent conformers A and B. One I^- anion has six such contacts with conformers of each kind (A or B), with the H···I distances varying within 3.02–3.20 Å. The shortest of these contacts (those with the hydrogen atoms at C^{2A} and C^{9A}, or at C^{2B}, C^{6B}, and C^{9B}), apparently, can be considered as very weak interionic hydrogen bonds of the $C–H\cdots I^-$ type.

EXPERIMENTAL

Ionic complex (salt) **I** was prepared as follows. A small molar excess of undiluted HI was added to a solution of 2.2.2-cryptand in a 1 : 1 acetone–ethanol mixture. The mixture was left to evaporate at room temperature. Within some time, colorless transparent crystals of this complex (salt) formed.

The unit cell parameters and three-dimensional set of reflection intensities were obtained on an Enraf-Nonius CAD-4 automatic diffractometer (MoK_α radiation, graphite monochromator). Compound **I** $[(C_{18}H_{38}N_2O_6)^{2+} \cdot 2I^-$, M 632.30] crystallizes in the rhombic system; a 19.892(3), b 9.732(2), c 12.830(2) Å; V 2483.7(7) Å^3, Z 4, d_{calc} 1.691 g cm^{-3}, $\mu(MoK_\alpha)$ 25.65 cm^{-1}, space group *Pbcn* (no. 60).

The intensities of 4053 reflections were measured in the reciprocal space octant ($2\theta \le 60°$) by the $\omega/2\theta$ scanning method from a 0.21 × 0.36 × 0.57-mm single crystal of **I**. A special mode was used in which the final scanning was performed for all (including very weak) reflections. The reflection intensities were corrected for absorption by the semiempirical method [5]. After exclusion of 457 systematically absent reflections, the working set of the measured $F^2(hkl)$ and $\sigma(F^2)$ values included 3596 unique reflections.

The structure of **I** was solved by the direct method using the SHELXS 97 program [6] and refined by the full-matrix least-squares method (with respect to F^2) using the SHELXL 97 program [6] in the approximation of anisotropic thermal vibrations for all nonhydrogen atoms. The structure was refined using almost all the reflections from the working set [including very weak reflections with $I < 2\sigma(I)$], except several reflections for which the measured and calculated F^2 values showed poor agreement.

First, we obtained from the direct method a structural model with the ordered 2.2.2-cryptand dication in which the nonhydrogen atom coordinates corresponded to conformer A. However, after anisotropic refinement of this ordered model (with geometrically set hydrogen atoms), the detailed analysis of the peaks of the control differential electron density synthesis revealed disordering of all the nonhydrogen atoms of the dication (and hence of all its hydrogen atoms) over two positions A and B, with the occupancy of positions B being by a factor of ~3 lower than that of positions A. These positions A and B correspond to two different conformers A and B of the 2.2.2-cryptand dication (see discussion above). Then, when refining the disordered structure of **I** by the least-squares method, we imposed soft equality conditions of the SAME, SADI, and DFIX type on the structurally equivalent (in conformers A and B) 1,2 and 1,3 interatomic distances [6]. The total occupancy of positions A and B of these two conformers was also refined by the least-squares method.

All the symmetrically independent hydrogen atoms of conformer A were objectively localized in the differential electron density synthesis in the intermediate refinement step. However, because of the disordering of **I**, in the subsequent refinement the coordinates of all the independent H atoms of conformers A and B were calculated geometrically by the rider model [6]; for conformer A, we refined the individual isotropic thermal parameters U_{iso} of the hydrogen atoms by the least-squares method.

For the exposed crystal of **I**, we also refined by the least-squares method the isotropic extinction coefficient: g 0.0020(2) [6]. In the last cycle of the full-matrix refinement of the disordered structure of **I**, the absolute shifts of all the 265 varied parameters were less than 0.003σ. The final coordinates and thermal parameters of the basis atoms are given in Table 4.

The final R factors are as follows: $R1$ 0.026 and $wR2$ 0.054 for 2375 observed reflections with $I \geq 2\sigma(I)$; $R1$ 0.048 and $wR2$ 0.091 for all the 3596 measured reflections; goodness of fit S 1.00 (for the definitions of $wR2$ and S, see [6]). In the final differential electron density synthesis, $-0.24 < \Delta\rho < 0.26$ eÅ^{-3}. The f curves used and anomalous-dispersion corrections to them ($\Delta f'$, $\Delta f''$) were taken from the International Tables [7]. All the X-ray structural calculations were performed with a PC.

Table 4. Coordinates ($\times 10^4$) and isotropic thermal parameters (Å^2, $\times 10^3$) of basis atoms in the crystal structure of **I**[a]

Atom	x	y	z	U[b]
I^-	3198.6(1)	–295.0(2)	4464.6(2)	63.41(9)
N^{1A}	1345(2)	132(3)	2694(3)	46(1)
C^{2A}	1211(2)	–262(3)	3804(2)	55.4(8)
C^{3A}	887(2)	888(4)	4406(3)	51.5(9)
O^{4A}	319(3)	1343(9)	3840(5)	56(1)
C^{5A}	–14(3)	2462(6)	4339(6)	67(1)
C^{6A}	–645(2)	2790(5)	3757(9)	54.5(7)
O^{7A}	–1112(3)	1742(7)	4002(5)	53(1)
C^{8A}	–1748(2)	1937(5)	3512(3)	51(1)
C^{9A}	–1722(1)	1461(3)	2397(2)	51.7(8)
C^{11A}	1698(1)	–995(3)	2112(2)	59.2(9)
C^{12A}	1384(2)	–2383(4)	2240(6)	69(1)
O^{13A}	680(2)	–2310(5)	2053(4)	69(1)
C^{14A}	371(1)	–3418(4)	2596(4)	88(1)
H^{1A}	938	257	2383	49(7)
N^{1B}	1445(5)	–37(7)	2817(6)	60(4)
C^{2B}	1375(4)	640(10)	3862(6)	79(3)
C^{3B}	687(4)	439(12)	4320(8)	83(4)
O^{4B}	218(6)	1169(15)	3700(12)	62(4)
C^{5B}	49(5)	2467(13)	4136(15)	42(3)
C^{6B}	–617(5)	2930(12)	3720(16)	55(4)
O^{7B}	–1052(6)	1779(15)	3780(13)	60(4)
C^{8B}	–1677(6)	2011(11)	3268(13)	95(7)
C^{9B}	–1954(4)	682(9)	2851(6)	77(3)
C^{11B}	1598(4)	–1542(7)	2911(8)	88(4)
C^{12B}	1272(4)	–2419(11)	2093(13)	79(6)
O^{13B}	586(4)	–2105(10)	1934(9)	71(4)
C^{14B}	191(4)	–3326(8)	1993(4)	61(3)
H^{1B}	1041	38	2490	65

[a] The occupancies of the atomic positions of the disordered 2.2.2-cryptand dication are 0.715(4) for all the positions with index A (conformer A) and 0.285(4) for all the positions with index B (conformer B). [b] Equivalent isotropic thermal parameters U_{eq} calculated as 1/3 of the trace of the orthogonalized U_{ij} tensor are given for all the nonhydrogen atoms, and the parameters U_{iso}, for the hydrogen atoms.

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