WATER CLUSTERS IN SUPRAMOLECULAR INCLUSION HYDRATES. CRYSTAL STRUCTURE OF DECAAZATRICYCLO[28.2.2.2^{13.16}]TETRATRIACONTANE NANOHYDRATE

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Inclusion compounds of solvate water molecules in a crystal matrix are investigated by X-ray diffraction analysis of a macrocyclic polyamine decaazatricyclo[$28.2.2.2^{13.16}$] tetratriacontane nanohydrate (I). When included in a crystal, water molecules are bonded by water-water (O-H...O) and water-macrocycle (O-H...N and N-H...O) hydrogen bonds, forming a linear cluster.

INTRODUCTION

Investigating the laws governing the formation of inorganic and organic clusters was a top priority in Powell's scientific activities [1, 2]. He was the first to show that clusters enter into the structure of clathrate compounds, including clathrate hydrates. During the recent decade, XRD analyses revealed a great number of compounds in which the clathrate component forms "partial" structures [2, 3]. The latter display the main features of a clathrate on the one hand but are not coordinationally saturated compounds on the other. The most striking examples are supramolecular crystal hydrates, where the linear, planar, or framework water associates (water clusters) define the principal motif of a crystal structure [3, 4].

It should be stressed once again that the main characteristic feature of such structures is coexistence of the hydrophilic and hydrophobic types of hydration [3, 4]. To establish the type of hydration of macrocyclic molecules is the primary object of a study of this kind.

The aim of this work is to perform an X-ray diffraction analysis of the clathrate hydrate decaazatricyclo[$28.2.2.2^{13.16}$]tetratriacontane nanohydrate (I). This compound is a supramolecular hydrate with a ratio macrocycle:water = 1:9. The macrocycle has the capability of hydrophilic hydration of ring nitrogens, whereas the major part of the macromolecule is hydrophobic.



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EXPERIMENTAL

Synthesis

The synthetic procedure and the complex-forming ability of a 30-membered macrocyclic polyamine are described in [5]. To synthesize decaazatricyclo[28.2.2.2^{13.16}]tetratriacontane we used the general procedure suggested by Richman and Atkins [6]. The starting N,N'-bis(2-p-toluenesulfonylaminoethyl)piperazine (2) may be prepared by various procedures [7, 8], one of which is shown in the scheme:



Cyclization of (2) with *tris*-(*p*-toluenesulfonyl)diethanolamine (3) in dry DMF at 100-110°C in the presence of K_2CO_3 proceeds via *in situ* formation of the dipotassium salt of (2), giving many by-products. To reduce their number, the disodium salt of N.N'-*bis*(2-*p*-toluenesulfonylaminoethyl)piperazine was previously isolated in a free form. This scheme also yields a [1+ 1] condensation product, which may be separated from (4) by recrystallization. The tosyl protecting groups were removed with concentrated H₂SO₄ with further treatment of the reaction mixture with a concentrated alkali and extraction of the target product (I) with hot benzene.

X-Ray Structure Analysis

For XRD analysis, a colorless prismatic single crystal was selected. The crystal is monoclinic with cell parameters (Table 1) refined from 30 reflections (DAR-UMB diffractometer, MoK_{α} radiation, graphite monochromator). Data were collected in an ω - $\theta/2\theta$ scan mode with scanning of reflections on a DAR-UMB diffractometer. Table 1 lists the conditions of data collection and the crystal and refinement data.

The structure was solved by direct methods using 1673 reflections with $l \ge 2\sigma(l)$ with the program package SHELX-86 [9] and refined by the least-squares procedure anisotropically for nonhydrogen atoms. The NH and water hydrogens were located on difference Fourier maps, and the parameters of the CH₂ groups were calculated geometrically. In the course of crystal structure determination it was found that the compound is a crystal hydrate. The ratio macrocycle:water is 1:9. Water occupies three general and three special (on twofold symmetry axes) positions in space group C2/c. The structure was refined with the SHELXL-93 [10]. The final coordinates of basic atoms are given in Table 2, and the interatomic distances and bond angles of I are listed in Table 3.

TABLE 1. Data	Collection and	Crystal and	Refinement	Data	for	I
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Molecular formula	$C_{24}H_{72}N_{10}O_{9}$		
Mol. wt.	644.92		
Wavelength, MoK_{α} , Å	0.71073		
Crystal system, space group	Monoclinic, C2/c		
Lattice parameters			
a, Å	14.117(3)		
b, Å	19.285(4)		
<i>c</i> , Å	14.344(3)		
β, deg	99.09(3)		
<i>V</i> . Å ³	3856.1(14)		
Z, ρ_{calc} , g/cm ³	4, 1.111		
$\mu(Mo), mm^{-1}$	0.084		
Crystal size, mm	0.30× 0.25× 0.70		
θ range, deg	2.11-25.22		
Range of indices	$-15 \le h \le 15, 0 \le k \le 22, 0 \le l \le 15$		
No. of refins measd	1673/1584 [R(int) = 0.0633]		
No. of reflns in LSA/No. of params	1584/244		
GOOF	1.090		
Final R factor			
$[I > 2\sigma(I)]$	$R_1 = 0.0674, wR_2 = 0.1719$		
R factor (for all reflections)	$R_1 = 0.0674, wR_2 = 0.1719$		
Residual peaks $\Delta\rho(max)$ and $\Delta\rho(min),~e\cdot~{\rm \AA}^{-3}$	0.283 and -0.253		

TABLE 2. Coordinates (× 10⁴) and Equivalent Isotropic Parameters (Å²× 10³) for I $[U_{eq} \text{ defined as } 1/3(U_{11} + U_{22} + U_{33})]$

Atom	x	у	Ξ	U _{eq}	Atom	X	у	Ξ	U _{eq}
N(1)	-3361(3)	5847(2)	-3686(3)	50(1)	N(13)	2143(3)	3364(2)	2185(2)	45(1)
C(2)	-3401(4)	5225(2)	-4280(3)	63(2)	C(14)	2513(4)	3088(2)	3136(3)	54(1)
C(3)	-3934(4)	4646(2)	-3857(3)	68(2)	C(15)	2686(4)	3633(3)	3913(3)	57(1)
N(4)	-3537(3)	4430(2)	-2872(3)	54(1)	C(16)	1674(3)	3063(3)	485(3)	61(1)
C(5)	-2525(4)	4225(2)	-2761(3)	55(1)	C(17)	2084(4)	2807(3)	1480(3)	59(1)
C(6)	-2165(3)	4026(2)	-1738(3)	53(1)	O(1w)	0	1513(3)	2500	63(2)
N(7)	-1139(3)	3872(2)	-1600(3)	51(1)	O(2w)	5000	2509(3)	2500	84(2)
C(8)	-739(4)	3737(3)	-606(3)	60(1)	O(3w)	-415(4)	2152(3)	707(3)	78(1)
C(9)	327(3)	3601(3)	-502(3)	53(1)	O(4w)	4908(3)	3456(2)	939(3)	69(1)
N(10)	722(3)	3365(2)	467(3)	48(1)	O(5w)	3436(4)	4345(2)	1407(3)	72(1)
C(11)	783(4)	3929(2)	1172(3)	51(1)	O(6w)	5000	116(3)	2500	82(2)
C(12)	1189(4)	3665(3)	2155(3)	55(1)					

TABLE 3. Interatomic Distances d (Å) and Bond Angles ω (deg) for I

Bond	d	Bond	d
1	2	3	4
N(1)-C(2)	1.467(6)	N(10)-C(16)	1.461(6)
C(2)–C(3)	1.527(7)	N(10)-C(11)	1.479(5)
C(3)–N(4)	1.494(6)	C(11)–C(12)	1.523(6)
N(4)-C(5)	1.466(6)	C(12)–N(13)	1.461(6)

TABLE 3 (Continued)

1	2	3	4
C(5)-C(6)	1.524(6)	N(13)-C(17)	1.468(6)
C(6)–N(7)	1.462(6)	N(13)–C(14)	1.481(6)
N(7)–C(8)	1.471(6)	C(14)–C(15)	1.523(7)
C(8)-C(9)	1.512(7)	C(15)–N(1)# 1	1.456(6)
C(9)–N(10)	1.485(6)	C(16)–C(17)	1.535(7)
Angle	ω	Angle	ω
C(15)# 1–N(1)–C(2)	113.5(4)	C(11)–N(10)–C(9)	112.8(3)
N(1)-C(2)-C(3)	110.0(4)	N(10)-C(11)-C(12)	111.1(4)
N(4)-C(3)-C(2)	116.4(4)	N(13)-C(12)-C(11)	111.7(4)
C(5)-N(4)-C(3)	113.1(4)	C(12)–N(13)–C(17)	108.6(3)
N(4)-C(5)-C(6)	110.1(4)	C(12)–N(13)–C(14)	111.1(4)
N(7)-C(6)-C(5)	110.7(4)	C(17)-N(13)-C(14)	110.2(3)
C(6)–N(7)–C(8)	112.8(4)	N(13)-C(14)-C(15)	114.8(4)
N(7)C(8)C(9)	110.5(4)	N(1)# 1-C(15)-C(14)	110.3(4)
N(10)-C(9)-C(8)	111.5(4)	N(10)-C(16)-C(17)	110.8(4)
C(16)–N(10)–C(11)	109.1(4)	N(13)-C(17)-C(16)	112.1(4)
C(16) - N(10) - C(9)	110.3(4)	_	

Note. Symmetry operation: # 1|| - x - y + 1, -z.

RESULTS AND DISCUSSION

The Structure-Forming Role of Water in I

Figure 1 shows a fragment of the crystal structure of I. By the nature of interactions between the components of the supramolecular complex, the latter may be regarded as a semiclathrate compound. Apart from the packing forces (according to Kitaigorodskii [11]), the structure-forming forces in a semiclathrate are the hydrogen bonds between the water molecules and between the solvate water and the macrocycle. Water molecules may be strictly classified into three groups according to their structural function. They all form a branched system of H-bonds, whose parameters are given in Table 4.

The O6w water molecule is not involved in interactions with the other solvate molecules. It is responsible for the formation of a dimer from two macrocycles related by a twofold axis. The parameters of the hydrogen bond are O6w...N7 2.952 Å, H...N7 2.10 Å; the angle at H is 172°.

The O5w water molecule is bonded to three nitrogen atoms, N1 (3.308 Å), N4 (3.151 Å), and N13 (2.966 Å), and to the O4w molecule. In the asymmetric fragment, the other four water molecules O1w–O4w are hydrogen-bonded into a chain structure directed along the z axis of the crystal. All water molecules of the chain interact with the hydrophilic part of the macrocycle via the O–H...N hydrogen bonds (Table 4).

Thus the chains of H_2O molecules (Figs. 1 and 2) consolidate all components of the supramolecular complex I into a three-dimensional framework. At the same time, the chains of water molecules fill the intermolecular space formed during the packing of bulky 30-membered macrocyclic polyamines.

A complex of 18-crown-6 with glycine-glycine and water may be considered the closest analog of this type of supramolecular inclusion hydrate [3]. In this structure, the linear associates of water molecules are bonded to the hydrophilic part of the dipeptide [3]. It is noteworthy that, while the compound is formally regarded as a guest-host complex, the basic host element of the system is difficult to determine. This may be either the macrocycle or the linear cluster of water molecules, which dictate the crystal architecture.

As can be seen in Fig. 2, the water associates fill the voids in the packing of macrocycles. At the same time,



Fig. 1. Crystal structure of I with numbering of water molecules.

DH	HA	DA	∠(DHA)	Symmetry transformation
0.92(5)	2.43(5)	3.308(6)	162(4)	N1–H1N1O5w_# 1
0.82(4)	2.34(5)	3.151(6)	166(4)	N4-H1N4O5w_# 1
0.83(6)	2.06(6)	2.865(5)	164(7)	O1w-H1w1N4_# 2
1.00(7)	1.89(8)	2.877(5)	171(7)	O2w-H2w2O4w
0.87(9)	1.96(9)	2.829(5)	170(7)	O3w–H2w3O1w
0.78(10)	2.12(10)	2.888(7)	171(9)	O3w-H2w3N10
0.98(6)	1.85(6)	2.827(7)	175(5)	O4w-H1w4O3w_# 3
0.86(8)	1.93(8)	2.766(6)	165(7)	O4w-H2w4N1_# 4
0.87(5)	1.99(6)	2.855(7)	173(4)	O5w-H1w5O4w
1.01(11)	1.98(1)	2.967(6)	164(8)	O5w-H2w5N13
0.86(5)	2.10(5)	2.953(5)	172(5)	O6w-H1w6N7_# 3

TABLE 4. Geometrical Parameters of Hydrogen Bonds in I

Note. Symmetry operations: # 1 - x, -y + 1, -z, # 2 x + 1/2, -y + 1/2, z + 1/2, # 3 - x + 1/2, -y + 1/2, -z, # 4 x + 1, -y + 1, z + 1/2.

water linked to the hydrophilic elements of the macrocycle is a structure-forming element of the system. The analysis of the structure-forming role of water in this crystal illustrates the diversity of water associates in supramolecular crystals, including point (D_0) , linear (D_1) , planar (D_2) , and framework (D_3) types.

An analysis of the packing in compound I shows that the O6w molecule forms point type (D_0) associates, whereas the O1w–O4w molecules form one-dimensional (D_1) clusters. Examples of three- and two-dimensional water



Fig. 2. Linear water cluster and its interaction with the macrocycle.

associates in supramolecular systems are 1,10-diaza-18-crown-6·9H₂O (framework D_3 type) [12] and 18-crown-6-C₃H₇NH₃F·10H₂O (layered D_2 type) [13].

Molecular Structure of Decaazatricyclo[28.2.2.2^{13.16}]tetratriacontane

Large macrocyclic polyamines can serve as substrates for syntheses of new hydrates of organic/inorganic materials and also as supramolecular semiconductors, photo and electric catalysts, magnetic materials, etc. [14, 15]. Their complexation reactions generally form binuclear complexes with 3*d*-metals [16]. In this case, they act as neutral ligands or cations protonating their amino groups.

Of special interest are the geometrical and conformational parameters of decaazatricyclo[28.2.2.2^{13.16}]tetratriacontane, which are missing in the literature.

Figure 3 presents an individual macrocycle molecule projected on the plane of donor atoms. The molecule is essentially nonplanar, the deviation of the donor atoms from the mean plane being up to ± 0.635 Å. The torsion angles in the independent part of the ring are given in Table 5. Two of the three $C(sp^3) - C(sp^3)$ bonds in the ethyleneamine fragments are in the *trans(anti)* configuration, which is less favorable for classical crown ethers than the *gosh* conformation.

The 30-membered centrosymmetric macrocyclic amide in general may be considered a two-angle amide [17, 18] with "pseudo" angles at the C(3) and C(3)* atoms. Most C-N bonds in the ethylamine chain are in the *trans* conformation. The distances in the ring are as typically observed in macrocyclic polyamides [19, 20]. The mean distances



Fig. 3. Molecular structure of decaazatricyclo $[28.2.2.2^{13.16}]$ tetratriacontane I with the atomic numbering scheme.

TABLE 5. Torsion	Angles	ω (deg)	in	I
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Angle	ω	Angle	ω
C15_# 1-N1-C2-C3	166.78(0.39)	N10-C11-C12-N13	58.59(0.55)
N1-C2-C3-N4	-57.73(0.62)	C11-C12-N13-C17	-56.75(0.50)
C2-C3-N4-C5	-55.57(0.61)	C11-C12-N13-C14	-178.10(0.38)
C3-N4-C5-C6	178.90(0.40)	C12–N13–C14–C15	-64.62(0.53)
N4C5C6N7	-175.59(0.38)	C17–N13–C14–C15	174.95(0.40)
C5-C6-N7-C8	174.90(0.40)	N13-C14-C15-N1_# 1	-58.07(0.53)
C6-N7-C8-C9	-178.38(0.40)	C14-C15-N1# 1-C2# 1	166.90(0.50)
N7-C8-C9-N10	-171.79(0.38)	C11-N10-C16-C17	56.48(0.52)
C8-C9-N10-C16	164.88(0.40)	C9-N10-C16-C17	-179.16(0.39)
C8C9N10C11	-72.89(0.50)	C12-N13-C17-C16	56.38(0.51)
C16-N10-C11-C12	-57.21(0.51)	C14-N13-C17-C16	178.28(0.40)
C9-N10-C11-C12	179.89(0.40)	N10-C16-C17-N13	-57.79(0.56)

Note. Symmetry operation: # 1 - x, -y + 1, -z.

in the polyethylamine chain $C(sp^3) - C(sp^3) 1.521$ Å, $C(sp^3) - N 1.470$ Å, and $C(sp^3) - N(pip) 1.483$ Å; the CNC angles are close to tetrahedral (Table 3). The geometrical parameters do not significantly differ from those of other cyclic polyamides [4, 7, 13, 16, 20]. Thus in the polyamide described in [20], C-N is 1.448-1.463, and C-C is 1.492-1.507 Å. The piperazine fragments have a chair conformation. Formation of a binuclear complex with a 3*d* metal demands an extensive conformational rearrangement of the macrocycle, providing the orientation of the nitrogen electron pairs needed for coordination to copper. At least two different complexes of copper(II) with macrocycle I are formed in solution according to the data of [5].

CONCLUSIONS

Recent experimental results, primarily X-ray data, permit an extended interpretation of the clathrate formation discovered by Powell. Kitaigorodskii's classification [11] according to the interaction between the components of mixed

crystals (which are often supramolecular systems) considers two groups of mixed crystals: packing and lattice ones. In real supramolecular systems, we never have one of the two extreme cases but we have both. In the compound under discussion, there are H_2O molecules united in a cluster, the O5w bridging molecule, and the O6w water molecule not linked with the rest of the hydration shell of the crystal.

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REFERENCES

- 1. H. M. Powell, J. Chem. Soc., 1, 61-73 (1948).
- 2. J. E. D. Davies, W. Kemula, H. M. Powell, and N. O. Smith, J. Incl. Phenom., 1, No. 1, 3-45 (1983).
- 3. J. Lipkowski, K. Udachin, Yu. A. Simonov, and D. Soldatov, *Current Challenges on Large Supramolecular Assemblies, NATO Science Series*, G. Tsoncaries (ed.), Kluwer (1999), pp. 157-171.
- 4. J. Lipkowski, O. V. Kulikov, and W. Zielenkiewicz, Supramol. Chem., 1, No. 1, 73-79 (1992).
- 5. I. I. Zheltvai, Yu. A. Popkov, and S. V. Dzyuba, Ukr. Khim. Zh., 64, No. 12, 132-136 (1998).
- 6. J. E. Richman and T. J. Atkins, J. Am. Chem. Soc., 96, No. 7, 2268-2270 (1974).
- 7. O. I. Dragomiretskaya, V. S. Orfeev, Yu. A. Popkov, and S. A. Andronati, *Dokl. Akad. Nauk USSR*, No. 1, 38-42 (1987).
- 8. Yu. A. Popkov, É. V. Ganin, and I. I. Zheltvai, Ukr. Khim. Zh., 60, No. 10, 718-720 (1994).
- 9. G. M. Sheldrick, Acta Crystallogr., A46, No. 6, 467-473 (1990).
- 10. G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, Germany (1993).
- 11. A. I. Kitaigorodskii, Mixed Crystals [in Russian], Nauka, Moscow (1983).
- 12. K. A. Udachin and J. Lipkowski, Mendel. Commun., 3, 237-238 (1995).
- 13. K. A. Udachin and J. Lipkowski, *ibid.*, **2**, 237-238.
- 14. M. Munakata, L. P. Wu, and T. Kuroda-Sowa, Bull. Chem. Soc. Jpn., 70, 1727-1734 (1997).
- 15. M. Petraszkiewicz, J. Mrozinski, R. Sat, et al., Collected Abstracts from the 10th International Symposium on Molecular Recognition and Inclusion, Warsaw (1998), pp. 4-27.
- 16. F. H. Allen and O. Kennard, Chem. Des. Autom. News, 8, No. 1, 31-37 (1993).
- 17. J. Dale, Acta Chem. Scand., 27, No. 12, 1115-1129 (1973).
- 18. J. Dale, Isr. J. Chem., 20, No. 1, 3-11 (1980).
- 19. P. Thuery, N. Keller, M. Lance, J.-D. Vigner, and M. Nierlich, Acta Crystallogr., C51, No. 10, 1407-1411 (1995).
- 20. H. Schumann, U. A. Bottger, K. Zietzke, et al., Chem. Ber. Recueil., 130, No. 2, 267-277 (1997).