

**SYNTHESIS AND STRUCTURE OF NONCOORDINATED CURTIS
MACROCYCLE AS A FREE BASE AND DIHYDROBROMIDE DIHYDRATE**Jan ROHOVEC¹, Pavel VOJTÍŠEK² and Ivan LUKEŠ^{3,*}

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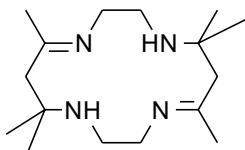
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5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (**1**) (Curtis macrocycle) was synthesized and studied by X-ray diffraction and NMR spectroscopy. In addition, a product of its decomposition 5,7,7-trimethyl-2,3,6,7-tetrahydro-1,4-diazepine (**2**) was found and identified by NMR spectroscopy. The X-ray structure of **1**·H₂O and **1**·2 HBr·2 H₂O is given.

Key words: Curtis macrocycle; Tetraazacyclotetradecadiene; Template synthesis; NMR spectroscopy; IR spectroscopy; X-Ray diffraction; Polyazamacrocyclic compounds; Azacrown compounds.

The macrocyclic compound 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (**1**) played an important role in the history of template syntheses of polyazamacrocyclic compounds.

The first synthesis of [Ni(**1**)]²⁺ was carried out by Curtis¹ using Ni²⁺ as a template cation for macrocyclization. Product was considered to be diimine

**1**

(CH₃)₂C=NCH₂CH₂N=C(CH₃)₂. Its macrocyclic nature was recognized later. The type of reaction is also called template synthesis or cyclization organic reactions using a metal ion as a template. Using that reaction, basic principles of the template synthesis were established². Consequently, the synthesis accelerated preparations of complexes of **1** with other transition metals³

and complexes of analogous azacycles⁴. Those complexes were studied from synthetical⁵, spectroscopic⁶ and magnetochemical⁷ points of view. About thirty complexes of **1** with various cations were investigated by diffraction techniques until 1997 (ref.⁸); however, the X-ray structure of **1**, which would be useful for comparison with structure of the complexes, has been unknown.

The free ligand **1** has never been isolated *via* decomplexation, for instance from $[\text{Ni}(\mathbf{1})]^{2+}$. During the procedure, decomposition was always observed. Compound **1** has been also considered unstable towards hydrolysis. The attempts to synthesize free **1** and similar compounds had not been successful until 1966 when its protonated salts with HClO_4 and HBr were prepared by the template synthesis on H^+ in the system of hydrogen bonds^{9,10}. In accordance with instability expected, anhydrous conditions were used^{9,10}. Unfortunately, these salts are reported not to form crystals suitable for X-ray investigation to obtain information on the geometry of the protonated molecule. On the other hand, they became useful starting materials for syntheses of a number of new complexes.

The papers mentioned above represent a "classic" period of template synthesis of azacrowns and their complexes. Now, these and similar tetraazaligands are important in medicine and supramolecular chemistry as well¹¹. An increasing interest concentrates on macrocyclic ligands with pendant groups¹². The Curtis-like ligands are also promising due to the presence of reactive $\text{N}=\text{C}$ bonds.

Preparation of a single crystal of **1** and its characterization including X-ray diffraction study is reported in this paper. Preparation of the single crystal of $\mathbf{1} \cdot 2 \text{HBr} \cdot 2 \text{H}_2\text{O}$ is also given. Structure of **1** is compared with the structures of the known complexes and $\mathbf{1} \cdot 2 \text{HBr} \cdot 2 \text{H}_2\text{O}$. Previous structures of the complexes⁸ described make possible broad discussion of geometry of the coordinated Curtis macrocycle and the noncoordinated ligand.

EXPERIMENTAL

Solvents and chemicals were obtained from Fluka (reagent grade) and were used as supplied. $\mathbf{1} \cdot 2 \text{HBr} \cdot 2 \text{H}_2\text{O}$ was prepared according to the literature¹⁰ and was used for further reaction without purification. Compound $[\text{Ni}(\mathbf{1})(\text{SCN})_2]$ (ref.¹³) was purified by recrystallization from H_2O . Silufol (Kavalier) silica plates were used for TLC.

Measurements

Infrared spectra in Nujol mulls were recorded on an ATI Mattson Genesis FTIR spectrometer (2 cm^{-1} resolution, Beer-Norton medium apodization) in the region $400\text{--}4\,000 \text{ cm}^{-1}$ at room temperature. All ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 400 spec-

trometer in CDCl_3 solutions at room temperature with TMS as internal standard. The ^{15}N NMR spectrum was taken in CDCl_3 using 5-mm broad band probe, 120 s delay and CH_3NO_2 as external reference. ^{13}C NMR spectra of solid samples were measured at room temperature using the CP/MAS technique and standard procedure (100.575 MHz, spinning rate 3 800 Hz, contact time 3 500 ms, the pulse repetition rate 5 s and adamantane as reference). Mass spectra were recorded on Incos 50 (Finnigan MAT) mass spectrometer, ionizing electron energy 70 eV, ion source temperature 150 °C. Samples were evaporated from a direct exposure probe (heating rate 10 mA s^{-1}).

Synthesis and Preparation of Single Crystals

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene hemihydrate (1·0.5 H₂O). Finely ground freshly prepared 1·2 HBr·2 H₂O (2.5 g, 5.2 mmol) was added in 0.1 g portions during 20 min into a vigorously stirred mixture of 8 M KOH (10 ml) and toluene (20 ml) at ambient temperature. The mixture was stirred vigorously until all the solid was dissolved (approximately 10 min). The toluene layer was separated and the water layer was twice extracted with 10 ml portions of toluene. The combined toluene extracts were dried using Na_2SO_4 and evaporated to dryness using rotary evaporator. The oily residue solidified to off-white crystals of **1**, which were purified by recrystallization from light petroleum. The isolated yield of 1·0.5 H₂O was 1.1 g (67%) as colourless crystals, soluble in toluene, CHCl_3 , light petroleum; m.p. 87–89 °C. For $\text{C}_{16}\text{H}_{32}\text{N}_4 \cdot 0.5 \text{H}_2\text{O}$ (289.46) calculated: 66.39% C, 11.49% H, 19.36% N; found: 66.78% C, 11.53% H, 19.32% N. IR (600–1 700 cm^{-1}): 640 vw; 737 m; 790 m; 815 m; 852 vw; 929 vw; 1 063 vw; 1 079 w; 1 111 m; 1 148 m; 1 174 m; 1 213 s; 1 231 s; 1 254 s; 1 269 w; 1 343 m; 1 354 s; 1 415 m; 1 463 vs; 1 650 vs (C=N). The purity of this compound can be checked by TLC (BuOH–25% NH_3 –EtOH 15 : 7 : 3 v/v, R_f 0.4). NMR data of are given in Tables I and II. MS, m/z (rel.%): 280 (M^+ , 0.2), 223 (0.2), 210 (0.3), 180 (0.6), 153 (1.8), 140 (8), 83 (27), 70 (100), 55 (32), 42 (25), 36 (10).

TABLE I
 ^1H NMR data for 1·0.5 H₂O and **2**

1·0.5 H ₂ O					2			
	δ , ppm	J , Hz			δ , ppm			
s	1.16	–	12 H	$(\text{CH}_3)_2\text{C}$	s	1.16	6 H	$(\text{CH}_3)_2\text{C}$
s	2.35	–	4 H	CCH_2C	s	2.03	3 H	$\text{CH}_3\text{C}=\text{N}$
s	1.81	–	6 H	$\text{CH}_3\text{C}=\text{N}$	s	2.53	2 H	CCH_2C
bt	3.32	4.4	4 H	$=\text{NCH}_2$	m	2.91	2 H	CH_2NH
bm	2.75	–	4 H	CH_2NH	m	3.62	2 H	$\text{CH}_2\text{N}=\text{}$
bm	3.9	–	2 H	NH				

Crystals of $1 \cdot 0.5 \text{ H}_2\text{O}$ can be stored in a tightly closed vessel in a refrigerator for about three months without significant decomposition. Any attempts to prepare anhydrous form by standing of $1 \cdot 0.5 \text{ H}_2\text{O}$ over P_2O_5 at room temperature lead to decomposition of **1** without a possibility to characterise the anhydrous **1**.

Identity of the decomposition product of sample of $1 \cdot 0.5 \text{ H}_2\text{O}$ (0.1 g, 0.3 mmol) after storage of the sample at ambient temperature for 3 months was confirmed by ^1H and ^{13}C NMR (Table I and II). According NMR spectra the product is *5,7,7-trimethyl-2,3,6,7-tetrahydro-1H-1,4-diazepine 2*. It is possible to isolate **2** by chromatography (TLC, the same mobile phase, R_F 0.6) in low yield (6.8 mg, 7%). MS, m/z (rel.%): 121 (0.5), 84 (30), 70 (19), 46 (87), 42 (31), 36 (100).

Recrystallization of **1** from light petroleum in the air by cooling of a hot (40°C) saturated solution in a refrigerator (-1°C) overnight gives large, well formed colourless crystals suitable for X-ray measurements. The composition of these crystals corresponds to the formula $1 \cdot \text{H}_2\text{O}$ suggesting an increase of hydration in the process of recrystallization.

Single crystals of $1 \cdot 2 \text{ HBr} \cdot 2 \text{ H}_2\text{O}$ were obtained by standing of aqueous solution saturated at 25°C in a refrigerator (-1°C) for one week. They do not lose water of crystallization at room temperature.

Crystallography

Single crystals of $1 \cdot \text{H}_2\text{O}$ and $1 \cdot 2 \text{ HBr} \cdot 2 \text{ H}_2\text{O}$ were mounted on a glass fiber using epoxy adhesive and coated by paraffin film. All diffraction data were collected on an Enraf-Nonius

TABLE II
 $^{13}\text{C}\{^1\text{H}\}$ NMR data for $1 \cdot 0.5 \text{ H}_2\text{O}$ and **2**, and $^{15}\text{N}\{^1\text{H}\}$ NMR data for $1 \cdot 0.5 \text{ H}_2\text{O}$

$1 \cdot 0.5 \text{ H}_2\text{O}$		2	
δ , ppm		δ , ppm	
$^{13}\text{C}\{^1\text{H}\}$			
27.09	$(\text{CH}_3)_2\text{C}$	30.65	$(\text{CH}_3)_2\text{C}$
52.54	$(\text{CH}_3)_2\text{C}$	28.19	$\text{CH}_3\text{C}=\text{N}$
49.60	CCH_2C	41.25	$=\text{NCH}_2$
169.37	$\text{C}=\text{N}$	42.10	HNCH_2
20.70	$\text{CH}_3\text{C}=\text{N}$	49.34	CCH_2C
50.80	$=\text{NCH}_2$	54.65	$(\text{CH}_3)_2\text{C}$
42.26	NHCH_2	173.98	$\text{C}=\text{N}$
$^{15}\text{N}\{^1\text{H}\}$			
-70.5	$\text{N}=\text{C}$		
-333.1	$\text{NH}-\text{C}$		

CAD4 diffractometer at random orientation using MoK α -radiation ($\lambda = 0.71073 \text{ \AA}$) and graphite monochromator.

Crystal data for 1-H₂O: C₁₆H₃₂N₄·H₂O, $M_r = 280.46$; monoclinic, space group $P2_1/c$ (No. 14), $a = 10.0449(4) \text{ \AA}$, $b = 10.4864(4) \text{ \AA}$, $c = 17.8597(7) \text{ \AA}$, $\beta = 97.227(3)^\circ$, $V = 1\,866.4(1) \text{ \AA}^3$, $Z = 4$, $D_c = 1.062 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 0.068 \text{ mm}^{-1}$, $F(000) = 664$. A colourless irregular crystal of dimensions $0.9 \times 0.8 \times 0.8 \text{ mm}$ was measured at room temperature. Its lattice parameters were determined from 25 reflections ($\theta = 15.5\text{--}16.5^\circ$). The intensities were measured by θ - 2θ scan in θ interval of $\langle 2.04, 26.97^\circ \rangle$, h interval of $\langle -12, 12 \rangle$, k interval of $\langle 0, 13 \rangle$, l interval of $\langle 0, 22 \rangle$. Three reflections were measured always after 1 h and their intensities varied the range from -6.0 to $+0.2\%$. Total 4 413 reflections were measured, $R_\sigma = 0.0170$ (4 057 independent, $R_{\text{int}} = 0.0179$). Lorentzian polarization correction (but not correction for absorption) were applied using program JANA98 (ref.¹⁴).

Crystal data for 1-2 HBr·2 H₂O: C₁₆H₃₂N₄·2 HBr·2 H₂O, $M_r = 478.32$; triclinic, space group $P(-1)$ (No. 2); $a = 8.2873(14) \text{ \AA}$, $b = 8.6144(11) \text{ \AA}$, $c = 8.7851(9) \text{ \AA}$, $\alpha = 73.045(9)^\circ$, $\beta = 75.303(13)^\circ$, $\gamma = 66.611(13)^\circ$, $V = 543.8(1) \text{ \AA}^3$, $Z = 1$, $D_c = 1.461 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 3.74 \text{ mm}^{-1}$, $F(000) = 248$. A colourless prismatic crystal of dimensions $0.4 \times 0.5 \times 0.5 \text{ mm}$ was measured at room temperature. Its lattice parameters were determined from 25 reflections ($\theta = 13\text{--}14^\circ$). The intensities were measured by θ - 2θ scan in θ interval of $\langle 2.45, 24.97^\circ \rangle$, h interval of $\langle -9, 9 \rangle$, k interval of $\langle -9, 10 \rangle$, l interval of $\langle 0, 10 \rangle$. Three reflections were measured always after 1 h and their intensities varied the range from -5.8 to $+0.9\%$. Total 1 912 reflections were measured, $R_\sigma = 0.0144$. Lorentzian polarization correction (but not correction for absorption) were applied using program JANA98 (ref.¹⁴).

The structures were solved by direct methods (SHELXS86, ref.¹⁵) and refined using the least-squares treatment (full-matrix, based on F^2) (SHELXL97, ref.¹⁶). The hydrogen atoms were found from difference Fourier map and refined isotropically. The minimized function was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2|F|^2 + (0.0659P)^2 + 0.2488P]$ for 1-H₂O and $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2|F|^2 + (0.0795P)^2 + 0.0681P]$ for 1-2 HBr·2 H₂O, where $P = (F_o^2 + 2F_c^2)/3$. The final values of refinement were:

a) for 1-H₂O: 327 parameters, $\Delta_{\text{max}}/\sigma = -0.005$ (for H-atom), $R_1 = 0.0428$, $wR_2 = 0.1185$ (SHELXL97, ref.¹⁶) for 3 067 observed ($I > 2\sigma(I)$) reflections, GOF = 1.081, the residual electron densities -0.22 and $+0.27 \text{ e \AA}^{-3}$;

b) for 1-2 HBr·2 H₂O: 186 parameters, $\Delta_{\text{max}}/\sigma = 0.070$ (for H-atom), $R_1 = 0.0392$, $wR_2 = 0.1062$ (SHELXL97, ref.¹⁶) for 1 652 observed ($I > 2\sigma(I)$) reflections, GOF = 1.080, the residual electron densities -0.97 and $+0.68 \text{ e \AA}^{-3}$.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-110245 (dibromid) and CCDC-110246 (curtis). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.ca.ac.uk.

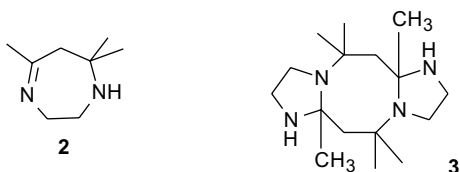
RESULTS AND DISCUSSION

Synthesis of 1·0.5 H₂O and Formation of 2

The Curtis macrocycle as a free base **1** was prepared from the easily accessible compound **1-2 HBr·2 H₂O** by neutralization of its aqueous solution with KOH. The crucial point of the preparation is a quick removal of **1** from the

aqueous phase to toluene. Contrary to expectations and to the well known instability of aliphatic imines in water, **1** was found to be extraordinarily stable toward hydrolysis at room temperature. To our surprise the elemental analysis of microcrystalline product suggests to the presence of crystal water that corresponding to the formula $1 \cdot 0.5 \text{H}_2\text{O}$. The explanation of this unexpected stability follows from geometry of the molecule of **1** discussed in the following section.

Compound $1 \cdot 0.5 \text{H}_2\text{O}$ slowly decomposes in the solid state. A similar behaviour was observed for $1 \cdot 2 \text{HBr} \cdot 2 \text{H}_2\text{O}$ and $1 \cdot 2 \text{HClO}_4$ (ref.⁹); however, the product of decomposition has not been investigated. The product of the decomposition is assumed to be **2** or **3**.



Compound **2** is formed by degradation of **1** into two parts whereas **3** is a product of double intramolecular addition of NH to the N=C bond. According to ^1H and ^{13}C NMR spectra (Tables I and II), it is possible to distinguish between **2** and **3**. The spectra of the products are in full agreement with the proposed structure **2**, mainly due to the presence of signal N=C double bond and the absence of signal N-CR₂-N (ref.¹⁷) in the ^{13}C NMR spectra. MS spectroscopy was not found to be convenient method for identification of **2** due to absence of M⁺⁺ in the spectrum. Only fragment ion of low molecular weight was observed, which does not lead to unequivocal conclusion.

Preparation of Single Crystals $1 \cdot \text{H}_2\text{O}$ and $1 \cdot 2 \text{HBr} \cdot 2 \text{H}_2\text{O}$

Compound $1 \cdot \text{H}_2\text{O}$ easily crystallizes after cooling of solution in light petroleum saturated at elevated temperature. A presence of H_2O seems to be necessary for formation of hydrogen bonds network in solid state. Compound $1 \cdot 2 \text{HBr} \cdot 2 \text{H}_2\text{O}$ is only soluble in H_2O . On the other hand instability of the compound titled is aqueous solution is also known, thus preparation of

1:2 HBr:2 H₂O in the single crystal form is rather difficult. We found that single crystals of this compound for X-ray analysis can be obtained by cooling its solution saturated at room temperature. An attempt to obtain crystals by slow evaporation of solution of titled compound in H₂O at room temperature offered a viscous mixture of products of hydrolysis after one week. It is possible to obtain single crystals by cooling of solution saturated at room temperature in a refrigerator.

TABLE III
¹³C CP MAS NMR data for 1·0.5 H₂O, 1·2 HBr·2 H₂O and [Ni(1)](SCN)₂

Carbon atom	1·0.5 H ₂ O δ, ppm	1·2 HBr·2 H ₂ O δ, ppm	[Ni(1)](SCN) ₂ δ, ppm
C=N	172.38	174.92	174.57
C(CH ₃) ₂	54.32	60.03	56.67
=NCH ₂	52.56	48.04	53.80
CCH ₂ C	42.91	44.64	47.50
NHCH ₂	29.56	43.18	45.31
(CH ₃) ₂ C	24.16	26.53	26.16
CH ₃ C=N	22.88	22.48	23.55
SCN	-	-	182.09
			180.10

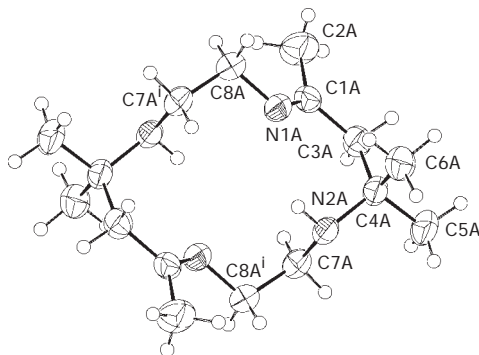


FIG. 1
 Perspective view of molecule A of 1 in the structure 1·H₂O with atom labels. (The labelling of molecule B is analogous)

TABLE IV
Selected bonds (Å) and angles (°)ⁱ in 1-H₂O. The geometry of the symmetrically independent parts

Atoms	Bond lengths	Atoms	Angles	Atoms	Torsion angles
Molecule A					
N1-C1	1.266(2)	C8 ⁱ -N1-C1	120.9(1)	C8 ⁱ -N1-C1-C3	178.6(1)
C1-C3	1.509(2)	N1-C1-C3	120.4(1)	N1-C1-C3-C4	7.2(2)
C3-C4	1.541(2)	C1-C3-C4	119.0(1)	C1-C3-C4-N2	-57.0(2)
C4-N2	1.482(2)	C3-C4-N2	113.7(1)	C3-C4-N2-C7	-60.4(2)
N2-C7	1.459(2)	C4-N2-C7	116.3(1)	C4-N2-C7-C8	175.8(1)
C7-C8	1.515(2)	N2-C7-C8	110.0(1)	N2-C7-C8-N1 ⁱ	-69.0(1)
C8-N1 ⁱ	1.461(2)	C7-C8-N1 ⁱ	109.3(1)	C7-C8-N1 ⁱ -C1 ⁱ	140.1(2)
C1-C2	1.508(2)	C2-C1-C3	113.8(1)	C8 ⁱ N1-C1-C2	1.8(2)
C4-C5	1.531(2)	C5-C4-C6	108.7(1)	C1-C3-C4-C5	-178.2(1)
C4-C6	1.526(2)			C1-C3-C4-C6	63.5(2)
N1...N1 ⁱ	3.812(3)				
N2...N2 ⁱ	4.509(2)				
Molecule B					
N1-C1	1.265(2)	C8 ⁱⁱ -N1-C1	121.3(1)	C8 ⁱⁱ -N1-C1-C3	180.6(1)
C1-C3	1.505(2)	N1-C1-C3	120.3(1)	N1-C1-C3-C4	-18.7(2)
C3-C4	1.542(2)	C1-C3-C4	119.1(1)	C1-C3-C4-N2	57.3(2)
C4-N2	1.481(2)	C3-C4-N2	113.7(1)	C3-C4-N2-C7	62.9(2)
N2-C7	1.460(2)	C4-N2-C7	116.0(1)	C4-N2-C7-C8	-176.8(1)
C7-C8	1.510(2)	N2-C7-C8	110.3(1)	N2-C7-C8-N1 ⁱⁱ	67.8(2)
C8-N1 ⁱⁱ	1.461(2)	C7-C8-N1 ⁱⁱ	109.7(1)	C7-C8-N1 ⁱⁱ -C1 ⁱⁱ	-150.3(2)
C1-C2	1.505(2)	C2-C1-C3	114.5(2)	C8 ⁱⁱ N1-C1-C2	0.0(3)
C4-C5	1.526(2)	C5-C4-C6	108.9(1)	C1-C3-C4-C5	179.3(1)
C4-C6	1.529(2)			C1-C3-C4-C6	-61.8(2)
N1...N1 ⁱⁱ	3.723(3)				
N2...N2 ⁱⁱ	4.521(3)				

i = -x, -y, 1 - z; ii = 1 - x, -y, -z.

Crystallography

The results of the room-temperature single-crystal structure determination of compound **1**·H₂O are listed in Table IV. The view of this structure (molecule A only) with the atom-labelling scheme is shown in Fig. 1, packing in Fig. 2. The structure consists of two crystallographically different macrocycle molecules which belong to the unit cell only by one half. Both are situated on the inverse centres ((0,0,1/2) and (1/2,0,0)) and they are linked through mediator molecules H₂O. This structure is stabilized by a network of weak hydrogen bonds. Each H₂O molecule participates in two hydrogen bonds of approximately the same lengths (O...N2 = 2.974(2) Å for molecule A and O...N2ⁱⁱⁱ = 2.930(2) Å; iii = -x + 1, -y - 1/2, z + 1/2 for molecule B). The system of hydrogen bonds is completed by two intramolecular bonds N1...N2 = 2.962(2) Å in molecule A and N1...N2 = 2.917(2) Å in molecule B.

The geometries of both the macrocycle molecules are nearly identical (Table IV) and representing the geometry of the Curtis macrocycle in an "intact" state without any bonding interaction except the weak hydrogen bonds. We can compare it with some complexes of the Curtis ligand. 24 independent coordinated molecules of the Curtis macrocycle were found in CCDC (ref.⁸). Selected bond lengths, angles and torsion angles for **1** are given in Table IV. The C-H bond lengths are in the range expected, from 0.89(2) to 1.04(2) Å. The values of C-C and C-N single bond lengths are nearly identical in both the crystallographically independent molecules and are in accordance with the expected values for this type of compound.

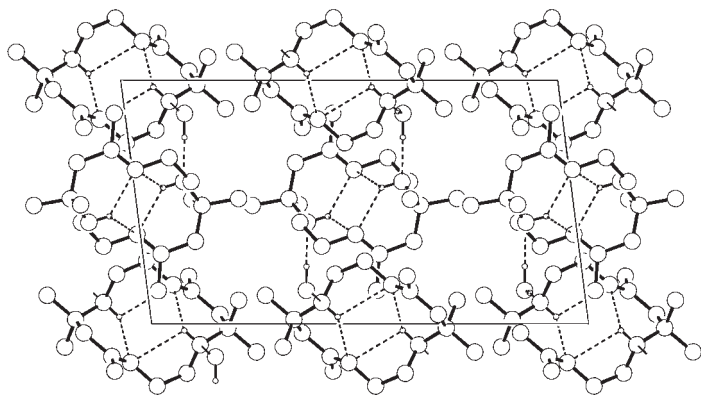


FIG. 2
Crystal packing of **1**·H₂O, view along (010) direction

The explanation of the stability of $1 \cdot \text{H}_2\text{O}$ in the solid state, mentioned above, follows from the structure shown in Fig. 1. All C=N bonds are sterically hindered by hydrophobic methyl groups and the ring conformation and water molecules are immobilized by the network of hydrogen bonds (Table V).

The X-ray data of $1 \cdot 2 \text{HBr} \cdot 2 \text{H}_2\text{O}$ are summarized in Table VI. The view of this structure with the atom-labelling scheme is shown in Fig. 3, packing in Fig. 4. The structure consists of the macrocycle molecule, being situated on

TABLE V
The geometry of water molecule and hydrogen bonds in $1 \cdot \text{H}_2\text{O}$

Atoms	Bond lengths	Atoms	Angles
O-H1	0.90(3)	H1-O-H2	108(2)
O-H2	0.90(3)	N2A...H2A...N1A	133(1)
N2A-H2A	0.89(1)	N2B...H2B...N1B	136(1)
N2B-H2B	0.89(2)	O...H1...N2A	173(1)
N2A...N1A	2.962(3)	O...H2...N2B ⁱⁱⁱ	165(1)
N2B...N1B	2.917(3)		
O...N2A	2.974(3)		
O...N2B ⁱⁱⁱ	2.930(3)		

iii = $x - 1, -y - 1/2, 1/2 + z$.

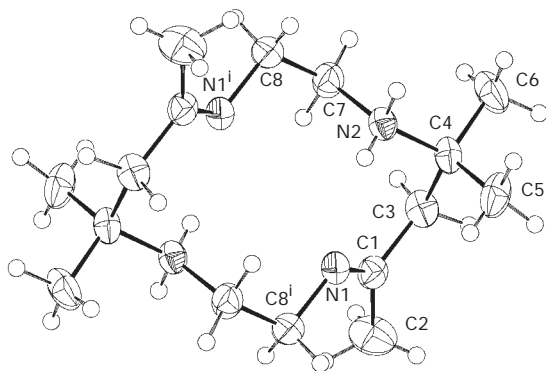


FIG. 3
Perspective view of molecule of **1** in the structure $1 \cdot 2 \text{HBr} \cdot 2 \text{H}_2\text{O}$ with atom labels

TABLE VI
Selected bonds (Å) and angles (°) in 1:2 HBr:2 H₂O. The geometry of the symmetrically independent part

Atoms	Bond lengths	Atoms	Angles	Atoms	Torsion angles
N1-C1	1.265(4)	C8 ⁱ -N1-C1	120.4(3)	C8 ⁱ -N1-C1-C3	179.6(2)
C1-C3	1.509(4)	N1-C1-C3	119.5(2)	N1-C1-C3-C4	-22.7(4)
C3-C4	1.521(4)	C1-C3-C4	118.3(2)	C1-C3-C4-N2	54.9(3)
C4-N2	1.517(3)	C3-C4-N2	110.3(2)	C3-C4-N2-C7	-61.3(3)
N2-C7	1.481(4)	C4-N2-C7	117.2(2)	C4-N2-C7-C8	179.1(2)
C7-C8	1.515(4)	N2-C7-C8	109.8(3)	N2-C7-C8-N1 ⁱ	71.6(4)
C8-N1 ⁱ	1.458(3)	C7-C8-N1 ⁱ	110.3(2)	C7-C8-N1 ⁱ -C1 ⁱ	-15.6(3)
C1-C2	1.498(4)	C2-C1-C3	113.7(3)	C8 ⁱ -N1-C1-C2	-1.8(4)
C4-C5	1.521(4)	C5-C4-C6	111.0(3)	C1-C3-C4-C5	175.1(2)
C4-C6	1.527(4)			C1-C3-C4-C6	-62.3(3)
N1...N1 ⁱ	3.598(4)				
N2...N2 ⁱ	4.496(4)				

$i = 1 - x, -y, 2 - z.$

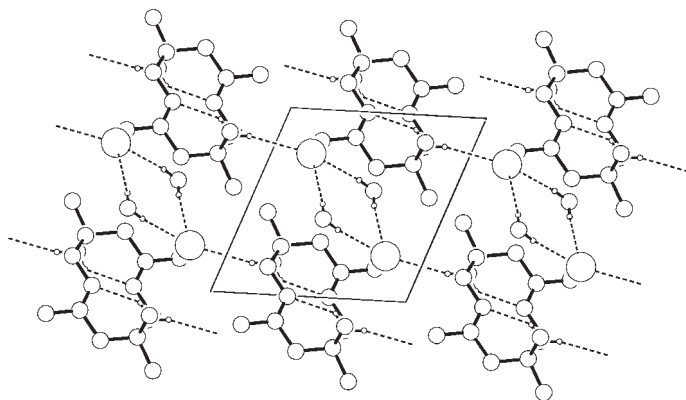


FIG. 4
Crystal packing of 1:2 HBr:2 H₂O, view along (001) direction

the inverse centre. The crystal structure of $1 \cdot 2 \text{ HBr} \cdot 2 \text{ H}_2\text{O}$ is stabilized by intramolecular and intermolecular hydrogen bond network, simillary to the previous one.

All nitrogen atoms in the $1 \cdot 2 \text{ HBr} \cdot 2 \text{ H}_2\text{O}$ take part in hydrogen bonds network (see Table VII). Two intramolecular hydrogen bonds $\text{N}2 \cdots \text{N}1$ and $\text{N}2^i \cdots \text{N}1^i$ ($i = 1 - x, -y, 2 - z$) in each molecule of macrocycle are relatively strong (2.757(4) Å). This array of hydrogen bonds observed in this structure in the solid state is in a good agreement with the hydrogen bond array expected in solution¹⁰. This system of hydrogen bonds is responsible for extraordinary high yields of macrocyclization reaction during the formation of this cyclic system¹⁰. The atom $\text{HN}21$ and $\text{HN}22$ participate on the bonding to bromide anion in the structure (Table VII). Both hydrogen atoms of water molecule interact with bromide anions.

The bond lengths and angles in $1 \cdot 2 \text{ HBr} \cdot 2 \text{ H}_2\text{O}$ are similar to $1 \cdot \text{H}_2\text{O}$, excluding bonds from protonized nitrogen atom $\text{N}2$. This prolongation is given by protonation of the macrocycle on $\text{N}2$ atoms. The geometry of the macrocycle is the same in both cases.

Comparison of the lengths of double bonds $\text{C}=\text{N}$ in the free ligand $1 \cdot \text{H}_2\text{O}$, $1 \cdot 2 \text{ HBr} \cdot 2 \text{ H}_2\text{O}$ and in complexes shows only small differences. Except the three values (two for one molecule of $[\text{Co}(1)]_2(\text{CO}_2\text{H})(\text{ClO}_4)_3$ (= GEYFUL)¹⁸ and one for one molecule of $[\text{Co}(\text{H}_2\text{O})(1)](\text{ClO}_4)_2 \cdot 0.6 \text{ H}_2\text{O}$ (= JASKUJ)¹⁹,

TABLE VII
The geometry of water molecule and hydrogen bonds in $1 \cdot 2 \text{ HBr} \cdot 2 \text{ H}_2\text{O}$

Atoms	Bond lengths	Atoms	Angles
O-HO1	0.72(5)	HO1-O-HO2	108(5)
O-HO2	0.80(6)	HN21-N2-HN22	113(4)
N2-HN21	0.84(4)	N2...HN21...Br	163.6(8)
N2-HN22	0.78(4)	N2...HN22...N1	133(1)
N2...Br	3.484(2)	N2...HN22...Br ⁱⁱ	116.2(8)
N2...N1	2.757(3)	O...HO1...Br ⁱⁱⁱ	169.5(8)
N2...Br ⁱⁱ	3.548(2)	O...HO2...Br	166.5(8)
O...Br ⁱⁱⁱ	3.388(2)		
O...Br	3.394(2)		

ii = $-x, -y, 2 - z$; iii = $-x - 1, 1 - y, 2 - z$.

probably due to the hydrogen bond present in these structures, the average C=N distance is 1.286(8) Å (from 45 hits⁸) being only a little higher than in the free macrocycle **1**·H₂O (average value for molecule A and B 1.265 (2) Å) or **1**·2 HBr·2 H₂O (1.265(4) Å). This fact can be expected due to affecting the double bonds by coordination. A similar effect can be observed in IR spectrum of the Curtis macrocycle (see below).

The carbon atoms in the ligand are pucker from the plane formed by four nitrogen atoms. The total puckering amplitude for *n*-membered ring can be generally expressed, according to Cremer and Pople²⁰,

$$Q = (\sum z_j^2)^{1/2} ,$$

where z_j is perpendicular atomic displacement of *j*-th atom from the reference plane defined by four nitrogen atoms. The values of *Q* are listed in Table VIII for two crystallographically independent molecules **1**·H₂O and for **1**·2 HBr·2 H₂O together with the values for some complexes. The average value of *Q* for 24 hits of coordinated ligands from CCDC (ref.⁸), 1.56(1) Å, is lower than the values for the free **1**·H₂O (3.02(1) and 3.14(1) Å for molecule A and B, respectively) and for **1**·2 HBr·2 H₂O (2.90(1) Å). This corresponds to a higher rigidity of coordinated ligand due to the presence of four coordination bonds.

NMR and IR Spectroscopy

NMR data for **1** and **2** are listed in Tables I and II. The assignment of ¹H and ¹³C NMR spectra was proved using H,H-COSY and C,H-HMQC techniques. ¹H and ¹³C spectra of **1**·0.5 H₂O and **2** in CDCl₃ at room temperature are in accordance with the proposed structures.

The ¹³C NMR spectrum of **1**·0.5 H₂O in the solid state is very similar to that in CHCl₃ (see Tables II and III) and hence, we assume that the conformation of **1** does not change significantly from that observed in the solid state. This was also confirmed a the NOESY experiment. In the ¹³C NMR spectra, we can also observe a shift of the 29.56 ppm NHCH₂ peak in **1** to the values of 43.18 ppm in **1**·2 HBr·2 H₂O and 45.31 ppm in [Ni(**1**)](SCN)₂ due to protonation and coordination of the nitrogen atom.

In contrast to the mentioned changes in the chemical shifts of carbon atom adjacent to the amine N atom, the imine N atom remains unaffected as expected due to general trends of p*K*_b of amines and imines. The observed ¹³C NMR shifts of [Ni(**1**)](SCN)₂ are close to the values of the noncoordinated Curtis macrocycle except for the NHCH₂ chemical shift

TABLE VIII
Values of puckering parameters of Curtis macrocycle (in complexes and in noncoordinated and protonized form)

CCDC-coden	Formula	Q, Å
BADFIV	[Co(H ₂)(CH ₃)(1))(ClO ₄) ₂ ·3 H ₂ O	1.419
BAPPUD	[Cu((1))(ClO ₄) ₂ , red isomer	1.548
BAPPUD01	[Cu((1))(ClO ₄) ₂ , orange isomer	1.239
CMZCFE	[FeCl(1)]	2.818
DENLIR	[Ni ₂ (μ-CN) ₂ (CN) ₂ (1)] _n ·n H ₂ O	1.282
DNCOPC10	[Co(NH ₃)(1))(ClO ₄) ₂	1.123
GEYFUL (molecule 1)	[Co(1) ₂ (CO ₂ H)(ClO ₄) ₃ ·3 CH ₃ CN	1.872
GEYFUL (molecule 2)	[Co(1) ₂ (CO ₂ H)(ClO ₄) ₃ ·3 CH ₃ CN	1.596
HMACNI	Ni(1)(SCN) ₂ ·H ₂ O	1.854
HMTZCR	[Cr(NO)(NO ₂)(1)PF ₆	1.317
JASKUJ (molecule 1)	[Co(H ₂ O)(1))(ClO ₄) ₂ ·0.6 H ₂ O	1.677
JASKUJ (molecule 2)	[Co(H ₂ O)(1))(ClO ₄) ₂ ·0.6 H ₂ O	1.708
JASKUJ (molecule 3)	[Co(H ₂ O)(1))(ClO ₄) ₂ ·0.6 H ₂ O	1.775
JASLEU	[Co(OCIO ₃)(1))(ClO ₄)	1.576
JETSIK	[Co(H ₂ O)(CCH ₂)(1))(ClO ₄) ₂	1.386
JIMJEU	[Co(H ₂ O)(CH ₃)(1))(CF ₃ SO ₃) ₂	1.684
KINNOK (molecule 1)	[Cu((1))ClO ₄	1.240
KINNOK (molecule 2)	[Cu((1))ClO ₄	1.214
KUFNEF	<i>meso</i> -[Ni((1))(ClO ₄) ₂	1.203
MAZTN102	<i>rac</i> -[Ni((1))(ClO ₄) ₂	1.616
TEKZEO	[Co(NCS) ₂ (1)]SCN	1.541
VAKTIK	[Co(CO)(1)]	1.832
VAKTUW	[CoCl ₂ (1)]	1.122
Average value		1.561
1·H ₂ O (molecule 1)		3.018
1·H ₂ O (molecula 2)		3.139
1·2 HBr·2 H ₂ O		2.901

mentioned above. This is in accordance with the assumption of a minute changes in the macrocycle geometry during the coordination. Two signals of the carbon atoms of SCN^- probably correspond to two chemically non-equivalent anions.

The IR spectrum of $1 \cdot 0.5 \text{ H}_2\text{O}$ is rather complex, however, the sharp band in the range $1\ 600\text{--}1\ 700 \text{ cm}^{-1}$ can be unambiguously assigned to $\nu(\text{C}=\text{N})$. This band was observed at $1\ 650 \text{ cm}^{-1}$ in the spectrum of noncoordinated ligand; but at $1\ 670 \text{ cm}^{-1}$ in the spectrum of $1 \cdot 2 \text{ HBr} \cdot 2 \text{ H}_2\text{O}$ (ref.⁹). The values for $[\text{Ni}(\mathbf{1})](\text{SCN})_2$ are close to those for the noncoordinated Curtis macrocycle ($1\ 654$ and $1\ 662 \text{ cm}^{-1}$ for *N-rac*-isomer and *N-meso*-isomer, respectively)²¹. Generally, the values of $\nu(\text{C}=\text{N})$ are not sensitive to the coordination or protonization effect and they would be found in a relatively narrow range $1\ 640\text{--}1\ 680 \text{ cm}^{-1}$ for $\text{Ni}(2+)$ complexes of Curtis-like ligands in solid state.

The results indicate that hydrophobic methyl groups in the Curtis cycle protect the $\text{C}=\text{N}$ bonds against attack by water molecules in both the solid state and solution. In contrast to the literature, we assume that crystal water stabilizes the structure by network of hydrogen bonds and hence, its presence in the solid state seems to be important.

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