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Full Papers

Binding of water and solvent molecules in a 25-membered-ring host compound

Fritz Vögtle *#, Gisela Brodesser #, Martin Nieger § and Kari Rissanen (a)

 # Institut für Organische Chemie und Biochemie der Universität Bonn,
§ Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Strasse 1, W-5300 Bonn 1
(a) Department of Chemistry, University of Jyväskylä PL 35, SF-40351 Jyväskylä, Finland
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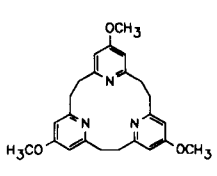
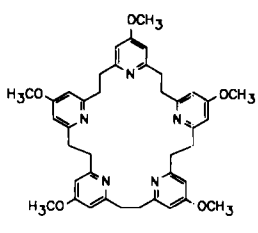
Abstract. The macrocyclic 15- and 25-membered-ring pyridine oligomers **1** and **2** containing three and five methoxy substituents in the 4-position of the pyridine rings were prepared by *Müller–Röscheisen* cyclization and then isolated by chromatography. They are attractive as synthetic endobasic receptor molecules. X-ray structure analysis exhibits the inclusion of hydrogen-bonded solvent molecules (water and trichloromethane) inside the pentameric macrocycle **2**.

Introduction

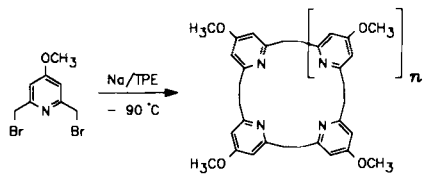
Recently, we reported the advantages of using many-membered and donor-substituted hydrocarbon rings[1]. While these hydrocarbon macrocycles are intraannular methoxy-substituted [2$_n$]cyclophanes and aimed at "endo-acidic receptor molecules", we wish to report now on macrocycles with reversed functionalization that unfold endobasic properties. Concerning the macrobicyclic domain[2], we had already successfully complexed acidic guests in molecular cavities containing bipyridine moieties[3].
The macromonocycles **1** and **2** described here are easily available from a simple one-step cyclization reaction, which is, moreover, an advantage with respect to the macrobicyclic analogues. In contrast to ordinary pyridinophanes[4], we fixed OCH_3 groups in the 4-position of each pyridine ring for strengthening basicity, donor capacity and cooperativity of the pyridine nitrogen atoms[5]. A certain conformational flexibility is achieved by alternate arrangement of rigid aromatic (pyridine rings) and flexible aliphatic moieties (ethano bridges). In this way, unfavourable rigid conformers, which are unable to enclose guest molecules, are avoided, as are mixtures of stable conformers, which must then be characterized and separated.



1



2



3

1: $n = 0$
2: $n = 2$

Preparation of macrocycles

The many-membered pyridinophanes **1** and **2** are prepared by cyclization of the bis(bromomethyl) compound **3**[6] according to the *Müller–Röscheisen* reaction[7]. This modified Wurtz coupling was employed first by *Jenny* et al.[8] for the synthesis of unsubstituted [2$_n$]metacyclophanes with no host character. Similar to the unsubstituted parent compounds[4], a mixture of cyclic and open-chained oligomers was obtained in the donor-substituted pyridinophane series. In order to exercise an influence on the distribution of products, we modified the reaction conditions: A solution of the dibromo compound **3** was added in small doses by a perfusor to the tetraphenylethane disodium complex (TDNa), as the red colour of the reaction mixture does not turn to yellow. Whereas tetraphenylethene (TPE) is used in catalytic amounts, we chose a ten-fold excess of sodium in relation to the dibromo compound **3**. For the purpose of keeping the amount of by-products as low as possible, cyclization was carried out at −90°C, underlined by slow addition of the dibromo compound **3** and high dilution, contrary to the original reaction conditions of *Burri* and *Jenny*[8a,b]. As a result of these conditions the trimeric and pentameric macrocycles **1** and **2** were obtained in higher yields. Their separation by column chromatography proceeded quickly and yielded pure products without further purification.

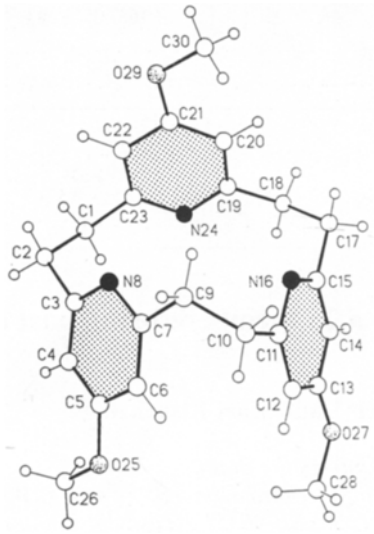


Figure 1. Crystal structure of trimeric pyridinophane **1**.

FAB mass spectra indicated oligomers with four to twelve 4-methoxy pyridine units (20–60 ring members).

X-ray structure analyses of 1 and of $2 \cdot (H_2O)_5 \cdot CHCl_3$

X-ray structure analysis of the pyridinophane **1** ("trimer") showed that the nitrogen atoms of the pyridine rings nearly project into the 15-membered ring, while the three pyridine rings do not form a plane. Figure 1 reveals that two methoxy pyridine rings are oriented in the same direction, with the third one in the opposite direction. The distances of the nitrogen atoms projecting inwards are: 408.4 pm (N8 · · · N16), 356.1 pm (N8 · · · N24) and 395.3 pm (N16 · · · N24) (Figure 1) (pm = picometre = 10^{-12} m).

X-ray structure analysis of the pyridinophane **2** ("pentamer") confirmed the inclusion of five water molecules and one trichloromethane molecule inside the cavity of the macrocycle. Four of the water molecules form hydrogen bridges with the nitrogen atoms of the pyridine rings directed inwards. In particular, the atom O4w forms hydrogen bridges with two nitrogen atoms (Figure 2): (N1A · · · O4w: 290.8 pm, N1B · · · O4w: 285.2 pm). The N–O distances of the other water molecules range from 284.3 pm (N1 · · · O1w) to 306.7 pm (N1D · · · O3w). The distance of N1A · · · N1D with a value of 856 pm is twice as long as the largest N–N distance in the 15-membered trimer **1**.

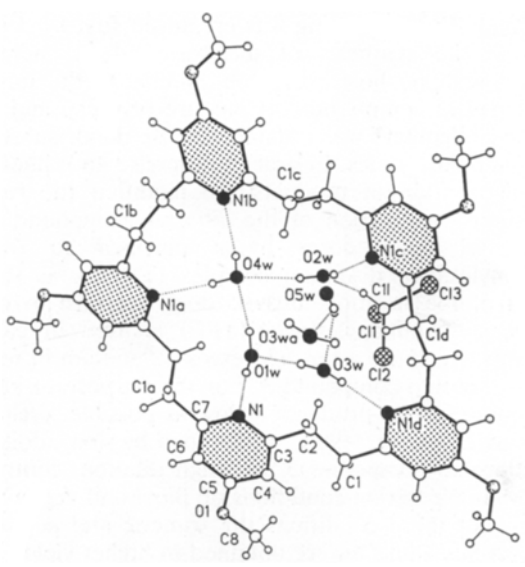


Figure 2. Crystal structure of pentameric pyridinophane $2 \cdot (H_2O)_5 \cdot CHCl_3$ *(O3wa generated by transformation: 1 − x, 1 − y, − z).*

Conclusions

The inclusion of water inside macrocyclic compounds containing pyridine moieties has attracted much attention since studies of the cyclodextrins[9], and some reports have been published[10]. Nevertheless, cluster-type inclusion of more than one water molecule inside the cavity of a synthetic macrocycle forming hydrogen bridges as shown here, seems quite rare[10b]. So far, the inclusion of water combined with trichloromethane forming a hydrogen bridge with one of the water molecules is an exceptional case. This type of donor-substituted pyridinophanes are also interesting for their host character towards neutral molecules (such as phenols); cations are also conceivable guests, in analogy to calixarenes or cyclodextrins[11]. Synthesis via *Müller–Röscheisen* reaction permits the design of tailored macrocycles containing substituted pyridine units and combining functional ether groups or longer alkyl chains with widely variable cavity size. Due to the chemical stability of the carbon ring members, methoxy cleavage[5b] and other refunctionalization are expected to be easy to realize. Macrocycles of this type form a basis for the design and construction of ligands and host compounds complementary to heteroaromatic calixarenes which are rare at present[12].

Experimental

Melting points were determined with a Kofler melting point apparatus and are uncorrected. ^{1}H-NMR spectra were recorded with a Bruker WH-90 (90 MHz), AC-200 (200 MHz) and WM-250 (250 MHz). ^{13}C-NMR spectra were recorded with a Bruker WH-400 (100.6 MHz) and WM-250 (62.90 MHz). FAB mass spectra were obtained with a Kratos Concept 1H and 3-nitrobenzyl alcohol as a matrix. IR spectra were recorded on a Infrared Spectrometer, Pye Unicam Ltd. Chromatography separations were performed on silica gel 60 (SiO_2, E. Merck, particle size: 0.040–0.063 mm); TLC was performed on $60F_{254}$ (SiO_2, E. Merck).

2,6-Bis(hydroxymethyl)-4-methoxypyridine[13]

$NaBH_4$ (33.40 g, 883 mmol) was added to an ice cooled suspension of 2,6-dimethyl-4-methoxypyridine-2,6-dicarboxylate[14] (40.00 g, 178 mmol) in dry MeOH (*ca.* 750 ml) in portions so that the temperature did not exceed 10°C. The mixture was then stirred at room temperature for 3 h and further heated at reflux overnight. The solvent was then evaporated *in vacuo* and the residue taken up in acetone (150 ml). After refluxing for 1 h and evaporating again, the residue was dissolved in a saturated solution of $NaHCO_3$ (150 ml) and heated at reflux. The mixture was concentrated and, after adding water (200 ml), it was neutralized with 2N hydrochloric acid. The aqueous phase was extracted continuously with $CHCl_3$ for $1\frac{1}{2}$ day. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Recrystallization from acetone gave the product as a light-coloured powder; 22.00 g (74%); m.p. 128°C. ^{1}H NMR (90 MHz, DMSO-d_6) δ: 3.80; s, 3H, CH_3; 4.50, d, 4H, CH_2O; 5.36, t, 2H, OH; 6.85, s, 2H, Ar-H.

2,6-Bis(bromomethyl)-4-methoxypyridine (**3**)[6]

A solution of PBr_3 (15.00 g, 88.7 mmol) in dry $CHCl_3$ (550 ml) was added dropwise to a stirred suspension of 2,6-bis(hydroxymethyl)-4-methoxypyridine[13] in dry $CHCl_3$ at room temperature. The resulting mixture was heated at reflux for 2 h. The mixture was then allowed to cool to room temperature and neutralized with saturated $NaHCO_3$ solution to pH 6. The resultant two layers were refluxed for 1 h and then separated. The aqueous layer was extracted twice with $CHCl_3$. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated *in vacuo*. Recrystallization from MeOH gave the

Table I Crystal data of macrocycles **1** *and* **2**.

	1	**2**
Crystal data		
Empirical formula	$C_{24}H_{27}N_3O_3$	$C_{40}H_{45}N_5O_5 \cdot (H_2O)_5 \cdot CHCl_3$
Formula weight	405.5	885.3
Crystal colour	colourless	colourless
Crystal size [mm]	$0.2 \times 0.18 \times 0.23$	$0.3 \times 0.4 \times 0.5$
Crystal system	orthorhombic	triclinic
Space group	$Pca2_1$ (no. 29)	$P\bar{1}$ (no. 2)
a (pm)	2854.4(2)	1064.8(6)
b (pm)	815.8(1)	1274.5(1)
c (pm)	915.7(1)	1751.5(3)
α (°)	90	74.26(1)
β (°)	90	83.87(4)
τ (°)	90	75.26(2)
V (nm^3)	2.1324(4)	2.211(1)
Z	4	2
D_c (g/cm)	1.263	1.330
μ (mm^{-1})	0.640 (Cu-K_α)	0.265 (Mo-K_α)
$F(000)$	864	936
Solution and refinement		
Parameter	271	562
Coll. Reflections	5175	8053
Indep. reflections	2733	7776
Obs. reflections	2177 [$I > 3\sigma(I)$]	6033 [$\|F\| > 3\sigma(F)$]
R	0.040	0.043
R_w	0.047	0.043
Weighting scheme	$w = w' \cdot [1.0 - [(\Delta F/6) \cdot \sigma F]^2$	$w^{-1} = \sigma^2(F) + 0.0005F^2$
Largest difference peak (max.) ($e \cdot Å^{-3}$)	0.20	0.34
Data collection		
Scan type	$\omega/2\theta$	ω
Scan range	$0.75° + 0.15 \tan\theta$	$0.90° + 0.35 \tan\theta$
Temperature (K)	296	193
Index ranges	$2\theta_{max} = 150°$ $-1 \le h \le 35$ $-1 \le k \le 10$ $-10 \le l \le 10$	$2\theta_{max} = 50°$ $-12 \le h \le 12$ $-14 \le k \le 15$ $0 \le l \le 20$

[a] w′ = Chebychev polynomial for Fc with three coefficients (3.08, 2.81 and 1.70).

product as colourless crystals; 24.00 g (91%); m.p. 99°C. ^{1}H NMR (90 MHz, $CDCl_3$) δ: 3.88, s, 3H, OCH_3; 4.50, s, 4H, CH_2Br; 6.89, s, 2H, Ar-H.

[2$_n$](2,6)Pyridinophanes

Under inert conditions (argon atmosphere), tetraphenylethene (TPE) (3.00 g, 9 mmol) was dissolved in dry THF (500 ml). Powdered sodium (9.50 g, 407 mmol)[1] was suspended in dry THF (500 ml) and added at once. While stirring vigorously, the mixture became deep red. It was stirred additional 2 h at −90°C. **3** (12.00 g, 41 mmol) dissolved in dry THF (250 ml) was added dropwise by a perfusor over 12 days at −90°C as fast as the red colour is present. Afterwards, the mixture was treated with MeOH (1 ml), whereby the colour turned from red to yellow. The excess of sodium was filtered off. For safety, the mixture was treated with MeOH once again to be sure that there was no sodium in the mixture before evaporating the solvent and taking up the residue with $CHCl_3$. The resultant mixture was refluxed for 1 h and inorganic solids were filtered off. Removing the solvent gave a mixture of products as a yellow oil, which was further separated by column chromatography[15] (SiO_2, CH_2Cl_2/MeOH/concd.-NH_3 100:5:1). After eluting an open-chained dimeric pyridino compound (R_f 0.7, in eluent), the evaporation of the second eluate gave pure **1** (R_f 0.3, in eluent). The cyclic pentameric compound **2** (R_f 0.8, in eluent) was eluted with (SiO_2, CH_2Cl_2/MeOH/concd.-NH_3 100:10:1).

5,13,21-Trimethoxy[2$_3$](2,6)pyridinophane (**1**). 640 mg (12%) as colourless crystals; m.p. 171°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.94, s, 12H, CH_2; 3.73, s, 9H, OCH_3; 6.35, s, 6H, Ar-H. ^{13}C NMR (100.61 MHz, $CDCl_3$) δ: 165.78, C; 161.17, C; 106.24,CH; 54.85, CH_3; 37.91, CH_2. IR (KBr): $\bar{\nu}$ 2980 m, 2855 m, 1610 vs, 1590 s, 1375 m, 1310 m, 1210 m, 1185 s, 1060 s, 920 w, 855 w, 845 w. Ms (FAB), m/z (%, fragment): 406.2, 100, $M^+ + H$.

Table II Atomic coordinates (Å^2) of **1** *and equivalent isotropic displacement coefficients. Equivalent isotropic U defined as one third of trace of orthogonalized U_{ij} tensor.*

Atom	x	y	z	U(eq)
C(1)	0.50078(8)	0.3341(3)	0.0485(3)	0.0449
C(2)	0.52280(7)	0.3406(3)	−0.1050(3)	0.0427
C(3)	0.57266(7)	0.4018(2)	−0.1021(2)	0.0363
C(4)	0.58236(7)	0.5639(2)	−0.1383(2)	0.0403
C(5)	0.62830(8)	0.6152(2)	−0.1301(3)	0.0420
C(6)	0.66290(7)	0.5051(3)	−0.0857(3)	0.0429
C(7)	0.64984(7)	0.3462(2)	−0.0500(2)	0.0369
N(8)	0.60541(6)	0.2935(2)	−0.0595(2)	0.0378
C(9)	0.68493(8)	0.2193(3)	0.0013(3)	0.0437
C(10)	0.72420(7)	0.2861(3)	0.0974(3)	0.0450
C(11)	0.70595(6)	0.3699(2)	0.2327(2)	0.0380
C(12)	0.71574(7)	0.5348(3)	0.2597(3)	0.0439
C(13)	0.69657(8)	0.6065(2)	0.3831(3)	0.0449
C(14)	0.66924(8)	0.5115(3)	0.4773(3)	0.0450
C(15)	0.66197(7)	0.3475(2)	0.4425(2)	0.0366
N(16)	0.68005(5)	0.2772(2)	0.3225(2)	0.0384
C(17)	0.63332(8)	0.2391(3)	0.5413(2)	0.0420
C(18)	0.58047(8)	0.2487(3)	0.5101(3)	0.0430
C(19)	0.56497(6)	0.1777(2)	0.3654(2)	0.0368
C(20)	0.57360(7)	0.0134(2)	0.3324(2)	0.0384
C(21)	0.55487(7)	−0.0502(2)	0.2045(2)	0.0368
C(22)	0.52867(7)	0.0512(2)	0.1143(2)	0.0389
C(23)	0.52456(7)	0.2155(2)	0.1515(3)	0.0373
N(24)	0.54141(6)	0.2788(2)	0.2763(2)	0.0381
O(25)	0.64374(7)	0.7696(2)	−0.1617(3)	0.0579
C(26)	0.6097(1)	0.8881(3)	−0.2025(4)	0.0636
O(27)	0.70244(8)	0.7659(2)	0.4241(3)	0.0667
C(28)	0.7278(1)	0.8708(3)	0.3261(6)	0.0779
O(29)	0.55979(5)	−0.2075(2)	0.1578(2)	0.0451
C(30)	0.59314(9)	−0.3089(3)	0.2322(3)	0.0493

5,13,21,29,37-Pentamethoxy[2$_5$](2,6)pyridinophane (**2**). 100 mg (2%) as colourless crystals; m.p. 202°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.05, s, 20H, CH_2; 3.79, s, 15H, OCH_3; 6.53, s, 10H, Ar-H. ^{13}C NMR (62.90 MHz, $CDCl_3$) δ: 166.0, C; 161.77, C; 106.04, CH; 54.76, CH_3; 37.72, CH_2. IR(KBr): $\tilde{\nu}$ 2980 m, 2900 m, 1605 vs, 1595 s, 1365 m, 1315 m, 1210 s, 1185 s, 945 w, 870 w. Ms (FAB), m/z (%, fragment): 676.3, 100, $M^+ + H$.

X-ray structure analysis of **1**

A single crystal of **1** suitable for the crystallography study was obtained by vapour diffusion from petroleum ether (40/60) in a solution of dichloromethane. Data were collected on a CAD4 diffractometer (Enraf Nonius) equipped with Cu-$K\alpha$ radiation (λ 154.18 pm) and a graphite monochromator. The structure was solved by direct methods and subjected to full-matrix anisotropic refinement. Structure solution and refinement were carried out with the programs SHELXS-86[16] and CRYSTALS[17]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated to their idealised positions (C–H distance 100 pm) and included in the final structure factor calculations with fixed isotropic temperature factors (U 0.9·U_{carbon}), but were not refined. The program DIFABS[18] was used for empirical absorption correction.

Table III Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($Å^2 \cdot 10^4$) of **2**. *Equivalent isotropic U defined as one third of trace of orthogonalized U_{ij} tensor.*

Atom	x	y	z	U(eq)
C(1)	−1052(2)	5043(2)	883(1)	288(8)
C(2)	−8(2)	4133(2)	1338(1)	305(8)
C(3)	−240(2)	2965(2)	1545(1)	237(8)
C(4)	−1409(2)	2744(2)	1440(1)	252(8)
C(5)	−1507(2)	1638(2)	1644(1)	294(8)
C(6)	−436(2)	799(2)	1941(1)	334(9)
C(7)	690(2)	1086(2)	2031(1)	276(8)
N(1)	793(2)	2159(1)	1837(1)	261(7)
O(1)	−2581(2)	1296(1)	1576(1)	450(7)
C(8)	−3750(2)	2119(2)	1344(2)	450(11)
C(1A)	1867(2)	229(2)	2381(1)	305(8)
C(2A)	2024(2)	255(2)	3229(1)	307(8)
C(3A)	3255(2)	−526(2)	3570(1)	256(8)
C(4A)	3302(2)	−1658(2)	3897(1)	254(8)
C(5A)	4455(2)	−2357(2)	4191(1)	246(8)
C(6A)	5538(2)	−1910(2)	4135(1)	282(8)
C(7A)	5418(2)	−780(2)	3793(1)	258(8)
N(1A)	4286(2)	−84(1)	3519(1)	267(7)
O(1A)	4627(2)	−3469(1)	4532(1)	309(6)
C(8A)	3510(2)	−3932(2)	4600(1)	319(9)
C(1B)	6535(2)	−229(2)	3715(1)	304(8)
C(2B)	6477(2)	381(2)	4369(1)	290(8)
C(3B)	7236(2)	1275(2)	4124(1)	242(8)
C(4B)	8453(2)	1111(2)	4394(1)	256(8)
C(5B)	9109(2)	1967(2)	4135(1)	245(8)
C(6B)	8520(2)	2952(2)	3610(1)	281(8)
C(7B)	7288(2)	3050(2)	3361(1)	265(8)
N(1B)	6648(2)	2237(1)	3614(1)	264(7)
O(1B)	10296(2)	1757(1)	4439(1)	333(6)
C(8B)	11001(2)	2621(2)	4174(2)	418(10)
C(1C)	6595(2)	4122(2)	2815(1)	322(9)
C(2C)	5739(2)	4931(2)	3261(1)	277(8)
C(3C)	5092(2)	6013(2)	2701(1)	232(8)
C(4C)	5745(2)	6872(2)	2435(1)	256(8)
C(5C)	5158(2)	7836(2)	1894(1)	267(8)
C(6C)	3948(2)	7912(2)	1629(1)	275(8)
C(7C)	3349(2)	7036(2)	1929(1)	247(8)
N(1C)	3912(2)	6088(1)	2465(1)	252(7)
O(1C)	5676(2)	8741(1)	1594(1)	372(6)
C(8C)	6908(2)	8701(2)	1862(2)	385(10)
C(1D)	2015(2)	7089(2)	1691(1)	297(8)
C(2D)	1780(2)	7556(2)	805(1)	328(9)
C(3D)	490(2)	7426(2)	606(1)	277(8)
C(4D)	−464(2)	8332(2)	260(1)	301(8)
C(5D)	−1643(2)	8164(2)	105(1)	271(8)
C(6D)	−1830(2)	7088(2)	319(1)	272(8)
C(7D)	−815(2)	6212(2)	660(1)	246(8)
N(1D)	337(2)	6354(1)	795(1)	271(7)
O(1D)	−2545(2)	9086(1)	−238(1)	369(6)
C(8D)	−3755(2)	8904(2)	−407(2)	366(9)
C(1L)	−203(2)	5981(2)	3708(1)	361(9)
Cl(1)	−1411(1)	5606(1)	4430(1)	456(3)
Cl(2)	−644(1)	6003(1)	2770(1)	500(3)
Cl(3)	20(1)	7296(1)	3724(1)	587(3)
O(1W)	3171(2)	2830(2)	1727(1)	430(7)
O(2W)	2510(2)	4499(2)	3454(1)	476(8)
O(3W)	3101(2)	4892(2)	737(1)	438(7)
O(4W)	4070(2)	2306(1)	3265(1)	398(7)
O(5W)	5767(2)	5226(3)	809(1)	782(12)

X-ray structure analysis of **2**·$(H_2O)_5$·$CHCl_3$

Vapour diffusion from petroleum ether (40/60) in a solution of dichloromethane gave a single crystal of **2** suitable for the crystallography study. X-ray analysis was performed on a CAD4 diffractometer (Enraf Nonius) equipped with Mo-$K\alpha$ radiation (ω scans, λ 71.103 pm) and a graphite monochromator. The structure was solved by direct methods; structure solution and refinement were carried out with the program system SHELXTL-plus[19]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized by difference electron density determination and refined using "riding model". Hydrogen atoms of the water molecules were refined with r_{OH} 85(1) pm. Crystal data and atomic coordinates are listed in tables I–III.

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