Tetrahedron Vol. 42, No. 6, pp. 1859 to 1872, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
© 1986 Pergamon Press Ltd.

Large Oligocyclic Cavities for Strong Cation Complexation

W.KIGGEN[a], F.VÖGTLE[a*], S.FRANKEN, H.PUFF

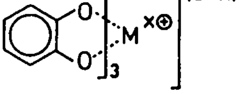
[a]Institut für Organische Chemie und Biochemie
und
Anorganisch-Chemisches Institut
Universität Bonn, Gerhard-Domagk-Straße 1, D-5300 Bonn 1, FRG

(*Received in USA* 1 *May* 1985)

Abstract. The syntheses of oligocyclic large cavities containing two or three catechol subunits are described. The X-ray analysis of a heptacyclic molecule composed of three triply clamped dimethyl catechol ether units demonstrates the size and shape of the cavity formed by this skeleton. Properties of the Fe^{3+}- and Ga^{3+}-complexes are elucidated by ^1H-NMR, IR, UV/Vis spectra, and by competition experiments with an open-chained reference ligand.

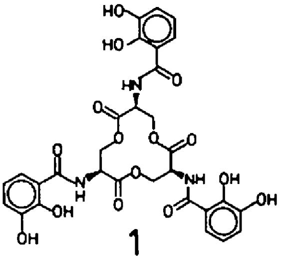
1. INTRODUCTION

The oxygen atoms of the catechol anion, which are of hard basic nature according to the HSAB principle, are good ligand donors for the complexation of main group-, side group and "inner" side group metals as e.g. Al, Fe, U.[1] In addition to this, with non-metals and semimetals as e.g. P,[2] and Si[3] bonds are also formed. In the course of complexation the remarkably stable five-membered chelate ring is formed.[4] In general, the ideal for distorted octahedral donor geometry is observed.[5]



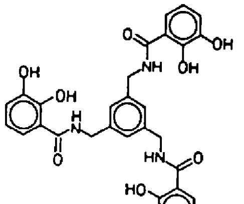
Three catechol units are arranged around the central atom leading to a helical-chiral structure.[6]

In nature, hexadentate ligand molecules containing substituted catechol units are encountered. In 1970, Neilands [7] and Gibson [8] were able to isolate enterobactin 1 from Salmonella typhimurium and Aerobacter aerogenes. This compound belongs to the siderophores (Greek: σιδερος = iron, φορεας = carrier) which supply microorganisms with iron,[9] and play a role in the regulation of their growth.



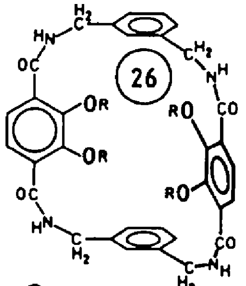
1

Enterobactin binds Fe^{3+} very strongly and shows a complex constant of approx. 10^{52}.[10] It has been synthesized by Corey,[11], Rastetter [12] and Shanzer.[13] For applications of enterobactin the lack of stability is disadvantageous: the triester ring is prone to hydrolysis and the catechol units are sensitive to oxidation.[14] To circumvent this lack of stability, analogous compounds, such as MECAM (2), have been synthesized by Raymond,[15] Rastetter [16] and Venuti.[17]

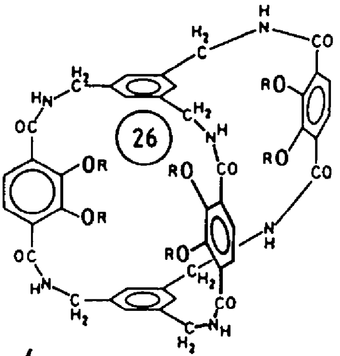


2

Despite the synthetic approaches to siderophores and siderophore analogues, no ligands have been described as yet which are hindered in their conformational flexibility and in which the donor geometry necessary for complexation is partially or completely preformed as e.g. in the porphyrins. The synthesis and the properties of such ligands with hindered conformational flexibility are the subject of this paper.[18] For the first time, to reach this aim, 2,3-dihydroxy terephthalic acid has been built into macrocyclic ring compounds as a building unit to the cyclic ligands 3 and 4.



3 R:CH$_3$



4 a: R:CH$_3$ b: R:H

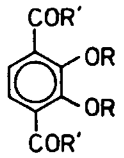
(26) means 26-membered ring.

Whereas catechol in alkaline solution is extremely air sensitive, 2,3-dihydroxy terephthalic acid is much more stable against oxidation. The fact that air can be bubbled through the alkaline solution of the latter compound for hours without appreciable oxidation, stimulated us to use this structure as a building block in macrocyclic ligand rings.

2. SYNTHESES

2.1. Synthesis of the monomacrocyclic catechol ligand 3

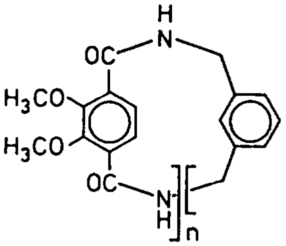
Twofold Kolbe-Schmidt reaction starting with catechol gives the 2,3-dihydroxy terephthalic acid 5a.[19] Complete methylation with dimethylsulfate leads to 5b; the ester is split with KOH yielding 5c and converted with thionyl chloride to 2,3-dimethoxy terephthaloyl dichloride 5d.[20]

5


	R'	R
a	OH	H
b	OCH_3	CH_3
c	OH	CH_3
d	Cl	CH_3

5d is reacted with 1,3-xylylene diamine in a high dilution reaction [21] to yield 3. The reaction conditions have been varied with the results shown in Table 1.

The product obtained was purified by column chromatography on silica gel using chloroform/ethanol as the eluent. Osmometric molecular weight determination of the cyclization product gave a molecular mass of 710 (≙ +9% dev.), which hints at 3. The monocycle 3 forms colourless crystals (powder) and is only sparingly soluble in chloroform. The smaller and the larger monocycles 6a,b have not been detected as yet.

6


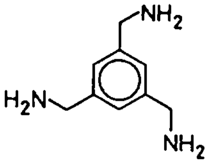
a: n = 1
b: n = 3

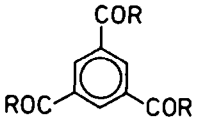
Table 1. Conditions for the synthesis of 3 and yields obtained (DMF = N,N-dimethylformamide, DMA = N,N-dimethylacetamide)

Assistant amine (for removal of HCl)	Solvent	Temp. [°C]	Yield [%]
NEt_3	DMF	ca.25	4.6
m-xylylene-diamine	DMA	ca.25	6.4
m-xylylene-diamine	benzene	ca.25	7.4
m-xylylene-diamine	benzene	80	9.0

2.2. Synthesis of the macrobicyclic ligand 4a

The synthesis of the oligocycle 4a was achieved in different ways, both starting with the amine 7.


7


8

a: R = Cl
b: R = NH_2

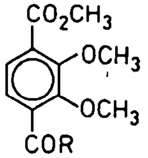
Starting with the 1,3,5-benzene tricarboxylic acid trichloride 8a [22] via the triamide 8b [15] the triamine 7 is obtained by reduction with diborane. Attempts at the reduction of 8b with $LiAlH_4$ were unsuccessful. The amine 7 is a colourless solid which is air sensitive.

2.2.1. Short synthesis of 4a

A quick synthesis of 4a starts with the cyclization under high dilution conditions of the components 5d and 7 in boiling benzene. 4a is obtained in only 1.5% yield.

2.2. Step-by-step synthesis of 4a

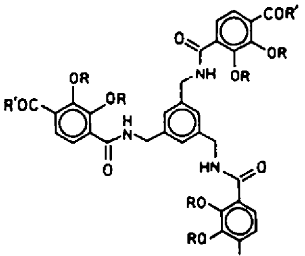
A step-by-step synthesis of 4a leads to significant higher yields. The procedure describing the synthesis of 9a by saponification of 5b [19a] has been improved in the course of our work and is described in detail in the experimental section. With thionyl chloride 9b is obtained and has been characterized.

9


a: R = ONa
b: R = Cl

Reaction of 7 with 9b gives 10a in quantitative yield.

10a can be hydrolized quantitatively using NaOH to yield 10b, which can be converted to 10c using thionyl chloride. Under high dilution conditions 10c is reacted with 7 in boiling benzene and gives rise to 4a in 13% yield. The reaction conditions have been varied as shown in Table 2.



10

a : R = CH_3, R' = CH_3O
b : R = CH_3, R' = NaO
c : R = CH_3, R' = Cl
d : R = H, R' = HO

Table 2. Varied conditions for the synthesis of 4a

Assistant amine (for removal of HCl)	Solvent	Temp. [°C]	Yield [%]
NEt_3	DMA	ca. 25	0
7	DMA	ca. 25	0
7	toluene	112	low, impure
7	benzene	25	8
7	benzene	80	13

Compound 4a was purified by chromatography on silica gel with chloroform/ethanol as the eluent. The solubility of 4a in chloroform at room temperature (50 mg in 0.6 ml) is significantly higher than the solubility in dichloromethane (50 mg in 3.5 ml). In 1,1,1-trichloroethane, acetone and CS_2 4a is only sparingly soluble.

3 and 4a chromatographically behave rather similarly. Demethylation with excess BBr_3 provided the free ligands 4b and 10d.

2.3. Syntheses of Fe^{3+}-complexes of 4b and 10d and of the Ga^{3+}-complex of 4b

10d as well as 4b are easily soluble in diluted NaOH. Alkaline solutions of 10d are stable for several days, and, in frozen form, can be stored for weeks. A solution of 4b is stable for many hours. Both solutions can be handled in air without precautions like protecting gas.

Addition of Fe^{3+} salts to these solutions at pH= 11 yields the red-brown Fe-complex of 10d and the red-violet Fe-complex of 4b. If these iron complex solutions are acidified, the negatively charged complexes are protonated, and they precipitate as electrically neutral complexes in the form of blue-black solids. The three-fold protonated Fe-complex of 4b has been determined through FAB mass spectrometry from a diethanolamine matrix. The colourless Ga-complex of 4b is obtained analogously to the Fe-complex.

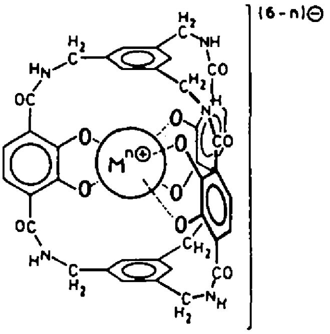


Fig. 1. Octahedral metal complex of 4b M= Fe^{3+}, Ga^{3+})

3. ^{1}H-NMR-STUDY OF THE COMPOUNDS 3, 4a, AND 10a

The strong highfield shift of the OCH_3 groups in 4a compared to 10a is striking. In 3 this highfield shift is still present, but less pronounced. The NH protons in 4a also seem to be shielded. The rotation around the para-phenylene axis apparently is only slightly hindered in 4a so that the OCH_3 groups gain access to the anisotropic region of the 1,3,5-substituted benzene rings.

Table 3 lists the chemical shifts of the ^{1}H-NMR signals of 3, 4a, and 10a.

Table 4 demonstrates that at low temperature the highfield shift of the OCH_3 groups in 4a is still marked, but all signals are broadened and the couplings are no longer resolved.

Table 3. ^{1}H-NMR chemical shifts of 3, 4a, and 10a (at room temperature, $CDCl_3/TMS_{int.}$)

No.	δ OCH_3 s	δ CH_2, d (^3J [Hz])	δ Ar-H (amine)	δ Ar-H (acid)	δ NH, t (^3J[Hz])
3	3.48	4.69 (6.2)	7.2-7.4	7.96	8.47 (6.2)
4a	2.82	4.55 (6)	7.41	7.90	7.93 (6)
10a	3.89	4.67 (6)	7.30	7.55, 7.88 (AB)	8.32 (6)

Table 4. ^{1}H-NMR chemical shifts of 4a at different temperatures, $CD_2Cl_2/TMS_{int.}$

Temp. °C	s (OCH_3)	d (CH_2)	s (Ar-H, amine)	s (Ar-H, acid)	t (NH)
+27	2.90	4.53	7.41	7.83	7.88
-81	3.16	4.56	7.45	7.82	8.10
-109	3.37	4.58	7.44	7.79	8.17

Examination of molecular models shows that not all of the six methoxy groups of 4a can be accomodated simultaneously in the interior of the molecular cavity. This provides an explanation as to why 4a, unlike other ligands (e.g. spherands) is not able to transfer inorganic salts into lipophilic phases. In the ^{1}H-NMR spectra significant interactions of the ligand 4a with various ions have not been observed: addition of $LiClO_4$, $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$, $Ca(SCN)_2$, $SrCl_2$, $Ba(SCN)_2$, NH_4SCN, $Ga_3(SO)_4)_3$ to a solution of 4a in $CDCl_3$ did not shift the signals of the ligand. The shifts of the proton signals of 4a in different solvents are listed in Table 5.

Table 5. ^{1}H-NMR chemical shifts of 4a in various solvents (at room temperature, TMS as internal standard)

Solvent	s (OCH_3)	d (CH_2) (^3J[Hz])	s (Ar-H, amine)	s (Ar-H, acid)	t (NH) (^3J[Hz])
$CDCl_3$	2.82	4.55 (6)	7.41	7.90	7.93 (6)
CD_2Cl_2	2.90	4.53 (6)	7.41	7.83	7.88 (6)
C_2D_6SO	3.04	4.40 (4)	7.35	7.41	8.08 (4)
CF_3CO_2H	3.24	4.80 (6)	7.70	7.80	8.80 (6)

Obviously, because of different interactions between the ligand 4a and the various solvents, the shielding of the OCH_3 groups is varying from solvent to solvent. Strong deshielding of +0.92 ppm is exerted on the NH protons on switching from $CDCl_3$ to CF_3CO_2H. In DMSO the small coupling constant ^3J N$\underline{H}$-C$\underline{H}$ attracts attention.

4. X-RAY STRUCTURAL ANALYSIS OF 4a

Small flat needles of 4a could be obtained by crystallization from a mixture of chlorobenzene and N,N-dimethylacetamide. As the elemental analysis and the X-ray structural investigation discussed in the following show, the crystal lattice of 4a selectively takes up chlorobenzene in between the molecules. This means that a clathrate is present.[23]

Crystal data: $C_{48}H_{48}N_6O_{12} \cdot \frac{1}{2} C_6H_4Cl_2$, M= 974.5, crystal dimensions 0.45 · 0.3 · 0.2 mm, triclinic, space group $P\bar{1}$, a= 1142.7(6), b= 1314.3(1), c= 1712.3(3) pm, α= 81.43(1), β= 85.09(3), γ= 68.09(3)°, V= 2.358 nm^3, Z= 2, d= 1.37 g cm^{-3}, μ= 1.12 cm^{-1}. Final R= 0.095 for 4697 unique reflexions [$\Theta < 25°$, $F > 3\sigma(F)$], using unit weights. The intensity data were measured at 293 K on a four-circle diffractometer CAD4 (Enraf-Nonius) using Mo-K_α-radiation and graphite monochromator. The structure was solved by Direct Methods (MITHRIL).[24]

Most of the H atoms of the benzenophane molecule could be localized in a difference fourier map. The asymmetric unit contains one half of the chlorobenzene molecule, the other half is generated by the inversion centre, giving a second chlorine atom. Obviously, two orientations of the solvent molecule are possible. Large temperature factors and differences of the bond angles and distances from expected values suggest a disorder of the solvent.- Figure 2 shows the elementary cell of the crystal.

The refinement was carried out by blocked matrix least squares methods (640 parameters, SHELX 76).[25] Anisotropic temperature factors for all C, O, N atoms of the benzenophane molecule and isotropic temperature factors for the nitrogen bound H atoms and for the chlorobenzene atoms were applied. H atoms of the methylene groups were included with constraints (C-H 108 pm) and common temperature factors for each block.

Figure 3 shows a single molecule of 4a, as is present in the crystal lattice. The rotational ellipsoids, which show the vibrations of the oxygen atoms, are rather large. Both 1,3,5-substituted benzene rings are plane (maximum distance

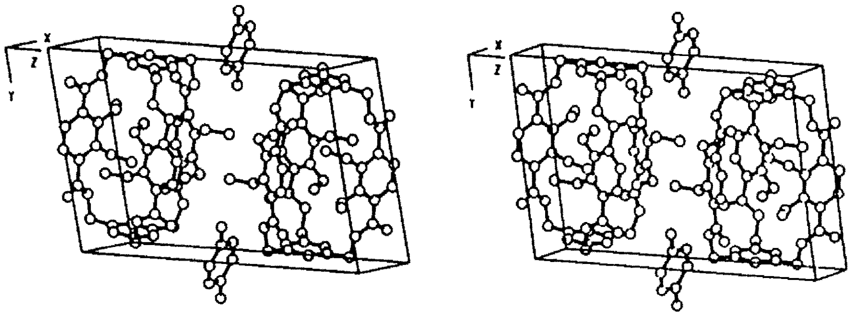


Fig.2. Stereoscopic view of the elementary cell of the clathrate of 4a with chlorobenzene (disordered)

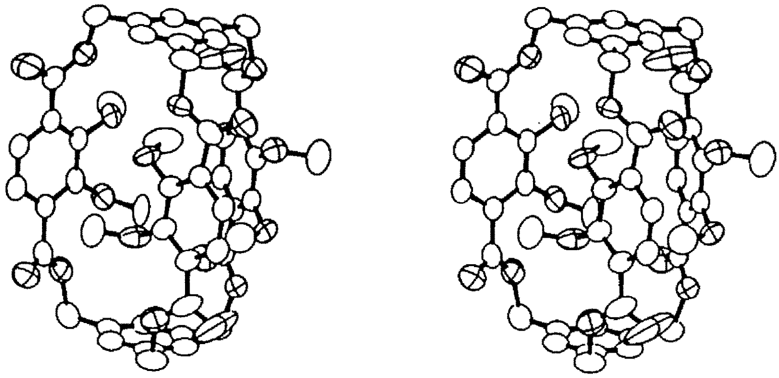


Fig.3. Stereoscopic view of 4a (the rotational ellipsoids correspond to a propability of 50%)

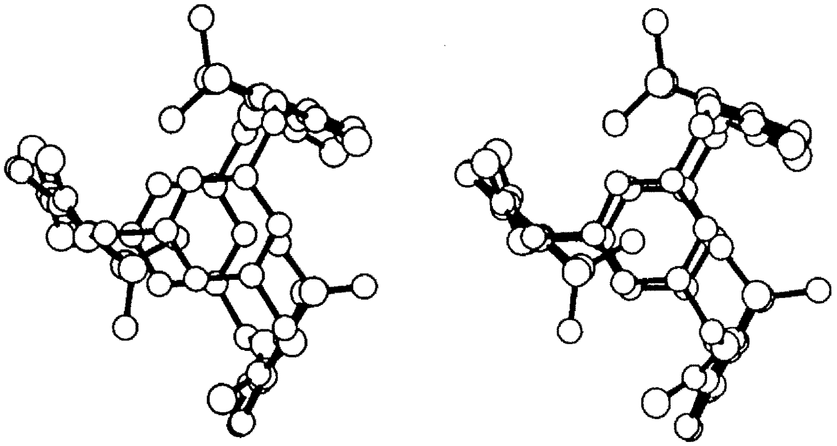


Fig.4. Stereo view of 4a (top plane view)

from the least squares plane 0.6 pm), and they lie in parallel planes (angle between the planes 0.2°) - their distance is 1030 pm.

Figure 4 gives the top plane view of the molecule. It can be seen that the three approx. planar para-phenylene groups (maximum distance from the least squares plane 2.9 pm) are arranged around a rotational axis, but this axis is not a symmetry element of the molecule. Consequently, the molecule belongs to the point group C1.

To fill up the space formed by the cavity of the molecular skeleton, one of the OCH_3 groups is projecting into this cavity. This is in agreement, on one hand, with Stuart Briegleb space filling models, and, on the other hand, with the ^1H-NMR highfield shifts of the OCH_3 protons in solution. The carbonyl groups are situated only a little outside the plane of the para-phenylene rings. Figure 5 gives an impression of the space filling of the ligand molecule 4a.

DMSO as the solvent. For an NMR study of the complexes the paramagnetic Fe^{3+} ion is not suitable, as it leads to signal broadenings. Diamagnetic Ga^{3+} salts however are well suitable. Because of the same charge of these ions and the nearly identical ion radii, [26] the complex constants of these complexes can be taken as similar.[27]

Table 6 compares the chemical shifts of the free ligand 4b and of the Ga complex in DMSO as the solvent. The coupling ^3J N<u>H</u>-C<u>H</u> unfortunately is not resolved.

Table 6. ^1H-NMR shifts of the ligand 4b and of its Ga^{3+} complex in DMSO-d_6 at room temperature ($TMS_{int.}$)

	$Ar-CH_2$	Ar-H (amine)	Ar-H (acid)	N-H
4b	4.35	6.92	7.31	8.63
Ga complex of 4b	4.26	6.69	7.24	10.50

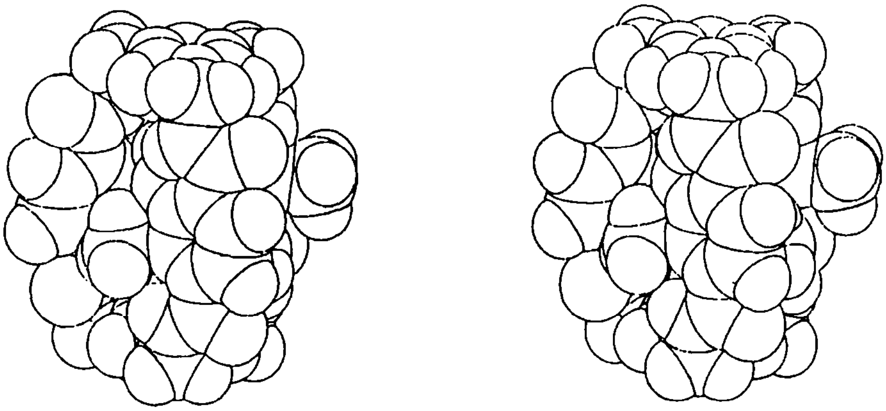


Fig.5. Space filling model of 4a (stereo view; from X-ray structural data)

5. ^1H-NMR INVESTIGATION OF THE FREE LIGAND 4b AND ITS Ga COMPLEX

The ^1H-NMR spectra of the ligands 10d and 4b can be measured in D_2O/NaOD solution. The chemical shifts of the ligands are strongly pD dependent. The amide H atoms rapidly exchange against D atoms. The spectra have also been measured using

The lowfield shift of the NH signal (Δδ= +1.87 ppm) in the course of the complex formation is especially striking. A similar deshielding (Δδ= +2.66 ppm) has also been observed by Llinas with regard to the Ga complex of enterobactin [27b] and by Bergeron regarding the Ga complex of parabactin.[28] This seems to be due to a change of the electron density at the nitrogen, which diminishes the amine carbonyl resonance, responsible for the usually planar amide bond.[27b]

A rectangular arrangement of the amide bonds has been proposed according to LCAO-MO calculations of Yan at the positively polarized nitrogen.[29] Space filling molecular models of the Ga complex also favour a dihedral angle of approx. 90°.

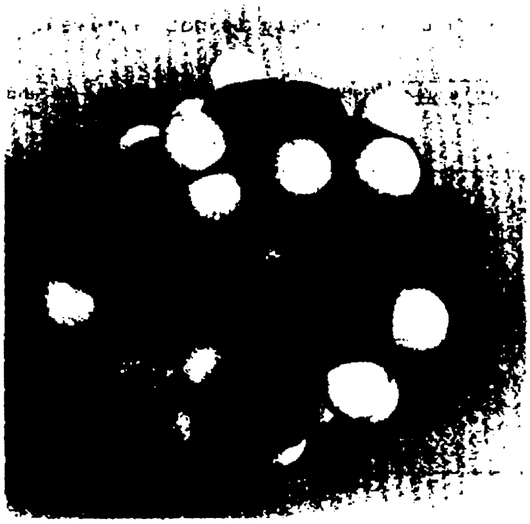


Fig.6. Space filling model (Stuart Briegleb) of the Ga^{3+} complex of 4b.[30] Shown here is the Δ configuration.

In the anion of the complex the negative charge can be stabilized by delocalization. This leads to a loss in aromaticity of the terephthalic acid rings, which is expressed as highfield shifts of the aromatic protons. Because of the same signal intensity of both singlets of the aromatic protons the value of the shift cannot be exactly determined. Most probably the signal at 7.31 ppm is shifted (Δδ= -0.62 ppm) to 6.69 ppm. Shifts of this order of magnitude have also been found in enterobactin. A deshielding of the 1,3,5-substituted benzene ring from 6.92 ppm (Δδ= +0.32 ppm) to 7.24 ppm seems to be plausible.

6. INFRARED SPECTRA OF 4b AND OF ITS Fe^{3+} COMPLEX

The IR spectra have been measured in solid phase (KBr pellet). The mostly broader absorption bands of the protonated Fe complex of 4b are in striking contrast to the absorptions of the free ligand.

The band at 1670 cm^{-1} in 4b is missing in the Fe complex. Whereas the band at 1615 cm^{-1} (CO valence vibration, amide band I) is well resolved in 4b, in the complex only a less resolved absorption is observed. In addition to that, the band at 1550 cm^{-1} (NH deformation, amide band II) is well resolved in 4b, but in the Fe complex a broad band at 1575 cm^{-1} is found. In the course of the complexation the amide bonds therefore are significantly altered. The OH deformation vibrations of the phenolic groups are well marked in 4b at 1330 cm^{-1}. In the Fe complex this band is shifted to 1335 cm^{-1} and somewhat weaker, but easily detectable.

7. UV/VIS SPECTROSCOPIC INVESTIGATION of 4b AND 10d

Figure 8 shows the spectra of the colourless compounds 4b amd 10d as well as the characteristic redviolet and redbrown Fe^{3+} complexes of 4b and 10d.

The octahedral $3d^5$ complexes of the type $[Fe^{3+}O_6]$ have a high spin ground state $^6A1g(t2g)^3(eg)^2$. d-d optical transitions are spin-forbidden.[31] Therefore, the characteristic spectral property is the broad absorption band of relatively weak extinction in the visible area of the spectrum (4b: λ_{max}= 544 nm, ε= 4400; 10d: λ_{max}= 508 nm, ε= 4660) due to the charge transfer transition. In addition to that in 4b the maximum of the broad band at 382 nm is shifted in the course of the complexation with Fe^{3+} (Δλ= -14 nm) to 368 nm. In 10d this hypsochromic shift from 364 to 360 nm is less pronounced. Controlling the titration of the solutions of 4b and 10d with the $FeCl_3$ solution spectroscopically at constant pH (11), a 1:1 stoichiometry for ligand:metal becomes obvious.

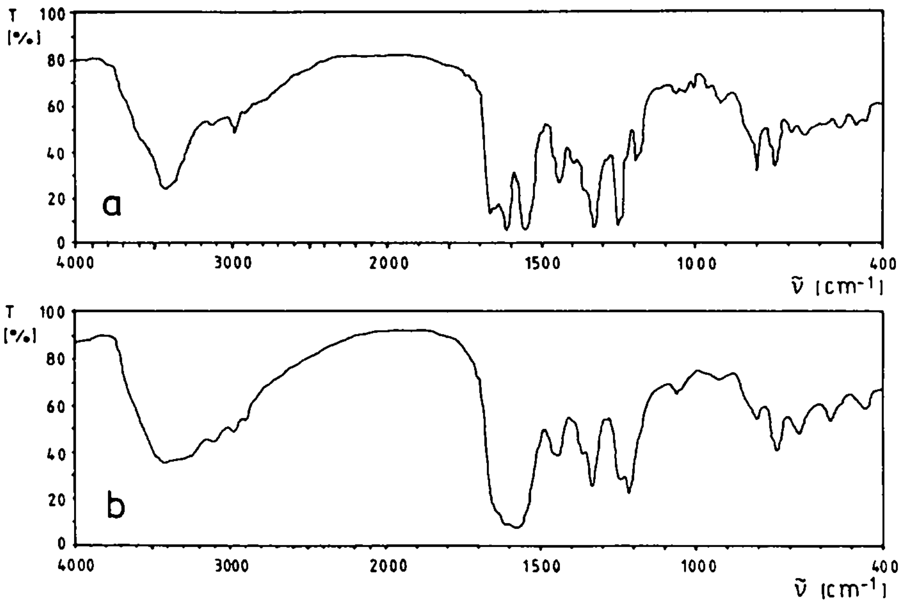


Fig.7. IR spectra of KBr pellets of 4b (a) and of the protonated Fe^{3+} complex of 4b (b)

A comparison of the pH dependence of the visible spectra of the iron complexes of 4b and 10d reveals strong differences. The redbrown ferric ion complex of 10d on acidification changes its colour to violet-red, grey-violet and at last grey-blueish and finally precipitates at pH 2.

In contrast, the ferric ion complex of 4b does not change its red-violet colour between pH 11 and pH 2.5, but also precipitates at pH 2 as a grey-blueish solid. Figure 9 shows this behaviour. The complex of 10d therewith shows a similar behaviour as that of MECAM (2).[32] In contrast to this the complex of 4b doesn't change its optical properties on protonation in a wide pH range. From this, some interesting properties can be derived. In competition experiments between 4b and 10d with respect to Fe^{3+} ions the stronger complex forming capability of the oligocyclic compound 4b is demonstrated clearly.

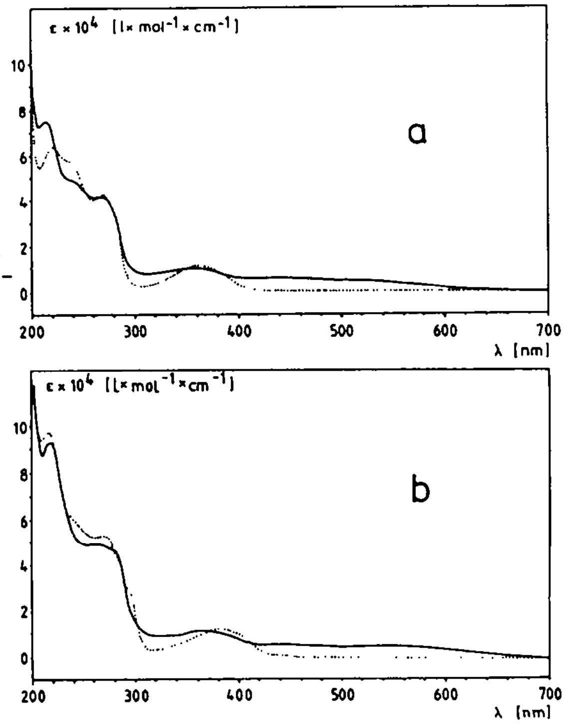


Fig.8. UV/Vis spectra: a) of 10d (···) and of its Fe^{3+} complex (——); b) of 4b (···) and of its Fe^{3+} complex (——) [in H_2O, c= 1.77 x 10^{-5} mol l^{-1}, T= 20.5°C, pH= 11.0, μ= 0.1 M (KCl)]

The comparison of the visible spectra of the Fe^{3+} salts in water at pH 11 shows that approx. 70% of the iron is bound by 4b. At pH 7, this relation is further shifted in favour of 4b. As the behaviour against protonation shows, it can be expected that 4b at pH 3 complexes nearly all of the iron. The absorption curve of the solution containing equimolar amounts of 4b, 10d and Fe^{3+} at pH 3, is most similar to that of the pure complexes of 4b as is shown by Figure 10.

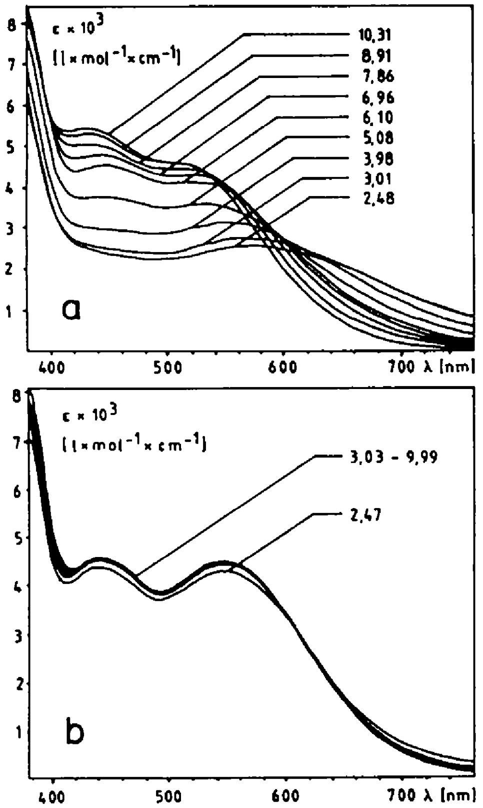


Fig.9. Visible spectra at various pH values of the Fe^{3+} complexes of a) 10d and b) 4b [in H_2O, c= 3.54 x 10^{-5} M, T= 21.5°C, μ= 0.1 M (KCl)]

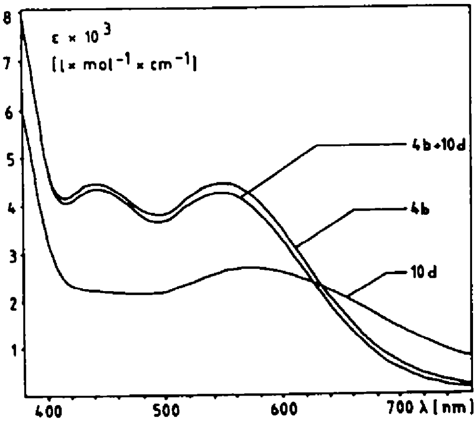


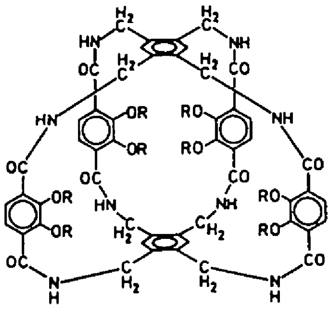
Fig.10. Visible spectra of solutions of equimolar amounts of 4b and $FeCl_3$, 10d and $FeCl_3$, and 4b, 10d and $FeCl_3$ [in H_2O, pH 3, c 4b= c 10d = c $FeCl_3$= 1.77 x 10^{-5} M, T=21.5°C, μ= 0.05 M (KCl)]

8. OUTLOOK

An oligomacrocyclic skeleton, containing substituents projecting into the interior of a cavity, seems to be the key for the development of similar ligands with preformed smaller or larger cavities. A variation of the cavity size can be achieved synthetically by using larger 1,3,5-substituted aromatic or aliphatic spacer units, e.g. triphenylmethyl instead of benzene. In such a way, new water soluble metal and molecule binding cavities will become available which will exhibit varying binding strength and guest selectivities.

In addition to a variation of the cavity size of compounds analogous to 4b, fourfold bridged molecules like 11 also are of interest. These have eight coordination centers instead of six. Such coordination numbers are important for the binding of actinide ions.

The syntheses of ligands of these types are in progress.



11 R = H

EXPERIMENTAL SECTION

Physical Measurements.

Melting points were taken on a Reichert microscope melting point apparatus and are uncorrected. ^1H-NMR spectra were recorded on Varian EM-360, EM-390, Bruker WH-90 and WM-400 instruments. Infrared spectra were recorded on a Pye Unicam SP-1100 instrument. Ultraviolet-visible spectra were recorded on a Cary model 219 spectrophotometer with quartz cuvettes. Mass spectra were recorded on MS-30 and MS-50, A.E.I., Manchester, U.K. FAB mass spectra were performed at the Institut für Physikalische Chemie, Universität

Bonn, by Prof.Dr.F.Röllgen and Dipl.-Phys. S.S.Wong. Microanalyses were performed by the Microanalytical Laboratory, Institut für Organische Chemie und Biochemie, Universität Bonn, and by the Microanalytical Laboratory Dr.Pascher, Bonn. X-ray analyses were performed at the Anorganisch Chemisches Institut, Universität Bonn. All calculations were made on an IBM 3081K computer of the "Regionales Rechenzentrum der Universität Bonn". TLC and column chromatography were performed on silica gel coated Al sheets and silica gel (0.063-0.1 mm) from E.Merck, Darmstadt. pH measurements were done with a Corning 130 pH-meter and an Orion 91-02 glass electrode, which had been standardized at pH 7.00 and 4.00.

1,3,5-Benzenetriyltris(methanamine) (7)
Reagents: Tetrahydrofurane is refluxed with sodium and benzophenone till the solution is deep-blue, then the solvent is distilled. $BF_3 \cdot OEt_2$ has to be colourless, otherwise it is purified by distillation.
Procedure: In a hood trimesyltriamide (8b) (30 g, 0.14 mol) and powdered sodium boranate (Bayer AG, 44 g, 1.16 mol) are added to 1 L of THF in a 2 L three-necked flask. Under nitrogen and intensive stirring borontrifluoride etherate (BASF AG, 175 mL, 1.42 mol) is added first dropwise (caution, foam), then quickly. Shortly after addition the suspension turns pink, but this colour soon disappears. Stirring is continued for three days, then the well stirred suspension is refluxed for another four days. Very cautiously 100 mL of concentrated hydrochlorid acid are added (vigorous evolution of hydrogen, foam) and the suspension is refluxed for 4 hours. The mixture is evaporated to dryness. The residue is triturated with 600 mL of water and filtered by suction. The clear solution is reduced to 400 mL by evaporation. The solution is poured into a 2 L liquid/liquid extractor (according to Ludwig, NORMAG, Otto Fritz GmbH, Feldstraße 1, D-6238 Hofheim/Taunus), superposed with ether and slowly solid KOH (250 g) is added. The mixture is extracted with ether for 24 hrs. In the ether phase of the extraction flask a nearly colourless oil separates. The ether is distilled off at the rotary evaporator. With few dichloromethane or trichloromethane the product is transferred to a 25 mL flask and the solvent is distilled off again (Note a). The product is distilled at 210°C/0.01 Torr (1.3 Pa) by ball tube distillation (Büchi GKR-50). Still hot the liquid is sucked into a warm syringe and the cannula is closed with a rubber stopper. 8.4 g (34% yield) colourless liquid are obtained, which solidifies quickly and melts again at 44-46°C (Note b). ^{1}H-NMR (60 MHz, $CDCl_3$/$TMS_{int.}$): δ= 1.6 (s, 6H, NH_2), 3.90 (s, 6H, CH_2), 7.15 (s, 3H, Ar-H). MS [70 eV, selection, m/e (rel. intens.)]: 165 (M^+, 5%), 147 (80), 135 (100), 118 (76), 104 (40). $C_9H_{15}N_3$ (165.24).

Notes: a) Attention should be paid that no acidic vapours are in the rotary evaporator; otherwise the apparatus should be set alkaline with ammonia.- b) In smaller charges yields up to 58% were obtained, but never as much as 8.4 g product were collected. The amine is very air-sensitive. To remove the amine from the syringe, it is melted with hot air.

2,3-Dimethoxyterephthaloyl dichloride (5d): 2,3-Dimethoxyterephthalic acid (5c) (9.0 g, 39.8 mmol) are boiled in 50 mL of thionyl chloride for ca. 0.5 hrs under reflux. A clear solution is obtained. The thionyl chloride is distilled off and the product distilled at 140°C/0.05 Torr (6.6 Pa): pale yellow oil (9.8 g, 94% yield), which solidifies in the refrigerator and melts at 20-21°C. ^{1}H-NMR (60 MHz, $CDCl_3$/$TMS_{int.}$): δ= 3.95 (s, 6H, OCH_3), 7.70 (s, 2H, Ar-H). $C_{10}H_8Cl_2O_4$ (263.08).

Sodium methyl 2,3-dimethoxyterephthalate (9a): In a solution of dimethyl 2,3-dimethoxyterephthalate (5b) (20.2 g, 79.5 mmol) in 500 mL of methanol and 5 mL of water solid sodium hydroxide (DAB 7, 3.2 g, 80 mmol) is added. The mixture is boiled under reflux over night. The solution is reduced to 100 mL at the rotary evaporator. 300 mL of dry acetone are added dropwise under stirring. The colourless precipitate is filtered by suction (Note a). 3 L of ethyl ether are added to the stirred filtrate. The fluffy precipitate of the product is filtered by suction, washed with ether and dried. The colourless solid is powdered and dried again at 95°C/0.05 Torr (6.6 Pa): 12.4 g (60% yield) of a colourless powder with mp. 210-213°C (Note b). ^{1}H-NMR (60 MHz, D_2O, HOD= 4.80 ppm): δ = 3.9-4.0 (2 s, 9H, OCH_3), 7.24, 7.57 (AB system, 2H, J_{AB}= 8 Hz, Ar-H). $C_{11}H_{11}NaO_6$ (262.11)

Notes: a) This precipitated byproduct is dried. One obtains 4.8 g of a colourless powder. This contains disodium 2,3-dimethoxyterephthalate as a major component, but is mixed with the main product. It can either be hydrolized to yield pure 2,3-dimethoxyterephthalic acid or may be used as starting material for the production of dimethyl-2,3-dimethoxyterephthalate.- b) Distilling off the solvent of the filtrate yields 3.2 g of dimethyl-2,3-dimethoxyterephthalate, which is not completely pure.

Methyl 2,3-dimethoxyterephthaloyl chloride (9b): Sodium methyl 2,3-dimethoxyterephthalate (9a) (12.4 g, 47.3 mmol) was added to thionyl chloride and refluxed for ca. 0.5 hrs. After cooling to room temperature 40 mL of dry tetrachloromethane are added. The sodium chloride gel is collected on a sinter (Note). The clear filtrate is evaporated, the residue is distilled by ball tube distillation (Büchi GKR-50) at 155°C/0.2 Torr (27 Pa). Colourless oil (10.9 g, 90% yield). ^{1}H-NMR (60 MHz, CCl_4/$TMS_{int.}$): δ= 3.9-4.0 (2 s, 9H, OCH_3), 7.40, 7.60 (AB, 2H, J_{AB}= 9 Hz, Ar-H). Anal. calc. for $C_{11}H_{11}ClO_5$ (258.66) C 51.08, H 4.29; found C 51.12, H 4.36.

Note: Before use, the sinter is flushed with thionyl chloride. Sometimes the sodium chloride gel passes the sinter. In this case the product can be distilled from the sodium chloride directly.

Trimethyl-2,2',2",3,3',3"-hexamethoxy-4,4',4"-[1,3,5-benzenetriyltris(methyleniminocarbonyl)]tris benzoate (10a): Triethylamine (6.3 mL, 45.0 mmol, dried with KOH and distilled after addition of 2% phenylisocyanate) and 1,3,5-benzenetriyltris(methanamine) (7) (2.19 g, 13.32 mmol) are dissolved in 100 mL of N,N-dimethylacetamide (Janssen, Nr. 18588-4). Methyl 2,3-dimethoxyterephthaloyl chloride (9b) (10.34 g, 39.97 mmol) is added dropwise to the stirred solution. Colourless ammonium salts precipitate. After 4 hrs stirring in the closed flask the precipitated salts are filtered by suction. The solvent is evaporated. The residue is dissolved in chloroform, washed with 2% NaOH, 2% HCl and water, dried with Na_2SO_4 and again evaporated. To remove the solvent completely, the crude product is melted at 150°C and evacuated (0.05 Torr, 6.6 Pa) for 1 hr. After cooling to room temperature, 10.4 g of a fair brown glassy material are obtained (95% yield). At room temperature the material is soft, whereas at 5°C it is hard. To remove the material out of the flask, the latter is cooled with liquid nitrogen. The product thereby cracks and is easily removed. It is stored at 5°C. TLC control (silica gel 60, $CHCl_3$/EtOH 25:2, v/v, R_F= 0.57) shows that there are scarcely impurities. The purity of this material is high enough to proceed with the following synthetic steps. A purer material is obtained by column chromatography on silica gel with $CHCl_3$/EtOH (see above). ^{1}H-NMR see Table 3. MS (70 eV, selection): m/e= 831 (M^+), 817, 800, 608, 592, 576, 369, 223. IR (KBr, cm^{-1}): 3310 (s), 2975 (m), 1745 (s), 1655 (s), 1550 (s), 1465 (m), 1410 (s), 1305 (s), 1245 (s), 1055 (s), 1035 (s), 813 (m), 760 (m), 715 (w). Anal. calc. for $C_{42}H_{45}N_3O_{15}$ (831.83): C 60.64, H 5.45, N 5.05; found C 60.56, H 5.47, N 4.80.

Trisodium 2,2',2",3,3',3"-hexamethoxy-4,4'-4"-[1,3,5-benzenetriyltris(methyleniminocarbonyl)]tris benzoate (10b): To a solution of 10a (7.64 g, 9.18 mmol) dissolved in 150 mL of methanol (disstilled) and 3 mL of water sodium hydroxide (1.148 g, 27.7 mmol, p.a.) is added. The mixture is stirred until the sodium hydroxide is dissolved completely and refluxed over night. After cooling the solvents are distilled off. The foam produced is dried in vacuo, pulverized and dried at 100°C/0.05 Torr (6.6 Pa). The substance decomposes at 245°C, the yield is nearly quantitative. ^{1}H-NMR (60 MHz, D_2O, HOD= 4.80 ppm): δ= 3.73 (s, 9H, OCH_3), 3.83 (s, 9H, OCH_3), 4.50 (s, broad, 6H, CH_2), 7.05-7.40 (m, 9H, Ar-H). ^{1}H-NMR (60 MHz, CD_3OD/TMS_{int}): δ= 3.85 (s, 9H, OCH_3), 3.90 (s, 9H, OCH_3), 4.60 (s, broad, 6H, CH_2), 7.21, 7.47 (AB, 6H, Ar-H, J_{AB}= 8 Hz), 7.34 (s, 3H, Ar-H). $C_{39}H_{36}N_3Na_3O_{15}$ (855.69).

2,2',2",3,3',3"-Hexamethoxy-4,4',4"-[1,3,5-benzenetriyltris(methyleniminocarbonyl)]-tris benzoylchloride (10c): A 100 mL flask filled with 50 mL of thionyl chloride (colourless, otherwise distilled) is cooled with liquid nitrogen until the thionyl chloride begins to solidify. After that, 5.00 g (ca. 5.8 mmol) of the trisodium salt 10b are added. The mixture is stirred, while the flask is warmed to room temperature by the surrounding air. Stirring is continued at 20°C for additional 0.5 hr; after this, no educt should swim on the thionyl chloride surface. The mixture is filtered by suction through a glass frit (flushed with thionyl chloride). Usually, NaCl is easily filtered off in this way. The thionyl chloride is distilled off in vacuo from the yellow filtrate at a temperature <25°C! A pale yellow foam is formed, from which the thionyl chloride is completely removed in vacuo (0.05 Torr, 6.6 Pa). After some hrs the material changes to a pale solid with mp. 130-132°C. The yield is quantitative. ^{1}H-NMR (60 MHz, $CDCl_3/TMS_{int.}$): δ= 3.95 (s, 18H, OCH_3), 4.70 (d, 6H, CH_2, J= 6 Hz), 7.30 (s, 3H, Ar-H), 7.74, 7.90 (AB, 6H, Ar-H, J_{AB}= 8 Hz), 8.30 (t, broad, 3H, NH, J= 6 Hz). Anal. calc. for $C_{39}H_{36}Cl_3N_3O_{12}$ (845.08) C 55.43, H 4.29, N 4.97; found C 55.70, H 4.64, N 4.74.

2,2',2"-3,3',3"-Hexahydroxy-4,4',4"-[1,3,5-benzenetriyltris(methyleniminocarbonyl)]tris benzoic acid (10d): In the following preparation nitrogen was always used for protection. To a solution of 2 mL of boron tribromide (21.15 mmol) in 20 mL of dry dichloromethane (distilled from P_4O_{10}) under cooling with ice a solution of the triester 10a (1.0 g, 1.2 mmol) in 10 mL of dry dichloromethane is added dropwise. After complete addition the mixture is warmed up to room temperature and stirred over night. Under cooling with ice 20 mL of water are added dropwise and the mixture stirred vigorously for 4 hrs. The colourless residue is filtered by suction and washed with water/dichloromethane. It is then dissolved in some mL of water and set to pH 10 using NaOH. The nearly clear solution is filtered and the filtrate acidified using diluted HCl. The gel is filtered by suction, washed five times with water and dried at 100°C/0.05 Torr (6.6 Pa): 640 mg (73% yield) colourless powder, softening at 205°C, oil at 230°C. The powder is insensitive to air. H-NMR (400 MHz, DMSO-d_6, DMSO= 2.58 ppm): δ= 4.59 (d, 6H, CH_2, J= 6 Hz), 7.20-7.45 (m, 9H, Ar-H), 9.57 (m, 3H, NH). Anal. calc. for $C_{33}H_{27}N_3O_{15} \cdot H_2O$ (723.59) C 54.78, H 4.04, N 5.81; found C 54.49, H 3.95, N 5.61. FAB mass spectrum in glycerol matrix: 706 $[M+H]^+$. In addition there are peaks at 720 $[M+14+H]^+$, 734 $[M+28+H]^+$, 748 $[M+42+H]^+$, 762 $[M+56+H]^+$. These peaks hint to incompletely demethylated byproducts.- IR (KBr, cm^{-1}): 3430 (s, broad), 1692 (s), 1650 (s), 1620 (s), 1560 (s), 1450 (s), 1330 (s), 1236 (s), 1185 (s), 1040 (m), 757 (s).

6,7,19,20-Tetramethoxy-3,10,16,23-tetraazapentacyclo[12.12.3^{1,25}.3^{12,14}.2^{5,8}.2^{18,21}]hexatriaconta-1(29),5,7,12,14(32),18,20,25,27,30,33,35-dodecaen-4,9,17,22-tetrone (3): In a high dilution apparatus (according to Vögtle, NORMAG) under nitrogen atmosphere in the course of 9 hrs synchronously the following two solutions are added dropwise (about 1 drop in 3 seconds) to 1.3 L of intensively stirred boiling benzene (distilled from sodium/benzophenone): a) 2,3-dimethoxy terephthaloyl chloride (3.00 g, 11.4 mmol) dissolved in 250 mL of benzene, and b) m-xylylene diamine (3.11 g, 22.8 mmol, Bayer AG) in 250 mL of benzene. A colourless precipitate is formed. The solvent is distilled off from the suspension. The solid residue is dried in vacuo and extracted in a soxhlet extractor for 24 hrs using dichloromethane. The solution is washed with HCl (2%), NaOH (2%) and water, dried with Na_2SO_4 and the dichloromethane is distilled off. The residue is stirred with some mL of methanol and filtered. The residue is washed with methanol, ether and petroleum ether (40/60°C) and dried. 1.32 g of a pale brown powder are obtained. Though the solubility in chloroform is not very high, the material can be chromatographed on a silica gel column (35 x 300 mm) using chloroform/ethanol (9:1, v/v, R_F = 0.53). The solvents are removed by distillation, the product is stirred with a little methanol and collected in a sinter. 670 mg (9% yield) of a colourless powder are obtained after drying at 80°C/0.05 Torr (6.6 Pa), which decomposes at 295°C. For an elemental analysis the product was again dried at 100°C/10^{-5} Torr. Anal. calc. for $C_{36}H_{36}N_4O_8$ (652.70) C 66.24, H 5.56, N 8.58; found C 65.93, H 5.60, N 8.56. Osmometric molecular weight determination (Dr.Pascher, Bonn): 710 (+9%). There is no indication to a smaller (molecular mass 325.13) and to a larger cycle (molecular mass 978.38) (6a,b). ^{1}H-NMR see Table 3.- MS (70 eV, selection): m/e = 652 (M^+), 651, 650, 620, 609, 593, 592, 489, 449, 327, 326, 325.- IR (KBr, cm^{-1}): 3425 (s), 2965 (m), 1675 (s), 1535 (s), 1460 (m), 1407 (m), 1300 (s), 1250 (m), 1055 (m), 1025 (m), 1000 (m), 797 (m), 480 (m).

8,9,23,24,35,36-Hexamethoxy-5,12,20,27,32,39-hexaazaheptacyclo[14.14.10.$2^{7,10}$.$2^{22,25}$.$2^{34,37}$.$1^{3,29}$.$1^{14,18}$]octatetraconta-1,3(43),7,9,14,16,18(46),22,24,29,34,36,41,44,47-pentadecaene-6,11,21,26,33,38-hexone (4a): In a high dilution apparatus (according to Vögtle, NORMAG) solutions of the trichloride 10c (5.60 g, 6.63 mmol) in 235 mL of benzene (dried on sodium/benzophenone) and 15 mL of dimethylacetamide (99+%, Janssen) and a solution of 1,3,5-benzenetriyltris(methanamine) (2.18 g, 13.2 mmol) in 250 mL of benzene are added dropwise and synchronously within 12 hrs in a nitrogen atmosphere to 1 L of vigorously stirred boiling benzene (see above). During this addition colourless fluffy precipitates are formed. After cooling to room temperature the suspension is filtered. Precipitate 1 is collected. The solvents of the filtrate are distilled off, the residue stirred with little methanol, the resulting solid collected on a glass frit. After drying 640 mg colourless powder are obtained. Precipitate 1 is extracted in a soxhlet extractor with dichloromethane for 24 hrs. The solution is washed with 2% HCl, 2% NaOH and water, dried with Na_2SO_4 and evaporated. The residue is chromatographed on a silica gel column with chloroform/ethanol (9:1 v/v). 160 mg crude product are collected. The combined crude products are chromatographed again on a silica gel column (35 x 300 mm, see above; R_F = 0.48). Three fractions are collected. The solvents are distilled off, the residue again stirred with methanol, the remaining solid is collected on a glass frit and dried at 100°C/0.05 Torr. The first fraction is somewhat purer than the second and third fraction. The total yield is 790 mg (13%) colourless powder, which decomposed at 290°C. ^{1}H-NMR see Tables 3-5. MS (70 eV, selection): m/e = 900 (M^+), 882, 881, 868, 867, 208.- IR (KBr, cm^{-1}): 3420 (s), 2970 (m), 1665 (s), 1545 (s), 1465 (m), 1407 (m), 1300 (m), 1240 (m), 1060 (m), 1020 (m), 995 (m), 735 (m).- Anal. calc. for $C_{48}H_{48}N_6O_{12}$ x $\frac{1}{2}$ H_2O (909.65) C 63.38, H 5.39, N 9.24; found C 63.29, H 5.40, N 9.06. Crystals for X-ray diffraction were obtained by crystallization from a mixture of chlorobenzene and N,N-dimethylformamide. Anal. calc. for $C_{48}H_{48}N_6O_{12}$ x $\frac{1}{2}$ C_6H_5Cl (957.22) C 63.99, H 5.32, N 8.78; found C 63.47, H 5.32, N 8.57.

8,9,23,24,35,36-Hexahydroxy-5,12,20,27,32,39-hexaazaheptacyclo[14.14.10.$2^{7,10}$.$2^{22,25}$.$2^{34,37}$.$1^{3,29}$.$1^{14,18}$]octatetraconta-1,3(43),7,9,14,16,18(46),22,24,29,34,36,41,44,47-pentadecaene-6,11,21,26,33,38-hexone (4b): The following procedure has been carried out under nitrogen atmosphere. It is not really known if this is necessary. To a 1 M solution of BBr_3 in dichloromethane (7.5 mL, 7.5 mmol) under cooling with ice a solution of 4a (200 mg, 0.22 mol) in 15 mL of dichloromethane (distilled from P_4O_{10}) is added dropwise. After completed addition the mixture is stirred at room temperature for 24 hrs. Under cooling with ice 18 mL of water are added dropwise. The mixture is stirred intensively at room temperature for 4 hrs, afterwards filtered by suction (frit) 4nd several times washed with water and dichloromethane. The residue is dissolved in some mL of water and the pH set to 11 using NaOH. The nearly clear solution is filtered, the filtrate is acidified using diluted HCl. The fine flocky precipitate is filtered by suction, washed five times with water and finally dried at 100°C/0.05 Torr (6.6 Pa): 134 mg (72% yield) colourless powder, insensitive to air, thermal decomposition at 285°C.- ^{1}H-NMR see Table 6. IR see Figure 7. FAB mass spectrum in glycerol matrix: 817 $[M+H]^+$. In addition there are peaks at $[M+n+14+H]^+$, n=1-5, which hint to byproducts not completely demethylated. Anal. calc. for $C_{42}H_{36}N_6O_{12}$ x 1.5 H_2O (843.80) C 59.78, H 4.66, N 9.96; found C 59.75, H 4.55, N 9.86.

Fe^{3+} complex of 4b: Fe_2O_3 (21.0 mg, 0.132 mmol) is dissolved under warming in 1 mL of conc. HCl. The solution is filled up to 100 mL with water. Under nitrogen the oligocyclic ligand 4b (20.0 mg, 0.024 mmol) is suspended in some mL of water and dissolved with little NaOH. To this solution 10.0 mL of the diluted $FeCl_3$ solution is added. A blue-black precipitate is formed. The pH is raised to 11 using NaOH. A dark red solution is obtained. This solution is filtered

and pH 1 adjusted with diluted HCl. The fine black precipitate is centrifugated, washed three times with 0.1 N HCl and each time centrifugated. The precipitate is dried at 0.05 Torr (6.6 Pa) finally at 100°C: 17.3 mg (75% yield) blue-black powder. IR see Figure 7. Anal. calc. for $C_{42}H_{33}FeN_6O_{12}$ x 5 H_2O (959.66) C 52.57, H 4.52, Fe 5.82; found C 52.73, H 4.51, Fe 5.40. FAB mass spectrum in diethanolamine matrix: 870 $[M+H]^+$.

Ga^{3+} complex of 4b: Under nitrogen the oligocyclic ligand 4b (8.4 mg, 10.0 µmol) is suspended in 2 mL of water and dissolved with little NaOH. $Ga_2(SO_4)_3$ (3.2 mg, 7.4 µmol, Fluka AG) is dissolved in some drops of hot HCl, with dilute NaOH pH 12 is adjusted. Both solutions are mixed and with dilute HCl pH 7.5 is adjusted. At this pH excess $Ga(OH)_3$ is insoluble and separated by centrifugation. The clear solution is freeze-dried, then dried at 60°C/0.05 Torr (6.6 Pa). The remaining colourless residue is divided. The first half is analyzed by ^1H-NMR spectroscopy: ^1H-NMR (90 MHz, D_2O, pD= 7.2, HOD= 4.80 ppm): δ= 4.60 (s, 12H, Ar-H). The second half is stirred with 0.6 mL of DMSO-d_6 for 15 min, inorganic salts are filtered off (glass frit) and the clear solution is analyzed by ^1H-NMR (see Table 6).

ACKNOWLEDGEMENT

We wish to thank Prof.Dr.F.Röllgen and Dipl.-Phys. S.S.Wong for recording FAB mass spectra and for discussions. This work was supported by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen.

REFERENCES

1) Beilstein, VI, EI 381, EII 773, EIII 4197.
2) Allcock, H.R.; Bisell, E.C. J.Am.Chem.Soc. 1973, 95, 3154.
3) Flynn, J.J.; Boer, F.P. J.Am.Chem.Soc. 1969, 91, 5756.
4) a) Munro, D. Chem.Brit. 1977, 13, 100; b) Schwarzenbach, G. Helv.Chim.Acta 1952, 35, 2344.
5) Buckingham, D.A. in "Inorganic Biochemistry" (Eichhorn, G.L., ed.), Elsevier Scientific Publishing Company, Amsterdam - London - New York, 1973,3.
6) Raymond, K.N.; Isied, St.S.; Brown, L.D.; Fronczek, F.R.; Nibert, J.H. J.Am.Chem.Soc. 1976, 98, 1767.
7) Pollack, J.R.; Neilands, J.B. Biochem.Biophys.Res.Commun. 1970, 38, 989.
8) O'Brien, J.G.; Gibson, F. Biochem. Biophys.Acta 1970, 215, 393.
9) Schlegel, H.G. Allgemeine Mikrobiologie, 5th ed., Thieme-Verlag, Stuttgart - New York, 1981.
10) Raymond, K.N.; Müller, G.; Matzanke, B.F. Top.Curr.Chem. 1984, 123, 49.
11) Corey, E.J.; Bhattacharyya, S. Tetrahedron Lett. 1977, 3919.
12) Rastetter, W.H.; Erichson, T.J.; Venuti, M.C. J.Org.Chem. 1981, 46, 3579.
13) Shanzer, A.; Libman, J. J.Chem.Soc. Chem.Commun. 1983, 846.
14) Isied, S.S.; Kuo, G.; Raymond, K.N. J.Am.Chem.Soc. 1976, 98, 1763.
15) Weitl, F.L.; Raymond, K.N. J.Am. Chem.Soc. 1979, 101, 2728.
16) Venuti, M.C.; Rastetter, W.H.; Neilands, J.B. J.Med.Chem. 1979, 22, 123.
17) Schuda, P.F.; Botti, C.M.; Venuti, M.C. Org.Prep.Proc.Int. 1984, 16, 119.
18) Kiggen, W.; Vögtle, F. Angew.Chem. 1984, 96, 712; Angew.Chem., Int.Ed. Engl. 1984, 23, 714.
19) a) Weitl, F.L.; Raymond, K.N.; Durbin, P.W. J.Med.Chem. 1981, 24, 203; b) Cason, J.; Dyke, Jr., G.O. J.Am. Chem.Soc. 1950 , 72, 621; c) Schmitt, R.; Hähle, H. J.prakt.Chem. 1891, 44, 1.
20) Dallacker, F.; Korb, W. Justus Liebigs Ann.Chem. 1966, 694, 98.
21) Cf. Rossa, L.; Vögtle, F. Top.Curr. Chem. 1983, 113, 1.
22) Ried, W.; Königstein, F.J. Chem.Ber. 1959, 92, 2532.
23) Weber, E.; Josel, H.-P. J.Incl.Phenom. 1983, 1, 79.
24) a) Gilmore, C. MITHRIL - A computer program for the automatic solution of crystal structures from X-Ray data, Glasgow, 1983; b) Complete data of the X-Ray analysis can be requested at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG, with No.CSD 51365, name of the authors and this journal.
25) Sheldrick, G.M. SHELX 76: Program for Crystal Structure Determination, Cambridge, 1976.
26) Schannon, R.D. Acta Crystallogr. 1976, A32, 751.
27) a) Taliaferro, C.H.; Motekaitis, R. J.; Martell, A.E. Inorg.Chem. 1984, 23, 1188; b) Llinas, M.; Wilson, D.M.; Neilands, J.B. Biochemistry 1973, 12, 3836.
28) Bergeron, R.J.; Kline, S.J. J.Am. Chem.Soc. 1984, 106, 3089.
29) Yan, L.F.; Momany, F.A.; Hoffmann, R.; Scheraga, H.A. J.Phys.Chem. 1970, 74, 420.
30) Jensen, K.A. Inorg.Chem. 1970, 9, 1.
31) a) Gray, H.B.; Schugar, H.-J. in "Inorganic Biochemistry" (Eichhorn, G.L., ed.), Elsevier Scientific Publishing Company, Amsterdam - London - New York, 1973, 102; b) Raymond, K.N.; Carrano, C.J. Acc.Chem. Res. 1979, 12, 183.
32) Harris, W.R.; Raymond, K.N. J.Am. Chem.Soc. 1979, 101, 6534.