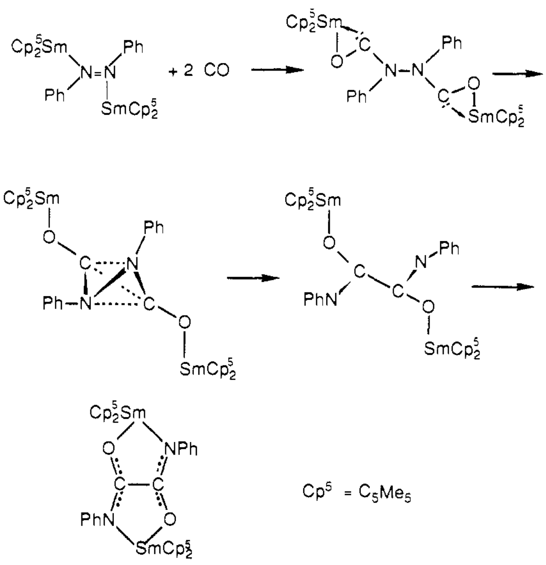
Scheme III



four-membered rings not the five-membered rings observed in **5**. To get to **5**, a second rotation of the molecule is necessary.

A major drawback in Scheme II is that two rotations are required. As Figure 5 shows, this system is sterically bulky. A sequence which does not involve rotations of such large fragments would be more desirable. Scheme III shows such an alternative. The first part of Scheme III is the same as in Scheme II. However, rather than rotate the CO inserted intermediate to bring the carbon atoms together in a planar four-center transition state, Scheme III shows the formation of a tetrahedral intermediate. Once the multiple bonds are reorganized in this intermediate, the nitrogen atoms are in the proper position to coordinate to the samarium atoms without any rotation. In terms of simplicity, Scheme III is more appealing and it is possible that a tetrahedral rather than square-planar intermediate is present in this reaction.

Conclusion

$(C_5Me_5)_2Sm(THF)_2$ reduces azobenzene to form both mono- and dianionic species. At both levels of reduction, complexes containing η^2-coordination of two adjacent nitrogen atoms can be formed. In addition, an unusual η^1,η^1-$Ph_2N_2^{2-}$ complex can be obtained. The complex containing the $Ph_2N_2^-$ monoanion is not activated for reaction with CO, but the dianion-containing complexes are reactive with CO. The product obtained from the $[(C_5Me_5)_2Sm]_2(\mu$-η^1:η^1-$N_2Ph_2)$ reaction shows an unusual reorganization of the multiple bonds in CO and azobenzene. This example shows that $(C_5Me_5)_2Sm(THF)_2$ can generate unusual multiple bond "metathesis" reactions with heteroatomic unsaturated substrates and should be considered as a possible reagent when multiple bond cleavage and activation is desirable. This system also suggests that tetrahedral intermediates may provide viable pathways for reactions of this type.

Acknowledgment. We thank the National Science Foundation for support of the research.

Registry No. 1, 114251-64-8; **1**·0.5THF, 114251-71-7; **2**, 105140-21-4; **3**, 114251-65-9; **3**·2THF, 114251-72-8; **4**, 114251-66-0; **4**·C_7H_8, 114273-26-6; **5**, 105140-22-5; **5**·$2C_7H_8$, 114251-73-9; **6**, 114251-67-1; **7**, 114251-68-2; **8**, 114251-69-3; **9**, 114251-70-6; $(C_5Me_5)_2Sm(THF)_2$, 79372-14-8; $(C_5H_5)_2Yb(THF)$, 99593-36-9; $C_6H_5N{=}NC_6H_4$-NMe_2-4, 60-11-7; CO, 630-08-0; azobenzene, 103-33-3; 3,3'-azotoluene, 588-04-5.

Supplementary Material Available: Tables of bond distances and angles and thermal parameters (17 pages); a listing of observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

Cocomplexation of Neutral Guests and Electrophilic Metal Cations in Synthetic Macrocyclic Hosts[1]

Catherina J. van Staveren,[†] Johan van Eerden,[‡] Frank C. J. M. van Veggel,[†] Sybolt Harkema,[‡] and David N. Reinhoudt*[,†]

Contribution from the Laboratories of Organic Chemistry and Chemical Physics, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands. *Received January 12, 1988*

Abstract: A novel method for the cocomplexation of neutral guest molecules by macrocyclic hosts, using an electrophilic metal cation, "immobilized" within a Schiff base moiety of a macrocyclic ligand, is described. The synthesis, IR and NMR spectral data, and X-ray crystal structures of the complexes are discussed. In 2,6-pyrido-27-crown-9·$LiClO_4$·urea (1:1:2) Li^+ and one urea are encapsulated by the host molecule, and urea is coordinated to the lithium ion via the oxygen atom. In the $Ba(ClO_4)_2$ and $Ba(CF_3SO_3)_2$ complexes of two Schiff base macrocycles, **11c**·MeOH and **12a**, the barium cation is coordinated in the polyether moiety of the ligand. In the $Ni^{(II)}$-H_2O and $Ni^{(II)}$-urea complexes of two Schiff base macrocycles, **19a**·H_2O and **16e**·urea, the nickel ion is complexed in the Schiff base moiety, whereas the neutral molecule is complexed in the polyether cavity, without short contact between the metal ion and the neutral guest. In the UO_2-urea complexes, the coordination of the neutral guest with the uranyl cation, located in the Schiff base moiety, was proven by IR spectroscopy and X-ray crystallography in the case of **20e**·urea. Similar complexes were obtained with substituted amides and ureas.

The synthesis of tailor-made receptor molecules is one of the main aims in host-guest chemistry. Although most of the efforts in this field used to be focussed on the complexation of cations,[2] more recently also the complexation of neutral guest species has become a rapidly growing field of interest.[3] Whereas relatively stable complexes have been reported when cations are the guest species, the interaction of macrocyclic ligands and neutral guests is generally very weak, especially when the host-guest interaction is the result of hydrogen bonding.[4] We are particularly interested

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[†] Laboratory of Organic Chemistry.

[‡] Laboratory of Chemical Physics.

(1) Part of this work appeared as a preliminary communication: van Staveren, C. J.; Fenton, D. E.; Reinhoudt, D. N.; van Eerden, J.; Harkema, S. *J. Am. Chem. Soc.* **1987**, *109*, 3456-3458.

(2) (a) de Jong, F.; Reinhoudt, D. N. *Adv. Phys. Org. Chem.* **1980**, *17*, 279-433. (b) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sew, D. *Chem. Rev.* **1985**, *85*, 271-339.

(3) (a) Vögtle, F.; Müller, W. M. *J. Incl. Phenom.* **1983**, *1*, 369-386. (b) Vögtle, F.; Sieger, H.; Müller, W. M. *Top. Curr. Chem.* **1981**, *98*, 107-162.

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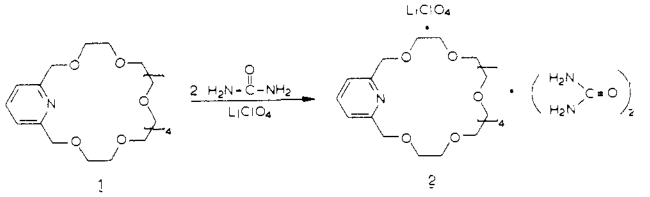
Scheme I



in the complexation of (polyfunctional) organic guest species of biological and industrial importance, such as urea, guanidine, methanol, etc.[5]

During the complexation of guanidine by 2,6-pyrido crown ethers a proton is transferred from the protonated pyridine nitrogen to the guanidine, yielding a protonated guest and a neutral macrocycle.[6] The proton transfer contributes to the complexation process because a macrocyclic polyether can complex a positively charged species much more effectively than a neutral guest.[4b]

The complexation of water molecules by protonated pyrido crown ethers shows that complexation can also occur if the proton is not transferred to the guest molecule.[5a] The same is observed in the complex of urea and 2-carboxyl-1,3-xylyl-30-crown-9, in which the carboxylic proton is not transferred from the carboxylic group to the urea oxygen.[7] In these two examples the guest molecule accepts a strong hydrogen bond from the acidic functionality of the crown ether. However, the relative acidities of host and guest prevent proton transfer.

The disadvantage of using a proton in the complexation of a neutral guest becomes clear when the complexation of urea by 2,6-pyrido crown ethers is examined. The unfavorable basicity of urea (pK_a (H_2O, 25 °C) = 0.1) makes it difficult to protonate the molecule. If the solution is not sufficiently acidic the macrocyclic polyether will be deprotonated, and proton transfer to the solvent instead of hydrogen bonding to urea will occur. It is virtually impossible to immobilize a proton of an acidic group within a macrocycle such that it is available for either proton transfer or hydrogen bonding at all pH values.

Although up to this point only the proton has been considered as a means to assist in the complexation of a neutral molecule it is possible to generalize the concept. A proton, either free or present as an acidic functionality in a macrocyclic cavity, is only one representative of an electrophilic center within the macrocycle. In principle other electrophiles may also serve to assist in the complexation of a neutral guest with a macrocyclic polyether.

It is known from the literature that urea can form complexes with many metal salts. In a number of cases structural information is available from X-ray crystallography. In complexes of urea with the alkali metal salts LiI[8a] and NaCl,[8b] the urea carbonyl forms a bond with two cations in a bridging fashion. In complexes of urea with transition-metal salts, e.g., $Mn(ClO_4)_2$,[8c] $Ni(SCN)_2$,[8d] and $Zn(NO_3)_2$,[8e] urea is bound via the oxygen atom to one metal cation. The geometry of the urea–cation binding has been studied by Lebioda.[9] He has found that the angle between the $O-M^{2+}$ bond and the plane of urea is normally small, i.e., the cation tends to lie in the plane of the urea molecule. The angle between the C=O bond and the $O-M^{2+}$ bond has a mean value of 138°. In most complexes the angle is between 135 and 140°. In the enzyme urease, urea is thought to bind to the active site via $C{=}O\cdots Ni^{2+}$ coordination.[10] Furthermore macrocyclic polyethers are well known for their ability to form complexes with metal ions.

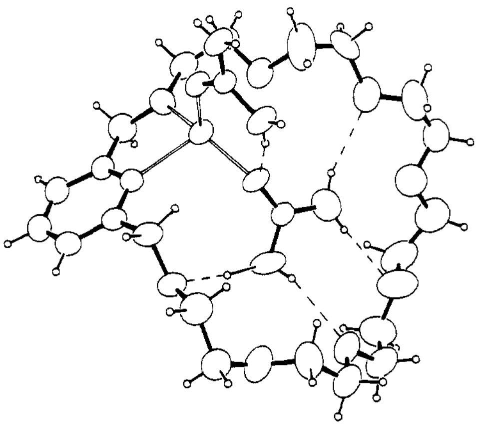
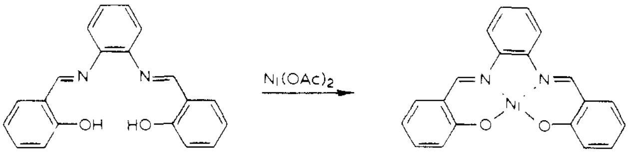


Figure 1. View of the structure of 2; the perchlorate anion is not shown.

Scheme II



We decided to test this novel and probably more general concept by using a small metal cation as the electrophile in the complexation of urea and other neutral polar molecules. Our aim was to complex both urea and the metal cation together in the macrocyclic cavity, in such a way that the metal ion is bound both to the urea carbonyl oxygen and to the macrocycle. The metal cation thus serves as a bridging electrophile that induces a partial positive charge on the urea NH_2 groups and therefore increases the hydrogen bonding between host and guest in a ternary complex.

Results and Discussion

As reported previously,[7] upon reaction of 2,6-pyrido-27-crown-9[6] (**1**) with 1 equiv of $LiClO_4$ and 2 equiv of urea, a 1:1:2 complex 2,6-pyrido-27-crown-9·$LiClO_4$·urea (**2**) was formed, mp 107–109 °C (Scheme I). X-ray analysis of this complex proved that the lithium cation and one of the urea molecules are encapsulated in the crown ether cavity (Figure 1).

The lithium ion is coordinated to the pyridyl nitrogen, to one of the benzylic oxygen atoms, and to both of the oxygen atoms of the two urea molecules. The encapsulated urea is coordinated to lithium via the oxygen atom and forms four hydrogen bonds to polyether oxygens. The second urea, which is not encapsulated by the crown ether, completes the tetrahedral coordination of the lithium cation and is further hydrogen bonded to the encapsulated urea molecule.

By synthesizing this complex, in which a metal cation is used as an electrophile that can bind both to the macrocycle and to the guest, we concluded that not only a proton but also a metal cation can be used to assist the complexation of a neutral guest with a macrocyclic polyether.[11]

However, in the 2,6-pyrido-27-crown-9·$LiClO_4$·urea (1:1:2) complex (**2**) four species have to combine to form a complex.

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(4) de Boer, J. A. A.; Reinhoudt, D. N.; Harkema, S.; van Hummel, G. J.; de Jong, F. *J. Am. Chem. Soc.* **1982**, *104*, 4073–4076. (b) van Staveren, C. J.; Aarts, V. M. L. J.; Grootenhuis, P. D. J.; van Eerden, J.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 5271–5276.

(5) (a) Grootenhuis, P. D. J.; Uiterwijk, J. W. H. M.; Reinhoudt, D. N.; van Staveren, C. J.; Sudhölter, E. J. R.; Bos, M.; van Eerden, J.; Klooster, W. T.; Kruise, L.; Harkema, S. *J. Am. Chem. Soc.* **1986**, *108*, 780–788. (b) de Boer, J. A. A.; Uiterwijk, J. W. H. M.; Geevers, J.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1983**, *48*, 4821–4830.

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(7) Aarts, V. M. L. J.; van Staveren, C. J.; Grootenhuis, P. D. J.; van Eerden, J.; Kruise, L.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 5035–5036.

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(9) Lebioda, L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36*, 271–275.

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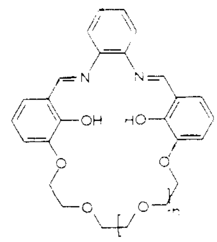
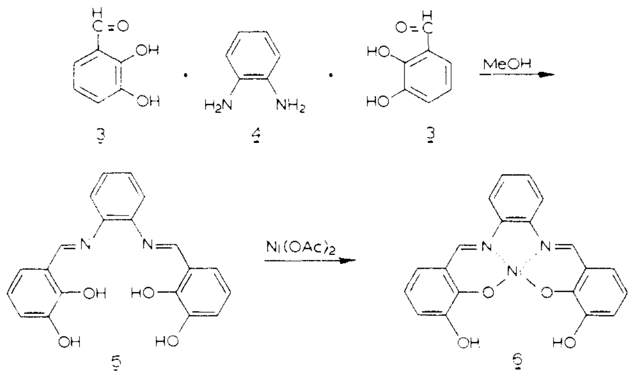
(11) We have attempted to obtain similar complexes with $NiBr_2$ or $MgBr_2$ as the metal salts. However, extremely hygroscopic products were obtained and no extensive analysis of these products was attempted.

Chart I



Scheme III



Therefore, with the 2,6-pyrido-27-crown-9·$LiClO_4$·urea (1:1:2) complex (**2**) as a starting point we investigated the possibility of "immobilizing" an electrophilic cation in a macrocyclic cavity. The advantage of this approach is that only two species will have to combine to form a complex, namely the neutral guest and the macrocycle in which the electrophile is permanently present. In these novel ligands the electrophile will not be lost to the solvent. The prerequisite for "immobilization" is a very high association constant of the complex between the metal cation and the macrocyclic ligand.

Design and Synthesis of a Ligand with an Immobilized Electrophile. From the literature it is known that some biological or synthetic receptor molecules are able to complex metal cations in such a way that very high association constants can be achieved. Examples of such natural ligands are porphyrins[12a] and the Fe^{3+} binding ligand enterobactin.[12b] Both types of receptors have been modified to give compounds with similar binding properties, e.g., capped porphyrins[13a] and synthetic analogues of enterobactin.[13b] The Schiff base condensation products of salicylaldehyde and aromatic or aliphatic diamines, the so-called salen type ligands (salen = *N,N'*-ethylenebis(salicylideneaminato)), are known to form very stable complexes with transition-metal cations.[14] Upon reaction of these ligands with a transition-metal acetate the phenolic OH groups are deprotonated, and a neutral complex is formed (Scheme II).

We decided to incorporate such a salen moiety in a new type of ligand. Our target molecules were the compounds shown in Chart I with a total ring size of 22–34 ring atoms. In this paper the part of the macrocycle that corresponds to the ligand shown in Scheme II will be referred to as the Schiff base moiety or as the salen moiety.

Potentially, two approaches to these compounds are possible. In the first approach (Scheme III) the Schiff base unit was synthesized from 2,3-dihydroxybenzaldehyde (**3**) and *o*-phenylenediamine (**4**) in a facile condensation reaction. Unfortunately, the direct reaction of the Schiff base component **5** or **6** with a polyethylene glycol ditosylate failed. Therefore the second route, outlined in Scheme IV was used.

The dialdehydes **9a** and **9b** were prepared in a one-step procedure. Reaction of 2,3-dihydroxybenzaldehyde with 2 equiv of NaH in DMSO gave the dianion,[15] which was treated with tri- or tetraethylene glycol ditosylate to give the desired dialdehydes **9a** and **9b** in 61–63% yield after acidic aqueous workup and chromatography.

For the synthesis of the larger analogues a different procedure was followed. Selective protection of 2,3-dihydroxybenzaldehyde was carried out by reaction of **3** with 1 equiv of NaH, to form the stabilized phenolate anion,[15] which reacted with 3-bromo-1-propene to give the 2-allyloxy-3-hydroxybenzaldehyde **7** in 60% yield after aqueous workup and recrystallization from petroleum ether. Compound **7** was reacted with pentaethylene glycol ditosylate in acetonitrile with excess potassium carbonate as a base to give the linear dialdehyde **8c** in 64% yield. Analogous reactions were carried out with hexaethylene glycol ditosylate and heptaethylene glycol ditosylate to give the corresponding homologues **8d** and **8e** in 64% and 68% yield, respectively. The protecting allyl groups in the linear dialdehydes were removed by reaction with 5% Pd/C and a trace of acid in $MeOH/H_2O$ under reflux, and compounds **9** were isolated in 85–88% yield.

Macrocyclization with *o*-phenylenediamine was attempted under high dilution conditions in MeOH. Without a template ion only traces of monomeric cyclic products were obtained, but when $Ni(OAc)_2$ was used as a template, small amounts of a cyclic nickel complex were formed as was proven by mass spectrometry. However, even under these conditions mostly polymeric material was isolated. Potassium, rubidium, and cesium salts were not satisfactory, but $Ba(ClO_4)_2$ and $Ba(CF_3SO_3)_2$[16] were found to be suitable template salts for the cyclization reaction. The complexes **10c** and **10d** were prepared by reaction of the dialdehyde with 1 equiv of $Ba(ClO_4)_2$ in $EtOH/CHCl_3$, which yielded the complexes **10c** and **10d** as pale yellow crystalline solids. In the case of the larger or smaller dialdehydes **9a,b,e** a solid product could not be isolated.

The subsequent ring closure was carried out by slow addition of separate solutions of the $Ba(ClO_4)_2$ complexes **10c,d** and of *o*-phenylenediamine to refluxing methanol. The cyclizations of the smaller and larger aldehydes were carried out by slow addition of a solution of the dialdehyde **9a,b,e** in MeOH or THF and of *o*-phenylenediamine in MeOH to a solution of the template salt in MeOH. As an alternative to the potentially explosive perchlorate, barium triflate[16] could also be used as the template salt in the cyclization reaction. The bright orange $Ba(ClO_4)_2$ complexes **11** and $Ba(CF_3SO_3)_2$ complexes **12** crystallized upon cooling and addition of a small amount of petroleum ether. The yields of the $Ba(ClO_4)_2$ complexes **11** were 59–68%, and of the $Ba(CF_3SO_3)_2$ complexes **12** the yields were 72–81%.

We were able to isolate the substituted barium triflate complexes **13a,b** by using 3,4-diaminotoluene and 3,4-diaminobenzophenone as the diamines in yields of 89% and 47%, respectively. The N=C stretching frequency was observed at 1620–1625 cm^{-1} for **12a**, **13a**, and **13b**, indicating that the N=C bond is not affected by the electron-withdrawing properties of the benzoyl group.

In the ^1H NMR spectrum of the complexes **11c–e** and **12b** a singlet in the region δ 8.9–9.2 ppm showed that the imine linkage is present, and a signal between 13.0 and 14.5 ppm proved that in these complexes the phenolic OH group is not deprotonated by Ba^{2+}. Unexpectedly the complexes **11a** and **12a** showed two sharp singlets for the imine protons, at δ 9.13 and 9.10 ppm for **11a**, and at δ 9.17 and 9.14 ppm for **12a**. This may be explained by proton transfer from one OH to one of the imine nitrogen atoms.[17] This proton transfer from a phenolic oxygen to an imine

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[12] (a) Falk, J. E. *Porphyrines and Metalloporphyrines*; Elsevier Publishing Company: Amsterdam, London, New York, 1964. (b) Harris, W. R.; Carrano, C. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 2722–2727.

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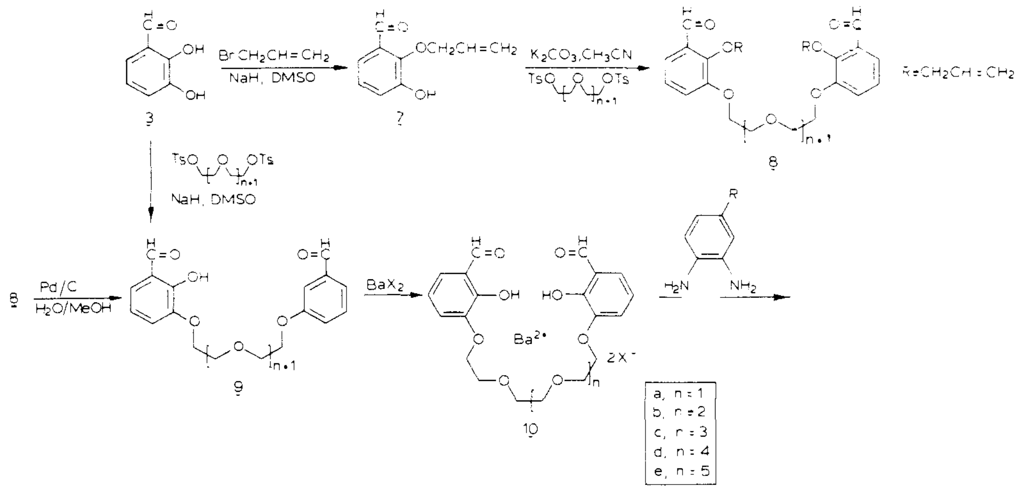
[14] (a) Dabrowska, D.; Rzoska, W. *Acta Pol. Pharm.* **1978**, *35*, 69–76. (b) Stronski, I.; Zielinski, A.; Samotus, A.; Stasicka, Z.; Budesinsky, B. *Z. Anal. Chem.* **1966**, *222*, 14–22.

[15] Kessar, S. V.; Gupta, Y. P.; Mohammed, T.; Goyal, M.; Sawal, K. K. *J. Chem. Soc., Chem. Commun.* **1983**, 400–401.

[16] Barium triflate was prepared by reaction of trifluoromethanesulfonic acid with barium hydroxide in MeOH. Evaporation of the solvent gave the product as white crystals.

[17] Jadamus, H.; Fernando, Q.; Freiser, H. *J. Am. Chem. Soc.* **1964**, *86*, 3056–3059.

Scheme IV



nitrogen results in the loss of symmetry of the Schiff base moiety, which explains the observation of two signals for the imine protons (vide infra). The ^{13}C NMR spectra of **11** and **12** reflect the structures of the macrocycles. The small macrocycles **11a** and **12a** show broad resonances at 154.0 and 154.6, respectively, for Ar C-3 and at 139.0 and 137.6, respectively, for Ar′ C-1. However, in the spectra of the larger macrocycles **11c–e** and **12b** these resonances appear at approximately 151 and 141 ppm. In the small rings of **11a** and **12a** the Schiff base moiety is almost planar, whereas in the larger rings there is a substantial deviation from planarity. For the latter rings this may result in a loss of conjugation, which explains the shift of the ^{13}C NMR signals for the larger macrocycles.

In the mass spectra of the complexes **11** and **12** the signal with the highest *m/e* corresponds to the mass of the salt-free ligand. Fast atom bombardment mass spectrometry of **11e** showed a signal at *m/e* 974 which corresponds to the complex **11e** with loss of one perchlorate anion.

Suitable crystals for X-ray analysis were obtained by allowing petroleum ether 40–60 to diffuse[18] into a methanolic solution of **11c** and **12a**, respectively. The structures of the $Ba(ClO_4)_2$ complex **11c**,[19] which appeared to contain a solvent molecule MeOH, and of the $Ba(CF_3SO_3)_2$ complex **12a** were determined by X-ray crystallography (vide infra) and are shown in Figure 2. In **11c·MeOH** the macrocycle is folded around the barium ion in order to achieve coordination of the cation by all eight oxygens of the host. A perchlorate anion and a methanol oxygen complete the coordination. In **12a**, which has a shorter polyether bridge, also all macrocyclic oxygens coordinate the barium cation, but here the six hetero atoms form an almost planar arrangement. Triflate anions above and below this plane complete the ninefold coordination of the cation. In the Schiff base cavity of **12a** proton transfer from one of the phenolic oxygens to the adjacent imine nitrogen is indeed observed. For **11c·MeOH** these protons could not be located.

Starting from the complexes **11**, **12**, and **13** there are two ways to synthesize the desired compounds **16**, **17**, or **18**, which have an empty polyether cavity and an electrophilic cation coordinated within the Schiff base moiety (Scheme V).

In the first method to obtain the mononuclear nickel, copper, or zinc complexes **16**, **17**, or **18** the barium ion was first removed from the cavity by reaction of the complexes **11**, **12**, or **13** with guanidinium sulfate (excess) in a two-phase system of water and chloroform. The uncomplexed macrocycles **15** are soluble in chloroform, and barium sulfate precipitated, which allowed for an easy isolation of the free macrocycles. The free ligands were obtained as orange oils, of which the larger free macrocycles (*n* = 3, 4, 5) slowly decomposed to form aldehyde **9**. Therefore the second method for the preparation of the corresponding mononuclear transition-metal complexes was more convenient for these larger macrocycles (vide infra).

When the ligands **15** were allowed to react with $Ni(OAc)_2$, $Cu(OAc)_2$, or $Zn(OAc)_2$ in EtOH or MeOH the nickel, copper, or zinc complexes **16**, **17**, and **18** were obtained.

In most cases the mononuclear complexes of the smaller rings (*n* = 1, 2) precipitated during the reaction. The products **16a,f,g**, **17a–c**, and **18a–c** were insoluble in most common solvents, except for DMSO and pyridine. Most of the mononuclear compounds

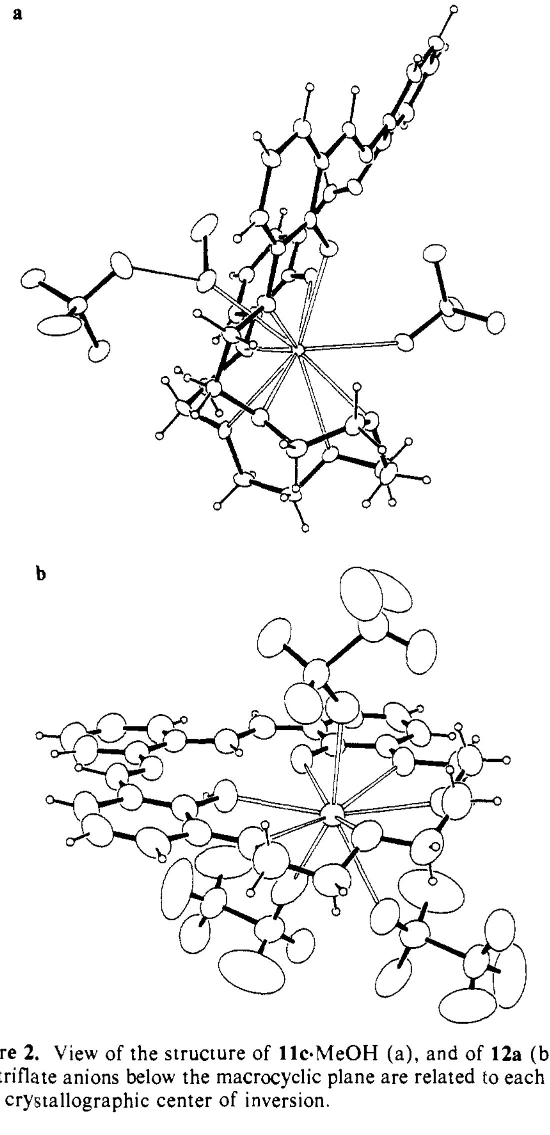


Figure 2. View of the structure of **11c·MeOH** (a), and of **12a** (b); the two triflate anions below the macrocyclic plane are related to each other by a crystallographic center of inversion.

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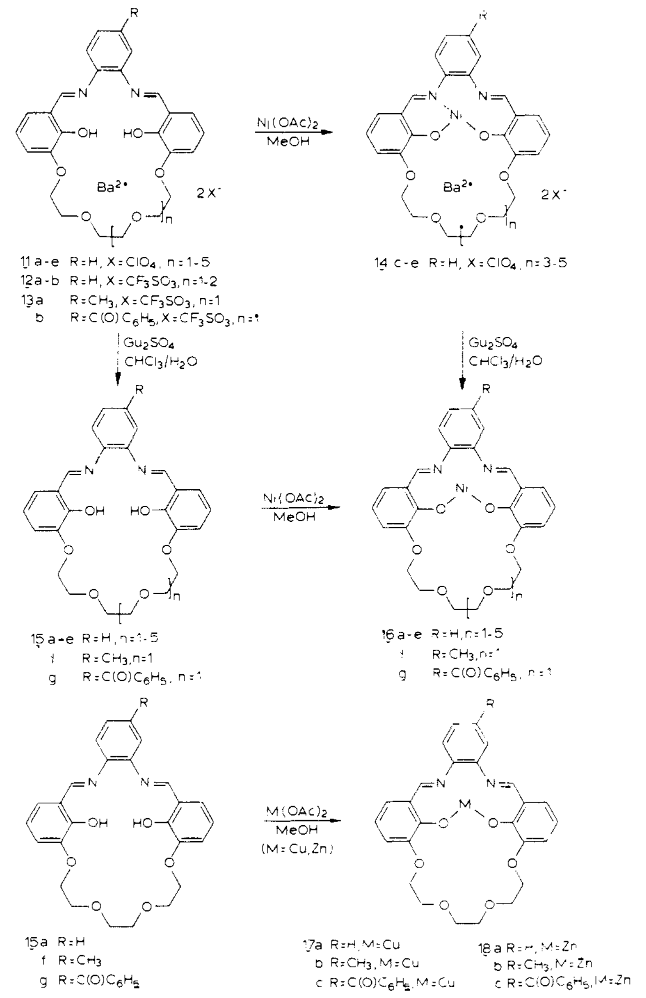
(18) Jones, P. G. *Chem. Brit.* **1981**, *17*, 222–224.

Scheme V



of the small rings contained water of crystallization, as concluded from elemental analysis. For all of the above mentioned nickel, copper, and zinc complexes except **18c**, the molecular ion peak was observed by mass spectroscopy. The nickel complex **16g** proved to be unstable in solution ($CHCl_3$/MeOH) at room temperature, but it could be detected by mass spectrometry. It showed a molecular ion peak at *m/e* 622 with the correct ratio of the nickel isotopes. Also the ^1H NMR spectrum taken immediately after isolation of the product was in agreement with the proposed structure.

In the second approach, which was the most convenient for the larger macrocycles **11c–e**, a solution of the mononuclear barium perchlorate complex **11** in MeOH was treated with a solution of nickel acetate in MeOH to give the hetero-binuclear complexes **14** in 56–82% yield.[19] The binuclear Ni-Ba$(ClO_4)_2$ complexes **14c–e** were subsequently decomplexed by reaction with guanidinium sulfate in $H_2O/CHCl_3$ to form the desired mononuclear nickel complexes **16c–e**. The products were soluble in $CHCl_3$, and the barium ion precipitated as barium sulfate. After evaporation of the solvent the products **16c–e** were obtained as deep-red crystalline products.

In the ^1H and ^{13}C NMR spectra the influence of complexation in either of the two cavities of the macrocycle is rather large. Both in the free macrocycle **15c** and in the mononuclear barium complex **11c** the OH protons were observed as a singlet near δ 13.15 ppm, owing to hydrogen bonding with the imine nitrogen.

The CH=N signal, which in the free macrocycle **15c** was observed at δ 8.60 ppm, shifted to slightly lower field, δ 8.91 ppm, upon complexation of barium perchlorate to give **11c**. This may be due to the electron-withdrawing properties of the Ba^{2+} ion coordinated to the phenolic oxygens. The complexation of barium perchlorate had little influence on the aromatic protons or on the protons of the polyether ring.

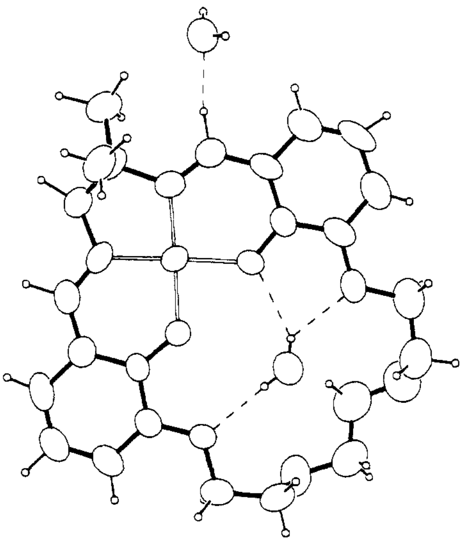
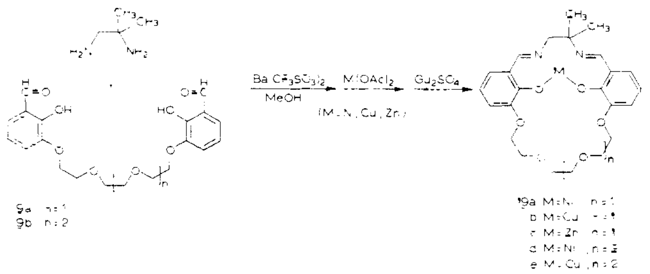


Figure 3. View of the structure of **19a**·H_2O; the two water molecules are symmetry-related.

Scheme VI



Complexation of the Schiff base moiety with Ni^{2+} had a considerable influence on the ^1H NMR spectrum. In the mononuclear complex **16c** the hydroxyl proton was not observed, indicating that deprotonation of the phenolic hydroxyl groups had taken place. The CH=N protons shifted from δ 8.91 ppm in the barium complex **11c** to δ 8.57 ppm in the nickel complex **16c** as a result of the absence of the Ba^{2+} ion in the polyether cavity and the deprotonation of the phenolic hydroxyl groups. It is interesting to note that in the mononuclear nickel complex **16c** the CH=N proton is shifted to higher field than in the corresponding free macrocycle, because the negative charge of the deprotonated phenolic groups is delocalized through the conjugated system to render the CH=N bond more electron rich than in the uncomplexed macrocycle. In the nickel complex, conjugation is possible, because the Schiff base moiety most probably assumes an almost planar conformation (vide infra).

Because of the rather low solubility of most of the mononuclear complexes **16**, **17**, and **18**, we decided to incorporate a nonsymmetrical aliphatic diamine instead of an aromatic diamine, because the lack of symmetry could prevent an easy packing in the crystal and thus increase solubility. In the synthesis of the compounds **19** a slightly modified route was used, because the imine linkage is less stable in this type of compound.[20] The compounds **19** were prepared in high yields in a one-pot synthesis, starting from the dialdehydes **9a,b** and 2-methyl-1,2-propanediamine, using Ba$(CF_3SO_3)_2$ as a template and employing a high dilution reaction (Scheme VI). The resulting barium triflate complexes were reacted in situ with $Ni(OAc)_2$, $Cu(OAc)_2$, or $Zn(OAc)_2$ to give the binuclear complexes. These were isolated, and the barium

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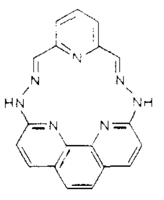
[19] van Staveren, C. J.; Reinhoudt, D. N.; van Eerden, J.; Harkema, S. *J. Chem. Soc., Chem. Commun.* **1987**, 974–977.

[20] *The Chemistry of the Carbon–Nitrogen Double Bond*; Patai, S., Ed.; Interscience: 1970; New York.

Chart II



salt was removed to give the mononuclear complexes **19**. The complexes **19** are readily soluble in $CHCl_3$, except for **19c**. All complexes showed a molecular ion peak in their mass spectra. In the ^1H NMR spectrum the nonsymmetrical nature of the compounds is reflected by two signals for the imine protons.

Deep red crystals suitable for X-ray crystallography were obtained by slow saturation with petroleum ether (bp 40-60 °C) of a solution of **19a** in $CHCl_3$. The crystal structure was determined (vide infra) and is shown in Figure 3. The nickel cation has the well-known square-planar coordination in the Schiff base moiety. The macrocyclic cavity is occupied by a water molecule, which is bound to a phenolic oxygen atom, and to two ether oxygens, via one linear and one bifurcated hydrogen bond. The water oxygen accepts a hydrogen bond from an imine carbon of a neighboring host molecule (or, vice versa, two symmetry-related water molecules are bound to one host, as shown in Figure 3). There is no short contact between the nickel ion and the water oxygen.

Complexation of the Nickel(II) Complexes 16 with Urea. The complexes **16** contain an immobilized electrophilic nickel cation in the Schiff base cavity. From the literature it is known that the enzyme urease, which catalyzes the hydrolysis of urea, probably employs a nickel ion to bind and activate urea in the hydrolysis reaction.[10] There are a few examples of a pentagonal planar coordination of nickel ions in complexes of cyclic ligands in the literature.[21] One example is the complex of Ni^{2+} with the ligand shown in Chart II. It might therefore be possible to induce such a pentagonal planar coordination of the nickel ion in a Schiff base cavity by coordination with urea, which could further be hydrogen bonded to the polyether moiety.

The complexation experiment was carried out by recrystallizing the nickel complexes **16c–e** from a 0.1 M solution of urea in MeOH (excess urea). The melting points of the products were identical with those of the free nickel complexes. In the case of the largest macrocycle, **16e**, in the IR spectrum the urea carbonyl group was observed at 1670 cm^{-1}. For the smaller rings there was no difference between the IR spectra of the macrocycle before and after treatment with urea. Elemental analysis showed that the largest macrocycle (**16e**) had formed a 1:1 complex with urea. An X-ray crystal structure determination showed that indeed a 1:1 complex of urea and the nickel complex **16e** had been formed. However, as shown in Figure 4, urea was not complexed within the macrocyclic cavity in an encapsulated fashion nor coordinated to the nickel ion. Instead three crystallographically equivalent urea molecules are hydrogen bonded to each macrocycle and vice versa.

One urea is coordinated to the polyether moiety in a perching fashion with one NH_2 group forming two hydrogen bonds, and the other NH_2 group forming one hydrogen bond. A second urea forms a bifurcated hydrogen bond with one of the NH protons to two oxygen atoms, whereas the third interaction involves short contacts of a urea oxygen with both an aromatic and an imine proton. Each urea molecule is involved in all three of the above mentioned interactions. In Figure 4 only one macrocycle is drawn for clarity.

Obviously the preferred coordination for the nickel(II) ion is the square-planar coordination, which prevents the cooperative interaction with a urea bound in the polyether cavity. The planar pentagonal coordination required for the cocomplexation of urea with assistance by the polyether moiety is not energetically favorable enough for the nickel cation. Therefore a cation with preferential planar pentagonal coordination was used for further complexation studies.

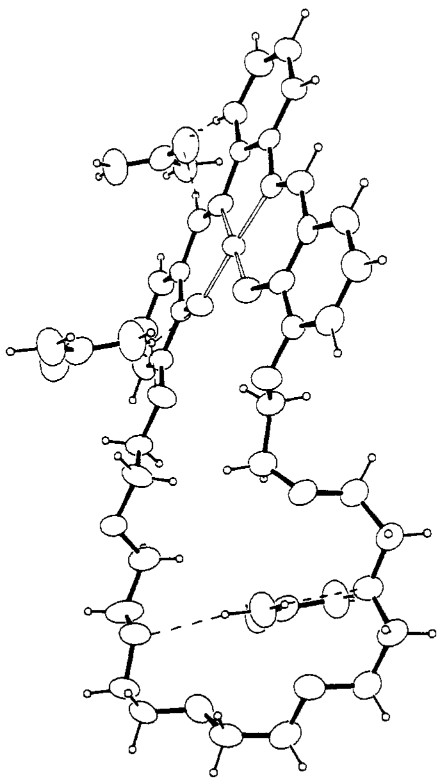
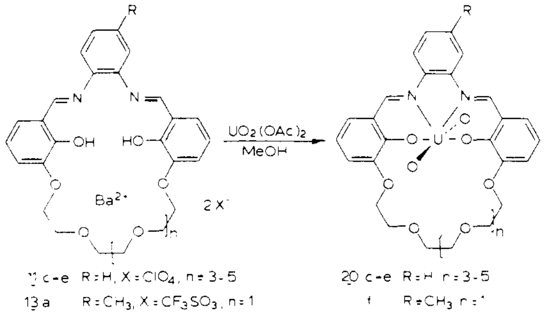


Figure 4. View of the structure of **16e**·urea; the three urea molecules are symmetry-related.

Scheme VII



Uranyl Complexes. Complexes of uranyl salts with neutral ligands such as substituted ureas, ketones, aldehydes, and many other neutral polar molecules are abundant in the literature.[22] Many of the complexes of uranyl salts have a pentagonal bipyramidal structure as determined from X-ray crystal structures.[23] The infrared spectral data of complexes of urea and uranyl salts show that urea is bound through the urea oxygen atom.[24]

Complexes of the uranyl cation with salen (salen = *N*,*N*'-ethylenebis(salicylideneaminato)) type ligands show also that the uranyl ion preferentially forms a pentagonal bipyramidal coordination, with the oxygen atoms at the axial positions. The X-ray structure of the UO_2 complex of salen shows that a molecule of H_2O is coordinated at the fifth equatorial position.[25] In the

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(21) Ansell, C. W. G.; Lewis, J.; Raithby, P. R.; Ramsden, J. N.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1982**, 546–547.

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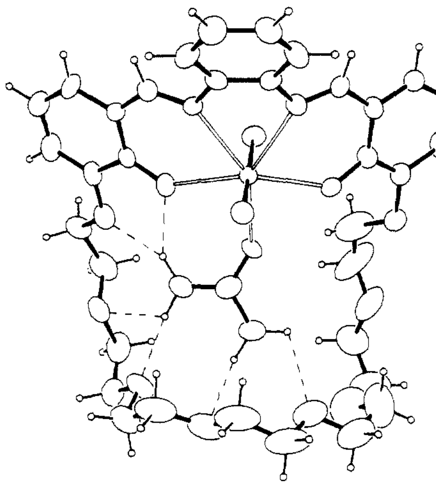

Figure 5. View of the structure of **20e**·urea.

complex of UO_2 with saloph (saloph = *N,N'*-phenylenebis(salicylideneaminato)) a solvent molecule (EtOH or H_2O) also occupies the fifth equatorial position.[26]

A different ligand, derived from a 1,3,5-triketone and ethylenediamine, complexes the uranyl cation with a molecule of dimethyl formamide at the fifth equatorial position.[27] In all the complexes mentioned so far, the uranyl cation is coordinated in a pentagonal bipyramid.

Therefore we decided to use the uranyl cation as the electrophile in the Schiff base cavity. Reaction of the $Ba(ClO_4)_2$ complexes **11** with uranyl acetate in refluxing methanol yielded the hydrated uranyl complexes **20** as deep red crystals that formed after cooling to room temperature and partial evaporation of the solvent (Scheme VII). The mass spectra of the complexes show a molecular ion peak that corresponds to an m/e of the deprotonated macrocycle plus UO_2, which indicates that the uranyl cation is tightly bound to the macrocycle. In the NMR spectrum (DMSO-d_6) the signal for the phenolic hydroxyl groups is absent, indicating that the phenolic OH groups are deprotonated. Moreover, in the IR spectra the absorption of the C=N bonds is located at 1600–1602 cm^{-1}. These observations indicate that the uranyl cation occupies the Schiff base cavity (Scheme VII).

When the uranyl complex **20e** was treated with guanidinium sulfate in a two-phase system of chloroform and water, no barium sulfate was formed. Therefore we concluded that the barium perchlorate is no longer present in the complex. The decomplexation of $Ba(ClO_4)_2$ during the complexation of UO_2^{2+} is probably due to the large size of the UO_2^{2+} cation. For the X-ray crystal structures of UO_2^{2+} complexes of salen type ligands O···O distances of 4.29 Å were reported.[25,26] Therefore the electrostatic repulsion that results from the complexation of UO_2^{2+} may cause the decomplexation of the barium cation. The IR spectrum of the UO_2^{2+} complexes **20** show strong absorptions at 897–900 cm^{-1} (ν_{as}(O–U–O)) and 1600–1602 cm^{-1} (ν(C=N)).

When a solution of the uranyl complex **20e** in MeOH was treated with 1 equiv of urea in MeOH, the 1:1 complex of **20e** and urea precipitated immediately as a red powder, mp 247–249 °C. The NMR spectrum (DMSO-d_6) shows a broad singlet at 5.4 ppm indicating the presence of urea. The mass spectrum exhibited a signal at m/e 906.299 which corresponds to the mass of the uranyl complex without urea. However, a strong signal at m/e = 60.0257 was present which was not observed for the complex **20e**. Satisfactory elemental analysis for the 1:1 complex **20e**·urea was obtained.' In the IR spectrum strong absorptions are present at 1640 cm^{-1} (ν(C=O)), 1602 cm^{-1} (ν(C=N)), and 896 cm^{-1} (ν_{as}(O–U–O)). The signal at 1640 cm^{-1} is in agreement with the C=O stretching frequency of complexes of urea and uranyl salts reported in the literature.[22] This indicates that the urea molecule is bound via the carbonyl oxygen atom and that a strong interaction is present.

Table I. Infrared Spectral Data (cm^{-1}) for the Complexes of **20** with Neutral Guests

	host			
guest	none	**20c**	**20d**	**20e**
formamide	1680	*a*	1670	1671
acetamide	1685	*a*	*a*	*a*
urea	1683	1630	1630	1640
N-methylurea	1650	*a*	*a*	1639
(2-pyridylmethyl)urea	1664	*a*	*b*	1642
acetone	1700	*b*	*a*	*a*
DMSO	1050	*a*	*a*	1005

[a] No crystalline products isolated. [b] Not attempted.

An X-ray crystal structure determination carried out for this compound (vide infra) proved that urea is coordinated within the macrocyclic cavity (Figure 5). The uranyl cation, owing to its size opens up the Schiff base moiety, allowing the approach of the urea carbonyl oxygen, resulting in a pentagonal planar coordination of the cation. Urea is also coordinated to one of the phenolate oxygens and to five oxygen atoms of the polyether chain via hydrogen bonds donated by the NH_2 groups. The result is a highly structured complex with a large number of host–guest interactions.

The structure of the urea–uranyl complex **20e**·urea confirms that it is possible to complex a neutral molecule within a macrocyclic ligand that possesses an immobilized electrophilic cation, provided that the geometry of the coordination of the cation is in agreement with the geometry necessary for the complexation of the neutral guest.

Complexation of the Uranyl Complexes 20 with Neutral Guests. In order to demonstrate the scope and the selectivity of the UO_2 complexes **20** in the complexation of neutral polar molecules, the complexation of the UO_2 complexes **20** with other neutral guests to form ternary complexes was studied. From the X-ray crystal structure of the complex of urea and **20e**, we know that the guest molecule is bound not only through a coordinative bond of the carbonyl oxygen atom to the electrophilic uranyl cation but also by hydrogen bonds of the NH_2 groups to the polyether oxygens. Therefore both substituted urea derivatives and amides were used as guest species for the UO_2 complexes **20**. Furthermore, acetone and DMSO were tested for their ability to form a complex with the UO_2 complexes.

In some cases a complex crystallized immediately, otherwise the mixtures were left overnight, and when crystals were formed these were filtered off and analyzed. In all cases the melting points of the complexes with the neutral guests were higher than of the corresponding ligands **20**. This probably reflects the increased rigidity of the complexed, relative to the uncomplexed species.

All elemental analyses were in agreement with the formation of 1:1 complexes, and in the mass spectra both the molecular ion peak of the complexes **20** and of the guest molecules were observed. When the spectra of the "uncomplexed" ligand **20** and the corresponding complexes with the neutral guests are compared, it is clear that the peaks corresponding to the guest molecules are not observed in the mass spectrum of the "uncomplexed" host, i.e., these signals are not the result of fragmentation of **20**.

The complexes of **20** and the neutral guests are only slightly soluble in most common solvents. The 200 MHz ^{1}H NMR spectra in DMSO-d_6 showed the signals of both host and guest. In general no chemical shift differences for the complexes were observed relative to the "free" uranyl complexes.

In the infrared spectra (KBr pellets) of the complexes the absorptions for the guest molecules are observed. The complexes of formamide, urea, *N*-methylurea, and (2-pyridylmethyl)urea exhibit a C=O stretching frequency at lower frequency relative to the uncomplexed guest species. This indicates a strong interaction between the guest molecule and the electrophilic uranyl

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Table II. Metal Cation Coordination in the Crystal Structures[e]

compd	**2**	**11c**-MeOH	**12a**	**19a**·H_2O	**16e**·urea	**20e**·urea
cation	Li^+	Ba^{2+}	Ba^{2+}	Ni^{2+}	Ni^{2+}	UO_2^{2+}
ligand						
O_{ether}	1.98	2.84–2.99	2.82–2.86			
O_{phen}[a]		2.72–2.75	2.70	1.85–1.87	1.82	2.24–2.30
O_{urea}	1.90–1.95					2.37
N	2.20			1.86–1.88	1.84–1.85	2.55–2.59
coord number	4	10[b]	9[c]	4	4	7[d]

[a] O_{phen} = phenolic or phenolate oxygen. [b] Including a methanol oxygen ($Ba^{2+}\cdots O$ 2.81 Å) and a perchlorate oxygen ($Ba^{2+}\cdots O$ 2.74 Å). [c] Including three triflate oxygens ($Ba^{2+}\cdots O$ 2.71–2.85 Å). [d] Including the two uranyl oxygens ($U\cdots O$ 1.78 Å). [e] Range of cation–ligand distances (Å) and coordination numbers. Data of **2** and **11c**·MeOH are included for comparison.

cation. Similarly in the DMSO complex a shift of the S=O stretching frequency was observed (Table I).

The interaction of the polar guest molecules with the uranyl cation is clearly not the only important interaction between host and guest. The effect of the polyether ring is obvious, because a certain degree of selectivity was observed. The largest macrocycle **20e** forms complexes with *N*-methylurea, (2-pyridylmethyl)urea and DMSO, whereas these guests are not encapsulated by the smaller macrocycles. However, the smaller guest molecules urea and formamide are complexed by both the smaller and the larger macrocyclic ligands.

X-ray Structures. The structures of the compounds **12a**, **19a**·H_2O, **16e**·urea, and **20e**·urea were determined by X-ray crystallography. Details of the structure determinations are in the Experimental Section. ORTEP[28] views of the structures are shown in Figures 2b–5. Metal coordination is depicted by open bonds; hydrogen bonds are indicated by dashed lines. Table II contains data on the metal cation coordination. The structures of **2**[7] and of **11c**·MeOH[19] (Figures 1 and 2a) are included in the discussion for comparison.

In the structure of **2** the Li^+ has a fourfold coordination which is approximately tetrahedral, very similar to that observed for complexes of crown ethers with hydrated lithium salts.[29] In all cases Li^+ is four- or five-coordinated to adjacent hetero atoms of the host and oxygen atoms of the anion or of the neutral guest molecule (urea or water), which can be hydrogen bonded in the remaining part of the macrocyclic host.

In the structure of **11c**·MeOH, Ba^{2+} is tenfold coordinated by eight oxygen atoms of the macrocyclic host, a perchlorate anion, and a methanol oxygen. The Schiff base moiety exhibits a rather large distortion (angles between adjacent aromatic rings are 25° and 27°) in order to allow the phenolic oxygens to participate in the coordination of the Ba^{2+}. The folding of the macrocycle around the barium has also been observed in the complex of dibenzo-24-crown-8 with barium perchlorate,[30] where all eight macrocyclic oxygens and two perchlorate anions coordinate Ba^{2+}. Complexes of linear polyethers with alkaline earth metal ions[31] show also a folding of the ether chain around the cation and additional coordination by anion and solvent.

The six macrocyclic oxygens of **12a** are within 0.14 Å of their mean plane. The barium cation is displaced by 0.46 Å out of this plane toward the two triflate anions (which are symmetry-related to each other) on one side of the macrocyclic plane. At the other side only one anion can approach the cation within coordinating distance. This combination of equatorial coordination by a crown ether and apical coordination by the anion and possibly a water molecule has been observed before times for barium.[32] In all cases there is a hexagonal planar coordination, with three or four apical ligands. The macrocyclic cavity of **12a** is slightly too small for a perfect fit of the Ba^{2+} cation, resulting in a displacement of the cation out of the mean ligand plane. If the cavity is even smaller, the displacement will be larger, and optimal coordination is then achieved by sandwiching the cation with two hosts.[33] In **12a** the distortion of the Schiff base moiety is small, and the two angles between adjacent aromatic rings are 5° and 10°, contrary to the observation for **11c**·MeOH, where the macrocycle is too large and is distorted by coordination. In the Schiff base cavity of **12a** the two protons were located. One is located on an imine nitrogen, the other on the phenolic oxygen. These protons have short contacts with the unprotonated hetero atoms in the Schiff base cavity. The $O\cdots N$ distances are 2.63 and 2.64 Å and the $O–H\cdots N$ or $N–H\cdots O$ angles are 142° and 139°, respectively.

In both the structures of **19a**·H_2O and **16e**·urea, the nickel ion has a square-planar coordination. It is within 0.01 Å of the mean plane of its four ligands. In both cases a neutral guest molecule is included in the crystal. The host–guest interactions consist of hydrogen bonds, donated by O–H or N–H groups of the guest, to macrocyclic oxygens, and of short contacts between C–H groups of the host and the oxygen atoms of the guests, which can be denoted as $C–H\cdots O$ hydrogen bonds.[34] There is no short contact between the nickel cation and the oxygen atom of the guest, which therefore is hydrogen bonded to another host, as this oxygen cannot be coordinated in the macrocyclic cavity. This explains the 2:2 host–guest interaction stoichiometry for **19a**·H_2O and the 3:3 ratio for **16e**·urea, instead of a 1:1 ratio, expected for an encapsulated complex. From the distance between the phenolate oxygens, 2.51 Å (**19a**·H_2O) and 2.44 Å (**16e**·urea), it is clear that there is no space for a fifth equatorial ligand to achieve a pentagonal planar coordination. This short distance is due to the presence of the nickel cation. When the Schiff base moiety is not complexed, larger distances are found, due to the repulsion of the phenolic oxygens, 3.01 Å (**11c**·MeOH) and 2.86 Å (**12a**). The optimal fit of the nickel ion in the Schiff base cavity is also reflected in the nearly planar conformation of this moiety in the structure of **16e**·urea, with angles between adjacent aromatic rings of 6° and 9°. Apical coordination of Ni^{2+} has been observed[35] and is sterically possible here but seems unfavorable without additional coordination of the guest by the polyether chain, which would have to fold backwards to achieve this.

In the structure of **20e**·urea a pentagonal planar coordination of the cation is possible, owing to the large size of the uranyl ion. The distance between the phenolate oxygens is 4.44 Å, which facilitates an equatorial approach of the urea carbonyl oxygen. The urea comes within normal coordination distance (2.37 Å)[23] of the cation, with a $C{=}O\cdots U$ angle of 141°,[9] and an angle between the plane of urea and the $U\cdots O$ bond of 26°, which is a rather large value.[9] It has distances to the two phenolate oxygens

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of 2.89 and 2.98 Å, while values of 2.81–3.18 have been reported for such geometries.[25,26,36] The five equatorial ligands are within 0.13 Å of their mean plane, from which the uranium is displaced by 0.04 Å. The deformation of the Schiff base moiety is reflected in values of 37° and 46° for the angles between adjacent aromatic rings. As a result, the polyether chain attached to this moiety does not have the optimal orientation to encapsulate the urea molecule, and the hydrogen bonds between the ether oxygens and urea are rather nonlinear. Thus, as a compromise, the coordination of urea both to the uranyl cation and to the polyether bridge is not optimal. The uranyl cation is slightly distorted from linearity[37] with a O–U–O angle of 176.6 (2)°.

Conclusions

An electrophilic metal cation can assist in the complexation of neutral molecules with macrocyclic ligands. The electrophilic metal cation can either be added as a third component to the neutral guest and the ligand, as was shown in the synthesis of 2,6-pyrido-27-crown-9·urea·LiClO$_4$ (1:2:1), or it can be immobilized in the macrocycle as in the macrocycles that contain a salen moiety. By synthesizing the nickel–urea complex **16e** we have shown that a cation that prefers a square-planar coordination is not satisfactory for the formation of an encapsulated ternary complex in these ligands. The formation of the UO$_2$–urea complex proves that encapsulation of the guest results in both coordination of the neutral guest to the metal ion and in hydrogen bonding with the polyether moiety when the cation prefers a pentagonal planar coordination. The interaction of the neutral guest with the metal cation is rather strong as observed by infrared spectroscopy. The hydrogen bonding with the polyether ring determines the shape selectivity.

Experimental Section

Caution. Although during these experiments no accidents have occurred, extreme care should be taken when perchlorates are handled, because they may explode spontaneously and may be sensitive to shock. The perchlorates should only be prepared in small quantities.

Melting points were determined with a Reichert melting point apparatus and are uncorrected. The ^{1}H NMR spectra were recorded with Bruker WP-80 or Nicolet NT-200 WB spectrometers in CDCl$_3$ or DMSO-d_6, and the ^{13}C NMR spectra were recorded with a Nicolet NT-200 WB spectrometer, with Me$_4$Si as an internal standard. Mass spectra were obtained with a Varian Mat 311A. Elemental analyses were carried out by the department of analytical chemistry. Infrared spectra were recorded with a Perkin Elmer 257 spectrophotometer

Materials. All chemicals were reagent grade and were used without further purification.

2,6-Pyrido-27-crown-9·LiClO$_4$·urea (1:1:2) (2). 2,6-Pyrido-27-crown-9 (0.429 g, 1.0 mmol), urea (0.120 g, 2.0 mmol), and LiClO$_4$ (0.106 g, 1.0 mmol) were dissolved in 10 mL of refluxing ethanol. The solvent was allowed to evaporate slowly at room temperature until crystals were formed. The crystals were filtered off and washed with cold ethanol: yield 80%; mp 107–109 °C; ^{1}H NMR (CDCl$_3$) δ 7.9–7.2 (m, 3 H, ArH), 4.73 (s, 4 H, ArCH$_2$), 3.8–3.2 (m, 28 H, CH$_2$O); ^{13}C NMR (CDCl$_3$) δ 161.9 (C-NH$_2$), 157.1 (Ar C-2, C-6), 138.1 (Ar C-4), 120.8 (Ar C-3, C-5), 73.1 (ArCH$_2$), 70.1–69.1 (CH$_2$). Anal. Calcd for C$_{23}$H$_{43}$ClLiN$_5$O$_{14}$: C, 42.11; H, 6.61; N, 10.68. Found: C, 42.36; H, 6.59; N, 10.63.

2-(2-Propenyloxy)-3-hydroxybenzaldehyde (7). To a mixture of 10.00 g (0.072 mol) of 2,3-dihydroxybenzaldehyde in 150 mL of DMSO was added 2.20 g (0.073 mol) of NaH (80% in oil) which was washed with petroleum ether 40–60 before use. The mixture was stirred at room temperature for 1 h, and subsequently 8.7 g (0.073 mol) of 3-bromo-1-propene was added. The mixture was stirred for 20 h. The product was poured into 250 mL of water and was extracted with 3 × 200 mL of CHCl$_3$. The organic phase was washed with 3 × 100 mL of water. After drying on MgSO$_4$, the organic phase was concentrated, and the product was purified by chromatography (silica gel/CHCl$_3$) and recrystallization from petroleum ether (bp 40–60 °C)/ether 95/5: yield 60%; mp 80–81 °C; ^{1}H NMR (CDCl$_3$) δ 10.26 (s, 1 H, CHO), 7.5–7.0 (m, 3 H, ArH), 6.3–5.8 (m, 1 H, =CH), 5.86 (s, 1 H, OH), 5.6–5.2 (m, 2 H, CH$_2$), 4.7–4.5 (m, 2 H, CH$_2$); ^{13}C NMR (CDCl$_3$) δ 190.3 (CHO), 149.8, 148.3 (Ar C-2, C-3), 132.5 (=CH), 129.4 (Ar C-1), 124.9, 122.3, 121.0 (Ar C-4, C-5, C-6), 119.9 (=CH$_2$), 77.0 (OCH$_2$); mass spectrum, m/e 178.064 (M$^+$; calcd 178.063). Anal. Calcd for C$_{10}$H$_{10}$O$_3$: C, 67.41; H, 5.66. Found: C, 67.09; H, 5.75.

3,3′-(3,6,9,12-Tetraoxatetradecane-1,14-diyldioxy)bis(2-(2-propenyloxy)benzaldehyde) (8a). A mixture of 1.78 g (0.01 mol) of 2-(2-propenyloxy)-3-hydroxybenzaldehyde and 2.72 g (0.005 mol) of pentaethylene glycol ditosylate was refluxed for 16 h in 50 mL of CH$_3$CN containing 1.38 g (0.01 mol) of K$_2$CO$_3$. After cooling, the mixture was filtered from salts, and the solvent was evaporated. The product was purified by chromatography to give an oil: yield 71%; ^{1}H NMR (CDCl$_3$) δ 10.43 (s, 2 H, CHO), 7.5–6.9 (m, 6 H, ArH), 6.4–5.8 (m, 2 H, =CH), 5.5–5.1 (m, 4 H, CH$_2$), 4.8–4.6 (m, 4 H, CH$_2$), 4.3–3.8 (m, 8 H, OCH$_2$), 3.7–3.6 (m, 12 H, OCH$_2$); ^{13}C NMR (CDCl$_3$) δ 190.3 (CHO), 152.1, 151.5 (Ar C-2, C-3), 133.3 (=CH), 130.1 (Ar C-1), 124.0, 119.6, 119.4 (Ar C-4, C-5, C-6), 118.8 (=CH$_2$), 75.0 (OCH$_2$), 70.8–68.6 (OCH$_2$); mass spectrum, m/e 558.247 (M$^+$; calcd 558.247).

3,3′-(3,6,9,12,15-Pentaoxaheptadecane-1,17-diyldioxy)bis(2-(2-propenyloxy)benzaldehyde) (8b). The compound **8b** was synthesized by using the same procedure as for **8a**, from 2-(2-propenyloxy)-3-hydroxybenzaldehyde and hexaethylene glycol ditosylate, to give an oil: yield 68%; ^{1}H NMR (CDCl$_3$) δ 10.44 (s, 2 H, CHO), 7.4–7.0 (m, 6 H, ArH), 6.3–5.8 (m, 2 H, =CH), 5.5–5.1 (m, 4 H, CH$_2$), 4.8–4.6 (m, 4 H, CH$_2$), 4.3–3.7 (m, 8 H, OCH$_2$), 3.7–3.6 (m, 16 H, OCH$_2$); ^{13}C NMR (CDCl$_3$) δ 190.3 (CHO), 152.1, 151.5 (Ar C-2, C-3), 133.3 (=CH), 130.1 (Ar C-1), 123.9, 119.7, 119.4 (Ar C-4, C-5, C-6), 118.7 (=CH$_2$), 75.0 (OCH$_2$), 70.7–68.6 (OCH$_2$); mass spectrum, m/e 602.266 (M$^+$; calcd 602.273).

3,3′-(3,6,9,12,15,18-Hexaoxaeicosane-1,20-diyldioxy)bis(2-(2-propenyloxy)benzaldehyde) (8c). The compound **8c** was synthesized by using the same procedure as for **8a**, from 2-(2-propenyloxy)-3-hydroxybenzaldehyde and heptaethylene glycol ditosylate, to give an oil: yield 64%; ^{1}H NMR (CDCl$_3$) δ 10.44 (s, 2 H, CHO), 7.5–6.9 (m, 6 H, ArH), 6.4–5.8 (m, 2 H, =CH), 5.5–5.1 (m, 4 H, CH$_2$), 4.8–4.6 (m, 4 H, CH$_2$), 4.3–3.8 (m, 8 H, OCH$_2$), 3.7–3.6 (m, 20 H, OCH$_2$); ^{13}C NMR (CDCl$_3$) δ 190.2 (CHO), 152.1, 151.5 (Ar C-2, C-3), 133.3 (=CH), 130.1 (Ar C-1), 123.9, 119.6, 119.4 (Ar C-4, C-5, C-6), 118.7 (CH$_2$), 74.9 (OCH$_2$), 70.8–68.5 (OCH$_2$); mass spectrum, m/e 646.304 (M$^+$; calcd 646.299).

3,3′-(3,6-Dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) (9a). To a suspension of NaH under N$_2$ (2.64 g, 0.11 mol) in 25 mL of dry DMSO a solution of 2,3-dihydroxybenzaldehyde (6.95 g, 0.050 mol) in 25 mL of dry DMSO was added over a period of 2 h, under vigorous stirring. The temperature was kept below 25 °C. After stirring for 1 h triethylene glycol ditosylate (11.45 g, 0.025 mol) was added in 1 portion. This mixture was stirred for 24 h. Subsequently 300 mL of water was added, and the resulting dark brown solution was extracted twice with CHCl$_3$. These organic layers contain only small amounts of unreacted ditosylate and were thrown away. The aqueous layer was acidified with 6 M HCl to pH = 1 and extracted with CHCl$_3$ (3 × 50 mL). These combined organic layers were well washed with 1 M HCl and dried over MgSO$_4$. After removal of the solvent a crude product was obtained which was purified by column chromatography (silica gel, CHCl$_3$) to give the product as a slightly yellow solid in 61% yield: mp 98–99 °C (MeOH/petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 10.81 (s, 2 H, OH), 9.94 (s, 2 H, CHO), 7.3–6.8 (m, 6 H, ArH), 4.3–4.1 (m, 4 H, ArOCH$_2$), 4.0–3.8 (m, 4 H, OCH$_2$), 3.77 (s, 4 H, OCH$_2$); ^{13}C NMR δ 195.9 (CHO), 152.1 (Ar C-2), 147.4 (Ar C-3), 125.0, 121.0, 119.4 (Ar C-4-C-6), 121.2 (Ar C-1), 70.9, 69.6, 69.4 (OCH$_2$); mass spectrum, m/e 390.132 (M$^+$; calcd 390.132); IR (KBr) 1650 (C=O) cm^{-1}. Anal. Calcd for C$_{20}$H$_{22}$O$_8$: C, 61.53; H, 5.68. Found: C, 61.32; H, 5.64.

3,3′-(3,6,9-Trioxaundecane-1,11-diyldioxy)bis(2-hydroxybenzaldehyde) (9b). This compound was prepared from 2,3-dihydroxybenzaldehyde and tetraethylene glycol ditosylate, by using the same procedure and the same scale as for compound **9a**. The crude product was purified by column chromatography (silica gel, CHCl$_3$:MeOH = 99:1) to give the product as a slightly yellow solid in 63% yield: mp 81–82 °C (MeOH/petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 10.78 (br s, 2 H, OH), 9.94 (s, 2 H, CHO), 7.3–6.8 (m, 6 H, ArH), 4.2–4.1 (m, 4 H, ArOCH$_2$), 3.9–3.7 (m, 12 H, OCH$_2$); ^{13}C NMR δ 195.8 (CHO), 152.3 (Ar C-2), 147.5 (Ar C-3), 125.0, 121.8, 119.4 (Ar C-4-C-6), 121.4 (Ar C-1), 70.9, 70.6, 69.7, 69.5 (OCH$_2$); mass spectrum, m/e 434.153 (M$^+$; calcd 434.158; IR (KBr 1645 (C=O) cm^{-1}. Anal. Calcd for C$_{22}$H$_{26}$O$_9$: C, 60.82; H, 6.03. Found: C, 60.74; H, 5.97.

3,3′-(3,6,9,12-Tetraoxatetradecane-1,14-diyldioxy)bis(2-hydroxybenzaldehyde) (9c). To 40 mL of water under N$_2$ were added 0.5 g of 5% Pd/C and 0.1 mL of 70% HClO$_4$. Subsequently a solution of 5 g of the condensation product of 2-(2-propenyloxy)-3-hydroxybenzaldehyde and pentaethylene glycol ditosylate (**8a**) in 160 mL of methanol was

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added. The mixture was refluxed for 48 h. The catalyst was filtered off, and most of the solvent was evaporated. The residue was mixed with water and extracted with $CHCl_3$, the organic phase was dried over $MgSO_4$, and the solvent was evaporated to yield an oil which slowly solidified on standing: yield 85%; ^{1}H NMR ($CDCl_3$) δ 10.78 (s, 2 H, OH), 9.94 (s, 2 H, CHO), 7.3–6.8 (m, 6 H, ArH), 4.3–3.7 (m, 8 H, OCH_2), 3.7–3.6 (m, 12 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 195.3 (CHO), 151.9 (Ar C-2), 147.3 (Ar C-3), 124.2, 120.3, 119.3 (Ar C-4, C-5, C-6), 121.3 (Ar C-1), 70.6–68.9 (OCH_2); mass spectrum, *m/e* 478.188 (M^+; calcd 478.184).

3,3′-(3,6,9,12,15-Pentaoxaheptadecane-1,17-diyldioxy)bis(2-hydroxybenzaldehyde) (9d). Compound **9d** was synthesized from **8b** by using the same procedure as for the synthesis of **9c**, to give an oil: yield 88%; ^{1}H NMR ($CDCl_3$) δ 10.80 (s, 2 H, OH), 9.95 (s, 2 H, CHO), 7.3–6.8 (m, 6 H, ArH), 4.3–3.7 (m, 8 H, OCH_2) 3.7–3.6 (m, 16 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 195.5 (CHO), 152.0 (Ar C-2), 147.4 (Ar C-3), 124.4, 120.4, 119.3 (Ar C-4, C-5, C-6), 121.4 (Ar C-1), 70.8–69.0 (OCH_2); mass spectrum, *m/e* 522.202 (M^+; calcd 522.210).

3,3′-(3,6,9,12,15,18-Hexaoxaeicosane-1,20-diyldioxy)bis(2-hydroxybenzaldehyde) (9e). Compound **9e** was synthesized from **8c** by using the same procedure as for the synthesis of **9c**, to give an oil: yield 85%; ^{1}H NMR ($CDCl_3$) δ 10.79 (s, 2 H, OH), 9.96 (s, 2 H, CHO), 7.3–6.8 (m, 6 H, ArH), 4.3–3.7 (m, 8 H, OCH_2), 3.7–3.6 (m, 20 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 195.8 (CHO), 152.1 (Ar C-2), 147.4 (Ar C-3), 124.9, 120.9, 119.4 (Ar C-4, C-5, C-6), 121.3 (Ar C-1), 70.7–69.3 (OCH_2); mass spectrum, *m/e* 566.236 (M^+; calcd 566.236).

3,3′-(3,6,9,12-Tetraoxatetradecane-1,14-diyldioxy)bis(2-hydroxybenzaldehyde)barium(2+) Diperchlorate (10c). A solution of 0.478 g (1 mmol) of the ligand **9c** in EtOH/MeOH (4:1 v/v) and a solution of 0.336 g (1 mmol) of $Ba(ClO_4)_2$ in EtOH were mixed and allowed to stand overnight at room temperature. The product crystallized and was filtered off: yield 84%; mp 234–235 °C; ^{1}H NMR (DMSO-d_6) δ 10.22 (s, 2 H, CHO), 7.3–6.7 (m, 6 H, ArH), 4.2–3.6 (m, 8 H, OCH_2), 3.6–3.4 (m, 12 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 192.8 (CHO), 150.9 (Ar C-2), 147.4 (Ar C-3), 122.3 (Ar C-1), 121.2, 119.4, 119.2 (Ar C-4, C-5, C-6), 69.9–68.6 (OCH_2); mass spectrum, *m/e* 478 ($M^+ - Ba(ClO_4)_2$; calcd 478). No satisfactory analysis was obtained.

3,3′-(3,6,9,12,15-Pentaoxaheptadecane-1,17-diyldioxy)bis(2-hydroxybenzaldehyde)barium(2+) Diperchlorate (10d). A solution of 0.522 g (1 mmol) of the ligand **9d** in EtOH/MeOH (4:1 v/v) and a solution of 0.336 g (1 mmol) of $Ba(ClO_4)_2$ in EtOH were mixed and left overnight at room temperature. The product crystallized and was filtered off: yield 72%; mp 170–172 °C; ^{1}H NMR (DMSO-d_6) δ 11.09 (s, 2 H, OH), 9.96 (s, 2 H, CHO), 7.4–6.9 (m, 6 H, ArH), 4.3–3.7 (m, 8 H, OCH_2), 3.7–3.6 (m, 16 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 192.2 (CHO), 150.4 (Ar C-2), 146.9 (Ar C-3), 121.9 (Ar C-1), 120.7, 119.0, 118.7 (Ar C-4, C-5, C-6), 69.4–68.2 (OCH_2); mass spectrum, *m/e* 522.201 ($M^+ - Ba(ClO_4)_2$; calcd 522.210). Anal. Calcd for $C_{26}H_{34}BaCl_2O_{19}$: C, 36.36; H, 3.99. Found: C, 36.38; H, 4.19.

General Procedure for the Preparation of the Barium Complexes 11a, 12a, 12b, 13a, and 13b. Method A1. To a refluxing solution of $Ba(CF_3SO_3)_2$ or $Ba(ClO_4)_2$ in MeOH (0.01 M) were added a solution of 1 equiv of the dialdehyde **9a** or **9b** in THF (0.1 M) and a solution of 1 equiv of the appropriate aromatic diamine in MeOH (0.1 M) dropwise over a period of several hours (1–3, depending on the scale). After the addition was complete the solution was refluxed for 0.5 h.

General Procedure for the Synthesis of $Ba(ClO_4)_2$ Complexes 11. Method B1. A solution of 1.0 mmol of the $Ba(ClO_4)_2$ complex **10** in 100 mL of MeOH and a solution of 1.0 mmol of 1,2-benzenediamine in 100 mL of MeOH were added dropwise to 100 mL of refluxing MeOH over 3 h. After the addition was complete, the mixture was refluxed for 30 min. The orange solution was concentrated to 150 mL, and 100 mL of petroleum ether 40–60 was added. The product crystallized and was filtered off.

(9,10,12,13,15,16-Hexahydro-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diol-O^8,O^{11},O^{14},O^{17},O^{29},O^{30})bariun(2+) Diperchlorate (11a). This reaction was carried out according to method A1 by using $Ba(ClO_4)_2$ (3.94 g, 11.71 mmol), the dialdehyde **9a** (4.57 g, 11.71 mmol), and 1,2-benzenediamine (1.27 g, 11.71 mmol). The barium complex crystallized during the reaction. After the reaction was complete, the reaction mixture was slowly cooled to room temperature, and the orange precipitate was filtered off and was washed twice with MeOH: yield 62%; mp > 320 °C; ^{1}H NMR (DMSO-d_6) δ 14.1 (br s, 2 H, OH), 9.13, 9.10 (s, 1 H, N=CH), 7.8–7.6 (m, 2 H, Ar′H), 7.6–7.4 (m, 2 H, Ar′H), 7.3–7.1 (m, 4 H, ArH), 7.0–6.8 (m, 2 H, ArH), 4.3–4.1 (m, 4 H, $ArOCH_2$), 4.0–3.8 (m, 4 H, OCH_2), 3.70 (s, 4 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 163.8 (N=CH), 154.0 (Ar C-3), 147.4 (Ar C-2), 139.0 (Ar′ C-1, C-2), 128.4, 124.6, 119.0, 117.8, 115.5 (Ar C-4-C-6, Ar′ C-3-C-6), 117.9 (Ar C-1), 69.8, 68.6, 67.2 (OCH_2); mass spectrum, *m/e* 462.179 ($M^+ - Ba(ClO_4)_2$; calcd 462.179); IR (KBr) 3440 (OH), 1622 (N=C) cm^{-1}.

(9,10,12,13,15,16,18,19,21,22-Decahydro-3,7:24,28-dimetheno-8,11,14,17,20,23,1,30-benzohexaoxadiazacyclodotriacontine-35,36-diol-O^8,O^{11},O^{14},O^{17},O^{20},O^{23},O^{35},O^{36})barium(2+) Diperchlorate (11c). Compound **11c** was synthesized by using **10c**, according to method B1, to give an orange crystalline product: yield 65%; mp 270–274 °C; ^{1}H NMR (DMSO-d_6) δ 13.13 (s, 2 H, OH), 8.91 (s, 2 H, CH=N), 7.43 (s, 4 H, Ar′H), 7.3–6.7 (m, 6 H, ArH), 4.2–3.7 (m, 8 H, OCH_2), 3.6–3.5 (m, 12 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 164.3 (CH=N), 150.5 (Ar C-3), 146.6 (Ar C-2), 141.5 (Ar′ C-1, C-2), 127.5, 124.2 (Ar C-6, Ar′ C-4, C-5), 118.8 (Ar C-1), 119.2, 118.1, 116.8 (Ar C-4, C-5, Ar′ C-3, C-6), 69.9–67.9 (OCH_2); mass spectrum, *m/e* 550.228 ($M^+ - Ba(ClO_4)_2$; calcd 550.225). Anal. Calcd for $C_{30}H_{34}BaCl_2N_2O_{16}{\cdot}CH_3OH$: C, 40.52; H, 4.17; N, 3.05. Found: C, 40.58; H, 4.40; N, 2.99.

(9,10,12,13,15,16,18,19,21,22,24,25-Dodecahydro-3,7:27,31-dimetheno-8,11,14,17,20,23,26,1,33-benzoheptaoxadiazacyclopentatriacontine-38,39-diol-O^8,O^{11},O^{14},O^{17},O^{20},O^{23},O^{26},O^{38},O^{39})barium(2+) Diperchlorate (11d). Compound **11d** was synthesized by using **10d**, according to method B1, to give an orange crystalline product: yield 59%; mp 288–290 °C; ^{1}H NMR (DMSO-d_6) δ 13.10 (s, 2 H, OH), 8.90 (s, 2 H, CH=N), 7.42 (s, 4 H, Ar′H), 7.4–6.8 (m, 6 H, ArH), 4.2–3.6 (m, 8 H, OCH_2), 3.6–3.5 (m, 16 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 164.4 (CH=N), 151.1 (Ar C-3), 146.9 (Ar C-2), 141.8 (Ar′ C-1, C-2), 127.8, 124.6 (Ar C-6, Ar′ C-4, C-5), 119.4 (Ar C-1), 119.6, 118.4, 117.6 (Ar C-4, C-5, Ar′ C-3, C-6), 69.9–68.3 (OCH_2); mass spectrum, *m/e* 594.257 ($M^+ - Ba(ClO_4)_2$; calcd 594.258). Anal. Calcd for $C_{32}H_{38}BaCl_2N_2O_{17}{\cdot}2H_2O$: C, 39.75; H, 4.38; N, 2.90. Found: C, 39.69; H, 3.98; N, 2.88.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diol-O^8,O^{11},O^{14},O^{17},O^{20},O^{23},O^{26},O^{29},O^{41},O^{42})barium(2+) Diperchlorate (11e). Compound **11e** was synthesized by using the dialdehyde **9e** (0.57 g, 1.0 mmol), 1,2-benzenediamine (0.11 g, 1.0 mmol), and $Ba(ClO_4)_2$ (0.34 g, 1.0 mmol) with method A1, to give an orange crystalline product: yield 68%; mp 240–244 °C; ^{1}H NMR (DMSO-d_6) δ 13.13 (s, 2 H, OH), 8.91 (s, 2 H, CH=N), 7.44 (s, 4 H, Ar′H), 7.2–6.8 (m, 6 H, ArH), 3.9–3.6 (m, 8 H, OCH_2), 3.6–3.5 (m, 20 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 164.5 (CH=N), 151.2 (Ar C-3), 146.9 (Ar C-2), 141.7 (Ar′ C-1, C-2), 127.8, 124.6 (Ar C-6, Ar′ C-4, C-5), 119.3 (Ar C-1), 119.7, 118.4, 117.5 (Ar C-4, C-5, Ar′ C-3, C-6), 69.7–68.3 (OCH_2); mass spectrum, *m/e* 638.282 ($M^+ - Ba(ClO_4)_2$; calcd 638.284). Anal. Calcd for $C_{34}H_{42}BaCl_2N_2O_{18}{\cdot}H_2O$: C, 41.13; H, 4.47; N, 2.82. Found: C, 41.06; H, 4.47; N, 2.72.

(9,10,12,13,15,16-Hexahydro-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diol-O^8,O^{11},O^{14},O^{17},O^{29},O^{30})barium(2+) Bis(trifluoromethanesulfonate) (12a). This reaction was carried out according to method A1 by using $Ba(CF_3SO_3)_2$ (2.18 g, 5.00 mmol), the dialdehyde **9a** (1.95 g, 5.00 mmol), and 1,2-benzenediamine (0.54 g, 5.00 mmol). After the reaction was complete, the resulting orange solution was concentrated to 200 mL and saturated with petroleum ether (bp 40–60 °C). The orange product crystallized, was filtered off, and was washed once with petroleum ether: yield 72%; mp > 320 °C (MeOH/petroleum ether (bp 40–60 °C)); ^{1}H NMR (DMSO-d_6) δ 14.48 (br s, 2 H, OH), 9.17, 9.14 (s, 1 H, N=CH), 7.9–7.7 (m, 2 H, Ar′H), 7.6–7.4 (m, 2 H, Ar′H), 7.3–7.1 (m, 4 H, ArH), 7.0–6.8 (m, 2 H, ArH), 4.2–4.0 (m, 4 H, $ArOCH_2$), 4.0–3.8 (m, 4 H, OCH_2), 3.74 (s, 4 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 163.2 (N=CH), 154.6 (Ar C-3), 147.1 (Ar C-2), 137.6 (Ar′ C-1, C-2), 128.1, 124.4, 118.6, 117.3, 115.1 (Ar C-4-C-6, Ar′ C-3-C-6), 117.2 (Ar C-1), 69.4, 68.2, 66.6 (OCH_2); mass spectrum, *m/e* 462.182 ($M^+ - Ba(CF_3SO_3)_2$; calcd 462.179); IR (KBr) 3460 (OH), 1625 (N=C) cm^{-1}. Anal. Calcd for $C_{28}H_{26}BaF_6N_2O_{12}S_2{\cdot}H_2O$: C, 36.72; H, 3.08; N, 3.06. Found: C, 36.86; H, 3.14; N, 2.91.

(9,10,12,13,15,16,18,19-Octahydro-3,7:21,25-dimetheno-8,11,14,17,20,1,27-benzopentaoxadiazacyclononacosine-32,33-diol-O^8,O^{11},O^{14},O^{17},O^{20},O^{32},O^{33})barium(2+) Bis(trifluoromethanesulfonate) (12b). This reaction was carried out according to method A1 by using $Ba(CF_3SO_3)_2$ (0.72 g, 1.66 mmol), the dialdehyde **9b** (0.72 g, 1.66 mmol), and 1,2-benzenediamine (0.18 g, 1.66 mmol). After the reaction was complete, the mixture was cooled to room temperature and concentrated to 15 mL. After the addition of some diisopropyl ether (DIP), the orange product precipitated. It was filtered off and was washed once with DIP: yield 81%; mp 318 °C (dec, MeOH/DIP); ^{1}H NMR (DMSO-d_6) δ 13.47 (br s, 2 H, OH), 8.98 (s, 2 H, N=CH), 7.6–7.3 (m, 4 H, Ar′H), 7.3–7.0 (m, 4 H, ArH), 7.0–6.8 (m, 2 H, ArH), 4.2–4.0 (m, 4 H, $ArOCH_2$), 4.0–3.8 (m, 4 H, OCH_2), 3.62 (s, 8 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 164.3 (N=CH), 151.1 (Ar C-3), 146.6 (Ar C-2), 140.8 (Ar′ C-1, C-2), 127.7, 124.1, 119.1, 117.9, 115.8 (Ar C-4-C-6, Ar′ C-3-C-6), 118.4 (Ar C-1), 69.6, 69.5, 68.6, 67.4 (OCH_2); mass spectrum, *m/e* 506.209 ($M^+ - Ba(CF_3SO_3)_2$; calcd 506.205); IR (KBr) 3460 (OH), 1625 (N=C) cm^{-1}. Anal. Calcd for $C_{30}H_{30}BaF_6N_2O_{13}S_2$: C, 38.25; H, 3.21; N, 2.97. Found: C, 37.97; H, 3.20; N, 2.68.

(9,10,12,13,15,16-Hexahydro-26-methyl-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diol-O^8,O^{11},O^{14},O^{17},O^{29},O^{30})barium(2+) Bis(trifluoromethanesulfonate) (13a). This reaction was carried out according to method A1 by using $Ba(CF_3SO_3)_2$ (1.12 g, 2.56 mmol), the dialdehyde **9a** (1.00 g, 2.56 mmol), and 4-methyl-1,2-benzenediamine (0.31 g, 2.56 mmol). After the reaction was complete, the reaction mixture was concentrated to 50 mL. After saturation with petroleum ether (bp 40–60 °C). the orange product crystallized. It was filtered off and was washed with petroleum ether: yield 89%; mp > 320 °C (MeOH/petroleum ether (bp 40–60 °C)); ^{1}H NMR (DMSO-d_6) δ 14.5 (br s, 2 H, OH), 9.17, 9.16 (s, 1 H, N=CH), 7.8–7.6 (m, 2 H, Ar″H), 7.4–7.1 (m, 5 H, Ar H, Ar′H, Ar″H), 7.0–6.8 (m, 2 H, ArH, Ar′H), 4.3–4.1 (m, 4 H, OCH_2), 4.0–3.8 (m, 4 H, OCH_2), 3.72 (s, 4 H, OCH_2), 3.16 (d, 3 H, J = 5.0 Hz, CH_3OH), 2.44 (s, 3 H, Me); ^{13}C NMR (DMSO-d_6) δ 163.5, 162.9 (N=CH), 154.0 (Ar C-3, Ar′ C-3), 147.5, 147.4 (Ar C-2, Ar′ C-2), 138.4 (Ar″ C-1, C-2), 129.0, 124.6, 119.3, 118.7, 117.7. 115.4, 115.3 (Ar C-4-C-6, Ar′ C-4-C-6, Ar″ C-3, C-5, C-6), 117.8 (Ar C- 1, Ar′ C-1), 69.8, 68.6, 67.2 (OCH_2), 45.8 (CH_3OH), 20.7 (Me); mass spectrum, *m/e* 476.195 (M^+ – $Ba(CF_3SO_3)_2$; calcd 476.195); IR (KBr) 3410 (OH), 1620 (N=C) cm^{-1}. Anal. Calcd for $C_{29}H_{28}BaF_6N_2O_{12}S_2\cdot MeOH$: C, 38.17; H, 3.42; N, 2.97. Found: C, 38.22; H, 3.31; N, 2.91.

(26-Benzoyl-9,10,12,13,15,16-hexahydro-29,30-dihydroxy-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-O^8,O^{11},O^{14},O^{17},O^{29},O^{30})barium(2+) Bis(trifluoromethanesulfonate) (13b). This reaction was carried out according to method A1 by using $Ba(CF_3SO_3)_2$ (1.12 g, 2.56 mmol), the dialdehyde **9a** (1.00 g, 2.56 mmol), and 3,4-diaminobenzophenone (0.54 g, 2.56 mmol). After the reaction was complete the resulting red solution was evaporated to dryness. The residue was dissolved in EtOH and the red product crystallized after the addition of some petroleum ether (bp 60–80 °C). It was filtered off and was washed once with petroleum ether: yield 47%; mp 151–158 °C (EtOH/petroleum ether (bp 40–60 °C)); ^{1}H NMR (DMSO-d_6) δ 14.0 (br s, 2 H, OH), 9.17 (br s, 2 H, N=CH), 8.0–7.6 (m, 8 H, Ar″H, Ar‴H), 7.3–7.1 (m, 4 H, ArH, Ar′H), 7.0–6.8 (m, 2 H, ArH, Ar′H), 4.2–4.0 (m, 4 H, $ArOCH_2$), 4.0–3.8 (m, 4 H, OCH_2), 3.70 (s, 4 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 194.0 (C=O), 164.8, 164.7 (N=CH), 153.9, 152.8 (Ar C-3, Ar′ C-3), 147.0, 146.8 (Ar C-2, Ar′ C-2), 136.1 (Ar″ C-1, C-2), 117.5 (Ar C-1, Ar′ C-1), 132.5, 129.0, 128.2, 124.4, 119.7, 118.8, 117.7, 115.5, 115.3 (Ar C-4-C-6, Ar′ C-4-C-6, Ar″ C-3, C-5, C-6, Ar‴ C-2-C-4), 69.4, 68.2, 66.8 (OCH_2); mass spectrum, *m/e* 566.202 (M^+ – $Ba(CF_3SO_3)_2$; calcd 566.205); IR (KBr) 3450 (OH), 1650 (C=O, shoulder), 1620 (N=C) cm^{-1}. Anal. Calcd for $C_{35}H_{30}BaF_6N_2O_{13}S_2\cdot H_2O$; C, 41.21; H, 3.16; N, 2.75. Found: C, 41.30; H, 3.09; N, 2.63.

(μ-(9,10,12,13,15,16,18,19,21,22-Decahydro-3,7:24,28-dimetheno-8,11,14,17,20,23,1,30-benzohexaoxadiazacyclodotriacontine-35,36-diolato(2–)-N^1,N^{30},O^{35},O^{36}:O^8,O^{11},O^{14},O^{17},O^{20},O^{23},O^{35},O^{36}))nickelbarium(2+) Diperchlorate (14c). Complex **11c** (0.45 g, 0.5 mmol) was dissolved in 50 mL of MeOH, and a solution of 0.12 g (0.5 mmol) of $Ni(OAc)_2\cdot 4H_2O$ in 50 mL of MeOH was added. The mixture turned deep red and was heated to reflux for 5 min, filtered while hot, and concentrated to 50 mL. After addition of 50 mL of petroleum ether (bp 40–60 °C) the product crystallized and was filtered off: yield 56%; mp > 310 °C; ^{1}H NMR (DMSO-d_6, 358 K) δ 9.6 (br s, 2 H, CH=N), 8.2–8.0 (m, 2 H, Ar′H), 7.5–7.3 (m, 2 H, Ar′H), 7.5–7.0 (m, 4 H, ArH), 6.8–6.5 (m, 2 H, ArH), 4.3–3.8 (m, 8 H, OCH_2), 3.7–3.5 (m, 12 H, OCH_2); ^{13}C NMR (DMSO-d_6, 358 K) δ 157.3 (CH=N), 154.9 (Ar C-2), 151.8 (Ar C-3), 140.2 (Ar′ C-1, C-2), 127.9, 126.3 (Ar C-6, Ar′ C-4, C-5), 120.6 (Ar C-1), 117.5, 116.8, 115.3 (Ar C-4, C-5, Ar′ C-3, C-6), 68.7–67.1 (OCH_2); mass spectrum, *m/e* 606.141 (M^+ – $Ba(ClO_4)_2$; calcd 606.151). Anal. Calcd for $C_{30}H_{32}BaCl_2N_2NiO_{16}$: C, 38.19; H, 3.42; N, 2.97. Found: C, 38.36; H, 3.53; N, 3.21.

(μ-(9,10,12,13,15,16,18,19,21,22,24,25-Dodecahydro-3,7:27,31-dimetheno-8,11,14,17,20,23,26,1,33-benzoheptaoxadiazacyclopentatriacontine-38,39-diolato(2–)-N^1,N^{33},O^{38},O^{39}:O^8,O^{11},O^{14},O^{17},O^{20},O^{23},-O^{26},O^{38},O^{39}))nickelbarium(2+) Diperchlorate (14d). The binuclear complex **14d** was synthesized from **11d** and $Ni(OAc)_2\cdot 4H_2O$ by using the same procedure as for **14c**, to give deep red crystals: yield 72%; mp > 310 °C; ^{1}H NMR (DMSO-d_6, 353 K) δ 9.55 (s, 2 H, CH=N), 8.2–8.0 (m, 2 H, Ar′H), 7.5–7.3 (m, 2 H, Ar′H), 7.3–6.5 (m, 6 H, ArH), 4.3–4.1 (m, 4 H, OCH_2), 3.9–3.7 (m, 4 H, OCH_2), 3.7–3.4 (m, 16 H. OCH_2); ^{13}C NMR (DMSO-d_6, 353 K) δ 156.4 (CH=N), 155.0 (Ar C-2). 150.3 (Ar C-3). 140.2 (Ar′ C-1, C-2), 127.2, 126.0 (Ar C-6, Ar′ C-4, C-5). 120.1 (Ar C-1), 117.9, 115.9, 114.7 (Ar C-4, C-5, Ar′ C-3, C-6), 68.9–67.1 (OCH_2); mass spectrum, *m/e* 650.175 (M^+ – $Ba(ClO_4)_2$; calcd 650.177). Anal. Calcd for $C_{32}H_{36}BaCl_2N_2NiO_{17}\cdot H_2O$: C, 38.22; H. 3.81; N, 2.79. Found: C, 38.37; H, 3.76; N, 2.64.

(μ-(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2–)-N^1,N^{36},O^{41},O^{42}-:O^8,O^{11},O^{14},O^{17},O^{20},O^{23},O^{26},O^{29},O^{41},O^{42}))nickelbarium(2+) Diperchlorate (14e). The binuclear complex **14e** was synthesized from **11e** and $Ni(OAc)_2\cdot 4H_2O$ by using the procedure for the synthesis of **14c**: yield 82%; mp > 310 °C; ^{1}H NMR (DMSO-d_6, 353 K) δ 9.83 (s, 2 H, CH=N), 8.2–8.0 (m, 2 H, Ar′H), 7.5–7.3 (m, 2 H, Ar′H), 7.3–6.6 (m. 6 H, ArH), 4.3–4.1 (m, 4 H, OCH_2), 4.0–3.8 (m, 4 H, OCH_2). 3.8–3.5 (m, 20 H, OCH_2); ^{13}C NMR (DMSO-d_6, 353 K) δ 157.0 (CH=N), 153.3 (Ar C-2), 149.8 (Ar C-3), 140.4 (Ar′ C-1, C-2), 127.5, 126.0 (Ar C-6, Ar′ C-4, C-5), 119.8 (Ar C-1), 116.9, 116.0, 115.3 (Ar C-4, C-5, Ar′ C-3, C-6), 69.0–66.5 (OCH_2); mass spectrum, *m/e* 694.198 (M^+ – $Ba(ClO_4)_2$; calcd 694.204). Anal. Calcd for $C_{34}H_{40}BaCl_2N_2NiO_{18}\cdot H_2O$: C, 38.91; H, 4.03; N, 2.67. Found: C, 39.12; H, 4.06; N. 2.65.

(9,10,12,13,15,16,18,19,21,22-Decahydro-3,7:24,28-dimetheno-8,11,14,17,20,23,1,30-benzohexaoxadiazacyclodotriacontine-35,36-diol (15c). A suspension of 1.0 g of $Ba(ClO_4)_2$ complex **11c** in 50 mL $CHCl_3$ was stirred with a solution of guanidinium sulfate (excess) in H_2O (50 mL). The $CHCl_3$ layer was separated off and dried over $MgSO_4$. After evaporation of the solvent the free macrocycle was obtained as an orange oil: ^{1}H NMR ($CDCl_3$) δ 13.18 (s, 2 H, OH), 8.60 (s, 2 H, CH=N), 7.27, 7.26 (s, 2 H, Ar′H), 7.2–6.8 (m, 6 H, ArH), 4.3–3.6 (m, 20 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 164.2 (CH=N), 152.0 (Ar C-3), 147.4 (Ar C-2), 142.2 (Ar′ C-1, C-2), 127.5, 124.8 (Ar C-4, C-5), 120.5 (Ar C-1), 119.5, 118.5, 118.4 (Ar C-4, C-5, Ar′ C-3, C-6), 70.7–69.0 (OCH_2); mass spectrum, *m/e* 550.225 (M^+; calcd 550.232).

General Procedure for the Mononuclear Complexes 16a, 16b, 16f, 17a, 17b, 17c, 18a, 18b, 18c, and 20f. Method A2. A suspension of the barium complex **11a**, **12a**, **12b**, **13a**, or **13b** (0.53–1.25 mmol) in chloroform (50–110 mL) was stirred with a solution of guanidinium sulfate (excess) in water (50–100 mL) until the organic layer was clear. The organic layer was separated off, concentrated, and diluted with MeOH or EtOH (30–50 mL). To the resulting orange or red solution was added 1 equiv of $Ni(OAc)_2$, $Cu(OAc)_2$, $Zn(OAc)_2$, or $UO_2(OAc)_2$ dissolved in MeOH or EtOH (10–20 mL), and after the addition the reaction mixture was stirred for 15 min.

General Procedure for the Synthesis of Mononuclear Complexes 16. Method B2. A suspension of the Ni–$Ba(ClO_4)_2$ complex **16** (1.0 mmol) in $CHCl_3$ (50 mL) was stirred with a solution of guanidinium sulfate (excess) in H_2O (50 mL) for 1 h. The clear organic layer was separated off, dried over $MgSO_4$, and concentrated to 5 mL. This solution was poured into 50 mL of diisopropyl ether. The product crystallized as a red powder and was filtered off.

(9,10,12,13,15,16-Hexahydro-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diolato(2–)-N^1,N^{24},O^{29},O^{30})-nickel (16a). This reaction was carried out according to method A2 by using the barium complex **12a** (0.50 g, 0.54 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (0.13 g, 0.54 mmol) in MeOH. The product crystallized during the reaction, was filtered off, and was washed with $CHCl_3$: yield 89%. A sample of the red product was dissolved in a mixture of pyridine and chloroform (1:1) and was precipitated with petroleum ether (bp 40–60 °C): mp 280–285 °C; ^{1}H NMR δ (DMSO-d_6) 8.84 (br s, 2 H, N=CH), 8.2–8.0 (m, 2 H, Ar′H), 7.3–7.1 (m, 4 H, ArH, Ar′H), 7.0–6.8 (m, 2 H. ArH), 6.7–6.5 (m, 2 H, ArH), 4.1–3.9 (m, 4 H, $ArOCH_2$), 3.9–3.7 (m, 4 H, OCH_2), 3.69 (s, 4 H, OCH_2); mass spectrum, *m/e* 518.099 (M^+; calcd 518.099); IR (KBr) 1605 (N=C) cm^{-1}. Anal. Calcd for $C_{26}H_{24}N_2NiO_6$: C, 60.15; H, 4.66; N, 5.40. Found: C, 60.53; H. 4.73; N, 5.45.

(9,10,12,13,15,16,18,19-Octahydro-3,7:21,25-dimetheno-8,11,14,17,20,1,27-benzopentaoxadiazacyclononacosine-32,33-diocta-(2–)-N^1,N^{27},O^{32},O^{33})nickel (16b). This reaction was carried out according to method A2 by using the barium complex **12b** (0.50 g, 0.53 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (0.13 g, 0.53 mmol) in MeOH. After the reaction was complete the solvent was evaporated. The residue was dissolved in a mixture of chloroform and pyridine (1:1) and the product precipitated upon the addition of petroleum ether (bp 40–60 °C): yield 70%; mp 229–231 °C; ^{1}H NMR (DMSO-d_6) δ 8.92 (s, 2 H, N=CH), 8.2–8.1 (m, 2 H, Ar′H), 7.5–7.1 (m, 4 H, ArH, Ar′H), 7.0–6.9 (m, 2 H, ArH), 6.7–6.5 (m, 2 H, ArH), 4.2–4.1 (m, 4 H. $ArOCH_2$), 4.0–3.8 (m. 4 H, OCH_2), 3.65 (s, 8 H, OCH_2); ^{13}C NMR (DMSO-d_6) δ 156.8 (Ar C-2), 156.4 (N=CH), 149.3 (Ar C-3), 142.1 (Ar′ C-1, C-2), 127.3, 126.0, 117.3, 116.1, 114.6 (Ar C-4-C-6, Ar′ C-3-C-6), 120.4 (Ar C-1), 70.7, 69.7, 69.2, 68.1 (OCH_2); mass spectrum, *m/e* 562.136 (M^+; calcd 562.135); IR (KBr) 1610 (N=C) cm^{-1}. Anal. Calcd for $C_{28}H_{28}N_2NiO_7$: C, 59.71; H, 5.01; N, 4.97. Found: C, 59.18; H, 4.93; N, 4.87.

(9,10,12,13,15,16,18,19,21,22-Decahydro-3,7:24,28-dimetheno-8,11,14,17,20,23,1,30-benzohexaoxadiazacyclotriacontine-35,36-diolato-(2–)-N^1,N^{30},O^{35},O^{36})nickel (16c). Complex **16c** was synthesized according to method B2: yield 68%; mp 130–132 °C; ^{1}H NMR ($CDCl_3$)

δ 8.57 (s, 2 H, CH=N), 7.8–7.5 (m, 2 H, Ar′H), 7.2–6.9 (m, 2 H, Ar′H), 7.0–6.3 (m, 6 H, ArH), 4.3–3.8 (m, 8 H, OCH_2), 3.8–3.5 (m, 12 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 156.8 (Ar C-2), 155.4 (CH=N), 148.6 (Ar C-3), 141.5 (Ar′ C-1, C-2), 126.6, 125.8 (Ar C-6, Ar′ C-4, C-5), 119.9 (Ar C-1), 118.3, 115.1, 113.7 (Ar C-4, C-5, Ar′ C-3, C-6), 69.1–67.9 (OCH_2); mass spectrum, *m/e* 606.146 (M^+; calcd 606.151). Anal. Calcd for $C_{30}H_{32}N_2NiO_8\cdot 3H_2O$: C, 54.49; H, 5.79; N, 4.24. Found: C, 54.55; H, 5.25; N, 4.15.

(9,10,12,13,15,16,18,19,21,22,24,25-Dodecahydro-3,7:27,31-dimetheno-8,11,14,17,20,23,26,1,33-benzoheptaoxadiazacyclopentatriacontine-38,39-diolato(2−)-N^1,N^{33},O^{38},O^{39})nickel (16d). Complex **16d** was synthesized according to method B2: yield 82%; mp 162–163 °C. (MeOH): ^1H NMR ($CDCl_3$) δ 8.15 (s, 2 H, CH=N), 7.7–7.5 (m, 2 H, Ar′H), 7.2–7.0 (m, 2 H, Ar′H), 7.0–6.3 (m, 6 H, ArH), 4.2–3.8 (m, 8 H, OCH_2), 3.8–3.6 (m, 16 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 158.8 (Ar C-2), 154.1 (CH=N), 150.2 (Ar C-3), 142.8 (Ar′ C-1, C-2), 127.3, 125.9 (Ar C-6, Ar′ C-4, C-5), 120.6 (Ar C-1), 118.2, 115.0 (Ar C-4, C-5, Ar′ C-3, C-6), 71.1–68.8 (OCH_2); mass spectrum, *m/e* 650.187 (M^+; calcd 650.177). Anal. Calcd for $C_{32}H_{36}N_2NiO_9$: C, 59.01; H, 5.57; N, 4.30. Found: C, 58.87; H, 5.46; N, 4.21.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2−)-N^1,N^{36},O^{41},O^{42})nickel (16e). Complex **16e** was synthesized according to method B2: yield 76%; mp 167–168 °C; ^1H NMR ($CDCl_3$) δ 8.23 (s, 2 H, CH=N), 7.8–7.6 (m, 2 H, Ar′H), 7.1–6.3 (m, 8 H, Ar′H, ArH), 4.2–3.9 (m, 8 H, OCH_2), 3.9–3.5 (m, 20 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 157.5 (Ar C-2), 154.3 (CH=N), 149.6 (Ar C-3), 142.5 (Ar′ C-1, C-2), 127.5, 125.6 (Ar C-6, Ar′ C-4, C-5), 120.1 (Ar C-1), 116.3, 115.0 (Ar C-4, C-5, Ar′ C-3, C-6), 70.8–67.6 (OCH_2); mass spectrum, *m/e* 694.197 (M^+; calcd 694.204). The product was analyzed as the corresponding complex with urea.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2−)-N^1,N^{36},O^{41},O^{42})nickel–urea (1:1) (16e·urea). Ligand **16e** was recrystallized from a 0.1 M solution of urea in MeOH, to give red needles: mp 162–163 °C; ^1H NMR ($CDCl_3$) δ 8.24 (s, 2 H, CH=N), 7.8–7.6 (m, 2 H, Ar′H), 7.3–7.1 (m, 2 H, Ar′H), 7.0–6.5 (m, 6 H, ArH), 4.2–3.8 (m, 8 H, OCH_2), 3.8–3.6 (m, 20 H, OCH_2); IR (KBr) 1670 (C=O urea), 1607 cm^{-1} (C=N). Anal. Calcd for $C_{35}H_{44}N_4NiO_{11}$: C, 55.65; H, 5.87; N, 7.42. Found: C, 55.38; H, 5.73; N, 7.09.

(9,10,12,13,15,16-Hexahydro-26-methyl-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diolato(2−)-N^1,N^{24},O^{29},O^{30})nickel (16f). This reaction was carried out according to method A2 by using the barium complex **13a** (0.51 g, 0.56 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (0.15 g, 0.56 mmol) in MeOH. The red product precipitated during the reaction was filtered off and was washed once with MeOH: yield 74%. A sample of the product was dissolved in a mixture of pyridine and chloroform (1:1) and precipitated with petroleum ether (bp 40–60 °C): mp 274–278 °C; ^1H NMR δ (DMSO-d_6) 8.75, 8.71 (s, 1 H, N=CH), 8.1–7.9 (m, 2 H, Ar″H), 7.2–7.0 (m, 3 H, ArH, Ar′H, Ar″H), 6.9–6.8 (m, 2 H, ArH, Ar′H), 6.7–6.5 (m, 2 H, ArH, Ar′H), 4.1–3.9 (m, 4 H, $ArOCH_2$), 3.9–3.7 (m, 4 H, OCH_2), 3.64 (s, 4 H, OCH_2), 2.37 (s, 3 H, Me); mass spectrum, *m/e* 532.113 (M^+; calcd 532.114); IR (KBr) 1610 (N=C) cm^{-1}. Anal. Calcd for $C_{27}H_{26}N_2NiO_6$: C, 60.82; H, 4.91; N, 5.25. Found: C, 60.95; H, 4.97; N, 5.25.

(9,10,12,13,15,16-Hexahydro-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diolato(2−)-N^1,N^{24},O^{29},O^{30})copper (17a). This reaction was carried out according to method A2 by using the barium complex **12a** (0.50 g, 0.54 mmol) and $Cu(OAc)_2\cdot H_2O$ (0.11 g, 0.54 mmol) in MeOH. During the reaction the green copper complex precipitated, was filtered off, and was washed with MeOH: yield 82%; mp 287–289 °C (pyridine/petroleum ether (bp 40–60 °C)); mass spectrum, *m/e* 523.090 (M^+; calcd 523.093); IR (KBr) 3480 and 3430 (OH), 1605 (N=C) cm^{-1}. Anal. Calcd for $C_{26}H_{24}CuN_2O_6\cdot H_2O$: C, 57.61; H, 4.83; N, 5.17. Found: C, 58.02; H, 4.87; N, 5.27.

(9,10,12,13,15,16-Hexahydro-26-methyl-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diolato(2−)-N^1,N^{24},O^{29},O^{30})copper (17b). This reaction was carried out according to method A2 by using the barium complex **12a** (0.50 g, 0.54 mmol) and $Cu(OAc)_2\cdot H_2O$ (0.11 g, 0.54 mmol) in MeOH. The green reaction product precipitated during the reaction, was filtered off, and was washed with MeOH: yield 74%. A sample of the product was dissolved in a mixture of pyridine and chloroform (1:1) and was precipitated with petroleum ether (bp 40–60 °C): mp > 320 °C; mass spectrum, *m/e* 537.109 (M^+; calcd 537.109); IR (KBr) 3480, 3430 (OH), 1610 (N=C) cm^{-1}. Anal. Calcd for $C_{27}H_{26}CuN_2O_6\cdot H_2O$: C, 58.32; H, 5.08; N, 5.04. Found: C, 58.43; H, 5.08; N, 4.91.

(26-Benzoyl-9,10,12,13,15,16-hexahydro-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diolato(2−)-N^1,N^{24},O^{29},O^{30})copper (17c). This reaction was carried out according to method A2 by using the barium complex **13b** (0.70 g, 0.70 mmol) and $Cu(OAc)_2\cdot H_2O$ (0.14 g, 0.70 mmol) in EtOH. After the reaction was complete, a small portion of petroleum ether (bp 60–80 °C) was added after which the dark brown product precipitated. It was filtered off and was washed once with petroleum ether: yield 64%. A sample of the product was dissolved in a mixture of pyridine and chloroform (1:1) and was precipitated with petroleum ether (bp 40–60 °C): mp 287–291 °C; mass spectrum, *m/e* 627.109 (M^+; calcd 627.119); IR (KBr) 3440, 3410 (OH), 1648 (C=O), 1605 (C=N) cm^{-1}. Anal. Calcd for $C_{33}H_{28}CuN_2O_7\cdot 2H_2O$: C, 59.68; H, 4.86; N, 4.22. Found: C, 59.60; H, 4.49; N, 4.27.

(9,10,12,13,15,16-Hexahydro-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diolato(2−)-N^1,N^{24},O^{29},O^{30})zinc (18a). This reaction was carried out according to method A2 by using the barium complex **11a** (1.00 g, 1.25 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (0.28 g, 1.25 mmol) in MeOH. During the reaction the product crystallized, was filtered off, and was washed with chloroform: yield 91%. A sample of the product was dissolved in a mixture of pyridine and chloroform (1:1) and was precipitated with petroleum ether (bp 40–60 °C): mp > 320 °C; ^1H NMR δ (DMSO-d_6 and pyridine-d_5) 9.14 (s, 2 H, N=CH), 8.0–7.8 (m, 2 H, Ar′H), 7.4–7.2 (m, 4 H, ArH, Ar′H), 7.1–6.9 (m, 2 H, ArH), 6.7–6.5 (m, 2 H, ArH), 4.1–3.9 (m, 8 H, OCH_2), 3.78 (s, 4 H, OCH_2); ^{13}C NMR δ (DMSO-d_6 and pyridine-d_5) 162.0 (N=CH), 151.4 (Ar C-3), 138.9 (Ar′ C-1, C-2), 118.6 (Ar C-1), 69.0, 68.5, 68.1 (OCH_2); mass spectrum, *m/e* 524.094 (M^+; calcd 524.093); IR (KBr) 1610 (N=C) cm^{-1}. Anal. Calcd for $C_{26}H_{24}N_2O_6Zn\cdot H_2O$: C, 57.42; H, 4.82; N, 5.15. Found: C, 57.15; H, 4.89; N, 5.08.

(9,10,12,13,15,16-Hexahydro-26-methyl-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazahexacosine-29,30-diolato(2−)-N^1,N^{24},O^{29},O^{30})zinc (18b). This reaction was carried out according to method A2 by using the barium complex **12a** (0.50 g, 0.54 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (0.12 g, 0.54 mmol) in MeOH. The yellow product precipitated almost immediately after the addition of zinc acetate. The product was filtered off and was washed once with MeOH: yield 54%; mp > 320 °C; ^1H NMR δ (DMSO-d_6) 9.00, 8.98 (s, 1 H, N=CH), 7.8–7.7 (m, 2 H, Ar″H), 7.2–6.8 (m, 5 H, ArH, Ar′H, Ar″H), 6.5–6.3 (m, 2 H, ArH, Ar′H), 4.1–3.9 (m, 4 H, $ArOCH_2$), 3.9–3.8 (m, 4 H, OCH_2), 3.71 (s, 4 H, OCH_2), 2.41 (s, 3 H, Me); mass spectrum, *m/e* 538.114 (M^+; calcd 538.108); IR (KBr) 1610 (N=C) cm^{-1}.

(26-Benzoyl-9,10,12,13,15,16-hexahydro-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diolato(2−)-N^1,N^{24},O^{29},O^{30})zinc (18c). This reaction was carried out according to method A2 by using the barium complex **13b** (0.70 g, 0.70 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (0.15 g, 0.70 mmol) in EtOH. After the reaction was complete the red product precipitated after the addition of a small amount of petroleum ether (bp 60–80 °C). It was filtered off and was washed once with petroleum ether: yield 73%. A sample of the product was dissolved in a mixture of pyridine and chloroform (4:1) and precipitated upon addition of petroleum ether (bp 40–60 °C): mp 202–205 °C; ^1H NMR δ (DMSO-d_6) 9.11, 9.07 (s, 1 H, N=CH), 8.1–7.5 (m, 8 H, Ar″H, Ar‴H), 7.1–6.8 (m, 4 H, ArH, Ar′H), 6.5–6.3 (m, 2 H, ArH, Ar′H), 4.1–3.9 (m, 4 H, $ArOCH_2$), 3.9–3.7 (m, 4 H, OCH_2), 3.71 (s, 4 H, OCH_2); ^{13}C NMR δ (DMSO-d_6 and pyridine-d_5) 193.8 (C=O), 165.2, 164.7 (Ar″ C-4, Ar‴ C-1), 163.4, 162.9 (N=CH), 151.7, 151.6 (Ar C-3, Ar′ C-3), 118.7, 118.6 (Ar C-1, Ar′ C-1), 69.1, 68.6, 68.3 (OCH_2); IR (KBr) 1650 (C=O), 1608 (C=N) cm^{-1}. Anal. Calcd for $C_{33}H_{28}N_2O_7Zn\cdot 1.5H_2O$: C, 60.33; H, 4.76; N, 4.26. Found: C, 60.38; H, 4.58; N, 4.27.

General Procedure for the Preparation of the Complexes 19a–e. Method C. To a refluxing solution of $Ba(CF_3SO_3)_2$ (0.56 g, 1.28 mmol) in 100 mL of MeOH were added dropwise a solution of the dialdehyde **9a** (0.50 g, 1.28 mmol) or the dialdehyde **9b** (0.56 g, 1.28 mmol) in 25 mL of THF and a solution of 2-methyl-1,2-propanediamine (0.11 g, 1.28 mmol) in 25 mL of MeOH over a period of 3 h. The resulting yellow solution was refluxed for 15 min after which a solution of $Ni(OAc)_2$, $Cu(OAc)_2$, or $Zn(OAc)_2$ (1.28 mmol) in MeOH (10–20 mL) was added in 1 portion. Subsequently the colored solution was cooled to room temperature, and the solvent was evaporated. Unless otherwise stated the residue was dissolved in EtOH, and after the addition of some petroleum ether (bp 60–80 °C) the product precipitated. It was filtered off and was washed with petroleum ether to give the binuclear complex. The barium salt was quantitatively removed by stirring a suspension in $CHCl_3$ for 1 h with a solution of guanidinium sulfate (excess) in water.

[5,5-Dimethyl-13,16,19,22-tetraoxa-3,6-diazatricyclo[21.3.1.1^{8,12}]octacosa-1(27),2,6,8,10,12(28),23,25-octaene-27,28-diolato(2−)-N^3,N^6,O^{27},O^{28}]nickel (19a). The nickel–barium complex was obtained according to method C as a brown solid in 72% yield. After removal of the barium salt a red solution of the nickel complex resulted. The solvent was removed, and the residue was dissolved in a little $CHCl_3$ and slowly precipitated with petroleum ether (bp 40–60 °C) to give ruby red crystals: mp 281–289 °C; ^{1}H NMR δ 7.27, 7.20 (s, 1 H, N=CH), 6.7–6.2 (m, 6 H, ArH), 3.97 (s, 8 H, OCH$_2$), 3.85 (s, 4 H, OCH$_2$), 3.25 (s, 2 H, NCH$_2$), 1.40 (s, 6 H, Me); mass spectrum, *m/e* 498.131 (M$^+$; calcd 498.130); IR (KBr) 3520, 3480 (OH), 1615 (N=C) cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2NiO_6\cdot 1.5H_2O$: C, 54.78; H, 5.94; N, 5.32. Found: C, 54.82; H, 5.78; N, 5.28.

[5,5-Dimethyl-13,16,19,22-tetraoxa-3,6-diazatricyclo[21.3.1.1^{8,12}]octacosa-1(27),2,6,8,10,12(28),23,25-octaene-27,28-diolato(2−)-*N*^{3},*N*^{6},*O*^{27},*O*^{28}]copper (19b). The copper–barium complex was obtained according to method C in 82% yield. After the removal of the barium salt a dark green solution of the copper complex resulted. The solvent was evaporated to give a green solid. This was dissolved in a little chloroform and precipitated with petroleum ether (bp 40–60 °C): mp 254–258 °C; mass spectrum, *m/e* 503.128 (M$^+$; calcd 503.124); IR (KBr) 3490 (OH), 1620 (N=C) cm^{-1}. Anal. Calcd for $C_{24}H_{28}CuN_2O_6\cdot 2H_2O$: C, 53.38; H, 5.97; N, 5.19. Found: C, 53.42; H, 5.62; N, 4.99.

[5,5-Dimethyl-13,16,19,22-tetraoxa-3,6-diazatricyclo[21.3.1.1^{8,12}]octacosa-1(27),2,6,8,10,12(28),23,25-octaene-27,28-diolato(2−)-*N*^{3},*N*^{6},*O*^{27},*O*^{28}]zinc (19c). The zinc–barium complex was obtained according to method C in 84% yield. After the removal of the barium salt a suspension resulted. The slightly yellow solid was filtered off and was washed with CHCl$_3$. It was dissolved in a mixture of pyridine and chloroform (2:1) and was precipitated with petroleum ether (bp 40–60 °C): mp > 320 °C; ^{1}H NMR δ (DMSO-*d*$_6$) 8.45, 8.38 (s, 1 H, N=CH), 6.9–6.7 (m, 4 H, ArH, Ar′H), 6.4–6.2 (m, 2 H, ArH, Ar′H), 4.1–3.9 (m, 4 H, ArOCH$_2$), 3.8–3.7 (m, 4 H, OCH$_2$), 3.68 (s, 4 H, OCH$_2$), 3.49 (s, 2 H, NCH$_2$), 1.27 (s, 6 H, Me); ^{13}C NMR δ (DMSO-*d*$_6$) 167.6, 165.1 (N=CH), 163.4, 162.8 (Ar C-2, Ar′ C-2), 151.6, 151.4 (Ar C-3, Ar′ C-3), 127.2, 126.6, 116.0, 115.9, 110.5, 110.4 (Ar C-4-C-6, Ar′ C-4-C-6), 118.6, 118.5 (Ar C-1, Ar′ C-1), 69.1, 68.7, 68.5 (OCH$_2$), 67.0 (NCH$_2$), 58.1 (NC(Me)$_2$), 24.9 (Me); mass spectrum, *m/e* 504.121 (M$^+$; calcd 504.124); IR (KBr) 3350 (OH), 1625 (N=C) cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2O_6Zn\cdot H_2O$: C, 55.02; H, 5.77; N, 5.35. Found: C, 54.93; H, 5.78; N, 5.42.

[5,5-Dimethyl-13,16,19,22,25-pentaoxa-3,6-diazatricyclo[24.3.1.1^{8,12}]hentriacontane-1(30),2,6,8,10,12(31),26,28-octaene-30,31-diolato(2−)-*N*^{3},*N*^{6},*O*^{30},*O*^{31}]nickel (19d). In this case the residue, obtained according to method C, was dissolved in a mixture of pyridine and chloroform (1:1), and after precipitation with petroleum ether (bp 40–60 °C) the nickel–barium complex was obtained as a brown solid: yield 75%. After removal of the barium salt the nickel complex resulted as a deep red solid: mp 224–226 °C (CHCl$_3$/petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 7.43, 7.31 (s, 1 H, N=CH), 6.9–6.5 (m, 4 H, ArH), 6.4–6.1 (m, 2 H, ArH), 4.10 (s, 8 H, OCH$_2$), 3.8–3.6 (m, 8 H, OCH$_2$), 3.24 (s, 2 H, NCH$_2$), 1.89 (s, 3 H, H$_2$O), 1.45 (s, 6 H, Me); mass spectrum, *m/e* 542.158 (M$^+$; calcd 542.156); IR (KBr) 1620 (N=C) cm^{-1}. Anal. Calcd for $C_{26}H_{32}N_2NiO_7\cdot 1.5H_2O$: C, 54.76; H, 6.19; N, 4.91. Found: C, 54.95; H, 5.84; N, 4.81.

[5,5-Dimethyl-13,16,19,22,25-pentaoxa-3,6-diazatricyclo[24.3.1.1^{8,12}]hentriacontane-1(30),2,6,8,10,12(31),26,28-octaene-30,31-diolato(2−)-*N*^{3},*N*^{6},*O*^{30},*O*^{31}]copper (19e). The reaction product, obtained according to method C, was treated in the same way as **19d**. The copper–barium complex was obtained in 71% yield. After removal of the barium salt, the copper complex resulted as a green blue solid: mp 172–173 °C (CHCl$_3$/petroleum ether (bp 40–60 °C)); mass spectrum, *m/e* 547.146 (M$^+$; calcd 547.151); IR (KBr) 1625 (N=C) cm^{-1}. Anal. Calcd for $C_{26}H_{32}CuN_2O_7\cdot 2H_2O$: C, 53.46; H, 6.21; N, 4.80. Found: C, 53.08; H, 5.93; N, 4.48.

(9,10,12,13,15,16,18,19,21,22-Decahydro-3,7:24,28-dimetheno-8,11,14,17,20,23,1,30-benzohexaoxadiazacyclotriacontine-35,36-diolato-(2−)-*N*^{1},*N*^{30},*O*^{35},*O*^{36})dioxouranium (20c). To a solution of 0.44 g (0.5 mmol) of the Ba(ClO$_4$)$_2$ complex **11c** in 200 mL of MeOH was added a solution of 0.20 g (0.5 mmol) of uranyl acetate dihydrate, and the mixture was heated at 80 °C for 1 h. The solvent was partially evaporated, and 25 mL of water was added. The product crystallized and was filtered off: yield 65%; mp 172–174 °C; ^{1}H NMR (DMSO-*d*$_6$) δ 9.60 (s, 2 H, CH=N), 7.8–7.1 (m, 8 H, ArH, Ar′H), 6.61 (t, *J* = 8 Hz, 2 H, ArH), 4.5–3.5 (m, 20 H, OCH$_2$); IR (KBr) 1600 (C=N), 900 (as O-U-O) cm^{-1}. Anal. Calcd for $C_{30}H_{32}N_2O_{10}U\cdot 3H_2O$: C, 41.29; H, 4.39; N, 3.21. Found: C, 41.28; H, 4.00; N, 3.21.

(9,10,12,13,15,16,18,19,21,22-Decahydro-3,7:24,28-dimetheno-8,11,14,17,20,23,1,30-benzohexaoxadiazacyclotriacontine-35,36-diolato-(2−)-*N*^{1},*N*^{30},*O*^{35},*O*^{36})dioxouranium–Urea (20c·urea). A solution of 0.06 g of the UO$_2$ complex **20c** in 25 mL of MeOH/CHCl$_3$ was treated with a solution of 0.05 g of urea in 10 mL of MeOH. The product crystallized slowly and was filtered off: mp 198–200 °C; ^{1}H NMR (DMSO-*d*$_6$) δ 9.60 (s, 2 H, CH=N), 7.9–7.1 (m, 8 H, ArH, Ar′H), 6.61 (t, *J* = 8 Hz, 2 H, ArH), 5.4 (br s, 4 H, NH$_2$), 4.5–3.5 (m, 20 H, OCH$_2$); mass spectrum, *m/e* 818.244 ($C_{30}H_{32}N_2O_{10}U^+$; calcd 818.256), 60.034 ($CH_4N_2O^+$, calcd 60.032); IR (KBr) 1630 (C=O), 1602 (C=N), 900 (as O-U-O) cm^{-1}. Anal. Calcd for $C_{30}H_{32}N_2O_{10}U\cdot CH_4N_2O\cdot {}^1/_2CHCl_3$: C, 40.32; H, 3.92; N, 5.97. Found: C, 40.24; H, 3.85; N, 5.30.

(9,10,12,13,15,16,18,19,21,22,24,25-Dodecahydro-3,7:27,31-dimetheno-8,11,14,17,20,23,26,1,33-benzoheptaoxadiazacyclopentatriacontine-38,39-diolato(2−)-*N*^{1},*N*^{33},*O*^{38},*O*^{39})dioxouranium (20d). To a solution of 0.47 g (0.5 mmol) of the Ba(ClO$_4$)$_2$ complex **11d** in 200 mL of MeOH was added a solution of 0.20 g (1.0 mmol) of uranyl acetate dihydrate. The mixture turned dark red and was heated for 1 h at 80 °C. The solvent was partially evaporated. Crystals formed, and these were filtered off: yield 80%; mp 144–146 °C; 200 MHz ^{1}H NMR (DMSO-*d*$_6$) δ 9.61 (s, 2 H, CH=N), 7.79–7.74 (m, 2 H, Ar′H), 7.55–7.50 (m, 2 H, Ar′H), 7.43 (d, *J* = 8 Hz, 2 H, ArH), 7.27 (d, *J* = 8 Hz, 2 H, ArH), 6.62 (t, *J* = 8 Hz, 2 H, ArH), 4.39–4.35 (m, 4 H, OCH$_2$), 3.95–3.90 (m, 4 H, OCH$_2$), 3.72–3.66 (m, 4 H, OCH$_2$), 3.63–3.58 (m, 4 H, OCH$_2$), 3.55 (s, 8 H, OCH$_2$); mass spectrum, *m/e* 862.287 (M$^+$; calcd 862.283); IR (KBr) 899 (as O-U-O), 1600 (C=N) cm^{-1}. Anal. Calcd for $C_{32}H_{36}N_2O_{11}U\text{-}H_2O$: C, 43.64; H, 4.35; N, 3.18. Found: C, 43.77; H, 4.50; N, 3.01.

(9,10,12,13,15,16,18,19,21,22,24,25-Dodecahydro-3,7:27,31-dimetheno-8,11,14,17,20,23,26,1,33-benzoheptaoxadiazacyclopentatriacontine-38,39-diolato(2−)-*N*^{1},*N*^{33},*O*^{38},*O*^{39})dioxouranium–Urea (20d·urea). A solution of 0.059 g (0.063 mmol) of the UO$_2$ complex **20d** in 25 mL of MeOH was treated with a solution of 0.01 g (0.17 mmol) of urea in 10 mL of MeOH. The product crystallized immediately and was filtered off: mp 260–261 °C; 200 MHz ^{1}H NMR (DMSO-*d*$_6$) δ 9.61 (s, 2 H, CH=N), 7.79–7.74 (m, 2 H, Ar′H), 7.55–7.50 (m, 2 H, Ar′H), 7.44 (d, *J* = 8 Hz, 2 H, ArH), 7.27 (d, *J* = 8 Hz, 2 H, ArH), 6.62 (t, *J* = 8 Hz, 2 H, ArH), 5.40 (br s, 4 H, NH$_2$ urea), 4.39–4.33 (m, 4 H, OCH$_2$), 3.94–3.90 (m, 4 H, OCH$_2$), 3.71–3.67 (m, 4 H, OCH$_2$), 3.63–3.58 (m, 4 H, OCH$_2$), 3.55 (s, 8 H, OCH$_2$); mass spectrum, *m/e* 862.288 ($C_{32}H_{36}N_2O_{11}U^+$; calcd 862.283), *m/e* 60.031 ($CH_4N_2O^+$; calcd 60.032); IR (KBr) 1630 (C=O), 1602 (C=N), 900 (as O-U-O) cm^{-1}. Anal. Calcd for $C_{32}H_{36}N_2O_{11}U\cdot CH_4N_2O$: C, 42.96; H, 4.37; N, 6.07. Found: C, 43.22; N, 4.50; N, 5.82.

(9,10,12,13,15,16,18,19,21,22,24,25-Dodecahydro-3,7:27,31-dimetheno-8,11,14,17,20,23,26,1,33-benzoheptaoxadiazacyclopentatriacontine-38,39-diolato(2−)-*N*^{1},*N*^{33},*O*^{38},*O*^{39})dioxouranium–Formamide (20d·formamide). A solution of 0.059 g (0.063 mmol) of the UO$_2$ complex **20d** in 25 mL of MeOH was treated with 0.1 mL of formamide. The mixture was allowed to crystallize overnight, and the crystals were filtered off: mp 225–227 °C; 200 MHz ^{1}H NMR (DMSO-*d*$_6$) δ 9.61 (s, 2 H, CH=N), 7.97 (dd, *J* = 13 Hz, *J* = 1 Hz, 1 H, HC=O formamide), 7.79–7.74 (m, 2 H, Ar′H), 7.55–7.50 (m, 2 H, Ar′H), 7.43 (d, *J* = 8 Hz, 2 H, ArH), 7.4 (br s, 2 H, NH$_2$), 7.27 (d, *J* = 8 Hz, 2 H, ArH), 6.62 (t, *J* = 8 Hz, 2 H, ArH), 4.38–4.35 (m, 4 H, OCH$_2$), 3.95–3.91 (m, 4 H, OCH$_2$), 3.74–3.69 (m, 4 H, OCH$_2$), 3.63–3.60 (m, 4 H, OCH$_2$), 3.55 (s, 8 H, OCH$_2$); mass spectrum, *m/e* 862.287 ($C_{32}H_{36}N_2O_{11}U^+$; calcd 862.283), *m/e* 45.020 (CH_3NO^+; calcd 45.022); IR (KBr) 1670 (C=O), 1602 (C=N), 895 (as O-U-O) cm^{-1}. Anal. Calcd for $C_{32}H_{36}N_2O_{11}U\cdot CH_3NO$: C, 43.67; H, 4.33; N, 4.63. Found: C, 43.88; H, 4.41; N, 4.51.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2−)-*N*^{1},*N*^{36},*O*^{41},*O*^{42})dioxouranium (20e). To a solution of 0.97 g (1.0 mmol) of the Ba(ClO$_4$)$_2$ complex **11e** in 200 mL of MeOH was added a solution of 0.42 g (1.0 mmol) of uranyl acetate dihydrate. The mixture turned dark red and was heated for 1 h at 80 °C. The solvent was partially evaporated. Crystals formed, and these were filtered off: yield 80%; mp 110–112 °C; 200 MHz ^{1}H NMR (DMSO-*d*$_6$) δ 9.60 (s, 2 H, CH=N), 7.78–7.73 (m, 2 H, Ar′H), 7.55–7.50 (m, 2 H, Ar′H), 7.42 (d, *J* = 8 Hz, 2 H, ArH), 7.26 (d, *J* = 8 Hz, 2 H, ArH), 6.61 (t, *J* = 8 Hz, 2 H, ArH), 4.37–4.32 (m, 4 H, OCH$_2$), 3.95–3.91 (m, 4 H, OCH$_2$), 3.74–3.70 (m, 4 H, OCH$_2$), 3.65–3.61 (m, 4 H, OCH$_2$), 3.60–3.50 (m, 12 H, OCH$_2$); ^{13}C NMR (DMSO-*d*$_6$) δ 165.7 (CH=N), 161.2 (Ar C-2), 150.0 (Ar C-3), 146.4 (Ar′ C-1, C-2), 128.1, 127.7 (Ar C-6, Ar′ C-4, C-5), 124.2 (Ar C-1), 119.7, 119.6, 115.3 (Ar C-4, C-5, Ar′ C-3, C-6), 69.8–68.7 (CH$_2$O); mass spectrum, *m/e* 906.298 (M$^+$; calcd 906.309); IR (KBr) 897 (as O-U-O), 1602 (C=N), 3450 (H$_2$O) cm^{-1}. Anal. Calcd for $C_{34}H_{40}N_2O_{12}U\cdot 7H_2O$: C, 39.54; H, 5.27; N, 2.71. Found: C, 39.32; H, 4.84; N, 2.63.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2−)-*N*^{1},*N*^{36},*O*^{41},*O*^{42})dioxouranium–Urea (20e·urea). A solution of 0.13 g of the UO$_2$ complex **20e** in 50 mL of MeOH was treated with a solution of 0.01 g of urea in 1 mL of MeOH. The product crystallized immediately and was filtered off: mp 247–249 °C; 200 MHz ^{1}H NMR (DMSO-*d*$_6$) δ 9.61 (s, 2 H, CH=N), 7.78–7.74 (m, 2 H, Ar′H), 7.55–7.50 (m, 2 H, Ar′H), 7.42 (d, *J* = 8 Hz, 2 H, ArH),

Table III. Crystal Data and Data Collection Parameters

	12a	**19a**·H_2O	**16e**·urea	**20e**·urea
formula	$C_{28}H_{32}BaF_6N_2O_{13}S_2$	$C_{24}H_{30}N_2NiO_7$	$C_{35}H_{44}N_4NiO_{11}$	$C_{35}H_{44}N_4O_{13}U$
fw	920.03	517.23	755.47	966.79
lattice type	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$
T, K	293	293	293	180
cell dimensions				
a, Å	10.075 (2)	12.142 (1)	8.584 (4)	16.280 (5)
b, Å	12.279 (4)	12.290 (3)	22.435 (8)	11.734 (3)
c, Å	14.012 (3)	16.595 (4)	18.156 (5)	20.531 (5)
α, deg	102.91 (2)			
β, deg	90.30 (2)	107.51 (1)	90.41 (4)	109.11 (3)
γ, deg	102.03 (2)			
V, Å^3	1650 (2)	2362 (2)	3496 (4)	3706 (4)
Z	2	4	4	4
D_c, g cm^{-3}	1.85	1.46	1.44	1.73
F(000)	920	1088	1592	1912
μ cm^{-1}	14.2	8.7	6.2	42.2
θ range, deg	3–25	3–25	3–22.5	3–25
no. of unique reflcns				
measd	5798	4170	4525	6467
obsd	5092	2586	2561	3331
no. of variables	565	403	460	478
R, %	2.9	5.4	5.2	2.8
R_w, %	3.8	6.2	6.5	3.4
weighting factor p	0.03	0.03	a	0.05
extinction g ($\times 10^{-7}$)	7.1	0	0	0

[a] Unit weights.

7.26 (d, J = 8 Hz, 2 H, ArH), 6.62 (t, J = 8 Hz, 2 H, ArH), 5.40 (br s, 4 H, NH_2 urea), 4.37–4.33 (m, 4 H, OCH_2), 3.95–3.91 (m, 4 H, OCH_2), 3.74–3.70 (m, 4 H, OCH_2), 3.65–3.61 (m, 4 H, OCH_2), 3.55–3.50 (m, 12 H, OCH_2); ^{13}C NMR (DMSO-d_6, 353 K) δ 164.4 (CH=N), 160.7 (Ar C-2), 158.5 (C=O urea), 149.5 (Ar C-3), 146.0 (Ar′ C-1, C-2), 127.7, 127.2 (Ar C-6, Ar′ C-4, C-5), 123.8 (Ar C-1), 119.2, 119.1, 115.0 (Ar C-4, C-5, Ar′ C-3, C-6), 69.4–68.3 (OCH_2); mass spectrum, m/e 906.299 ($C_{34}H_{40}N_2O_{12}U^+$; calcd 906.306), m/e 60.025 ($CH_4N_2O^+$; calcd 60.032); IR (KBr) 1640 (C=O), 1602 (C=N), 896 (as O–U–O) cm^{-1}. Anal. Calcd for $C_{35}H_{44}N_4O_{13}U$: C, 43.48; H, 4.59; N, 5.80. Found: C, 43.11; H, 4.49; N, 5.72.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2−)-N^1,N^{36},O^{41},O^{42})dioxouranium–N-Methylurea (20e·N-methylurea). A solution of 0.06 g of the UO_2 complex **20e** in 25 mL of MeOH was treated with a solution of 0.01 g of N-methylurea in 10 mL of MeOH. The product crystallized immediately and was filtered off: mp 145–148 °C; 200 MHz ^1H NMR (DMSO-d_6) δ 9.61 (s, 2 H, CH=N), 7.78–7.73 (m, 2 H, Ar′H), 7.55–7.50 (m, 2 H, Ar′H), 7.43 (d, J = 8 Hz, 2 H, ArH), 7.26 (d, J = 8 Hz, 2 H, ArH), 6.61 (t, J = 8 Hz, 2 H, ArH), 5.79 (br s, 1 H, NH), 5.41 (br s, 2 H, NH_2), 4.35–4.33 (m, 4 H, OCH_2), 3.94–3.90 (m, 4 H, OCH_2), 3.73–3.70 (m, 4 H, OCH_2), 3.65–3.61 (m, 4 H, OCH_2), 3.55–3.51 (m, 12 H, OCH_2), methyl signal of N-methylurea obscured by DMSO; mass spectrum, m/e 906.323 ($C_{34}H_{40}N_2O_{12}U^+$; calcd 906.309), m/e 74.050 (C_2H_6 N_2O^+; calcd 74.048); IR (KBr) 1639 (C=O), 1601 (C=N), 899 (as O–U–O) cm^{-1}. Anal. Calcd for $C_{34}H_{40}N_2O_{12}U{\cdot}C_2H_6N_2O{\cdot}2H_2O$: C, 42.52; H, 4.96; N, 5.51. Found: C, 42.71; H, 4.67; N, 5.23.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2−)-N^1,N^{36},O^{41},O^{42})dioxouranium–Formamide (20e·formamide). A solution of 0.06 g of the UO_2 complex **20e** in 25 mL of MeOH was treated with 0.1 mL of formamide. The product was allowed to crystallize overnight, and the crystals were filtered off: mp 185–190 °C; 200 MHz ^1H NMR (DMSO-d_6) δ 9.61 (s, 2 H, CH=N), 7.97 (dd, J = 13 Hz, J = 1 Hz, 1 H, HC=O formamide), 7.78–7.73 (m, 2 H, Ar′H), 7.55–7.50 (m, 2 H, Ar′H), 7.43 (d, J = 8 Hz, 2 H, ArH), 7.3 (br s, 2 H, NH_2), 7.26 (d, J = 8 Hz, 2 H, ArH), 6.62 (t, J = 8 Hz, 2 H, ArH), 4.37–4.32 (m, 4 H, OCH_2), 3.95–3.90 (m, 4 H, OCH_2), 3.74–3.70 (m, 4 H, OCH_2), 3.65–3.60 (m, 4 H, OCH_2), 3.55–3.51 (m, 12 H, OCH_2); mass spectrum, m/e 906.323 ($C_{34}H_{40}N_2O_{12}U^+$; calcd 906.309), m/e 45.020 (CH_3NO^+; calcd 45.022); IR (KBr) 1671 (C=O), 1602 (C=N), 899 (as O–U–O) cm^{-1}. Anal. Calcd for $C_{34}H_{40}N_2O_{12}U{\cdot}CH_3NO$: C, 44.17; H, 4.55; N, 4.41. Found: C, 44.35; H, 4.59; N, 4.37.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2−)-N^1,N^{36},O^{41},O^{42})dioxouranium–DMSO (20e·DMSO). A solution of 0.06 g of the UO_2 complex **20e** in 25 mL of MeOH was treated with 1 mL of DMSO. The product crystallized immediately and was filtered off: mp 113–114 °C; mass spectrum, m/e 906.339 ($C_{34}H_{40}N_2O_{12}U^+$; calcd 906.309), m/e 78.015 ($C_2H_6SO^+$; calcd 78.014); IR (KBr) 1600 (C=N), 1005 (S=O), 898 (as O–U–O) cm^{-1}.

(9,10,12,13,15,16,18,19,21,22,24,25,27,28-Tetradecahydro-3,7:30,34-dimetheno-8,11,14,17,20,23,26,29,1,36-benzoctaoxadiazacyclooctatriacontine-41,42-diolato(2−)-N^1,N^{36},O^{41},O^{42})dioxouranium–(2-Pyridylmethyl)urea (20e·(2-pyridylmethyl)urea). A solution of 0.06 g of the UO_2 complex **20e** in 25 mL of MeOH was treated with 0.1 g of (2-pyridylmethyl)urea. The product crystallized immediately and was filtered off: mp 157–159 °C; 200 MHz ^1H NMR (DMSO-d_6) δ 9.61 (s, 2 H, CH=N), 8.54 (d, J = 5 Hz, 1 H, Ar″H-6), 7.90 (t, J = 8 Hz, 1 H, Ar″ H-4), 7.78–7.73 (m, 2 H, Ar′H), 7.55–7.50 (m, 2 H, Ar′H), 7.50–7.24 (m, 8 H, ArH, A′H, NH_2, Ar″ H-3, H-5), 6.62 (t, J = 8 Hz, 2 H, ArH), 5.7 (bs, 1 H, NH), 4.32–4.27 (m, 6 H, OCH_2, Ar″CH_2), 3.94–3.90 (m, 4 H, OCH_2), 3.72–3.69 (m, 4 H, OCH_2), 3.64–3.60 (m, 4 H, OCH_2), 3.54–3.51 (m, 12 H, OCH_2); IR (KBr) 1642 (C=O), 1602 (C=N), 900 (as O–U–O) cm^{-1}.

(9,10,12,13,15,16-Hexahydro-26-methyl-3,7:18,22-dimetheno-8,11,14,17,1,24-benzotetraoxadiazacyclohexacosine-29,30-diolato(2−)-N^1,N^{24},O^{29},O^{30})dioxouranium (20f). This reaction was carried out according to method A2 using the barium complex **13a** (0.50 g, 0.55 mmol) and $UO_2(OAc)_2{\cdot}2H_2O$ (0.23 g, 0.55 mmol) in MeOH. After the reaction was complete the organic layer was saturated with petroleum ether (bp 40–60 °C) and the orange product precipitated. It was filtered off and was washed with petroleum ether: yield 73%; mp 195–199 °C ($CHCl_3$/petroleum ether (bp 40–60 °C)); ^1H NMR δ 9.26 (s, 2 H, N=CH), 7.5–7.0 (m, 7 H, ArH, Ar′H, Ar″H), 6.7–6.5 (m, 2 H, ArH, Ar′H), 4.3–4.1 (m, 4 H, ArOCH_2), 4.1–3.9 (m, 4 H, OCH_2), 3.82 (s, 4 H, OCH_2), 2.50 (s, 3 H, Me); ^{13}C NMR δ 164.9, 164.2 (N=CH), 161.7, 161.5 (Ar C-2, Ar′ C-2), 149.5 (Ar C-3, Ar′ C-3), 145.9, 143.9 (Ar″ C-1, C-2), 123.8, 123.7 (Ar C-1, Ar′ C-1), 70.9, 68.8, 68.7 (OCH_2), 21.4 (Me); mass spectrum, m/e 744.227 (M$^+$; calcd 744.220); IR (KBr) 3450 (OH), 1600 (N=C), 900 (O–U–O) cm^{-1}. Anal. Calcd for $C_{27}H_{26}N_2O_8U{\cdot}3H_2O$: C, 40.61; H, 4.04; N, 3.51. Found: C, 40.62; H, 3.72; N, 3.23.

X-ray Crystallography. X-ray diffraction measurements were performed on a Philips PW1100 or an Enraf-Nonius CAD4 diffractometer, by using graphite monochromated Mo Kα radiation. Crystal data and data collection parameters are in Table III. Lattice parameters were determined by least squares from 20–25 centered reflections. Intensities were measured in the $\omega/2\theta$ scan mode and corrected for the decay of three control reflections, measured every hour, and for Lorentz and polarization factors.

The structures were solved by direct methods.[38] In some cases initially only the heavy atom and part of the macrocycle were located. The

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[38] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *27*, 368–376.

structures were then completed by successive difference Fourier syntheses. Reflections with $F_o^2 > 3\sigma(F_o^2)$ were considered observed and were included in the refinement (on F) by full-matrix least squares. Weights were calculated as $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$, $\sigma(I)$ based on counting statistics, and p an instability factor obtained from plots of F_o versus weighted error. After completion of the isotropic refinement of the non-H atoms an empirical absorption correction, using the DIFABS[39] routine, was performed for all structures. Due to the presence of a heavy atom not all H atoms were located on difference Fourier maps of the structures. In some cases macrocyclic and/or urea H atoms were put in calculated positions and treated as riding on their parent atoms. Details concerning the treatment of the H-atoms are in the Supplementary Material. Parameters refined were the overall scale factor, an isotropic extinction parameter g ($F_o = F_c/(1 + gI_c)$), positional and anisotropic thermal parameters for non-H atoms, and positional and isotropic thermal parameters for H-atoms. Refinement converged with shift/error ratios less than unity. Final difference Fourier maps showed features less than 1.0 eÅ^{-3}, mostly near the heavy atom. All calculations were done with SDP.[40]

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Supplementary Material Available: Tables of positional and thermal parameters of all atoms, bond distances and angles, and torsion angles in the macrocycle for the crystal structures of the compounds **12a**, **19a**·H_2O, **16e**·urea, and **20e**·urea (26 pages). Ordering information is given on any current masthead page.

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Synthesis and Catalysis of Novel Mono- and Bis(diene) Complexes of Niobium and X-ray Structures of Binuclear $[Nb(\mu\text{-}Cl)(C_5H_5)(s\text{-}cis\text{-butadiene})]_2$ and Mononuclear $Nb(C_5H_5)(s\text{-}cis\text{-}2,3\text{-dimethylbutadiene})_2$

Takuji Okamoto,[†] Hajime Yasuda,*,[†] Akira Nakamura,*,[†] Yasushi Kai,*,[‡] Nobuko Kanehisa,[‡] and Nobutami Kasai*,[‡]

Contribution from the Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan, and the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan. *Received November 18, 1987*

Abstract: A series of novel mono(diene)-niobium complexes of the type $NbCl_2(C_5R_5)(s\text{-}cis\text{-diene})$ (R = CH_3, H; diene = 2,3-dimethylbutadiene, isoprene, butadiene) of supine (exo) conformation was synthesized by the 1:1 reaction of $NbCl_4(C_5R_5)$ with (2-butene-1,4-diyl)magnesium or its higher homologue. Using a similar procedure, binuclear niobium-diene complexes, $[Nb(\mu\text{-}Cl)(C_5H_5)(\text{butadiene})]_2$ and $[Nb(\mu\text{-}Cl)(C_5H_5)(\text{isoprene})]_2$, could also be isolated as crystals and the X-ray analysis was applied for the former. The 1:2 reaction of $NbCl_4(C_5R_5)$ with (2-butene-1,4-diyl)magnesium or its derivatives leads to $Nb(C_5R_5)(s\text{-}cis\text{-diene})_2$ of supine-prone (exo-endo) conformation in good yields. A very unusual s-cis,s-trans mixed bis(diene)-metal complex was obtained in the case of $Nb(C_5H_5)(\text{butadiene})_2$ as a mixture with its geometrical isomer bearing two $s\text{-}cis\text{-}C_4H_6$ ligands. The addition reaction of a deuterium labeled complex $Nb(C_5H_5)(C_6H_6D_4)(C_6H_{10})$ with 2,4-dimethyl-3-pentanone proved the exceedingly high reactivity of the prone-oriented diene relative to the supine diene toward electrophiles. The isolated binuclear Nb-diene complexes and bis(diene)niobium complexes exhibit a fairly good catalytic activity for the polymerization of butadiene, linear dimerization of isoprene, and cyclic trimerization of 1-alkynes. $[Nb(\mu\text{-}Cl)(C_5H_5)(s\text{-}cis\text{-}C_4H_6)]_2$ crystallizes as monoclinic crystals, space group $P2_1/c$ with a = 12.257 (2) Å, b = 8.088 (1) Å, c = 19.049 (4) Å, β = 108.39 (1)°, and z = 4. The complex is diamagnetic in spite of the presence of a long Nb-Nb bond (3.364 (1) Å). A bis(s-cis-diene)niobium complex of supine-prone conformation, $Nb(C_5H_5)(2,3\text{-dimethylbutadiene})_2$, crystallizes as orthorhombic crystals, space group $Pnma$ with a = 8.961 (1) Å, b = 12.305 (2) Å, c = 13.530 (2) Å, and z = 4.

The chemistry of diene complexes of d-block along with f-block early transition metals (Zr,[1] Ti,[2] Hf,[3] Ta,[4] Th,[5,6] U,[6] etc.) is attracting increasing interests, since these complexes display a distinctive chemistry reflecting their unique M-C bonding property and their ability to perform the highly selective reactions. Previously we have reported unusual orientation of coordinated dienes and remarkable structures for group 5A tantalum-diene complexes (a third transition series metal complex) of the type $TaCl_2(C_5R_5)(\text{diene})$ and $Ta(C_5R_5)(\text{diene})_2$,[4] which became accessible by employing (2-butene-1,4-diyl)magnesium or its derivatives as an effective diene-incorporating reagent.[7] The extension of the above chemistry to niobium-diene complexes is of fundamental importance to prove the notable chemical and structural features of the second transition series group 5A metal species, since the

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[†] Faculty of Science.

[‡] Faculty of Engineering.

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