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Incorporation of N–O Bonds in Metallomacrocycles: Synthesis, X-ray Structure, and Electrochemistry of Hetero-Dinuclear Complexes

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A novel class of acyclic (**4** and **10**) and cyclic (**7**) hetero-dinucleating ligands that have a compartment suitable for the complexation of transition-metal cations and a compartment for the complexation of alkaline or alkaline-earth cations has been synthesized. The reaction of **7** and the Ba^{2+}-templated reaction of the ligands **4** and **10** with nickel, copper, or zinc acetate resulted in the hetero-dinuclear complexes **8**, **5**, and **11**, respectively, except for **5a**, which was isolated as the nickel complex. The barium complex **7** and three hetero-dinuclear complexes (**8b**, **11b**, and **11c**) have been analyzed by X-ray crystallography. The copper cation in the complexes **8b** and **11b** has a distorted square-planar coordination whereas the zinc cation in **11c** has a trigonal-bipyrimidal coordination. The barium cation in the four complexes discussed is approximate hexagonal-planar coordinated by the crown ether and by water and/or anions in the apical positions. The distance between the two metal centers in the complexes **8**, **11b**, and **11c** is 3.69–3.73 Å. The electrochemical properties of the complexed transition-metal cations have been investigated by polarography, cyclic voltammetry, and coulometry. The copper/barium complexes **5b** and **8b** undergo a one-electron reduction at $E_{1/2}$ = −0.999 and −0.438 V, respectively. The copper/barium complex **11b** exhibits a two-electron reduction in two separated one-electron steps at $E_{1/2}$ = −0.284 and −0.863 V. Cyclic voltammetry revealed that the reductions of the copper/barium complexes **8b** and **11b** are chemically reversible and that the oxidation of the **11b**$^{2-}$ species is a single-step, two-electron transfer. The one-electron reductions of the nickel/barium complexes **8a** ($E_{1/2}$ = −0.931 V) and **11a** ($E_{1/2}$ = −0.959 V) are chemically irreversible.

Introduction

Hitherto, the majority of hetero-dinuclear complexes are combinations of two transition-metal ions and little is known about (cyclic) ligands with two totally different cavities, viz., one "hard" cavity that can bind alkaline or alkaline-earth cations and a "soft" cavity capable of binding cations like Ni^{2+}, Cu^{2+}, Co^{2+}, and Zn^{2+}. Recently we have published studies on a number of cyclic ligands with a soft, salen type, N$_2$O$_2$ cavity and a hard polyether cavity together with the monobarium, mono-transition-metal, and hetero-dinuclear complexes (Chart I).[1,2] Our investigations showed a large influence by the complexed hard cation on the properties of the complexed transition-metal ion. Polarography revealed that complexation of hard cations in the polyether cavity resulted in anodic shifts of the half-wave potential corresponding to the reduction of the complexed transition-metal ion, as large as 213 mV. Furthermore, we have shown that the behavior of the complexed transition-metal cation in a hetero-dinuclear complex depends on the ring size and the rigidity of the polyether cavity. To the best of our knowledge, only Carroy and Lehn[3] very recently published dinuclear complexes of cyclic ligands that contain both a transition-metal ion and a non-transition-metal ion (Li^{+}, Ba^{2+}, Al^{3+}).

The area of dinucleating ligands able to form homo- and hetero-dinuclear complexes is of great interest for several reasons.[4] Firstly, such dinuclear complexes may bind and activate small molecules. Floriani and co-workers have shown this for CO$_2$ and CO$_2$-like molecules.[5] They prepared an acyclic $[L^{2-}\cdot Co^{I}]^{-}M^{+}$ (M = Na, K, Cs) complex in which the Co^{I} center acts as a Lewis base and the M^{+} center as a Lewis acid. Secondly, they may serve as models for metalloproteins like superoxide dismutase, oxidases, and peptidases.[6] In particular the dinuclear copper containing complexes recently attract much attention because of the presence of two copper centers in the active site of copper-proteins like hemocyanin, which transports O$_2$, and the monooxygenases tyrosinase and dopamine β-hydroxylase, which introduce oxygen (from O$_2$) into organic substrates.[7] Thirdly, the dinuclear complexes can be applied as bifunctional catalysts.[8]

In principle the behavior of dimetallic complexes can be quite different from the monometallic analogues when the distance between the two metal centers is small.[9]

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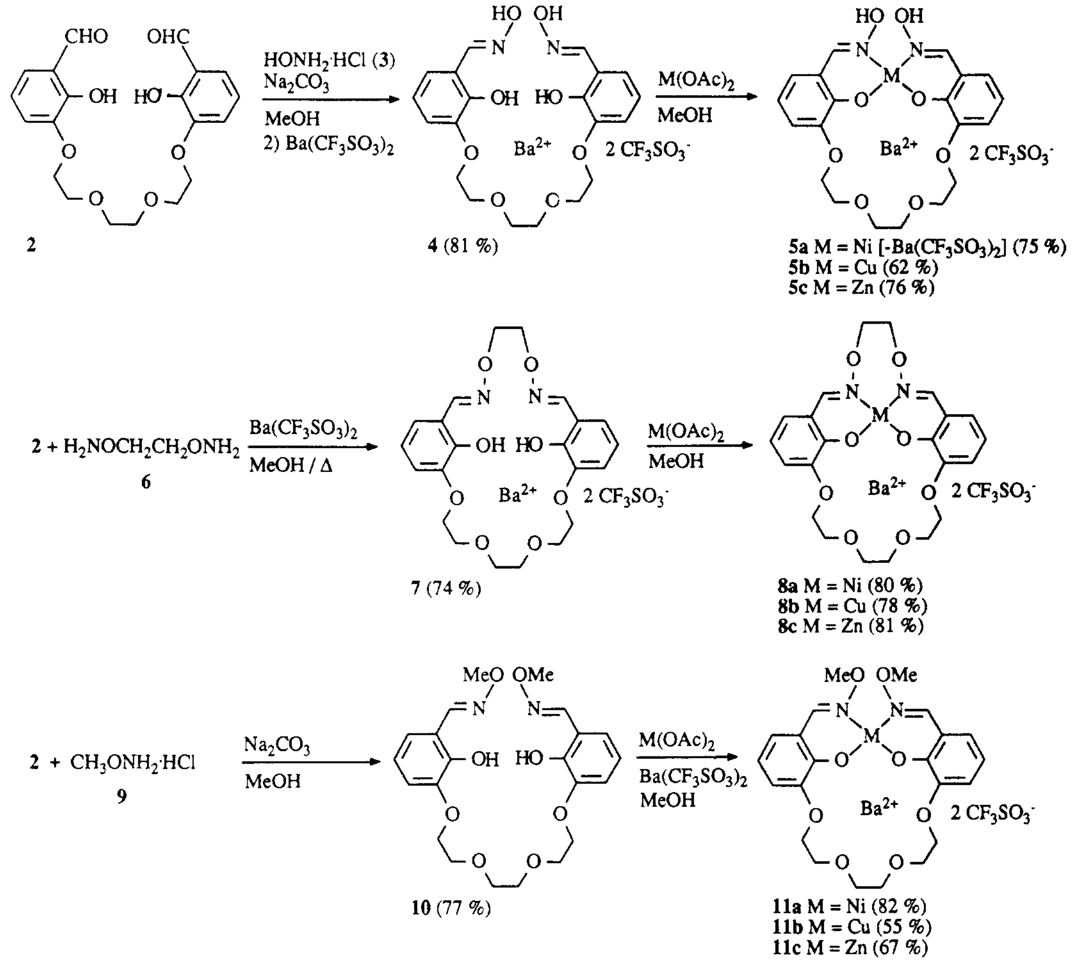
0022-3263/89/1954-2351$01.50/0

Scheme I



Nickel, copper, and zinc complexes of salicylaldoxime (1:2) in which the nitrogen and the phenolate oxygen are coordinated to the metal center are known,[10] but to our knowledge this complexing unit has not been used for the synthesis of dinucleating ligands. We decided to incorporate this complexing moiety in dinucleating ligands in order to investigate systematically the properties of (cyclic) hetero-dinuclear complexes. Since the nitrogen of the oxime linkage has a different basicity compared with the imine bond, other electrochemical properties are expected. In addition alkylation of the hydroxyl group of the oxime bond is expected to change the properties. In this paper we report the syntheses of three novel types of dinucleating ligands with soft, oxime-containing, N_2O_2 cavities and hard polyether cavities. Their properties were studied by X-ray crystallography, polarography, cyclic voltammetry, and coulometry.

Results and Discussion

Synthesis. The dialdehyde **2**[1] was converted into the corresponding dioxime by reaction with excess of hydroxylamine under slightly basic conditions, and the dioxime derivative was isolated and characterized as the barium complex **4** in 81% yield. The ^{1}H NMR spectrum (DMSO-d_6) shows a singlet at 8.33 ppm, indicating the presence of oxime bonds, and in the IR spectrum these oxime double bonds exhibit an absorption at 1621 cm^{-1}. Because of a favorable intramolecular hydrogen bond between the phenol group and the oxime nitrogen, the oxime bonds most likely have a trans configuration. The barium complex **4** was converted into the complexes **5** upon slow addition of a solution of nickel, copper, or zinc acetate to a solution of the barium complex in methanol. The IR spectra of **5a–c** show a signal at 1602 cm^{-1} for the N=C bonds, which indicates that upon complexation these double bonds have less double-bond character than the oxime moieties in **4**. From the elemental analysis, it was concluded that **5a** was obtained as a nickel complex instead of the dinuclear complex as was the case for **5b** and **5c**. The ^{1}H NMR spectrum of **5c** shows an upfield shift of the N=CH protons (7.99 ppm) with respect to the barium complex **4** (8.33 ppm)[11] (Scheme I).

In order to study the effect of alkylation and alkylation combined with cyclization of the alcohol moieties on the physical properties of the oxime-containing complexes **5**, we have prepared the dinucleating ligands **7** and **10**. The synthesis was accomplished starting from 1,2-bis(aminooxy)ethane (**6**)[12] and *O*-methylhydroxylamine (**9**). The macrocyclization of the dialdehyde **2** with the diamine **6** was carried out by slow addition of both a solution of **2** and a solution of **6** to a refluxing solution of $Ba(CF_3SO_3)_2$[13] in methanol to afford **7** in 74% yield. We have demonstrated for similar cyclic ligands that this combination of barium, acting as a template ion, and high dilution conditions is necessary in order to achieve cyclic compounds in high yields.[1,2] The ^{1}H NMR spectrum of **7** exhibits a signal at 8.47 ppm and in the IR spectrum an absorption

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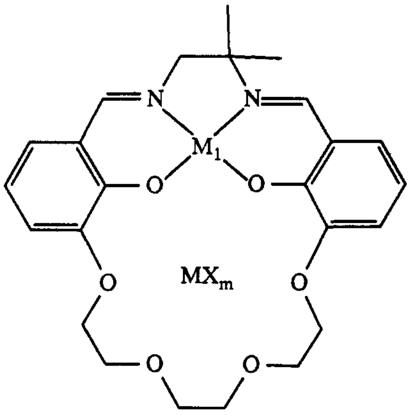
Table I. Crystal Data and Data Collection Parameters

compd	**7**	**8b**·2H$_2$O	**11b**	**11c**
formula	$C_{24}H_{26}BaF_6N_2O_{14}S_2$	$C_{24}H_{28}BaCuF_6N_2O_{16}S_2$	$C_{24}H_{26}BaCuF_6N_2O_{14}S_2$	$C_{24}H_{26}BaF_6N_2O_{14}S_2Zn$
fw	881.00	979.41	945.48	947.31
lattice type	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	Pn	$Pbcn$
T(K)	293	293	293	293
cell dimensions				
a(Å)	16.592 (4)	12.915 (1)	12.213 (6)	23.056 (7)
b(Å)	23.415 (6)	12.501 (3)	10.558 (2)	21.078 (10)
c(Å)	18.421 (7)	12.020 (1)	26.831 (9)	14.256 (3)
α (deg)		61.87 (1)		
β (deg)	114.27 (2)	81.73 (1)	102.83 (1)	
γ (deg)		78.97 (1)		
V(Å^3)	6524 (2)	1677 (2)	3373 (3)	6928 (7)
Z	8	2	4	8
D_c (g/cm^3)	1.79	1.88	1.86	1.82
F(000)	3504	970	1836	3680
μ(cm^{-1})	1.44	2.02	2.01	2.05
θ range (deg)	3–22.5	3–30	3–30	3–22.5
no. of unique refln				
measd	8482	8757	10370	4450
obsd [$I > 3\sigma(I)$]	5573	4976	7472	2065
no. of variables	554	574	587	242
R(%)	5.4	3.2	5.2	7.1
R_w(%)	6.5	4.2	6.7	7.9
weighting factor p	0.05	0.04	0.05	0.05
extinction g (*10^{-7})				0.17

Chart I



1a M_1 = Ni; MX_m = -
1b M_1 = Ni; MX_m = $Ba(CF_3SO_3)_2$
1c M_1 = Cu; MX_m = -
1d M_1 = Cu; MX_m = $Ba(CF_3SO_3)_2$

is located at 1618 cm^{-1}, which shows that the oxime linkages are present. In the mass spectrum the M$^+$ peak is found at 446.169, which is in agreement with the calculated value for **7** upon loss of $Ba(CF_3SO_3)_2$ (calcd 446.169). The solid-state structure of **7** was determined by X-ray crystallography (vide infra). The dinuclear complexes **8a–c** were easily obtained in high yields by reaction of the barium complex **7** with 1 equiv of nickel, copper, and zinc acetate, respectively, in methanol. In the IR spectra the absorption of the N=C linkages is observed at 1606–1608 cm^{-1}, compared with 1618 cm^{-1} for **7**. Also in these complexes the complexation of a metal ion in the soft cavity results in N=C bonds with less double-bond character. For the zinc/barium complex **8c**, a downfield shift was observed for the N=CH protons compared with **7** (8.73 and 8.47 ppm, respectively), which is the opposite effect as observed for **5c** and **4**. The solid-state structure of the copper/barium complex **8b** was also determined by X-ray diffraction (vide infra). The oxime derivative **10** was obtained in 77% yield upon reaction of the dialdehyde **2** and an excess of *O*-methylhydroxylamine (**9**) in methanol under slightly basic conditions. The ^{1}H NMR spectrum exhibits a signal for the N=CH protons at 8.17 ppm and the IR spectrum shows an absorption for the N=C bonds at 1609 cm^{-1}. The dinuclear complexes **11a–c** were obtained by reaction under high dilution conditions of the dioxime derivative **10** and 1 equiv of nickel, copper, or zinc acetate, respectively, in methanol using barium triflate as template salt. The IR spectra of the dinuclear complexes **11a–c** show almost the same absorption for the N=C bonds as those for the precursor **10** (1605–1609 and 1609 cm^{-1}, respectively), indicating that this double bond is hardly affected upon complexation. The solid-state structures of **11b** and **11c** were determined by X-ray diffraction (vide infra).

X-ray Structures

The solid-state structures of the compounds **7**, **8b**, **11b**, and **11c** were determined by X-ray crystallography. Details of the structure determination are given in the Experimental Section. ORTEP[14] views of the structures are shown in the Figures 1–4. Metal coordination is depicted by open bonds. Table I contains the crystal data and data collection parameters and Table II contains data on the metal cation coordination.

Suitable crystals of the barium complex **7** were grown by slow diffusion of diisopropyl ether into a solution of **7** in methanol.[15] The structure is shown in Figure 1.

The asymmetric unit contains two independent molecules. Beside minor differences in the conformation of the macrocycle, the coordination of the barium cations is

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(11) The ^{1}H NMR spectrum of **5a** in DMSO-d_6 exhibits broad signals between 3.5 and 6.0 ppm. This is probably due to a partially paramagnetic nickel cation. Bis(salicylaldoxime)nickel(II), which is diamagnetic in the solid state, is partially paramagnetic in chloroform probably due to molecular association.[10a] The ^{1}H NMR spectrum of the copper(II) complex **5b** could not be obtained because of paramagnetism.

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(13) Barium triflate ($Ba(CF_3SO_3)_2$) was prepared from $Ba(OH)_2$ and CF_3SO_3H in water.

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Table II. Metal Coordination in the Crystal Structures: Range of Cation-Coordinating Atom Distances (Å) and Coordination Number

compd	7		$8b \cdot 2H_2O$		11b				11c	
cation	$Ba1^{2+}$	$Ba2^{2+}$	Cu^{2+}	Ba^{2+}	$Cu1^{2+}$	$Ba1^{2+}$	$Cu2^{2+}$	$Ba2^{2+}$	Zn^{2+}	Ba^{2+}
coord. atom										
O_{ether}	2.83–2.95	2.28–2.85		2.81–2.91		2.82–2.89		2.80–2.85		2.79–2.85
O_{phen}	2.79–2.83	2.79–2.93	1.92–1.95	2.68–2.73	1.89–1.90	2.65–2.70	1.90–1.92	2.66–2.70	1.98–1.99	2.65–2.70
N			1.94–1.99		1.94–1.96		1.96–1.98		2.07–2.11	
coord. no.	10[a]	9[b]	4	9[c]	4	10[d]	4	10[e]	5[f]	10[g]

[a] +4 oxygens of three anions ($Ba^{2+} \cdots O$ 2.68–3.05 Å). [b] +3 oxygens of three anions ($Ba^{2+} \cdots O$ 2.70–2.71 Å). [c] +1 H_2O ($Ba^{2+} \cdots O$ 2.82 Å) and 2 oxygens of one anion ($Ba^{2+} \cdots O$ 2.76–2.86 Å). [d] +4 oxygens of three anions ($Ba^{2+} \cdots O$ 2.73–3.03 Å). [e] +4 oxygens of three anions ($Ba^{2+} \cdots O$ 2.78–2.98 Å). [f] +1 oxygen of an anion ($Zn^{2+} \cdots O$ 2.13 Å). [g] +4 oxygens of three anions ($Ba^{2+} \cdots O$ 2.72–3.15 Å).

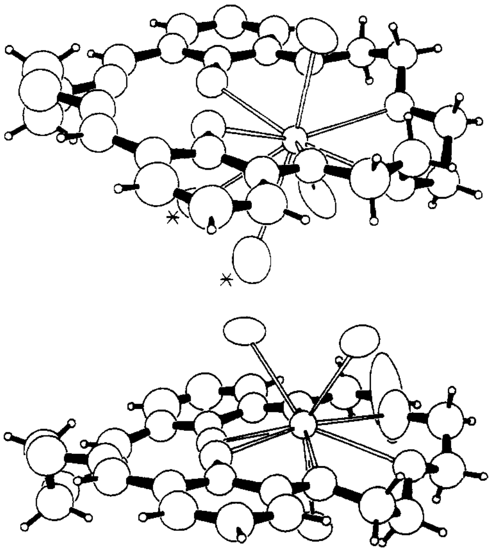

Figure 1. View of **7**: molecule 1 (top, a) and molecule 2 (bottom, b). Only the coordinated oxygens of the anions are shown for clarity. Oxygens marked with an asterisk are of one anion.

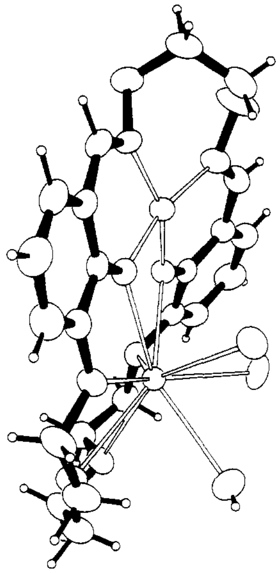

Figure 2. View of $\mathbf{8b} \cdot 2H_2O$. Only the oxygens of the coordinated anion are shown for clarity.

significantly different. In molecule 1 the barium has a 10-fold coordination. The macrocycle is coordinated to the barium by two phenolic oxygens ($Ba^{2+} \cdots O$ 2.79–2.83 Å) and four ether oxygens ($Ba^{2+} \cdots O$ 2.83–2.95 Å). Furthermore three triflate ($CF_3SO_3^-$) anions are coordinated to the barium. At one side of the macrocycle two anions are coordinated, one with two oxygens ($Ba^{2+} \cdots O$ 2.94–3.05 Å) and the other one with one oxygen ($Ba^{2+} \cdots O$ 2.71 Å). At the other face of the macrocycle the apical position is occupied by one coordinating oxygen of an anion ($Ba^{2+} \cdots O$ 2.68 Å). The barium cation is displaced 0.58 Å out of the mean plane of the six oxygens of the macrocycle toward the two coordinating triflate anions. In molecule 2 the barium has a 9-fold coordination, formed by two phenolic oxygens ($Ba^{2+} \cdots O$ 2.79–2.93 Å), four ether oxygens ($Ba^{2+} \cdots O$ 2.82–2.85 Å), and three triflate anions via one oxygen ($Ba^{2+} \cdots O$ 2.70–2.71 Å). Also in this complex the barium is displaced (0.50 Å) out of the mean plane of the six oxygens of the macrocycle toward the two coordinating triflate anions.

Green single crystals of the copper/barium complex $\mathbf{8b} \cdot 2H_2O$ were obtained by slow evaporation to dryness of a solution in methanol. The structure of this hetero-dinuclear complex is shown in Figure 2.

The copper cation is coordinated in the soft cavity by the nitrogens ($Cu^{2+} \cdots N$ 1.94–1.99 Å) and the phenolate oxygens ($Cu^{2+} \cdots O$ 1.92–1.95 Å). These four coordinating atoms are within 0.29 Å of their mean plane. The copper cation is displaced 0.07 Å out of this mean plane, resulting in a distorted square-planar coordination. The barium is complexed in a perching fashion by the macrocycle. The 9-fold coordination is formed by two phenolate oxygens ($Ba^{2+} \cdots O$ 2.68–2.73 Å), four ether oxygens ($Ba^{2+} \cdots O$ 2.81–2.91 Å), two oxygens of one anion ($Ba^{2+} \cdots O$ 2.76–2.86 Å), and one water molecule ($Ba^{2+} \cdots O$ 2.82 Å). At the other side of the macrocyclic ring no coordinating anion or water molecule was found. The displacement of the barium out of the mean plane of the six macrocyclic oxygens is 0.90 Å, which is larger than that for the barium complex **7** (0.58 and 0.50 Å). This is due to a contraction of the macrocycle upon complexation of the copper cation. This is reflected in a shorter distance between the two phenolate oxygens (2.60 Å), whereas the distances between the two phenolic oxygens in **7** are 3.45 and 3.49 Å. The angle between the two aromatic rings is 30.8°, whereas the angles in the barium complex **7** are 13.2° and 15.4°. The distance between the two metal ions is 3.73 Å.

Dark brown crystals of the copper/barium complex **11b** were obtained by slow diffusion of diisopropyl ether into a solution of **11b** in acetonitrile. The structure of this hetero-dinuclear complex is shown in Figure 3.

The asymmetric unit contains two independent molecules that have different conformations. In molecule 1 the copper is coordinated by two nitrogens ($Cu^{2+} \cdots N$ 1.94–1.96 Å) and two phenolate oxygens ($Cu^{2+} \cdots O$ 1.98–1.90 Å) in a distorted square-planar complex. The copper cation is displaced 0.04 Å out of the mean plane of the four coordinating atoms, which are within 0.37 Å of their mean plane. The barium cation is complexed in a perching fashion by the crown ether. The macrocycle is coordinated with the two phenolate oxygens ($Ba^{2+} \cdots O$ 2.65–2.69 Å) and the four ether oxygens ($Ba^{2+} \cdots O$ 2.82–2.85 Å). At one side

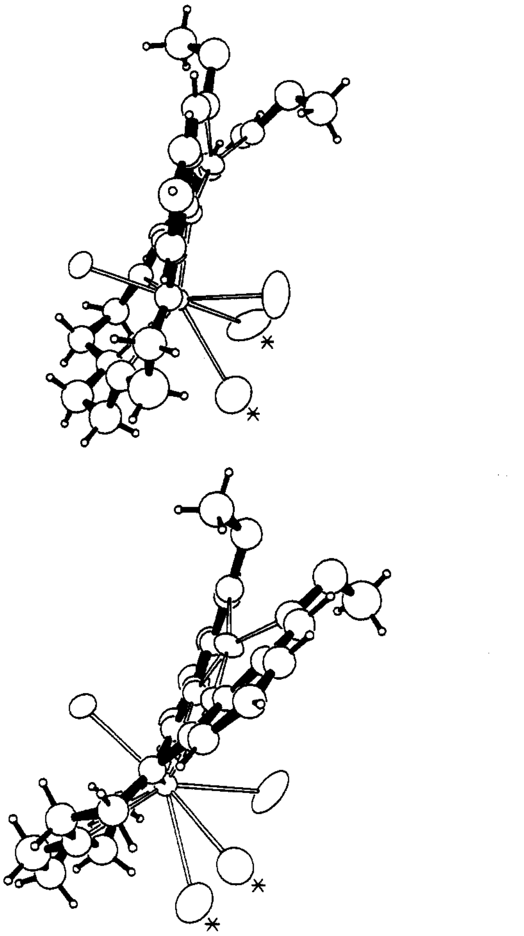

Figure 3. View of **11b**: molecule 1 (top, a) and molecule 2 (bottom, b). Only the coordinated oxygens are shown for clarity. Oxygens marked with an asterisk are belonging to one anion.

of the macrocycle two anions are coordinated, one with two oxygens (Ba^{2+}···O 2.81–3.03 Å) and the other with one oxygen (Ba^{2+}···O 2.75 Å). At the other side of the ring the apical position is occupied by one coordinating oxygen of an anion (Ba^{2+}···O 2.73 Å). The barium is displaced 0.71 Å out of the mean plane of the six oxygens of the macrocycle toward the two coordinating anions. The angle between the two aromatic rings is 26.4°. In molecule 2 the copper cation is also coordinated by two nitrogens (Cu^{2+}···N 1.96–1.98 Å) and two phenolate oxygens (Cu^{2+}···O 1.90–1.92 Å) in a distorted square-planar complex. The copper cation is displaced 0.11 Å out of the mean plane of the four coordinating atoms, which are within 0.30 Å of their mean plane. The barium is complexed in a similar perching complex as in molecule 1. The macrocycle is coordinated by two phenolate oxygens (Ba^{2+}···O 2.66–2.70 Å) and four ether oxygens (Ba^{2+}···O 2.80–2.85 Å). At one side of the ring two anions are coordinated, one with two oxygens (Ba^{2+}···O 2.96–2.98 Å) and the other one with one oxygen (Ba^{2+}···O 2.83 Å). At the other side one oxygen of an anion is coordinated (Ba^{2+}···O 2.78 Å). The barium cation is displaced 0.65 Å out of the mean plane of the six oxygens of the ring toward the two coordinating anions. The angle between the two aromatic rings is somewhat smaller than in molecule 1 (21.9° and 26.4°, respectively). In both molecules the distance between the copper and the barium is 3.69 Å. The distance between the phenolate oxygens (2.59 and 2.66 Å) is comparable with the distance in the copper/barium complex **8b** (2.60 Å).

Pale yellow crystals of **11c** were obtained by slow saturation of a solution of **11c** in acetonitrile with diisopropyl ether. The structure is shown in Figure 4.

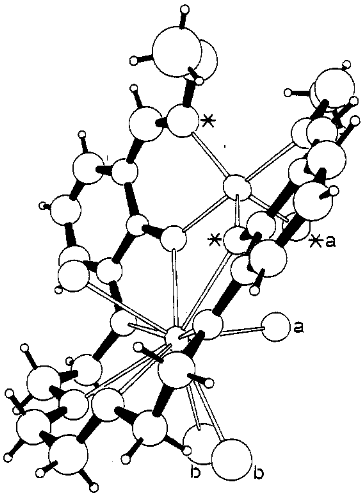

Figure 4. View of **11c**. Atoms labeled with an asterisk are the equatorial ligands of the complexed zinc cation. Oxygens marked with an "a" are of the anion that is coordinated both to zinc and barium. Oxygens marked with a "b" are of the anion that is only coordinated to the barium.

In contrast to the four-coordination of the copper cation in the complexes **8b** and **11b**, the zinc cation has a trigonal-bipyrimidal coordination sphere. The ground plane is formed by one phenolate oxygen and one nitrogen of the macrocycle and an oxygen of an anion (these atoms are labeled with an asterisk). The zinc cation is displaced 0.10 Å out of this plane toward the axial nitrogen atom. The angles in the equatorial plane are 105°, 123°, and 131° and the angles between an equatorial and an axial atom are in the range of 84° to 97°. The angle O_{ax}–Zn–N_{ax} is 176°. The result of this coordination of zinc with respect to the copper/barium complex **11b** is a longer distance between the phenolate oxygens (2.74 Å in **11c** to 2.59 and 2.66 Å in **11b**) and a larger angle between the aromatic rings (42° in **11c** to 21.9 and 26.4° in **11b**). The barium cation is complexed in the hard polyether cavity in a perching fashion. The macrocyclic ring is coordinated with two phenolate oxygens (Ba^{2+}···O 2.65–2.70 Å) and four ether oxygens (Ba^{2+}···O 2.79–2.85 Å). At one side of the ring two anions are coordinated, one with two oxygens (Ba^{2+}···O 2.90–3.15 Å) and the other one with one oxygen (Ba^{2+}···O 2.74 Å). This latter anion is bridged via an other oxygen to the zinc cation. At the other side of the macrocycle the apical position is occupied by an oxygen of an anion (Ba^{2+}···O 2.72 Å). The barium cation is displaced 0.70 Å out of the mean plane of the six oxygens of the ring toward the two coordinating anions. The distance between the two metal ions is 3.69 Å.

In the four structures discussed, an approximate hexagonal-planar coordination of the crown ether to the barium cation and apical coordination by anions and water molecules is observed. This combination of equatorial coordination of a crown ether and three or four apical ligands is not uncommon for barium.[1,2,16]

Electrochemistry

The reduction properties of the complexes **5a**, **5b**, **8a**, **8b**, **11a**, and **11b** were investigated by sampled DC po-

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(16) (a) Drew, M. G. B.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1678. (b) Dyer, R. B.; Metcalf, D. H.; Ghirardelli, R. G.; Dalmer, R. A.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 3621. (c) Wei, Y. Y.; Tinant, B.; Declercq, J.-P.; van Meerssche, M. *Acta Crystallogr., Sect. C* **1988**, *44*, 77. (d) Dalley, N. K.; Sypherd, D.; George, R. D. *J. Heterocycl. Chem.* **1984**, *21*, 497.

Table III. Polarographic Data for the Reduction at a Dropping Mercury Electrode at 20 °C in 0.1 M TEAP in DMSO vs Ag/AgCl

compd	$E_{1/2}$, V	i_l, μA	slope log plot, mV	concn, mM
5a	−1.231	0.139	60	*a*
5b	−0.998	0.903	55	1.48
8a	−0.931	1.081	60	1.57
8b	−0.438	1.446	61	1.82
11a	−0.959	0.808	58	1.23
11b[b]	−0.284	0.801	51	1.14
	−0.863	0.549	129	

[a] Saturated but unknown concentration. [b] "Total" limiting current is 2.0 μA.

larography in DMSO with TEAP ($Et_4N^+ClO_4^-$) as supporting electrolyte. The polarograms in the range of −0.2 to −1.5 V were recorded and evaluated by a computerized method described by Zollinger et al.[17] and are given in Table III. The complexes **8a**, **8b**, **11a**, and **11b** were also studied with cyclic voltammetry, in DMSO also with TEAP as supporting electrolyte. Potentials are reported vs an Ag/AgCl reference electrode.

The polarograms of the copper/barium complexes **5b** and **8b** show one wave with a half-wave potential ($E_{1/2}$) of −0.998 and −0.438 V, respectively. The reduction of the complex **8b** is a one-electron transfer, which was determined by using coulometry at −0.6 V. With the assumption that the diffusion coefficients are the same for **5b** and **8b** also the reduction of the former involves one electron. The slope for these reductions are 55 and 61 mV, respectively, which indicates an electrochemically reversible electron transfer. The copper/barium complex **8b** was also studied by using cyclic voltammetry. At scan rates of 0.5 to 6 V/s a diffusion-controlled mechanism is observed with differences in the peak potentials ($\Delta E_p = E_{pa} - E_{pc}$) of 58 to 78 mV. The peak surfaces, i.e., charge transfered, of the cathodic and anodic sweep are within 10% equal, which shows that the reduction is *chemically* reversible; the generated Cu^I species is stable in solution in the absence of oxygen. The remarkable difference in the half-wave potentials of the complexes **5b** and **8b** (−0.998 and −0.438 V, respectively) may be due to the combined effect of alkylation of the hydroxyl group in the oxime moiety and cyclization of the ligand. In order to determine which effect provides the major contribution, the copper/barium complex **11b**, which contains only alkylated oxime moieties, was synthesized.

The polarogram of the complex **11b** is more complicated and shows two major waves with half-wave potentials of −0.284 and −0.863 V.[18] Between these two waves two small waves are visible, which may be due to adsorption at the mercury drop.[19] The ratio of the limiting currents of a major wave plus the closest minor wave was about one. The first major wave is more or less electrochemically reversible (slope is 51 mV) but the second major one is electrochemically irreversible (slope 129 mV). Coulometry at a potential of −1.0 V revealed that two electrons were transfered, hence the reduction proceeds via a formally Cu^I species to a formally Cu^0 species. In order to obtain more detailed information about this reduction process, this complex was also studied by using cyclic voltammetry.

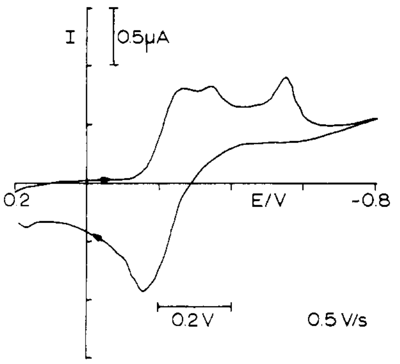

Figure 5. Cyclic voltammogram of **11b** in DMSO at scan rate of 0.5 V/s.

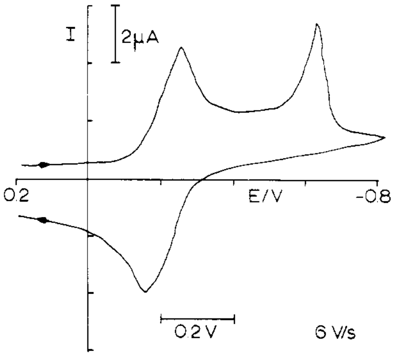

Figure 6. Cyclic voltammogram of **11b** in DMSO at scan rate of 6 V/s.

The cyclic voltammograms between 0.2 and −0.800 V at scan rates of 0.5 to 6 V/s show two peaks in the cathodic (reductive) sweep and one peak in the anodic (oxidative) sweep (see Figures 5 and 6). At the scan rates of 0.5 and 1 V/s a small peak right after the first peak was observed, presumably due to adsorption of the generated Cu^I species at the mercury drop. The cathodic peak surface was within 10% equal to the anodic peak surface, which leads to two conclusions. Firstly, this two-electron reduction is chemically reversible, and, secondly, the oxidation is a one-step two-electron transfer, whereas the reduction occurs in two steps.[20] When five scans at a scan rate of 6 V/s were applied, five essentially identical voltammograms were recorded, supporting the chemical reversibility of this reduction and oxidation. We had expected a more or less "intermediate" behavior of this complex **11b** with respect to the behavior of the complexes **5b** and **8b**, but instead strikingly different properties were observed.

The polarogram of the nickel complex **5a** shows one wave at a half-wave potential of −1.231 V and a slope of 60 mV. We assume that this reduction is a one-electron transfer (vide infra). This reduction occurs at a less negative potential than that for the nickel complex **1a**,[2] which contains imine bonds instead of oxime linkages, indicating that the nitrogen in the oxime bond is less basic.[21] As a result the electron-donating ability toward the metal is lower and hence the reduction of the more positively charged metal cation is easier.

The reduction of the nickel/barium complexes **8a** and **11a** is a single step with a half-wave potential of −0.931

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[17] Zollinger, D. P.; Bos, M.; van Veen-Blaauw, A. M. W.; van der Linden, W. E. *Anal. Chim. Acta* **1985**, *167*, 89.

[18] The differences in the polarographic and cyclic voltammetric data for the copper/barium complex **11b** are surprising; in the two techniques a very different scan rate is used and hence a direct comparison of the results is not always possible.

[19] Heyrovski, J.; Kuta, J. *Grundlagen der Polarographie*; Akademie-Verlag: Berlin, 1965.

[20] Several tentative explanations can be given for the observed reduction/oxidation behavior of **11b**, but no detailed mechanistic study has been carried out to reveal the actual mechanism. Therefore we prefer to give only an accurate description of the observed phenomena.

[21] We assume a square-planar complex, as is reported for the nickel complex of salicylaldoxime.[10d]

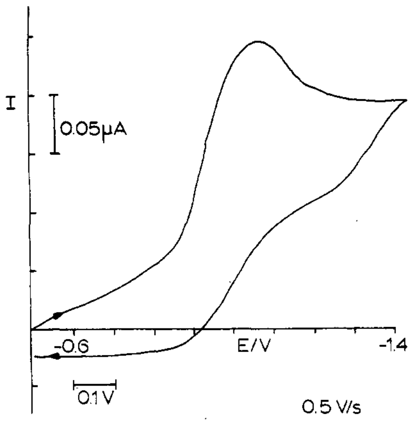

Figure 7. Cyclic voltammogram of **8a** in DMSO at scan rate of 0.5 V/s.

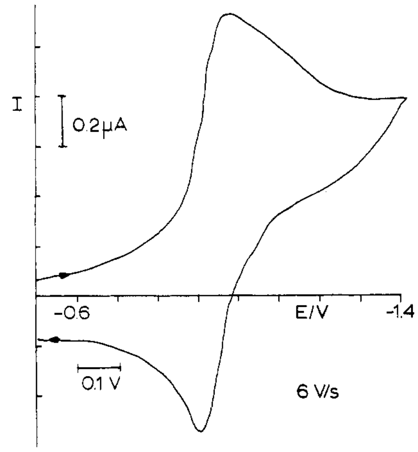

Figure 8. Cyclic voltammogram of **8a** in DMSO at scan rate of 6 V/s.

and −0.959 V, respectively. When we assume equal diffusion coefficients of nickel/barium complexes **8a** and **11a** and the copper/barium complexes **8b** and **11b** the diffusion current constant is proportional to the number of electrons transfered.[19] Based on this assumption, it can be concluded that the reductions of the nickel/barium complexes are one-electron transfers. Cyclic voltammetry at scan rates of 0.5 to 6 V/s of **8a** and **11a** revealed that the generated Ni^I species are not stable. At low scan rates a peak is observed in the cathodic sweep but virtually no peak is seen in the anodic sweep (see Figures 7 and 8). Upon increasing the scan rate also a peak in the anodic sweep becomes visible. This indicates an EC mechanism: firstly an electrochemical step followed by a chemical step.

The reduction of the hetero-dinuclear complexes **5b**, **8a**, **8b**, **11a**, and **11b** takes place at a less negative half-wave potential[22] than those for the similar hetero-dinuclear complexes **1b** and **1d**, which contain imine bonds, confirming that the nitrogen in an oxime bond is less basic than that in an imine bond. The deviation from planarity of the atoms complexing the transition-metal cation, as observed in the solid state (vide supra), may also play a role in decreasing the donation of electrons to the cation (the complexation of the transition-metal cation in the salen-type macrocycles, Chart I, is essentially square planar[1,2]). Therefore the cation is more positively charged and the reduction will occur at less negative potential.

Conclusions

The Ba^{2+}-templated synthesis of the hetero-dinuclear complexes **5** and **11** from the dioximes **4** and **10** with nickel, copper, or zinc acetate is a convenient route. The Ba^{2+}-templated (1:1) macrocyclization of the dialdehyde **2** and the diamine **6** could be performed in high yield and the resulting barium complex could be easily transformed into the hetero-dinuclear complexes **8** upon reaction with nickel, copper, or zinc acetate. The coordination sphere of the zinc cation in **11c** is a trigonal bipyrimid, whereas the copper cation in the complexes **8b** and **11b** has a distorted square-planar coordination. Our electrochemical studies revealed that the copper/barium complexes **5b** and **8b** undergo a one-electron reduction, whereas the copper/barium complex **11b** exhibits a two-electron reduction in two steps below −1.5 V. Cyclic voltammetry showed that the reductions of **8b** (one electron) and **11b** (two electrons) are chemically reversible. The oxidation of the $\mathbf{11b}^{2-}$ species to **11b** occurs in one step. The one-electron reductions of the nickel/barium complexes **8a** and **11a** are chemically irreversible. As is clearly demonstrated the electrochemical behavior of oxime bonds containing complexes is quite different from those having imine bonds. We are currently studying the interactions of these hetero-dinuclear complexes with small molecules like CO_2, CO, NO_x, and SO_x. Our ultimate goal is the application of a hetero-dinuclear complex as a bifunctional catalyst.

Experimental Section

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Bruker WP-80 spectrometer and ^{13}C NMR spectra were recorded with a Nicolet NT-200 WB spectrometer. The spectra were recorded in DMSO-d_6 with Me_4Si as an internal standard unless otherwise stated. Mass spectra were obtained with a Varian MAT 311A spectrometer. Infrared spectra were recorded with a Nicolet 5SXC FT-IR spectrophotometer. Elemental analyses were carried out by the Department of Chemical Analysis of our institute.

All chemicals were reagent grade and were used without further purification. DIP refers to diisopropyl ether, DMSO to dimethyl sulfoxide, and THF to tetrahydrofuran. Dropwise addition over a period of several hours was always carried out with a perfusor.

[3,3′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bis(2-hydroxybenzaldehyde) dioxime]barium(2+) Bis(trifluoromethanesulfonate) (4). To a solution of $HONH_2{\cdot}HCl$ (**3**) (2.10 g, 30.2 mmol) in 15 mL of H_2O was added solid Na_2CO_3 to pH = 8. To the resulting slightly basic solution was added the dialdehyde **2** (3.00 g, 7.69 mmol) dissolved in 50 mL of warm methanol, and the reaction mixture was stirred for 20 h at 50 °C. The mixture was cooled to room temperature and the methanol was evaporated. The aqueous solution was acidified with acetic acid to pH = 6 and extracted twice with $CHCl_3$ (10 mL). The combined organic layers were washed three times with water (10 mL), dried with $MgSO_4$, and concentrated. The residue was dissolved in 25 mL of MeOH and 1 equiv of $Ba(CF_3SO_3)_2$ was added. The mixture was stirred for 15 min and concentrated to 15 mL, after which some DIP was added. The resulting white precipitate was filtered off to give the barium complex **4**: yield 81%; mp 186–187 °C (MeOH/DIP); ^{1}H NMR δ 11.3 (bs, 2 H, OH), 9.6 (bs, 2 H, OH), 8.33 (s, 2 H, N═CH), 7.1–6.8 (m, 6 H, Ar H), 4.2–4.1 (m, 4 H, Ar OCH_2), 3.8–3.7 (m, 4 H, OCH_2), 3.63 (s, 4 H, OCH_2); ^{13}C NMR δ 147.9 (d, N═CH), 146.9 and 145.9 (s, Ar C-2,3), 120.1, 119.1, and 114.6 (d, Ar C-4-6), 118.5 (s, Ar C-1), 69.3, 68.7, and 68.2 (t, OCH_2); IR (KBr) 3445 (OH) and 1621 (N═C) cm^{-1}.

General Procedure for the Synthesis of 5a, 5b, and 5c. To a solution of the barium complex **4** (0.30 g, 0.35 mmol) in 100 mL of MeOH was added a solution of 1 equiv of nickel, copper, or zinc acetate in 24 mL of MeOH dropwise over a period of 1.5 h. After the addition was completed, the reaction mixture was stirred for 0.5 h, after which it was concentrated to dryness. The colored

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[22] Although it is formally not correct to compare reductions that have different mechanisms, we are allowed to do so because the value $(E_{pc} + E_{pa})/2$ for **8a** and **11a** at scan rates of 6 V/s (−0.932 and −0.972 V, respectively), where a reversible E mechanism is observed, are equal to the half-wave potentials.

residue was dissolved in a little CH_3CN and some DIP was added, after which a precipitate was formed, which was filtered off and was washed once with DIP.

[3,3′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bis(2-hydroxybenzaldehyde oximato-N^1,O^2)]nickel (5a): yield 75%; mp 216–218 °C (MeOH/DIP); IR (KBr) 3540 (OH) and 1602 (N=C) cm^{-1}.

Anal. Calcd for $C_{20}H_{22}N_2NiO_8 \cdot 0.5H_2O$: C, 49.42; H, 4.77; N, 5.76. Found: C, 49.27; H, 4.61; N, 5.56.

[[3,3′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bis(2-hydroxybenzaldehyde oximato-N^1,O^2)]copper]barium(2+) bis(trifluoromethanesulfonate) (5b): yield 62%; mp >300 °C (CH_3CN/DIP); IR (KBr) 3450 (OH) and 1602 (N=C) cm^{-1}.

Anal. Calcd for $C_{22}H_{22}BaCuF_6N_2O_{14}S_2$: C, 28.80; H, 2.42; N, 3.05. Found: C, 28.53; H, 2.45; N, 3.31.

[[3,3′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bis(2-hydroxybenzaldehyde oximato-N^1,O^2)]zinc]barium(2+) bis(trifluoromethanesulfonate) (5c): yield 76%; mp >300 °C (MeOH/DIP); ^{1}H NMR δ 7.99 (s, 2 H, N=CH), 6.9–6.4 (m, 6 H, Ar H), 4.1–4.0 (m, 8 H, $ArOCH_2$ and OCH_2), 3.79 (s, 4 H, OCH_2); ^{13}C NMR δ 155.3 and 149.4 (s, Ar C-2,3), 153.5 (d, N=C), 123.9, 112.8, and 110.4 (d, Ar C-4-6), 117.2 (s, Ar C-1), 68.9, 67.9, and 66.0 (t, OCH_2); IR (KBr) 3460 (OH) and 1602 (N=C) cm^{-1}.

Anal. Calcd for $C_{22}H_{22}BaF_6N_2O_{14}S_2Zn \cdot 0.5DIP$: C, 30.95; H, 3.01; N, 2.89. Found: C, 30.53; H, 2.85; N, 3.26.

(4,7,15,18,21,24-Hexaoxa-3,8-diazatricyclo[23.3.1.1^{10,14}]triaconta-1(29),2,8,10,12,14(30),25,27-octaene-29,30-diol-O^{15},O^{18},O^{21},O^{24},O^{29},O^{30})barium(2+) Bis(trifluoromethanesulfonate) (7). To a refluxing solution of $Ba(CF_3SO_3)_2$ (0.84 g, 1.92 mmol) in 250 mL of MeOH both a solution of the dialdehyde 2 (0.75 g, 1.92 mmol) in 40 mL of THF and a solution of the diamine 6 (0.18 g, 1.92 mmol) in 40 mL of MeOH were added dropwise over a period of 2.5 h. After the addition was completed, the mixture was stirred for 15 min and cooled to room temperature. The resulting reaction mixture was partly concentrated and some DIP was carefully added until the solution became just turbid. It was left overnight, after which the colorless crystals were filtered off: yield 74%; mp >300 °C (MeOH/DIP); ^{1}H NMR δ 9.33 (bs, 2 H, OH), 8.47 (s, 2 H, N=CH), 7.2–6.8 (m, 6 H, Ar H), 4.42 (s, 4 H, $NOCH_2$), 4.2–4.1 (m, 4 H, Ar OCH_2), 3.8–3.7 (m, 4 H, OCH_2), 3.63 (s, 4 H, OCH_2); ^{13}C NMR δ 148.2 (d, N=C), 146.6 and 146.3 (s, Ar C-2,3), 120.8, 118.2, and 116.7 (d, Ar C-4-6), 117.0 (s, Ar C-1), 72.7 (t, $NOCH_2$), 69.5, 68.4, and 68.3 (t, OCH_2); IR (KBr) 3496 (OH) and 1618 (N=C) cm^{-1}; mass spectrum, *m/e* 446.169 ($M^+ - Ba(CF_3SO_3)_2$, calcd 446.169).

Anal. Calcd for $C_{24}H_{26}BaF_6N_2O_{14}S_2$: C, 32.69; H, 2.97; N, 3.18. Found: C, 32.30; H, 3.07; N, 3.08.

General Procedure for the Synthesis of 8a, 8b, and 8c. To a solution of the barium complex 7 (0.25 g, 0.28 mmol) in 100 mL of MeOH was added a solution of 1 equiv of nickel, copper, or zinc acetate in MeOH (10–15 mL) in one portion. The reaction mixture was stirred for 0.5 h at room temperature, after which the solvent was partly evaporated. DIP was carefully added until the solution became just turbid. It was left overnight and the precipitate formed was filtered off and was washed once with DIP.

[μ-(4,7,15,18,21,24-Hexaoxa-3,8-diazatricyclo[23.3.1.1^{10,14}]-triaconta-1(29),2,8,10,12,14(30),25,27-octaene-29,30-diolato-(2−)-N^3,N^8,O^{29},O^{30}:O^{15},O^{18},O^{21},O^{24},O^{29},O^{30})(nickel)]barium(2+) (8a): yield mp >300 °C (MeOH/DIP); IR (KBr) 1608 (N=C) cm^{-1}.

Anal. Calcd for $C_{24}H_{24}BaF_6N_2NiO_{14}S_2 \cdot H_2O$: C, 30.13; H, 2.74; N, 2.93. Found: C, 30.18; H, 2.94; N, 2.93.

[μ-(4,7,15,18,21,24-Hexaoxa-3,8-diazatricyclo[23.3.1.1^{10,14}]-triaconta-1(29),2,8,10,12,14(30),25,27-octaene-29,30-diolato-(2−)-N^3,N^8,O^{29},O^{30}:O^{15},O^{18},O^{21},O^{24},O^{29},O^{30})(copper)]barium(2+) bis(trifluoromethanesulfonate) (8b): yield 78%; mp >300 °C (MeOH/DIP); IR (KBr) 1607 (N=C) cm^{-1}.

Anal. Calcd for $C_{24}H_{24}BaCuF_6N_2O_{14}S_2$: C, 30.55; H, 2.56; N, 2.97. Found: C, 30.37; H, 2.54; N, 2.93.

[μ-(4,7,15,18,21,24-Hexaoxa-3,8-diazatricyclo[23.3.1.1^{10,14}]-triaconta-1(29),2,8,10,12,14(30),25,27-octaene-29,30-diolato-(2−)-N^3,N^8,O^{29},O^{30}:O^{15},O^{18},O^{21},O^{24},O^{29},O^{30})(zinc)]barium(2+) bis(trifluoromethanesulfonate) (8c): yield 81%; mp >300 °C (MeOH/DIP); ^{1}H NMR δ 8.73 (s, 2 H, N=CH), 7.1–7.0 (m, 4 H, Ar H), 6.7–6.5 (m, 2 H, Ar H), 4.46 (s, 4 H, $NOCH_2$), 4.2–3.7 (m, 12 H, OCH_2); ^{13}C NMR δ 162.6 (d, N=C), 157.4 and 149.5 (s, Ar C-2,3), 126.1 and 113.7 (d, Ar C-4-6), 70.0, 69.1, 68.0, and 66.4 (t, OCH_2); IR (KBr) 1606 (N=C) cm^{-1}.

Anal. Calcd for $C_{24}H_{24}BaF_6N_2O_{14}S_2Zn \cdot 1.5H_2O$: C, 29.65; H, 2.80; N, 2.88. Found: C, 29.55; H, 2.80; N, 2.81.

3,3′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bis(2-hydroxybenzaldehyde) Bis(*O*-methyloxime) (10). To a solution of the dialdehyde 2 (1.30 g, 3.33 mmol) in 40 mL of MeOH was added a solution of $CH_3ONH_2 \cdot HCl$ (9) (1.11 g, 13.33 mmol) in 10 mL of H_2O at pH = 8 (solid Na_2CO_3) at 50 °C. The resulting mixture was stirred for 0.5 h at 50 °C and poored into 150 mL of H_2O. The aqueous solution was acidified with 1 M HCl to pH = 4 and extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were washed once with H_2O, dried with $MgSO_4$, and concentrated to dryness. The solid residue was triturated with MeOH to afford 10 as a white solid: yield 77%; mp 87–89 °C (MeOH); ^{1}H NMR δ ($CDCl_3$) 9.62 (s, 2 H, OH), 8.17 (s, 2 H, N=CH), 7.0–6.8 (m, 6 H, ArH), 4.3–4.1 (m, 4 H, $ArOCH_2$), 3.96 (s, 6 H, OCH_3), 3.9–3.8 (m, 4 H, OCH_2), 3.77 (s, 4 H, OCH_2); ^{13}C NMR δ ($CDCl_3$) 150.4 (d, N=C), 147.9 and 147.3 (s, Ar C-2,3), 122.7, 119.3, and 116.7 (d, Ar C-4-6), 119.1 (s, Ar C-1), 70.9, 69.8, and 69.4 (t, OCH_2), 62.4 (q, OCH_3); IR (KBr) 1609 (N=C) cm^{-1}; mass spectrum, *m/e* 448.180 (M^+, calcd 448.185).

Anal. Calcd for $C_{22}H_{28}N_2O_8$: C, 58.92; H, 6.29; N, 6.25. Found: C, 58.90; H, 6.22; N, 6.08.

General Procedure for the Synthesis of 11a, 11b, and 11c. To a solution of $Ba(CF_3SO_3)_2$ (0.49 g, 1.12 mmol) in 150 mL of MeOH were added both a solution of the dioxime 10 (0.50 g, 1.12 mmol) in a mixture of 40 mL of MeOH and 10 mL of CH_2Cl_2 and a solution of 1 equiv of nickel, copper, or zinc acetate in 50 mL of MeOH dropwise over a period of 2.5 h. The resulting colored solution was concentrated to about 10 mL and after the addition of some DIP the dinuclear complex precipitated and was filtered off.

[[3,3′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bis(2-hydroxybenzaldehyde *O*-methyloximato-N^1,O^2)]nickel]-barium(2+) bis(trifluoromethanesulfonate) (11a): yield 82%; mp 241 °C dec (MeOH/DIP); IR (KBr) 1609 (N=C) cm^{-1}.

Anal. Calcd for $C_{24}H_{26}BaF_6N_2NiO_{14}S_2$: C, 30.65; H, 2.79; N, 2.98. Found: C, 30.73; H, 2.79; N, 3.04.

[[3,3′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bis(2-hydroxybenzaldehyde *O*-methyloximato-N^1,O^2)]copper]-barium(2+) bis(trifluoromethanesulfonate) (11b): yield 55%; mp >300 °C (MeOH/DIP); IR (KBr) 1606 (N=C) cm^{-1}.

Anal. Calcd for $C_{24}H_{26}BaCuF_6N_2O_{14}S_2$: C, 30.49; H, 2.77; N, 2.96. Found: C, 30.45; H, 2.87; N, 2.67.

[[3,3′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bis(2-hydroxybenzaldehyde *O*-methyloximato-N^1,O^2)]zinc]barium(2+) bis(trifluoromethanesulfonate) (11c): yield 67%; mp >300 °C (CH_3CN/DIP); ^{1}H NMR δ 8.63 (s, 2 H, N=CH), 7.0–6.9 (m, 4 H, ArH), 6.6–6.4 (m, 2 H, ArH), 4.2–3.7 (m, 12 H, OCH_2), 3.83 (s, 6 H, OCH_3); IR (KBr) 1605 (N=C) cm^{-1}.

Anal. Calcd for $C_{24}H_{26}BaF_6N_2O_{14}S_2Zn \cdot 0.5CH_3CN$: C, 31.03; H, 2.86; N, 3.62. Found: C, 30.84; H, 2.76; N, 3.35.

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

The metal ions were located by Patterson methods and the rest of the heavy atoms 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 vs weighted error. In all structures the metal ions were refined with anisotropic thermal parameters and depending on the ratio of data/parameters other atoms were also refined anisotropically. For all four structures an empirical absorption correction, using DIFABS,[23] was performed. In structures

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[23] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

7 and **11c** the hydrogen atoms are placed at the calculated positions and treated as riding on their parent carbon atom. In structure **8b** all hydrogens except one of each water molecule were located by difference Fourier synthesis and they were refined with isotropic thermal parameters. In structure **11b** the hydrogens were placed on their calculated positions and all but two were treated as riding on their parent carbon atom. The remaining two hydrogens were, for reasons of calculation efficiency, refined with isotropic thermal parameters. Parameters refined were the overall scale factor, an isotropic extinction parameter g [$F_o = F_c/(1 + gI_c)$] for **11c**, positional and isotropic cq anisotropic thermal parameters for non-hydrogen atoms, and positional and isotropic thermal parameters for hydrogen atoms (if included). Refinements converged with shift/error ratios less than unity, except for 7, where convergence in the parameters of one highly disordered anion was poor. Final difference Fourier maps showed no significant features. All calculation were done using SDP.[24]

Electrochemistry. The polarographic measurements were carried out with a Metrohm E505 polarograph. This polarograph was operated in a three-electrode mode with a dropping mercury electrode (DME) as cathode, a platinum wire as auxiliary electrode, and an Ag/AgCl electrode (Metrohm EA 441/5) as reference. The reference electrode was filled with 1 M $Et_4N^+Cl^-$ (Merck, synthetic quality, recrystallized from ethyl acetate/$CHCl_3$) in MeOH (Merck, pa quality). The measurements were performed at 20 °C in a 0.1 M solution of TEAP ($Et_4N^+ClO_4^-$, Fluka, purum, recrystallized from EtOH) in DMSO (pa quality of Merck, max 0.03% H_2O). The reference electrode was brought into contact with the sample via a double salt bridge of the following configuration:

$$\text{Ag; AgCl, Et}_4\text{N}^+\text{Cl}^- - \text{MeOH:TEAP–DMSO:sample.}$$

The characteristics of the DME electrode were $m = 1.065$ mg/s, natural drop time = 5.30 s, and height of the mercury colomn 64 cm^{-1}. A mechanical drop time of 1.000 s was maintained during all experiments. The sample concentrations were 1.14–1.82 mM. Oxygen was expelled by bubbling with nitrogen (Hoekloos, very pure) for at least 10 min. Polarograms were recorded and evaluated by a computerized method described by Zollinger et al.[17] The nickel/barium complex **1b**[2] was used as a reference and measured several times during the day to detect fluctuations ($\Delta E_{1/2} < 3$ mV).

Cyclic voltammetry was carried out with an AUTOLAB computerized system for electrochemistry (ECO CHEMIE, Utrecht, The Netherlands). The measurements were performed at a stationary hanging mercury drop electrode (Metrohm, 663 VA Stand). The same reference and auxiliary electrode were used as in the polarographic experiments. The solvent and the supporting electrolyte were also the same as used in the polarography.

Coulometry was carried out with a Metrohm coulostat E524 and a Metrohm integrator E525. The measurements were carried out in the same solvent and supporting electrolyte as were used for the polarographic experiments. A mercury pool was used as cathode and it was seperated from the platinum counterelectrode by one salt bridge. The reference electrode was the same as used for the other electrochemical experiments. The coulostat was operated with a constant potential (potentiostatic coulometry).

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Registry No. **2**, 115142-66-0; **3**, 5470-11-1; **4**, 119655-83-3; **5a**, 119655-84-4; **5b**, 119655-86-6; **5c**, 119655-88-8; **6**, 5627-11-2; **7**, 119655-90-2; **8a**[Ni(II)], 119655-97-9; **8a**[Ni(I)], 119656-07-4; **8b**[Cu(II)], 119655-93-5; **8b**[Cu(I)], 119656-04-1; **8c**, 119655-95-7; **9**, 593-56-6; **10**, 119638-40-3; **11a**[Ni(II)], 119655-99-1; **11a**[Ni(I)], 119656-08-5; **11b**[Cu(II)], 119656-01-8; **11b**[Cu(I)], 119656-06-3; **11b**[Cu(0)], 119656-05-2; **11c**, 119656-03-0.

Supplementary Material Available: Tables of positional and thermal parameters of all atoms, bond distances, and bond angles in the complexes 7, **8b**·$2H_2O$, **11b**, and **11c** (18 pages). Ordering information is given on any current masthead page.

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[24] *Structure Determination Package*; B. A. Frenz and Associates Inc.; College Station, TX, and Enraf-Nonius, Delft, 1983.

Photochemical Reactions of *N,N'*-Dimethylimidazolidinetrione with Alkenes. Solvent-Incorporated Addition via Hydrogen Abstraction

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Photoreactions of *N,N'*-dimethylimidazolidinetrione (**1**) with alkenes in benzene gave oxetanes in high yields. The reaction of **1** with stilbene proceeded via excitation of the alkene rather than **1**, whereas that with 2,5-dimethylhexadiene took place via excitation of the ground-state complex of **1** with the diene. On irradiation in hydrogen-donating solvents such as alcohols, toluene, or cyclohexane, **1** underwent a quite rare solvent-incorporated addition to the alkenes via intermolecular hydrogen abstraction.

The photochemical reactivity of **1** is of interest in connection with that of extensively investigated cyclic imides[1] and acylureas,[2] since imidazolidinetriones may be viewed as a composite of (a) one imide and one amide and (b) urea and *cis*-glyoxal.[3] In relation to our studies on photoreactions of nitrogen-containing α-dicarbonyl compounds,[4] we have reported photochemical intramolecular hydrogen abstraction of *N,N'*-dialkylimidazolidinetriones.[5] Kanaoka et al. have independently reported intermolecular hydro-

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