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Synthesis, Characterization, and Electrochemical Properties of a Novel Macrocylic Ligand and its Transition Metal Complexes

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Summary. 2,3-Dibromo-6,7,13,14,15,16,22,23-octahydro-14,15-*bis*-(hydroxyimino)-tribenzo [*e*,*k*,*q*][1,4,7,10,13,16]tetraoxadiazacyclohexadecine (LH_4) was prepared by condensation of 1,2-*bis*-(2′-aminophenoxyethoxy)-4,5-dibromobenzene with cyanogen-di-N-oxide. Mono-, di-, and tri-nuclear transition metal complexes of this ligand (($(LH_3)_2$Ni, $(LH_3)_2$Zn, $(LH_3)_2$Co, $(LH_3)_2$Cu, $(LH_3)_2$Fe, $(LH_3)_2(UO_2)_2(OH)_2$, $(LH)_2Cu_3$, $(LH)_2Co_3$) were synthesized under basic conditions. The electrochemical properties of the mono- and dinuclear complexes were studied by cyclic voltammetry in *DMSO* solution containing *TBAP*. The results showed that all redox processes are based on the metal center and the oxime ligands stabilize the Ni(III), Fe(III), Co(III), and Cu(III) species formed during oxidation. The Fe(II) and U(VI)O_2 complexes displayed a different behaviour: a reduction peak with the corresponding anodic signal during the reverse scan was observed. The oxime moiety also stabilizes U(V)O_2 which forms during the reduction process of the uranyl complex. Cu(II) was adsorbed on the electrode surface upon scanning cathodically.

Keywords. *vic*-Dioxime; Macrocycle; Co(II); U(IV); Electrochemistry.

Introduction

Oxime ligands are widely recognized for their physicochemical properties, reactivity patterns, and potential applications in medicinal chemistry [1–4], bioorganic systems [5–7] and the field of electrochemical and electrooptical sensors [8–10]. The synthesis of purpose-designed macrocyclic ligands, which are capable of forming multinuclear complexes, is of great interest for special applications. For these purposes, the ligands need to carry multidonor groups to be able to bind more than one metal ion simultaneously [11–14]. Various *vic*-dioximes and their mono-, di-, and trinuclear complexes have been topics of recent research [15–18].

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Since the first observations of the transition metal binding ability and selectivity of secondary amine functions in macrocycles, considerable efforts have been undertaken to incorporate these functional groups into new compounds. The main interest in these compounds which contain both macrocycles and a *vic*-dioxime moiety arises from an investigation of the transition metal ion coordination of the macrocycles [19–26].

We have previously reported on the synthesis of MN_4-core containing compounds [27–35]. Recently, we have also focused on monophthalocyanines and double-decker phthalocyanines which have been the subject of extensive investigations with respect to their electrochromic properties and intrinsic semiconductivity [36].

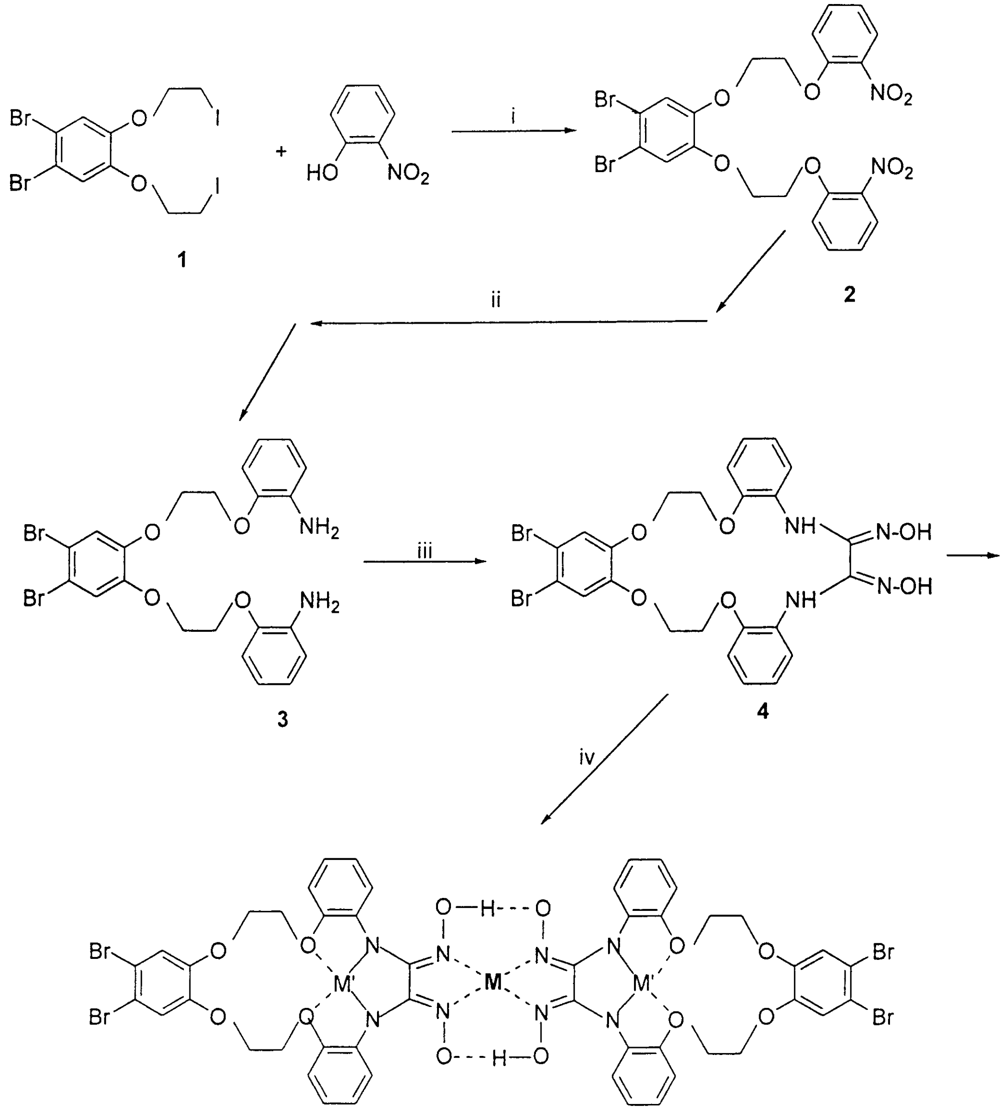
The ability of oxime-containing ligands to stabilize reduced and oxidized forms of metal ions is of vital importance in their application in electrochemical and electrooptical sensors [8–10]. However, literature dealing with the electrochemistry of metal oximes, especially in organic solvents, is scarce [37–39]. Only the reduction of neutral and anionic benzaldoxime, different aldoximes and ketoximes derivatives, and, more recently, the electrochemical properties of rhenium ketoxime have been published [40, 41]. Thus, we concentrated our attention to the investigation of the electrochemical properties of metal oximes in nonaqueous media.

In the present work we introduce for the first time a new generation of higher-membered macrocyclic derivatives of a *vic*-dioxime ligand carrying an 18-membered N_2O_4 macrocycle and its complexes with Cu, Co, Ni, UO_2, Fe, and Zn ions. The electrochemical behaviour of mono- and dinuclear complexes was studied.

Results and Discussion

Synthesis

1,2-*Bis*-(2′-nitro phenoxyethoxy)-4,5-dibromobenzene (**2**) was synthesized by reaction of 2-nitrophenol with 1,2-*bis*-(iodoethoxy)-4,5-dibromobenzene (**1**) which was obtained from a multi-step reaction sequence according to published methods [42–45]. **2** was reduced to 1,2-*bis*-(2′-aminophenoxyethoxy)-4,5-dibromobenzene (**3**) by iron powder in a weakly acidic medium maintained below $pH = 7$ by addition of acetic acid [21]. 2,3-Dibromo-6,7,3,14,15,16,22,23-ocyahydro-14,15-*bis*-(hydroxyimino)-tribenzo[*e*,*k*,*q*],[1,4,7,10,13,16]tetraoxadiazacyclohexadecine (**4**, LH_4) was prepared in moderate yield by condensation of **3** with cyanogen-di-N-oxide which was prepared by treatment of a suspension of *anti*-dichloro glyoxime in CH_2Cl_2 with 1 *N* aqueous Na_2CO_3 at −20°C (Scheme 1). The high-dilution technique was used to prevent polymer formation in CH_2Cl_2. Compound **4** is light sensitive; therefore, its grey color gradually turns to red-brown. The mono-, bi-, and trinuclear complexes $(LH_3)_2Ni$ (**5**), $(LH_3)_2Zn$ (**6**), $(LH_3)_2Cu$ (**7**), $(LH_3)_2Co$ (**8**), $(LH_3)_2Fe$ (**9**), $(LH_3)_2(UO_2)_2$ (**12**), $(LH)_2Cu_3$ (**10**), and $(LH)_2Co_3$ (**11**) were synthesized by reaction of **4** with nitrates of Ni(II), Zn(II), Cu(II), Co(II), Fe(II), and UO_2(VI). The mononuclear complexes have a metal:ligand ratio of 1:2, and the ligand is coordinated only by the N,N′ atoms of the *vic*-dioxime moiety. In contrast, two metal ions are coordinated to the two nitrogen and two oxygen atoms of each



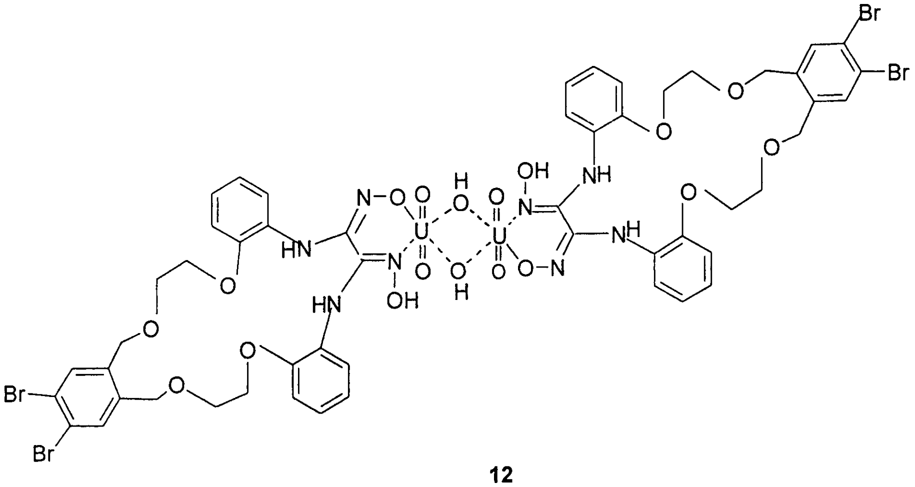
	M	*M'*
5	Ni	H_2
6	Zn	H_2
7	Cu	H_2
8	Co	H_2
9	Fe	H_2
10	Cu	Cu
11	Co	Co

Scheme 1. *i*: *DMF*, $K_2(CO_3)$; *ii*: Fe, CH_3COOH; *iii*: cyanogen-di-N-oxide, CH_2Cl_2, −40°C; *iv*: *THF*, $ML_2 \cdot 6H_2O$ ($L = NO_3$, $M =$ Ni, Zn, Cu, Co, Fe, UO_2), Et_3N, *DMF*, KOH

macrocycle in trinuclear complexes, whereas the third metal ion is coordinated by the N,N′ atoms of each oxime group in the two ligand molecules (Scheme 1). These complexes have a metal:ligand ratio of 3:2.

The new compounds were characterized by elemental analyses and spectroscopic techniques. The IR spectra of **2** and **3** exhibited characteristic frequencies at 3080, 3030 (CH–Ar), 2930–2860 (CH aliph.), 1350, 1150 (–SO_2), 640 (C–Br), 3460–3350 (Ar–NH_2), 3055, 3030 (Ar–H), 2960, 2850, (CH-Aliph), and 660 (C–Br) cm^{-1}. The remainder of the spectrum of **2** was closely similar to that of **3**. In the spectrum of **4** the NH and OH stretching vibrations were observed at 3370 and 3240 cm^{-1} as slightly broadened absorptions in addition to the C=N and N–O stretching vibrations at 1640 and 950 cm^{-1}. In the IR spectra of the mono- and trinuclear complexes, weak O–H···O deformation vibrations were observed at 1700–1710 cm^{-1}, and the stretching vibration of the NH group in **10** and **11** disappeared which also confirmed the formation of trinuclear complexes. The disappearance of the O–H band and the shift of peaks assigned to C=N, C=C, and N–O frequencies in the IR spectra of mono- and dinuclear complexes could be attributed to N,N′-chelating [25]. The appearance of weak O–H···O bending vibrations around 1700–1710 cm^{-1} indicated the coordination of the metal ion by two hydrogen bridges. In addition to the O–H···O bending vibrations around 1700 cm^{-1}, **10** and **11** showed two strong sharp bands at around 1230 and 950 cm^{-1} which could be assigned to ν(C–O–C) and ν(N–O···). The IR spectrum of **12** was also consistent with the dimeric formula (Fig. 1). A strong band around 900 cm^{-1} was characteristic for ν(O=U=O) vibrations; NH and OH stretching vibrations of the oxime groups still appeared as broad bands at 3370 and 3250 cm^{-1}.

The ^{1}H NMR spectra of **2**, **3**, and **4** were consistent with the proposed formulae. For **2** and **3**, the signals of all aromatic protons could be assigned. The aliphatic protons of these compounds appeared at 4.26 (t), 3.99 (t), 4.17 (t), and 3.90 (t) ppm. In the ^{1}H NMR spectrum of **3**, the primary aromatic amine protons were also observed at 5.36 ppm as a singlet, easily identified by deuterium exchange. In the ^{1}H NMR spectrum of **4**, the singlet assigned to the NH_2 protons in **3** disappeared, and signals at 10.74 and 8.66 ppm were observed due to the exchangeable NOH and NH protons. These singlets indicated the (*E*,*E*)-configuration of the *vic*-dioxime [15]



12

Fig. 1. Binuclear uranyl complex **12**

(Scheme 1). The chemical shifts of the aromatic and methylene protons of **4** were in accordance with those of the macrocyclic compounds described in Refs. [21, 25]. The ^{1}H NMR spectrum of **4** indicated the *anti*-isomer of the *vic*-dioxime by the presence of only one singlet for the NOH protons at low field (10.74 ppm). The signals corresponding to aromatic and aliphatic protons of **4** were slightly shifted compared to those of **2** and **3**.

The ^{1}H NMR spectra of the diamagnetic complexes **5** and **6** were characterized by the disappearance of the NOH signal at 10.74 ppm, and the formation of an intermolecular hydrogen bond was observed (signals at 16.40 and 16.78 ppm in addition to those of the NH protons at 8.61 and 8.63 ppm). The bridge protons could also easily be identified by deuterium exchange. The signals of NH, aromatic protons, and aliphatic protons were similar to what was observed for **4** except for a slight shift.

The ^{1}H NMR spectrum of **12** showed two chemical shifts for the deuterium-exchangeable NOH protons at 10.90 and 10.35 ppm and the NH protons at 8.44 and 8.15 ppm, which could be attributed to the magnetic anisotropy of the uranyl ion as discussed previously in relation to some carboxylate and amine complexes [12, 21, 23]. It is known that the uranyl ion enhances the chemical shift difference between non-equivalent protons.

In the UV/Vis spectrum of **12** a strong absorption at 400 nm, which was assigned to a charge transfer transition from the π-orbitals of the donor atoms to the 5f and 6d orbitals of uranium, appeared as reported previously for similar compounds [12, 21]. The mass spectra of **2**, **3** (EI), and **4** (FAB) showed the proper molecular ion peaks in addition to major fragments at $m/z = 552.0$ $[M\text{-}46]^+$, 506.1 $[M\text{-}93]^+$, 459.0 $[M\text{-}139]^+$, and 324.0 $[M\text{-}278]^+$ for **2**, $m/z = 458.2$ $[M\text{-}80]^+$, 430.1 $[M\text{-}108]^+$, 403 $[M\text{-}135]^+$, 323.1 $[M\text{-}216]^+$, 136.1, 108.0, 92.0, and 80.0 for **3**, and $m/z = 707$ $[M^+ + \text{cyanogen-di-N-oxide} + 1]^+$, 606 $[M^+\text{-}17]^+$, 522 $[M^+\text{-}101]$, and 323.2 $[M^+\text{-}300]$ for **4**.

In the mass spectra of the complexes, fragment ions corresponding to $[M\text{-Ni}]^+$, $[M\text{-Co-}1]^+$, $[M\text{-Cu-}1]^+$, and $[M\text{-Zn}]^+$ (mononuclear compounds) and $[M\text{-2Cu-}1]^+$ and $[M\text{-2Co} + \text{Cl}]^+$ (trinuclear compounds) were easily identified.

Electrochemical Measurements

The electrochemical properties of complexes **5**–**9** and **12** were investigated using voltammetric techniques. The cyclic voltammograms of all complexes are presented in Figs. 2 and 4–7; the results are summarized in Table 1. Compound **6** did not display any peak within the available potential scale. CPC (controlled potentials coulometry) measurements showed that the number of electrons transferred is 1 for the redox processes of all complexes.

A one-electron reduction and a one-electron oxidation peak were recorded for all complexes except for **12** which exhibited only a one-electron reduction within the accessible potential range of the *DMSO*/*TBAP* solvent/electrolyte system. Scanning the potential to the positive side, all complexes gave an oxidation couple within the positive potential window, which was attributed to the *M*(II)/*M*(III) process. These redox couples have reversible character with peak separation values (ΔE_p) between 55 and 80 mV at a scan rate of $10\,\mathrm{mV \cdot s^{-1}}$. ΔE_p values of all

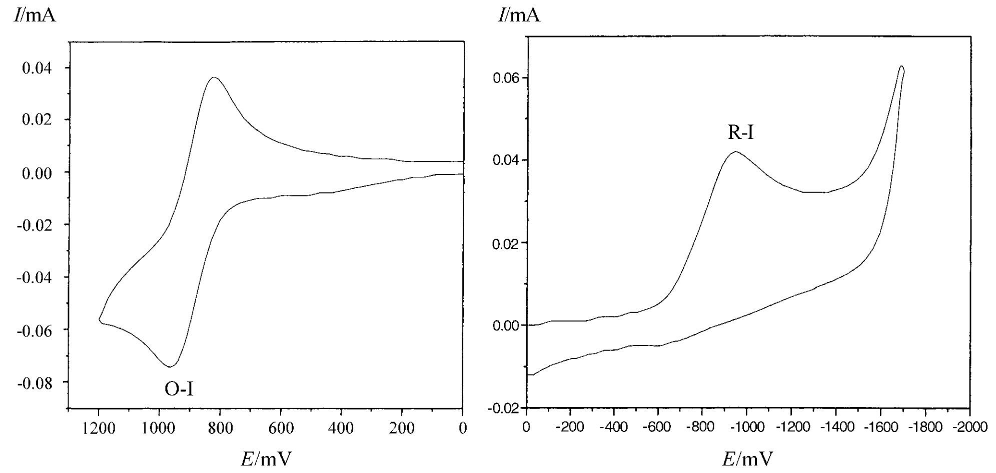


Fig. 2. Cyclic voltammogram of 1.0×10^{-4} *M* $(LH_3)_2$Ni (**5**) in *DMSO*/0.1 *M TBAP* at 100 mV · s^{-1} *vs.* SCE

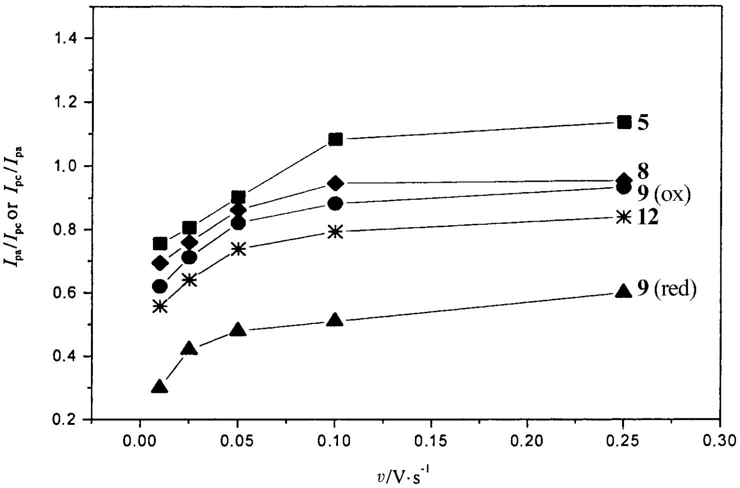


Fig. 3. Peak current ratio ($I_{p,a}/I_{p,c}$ for reduction, $I_{p,c}/I_{p,a}$ for oxidation) *vs.* scan rate (v) for the redox couples of all complexes

complexes increased with the scan rate but remained in the range for *quasi*-reversible systems (Table 1). As shown in Fig. 7, **7** gave an oxidation couple of different character: it is located at less positive potentials than the reduction signal and has a shoulder. Moreover, the anodic peak current is directly proportional to the scan rate. These results indicate that **7** is adsorbed on the electrode surface.

Upon scanning cathodically, each of **5**, **7**, and **8** displayed a reduction peak without the corresponding anodic waves on the reverse scan, whereas both **9** and **12** gave a couple. These processes cannot be due to the oxime moieties because in the highly polar solvent *DMSO* polarization of the hydroxyl groups of the oxime moiety occurs and this causes an increase in negative charge in the coordinated oxime moieties which become harder to reduce. Thus, these peaks could be assigned to Fe(II)/Fe(I) for **9** and U(VI)O_2/U(V)O_2 for **12**. The absence of the

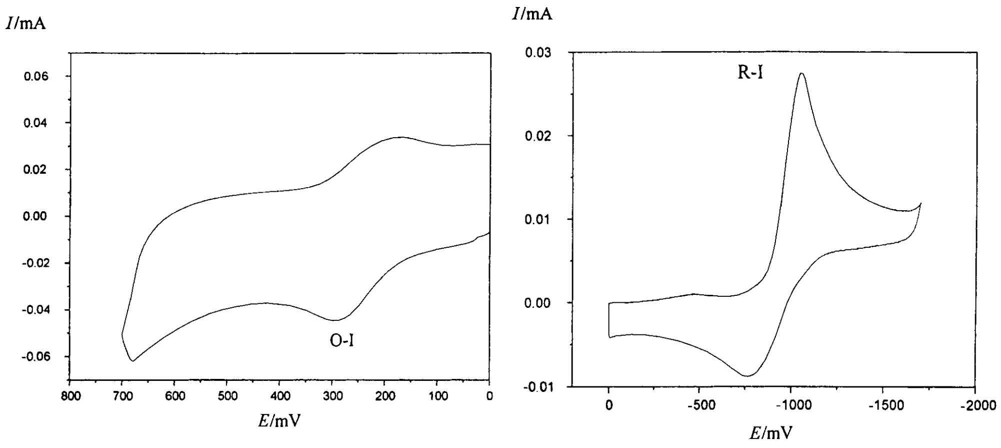


Fig. 4. Cyclic voltammogram of 1.0×10^{-4} *M* ($(LH_3)_2Fe$) (**9**) in *DMSO*/0.1 *M TBAP* at 100 mV · s^{-1} *vs.* SCE

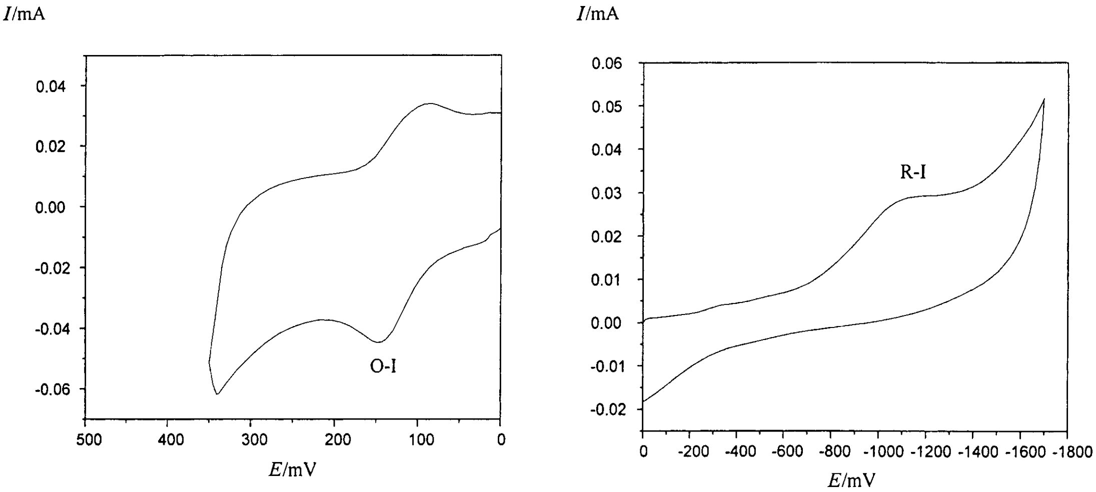


Fig. 5. Cyclic voltammogram of 1.0×10^{-4} *M* ($(LH_3)_2Co$) (**8**) in *DMSO*/0.1 *M TBAP* at 100 mV · s^{-1} *vs.* SCE

anodic signal for **5**, **7**, and **8** indicated that the charge transfer step was followed by a fast chemical reaction, and instable electrochemically generated *M*(I) species were formed. $\partial E_p/\partial \log v$ values given in Table 1 indicate that these reduction peaks are not totally irreversible, although they deviate from reversibility. The absence of an anodic signal even at high scan rates results from the fast chemical reaction following the electron transfer reactions. Differently, both **9** and **12** gave a reduction couple within the range of *quasi*-reversible electron transfer processes ($\Delta E_p =$ 65 and 75 mV at 10 mV · s^{-1}; 240 and 280 mV at 100 mV · s^{-1}).

The variations of peak current ratios with scan rate for redox couples of all complexes are presented in Fig. 3. The $I_{p,c}/I_{p,a}$ ratios deviated from unity and increased with increasing scan rate. This indicated the existence of a chemical reaction following the electron transfer reaction for each complex.

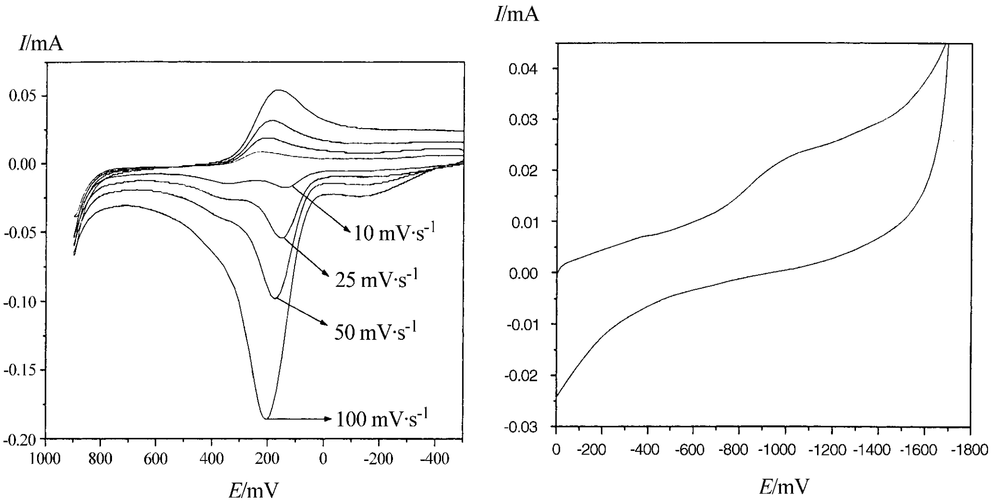


Fig. 6. Cyclic voltammogram of 1.0×10^{-4} *M* $(LH_3)_2Cu$ (**7**) in *DMSO*/0.1 *M TBAP* at 100 mV · s^{-1} *vs.* SCE

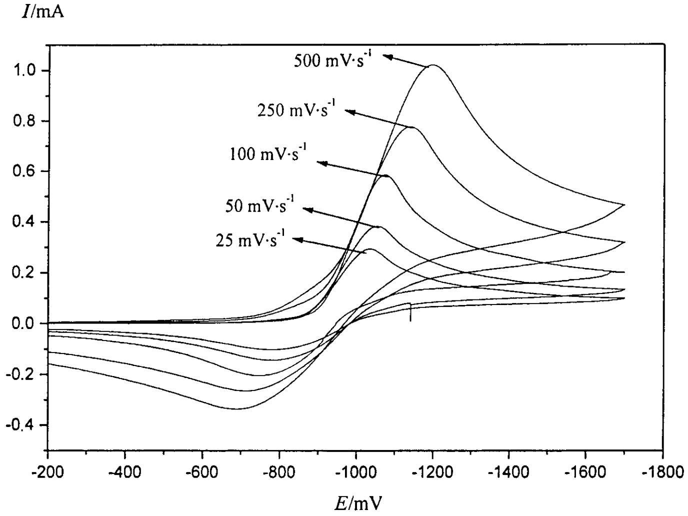


Fig. 7. Cyclic voltammogram of 1.0×10^{-4} *M* $(LH_3)_2(UO_2)_2(OH)_2$ (**12**) in *DMSO*/0.1 *M TBAP* at 100 mV · s^{-1} *vs.* SCE

The voltammetric results obtained in this study showed that oxime-containing ligands stabilize Ni(III), Fe(III), Co(III), and Cu(III), since in these cases oxidation peaks with the corresponding cathodic signals were observed. Higher oxidation states of the complexes appeared to be accessible in systems with oximato-nitrogen donors, probably as a result of the coulombic influence of the negative charge on the HOMO energy and of σ-donation effects [46]. Complexes **9** and **12** behaved differently; a reduction peak with the corresponding anodic signal during the return scan was observed only for **9** and **12**. This indicated that both Fe(III) and Fe(I) species are stable because the oxime containing ligands tend to stabilize only one of the oxidized forms of the metal center of the complexes. The stabilization of

Table 1. Cyclic voltammetric parameters of complexes *vs.* SCE (*Fc*/*Fc*$^+$); values in parentheses: *vs.* *Fc*/*Fc*$^+$

	Redox process	$E^a_{1/2}$ (V)	$\partial E^b_p/\partial \log v$ (V)	ΔE^c_p (V)	Peak ratio[d]
5	Oxidation	0.875 (0.375)	0.056	0.075	0.97
	Reduction	−0.850 (−1.350)	0.050	–	–
7	Oxidation	0.220 (−0.280)	0.020	−0.035[e]	0.88
	Reduction	−1.090 (−1.590)	0.135	–	–
8	Oxidation	0.110 (−0.390)	0.044	0.080	0.90
	Reduction	−1.125 (−1.625)	0.079	–	–
9	Oxidation	0.270 (−0.230)	0.035	0.078	0.30
	Reduction	−0.920 (−1.420)	0.055	0.065	0.94
12	Reduction	−0.975 (−1.475)	0.040	0.075	0.52
	Oxidation	–	–	–	–

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$ for redox couple, E_{pc} for irreversible peaks at a scan rate of $0.010\,V \cdot s^{-1}$; [b] E_{pc} for reduction, E_{pa} for oxidation; [c] $\Delta E_p = E_{pa} - E_{pc}$ at $0.010\,V \cdot s^{-1}$; [d] $I_{p,a}/I_{p,c}$ for reduction, $I_{p,c}/I_{p,a}$ for oxidation at $0.010\,V \cdot s^{-1}$; [e] the cathodic peak potential is more negative than the anodic one due to adsorption

both *M*(I) and *M*(III) by the same ligand is quite uncommon. It was generally observed that larger numbers of imino oxime nitrogen donors stabilize the formation of Ni(III), Fe(III), Co(III), and Cu(III), whereas ethoxy groups may stabilize Fe(I). In the case of **12**, the lowest oxidation state of the complex (U(V)O_2 species) was stable.

Experimental

(*E*,*E*)-Dichloroglyoxime and 1,2-*bis*-(2′-iodoethoxy)-4,5-dibromobenzene were prepared by a known procedure [15]. ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer using *TMS* as internal standard. Mass spectra were obtained with a VG Zabspec GS-MS spectrometer. IR spectra were run on a Mattison 1000 FTIR spectrophotometer (KBr pellets), UV/Vis spectra on an unicam UV2 spectrophotometer. Elemental analyses were performed by the instrumental laboratory of the Tubıtak Marmara Research Center; their results were in good agreement with the calculated values.

The metal content of the complexes were determined with a Hitachi 180–80 atomic absorption spectrometer from solutions prepared by decomposition of the compounds in concentrated HCl and concentrated HNO_3 (3:1) followed by dilution with water. The homogeneity of the products was tested at each step by TLC (SiO_2, $CHCl_3$/MeOH).

Cyclic voltammetric and controlled potential coulometric (CPC) measurements were carried out with a Princeton Applied Research Model 273 potentiostat controlled by an external PC using the computer program HEADSTRT and utilizing a three-electrode configuration at 25°C. The Origin 5.0 graph program was used to evaluate the HEADSTRT data, to draw voltammograms, and to analyze them. A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and was separated from the bulk of the solution by a glass bridge. The ferrocene/ferrocenium couple (*Fc*/*Fc*$^+$) was used as internal standard. The working electrode was a Pt plate with an area of $1.0\,cm^2$. A solution of $0.1\,mol \cdot dm^{-3}$ tetrabutylammoniumperchlorate (*TBAP*) in extra pure *DMSO* was employed as the supporting electrolyte. High purity N_2 was used for deaeration at least 15 minute prior to each run. For CPC studies, a Pt gauze working electrode ($10.5\,cm^2$ surface area), a platinum wire counter electrode separated by a glass bridge, a saturated calomel reference electrode, and a model 377/12 synchronous stirrer were used.

All reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried and purified as described by *Perrin* and *Armarego* [47]. The solvents were stored over molecular sieves (4 Å). 1,2-*Bis*-(2-iodoethoxy)-4,5-dibromobenzene [43] and *anti*-dichloroglyoxime [48] were prepared by reported procedures.

1,2-Bis-(2′-nitrophenoxyethoxy)-4,5-dibromobenzene (**2**; $C_{22}H_{18}Br_2N_2O_6$)

To 20 cm^3 of a solution of 1.93 g (13.88 mmol) 2-nitrophenol and 1.91 g anhydrous K_2CO_3 in DMF which was stirred at room temperature for 1 h under an N_2 atmosphere, 20 cm^3 of a solution of 4.00 g (6.94 mmol) **1** in *DMF* was added dropwise. After the mixture was kept at 30°C for 24 h with stirring, the yellow solution was slowly poured into 200 cm^3 ice water. The precipitated white nitro compound was collected by filtration, washed successively with cold H_2O, cold EtOH, and diethyl ether, and finally dried *in vacuo*.

Yield: 2.24 g (54%); m.p.: 158°C; IR (KBr): $\nu = 3080$, 3030 (Ar–CH), 2930–2860 (CH-aliph.), 1350, 1150 (NO_2), 1260, 1240 (C–O–C), 640 (C–Br) cm^{-1}; ^{1}H NMR (250 MHz, δ, *DMSO*-d$_6$): 7.74 (s, 2H, Ar–H), 7.37 (dd, $^3J = 7.5$ Hz, $^4J = 1.6$ Hz, 2H, phenyl-H3), 7.12 (dt, $^3J = 7.7$ Hz, $^4J = 1.5$ Hz, 2H, phenyl-H5), 6.90 (dt, $^3J = 7.8$ Hz, $^4J = 1.7$ Hz, 2H, phenyl-H4), 6.62 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H, phenyl-H6), 4.26 (t, $^3J = 6.5$ Hz, 4H, Ar–O–CH_2CH_2), 3.99 (s, 4H, CH_2CH_2–O–Ar) ppm; MS (EI): m/z (%) = 598 (90) [M$^+$], 552.0 [M-46]$^+$, 506.1 [M-93]$^+$, 459.0 [M-139]$^+$, 324.0 [M-278]$^+$.

1,2-Bis-(2′-aminophenoxyethoxy)-4,5-dibromobenzene (**3**; $C_{22}H_{18}Br_2N_2O_6$)

1.00 g (1.67 mmol) **2** and 0.80 g Fe powder (14.28 mmol) were suspended in 100 cm^3 EtOH: $H_2O = 2{:}1$, and the mixture was heated at reflux for about 1 h. Then, glacial acetic acid was added dropwise. Heating of the mixture was continued for further 18 h, and the hot mixture was filtered. White cream colored crystals were formed after cooling which were filtered off, washed with cold EtOH, and dried over P_2O_5.

Yield: 0.55 g (61%); m.p.: 134°C; IR (KBr): $\nu = 3460$–3350 (Ar–NH_2), 3055–3030 (Ar–CH), 2960, 2850 (aliph.-CH), 1615 (NH-bend.), 1540–1450 (Ar), 1240, 1260 (Ar–O-aliph. and aliph-O–Ar), 660 (C–Br) cm^{-1}; ^{1}H NMR (250 MHz, δ, *DMSO*-d$_6$): 7.37 (s, 2H, Ar–H), 7.27 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H, phenyl-H3), 7.07 (dt, $^3J = 7.8$ Hz, $^4J = 1.7$ Hz, 2H, phenyl-H5), 6.73 (d, $^3J = 7.2$ Hz, 2H, phenyl-H4), 6.53 (t, $^3J = 7.2$ Hz, 2H, phenyl-H6), 5.36 (s, 4H, Ar–NH_2), 4.17 (t, $^3J = 6.4$ Hz, 4H, Ar–O–CH_2CH_2), 3.90 (t, $^3J = 6.2$ Hz, 4H, CH_2CH_2–O–Ar) ppm; MS (EI): m/z (%) = 538.1 (100) [M$^+$], 458.2 [M-80]$^+$, 430.1 [M-108]$^+$, 403 [M-135]$^+$, 323.1 [M-216]$^+$.

5,6,17,18-Dibenzo-11,12-dibromobenzo-2,3-bishydroxyimino-1,4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine (**4**; $C_{24}H_{22}Br_2O_6N_4$)

Compound **3** (1.00 g, 1.85 mmol) was dissolved in 200 cm^3 of dry CH_2Cl_2 and cooled to −40°C. This solution was added dropwise to a solution of cyanogen di-N-oxide in 50 cm^3 CH_2Cl_2 which was obtained by treating a suspension of 0.70 g (4.45 mmol) dichloroglyoxime in CH_2Cl_2 with 25 cm^3 1 *N* Na_2CO_3 cooled to −40°C. The mixture was stirred at −40°C for another 4 h. When the mixture was allowed to warm slowly to room temperature a white precipitate occurred which was separated by filtration, washed with cold CH_2Cl_2 and diethyl ether to remove any unreacted starting materials, and dried *in vacuo*. Finally, the creamy product was recrystallized from EtOH.

Yield: 0.44 g (38%); m.p.: 164°C; IR (KBr): $\nu = 3370$ (NH), 3240 (br, OH), 3050–3020 (Ar–H), 2980–2850 (aliph.-H), 1640 (C=N), 1595 (w), 1250–1240 (C–O–C), 950 (N–O), 640 (C–Br) cm^{-1}; ^{1}H NMR (250 MHz, δ, *DMSO*-d$_6$): 10.74 (s, 2H, =N–OH, D-exchangeable), 8.66 (s, 2H, Ar–NH, D-exchangeable), 7.70–7.27 (s, 2H, Ar–H superimposed by phenyl-H3), 7.07 (dt, $^3J = 8.5$ Hz, $^4J = 1.8$ Hz, 2H, phenyl-H5), 6.80 (dd, $^3J = 7.7$ Hz, $^4J = 1.6$ Hz, 2H, phenyl-H4), 6.68 (d, $^3J = 7.2$ Hz, 2H, phenyl-H6), 4.25 (t, $^3J = 6.8$ Hz, 4H, Ar–O–CH_2CH_2), 4.02 (t, $^3J = 6.2$ Hz, 4H, O–CH_2CH_2) ppm; UV/Vis (*DMSO*): λ_{max} (ε) = 307 (9840) (sh), 290 (12500) nm; MS (positive FAB, matrix: *p*-nitrobenzylalcohol): *m/z* (%) = 622 (54) [M^+], 707 [M^+ + cyanogen-di-N-oxide + 1]$^+$, 606 [M^+-17]$^+$, 522 [M^+-101], 323.2 [M^+-300].

Bis-(5,6,17,18-dibenzo-11,12-dibromobenzo-2,3-bishydroxyiminato-1,4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine)-Ni(II)
(**5**; $C_{48}H_{42}Br_4N_8O_{12}Ni$)

A solution of 0.01 g $Ni(NO_3)_2 \cdot 6H_2O$ (0.05 mmol) in 20 cm^3 *THF* was added dropwise to a solution of 0.05 g (0.09 mmol) **4** in 20 cm^3 *THF* at room temperature. The color of the solution turned into dark brown, and the *pH* dropped to ~4–5; it was raised to ~7 by addition of triethylamine under stirring. The reaction mixture was heated to 60–70°C for 2 h and then brought to room temperature. The precipitate formed was filtered off, washed with cold *THF*, H_2O, EtOH, and diethyl ether to remove metal salts and unreacted organic impurities, and dried *in vacuo*.

Yield: 0.04 mg (58%); m.p.: >200°C; IR (KBr): ν = 3360 (NH), 3085 (Ar–H), 2963–2840 (aliph.-H), 1710 (O–H···O), 1610 (CN), 1590, 1560–1440 (Ar), 1260, 1210 (Ar–O-aliph., aliph.-O–Ar), 1100, 1010, 1000 (N–O), 710, 650 (C–Br) cm^{-1}; ^{1}H NMR (250 MHz, δ, *DMSO*-d$_6$): 16.40 (s, 2H, O–H···O, D-exchangeable), 8.61 (s, 4H, NH, D-exchangeable), 7.70–7.55 (s, 2H, Ar–H superimposed by dd, 4H, phenyl-H3), 7.15 (dt, $^3J = 7.8$ Hz, $^4J = 1.5$ Hz, 4H, phenyl-H5), 7.03 (dt, $^3J = 7.2$ Hz, $^4J = 1.5$ Hz, 4H, phenyl-H4), 6.55 (dd, $^3J = 7.5$ Hz, $^4J = 1.6$ Hz, 4H, phenyl-H6), 4.20 (t, $^3J = 6.2$ Hz, 8H, Ar–O–CH_2CH_2), 3.92 (t, $^3J = 6.1$ Hz, 8H, Ar–O–CH_2CH_2); UV/Vis (*DMSO*): λ_{max} (ε) = 350 (6700), 321 (11090), 303 (13030) nm; MS (positive FAB, matrix: *p*-nitrobenzylalcohol): *m/z* (%) = 1301 (9) [M^+], 1242 [M-Ni]$^+$.

Bis-(5,6,17,18-dibenzo-11,12-dibromobenzo-2,3-bishydroxyiminato-1,4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine)-Zn(II)
(**6**; $C_{48}H_{42}Br_4N_8O_{12}Zn$)

6 was prepared following the same procedure as described for **5** starting from 0.05 g (0.09 mmol) **4** and 0.01 g (0.05 mmol) $Zn(NO_3)_2 \cdot 6H_2O$.

Yield: 0.019 g (31%); m.p.: >200°C; IR (KBr): ν = 3370 (NH), 3070, 3030 (Ar–H), 2970, 2850 (aliph.-H), 1710, 1620 (CN), 1590 (w), 1515–1450, 1270–1240 (C–O–C), 1030 (N–O), 695, 660 (C–Br) cm^{-1}; ^{1}H NMR (250 MHz, δ, *DMSO*-d$_6$): 16.78 (s, 2H, O–H···O, D-exchangeable), 8.63 (s, 4H, NH, D-exchangeable), 7.44–7.38 (s, 2H, Ar–H superimposed by dd, 4H, phenyl-H3), 7.12 (dt, $^3J = 7.2$ Hz, $^4J = 1.5$ Hz, 4H, phenyl-H5), 6.78 (dd, $^3J = 7.8$ Hz, $^4J = 1.7$ Hz, 4H, phenyl-H4), 6.55 (d, $^3J = 7.2$ Hz, 4H, phenyl-H6), 4.11 (t, $^3J = 6.5$ Hz, 8H, Ar–O–CH_2CH_2), 3.90 (t, $^3J = 6.1$ Hz, 8H, CH_2CH_2–O–Ar) ppm; UV/Vis (*DMSO*): λ_{max} (ε) = 328 (1150, sh), 319 (1460), 303 (9100) nm; MS (positive FAB, matrix: *p*-nitrobenzylalcohol): *m/z* (%) = 1307 (15) [M^+], 1242 [M-Zn]$^+$.

Bis-(5,6,17,18-dibenzo-11,12-dibromobenzo-2,3-bishydroxyiminato-1,4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine)-Cu(II)
(**7**; $C_{48}H_{42}Br_4N_8O_{12}Cu$)

7 was prepared following the same procedure as described for **5** starting from 0.05 g (0.09 mmol) **4** and (0.05 mmol) 0.01 g $Cu(NO_3)_2 \cdot 6H_2O$.

Yield: 0.03 g (53%); m.p.: >200°C; IR (KBr): ν = 3365 (NH), 3075 (Ar–H), 2980, 2870–2830 (aliph.-H), 1710, 1650 (CN), 1590, 1520–1460, 1270–12550 (C–O–C), 1000 (N–O), 700, 650

(C–Br) cm^{-1}; UV/Vis (*DMSO*): λ_{max} (ε) = 348 (2240) (sh), 302 (10500) nm; MS (positive FAB, matrix: *p*-nitrobenzylalcohol): m/z (%) = 1304.3 (20) [M^+-1], 1242 $[M\text{-}Cu\text{-}1]^+$.

Bis-(5,6,17,18-dibenzo-11,12-dibromobenzo-2,3-bishydroxyiminato-1,4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine)-Co(II) (**8**; $C_{48}H_{42}Br_4N_8O_{12}Co$)

8 was prepared following the same procedure as described for **5** starting from 0.05 g (0.09 mmol) **4** and 0.014 g (0.05 mmol) $Co(NO_3)_2 \cdot 6H_2O$.

Yield: 0.03 g (50%); m.p.: >200°C; IR (KBr): ν = 3365 (NH), 3075 (Ar–H), 2980, 2870–2830 (aliph.-H), 1710, 1650 (CN), 1590, 1520–1460, 1270–12550 (C–O–C), 1010 (N–O), 700, 650 (C–Br) cm^{-1}; UV/Vis (*DMSO*): λ_{max} (ε) = 350 (1550) (sh), 305 (4670) nm; MS (positive FAB, matrix: *p*-nitrobenzylalcohol): m/z (%) = 1301 (17) [M^+], 1243 $[M\text{-}Co\text{-}1]^+$.

Bis-(5,6,17,18-dibenzo-11,12-dibromobenzo-2,3-bishydroxyiminato-1,4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine)-Fe(II) (**9**; $C_{48}H_{42}Br_4N_8O_{12}Fe$)

9 was prepared following the same procedure as described for of **5** starting from 0.05 g (0.09 mmol) **4** and 0.01 g (0.05 mmol) $Fe(NO_3)_2 \cdot 6H_2O$.

Yield: 0.03 g (51%); m.p.: >200°C; IR (KBr): ν = 3360 (N–H), 3060 (Ar–H), 2975, 2860, 2830 (aliph.-H), 1700 (O–H–O), 1650 (C=N), 1520–1460, 1430, 1260–1240 (C–O–C), 1080, 1030, 1010 (N–O), 720, 660 (C–Br) cm^{-1}; UV/Vis (*DMSO*) λ_{max} (ε) = 437 (2350, sh), 307 (5600), 291 (12800) nm; MS (positive FAB, *p*-nitrobenzylalcohol): m/z (%) = 1298 (12) [M^+].

Bis-(5,6,17,18-dibenzo-11,12-dibromobenzo-2,3-bishydroxyiminato-1,4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine)-tricopper(II) (**10**; $C_{48}H_{38}Br_4N_8O_{12}Cu_3$)

0.05 g (0.04 mmol) of **7** were dissolved in 10 cm^3 *DMF* with heating and stirring. A solution of 0.12 g (0.07 mmol) $CuCl_2 \cdot 2H_2O$ in 10 cm^3 *DMF* was added, and the mixture was stirred for 3 h at 40°C. The *pH* of the solution decreased and was raised to 7 by the addition of KOH. After the solvent was removed under reduced pressure to about dryness, the precipitate was filtered off, washed with H_2O, EtOH, and diethyl ether, and dried *in vacuo*. **10** is slightly soluble in *DMF*, *DMSO*, and pyridine.

Yield: 0.017 g (29%); m.p.: >200°C; IR (KBr): ν = 3070–3030 (Ar–H), 2930–2850, (aliph.-H), 1700 (O–H–O), 1610 (C=N), 1510, 1460, 1240 (C–O–C), 1120, 1100, 950 (N–O), 670, 640, 540 cm^{-1}; UV/Vis (*DMSO*): λ_{max} (ε) = 375 (1940), 310 (8820) nm; MS (positive FAB, *p*-nitrobenzylalcohol): m/z (%) = 1431.3 (5) $[M+3]^+$.

Bis-(5,6,17,18-dibenzo-11,12-dibromobenzo-2,3-bishydroxyiminato-1,4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine)-tricobalt(II) (**11**; $C_{48}H_{38}Br_4N_8O_{12}Co_3$)

11 was prepared following the same procedure as described for **10** starting from 0.05 g (0.04 mmol) **8** and 0.02 g (0.08 mmol) $CoCl_2 \cdot 6H_2O$. The dark brown complex is moderately soluble in *DMF*, *DMSO*, and pyridine.

Yield: 0.02 g (32%); m.p.: >200°C; IR (KBr): ν = 3080, (Ar–H), 2925, 2840 (aliph.-H), 1705 (O–H···O), 1595 (CN), 1230, 1210 (Ar–O-aliph., aliph.-O–Ar), 1100, 960 (N–O), 685, 650 (C–Br) cm^{-1}; UV/Vis (*DMSO*): λ_{max} (ε) = 390 (2400, sh), 350 (6700), 302 (12350) nm; MS (positive FAB, *p*-nitrobenzylalcohol): m/z (%) = 1416 (8) $[M+1]^+$.

Bis-(5,6,17,18-dibenzo-11,12-dibromobenzo-2,3-bishydroxyiminato-1,
4-diaza-7,10,13,16-tetraoxa-2,3,8,9,14,15-hexahydrocyclodecine-μ-hydroxo-uranyl)
(**12**; $C_{48}H_{44}Br_4N_8O_{18}U_2$)

A solution of 0.04 g (0.09 mmol) $UO_2(NO_3)_2 \cdot 2H_2O$ in 30 cm^3 dry *THF* was added portion wise to a solution of 0.05 g (0.09 mmol) **4** in 30 cm^3 dry *THF* at room temperature. The color of the solution turned orange. The mixture was heated for 20 min under stirring. The *pH* of the solution rose to ~7. After the volume of the reaction mixture was reduced to ~15 cm^3, an orange precipitated formed which was filtered off, washed with H_2O, EtOH, and diethyl ether, and finally dried *in vacuo*.

Yield: 0.040 g (47%); m.p.: >200°C; IR (KBr): $\nu = 3370$ (N–H), 3250 (OH), 3060, 3040 (Ar–H), 2930–2840 (CH-aliph.), 1630 (C=N), 1580 (N–H), 1500–1450 (Ar), 1260, 1210 (Ar–O–C), 1010 (N–O), 900 (O=U=O), 635 (C–Br) cm^{-1}; ^1H NMR (250 MHz, δ, *DMSO*-d_6): 10.90 (s, 1H, N–OH, D-exchangeable), 10.35 (s, 1H, N–OH, D-exchangeable), 8.44 and 8.15 (s, s, 4H, NH, D-exchangeable), 7.53–7.45 (s, 4H, Ar–H superimposed by phenyl H3), 7.20 (dt, $^3J = 7.2$ Hz, $^4J = 1.5$ Hz, 4H, phenyl-H5), 6.89 (dt, $^3J = 7.8$ Hz, $^4J = 1.6$ Hz, 4H, phenyl-H4), 6.78 (d, $^3J = 7.5$ Hz, $^4J = 1.4$ Hz, 4H, phenyl-H6), 4.35 (t, $^3J = 12.0$ Hz, 8H, Ar–O–CH_2CH_2), 3.92 (t, 8H, CH_2CH_2–O–Ar) ppm; UV/Vis (*DMSO*): λ_{max} (ε) = 405 (4350), 321 (8900), 303 (11300) nm.

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