Synthesis and Complexation of a New 14-Membered N_2O_2 Macrocycle with *vic*-Dioxime Moieties

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The new vic-dioxime ligand **2** (LH_4) carrying a 14-membered N_2O_2 macrocycle has been prepared. Mononuclear complex $(LH_3)_2Ni$, trinuclear complexes $(LH)_2Cu_3$, $(LH)_2Co_3$, $(LH)_2Pd_3$, and $(LH)_2Co_3(py)_3Cl_3$, dinuclear complex $(LH_3)_2(UO_2)_2(OH)_2$, and pentanuclear complex $[L_2Cu_5(phen)_2](NO_3)_2$ have been synthesized from LH_4. The electrochemical properties of tri- and pentanuclear complexes were investigated by cyclic voltammetry. For $(LH)_2Cu_3$ two reduction waves appeared at 0.215 and −0.870 V. $[L_2Cu_5(phen)_2](NO_3)_2$ exhibited four reduction waves at 0.200, −0.025, −0.670, and −1.170 V.

The successful design and synthesis of ligands capable of forming multinuclear complexes are of great interest for obtaining special effects in magnetic, optical, and electrical properties. For this purpose, the ligands need to carry multidonor groups to be able to bind more than one metal ion simultaneously. Macrocyclic ligands can be considered as important candidates for one of the components of these ligands. Although many examples of macrocyclic synthetic ligands contain identical donor groups being liable to coordinate with either hard or soft metal ions, a mixture of two or more donor sites has been also employed to tune the selectivity and stability[1]. Incorporation of a *vic*-dioxime moiety onto the macrocycle provides an efficient binding site for transition metal ions by formation of an MN_4 core with additional two hydrogen bridges[2].

The high stability of the complexes prepared with *vic*-dioxime ligands has been extensively used for various purposes including model compounds for vitamin B_{12}[3] or trace metal analysis[4]. Recently, the two H bridges have been substituted with metal complexes to obtain trinuclear compounds in order to investigate the magnetic interactions of the metal ions[5].

We have previously reported on the synthetic chemistry of MN_4 core-containing complexes, namely phthalocyanines[6,7] and *vic*-dioximates[8,9], with additional macrocyclic substituents. These macrocyclic *vic*-dioximes with four aza[10] or four thia[11] groups are shown to be capable of forming trinuclear complexes.

In the present work, our aim has been to undertake the synthesis of a *vic*-dioxime ligand carrying a 14-membered N_2O_2 macrocycle. The basicity of N donors in this macrocycle is rather low because of their position just near the oxime groups; i.e. their basicity is comparable with amides. However, three-nuclear complexes have been obtained by deprotonation of these NH groups. The synthesis of a pentanuclear complex has been also accomplished by insertion of the 1,10-phenanthroline complex of Cu in the place of bridge hydrogen atoms.

Results and Discussion

2,3-Dibromo-5,11,12,13,14,20-hexahydro-12,13-bis(hydroxyimino)tribenzo[*b.h.l.*][1,10,4,7]dioxadiazacyclotetradecine (**2** = LH_4) was prepared by the reaction of 1,2-bis[(2-aminophenoxy)methyl]-4,5-dibromobenzene[12] with *anti*-dichloroglyoxime in ethanol with excess of $NaHCO_3$ as a buffer to neutralize HCl formed during the reaction (Scheme 1). The colours, yields, and elemental analyses of LH_4 and its metal derivatives are listed in Table 1.

Scheme 1. Synthetic route to *vic*-dioxime **2** (LH_4) and its metal complexes

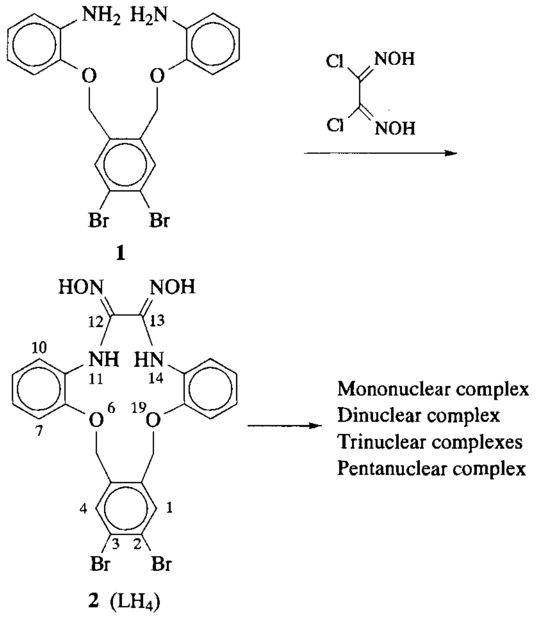

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Table 1. Analytical and physical data for **2** (LH_4) and its complexes. Required values are given in parentheses

			Analysis			
Compounds	Colour	Yields (%)	C	H	N	M
LH_4	light yellow	52	(46.90) 46.50	(3.20) 3.15	(9.96) 9.60	–
$(LH_3)_2Ni$	reddish brown	76	(44.74) 44.12	(2.87) 2.95	(9.48) 9.24	(4.97) 4.52
$(LH)_2Cu_3$	brown–green	60	(40.38) 40.54	(2.29) 2.59	(8.55) 8.41	(14.56) 14.16
$(LH)_2Co_3$	dark brown	56	(40.77) 40.18	(2.32) 2.43	(8.65) 8.32	(13.60) 12.95
$(LH)_2Pd_3$	brown	39	(36.73) 35.84	(2.08) 2.30	(7.79) 7.60	(22.20) 21.90
$(LH)_2Co_3\ (Py)_3Cl_3$	light brown	69	(43.21) 43.12	(2.74) 3.00	(9.30) 8.93	(10.78) 10.55
$(LH_3)_2\ (UO_2)_2(OH)_2$	orange	54	(31.13) 31.49	(2.12) 2.42	(6.60) 6.60	(28.06) 28.25
$[L_2Cu_6\ (Phen)_2](NO_3)_2$	black	34	(42.55) 42.35	(2.29) 2.19	(10.01) 9.85	(16.55) 16.13

In the ^{1}H-NMR spectrum of LH_4, the OH and NH proton resonances appear as two singlets at $\delta = 9.4$ and 9.2, respectively (Table 2). These singlets disappear by deuterium exchange. A single chemical shift for OH protons indicates that the oxime groups are in the *anti* form[8,11].

Table 2. ^{1}H-NMR spectral data for **2** (LH_4) and its complexes in DMSO

Compound	OH...O	-OH	N-H	Ar-H	Ar-H	$-CH_2-$	Others
LH_4	–	9.4(s,2H)	9.2(s,2H)	8.0(s,2H)	7.4-6.7(m,8H)	5.0(s,4H)	
$(LH_3)_2Ni$	16.8(s,2H)	–	7.5(s,4H)	8.0(s,4H)	7.3-6.8(m,16H)	5.0(s,8H)	
$(LH)_2Pd_3$	[a]	–	–	7.9(s,4H)	7.1-6.8(m,16H)	4.8(s,8H)	
$(LH)_2Co_3(Py)_3Cl_3$	[a]	–	–	8.0(s,4H)	7.0-6.5(m,16H)	5.1(s,8H)	7.9-7.0 (m,15H) (py)
$(LH_3)_2(UO_2)_2(OH)_2$	–	10.9 and 10.3(s,2H)	9.7 and 9.5(s,4H)	8.0(s,4H)	7.2-6.6(m,16H)	5.2(s,8H)	

[a] Not observed.

In the IR spectrum of LH_4, an OH stretching vibration is observed at 3220 cm^{-1} as a broad absorption. C=N and N–O stretching vibrations are at 1620 and 920 cm^{-1}, respectively (Table 3). These values are in harmony with the previously reported diaminoglyoxime derivatives[8,11].

Table 3. Characteristic IR bands (cm^{-1}) of **2** (LH_4) and its complexes (KBr pellets)

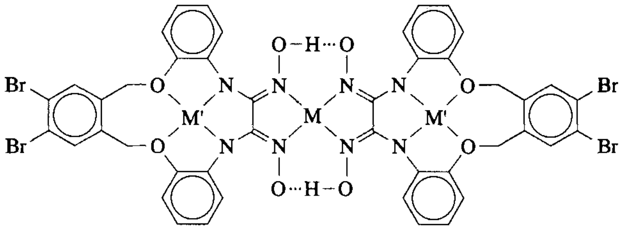
Compound	N-H	O-H	OH..O	C=N	N-H	Ar-O-C	N-O	Others
LH_4	3360	3220	–	1620	1595	1250	920	
$(LH_3)_2Ni$	3420	–	1720	1600	1570	1260	920	
$(LH)_2Cu_3$	–	–	1720	1600	–	1270	930	
$(LH)_2Co_3$	–	–	1700	1580	–	1250	920	
$(LH)_2Pd_3$	–	–	1710	1580	–	1250	920	
$(LH)_2Co_3(Py)_3Cl_3$	–	–	1710	1600	–	1260	910	1580(py)
$(LH_3)_2(UO_2)_2(OH)_2$	3380	–	–	1620	1580	1250	920	900(O=U=O)
$[L_2Cu_5(Phen)_2](NO_3)_2$	–	–	–	1590	–	1250	920	1380(NO_3^-)

Mono-, di-, tri-, and pentanuclear complexes have been synthesized from LH_4 with Ni(II), Cu(II), Co(II), Co(III), UO_2(VI), and Pd(II) (Table 1).

The Ni(II) complex of LH_4 has a metal:ligand ratio of 1:2, and the ligand is coordinated only by the N,N′ atoms of the *vic*-dioxime. It shows the characteristic features of *vic*-dioxime complexes (Figure 1). The disappearance of the OH stretching band and the shift of the C=N band to lower frequency in IR spectra of $(LH_3)_2Ni$ can be attributed to *N,N′*-chelation[8,13]. The (OH···O) bridge is characterized by a broad absorption for the bending vibrations at 1720 cm^{-1} (Table 3). As expected for a d^8 configuration in a square-planar field, $(LH_3)_2Ni$ is diamagnetic as confirmed by the NMR spectrum[2,8]. ^{1}H-NMR spectral data confirm the hydrogen bridge structure with a chemical shift at lower field ($\delta = 16.8$) for the deuterium exchangeable OH protons[8,14]. Also an NH proton has been observed at $\delta = 7.5$ (Table 2).

In contrast to the Ni(II) ion which gives only mononuclear complexes with LH_4, trinuclear complexes are obtained with Cu(II), Co(II), Co(III), and Pd(II). For each macrocycle one metal ion is coordinated to two aza and two oxa atoms of each macrocycle, while the third metal ion is coordinated by the N,N′ atoms of each oxime group in the two ligand molecules (Figure 1). These complexes have a metal:ligand ratio of 3:2. Trinuclear complexation is also confirmed by the mass spectrum of $(LH)_2Cu_3$ which gives a molecular ion peak at *m/z* 1307 using FAB technique.

$(LH)_2Co_3$ is oxidized to a diamagnetic octahedral Co(III) derivative by bubbling air through a solution of the complex in the presence of pyridine[3,15]. However, attempts to reduce the Co(III) complex to Co(I), a procedure used extensively to prepare alkylcobaloxime derivatives of dimethylglyoxime and other vic-dioximes, were not successful[3,15]. It is suggested that the six coordinated complexes with Co(III) are of the type $(LH)_2Co_3(py)_3Cl_3$. Pyridine ligands are coordinated axially to the metal in these octahedral complexes.



Complex	M	M'
$(LH_3)_2Ni$	Ni	–
$(LH)_2Cu_3$	Cu	Cu
$(LH)_2Co_3$	Co	Co
$(LH)_2Co_3(py)_3Cl_3$	Co(py)Cl	Co(py)Cl
$(LH)_2Pd_3$	Pd	Pd

Figure 1. Mono and trinuclear complexes of **2** (LH_4)

In the IR spectrum of $(LH)_2Co_3(py)_3Cl_3$ the weak band assigned to the intramolecular hydrogen-bonded OH bending vibration is observed at 1710 cm^{-1}. The C=N bands due to the oxime groups and pyridine are observed as a combined band at 1600−1580 cm^{-1} (Table 3). In the ^{1}H-NMR spectrum of $(LH)_2Co_3(py)_3Cl_3$ protons of pyridine appear at δ = 7.9−7.0 (Table 2). In the proton NMR spectrum the presence of intramolecular OH···O bands are not identifiable for either the Co(III) or Pd(II) complexes.

A dinuclear UO_2 complex was prepared from uranyl acetate and the ligand in methanol (Figure 2). The $(LH_3)_2(UO_2)_2(OH)_2$ complex precipitated immediately without any need to raise the pH of the solution. The elemental analysis of the complex indicated a metal:ligand ratio of 1:1 (Table 1). Uranyl complexes of vic-dioximes with this metal:ligand ratio are rare although we have reported on a dinuclear complex with μ-hydroxo bridges[8]. The IR spectrum is also consistent with the dimeric structure. A strong band around 900 cm^{-1} is the characteristic frequency for ν(O=U=O) vibrations (Table 3). The ^{1}H-NMR spectrum of the uranyl complex shows two chemical shifts for the deuterium-exchangeable N−OH (δ = 10.9 and 10.3) and NH protons (δ = 9.7 and 9.5) (Table 2), which can be attributed to the magnetic anisotropy of the uranyl ion as discussed in relation to some carboxylate and amine complexes[16]. It is known that uranyl ion enhances the chemical shift difference between non-equivalent protons. This effect is equivalent to increasing the proton NMR observing frequency by a few orders of magnitude[17].

It is known that the oximate group ($=N-O^-$) can function as a bridge[3] between two metal ions by means of the imino nitrogen and the deprotonated oxygen to afford di- and trinuclear complexes[5].

In this study we have accomplished the synthesis of the pentanuclear Cu(II) complex $[L_2Cu_5(phen)_2](NO_3)_2$ (Figure 3) with $(LH)_2Cu_3$ as the bridging ligand and 1,10-phenanthroline (phen) as an end-cap ligand. Formation of this pentanuclear complex is verified by the M^+ peak at *m/z* 1917 which has been obtained by fast-atom bombardment mass spectrometry. The secondary ions corresponding to the loss of two phenanthroline groups together with two Cu and two nitrates also appear at 1306 daltons. As in the case of the copper(II) ions in the trinuclear $(LH)_2Cu_3$ complex, the last two copper ions in the pentanuclear complex need to be tetracoordinated with two nitrogen atoms of phen and two oxygens of oxime. The nitrate ions are out of the coordination sphere as observed by the NO stretching vibrations around 1380 cm^{-1} which is a typical value for an ionic nitrate group[18].

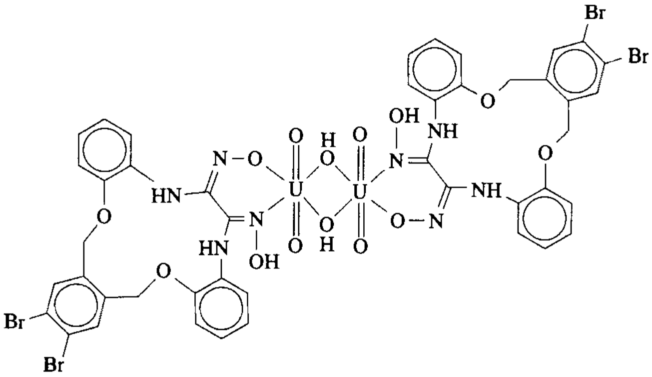


Figure 2. Dinuclear uranyl complex of LH_4

This complex is deeply coloured (black) and is stable at atmospheric pressure. $[L_2Cu_5(phen)_2](NO_3)_2$ is soluble in dimethylformamide, pyridine, or dimethyl sulfoxide.

In the IR spectrum of this complex no absorption attributable to a ν(OH) vibration in the region 1600−2000 cm^{-1} indicates that all dioxime oxygen atoms are deprotonated. In addition, IR spectroscopy indicates the presence of phen at 3060, 1520, 1430, and 740 cm^{-1} (Table 2).

Table 4. Current functions and diffusion coefficients for the trinuclear Cu(II) and pentanuclear Cu(II) complexes of LH_4 in 0.1 M TBAP supporting electrolyte (ν=0.05 Vs^{-1})

Compound	Peak no	ΔC^a/V	E_p/V	n	$\alpha^b n$	I_p/μA	$10^{12}D/m^2.s^{-1}$
$(LH_2)_2Cu_3$	1	0.0416	+0.2150	1	0.7090	0.2500	0.0740
	2	0.0390	−0.8700	1	0.7560	0.7350	0.5940
	3	0.0597	−0.6600	1	0.4940	0.1000	0.0170
	4	0.0830	+0.1000	1	0.3540	0.3500	0.2890
$[L_2Cu_5(phen)_2](NO_3)_2$	1	0.0434	+0.2000	1	0.6800	0.1500	0.0280
	2	0.0410	−0.0250	1	0.7190	0.1350	0.0210
	3	0.0928	−0.6700	1	0.3170	0.2750	0.1980
	4	0.0597	−1.1700	1	0.4940	0.1500	0.0380
	5	0.0726	+0.0500	1	0.4060	0.5250	0.5640
	6	0.0839	+0.3000	1	0.3510	0.2000	0.0950

[a] $\Delta C = E_p/\lg V$. − [b] $\Delta C = 0.0295/\alpha n$; hence α can be obtained. $Ip = 2.98 \times 10^5\, n(\alpha n)^{1/2} D^{1/2} C A \nu^{1/2}$ hence *D* can be obtained when αn is known for ν = 0.05 Vs^{-1}.

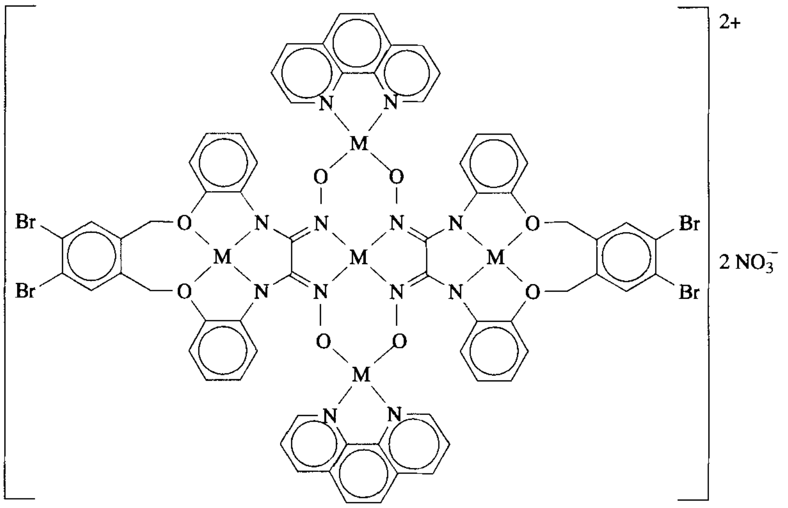


Figure 3. Pentanuclear complex of LH_4

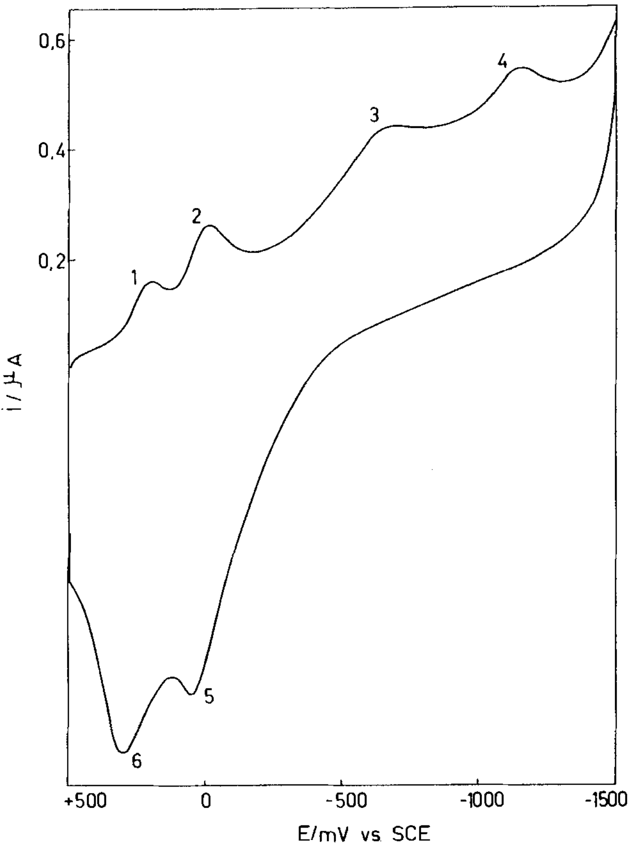


Figure 4. Cyclic voltammogram of $L_2Cu_5(phen)_2(NO_3)_2$

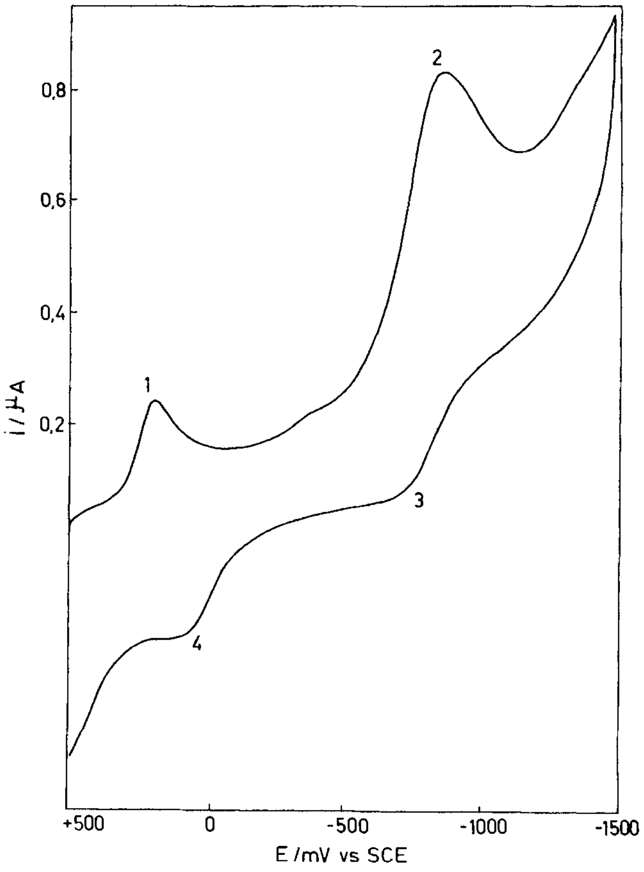


Figure 5. Cyclic voltammogram of $(LH)_2Cu_3$

All complexes show an intense charge-transfer absorption at ca. 400 nm. A weak d-d transition can not be observed.

Electrochemical Measurements

A typical voltammogram of the pentanuclear Cu(II) complex $[L_2Cu_5(phen)_2](NO_3)_2$ is shown in Figure 4. Four one-electron reduction waves were observed for this complex. For the trinuclear Cu(II) complex the cyclic voltammogram is characterized by two one-electron reduction waves (Figure 5). The waves of the trinuclear Cu(II) and pentanuclear Cu(II) species show a quasi-reversible behaviour at all sweep rates studied. The heterogenous electron transfer rate is relatively slow, so that the separation between the cathodic and anodic peaks varies with the sweep rate. The variation of E_p with sweep rate changed from the quasi-reversible case to the charge transfer rate-determining case within sweep rates studied (Table 4).

According to the slopes obtained these reactions are electron transfers with the following chemical reactions.

The difference of the reduction peak numbers between trinuclear Cu(II) and pentanuclear Cu(II) may be attributed to the different coordination spheres of copper ions in both species. Cyclic voltammetry of the copper-containing polynuclear complexes clearly shows that the reduction proceeds in two distinct one-electron steps. After the first one-electron reduction the redox properties of the other complexed transition metal cation are changed[19].

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Experimental

IR: Perkin-Elmer 598, KBr pellets. – Elemental analyses: Instrumental Analysis Laboratory of TUBITAK Gebze Research Center. – ^1H NMR: Bruker 200 MHz. – UV/Vis: DMS 90 spectrometer. – MS: VG ZabSpec with fast atom bombardment. – Cyclic voltammograms: Analytical cyclic voltammetry instrument CV EG & G PARC model 273, controlled by an external computer. A three-electrode system with a saturated calomel reference electrode and a platinum wire counter electrode was used. The working electrode was a platinum plate. Tridistilled water and Spectrosel grade DMSO, dried with 4 Å molecular sieves, were used in the voltammetric experiments. Tetrabutylammonium perchlorate (0.1 M) was the supporting electrolyte in DMSO. Solutions were purged with nitrogen prior to each voltammetric measurements.

1,2-Dibromo-4,5-bis(bromomethyl)benzene[20,21], 1,2-bis[(2-aminophenoxy)methyl]-4,5-dibromobenzene[12], and *anti*-dichloroglyoxime[22] were prepared by reported procedures. For colours and yields of the following products, see Table 1.

Dioxadiaza Macrocycle **2** (LH_4): A solution of *anti*-dichloroglyoxime (0.164 g, 1.0 mmol) in anhydrous ethanol (20 ml) was added dropwise to a solution of 1,2-bis[(2-aminophenoxy)methyl]-4,5-dibromobenzene (0.50 g, 1.0 mmol) in anhydrous ethanol (150 ml), which also contained sodium hydrogen carbonate (0.504 g, 6.0 mmol) in excess. The reaction mixture was heated on a water-bath at 60–70°C for 5 h. After cooling to room temp. it was filtered. The filtrate was added to 100 ml of water which contained 0.5 g of Na_2SO_4 in order to prevent colloidal dispersion. The precipitated dark-yellow compound was filtered off, washed with water, and dried in vacuo. Yield: 0.30 g (52%), m.p. 145–150°C.

Mononuclear Ni Complex $(LH_3)_2Ni$: To a solution of LH_4 (0.300 g, 0.534 mmol) in methanol (30 ml) was added a solution of $NiCl_2 \cdot 6\,H_2O$ (0.064 g, 0.280 mmol) in methanol (20 ml). The mixture was heated on a water-bath for 15 min. A reddish-brown complex was precipitated after the addition of 0.1 N KOH solution in ethanol up to pH 5. The product was filtered off, washed with hot methanol and diethyl ether and dried in vacuo at room temp. Yield: 0.24 g (76%).

Trinuclear Complexes $(LH)_2Cu_3$, $(LH)_2Co_3$, *and* $(LH)_2Pd_3$

a) *For* $(LH)_2Cu_3$ *and* $(LH)_2Co_3$: LH_4 (0.40 g, 0.710 mmol) was dissolved in methanol (40 ml) with heating and stirring. A solution of metal salt (1.067 mmol, 0.182 g of $CuCl_2 \cdot 2\,H_2O$, 0.253 g of $CoCl_2 \cdot 6\,H_2O$) in methanol (40 ml) was added to the dioxime solution with stirring. The mixture was heated on a water-bath for 15 min. 0.1 N KOH in ethanol was added to adjust the pH of the solution to about 4.5 where the precipitation of the complex started. After heating for another hour, the complex precipitated completely. It was filtered off, washed with hot and cold methanol and diethyl ether and dried in vacuo at room temp. For $(LH)_2Cu_3$ yield: 0.28 g (60%), $(LH)_2Co_3$ yield: 0.26 g (56%).

b) *For* $(LH)_2Pd_3$: A mixture of $PdCl_2$ (0.142 g, 0.8 mmol) and NaCl (0.094 g, 1.6 mmol) was dissolved in ethanol (40 ml). The solution was stirred at 70°C until $PdCl_2$ dissolved completely. A solution of LH_4 (0.3 g, 0.534 mmol) in ethanol (20 ml) was added to this Na_2PdCl_4 solution, and the procedures described above for the copper(II) and cobalt(II) analogs followed. Yield: 0.15 g (39%) of $(LH)_2Pd_3$. – MS (FAB), *m/z* (%): 1307 (3) [M^+], 1264 (6), 1205 (3), 1140 (2), 1124 (4), 1056 (6), 1013 (10), 625 (9), 537 (13), 244 (19), 185 (100), 133 (16).

Dinuclear $UO_2(VI)$ *Complex* $(LH_3)_2(UO_2)_2(OH)_2$: To a solution of LH_4 (0.30 g, 0.534 mmol) in methanol (30 ml) a solution of $UO_2(CH_3CO_2)_2 \cdot 2\,H_2O$ (0.228 g, 0.534 mmol) in methanol (20 ml) was added, and the mixture was heated on a water-bath for 10 min. The complex was precipitated immediately. The precipitate was filtered off, washed with hot and cold methanol and diethyl ether. The product was dried in vacuo. Yield: 0.24 g (54%).

Co(III) Complex $(LH)_2Co_3(Py)_3Cl_3$: LH_4 (0.30 g, 0.534 mmol) was dissolved in methanol (30 ml) with heating and stirring. To this solution was added a solution of $CoCl_2 \cdot 6\,H_2O$ (0.190 g, 0.8 mmol) in methanol (30 ml). The solution was filtered hot, pyridine (3.2 mmol) in methanol (10 ml) was added, and air was bubbled through the solution for 1 h. During this time precipitation occurred. The mixture was allowed to stand overnight. The brown precipitate was filtered, washed first with water, than with methanol and diethyl ether and dried in vacuo. Yield: 0.30 g (69%).

Pentanuclear Cu(II) Complex $[L_2Cu_5(phen)_2](NO_3)_2$: To a solution of the $(LH)_2Cu_3$ complex (0.200 g, 0.172 mmol) in tetrahydrofuran (THF 30 ml) was added a solution of 1,10-phenanthroline (0.080 g, 0.4 mmol) in THF (10 ml) and a solution of $Cu(NO_3)_2 \cdot 3\,H_2O$ (0.096 g, 0.4 mmol) in THF (10 ml). The mixture was stirred and heated at reflux. Reflux was maintained for 5 h after which the mixture was filtered. The volume of the filtrate was reduced to 10–15 ml on a rotary evaporator, and diethyl ether was slowly added with continuous stirring to the precipitated complex. This was filtered off, washed with water, ethanol, and diethyl ether and dried in vacuo at room temp. Yield: 0.10 g (34%). – MS (FAB), *m/z* (%): 1917 (7) [M^+], 1860 (3), 1813 (6), 1507 (2), 1467 (6), 1436 (3), 1370 (3), 1342 (3), 1306 (4), 1268 (12), 1215 (6), 895 (10), 746 (16), 530 (13), 314 (32), 197 (100).

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