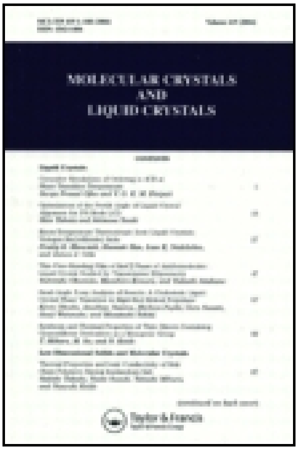

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Synthesis and Mesomorphism of [N,N′-Bis(3′,4′-didodecyloxyphenyl) diaminoglyoxime] Complexes with Nickel and Palladium

G. Gümüş [a] & V. Ahsen [a b]

[a] TÜBITAK Marmara Research Center, Department of Chemistry, P.O. Box 21, 41470, Gebze, Kocaeli, Turkey

[b] Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, 41400, Gebze, Kocaeli, Turkey

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Synthesis and Mesomorphism of [N,N′-Bis(3′,4′-didodecyloxyphenyl) diaminoglyoxime] Complexes with Nickel and Palladium

G. GÜMÜŞ[a] and V. AHSEN[ab*]

[a]*TÜBİTAK Marmara Research Center, Department of Chemistry, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey and* [b]*Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, 41400 Gebze, Kocaeli, Turkey*

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A new *vic*-dioxime, [N,N′-Bis(3′,4′-didodecyloxyphenyl)diaminoglyoxime](H_2L) has been prepared from 3,4-didodecyloxyaniline and *(E,E)*-dichloroglyoxime. The *(E,E)*- and *(E,Z)*-forms of Ni(II) complex have been isolated, but palladium complex could be isolated only as *(E,E)*-isomer. The mesomorphic properties of these complexes were investigated by polarizing microscopy, differential scanning calorimetry (DSC) and X-ray diffraction analysis. These complexes form columnar hexagonal disordered (Col_{hd}) mesophases. All complexes are very soluble in common organic solvents. ^1H and ^{13}C NMR, IR, MS and UV/Vis data are presented.

Keywords: Oximes; transition metal complexes; liquid crystal; columnar mesophases

1. INTRODUCTION

Due to the formation of interesting and coloured complexes with transition metal ions as metalomesogens, the oximes have gained importance in recent years[1,2].

The reaction of amines or thiols with *(E,E)*-dichloroglyoxime or cyanogen di-N-oxide yielded various symmetrically substituted diaminoglyoxime or dithioglyoxime derivatives[3]. The *(E,E)*-and *(E,Z)*- stereoisomers of vicinal dioximes are capable of coordinating through N,N or N,O sites of the oxime groups, though transition metal complexes of these vicinal dioximes are essentially N,N-coordinated square-planar structures.

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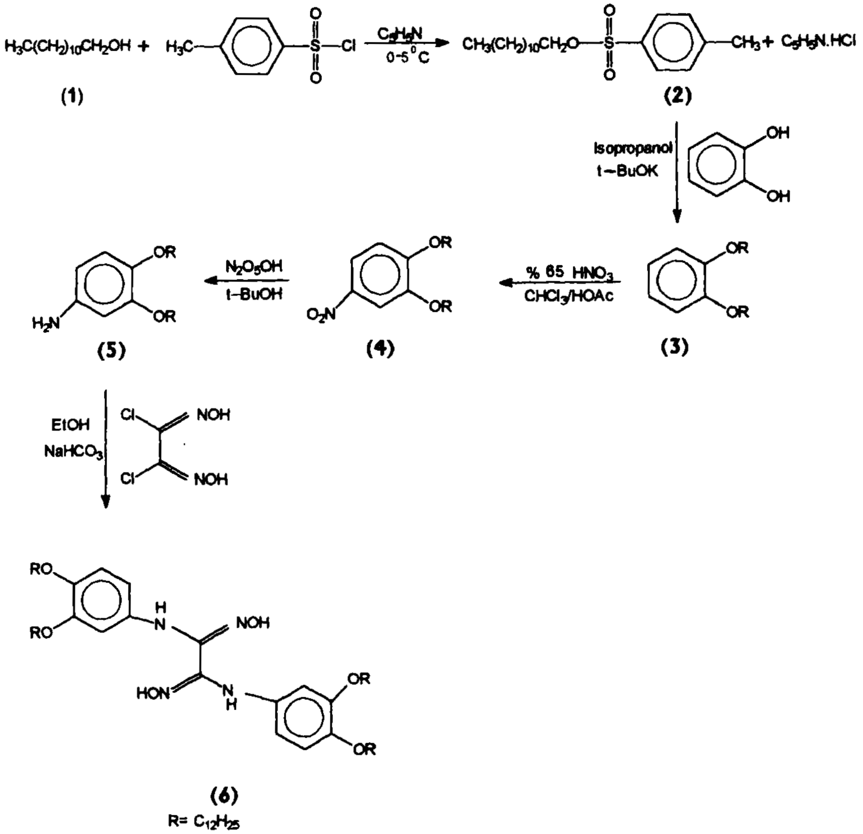
* Correspondence Author.

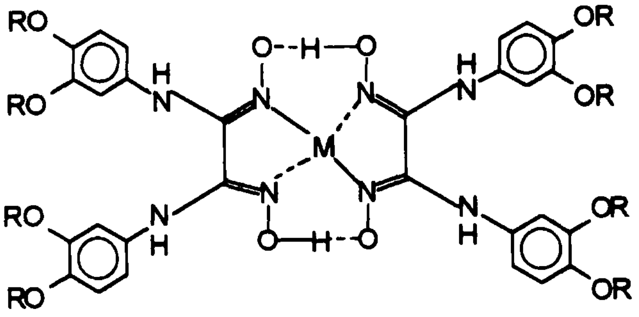


SCHEME 1 Synthesis of the H_2L (6)

The low solubility of the *vic*-dioximes complexes has hindered the study of their structures and their reactions. In order to increase their solubility and also promote them to gain liquid crystalline properties, additional groups need to be added to the rigid core composed of MN_4 group. These can be polarity enhancing groups such as ester, oxyether, nitrile and long alkyl chains. The solubility of *vic*-dioximes can be increased by adding long alkyl chains into the molecule[4].

Recently, Ohta and co-workers described the synthesis and mesomorphism of benzil-derived discotic columnar dioximato metal complexes, which constitute the first examples of liquid crystals in the bis(dionedioximato) metal (II) system[1].

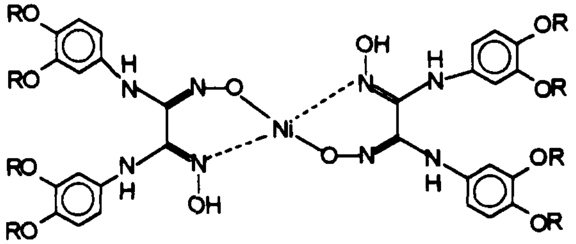
In the second study, Wegner and co-workers[2] synthesized 2,3,6,7-tetra-n-alkyl-substituted phenanthrene-9,10-dionedioximes (with alkyl=hexyl and decyl) and



(7) M=Ni
(8) M=Pd

R= $C_{12}H_{25}$

FIGURE 1 Structure of the *(E,E)*-Ni(II) (7) and *(E,E)*-Pd(II) (8)



(9)

R= $C_{12}H_{25}$

FIGURE 2 Structure of the *(E,Z)*-Ni(II) (9)

their complexes with the metals such as nickel, palladium and platinum to form the corresponding complexes as *(E,E)*-and *(E,Z)*- isomers which were identified as columnar mesophases. These properties were apparently caused by the introduction of alkoxy chains. On the other hand, it is well known that the mesomorphic properties and structures of transition metal complexes are also extremely influenced by the central metal ion.

In this paper, we describe the synthesis of the ligand (**6**) and the mesomorphic properties of its complexes with *(E,E)*-Ni(II), *(E,E)*-Pd(II) (Fig 1) and *(E,Z)*-Ni(II) (Fig 2).

2. RESULTS AND DISCUSSION

2.1.Synthesis

[N,N′-Bis(3′,4′-didodecyloxyphenyl)diaminoglyoxime] (H_2L) was prepared by the reaction of 3,4-didodecyloxyaniline with *(E,E)*- dichloroglyoxime in ethanol with excess of $NaHCO_3$ as a buffer to neutralize HCl formed during the reaction (Scheme 1).

In the IR spectrum of H_2L, the OH, C=N and N-O streching vibrations are observed at 3200, 1620 and 960 cm^{-1}, respectively, in agreement with the values reported for similar compounds[5,6,7]. The ^1H NMR spectrum of H_2L in DMSO-d_6 exhibits signals for OH (10 ppm) and NH (7.6 ppm). When $CDCl_3$ is used as solvent, the OH signal is not observed due to self-association through H-bridges[8,9]. The single chemical shift for OH protons indicates that the oxime groups are in *(E,E)* structure for H_2L[10]. The aromatic protons at 6.7–6.2 ppm, aliphatic (CH_2-O) protons around 3.8–3.6 ppm, aliphatic methylene protons at 1.3 ppm and methyl protons at 0.8 ppm as triplet were appeared. More detailed information about the structure of H_2L is provided by ^{13}C APT NMR spectroscopy. The carbon resonance of the oxime groups is found to be at lower fields (146 ppm) as given in the literature[11]. The mass spectrum of H_2L has been obtained by FAB technique using a m-nitrobenzylalcohol as matrix and $[M]^+$ peak is observed at m/z 1007.7.

To prepare *(E,E)*-Ni(II), *(E,E)*-Pd(II) and *(E,Z)*-Ni(II) complexes, a solution of the ligand and a metal salt in ethanol was heated to 65°C for 15 min. The complexes of H_2L with Ni(II) was isolated as *(E,E)*-Ni(II) or *(E,Z)*-Ni(II) complexes depending on the applied reaction conditions. Complexation at pH=2 yields the *(E,Z)*-isomer, whereas at pH=5 formation of the *(E,E)*-isomer prevails. However, only nickel complexes could be isolated in *(E,Z)*and *(E,E)* conformation, while the palladium complex was completely isomerized to the (E,E)-isomer during complex formation.

As in the cases of most *(E,E)*-dioximes, H_2L forms complexes with Ni(II) and Pd(II) with a metal / ligand ratio of 1:2. As expected for d^8configuration in square planar field, Ni(II) and Pd(II) complexes with *(E,E)*isomer are diamagnetic according to the NMR spectrum[10,12]. The ^1H NMR spectrum in $CDCl_3$

proved the hydrogen-bridged structure for *(E,E)*-Ni(II) complex with a deuterium exchangeable chemical shift at 17 ppm[6]. *(E,Z)*-Ni(II) complex on the other hand, showed a broad resonance at 9.2 ppm for the deuterium exchangable free O-H protons. But O-H--O proton of *(E,E)*-Pd(II) complex was not observed. As expected, the *(E,Z)*-Ni(II) complex is tetrahedral and paramagnetic, so its NMR signals are broad[12,13].

All complexes have similar IR spectra. But, while C=N streching absorption of *(E,E)*-Ni(II) complex has a single band at 1600 cm^{-1}, *(E,Z)*-Ni(II) complex has two absorptions at 1600 and 1640 cm^{-1} corresponding to the two different coordination modes of each oxime moiety. The color of *(E,E)*-Ni(II) complex is yellowish orange, *(E,Z)*-Ni(II) complex is yellowish green due to their structural conformation[10,12]. The ^{13}C NMR spectra of H_2L and its complexes agreed with the data reported for similary compounds[14].

The mass spectra of the both *(E,E)*-Ni(II), *(E,Z)*-Ni(II) and *(E,E)*-Pd(II) complexes have been obtained by FAB technique using m-nitrobenzylalcohol as matrix and $[M+1]^+$ peaks are observed at m/z 2071, 2071 and 2118.4, respectively.

2.2.Mesogenic behaviour of metal complexes

The phase transformation behaviour of *(E,E)*-Ni(II) metal complex was studied by microscopy and differential scanning calorimetry (DSC).

When the virgin powder crystals were started heating from room temperature with a rate of 3°C /min under the microscope, they were transformed at 77.7°C into a viscous liquid with birefringence, a characteristic of liquid crystalline phases. On further heating, the sample cleared to form an isotropic liquid at 117.2°C. When the isotropic liquid was cooled from 120°C at a cooling rate of 3°C/min, broken spherolithic textures appeared at 115°C (Fig 3). The textures are compatible with that of the columnar hexagonal disordered (Col_{hd}) mesophase reported in the literature[1,2]. On further cooling, these broken spherolithic textures remained even at room temperature. This behaviour was also observed by DSC.

The DSC thermogram of the virgin sample at a first heating rate of 5°C /min gave two endothermic peaks at 77.7°C (ΔH=50.08 J/g) and 117.2°C (ΔH=2.62 J/g). While the melting point of this sample is 77.7°C, the peak at 117.2°C correspond to the clearing point.

In the first cooling cycle at 115.2°C, transition from isotropic phase to liquid crystalline phase was observed. The sample was cooled to –25°C, but the transition from liquid crystalline phases to crystalline phases had not been observed. In

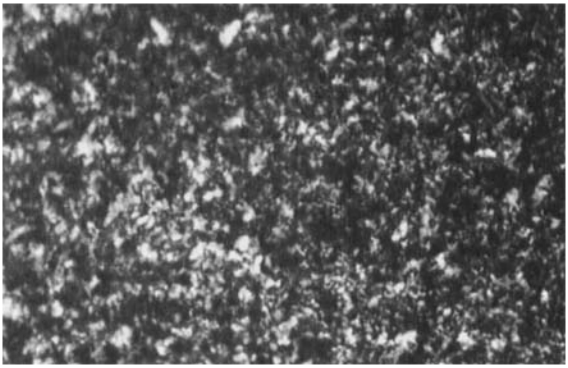


FIGURE 3 Broken spherolithic texture at 35°C of compound (7) (See Color Plate VI at the back of this issue)

the second heating run (5°C/ min) it gave only one peak (clearing point) at 117.2°C.

Although the *(E,E)*-Ni(II) (Fig 3) and *(E,E)*-Pd(II) (Fig 4) complexes exhibit the same properties of mesomorphism, for *(E,Z)*-Ni(II) complex the clearing point could not be observed by DSC, but it was identified by polarizing microscop with the typical textures (Fig 5). The phase transition temperatures and enthalpy changes, measured by the DSC and the polarizing microscope are summarized in Table I.

TABLE I Phase transition temperatures (T_t) and enthalpy changes (ΔH_t) of the complexes

Compound	*Phase* $T_t/°C$ ΔH_t J/g	*Phase*
(E,E)-Ni (II)	$K \xrightarrow{77.7\ [50.80]} Col_{hd}$	$Col_{hd} \underset{115}{\overset{117.2\ [2.62]}{\rightleftarrows}} I.L.$
(E,Z)-Ni (II)	$K \xrightarrow{65.7\ [71.35]} Col_{hd}$	$Col_{hd} \underset{140}{\overset{145}{\rightleftarrows}} I.L.$
(E,E)-Pd (II)	$K \xrightarrow{80\ [7.02]} Col_{hd}$	$Col_{hd} \underset{129.5}{\overset{131.2\ [3.21]}{\rightleftarrows}} I.L.$

Col_{hd}= Columnar hexagonal disordered mesophase. I.L.= Isotropic liquid.

As confirmed by X-ray powder diffraction *(E,E)*-Ni(II) complex has a columnar hexagonal disordered (Col_{hd}) mesophase. The X-ray results show three narrow reflections, which are assigned to (100), (110) and (200) in a two-dimensional hexagonal lattice. The lattice constant is 38.20 Å. The pattern also gives a diffuse band at $2\theta \cong 20°C$ (d= 4.44 Å) which corresponds to the melt of the alkyl chains. While a full spherolitic texture is observed for the palladium compound **8** (Fig. 4), pseudo-focal conic or spherolithic textures are obtained for nickel complexes **7** and **9** (Fig 3 and 5). In the columnar hexagonal phases, the observed and calculated spacing ratios are very close to each other. Here it is not the case for compound **7** (d_{100}/d_{110}=1.762) and for compound **9** (d_{100}/d_{110}=1.708). Consequently, a slightly distorted hexagonal lattice (i.e. a rectangular one) can be proposed for these systems.

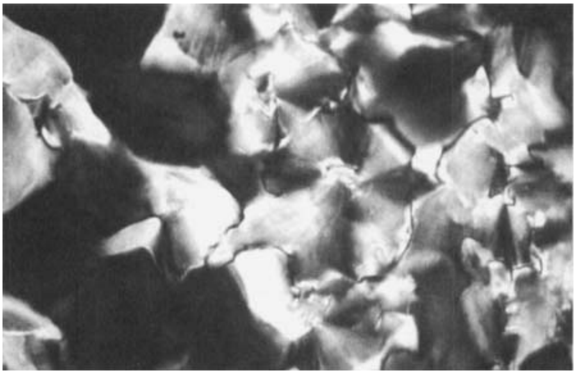


FIGURE 4 Spherolithic texture at 31.5°C of compound (**8**) (See Color Plate VII at the back of this issue)

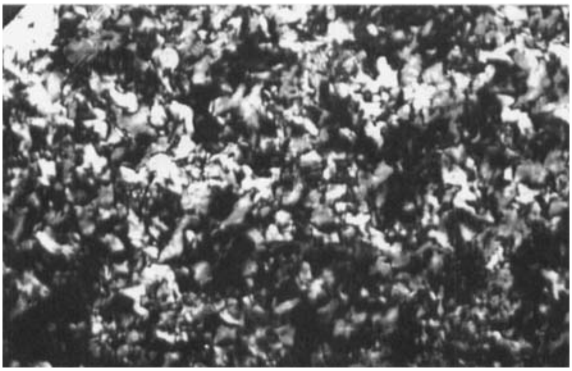


FIGURE 5 Broken spherolithic texture at 33°C of compound (**9**) (See Color Plate VIII at the back of this issue)

TABLE II X-Ray Diffraction Data of the Complexes at Room Temperature

Compound	*Spacing (Å)*		*Miller Indices*	*Lattice constant*
	d_{obsd}	d_{calcd}		
(E,E)-Ni (II)	33.09	33.09	(100)	
	18.78	19.10	(110)	a=38.20Å
	15.69	16.55	(200)	
	≅ 4.44	–	*	
(E,E)-Pd (II)	32.41	32.41	(100)	
	18.82	18.71	(110)	
	16.32	16.21	(200)	
	12.36	12.25	(210)	a=37.42Å
	10.80	10.80	(300)	
		9.35	(220)	
	9.08	8.98	(310)	
	≅ 4.52	–	*	
(E,Z)-Ni (II)	31.57	31.57	(100)	
	18.48	18.23	(110)	a=36.46Å
	15.30	15.79	(200)	
	≅ 4.44	–	*	

*. the melt of alkyl chains.

3. EXPERIMENTAL SECTION

(E,E)-dichloroglyoxime[15], dodecyltosylate[16] **(2)**, 1,2-didodecyloxybenzene **(3)** and 1,2-didodecyloxy-4-nitrobenzene[17,18] **(4)** were synthesized according to a described procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz Spectrometer, Mass spectra were recorded on a VG Zab Spec GC-Ms spectrometer with fast atom bombardment (FAB) method (35 KV). MNBA was used as the matrix.

Routine IR spectra were recorded on a Perkin-Elmer 983 Spectrophotometer as KBr pellets. Electronic spectra were recorded on a Schimadzu 2001 UV Pc Spectrophotometer. Elemental analyses were obtained using a Carlo Erba 1106 Instrument. X-ray measurements were carried out by using Rigaku X-Ray Diffractometer Sesi D_{max} 2200. Differential Scanning Calorimetry (DSC) experiments have been carried out on a Perkin-Elmer DSC-7 series thermal analysis system.

3,4-Didodecyloxyaniline (5)

This compound was prepared by making slight changes on the procedure given in the literature [18].

Compound (**4**) (19 g, 0.04 mol) was dissolved in hot n-butanol (170 ml) and palladium-charcoal activated (10 % Pd) (1.9 g) was added under argon. When the mixture was refluxing, hydrazinium hydroxide (9.5 ml, 80 %) was added dropwise in 1h. After the reaction mixture had been refluxed for 2h, it was filtered hot. The product was soluble in chloroform, n-hexane, ethanol, acetone, DMF and THF. Yield: 16.5 g (% 89); m.p.54°C; Found C, 77.00; H, 11.35; N, 3.02 %, $C_{30}H_{55}NO_2$; requires C, 77.86; H, 11.98; N, 3.03 %; IR (ν_{max}/cm^{-1}): 3393 and 3306 (NH), 2920 and 2850 (CH_2), 1600, 1500, 1470, 1235 ($C\text{-}O\text{-}C_{aryl}$), 1120 and 1071 (C-O-C), 844, 604; MS (EI), m/z (%): 462.5 (94) $[M{+}1]^+$, 446 (15) $[M\text{-}CH_3]^+$, 293 (80) $[M\text{-}C_{12}H_{25}]^+$, 276 (4) $[M\text{-}OC_{12}H_{25}]^+$, 125 (100) $[M\text{-}2(C_{12}H_{25})]^+$, 109 (23) $[M\text{-}2(OC_{12}H_{25})]^+$; ^{1}H-NMR ($CDCl_3$) δ ppm: 6.7 (d, 1H, Ar-H), 6.3 (d, 1H, Ar-H), 6.2 (dd, 1H, Ar-H), 3.9 (q, 4H, CH_2-O), 3.4 (s, 2H, C-NH_2), 1.7 (m, 4H, $\underline{CH_2}$-CH_2-O), 1.3 (m, 36H, CH_2), 0.8 (t, 6H, CH_3); ^{13}C-NMR ($CDCl_3$) δ ppm: 152, 143, 137, 117, 109 and 104 (Ar-C), 71 and 69 (CH_2-O), 33 ($\underline{CH_2}$-CH_2-O), 30, 27 and 23 (CH_2), 14 (CH_3).

[N,N′-Bis(3′,4′-didodecyloxyphenyl)diaminoglyoxime](H_2L)(6)

3,4-Didodecyloxyaniline (**5**) (12 g, 0.026 mol) was dissolved in absolute ethanol (300 ml) under argon at 40°C and sodium hydrogen carbonate (4.32 g, 0.052 mol) was added in excess. The mixture was stirred for 1h at room temperature. To this mixture, a solution of *(E,E)*-dichloroglyoxime (2.4 g, 0.015 mol) in 80 ml of absolute ethanol was added dropwise during 2h and stirred at room temperature overnight. Water was added dropwise until precipitation occurred. The product was filtered off, washed with water and then dried. The ligand was soluble in n-hexane, dichloromethane and slightly soluble ethanol, DMF and THF. Yield: 8 g (% 62); m.p. 120–123°C; Found C, 73.00; H, 11.21; N, 5.20 %, $C_{62}H_{110}N_4O_6$; requires C, 73.91; H, 11.80; N, 5.56 %; IR (ν_{max}/cm^{-1}): 3395 (NH), 3200 (OH), 2920 and 2850 (CH_2), 1620 (C=N), 1450, 1260, 1240, 1135, 960 (N-O), 720; MS (FAB), m/z (%): 1007.7 (100) $[M]^+$, 821.5 (13) $[M\text{-}OC_{12}H_{25}]^+$, 635 (9) $[M\text{-}2(OC_{12}H_{25})]^+$, 472 (43), 304 (23), 261; λ_{max}/nm ($CHCl_3$) 250 and 216 ($\epsilon/dm^3\ mol\ cm^{-1}$74000 and 51600); ^{1}H-NMR (DMSO) δ ppm: 10.0 (s, 2H, OH), 7.6 (s, 2H, C-NH), 6.7 (d, 2H, Ar-H), 6.3 (d, 2H, Ar-H), 6.2 (dd, 2H, Ar-H), 3.8 (t, 4H, CH_2-O), 3.6 (t, 4H, CH_2-O), 1.8 (s, 8H, $\underline{CH_2}$-CH_2-O), 1.3 (m, 72H, CH_2), 0.8 (t, 12H, CH_3); ^{13}C-NMR ($CDCl_3$) δ ppm:

151 (Ar-C), 150 (C=NOH), 141, 130, 117, 107 and 102 (Ar-C), 72 and 68 (CH_2-O), 32 ($\underline{CH_2}$-CH_2-O), 30, 25 and 22 (CH_2), 12 (CH_3).

N,N-Coordinated Complexes [(E,E)-Ni(HL)$_2$ (7) and (E,E)-Pd(HL)$_2$(8)]

To the warm ethanol solution (40 ml) of H_2L (**6**) (0.500 g, 5.10^{-4} mol) was added a warm ethanol (60°C) solution (10 ml) of the appropriate metal salt [$NiCl_2$. $6H_2O$ (0.058 g, 2.5 10^{-4} mol) or solution of Na_2PdCl_4 (12 ml) (prepared by stirring 0.369 g, 2.08.10^{-3} mol of $PdCl_2$ and 0.244 g, 4.17.10^{-3} mol of NaCl in 100 ml ethanol)] with stirring at 60°C for 15 min. A distinct change in color and a decrease in the pH value of the solution was observed. An equivalent amount of KOH (0.1 M in EtOH) was added dropwise to maintain pH value at 5. The complexes were separeted as oily products in ethanol at this temperature (60°C). After, the complexes were dissolved in dichloromethane (5 ml) and were precipitated with ethanol (25ml). The products were filtered off, washed with water and ethanol and then dried. These compounds were soluble in chloroform, ethylacetate, benzene, THF, and CCl_4.

(E,E)-Ni(HL)$_2$

Yield: 0.250 g (% 49); Found C, 71.32; H, 11.02; N, 4.97 %, $C_{124}H_{218}N_8O_{12}Ni$; requires C, 71.89; H, 10.60; N, 5.41 %; IR (ν_{max}/cm^{-1}) 3400 (NH), 3220 (OH), 2920 and 2850 (CH_2), 1600 (C=N), 1060 (N-O); MS (FAB), m/z (%): 2071 (100) $[M+1]^+$, 1902 (11) $[M-C_{12}H_{25}]^+$, 1231 (89) $[M-5(C_{12}H_{25})]^+$, 1061 (23) $[M-6(C_{12}H_{25})]^+$, 975 (77) $[(M-7(C_{12}H_{25})]^+$, 806 (14), 634 (12), 472 (52); λ_{max}/nm ($CHCl_3$) 384, 255 and 241 (ε/dm^3 mol cm^{-1} 12870, 20480 and 20330); ^{1}H-NMR ($CDCl_3$) δ ppm: 17 (s, 2H, O-H--O), 6.8 (s, 4H, NH), 6.6 (d, 4H, Ar-H), 6.2 (d, 4H, Ar-H), 6.1 (s, 4H, Ar-H), 3.8 (d, 16H, CH_2-O), 1.8 (s, 16H, $\underline{CH_2}$-CH_2-O), 1.4 (s, 144H, CH_2), 0.8 (s, 24H, CH_3); ^{13}C-NMR ($CDCl_3$) δ ppm: 148 (Ar-C), 146 (C=N-O), 143, 132, 117, 114 and 108 (Ar-C), 70 and 69 (CH_2-O), 32 ($\underline{CH_2}$-CH_2-O), 30, 26 and 23 (CH_2), 14 (CH_3).

(E,E)-Pd(HL)$_2$

Yield: 0.100 g (% 20); Found C, 70.97; H, 11.13; N, 5.22 %, $C_{124}H_{218}N_8O_{12}Pd$; requires C, 70.27; H, 10.37; N, 5.29 %; IR (ν_{max}/cm^{-1}) 3400 (NH), 3220 (OH), 2920 and 2850 (CH_2), 1600 (C=N), 1060 (N-O); MS (FAB), m/z (%): 2118.4 (20) $[M+1]^+$, 1949 (5), $[M-C_{12}H_{25}]^+$, 1658 (5), 1160 (7), 1007 (100), 821 (15), 600 (21); λ_{max}/nm ($CHCl_3$) 366, 241 and 204 (ε/dm^3 mol cm^{-1} 10790, 20440 and 11120); ^{1}H-NMR ($CDCl_3$) δ ppm: 7.6 (s, 4H, NH), 6.8 (d, 4H, Ar-H), 6.2 (d, 4H, Ar-H), 5.8 (s, 4H, Ar-H), 3.8 (t, 8H, CH_2-O), 3.6 (t, 8H, CH_2-O), 1.8 (s, 16H,

$\underline{CH_2}$-CH_2-O), 1.4 (s, 144H, CH_2), 0.8 (s, 24H, CH_3); ^{13}C-NMR ($CDCl_3$) δ ppm: 148 (Ar-C), 146 (C=N-O), 143, 131, 114 and 108 (Ar-C), 70 and 69 (CH_2-O), 32 ($\underline{CH_2}$-CH_2-O), 30, 26 and 23 (CH_2), 14 (CH_3).

N,O-Coordinated Ni (II) Complex (9)

To a solution (0.500 g, 5.10^{-4} mol) of H_2L (**6**) in 40 ml of warm ethanol was added $NiCl_2.6H_2O$ (0.058 g, $2.5.10^{-4}$ mol) in 10 ml of warm ethanol. The color change from yellow to green together and a decrease in the pH value (≈ 2) of the solution was observed. After cooling to deepfreeze, the yellowish-green precipitate was filtered off, washed with water and dried. The compound *(E,Z)*-Ni $(HL)_2$ was soluble in chloroform, ethylacetate, benzene, THF and CCl_4.

(E,Z)-Ni(HL)$_2$

Yield: 0.100 g (20 %); Found C, 70.88; H, 10.77; N, 5.02 %, $C_{124}H_{218}N_8O_{12}Ni$; requires C, 71.89; H, 10.60; N, 5.41 %; IR (ν_{max}/cm^{-1}) 3400 (NH), 3220 (OH), 2920 and 2840 (CH_2), 1640 and 1600 (C=N), 1460, 1260, 1240, 1120, 1060 (N-O), 860, 840, MS (FAB), m/z (%): 2071 (100) $[M+1]^+$, 1903 (9) $[M-C_{12}H_{25}]^+$, 1231 (74) $[M-5(C_{12}H_{25})]^+$, 1061 (14) $[M-6(C_{12}H_{25})]^+$, 975 (77) $[(M-7(C_{12}H_{25})]^+$, 472.5 (38), 206 (47), λ_{max}/nm (in acidic $CHCl_3$) 242 and 212 (ε/dm^3 mol^{-1} cm^{-1} 18400 and 12220); ^{1}H-NMR ($CDCl_3$) δ ppm: 9.2 (b, 2H, OH), 6.6–6.2 (b, 12H, Ar-H), 4.4–3.8 (b, 16H, CH_2-O), 1.8 (s, 16H, $\underline{CH_2}$-CH_2-O), 1.4 (m, 144H, CH_2), 0.8 (s, 24H, CH_3).

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