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Synthesis, Mesomorphism, and Spectroscopic Characterization of New Schiff Bases and Their Cu(II), Pd(II) Complexes

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New Schiff bases have been prepared from 1,2-dialkyloxy-4-formyl-5-hydroxybenzene and 4,5-diamino-1,2-didodecyloxybenzene. Pd(II) and Cu(II) complexes are obtained with metal Schiff base ratio of 1:1. The new compounds have been characterized by elemental analyses; IR; and, ^{1}H NMR, ^{13}C NMR, and mass spectra. The mesomorphic properties of these complexes were investigated by polarizing microscopy and X-ray diffraction analysis. These complexes form columnar hexagonal (Col_h) mesophases. The influence of the metal centers on the mesomorphic temperatures may be attributed to better intermolecular dative association in the palladium complexes than in the copper complexes.

Keywords: liquid crystal; metallomesogen; Schiff base

INTRODUCTION

Liquid crystals are fascinating materials because they exhibit properties of both solids and liquids. Many liquid crystals with metal-containing molecules (metallomesogens) have been synthesized, and molecular design and synthesis of mesogenic metal complexes with new structures or improved physical properties constitute an active research area [1–6]. The most popular molecular method of building

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liquid crystals is to confine the core and the chains of the molecule near a plane. Metallomesogens introduce to metal-based coordination chemistry [7] the unusual physical properties exhibited by liquid crystals that are so useful in electronic devices and elsewhere. The relationship between chemical structure and mesogenic properties is an extensively investigated area in the field of liquid-crystal chemistry [8–10]. Especially over the past few years, a number of metal complexes of Schiff bases have been reported that show liquid-crystal phases [1,8,9,11–15]. There have been a few reports of complexes containing 1,2-diaminobenzene with salicylaldehyde [16–20].

We are currently focused on the design and synthesis of metallomesogens [21–23]. Some compounds that are mesomorphic at room temperature are used in ordered and disordered forms. The ordered films on quartz crystal microbalance (QCM) devices show higher sensitivity and partition coefficients for all solvent molecules investigated such as ethanol, dichloromethane, acetone, and n-hexane [24]. In this article, we report the synthesis of symmetrically substituted Schiff base-copper and palladium complexes in order to better understand the effect of the type of the metal ion incorporated to the formation of their mesomorphic properties. In addition, we investigated the possibility that the presence of both four rigid alkyloxyaldehyde and 4,5-dialkyloxy-1,2-diaminobenzene can effect dative mesomorphic properties. These complexes are mesomorphic in room temperature and are examined as chemical sensors.

EXPERIMENTAL

Alkyl tosylate [25] **4**, **5**, and **6**; 1,2-dialkyloxy benzene compounds **7**, **8**, and **9**, and 4,5-diamino 1,2-didodecyloxybenzene [26] were prepared by a reported procedure. Routine IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200-MHz spectrometer. Elemental analyses were performed on a Carlo Erba elemental analyser. Electronic spectra were recorded on a Schimatzu 2001 UV spectrophotometer. Mass spectra were recorded on a VG Zab Spec GC-Ms spectrometer using the electron ionization (EI) and LSIMS-Fast Atom Bombardment (FAB) methods. MNBA (m-nitrobenzylalcohol) was used as a matrix.

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 Mettler Toledo TGA/SDTA 851^{e}.

Synthesis of 1,2-dioctyloxy-4-acetylbenzenes (10, 11, and 12)

Phosphorus pentoxide (37 g, 0.26 mol) was dissolved in orthophosporic acide (17 ml) under argon at 120°C for 1 h and then cooled at 90°C, and acetic acide (7.5 ml) was added in the mixture. After the reaction mixture was cooled to 45°C, acetic anhydride (2.2 ml) was added to this mixture, and the solution of compound **7** (6.69 g, 0.02 mol) in acetic acide (29 ml) was added to the reaction mixture.

The mixture was stirred under argon at 120°C for 48 h. Then water (65 ml) was added and the aqueous phase was extracted with dichlorometane (3 × 30 ml). The combined extract was threated with sodium carbonate solution (5%) and then with water, and dried over anhydrous sodium sulfate. Purification of the product was accomplished by column chromatograpy with silicagel (60–230 mesh) (eluent dichlorometane/n-hexane 2:5).

This compound was soluble in n-hexane, diethyl ether, and chloroform. The results of elemental analysis are given in Table 1.

TABLE 1 Analytical and Physical Data for Schiff Bases and Their Complexes

			Analysis (%)		
Compound	Yield (%)	Mp (θ/°C)	C	H	N
10	77	68	(76.54) 76.31	(10.71) 10.63	—
11	76	65	(77.72) 77.86	(11.18) 11.87	—
12	73	65	(78.63) 78.80	(11.55) 11.38	—
13	40	53	(73.43) 73.45	(10.27) 10.24	—
14	49	53	(74.90) 74.48	(10.78) 10.91	—
15	43	54	(74.90) 74.92	(11.78) 11.04	—
16	90	70	(75.38) 75.03	(10.93) 10.68	—
17	89	75	(76.79) 76.12	(11.40) 11.34	—
18	89	78	(77.86) 77.79	(11.76) 11.05	—
19	26	45	(72.98) 72.92	(10.12) 10.13	—
20	27	58	(74.61) 74.19	(10.67) 10.85	—
21	35	73	(75.87) 75.21	(11.09) 11.60	—
22	66	128	(73.10) 73.20	(10.37) 10.27	(3.33) 3.34
22a	42	230	(72.36) 71.39	(10.07) 9.45	(2.22) 2.24
22b	42	240	(70.09) 69.93	(9.75) 9.70	(2.15) 1.97
23	66	128	(77.01) 76.91	(11.08) 10.95	(2.14) 1.97
23a	44	210	(73.55) 73.34	(10.44) 9.36	(2.04) 1.98
23b	47	230	(71.33) 71.00	(10.12) 10.11	(1.98) 1.95
24	66	127	(77.69) 77.62	(11.34) 11.27	(1.97) 1.97
24a	45	169	(74.47) 74.05	(10.73) 10.45	(1.89) 1.79
24b	44	210	(72.38) 72.13	(10.43) 10.17	(1.83) 1.82

- IR (KBr): $\nu_{max}/\,cm^{-1} = 3040$, 2980–2820, 1665 (C=O), 1580–1500, 1460, 1380, 1260, 810–720.
- ^{1}H NMR ($CDCl_3$): δ 7.56 (d, 1H, Ar−H), 6.88 (d, 1H, Ar−H), 7.50 (s, 1H, Ar−H), 4.08 (m, 4H, OCH_2), 2.57 (s, 3H, O=C−CH_3), 1.83 (m, 4H, $OCH_2\underline{CH_2}$), 1.30 (m, 20H, CH_2), 0.88 (q, 6H, CH_3).
- ^{13}C NMR (APT) ($CDCl_3$): δ 198.4 (Ar−$\underline{C}$=O), 153.54 (C_{Ar}), 148.85 (C_{Ar}), 130.28 (C_{Ar}), 123.16 (Ar−CH), 112.53 (Ar−CH), 111.68 (Ar−CH), 69.30–69.08 (OCH_2), 26.16 (OC−$\underline{CH_3}$), 31.92–22.68 (CH_2), 14.09 (CH_3).
- MS (EI), m/z (%): 376.2 (100) $[M]^+$, 264.1 (50) $[M^+ - C_8H_{17}]$, 152.0 (100) $[M^+ - 2(C_8H_{17})]$, 137.0 (73) $[M^+ - 2(C_8H_{17}) + CH_3]$.

Compounds **11** and **12** were prepared according to the procedure described for **10**.

11: MS (EI), m/z (%): 432.3 (100) $[M]^+$, 292.2 (45) $[M^+ - C_{10}H_{21}]$, 152.0 (100) $[M^+ - 2(C_{10}H_{21})]$, 137.0 (68) $[M^+ - 2(C_{10}H_{21}) + CH_3]$.
12: MS (EI), m/z (%): 488.4 (100) $[M]^+$, 320.2 (9) $[M^+ - C_{12}H_{25}]$, 152.0 (76) $[M^+ - 2(C_{12}H_{25})]$, 137.0 (23) $[M^+ - 2(C_{12}H_{25}) + CH_3]$.

Synthesis of 1,2-Dioctyloxy-4-acetoxylbenzene (13, 14, and 15)

Compound **10** (2.5 g, 6.6×10^{-3} mol) was dissolved in acetic acid (14.5 ml) at 80°C and per acetic acid (9%, 11 ml) was added. The mixture was stirred for 5 h. After cooling to room temperature, the solution of sodium metabisulfite (3.64 g, 0.013 mol) in water (15 ml) was added while cooling in an ice bath. Then, the mixture was extracted with dichloromethane (3×30 ml). The combined extract was extracted first with sodium carbonate solution (5%) and then with water, and dried over anhydrous sodium sulfate. Purification of the product was accomplished by column chromatography with silica gel (eluent: dichloromethane/n-hexane; 2:5). This compound was soluble in n-hexane, diethyl ether, and chloroform. The results of elemental analysis are given in Table 1.

- IR (KBr): $\nu_{max}\,/\,cm^{-1} = 3040$, 2980–2820, 1750 (C=O), 1580–1500, 1460, 1380, 1260, 810–720.
- ^{1}H NMR ($CDCl_3$) : δ 6.81 (d, 1H, Ar−H), 6.60 (s, 1H, Ar−H), 6.59 (d, 1H, Ar−H), 3.98 (m, 4H, OCH_2), 2.20 (s, 3H, O=C−CH_3), 1.80 (m, 4H, $OCH_2\underline{CH_2}$), 1.42 (m, 20H, CH_2), 0.86 (q, 6H, CH_3).
- ^{13}C NMR (APT) ($CDCl_3$): δ 169.14 (Ar−O−$\underline{C}$=O), 149.72 (C_{Ar}), 146.90 (C_{Ar}), 144.60 (C_{Ar}), 114.19 (Ar−CH), 112.88 (Ar−CH),

107.82 (Ar−CH), 69.65–69.07 (OCH_2), 22.60 (O=C−$\underline{CH_3}$), 31.79–22.60 (CH_2), 13.94 (CH_3).

- MS (EI), m/z (%): 392.5 (39) $[M]^+$, 350.4 (100) $[M^+ - OC_2H_3]$, 238.3 (46) $[M^+ - OC_2H_3 + (C_8H_{17})]$, 126.1 (79) $[M^+ - 2(C_8H_{17}) + OC_2H_3]$.

Compounds **14** and **15** were prepared according to the procedure described for **13**.

14: MS (EI), m/z (%): 448.3 (84) $[M]^+$, 406.3 (100) $[M^+ - OC_2H_3]$, 266.2 (52) $[M^+ - OC_2H_3 + (C_{10}H_{21})]$, 126.1 (82) $[M^+ - 2(C_{10}H_{21}) + OC_2H_3]$.

15: MS (EI), m/z (%): 504.4 (74) $[M]^+$, 462.4 (100) $[M^+ - OC_2H_3]$, 294.2 (31) $[M^+ - OC_2H_3 + (C_{12}H_{25})]$, 126.1 (89) $[M^+ - 2(C_{12}H_{25}) + OC_2H_3]$.

Synthesis of 1,2-Dioctyloxy-4-hydroxylbenzene (16, 17, and 18)

A solution of NaOH (10%, 26 ml) was added dropwise over 15 min to compound **13** (3 g, 7.64×10^{-3} mol). The mixture was heated under argon at 70°C for 5 h. Then, H_2SO_4 (25%, 10.5 ml) was added dropwise until the pH reached 2 while cooling in an ice bath. The product was filtered off, washed with water, and then dried. The ligand was soluble in chloroform and diethyl ether. The results of elemental analysis are given in Table 1.

- IR (KBr): ν_{max} / cm^{-1} = 3300 (OH), 3040, 2980–2820, 1600, 1500, 1460, 1260, 810–720.
- ^1H NMR ($CDCl_3$): δ 6.76 (d, 1H, Ar−H), 6.43 (s, 1H, Ar−H), 6.32 (d, 1H, Ar−H), 5.21 (s, 1H, OH), 3.94 (m, 4H, OCH_2), 1.85 (m, 4H, $OCH_2\underline{CH_2}$), 1.41 (m, 20H, CH_2), 0.90 (t, 6H, CH_3).
- ^{13}C NMR (APT) ($CDCl_3$): δ 150.58 (C_{Ar}), 150. 01 (C_{Ar}), 142.94 (C_{Ar}), 116.53 (Ar−CH), 106.21 (Ar−CH), 102.37 (Ar−CH), 70.90, 69.03 (OCH_2), 31.83–22.66(CH_2), 14.07 (CH_3).
- MS (EI), m/z (%): 350.4 (100) $[M]^+$, 237.1 (60) $[M^+ - C_8H_{17}]$, 122.0 (98) $[M^+ - 2(C_8H_{17})]$.

Compounds **17** and **18** were prepared according to the procedure described for **16**.

17: MS (EI), m/z (%): 406.2 (100) $[M]^+$, 266.2 (58) $[M^+ - C_{10}H_{21}]$, 126.0 (100) $[M^+ - 2(C_{10}H_{21})]$.

18: MS (EI), m/z (%): 462.4 (100) $[M]^+$, 294.2 (40) $[M^+ - C_{12}H_{25}]$, 126.0 (96) $[M^+ - 2(C_{12}H_{25})]$.

Synthesis of 1,2-Dioctyloxy-4-formyl-5-hydroxybenzene (19, 20, and 21)

The compound **16** (2.5 g, 6.86×10^{-3} mol) was dissolved in anhydrous trifluoroacetic acid (6.5 ml) under N_2 and hexamethylenetetramine (0.96 g, 6.88×10^{-3}) was added in one portion. The brown solution was refluxed until all starting material was converted, and the mixture was then cooled to room temperature. The cooled solution was poured into 4 M HCl (7 ml) and stirred for 15 min, and the product was extracted with dichloromethane (2×10 ml). The combined organic extracts were washed with 4 M HCl (7 ml) and saturated brine (7 ml), and then dried (Na_2SO_4) and the solvent removed in vacuo. The dark orange residue was purified by column chromatography (silica gel, CH_2Cl_2/n-hexane 1:1). After evaporation **19** was isolated as a yellow precipitate. The results of elemental analysis are given in Table 1.

- IR (KBr): $\nu_{max}/\,cm^{-1} = 3300$ (OH), 3040, 2980–2820, 1635 (C=O), 1600, 1500, 1460, 1380, 1260, 810–720.
- ^{1}H NMR ($CDCl_3$): δ 11.36 (s, 1H, OH), 9.65 (s, 1H, COH), 6.92 (s, 1H, Ar−H), 6.42 (s, 1H, Ar−H), 4.06 (m, 4H, OCH_2), 1.88 (m, 4H, $OCH_2\underline{CH_2}$), 1.60 (m, 20H, CH_2), 0.91 (t, 6H, CH_3).
- ^{13}C $\overline{NMR}$ (APT) ($CDCl_3$): δ 193.87 (COH), 159.51 (C_{Ar}), 157.48 (C_{Ar}), 142.46 (C_{Ar}), 116.90 (Ar−CH), 112.84 (Ar−CH), 100.75 (Ar−CH), 70.51, 69.12 (OCH_2), 31.76–22.62 (CH_2), 14.04 (CH_3).
- MS (EI), m/z (%): 378.1 (100) $[M]^+$, 266.1 (74) $[M^+ - C_8H_{17}]$, 154.0 (89) $[M^+ - 2(C_8H_{17})]$.

Compounds **20** and **21** were prepared according to the procedure described for **19**.

20: MS (EI), m/z (%): 434.2 (100) $[M]^+$, 294.1 (64) $[M^+ - C_{10}H_{21}]$, 154.0 (98) $[M^+ - 2(C_{10}H_{21})]$.

21: MS (EI), m/z (%): 490.4 (100) $[M]^+$, 322.2 (33) $[M^+ - C_{12}H_{25}]$, 154.0 (74) $[M^+ - 2(C_{12}H_{25})]$.

Preparation of the Schiff bases (22, 23, and 24)

To a solution of 4,5-diamino-1,2-didodecyloxybenzene (0.84 g, 1.77×10^{-3} mol) in dry MeOH (40 ml) was added a solution of **19** (0.5 g, 1.27×10^{-3} mol) in dry MeOH (29 ml) under argon at 60°C. The mixture was stirred and refluxed for 3 h, and orange precipitate formed. The product was filtered off and washed with MeOH. The orange residue was purified by column chromatography (silica gel

CH_2Cl_2/n-hexane 1:1). The results of elemental analysis are given in Table 1.

- IR (KBr): $\nu_{max}/\,cm^{-1} = 3300$ (OH), 3040, 2980–2820, 1610, 1560, 1500, 1460, 1380, 1360, 1260, 800.
- ^1H NMR ($CDCl_3$): δ 11.51 (s, 2H, OH), 8.52 (s, 2H, N=CH), 6.78 (s, 2H, Ar−H), 6.52 (s, 4H, Ar−H), 4.05 (m, 12H, OCH_2), 1.88 (m, 12H, OCH_2CH_2), 1.45 (m, 76H, CH_2), 0.88 (t, 18H, CH_3).
- ^{13}C NMR (APT) ($CDCl_3$): δ 162.44 (N=CH), 156.36 (C_{Ar}), 154.47 (C_{Ar}), 142.26 (C_{Ar}), 117.52 (Ar−CH), 108.94 (Ar−C−CH=N), 101.46 (Ar−CH), 70.85–68.90 (OCH_2), 31.82–22.66 (CH_2), 14.07 (CH_3).
- MS (LSIMS-FAB), m/z (%): 1197.1 (80) $[M+1]^+$, 752.6 (100) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O))]$, 640.4 (16) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2)+(C_8H_{17})]$, 527.3 (5) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2)+(C_8H_{17})_2]$.

Compounds **23** and **24** were prepared according to the procedure described for **22**.

23: MS (LSIMS-FAB), m/z (%): 1309.1 (89) $[M+1]^+$, 865.8 (100) $[M^+-(^+-(o-(C_6H_2)-(C_{12}H_{25}O))]$, 724.6 (12) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2)+(C_{10}H_{21})]$, 583.4 (6) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2)+(C_{10}H_{21})_2]$.

24: MS (LSIMS-FAB), m/z (%): 1422.4 (52) $[M+1]^+$, 977.1 (100) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O))]$, 810.1 (10) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2)+(C_{12}H_{25})]$, 640.3 (6) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2)+(C_{12}H_{25})_2]$.

Preparation of the Copper (II) Complexes of 22a

A mixture of copper (II) acetate dihidrate (0.008 g, 4.21×10^{-5}) was dissolved in dry THF (2 ml) by warming in an oil bath. An equimolar amount of **22** (0.05 g, 4.17×10^{-5} mol) dissolved in dry THF (5.5 ml) was added to the acetate of metal ion. The mixture was boiled in a oil bath for 2 h. After evaporation of the solvent, the product was washed with MeOH until the washings were colorless and dried in vacuo. The results of elemental analysis are given in Table 1.

- IR (KBr): $\nu_{max}/\,cm^{-1} = 3040$, 2980–2820, 1620, 1560, 1500, 1480, 1380, 1360, 1260, 800.
- MS (LSIMS-FAB), m/z (%): 1258.4 (81) $[M+1]^+$, 753.6 (100) $[M-(o-(C_6H_2)-(C_{12}H_{25}O)+Cu)]^+$, 639.4 (14) $[M-(o-(C_6H_2)-(C_{12}H_{25}O)_2+Cu)+(C_8H_{17})]^+$, 527.2 (5) $[M-(o-(C_6H_2)-(C_{12}H_{25}O)_2+Cu)+(C_8H_{17})_2]^+$.

Compounds **23a** and **24a** were prepared according to the procedure described for **22a**.

23a: MS (LSIMS-FAB), m/z (%): 1370.7 (92) $[M+1]^+$, 864.6 (100) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)+Cu)]$, 723.4 (16) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2+Cu)+(C_{10}H_{21})]$, 581.0 (24) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2+Cu)+(C_{10}H_{21})_2]$.

24a: MS (LSIMS-FAB), m/z (%): 1485.4 (94) $[M+1]^+$, 977.9 (41) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)+Cu)]$, 806.0 (7) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2+Cu)+(C_{12}H_{25})]$, 637.3 (5) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2+Cu)+(C_{12}H_{25})_2]$.

Preparation of the Palladium (II) Complexes of 22b

A mixture of palladium (II) acetate monohidrate (0.009 g, 4.21×10^{-5}) was dissolved in dry THF (2 ml) by warming in a oil bath. An equimolar amount of **22** (0.05 g, $4.17\times10^{\times5}$ mol) dissolved in dry THF (5.5 ml) was added to the acetate of metal ion. The mixture was boiled in an oil bath for 2 h. After evaporation of the solvent the product was washed with MeOH until the washings were colorless, and dried in vacuo. It was yellow orange. The results of elemental analysis are given in Table 1.

- IR (KBr): $\nu_{max}/\,cm^{-1}=3040$, 2980–2820, 1610, 1560, 1500, 1480, 1380, 1360, 1260, 800.
- ^1H NMR ($CDCl_3$): δ 8.67 (s, 2H, N=CH), 7.64 (s, 2H, Ar−H), 6.67 (s, 2H, Ar−H), 6.54 (s, 2H, Ar−H), 4.01 (m, 12H, OCH_2), 1.82 (m, 12H, $OCH_2\underline{CH_2}$), 1.53 (m, 76H, CH_2), 0.88 (t, 18H, CH_3).
- ^{13}C NMR (APT) ($CDCl_3$): δ 162.01 (N=CH), 156.98 (C_{Ar}), 156.05 (C_{Ar}), 142.52 (C_{Ar}), 140.20 (C_{Ar}), 117. 03 (Ar−CH), 108.13 (Ar−C−CH=N), 101.35 (Ar−CH), 69.97–68.35 (OCH_2), 31.97–22.70 (CH_2), 14.20 (CH_3).
- MS (LSIMS-FAB), m/z (%): 1301.2 (55) $[M+1]^+$, 753.6 (40) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)+Pd)]$, 638.0 (8) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2+Pd)+(C_8H_{17})]$, 525.3 (5) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)_2+Pd)+(C_8H_{17})_2]$.

Compounds **23b** and **24b** were prepared according to the procedure described for **22b**.

23b: MS (LSIMS-FAB), m/z (%): 1413.4 (70) $[M+1]^+$, 864.5 (41) $[M^+-(o-(C_6H_2)-(C_{12}H_{25}O)+Pd)]$, 722.1(7) $[M^+-(o-(C_6H_2)$

$-(C_{12}H_{25}O)_2 + Pd) + (C_{10}H_{21})]$, 581.3 (5) $[M^+ - (o-(C_6H_2)-(C_{12}H_{25}O)_2 + Pd) + (C_{10}H_{21})_2]$.

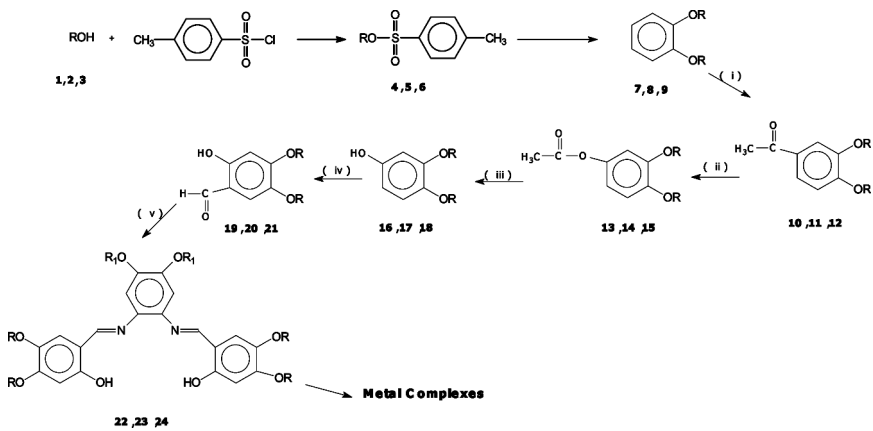
24b: MS (LSIMS-FAB), m/z (%): 1527.0 (70) $[M+1]^+$, 976.7 (50) $[M^+ - (o-(C_6H_2)-(C_{12}H_{25}O) + Pd)]$, 807.8 (12) $[M^+ - (o-(C_6H_2)-(C_{12}H_{25}O)_2 + Pd) + (C_{12}H_{25})]$, 639.4 (7) $[M^+ - (o-(C_6H_2)-(C_{12}H_{25}O)_2 + Pd) + (C_{12}H_{25})_2]$.

RESULTS AND DISCUSSION

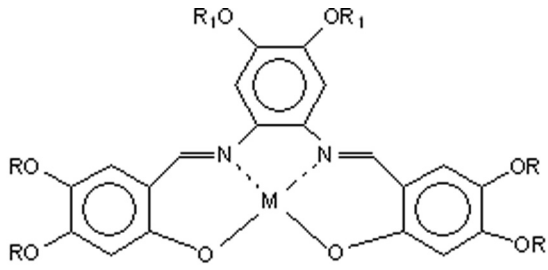
The preparation of the ligands (**22–24**) (Scheme 1) was accomplished by condensation of the selected 4,5-diamino-1,2 didodecyloxybenzene with the **19, 20**, and **21**. Ligands are yellow-orange solids (yields, melting points, analytical data, and ^1H and ^{13}C NMR spectra are given in the Experimental section and Table 1). The metal complexes were obtained in THF by the reaction of copper acetate and palladium acetate with the ligands (Figure 1).

For **22**, **23**, and **24**, the OH vibration is observed at 3300 cm^{-1} as a broad peak. Conversion of the compounds **19**, **20**, and **21** to **22**, **23**, and **24** was confirmed by the disappearance of the C=O vibrations at 1635 cm^{-1}. Characteristic intense absorptions of C=N groups appeared at 1625 cm^{-1} in **22**, **23**, and **24** derivatives after the Schiff base reaction.

In the ^1H NMR spectra of **22**, **23**, and **24** in $CDCl_3$, the OH proton resonance appears at low field as singlet peak at 11.49 ppm. This peak



SCHEME 1 Synthesis of Schiff base ligand: (i) acetic anhydride, polyphosporic acid; (ii) peracetic acide, acetic acide; (iii) NaOH, H_2SO_4; (iv) hexamethylenetetramine, CF_3COOH; (v) 4,5-diamino-1,2-didodecyloxybenzene, MeOH.



	R_1	R	M
22a	$C_{12}H_{25}$	C_8H_{17}	Cu^{2+}
22b	$C_{12}H_{25}$	C_8H_{17}	Pd^{2+}
23a	$C_{12}H_{25}$	$C_{10}H_{21}$	Cu^{2+}
23b	$C_{12}H_{25}$	$C_{10}H_{21}$	Pd^{2+}
24a	$C_{12}H_{25}$	$C_{12}H_{25}$	Cu^{2+}
24b	$C_{12}H_{25}$	$C_{12}H_{25}$	Pd^{2+}

FIGURE 1 Structure of Schiff base complexes.

disappears by deuterium exchange; N=CH protons appeared at 8.52 ppm. The aromatic protons are observed at 6.78 and 6.52 ppm as singlets for each different benzene. OCH_2 protons appeared as multiplets at 4.05–3.90 ppm. OCH_2CH_2 and CH_2 and CH_3 protons appeared at 1.88–1.58 ppm as a multiplet, 1.45–1.25 ppm as a multiplet, and 0.88–0.84 ppm as a triplet respectively. More detailed information about the structure of **22**, **23**, and **24** is provided by ^{13}C APT (attached proton test) NMR spectroscopy. The formation of an azomethine band causes a shift from 193.87 ppm in **19**, **20**, and **21** to 166.23 ppm in **22**, **23**, and **24** for N=CH as reported in the literature [27–30].

At the mass spectrum of the ligands moleculer ion peaks were observed with LSIMS-FAB technique. A close investigation of the mass spectra of Schiff base compound **22**, **23**, and **24** confirmed the proposed structures. In the case of Schiff base complexes **22a**, **22b**, **23a**, **23b**, **24a**, and **24b**, the $[M+1]^+$ peaks and fragments ions

corresponding to the loss of M–[o–(C_6H_2)–($OC_{12}H_{25}$)$_2$ + Pd or Cu], M–[(o–(C_6H_2)–($OC_{12}H_{25}$)$_2$ + Pd or Cu) + R] and M–[(o–(C_6H_2)–($OC_{12}H_{25}$)$_2$ + Pd or Cu) + (R)$_2$] were easily identified.

All of the metal complexes were characterized by elemental analysis, IR, and, in the case of the diamagnetic Pd (II) species, by ^{1}H and ^{13}C APT NMR spectra (Experimental section). The bonding mode of the **22**, **23**, and **24** ligands for the Pd complexes have been inferred by ^{1}H NMR evidence. This shows that the Pd (II) ion selectively binds the O, N, N, O-tetradentate salen-type functionality. Strong indications of Pd binding arise from both the large shielding experienced by the imine proton N=CH ($\Delta\delta = \delta_{\text{ligand}} - \delta_{\text{complex}} = 0.2$) and the disappearance of the proton signal corresponding to the OH group of free ligands. The ^{13}C NMR spectra of **22**, **23**, and **24** and its complexes agreed with the data reported for similarly compounds [27,30]. Infrared data are much less informative [8] (C=N and N=N stretching modes superimpose in the same region), although they are not in contrast with the presence of tetradentate ligands with an N_2O_2 donor set. The IR spectra of the complexes show most ligand absorptions at the same frequencies except for the C=N stretches, which are shifted slightly (ca. 10 cm^{-1}) to lower energy after complex formation [25]. Similar shifts have been reported for the N, N′-coordinated *vic*-dioxime complexes of various transition metal ions [31–33]. By analogy, a similar bonding mode has been proposed for the homologous paramagnetic Cu (II) compound (Figure 1).

Mesogenic Behavior of Metal Complexes

The phase transformation behavior of the **24a** complex was studied by polarized microscopy and differential scanning calorimetry (DSC).

The virgin powder crystals were heated from 15°C with a rate of 5°C/min under the microscope and the sample cleared to form an isotropic liquid at 169°C. When the isotropic liquid was cooled from 170°C at a cooling rate of 5°C/min, textures appeared at 162°C. Upon further cooling, these fan-like textures remained even at room temperature. All complexes show similar behavior to **24a**. The textures are compatible with that of the discotic liquid crystalline reported in the literature [15,16,19,34]. Good textures of the samples were obtained by slowly cooling from the isotropic melt. Phase transition from mesophase to isotropic liquid are **22a**, **22b**, **23a**, **23b**, and **24b** $\geq$ 210°C. They appear to have a fan-like or star-like texture (Figure 2).

Increasing the carbon length in the alkoxy side chains decreased the clearing temperature. So, the columnar mesophases existed over a wide range of temperatures including room temperature; the

FIGURE 2 Star-like texture at room temperature of compound **22b**.

clearing points ranged from 240 to 169°C depending on the alkoxy side chain length ($n = 8$, 10, 12). The size of the metal ions also affect the clearing temperature. For example the difference of clearing

TABLE 2 Phase Transition Temperature from DSC Measurements and Entalphy Changes (ΔH) of the Complexes

Compound	Transition	T (°C)	ΔH (kJ mol^{-1})
22b	K-CoI_h	110	10.93
	CoI_h-I	240	39.01
23b	K- CoI_h	112	10.83
	CoI_h-I	231	38.52
24b	K- CoI_h	117	9.10
	CoI_h-I	200	35.07
22a	K-CoI_h	86	2.11
	CoI_h-I	230	2.82
23a	K-CoI_h		
	CoI_h-I	210	
24a	K-CoI_h		
	CoI_h-I	169	

TABLE 3 X-Ray Diffraction Data of the Complexes at 25°C

Compound	Spacing (Å)		Ratio	Lattice constant
	d_{obs}	d_{calc}		
22a	23.11	23.11	1	
	14.28	13.36	$\sqrt{3}$	
	11.56	11.55	$\sqrt{4}$	
	8.91	8.73	$\sqrt{7}$	a = 26.68
	7.49	7.70	$\sqrt{9}$	
	6.82	6.67	$\sqrt{12}$	
	6.37	6.41	$\sqrt{13}$	
	4.43	—		
22b	27.76	27.76	1	
	16.31	16.05	$\sqrt{3}$	
	13.63	13.88	$\sqrt{4}$	
	11.12	10.49	$\sqrt{7}$	a = 32.09
	9.04	9.25	$\sqrt{9}$	
	8.02	8.01	$\sqrt{12}$	
	7.26	7.70	$\sqrt{13}$	
	4.33	—		
23a	26.65	26.65	1	
	15.26	15.40	$\sqrt{3}$	
	13.31	13.32	$\sqrt{4}$	
	10.25	10.07	$\sqrt{7}$	a = 30.81
	7.73	7.69	$\sqrt{12}$	
	4.52	—		
23b	30.88	30.88	1	
	17.53	17.85	$\sqrt{3}$	
	15.43	15.44	$\sqrt{4}$	
	10.25	10.29	$\sqrt{9}$	a = 35.70
	8.41	8.56	$\sqrt{13}$	
	4.32	—		
24a	29.54	29.54	1	
	16.93	17.08	$\sqrt{3}$	a = 34.15
	14.53	14.77	$\sqrt{4}$	
	4.43	—		
24b	35.31	35.31	1	
	19.49	20.41	$\sqrt{3}$	
	17.11	17.66	$\sqrt{4}$	a = 40.82
	11.81	11.77	$\sqrt{9}$	
	10.20	10.19	$\sqrt{12}$	
	4.29	—		

temperature was 10°C for Pd and Cu complexes substituted with octyl. The crystal to mesophase transition temperatures were determined by DSC. The DSC measurements of the complexes **22a**, **23a**, and **24a** show no significant sharp peaks from −25 to 250°C. The absence of

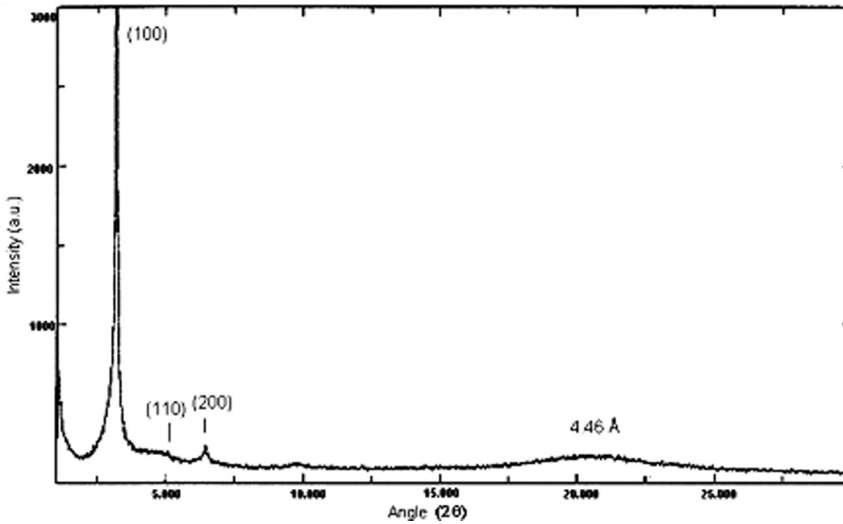


FIGURE 3 X-ray diffraction of **22b**.

the isotropic peak at DSC curve might be due to a relatively low transition enthalpy change for the transition, indicating that the columnar phase was a highly disordered phase. The results for other complexes (**22b**, **23b**, and **24b**) measured by the DSC are summarized in Table 2.

X-Ray Diffraction

X-ray diffraction measurements were performed with Cu-K_α radiation using a Rigaku Kristalloflex diffractometer (D_{max} 2200). X-ray studies are shown in Table 3. The diffractogram of all compounds confirms the nature of the columnar hexagonal phase [35]. The X-ray results show three narrow reflections, which are assigned to (100), (110), and (200) in a two-dimentional hexagonal lattice. The lattice constant is given in Table 3.

The low angle of the X-ray diffraction diagrams of the compounds **22a**, **22b**, **23a**, **23b**, **24a**, and **24b** show sharp Bragg reflections with d-spacing ratio $1:1\sqrt{3}:1\sqrt{4}:1\sqrt{7}:1\sqrt{9}$ (Table 3) [20–22,36]. This result suggests a two-dimentional hexagonal lattice with disk-like molecules stacked in columns in a hexagonal arrangement. The hexagonal lattices also correlated well with increasing side-chain lengths and with the size of the metal ions. The sharpness of this reflection of Schiff base complexes suggest good order within the columns and are consistent with the strong intramolecular periodicity associated with the discotic hexagonal CoI_h mesophase (Figure 3).

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