Ferroelectric Behavior of Chiral Bis(salicylideneaniline) Copper(II), Vanadium(IV), and Palladium(II) Liquid Crystals

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Three series of chiral bis(salicylideneaniline)copper(II), -oxovanadium(IV), and -palladium-(II) complexes, namely, series X = −CH=CH−COO−, series X = −COO−, and series X = −O−, have been synthesized, and their mesogenic and ferroelectric properties evaluated. The potentially ferroelectric S_C^* phase has been found for all four compounds of the series X = −CH=CH−COO− and the three complexes of the series X = −COO−. The values of the spontaneous polarization (Ps) of these compounds have been measured ranging from ca. 20 to 90 nC/cm^2. A packing arrangement in which the molecules are tilted to one edge within the S_C^* phase is proposed. In this situation the net molecular dipole must principally lie with the polar axis of the ferroelectric phase, thus explaining the Ps values measured. In addition, all the compounds have been studied as chiral dopants for ferroelectric liquid-crystalline mixtures.

Introduction

Soon after some metal-containing compounds appeared as promesogenic structures, researchers in the field of liquid crystals envisioned the enormous possibilities of these new mesogens.[1−5] One of the aspects that makes them different from typical organic liquid crystals is the rich variety of molecular geometries that can be obtained by introducing metals into the chemical structure. Similar to organic mesogens, these compounds exhibit either calamitic or discotic mesophases. However, a wider diversity of molecular shapes can be found that display either type of mesomorphic behavior.[6]

Investigation of ferroelectric behavior in liquid crystals has mainly centered on "rodlike", chiral organic mesogens. Models have been proposed[7] to explain the molecular origin of the spontaneous polarization (Ps) within the chiral smectic C (S_C^*) phase. However, ferroelectricity has been proposed to exist, and in a few cases the spontaneous polarization evaluated in S_C^* phases consisting of molecules that are not rod-shaped.

Thus, the ferroelectric behavior of salicylideneamine complexes,[8] open-book dinuclear palladium complexes,[9] H-shaped chloro-bridged dinuclear palladium complexes,[10] and K-shaped benzylideneamine β-diketone palladium complexes[11] have been studied. Furthermore, in a similar way to organic ferroelectric liquid crystals, ferroelectric metallomesogens have demonstrated second-order nonlinear optical properties.[6,12,13]

As a consequence, we consider it of great interest to examine more deeply the ferroelectric properties derived from the presence of chiral lateral−lateral fused twin[14] molecules within the S_C^* phase. As a first step to achieve this goal, we have carried out the synthesis, structural characterization, and a detailed study of mesogenic and ferroelectric properties of three series of salicylideneaniline compounds. Each series consists of the ligand and three derived complexes with

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⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1996.
(1) Giroud-Godquin, A. M.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1191,** *30,* 375.
(2) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992,** *117,* 215.
(3) Bruce, D. W. *Inorg. Mater.* **1992,** 407.
(4) Hudson, S. A.; Maitlis, P. M. *Chem. Rev.* **1993,** *93,* 861.
(5) Polishchuk, A. P.; Timofeeva, T. V. *Russ. Chem. Rev.* **1993,** *62,* 291.
(6) Serrano, J. L., Ed. *Metallomesogens. Synthesis, Properties, and Applications*; VCH: Weinheim, 1996.
(7) (a) Walba, D. M. In *Advances in the Synthesis and Reactivity of Solids*; JAI Press, Ltd.: London, 1991; Vol. 1, p 173. (b) Pikin, S. A.; Osipov, M. A. In *Ferroelectric Liquid Crystals. Principles, Properties and Applications*; Gordon and Breach: Philadelphia, 1991; p 249. (c) Photinos, D. J.; Samulski, E. T. *Science* **1995,** *270,* 783.

(8) (a) Marcos, M.; Serrano, J. L.; Sierra, T.; Giménez, M. J. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1471. (b) Marcos, M.; Serrano, J. L.; Sierra, T.; Giménez, M. J. *Chem. Mater.* **1993,** *5,* 1332. (c) Athanassopoulou, M. A.; Hiller, S.; Beresnev, L. A.; Galyametdinov, Y. G.; Schweissguth, M.; Haase, W. *15th International Liquid Crystal Conference*, 1994, Budapest, Hungary. (d) Ghedini, M.; Pucci, D.; Scaramuzza, N.; Komitov, L.; Lagerwall, S. T. *Adv. Mater.* **1995,** *7,* 659.
(9) Espinet, P.; Etxebarría, J.; Marcos, M.; Pérez, J.; Remón, A.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1065.
(10) Baena, M. J.; Barberá, J.; Espinet, P.; Ezcurra, A.; Ros, M. B.; Serrano, J. L. *J. Am. Chem. Soc.* **1994,** *116,* 1899.
(11) (a) Baena, M. J.; Espinet, P.; Ros, M. B.; Serrano, J. L.; Ezcurra, A. *Angew. Chem., Int. Ed. Eng.* **1993,** *32,* 1203. (b) Thompson, N.; Serrano, J. L.; Baena, M. J.; Espinet, P. *Chemistry. A European Journal* **1996,** *2,* 214.
(12) Ciparrone, G.; Versace, C.; Duca, D.; Pucci, D.; Ghedini, M.; Umeton, C. *Mol. Cryst. Liq. Cryst.* **1992,** *212,* 217.
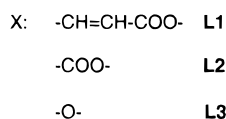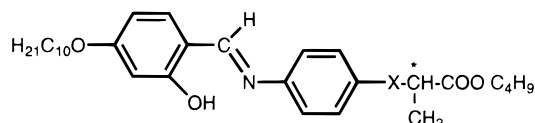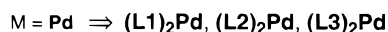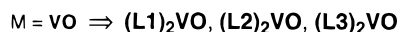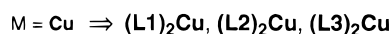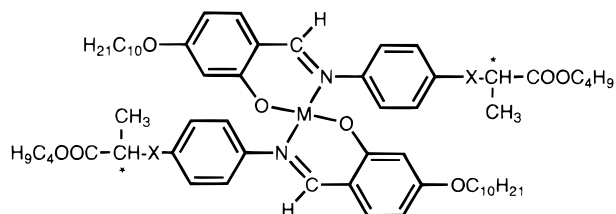(13) (a) Espinet, P.; Etxebarría, J.; Marcos, M.; Pérez-Jubindo, M. A.; Ros, M. B.; Serrano, J. L. *Mater. Res. Soc. Symp. Proc.* **1995,** *392,* 123. (b) Espinet, P.; Etxebarría, J.; Folcia, C. L.; Ortega, J.; Ros, M. B.; Serrano, J. L. *Adv. Mater.*, in press.
(14) Demus, D. *Liq. Cryst.* **1989,** *5,* 75.

Table 1. Ferroelectric Properties [Ps_{max}, $Ps(-10\ °C)$, $\tau(-10\ °C)$ and $\gamma(-10\ °C)$] of Compounds Maximum Ps Values Were Adequately Measured[a]

compound	x	Ps_{max} (nC/cm²)	$Ps(-10\ °C)$ (nC/cm²)	$\tau(-10\ °C)$ (ms V/μm)	$\gamma(-10\ °C)$ (Pa s)
L1	−CH=CH−COO−	57	41	1.1	0.25
(L1)₂Cu	−CH=CH−COO−	50 (90 °C)	38	8.5	1.87
(L1)₂VO	−CH=CH−COO−	30 (111 °C)	29	18.4	3.01
(L1)₂Pd	−CH=CH−COO−	55	40	1.9	0.44
(L2)₂Cu	−COO−		(−2 °C) 80	(−2 °C) 91.2	(−2 °C) 17.11
(L2)₂VO	−COO−		(−7 °C) 36	(−7 °C) 37.7	(−7 °C) 7.82
(L2)₂Pd	−COO−	90 (89 °C)	72	3.5	1.46
			(−7 °C) 64		
			(−2 °C) 40		

[a] At lower temperatures, viscosity was too high to obtain a good value of Ps.

Chart 1

Ligands

X: -CH=CH-COO-   **L1**

       -COO-   **L2**

       -O-   **L3**

Complexes

M = **Cu** ⇒ **(L1)₂Cu, (L2)₂Cu, (L3)₂Cu**

M = **VO** ⇒ **(L1)₂VO, (L2)₂VO, (L3)₂VO**

M = **Pd** ⇒ **(L1)₂Pd, (L2)₂Pd, (L3)₂Pd**

copper(II), vanadium(IV), and palladium(II) as metal centers (see Chart 1). Some of these compounds have already been studied.[8a,b] However, to make our investigations most rigorous and our conclusions reliable, we have prepared fresh samples of all of them, and we have evaluated their mesogenic and ferroelectric properties under the same conditions. Since not all the complexes show the S_C^* phase, binary mixtures of all the compounds have been prepared and evaluated to allow a comparative study of all the structures.

All experimental results together with the knowledge of the structure of these molecules will enable us to elucidate the type of packing arrangement of these molecules within the S_C^* phase which allows the alignment of net molecular dipoles along the polar axis of the S_C^* phase giving rise to measurable spontaneous polarization values. Supporting our conclusions, studies based on dielectric spectroscopy are in progress and will be published elsewhere.[15]

(15) de Daran, F.; Merino, S.; de la Fuente, M. R.; Pérez-Jubindo, M. A.; Iglesias, R.; Marcos, M. *Adv. Mater.*, in press.

Results and Discussion

Mesomorphic Behavior. Once the complexes melt from the crystal obtained from the synthetic process (see Experimental Section) no crystallization but solidification into a glassy state is observed for most cases (except (L1)₂Pd). For this reason, only transition temperatures corresponding to the second heating and cooling scans, being these reproducible in subsequent heating−cooling cycles, are represented in Table 1. This behavior, which is rarely found in low molecular weight organic LCs, turns out to be quite usual in metal-containing LCs.[6] As a consequence, the complexes, except for (L3)₂Cu which is not mesogenic, retain the structure of the S_C^* phase in the glass. In our case, this is advantageous as the polar order of the S_C^* phase can be fixed together with the nonmobility of the molecules, and consequently some properties such as second-order nonlinear optical phenomena are new possibilities for these glassy materials. Three of the complexes, i.e., (L1)₂VO, (L2)₂Pd, and (L3)₂Pd, undergo a cold crystallization on heating the S_C^* phase obtained from the glass; this phenomenon makes the ferroelectric phase monotropic for both palladium compounds.

A general lowering of transition temperatures is observed on going from the [X = −CH=CH−COO−] series to the [X = −COO−] and [X = −O−] ones. It is also worth noting the effectiveness of the complexation on the appearance of mesomorphic properties. This phenomenon is more pronounced for the [X = −COO−] and [X = −O−] series whose ligands are not mesogenic. The formation of the dimer through chelation to a metal overcomes the weak tendency of the metal-free Schiff base to interact laterally and promotes liquid-crystalline behavior.

The [X = −CH=CH−COO−] series shows a continuous increase in the S_C^*−S_A transition temperatures and clearing points on passing from the metal-free compound to the three different metal complexes following the sequence Cu < VO < Pd. S_A and S_C^* phases appear for the four compounds in the series, with a widening of mesomorphic ranges being noticeable upon formation of the dimer through metal complexation. Along with the decrease in transition temperatures, a weakening of the mesogenic character is observed for compounds of the [X = −COO−] and [X = −O−] series. Steric factors such as the closeness of the stereogenic center to the rigid core, and electronic factors related to the decrease in the anisotropy of the polarizability, making intermolecular interactions within the solid and the mesophase difficult, can account for both phenomena. Indeed, the ligand corresponding to the [X = −COO−]

series does not show mesomorphic behavior. All three complexes (i.e., (L2)₂Cu, (L2)₂VO, and (L2)₂Pd) are mesogenic. The S$_C$* phase is common to all of them. The presence of the carboxylato linkage group seems to favor the formation of the chiral nematic phase for the (L2)₂Cu and (L2)₂Pd complexes which is, otherwise, unusual for 4-alkoxysalicylideneaniline complexes. However, an oxovanadium group with a dipole moment perpendicular to the molecular plane might be responsible for the preference of the orthogonal smectic phase over a nematic one for the (L2)₂VO complex. When the sterogenic center is close to the rigid mesogenic core as for the [X = −O−] series, the mesomorphic properties degrade. Neither the ligand nor the copper complex [(L3)₂Cu] display mesophases. Only the oxovanadium [(L3)₂VO] and palladium [(L3)₂Pd] derivatives are mesogenic. A S$_C$* phase appears for both of them at very low temperatures, in addition to a monotropic S$_A$ phase for the palladium complex.

Ferroelectric Properties. *Pure Compounds.* The ferroelectric properties of all the four compounds from the [X = −CH=CH−COO−] series and the three complexes from the [X = −COO−] series that show the ferroelectric S$_C$* phase have been evaluated in their pure states. The high viscosities of complexes (L3)₂VO and (L3)₂Pd made their study impossible. The results are gathered in Table 1. All three magnitudes (Ps, spontaneous polarization; τ, response time; γ, rotational viscosity) were determined simultaneously using 4 μm ITO-coated cells. Electric fields and frequencies had to be adjusted for every material due to their different viscosities, and in all cases, at certain low temperatures, samples became so viscous that a good value for Ps$_{max}$ could not be determined. For this reason the maximum Ps data obtained for each complex are gathered in Table 1 together with the temperature at which it was evaluated. For the organic ligand L1, the usual settings (30 Vpp and 50 Hz) were used. However, either high-field amplitudes or low frequencies, or both, had to be employed for the complexes. Frequencies lower than 30 Hz were used in general. The most viscous complex (L2)₂Cu had to be evaluated at an extremely low frequency of 2 Hz as high electric fields could not be used due to the risk of decomposition. For both oxovanadium complexes [(L1)₂VO and (L2)₂VO], fields as high as 100 and 80 Vpp had to be employed. The dependence of the Ps values on temperature is plotted in Figure 2.

As the stereogenic center approaches the rigid part of the molecule, a strong increase in Ps values for the complexes of the [X = −COO−] series is observed. This phenomenon occurs together with a worsening in mesomorphic properties as discussed previously.

Within the [X = −CH=CH−COO−] series, the lowest Ps value corresponds to the oxovanadium complex [(L1)₂VO] whereas similar values were measured for the ligand (L1), copper [(L1)₂Cu], and palladium [(L1)₂Pd] complexes. A difference of 10 nC/cm² is observed 10 °C below the S$_A$−S$_C$* transition for the oxovanadium complex. For the [X = −COO−] series, the oxovanadium complex shows, again, the lowest Ps value if we compare data corresponding to 2 or 7 °C below the S$_A$−S$_C$* transition.

With regard to their responses in an ac electric field, all the complexes show switching times in the millisecond range, comparable to some polymeric ferroelec-
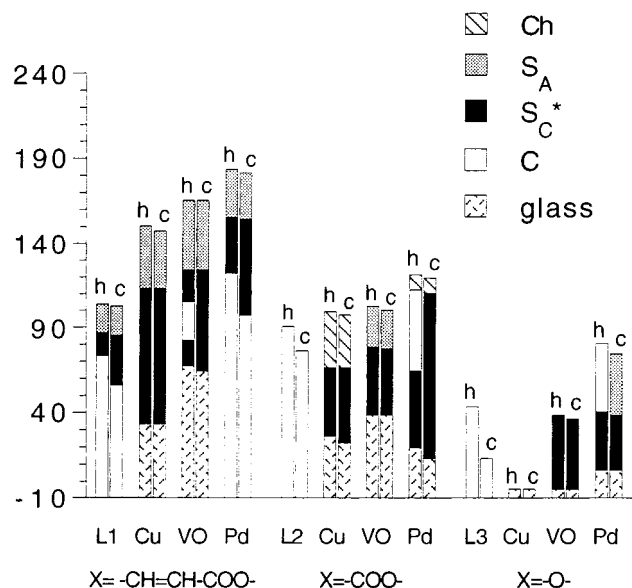

Figure 1. Mesomorphic behavior of the three series of compounds. Transition temperatures correspond to the second heating (h) and cooling (c) DSC scans.
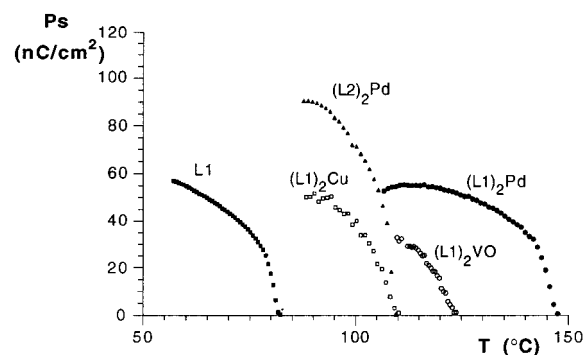

Figure 2. Plot of the Ps values of the complexes with wide S$_C$* range vs temperature.

tric liquid-crystalline materials.[16] As was expected, the longest switching times correspond to the more viscous complexes (L1)₂VO, (L2)₂Cu, and (L2)₂VO.

As was discussed previously in the Introduction, little work has been carried out on the evaluation of the ferroelectric behavior of chiral metallomesogens. Furthermore, no detailed study has been carried out on the origin of the spontaneous polarization in these lateral−lateral fused twin molecules. In an attempt to establish the origin of the polar order of these materials, it is essential to be aware of two main characteristics inherent in their molecular structure. Firstly, the structure deviates considerably form the classical rodlike shape.[14] Indeed, the molecular aspect ratio (L/d) is rather smaller in these molecules than in corresponding rodlike systems, and three main axes can be defined; a longitudinal axis (a) and two transverse axes (b and c). Axes a and b are both contained in the plane of coordination of the metal and therefore $a > b \gg c$ (Figure 3). Second, it is necessary to take into account the C_2 symmetry of these molecules. To arrive at the origin of this molecule's space group, we must go back to the synthetic step in which the complex is formed. During the chelation process, two salicylideneaniline ligands must face each

(16) Poths, H.; Schönfeld, A.; Zentel, R.; Kremer, F.; Siemensmeyer, K. *Adv. Mater.* **1992**, *4*, 351.
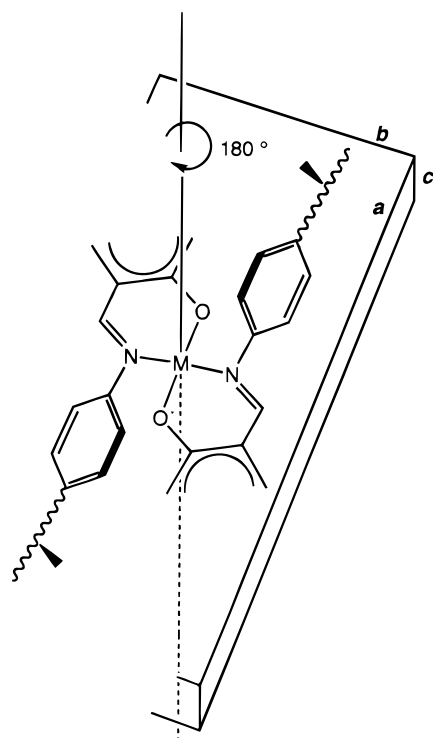
Figure 3. Schematic representation of the C_2 symmetry of the square-planar salicylideneaniline metal complexes.

other in such a way that all four chelating heteroatoms together with the metal are in the same plane as represented in Figure 3. Thus to achieve the correct disposition, one of the ligands must be rotated by 180° with respect to the other ligand. As a result of this, a C_2 symmetry axis perpendicular to the plane that contains the metal and the coordination atoms is the only symmetry element of the molecule provided that one stereogenic center is present in one of the tails of each ligand. Thus, on average, a net dipole moment for these molecules can only be found parallel to their C_2 axis.

If the first consideration is taken into account, two possibilities exist for the disposition of the molecular tilt of these molecules within the S_C^* phase. The molecules could be tilted to one side (i.e., axes a and c are contained within the tilting plane) or tilted to one edge (i.e., axes a and b are contained within the tilting plane). Considering the bulk material, if Ps values ranging from 30 to 90 nC/cm² have been measured, it seems plausible that the net molecular dipole must principally lie with the polar axis of the ferroelectric phase. Consequently, both the molecular C_2 axis and the S_C^* phase C_2 axis (namely, the polar axis) must be coincident. In this situation the plane of inclination is that containing the a and b axes, and hence the molecules are tilted to one edge within the ferroelectric phase (Figure 4).

On the basis of this proposed model, it is tempting to speculate on the role of the oxovanadium group in the ferroelectric behavior of these materials. Because the vanadyl ion is lopsided, the square-pyramidal geometry of the vanadium complexes is noncentrosymmetric. This means that when the complex is obtained from achiral salicylideneaniline ligands a racemic mixture must result. However, if ligands are chiral the subsequent optically active diastereomeric mixture is ob-
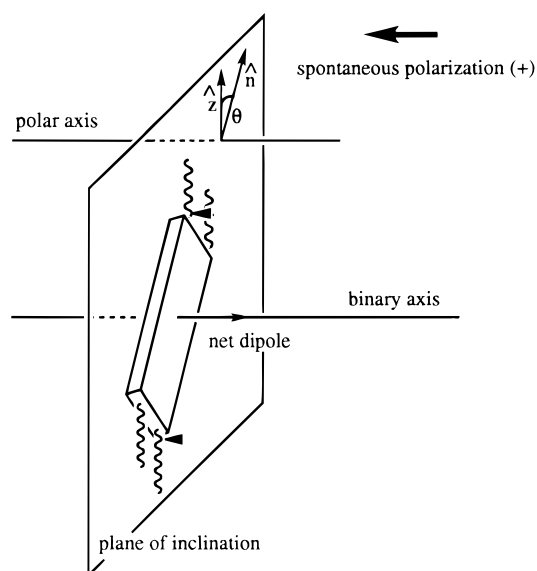

Figure 4. Model proposed for the average position of a bis-(salicylideneaniline)metal molecule within the SmC* phase, showing the origin of the spontaneous polarization in complexes. $\hat{n}$, molecular director; $\hat{z}$, layer normal; θ, tilt angle.

tained.[17] As a consequence, a preferred direction either toward or away from the molecular tilt plane of the oxovanadium group should be expected. Thus, the dipole associated with this group will contribute either negatively (as it would be in this case) or positively to the effective molecular dipole in the Ps values.

Mixtures. A study of the physical properties of binary mixtures of all the compounds synthesized has been carried out to determine their potential *as* ferroelectric dopants. A salicylideneaniline compound, namely, *N*-(4-decyloxy)-2-hydroxy-4-(pentyloxy)benzylideneaniline, C 71.2 °C S_C 115 °C N 117 °C I, was chosen as an achiral matrix. The transition temperatures together with the ferroelectric properties [Ps$_{max}$, Ps(−10 °C), τ(−10 °C), γ(−10 °C), θ(−10 °C) and Po(−10 °C)] are gathered in Table 2. Comparing the Ps values of the mixtures with the same proportion of stereogenic centers either in the free ligands or in the dimer complexes (i.e., 20 and 10 mol %, respectively), it seems that complexation does not provide a noticeable improvement in Ps$_{max}$ values.

For a more accurate discussion let us compare the reduced Ps values (Po = Ps/sin θ). The phase sequence differs for these mixtures such that the tilt angles, measured 10 °C below the transition to the S_C^* phase, are higher for L2 ligand and the compounds of the [X = −O−] series compounds than for the compounds of the [X = −CH=CH−COO−] series and complexes of the [X = −COO−] series given the first-order character of the Ch−S_C^* transition. As a general trend, the highest Po(−10 °C) values correspond to the palladium complexes of all three series, which is comparable to the presence of the free ligand in a 20 mol % proportion. We emphasize that the ferroelectric behavior of these mixtures gives rise to considerably high Ps values considering that we are dealing with small amounts of the chiral dopant. It is also worth noting the low viscosity, and hence low switching times, of these

(17) *Comprehensive Coordination Chemistry. The Synthesis, Reactions, Properties and Applications of Coordination Compounds*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 3, p 532.

Table 2. Mesomorphic and Ferroelectric Properties [Spontaneous Polarization, Ps$_{max}$, Ps(−10 °C), Response Time, τ(−10 °C), Rotational Viscosity, γ(−10 °C), Tilt Angle, θ(−10 °C) and Reduced Polarization, Po(−10 °C)] of the Binary Mixtures of All the Compounds

compound[a]	mesomorphic properties					Ps$_{max}$ (nC/cm^2)	Ps (−10 °C) (nC/cm^2)	τ(−10 °C) (μs V/μm)	γ(−10 °C) (Pa s)	θ(−10 °C)	Po(−20 °C) (nC/cm^2)
	I	Ch	S$_A$	S$_C$*	C						
L1	117			107	34	+10.2	4.4	191	0.005	23	11.3
L1[b]	117			112	33	+27.6	11.8	370	0.025	19	36.2
(Li)$_2$Cu	127			109	30	+28.8	10.4	260	0.016	23	26.6
(L1)$_2$VO	127			113	28	+22.0	9.7	276	0.015	20	28.4
(L1)$_2$Pd	131			114	34	+33.4	12.6	387	0.028	20	36.8
L2	113	108			38	+9.0	4.9	233	0.007	25	11.6
L2[b]	107	101			33	+21.2	11.6	186	0.012	27	25.6
(L2)$_2$Cu	114			107	28	+21.3	9.6	272	0.015	24	23.6
(L2)$_2$VO	114			112	31	+19.1	8.3	389	0.018	22	22.2
(L2)$_2$Pd	120	118	113		31	+23.5	11.1	307	0.020	23	28.4
L3	113	107			39	+5.8	4.0	359	0.008	29	8.3
L3[b]	101	93			38	+14.7	8.8	497	0.025	32	16.6
(L3)$_2$Cu	101	93			30	+13.6	6.4	290	0.011	26	14.6
(L3)$_2$VO	108	92			29	+15.6	8.8	351	0.018	28	18.7
(L3)$_2$Pd	109	101			37	+13.6	9.5	435	0.026	28	20.2

[a] All the binary mixtures were 10 mol % of the chiral dopant, except (b) which are 20 mol % of the ligand.

materials despite the presence of metal-containing molecules.

The previously mentioned phenomenon concerning the V=O group appears negligible in binary mixtures containing a small amount of the chiral complex (10 mol %).

Conclusions

Lateral−lateral fused twin ferroelectric metal−organic liquid crystals incorporating copper(II), vanadium-(IV), and palladium(II) atoms in their structure have been synthesized and characterized. Results reported in this paper show that wide S$_C$* ranges (together with glassy S$_C$* phases) and high Ps values can be obtained from some of these materials.

The study of the ferroelectric behavior of these complexes has led us to propose a model for the disposition of the molecules within the ferroelectric phase (S$_C$*) which accounts for the existence of nonzero Ps values. In this model the molecules are tilted to one edge in such a way that the plane of inclination of the phase is that containing the plane defined by the metal and the four chelating atoms, i.e., the two main axes of the molecules (*a* and *b*).

In addition, all the compounds have been used as dopants for binary mixtures. Evaluation of the ferroelectric properties of the mixtures has been carried out and has shown Ps values ranging from 10 to 30 nC/cm^2 and low response times.

Experimental Section

Synthesis. Even though the syntheses of some of the compounds of the present study (compounds of series [X = −CH=CH−COO−] and palladium complexes of series [X = −COO−] and [X = −O−]) have already been described,[8a,b] freshly prepared samples of all of them were used in this study. *No significant changes of transition temperatures (only 2 or 3 °C in clearing points) have been observed with regard to the old compounds.* Their analytical data are gathered in the Experimental Section.

The synthetic path used to prepare the ligands and the complexes is outlined in Scheme 1. The chiral Schiff bases were synthesized from the 4-(decyloxy)-2-hydroxybenzaldehyde and the corresponding chiral aniline. The chiral starting material was *S*-(−)-butyl lactate commercially available from Fluka in 97% enantiomeric purity.

The chiral anilines were obtained from the corresponding nitro compound using tin(II) chloride dihydrate as reducing agent following the Bellamy method.[18] To avoid some trans-esterification problems detected in the reduction process, 2-propanol was used as solvent instead of ethanol (employed in ref 8a,b).

Preparation of the Complexes. All the complexes were prepared from the corresponding metal salt (palladium(II) acetate, copper(II) acetate monohydrate, and oxovanadium-(IV) sulfate pentahydrate): an ethanolic solution containing the metal salt (1 mmol) was added to a hot ethanolic solution of the ligand (2 mmol). The solution was refluxed for 1 h and then cooled. The precipitate was filtered off and dissolved in chloroform. The complex was reprecipitated by adding ethanol.

Analytical Data of the ligand and the complexes derived from *(1-butoxycarbonyl)ethyl 4′-aminocinnamate*: **L1**. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H), 1.28 (m, 12H), 1.31 (m, 2H), 1.41 (m, 2H), 1.57 (d, J = 7.1 Hz, 3H), 1.62 (m, 2H), 1.80 (m, 2H), 4.01 (t, J = 6.6 Hz, 2H), 4.18 (t, J = 6.6 Hz, 2H), 5.22 (c, J = 7.1 Hz, 1H), 6.46 (m, 2H), 6.47 (d, J = 15.9 Hz, 1H), 7.25 (m, 3H), 7.56 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 15.9 Hz, 1H), 8.55 (s, 1H), 13.52 (s, 1H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.6, 14.0, 17.0, 18.9, 22.6, 25.9, 28.9, 29.2, 29.2, 29.5, 30.4, 31.8, 65.1, 68.2, 68.7, 101.4, 107.8, 112.8, 116.6, 121.5, 129.3, 132.2, 133.7, 144.9, 150.2, 161.9, 163.9, 163.9, 166.1, 170.9. IR (Nujol) 1750, 1716, 1633, 1162 cm^{-1}. Anal. Calcd for C$_{33}$H$_{45}$O$_6$N: C, 71.84; H, 8.22; N, 2.54. Found: C, 71.22; H, 7.97; N, 2.20.

(L1)$_2$Cu. IR (Nujol 1755, 1693, 1606, 1589, 1199 cm^{-1}. Anal. Calcd for C$_{66}$H$_{88}$N$_2$O$_{12}$Cu: C, 68.07; H, 7.56; N, 2.41. Found: C, 68.11; H, 7.62; N, 2.40.

(L1)$_2$VO. IR (Nujol) 1759, 1717, 1634, 1608, 1581, 1204, 1162, 981 cm^{-1}. Anal. Calcd for C$_{66}$H$_{88}$N$_2$O$_{13}$V: C, 67; H, 7.54; N, 2.40. Found: C, 87; H, 7.47; N, 2.43.

(L1)$_2$Pd. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.86 (t, J = 6.9 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H), 1.25 (m, 12H), 1.37 (m, 4H), 1.56 (d, J = 7.1 Hz, 3H), 1.64 (m, 4H), 3.72 (t, J = 6.3 Hz, 2H), 4.17 (t, J = 6.7 Hz, 2H), 5.21 (c, J = 7.1 Hz, 1H), 5.47 (d, J = 2.2 Hz, 1H), 6.13 (dd, J = 8.8, 2.3 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 7.01 (d, J = 8.9 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.54 (s, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 16.0 Hz, 1H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.6, 14.1, 17.1, 19.0, 22.6, 25.9, 28.8, 29.3, 29.5, 29.5, 30.5, 31.8, 65.2, 67.8, 68.7, 101.9, 107.1, 114.4, 116.7, 125.6, 128.0, 132.0, 135.6, 145.2, 151.7, 160.8, 165.5, 166.1, 166.9, 170.9. IR (Nujol) 1756, 1692, 1592, 1203 cm^{-1}. Anal. Calcd for C$_{66}$H$_{88}$O$_{12}$N$_2$Pd: C, 65.65; H, 7.29; N, 2.32. Found: C, 65.86; H, 7.34; N, 2.48.

Analytical Data of the ligand and the complexes derived from *(1-butoxycarbonyl)ethyl 4′-aminobenzoate*: **L2**. ^{1}H NMR

(18) Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, *25*, 839.

Scheme 1

DCC/PPY/THF   DCC/PPY/THF   DEAD/Ph$_3$P/THF

SnCl$_2$·2H$_2$O/^{i}PrOH   SnCl$_2$·2H$_2$O/^{i}PrOH   SnCl$_2$·2H$_2$O/^{i}PrOH

H$_{21}$C$_{10}$O—CHO   H$_{21}$C$_{10}$O—CHO   H$_{21}$C$_{10}$O—CHO

EtOH/AcOH   EtOH/AcOH   EtOH/AcOH

L1   **L2**   **L3**

L1, L2, L3 + { Cu(OAc)$_2$·H$_2$O, VOSO$_4$·5H$_2$O, Pd(OAc)$_2$ } → EtOH →
(L1)$_2$Cu, (L1)$_2$VO, (L1)$_2$Pd
(L2)$_2$Cu, (L2)$_2$VO, (L2)$_2$Pd
(L3)$_2$Cu, (L3)$_2$VO, (L3)$_2$Pd
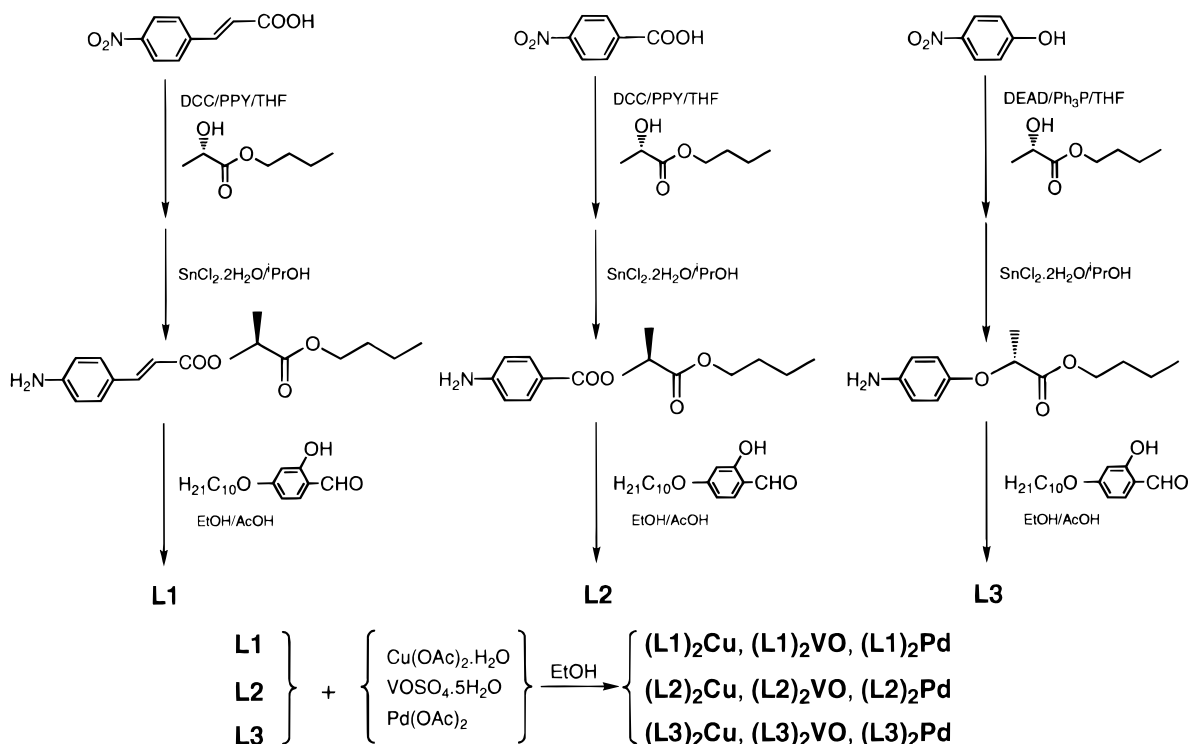
(300 MHz, CDCl$_3$) δ 0.82 (t, 3H), 0.86 (t, J = 7.3 Hz, 3H), 1.22 (m, 12H), 1.30 (m, 2H), 1.38 (m, 2H), 1.57 (m, 2H), 1.58 (d, J = 7.1 Hz, 3H), 1.74 (m, 2H), 3.94 (t, J = 6.6 Hz, 2H), 4.12 (dt, J = 1.4, 6.6 Hz, 2H), 5.26 (c, J = 7.0 Hz, 1H), 6.46 (m, 2H), 7.22 (d, J = 8.8 Hz, 1H), 7.22 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.6 Hz, 2H), 8.47 (s, 1H), 13.36 (s, 1H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.6, 14.1, 17.1, 19.0, 22.7, 26.0, 29.0, 29.3, 29.3, 29.5, 30.5, 31.9, 65.2, 68.3, 69.2, 101.5, 108.0, 112.8, 121.0, 127.1, 131.3, 133.9, 152.9, 162.9, 164.1, 164.2, 165.5, 170.9 IR (Nujol) 1750, 1727, 1628 cm^{-1}. Anal. Calcd for C$_{31}$H$_{43}$O$_6$N: C, 70.83; H, 8.24; N, 2.66. Found: C, 70.45; H, 8.11; N, 2.43.

(L2)$_2$Cu. IR (Nujol) 1754, 1716, 1608, 1585, 1198, 1103 cm^{-1}. Anal. Calcd for C$_{62}$H$_{28}$O$_{12}$N$_2$Cu: C, 66.94; H, 7.56; N, 2.52. Found: C, 67.92; H, 7.68; N, 2.57.

(L2)$_2$VO. IR (Nujol) 1750, 1727, 1601, 1196, 1114, 978 cm^{-1}. Anal. Calcd for C$_{62}$H$_{84}$O$_{13}$N$_2$V: C, 66.73; H, 7.53; N, 2.51. Found: C, 66.30; H, 6.73; N, 2.51.

(L2)$_2$Pd. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.86 (t, J = 6.8 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H), 1.25 (m, 12H), 1.26 (m, 4H), 1.62 (d, J = 7.1 Hz, 3H), 1.64 (m, 4H), 3.74 (t, J = 6.4 Hz, 2H), 4.16 (dt, J = 2.8, 6.6 Hz, 2H), 5.31 (c, J = 7.1 Hz, 1H), 5.47 (d, J = 2.2 Hz, 1H), 6.14 (dd, J = 2.4, 8.8 Hz, 1H), 7.02 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.5 (s, 1H), 8.11 (d, J = 8.4 Hz, 2H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.7, 14.1, 17.1, 19.0, 22.7, 26.0, 29.0, 29.3, 29.5, 29.6, 30.5, 31.9, 65.2, 67.8, 69.1, 102.0, 107.3, 114.4, 125.2, 127.1, 130.0, 135.7, 154.1, 160.9, 165.5, 165.7, 167.1, 170.7. IR (Nujol) 1758, 1712, 1609, 1573, 1203, 1109 cm^{-1}. Anal. Calcd for C$_{64}$H$_{84}$O$_{12}$N$_2$Pd: C, 64.45; H, 7.28; N, 2.43. Found: C, 64.56; H, 6.77; N, 2.71.

Analytical Data of the ligand and the complexes derived from *4-(1-butoxycarbonyl)ethoxyaniline*: **L3**. ^{1}H NMR (300 MHz) δ 0.91 (t, J = 6.6 Hz, 3H), 0.93 (t, J = 7.1 Hz, 3H), 1.31 (m, 14H), 1.41 (m, 2H), 1.64 (m, 2H), 1.60 (d, J = 6.8 Hz, 3H), 1.82 (m, 2H), 4.00 (t, J = 6.6 Hz, 2H), 4.20 (dt, J = 6.6, 3.1 Hz, 2H), 4.79 (c, J = 6.8 Hz, 1H), 6.52 (m, 2H), 6.93 (d, J = 8.8 Hz, 2H), 7.24 (m, 3H), 8.51 (s, 1H), 13.82 (s, 1H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.6, 14.1, 18.6, 18.9, 22.7, 26.0, 29.1, 29.3, 29.3, 29.5, 29.5, 30.5, 31.9, 65.1, 68.2, 72.9, 101.5, 107.4, 113.0, 115.8, 122.0, 133.2, 142.2, 156.3, 160.0, 163.3, 163.7, 172.2. IR (Nujol) 1731, 1623 cm^{-1}. Anal. Calcd for C$_{30}$H$_{43}$O$_5$N: C, 72.40; H, 8.71; N, 2.81. Found: C, 71.86; H, 8.29; N, 2.67.

(L3)$_2$Cu. IR (Nujol) 1738, 1613, 1503, 1185 cm^{-1}. Anal. Calcd for C$_{60}$H$_{84}$O$_{10}$N$_2$Cu: C, 68.21; H, 7.96; N, 2.65. Found: C, 67.89; H, 8.00; N, 2.52.

(L3)$_2$VO. IR (Nujol) 1747, 1612, 1585, 1194, 975 cm^{-1}. Anal. Calcd for C$_{60}$H$_{84}$O$_{11}$N$_2$V: C, 67.99; H, 7.93; N, 2.64. Found: C, 67.97; H, 7.97; N, 2.54.

(L3)$_2$Pd. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.86 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H), 1.25 (m, 14H), 1.31 (m, 2H), 1.61 (m, 2H), 1.62 (d, J = 6.8 Hz, 3H), 1.69 (m, 2H), 3.81 (dt, J = 2.3, 6.1 Hz, 2H), 4.15 (dt, J = 2.7, 6.6 Hz, 2H), 4.74 (c, J = 6.8 Hz, 1H), 5.61 (d, J = 2.2 Hz, 1H), 6.12 (dd, J = 8.7, 2.3 Hz, 1H), 6.85 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.9 Hz, 1H), 7.20 (d, J = 8.8 Hz, 2H), 7.51 (s, 1H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 13.6, 14.1, 18.6, 19.0, 22.6, 26.0, 29.1, 29.3, 29.4, 29.5, 30.5, 31.8, 65.1, 67.8, 72.8, 102.1, 106.4, 114.4, 114.4, 125.8, 135.3, 143.7, 155.7, 161.0, 165.1, 166.8, 172.0. IR (Nujol) 1724, 1609, 1583, 1200 cm^{-1}. Anal. Calcd for C$_{60}$H$_{84}$O$_{10}$N$_2$Pd: C, 65.54; H, 7.65; N, 2.55. Found: C, 65.66; H, 6.75; N, 2.25.

Mesophase Characterization. The mesophases were identified according to their textures which were observed by optical microscopy.

The cholesteric phase (Ch) showed by complexes was identified by the typical focal-conic texture (and oily-streak texture was observed when the sample was manipulated). On cooling the Ch focal conic phase transforms in a chiral smectic C* phase (S$_C$*) which exhibit broken fan-shaped texture. Dechiralization lines were observed. Smectic A mesophase (S$_A$) was clearly identified by its fan-shaped texture, which appears when the sample is cooled from the isotropic liquid and the phase becomes homeotropic when the sample is submitted to mechanical stress. The S$_C$* phase showed broken fan-shaped texture on cooling the fan-shaped S$_A$ phase. Dechiralization lines were observed in the ferroelectric mesophase. A pseudohomeotropic texture can be obtained on applying mechanical stress to the sample. The textures observed for ligands and complexes are optically similar; however, those showed by the complexes were more viscous than the corresponding mesophases exhibited by the ligands.

Techniques. Microanalysis was performed with a Perkin-Elmer 240 B microanalyzer. Infrared spectra for all the complexes were obtained by using a Perkin-Elmer 1600 (FTIR) spectrophotometer in the 400−4000 cm^{-1} spectral range. ^{1}H NMR spectra were recorded on a Varian Unity 300-MHz spectrometer in deuteriochloroform solutions.

The textures of the mesophases were studied with an optical microscope (Nikon) with crossed polarizers and connected to a Mettler FP82 hot stage and a Mettler central processor.

Measurements of the transition temperatures were made using a TA2910 differential calorimeter with a heating or cooling rate of 10 °C/min. The apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g).

The spontaneous polarization and the response time were obtained simultaneously using the triangular wave form method.[19] In the experimental setup the triangular wave voltage was supplied by a HP3245A function generator. The current—voltage cycles were recorded by a Digital Acquisition System Tech ADC488/16A. All the equipment was interfaced to a microcomputer. The cells used for the measurements are coated with polyimide and with indium tin oxide (ITO) electrodes. *Experimental details of the ferroelectric measurements:* The values of the spontaneous polarization (Ps) were determined by integrating the displacement current peak which appears due to the reversal of the Ps, in response to an applied triangular voltage.[19b] The maximum amplitudes and frequencies in the pure compounds have been discussed previously. A complete alignment of the sample could not be obtained in every case. For the mixtures, the maximum amplitude, frequency and cell thickness were 20 Vpp, 50 Hz,

and 4 μm, respectively. Good alignment was obtained by slow cooling (0.5 or 1 °C/min) of the filled cell from the isotropic liquid.

The rotational viscosity, γ_c, was obtained from the parameters of the current peak calculated from the Ps measurement. Using both values the response time was calculated using the equation $\tau = 1.75 \; \gamma_c/\text{Ps E}$.[20]

The sign of Ps was determined by the field reversal method by optical observation of the extinction direction by rotating the stage according to Lagerwall's convention.[21]

The tilt angles were measured as a function of temperature between crossed Nicol polarizers and were recorded as half the rotation angle between the two extinction positions associated with oppositely directed polarization. The extinction positions were determined using a photomultiplier tube, the applied electrical dc field was 5 V/μm.

(19) (a) Miyasato, K.; Abe, S.; Takezoe, H.; Fukuda, A.; Kuze, E. *Jpn. J. Appl. Phys.* **1983**, *22*, L661. (b) De la Fuente, M. R.; Ezcurra, A.; Pérez-Jubindo, M. A.; Zubía, J. *Liq. Cryst.* **1990**, *7*, 51.

(20) Kimura, S.; Nishiyama, S.; Ouchi, Y.; Takezoe, H.; Fukuda, A. *Jpn. J. Appl. Phys.* **1987**, *26*, L255.
(21) Lagerwall, S. T.; Dahl, I. *Mol. Cryst. Liq. Cryst.* **1984**, *114*, 151.