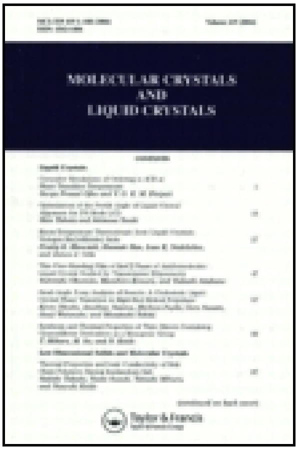

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Organometallic Ferroelectric Liquid Crystals. II. Syntheses, Characterization and Mesogenic Properties of Amino-Acid Chelated-Palladated Azine, Azo and Imine Mononuclear Complexes

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Organometallic Ferroelectric Liquid Crystals. II. Syntheses, Characterization and Mesogenic Properties of Amino-Acid Chelated-Palladated Azine, Azo and Imine Mononuclear Complexes

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Six mononuclear ortho-palladated complexes containing amino-acid chelate ligands and azine or azo, imine ligands have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR and ^{13}C NMR. Their thermotropic behaviors and mesogenic properties were studied. The relation between mesogenic properties and molecular structures of complexes were also discussed. As a result, three novel organometallic ferroelectric liquid crystals were found.

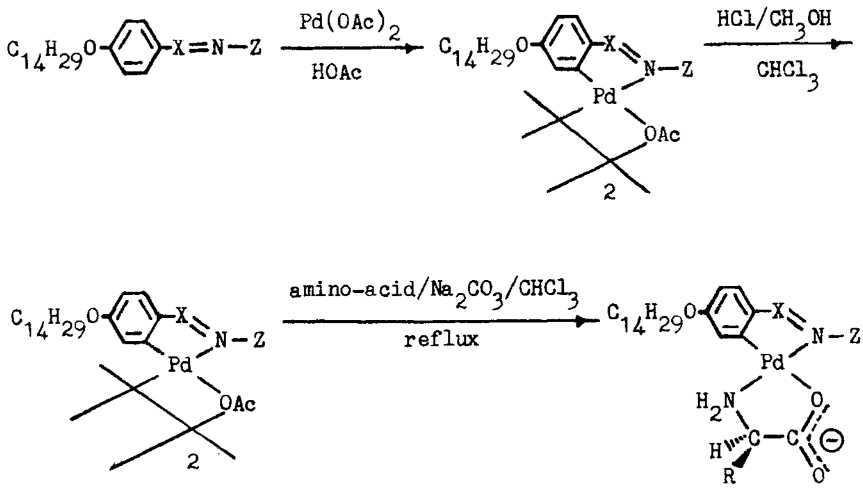
Keywords: organometallic complexes, ferroelectric liquid crystal, syntheses

Ferroelectric liquid crystals (FLCs) are nowadays a major area of interest in mesogenic materials, both in basic and applied research.[1] In 1989, P. Espinet *et al.* reported the first organometallic ferroelectric liquid crystal (OMFLC) which was a binuclear ortho-palladated complex derived from azine and $CH_3C^*HClCOO^-$ as bridged ligand.[2] Their work marked the beginning of the effort to seek advanced FLC materials in organometallics. To reach this goal, it is naturally of great importance to design and synthesize varieties of new types of organometallic ferroelectric liquid crystals to fit different practical aspects. We report here the syntheses and mesomorphism of novel *l*-aminoacid chelate ortho-palladated mononuclear complexes derived from azine, azo and imine.

EXPERIMENTAL SECTION

General Procedures: The ^{1}H NMR spectra were recorded on 300 MHz Brucker AC-P300 spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. The IR spectra (nujol) were performed on NICOLET FT-MX-1E spectrometer. Elemental analyses were obtained from CARLO ERAB-1106 microanalyzer. The thermotropic behaviors were determined by DSC using Perkin-Elmer 7 series analysis system. The textures of mesophases were observed under ORTHLUX-IIPOL-BK polarizing microscope.

The azine, azo and imine long-chain ligands were synthesized by similar methods previously described.[3] The aceto-bridged binuclear complexes were obtained through ortho-palladated reaction of above ligand with palladium (II) acetate.[4] The corresponding chloro-bridged complexes were prepared by ligand exchange reaction. Finally, using *l*-amino acids to split the chloro-bridges, the mononuclear complexes were formed. The synthetical route is shown as follows:



ID: X=CH, $Z=C_{14}H_{29}OC_6H_4CHN$, $R=CH_3$;
IID: X=N, $Z=C_{14}H_{29}OC_6H_4$, $R=CH_3$;
IIID: X=CH, $Z=C_{14}H_{29}OC_6H_4$, $R=CH_3$;
IIIE: X=CH, $Z=C_{14}H_{29}OC_6H_4$, $R=C_6H_5CH_2$;
IIIF: X=CH, $Z=C_{14}H_{29}OC_6H_4$, $R=(CH_3)_2CH$;
IIIG: X=CH, $Z=C_{14}H_{29}OC_6H_4$, $R=(CH_3)_2CHCH_2$;

SCHEME 1 Syntheses of organometallic liquid crystals

Aceto-bridge ortho-palladated dimers: A mixture of Pd $(OAc)_2$ and azine (azo, or imine) ligand (Pd/ligand = 1:1) in acetic acid was refluxed until the appearance of palladium black, cooled, filtered and washed the residue with acetic acid. The crude product was soluted in $CHCl_3$ and filtered to remove non-soluble impurities, the filtrate was concentrated and poured into alcohol to separate out the product, which was filtered off, washed with alcohol and dried.

Chloro-bridged ortho-palladated dimers: to the solution of aceto-bridged dimers in $CHCl_3$ was dropwise added 0.7026 $mol \cdot L^{-1}$ methanolic solution of HCl (Cl/Pd = 1:1), the mixture was stirred for 1 h, concentrated, precipitated the product by addition of acetone, filtered off, washed with acetone and dried in vacuo, and the products are pure enough for further reaction.

ID, IID and IIID-G: Typically, to the suspension of 1.1 g (6.76×10^{-4} mol)

TABLE I

Elemental analyses data of organometallic complexes

Compd.	C%		H%		N%		Color
	Found	Cald.	Found	Cald.	Found	Cald.	
ID	65.03	65.4	9.06	8.90	4.52	5.08	yellow
IID	63.99	64.54	9.29	9.19	4.56	5.25	red
IIID	64.19	64.65	8.91	8.80	1.69	1.73	yellow
IIIE	67.68	67.11	9.28	8.80	2.62	3.12	yellow
IIIF	66.85	66.77	9.58	9.26	3.32	3.38	yellow
IIIG	66.79	67.08	9.80	9.34	3.04	3.32	yellow

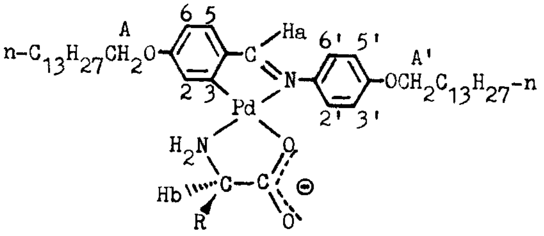


TABLE II

^1H NMR data of organometallic complexes

Compd.	.^1H Chemical Shift, ppm									J,Hz		
	H_5	H_6	H_3	$H_{2',6'}$	$H_{3',5'}$	H_a	H_b	A	A′	H_5–H_6	H_6–H_2	$H_{2'}$–$H_{3'}$
IIID	7.25 (d)	6.54 (dd)	6.26 (d)	7.33 (d)	6.66 (d)	7.84 (s)	3.71 (m)	3.93 (t)	3.81 (t)	9.0	3.0	9.0
IIIE	7.27 (d)	6.59 (dd)	5.94 (d)	7.34 (d)	6.53 (d)	7.84 (s)	4.75 (m)	3.77 (t)	3.73 (t)	9.0	3.0	9.0
IIIF	7.27 (d)	6.58 (dd)	6.23 (d)	7.35 (d)	6.60 (d)	7.83 (s)	3.47 (m)	3.92 (t)	3.78 (t)	9.0	3.0	9.0

[Pd (n—$C_{14}H_{29}OC_6H_3CHNC_6H_4OC_{14}H_{29}$—$n$)($\mu$ − Cl)]$_2$ in 40 ml acetone, 0.263 g (6.76×10^{-4} mol) $AgBF_4$ was added, the mixture was refluxed in dark for 12 hrs, filtered the white precipitate off. To the filtrate, 0.24 g *l*-alanine and 0.36 g Na_2CO_3 was added. The solution was refluxed for 20 hrs, filtered, upon cooling yellow crystal was separated out from the filtrate, filtered, washed the residue with acetone several times, after recrystallization from acetone 0.84 g IIID was obtained, similarly, ID, IID, and IIIE-G were synthesized.

The elemental analyses data of these organometallic complexes are summarized in Table I.

RESULTS AND DISCUSSION

Characterization of the complexes: NMR and IR data of title complexes were shown in Tables II, III and IV, respectively.

TABLE III

^{13}C NMR data of organometallic complexes

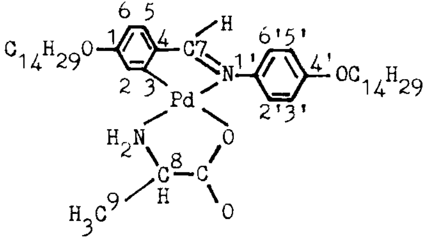
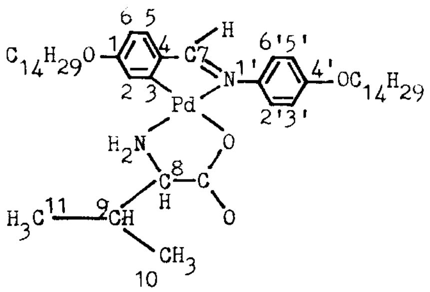
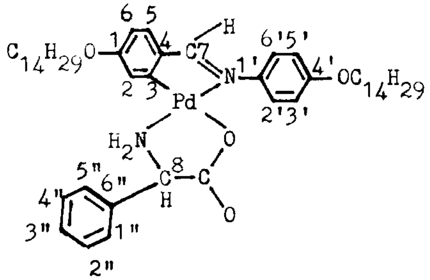
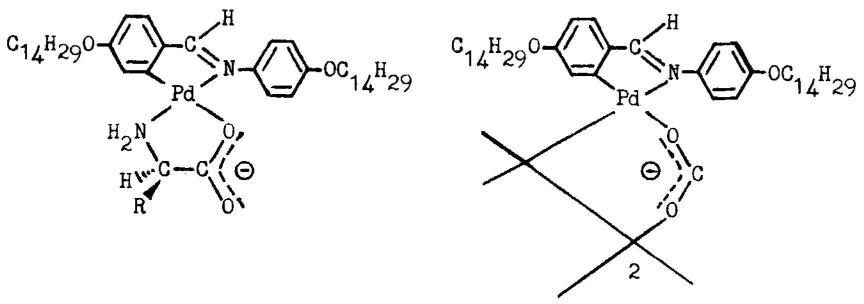
Complexes	**^{13}C NMR Chemical Shift, ppm**
	$C_9(CH_3)$ 26.01; $C_8(C^*H)$ 65.24; $C_{3'},C_{5'}$ 114.75; $C_{2'},C_6$ 103.77; C_6 109.31; C_2 119.54; C_5 130.17; C_1 139.80; $C_{4'}$ 141.10; $C_{1'}$ 157.43; C_4 158.82; C_3 160.22; COO^- 180.23; C_7 170.39;
	$C_{10}(CH_3)$ 18.26; $C_{11}(CH_3)$ 19.75; $C_9(CH)$ 31.93; $C_8(C^*H)$ 65.25; $C_{3'},C_{5'}$ 114.47; $C_{2'},C_{6'}$ 123.69; C_6 104.65; C_2 117.87; C_5 130.05; C_1 139.82; $C_{4'}$ 140.83; $C_{1'}$ 156.86; C_4 158.67; C_3 159.91; $C_7(CH=N)$ 169.40; COO^- 180.04.
	C_8 61.28; C_6 111.05; $C_{3'},C_{5'}$ 114.39; C_2 117.11; $C_{2'},C_{6'}$ 123.64; C_5 127.46; $C_{2''},C_{6''}$ 129.21; $C_{3''},C_{5''}$ 129.53; $C_{4''}$ 129.89; $C_{1''}$ 136.84; C_1 139.55; $C_{4'}$ 140.72; $C_{1'}$ 156.94; C_4 158.63; C_3 159.90; $C_7(CH=N)$ 169.33; COO^- 180.24.

TABLE IV

IR data of organometallic complexes

Compd.	ID	IID	IIID	IIIE	IIIF	IIIG
ν_{N-H},cm^{-1}	3200 3100	3220 3060	3200 3100	3200 3100	3200 3100	3200 3100

ID, IID, and IIID-G may exist in two forms: binuclear or mononuclear. For example, the two possible structures for IIID are shown in Scheme 2. It is difficult to distinguish them by elemental analysis, ^{1}H-NMR, or ^{13}C-NMR. However, some important structural information was found in the IR spectra (Table IV): ν_{N-H} absorption bands of the complexes are reduced from 3500–3300 cm^{-1} (ν_{N-H} absorbance of free NH_2) to 3200–3100 cm^{-1}. Therefore, we predicted that ID, IID,



A: Mononuclear Complex B: Binuclear Complex

SCHEME 2 Two possible structures of IIID

TABLE V

DSC results of the complexes

Compd.	Phase transition	Temperature T(°C)	Enthalpy (KJ / mol)
ID	C—Sc^*	99.3	11.69
	Sc^*—I	135.9	7.27
IID	C—Sc^*	92.3	19.24
	Sc^*—I	104.0	2.54
IIID	C—Sc^*	81.5	46.48
	Sc^*—I	174.0	19.12
IIIE	C—S_A	64.2	24.81
	S_A—I	211.9 (dec.)	16.29
IIIF	C—S_A	100.7	38.34
	S_A—I	136.3	11.59
IIIG	C—S_A	75.2	20.02
	S_A—I	120.2	1.95

and IIID-G exist in the form of mononuclear complexes, the amino acid anion were chelated with Pd^{2+}.

Mesogenic properties: The thermotropic data for the complexes are summarized in Table V.

Owing to the long terminal chains ($n = 14$), the complexes show smectic phases only. The effects of bridging groups of long chain ligands and amino acids with different R on the phase transition temperatures of the complexes are shown in Figures 1 and 2, respectively.

As shown in Figure 1, the clearing points of ID and IIID are higher than IID, and the mesogenic ranges of ID and IIID are wider than IID. The reason may be that IID contains azo which has the smallest molecular anisotropy of polarizability among the three long chain ligands. It is observed from Figure 2 that the clearing

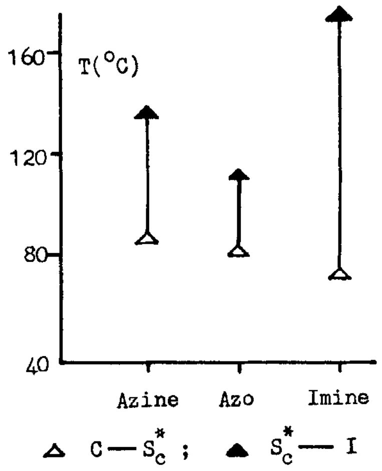


FIGURE 1 Effect of central bridged groups on the transition temperature.

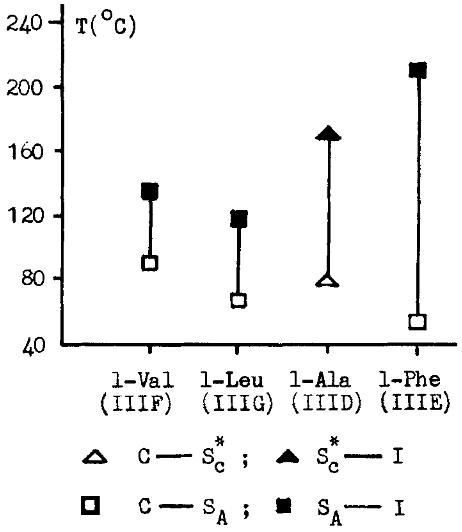
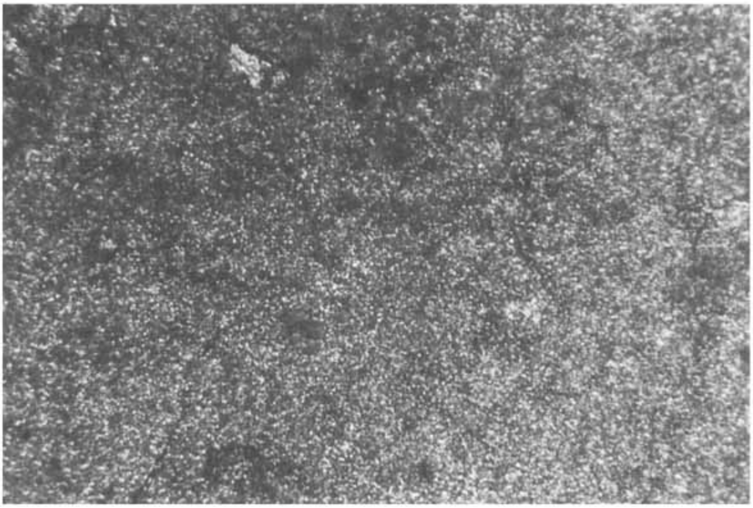
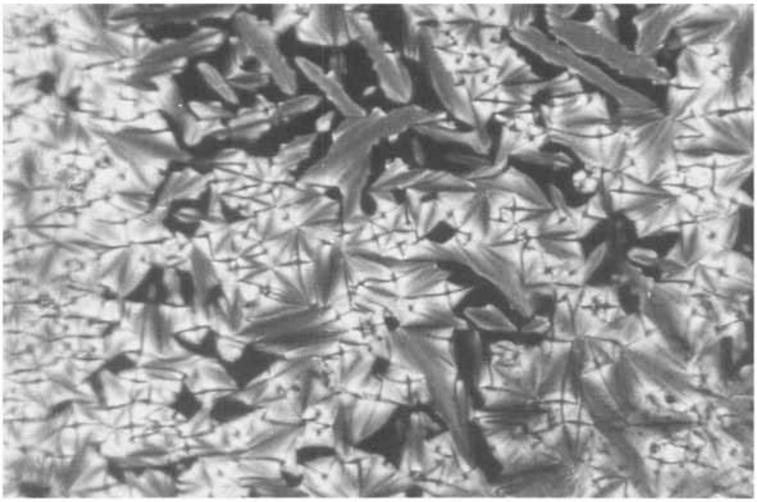


FIGURE 2 Effect of amino-acid group on the mesogenic properties.

point temperature of IIID-G reduced in the order of Phe > Ala > Val > Leu. Among the four complexes, IIIE possesses the widest mesogenic range, this is due to the aromatic ring of Phe which increases the molecular anisotropy and intermolecular action. By contrast, when the *R* groups of amino acids change from CH_3, $(CH_3)_2CH$ to $(CH_3)_2CHCH_2$, the width of the central part of the molecule increases consequently; this is disadvantage to the arrangement of the molecules and the formation of mesophases, as a result, the clearing point and mesogenic range of the remaining complexes decrease: ID, IID, and IIID show chiral smectic



(a) ID



(b) IIIE

FIGURE 3 (a) ID: T = 110°C: chiral smectic C phase, (b) IIIE: T = 160°C; smectic A phase. Observed during a cooling run. Crossed polarizers, 200×.

C phases, the others exhibit smectic A phases. Two typical textures of the complexes are shown in Figure 3.

Acknowledgment

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