to the two isomers of the DACH ligand). The low solubility of these compounds made further separations and purifications extremely difficult.

Conclusions

In this study we have shown that the initial product formed upon reaction between diaminediaquaplatinum(II) complexes and aminomalonate is the O,O chelate $[PtAm_2(amal\text{-}O,O)]^+$. As the reaction progresses, the kinetic product isomerizes to give the thermodynamically stable $PtAm_2(amal\text{-}N,O)$. The inertness of the Pt–N bond is responsible for the formation and for the stability of the thermodynamic products.

Registry No. **1**, 20115-64-4; **3**, 129365-85-1; **4**, 129365-87-3; **5**, 129965-00-0; **6**, 129965-01-1; **7**, 129964-99-4; **8**, 129965-02-2; **9**, 129965-03-3; **10**, 129965-04-4; **12**, 129965-05-5; **13**, 129965-06-6; **14**, 121858-78-4; **15** (O,O isomer), 125445-71-8; **15** (N,O isomer), 129965-08-8; **16** (O,O isomer), 121857-22-5; **16** (N,O isomer), 129965-09-9; **17** (O,O isomer), 121864-98-0; **17** (N,O isomer), 129965-10-2; **18**, 121857-31-6; **19**, 129965-07-7; ^{195}Pt, 14191-88-9; $Pt(NH_3)_2(SO_4)(H_2O)$, 86493-49-4.

Notes

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Mesomorphic Properties of Metallonematogens, Bis[4-((4-alkoxybenzoyl)oxy)-*N*-(*n*-alkyl)salicylaldiminato]copper(II) Complexes

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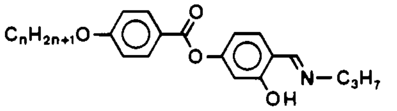
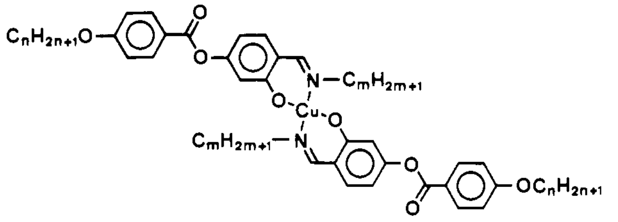
Introduction

We have previously reported a synthetic and structural study on a homologous series of liquid crystalline copper(II) complexes of *N*-salicylideneaniline derivatives, which exhibit both nematic and smectic C phases.[1] As an extension of this work, we have replaced the *N*-phenyl moieties by *N*-alkyl groups in the hope of obtaining the nematic phase over a manageable temperature range and prepared homologous series of 3-hydroxy-4-((propylimino)methyl)phenyl 4-alkoxybenzoates (LA) and copper(II) complexes having various terminal and lateral alkyl chains, bis[4-((4-alkoxybenzoyl)oxy)-*N*-(*n*-propyl)salicylaldiminato]copper(II) ($Cu(LA)_2$) and bis[4-((4-(hexyloxy)benzoyl)oxy)-*N*-(*n*-alkyl)salicylaldiminato]copper(II) ($Cu(LB)_2$), respectively. The terms terminal and lateral are based on a view that the bis(4-(benzoyloxy)salicylaldiminato)copper core constitutes a rigid core part of this mesogenic molecule. All of the compounds proved to show the nematic phases.



LA; n=4-12, 14, 16, 18



$Cu(LA)_2$: m=3, n=4-12, 14, 16, 18

$Cu(LB)_2$: n=6, m=1, 2, 4-13

Results and Discussion

The phase behavior was studied by polarizing microscopic observation and by differential scanning calorimetry. Table I summarizes the mesomorphic transition temperatures and enthalpy changes determined by the latter means for the homologous series of LA, $Cu(LA)_2$, and $Cu(LB)_2$. Here K,[2] N, and I denote crystalline, nematic, and isotropic phases, respectively, and each homologue is designated by the number of carbon atoms in the terminal alkyl chains, *n*, for LA and $Cu(LA)_2$, and in the lateral alkyl groups, *m*, for $Cu(LB)_2$.

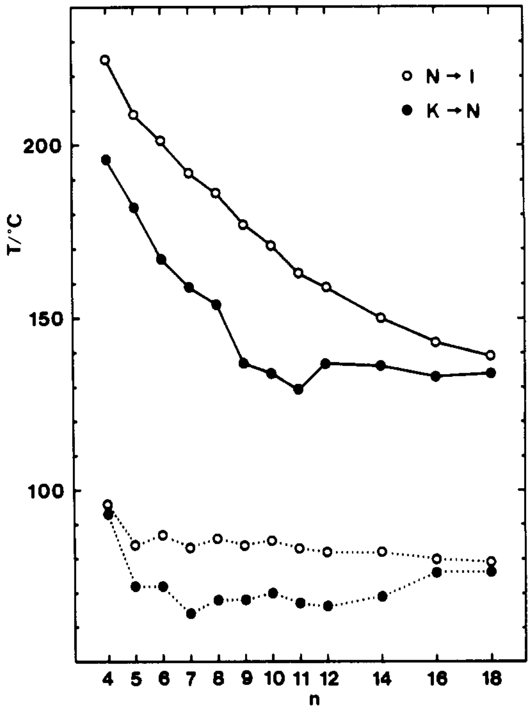


Figure 1. Plots of mesomorphic transition temperatures vs terminal alkyl chain length (*n*) for LA (dotted line) and $Cu(LA)_2$ (solid line).

Mesomorphic Properties of LA and $Cu(LA)_2$. Figure 1 gives a graphic comparison of phase behaviors of LA and $Cu(LA)_2$. It is seen that all of the ligand homologues exhibit enantiotropic nematic phases, though only over narrow temperature ranges. The phases were characterized by their marble textures under a crossed polarizing microscope, and the magnitude of isotropization enthalpies also supports the identification.[3] The mesomorphic property of 4-((propylimino)methyl)phenyl 4-(pentyloxy)benzoate, a two-ring compound analogous to LA (*n* = 5) but lacking the 3-hydroxyl group, has been reported by Weissflog et al.[4] to show

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(1) Hoshino, N.; Murakami, H.; Matsunaga, Y.; Inabe, T.; Maruyama, Y. *Inorg. Chem.* **1990**, *29*(6), 1177-1181.

(2) Melting points and enthalpies were determined also with annealed specimens whenever the presence of lower melting metastable forms in virgin crystals was indicated by solid–solid transition peaks and/or double melting behavior on DSC thermograms.

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Table I. Mesomorphic Transition Temperatures (°C) and Enthalpies (ΔH/kJ mol^{-1})[a] for LA, Cu(LA)$_2$, and Cu(LB)$_2$

	LA		Cu(LA)$_2$			Cu(LB)$_2$	
n	K[b] → N	N–I	K[b] → N	N–I	*m*	K[b] → N	N–I
4	93 (33)	96 (1.0)	196 (56)	225 (3.6)	1	212 (59)	267[c]
5	72 (35)	84 (0.77)	182 (52)	209 (3.1)	2	214 (66)	247[c]
6	72 (23)	87 (0.90)	167 (54)	201 (2.8)	4	151 (68)	176 (2.7)
7	64 (27)	83 (0.85)	159 (54)	192 (2.4)	5	132 (52)	173 (2.7)
8	68 (27)	86 (0.93)	154 (57)	186 (2.5)	6	132 (48)	168 (2.3)
9	68 (34)	84 (0.95)	137 (55)	177 (2.3)	7	126 (49)	167 (2.4)
10	70 (33)	85 (1.1)	134 (59)	171 (2.2)	8	111 (69)	153 (2.1)
11	67 (33)	83 (1.0)	129 (58)	163 (2.0)	9	123 (46)	151 (2.2)
12	66 (32)	82 (1.2)	137 (67)	159 (1.9)	10	120 (42)	146 (2.1)
14	69 (37)	82 (1.4)	136 (74)	150 (1.9)	11	130 (52)	145 (2.0)
16	76 (47)	80 (1.6)	133 (79)	143 (1.9)	12	129 (55)	140 (2.1)
18	76 (71)	79 (1.9)	134 (91)	139 (2.0)	13	133 (61)	139 (2.0)

[a] Values in parentheses. [b] Determined with annealed samples for n = 6, 7, 12, 16, and 18 homologues of LA, for n = 9–11, 14, and 16 homologues of Cu(LA)$_2$, and for m = 6–13 homologues of Cu(LB)$_2$. [c] Onset of exothermic decomposition.

a nematic phase from 73 to 78 °C. They have also described the emergence and stabilization of a smectic A phase among other homologues having the alkoxy chains longer than the alkylimino end. Such a tendency was not observed with the present LA series, which is purely nematogenic, though $n > 3$ throughout the series. Thus introduction of the hydroxy group ortho to the azomethine functionality seems not only to increase the nematic stability but also to suppress the smectic phases. This may be a consequence of intramolecular hydrogen bonding, which will constrain the *N*-alkyl group within the salicylidene plane. The same nematic-favoring effect may be anticipated for chelated species, but a much more drastic change in the molecular structure and symmetry takes place in formation of complexes of the bis(ligand) type.

Figure 1 shows that all of the Cu(LA)$_2$ homologues are also nematogenic, but both melting and clearing temperatures are raised by more than 58 °C (n = 18) compared to the ligands, and they increase more sharply as the series is descended. The optical textures were of a marble type similar to those of the ligands, but the greater magnitude of N–I transition enthalpies suggests that the nematic phases of Cu(LA)$_2$ are more ordered than LA.

Terminal vs Lateral Chain Elongation. Next, we turn to comparison between Cu(LA)$_2$ and Cu(LB)$_2$. The latter series also showed the nematic phases, which are similar to those of the former in terms of both optical texture and the magnitude of N–I transition enthalpy. In Figure 2 are plotted mesomorphic transition temperatures for these complexes together with the data reported recently by Marcos et al.[5] for bis[4-((4-(decyloxy)benzoyl)oxy)-*N*-(*n*-alkyl)salicylaldiminato]copper(II), n = 10 homologues of our Cu(LB)$_2$ series.[6] With regard to the thermal stability of the mesophases, extension of the lateral alkyl groups (increasing m) leads to a drastic depression of the clearing points up to m = 4 and the curves show more gradual decreases thereafter in both cases of n = 6 and 10. On the other hand, elongation of the terminal alkyl chains beyond n = 3 (=m) brings down the clearing temperature only gradually. The destabilizing effect of the extended lateral groups appears to work better on a more ordered phase, and melting point curves[6] also fall rapidly along the m axis, but there is a sign of reversal after the minimum at m = 8.

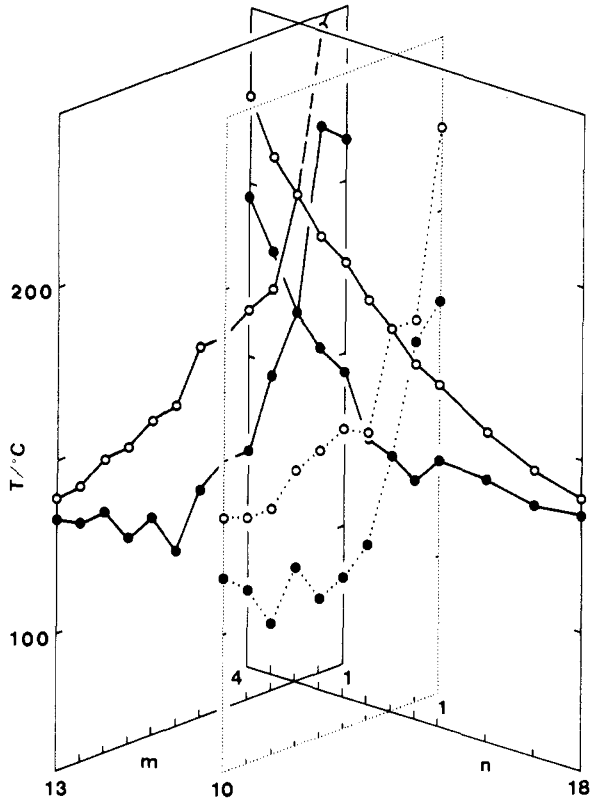

Figure 2. Plots of mesomorphic transition temperatures vs terminal alkyl chain length (n) for Cu(LA)$_2$ and lateral alkyl chain length (m) for Cu(LB)$_2$. Data from ref 5 for n = 10 analogues to Cu(LB)$_2$ (dotted line) are indicated for comparison. Full and empty circles represent melting and clearing temperatures, respectively.

If more data points were in hand, we could construct "contour" plots, projected onto the mn plane, which outline surfaces defined by the existence limit of each phase. Still, concavity of such plots is clearly conceivable with the available set of data in Figure 2. Since the melting curves along the m axis appear to have shallow wells, a region on the mn plane may be found where the nematic range can be maximized. We have proceeded instead to carry out physical measurements in the available nematic phases, including supercooled ranges, of these and analogous complexes, the results of which will be the subject of a forthcoming publication.[7]

It is worth noting the tendency of melting curves, reversing upward as m increases. Charles has previously reported on the melting behavior of bis[*N*-(*n*-alkyl)salicylaldiminato]copper(II) and stated that the melting points of these complexes generally decrease from methyl (158.5–159.0 °C) to *n*-tetradecyl (56.5–58.0 °C) homologues.[8] Therefore, the above tendency can be ascribed to the presence of (4-alkoxybenzoyl)oxy groups in our Cu(LB)$_2$ system. These groups were introduced actually to generate orientational order in the liquid phase of the unsubstituted complexes by bringing in molecular shape anisotropy. The approach was successful, but it was inevitably effective in stabilizing the crystalline phase as well, particularly for the higher homologues.

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(5) Marcos, M.; Romero, P.; Serrano, J.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 1641–1643.

(6) The melting points reported in ref 5 are not always for the most stable crystalline form. Reported values of the phase transition (both K → N and N–I) temperatures for Cu(LA)$_2$ (n = 10) are 3–4 °C lower than our data.

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A question may arise as to the coordination geometry of the copper atom of higher homologues of Cu(LB)$_2$ complexes in the mesophase. On the basis of the following information, we think that destabilization of the mesophases of these complexes is not caused by tetrahedral distortion alone to a serious degree and their coordination geometries are planar, or nearly so, ensuring a lathlike molecular structure even at very large m. First of all, the mesomorphic behavior is completely lost in tetrahedral zinc(II) analogues of Cu(LA)$_2$ (n = 10 and 14); their isotropic melts can be supercooled down to about 20 °C below their melting points (153 and 148 °C, respectively) but yield no mesophase whatsoever. Besides, Marcos et al. mentioned on ESR (negative) evidence that the nickel(II) analogue of our Cu(LB)$_2$ (m = 10) is not paramagnetic,[5] supporting its square-planar configuration. Square planarity of related complexes in other phases has been established; bis[*N*-(*n*-alkyl)salicylaldiminato]copper(II) complexes containing up to six carbon alkyl chains also have a planar structure with minimal distortion in toluene,[9] and the Cu(LA)$_2$ (n = 5) containing propyl substituents is of planar configuration in the solid state, since the near-infrared band(s) is(are) absent from its reflectance spectrum.[10]

Experimental Section

Materials. Typical procedures for preparation of the compounds are outlined below.

Ligands (LA). 2,4-Dihydroxybenzaldehyde was subjected to DCC esterification[11] by an appropriate *p*-alkoxybenzoic acid[1] and purified by two or three recrystallizations from methanol (or ethanol for higher homologues). Yields: 40–60%. The product was then condensed with an equimolar amount of propylamine by refluxing in benzene with a Dean-Stark trap attached. After the solvent was removed by rotary evaporation, the desired Schiff base was isolated from the methanol-triturated residue by filtration and recrystallized twice from methanol. Yields: 70–80%, pale yellow microcrystals. ^{1}H NMR (CDCl$_3$) for L (n = 9): δ 14.08 (br s, 1 H, OH), 8.31 (s, 1 H, CH=N), 8.12 (d, J = 8.8 Hz, 2 H, benzoyl), 7.26 (d, J = 8.2 Hz, 1 H, salicylidene), 6.96 (d, 2 H, benzoyl), 6.79 (d, J = 2.2 Hz, 1 H, salicylidene), 6.72 (dd, 1 H, salicylidene), 4.04 (t, J = 6.6 Hz, 2 H, CH$_2$—O), 3.55 (t, J = 6.6 Hz, 2 H, CH$_2$—N), 1.82 (quintet, J = 7 Hz, 2 H, CH$_2$), 1.71 (hextet, J = 7 Hz, 2 H, CH$_2$), 1.47–1.29 (br m, 12 H, CH$_2$'s), 0.98 (t, J = 7 Hz, 3 H, CH$_3$), 0.89 (t, J = 7 Hz, 3 H, CH$_3$). Anal. Found (calcd) for $C_{25}H_{33}NO_4$ (n = 8): C, 72.80 (72.96); H, 8.04 (8.09); N, 2.99 (3.40). Found (calcd) for $C_{26}H_{35}NO_4$ (n = 9): C, 73.36 (73.38); H, 8.45 (8.29); N, 3.49 (3.29).

Copper(II) Complexes (Cu(LA)$_2$). A 5-mmol sample of an LA homologue was dissolved in 30 mL of hot methanol, and to this was added a methanolic solution of 2.55 mmol of cupric acetate dihydrate. After refluxing for several hours, a greenish brown solid was collected by filtration, washed with methanol, and recrystallized from ethanol/chloroform mixtures until sharp and constant phase transitions were obtained. Yields: 50–70%, fibrous to platelike ($n \leq 12$) or powdery microcrystals (n = 14, 16, and 18). Anal. Found (calcd) for $C_{50}H_{64}N_2O_8Cu$ (n = 8): C, 67.73 (67.89); H, 7.30 (7.29); N, 3.13 (3.17). Found (calcd) for $C_{52}H_{68}N_2O_8Cu$ (n = 9): C, 68.34 (68.43); H, 7.58 (7.51); N, 3.00 (3.07).

Cu(LB)$_2$. Bis[4-((4-(hexyloxy)benzoyl)oxy)salicylaldehydato]copper(II) was prepared by using the aldehyde ligand, prepared above, in a manner similar to that for Cu(LA)$_2$. A 1-mmol quantity of this complex was allowed to react with 3 equiv of an alkylamine in 40 mL of boiling chloroform for several hours and then evaporated nearly to dryness. Crude solid was isolated and washed with methanol and purified as above. Yields: 30–60%, greenish brown fibrous to platelike crystals. Anal. Found (calcd) for $C_{58}H_{80}N_2O_8Cu$ (m = 9): C, 69.75 (69.89); H, 8.21 (8.09); N, 2.78 (2.81).

Physical Measurements. Calorimetric measurements were performed by using Rigaku Thermoflex, Rigaku TAS100, and Du Pont 9900 differential scanning calorimeters. The heating or cooling rate was 5 K min^{-1}.

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Nitronium (Trifluoroacetato)metalates. 1. Nitronium Hexakis(trifluoroacetato)stannate(IV)

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During an investigation by ^{14}NMR spectroscopy of the nature of the nitrogen species present in the solution of covalent tin(IV) nitrate in the reactive solvent (CF$_3$CO)$_2$O, it became apparent that solvolysis of the tin(IV) nitrate with the anhydride provides a synthetic method for the hitherto unknown nitronium salt of the hexakis(trifluoroacetato)stannate(IV) anion.

Addison has postulated a free radical mechanism[1,2] to account for the vigor of the bidentate nitrate reactions in nonaqueous media. Such a hypothesis would involve reduction of the metal ion, e.g.

$$Sn(NO_3)_4 \rightleftharpoons Sn(NO_3)_3 + NO_3^{\bullet}$$

The existence of the NO$_3^{\bullet}$ free radical is well established.[3–6]

However, the reactions of the bidentate tin(IV) nitrate described here can alternatively be regarded as reactions of coordinated nitrate ligands. The reactivity of the bidentate nitrate, due to perturbed electronic distribution, appears to be related to the oxidation state, electronic configuration, and the polarizing power of the metal, with small highly charged cations possessing a spherically symmetric electron distribution, such as d^{10} in Sn(NO$_3$)$_4$.

On the other hand the fluoroacetato compounds are well-known and established.[7–10]

Here, we report the synthesis, characterization, and spectroscopic properties of nitronium hexakis(trifluoroacetato)stannate(IV).

Experimental Section

Reagents. Tin(IV) nitrate was prepared as described in the literature.[1] Pure N$_2$O$_5$ was collected at −78°C, and SnCl$_4$ was added in portions with continuous shaking. Excess of the reagents was removed by evacuating the flask, and the crude product was sublimed under vacuum at 50 °C.

Carbon tetrachloride, nitromethane, and acetonitrile were distilled twice from P$_2$O$_5$. Molecular sieves were used to dry other solvents.

Preparation of (NO$_2$)$_2$[Sn(O$_2$C$_2$F$_3$)$_6$]. The nitronium hexakis(trifluoroacetato)stannate(IV) is prepared by dissolving powdered Sn(NO$_3$)$_4$ (0.5 g) in pure and dry (CF$_3$CO)$_2$O (ca. 5 mL). All manipulations were carried out in inert media. The mixture was allowed to stand overnight whereupon white needles and a clear supernatant liquid were obtained. The precipitate was filtered off under a nitrogen current, washed with dry CCl$_4$, and dried in vacuum at room temperature. Analysis was consistent with the formula [$SnO_{16}C_{12}N_2F_{18}$]. [Cald for $SnC_{12}F_{18}N_2O_{16}$: Sn, 13.35; C, 16.21; N, 3.15. Found: Sn, 13.55; C, 16.21, N, 3.15; H, 0.12.] The product is readily soluble and stable in acetonitrile and ethyl acetate, insoluble in CCl$_4$, CH$_3$Cl, and CH$_2$Cl$_2$, and reacts with effervescence with alcohol, acetone, and water.

Analysis. Nitrogen was determined by the refined Kjeldah method using stoppered breakable bulbs for the hydrolysis of the compound. Tin was determined as SnO$_2$.

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