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Metalloorganic Liquid Crystals: Bis(*N*-aryl-4-substituted salicylaldimine)nickel(II) and -copper(II) Complexes

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The synthesis and mesogenic behavior of new metalloorganic complexes are described: the bis(*N*-aryl-4-[((decyloxy)benzoyl)oxy]salicylaldimine)nickel(II) and -copper(II) in which aryl = $C_6H_4OC_nH_{2n+1}$ and n = 1–6, 8, 10, 14. All the copper(II) complexes show liquid-crystal properties (nematic and/or smectic C phases) with a broad temperature range, whereas nickel(II) complexes show fluid liquid-crystal properties (nematic mesophase) when n = 1, 2, 3, 4.

Introduction

The syntheses of new metal-containing liquid crystals is currently in progress[1] due to the special combination of liquid-crystalline properties and the presence of a transition metal in the structure of the molecules, which can introduce unusual electrooptic and magnetic properties[2–6] that make these materials potentially very useful for several applications.

Bartkowski and Morosin have investigated the exchange couple one-dimensional behavior of bis(*N*-methylsalicylaldimine)copper(II) by X-ray diffraction and ESR and found that this compound had the properties of a one-dimensional spin $^1/_2$ Heisenberg antiferromagnet.[7]

We report here the syntheses and liquid-crystalline properties of two new families with four side chains derived from *N*-arylimine complexes of nickel(II) and copper(II) (series I and II, respectively), which we believe to be of special interest because the complexes in series I are the first mesogenic *N*-arylimine complexes of Ni(II) described (previous attempts to obtain *N*-aryl Schiff bases of Ni(II) complexes with liquid-crystal properties have been unsuccessful to date,[8,9] and we present a systematic study of two homologous series of complexes that allow us to study (a) the influence of the nature of the metal on the liquid-crystal properties, (b) the influence of the terminal chain's length, and (c) to go deeply into the relationship between the molecular structure and the mesogenic behavior of these complexes.

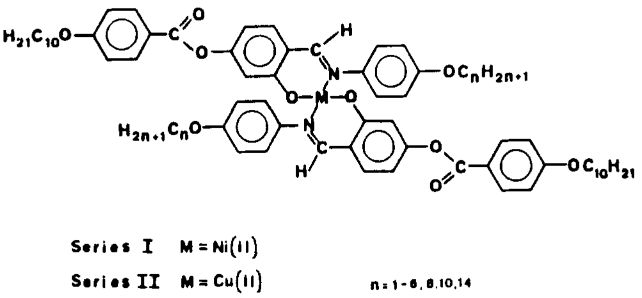

Table I. Elemental Analyses (percent) for Complexes of Series I and II (Calculated Values in Parentheses) and Yields

series	*n*	C	H	N	yield, %
I	1	69.7 (70.0)	7.2 (6.8)	2.7 (2.6)	56.8
	2	70.6 (70.4)	7.4 (7.0)	2.6 (2.6)	94.1
	3	71.2 (70.8)	7.6 (7.2)	2.5 (2.5)	57.0
	4	71.7 (71.2)	8.2 (7.3)	2.4 (2.4)	83.8
	5	71.2 (71.5)	8.3 (7.5)	2.4 (2.4)	76.6
	6	71.1 (71.4)	8.0 (7.7)	2.2 (2.3)	83.4
	8	72.7 (72.5)	8.7 (7.9)	2.3 (2.2)	87.8
	10	72.5 (73.0)	8.5 (8.2)	2.1 (2.1)	76.0
	14	74.4 (74.0)	9.2 (8.7)	1.9 (2.0)	88.3
II	1	69.7 (69.7)	7.4 (6.7)	2.6 (2.6)	94.3
	2	70.3 (70.1)	7.6 (6.9)	2.6 (2.6)	94.3
	3	70.3 (70.5)	7.7 (7.1)	2.4 (2.5)	94.7
	4	70.5 (70.9)	7.9 (7.3)	2.4 (2.4)	94.8
	5	71.9 (71.2)	7.6 (7.5)	2.6 (2.4)	87.2
	6	72.1 (72.6)	8.4 (7.6)	2.3 (2.3)	94.0
	8	72.3 (72.2)	8.7 (7.9)	2.2 (2.2)	83.7
	10	72.3 (72.8)	8.7 (8.2)	2.2 (2.1)	92.0
	14	73.3 (73.8)	9.9 (8.7)	1.8 (2.0)	95.5

Experimental Section

The synthetic procedure leading to the target complexes is outlined in Scheme I.

The free ligands were synthesized by using a well-known method[10] by mixing an ethanolic solution of the 4-(4′-[(decyloxy)benzoyl]oxy)-2-hydroxybenzaldehyde with the corresponding amine.

Preparation of the Complexes. The nickel(II) and copper(II) complexes were prepared by addition of an ethanolic solution (20 mL) containing nickel acetate ($Ni(OAc)_2 \cdot 4H_2O$) or copper acetate ($Cu(OAc)_2 \cdot H_2O$) (1 mmol) to a hot solution of the appropriate imine (2 mmol) in a mixture of chloroform and ethanol (100 mL). The solution was refluxed for 1 h. After cooling, the precipitate was collected by filtration and recrystallized from ethyl acetate

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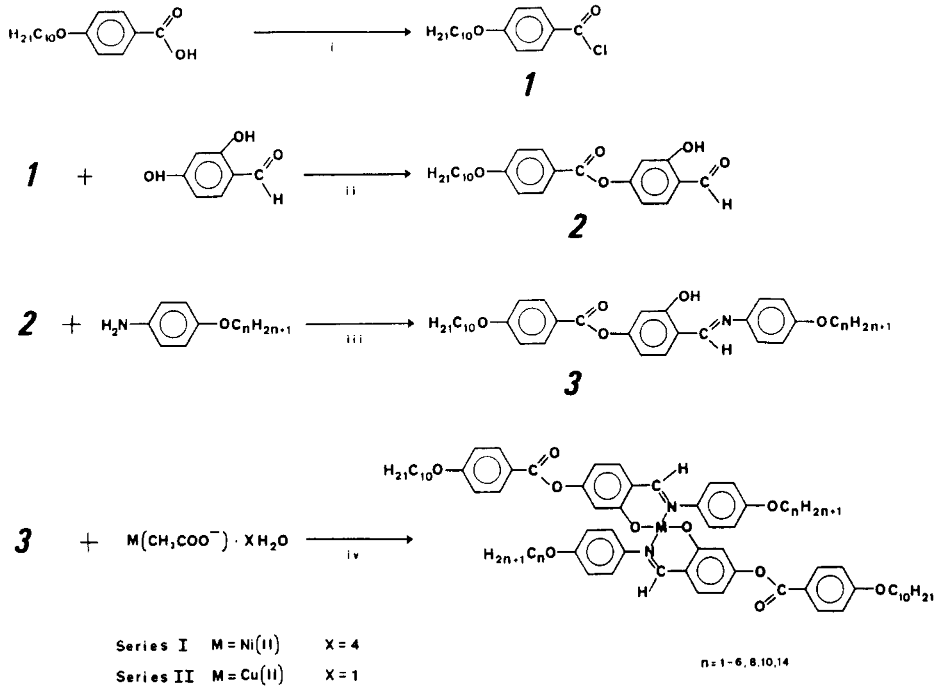
Scheme I[a]



[a] Reagents and conditions: i, $SOCl_2$, DMF, reflux, 2 h; ii, CH_2Cl_2, Et_3N, room temperature, several hours; iii, EtOH, AcOH, reflux; iv, EtOH/ethyl acetate, reflux, 0.5 h.

(for n = 1-6) or from a mixture of chloroform-ethanol (for n = 8, 10, 14).

Elemental analysis and yields are collected in Table I.

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 (series FTIR) spectrometer using Nujol mulls between polyethylene plates in the 400-4000-cm^{-1} spectral range. The visible absorption spectra for the metal complexes were recorded in chloroform by using a Hitachi V-3400 spectrophotometer in the 400-1000-nm spectral range. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200 MHz for ^1H, in deuteriochloroform solutions.

The textures of the mesophases were studied with an optical microscope (Meiji) equipped with polarizing light, a Mettler FP82 hot stage, and a Mettler FP80 central processor.

Measurements of temperatures and enthalpies of transition were made using a Perkin-Elmer DSC-2 differential scanning calorimeter with a heating or cooling rate of 10 K/min (the apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g).

Thermogravimetric analyses were obtained on a Perkin-Elmer TGS-2 equipped with a system 4 microprocessor controller at a heating rate of 10 K/min under nitrogen.

Results and Discussion

Synthesis and Characterization. The complexes in series I and II are prepared by reacting the appropriate imine with nickel(II) acetate tetrahydrate or copper(II) acetate monohydrate, respectively, in warm ethanol. The complexes are isolated as green or green-brown solids with good yields and are soluble in toluene, chloroform, and dichloromethane and insoluble in ethanol and petroleum ether.

The elemental analyses of the complexes are consistent with their proposed structures, although repeated hydrogen analyses are always higher than the calculated values.

The infrared spectra of the metal complexes show a stretch band around 1614 cm^{-1} in both series, which is assigned to ν(C=N); it is found that this band shifts to a lower frequency by ca. 5-9 cm^{-1} compared to that of the free Schiff bases. There is a stretch band between 1716 and 1734 cm^{-1} assigned to the ester group ν(C=O), and in some cases this band show a double peak, which is attributed to the fact that the ester group allows the aromatic ring to revolve around the O-C(aromatic) bond. The metal-ligand bands were of difficult assignation.

The electronic spectra of complexes show a weak absorption band centered around λ = 600 nm for complexes derived from Ni(II) and λ = 662-670 nm for complexes derived from Cu(II) complexes. This band is much reduced in intensity in the case of the nickel complexes compared to the transition in the copper complexes.

NMR studies carried out with the nickel(II) complexes show that although these complexes are diamagnetic as solids, as was proved by EPR, they become partially paramagnetic in a chloroform solution because a distortion as well as a broadening of the signals is observed.

The stability of the complexes was studied by thermogravimetric analysis, and none of the complexes shows weight loss until 280 °C or higher temperatures: however, we have observed that most of the complexes decompose after the complex has become isotropic and the second DSC scan is different. For this reason first-scan DSC data were used.

Mesogenic Behavior. The optical, thermal and thermodynamic data of the complexes are summarized in Tables II and III.

Series I Complexes. Compounds with n = 5, 6, 8, 10, 14 are transformed on heating from the solid into a highly viscous birefringent phase. One of the textures observed with a polarizing microscope, between crossed polarizers, is shown in Figure 1. X-ray diffraction experiments to determine the structure of the phase show that the phase is of a crystalline nature and not of an ordered liquid crystal as the optical observations might lead one to think.

The complexes with n = 3, 4 show a nematic mesophase as well as a birefringent phase between 162.0 and 218.7 and 159.3 and 187.3, respectively, which is optically similar to the phase shown by the above-mentioned complexes.

The complexes with n = 1,2 show an enantiotropic nematic phase. The nematic phase shows textures that are

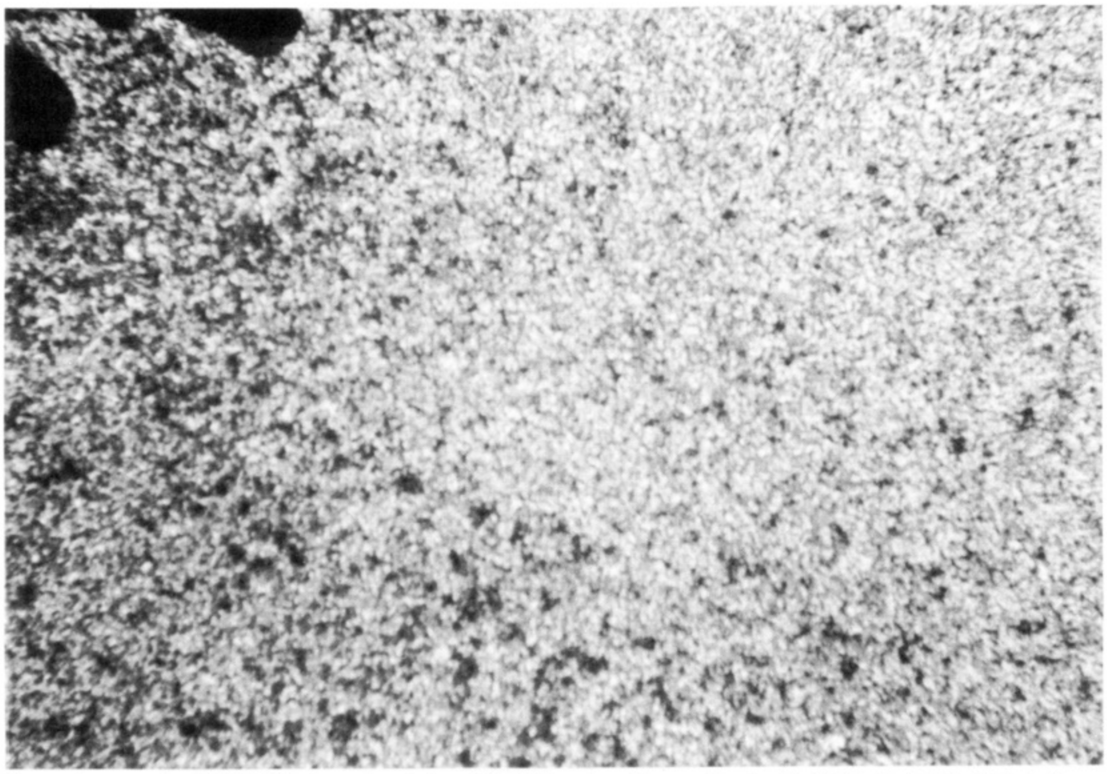


Figure 1. Photomicrograph of bis((*N*-(*p*-(octyloxy)phenyl))-4-((decyloxy)benzoyloxy)salicylaldimine)nickel(II) in its crystal phase at 195 °C, viewed between crossed polars.

Table II. Optical, Thermal, and Thermodynamic Data for Nickel(II) Complexes

n	transition[a]	temp,[b] °C	ΔH,[b] kJ/mol
1	C–N	182.6	20.39
	N–l	212.8	0.40
2	C–N	219.5	26.39
	N–l	230.4	1.20
3	C–C′	162.0	3.13
	C′–N	218.7	26.98
	N–l	222[c]	
4	C–C′	159.3	25.59
	C′–N	187.3	13.09
	N–l	217.1	1.54
5	C–C′	150.0	9.33
	C′–l	203.6	19.35
6	C–C′	138.0	18.47
	C′–l	191.7	22.37
8	C–C′	151.1	25.88
	C′–l	207.4	24.89
10	C–C′	151.5	26.18
	C′–l	196.8	39.80
14	C–C′	119.0	13.25
	C′–l	176.2	30.78

[a] C, C′, crystalline phases; N, nematic mesophase; l, isotropic liquid. [b] DSC data from first scan. [c] Optical data.

Table III. Optical, Thermal, and Thermodynamic Data for Copper(II) Complexes

n	transition[a]	temp,[b] °C	ΔH,[b] kJ/mol
1	C–N	166.6	69.00
	N–l	266.7	2.28
2	C–N	161.3	49.73
	N–l	254.7	1.37
3	C–S_C	179.8	38.65
	S_C–N	186.3	0.99
	N–l	274.1	2.44
4	C–S_C	173.9	35.81
	S_C–N	224.0	1.16
	N–l	274.0	2.02
5	C–C′	149.9	11.98
	C′–S_C	173.7	25.34
	S_C–N	230.1	1.48
	N–l	266.3	1.97
6	C–C′	143.0	8.36
	C′–S_C	166.8	25.21
	S_C–N	233.9	2.9
	N–l	255.7	2.83
8	C–C′	147.9	12.83
	C′–S_C	168.4	28.89
	S_C–N	242.4	6.60
	N–l	252.3	4.17
10	C–C′	120.6	32.21
	C′–S_C	163.6	28.95
	S_C–N	247.9	16.44
	N–l	248.5	7.50
14	C–C′	147.5	6.88
	C′–S_C	155.0	17.78
	S_C–l	232.3	13.62

[a] C, C′, crystalline phases; N, nematic mesophase; S_C, smectic C mesophase; l, isotropic liquid. [b] DSC data from first scan.

typical of this type of mesophase,[11] the marbled texture on heating and schlieren texture on cooling (see Figure 2).

Previous studies carried out by us with bis(*N*-aryl-4-(decyloxy)salicyaldimine)nickel(II), and by Galyametdinov et al.[8] showed that these complexes were not liquid crystals. During the preparation of this paper we found a report by Bayle et al.[9] on nickel(II) complexes derived from *n*-butyl-4-*N*-(4′-[(*n*-alkoxybenzoyl)oxy]-4-salicyliden)aniline which are also described as non-liquid crystals. All of this seems to indicate that the number of aromatic rings, the nature of the terminal chain in the aniline part (alkyl or alkoxy), and the chain length have a decisive influence on the appearance of mesomorphism in this kind of complex.

Series II Complexes. It was found that the complexes in series II where $n = 1, 2$ showed an enantiotropic nematic phase with a wide range. On extending the chain length of the terminal chains $n = 3, 4$ two enantiotropic phases were found (nematic (N) and smectic C (S_C)). The ho-

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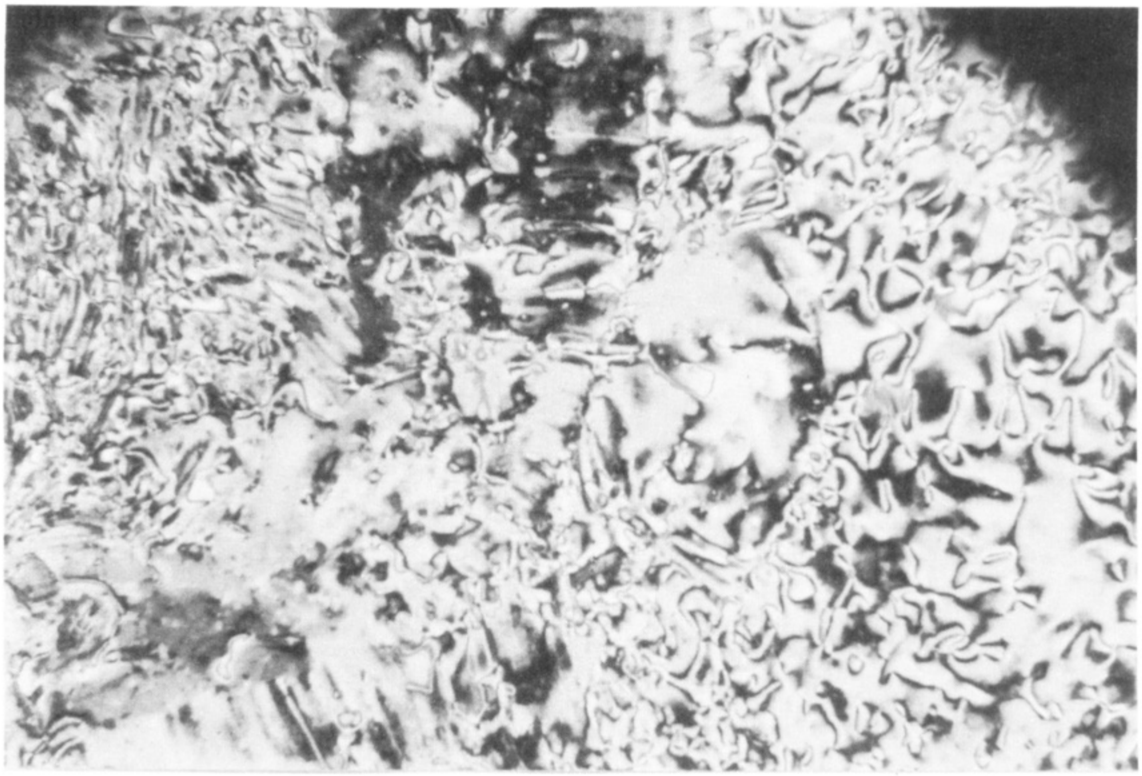

Figure 2. Photomicrograph of bis((*N*-(*p*-methoxyphenyl))-4-((decyloxy)benzoyloxy)salicylaldimine)nickel(II) in its nematic phase at 200 °C, viewed between crossed polars.

mologues $n = 5, 6, 8, 10$ show nematic and smectic C mesophases. And in complex where $n = 14$ only a smectic C phase appears.

The homologue where $n = 5, 6, 8, 10, 14$ together with the fluid liquid-crystal mesophases show at lower temperatures a more viscous phase. This phase was examined by X-ray diffraction in the copper complex where $n = 10$ and shown to be crystalline in nature.

The complexes melt at higher temperatures than the ligands, which are also liquid crystals. The transition temperatures of the ligands will be reported elsewhere.

The copper complexes have wider mesophase ranges than the nickel complexes where comparison was possible, and the melting temperatures are lower (Tables II and III).

The liquid-crystal properties of the two series are very different. However, both kinds of complex show nematic mesophase: series I when $n = 1$–4 and series II when $n = 1$–$6, 8, 10$.

It was reported[12] that some bis(*p*-substituted-*N*-arylsalicylaldimine)nickel(II) complexes are paramagnetic solids. However, EPR studies carried out at room temperature for the complexes when $n = 10$ show that whereas the copper(II) complex is paramagnetic, the nickel(II) complex is diamagnetic. Preliminary EPR studies at variable temperature (when $n = 4$) have shown that in copper complex the mesophases N and S_C are paramagnetic, whereas paramagnetism could not be observed with the nickel complex in any of its phases.

Conclusions

Two new series of Ni(II) and Cu(II) with Schiff base complexes having mesogenic properties have been synthesized and characterized. Interestingly, the results reported in this paper show that liquid crystal properties can be obtained by coordination to the nickel(II) of Schiff bases with a three-ring system derived from alkoxyanilines and that copper(II) complexes with the same molecular structure have better mesogenic properties than nickel complexes. The copper complexes are paramagnetic in solid, whereas the nickel ones are diamagnetic.

These complexes are good systems with which to carry out physical studies to elucidate their particular properties.

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Registry No. I ($n = 1$), 129103-06-6; I ($n = 2$), 129103-07-7; I ($n = 3$), 129103-08-8; I ($n = 4$), 129103-09-9; I ($n = 5$), 129103-10-2; I ($n = 6$), 129103-11-3; I ($n = 8$), 129103-12-4; I ($n = 10$), 129124-65-8; I ($n = 14$), 129103-13-5; II ($n = 1$), 129103-14-6; II ($n = 2$), 129172-27-6; II ($n = 3$), 129103-15-7; II ($n = 4$), 129103-16-8; II ($n = 5$), 129103-17-9; II ($n = 6$), 129103-18-0; II ($n = 8$), 129124-66-9; II ($n = 10$), 129172-28-7; II ($n = 14$), 129124-67-0.

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