

Communication

Smectic Bimetallo Mesogens: Synthesis and Mesomorphic Properties in Oxygen-Bridged Dicopper and Divanadyl Complexes

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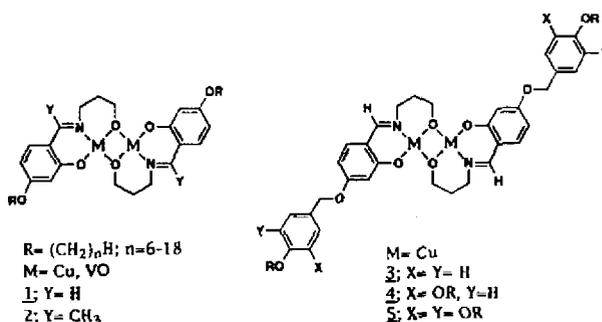
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The synthesis and mesomorphic properties of a homologous series of *N*-(3-hydroxypropyl)-4-alkoxy-salicylaldimine, *N*-(3-hydroxypropyl)-4-(4'-alkoxybenzoy)salicylaldimine, and their dicopper(II) and divanadium(VI) complexes are reported. Copper complexes exhibited monotropic smectic A phases; however, vanadyl complexes showed no mesomorphism. A systematic comparison revealed that the mesogenic behaviors of these bimetallic complexes are induced by the weak intermolecular force and determined mainly by the central metal. The effects on the structural variations near the metal central cores and side chain density are also discussed.

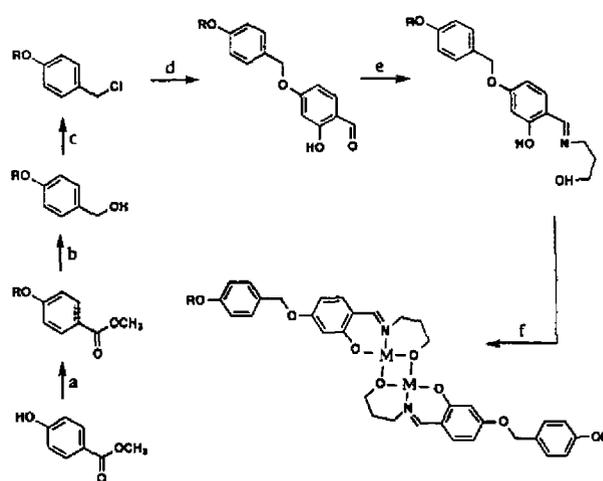
The incorporation of metal centers into ligand crystalline core groups, known as metallo mesogens, impart the physical properties which mainly arise from the large polarizable electron density of the metal atoms. Metallo mesogenic materials are fundamentally and technologically interesting since the incorporation of various metal centers offers many opportunities, not only to create novel materials, but also to study and investigate their potential physical properties. The induction of liquid crystallinity by intermolecular coordination² via direct metal-metal or ligand-mediated interaction has been widely applied to generate mesogenic superstructures with novel properties. The development of bimetallic mesogens³ opens new possibilities for the formation of materials which exhibit interesting properties, such as ferromagnetism and conductivity. A detailed understanding of the interactions in these homo- or hetero-bimetallic systems is of fundamental importance in the design of such materials, and it remains a challenging goal to materials researchers. We report herein our results on the development of smectic bimetallic liquid crystalline complexes.

We have prepared a number of dicopper and divanadyl complexes, 1-5, which are shown in Scheme I. The typical synthetic procedures are summarized in Scheme II. Reactions of 4-(4'-alkoxybenzoy)-2-hydroxybenzaldehyde⁴ with 3-amino-1-propanol in refluxing absolute ethanol gave the resulting Schiff bases: *N*-(3-hydroxypropyl)-4-(4'-alkoxybenzoy)salicylaldimine⁵ with a high yield of 92-95%. The metal complexes; bis[*N*-(3-hydroxypropyl)-4-(4'-alkoxybenzoy)salicylaldiminato]Cu(II) and VO(II) were obtained by the reaction⁶ of the Schiff bases with Cu(OAc)₂ and VO(OAc)₂ in CHCl₃/CH₃OH. Satisfactory elemental analyses for metal complexes were obtained by several re-

Scheme I



Scheme II



Reaction conditions:
a: RB(1.0eq), K₂CO₃(3.0eq), refluxed in CH₃COCH₃, 24 hr., 94%
b: LiAlH₄(1.1eq), stirred at RT in dried THF, 1 hr, refluxed 1/2 hr., 95%
c: SOCl₂(1.1eq), stirred in THF at RT, 10 min., 88%
d: 2,4-dihydroxybenzaldehyde(1.0eq), K₂CO₃(1.1eq), stirred at 50°C in CH₃COCH₃, 24 hr., 86%
e: H₂N(CH₂)₃OH(1.2eq), refluxed in absolute C₂H₅OH, 3 hr., 92%
f: M(OAc)₂; M = Cu, VO, refluxed in CHCl₃/CH₃OH, 2 hr., 85%.

crystallizations.

The liquid crystallinity of copper and vanadyl complexes of **1**, **2** and **3** was investigated by polarized optical microscope and DSC analysis. The phase behavior of copper and vanadyl complexes **1** and **3** is given in Table 1. Dicopper complexes **1** exhibited monotropic smectic A mesophases, which are often observed for long rod-like molecules; however, vanadyl complexes showed only crystalline phases. Smectic phases have been observed in complexes¹⁻² of various salicylaldehydes containing mono transition metals. Upon heating, the copper complexes melt directly into isotropic liquid at ca. 124 °C-145 °C and the smectic phase was obtained by cooling from the isotropic phase. The tem-

perature range of mesophases was fairly narrow and varied slightly with the sidechain length. The smectic A phase was identified by polarized optical microscope. Typical fan-shaped textures were observed by slow cooling the isotropic liquids. Vanadyl complexes **1** exhibited only crystal-to-isotropic transition at 210 °C-220 °C. The frequency of V=O stretching bands of these vanadyl complexes at around 988 cm⁻¹ (in Mujol) indicated a monomeric⁷ structure. Formation of polymeric structures in liquid crystalline phases of vanadyl compounds has been applied to produce polar ordering of linear chain structures. This type of macroscopic polar ordering could generate ferroelectric and NLO materials.⁸

The formation and stability of these mesophases are very sensitive to steric hindrance, and the position of alkoxy side chains. For example, liquid crystallinity is totally suppressed in dicopper complex **2**, presumably the increased bulk of a methyl group destroys the weak intermolecular force necessary to stabilize the liquid crystallinity. Crystal-to-isotropic transition ($T = 191$ °C; $n = 14$) was observed for these dicopper complexes. The copper complexes **3** showed similar phase behavior. Complexes; $n = 12$ and 14 exhibited enantropic S_A phases; however, complexes $n = 8, 10, 16,$ and 18 exhibited monotropic S_A phases. Clearing temperatures at 191 °C-203 °C of crystal-to-isotropic transitions were higher than those of dicopper complexes **1**. The temperature ranges of copper complexes **3** were wider than for complexes **1**, indicating that the mesophase of complexes **3** was more stable. Powder XRD measurements are in progress to confirm the structures of the mesophases in these bimetallic systems.

The effect of sidechain density on the mesomorphism was also studied. Copper complexes **4** and **5** all exhibited only crystalline phases. Induction of liquid crystallinity of these dicopper complexes was not accomplished by increasing the number of sidechains and substitution positions of sidechains. The results suggest that the formation of liquid crystalline phases is a combination of rigid core and sidechain density, e.g., the aspect ratio. Extra sidechain density in compounds **4** and **5**, compared with compound **3**, destroyed the weak mesophase.

In summary, we have developed bicopper complexes with rod-like shapes that exhibit smectic mesophases. The mesomorphic behavior is governed by the geometrical structures of these rod-like molecules, which in turn depends on the geometry of the metal centers. Copper complexes with planar or nearly planar arrangements around the central core produce flat elongated molecules, thus facilitate the formation of layered smectic phases. However, the lack of liquid crystalline phases in divanadyl systems was as-

Table 1. Phase Behaviors^a of Metal Complexes **1** and **3**

Metal	n	Heating(top) Cooling(bottom)			
1 , M = Cu	8	K	191.4(6.16)		I
		K	132.4(6.63)	S_A	137.2(0.24) I
	10	K	180.8(11.3)		I
		K	129.5(7.56)	S_A	145.2(1.18) I
	12	K	171.2(11.0)		I
		K	127.1(7.90)	S_A	144.4(1.23) I
	14	K	164.7(13.0)		I
		K	117.9(8.89)	S_A	140.4(1.43) I
	16	K	149.7(7.67)		I
		K	121.3(9.66)	S_A	133.9(1.71) I
18	K	150.3(1.62)		I	
	K	124.4 ^b	S_A	123.9 ^b I	
1 , M = VO	12	K	219.1(9.01)		I
		K	198.6(8.58)		I
	14	K	217.7(9.95)		I
		K	200.1(9.53)		I
	16	K	214.3(9.63)		I
		K	204.3(9.58)		I
18	K	209.3(8.04)		I	
	K	195.9(7.42)		I	
3 , M = Cu	8	K	213.6(12.9)		I
		K	188.9(9.56)	S_A	199.1(1.66) I
	10	K	206.9(8.32)		I
		K	187.9(6.04)	S_A	203.2(2.25) I
	12	K	187.2(5.08)	S_A	193.3(0.52) I
		K	161.1(3.30)	S_A	187.1(1.39) I
	14	K	197.9(3.67)	S_A	201.7(1.53) I
		K	179.2(4.89)	S_A	199.8(2.64) I
	16	K	198.3(5.72)		I
		K	178.0(5.46)	S_A	193.6(1.68) I
18	K	196.3(6.63)		I	
	K	174.5(5.41)	S_A	191.2(2.04) I	

^a The phase transition temperature (°C) and the enthalpies of transition (Kcal/mol, in parenthesis) are given between the phases. n represents the number of carbons in the alkoxy chains; K is the crystal phase; S_A is the smectic A phase; and I stands for isotropic.
^b unsolved peaks.

cribed to the stronger intermolecular forces between vanadyl centers. Geometry of both V = O bonding; either *trans* or *cis*, still remains unknown. Determination of the geometric structure of single crystals is important, since this affects the molecular shapes and hence the mesogenicity. Further research is continuing on similar bimetallic complexes as well as other multinuclear structures.

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SUPPLEMENTARY MATERIALS AVAILABLE

Tables of phase diagrams and elemental analysis data (7 pages) for all metal complexes reported. Ordering information is given on any current masthead page.

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Key Words

Liquid crystals; Metallomesogens; Smectic A; Bimetallic complexes; Schiff bases; Monotropic.

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- Temperature at 50 °C is controlled for the monoalkylation reactions to give better yields of 4-substituted aldehyde; 4-(4-dodecyloxybenzoxy)-2-hydroxybenzaldehyde. M.p. 85-86 °C; ¹H-NMR (200 MHz, ppm, CDCl₃): 0.86 (t, -CH₃, 3H), 1.06-1.80 (m, -(CH₂)₁₀, 20H), 3.98 (t, -OCH₂, 2H), 5.00 (s, -C₆H₄-OCH₂-, 2H), 6.48 (d, -C₆H₃, 1H), 6.59 (dd, -C₆H₃, 1H), 6.90 (d, -C₆H₄, 2H), 7.24 (d, -C₆H₄, 2H), 7.48 (d, -C₆H₃, 1H), 9.69 (s, -CHO, 1H), 11.46 (s, -C₆H₃OH, 1H). ¹³C-NMR (ppm, CDCl₃): 14.78, 23.37, 26.70, 29.91, 29.95, 30.01, 30.21, 30.56, 32.56, 68.76, 70.79, 102.2, 109.6, 115.3, 115.9, 128.0, 130.0, 135.9, 160.0, 165.1, 166.7, 195.0.
- Crude product of N-(3-hydroxypropyl)-4'-(4-dodecyloxybenzoxy)-salicylaldehyde was recrystallized from THF/CH₃OH to pale yellowish solids. M.p. 126-127 °C, ¹H-NMR (200 MHz, CDCl₃, TMS): 0.86 (t, -CH₃, 3H), 1.27-1.88 (m, -(CH₂)₁₀, 20H), 1.94 (m, -NCH₂CH₂-, 2H), 3.65 (t, -CH₂N=C, 2H), 3.74 (t, -CH₂OH, 2H), 3.95 (t, -OCH₂, 2H), 4.95 (s, -OCH₂C₆H₄, 2H), 6.43 (d, -C₆H₃, 2H), 6.87 (d, -C₆H₄, 2H), 7.01 (d, -C₆H₃, 1H), 8.10 (d, -N=CH, 1H). ¹³C-NMR (ppm, CDCl₃): 14.80, 23.40, 26.72, 29.91, 30.02, 30.58, 31.63, 32.58, 53.38, 59.78, 68.03, 69.77, 102.4, 107.0, 120.0, 114.6, 128.2, 129.3, 132.7, 159.1, 163.0, 163.9, 168.2.
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