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Hexagonal Columnar Mesophase D_h In Some Transition Metal Complexes

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A series of octasubstituted copper(II) complexes, including derivatives possessing two types of side chains was prepared. Some of these complexes exhibit a thermotropic D_h mesophase as determined by miscibility with a reference compound. For the first time, a columnar mesophase D_h is observed with an unsymmetrical product.

INTRODUCTION

Among the new class of hexagonal columnar mesophases discovered some years ago,[1,2,3] few compounds contain metals.[4,5,6,7] Some of us have previously reported the synthesis and some physical properties of two types[5,6] of thermotropic transition metal complexes which form a two dimensional hexagonal lattice of columns as determined by X-Ray diffraction.

The bis (3,4-nonyloxybenzoyl)methanato copper(II) ($\underline{1}$ R = C_9H_{19})

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has been clearly identified by miscibility with the D_h mesophase of a well-known hexasubstituted triphenylene derivative.[5]

In this paper, we wish to report some new results for other compounds of this series including derivatives exhibiting two different types of side chains.

SYNTHESIS

The transition metal complexes were synthesized by addition of a solution of transition metal chloride in ethanol to a solution of bis(3,4 alkoxybenzoyl) methane in the same solvent at a pH adjusted with ammonia to 7–8.

The bis(3,4 alkoxybenzoyl) methanes were obtained by reacting 3,4-alkoxybenzoic acid methyl ester with 3,4-alkoxyacetophenone in the presence of sodium hydride in anhydrous dimethoxy ethane. All compounds and complexes were recrystallized from heptane and/or isopropyl alcohol, and characterized by the usual analytical methods.

RESULTS

The bis (3,4 alkyloxy benzoyl) methanes were studied by Differential Scanning Calorimetry (Perkin Elmer DSC-2C) and observed by polarizing microscopy. The transition temperatures and melting enthalpies are given in Table I.

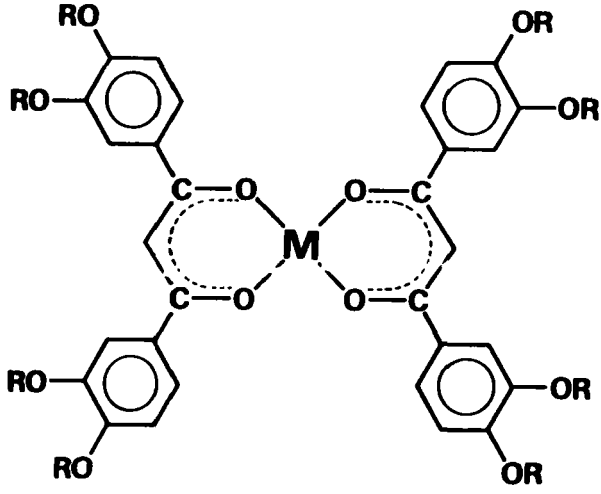

FIGURE 1 Octasubstituted transition metal complexes.

TABLE I

Melting points and melting enthalpies of bis(3,4-alkyloxybenzoyl) methanes

Substituents R		Melting temperatures	Melting enthalpies
3	4	°C	cal g^{-1}
C_7H_{15}	C_7H_{15}	81	24.5
C_9H_{19}	C_9H_{19}	81	26.4
$C_{11}H_{21}$	$C_{11}H_{21}$	73.5	24.2
C_3H_7	$C_{11}H_{21}$	70	21.3
C_7H_{15}	$C_{11}H_{21}$	74.5	18.4

The complexes were studied by the same way. The characterization of the mesophases was deduced from miscibility with the reference compound: bis(3,4-nonyloxy benzoyl methanato copper(II) (R = C_9H_{19} 1)[5] which is known to have a columnar mesophase D_h in the range of 102°C to 112°C.

The corresponding binary diagrams are shown in Figures 2 and 3. The transition temperatures and molar enthalpies of symmetrical compounds are given in Table II. The bis(3,4-heptyloxy benzoyl methanato copper(II) (R = C_7H_{15} 2) exhibits only a monotropic D_h mesophase whereas 3,4-nonyloxy (R = C_9H_{19} 1) and undecyloxy (R = $C_{11}H_{23}$ 3) contain the same but enantiotropic mesophases. The X-ray analysis (Guinier camera) clearly agrees with the miscibility identification: in particular, the lack of Bragg spot or intense diffuse scattering at wide angles confirms the liquid-like order inside each column.

Changing the alkyloxy substituent on the central core from the 3,4 to the 3,5 positions results in the disappearance of the mesomorphic properties (4 and 5). That probably comes from the steric interaction between chains which might bend the central core.

In the complex, substitution of the copper metal atom by nickel also destroys the liquid crystalline properties (6 table II).

The transition temperatures and molar enthalpies of the unsymmetrical compounds are given in Table III. The most important result of this study is that a slightly disymmetrical copper complex retains the D_h mesophase: the mesomorphic phase of (R = C_9H_{19}, R′ = $C_{11}H_{23}$ 9) is totally miscible with that of 1, taken as a reference (Figure 4).

To our knowledge, this is the first observation of a columnar mesophase D_h in a compound consisting of a non-symmetrical surrounding of paraffin chains. In fact, the addition of methylene groups around the central core and the small disymmetry induce very small differ-

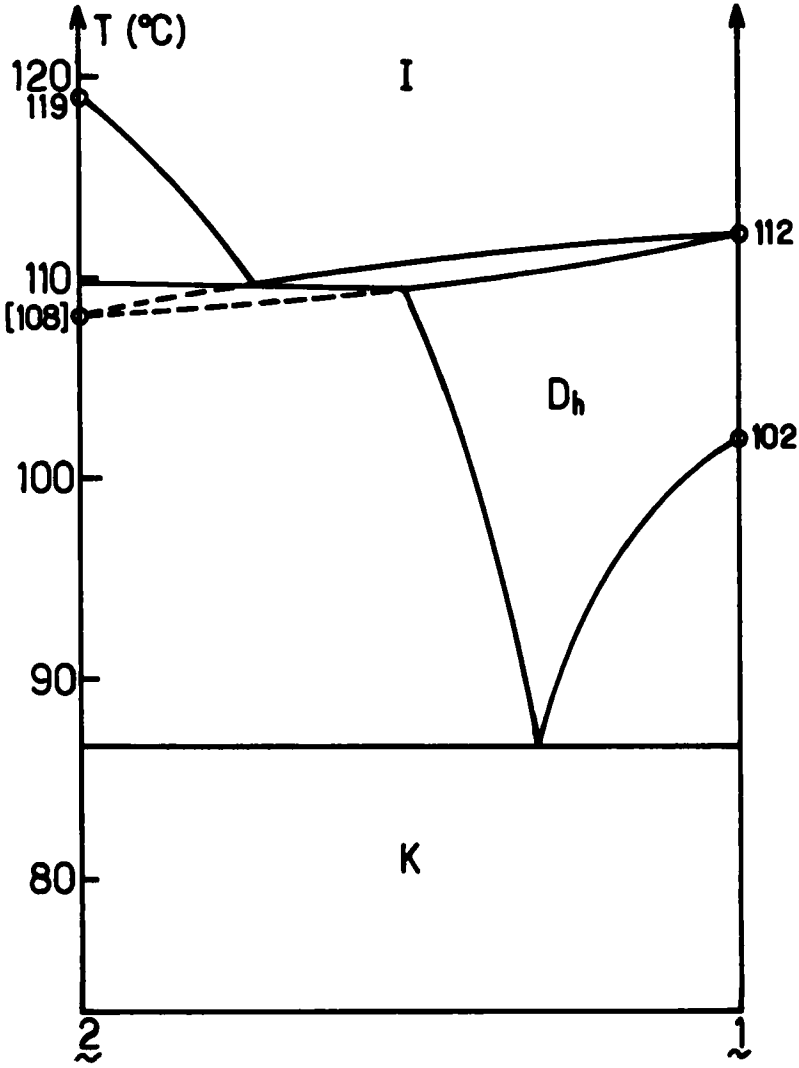

FIGURE 2 Diagram of isomorphy between Cu complex $\underset{\sim}{2}$ and the reference complex $\underset{\sim}{1}$. (contact method). The dotted spindle corresponds to monotropic I-D_h transitions.

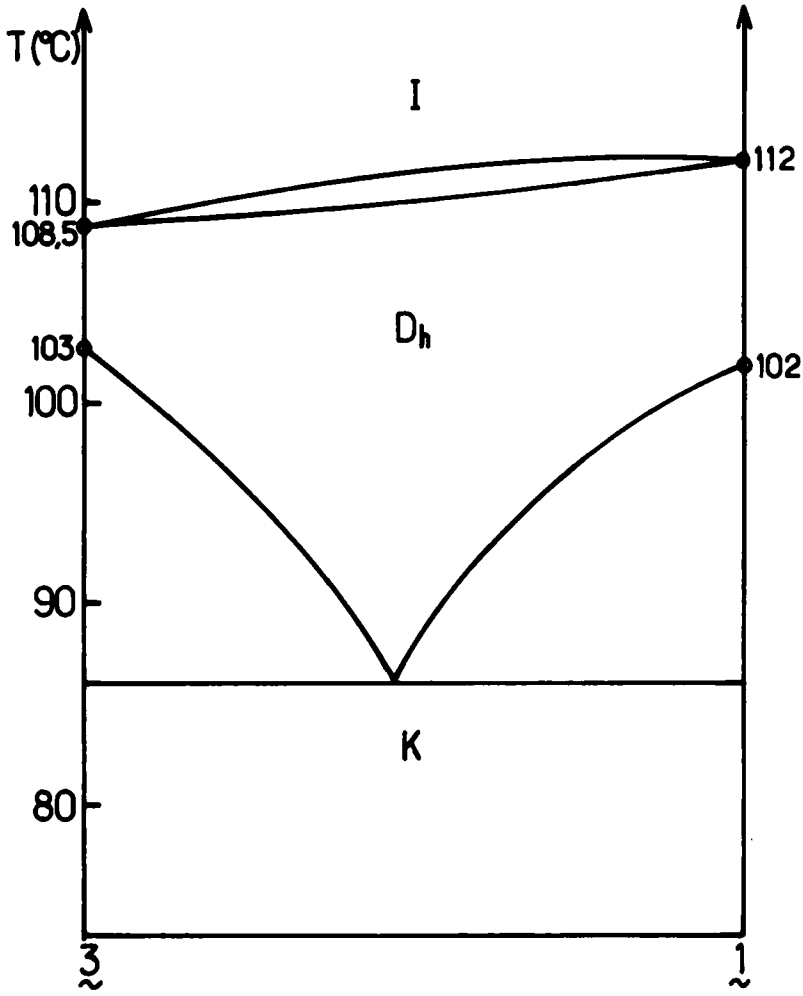

FIGURE 3 Diagram of isomorphy between Cu complex 3 and the reference compound 1.

ences upon the thermodynamic and the structural parameters. In particular, the distance between neighbouring columns is weakly influenced by the terminal methylene groups (Table IV) and is near 28–29 Å for both types of compounds: symmetrical or unsymmetrical.

Unfortunately, a larger dissymmetry of the flexible chains in the compounds of this series (7 and 8) results in loss of the mesogenic character.

TABLE II

Octa substituted complexes with the same length for the aliphatic chains

Metal	R			Polymorphism					
	3 3′	4 4′	5 5′	Melting point T_{KI} or T_{KDh}(°C)		D_h	Clearing point T_{Dhi}(°C)		
	C_9H_{19}	C_9H_{19}		102	[21.0]	Yes	112	[0.52]	1
	C_7H_{15}	C_7H_{15}		119	[17.4]	Yes	(108)	[a]	2
Cu	$C_{11}H_{23}$	$C_{11}H_{23}$		103	[11.5]	Yes	108.5	[0.58]	3
	$C_{11}H_{23}$		$C_{11}H_{23}$	85	[14.7]	No			4
	C_9H_{19}		C_9H_{19}	98	[14.6]	No			5
Ni	C_9H_{19}	C_9H_{19}		102	[24.3]	No			6

[a]this value is not obtained due to crystallization.
[ ] Enthalpy cal mole^{-1}.

TABLE III

Octasubstituted complexes with different lengths for the aliphatic chains

Metal	Substituents R				Polymorphism				
	3	4	3′	4′	Melting point T_{K1} or T_{KDh}(°C)		D_h	Clearing point T_{Dh1}(°C)	
Cu	C_3H_7	C_3H_7	$C_{11}H_{23}$	$C_{11}H_{23}$	114	[14.1]	No		7
	C_7H_{15}	C_7H_{15}	$C_{11}H_{23}$	$C_{11}H_{23}$	102	[11.2]	No		8
	C_9H_{19}	C_9H_{19}	$C_{11}H_{23}$	$C_{11}H_{23}$	101	[11.6]	Yes	118[0.63]	9

[ ]Enthalpy cal mole^{-1}

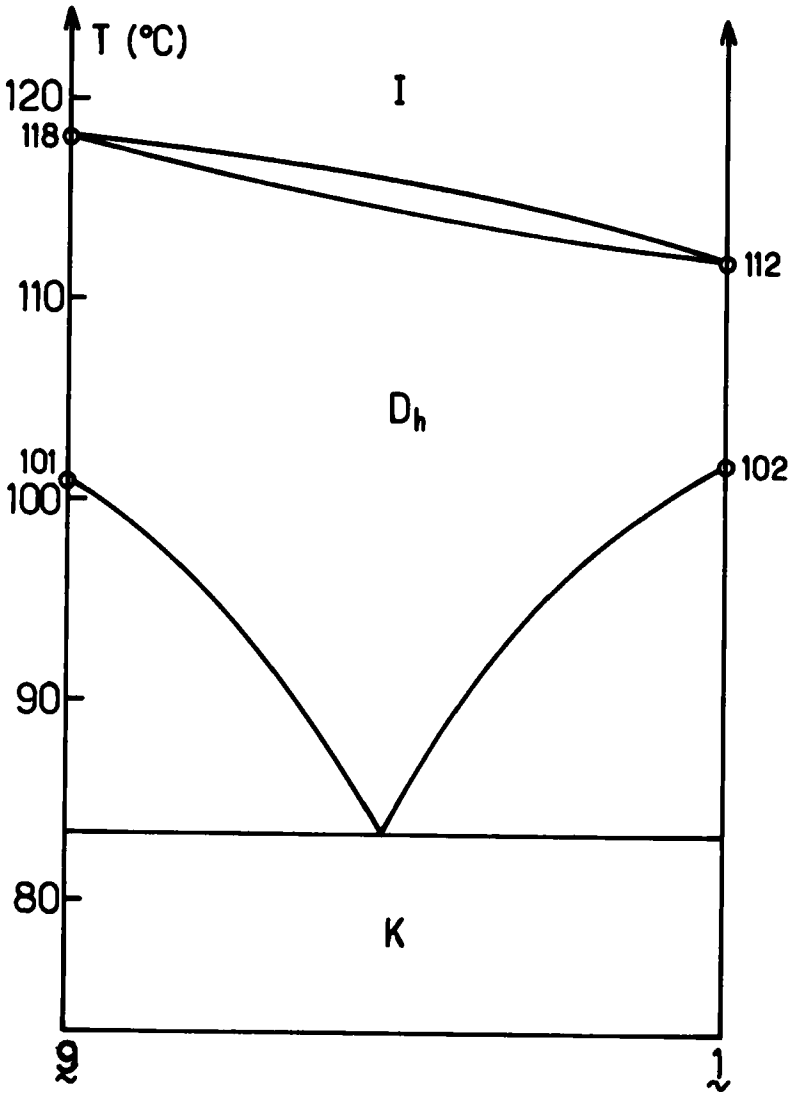

FIGURE 4 Diagram of isomorphy between Cu complex 9 and the reference compound 1.

TABLE IV

Parameter of the hexagonal lattice

Compound	a
1	27.90 Å
3	29.05 Å
9	28.10 Å

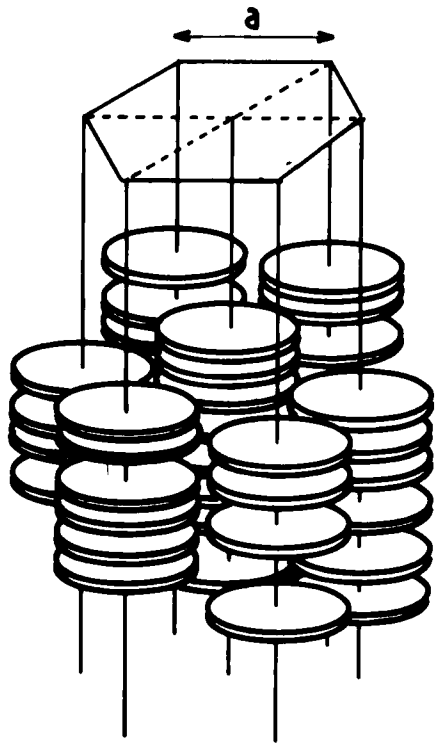

FIGURE 5 Schematic representation of the hexagonal structure in the columnar mesophase D_h.

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