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Novel liquid-crystalline derivatives of transition metals. The effect of the molecular geometry of the ligands on the mesogenic properties of tetracoordinated copper(II) complexes

Mercedes Marcos[a]; Pilar Romero[a]; José Luis Serrano[a]; Joaquín Barberá[b]; Anne Marie Levelut[b]
[a] Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza-C.S.I.C., Zaragoza, Spain [b] Laboratoire de Physique des Solides, Universite de Paris Sud, Orsay, France

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Novel liquid-crystalline derivatives of transition metals

The effect of the molecular geometry of the ligands on the mesogenic properties of tetracoordinated copper(II) complexes

by MERCEDES MARCOS, PILAR ROMERO and JOSÉ LUIS SERRANO
Química Orgánica, Instituto de Ciencia de Materiales de Aragón,
Facultad de Ciencias, Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza, Spain

JOAQUÍN BARBERÁ and ANNE MARIE LEVELUT
Laboratoire de Physique des Solides, Universite de Paris Sud, 91405 Orsay, France

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The synthesis, characterization and thermal behaviour of several new series of copper(II) complexes derived from carbonylic compounds and their Schiff's bases are reported. The complexes are of two types; $[Cu(C_6H_3O(R)\text{-}C(X)=O)_2]$, (type I) and $[Cu(C_6H_3O(R)\text{-}C(X)=N\text{-}R')_2]$ (type II) where $R = -OOC\text{-}C_6H_4OC_{10}H_{21}\text{-}p$, and the position of R is 4 or 5; $R' = CH_3$, $n\text{-}C_{10}H_{21}$, $p\text{-}n\text{-}C_{10}H_{21}O(C_6H_4)\text{-}$; $X = H, CH_3$. In type I complexes, only the compound with $X = H$ and R in position 5 showed mesomorphism. For type II complexes, all the Schiff's bases complexes of copper(II) derived from 2,4-dihydroxybenzaldehyde showed thermotropic mesophases (smectic C and nematic), whereas the complexes derived from 2,5-dihydroxybenzaldehyde were only mesogenic when the imine was derived from methylamine. None of the complexes derived from the ketone (2,4 or 2,5-dihydroxy derivatives) showed liquid-crystalline properties. X-ray studies of four complexes of type II were carried out. The anisotropy of the magnetic susceptibility has a negative sign for complexes with R in position 4 and a positive sign for 2,5-derivative complexes. The relationship between molecular structure and mesomorphic behaviour is discussed.

1. Introduction

The synthesis of mesogenic transition metal complexes is currently in progress due to the special combination of liquid-crystalline properties and the presence of a transition metal in the structure of the molecules [1–15]. Copper(II) complexes in particular have been studied [2–4, 8, 11–15] because the Cu(II) ion has a square-planar coordination geometry in most compounds, and also the complexes are paramagnetic species. Studies of crystalline one-dimensional systems containing Cu(II) have been reported; Bartkowski and Morosin investigated the exchange coupled one-dimensional behaviour of bis(*N*-methylsalicylaldiminato)-copper(II) by X-ray diffraction and E.S.R. spectroscopy and found that this compound has the properties of a one-dimensional spin 1/2 Heisenberg antiferromagnet [16]. Eastman *et al.* suggested that crystals of paramagnetic coordination complexes which exhibit discotic phases may exhibit the properties of one-dimensional exchange coupled systems either in the crystalline or in the discotic phase and that the interaction between paramagnetic centres in such complexes is altered by changes in molecular motion and spacing which occur during a discotic phase transition [17]. Ovchinnikov *et al.* reported the synthesis and E.S.R. spectra of several bis[salicylaldiminato]copper(II) complexes

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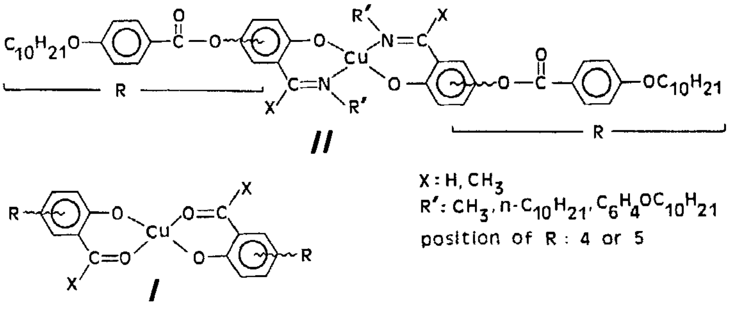
and found that they showed crystal–smectic discotic, smectic–nematic and nematic–isotropic transitions and that the configuration of the complexes is square-planar [3]. Otha *et al.* described tetrasubstituted β-diketonato copper(II) complexes and, established for the first time, from X-ray diffraction measurements that each of the discotic mesophases shown by these complexes is a discotic lamellar phase [4, 13].

Recently, we reported several copper(II) complexes of imines, $[Cu(p\text{-}RC_6H_3OC\text{-}(Y) = C_6H_4R'\text{-}p)]$ (R = alkoxy, R' = alkyl or alkoxy, Y = H or CH_3), many of which exhibited lamellar phases [14]. Other research groups have also studied this type of complex [6, 8, 12]. Here, we present the synthesis and mesogenic properties of several new tetracoordinate copper(II) complexes of two types, the general structures of which are;



Sketch 1

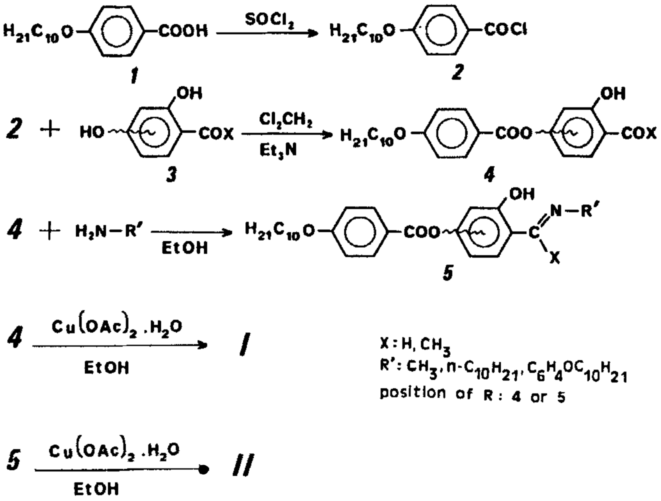
2. Experimental

2.1. *Synthesis*

The synthesis of the copper(II) complexes was carried out using the method illustrated in scheme 1.

2.2. *Preparation of the ligands*

The preparation of the ligands was involved conventional procedures [18].



Scheme 1

2.3. *Preparation of type I complexes*

The copper(II) complexes of type I were synthesized as described elsewhere [14].

2.4. *Preparation of type II complexes*

The copper(II) chelates of the Schiff's bases were prepared by the addition of an ethanolic solution (20 ml) containing $Cu(OAc)_2 . H_2O$ (1 mmole) to a hot ethanolic solution of the appropriate imine (2 mmole). The solution was refluxed for one hour. After cooling the precipitate was collected by filtration and recrystallized from a mixture of chloroform and ethanol. Table 1 lists the results from elemental analysis and yields for type I and type II complexes.

Table 1. The elemental analysis and yields for type I and type II complexes.

Complexes	*X*	Position of *R*	*R'*†	C/%	H/%	N/%	Yield/%
Type I	H	4	–	67·4(67·3)	6·9(6·5)		98·4
	H	5	–	66·8(67·3)	6·5(6·5)		90·1
	CH_3	4	–	67·6(67·8)	7·6(7·0)		82·3
	CH_3	5	–	66·9(67·8)	7·4(7·0)		96·4
Type II	H	4	ϕ-$OC_{10}H_{21}$	72·3(72·8)	9·1(8·2)	2·2(2·1)	92·0
	H	5	ϕ-$OC_{10}H_{21}$	72·7(72·8)	8·7(8·2)	2·3(2·1)	90·5
	H	4	n-$C_{10}H_{21}$	71·7(71·9)	9·7(8·8)	2·7(2·5)	94·7
	H	5	n-$C_{10}H_{21}$	71·3(71·9)	9·4(8·8)	2·6(2·5)	92·0
	H	4	CH_3	67·6(67·9)	7·9(7·2)	3·3(3·2)	87·9
	H	5	CH_3	67·3(67·9)	7·6(7·2)	3·1(3·2)	86·0
	CH_3	4	ϕ-$OC_{10}H_{21}$	73·2(73·0)	8·9(8·3)	1·9(2·1)	59·4
	CH_3	5	ϕ-$OC_{10}H_{21}$	72·5(73·0)	8·9(8·3)	1·9(2·1)	74·5
	CH_3	4	n-$C_{10}H_{21}$	71·8(72·2)	9·3(8·9)	2·9(2·4)	78·7
	CH_3	5	n-$C_{10}H_{21}$	72·9(72·2)	9·5(8·9)	2·8(2·4)	47·4

† The phenyl group is represented as ϕ.

2.5. *Characterization*

The microanalysis was performed using a Perkin–Elmer 240B microanalyser. Infrared spectra for all the complexes were obtained using a Perkin–Elmer 1600 (series FTIR) spectrometer. The visible absorption spectra for the metal complexes were recorded in chloroform using a Perkin–Elmer 200 spectrophotometer. The optical textures of the mesophases were studied with a Meiji polarizing microscope equipped with a Mettler FP82 hot stage and an FP80 central processor. The transition temperatures were measured by differential scanning calorimetry using a Perkin–Elmer DSC-2 operated at a scanning rate of 10°C/min on heating. The apparatus was calibrated with indium (156·6°C, 28·4 J/g) and tin (232·1°C; 60·46 J/g) as standards. Thermogravimetric analyses were obtained on a Perkin–Elmer TGS-2 equipped with a system 4 microprocessor controller at a heating rate of 10°C/min under a nitrogen atmosphere. X-ray diffraction patterns were obtained on magnetically aligned samples. We used a point focused monochromatic CuKα X-ray beam issued from the reflection by a double bent pyrolitic graphite. The sample was held in a Lindemann glass tube in the inlet of a magnet (0·3 to 1·7 Tesla) and the patterns were recorded on photographic film.

3. Results and discussion

3.1. *Synthesis and characterization*

Copper complexes of types I and II are prepared by reacting the appropriate ligand with copper(II) acetate monohydrate in warm ethanol. The complexes are isolated as green or green-brown solids in good yields and are soluble in dioxane, chloroform, benzene and insoluble in ethanol, petroleum ether and, hexane. The elemental analyses of the complexes are consistent with their proposed structures. The type I copper complexes show a $\nu(\mathrm{C}\underline{\cdot\cdot}\mathrm{O})$ stretch between 1615–1624 cm^{-1} and type II complexes show a $\nu(\mathrm{C}\underline{\cdot\cdot}\mathrm{N})$ stretch in the range 1615–1632 cm^{-1} for aldehyde derivatives and 1600–1610 cm^{-1} for ketone derivatives. The $\nu(\mathrm{C{=}O})$ stretch of the ester group appears between 1718–1735 depending on the ligand. In some cases this band shows a double peak due to the fact that the ester group allows the aromatic ring to revolve around the O–C (aromatic) bond. The I.R. data are collected in table 2. The electronic spectra of the type I complexes show an absorption band centred at $\lambda = 675$ nm for complexes derived from an aldehyde and $\lambda = 664$ nm for ketone derivatives, again the data is gathered in table 2. Data of visible spectra of type II complexes are more difficult to generalize and also are collected in table 2. The data are consistent with a square planar structure for the complexes. The stability of the complexes was studied by thermogravimetry, all the type II complexes are stable until 290°C at which decomposition is observed. Type I complexes are less stable and decompose at the temperature of transition to the isotropic liquid.

Table 2. The I.R. and visible spectroscopic data for type I and type II complexes.

Complex	X	Position of R	R'†	$\nu(\mathrm{C}\underline{\cdot\cdot}\mathrm{O})$	$\nu(\mathrm{C}\underline{\cdot\cdot}\mathrm{N})$§	$\nu(\mathrm{CO{=}O})$‖	λ
Type I	H	4	—	1620	—	1739, 1726	674
	H	5	—	1624	—	1718	676
	CH_3	4	—	1617	—	1721	664
	CH_3	5	—	1615	—	1725	666
Type II	H	4	ϕ-OC_{10}	—	1615	1730, 1720^{sh}	670
	H	5	ϕ-OC_{10}	—	1617	1725, 1738^{sh}	656
	H	4	n-$C_{10}H_{21}$	—	1620	1720	645
	H	5	n-$C_{10}H_{21}$	—	1631	1720	651
	H	4	CH_3	—	1625	1720, 1735^{sh}	651
	H	5	CH_3	—	1635	1725	639
	CH_3	4	ϕ-OC_{10}	—	1606	1739	645
	CH_3	5	ϕ-OC_{10}	—	1607	1731	653
	CH_3	4	n-$C_{10}H_{21}$	—	1602	1724	609
	CH_3	5	n-$C_{10}H_{21}$	—	1605	1728	610

† ϕ-OC_{10} represents $C_6H_4OC_{10}H_{21}$. ‡ I.R. stretch band of carbonylic group. § I.R. stretch band of imine group. ‖ I.R. stretch band of ester group; sh signifies shoulder.

3.2. *Mesogenic behaviour*

The phase transition temperatures and enthalpy changes of type I and type II complexes are given in tables 3 and 4 respectively. In type I complexes only the compound derived from 2,5-dihydroxybenzaldehyde exhibits liquid crystalline properties. All the copper(II) complexes with Schiff's bases derived from 2,4-dihydroxybenzaldehyde show thermotropic mesophases. The type II complexes derived from

Table 3. The optical, thermal and thermodynamic data for type I complexes.

n	*X*	Position of *R*	Transition	Temperature °C	Δ*H*/(kJ/mole)
10	H	4	C_1-C_2	135·5	11·8
			C_2-C_3	146·9	9·7
			C_3-I(dec·)	237·0	68·7
10	H	5	C_1-C_2	70·8	51·4
			C_2-S_C	190·3	14·3
			S_C-I(dec·)	240·8	26·5
10	CH_3	4	C_1-C_2	179·9	8·5
			C_2-I(dec·)	222·5	57·0
10	CH_3	5	C_1-C_2	65·7	90·3
			C_2-I(dec·)	206·6	51·3

Table 4. The optical, thermal and thermodynamic data for type II complexes.

n	*X*	Position of *R*	*R'*†	Transition	Temperature °C	Δ*H*/kJ/mole
10	H	4	ϕ-$OC_{10}H_{21}$	C-S_1	120·6	32·2
				S_1-S_C	163·6	28·9
				S_C-N	247·9	16·4
				N-I	248·5	7·5
10	H	5	ϕ-$OC_{10}H_{21}$	C_1-C_2	59·2	3·6
				C_2-C_3	119·0	
				C_3-I	119·2	7·8
10	H	4	*n*-$C_{10}H_{21}$	C-N	115·7	16·6
				N-I	134·0	0·8
10	H	5	*n*-$C_{10}H_{21}$	C-I	103·9	72·6
10	H	4	CH_3	C-S_C	173·9	
				S_C-N	178·2	64·9
				N-I	224·0	15·4
10	H	5	CH_3	C-S_C	187·4	36·9
				S_C-N	237·5	3·0
				N-I	265·7	2·1
10	CH_3	4	ϕ-$OC_{10}H_{21}$	C_1-C_2	106·5	46·1
				C_2-C_3	184·3	4·0
				C_3-C_4	201·0	2·9
				C_4-I	228·0	54·3
10	CH_3	5	ϕ-$OC_{10}H_{21}$	C-I	190·0	69·2
10	CH_3	4	*n*-$C_{10}H_{21}$	C-I	142·3	90·1
10	CH_3	5	*n*-$C_{10}H_{21}$	C-I	115·6	23·4

†The phenyl group is denoted by ϕ.

2,5-dihydroxybenzaldehyde are only mesogenic if derived from *N*-methylimine. None of the copper(II) complexes derived from ketoimine were liquid-crystalline.

3.3. *Type I complexes*

The geometry of the type I complexes (2,4- and 2,5-derivatives) accounts for their mesogenic behaviour. 2,4-derivatives have a geometry which does not favour mesogenic properties because the ester group does not lie in the direction of the main axis of the molecule; instead they form a Z-shape, which is unlikely to favour the ordering after melting (figure 1 (*a*)) and it can be seen from the thermal data (table 3) that these complexes are not liquid crystals. On the other hand, we can see in figure 1 (*b*), that in the 2,5-derivatives the ester group lies in the same direction as the main axis of the molecule, and this should favour the appearance of mesomorphism. In fact, the complex derived from 2,5-dihydroxybenzaldehyde displays a smectic C mesophase over a range of approximately 50°C. None of the ketone derivatives (neither the 2,4-substituted nor the 2,5-substituted derivatives) was liquid crystalline. We attributed this to the steric effect of the methyl group which when compared to hydrogen increases the molecular width. This methyl group also causes distortions from the planarity of the molecule which hinder mesogenic behaviour.

3.4. *Type II complexes*

Type II complexes were synthesized from imines as ligands. The 2,4-dihydroxy derivative complexes may be represented as two rod-like structures joined by a central group (figure 2) where the central part is planar and the terminal chains are parallel to each other. We have already seen that all the 4-substituted aldehyde complexes are mesogenic. The complex in which *R'* = $C_6H_4OC_{10}H_{21}$ exhibits two smectic mesophases, a S_C phase and the other, S_1, at a lower temperature which was identified as S_G by its optical textures [19, 20].

The results for the *N*-alkylimine complexes are even more interesting. The complex in which *R'* = CH_3 shows enantiotropic S_C and N mesophases and for the complex *R'* = *n*-$C_{10}H_{21}$ only a nematic mesophase was observed. This may be explained because the decyl group is long and is probably situated parallel to the main axis of the molecule and prevents the adequate molecular packing required to produce a smectic phase, whereas the smaller size of the methyl group allows greater interaction

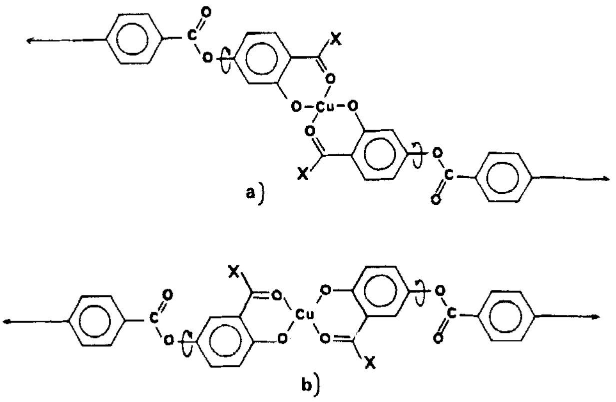


Figure 1.

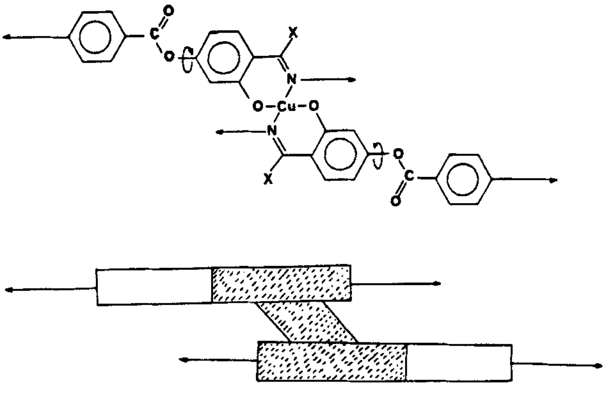


Figure 2.

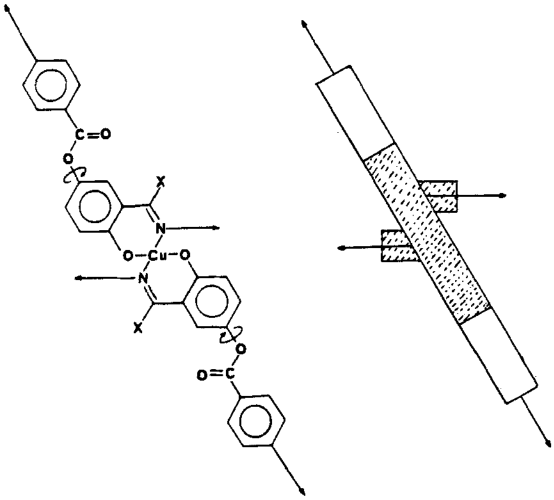


Figure 3.

between the aromatic parts of the molecular and, as a consequence, more ordered mesophases appear. The stability of the mesophase is also increased by about 90°.

The 2,5-dihydroxyderivative complexes have a molecular structure which is totally different from that of the 2,4-derivative complexes. The terminal chains form a cross. Schematically these complexes may be represented as a rod-like structure comprising a long mesogenic unit and two lateral substituents which may hinder the molecular packing necessary for liquid crystalline properties (figure 3). In fact, only the *N*-methylimine derivative exhibits mesomorphic properties (a smectic C and nematic phase). Neither the *N*-decyl nor the *N*-decyloxyphenyl imine derivative complexes are mesogenic. Only four complexes derived from *o*-hydroxyacetophenone were prepared. The *N*-methyl(*o*-hydroxyacetophenone)imine could not be synthesized in sufficient yields and due to this, their complexes could not be studied. None of the ketone derivatives display mesomorphism (see table 4). The steric effect of the methyl group is of fundamental importance. Not only does it increase the molecular width, but may well also distort the normal square-planar coordination geometry of the copper(II) towards a tetrahedral geometry [21].

3.5. *X-ray studies*

Four compounds of type II were studied by X-ray diffraction using an aligning magnetic field; the 4-substituted aldehyde complexes with $R' = C_6H_4OC_{10}H_{21}$, $R' = n\text{-}C_{10}H_{21}$ and $R' = CH_3$, and the 5-substituted aldehyde derivative with $R' = CH_3$. The samples of the 4-substituted complexes with $R' = n\text{-}C_{10}H_{21}$ and $R' = CH_3$ were studied in the nematic phase and the diffraction patterns indicate that the short axes of the molecules are orientated parallel to the magnetic field; this suggests that the anisotropy of the magnetic susceptibility is negative in these compounds. The long axes may adopt any orientation on a plane perpendicular to the field which precludes the formation of a single domain if the sample container is fixed. Therefore the sample is better orientated when the capillary tube rotates around its axis which is perpendicular to the magnetic field, the director then being aligned along this axis. The same procedure of orientation has proved to be effective for some lyotropic [22] and disc-like [23] mesophases of a nematic type. The other two compounds (4-substituted complex with $R' = C_6H_4OC_{10}H_{21}$ and 5-substituted complex with $R' = CH_3$) were studied in the smectic C phase and the alignment was more difficult. The anisotropy of the magnetic susceptibility appears to be negative for the 2,4-derivative complexes and positive for the 2,5-derivative complex.

The X-ray patterns obtained either in the nematic or in the smectic C phase show no appreciable differences if compared with those of conventional mesophases. In contrast to the copper diimino complexes described in [24] in which the molecules are coupled in a side-by-side array in the smectic A phase, in the present case there is no obvious evidence of the pairing of the ligands neither in the nematic nor in the smectic C phase. Fluctuations of smectic C ordering (skewed cybotatic groups) appear in the nematic phase and one can measure the apparent periodicity of such fluctuations as well as the tilt angle of the director with respect to the wave vector of the fluctuations. The experimental measurements will be examined in detail in a future paper.

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