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Thermotropic Mesomorphism in Some Cu(II) and Pd(II) Metallorganic Complexes

Ugo Caruso[a]; Antonio Roviello[a]; Augusto Sirigu[a]
[a] Dipartimento di Chimica, Universita' di Napoli, Napoli, Italy

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Thermotropic mesomorphism in some Cu(II) and Pd(II) metallorganic complexes

by UGO CARUSO, ANTONIO ROVIELLO and AUGUSTO SIRIGU
Universita' di Napoli, Dipartimento di Chimica, Via Mezzocannone 4,
80134 Napoli, Italy

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The synthesis and liquid crystal properties of some bis(*N*-*p*-(*n*-alkoxy)phenyl, *p*-(*n*-alkoxy)salicylaldiminato)copper(II), of a homologous series of bis(*N*-*p*-(*n*-alkanoyloxy)phenyl, *p*-(*n*-alkanoyloxy)salicylaldiminato)copper(II), and of some corresponding palladium(II) complexes are reported. All of the compounds examined exhibit enantiotropic smectic mesomorphism, predominantly of the C type. Palladium(II) complexes are mesomorphic up to higher temperatures than the copper(II) homologues.

1. Introduction

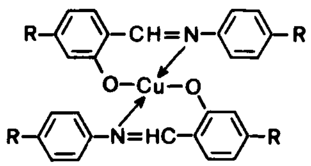
In the recent literature on liquid crystals the increasing number of mesogens containing Cu(II) or Pd(II) atoms underlines the versatility of the square-planar coordinate geometry, which is typical of those atomic species, in the building of molecular groups with actual or potential mesogenic properties. The occurrence of nematic, smectic or discotic mesomorphism has been reported [1-6]. Smectogenic properties have also been observed in polymeric molecules containing square-planar complexed Cu(II) in the monomer units [7].

A detailed investigation of metallorganic mesogens involves, in its most simple form, the examination of pairs of homologous compounds which differ only by the nature of the metal atom used in order to infer its specific role. On the other hand, the investigation of the influence of the chemical and structural peculiarities of the organic ligand on the mesophasic properties, including, as for the conventional organic mesogens, those with the flexible terminal chains (frequently but not necessarily four of them in this class of complexes and not necessarily equal). The results of such an investigation on some bis-salicylaldiminato square-planar metal complexes are reported in this paper.

2. Experimental

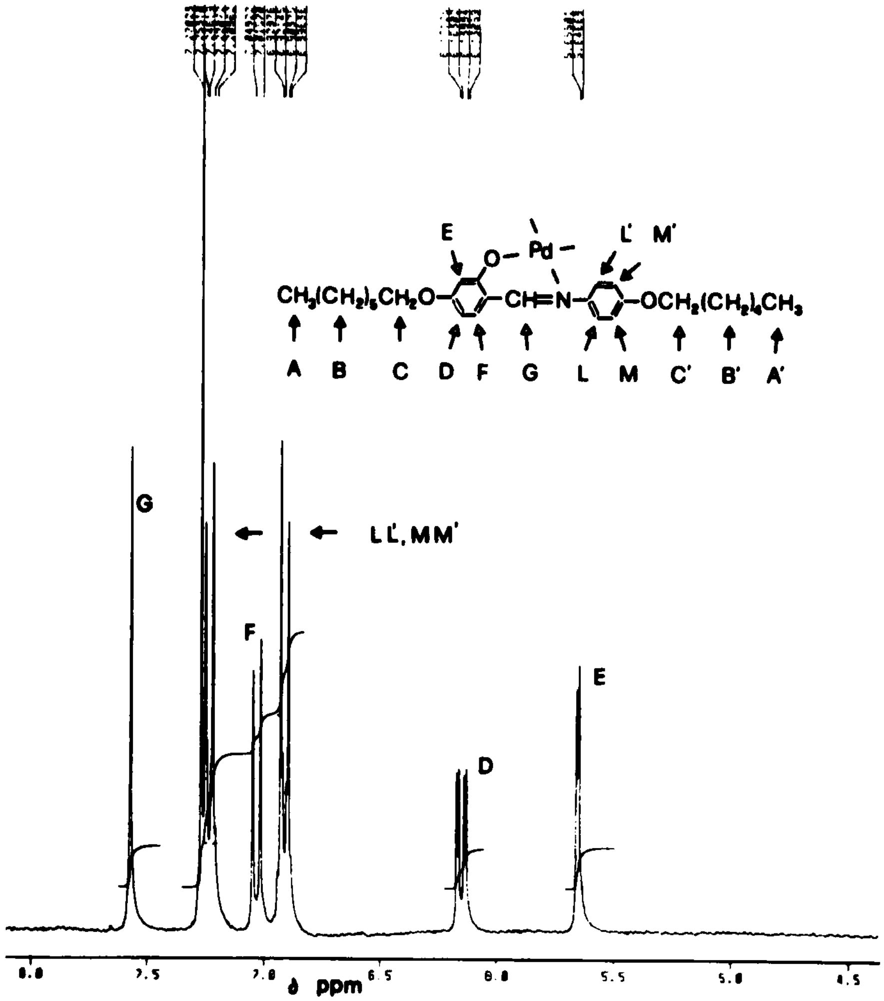
Copper(II) complexes with the formula

CuCnES =



$R = -OOC(CH_2)_{n-2}CH_3$

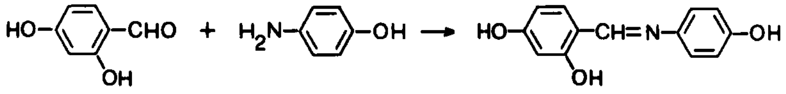
have been prepared for $n = 6$ to 12. They will be referred to as CuCnES. A single analogous compound, PdC8ES, containing Pd(II) in place of copper, was also



(*a*)

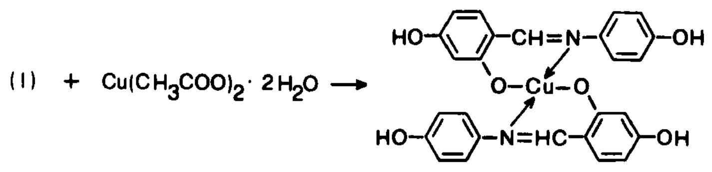
prepared. The synthesis involved the following steps:

(1)



(I)

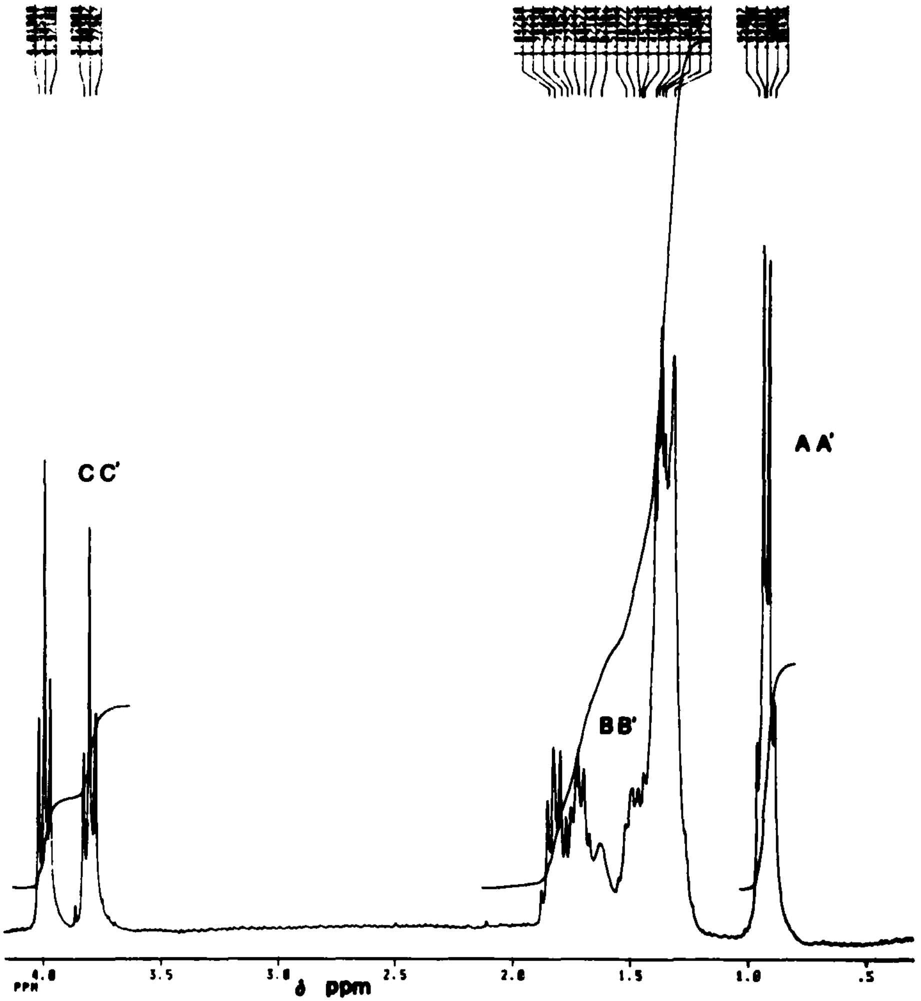
(2)



(II)

(3) (II) + $4CH_3(CH_2)_{n-2}COCl$ to give CuCnES

Step (1) is a straightforward reaction in refluxing absolute ethanol. The imine (I) (melting point 497 K) precipitates by cooling after dilution with water. (For example,



(*b*)

Figure 1. 270 MHz ^{1}H-N.M.R. spectrum of PdC76ET. Solvent $CDCl_3$, standard $CHCl_3$.

2·991 g of *p*-aminophenol and an equal amount of 2,4-dihydroxybenzaldehyde (3·786 g), dissolved in 50 ml absolute ethanol, were refluxed for 15 min. An equal volume of water was added and the solution cooled. 5·496 g of crystalline (I) were obtained (yield 87 per cent).)

The step (2) reaction was performed following two slightly different procedures for the copper and palladium complexes.

Copper complex: 5·496 g of imine (I) and 2·394 g of copper acetate previously dissolved in hot dioxane (respectively 50 ml and 30 ml) were mixed and kept for approximately 20 min at about 100°C. A cold solution of 3·00 g sodium acetate in 80 ml water was then added to the reaction mixture. From the cooled solution crystalline (II) is precipitated with a 91 per cent yield.

Palladium complex: a solution of 0·2522 g imine (I) in 30 ml dried dioxane and a solution of 0·2105 g $Pd(C_6H_5CN)_2Cl_2$ in 30 ml dried dioxane were mixed and allowed to react at room temperature for 15 min; 70 ml *n*-hexane were then added to the reaction mixture. Microcrystalline (II) was precipitated by cooling at about 0°C; yield 89 per cent.

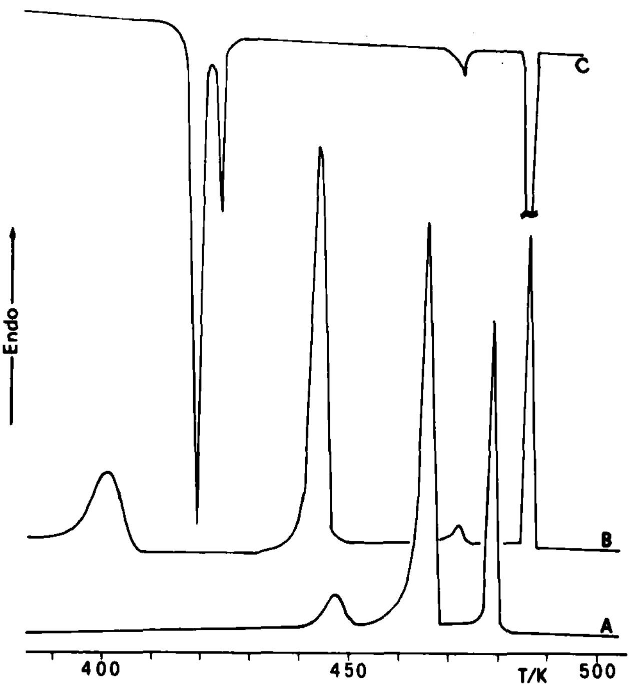


Figure 2. D.S.C. thermograms. (A) CuC8ES, heating run; (B) PdC76ET, heating run; (C) PdC76ET, cooling run.

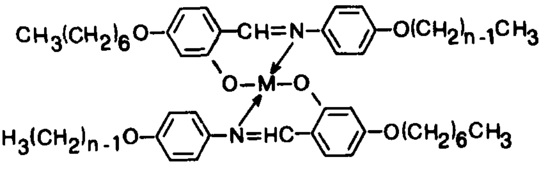
Compounds *M*C*n*ES (*M* = Cu or Pd) were obtained by interfacial esterification of (II) with the appropriate alkanoylchloride. As an example, the synthesis of CuC9ES is reported in some detail.

1·0030 g of (II) (*M* = Cu) were dissolved in 120 ml water containing 0·532 g of potassium hydroxide and 2·0 g benzyltriethylammoniumchloride. To this solution was added, stirring rapidly, a solution of 1·4040 g (3 per cent stoichiometric excess) *n*-nonanoylchloride in 50 ml chloroform. After about 10 min stirring the chloroform phase was separated and CuC9ES precipitated by addition of 150 ml ethanol. The compound, purified by column chromatography (Florisil, chloroform as eluent), crystallized in large deep-green crystals.

The ^{1}H-N.M.R. spectrum of PdC8ES in $CDCl_3$ solution is consistent with the formula. For CuC8ES and CuC11ES the copper content, given as Cu O per cent, has been determined quantitatively with the following result: CuC8ES, 7·71 calculated, 7·81 found; CuC11ES, 6·67 calculated, 6·65 found.

Palladium(II) and copper(II) complexes with the general formula

MC7nET =



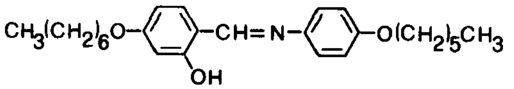
with *n* = 6, 10, have been prepared; they will be referred to as *M*C7*n*ET (*M* = Cu or Pd). The synthesis and the properties of CuC76ET have already been described [2, 7]; CuC710ET was prepared by an analogous procedure.

Figure 3. CuC9ES, smectic phase at 463 K, crossed polarizers.

The corresponding palladium complexes were prepared in a somewhat different way. As an example, we now outline the preparation of PdC76ET.

The ligand imine (III) was prepared according to a procedure already described [7] and its nature confirmed by ^{1}H-N.M.R. spectroscopy.

(III)



15 ml of a dioxane solution of 0·6440 g of imine (III) were added to 10 ml absolute ethanol solution containing 0·064 g sodium hydroxide at room temperature. To this mixture a solution containing 0·3000 g $Pd(C_6H_5CN)_2Cl_2$ in 15 ml dioxane was added at room temperature with stirring. After about 10 min 40 ml water was added to the reaction mixture; the palladium complex precipitated with 75 per cent yield. After a preliminary recrystallization from an 80/20 volume ethanol/chloroform mixture, the compound was further purified by column chromatography (Florisil, chloroform as eluent) and finally crystallized by the addition of 95 per cent ethanol to the chloroform

Figure 4. PdC76ET, smectic C phase at 460 K, crossed polarizers.

solution. The ^{1}H-N.M.R. spectrum of the metal complexes is consistent with their expected structure. Figures 1(*a*), (*b*) show the spectrum of PdC76ET.

The characterization of the liquid crystal properties was performed, for all the compounds, by differential scanning calorimetry (D.S.C.) with a Mettler TA3000 apparatus. A Leitz polarizing microscope and a Mettler FP5 microfurnace were used for the optical detection of the phase transitions and, in particular, for the textural analysis of the liquid crystal phases. A further characterization was performed by X-ray diffraction analysis (flat-film camera, CuK$_\alpha$ radiation) at the appropriate temperature.

3. Results and discussion

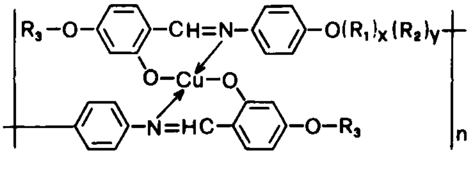
The table reports some thermodynamic data useful for the characterization of the complexes. Solid phase transition temperatures are also given, indicating that most of the compounds exhibit solid state polymorphism (see figure 2). This is, however, a rather peripheral point and no reference will be made to it.

All of the compounds exhibit smectic mesomorphism and many of them show smectic polymorphism. The smectic C phase, with both schlieren and broken fan

Figure 5. PdC76ET, smectic A phase at 477 K, crossed polarizers.

textures (see figure 3), is the only liquid crystal phase observed for most of the compounds CuCnES. Only CuC7ES shows both smectic A (fan and homeotropic textures) and enantiotropic smectic C (schlieren texture) phases. CuC6ES exhibits enantiotropic smectic A mesomorphism (fan and homeotropic textures) while a broken fan texture, possibly indicative of a monotropic smectic C phase, is sometimes observed, but only on cooling from the smectic A. All of the other compounds, including PdC8ES, exhibit enantiotropic smectic mesomorphism, both of the C (see figure 4) and of the A type (see figure 5). It is worth noting that smectic mesomorphism is also shown by polymeric compounds (*IV*) whose monomer units are strictly related to the copper complexes presented here [7].

(IV)



Thermodynamic data for the phase transitions.

n	T_k/K	T_m/K	T_l/K	T_i/K	ΔH_m/kJ mol^{-1}	ΔH_i/kJ mol^{-1}	d/Å	T/T_i
CuC*n*ES								
6	476	482	†	488	38·9	9·8	‡	
7	462	472	478	481	41·8	12·2	‡	
8	446	466		480	34·6	13·7	28·6	0·99
9	433	458		473	34·0	14·6	29·9	0·99
10	434	450		468	36·4	15·5	31·2	0·99
11	436	446		465	40·3	16·3	32·4	0·99
12		438		457	45·3	16·4	33·3	0·98
CuC7*n*ET								
6		423	428	441	46·3	10·9	26·1	0·97
10		413	424	433	47·8	10·8	30·8	0·99
PdC7*n*ET	§							
6	404	444	474	488	44·0	10·2	26·0	0·98
10	411	432	463	473	44·4	10·4	29·6	0·99
PdC8ES	486	511	520	523	49·7	11·9	‡	

T_k = solid phase transition temperature; T_m = melting temperature; T_l = smectic C–smectic A transition temperature, T_i = temperature for formation of the isotropic phase; ΔH_m = molar melting enthalpy, inclusive of solid phase transition enthalpy; ΔH_i = molar enthalpy for formation of the isotropic phase, inclusive of smectic–smectic transition enthalpy (1·3 kJ mol^{-1} for PdC76ET and PdC710ET, not separately measured for CuC7ES and PdC8ES); d = smectic periodicity measured at temperature T.

† Monotropic.

‡ Not measured.

§ Monotropic phase transition observed on cooling at 425 K for PdC76ET, at 410 K for PdC710ET. $\sigma T_i/T_i = 0{\cdot}003$; $0{\cdot}05 > \sigma\Delta H_i/\Delta H_i > 0{\cdot}01$; $\sigma d/d = 0{\cdot}02$.

R_1 = –$(CH_2)_{12}$–O–; R_2 = –$(CH_2–CH_2–O)_3$–; x, y = mole fractions, with $y = 1 - x = 0, 0{\cdot}25, 0{\cdot}50, 0{\cdot}75, 1$. R_3 = $CH_3(CH_2)_5CH_2$–.

The smectic structural periodicity, measured by X-ray diffraction methods at temperatures just below the transition to the isotropic phase, increases fairly regularly with increasing length of the aliphatic terminal chains for all types of compounds. The results of a crystal and molecular structure determination by single crystal X-ray diffraction on CuC76ET [8] show that the length of the molecule, in its almost completely extended conformation, is about 30 Å. The comparatively smaller structural periodicity measured for this compound (26·1 Å at T/T_i = 0·97) in the smectic A phase might be the consequence of a further substantial disordering of the alkyl chains occurring on melting. (Also, a moderate interdigitation would have analogous effects. However, this feature is virtually absent in the crystal packing). On similar grounds the periodicities measured for the other compounds and their variation with increasing length of the terminal chains (e.g. an average of 1·2 Å per added methylene group to each terminal chain for CuCnES compounds) might be accounted for, taking also into account, for the smectic C phases, a possible tilting of the long molecular axis with respect to the layer normal. The modest increase of the molar enthalpy for forming the isotropic phase with increasing length of the methylenic terminals (0·17 kJ per mole per additional methylene group going from CuC8ES to CuC12ES; there is essentially no increase for compounds *M*C7*n*ET) is consistent with a model for the smectic packing in which the terminal chains are still elongated but conformationally disordered.

Although the structural analogy between ES and ET compounds is only partial, the systematically higher temperatures for melting and isotropic phase formation found for the former appear to be significantly related to the different nature of the chemical link between alkyl chains and the molecular core. However, the explanation of such different behaviour is not straightforward. Existing data on homologous series of mesogens of largely different molecular structure show that the reverse trend may also occur [9, 10].

Replacing copper with palladium in totally homologous compounds has a drastic effect, raising the melting point and, even more, isotropic transition temperatures. In particular, for compounds of the class *M*C7*n*ET, the comparatively moderate increase of the melting point produces a considerable broadening of the thermal stability interval of the mesophase. A crystal structure determination of PdC76ET is underway to detect possible molecular structure and molecular packing differences from the analogous copper(II) complex.

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