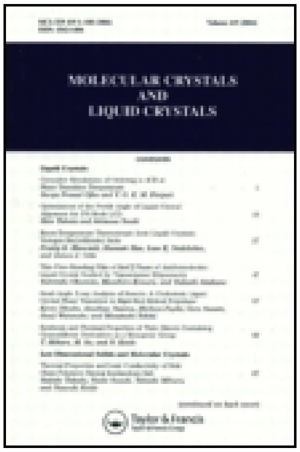


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Transition Metal Complexes with Ordered Mesophases: Cyclopalladated Compounds of (p-Ethoxyphenylazo)-p-Phenyl Heptanoate

M. Ghedini [a] , S. Licoccia [a] , S. Armentano [a] & R. Bartolino [b]
[a] Dipartimento di Fisica, Univesità della Calabria, Arcavacata(CS), 87030, Italy
[b] Dipartimento di Fisica, Università della Calabria, Arcavacata(CS), 87030, Italy

Version of record first published: 20 Apr 2011.

To cite this article: M. Ghedini , S. Licoccia , S. Armentano & R. Bartolino (1984): Transition Metal Complexes with Ordered Mesophases: Cyclopalladated Compounds of (p-Ethoxyphenylazo)-p-Phenyl Heptanoate, Molecular Crystals and Liquid Crystals, 108:3-4, 269-275

To link to this article: http://dx.doi.org/10.1080/00268948408078679

Mol. Cryst. Liq. Cryst., 1984, Vol. 108, pp. 269–275
0026-8941/84/1084-0269/$18.50/0

Printed in the United States of America

Transition Metal Complexes with Ordered Mesophases: Cyclopalladated Compounds of (*p*-Ethoxyphenylazo)-*p*-Phenyl Heptanoate

M. GHEDINI, S. LICOCCIA and S. ARMENTANO

Dipartimento di Chimica, Università della Calabria, 87030 Arcavacata (CS), Italy

and

R. BARTOLINO

Dipartimento di Fisica, Università della Calabria, 87030 Arcavacata (CS), Italy

(*Received August 1, 1983; in final form February 2, 1983*)

The synthesis, characterization and thermal behaviour of dinuclear and mononuclear cyclopalladated derivatives of (*p*-ethoxyphenylazo)-*p*-phenyl heptanoate are reported.

The dinuclear halo-bridged complexes show nematic phases at temperatures increasing in the order Cl < Br < I.

The breaking of the halogen bridge by pyridine or quinoline affords a new series of mononuclear liquid crystals in which a layered smectic phase is present. The connection between the nature of the neutral nitrogenous ligand and the thermal properties of the mononuclear complexes is also discussed.

INTRODUCTION

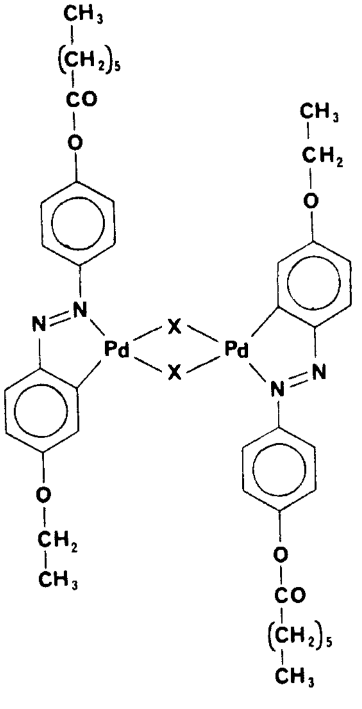
Liquid crystals are still receiving considerable attention because of their numerous applications.[1–5] To a large extent, most of the liquid crystals currently studied are organic in nature, while very little is know about organometallic species.

Recently we reported that palladium(II) complexes with mesogenic azobenzene ligands bonded through a metal-carbon σ bond and having a metal–metal chlorine bridge display ordered mesophases.[6] In this new class of organometallic compound, coordination increases the phase transition temperature by about 100°.

In order to elucidate the influence of the bridging halide on the thermal properties of these compounds, we have carried out a systematic study of a series of palladium(II) derivatives of (*p*-ethoxyphenylazo)-*p*-phenyl heptanoate (AB).

SYNTHESIS AND CHARACTERIZATION

The previously characterized[6] chloro-bridged complex 1



1; X = Cl, Br, I

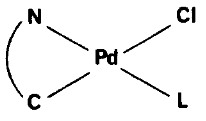
easily reacts with LiX to yield compounds for which the elemental analyses are in agreement with the formation of its metathetical products (X = Br, 2; X = I, 3. Table I).

Cyclometallated dinuclear compounds, such as 1, undergo bridge splitting reactions with nitrogenous neutral ligands.[7] Complex 1, in fact, reacts with pyridine, quinoline and aniline to give compounds 4–6 (see Table I) according to equation (1).

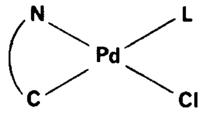
$$[PdX(AB\text{-}H)]_2 + 2L \rightarrow 2[PdX(AB\text{-}H)L] \qquad (1)$$

In the far infrared spectra of the mononuclear species 4–6, the Pd-Cl stretching absorptions occur at 345, 310 and 308 cm^{-1} respectively.

Reaction (1) may lead to two isomeric forms, **I** and **II**:



I



II

Crociani *et al.*[8] established that ν(Pd-Cl) frequencies, where Cl is in the *trans*-position to a Pd-C bond, (**I**), fall in the range 300–280 cm^{-1}, significantly lower than those (355–320 cm^{-1}) for the corresponding *cis*-isomer, (**II**).

TABLE I

Analytical and far infrared data for $[PdX(AB\text{-}H)]_2$[a] and [PdX(AB-H)L] complexes

	X	L	Yield (%)	Found (calc.) %C	%H	%N	ν(Pd-Cl), cm^{-1}[b]
1	Cl	—	55	50.8 (50.9)	5.3 (5.1)	5.8 (5.7)	341, 320, 242
2	Br	—	90	47.7 (46.7)	4.7 (4.7)	5.2 (5.2)	—
3	I	—	90	42.6 (43.0)	4.2 (4.3)	4.6 (4.8)	—
4	Cl	Pyridine	60	54.0 (54.4)	4.4 (5.3)	7.0 (7.3)	345
5	Cl	Quinoline	65	56.7 (57.7)	5.0 (5.2)	6.3 (6.7)	310
6	Cl	Aniline	60	54.6 (55.1)	5.3 (5.5)	6.5 (7.1)	308

[a] AB = (*p*-ethoxyphenylazo)-*p*-phenyl heptanoate.
[b] Nujol mulls.

Although for our complexes the far infrared evidence accounts for only one isomer (single ν(Pd-Cl) absorption), its nature (**II**) can be unequivocally established only for complex 4 (ν(Pd-Cl) = 345 cm^{-1}.

As far as we can judge, the palladium-nitrogen bond is very similar in compounds 4 and 5; therefore the lower ν(Pd-Cl) frequency observed in the spectrum of 5 leads us to suggest a *cis*-geometry, (*I*), for 5 as well as for complex 6.

THERMAL PROPERTIES

The nature of the mesophases displayed by complexes 1–6 was confirmed by miscibility experiments. In these experiments the reference compound was terephthal-*bis*-(4-*n*-butylaniline), (TBBA), a well characterized liquid crystalline material with transition temperatures similar to those observed for the compounds under investigation.[9] Attempts to obtain miscibility diagrams using other liquid crystalline materials such as *N*-(4-*n*-butyloxybenzylidene)-4′-*n*-heptylaniline (40.7) were unsuccessful.

Compound 1 displays a strongly birefringent and fluid nematic mesophase between 190 and 205°C.

Compound 2 shows, at 175°C, a solid–solid structural phase transition where larger domains aggregate. Between 210 and 215°C a polydomain texture S_A forms. Such a system is weakly birefringent and highly dense. The nematic phase, however, which has a very large temperature range, is fluid and spontaneously highly homeotropic, but with some textural imperfections. The sudden clearing to the isotropic

TABLE II

Thermal properties of metallated liquid crystals

Compd. no.	Mesophases and transition temperatures (°C)
1	K ↔ 190 (N) ↔ 205 (I)
2	$K \leftrightarrow 175(K') \rightarrow 210(S_A) \leftrightarrow 215(N) \leftrightarrow 250(I)$ $190 \nwarrow\ 205(S_B) \swarrow$
3	$K \rightarrow 220\ (S_A) \leftrightarrow 225\ (N) \leftrightarrow 230\ (I)$
4	$K \leftrightarrow 180\ (S_B) \leftrightarrow 198\ (N) \leftrightarrow 235\ (I)$
5	$K \leftrightarrow 136\ (S_A) \leftrightarrow 151\ (N) \leftrightarrow 180\ (I)$
6	K → 173–175 Decomposition
TBBA[a]	$K \rightarrow 113\ (S_H) \rightarrow 142\ (S_C) \rightarrow 172.5\ (S_A) \rightarrow 195.5\ (N) \rightarrow 235.5\ (I)$

[a] From ref. 9.

phase occurs uniformly. Upon cooling down, a S_B phase in a mosaic texture is observed between 205 and 190°C.

Compound 3 exhibits S_A and N phases (formed respectively on heating at 220°C and 225°C); both phases show little birefringence.

Compounds 4 and 5 both show a powder pattern behaviour in the solid phase; then upon heating, a very viscous lamellar mesophase, followed by a highly fluid nematic phase, is formed. All the transitions are quite well defined and all the phases are enantiotropic. Remarkably, in 5 the S_A phase spontaneously orientates very well.

Compound 6 does not display mesophases and melts with some decomposition.

CONCLUSIONS

The connection between molecular structure and thermal properties of these two series of organometallic mesomorphic compounds, 1–3 and 4–6, can be summarized as follows:

i) All the dinuclear halo-bridged complexes 1–3 exhibit roughly the same thermal behaviour, showing nematic phases with similar macroscopic characteristics. The temperatures at which the nematic phases appear seem to be related to the nature of the halogen atom, the transition temperatures increasing in the order Cl < Br < I.

ii) Mesomorphism occurs also for the mononuclear systems. Particularly, the breaking of the halogen bridge by nitrogenous neutral ligands (e.g., pyridine and quinoline) gives rise to liquid crystals in which a further smectic layered phase appears.

iii) Along the series of mononuclear complexes 4–6, we point out the different thermal behaviour observed when aniline, instead of pyridine or quinoline, is bonded to the metal center. No mesomorphism is observed in the case of aniline. These results indicate that the role played by such ligands is much more complicated than a simple steric effect. Further research must be conducted in order to elucidate the contribution of electronic affects, although, on the basis of the available data, the iminic ligands seem to be better than the aminic ones in relation to mesomorphic properties.

EXPERIMENTAL

Apparatus

Infrared spectra were obtained using a Perkin Elmer 180 spectrometer and nujol mulls. Elemental analyses were made by the Microanalysis

Laboratory of the Istituto di Farmacia of the University of Pisa, Pisa, Italy.

The transition temperatures and the textures of the various mesophases were observed by means of a Reichert Thermovar polarizing microscope equipped with a heating stage.

Preparation of the binuclear species

Complex 1 was prepared as previously described.[6] Complexes 2 and 3 were obtained by metathetical reactions with the appropriate lithium halide in acetone.

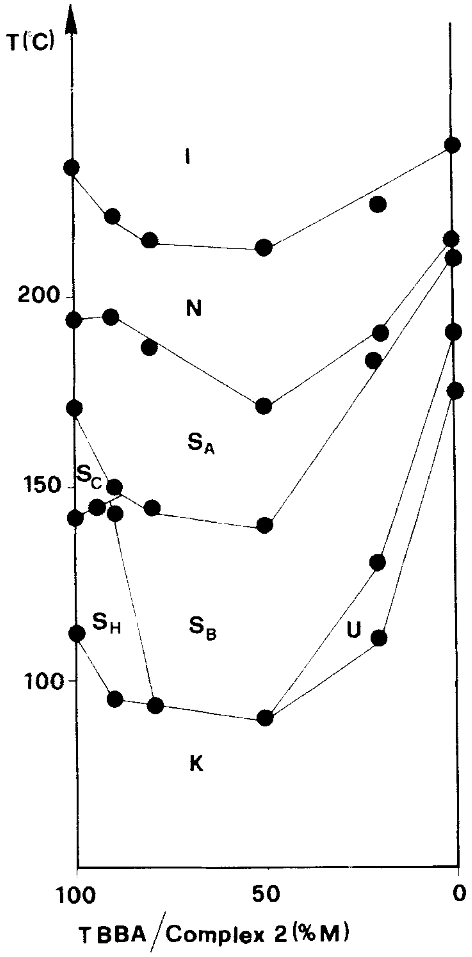


FIGURE 1 Miscibility phase diagram for complex 2 and TBBA: left side TBBA phase sequence; right side complex 2 phase sequence. Region U indicates an unidentified phase which could be either a solid phase (K′) or a S_H phase.

Bridge splitting reactions

An excess (about 4 : 1 molar ratio) of the entering ligand L (4, L = pyridine; 5, L = quinoline; 6, L = aniline) was added to a suspension of 1 in acetone. The mixture was stirred at room temperature for 48 hours, then evaporated under reduced pressure and chromatographed on a silica gel column (eluent: acetone). Evaporation of the solvent afforded pure products.

Miscibility experiments

Experiments were performed on mixtures in which the molecular ratios between TBBA and the appropriate complex 1–6 ranged from 0 to 100%. The miscibility diagram for complex 2 is reported in Figure 1, which is representative of the whole series.

Acknowledgment

This work was financed by the C.N.R. project "Chimica Fine e Secondaria."

References

1. G. J. Deboo and C. N. Burrows, "*Integrated Circuits and Semiconductor Devices: Theory and Applications*," McGraw-Hill, New York, 1982, pp. 303–311.
2. G. H. Brown and J. Walken, "*Liquid Crystals and Biological Structures*," Academic Press, New York, 1979.
3. O. Niwa, A. Kumano, T. Kajiyama, M. Takayamagi, T. Kumitake, and K. Kano, *Rept. Progr. Polym. Phys. Japan*, **24**, 741 (1981) and references therein.
4. B. Samorì and L. Fiocco, *J. Amer. Chem. Soc.*, **104**, 2634 (1982).
5. C. Eskenazi, J. F. Micaud and H. B. Kagan, *J. Org. Chem.*, **44**, 995 (1975).
6. M. Ghedini, M. Longeri, and R. Bartolino, *Mol. Cryst. Liq. Cryst.*, **84**, 207 (1982).
7. J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, **18**, 327 (1976).
8. B. Crociani, T. Boschi, R. Pietropaolo, and U. Belluco, *J. Chem. Soc. A*, 531 (1970).
9. R. Bartolino, J. Doucet, and G. Durand, *Ann. Phys. (Paris)*, **3**, 389 (1978).