

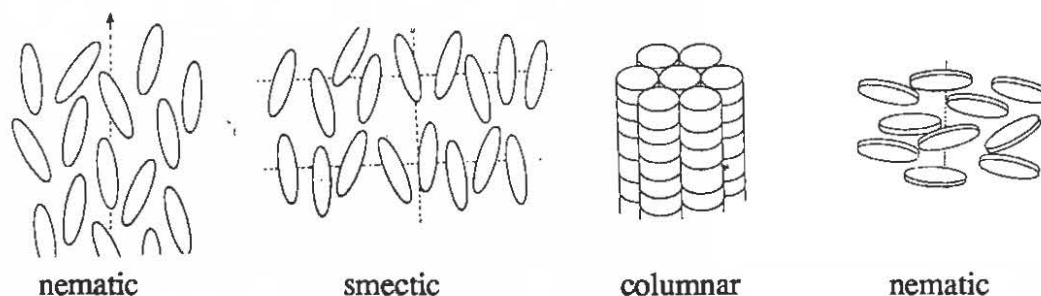
Transition Metals Complexed to Mesophases:
Palladium(II) Containing Metallomesogens

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Mesophase is an intermediate state of matter between the solid and the liquid, therefore the terms "liquid crystal" or "mesomorph" are also used. The liquid crystalline media have a unique combination of properties. They are fluids, and also have one or two-dimensional orientational order leading to anisotropic behavior. They form two big families, the thermotropics and the lyotropics. The thermotropics change phases by a change of temperature, and majority of the liquid crystals fall into this category. They can be divided into rod-like and disc-like liquid crystals. Polymeric liquid crystals are also known. Furthermore, the rod-like liquid crystals are sub-divided into smectics and nematics, whereas the disc-like type is divided into nematics and columnar.



Liquid crystalline compounds have been known for over a century. However, most of the liquid crystals that have been studied are organic in nature. Metallomesogens are a new class of compounds with liquid crystalline properties obtained by incorporation of one or more metal atoms into organic structures. This can extend the unique physical properties of liquid crystals by introducing metal-based chemistry. Many different types of metallomesogens have been made by inclusion of s-, p-, d-, even f- block elements [1-4,25]. Among them, palladium is one of the most versatile metals used so far, with all the main types of mesogenic complexes having been reported.

A great number of thermotropic rod-like metallomesogens have been synthesized [7,8,22-24] based on the ortho-metalation reaction between aromatic azo-compound and palladium(II) dichloride, which gives rise to the chloro-bridged planar dimer [5,6]. Metal complexation of organic ligands can give them quite different mesomorphic behavior from the free ligands, usually leading to higher phase transition temperature. Sometimes, metallomesogens are composed of ligands which are not mesomorphic [7]. The role played by the nature of halogen bridging atoms was studied by the substitution of chloride with bromide or iodide [9]. The breaking of the halogen bridge was also performed by neutral molecules, such as quinoline or PPh_3 , giving rise to new monometallic complexes [9,10].

In contrast to the planar structure of halogen-bridged complexes, carboxylato-bridged compounds usually show nonplanarity, which has been expected to disfavor the mesogenic behavior [11,12]. However, an open book shaped palladium(II)-azine mesogen has been synthesized through the bent acetato-bridge [13,14]. Furthermore, by using a similar reaction, chirality can be easily introduced into the liquid crystal leading to the potentially useful ferroelectric liquid crystals [15].

Discotic metallomesogens were first discovered in 1977. This type of complex normally contains a flattish platelike core with the metal in the center, surrounded by unsaturated organic ligands, such as diketones and porphyrins [16,17]. Many of these complexes adopt packing arrangements in which the molecules form columns [16].

Polymeric metallomesogens are another unusual type of complex in which the polymeric nature is likely to introduce more interesting properties. Among the examples of these species are the palladium(II)-polyne polymers [18,19]. They do not show thermotropic properties. However, they are lyotropic nematic in trichloroethylene. It has been shown that the main chain of these polymers can be aligned in a magnetic field, probably due to their diamagnetic anisotropy [20,21].

The characterization of thermotropic metallomesogens is carried out using hot stage polarizing microscopy, where different optical textures are observed for different phases as a function of temperature, and using differential scanning calorimetry. Sometimes, X-ray scattering investigations of the mesophases are also carried out.

Despite the many exciting developments in this area, metallomesogens constitute a challenging subject for both the design of new complexes and the exploration of technological applications.

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