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The effect of polyether terminal chains in the liquid crystalline behavior of *ortho*-palladated complexes

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Abstract

A series of benzylideneanilines bearing terminal polyether chains, HL (HL = R-C_6H_4–CH=N–C_6H_4-R′: R = OC_8H_{17}, R′ = $O(CH_2CH_2O)_2C_2H_5$; R = $O(CH_2CH_2O)_2C_2H_5$, R′ = OC_8H_{17}; R = R′ = $O(CH_2CH_2O)_2C_2H_5$; R = $OC_{12}H_{25}$, R′ = $O(CH_2CH_2O)_3C_2H_5$; R = $O(CH_2CH_2O)_3C_2H_5$, R′ = $OC_{12}H_{25}$; R = R′ = $O(CH_2CH_2O)_3C_2H_5$) have been prepared. Their dinuclear, $[Pd(\mu\text{-}X)L]_2$ (X = OAc, Cl, Br, SC_8), $[Pd_2(\mu\text{-}SCn)(\mu\text{-}X)L_2]$ (X = OAc, Cl; *n* = 8, 2) and mononuclear orthopalladated derivatives, Pd(acac)L, Pd(Ala)L, are reported and their mesogenic properties are compared with those of the analogous compounds with alkoxy chains. In general a great lowering in the melting points is produced for all the products. The free ligands and the alanine complexes are not liquid crystals. The chloro-bridged complexes bearing alkoxy and short polyether chains ($O(CH_2CH_2O)_2C_2H_5$) show the larger improvement of mesogenic properties. Longer polyether chains ($O(CH_2CH_2O)_3C_2H_5$) result usually in a destabilization of the mesophases. If only polyether chains are present, the destabilization is important regardless of the chain length. The ability of these molecules as ionic extractants and transporters was qualitatively evaluated for the more propitious *cis*-dinuclear complexes, which in fact showed some extracting ability, modest but improved compared to the free ligands.

Keywords: Metallomesogens; Palladium; Orthometalated imine; Polyether; Substituent effect; Liquid crystals

1. Introduction

Metallomesogens (metal-containing liquid crystals) is an area of research with a fast development in the last two decades. A great variety of such compounds have been synthesized, and some reviews have appeared [1]. Since the first report by Ghedini et al. [2] of orthopalladated mesogens other groups have developed these interesting systems, as they form thermally stable complexes, give rise to calamitic, discotic and lyotropic mesophases, and offer different possibilities for tuning the mesogenic properties. Our group has reported in the last years a variety of cyclometallated (Pd^{II}, Pt^{II}) imine complexes and studied the structure-mesogenic activity relationships in these different molecular types [3], where we have found the first cholesteric metallomesogens [4], as well as properties of non-linear optics [5], ferroelectricity [6] or lyotropism [7]. A few of these studies have been carried out on orthopalladated azines [8].

Important issues for the potential application of metallomesogens in liquid crystal displays are the reduction of transition temperatures, the expansion of mesogenic ranges, the increase of thermal stability, and the improvement of miscibility with other ingredients (such as polar solvents) in mixtures. It is known that polyether or polyethyleneglycol ligands can enhance the solubility of the complexes in organic solvents and in water due to the polarity introduced by the oxygen atoms [9]. It is also likely that the introduction of polyether chains

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may be beneficial for the mesogenic properties of orthopalladated derivatives [10]. The higher flexibility and the preferred gauche conformation of the $(OCH_2CH_2)_n$ units makes that these chains can adopt more easily a helical conformation and occupy a significantly larger mean lateral area per chain than comparable aliphatic chains of the same length. Thus, it is expected that they might lower the melting points and produce a significant perturbation in the range of smectic mesophases. Depending on the amphiphilicity of the molecule and its ability to induce microsegregation, these mesophases can result stabilized or destabilized [11].

Polyether chains have been utilized before in mesogenic materials. For example, rod shaped organic esters with a polyether terminal group show tilted and orthogonal smectic phases [12]. On the other hand, the addition of alkaline triflate to lamellar phases of mesogenic polyethers induces the formation of columnar phases [13]. By combining the ionophore activity of polyethers with the peculiarities of the mesomorphic state (i.e., sensitivity to small external influences and anisotropy) these systems could play the function of a membrane. The main advantages are the availability of low dimensional ionic conductivities and an easy processability. In fact, the investigation on liquid crystalline based membranes is an area of growing interest [14]. Usually, organic LC amphiphilic systems are used for this purpose and, to our knowledge, no metallomesogens have been tested. The cases of metal containing liquid crystals bearing polyethers are very few. For example, orthopalladated phenylpyrimidines [d,15] linked by oxyethylene units to form macrocyclic molecular structures displaying smectic and columnar mesophases have been reported. Phthalocyanine metallomesogens derivatives have been proposed as materials for the transport of either photons or electrons due to their stacking order, and they are considered also suitable for ion transport. 15-crown-5 ether copper phthalocyanine has been reported to form mesophases in which channels are defined along the columnar axis, but no data about their transport properties are available [16]. A third example is an annelide complex of cobalt (III) with a hydrophobic octadecyl chain and two hydrophylic fragments, the cationic cobalt centre and two oxyethylene chains. This compound behaves as lyotropic liquid crystal [17].

In this paper, we report the preparation and mesogenic properties of orthopalladated complexes containing polyether chains. In spite of the non-macrocyclic nature of the polyether moieties in the complexes, some of the compounds reported were checked towards extraction of potassium ion.

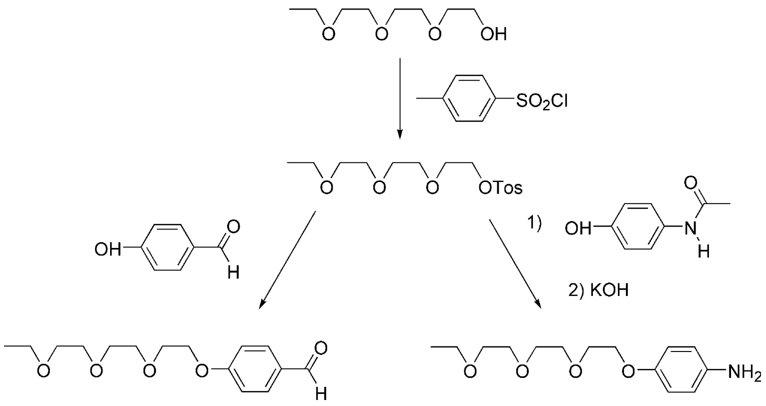
2. Results and discussion

In the text and Schemes to follow the chains $O(CH_2CH_2O)_2C_2H_5$ are abbreviated as $O_3C_6H_{13}O_2$, while $O_4C_8H_{17}$ stands for $O(CH_2CH_2O)_2C_2H_5$.

2.1. Synthesis and structures

The imines **1.1** and **1.2** were readily prepared in good yields by condensation of the corresponding aldehydes and anilines. Imine **1.1a** was already reported [3e]. The method followed to introduce the polyether chains on the *p*-hydroxybenzaldehyde or on the *p*-hydroxyacetanilide is depicted in Scheme 1. As expected, the solubility of the ligands depends on the nature and number of the substituents. Ligands with two alkoxy chains precipitate in ethanol, whereas ligands with a polyether chain are more soluble. The double-chained derivative is completely soluble.

The cyclopalladated complexes were synthesized as depicted in Scheme 2. The orthometallation of the imine ligands was carried out as described elsewhere [3f], but derivatives **2.2b** and **2.2c** could not be obtained sufficiently pure. In these cases, the crude acetate-complexes were treated with HCl, the chloro-complexes were purified by column chromatography and then reacted with sodium acetate in order to get the pure acetate bridged complexes. The trend of the solubility of the complexes is the same as for the free ligands. Chloro bridged



Scheme 1.