Journal of Organometallic Chemistry 836-837 (2017) 81–89

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Luminescent palladium(II) metallomesogens based on cyclometalated Schiff bases and *N*-benzoyl thiourea derivatives as co-ligands

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ARTICLE INFO

Article history:
Received 30 January 2017
Received in revised form
4 March 2017
Accepted 8 March 2017
Available online 10 March 2017

Keywords:
Schiff base
Palladium(II)
Metallomesogens
Liquid crystals
Luminescence

ABSTRACT

Luminescent cyclometalated palladium(II) complexes based on Schiff bases and *N*-benzoylthiourea (BTU) ligands with different numbers of alkoxy groups at their periphery were designed and prepared. The BTU ligands coordinate through the O and S atoms in a deprotonated bidentate fashion as confirmed by IR and NMR spectroscopy data. Additionally, giving the asymmetrical structure of BTU ligands, the ^{1}H-NMR showed the presence of only one of the two possible isomers. The liquid crystalline behavior of these palladium(II) complexes was investigated by a combination of polarized optical microscopy (POM) and differential scanning calorimetry (DSC) while their thermal stability was studied by thermogravimetric analysis (TGA). The mesomorphic behavior of palladium(II) complexes depends on the number and chain length of alkoxy groups grafted on BTU derivatives (monotropic smectic A and C phases). The palladium(II) complexes are thermally stable on a broad temperature range up to about 220 °C. Interestingly, when the number of alkoxy groups on the BTU ancillary ligands was increased, the corresponding palladium(II) complexes lost their mesogenicity and only melting to the isotropic state was observed. The solid-state emission spectra of palladium(II) complexes show two maxima around 580 and 650 nm, respectively, with a shoulder around 710 nm when the samples are irradiated in the 330–380 nm range.

1. Introduction

The design and investigation of metal-containing liquid crystals (metallomesogens) is still expanding considerably in the present time. [1,2] Liquid crystalline materials have found various applications such as the manufacturing of LCD, molecular sensors and detectors, optical switches, spatial light modulator, etc. [3–5] There is a growing interest to study the unique combination of properties of anisotropic fluids (anisotropy of physical properties and fast orientational response to external fields) specific to liquid crystals (LC) with the particular properties of metals (geometry of coordination, electronic, magnetic or the purely structural role, depending on the metal ion). [6] Metal ions with different coordination geometries enable rich structures and topologies of these metal complexes and, consequently, more interesting mesomorphic properties to those found for pure organic liquid crystals. [7] In particular, the liquid crystalline materials based on palladium(II) complexes were given a tremendous attention. [8–18] Amongst various advantages of such metal complexes, one can mention here that the square planar geometry favors the stabilization of LC phases, besides the relative ease of various complex systems preparation. Moreover, it is possible to control the LC and emission properties by a variety of available options to change the chemical structure around the palladium metal center. [19–23] Lower transition temperatures as well as improved mesophases stability near room temperature could be attained in such systems by using the right combination of ligands coordinated to palladium(II) metal. [24,25] Recently, we reported a new class of palladium(II) complexes with LC properties based on cyclometalated imine ligands and *N*-benzoylthiourea (BTU) derivatives as auxiliary ligands. [26–32] When simple *N*-benzoyl thiourea derivatives were used as co-ligands for palladium(II) metal accompanied by cyclometalated imine ligands, only monotropic nematic or smectic A phases were observed, depending on the number of alkoxy groups grafted on the Schiff bases. [28,29] There is a significant change of LC properties of palladium(II) complexes with BTU ligands having various number of long alkoxy terminal groups; mono- or dinuclear palladium(II) complexes with lower transition temperatures and rich mesomorphic behavior ranging from calamitic to discotic materials

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http://dx.doi.org/10.1016/j.jorganchem.2017.03.015

could be prepared. [27,30] Thus, the influence of the alkoxy-substituted BTU derivatives on the thermal behavior of square-planar Pd(II) and Pt(II) cyclometalated complexes together with their luminescent properties were reported. [26,30] This paper represents a continuation of the study on such mixed-ligands palladium(II) systems. [33] We were interested to perform a systematic investigation of the influence of BTU derivatives containing different numbers of long alkoxy mesogenic group in terminal positions in order to establish a correlation structure – mesomorphic behavior for such mononuclear cyclopalladated complexes. On the other hand, metallomesogens with luminescent properties are of great interest as they can find application in electrooptical devices, more specifically for light-emitting diode (OLED) technology. [34–37] There is a considerable lower number of emissive Pd(II) complexes at room temperature by comparison with their Pt(II) analogues, most of them with the metal center in a cyclometalated environment. [38–45] Therefore, an investigation of the solid state emission properties of the newly prepared palladium(II) complexes was undertaken and the results are included in this paper.

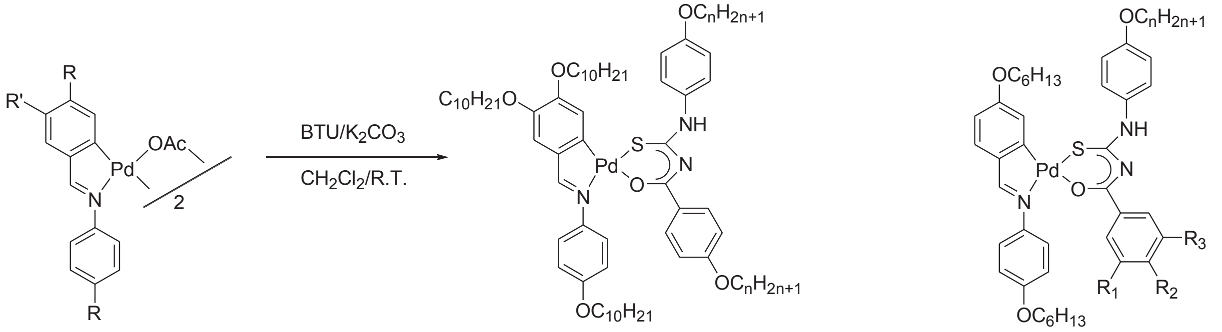
2. Results and discussion

The synthesis of mononuclear palladium(II) complexes with various BTU derivatives, along with their numbering scheme, is presented in Scheme 1. These complexes were obtained by treatment of the corresponding dinuclear μ-acetato-bridged species with BTU ligands in dichloromethane, by using potassium carbonate, at room temperature. The mononuclear palladium(II) complexes were purified on silica with dichloromethane as eluant. Final products were obtained by repeated recrystallization from a mixture of dichloromethane and ethanol. These compounds were prepared in good yields (65–85%) and they were separated as yellow to yellow-brown solid products. The structure of palladium(II) complexes was assigned by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy. The mesomorphic behavior was investigated by a combination of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

The *N*-benzoyl thiourea derivatives were found to coordinate to palladium(II) center in the chelating monodeprotonated form, as confirmed by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectra of the uncoordinated BTU derivatives contains two singlets, one in the range 12.50–12.30 ppm and a second one in the 9.10–9.00 ppm range, which were assigned to the two existing NH groups. These two signals were absent in the ^{1}H-NMR spectra of the corresponding palladium(II) complexes as a consequence of ligand coordination. [26,46] The other signals, sometimes overlapped as multiplets, assigned to aromatic protons show the normal splitting pattern of a 1,4-or 1,3,4-substitution of the aromatic rings. All these data confirmed the loss of the NH hydrogen atom located between the thiocarbonyl and carbonyl groups belonging to the *N*-benzoyl thiourea ligand. These suppositions were further confirmed by IR spectroscopy. The IR spectra of the palladium(II) compounds exhibit a sharp, medium absorption band around 3230 -3360 cm^{-1} assigned to the NH vibration of the remaining NH-R group. Furthermore, the infrared spectra of all palladium(II) complexes show no absorption bands in the range between 1610 and 1690 cm^{-1}, the normal range for $\nu_{C=O}$ stretches in the IR spectra of the uncoordinated BTU ligands, indicating the chelate formation with a high degree of electron delocalization within the chelate rings. Such behavior was reported previously for different simple complexes of BTU derivatives with various metals. [47–49] The asymmetrical structure of BTU ligands could give rise to a mixture of *cis* and *trans* isomers for mononuclear palladium(II) complexes. The ^{1}H-NMR spectroscopy is a useful tool in assessing the mixture proportion of different isomers for palladium(II) or platinum(II) complexes in solution. Thus, the presence of only one signal around 8.10 ppm, assigned to H–C=N- iminic hydrogen, together with the presence of only one set for the other signals suggested that the final products contained mainly one of the two possible isomers related to position of sulfur atom of the BTU ligand in respect to nitrogen atom of the cyclometalated Schiff base ligand.

In order to evaluate the nature of intermolecular interactions existing in crystalline state and in mesophase, complex **1d** was selected for variable-temperature FTIR spectroscopy. The FTIR spectra were recorded at different temperatures on heating from the crystalline state (room temperature) up to isotropic phase (110 °C) and on cooling down from isotropic state to crystallization temperature (60 °C) (Fig. 1).

The most important features were observed in the 3500-3200 cm^{-1} and 1650-1100 cm^{-1} regions. The NH stretching vibration at ~3370 cm^{-1} in the IR spectra of **1d** in crystalline state shifts to lower wavenumber at ~3237 cm^{-1} together with its broadening in the IR spectra recorded for **1d** in isotropic state and mesophase. Its position remains unchanged once the complex started to crystallize at 60 °C. The NH frequency shift on going from crystalline state to liquid crystalline state could be an indication of intermolecular hydrogen bonding. Such interactions between NH-R group and the O atom of the alkyl aryl ether fragment have been found previously in the crystalline state of a Pt(II) complex with similar ligands (Schiff base and BTU). [26] This supposition should be correlated with the change of position and intensity of IR bands located at 1473 and 1451 cm^{-1}, 1386 cm^{-1} and 1246 cm^{-1} assigned



R=OC_6H_{13}, R'=H
R=R'=$OC_{10}H_{21}$

1a-f: n=6,8,10,12,14,16

2: R_3=H, R_1=R_2=$OC_{10}H_{21}$, n=10
3: R_2=H, R_1=R_3=$OC_{12}H_{25}$, n=12
4: R_1=R_2=R_3=OC_mH_{2m+1}, m=12(**a**), 16(**b**), n=8

Scheme 1. Preparation of mononuclear palladium(II) complexes with mesogenic BTU derivatives.