Inorganica Chimica Acta 363 (2010) 729-736

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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



Synthesis, mesomorphism and luminescence properties of palladium(II) and platinum(II) complexes with dimeric Schiff base liquid crystals

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ARTICLE INFO

Article history: Received 12 July 2009 Received in revised form 12 November 2009 Accepted 19 November 2009 Available online 26 November 2009

Keywords: Liquid crystals Palladium Platinum Orthometallation N-benzoyl thiourea Imine Luminescence

ABSTRACT

A series of *ortho*-metallated Pd and Pt complexes containing dimeric liquid crystals Schiff base as cyclometallated ligands and *N*-benzoyl thiourea derivatives as co-ligands were prepared and investigated for their liquid crystalline properties. Their structures were assigned based on elemental analysis, IR and ¹H NMR spectroscopy while the mesogenic properties were investigated by DSC and polarising optical microscopy. The complexes show either monotropic or enantiotropic transitions with nematic and smectic A phases being displayed, with the mesomorphic behaviour strongly related to the type of *N*-benzoyl thiourea as well as the metal center used. The structure of a palladium(II) complex has been solved by Xray diffraction.

The platinum(II) complexes show photoluminescence properties both in solution and in solid state at room temperature, with the emission band centered around 600 nm. These are the first examples of metallomesogens based on Schiff base cyclometallated ligands that display luminescence properties.

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1. Introduction

The liquid crystal dimers (also known as dimesogens), composed of either two identical (symmetric) or non-identical (nonsymmetric) mesogenic units connected via a flexible central spacer, have been extensively studied for their ability to act as model compounds for semi-flexible main-chain liquid crystalline polymers and for their interesting physical properties [1].

Few studies have been reported so far concerning metallomesogens containing dimeric liquid crystals as ligands [2,3]. The first examples of metallomesogens derived from achiral non-symmetrical bidentate dimeric ligands, Pd(II) and Cu(II) complexes with ligands based on salicylaldimine core, were reported recently [2]. The same authors reported the synthesis and mesomorphism of the first examples of optically active (cholesterol-based) dimeric bidentate ligands and their Cu(II) and Pd(II) complexes [3]. Metallomesogens (liquid crystals containing metal ions) are intensively studied due to their interesting properties which are influenced by the presence of the metal ion, such as colour, polarisability, electrical and magnetic properties [4,5].

The non-symmetric dimeric liquid crystal Schiff bases α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-*n*-alkyloxyanilinebenzylidene-4'-oxy)hexane were reported previously to show SmA and N enantio-

* Corresponding author. E-mail address: viorel_carcu@yahoo.com (V. Cîrcu). tropic phases, with an intercalated arrangement within the SmA phase [6,7] in which specific molecular interactions between the two different mesogenic units account for this specific phase behaviour.

In this work, these Schiff bases were used in the *ortho*-metallation reaction with palladium(II) and platinum(II) precursors to give the nematogen dinuclear complexes which further leads to mononuclear complexes by reacting them with sodium salts of simple *N*,*N*-dialkyl-*N'*-benzoyl thiourea derivatives. Our previous results have shown that mixed-ligands palladium(II) and platinum(II) complexes with imine and *N*-benzoyl thioureas ligands show liquid crystals properties, with nematic and SmA phases being displayed, the mesomorphic behaviour of such complexes being strongly dependent on the type of the imine ligand employed as well as the type of co-ligand [8,9]. The liquid crystal properties of mononuclear compounds were investigated by mean of DSC and polarising light microscopy and they will be discussed in connection with the type of metal and the alkyl chain length of the *N*-benzoyl thiourea derivative used as co-ligands.

2. Results and discussion

The preparation of the palladium(II) and platinum(II) complexes is depicted in Scheme 1. The dinuclear acetato-bridged palladium complexes, intermediates in the preparation of the



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Scheme 1. The preparation of ortho-metallated palladium(II) and platinum(II) complexes (m = 1, 10; n = 2-4, 6, 8).

corresponding palladium(II) mononuclear species, were obtained with good yield by *ortho*-palladation reaction between $Pd(OAc)_2$ and the two Schiff bases **LH-***m* in glacial acetic acid. These dinuclear complexes were used in the next step for the preparation of the mononuclear palladium(II) complexes by reacting them with a series of sodium salts of *N*,*N*-dialkyl-*N'*-benzoyl thiourea derivatives. All the mononuclear palladium(II) complexes are microcrystalline yellow products, which are stable in normal conditions.

The dinuclear chloro-bridged *ortho*-platinated compound was prepared by *ortho*-platination reaction of the Schiff base **LH-1** using $[Pt(\mu-Cl)(\eta^3-C_4H_7)]_2$ as starting material [10]. In this case, the crude products were used in the next step without further characterisation and purification. Thus, the mononuclear platinum(II) complexe was prepared by a ligand exchange reaction of the chloro-bridged dinuclear platinum(II) complexes using the corresponding sodium salts of the *N*,*N*-dialkyl-*N'*-benzoyl thiourea derivatives. The new platinum(II) complexes were prepared in moderate to low yields as orange microcrystalline solid products which are stable under ambient conditions. Their structures were confirmed by elemental analysis, IR spectroscopy as well as ¹H and, in one case, by X-ray diffraction.

It was found that the ¹H NMR spectra indicate the presence of only one isomer in solution (one set of signals) for all prepared palladium(II) complexes, while in the case of their analogues with platinum(II), the ¹H NMR spectrum of complex **PtL-1,4** reveals two sets of signals corresponding to the imine proton and methyl group of the Schiff base, their integration showing a 50:50 mixture of the two possible isomers (the sulfur atom of the *N*-benzoyl thiourea ligand in a *trans* or *cis* position to the nitrogen atom of the imine group of the Schiff base ligand). This is the only case when a mixture of isomers was found.

The formation of the mixed-ligands *ortho*-platinated complexes can be confirmed readily by ¹H NMR spectroscopy where the signal corresponding to the imine proton of the Schiff base is accompanied by ¹⁹⁵Pt satellites with ³ J_{Pt-H} coupling constants within the expected range for such complexes [11,12].

3. Description of crystal structure of complex PdL-10,3

Single crystals of complex **PdL-10,3** suitable for X-ray diffraction were obtained by cooling a solution of this compound in a mixture of dichloromethane and ethanol (ca. 1/1 v/v) at -25 °C. The molecular structure of this compound is shown in Fig. 1, while crystallographic data are collected in Table 1 and selected bond and angles are presented in Table 2.

The crystal structure of this compound shows Pd(II) in a squareplanar environment bound to the imine ligand in an *ortho*-metallated fashion and chelated to the *N*,*N*-dipropyl-*N*'-benzoyl thiourea derivative with palladium surrounded by one aromatic carbon atom (metallated phenyl ring), one nitrogen atom (imine group) and one sulfur atom and one oxygen atom of the *N*-benzoyl thiourea derivative. The sulfur atom is situated *trans* to the nitrogen atom from the imine group of the Schiff base as it is the case for previously reported related palladium complexes bearing 4-hexyloxybenzylidene-4'-hexyloxyaniline as Schiff base [11]. The corre-



Fig. 1. The molecular structure of compound PdL-10,3.

Table 1

Crystallographic data for compound PdL-10,3.

Compound	PdL-10,3
Empirical formula Formula weight (g mol ⁻¹) T (K) Wavelength (Å) Crystal system Space group	C ₅₆ H ₆₈ N ₄ O ₄ PdS 999.60 293(2) 0.71073 triclinic <i>P</i> 1
Unit cell dimensions a (Å) b (Å) c (Å)	12.4533(9) 14.7928(9) 15.7227(10)
Unit cell angles α (°) β (°) γ (°) Volume (Å ³) Z Density (calculated) (Mg m ⁻³) Absorption coefficient (mm ⁻¹) $F(0 \ 0 \ 0)$ Crystal Crystal size (mm ³) θ Range for data collection (°) Index ranges	$\begin{array}{l} 85.368(5)\\ 77.773(5)\\ 69.040(5)\\ 2643.4(3)\\ 2\\ 1.256\\ 0.438\\ 1052\\ yellow\\ 0.50 \times 0.35 \times 0.20\\ 2.50-33.24\\ -16 \leqslant h \leqslant 19, -22 \leqslant k \leqslant 22, \end{array}$
Reflections collected Independent reflections Maximum and minimum transmission Data/restraints/parameters Goodness-of-fit (GOF) on F^2 Final <i>R</i> indices ($F^2 > 2\sigma(F^2)$] <i>R</i> indices (all data) Largest difference in peak and hole (e Å ⁻³)	$-24 \le l \le 24$ 50 224 19 514 [$R_{int} = 0.0485$] 0.8758 and 0.8317 19 514/4/613 1.020 $R_1 = 0.0669, wR_2 = 0.1362$ $R_1 = 0.1313, wR_2 = 0.1500$ 0.679 and -0.685

sponding chelate ring around the Pd center is essentially planar with a maximum deviation from the mean plane of 0.054 Å. However, while the metallated phenyl ring is almost coplanar with respect to the mean plane, the unmetallated ring of the Schiff base is twisted by 39.7° with respect to the core plane. Also, the two rings of the biphenyl group are rotated by ~31°.

An important factor that contributes to the crystal packing of this compound is intermolecular $C-N\cdots H^1$ hydrogen bonds which leads to the formation of dimers (Fig. 2). These type of interactions are usually found in the 4-*n*-alkyloxy-4'-cyanobiphenyls liquid crystals family of compounds [13].

Table 2	
Selected bond lengths (Å) and angles (°).	

	PdL-10,3
Pd-C	1.983(3)
Pd-N	2.096(2)
Pd–S	2.2324(9)
Pd–O	2.085(2)
$N(Pr_2)-C$	1.332(4)
N–C(S)	1.341(4)
N-C(O)	1.323(4)
C-0	1.262(4)
C–S	1.720(3)
C(O)-C(Ph)	1.505(4)
C-N(imine)	1.282(4)
C-N (cyano group)	1.140(5)
C-Pd-N	80.70(11)
N-Pd-O	96.58(9)
O–Pd–S	92.25(6)
S-Pd-C	90.31(9)

4. Thermal behaviour

All palladium and platinum complexes were investigated for their potential liquid crystal properties by hot stage polarising optical microscopy and differential scanning calorimetry. The thermal data are summarized in Table 3. Mesophases were assigned based on their optical texture and two examples are presented in Figs. 3 and 4. The mesogenic behaviour of these complexes is strongly influenced by the nature of the ortho-metallated imine fragment. All palladium(II) and platinum(II), except complexes PdL-1,6, PdL-1,8 and PtL-1,6, exhibit an enantiotropic or a monotropic nematic phase, which was identified on the basis of the characteristic Schlieren optical texture that show two- and fourpoint singularities observed when viewed under the polarised light microscope; this texture also flashed when subjected to mechanical stress. The influence of the N-benzoyl thiourea fragment on the mesogenic behaviour of the metal complexes is much more pronounced in the case of complexes bearing the LH-1 Schiff base. On cooling the nematic phases exhibited by PdL-1,4 and PtL-1,4 under the polarised light microscope a well defined focal conic fan texture is developed, as it can be seen in Fig. 3. For this series, either an enantiotropic (PdL-1,2) or a monotropic nematic phase (PdL-1,3) was observed for the short-chain length N,N-dialkyl-N'benzoyl thioureas, both monotropic SmA and N phases at intermediate-chain length (complexes PdL-1.4 and PtL-1.4), and only the SmA phase for the derivatives with two hexyl and octyl chains (complexes PdL-1,6, PdL-1,8 and PtL-1,6). The SmA phase of these late complexes could be assigned by the typical fan-shaped texture which can be aligned homeotropically. A similar influence of the co-ligands on the mesomorphic behaviour of palladium(II) complexes bearing imine ligands was found for ortho-metallated palladium(II) complexes with aliphatic β -diketonate derivatives [14].

¹ Hydrogen bonds for **PdL-10,3**: C(21)–H(21)···N(4) 3.49 Å, H(21)···N(4) 2.60 Å. Symmetry transformation used to generate equivalent atoms: x, y, z; -x. -y, -z.



Fig. 2. Hydrogen bonds CN...H in dimers.

Table 3						
Thermal data for	palladium(II) and	platinum(II) com	plexes.

=			-	
Compound	М	Transition	T (°C)	ΔH (kJ mol ⁻¹)
[PdL-10Ac] ₂		Cr–I (dec)	227	80.0
[PdL-100Ac] ₂		Cr-N	145	89.6
		N–I	186	13.4
PdL-1,2		Cr–Cr′	70	4.1
		Cr'-N	145	4.4*
		N–I	150	
		(I–N)	(148)	2.3
PdL-10,2		Cr–N	133	61.1
		N–I	141	1.8
PdL-1,3	Pd	Cr–Cr′	82	12.9
		Cr'-Cr''	143	10.4
		Cr''-I	167	23.2
		(I–N)	(149)	1.9
PdL-10,3		Cr–Cr′	135	47.9
		Cr'-N	139	10.4
		N–I	144	1.19
PdL-1,4		Cr–I	158	42.6
		(I–N)	(144)	(2.5)
		(N–SmA)	(114)	(0.3)
PdL-10,4		Cr–Cr′	104	12.9
		Cr'-N	118	33.6
		N–I	138	1.6
PdL-1,6		Cr–Cr′	61	4.1
		Cr'-SmA	145	24.7
		SmA–I	151	9.8
PdL-10,6		Cr–N	113	41.8
		N–I	130	1.4
PdL-1,8		Cr–SmA	111	33.8
		SmA–I	138	9.5
PdL-10,8		Cr–N	96	32.2
		N–I	118	1.3
PtL-1,3	Pt	Cr–Cr′	91	11.5
		Cr'-N	127	46.4
		N–I	180	2.5
PtL-1,4		Cr–Cr′	137	2.2
		Cr'-I	176	42.6
		(I–N)	(140)	(2.2)
		(N-SmA)	(126)	(0.4)
PtL-1,6		Cr–Cr′	98	10.2
		Cr'-I	154	30.6
		(I–SmA)	(142)	(4.0)

* Combined enthalpies.

On the other hand, the Pd(II) complexes bearing the Schiff base with decyloxy group (**LH-10**) show only an enantiotropic nematic phase with melting and clearing points that are influenced by the chain length of the *N*,*N*-dialkyl-*N'*-benzoyl thiourea derivative. There is a very small increase of thermal stability of the nematic phase on going from ethyl to propyl (ca. 3 °C) followed by a clear tendency of decrease of the stability of the nematic phase with the increasing the chain length from propyl to octyl (Fig. 5). Such a behaviour could be explained by considering the molecular anisotropy of these complexes [15]. Increasing the length of the al-kyl chain of the *N*-benzoyl thiourea derivatives leads to the increase of the molecular breadth with consequences on the mesogenic behaviour as it is the case for the previous reported complexes bearing such co-ligands [8].



Fig. 3. Polarised optical pictures of the nematic phase of compound PdL-1,4 at 120 $^\circ C$ (a) and of the SmA phase at 90 $^\circ C$, (b) (same region on cooling).



Fig. 4. Polarised optical picture of the Schlieren texture of the nematic phase of compound PtL-1,4 at 137 °C ($200 \times$).



Fig. 5. Dependence of the melting points and clearing temperatures on the chain lengths of the *N*,*N*-dialkyl-*N'*-benzoyl thiourea derivative for Pd(II) complexes with Schiff base bearing decyloxy group (**LH-10**).

If the mesomorphic behaviour of the palladium complexes is compared to that of the platinum complexes which posses the same structure, then the same type of mesophases is seen but with higher transition temperatures in the later case, as a result of substitution of palladium with much heavier platinum atom which brings an enhancement of the polarisation. A similar change in mesomorphic properties when the palladium is replaced with platinum was reported for other *ortho*-metallated complexes [16,17]. It is worth to note here that complex **PtL-1,6** shows an monotropic smectic phase while its analogue with palladium **PdL-1,6** shows an enantiotropic smectic A phase.

5. Absorption and luminescence properties

Metallomesogens with luminescent properties are of great interest for their promising application in electrooptical devices. Emissive properties were reported for a series of metallomesogens and these were recently reviewed by Binnemans [18]. There are several studies dealing with light-emitting metallomesogens incorporating palladium(II) and platinum(II) ions, all of them in cyclometallated environment [19–21]. The explanation is that one of the best strategies used to promote luminescence in platinum(II) complexes is to employ ligands with a very strong ligand field in order to raise the d-d state, as it is the case for cyclometalating ligands, mostly with 2-arylpyridine or 2-thienylpyridine derivatives, resulting both homoleptic or heteroleptic complexes [22–24].

The absorption data for platinum(II) complexes are summarized in Table 4 while the absorption spectrum of complex **PtL-1,3** is shown in Fig. 6. The absorption spectra of the platinum(II) complexes show intense bands in the ultraviolet region between 250 and 350 nm. These high energy bands can be assigned primarily to the allowed intraligand transitions (one around 290 nm and a shoulder around 345 nm). At lower energies two less intense bands in the range 380–500 nm, with low extinction coefficients, ε , ranging between 200 and 1500 M⁻¹ cm⁻¹ were also observed.



Complex	$\lambda_{max}(abs.) (nm) (\epsilon/M^{-1} cm^{-1})$	$\lambda_{max}(em.) (nm)$	
		Solution	Solid
PtL-1,3	290(6120), 343sh(2260), 385(810), 440sh(220)	371, 485, 604	608
PtL-1,4	283(6040), 343sh(2030), 387(1480), 440(410)	365, 493, 602	590
PtL-1,6	187(6080), 344sh(2150), 385(960), 441(370)	368, 502, 604	602



Fig. 6. The UV–Vis spectrum of Pt(II) complex PtL-1,3 recorded in CH_2Cl_2 solution ($c = 1.01 \times 10^{-4}$ M).



Fig. 7. Normalised luminescence and excitation spectra of **PtL-1,3** dissolved in CH₂Cl₂ (concentration 1×10^{-4} M) in the UV region (λ_{exc} = 295 nm) (a) and in Vis range (λ_{exc} = 385 nm) (b).



Fig. 8. Solid state luminescence spectrum of complex **PtL-1,4** (λ_{exc} = 380 nm).

The luminescence and excitation spectra of the platinum(II) complexes dissolved in CH_2Cl_2 and in solid state were measured at room temperature and the data are included in Table 4.

It was found that the excitation with the wavelength λ = 295 nm produced the emission around 370 nm while the excitation with λ = 385 nm produced two emission bands located at 470 and 600 nm (Fig. 7a and b). The solid state luminescence spectra of all three platinum(II) complexes recorded at room temperature using λ_{exc} = 380 nm exhibit an emission band around 600 nm (Fig. 8).

Unfortunately, the mesophase stability at high temperatures makes no possible the recording of luminescence properties in the mesophase.

In the heteroleptic *ortho*-metallated platinum(II) complexes the strong field associated with the *ortho*-metallated carbon should favour luminescence but it is not always necessarily sufficient to induce room temperature emission – in this case a strong influence has the ancillary ligands. It is obvious that for platinum(II) complexes the position of the emission bands both in the solution and solid state luminescence spectra is very little affected by the alkyl chain length of the *N*,*N*-dialkyl-*N*'-benzoyl thiourea used as ancillary ligands, but it proved that together with the *ortho*-metallated Schiff base fragment could constitute good candidates for luminescent metallomesogens and further investigations are currently underway.

6. Conclusions

A series of organometallic palladium(II) and platinum(II) complexes bearing dimeric liquid crystals Schiff bases and *N*,*N*-dialkyl-*N'*-benzoyl thiourea as co-ligands were prepared and investigated for their liquid crystal and photoluminescence properties. These complexes show either monotropic or enantiotropic transitions with nematic and smectic A phases being displayed, with the mesomorphic behaviour strongly related to the type of *N*-benzoyl thiourea as well as the metal center used. The structure of a palladium(II) complex has been solved by X-ray diffraction.

The platinum(II) complexes show photoluminescence properties both in solution and in solid state at room temperature, with the emission band centered around 600 nm. These are the first examples of metallomesogens based on Schiff base cyclometallated ligands that display luminescence properties.

7. Experimental

Dichloromethane was distilled from phosphorus pentaoxide; other chemicals were used as supplied.

Proton and carbon NMR spectra were recorded on a Varian Gemini 300 BB spectrometer operating at 300 MHz, using CDCl₃ as solvent. ¹H chemical shifts were referenced to the solvent peak position, δ 7.26 ppm. X-ray data for crystal **PdL-10,3** were collected at room temperature on a STOE IPDS II diffractometer. The structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package.

The UV–Vis absorption spectra of Pt(II) complexes were recorded in dichloromethane using a Cary 100 Bio (Varian Inc.) spectrophotometer.

Transition temperatures were measured using a Linkam THMS600 hot stage and a TMS94 temperature controller attached to a Nikon 50i Pol polarising microscope. These temperatures were confirmed by differential scanning calorimetry (Perkin–Elmer Diamond instrument using 10 °C/min heating rate). Two or more heating/cooling cycles were performed on each sample. Mesophases were assigned by their optical texture [25]. Solid state fluorescence spectra were recorded using a JASCO FP6500 spectrofluorimeter while fluorescence spectra in solution were recorded using a Per-kin–Elmer LS 50 B spectrofluorimeter.

The synthesis of the two Schiff bases (**LH-1** and **LH-10**) was carried out as described elsewhere [6,7]. The *N*-benzoyl thiourea derivatives as well as their sodium salts used in this work were prepared according to the methods published in literature [26,27].

8. Synthesis of dinuclear palladium(II) and platinum(II) complexes

A mixture of Schiff base (compound **LH-1** or **LH-10**, 0.55 mmol) and palladium acetate (0.55 mmol) in glacial acetic acid (10 ml) was heated under reflux for 7 h. The resulting green-yellow precipitate was filtered hot and washed several times with acetic acid. The crude product was recrystallised from a mixture of CH_2Cl_2/C_2H_5OH (1/1) at -25 °C to afford a green-yellow microcrystalline solid.

In the case of chloro-bridged dinuclear platinum(II) complex, the starting material was $[Pt(\mu-Cl)(\eta^3-C_4H_7)]_2$, which was prepared according to literature data [10]. The mixture of the Schiff base ligand and $[Pt(\mu-Cl)(\eta^3-C_4H_7)]_2$ in methanol, in molar ratio 2:1, was stirred for 1 day at room temperature. The resulting green-brown precipitate was filtered and washed several times with cold methanol. The preparation of the dinuclear platinum(II) complex followed the one described in literature [28]. The crude product was used in the next step, for the preparation of mononuclear species, without further purification.

9. Synthesis of mononuclear palladium(II) and platinum(II) complexes

The solid sodium salt of *N*,*N*-dialkyl-*N*'-benzoyl thiourea derivative (0.30 mmol) was added to a solution of the corresponding binuclear complex (0.10 mmol) in CH₂Cl₂ (15 ml) and the resulting mixture was stirred at room temperature for 1 day. The solvent was removed and the solid was purified on silica using CH₂Cl₂ as eluant. The crude yellow solid was recrystallised from a mixture of CH₂Cl₂/C₂H₅OH (1/1) at -25 °C in the case of palladium(II) complexes. The platinum(II) complexes were recrystallized from a mixture of acetone/methanol (1/1) at -25 °C.

The yields, elemental analysis results as well as ¹H NMR and IR data are presented below:

LH-1. Yield 68%, off-white solid. *Anal.* Calc. for C₃₃H₃₂N₂O₃: C, 78.6; H, 6.4; N, 5.6. Found: C, 78.3; H, 6.7; N, 5.3%.

¹H NMR (300 MHz, CDCl₃): 8.40 (s, 1H), 7.83 (AA'BB' system, ³J = 8.8 Hz, 2H), 7.67 (m, 4H), 7.53 (AA'BB' system, ³J = 9 Hz, 2H), 7.22 (AA'BB' system, ³J = 9.1 Hz, 2H), 7.01–6.91 (m, 6H), 4.04 (m, 4H), 3.84 (s, 3H), 1.87 (m, 4H), 1.59 (m, 4H).

IR (KBr pellet): v_{max} in cm⁻¹ 2237w, 1605s, 1574s, 1246vs.

LH-10. Yield 74%, off-white solid. *Anal.* Calc. for C₄₂H₅₀N₂O₅: C, 80.0; H, 8.0; N, 4.4. Found: C, 79.7; H, 8.2; N, 4.1%.

¹H NMR (300 MHz, CDCl₃): 8.40 (s, 1H), 7.82 (AA'BB' system, ³J = 8.5 Hz, 2H), 7.67 (m, 4H), 7.53 (AA'BB' system, ³J = 8.5 Hz, 2H), 7.22 (AA'BB' system, ³J = 8.8 Hz, 2H), 7.01–6.90 (m, 6H), 4.07–3.95 (m, 6H), 1.90–1.20 (m, 24H), 0.89 (m, 3H).

IR (KBr pellet): v_{max} in cm⁻¹ 2237w, 1606s, 1574s, 1250vs.

 $[\textit{PdL-10Ac}]_2$. Yield 21%, green-yellow crystals. Anal. Calc. for $C_{70}H_{70}N_4O_{10}Pd_2$: C, 62.7; H, 5.3; N, 4.2. Found: C, 62.4; H, 5.7; N, 4.0%.

¹H NMR (300 MHz, CDCl₃): 7.60 (m, 4H), 7.47 (AA'BB' system, ³J = 8.8 Hz, 2H), 7.41 (s, 1H), 7.05 (d, ³J = 8.2 Hz, 1H), 6.93 (AA'BB' system, ³J = 8.8 Hz, 2H), 6.60 (m, 4H), 6.48 (dd, ³J = 8.5 Hz, ⁴J = 2.5 Hz, 1H), 5.96 (d, ⁴J = 2.5 Hz, 1H), 3.97 (t, ³J = 6.3 Hz, 2H), 3.71 (m, 4H), 3.52 (m, 1H), 1.82–1.45 (m, 11H).

IR (KBr pellet): v_{max} in cm⁻¹ 2223w, 1603s, 1571s, 1250vs.

[PdL-100Ac]₂. Yield 32%, green-yellow crystals. *Anal.* Calc. for C₈₈H₁₀₄N₄O₁₀Pd₂: C, 66.5; H, 6.6; N, 3.5. Found: C, 66.1; H, 7.0; N, 3.2%.

¹H NMR (300 MHz, CDCl₃): 7.60 (m, 4H), 7.47 (AA'BB' system, ³J = 8.8 Hz, 2H), 7.41 (s, 1H), 7.05 (d, ³J = 8.2 Hz, 1H), 6.93 (AA'BB' system, ³J = 8.8 Hz, 2H), 6.60 (m, 4H), 6.48 (dd, ³J = 8.5 Hz, ⁴J = 2 Hz, 1H), 5.96 (d, ⁴J = 2.5 Hz, 1H), 4.09–3.87 (m, 4H), 3.80 (m, 1H), 3.59 (m, 1H), 1.89–1.20 (m, 27H), 0.88 (m, 3H).

IR (KBr pellet): v_{max} in cm⁻¹ 2224w, 1604s, 1570s, 1249vs.

PdL-1,2. Yield 53%, yellow crystals. Anal. Calc. for $C_{45}H_{46}$ -N₄O₄PdS: C, 63.9; H, 5.5; N, 6.6. Found: C, 63.8; H, 5.7; N, 6.3%.

¹H NMR (300 MHz, CDCl₃): 8.13 (s, 1H), 7.73 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ${}^{3}J$ = 8.7 Hz, 2H), 7.42–7.33 (m, 4H), 7.22 (m, 2H), 7.01–6.97 (m, 5H), 6.59 (dd, ${}^{3}J$ = 8.4 Hz, ${}^{4}J$ = 2.4 Hz, 1H), 4.05 (m, 6H), 3.89–3.82 (m, 5H), 1.86 (m, 4H), 1.62–1.38 (m, 7H), 1.25 (t, ${}^{3}J$ = 6.6 Hz, 3H).

IR (KBr pellet): $v_{\rm max}$ in cm⁻¹ 2223w, 1604 s, 1580s, 1418vs, 1249vs.

*PdL***-10,2**. Yield 79%, yellow crystals. Anal. Calc. for $C_{54}H_{64}N_4O_4PdS$: C, 66.8; H, 6.6; N, 5.8. Found: C, 66.5; H, 6.9; N, 5.6%.

¹H NMR (300 MHz, CDCl₃): 8.12 (s, 1H), 7.74 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ³*J* = 8 Hz, 2H), 7.42–7.33 (m, 4H), 7.22 (m, 2H), 7.01–6.97 (m, 5H), 6.59 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.4 Hz, 1H), 4.09–4.00 (m, 6H), 3.91–3.86 (m, 2H), 3.80–3.75 (m, 2H), 1.90–1.20 (m, 30H), 0.88 (t, ³*J* = 7.4 Hz, 3H).

IR (KBr pellet): $v_{\rm max}$ in cm⁻¹ 2223w, 1602s, 1582s, 1416vs, 1249vs.

*PdL***-1,3**. Yield 38%, yellow crystals. Anal. Calc. for $C_{47}H_{50}N_4O_4PdS$: C, 64.6; H, 5.8; N, 6.4. Found: C, 64.2; H, 6.2; N, 6.2%.

¹H NMR (300 MHz, CDCl₃): 8.13 (s, 1H), 7.74 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ${}^{3}J$ = 8.7 Hz, 2H), 7.42–7.33 (m, 4H), 7.25 (m, 2H), 7.01–6.97 (m, 5H), 6.59 (dd, ${}^{3}J$ = 8.4 Hz, ${}^{4}J$ = 2.4 Hz, 1H), 4.08 (t, ${}^{3}J$ = 6.5 Hz, 2H), 4.03 (t, ${}^{3}J$ = 6.5 Hz, 2H), 3.89–3.85 (m, 5H), 3.79–3.73 (m, 2H), 1.95–1.55 (m, 12H), 1.03 (t, ${}^{3}J$ = 7.4 Hz, 3H), 0.93 (t, ${}^{3}J$ = 7.4 Hz, 3H).

IR (KBr pellet): v_{max} in cm⁻¹ 2223w, 1604s, 1580s, 1416vs, 1249vs.

*PdL***-10,3**. Yield 45%, yellow crystals. Anal. Calc. for $C_{56}H_{68}N_4O_4PdS$: C, 67.3; H, 6.9; N, 5.6. Found: C, 67.0; H, 7.3; N, 5.3%.

¹H NMR (300 MHz, CDCl₃): 8.12 (s, 1H), 7.74 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ${}^{3}J$ = 8.7 Hz, 2H), 7.42–7.33 (m, 4H), 7.22 (m, 2H), 7.01–6.97 (m, 5H), 6.59 (dd, ${}^{3}J$ = 8.4 Hz, ${}^{4}J$ = 2.4 Hz, 1H),

4.09–4.00 (m, 6H), 3.91–3.86 (m, 2H), 3.80–3.75 (m, 2H), 1.95– 1.25 (m, 28H), 1.03 (t, ³*I* = 7.4 Hz, 3H), 0.95–0.87 (m, 6H).

IR (KBr pellet): v_{max} in cm⁻¹ 2224w, 1604s, 1579s, 1416vs, 1247vs.

*PdL***-1,4**. Yield 63%, yellow crystals. *Anal.* Calc. for $C_{49}H_{54}N_4O_4$ -PdS: C, 65.3; H, 6.0; N, 6.2. Found: C, 64.9; H, 6.4; N, 6.0%.

¹H NMR (300 MHz, CDCl₃): 8.12 (s, 1H), 7.74 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ³*J* = 8.7 Hz, 2H), 7.42–7.32 (m, 4H), 7.22 (m, 2H), 7.03–6.96 (m, 5H), 6.59 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.4 Hz, 1H), 4.09–4.00 (m, 4H), 3.89–3.85 (m, 5H), 3.82–3.77 (m, 2H), 1.90–1.30 (m, 16H), 1.04 (t, ³*J* = 7.4 Hz, 3H), 0.92 (t, ³*J* = 7.4 Hz, 3H).

IR (KBr pellet): v_{max} in cm⁻¹ 2224w, 1603s, 1579s, 1415vs, 1249vs.

*PdL***-10,4**. Yield 85%, yellow crystals. *Anal.* Calc. for $C_{58}H_{72}N_4$ -O₄PdS: C, 67.8; H, 7.1; N, 5.5. Found: C, 67.4; H, 7.5; N, 5.2%.

¹H NMR (300 MHz, CDCl₃): 8.12 (s, 1H), 7.74 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ³*J* = 8.7 Hz, 2H), 7.42–7.33 (m, 4H), 7.22 (m, 2H), 7.01–6.97 (m, 5H), 6.59 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.4 Hz, 1H), 4.09–4.00 (m, 6H), 3.91–3.86 (m, 2H), 3.80–3.75 (m, 2H), 1.95–1.25 (m, 32H), 1.05 (t, ³*J* = 7.2 Hz, 3H), 0.94–0.87 (m, 6H).

IR (KBr pellet): v_{max} in cm⁻¹ 2224w, 1604s, 1580s, 1415vs, 1249vs.

*PdL***-1,6**. Yield 53%, yellow crystals. *Anal.* Calc. for $C_{53}H_{62}N_4$ -O₄PdS: C, 66.5; H, 6.5; N, 5.9. Found: C, 66.3; H, 6.8; N, 5.6%.

¹H NMR (300 MHz, CDCl₃): 8.13 (s, 1H), 7.74 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ${}^{3}J = 8.7$ Hz, 2H), 7.42–7.33 (m, 4H), 7.22 (m, 2H), 7.01–6.97 (m, 5H), 6.59 (dd, ${}^{3}J = 8.4$ Hz, ${}^{4}J = 2.4$ Hz, 1H), 4.09–4.00 (m, 4H), 3.91–3.86 (m, 5H), 3.82–3.77 (m, 2H), 1.90–1.30 (m, 24H), 0.92 (t, ${}^{3}J = 7.0$ Hz, 3H), 0.85 (t, ${}^{3}J = 7.0$ Hz, 3H).

IR (KBr pellet): v_{max} in cm⁻¹ 2225w, 1604s, 1578s, 1416vs, 1248s.

*PdL***-10,6**. Yield 44%, yellow crystals. *Anal.* Calc. for $C_{62}H_{80}N_{4}$ -O₄PdS: C, 68.7; H, 7.4; N, 5.2. Found: C, 68.5; H, 7.7; N, 5.0%.

¹H NMR (300 MHz, CDCl₃): 8.12 (s, 1H), 7.74 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ${}^{3}J$ = 8.7 Hz, 2H), 7.42–7.33 (m, 4H), 7.22 (m, 2H), 7.01–6.97 (m, 5H), 6.59 (dd, ${}^{3}J$ = 8.4 Hz, ${}^{4}J$ = 2.4 Hz, 1H), 4.09–4.00 (m, 6H), 3.91–3.86 (m, 2H), 3.80–3.75 (m, 2H), 1.90–1.25 (m, 40H), 0.96–0.82 (m, 9H).

IR (KBr pellet): ν_{max} in cm⁻¹ 2223w, 1604s, 1579s, 1414vs, 1248s. *PdL***-1,8**. Yield 71%, yellow crystals. *Anal.* Calc. for C₅₇H₇₀N₄-O₄PdS: C, 67.5; H, 7.0; N, 5.5. Found: C, 67.2; H, 7.4; N, 5.2%.

¹H NMR (300 MHz, CDCl₃): 8.13 (s, 1H), 7.74 (d br, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ³*J* = 8.7 Hz, 2H), 7.42–7.32 (m, 4H), 7.22 (m, 2H), 7.03–6.96 (m, 5H), 6.59 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.4 Hz, 1H), 4.10–4.00 (m, 4H), 3.89 (m, 5H), 3.78 (m, 2H), 1.90–1.25 (m, 32H), 0.91–0.83 (m, 6H).

IR (KBr pellet): $v_{\rm max}$ in cm⁻¹ 2222w, 1602s, 1579s, 1415vs, 1246vs.

*PdL***-10,8**. Yield 43%, yellow crystals. *Anal.* Calc. for $C_{66}H_{88}N_{4}$ -O₄PdS: C, 69.5; H, 7.8; N, 4.9. Found: C, 69.1; H, 8.2; N, 4.6%.

¹H NMR (300 MHz, CDCl₃): 8.12 (s, 1H), 7.74 (m, 2H), 7.65 (m, 4H), 7.53 (AA'BB' system, ${}^{3}J = 8.7$ Hz, 2H), 7.42–7.33 (m, 4H), 7.22 (m, 2H), 7.01–6.97 (m, 5H), 6.59 (dd, ${}^{3}J = 8.4$ Hz, ${}^{4}J = 2.4$ Hz, 1H), 4.09–4.00 (m, 6H), 3.91–3.86 (m, 2H), 3.80–3.75 (m, 2H), 1.90–1.25 (m, 48H), 0.96–0.82 (m, 9H).

IR (KBr pellet): v_{max} in cm⁻¹ 2225w, 1606s, 1579s, 1416vs, 1247vs.

PtL-1,3. Yield 27%, orange crystals. Anal. Calc. for $C_{47}H_{50}N_4O_4PtS$: C, 58.7; H, 5.2; N, 5.8. Found: C, 58.4; H, 5.6; N, 5.5%.

¹H NMR (300 MHz, CDCl₃): 8.39 (s, 1H, ³*J*_{Pt-H} = 110 Hz), 8.26 (m, 2H), 7.69–7.62 (m, 5H), 7.55–7.48 (m, 3H), 7.44–7.35 (m, 4H), 7.19 (m, 2H), 7.09 (d, ³*J* = 2.5 Hz, 1H), 7.00 (AA'BB' system, ³*J* = 8.3 Hz, 2H), 6.59 (dd, ³*J* = 8.5 Hz, ⁴*J* = 2.5 Hz, 1H), 4.10–4.01 (m, 4H), 3.90 (s, 3H), 3.83–3.65 (m, 4H), 1.90–0.85 (m, 12H), 1.03 (t, ³*J* = 7.4 Hz, 3H), 0.93 (t, ³*J* = 7.4 Hz, 3H).

IR (KBr pellet): v_{max} in cm⁻¹ 2223w, 1605s, 1579s, 1417vs, 1246vs.

PtL-1,4. Yield 25%, orange crystals. *Anal.* Calc. for C₄₉H₅₄-N₄O₄PtS: C, 59.4; H, 5.5; N, 5.7. Found: C, 59.1; H, 5.9; N, 5.4%.

¹H NMR (300 MHz, CDCl₃): 8.39, 8.38 (2s (two isomers *syn* and *anti*), 1H, ${}^{3}J_{Pt-H} = 114$ Hz), 7.82 (AA'BB' system, ${}^{3}J = 8.5$ Hz, 2H), 7.70–7.62 (m, 4H), 7.53 (AA'BB' system, ${}^{3}J = 8.8$ Hz, 2H), 7.43–7.35 (m, 3H), 7.22–7.17 (m, 2H), 7.09 (d, ${}^{3}J = 2.5$ Hz, 1H), 6.99 (AA'BB' system, ${}^{3}J = 8.8$ Hz, 2H), 6.95–6.91 (m, 3H), 6.59 (dd, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 2.4$ Hz, 1H), 4.08–4.01 (m, 4H), 3.90, 3.83 (2s (*syn* + *anti*), 3H), 3.87–3.75 (m, 4H), 1.95–1.30 (m, 16H), 1.04 (t, {}^{3}J = 7.4 Hz, 3H), 0.92 (t, ${}^{3}J = 7.4$ Hz, 3H).

IR (KBr pellet): v_{max} in cm⁻¹ 2222w, 1602s, 1580s, 1415vs, 1245vs.

PtL-1,6. Yield 33%, orange crystals. Anal. Calc. for $C_{53}H_{62}$ -N₄O₄PtS: C, 60.8; H, 6.0; N, 5.4. Found: C, 60.3; H, 6.4; N, 5.3%.

¹H NMR (300 MHz, CDCl₃): 8.39 (s, 1H, ${}^{3}J_{Pt-H} = 108$ Hz), 8.26 (m, 2H), 7.69–7.62 (m, 5H), 7.55–7.48 (m, 3H), 7.44–7.35 (m, 4H), 7.19 (m, 2H), 7.09 (d, ${}^{3}J = 2.5$ Hz, 1H), 7.00 (AA'BB' system, ${}^{3}J = 8.3$ Hz, 2H), 6.59 (dd, ${}^{3}J = 8.5$ Hz, ${}^{4}J = 2.5$ Hz, 1H), 4.10–4.01 (m, 4H), 3.90 (s, 3H), 3.83–3.65 (m, 4H), 1.90–1.30 (m, 24H), 0.93–0.85 (m, 6H).

IR (KBr pellet): v_{max} in cm⁻¹ 2225w, 1606s, 1578s, 1414vs, 1248s.

Acknowledgements

The authors wish to thank MECI (Romanian Ministry of Education and Inovation, Project CNCSIS A1640, project PNII 210/2009 Brâncusi and Project PNII ID_954) for funding this study and to Dr. Augustin Madalan for his help with the X-ray diffraction study.

Appendix A. Supplementary material

CCDC 736202 contains the supplementary crystallographic data for compound **4b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2009.11.028.

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