Effect of Ion Coordination on the Conformational and Electronic Structure of 3,4-Bis(alkylthio)thiophenes

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A joint experimental and theoretical approach is used to study the coordination of soft transition metal ions with 3,4-bis(alkylthio)thiophenes. The synthesis of [$PdCl_2${3,4-bis(3-methylbutylthio)thiophene}], [$PtCl_2${3,4-bis(3-methylbutylthio)thiophene}] and [$PdCl_2${3′,4′-bis[2-(*S*)-methylbutylthio]-2,2′:5′,2′′-terthiophene}] by exchange of the benzonitrile ligands in [$PdCl_2(PhCN)_2$] and [$PtCl_2(PhCN)_2$] for the thiophene derivatives with thioether side chains is described. Changes in the conformational and electronic structure of the molecules were studied by X-ray diffraction, cyclic voltammetry, and optical and NMR spectroscopy; these experimental data are interpreted with the help of quantum mechanical calculations based on density functional theory. The complexes crystallize in a mixture of diastereoisomers, these stereoisomers are in equilibrium in solution, as observed by variable-temperature NMR spectroscopy. The complexation diminishes the electron-donor ability of the sulfur to the thiophene ring, as observed from the blueshift of the absorption maximum and from the absence of an oxidation wave in the positive potential regime for monomeric 3,4-bis(alkylthio)thiophenes. In this way it is possible to tune the properties of thiophene derivatives by ion coordination.

Introduction

Over the past two decades, thiophenes have attracted strong interest, because of the possible applications of the corresponding polymers in secondary batteries, sensors, photo- and electroluminescent devices, etc.[1−4] In particular, the development of side chain-substituted conjugated derivatives has led to the discovery of a number of interesting phenomena that are not observed in the unsubstituted parent polymers. For instance, the introduction of groups that could act as ligands opens possibilities for application in areas such as chemosensors and catalysis, as reported by Swager et al.[5,6] and Reynolds et al.,[7] respectively.

Because complexes with transition metal ions are of general use in fields such as catalysis, we are investigating the synthesis and properties of new conjugated polymers with alkylthio side groups, since thioether ligands are well known for their ability to complex soft transition metal ions.[8,9] Such conjugated polymers could act as probes or modulators of the activity of the catalytic centre. Furthermore, these systems could be used to anchor biomolecules in a reversible fashion by metal coordination. Similarly, Leclerc et al.[10] reported the possibility of fixing avidin to polythiophene through acid-base complexes. Finally, ion coordination can also be envisioned as an interesting approach to modulate the properties of the conjugated polymer in a noncovalent way.

In this paper we describe the synthesis of [$PdCl_2${3,4-bis(3-methylbutylthio)thiophene}] (**5**), [$PtCl_2${3,4-bis(3-methylbutylthio)thiophene}] (**6**) and [$PdCl_2${3′,4′-bis[2-(*S*)-methylbutylthio]-2,2′:5′,2′′-terthiophene}] (**7**) by exchange of the benzonitrile ligands in [$PdCl_2(PhCN)_2$] and *cis*-[$PtCl_2(PhCN)_2$] for the thiophene derivatives with thioether side chains. The complexes **5** and **6** crystallize in a mixture of diastereoisomers and these stereoisomers are in equilibrium in solution, as observed by variable temperature NMR spectrosocpy. The optical and electrochemical properties of the thiophene derivatives are strongly modified by the presence of the transition metal ions. To account for these properties, this paper also reports theoretical calculations on the geometries of the molecules and on their corresponding energies, together with the interpretation of the optical spectra.

Results and Discussion

Synthesis of the Complexes

The 3,4-bis(3-methylbutylthio)thiophenes **2** and 3,4-bis[2-(*S*)-methylbutylthio]thiophene **3** were conveniently synthesized by transetherification of 3,4-dimethoxythiophene (**1**) with the corresponding thiols, as we reported

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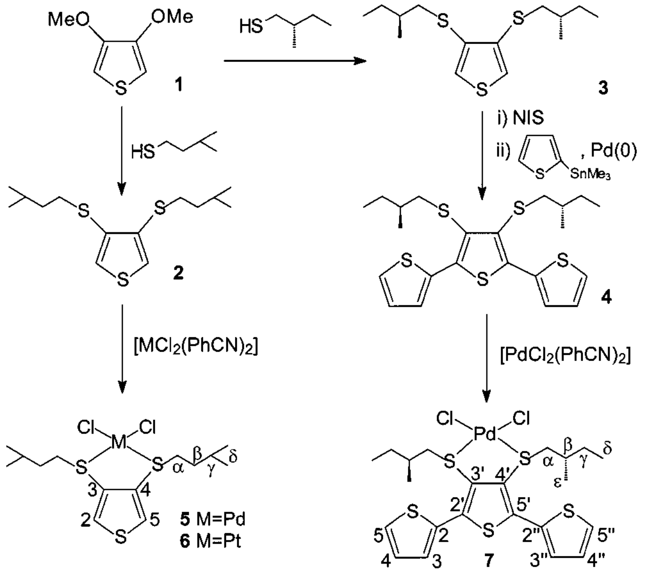

Scheme 1. Synthesis of the complexes **5−7**

previously.[11] Stille coupling of the diiodo derivative of **3** with two equivalents of 2-trimethyltinthiophene in the presence of catalytic amounts of Pd^0 produced the desired terthiophene **4**.[12]

The chelate Pd complexes **5** and **7** were obtained by the reaction of an equimolar amount of the dithioether in dichloromethane with $[PdCl_2(PhCN)_2]$, as shown in Scheme 1. The complexes were separated as orange-red solids upon addition of 2-propanol. Using the same conditions as for complex **5**, the corresponding Pt derivative *cis*-$[PtCl_2(PhCN)_2]$ did not react with the ligand at room temperature, as reported for other thioether ligands.[8] However, under UV irradiation in $CHCl_3$, chelate complexation of the dithioether ligand to the platinum centre took place and was completed in a few hours. Addition of hexane led to precipitation of complex **6** as a pale yellow solid. All new compounds **2−7** were fully analysed, including NMR spectroscopy and elemental analysis.

Crystal Structure

Both compounds **5** and **6** crystallize in the monoclinic $P2_1/c$ space group, in quasi-identical cells (the axes or

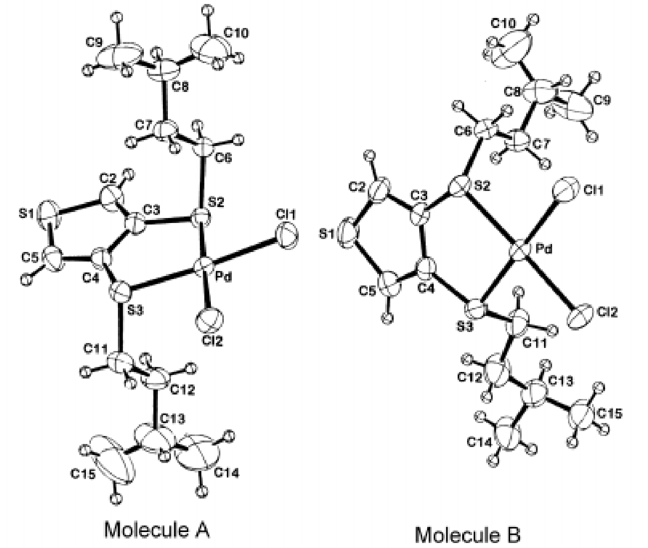

Figure 1. ORTEP drawing of the two independent molecules of compound **5**; thermal ellipsoids for non-H atoms enclose 30% probability

Table 1. X-ray data collection and processing for compounds **5** and **6**

	5	**6**
Empirical formula	$C_{14}H_{24}Cl_2PdS_3$	$C_{14}H_{24}Cl_2PtS_3$
Formula weight	465.81	554.50
Temperature (K)	293(2)	293(2)
Wwavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	14.305(2)	14.370(1)
b (Å)	16.299(3)	16.283(2)
c (Å)	17.101(3)	17.136(1)
α (°)	90	90
β (°)	100.01(2)	100.199(8)
γ (°)	90	90
V (Å^3)	3926.5(13)	3946.1(6)
Z	8	8
$\rho_{calcd.}$ (Mg/m^3)	1.576	1.867
μ (Mo-K_α, mm^{-1})	1.526	7.689
Crystal size (mm)	0.38 × 0.30 × 0.20	0.25 × 0.20 × 0.15
θ range (°)	2.12−26.96	1.91−26.00
Index ranges	$-18\leq h\leq18$ $-1\leq k\leq20$ $-1\leq l\leq21$	$-17\leq h\leq17$ $-1\leq k\leq20$ $-1\leq l\leq20$
Reflns collected	10049	9311
Unique reflns	8528 [R_{int} = 0.0273]	7721 [R_{int} = 0.0260]
Observed reflns [$I>2\sigma(I)$]	5656	5122
Abs. corr. transmission	0.711−1.000	0.657−1.000
Parameters refined	362	361
$R1 = \Sigma\Vert F_o\vert-\vert F_c\Vert/\Sigma\vert F_o\vert$	0.0370	0.0430
(Observed rflns) $wR2$	0.1016	0.0801
Largest diff. peak and hole (e· Å^3)	0.860 and −0.463	0.905 and −0.806

angles do not differ by more than 0.45%, see Table 1).[13] In both compounds the asymmetric unit contains two crystallographically independent *syn* and *anti* isomeric molecules, which are shown in Figure 1 and 2 along with the atom numbering. Selected bond lengths and angles are reported in Table 2.2

A comparison between all structural features of both isomers of complexes **5** and **6**, starting from atomic fractional coordinates, reveals such a close resemblance that the same description can be indifferently applied to either the Pd (**5**) or Pt (**6**) derivative. Most of the corresponding bond lengths, bond angles, and torsion angles in compounds **5** and **6** are equal within one or two standard deviations; moreover, this is equally true for their nonbonded intermolecular contacts. In both complexes, the metal atoms of the two independent molecules display nearly ideal square-planar four-coordination, with the two *cis* Cl atoms and the two sulfanyl S atoms from the substituted thiophene molecule binding in a chelating fashion. As expected, the thiophene rings are nearly coplanar with respect to the coordination planes. The metal atoms are coplanar with their donor atoms in A-labelled molecules, and slightly displaced from the plane in B-labelled ones (Table 2).

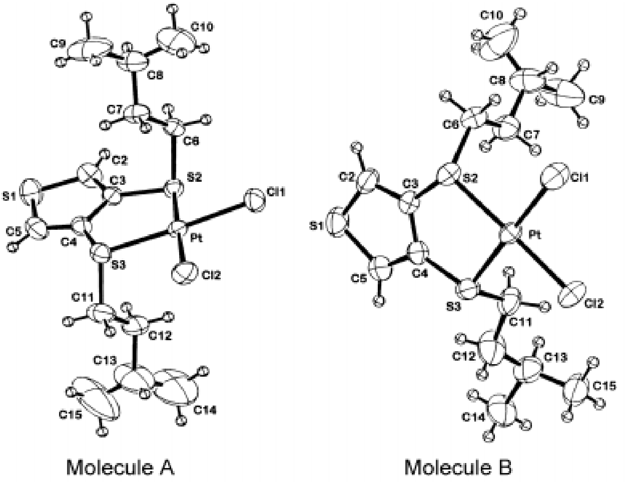

Figure 2. ORTEP drawing of the two independent molecules of compound **6**; thermal ellipsoids for non-H atoms enclose 30% probability

In order to estimate the relative energy of the different structures and to gain information on changes in the electronic density due to complexation, calculations were performed on representative models using a Density Functional Theory (DFT) approach. To keep the computational effort to a reasonable level, the alkylthio side chains were represented by methylthio groups. The theoretical description of the geometry obtained for [PdCl$_2${3,4-bis(methylthio)thiophene}] is fully consistent with the X-ray data of compound **5**. The largest difference between theoretical and experimental data is only about 0.02 Å and 3° for the bond lengths and bond angles, respectively. A comparison between the theoretical structures of 3,4-bis(methylthio)thiophene (Figure 3a) and [PdCl$_2${3,4-bis(methylthio)thiophene}] (Figure 3b,c) is reported in Table 3. These data indicate that the complexation does not lead to significant bond length or angle modifications in the thiophene moiety. The changes are large on the thioether groups where the complexation leads to an increase (0.03 Å) of the bond lengths between the C$_\beta$ of the thiophene ring and the sulfur atoms.

The nature of the bonds between the thioether groups and the Pd atom is clearly covalent: the calculated Pd−S distances (2.292 Å) are indeed slightly lower than the sum

Table 2. Selected bond lengths and angles in compounds **5** and **6**

	Compound **5** (Me = Pd)		Compound **6** (Me = Pt)	
	Molecule **A**	Molecule **B**	Molecule **A**	Molecule **B**
Bond lengths (Å)				
Me−Cl(1)	2.301(1)	2.291(1)	2.309(2)	2.300(3)
Me−Cl(2)	2.306(1)	2.304(1)	2.314(2)	2.311(2)
Me−S(2)	2.263(1)	2.266(1)	2.248(2)	2.252(2)
Me−S(3)	2.264(1)	2.263(1)	2.254(2)	2.250(2)
S(1)−C(2)	1.688(5)	1.697(6)	1.700(10)	1.693(10)
S(1)−C(5)	1.696(5)	1.690(5)	1.702(11)	1.694(10)
C(3)−S(2)	1.765(4)	1.771(5)	1.774(8)	1.780(9)
S(2)−C(6)	1.816(4)	1.807(4)	1.817(8)	1.810(9)
C(4)−S(3)	1.776(4)	1.782(4)	1.771(9)	1.763(9)
S(3)−C(11)	1.808(4)	1.818(5)	1.813(9)	1.814(9)
Bond angles (°)				
Cl(1)−Me−Cl(2)	92.83(5)	92.05(5)	91.61(10)	90.83(9)
Cl(1)−Me−S(2)	87.18(4)	88.13(4)	87.58(9)	88.69(9)
Cl(1)−Me−S(3)	176.35(5)	179.43(4)	176.63(9)	179.31(9)
Cl(2)−Me−S(2)	176.70(4)	176.53(5)	177.06(8)	176.98(9)
Cl(2)−Me−S(3)	88.46(5)	88.47(5)	88.67(9)	88.50(9)
S(2)−Me−S(3)	91.73(4)	91.36(4)	92.31(8)	91.98(9)
Torsion angles (°)				
Me−S(2)−C(6)−C(7)	−50.5(3)	48.3(4)	−51.1(7)	48.6(8)
C(3)−S(2)−C(6)−C(7)	57.0(3)	−60.7(4)	56.6(7)	−61.0(8)
Me−S(3)−C(11)−C(12)	−49.5(5)	168.2(4)	−47.7(9)	166.8(8)
C(4)−S(3)−C(11)−C(12)	58.8(5)	−84.4(4)	60.6(9)	−86.1(9)
out of plane (Å) of Me atom [a]	0.001(1)	0.032(1)	0.006(1)	0.031(1)

[a] The four donor atoms were used to define the plane.

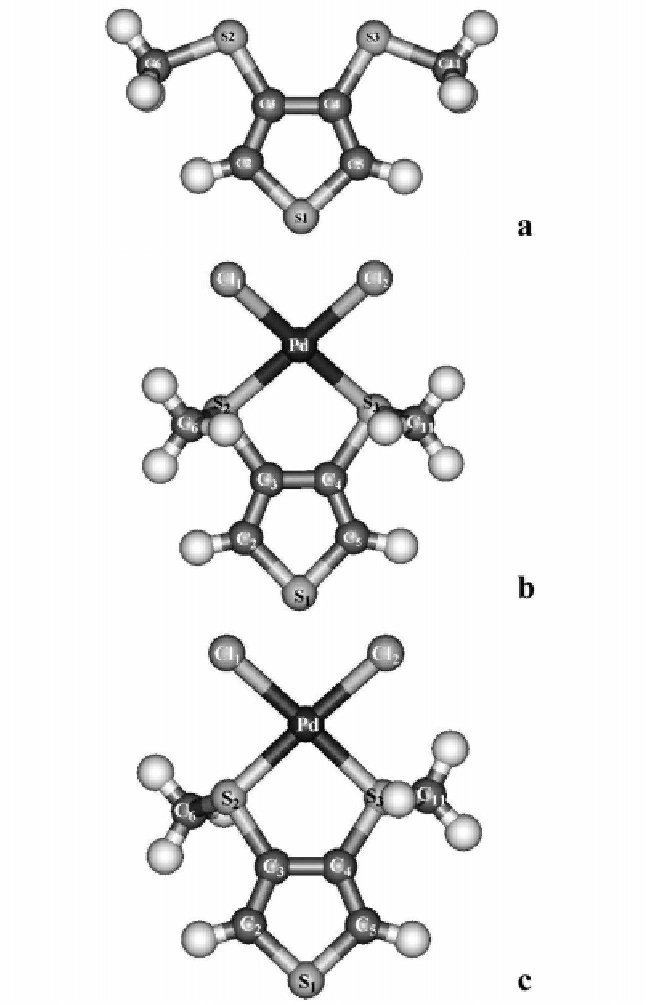

Figure 3. Chemical structure of 3,4-bis(methylthio)thiophene (**a**) and {$PdCl_2$[3,4-bis(methylthio)thiophene]} *syn* (**b**) and *anti* (**c**) isomers

of the covalent radii (2.330 Å).[14] The quasi-equivalent bond lengths to the two Cl atoms (2.304 Å) and to the two sulfanyl S atoms (2.292 Å) and their respective angles (about 90°) form a nearly square planar configuration around the Pd centre, as also observed in the X-ray structure.

From the calculations it is possible to evaluate the stability of the complex, i.e., the binding energy of $PdCl_2$ to 3,4-bis(methylthio)thiophene; this is obtained from the difference in total energy between the complex and the separate partners. The value calculated with a nonlocal-gradient-corrected DFT approach is -181 kJ mol^{-1} and -171 kJ mol^{-1} for the *syn* and *anti* isomers, respectively. We also checked that alternative bonding sites for the Pd atom (the sulfur atom of the thiophene ring and the π system of the thiophene ring) lead to complexes with much lower binding energies (-83 and -52 kJ mol^{-1}, respectively).

In both complexes, the two independent molecules in the crystallographic unit differ only by the absolute configuration around the metal-bonded S atoms, which are stereocentres. Both crystals contain all the diastereoisomeric forms. The S atoms of the A- and B-labelled molecules display *R,R* and *R,S* configurations, respectively. Due to the presence of an inversion centre (and of a glide plane), the inverted *S,S* and *R,S* configurations are also present, and hence the compounds crystallise in a racemic form. There are no significant differences between the corresponding bond lengths and angles of the two independent molecules, and their values compare well with the mean bond lengths retrieved from the Cambridge Structural Database.[15,16] It is of interest to note that the strong similarities between the two structures also apply to probable disorder problems, which involve, in particular, two terminal methyl groups of the alkyl chains. In both crystals, and in both independent molecules, the C(9) and C(10) atoms are affected by extremely high temperature factors, and, as a consequence, by extremely short (and unrealistic) bond lengths. Nevertheless, to observe this effect in both independent molecules and in both complexes could be of some significance with regard to their molecular packing mode. As reported above, both complexes exhibit the same molecular packing, characterised by only three nonbonded distances lower than 3.60 Å (two C···S and one C···C contacts). These interactions occur only between racemic pairs (A- or B-labelled) of molecules.

Table 3. Comparison of theoretical bond lengths and angles of {3,4-bis(methylthio)thiophene} (**a**) and [$PdCl_2${3,4-bis(methylthio)thiophene}] (**b**) with the experimental data for compound **5** (isomer B)

	a	**b**	X-ray structure of compound **5**
Bond lengths (Å)			
Pd−Cl(1)		2.304	2.291(1)
Pd−Cl(2)		2.304	2.304(1)
Pd−S(2)		2.292	2.266(10)
Pd−S(3)		2.292	2.262(13)
S(1)−C(2)	1.714	1.708	1.697(6)
C(2)−C(3)	1.371	1.370	1.347(6)
C(3)−C(4)	1.427	1.418	1.415(6)
C(4)−C(5)	1.371	1.370	1.346(6)
C(5)−S(1)	1.714	1.708	1.690(5)
C(3)−S(2)	1.741	1.770	1.771(5)
S(2)−C(6)	1.793	1.801	1.807(4)
C(4)−S(3)	1.741	1.770	1.782(4)
S(3)−C(11)	1.793	1.801	1.818(5)
Bond angles (°)			
Cl(1)−Pd−Cl(2)		95.50	92.05(5)
Cl(1)−Pd−S(2)		86.34	88.13(4)
Cl(1)−Pd−S(3)		178.03	179.43(4)
Cl(2)−Pd−S(2)		178.03	176.53(5)
Cl(2)−Pd−S(3)		86.34	88.47(5)
S(2)−Pd−S(3)		91.79	91.36(4)

Variable Temperature NMR Spectroscopy

The variable temperature ^1H NMR spectrum of the palladium complex **5** in chloroform solution is shown in Figure 4. At room temperature the compound shows a singlet for the α-proton of the thiophene, and broad peaks in the aliphatic region, corresponding to the thioether side chains, all deshielded relative to the values for uncomplexed com-

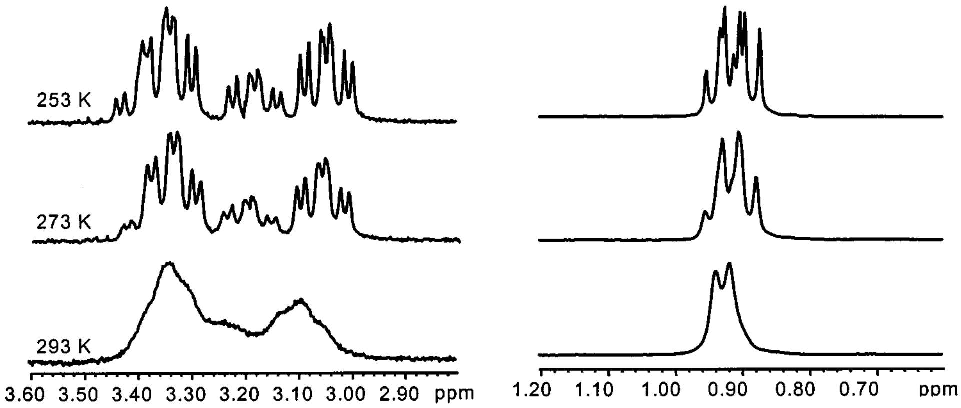

Figure 4. Variable temperature ^{1}H NMR spectrum of compound **5** in $CDCl_3$ in the regions corresponding to the signals of the SCH_2 and CH_3 protons

pound **2**. In the ^{13}C NMR spectrum at room temperature, there are two peaks in the aromatic region at $\delta = 128$ and 135, corresponding to the two α- and β-carbons of the thiophene ring, respectively, while five peaks for the aliphatic region are recorded, including two at $\delta = 21.9$ and 22.2 corresponding to the two methyl end groups, indicating that these groups have a reduced motional freedom. At −20 °C, the thioether side chains resolve into several multiplets. The diastereotopic $SCH_2(\alpha)$ is resolved into two groups of signals, each consisting of two double triplets, as shown in Figure 4. At lower temperatures, we also observe the presence of two doublets of doublets for the CH_3 group at the end of the chain, confirming the presence of two isomers.

The two *syn* and *anti* isomers are in equilibrium in solution, and from the coalescence temperature and the ratio of the integrated signals, we can deduce that one is preferred over the other in a 2:1 ratio. An approximate energy barrier of 68 kJ mol^{-1} can be calculated for the interconversion between the two isomers, and the difference in energy between the two forms is approximately 1.7 kJ mol^{-1}. The theoretical calculations on the corresponding [$PdCl_2${3,4-bis(methylthio)thiophene}] isomers (Figure 3) indicate that the *syn* form is more stable than the *anti* form by about 10 kJ mol^{-1}. Such an overestimation, relative to the experimental value, may be due to the fact that the calculations are performed on single isolated molecules, thereby neglecting the influence of the solvent. The two isomers can be identified with the two couples of diastereoisomeric molecules A and B observed in the crystal.

UV/Vis Spectroscopy

With respect to uncomplexed compound **2**, which presents an absorption maximum at 286 nm, the absorption maximum in complex **5** is blue-shifted by 29 nm, to 257 nm (Figure 5). The spectrum also shows two smaller bands at 315 nm ($\varepsilon = 2800$ dm^3 mol^{-1} cm^{-1}) and 412 nm ($\varepsilon = 1000$ dm^3 mol^{-1} cm^{-1}). INDO/SCI calculations on [$PdCl_2${3,4-bis(methylthio)thiophene}] indicate that the maximum at 257 nm is a HOMO to LUMO+1 transition localised on the thiophene moiety, and that the two bands at 315 nm and 412 nm are due to transitions involving the Pd atoms. The blue shift of 29 nm found for the main absorption is related to the stabilization of the HOMO due to the diminished electron-donating ability of the S atoms; as a result, the absorption maximum gets closer to that of thiophene itself (231 nm). The absorption coefficient is significantly increased from $\varepsilon = 4800$ dm^3 mol^{-1} cm^{-1} at 286 nm in the uncomplexed compound to 11100 dm^3 mol^{-1} cm^{-1} at 257 nm in compound **5**.

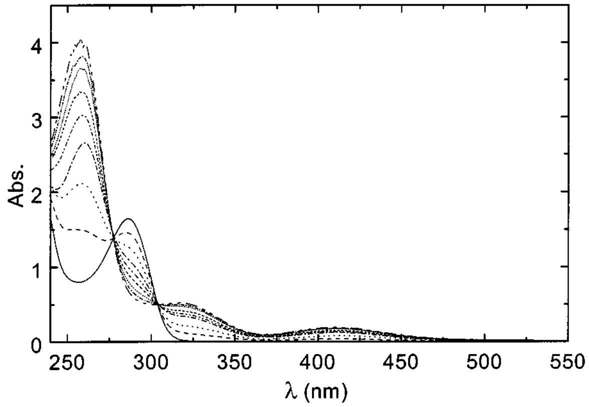

Figure 5. UV/Vis spectra of the titration of 3,4-bis(3-methylbutylthio)thiophene (**2**) with [$Pd(CH_3CN)_2Cl_2$] in acetonitrile

From the titration experiment, we can observe the presence of two clear isosbestic points, indicating the presence of the two species (complexed and uncomplexed) in solution (see Figure 5).

Cyclic Voltammetry and Electropolymerisation.

The electrochemical characterisation of **5** reveals one reversible reduction wave at −0.71 V, while **2** just presents an irreversible oxidation wave at 1.7 V. No oxidation wave is observed for **5** in the positive potential regime ($E \leq 1.8$ V), which is in contrast to what is found in electron-donor-substituted thiophenes.[17–19] Therefore compound **5** cannot be oxidatively electropolymerised.

In order to explain this behaviour, we computed the electronic properties of 3,4-bis(methylthio)thiophene and its $PdCl_2$ complex. The electrophilic character of $PdCl_2$ is clearly illustrated through the Mulliken charge-transfer analysis (Table 4).

Table 4. Mulliken charge analysis for [$PdCl_2${3,4-bis(methylthio)thiophene}]; the charge variation is defined as the difference between the DFT-calculated electronic charges in the complex and in the isolated compounds; a negative value corresponds to a gain of electronic density

Atoms	Charge variation |e|
Cl(1)	−0.16
Cl(2)	−0.16
Pd	−0.29
C(6)H_3 group	+.008
C(11)H_3 group	+.008
S(3)	+0.11
S(2)	+0.11
C(3)	−0.04
C(4)	−0.04
C(2)H	+0.10
C(5)H	+0.10
S(1)	+0.07

As a consequence of complexation, a partial charge transfer (−0.6 |e|) takes place from 3,4-bis(methylthio)thiophene to $PdCl_2$. The sulfur atoms of the thioether groups and the C_α atoms of the thiophene ring are the most depleted sites, while the alkyl side chains and the C_β atoms of the ring remain almost untouched. Globally, the decrease in electron density on the organic molecule upon complexation is consistent with the fact that oxidation becomes more difficult. Along the same lines, the redox properties can be qualitatively interpreted on the basis of the one-electron electronic structure of the molecule. Indeed, the oxidation process corresponds to the removal of one electron and can thus be roughly connected to the energy of the HOMO.[20] Similarly, the reduction process induces the addition of one electron that must be deposited on the LUMO.

The analysis of the electronic structure of 3,4-bis(methylthio)thiophene (**a**) and its $PdCl_2$ complex (Figure 6) shows two important points. Firstly, the HOMO of [$PdCl_2${3,4-bis(methylthio)thiophene}] is similar to that of 3,4-bis(methylthio)thiophene but is strongly stabilized (Table 5). This implies that oxidation becomes more difficult when going from 3,4-bis(methylthio)thiophene to its $PdCl_2$ complex. Secondly, the complexation leads to the localization of the LUMO on the Pd atom and to a strong energetic stabilization (Table 5). This is fully consistent with the appearance of a reduction peak at −0.71 V.

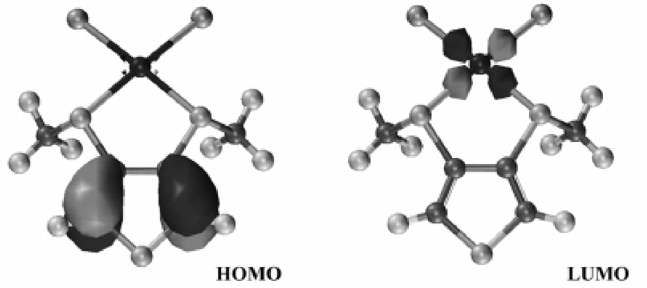

Figure 6. INDO-calculated HOMO and LUMO patterns of [$PdCl_2${3,4-bis(methylthio) thiophene}]

Table 5. Comparison of the INDO energies of the LUMO, and HOMO for 3,4-bis(methylthio)thiophene (**a**), {$PdCl_2$[3,4-bis(methylthio) thiophene]} (**b**), [3′,4′-bis(methylbutylthio)-2,2′:5′,2′′-terthiophene] (**4**), and {$PdCl_2$[3′,4′-bis(methylthio)-2,2′:5′,2′′-terthiophene} (**7**); the energies are in electron volts (eV)

	a	**b**	**4**	**7**
LUMO	0.34	−1.32	−0.88	−1.88
HOMO	−8.17	−9.70	−6.77	−7.75

Since complexation diminishes the electronic density on the α-positions of the thiophene ring (Table 4), electrochemical oxidation and monomer coupling at these positions become more difficult. This explains why the electropolymerisation of compound **5** was not successful. To overcome this problem, we therefore synthesized compound **7**, which possesses both a complexed Pd atom and two pristine C_α sites. This compound also has a reversible redox wave at −0.71 V and, most importantly, shows a highly irreversible oxidation wave at 1.7 V. This behaviour is consistent with the electronic structure of [$PdCl_2${3,4-bis(methylthio)thiophene}] and [$PdCl_2${3′,4′-bis(methylthio)-2,2′:5′,2′′-terthiophene}] (Table 5). The energetic values and the nature of the frontier molecular orbitals are modified when going from the thiophene complex to the terthiophene complex (Figure 7 and Table 5). In the terthiophene complex, both the HOMO and LUMO are mostly localized on the organic backbone, with strong similarities to those of the uncomplexed molecule. The HOMO of [$PdCl_2${3′,4′-bis(methylthio)-2,2′:5′,2′′-terthiophene}] is strongly destabilized (1.95 eV) relative to that of [$PdCl_2${3,4-bis(methylthio)thiophene}]. This destabilization of the HOMO implies that the oxidation process is much easier for [$PdCl_2${3′,4′-bis(methylthio)-2,2′:5′,2′′-terthiophene}] than for [$PdCl_2${3,4-bis(methylthio)thiophene}]. As for [$PdCl_2${3,4-bis(methylthio)thiophene}], complexation leads to the stabilization (1 eV) of the LUMO. However, the LUMO is no longer localized on the Pd atom but on the terthiophene part while the LUMO+1 is found on the Pd atom.

Based on these considerations, it is most likely that the oxidation wave at 1.7 V is due to the oxidation of the terthiophene moiety. Red films of electrochemically active, polymeric material can be grown on the Pt electrode by repetitive cycling, but the polymer is no longer soluble in organic solvents. The results of the electropolymerisation and of the complexation of the preformed polymers will be reported in a forthcoming paper.[21]

Conclusion

Complexes between thiophenes substituted with thioether ligands and transition metal ions were successfully synthesized. We have shown that complexation leads to the freezing of the rotation of the side chains, as the complexes

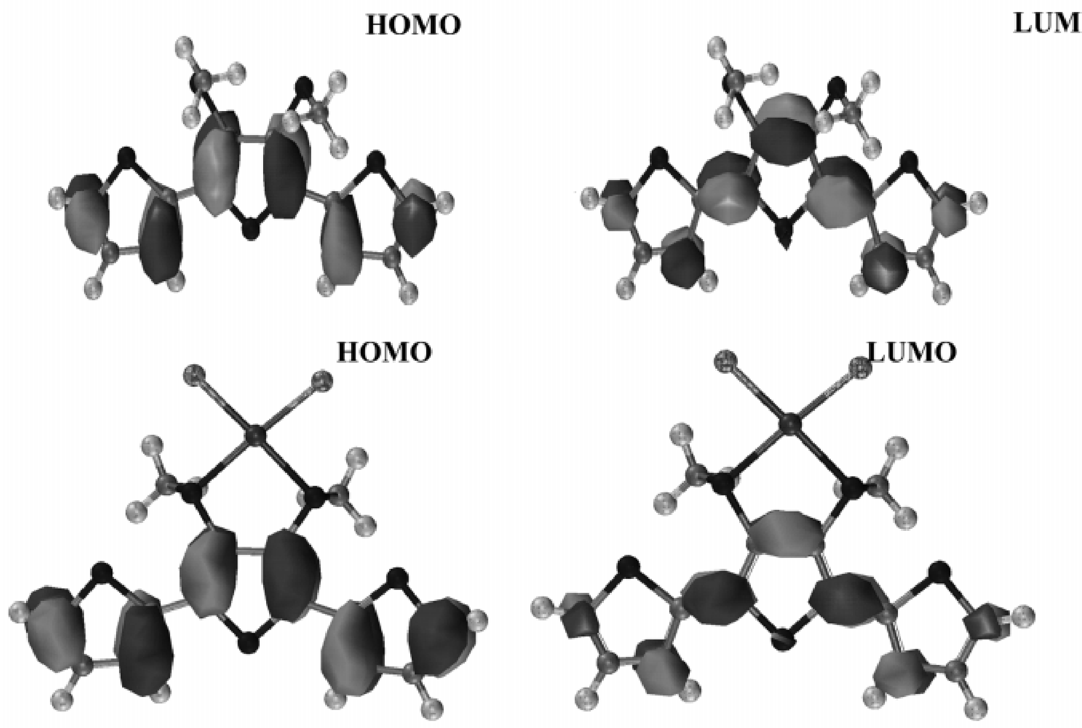

Figure 7. INDO-calculated HOMO and LUMO patterns of [$PdCl_2${3′,4′-bis(methylthio)-2,2′:5′,2′′-terthiophene} and -{3′,4′-bis(methylbutylthio)-2,2′:5′,2′′-terthiophene}]

are crystalline at room temperature. Furthermore, the reversible linkage with the metal ions modifies the optical and electrochemical properties of the thiophene derivatives. Thus, metal complexation can be used as a reversible tool for the modification of the properties in π-conjugated polymers.

Experimental Section

General Remarks: The IR spectra were recorded on a Perkin−Elmer 1600 series FT-IR spectrometer. NMR spectra were recorded on a Varian Gemini 300 spectrometer. Chemical shifts are reported in ppm downfield from TMS. The UV/Vis spectra were recorded on a Perkin−Elmer Lambda 900 spectrophotometer. Cyclic voltammograms were recorded with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte using a Potentioscan Wenking POS73 potentiostat. The working electrode was a platinum disc (0.2 cm^2), the counterelectrode was a platinum plate (0.5 cm^2) and the reference electrode was a saturated calomel electrode calibrated against a Fc/Fc^+ couple. Electrospray-MS (ESI/MS) measurements were performed on a Perkin−Elmer/Sciex API300 mass spectrometer. Elemental analysis (C, H, N) was obtained by combustion analysis using a Perkin−Elmer 2400. 3,4-Bis(3-methylbutylthio)thiophene (**2**)[11] and 3′,4′-bis[2-(*S*)-methylbutylthio]-2,2′:5′,2′′-terthiophene (**4**)[12] were prepared as previously reported. All other reagents were commercial products and were used as received. Solvents were dried by standard procedures.

[$PdCl_2${3,4-Bis(3-methylbutylthio)thiophene}] (5): The ligand 3,4-bis(3-methyl-butylthio)thiophene[11] (**2**; 75 mg, 0.26 mmol) was added to a solution of [$PdCl_2(PhCN)_2$] (100 mg, 0.26 mmol) in dry dichloromethane (5 mL). After stirring at room temperature for 20 min., 2-propanol was added to give an orange precipitate of **5** which was filtered off and dried in vacuo (115 mg, 95%). − ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 7.6 (s, 2 H, 2-H and 5-H), 3.3 (broad, 4 H, α-H), 2.06 (broad, 2 H, γ-H), 1.8−1.4 (broad, 4 H, β-H), 0.87 (broad, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 134 (C_4 and C_5), 128 (C_2 and C_3), 43 (α-C), 38 (δ-C), 27 (β-C), 22.2 (CH_3) and 21.9 (CH_3). − ES-MS; *m/z*: 395 [M − 2Cl]. − $C_{14}H_{24}Cl_2PdS_3$ (465.7): calcd. C 36.11, H 5.15; found C 36.11, H 5.24.

[$PtCl_2${3,4-Bis(3-methylbutylthio)thiophene}] (6): The ligand 3,4-bis(3-methyl-butylthio)thiophene[11] (**2**; 30.5 mg, 0.13 mmol) was added to a solution of [$PtCl_2(PhCN)_2$] (50 mg, 0.13 mmol) in chloroform (10 mL). The solution was irradiated (about 300 nm) at 35 °C for 11 h. The chloroform was evaporated and hexane was added. The solid was stirred in hot hexane, then the solvent was removed by decantation. The solid was then recrystallized from 2-propanol to give **6** (23.6 mg, 48%). − ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 7.56 and 7.54 (s, 2 H, 2-H and 5-H), 3.28 and 3.15 (two multiplets, 4 H, α-H), 2.00 (multiplet, 2 H, γ-H), 1.8−1.4 (three multiplets, 4 H, β-H), 0.95, 0.94, 0.91 and 0.89 (four doublets, 6 H, 2 CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 125 (C_2 and C_3), 43 (α-C), 37.7 and 37.6 (δ-C), 27.3 and 27.2 (β-C), 22.4, 22.3 and 22.0 (CH_3). − $C_{14}H_{24}Cl_2PtS_3$ (554.3): calcd. C 30.33, H 4.32; found C 30.70, H 3.99. Probably due to a broadening of the signals, the peaks of the C_4 and C_5 could not be detected, even after an overnight acquisition.

[$PdCl_2${3′,4′-Bis[2-(*S*)-methylbutylthio]-2,2′:5′,2′′-terthiophene}] (7): The ligand 3′,4′-bis[2-(*S*)-methylbutylthio]-2,2′:5′,2′′-terthiophene[12] (**4**; 100 mg, 0.22 mmol) was added to a solution of [$PdCl_2(PhCN)_2$] (84 mg, 0.22 mmol) in dichloromethane (10 mL). After stirring at room temperature for 20 min., the solvent was removed to give **7** (115 mg, 83%). − ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 7.54 (dd, J_{35} = 0.98 Hz, J_{45} = 5 Hz, 2 H, 5-H and 5"-H), 7.40 (broad dd, 2 H, 3-H and 3"-H), 7.16 (dd, J_{34} = 3.7 Hz,

J_{45} = 5 Hz, 2 H, 4-H and 4"-H), 3.4−2.8 (broad multiplets, 4 H, α-H), 2.1−1.6 (broad, 2 H, β-H), 1.4−1.0 (broad, 4 H, γ-H), 0.9−0.6 (broad, 6 H, δ- and ε-CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 130.6 (2C, 2-C and 2′′-C), 129.7 (2C, CH), 129.1 (2C, CH), 128.8 (2C, CH), 53.4, 52.8, 50.8, 50.2 [2C, CH_2(α)], 35.7, 34.3 [2C, CH(β)], 29.3, 29.2 [2C, CH_2 (γ)], 19.8, 18.9 [2C, CH_2(ε)], 11.3, 11.2 [2C, CH_2(δ)]. − $C_{22}H_{28}Cl_2PdS_5$ (629.9): calcd. C 41.95, H 4.47; found C 41.01, H 4.51. Probably due to a broadening of the signals, the peaks of the quaternary carbons could not be detected, even after an overnight acquisition.

Crystal Structure Determination for Compounds 5 and 6: Diffraction data for compound **5** were collected on a Enraf−Nonius CAD4 diffractometer, whereas those for compound **6** were obtained with a Siemens P4RA-M18X diffractometer equipped with a rotating anode (52 kV, 130 mA). In both cases, the ω-2θ scan mode was chosen. Crystal data and details of data collections and refinements are summarised in Table 1. The structures were solved by direct methods (SHELXS-86) and were refined by full-matrix least-square calculations based on F^2 (SHELXL-93). All non-hydrogen atoms were refined anisotropically, and H atoms were constrained to remain in ideal positions on the C atoms to which they are bonded. In both compounds, two methyl groups (C_9 and C_{10} in Figure 1 and 2) display unusually high thermal motion parameters and extremely short bond lengths, perhaps indicative of light disorder.

Theoretical Methodology: 3,4-Bis(methylthio)thiophene and [3′,4′-bis(methylthio)-2,2′:5′,2′′-terthiophene] were used as representative models for the 3,4-bis(3-methylbutylthio)thiophene (**2**) and [3′,4′-bis(methylbutylthio)-2,2′:5′,2′′-terthiophene] (**4**), respectively. The geometries of the isolated molecules as well as those of the complexes with $PdCl_2$ were fully optimized at the density functional level of calculation. The main advantage of Density Functional Theory (DFT) with respect to Hartree−Fock is that it allowed us to take electron correlation explicitly into account, which is of the utmost importance in the description of metal-organic interactions. The Vosko-Wilk-Nusair[22] function for the exchange-correlation potential in the local density approximation was used, along with a double numerical precision basis set (DNP) of 6−311 G* quality.[23] A frozen-core approximation equivalent to the use of a pseudopotential was used for the palladium and chlorine atoms. The binding energies and charge distributions calculations were carried out at the nonlocal level of DFT using the Becke-Lee-Yang-Parr gradient-corrected functional[24,25] for the exchange-correlation potential. This methodology has already been successfully applied to metal-organic systems containing aluminum, nickel, copper, and iron.[26,27] The interpretation of the optical spectra of [{$PdCl_2$(3,4-bis(methylthio) thiophene}] (**5**) was performed on the basis of Hartree−Fock INDO semiempirical calculations, coupled to a Single Configuration Interaction description (SCI).[28]

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