Spectral Studies on Pt(II) and Pd(II) Complexes with *N*-benzoyl-*N'*-aryl Thiourea derivatives

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A series of Pt(II) and Pd(II) complexes with N-benzoyl-N'-aryl thiourea derivatives were prepared and investigated by mean of several spectroscopic techniques: IR and UV-VIS, ^{1}H and ^{13}C NMR spectroscopy. These derivatives act as monodentate ligands through the sulphur atom to Pt(II) and as bidentate through the sulphur and oxygen atoms to Pd(II). The ^{1}H NMR spectroscopy shows the presence of a mixture of cis and trans isomers in solution for both Pt(II) and Pd(II) complexes.

Keywords: Pt(II) and Pd(II) complexes, N-benzoyl-N'-aryl thiourea, IR and UV-VIS, ^{1}H and ^{13}C NMR spectroscopy

The *N*-acyl-*N'*-aryl thiourea derivatives have been employed in the preparation of metal complexes much more rarely. One of the reason might be the capability of the two amino groups to loose their protons and hence to give polymeric structures. Thus, the most intensively studied derivatives are the *N*-benzoyl or *N*-acyl-*N'*-dialkyl thiourea derivatives which always give rise to neutral chelates in which the ligand is coordinated in a bidentate fashion [1, 2].

Recently, the latest examples of Pt(II), Pd(II) and Rh(III) complexes with *N*-alkyl and *N*,*N*-dialkyl-*N'*-acyl (aroyl) thiourea derivatives have been reviewed by Koch [3]. Most of these derivatives react with transition metals forming neutral complexes in which the monoanionic ligand acts as bidentate through sulphur and oxygen atoms. These derivatives have found many important applications, such as: biological properties [4], solvent extraction of platinum group metals [5] and, more recently, they have been used to prepare liquid crystalline materials [6, 7].

By attaching mesogenic groups, such as alkoxy group, in terminal positions, we prepared liquid crystalline materials showing smectic A and nematic phases [8].

In this paper we report the preparation and spectroscopic investigation of a series of Pt(II) and Pd(II) complexes with *N*-benzoyl-*N'*-aryl thiourea derivatives that contains alkyl, alkoxy or nitro groups on the benzene ring.

Experimental part

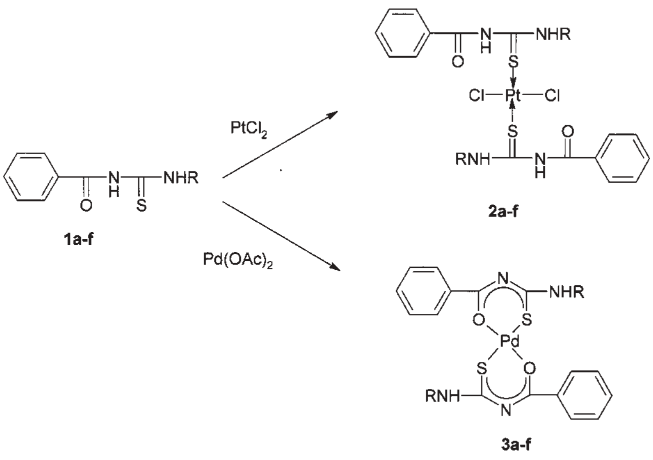
Elemental analysis of C and N was performed on a Carlo-Erba L-1108 analyser while metal content was evaluated by gravimetric methods.

Solid state UV-VIS spectra were recorded on a Carl Zeiss Jena Specord M40 spectrophotometer, using MgO, while solution UV-VIS spectra were recorded either on a Perkin Elmer Lambda-20 or Shimadzu UV 160 spectrophotometer. Analysis by IR was carried out using a BioRad FTS 135 spectrophotometer, in the range 4000-400 cm^{-1}, as KBr pellets.

^{1}H, ^{13}C and 2D-NMR were recorded on a Bruker DRX 400 MHz spectrometer using $CDCl_3$ solvent. The chemical shifts were referenced to the TMS peak position.

Preparation of Pt(II) and Pd(II) complexes

Pt(II) and Pd(II) complexes were prepared by a similar method described in literature [9, 10]. Anhydrous platinum chloride or palladium acetate were mixed together with the *N*-benzoyl thiourea derivative in a 1:2 metal to ligand ratio, in acetone. The resulting mixture was stirred at room temperature for 2h after which yellow-brown or yellow products separated. The products were filtered and washed several time with small portions of cold acetone and then air-dried.



a: R=3,4-dimethylphenyl; b: R=3,4-dimethylphenyl; c: R=2,5-dimethylphenyl ; d: R=2-ethyl-6-methylphenyl; e: R=2-nitro-4-methoxyphenyl; f: R=4-methoxyphenyl
Scheme 1

Compound **2e** was prepared using the method described in literature for comparison purposes [10].

Compound 2a. Yield 51%. Elemental analysis: calc. %C: 46.0; %N: 6.7; %Pt: 23.4; found %C: 45.4; %N: 6.5; %Pt: 23.1. IR (KBr, cm^{-1}): 1674s; 1557vs; 1529i; 1356s; 706m.

Compound 2b. Yield 45%. Elemental analysis: calc. %C: 46.0; %N: 6.7; %Pt: 23.4; found %C: 45.5; %N: 6.4; %Pt: 23.6. IR (KBr, cm^{-1}): 1673s; 1550 vs; 1522s; 1330s ; 681m.

Compound 2c. Yield 62%. Elemental analysis: calc. %C: 46.0; %N: 6.7; %Pt: 23.4; found %C: 45.6; %N: 6.3; %Pt: 23.7. IR (KBr, cm^{-1}): 1675s; 1555vs; 1530s; 1365s; 695m.

Compound 2d. Yield 43%. Elemental analysis: calc. %C: 47.5; %N: 6.5; %Pt: 22.6; found %C: 47.0; %N: 6.0; %Pt: 22.3. IR (KBr, cm^{-1}): 1677s; 1543vs; 1515s; 1319s ; 707m.

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Compound 2f. Yield 57%. Elemental analysis: calc. %C: 43.0; %N: 6.7; %Pt: 23.3; found %C: 42.4; %N : 6.4 ; %Pt : 23.4. IR (KBr, cm^{-1}): 1673s; 1540 vs; 1515i; 1355s; 696m.

Compound 3a. Yield 77%. Elemental analysis: calc. %C: 57.1; %N: 8.3; %Pd: 15.8; found %C: 56.2; %N: 8.2; %Pd: 15.3. IR (KBr, cm^{-1}): 1617s; 1522 vs; 1345; 1315s; 695m.

Compound 3b. Yield 82%. Elemental analysis: calc. %C: 57.1; %N: 8.3; %Pd: 15.8; found %C: 56.3; %N: 7.8; %Pd: 16.0. IR (KBr, cm^{-1}): 1615s ; 1538vs; 1360; 1315s; 693m.

Compound 3c. Yield 79%. Elemental analysis: calc. %C: 57.1; %N: 8.3; %Pd: 15.8; found %C: 56.4; %N: 7.9; %Pd: 15.7. IR (KBr, cm^{-1}): 1604s; 1554 vs; 1383, 1320s; 695m.

Compound 3d. Yield 80%. Elemental analysis: calc. %C: 58.3; %N: 8.0; %Pd: 15.2; found %C: 57.7; %N: 7.2; %Pd: 15.3. IR (KBr, cm^{-1}): 1616s; 1536 vs; 1351; 1317s; 693m.

Compound 3f. Yield 85%. Elemental analysis: calc. %C: 53.2; %N: 8.3; %Pd: 15.7; found %C: 52.8; %N: 8.0; %Pd: 15.5. IR (KBr, cm^{-1}): 1615s; 1504 vs; 1345s; 701m.

Results and Discussion

Pt(II) and Pd(II) complexes with *N*-benzoyl-*N*'-aryl thiourea are easily prepared by mixing palladium acetate or anhydrous platinum chloride with the ligand, in 1:2 molar ratio, using acetone as solvent, as depicted in scheme 1. The resulting products have yellow or yellow -brown colour and correspond to PtL_2Cl_2 or $Pd(L\text{-}H)_2$ formulae. The yields for Pd(II) complexes are higher than those for corresponding Pt(II) complexes. These complexes were characterised by elemental analysis, IR and UV-VIS spectroscopy and some of them by ^1H and ^{13}C NMR spectroscopy.

IR Spectroscopy

All IR spectra of Pt(II) complexes with *N*-benzoyl-*N*'-aryl thiourea show the same features. The $\nu_{C=O}$ absorbtion bands shift slightly to lower wavenumbers, thus the possibility of carbonyl group to be involved in coordination being ruled out. The very strong bands in the 1500-1560 cm^{-1} range of IR spectra of Pt(II) complexes are assigned to $\nu_{asN\text{-}C\text{-}N}$. These bands do not show any significant changes of their position or intensity compared to IR spectra of uncoordinated ligands. Major changes occur for $\nu_{sN\text{-}C\text{-}N}$ bands; these shift to higher wavenumbers, which lead to the assumption that the ligands coordinate to platinum through the sulphur atom. The positive shift of these bands can be explained by the partial double bond character of C-N bonds as a consequence of coordination of ligands through sulphur atoms [11]. This supposition is also confirmed by the shift of $\nu_{C=S}$ bands to lower wavenumbers. The splitting of this band in the IR spectrum of complex **2a** suggests the same coordination via the sulphur atom of the ligand to platinum centre.

The coordination of the ligands only through the sulphur atom is also supported by the ^1H NMR spectroscopy that will be discussed further.

IR spectra of Pd(II) complexes show an ~70 cm^{-1} shift to lower wavenumbers of $\nu_{C=O}$ band, thus confirming the coordination oxygen atom to palladium ion. Some authors reported an ~150 cm^{-1} shift of this band in the IR spectra of complexes, which is similar to the behaviour reported for acetylacetonate complexes [12, 13]. Another important feature of $\nu_{C=O}$ band, its position both in the IR spectra of ligands and Pd(II) complexes, is neither affected by the nature of substituents nor by their position on the benzene ring. The simple C-N bond changes to partial double bond as a result of the coordination of the ligand to palladium in deprotonated form. This process gives rise to a positive shift (towards higher wavenumbers) of ν_{CN} bands which are located in the 1480-1490 cm^{-1}, 1280-1290 cm^{-1} and 1350-1380 cm^{-1} ranges of IR spectra. On the other hand, the ν_{CS} bands shift to lower wavenumbers due to the coordination of the ligands through sulphur atom.

UV-VIS Spectroscopy

UV-VIS spectra of Pt(II) complexes **2a-f** were recorded in solid state using diffuse reflectance technique while the UV-VIS spectra of Pd(II) complexes **3a-f** were recorded in chloroform solution. The results are presented in table 1.

UV-VIS spectra of Pt(II) complexes **2a-f** show an absorbtion band in the UV region located around 240 nm which is assigned to intraligand $\pi \rightarrow \pi^*$ transition. The second absorbtion band assigned to intraligand transition couldn't be found for complexes **2c**, **2d** and **2f**. In these cases, this absorbtion band is overlapped by the wide band with maximum absorbtion at ~240 nm (fig. 1).

The other two absorbtion bands, which are located in the visible region of the UV-VIS spectra of complexes **2a-f**, are assigned to *d-d* transitions and they are characteristic to Pt(II) complexes with square-planar symmetry [14, 15].

The UV region of electronic spectra of Pd(II) complexes **3a-f** show two absorbtion bands assigned to intraligand transitions. The band situated around 340 nm in the UV

Table 1

POSITION OF ABSORBTION BANDS (NM) IN UV-VIS SPECTRA OF Pt(II) AND Pd(II) COMPLEXES

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	CT	$^1A_{1g} \rightarrow {}^1E_g$	$^1A_{1g} \rightarrow {}^1B_{1g}$
2a	241	277	-	330	471
2b	248	277	-	365	485
2c	245	-	-	365	484
2d	240	-	-	362	486
2f	245	-	-	365	435
3a	249	290	340	359	460
3b	245	380	-	-	427
3c	253	298	335	387	460
3d	248	290	340	380	453
3f	252	294	335	377	455

CT – charge transfer

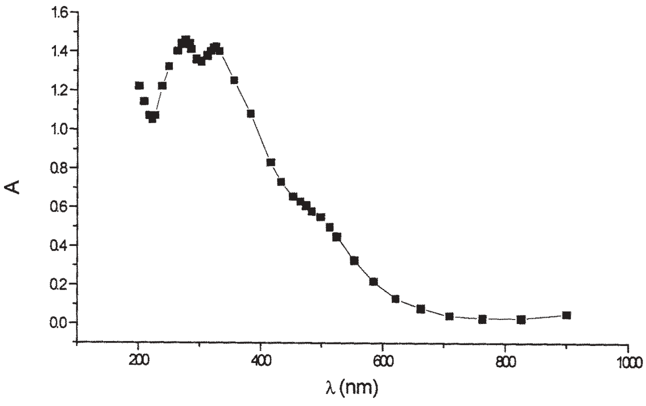


Fig. 1. UV-VIS spectrum of complex 2a

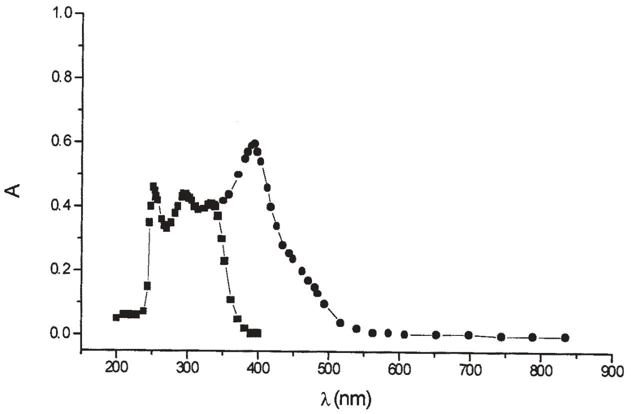


Fig. 2. UV-VIS spectrum of complex 3a in chloroform, recorded separately for 200 – 400 nm and 350 – 850 nm ranges

region could be assigned to a charge transfer metal→ ligand transition, its high intensity making possible this assignment (fig. 2) [14]. The other two transitions in the visible region of the electronic spectra were assigned to *d-d* transitions based on the energy levels diagram of D_{4h} symmetry [15, 16].

NMR Spectroscopy

^{1}H NMR spectra were recorded only for complexes **2a**, **2d** and **2e** due to the poor solubility of Pt(II) complexes in chloroform. Interpretation of ^{1}H NMR spectra of Pt(II) complexes was made with the help of previous assignment of the ^{1}H NMR spectra of the ligands and using the ^{1}H NMR spectra recorded for Cu(I) complexes with these derivatives. In the case of Cu(I) complexes the *N*-benzoyl-*N'*-aryl thioureas act as monodentate ligands, via the sulphur atom of thiocarbonyl group, the same coordination way as for Pt(II) complexes.

The ^{1}H NMR data for Pt(II) complexes are shown in table 2.

For Pt(II) complexes the most affected signals by coordination are expected to be the NH signals, these two protons being in the proximity of the coordination centre [17]. The ^{1}H NMR spectrum of complex **2e** shows two sets of signals for amino group protons. This can be explained by the presence of a mixture of *cis* and *trans* isomers, which is characteristic to square-planar Pt(II) complexes [18]. The H^a signal is shifted with 2.67 ppm and 2.81 ppm to low field while the H^b signal is shifted with 0.03 ppm and 0.19 ppm to low field compared with the positions of these signals in the ^{1}H NMR spectrum of ligand **1e** (fig. 3).

It is not unusual to obtain a mixture of *cis* and *trans* isomers for Pt(II) complexes with *N*-acyl thiourea derivatives. Koch et al. synthesized and characterized by X-ray diffraction the *cis* isomer of Pt(II) complex with *N*-benzoyl-*N'*-propyl thiourea. These authors have shown that the *cis* isomer is the major isomer in the mixture [19].

The proportion of the two isomers in the mixture could be estimated by integration of the two signals leading to 25% *trans* isomer and 75% *cis* isomer. ^{1}H NMR spectra of Pt(II) complexes **2a** and **2d** are different from complex **2e** showing the disappearance of H^1 proton. In the case of complexes **2a** and **2d** one can assume that in solution these complexes participate in a ring closure process, which is depicted in scheme 2.

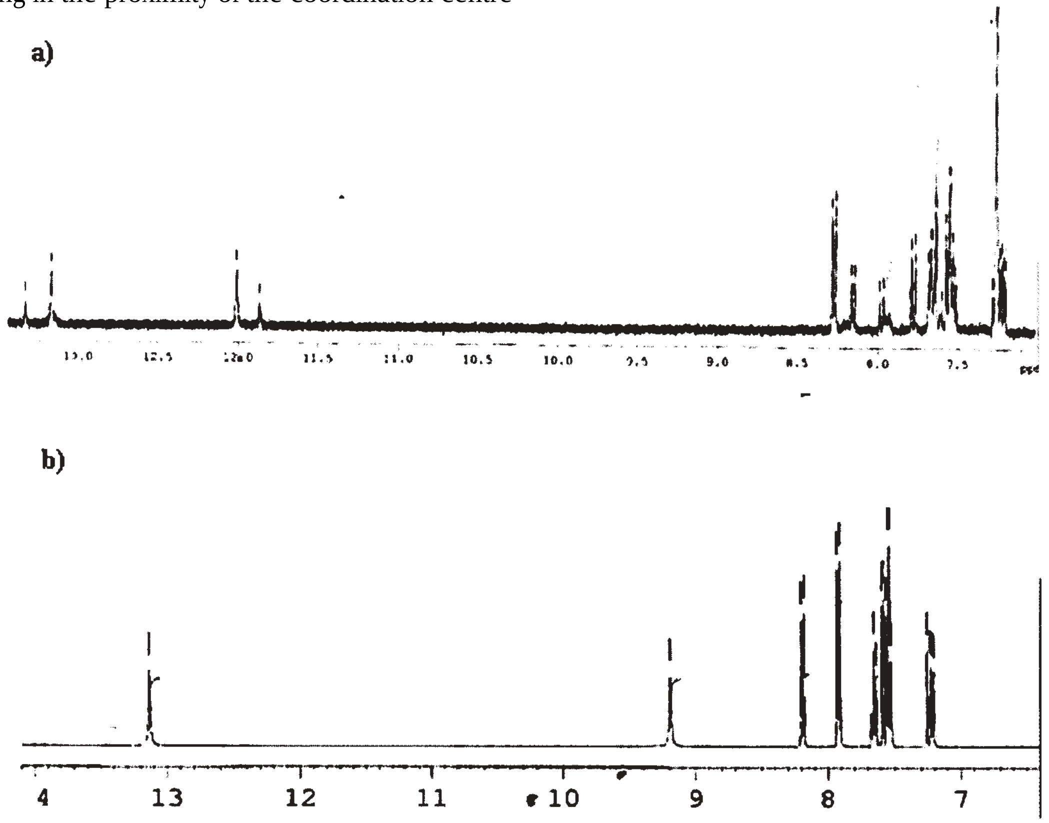
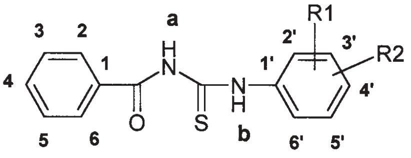


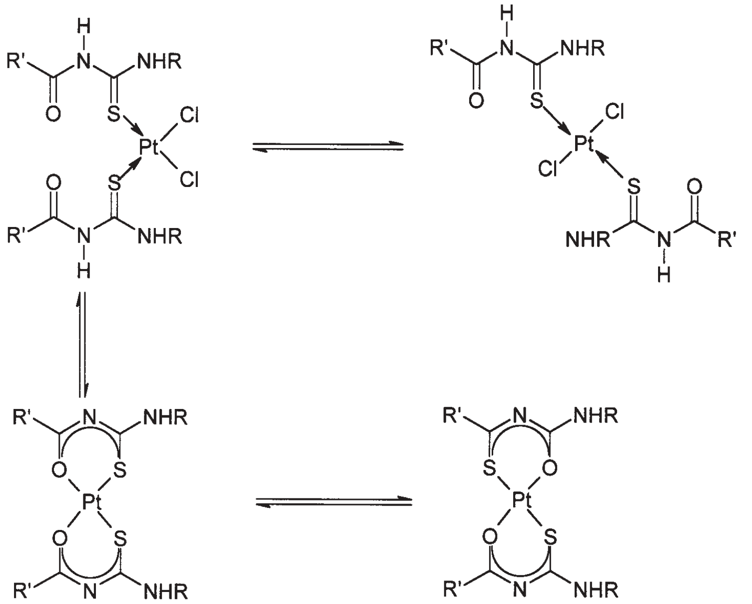
Fig. 3· ^{1}H NMR spectra of complex 2e (a) and ligand 1e (b)

Table 2

^{1}H RMN DATA OF Pt(II) AND Pd(II) COMPLEXES



Compound	H-2,6	H-2',6'	H-3,5	H-3',5'	H-4	H-4'	NH^a	NH^b	CH_3	CH_2 (Ethyl)	CH_3 (Ethyl)	OCH_3
2a	7.93	7.41	7.55	7.18	7.66	-	-	12.47	2.27 2.29	-	-	-
2d	8.28	-	7.57	7.16	7.66	7.30	-	12.49	2.17	2.47	1.27	-
2e	7.97	7.79	7.54	8.27 8.16 7.25	7.67	-	11.87 12.01	13.17 13.33	-	-	-	3.93 3.94
3a	7.83	7.08 7.17	7.41	7.03	7.41	-	-	12.49	2.23 2.22	-	-	-
3c	7.85	7.22	7.40	7.00	7.40	7.11	-	12.37	2.23 2.29	-	-	-
3d	7.87	-	7.32	7.09	7.32	7.21	-	11.89	2.25	2.58	1.20	-



Scheme 2

where R = 3,4-dimethylphenyl thiourea (**1a**) and 2-ethyl-6-methylphenyl (**1d**) and R'= phenyl.

The same authors have shown that there is equilibrium in solution between species containing bidentate (S, O) *N*-acyl thiourea ligands and species containing monodentate (S) *N*-acyl thiourea ligands as well as between *cis* and *trans* isomers, as a function of *p*H of solution. In the case of *N*-benzoyl-*N*'-aryl thiourea derivatives the alkyl substituents on phenyl ring play a major role on Pt(II) complexes behaviour in solution [20].

There is a difference between the nitro and methoxy group on one hand and alkyl groups on the other hand, the later have an inductive electron repelling effect that increase the electron density on sulphur and oxygen atoms which enhances the capability of losing the amino protons and labilise the Pt-Cl bonds by *trans* influence.

Thus, we can assume that in solution the labile Pt-Cl bonds can be broken and the ligands loose their amino protons during the ring closure process. This process leads to the disappearance of H^a signals in the NMR spectra.

The H^b signals shifts to low field with 0.03 ppm for complex **2a** and with 0.14 ppm and 0.21 ppm for complex **2d**. The ^{1}H NMR spectra of complex **2d** shows the splitting of H^2 signal due to the presence of a mixture of *cis* and *trans* isomers, with 49% *trans* isomer and 51% *cis* isomer. The presence of the two isomers almost in equal proportion in the mixture can be explained by the equal chances of formation of the two isomers when the two Pt – Cl bonds are broken followed by the chelate (S, O) rings formation.

The aromatic region of the ^{1}H NMR spectra of complexes **2d** and **2e** becomes more complex due to the overlapping of the two sets of signals assigned to the two isomers *cis* and *trans*.

Generally, for all complexes, the signals assigned to protons in *ortho* position of benzoyl fragment shift to low field region while the signals of protons in *meta* position shift to high field, which represents a common feature of complexes with *N*-acyl thiourea derivatives [13].

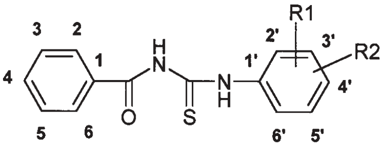


Table 3
^{13}C RMN DATA OF Pt(II) AND Pd(II) COMPLEXES

Complex	C-2,6	C-2',6'	C-3,5	C-3',5'	C-4	C-4'	C-1	C-1'	C=O	C=S	CH$_3$	CH$_2$ (ethyl)	CH$_3$ (Ethyl)
3a	128.6	130.3	128.1	132.2	131.3	135.0	135.9	137.8	177.6	188.2	19.8	-	-
											19.4		
3c	128.7	129.6	128.1	132.8	131.4	131.4	134.9	136.4	177.7	188.9	17.5	-	-
		125.4									20.9		
3d	128.9	130.7	-	126.8	-	128.5	131.1	141.5	177.5	190.8	18.3	24.8	14.7
		135.9		128.9									

Three Pd(II) complexes **3a**, **3c** and **3d** have been investigated by ^{1}H, ^{13}C and 2D-NMR (COSY and ^{1}H-^{13}C heterocorrelation) spectroscopy. The ^{1}H NMR data are presented in table 2 while the ^{13}C NMR chemical shifts are presented in table 3.

The most important feature of the ^{1}H NMR spectra of Pd(II) complexes is the disappearance of one of the two signals assigned to amino protons in the ^{1}H NMR spectra of ligands. This fact confirms that the *N*-benzoyl thiourea derivatives act as deprotonated bidentate ligands giving rise to neutral complexes, information which was confirmed by IR spectroscopy as well. The disappearance of signal located around 9 ppm in the ^{1}H NMR spectra of ligands is a result of coordination to Pd(II) with loosing of H^{a} proton, thus the signal situated in the 11-12 ppm range can be certainly assigned to H^{b} proton [20].

The aromatic region of ^{1}H NMR spectra of Pd(II) complexes show very interesting features. All signals assigned to aromatic protons shift to high field together with their overlapping as a consequence of perturbation of the whole aromatic system due to coordination to the Pd(II) centre. Thus, the signals assigned to H-2,6 shift with 0.03-0.05 ppm, H-3,5 with 0.13-0.16 ppm and H-4 with 0.16-0.17 ppm to high field compare to ^{1}H NMR spectra of ligands. The signals of aromatic protons of substituted phenyl ring show a much more pronounced shift to high field as follows: 0.22-0.33 ppm (H-2',6'); 0.07-0.16 ppm (H-3',5') and 0.04-0.09 ppm (H-4').

The ^{13}C NMR spectra of Pd(II) complexes show that both the signal assigned to carbon atom of thiocarbonyl group and the signal assigned to carbon atom of carbonyl group are shifted with ~10 ppm to low field as a result of coordination of the ligand through sulphur and oxygen atoms. The simultaneous shift of C=O and C=S signals is an indication of an extended electron delocalisation in the two chelate rings.

An interesting feature of square-planar Pd(II) complexes is the presence of *cis* and *trans* isomers. Beyer et al. [21] have prepared and analysed by X-ray diffraction the cis isomer of Pd(II) complex with *N*-benzoyl-*N'*,*N'*-diethyl thiourea ligand.

The ^{1}H NMR spectrum of complex **3a** shows two very weak signals at 2.26 ppm and 2.27 ppm besides the singlet signals of the two methyl groups at 2.22 ppm and 2.23 ppm, which can be explained by the presence of both *cis* and *trans* isomers in solution. Based on the results of Beyer et al. the strong signals can be assigned to *cis* major isomer while the weak signals can be assigned to *trans* isomer. The integration of these signals gives 82 % *cis* and 18% *trans* isomer. Also, the signals assigned to carbon atoms of these two methyl groups are accompanied by weak signals in the ^{13}C NMR spectrum of complex **3a**.

The presence of two sets of singlet signals assigned to methyl groups (2.23 and 2.29 ppm for strong signals and 2.17 ppm and 2.28 ppm for weak signals) was detected in the ^{1}H NMR spectrum of complex **3c**, but their integration gives a very low proportion of *trans* isomer in the mixture.

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