A series of Pt(II) and Pd(II) complexes with N-benzoyl-N'-aryl thiourea derivatives were prepared and investigated by means of several spectroscopic techniques: IR and UV-VIS, ¹H and ¹³C NMR spectroscopy. These derivatives act as monodentate ligands through the sulfur atom to Pt(II) and as bidentate through the sulfur and oxygen atoms to Pd(II). The ¹H 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, ¹H and ¹³C NMR spectroscopy

The N-acyl-N'-aryl thiourea derivatives have been employed in the preparation of metal complexes much more rarely. One of the reasons might be the capability of the two amino groups to lose 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.

¹H, ¹³C and ²D-NMR were recorded on a Bruker DRX 400 MHz spectrometer using CDCl₃ 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 chlorid 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.

**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): 1673; 1550 vs; 1522s; 1330s; 681m.

**Compound 2c.** Yield 62%. 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): 1673; 1550 vs; 1522s; 1330s; 681m.

**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): 1675; 1543vs; 1515s; 1319s; 707m.
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; 693m.

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 3e. 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, 1517s; 1345; 1315s; 695m.

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 for Pt(II) complexes with square-planar symmetry [14, 15]. Another important feature of ν(C=S) 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(C=S) bands due to 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 is ν(C=O) absorbtion band, which is assigned to intraligand ν(C=O) absorbtion band in the UV region located around 240 nm (fig. 1). The second absorbtion band is overlapped by the wide band with maximum absorption at ~240 nm (fig. 1).

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 two absorbtion bands assigned to intraligand 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](Image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>π→π*</th>
<th>n→π*</th>
<th>CT</th>
<th>1/2A1g→1/2Eg</th>
<th>1/2A1g→1/2B1g</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>248</td>
<td>277</td>
<td>-</td>
<td>330</td>
<td>471</td>
</tr>
<tr>
<td>2b</td>
<td>248</td>
<td>277</td>
<td>-</td>
<td>365</td>
<td>485</td>
</tr>
<tr>
<td>2c</td>
<td>245</td>
<td>-</td>
<td>-</td>
<td>365</td>
<td>484</td>
</tr>
<tr>
<td>2d</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>362</td>
<td>486</td>
</tr>
<tr>
<td>2f</td>
<td>245</td>
<td>-</td>
<td>-</td>
<td>365</td>
<td>445</td>
</tr>
<tr>
<td>3a</td>
<td>249</td>
<td>290</td>
<td>340</td>
<td>359</td>
<td>460</td>
</tr>
<tr>
<td>3b</td>
<td>245</td>
<td>380</td>
<td>-</td>
<td>-</td>
<td>427</td>
</tr>
<tr>
<td>3c</td>
<td>253</td>
<td>298</td>
<td>335</td>
<td>387</td>
<td>460</td>
</tr>
<tr>
<td>3d</td>
<td>248</td>
<td>290</td>
<td>340</td>
<td>380</td>
<td>453</td>
</tr>
<tr>
<td>3f</td>
<td>252</td>
<td>294</td>
<td>335</td>
<td>377</td>
<td>455</td>
</tr>
</tbody>
</table>

CT – charge transfer

REV. CHIM. (București) • 59 • Nr. 8 • 2008
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 D4h
symmetry [15, 16].

NMR Spectroscopy

1H NMR spectra were recorded only for complexes 2a,
2d and 2e due to the poor solubility of Pt(II) complexes in
chloroform. Interpretation of 1H NMR spectra of Pt(II)
complexes was made with the help of previous assignment
of the 1H NMR spectra of the ligands and using the 1H 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 1H 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 1H 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
H1 signal is shifted with 2.67 ppm and 2.81 ppm to low field
while the H2 signal is shifted with 0.03 ppm and 0.19 ppm
to low field compared with the positions of these signals
in the 1H 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. 1H NMR spectra of
Pt(II) complexes 2a and 2d are different from complex 2e
showing the disappearance of H1 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.
Table 2

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>H-2,6</th>
<th>H-2',6'</th>
<th>H-3,5</th>
<th>H-3',5'</th>
<th>H-4</th>
<th>H-4'</th>
<th>NH</th>
<th>NH</th>
<th>CH$_3$ (Ethyl)</th>
<th>CH$_3$ (Ethyl)</th>
<th>OCH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>7.93</td>
<td>7.41</td>
<td>7.55</td>
<td>7.18</td>
<td>7.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.47</td>
<td>2.27</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>8.28</td>
<td>-</td>
<td>7.57</td>
<td>7.16</td>
<td>7.66</td>
<td>7.30</td>
<td>-</td>
<td>-</td>
<td>12.49</td>
<td>2.17</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>7.97</td>
<td>7.79</td>
<td>7.54</td>
<td>8.27</td>
<td>7.67</td>
<td>-</td>
<td>11.87</td>
<td>13.17</td>
<td>-</td>
<td>-</td>
<td>3.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>7.83</td>
<td>7.08</td>
<td>7.41</td>
<td>7.03</td>
<td>7.41</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.49</td>
<td>2.23</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>7.85</td>
<td>7.22</td>
<td>7.40</td>
<td>7.00</td>
<td>7.40</td>
<td>7.11</td>
<td>-</td>
<td>-</td>
<td>12.37</td>
<td>2.23</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>7.87</td>
<td>-</td>
<td>7.32</td>
<td>7.09</td>
<td>7.32</td>
<td>7.21</td>
<td>-</td>
<td>-</td>
<td>11.89</td>
<td>2.25</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 pH 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$^+$ signals in the NMR spectra.

The H$^+$ 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 1H NMR spectra of complex 2d shows the splitting of H$^+$ 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 1H 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].
Three Pd(II) complexes 3a, 3c and 3d have been investigated by $^{1}$H, $^{13}$C and 2D-NMR (COSY and $^{1}$$^{13}$C heterocorrelation) spectroscopy. The $^{13}$C NMR data are presented in table 2 while the $^{1}$$^{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-proton, thus the signal situated in the 11-12 ppm range can be certainly assigned to H-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 compared 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 accompanied by weak signals at 2.26 ppm and 2.27 ppm besides the singlet signals of 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.

Acknowledgements

The authors wish to thank MEdC (Romanian Ministry of Education and Research) for funding this study.

References


Manuscript received: 17.12.2007

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>C-2,6</th>
<th>C-2',6'</th>
<th>C-3,5</th>
<th>C-3',5'</th>
<th>C-4</th>
<th>C-4'</th>
<th>C-1</th>
<th>C-1'</th>
<th>C=O</th>
<th>C=S</th>
<th>CH3</th>
<th>CH2</th>
<th>CH3 (ethyl)</th>
<th>(Ethyl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>128.6</td>
<td>130.3</td>
<td>128.1</td>
<td>132.2</td>
<td>131.3</td>
<td>135.0</td>
<td>135.9</td>
<td>137.8</td>
<td>177.6</td>
<td>188.2</td>
<td>19.8</td>
<td>-</td>
<td>-</td>
<td>19.4</td>
</tr>
<tr>
<td>3c</td>
<td>128.6</td>
<td>129.6</td>
<td>128.1</td>
<td>132.8</td>
<td>131.4</td>
<td>131.4</td>
<td>134.9</td>
<td>136.4</td>
<td>177.7</td>
<td>188.9</td>
<td>17.5</td>
<td>-</td>
<td>-</td>
<td>20.9</td>
</tr>
<tr>
<td>3d</td>
<td>128.9</td>
<td>130.7</td>
<td>-</td>
<td>126.8</td>
<td>-</td>
<td>128.5</td>
<td>131.1</td>
<td>141.5</td>
<td>177.5</td>
<td>190.8</td>
<td>18.3</td>
<td>24.8</td>
<td>14.7</td>
<td></td>
</tr>
</tbody>
</table>