Studies on platinum(II) and palladium(II) complexes of some N,N'-disubstituted thiourea derivatives

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Summary
A series of new PtⅡ and PdⅡ complexes of N,N'-disubstituted thiourea derivatives of general formulae [MLCl₂], [ML₂Cl₂] and [ML₄]Cl₂ have been prepared and characterised by physicochemical and spectroscopic methods. The reaction of these ligands with [M(DMSO)₂Cl₂], M = Pt, cis- or Pd, trans-, in CHCl₃ and EtOH at ambient temperature or under reflux, is described.

Introduction
Thiourea and its derivatives are important ligands for transition metals, especially platinum and to a lesser extent palladium. The high trans-effect caused by thiourea is a useful aid in the study of substitution reactions in square planar complexes. Thus, a large number of platinum complexes of thiourea and its derivatives have been synthesised and their chemistries studied. It has been concluded that the lowering of the v(C=S) value by ~25 cm⁻¹ compared to the free ligand, in the i.r. spectrum of the complex [PtCl₂L], in which L = tetramethylthiourea, is good evidence for monodentate ligation through sulphur and the complex should therefore have a dimeric structure. Conversely, Dunina studied the complexes [PdCl₂L], in which L = various mono-, di-, and tri-substituted thioureas by spectrophotometry and concluded that these ligands are monodentate and coordinate through nitrogen rather than sulphur. Kukushkin isolated a platinum(II) complex of allylthiourea and assigned Pt—N bonding, but they could not isolate a complex of the N,N'-diphenyl thiourea derivative. Furthermore, these workers assigned a cis-geometry to the complexes [PtL₂Cl₂] based on the small splitting of the v(Pt—Cl) frequencies, whereas Rochon et al. assigned a trans geometry to the complexes [PtL₂Cl₂] and [PtL₄Cl₂] in which L is a thiourea derivative and L' is a neutral ligand such as pyridine or ammonia. In view of the above, we have prepared various N,N'-disubstituted thiourea derivatives and their [MLCl₂], [ML₂Cl₂] and [ML₄]Cl₂ complexes, in which M = Pt or Pd and L = RNH(CS)NHR'(where R and R' = allyl (Al), cyclohexyl (Cy), ethyl (Et), 1-naphthyl (1-Np) or phenyl (Ph)).

Experimental
General
13C{'H} n.m.r. spectra were recorded in CDC1₃ or DMSO-d₆ at 25 °C on a Bruker—WH 90 DS spectrometer, operating at 22.63 MHz with a pulse width of 6 μs and a 3s delay. 1H n.m.r. spectra were recorded on the same spectrometer in CDC1₃.

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I.r. spectra were recorded on a Unicam SP 2000 spectrophotometer in the 200-4000 cm⁻¹ range using Nujol mulls and CsI discs.

Elemental analyses were carried out on a CHN Analyst, Type 1106 (Carlo Erba) and were performed in part at the laboratories of Prof. Dr. W. P. Neumann, Dortmund, Germany.

Conductivity measurements were made on 10⁻³ M solutions of the complexes at ambient temperature using a conductivity meter model 4070 (Jenway).

Starting materials
K₂PtCl₄ and K₂PdCl₄ were used as supplied from Fluka. The [M(DMSO)₂Cl₂] (M = Pt, cis-; Pd, trans-) complexes were prepared according to the literature.

The N,N'-disubstituted ureas, RNHC(O)NHR', where R = R' = Ph or R = Pd, R' = Cy, and the N,N'-disubstituted thioureas, RNHC(S)NHR', where R = R' = Ph; or R = Et, R' = Ph, Cy or 1-Np; or R = Ph, R' = Cy or 1-Np, were prepared by using the following standard method.

Equimolar quantities of the amino compound (RNH₂) and the corresponding isocyanate (RNCO) or isothiocyanate (RNCS) were dissolved in EtOH. The mixture was heated under reflux for 10 to 90 min. The solution thus formed was kept in ice-cold water for ~30 min, giving a white precipitate. This was recrystallised from EtOH and dried in vacuo for several hours. For all the isocyanates, the solid was obtained immediately on mixing with the amino compounds.

[MLCl₂]₂ complexes
These were prepared according to the following general procedure. K₂MCl₄ (1 mmol) was dissolved in distilled H₂O (15 cm³) and added gradually to a hot solution of the ligand (1 mmol) in EtOH (25 cm³). An immediate precipitate of the product was observed. The mixture was stirred for several hours at ambient temperature, to ensure complete reaction. The solid was then filtered off, washed several times with small portions of H₂O, EtOH and then with n-hexane and dried in vacuo for several hours. The yield in almost all cases was ≥80% based on the metal salt used.

[PtL₂Cl₂] complexes
These were prepared according to the method described by Bret et al. with a minor modification, as follows:

K₂PtCl₄ (1 mmol) was dissolved in distilled H₂O (10 cm³) and added gradually to a hot solution of the ligand (2 mmol) in EtOH (15 cm³). Immediate precipitation of the product was observed. The mixture was stirred for several hours at ambient temperature. The yellow solid was then filtered off, washed several times with small
portions of H₂O, EtOH and then with n-hexane and dried in vacuo for several hours. The yield in almost all cases was > 80% based on the Pt.

\[[\text{Pt(CPTU}_4]\text{Cl}_2\]

This complex was prepared by refluxing a mixture of PtCl₃ (1 mmol) and the ligand CPTU (6 mmol) in EtOH (50 cm³) for ~ 2 h. The yellow solution was filtered through celite and reduced in volume to ~ 15 cm³. The resulting precipitate was filtered off, washed with small portions of EtOH, Me₂CO and then with petroleum spirit (40–60 °C), and dried in vacuo for several hours. The yield was ~ 90%.

**Reaction of [M(DMSO)₂Cl₂] with thiourea in CHCl₃**

The complex [M(DMSO)₂Cl₂], (M = Pt, cis-; Pd, trans-) (1 mmol) was added to a suspension of the ligand (1.2 mmol) in CHCl₃ (50 cm³), and the mixture was stirred under reflux for ~30 min. The resulting yellow solution was filtered through celite and reduced in volume to ~ 15 cm³. The precipitate thus formed was filtered off, washed with petroleum spirit (40–60 °C), and dried in vacuo for several hours. The product was recrystallised from CHCl₃/pet. spirit.

**Results and discussion**

Physical data for the N,N'-disubstituted thiourea derivatives are listed in Table 1. Their ¹H and ¹³C n.m.r. spectral data have been reported previously.

The physical properties of the platinum(II) and palladium(II) complexes prepared from the reaction of K₂PtCl₄ and K₂PdCl₄ respectively with RNH(CS)NHR' are listed in Table 2; ¹H and ¹³C n.m.r. data for selected complexes are listed in Tables 3 and 4, respectively.

It has been reported previously that N,N'-diphenylthiourea (PPTU) does not give the bridged complex, [Pt(PPTU)Cl₂]₂. However, we repeated this reaction by adding an aqueous solution of K₂MC₁₄ (M = Pt or Pd) to a hot ethanolic solution of PPTU in 1:1 molar ratio and isolated a product whose elemental composition was in good agreement with the empirical formula MC₁₄·PPTU.

The i.r. spectrum showed two v(M—C₁) bands (Table 2); the one at higher frequency is assigned to terminal M—C₁, whilst the other may be assigned to bridging M—C₁—M ~12). The ¹³C n.m.r. spectrum (Table 4) is also consistent with the formulation [M(PPTU)Cl₂]₂ (vide infra).

**Table 1. Physical properties of the compounds RNHC(X)NHR' (X = S or O).**

<table>
<thead>
<tr>
<th>Species*</th>
<th>M.p. (°C)</th>
<th>Found (Calcd.)</th>
<th>Selected i.r. b</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>AINHC(S)NHCy (ACTU)</td>
<td>148–150</td>
<td>60.0</td>
<td>9.0</td>
<td>14.1</td>
</tr>
<tr>
<td>AINHC(S)NH-Np (ANTU)</td>
<td>146–147</td>
<td>68.9</td>
<td>6.0</td>
<td>11.45</td>
</tr>
<tr>
<td>AINHC(S)NHPh (APTU)</td>
<td>98–100</td>
<td>61.5</td>
<td>6.15</td>
<td>14.2</td>
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<tr>
<td>CyNHC(S)NH-Et (CETU)</td>
<td>104–105</td>
<td>58.0</td>
<td>9.4</td>
<td>14.8</td>
</tr>
<tr>
<td>CyNHC(S)NHPh (CPTU)</td>
<td>148–150</td>
<td>66.6</td>
<td>7.7</td>
<td>12.0</td>
</tr>
<tr>
<td>EtNHC(S)NH-Np (ENTU)</td>
<td>120–121</td>
<td>67.1</td>
<td>6.4</td>
<td>12.0</td>
</tr>
<tr>
<td>EtNHC(S)NHPh (EPTU)</td>
<td>98–99</td>
<td>59.4</td>
<td>6.65</td>
<td>14.9</td>
</tr>
<tr>
<td>1-NHC(S)NHPh (NPNU)</td>
<td>170–171</td>
<td>72.0</td>
<td>5.0</td>
<td>16.0</td>
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<tr>
<td>PhNHC(S)NHPh (PPTU)</td>
<td>154–155</td>
<td>67.8</td>
<td>5.2</td>
<td>11.9</td>
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<tr>
<td>CyNHC(O)NHPh (CPU)</td>
<td>185–186</td>
<td>71.0</td>
<td>8.1</td>
<td>12.8</td>
</tr>
<tr>
<td>PhNHC(O)NHPh (PPU)</td>
<td>242–244</td>
<td>72.9</td>
<td>5.55</td>
<td>13.0</td>
</tr>
</tbody>
</table>

*Abbreviations, A1, Cy, and 1-Np are for allyl, cyclohexyl, and 1-naphthyl groups, respectively. In Nujol mulls. Similar trends are observed for the complexes in Tables 2 and 5.