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Synthesis and NMR Spectra of Platinum Compounds with Thiourea Derivatives

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Abstract

Compounds *trans*-$[PtL_2(DPT)_2]Cl_2$ where L = NH_3, methylamine, dimethylamine, ethylamine and isopropylamine and DPT = *N,N'*-diphenylthiourea were synthesized from the reaction of *trans*-$[PtL_2Cl_2]$ with DPT in DMF. The IR and ^1H NMR spectra of the compounds were measured.

The resonance of the methyl protons in *N*-methylthiourea (MT), *N,N'*-dimethylthiourea (DMT) and in the complex $[Pt(DMT)_4]Cl_2$ was studied in the presence of pyridine in order to confirm the hypothesis of intramolecular interaction between the methyl group of the thiourea derivative and the aromatic ring in the complexes *trans*-$[PtL_2(MT \text{ or } DMT)_2]Cl_2$ (L = pyridine and 2-aminopyrimidine). $[Pt(DMT)_4]Cl_2$ reacts with pyridine in water to form *trans*-$[Pt(pyridine)_2(DMT)_2]Cl_2$. The ^{13}C NMR spectra of *trans*-$[Pt(pyridine)_2T_2]Cl_2$ (T = MT and DMT) are also reported.

Introduction

We have recently reported the synthesis of several compounds of the type *trans*-$[PtL_2(T)_2]Cl_2$ where L = nitrogen ligand and T = *N*-methylthiourea (MT), *N,N'*-dimethylthiourea (DMT) and *N,N,N',N'*-tetramethylthiourea (TMT) [1]. The ^1H NMR spectra of the compounds have confirmed that the thiourea derivatives were coordinated to platinum by the sulfur atom. The methyl protons of MT and one methyl group protons of DMT in the complexes where L is aromatic, showed resonance at higher field after coordination to the metal. This shielding was explained by an intramolecular interaction between the methyl group and the aromatic ring of pyridine or 2-aminopyrimidine.

In order to verify this hypothesis, we have continued this study by synthesizing platinum compounds containing a thiourea derivative with aromatic rings. We have chosen *N,N'*-diphenylthiourea (DPT). We were interested to know if the methyl groups of aliphatic amines could be shielded by the close environment of an aromatic ring located on the thiourea derivative. We have now synthesized several compounds *trans*-$[PtL_2(DPT)_2]Cl_2$ which were studied by ^1H NMR and by IR spectroscopy.

We have also studied the NMR of the methyl protons of the free ligands MT and DMT and of the complex $[Pt(DMT)_4]Cl_2$ in the presence of pyridine in different proportion, in order to confirm our hypothesis on intramolecular interaction.

The ^{13}C NMR spectra of *trans*-$[Pt(pyridine)_2(MT)_2]Cl_2$ and *trans*-$[Pt(pyridine)_2(DMT)_2]Cl_2$ were measured and will be discussed below.

Experimental

trans-[PtL$_2$Cl$_2$]

These compounds were synthesized by the method described by Kauffman [2, 3].

trans-[PtL$_2$(DPT)$_2$]Cl$_2$

The complex *trans*-$[PtL_2Cl_2]$ (0.7 mmol) was dissolved in 2 ml of DMF and the solution was filtered. An excess of DPT (3 mmol) was added to the filtrate, and the mixture was stirred during 6 h. The pale yellow precipitate was filtered, washed with ether and stirred with ether for 12 h in order to remove completely DMF and the excess DPT. The solid was filtered out and dissolved in water. The aqueous solution was filtered and evaporated to dryness under vacuum. The product was again washed several times with ether and dried under vacuum for 12 h. Compounds with L = NH_3, methylamine (MA), dimethylamine (DMA), ethylamine (EA) and isopropylamine (IPA) were synthesized.

trans-[Pt(NH$_3$)$_2$(DPT)$_2$]Cl$_2$

Yield 60%, dec. 190–200 °C. *Anal.* Calc.: C, 41.27; H, 3.97; Cl, 9.39. Found: C, 40.36; H, 3.88; Cl, 9.81%. IR: 3350s, 3310m, 3110l, 1590s, 1583s, 1535s, 1485s, 1290s, 1250s, 1205m, 1180w, 1065w, 761s, 725m, 680s, 620m, 600m, 580m, 500m, 435m, 260w cm^{-1}.

trans-[Pt(MA)$_2$(DPT)$_2$]Cl$_2$

Yield 70%, dec. ~125 °C. *Anal.* Calc.: C, 42.86; H, 4.35; Cl, 9.06. Found: C, 42.38; H, 4.54; Cl, 9.17%. IR: 3215s, 3195m, 3100l, 1594s, 1550s,

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1520s, 1490s, 1420m, 1400m, 1310m, 1270m, 1235m, 1215m, 1130s, 1085s, 1025w, 995w, 920w, 850w, 750s, 680s, 590s, 498s, 475w, 290w, 271w cm^{-1}.

trans-[Pt(DMA)$_2$(DPT)$_2$]Cl$_2$
Yield 50%, dec. 180–195 °C. *Anal.* Calc.: C, 44.33; H, 4.69; Cl, 8.74. Found: C, 43.95; H, 4.80; Cl, 9.10%. IR: 3355m, 3100l, 1590s, 1505s, 1488s, 1285m, 1250s, 1210m, 1130m, 1075s, 890m, 750s, 680s, 590m, 500m, 273w cm^{-1}.

trans-[Pt(EA)$_2$(DPT)$_2$]Cl$_2$
Yield 50%, dec. 160–165 °C. *Anal.* Calc.:, C, 44.33; H, 4.69; Cl, 8.74. Found: C, 43.69; H, 4.74; Cl, 9.02%. IR: 3340s, 3160l, 3070l, 1585m, 1535s, 1485s, 1280m, 1260s, 1220w, 1090w, 757s, 720m, 680s, 600w, 500w, 270vw cm^{-1}.

trans-[Pt(IPA)$_2$(DPT)$_2$]Cl$_2$
Yield 40%, dec. 130–140 °C. *Anal.* Calc.: C, 45.71; H, 5.00; Cl, 8.45. Found: C, 45.07; H, 5.48; Cl, 9.97%. IR: 3350m, 3180l, 3070l, 1590s, 1535s, 1480s, 1285s, 1265s, 1255s, 1245m, 1215m, 1190w, 1150w, 1110s, 1065w, 1020m, 930m, 753m, 725m, 685s, 505w, 440w, 271w cm^{-1}.

[Pt(DMT)$_4$]Cl$_2$, *trans*-[Pt(pyridine)$_2$(MT)$_2$]Cl$_2$ and *trans*-[Pt(pyridine)$_2$(DMT)$_2$]Cl$_2$ were prepared as already described [1].

The infrared spectra were measured as Nujol mulls on a P.E. 621 spectrometer. A 60 MHz Varian EM 360C was used to record the ^{1}H NMR spectra. These were measured in D_2O (~0.2 M) at 30 °C. For the *trans*-[PtL$_2$(DPT)$_2$]Cl$_2$ complexes, a very small quantity of DSS was used as internal standard. The spectra of MT, DMT and [Pt(DMT)$_4$]Cl$_2$ with pyridine were recorded with a small quantity of DSS as external standard (the chemical shifts as slightly different). The ^{13}C NMR spectra were recorded on a Bruker WP 80 MHz instrument in D_2O with 1,4-dioxane as standard.

Results and Discussion

The compounds *trans*-[PtL$_2$(DPT)$_2$]Cl$_2$ where L = NH_3, methylamine (MA), dimethylamine (DMA), ethylamine (EA) and isopropylamine (IPA) and DPT = diphenylthiourea were prepared according to the following equation:

$$\textit{trans}\text{-}[PtL_2Cl_2] + 2DPT \xrightarrow{DMF} \textit{trans}\text{-}[PtL_2(DPT)_2]Cl_2$$

The yields vary from 30 to 70%. We were not able to synthesize compounds with L = pyridine and 2-aminopyrimidine probably because the steric hindrance would be too large.

The compounds *trans*-[PtL$_2$(DPT)$_2$]Cl$_2$ must be washed several times with ether in order to remove completely the DMF. The compound with L = NH_3 is difficult to obtain pure. The first analytical results indicated a low %C and a high %Cl probably because of an incomplete reaction. Therefore great care should be taken to remove completely DMF, the excess DPT and the starting material. The results of the chemical analyses of the five compounds are shown in 'Experimental'.

The IR spectra of the synthesized complexes, *trans*-[PtL$_2$(DPT)$_2$]Cl$_2$ were measured, and the main bands appear in 'Experimental'. Most of the bands are due to combination vibrations. A strong band around 1590 cm^{-1} was assigned to ν(CN) + δ(NH) while another band around 755 cm^{-1} was assigned to ν(CS) + ν(CN) + ν(C'N). These bands appeared at 1595 and 754 cm^{-1} in free DPT. These assignments are based on the works of Gosavi and Rao [4] and Kukushkin *et al.* [5]. A very weak band observed around 270 cm^{-1} might be assigned to Pt–S stretching vibrations [5]. The bands caused by the –NH vibrations in coordinated DPT appear either at the same frequencies or at very slightly higher frequencies, compared to free DPT, indicating that the N atoms are not involved in coordination. Therefore diphenylthiourea is bonded to platinum through its sulfur atom, similarly to the other thiourea derivatives [1].

The ^{1}H NMR spectra of the five compounds *trans*-[PtL$_2$(DPT)$_2$]Cl$_2$ were measured in D_2O and the results are shown in Table I. All the protons are shifted towards lower field upon coordination, the amine, being more affected than DPT. The two methyl groups in dimethylamine appear separately indicating a different environment probably caused by steric hindrance. The rotation around the Pt–S and Pt–N bonds is hindered because of the presence of four bulky ligands. The methyl protons of MA and DMA couple with ^{195}Pt with a coupling constant $^3J(^{195}Pt-^1H)$ = 40 Hz. The α-protons in ethylamine and isopropylamine should also couple with ^{195}Pt, but the coupling constant could not be calculated since these peaks are multiplets of low intensity. The DPT protons appear as a singlet.

In our previous work [1], we have observed that the methyl protons of MT and one methyl group protons of DMT in the complexes *trans*-[PtL$_2$(MT or DMT)$_2$]Cl$_2$ (L = pyridine and 2-aminopyrimidine) were shifted to higher field upon coordination. This shielding was explained assuming that the methyl group of MT or one methyl group of DMT was in the close environment of the aromatic ring of L. For steric reasons, the rotations around the Pt–S and Pt–N bonds are hindered and the methyl protons of the thiourea derivative would be influenced by the π electrons of pyridine or 2-aminopyrimidine (Fig. 1). IR and X-ray diffraction have confirmed the double

TABLE I. ^{1}H NMR Chemical Shifts (δ(ppm)) and Coupling Constants (Hz) of the Complexes *trans*-$[Pt(L)_2(DPT)_2]Cl_2$ Measured in D_2O

L	L				DPT		
	Free	Complexed	Δ	^3J(Pt–H)	Free	Complexed	Δ
NH_3					7.33	7.39	0.06
Methylamine	2.30	2.50	0.20	42	7.33	7.48	0.15
Dimethylamine	2.30	2.68	0.38	40	7.33	7.50	0.17
		2.76	0.46	40			
Ethylamine	1.03	1.23	0.20		7.33	7.45	0.12
	2.66	2.86	0.20				
Isopropylamine	1.07	1.28	0.21		7.33	7.50	0.17
	3.05	3.31	0.26				

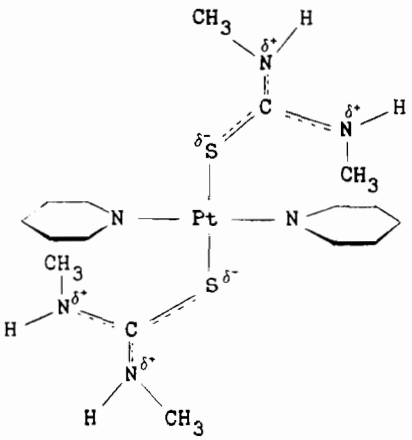

Fig. 1. Partial charge in dimethylthiourea and structure of *trans*-$[Pt(pyridine)_2(DMT)_2]^{2+}$.

bond character of the C–N bonds in the thiourea derivatives and the lower order of the C–S bond [1 and refs. therein]. Therefore there is some partial charge on the thiourea derivative as suggested for DMF [6], resulting in a close interaction of one methyl group with the aromatic ring.

It seemed interesting to study the NMR spectra of platinum(II) compounds with diphenylthiourea and amines containing methyl groups in order to determine if the methyl protons of the amines could be shielded by the close environment of the aromatic ring in DPT. No shielding was observed as expected (Table I) since the nitrogen atom of the amine ligand is not partly positively charged as the nitrogen atom in the thiourea derivatives (Fig. 1).

The ^{13}C NMR spectra of the complexes *trans*-$[Pt(pyridine)_2T_2]Cl_2$ where T = MT and DMT were measured in D_2O (Table II). The pyridine carbons in the complexes are observed at lower field than free pyridine as expected. The methyl carbon of MT and one methyl carbon of DMT are shielded compared to the free thiourea derivatives. These results are similar to those obtained from ^{1}H NMR [1]. The

TABLE II. ^{13}C NMR Spectra of the Complexes *trans*-$[Pt(pyridine)_2T_2]Cl_2$

T	δ (ppm) pyridine			δ(ppm)T	
	$C_{3,5}$	C_4	$C_{2,6}$	$-CH_3$	
Free Py	123.7	135.7	149.9		
Free MT				31.01	
$[Pt(Py)_2(MT)_2]Cl_2$	127.5	140.7	154.2	30.50	
Δδ	3.8	5.0	4.3	−0.51	
Free DMT				31.01	
$[Pt(Py)_2(DMT)_2]Cl_2$	127.4	140.7	153.9	29.77	32.47
Δδ	3.7	5.0	4.0	−1.24	1.46

meta carbons (C_3, C_5) of pyridine couple with ^{195}Pt in the DMT complex with a coupling constant $^3J(^{195}Pt-^{13}C) = 41$ Hz. No similar coupling was observed with C_2 and C_6 which are closer to the platinum atom. We have recently started a ^{13}C NMR study on several pyridine derivatives platinum(II) complexes. Similar results were obtained and this work will be published later. The absence of coupling between Pt and C_2 or C_6 can be explained by the spatial arrangement of the orbitals on the platinum atom related to those on C_2 or C_6.

The results on the diphenylthiourea are in agreement with our interaction hypothesis. We continued the study by measuring the ^{1}H NMR spectra of the ligands MT and DMT in water in the presence of different concentrations of pyridine (with DSS as external standard). The chemical shifts are shown in Fig. 2 as a function of the molar fraction of pyridine. The total concentration in water was 0.4 M. The thiourea derivatives showed a resonance at δ = 2.83 ppm for MT and 2.89 ppm for DMT. In the presence of pyridine, the methyl protons are slightly shielded. At a 0.05 molar fraction of thiourea derivative, the resonance appeared at δ = 2.77 ppm for MT and at 2.83 ppm for DMT. Therefore there is a gradual change for a maximum Δ of 0.06 ppm as the concentration of pyridine increases. The shielding

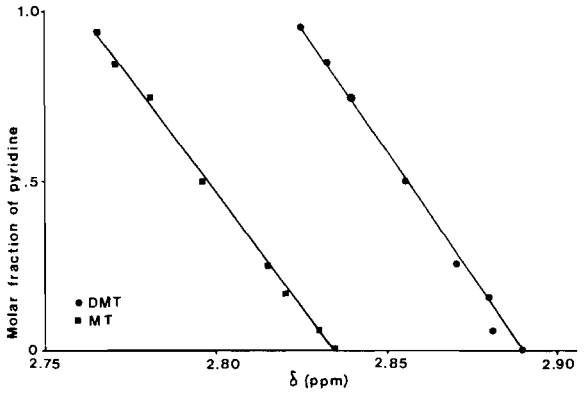

Fig. 2. Chemical shifts of MT and DMT in the presence of pyridine.

observed in the complexes *trans*-[Pt(pyridine)$_2$(MT or DMT)$_2$]Cl$_2$ was much greater, about 0.3 ppm. This can be explained by the fact that the partial charges in the thiourea derivatives are much more important in the coordinated ligand and therefore the interaction with the aromatic ring is enhanced. The hindered rotation of the ligands around the Pt atom results in a fairly rigid molecule and the inter-ligand interaction is again enhanced.

We then repeated the study with pyridine, using [Pt(DMT)$_4$]Cl$_2$ instead of the free ligands. We reported earlier that [Pt(DMT)$_4$]Cl$_2$ showed only one resonance peak, but when using scale expansion with accumulation of spectra, we observed two large peaks not very well resolved at approximately 3.05 and 2.92 ppm. When pyridine is added to the complex [Pt(DMT)$_4$]Cl$_2$, the two peaks become better resolved. As the concentration of pyridine is increased, the intensity of the peak at 2.9 ppm increases and we can also observe the appearance of a new peak at 2.59 ppm. Therefore we can conclude that [Pt(DMT)$_4$]Cl$_2$ decomposes in the presence of pyridine (Py) as follows:

$$[Pt(DMT)_4]Cl_2 + 2Py \xrightarrow{H_2O}$$

$$\textit{trans}\text{-}[Pt(Py)_2(DMT)_2]Cl_2 + 2DMT$$

trans-[Pt(Py)$_2$(DMT)$_2$]Cl$_2$ shows two peaks at 2.59 and 3.0 ppm while free DMT has one peak at 2.89 ppm.

These results are in agreement with our hypothesis on the structure of the complexes *trans*-[Pt(L)$_2$T$_2$]-Cl$_2$ where L = pyridine or 2-aminopyrimidine and T = MT or DMT (Fig. 1). Methylthiourea has only one methyl group and therefore has the *trans* configuration in the complex (thioamide hydrogen and thiocarbonyl bond are *trans*). DMT has two methyl groups, but only one interacts with the aromatic ring as shown by NMR spectroscopy. Coordinated DMT has either the *trans–trans* configuration as shown in Fig. 1 or the *trans–cis* configuration.

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