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Platinum and palladium complexes of thiosemicarbazones derived of 2-acetylthiophene: Synthesis and spectral studies

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Abstract

The reaction of 2-acetylthiophene thiosemicarbazone (2-HATT) and 2-acetylthiophene 4-phenylthiosemicarbazone (2-HAT-4-FT) with $Pd(COD)Cl_2$ (COD = 1,5-cyclooctadiene) and *trans*-$Pt_2PEt_3Cl_4$ yielded four new metal complexes: $[Pd(2\text{-}HATT)Cl_2]$ (**1**), $[Pd(2\text{-}ATT)_2]$ (**2**), [Pd(2-AT-4-FT)Cl] (**3**) and [Pt(2-ATT)(PEt_3)Cl] (**4**). Apart from compound **3** all the others were characterised by ^1H and $^{13}C\{^1H\}$ NMR, infrared spectroscopy, and elemental analysis. Multinuclear NMR experiments of $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ of complex **4** have revealed that the ligand 2-HATT behaves as a bidentate chelating agent towards $Pd(COD)Cl_2$ and *trans*-$Pt_2PEt_3Cl_4$ whereas ligand 2-HAT-4-FT forms a tridentate chelating complex with $Pd(COD)Cl_2$.

Keywords: Heterocyclic thiosemicarbazone; Metal complexes; Palladium(II) and platinum(II)

1. Introduction

Thiosemicarbazones and the corresponding metal complexes are widely known as having a large range of biological applications, such as antiviral, antibacterial, antimalarial, antifungal, etc. [1,2]. The compound *p*-acetamidobenzaldehyde thiosemicarbazone, commercially available as thiacetazone, has long been employed in the treatment of tuberculosis [3]. The activity of these compounds is strongly dependent upon the nature of the heteroaromatic ring and the position of attachment to the ring, as well as the form of the thiosemicarbazones moiety [4–6].

Thiosemicarbazones usually react with metallic cations giving complexes in which the ligand behaves as chelating agent bonding through the sulfur and hydrazine nitrogen atoms. Palladium and platinum complexes of thiosemicarbazones have been reported as compounds that present biological activity [7–9].

Previous works have reported the structural characterisations, the biological activity and coordination features of 2-acetylthiophene thiosemicarbazone [10–15]. The synthesis and crystallographic characterisation of 2-acetylthiophene 4-phenylthiosemicarbazone as well as the structural revision of 2-acetylthiophene thiosemicarbazone have been published by us [16]. Some of us have been interested in the biological aspects of such chemistry. In the last years the biological activity of thiosemicarbazone complexes of Pd(II), Pt(II), Cu(II), Zn(II) and organotin halides has been investigated. The later complexes have revealed interesting antifungal [17] and cytotoxic activity [18].

In this work we reported the synthesis and spectroscopic characterisation of new palladium(II) and platinum(II) complexes of thiosemicarbazones derived from 2-acetylthiophene.

2. Experimental

2.1. Material and procedures

Experimental work was carried out in air atmosphere. All solvents were distilled prior to use. The chemicals were obtained from Aldrich and Strem or prepared according

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to literature procedures [10–16,19–21]. NMR spectra were recorded in d_6-DMSO to complexes **1** and **2** and $CDCl_3$ to **4**, at 400.000 MHz ^1H, 100.577 MHz $^{13}C\{^1H\}$ using a Bruker DMX-400 spectrometer equipped with an 89 mm wide-bore magnet. $^{195}Pt\{^1H\}$ and $^{31}P\{^1H\}$ spectra were obtained for compound **4** at 85.996 and 161.923 MHz respectively. The IR spectra were recorded for CsI dies on a Perkin Elmer Paragon 1000 FTIR spectrophotometer in the frequency range of 4000–200 cm^{-1}. Microanalyses were carried out on a Perkin Elmer 2400 CHN Elemental Analyzer. Platinum and palladium analysis were performed using a Rigaku-Geiger Flex diffractometer with LiF crystal analyzer.

2.2. Synthesis of [Pd(2-HATT)Cl_2] (*1*)

To a round-bottom-flask containing 100 mL of ethanol under stirring, with 1.01 g (5.06 mmol) of 2-HATT, was added a solution of 1.37 g (4.79 mmol) of [Pd(COD)Cl_2] in 150 mL of ethanol. After 5 h of stirring at room temperature a red solid was filtered off and washed with ethanol and hexane. The product was dried in vacuum. Yield: 92%.

2.3. Synthesis of [Pd(2-ATT)$_2$] (*2*)

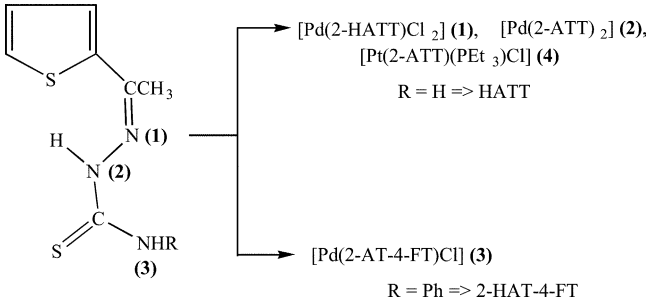
A round-bottom-flask was filled with 1.04 g (5.20 mmol) of 2-HATT and 100 mL of EtOH. When the solid was completely dissolved, 0.68 g (2.40 mmol) of [Pd(COD)Cl_2] in 150 mL of ethanol was added following the addition of 8.00 mL (5.20 mmol) of NH_4OH. An orange solid was immediately precipitated. After 5 h stirring at room temperature, the orange product was filtered off and washed with cold ethanol and hexane. The product was dried in vacuum. Yield: 53%.

2.4. Synthesis of [Pd(2-AT-4-FT)Cl] (*3*)

To a round-bottom-flask containing 100 mL of ethanol under stirring, were added 0.80 g (1.92 mmol) of 2-HAT-4-FT, following the addition of 0.50 g (1.75 mmol) of [Pd(COD)Cl_2] in 150 mL of ethanol. An orange solid precipitated and after 5 h stirring it was filtered off and washed with ethanol and hexane. The product was dried in vacuum. Yield: 75%.

2.5. Synthesis of [Pt(2-ATT)(PEt_3)Cl] (*4*)

To a round-bottom-flask charged with 100 mL of ethanol under stirring and 0.40 g (2.00 mmol) of 2-HATT, was were added a solution of 0.60 g (0.78 mmol) of [$Pt_2(PEt_3)_2Cl_4$] in 150 mL of ethanol. Within 5 h stirring a colour change from orange to red was observed. The solvent was removed in vacuum and a violet solid was obtained, with was washed with ethyl ether and hexane. Yield: 86%.



Scheme 1.

3. Results and discussion

Compounds [Pd(2-HATT)Cl_2] (**1**), [Pd(2-ATT)$_2$] (**2**) and [Pt(2-ATT)(PEt_3)Cl] (**4**) were prepared by reacting Pd(COD)Cl_2 or [$Pt_2(PEt_3)_2Cl_4$] with 2-acetylthiophene thiosemicarbazone (2-HATT) and [Pd(2-AT-4-FT)Cl] (**3**) with 2-acetylthiophene-4-phenylthiosemicarbazone (2-HAT-4-FT), according to Scheme 1.

All compounds were isolated as coloured air stable derivatives with acceptable melting points and elemental analysis (see Table 1 for analytical data).

Due to the low solubility of **1**, **2** and **3** it was not possible to obtain crystals for X-ray experiments. On the other hand compound **4** was fairly soluble in polar solvents, however the crystals obtained have not diffracted well, even after a number of attempts to obtain X-ray quality ones. Even though, the spectroscopic measurements employed were conclusive in determining the structures in solution (Tables 2–4).

For **1** the ^1H NMR spectrum, recorded in DMSO, have shown a signal at δ 11.3 indicating that the ligand remains protonated, as N(2)–H. In addition it was observed, as for the free ligand, two resonances for the NH_2 group, δ 8.4 and 9.3. The free ligand presents in the solid state a intra-molecular N(3)–H···N(1) hydrogen bond, which remains in solution, as attested by the ^1H NMR chemical shifts at δ 6.8 and 7.4. It is reasonable to conclude that the non-equivalence of the NH_2 hydrogen atoms still persists in complex **1**, Table 2 and 3. The

Table 1
Analytical data for complexes **1**–**4**

Complexes	Yield (%)	Colour	m.p. (°C)	Found (calcd.) (%)			
				C	H	N	M
[Pd(2-HATT)Cl_2] (**1**)	92	Red	230 (dec)	22.7 (22.3)	2.2 (2.4)	11.3 (11.1)	29.7 (28.3)
[Pd(2-ATT)$_2$] (**2**)	53	Orange	152–55	32.8 (33.4)	2.9 (3.2)	16.5 (16.7)	20.6 (21.2)
[Pd(2-AT-4-FT)Cl] (**3**)	75	Dark orange	280 (dec)	38.3 (37.5)	2.9 (2.9)	9.8 (10.1)	26.5 (25.6)
[Pt(2-ATT)(PEt_3)Cl] (**4**)	86	Violet	127–29	28.2 (28.6)	4.2 (4.2)	7.5 (7.7)	36.2 (35.6)

Table 2
^{1}H spectral assignments for ligands 2-HATT, 2-HAT-4-FT and Pd(II) and Pt(II) complexes

Compounds	CH_3(P)	CH_2(P)	CH_3	C_4H_3S	NH_2	NH
2-HATT[a]	–	–	2.3	7.1–7.3	6.8, 7.4	8.9
2-HA-4-FT[a]	–	–	2.3	7.1–7.7	8.8	9.3
1[b]	–	–	2.4	7.1–7.8	8.4, 9.3	11.3
2[b]	–	–	2.6	7.6–7.8	7.1	–
4[a]	1.2	1.9	2.6	6.7–7.4	7.9	–

[a] $CDCl_3$.
[b] $(CD_3)_2SO$.

Table 3
$^{13}C\{^1H\}$ spectral assignments for ligands 2-HATT, 2-HAT-4-FT and palladium(II) and platinum complexes

Compounds	CH_3(P)	CH_2(P)	CH_3	C_4H_3S	C=N	C=S
2-HATT[a]	–	–	14	129.2–127.3	144.2	178.0
2-HA-4-FT[a]	–	–	14	126.1–127.4	143.0	176.3
1[b]	–	–	15.8	125.5–130.2	141.5	172.0
2[b]	–	–	23.5	125.7–135.4	152.5	172.5
4[a]	8.7	17.8	15.8	132.2–164.8	178.3	183.0

[a] $CDCl_3$.
[b] $(CD_3)_2SO$.

IR spectrum of compound **1** has shown little change in the C=S bond upon coordination, since the vibration frequency vary from 825 to 830 cm^{-1}. On the other hand the C=N–N system changes from 1570 to 1555 cm^{-1} (C=N) and 1035 to 1088 cm^{-1} (N–N), Table 4. Therefore the coordination has occurred between $PdCl_2$ and both *S* of thiophene group and N(2), Fig. 1.

The ^{1}H and ^{13}C NMR spectra for **2** was little different from **1**, except by the absence of the signal corresponding to N(2)–*H*, and also because the other signals are all duplicated. At first we though it was impurity caused by an eventual excess of ligand, after several washing, the spectrum remained as it was. In addition the IR spectrum indicated, by analyzing the position of the two bands for ν(C=N) 1589 and 1511 cm^{-1}, that two ligand molecules were presented, Fig. 1.

Due to the low solubility of complex **3**, it was only characterised by IR and elemental analysis. In order to detect the deprotonation of the ligand we have monitored pH for the following solutions in ethanol: (i) [Pd(COD)Cl_2], 6.0; (ii) [2-HAT-4FT], 5.0 and (iii) mixture of (i) and (ii), 2.5. It has indicated that during the reaction the ligand stays deprotonated, causing a decrease in the reaction pH.

The reaction of [$Pt_2(PEt_3)_2Cl_4$] with 2-acetylthiophene thiosemicarbazone (2-HATT) yielded compound **4**, as represented in Fig. 1. The ^{1}H NMR spectrum of **4** has not displayed the signal corresponding to N(2)–*H*, indicating that the ligand is not protonated. It was also observed resonances corresponding to Ph group of the triphenylphosphine moiety. The $^{13}C\{^1H\}$ NMR spectrum has displayed the signals of the ligand. It has been observed in the $^{31}P\{^1H\}$ NMR spectrum a resonance at δ 11.4, revealing a $J^1(^{195}Pt–^{31}P) = 3698$ Hz. This coupling constant was also obtained in the $^{195}Pt\{^1H\}$ NMR experiment, where a doublet centered at δ −4418 was

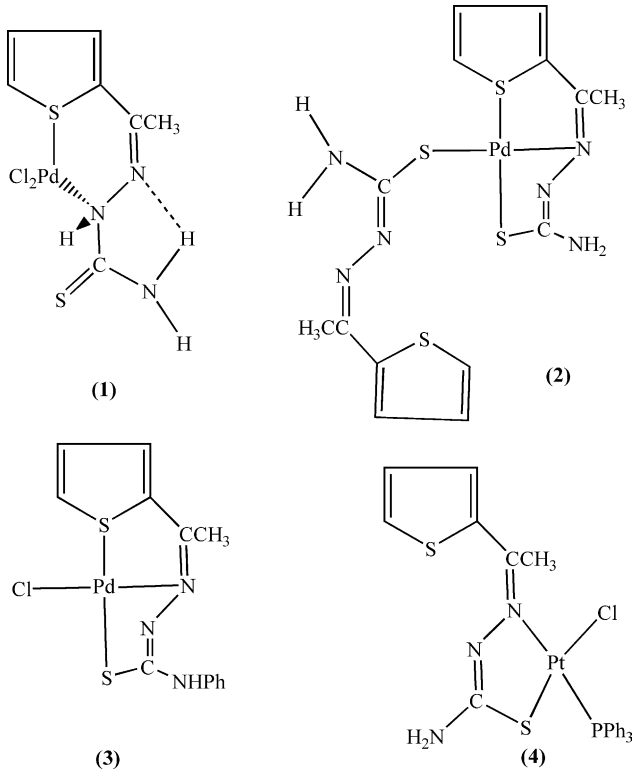


Fig. 1. Proposed structures of compounds **1**–**4**.

Table 4
Selected IR absorptions for ligands and complexes (cm^{-1})

Compounds	ν(N—H)	ν(C=N)	ν(N—N)	ν(C—S)	ν(M—N)	ν(M—S)	ν(M—Cl)	ν(P—C)	ν(M—P)
2-HATT	3445	1570	1035	825	–	–	–	–	–
2-HAT-4-FT	3295	1585	1030	830	–	–	–	–	–
1	3346	1555	1088	820	496	401	326, 305		
2	–	1511, 1589	1088, 1030	772, 796	474	405, 330	–	–	–
3	–	1529	1062	806	487	383, 345	300	–	–
4	–	1570	1082	808	456	340	292	1376	384

detected. According to the literature this coupling value is characteristic of a Pt–P trans to nitrogen bond system [22,23]. All the elemental analysis was consistent with the proposed structures in Fig. 1.

4. Summary of the results

Four new complexes of Pd and Pt were obtained by employing the ligands 2-acetylthiophene thiosemicarbazone (2-HATT) and 2-acetylthiophene 4-phenylthiosemicarbazone (2-HAT-4-FT). The compounds were characterised by multinuclear NMR experiments, infrared spectroscopy and elemental analysis.

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