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Coordination modes of 3-aminosalicylic and 3-hydroxyanthranilic acids in palladium(II), platinum(II) and rhenium(V) complexes. The crystal structure of *cis*-$[Pt(HsalNH)(PPh_3)_2]\cdot 0.25C_2H_5OH$

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Abstract

New Pd(II), Pt(II) and Re(V) complexes of 3-aminosalicylic acid (H_2salNH_2) and 3-hydroxyantranilic acid (HantOH) have been prepared, *cis*-[Pt (HsalNH)$(PPh_3)_2$]· $0.25C_2H_5OH$ (**1**), *trans*-[PdCl$(salNH_2)(PPh_3)_2$] (**2**), *trans*-[$ReOI_2(HsalNH_2)(PPh_3)$]$\cdot(CH_3)_2CO$ (**3**), *cis*-[Pt(HantO)$(PPh_3)_2$] (**4**), *trans*-[PdCl(antOH)$(PPh_3)_2$]$\cdot 4H_2O$ (**5**), [PdCl(antOH)(bipy)]$\cdot C_2H_5OH$ (**6**), [$PdCl_2$(HantOH)$_2$] (**7**) and *trans*-[ReOI(HantO)$(PPh_3)_2$]$\cdot(CH_3)_2CO$ (**8**). The crystal structure of complex **1** was determined showing chelation of $HsalNH^{2-}$ through the adjacent nitrogen and oxygen atoms of the amino and phenolate groups. Infrared and ^1H NMR spectroscopic data for the complexes are presented.

Keywords: 3-Aminosalicylic acid; 3-Hydroxyanthranilic acid; Crystal structure; Palladium; Platinum; Rhenium

1. Introduction

We have been studying the coordination modes of aromatic ambidentade ligands, such as 3-hydroxypicolinic acid [1,2], 2-hydroxynicotinic acid [3] and 2,3-, 3,4- and 2,6-dihydroxybenzoic acids, with 2nd and 3rd row transition metals and the lanthanides [4–6]. In the present work a comparative study was done on Pd(II), Pt(II) and Re(V) complexes with 3-aminosalicylic (H_2salNH_2) and 3-hydroxyantranilic acids (HantOH), respectively. The two ligands are constitutional isomers: 3-aminosalicylic acid is 3-amino-2-hydroxybenzoic acid (Fig. 1(a)), and 3-hydroxyanthranilic acid is 2-amino-3-hydroxybenzoic acid (Fig. 1(b)).

3-Aminosalicylic acid can bind to metals by several coordination modes: monodentate O or N donor, bridging, or by two different chelates either the O,O-chelate, involving the carboxylate group and the oxygen in position-2, resulting in a six-membered chelate-ring, or the N,O-chelate, involving the amino group nitrogen and the oxygen in position-2, with the formation of a five-membered chelate-ring. A similar O,O-chelate is found in complexes of salicylic acid and derivatives, such as $[MoO_2L_2]^{2-}$ (H_2L = salicylic acid, 4- or 5-methylsalicylic acids), $[PdL_2]$ (H_2L = salicylic acid) [7], $[MoO_2L_2]^{2-}$, $[OsO_2(py)_2L]$, [ReOIL(PPh_3)] (H_2L = 2,6-dihydroxybenzoic acid; py = pyridine) [8].

When deprotonated, 3-hydroxyanthranilic acid can also bind to metals by several coordination modes: monodentate O or N donor, bridging, or by two possible N,O-chelating modes, involving the nitrogen atom and the oxygen atom of either the hydroxyl group (forming a five-membered chelate-ring) or the carboxyl group (forming a six-membered chelate-ring). The former is found in complexes with 2-aminophenolate and

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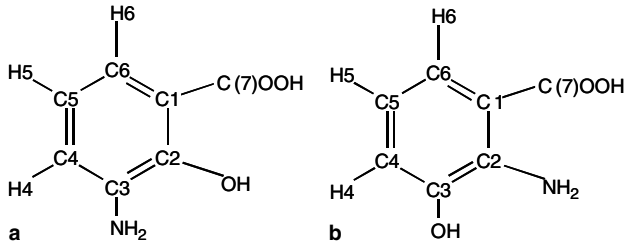

Fig. 1. 3-Aminosalicylic (a) and 3-hydroxyanthranilic (b) acids and numbering scheme adopted.

derivatives such as $[MoO_2(HL)_2]$ (H_2L = 2-amino-4-clorophenol, 2-amino-4-methylphenol) and $[OsL_3]$ (H_2L = 2-amino-4-methylphenol, 2-amino-4-^{t}butylphenol), $[MoO_2(HL)_2]$ [9] and $[PtL(PPh_3)_2]$ [10] (H_2L = 2-aminophenol), $[V(=NPh)(OC_6H_2(CH_2NMe_2)\text{-}2\text{-}Me_2\text{-}4,6)_2]$ [11], $[V(OC_6H_2(CH_2NMe_2)\text{-}2,6\text{-}Me\text{-}4)_3]$ and $[VCl(OC_6H_2(CH_2NMe_2)\text{-}2\text{-}Me\text{-}4)_2]$ [12]. The latter chelating mode is found in complexes of anthranilic acid like $[MoCl_3\{2\text{-}(HN)C_6H_4CO_2\}\{2\text{-}Me_3SiO_2CC_6H_4N\}]^-$, $[MoCl_3\{2\text{-}(HN)C_6H_4CO_2\}(NC_6H_3Pr^i_2\text{-}2,6)]^-$ [13] and $[Ba(2\text{-}NH_2C_6H_4CO_2)_2(OH_2)]_n$ [14].

The N,O-chelating mode in H_2salNH_2 is similar to the N,O-chelating mode with HantOH, forming five-membered chelate-rings. The formation of six-membered chelate-rings is in the case of H_2salNH_2 achieved through bonding to a carboxylate O atom and a hydroxyl O atom, and in the case of HantOH to a carboxylate O atom and an amino N atom. The coordination modes described were investigated in Pd(II), Pt(II) and Re(V) complexes using spectroscopic data and in one case X-ray diffraction data. The crystal structure of the Pt(II) compound **1** was determined and in this complex the 3-aminosalicylato ligand shows coordination through the nitrogen and oxygen atoms of the amino and phenolate groups (N,O-chelating mode). Spectroscopic characterisation of the remaining compounds suggests that other coordination modes may occur.

2. Results and discussion

2.1. Preparations

Suspensions of *cis*-$[PtCl_2(PPh_3)_2]$ or *trans*-$[PdCl_2(PPh_3)_2]$ and H_2salNH_2 or HantOH in an ethanol/methanol mixture in the presence of triethylamine gave complexes *cis*-$[Pt(HsalNH)(PPh_3)_2]\cdot 0.25C_2H_5OH$ (**1**), *trans*-$[PdCl(HsalNH_2)(PPh_3)_2]$ (**2**), *cis*-$[Pt(HantO)(PPh_3)_2]$ (**4**) and *trans*-$[PdCl(antOH)(PPh_3)_2]\cdot 4H_2O$ (**5**). When $K_2[PdCl_4]$ was used as starting material, the compound obtained was $[PdCl_2(HantOH)_2]$ (**7**). Reaction of the 2,2′-bipyridine (bipy) complex $[PdCl_2(bipy)]$ with HantOH gave compound **6**, $[PdCl(antOH)(bipy)]\cdot C_2H_5OH$. The complexes *trans*-$[ReOI_2(HsalNH_2)(PPh_3)]\cdot(CH_3)_2CO$ (**3**) and *trans*-$[ReOI(HantO)(PPh_3)_2]\cdot(CH_3)_2CO$ (**8**) were synthesised by refluxing *trans*-$[ReOI_2(OEt)(PPh_3)_2]$ with H_2salNH_2 or HantOH in acetone.

2.2. Crystal structure of *1*

The X-ray diffraction study of **1** shows that its crystal structure is built up from an asymmetric unit composed of one molecule of *cis*-$[Pt(HsalNH)(PPh_3)_2]$ and several solvent molecules of ethanol all with reduced occupancy. An ORTEP view showing the overall geometry of the complex and the atomic notation scheme is presented in Fig. 2. Bond lengths and angles are listed in Table 1 for complex **1**. The platinum(II) centre is surrounded by the nitrogen and oxygen atoms from the amino and phenol groups of the $HsalNH^{2-}$ ligand and the phosphorus atoms of the two PPh_3 ligands in a distorted square planar coordination environment. The angle N–Pt–O of 79.32(3)° is dictated by the O–N bite angle of the $HsalNH^{2-}$ ligand while the remaining angles in the metal coordination sphere are the result of

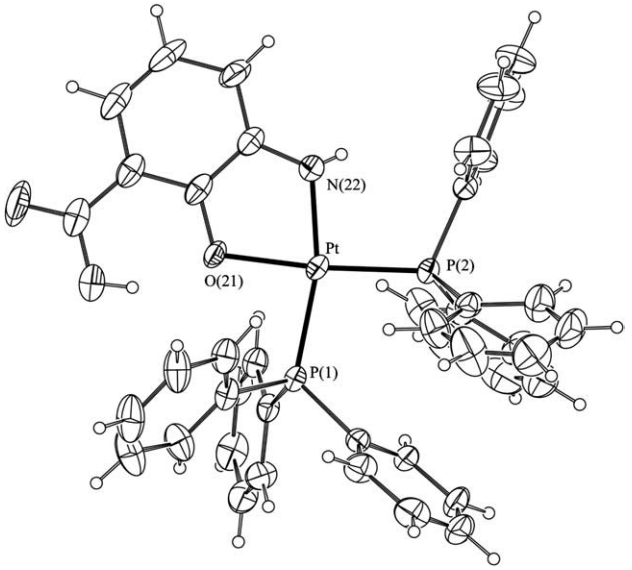

Fig. 2. An ORTEP view of *cis*-$[Pt(HsalNH)(PPh_3)_2]$ (**1**) showing the overall molecular geometry. Ellipsoids are drawn at 30% probability level.

Table 1
Selected distances (Å) and angles (°) for complex **1**

Pt–N(22)	2.014(6)
Pt–P(1)	2.289(2)
Pt–O(21)	2.069(5)
Pt–P(2)	2.226(2)
N(22)–Pt–P(1)	166.5(2)
P(2)–Pt–O(21)	174.2(2)
N(22)–Pt–P(2)	95.0(2)
P(1)–Pt–P(2)	99.4(1)
N(22)–Pt–O(21)	80.4(2)
P(1)–Pt–O(21)	86.1(2)

the minimisation of the steric interactions between the $HsalNH^{2-}$ ligand and the two bulky PPh_3 ligands. The bond lengths to the metal centre are within the values found for related complexes such as *cis*-[PtCl(picOH)$(PPh_3)_2$] [1] and *cis*-[PtCl(HnicO)$(PPh_3)_2$] [3].

2.3. Infrared spectra

Infrared data for H_2salNH_2, HantOH and complexes **1**–**8** are given in Table 2. Tentative assignments are based on those found in the literature for 3-aminosalicylic acid [15], salicylic acid [7], anthranilic acid and derivatives [16,17], 2-aminophenol [9], 3-hydroxypicolinic acid [1,2], and respective complexes. The most sensitive bands to metal coordination were selected, namely the C=O and C–O stretches of the carboxyl group, ν(C=O) and $\nu(C–O)_c$, the bending mode of the amino group, $\delta(NH_2)$, the C–O stretch of the phenolic group, $\nu(C–O)_{OH}$, and the C–NH_2 stretch, $\nu(C–NH_2)$.

The bending frequency of the NH_2 group, $\delta(NH_2)$, of 3-aminosalicylic acid is assigned at 1537 cm^{-1} and of 3-hydroxyanthranilic acid at 1548 cm^{-1}. In all complexes, this frequency shifts to higher wavenumbers. For complexes **5** and **6** it shifts only 3 cm^{-1}. For complexes **1**, **3**, **4**, **7** and **8** this shift is higher than 42 cm^{-1} showing that the amino group may be involved in the coordination to metals. It suggests that in complexes **5** and **6** the coordination may involve only the carboxylate or phenolate groups.

Two strong bands at 1651 and 1394 cm^{-1} in the spectrum of 3-aminosalicylic acid are assigned to the C=O and C–O stretches, ν(C=O) and $\nu(C–O)_c$, of the carboxyl group, respectively. In the spectrum of 3-hydroxyanthranilic acid these bands are seen at 1651 cm^{-1} and 1344 cm^{-1}, respectively. The ν(C=O) frequency decreases in complexes **5** and **6**, and the $\nu(C–O)_c$ frequency increases. The calculated $\Delta\nu(CO_2)$ values, defined by Deacon and Phillips as $\nu_{as}(CO_2) - \nu_s(CO_2)$, of 267 and 233 cm^{-1} for **5** and **6**, respectively, indicate a typical COO^- coordination fashion, possibly unidentate [18,19]. In **1**–**4**, **7** and **8**, the carboxyl group is possibly not involved in the coordination because of the increase of the ν(C=O) frequency. In complex **1**, the charge balance constrains a 2− charge in the deprotonated form of the 3-aminosalicylic acid. Assuming the 1721 cm^{-1} frequency as the C=O stretch, characteristic of the carboxyl group, the deprotonation possibly occurs in the phenolic and amino groups (according to crystal structure data). Similar deprotonation was described for $[MoCl_3\{2\text{-}(HN)C_6H_4CO_2\}\{2\text{-}Me_3SiO_2CC_6H_4N\}]^-$, $[MoCl_3\{2\text{-}(HN)C_6H_4CO_2\}(NC_6H_3Pr^i{}_2\text{-}2,6)]^-$ [13] and $[Pt\{2\text{-}(HN)C_6H_4O\}(PPh_3)_2]$ [10]. The stretching C–O frequency of the phenolic group, $\nu(C–O)_{OH}$, (1319 cm^{-1} in H_2salNH_2 spectra and 1299 cm^{-1} in HantOH) shifts to lower wavenumbers in the spectra of all complexes. It is particularly significant for complexes **1**–**4** and **8**, suggesting that in these complexes the oxygen atom of the phenolic group may be involved in coordination to the metals. The decrease in the C–NH_2 stretch frequency, $\nu(C–NH_2)$, in the spectra of the complexes **1**, **3**, **4**, **7** and **8** indicates that the amino group may be coordinated to the metals.

The results described suggest the following coordination modes of 3-aminosalicylic or 3-hydroxyanthranilic acids: in complexes **1**, **3**, **4** and **8** via chelation-NO through the nitrogen atom of the amino group and the oxygen atom of the phenolate group; in complexes **5** and **6** through one of the oxygen atoms of the carboxylate group; in complex **2** via monodentate-O of the phenolate group; and in complex **7** via monodentate-N.

The spectra of compounds **1**–**5** and **8** show three characteristic bands of the PPh_3 ligands, around 1480, 1435 and 1095 cm^{-1}, assigned to the symmetric and asymmetric stretching and bending of P–Ph bonds, respectively [17,19]. The strong bands at 974 and 979 cm^{-1} in the spectra of the rhenium complexes **3** and **8**, respectively, are assigned to Re=O stretch [1].

Table 2
Infrared data (cm^{-1}) for 3-aminosalicylic and 3-hydroxyanthranilic acids and complexes **1**–**8**

Compound	ν(C=O)	$\delta(NH_2)$[a]	$\nu(C–O)_c$	$\nu(C–O)_{OH}$	$\nu(C–NH_2)$[b]	ν(M–N)	ν(M–Cl)
3-Aminosalicylic acid	1651 vs	1537 vs	1394 vs	1319 vs	1262 vs		
cis-[Pt(HsalNH)$(PPh_3)_2]\cdot 0.25C_2H_5OH$ (**1**)	1721 vs	1587 m	1373 m	1302 vs	1227 s	399 w	
trans-[PdCl$(HsalNH_2)(PPh_3)_2$] (**2**)	1700 m	1571 m	1390 m	1308 m	1283 m		389 m
trans-[$ReOI_2(HsalNH_2)(PPh_3)]\cdot(CH_3)_2CO$ (**3**)	1671 m	1581 s	1370 s	1303 m	1240 m	457 m	
3-Hydroxyanthranilic acid	1651 vs	1548 vs	1344 s	1299 vs	1221 vs		
cis-[Pt(HantO)$(PPh_3)_2$] (**4**)	1679 sh	1615 s	1323 s	1251 vs	1213 vs	350 w	
trans-[PdCl(antOH)$(PPh_3)_2]\cdot 4H_2O$ (**5**)	1635 m	1551 m	1368 s	1275 vs	1249 m		350 w
[PdCl(antOH)(bipy)]$\cdot C_2H_5OH$ (**6**)	1603 vs	1551 s	1370 vs	1276 vs	1250 sh		336 m
$[PdCl_2(HantOH)_2]$ (**7**)	1666 vs	1590 s	1337 s	1293 vs	1215 vs		328 s, 307 s
trans-[ReOI(HantO)$(PPh_3)_2]\cdot(CH_3)_2CO$ (**8**)	1680 m	1602 m	1296 s	1242 vs	1215 s	458 m	

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.
[a] δ(NH) in complexes **1**, **4** and **8**.
[b] ν(C–NH) in complexes **1**, **4** and **8**.

Table 3
^{1}H NMR data for for 3-aminosalicylic and 3-hydroxyanthranilic acids and its complexes

Compound	Chemical shift (ppm)[A]		
	H4	H5	H6
3-Aminosalicylic acid[a]	7.02 dd (5, 26)	6.72 t (26)	7.37 dd (5, 26)
cis-[Pt(HsalNH)(PPh_3)$_2$] · 0.25C_2H_5OH (**1**)[b]	6.31 d (25)	6.44 t (26)	6.96 d (25)
trans-[$ReOI_2$(HsalNH_2)(PPh_3)] · (CH_3)$_2$CO (**3**)[c]	7.49 dd (5, 26)	6.99 t (26)	7.73 dd (5, 26)
3-Hydroxyanthranilic acid[a]	6.80 dd (5, 26)	6.45 t (26)	7.35 dd (5, 27)
cis-[Pt(HantO)(PPh_3)$_2$] (**4**)[b]	6.47 d (25)	6.25 t (25)	7.05 d (27)
[PdCl(antOH)(bipy)] (**6**)[d]	7.21 d (26)	6.74 t (26)	8.02 d (25)
[$PdCl_2$(HantOH)$_2$] (**7**)[c]	6.79 d (25)	6.36 t (26)	7.20 d (27)
trans-[ReOI(HantO)(PPh_3)$_2$] · (CH_3)$_2$CO (**8**)[c]	6.98 dd (5, 26)	6.74 t (26)	7.33 dd (5, 27)

[A] *J* values in parentheses (Hz); dd, doublet-doublet; t, triplet; d, doublet.
[a] In CD_3OD.
[b] In $CDCl_3$.
[c] In dmso-d_6.
[d] D_2O.

2.4. ^{1}H NMR spectra

^{1}H NMR data and tentative assignments for 3-aminosalicylic and 3-hydroxyanthranilic acids and its complexes are shown in Table 3. Assignments are based on those find in the literature for salicylic acid [20] and derivates [16] and 2-aminophenol [9,21], anthranilic acid [13,18] and derivates [17] and salicylic acid complexes [7].

The ^{1}H NMR spectrum of 3-aminosalicylic acid in CD_3OD shows a triplet at 6.72 ppm assigned to the H5 proton and two doublet-doublets at 7.02 and 7.37 ppm assigned to the H4 and H6 protons, respectively. Similarly the ^{1}H NMR spectrum of 3-hydroxyanthranilic acid in CD_3OD shows a triplet at 6.45 ppm assigned to the H5 proton, a doublet-doublet at 6.80 ppm assigned to the H4 proton and another doublet-doublet at 7.35 ppm assigned to the H6 proton.

The proton signals of $HsalNH_2^-$ in complex **2** and of $antOH^-$ in complex **5** are overlapped with the PPh_3 signals. In the spectra of complex **6**, the major shifts downfield are observed for H4 and H6 protons. These are higher than the shifts observed in complexes **4** and **8** with suggested NO-chelation. Relative to the free ligand, the protons of $HsalNH^{2-}$ ligand in the Pt complex **1** shift upfield and in the Re complex **3** shift downfield; the same trend is observed for the protons of $HantO^-$ ligand in complexes **4** (Pt) and **8** (Re), having all the suggested NO-chelation .

3. Experimental

3.1. Preparation of complexes

All chemicals were of at least reagent grade and used as supplied by Aldrich. The starting complexes, *trans*-[$PdCl_2$(PPh_3)$_2$] [22], *cis*-[$PtCl_2$(PPh_3)$_2$] [23], [$PdCl_2$(bipy)] [24] and *trans*-[$ReOI_2$(OEt)(PPh_3)$_2$] [25] were prepared by the respective literature procedures.

3.1.1. *cis*-[Pt(HsalNH)(PPh_3)$_2$] · 0.25C_2H_5OH (**1**)

To a stirred suspension of *cis*-[$PtCl_2$(PPh_3)$_2$] (0.12 g, 0.15 mmol) in ethanol (5 cm^3) was added a methanolic suspension (5 cm^3) of 3-aminosalicylic acid (0.05 g, 0.3 mmol) and triethylamine (0.08 cm^3, 0.6 mmol). The resulting yellow suspension was stirred for one day. It was centrifuged and a yellow solid isolated. Orange crystals were formed by recrystallisation in ethanol, washed whith water and dried over silica gel. Yield: 0.05 g, 0.06 mmol, 40%.

Elemental analysis. Calc.: C, 58.3; H, 4.3; N, 1.6. Exp.: C, 59.9; H, 4.1; N, 1.6%. MS = 871; MW = 870.768 calculated for [Pt(HsalNH)(PPh_3)$_2$].

3.1.2. *trans*-[PdCl(HsalNH_2)(PPh_3)$_2$] (**2**)

To a stirred suspension of *trans*-[$PdCl_2$(PPh_3)$_2$] (0.15 g, 0.15 mmol) in ethanol (5 cm^3) was added a methanolic suspension (5 cm^3) of 3-aminosalicylic acid (0.05 g, 0.3 mmol) and triethylamine (0.08 cm^3, 0.6 mmol). The resulting suspension was refluxed for 1 h and filtered. To the orange filtrate was added 10 cm^3 of water and a orange solid was formed. It was centrifuged, washed with water and dried over silica gel. Yield: 0.05 g, 0.06 mmol, 40%.

Elemental analysis. Calc.: C, 63.1; H, 4.4; N, 1.7. Exp.: C 61.4, H 4.6, N 1.7%.

3.1.3. *trans*-[$ReOI_2$(HsalNH_2)(PPh_3)] · (CH_3)$_2$CO (**3**)

A suspension of *trans*-[ReOI(OEt)$_2$(PPh_3)$_2$] (0.31 g, 0.3 mmol) and 3-aminosalicylic acid (0.05 g, 0.3 mmol) in acetone (20 cm^3) was refluxed for 1 h. It was centrifuged and a green solid obtained. It was washed with acetone and dried over silica gel. Yield: 0.20 g, 0.21 mmol, 68%.

Elemental analysis. Calc.: C, 36.2; H, 2.9; N, 1.5. Exp.: C, 36.3; H, 3.1; N, 1.6%.

3.1.4. *cis*-[Pt(HantO)(PPh$_3$)$_2$] (**4**)

To a stirred suspension of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.12 g, 0.15 mmol) in ethanol (5 cm^3) was added a methanolic suspension (5 cm^3) of 3-hydroxyanthranilic acid (0.05 g, 0.3 mmol) and triethylamine (0.08 cm^3, 0.6 mmol). The resulting yellow suspension was stirred for one day. It was centrifuged and a yellow solid isolated, washed with ethanol and dried over silica gel. Yield: 0.11 g, 0.13 mmol, 87%.

Elemental analysis. Calc.: C, 59.3; H, 4.1; N, 1.6. Exp.: C, 59.9; H, 4.1; N, 1.6%. MS = 871; MW = 870.768 calculated for [Pt(HantO)(PPh$_3$)$_2$].

3.1.5. *trans*-[PdCl(antOH)(PPh$_3$)$_2$] · 4H$_2$O (**5**)

To a stirred suspension of *trans*-[PdCl$_2$(PPh$_3$)$_2$] (0.35 g, 0.5 mmol) in ethanol (5 cm^3) was added a methanolic suspension (4 cm^3) of 3-hydroxyanthranilic acid (0.15 g, 1 mmol) and triethylamine (0.28 cm^3, 2 mmol). The resulting suspension was stirred for 1 h. It was centrifuged and a orange solution was obtained. Part of the solvent was evaporated and a red solid was obtained by addition of an equal amount of water. This solid was washed with water and dried over silica gel. Yield: 0.13 g, 0.27 mmol, 54%.

Elemental analysis. Calc.: C, 58.0; H, 5.0; N, 1.6. Exp.: C, 58.0; H, 5.3; N, 2.1%.

3.1.6. [PdCl(antOH)(bipy)] · C$_2$H$_5$OH (**6**)

To a stirred suspension of [PdCl$_2$(bipy)] (0.05 g, 0.15 mmol) in ethanol (5 cm^3) was added a methanolic suspension (5 cm^3) of 3-hydroxyanthanilic acid (0.05 g, 0.3 mmol) and triethylamine (0.08 cm^3, 0.6 mmol). The resulting yellow suspension was stirred for three days. It was centrifuged and a brownish solid isolated, washed with ethanol and dried over silica gel. Yield: 0.07 g, 0.14 mmol, 93%.

Elemental analysis. Calc.: C, 46.0; H, 4.1; N, 8.5. Exp.: C, 45.9; H, 4.1; N, 9.9%. MS = 413; MW = 414.731 calculated for [Pd(antOH)(bipy)]$^+$.

3.1.7. [PdCl$_2$(HantOH)$_2$] (**7**)

A methanolic suspension (4 cm^3) of 3-hydroxyanthranilic acid (0.15 g, 1 mmol) was added to an aqueous solution (5 cm^3) of K$_2$[PdCl$_4$] (0.16 g, 0.5 mmol). The resulting orange suspension was stirred for one day. It was centrifuged and a yellow solid isolated, washed with ethanol and dried over silica gel. Yield: 0.22 g, 0.45 mmol, 90%.

Elemental analysis. Calc.: C, 34.8; H, 2.9; N, 5.8. Exp.: C, 34.6; H, 3.4; N, 6.2%. MS = 485; MW = 483.596 calculated for [PdCl$_2$(antOH)$_2$]. MS = 411; MW = 412.690 calculated for [Pd(antOH)$_2$]$^{2+}$.

3.1.8. *trans*-[ReOI(HantO)(PPh$_3$)$_2$] · (CH$_3$)$_2$CO (**8**)

A suspension of *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] (0.31 g, 0.3 mmol) and 3-hydroxyantharanilic acid (0.05 g, 0.3 mmol) in acetone (10 cm^3) was refluxed for 30 min. After cooling to room temperature, 10 cm^3 of water were added and a brownish solid was formed, isolated, washed with water and dried over silica gel. Yield: 0.20 g, 0.19 mmol, 63%.

Elemental analysis. Calc.: C, 51.9; H, 4.0; N, 1.3. Exp.: C, 54.9; H, 4.1; N, 1.5%.

3.2. X-ray diffraction

$C_{44.50}H_{40}NO_{3.75}P_2Pt$ (**1**), $M_r = 905.80$, triclinic, space group $P\bar{1}$, $a = 9.749(12)$ Å; $b = 13.954(15)$ Å; $c = 16.333(17)$ Å; $\alpha = 74.23(1)°$; $\beta = 84.14(1)°$, $\gamma = 74.15(1)°$, $U = 2056.0$ Å^3, $Z = 2$, $\rho_{calc} = 1.463$ Mg m^{-3}, μ(Mo Kα) = 3.531 mm^{-1}.

X-ray data were collected at room temperature on a MAR research plate system using graphite monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å) at Reading University. The crystal was positioned at 70 mm from the image plate. 95 frames were taken at 2° intervals with an adequate counting time. Data analysis was performed with the XDS program [26]. Intensities were corrected empirically for absorption effects, using a DIFABS version modified for image plate geometry [27].

The structure was solved by a combination of direct methods and difference Fourier syntheses. The hydrogen atoms on the parent carbon atoms and aliphatic nitrogen atoms were included in calculated positions and giving thermal parameters equivalent 1.2 times those of the atom to which were attached. The non-hydrogen atoms were refined with anisotropic thermal parameters

The final refinement of 464 parameters by full-matrix least-squares method against F^2 until convergence to be achieved leading to final indices $R_1 = 0.0412$ and $wR_2 = 0.1126$ for 5710 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0521$ and $wR_2 = 0.1205$, for all intensity data comprising 6578 reflections. The residual electronic density was in the range −1.189 to 2.347 e Å^{-3}, with positive hole 0.96 Å within platinum coordination sphere while the negative one is only 1.44 Å way from the calculated position for an hydrogen atom. All calculations required to solve and to refine the structure were carried out using the SHELX-97 system programs [28]. Molecular diagrams were drawn with PLATON [29].

3.3. Instrumentation

Infrared spectra were measured as KBr pellets on a Mattson 7000 FT instrument. ^{1}H NMR spectra were recorded on a Brüker AMX300 spectrometer at 300 MHz and referenced to SiMe$_4$ or the solvent. Microanalyses

(C, H and N) were measured by the Department of Chemistry, University of Aveiro.

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Appendix A. Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 269712. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK (fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk, and http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.poly.2005.07.034.

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