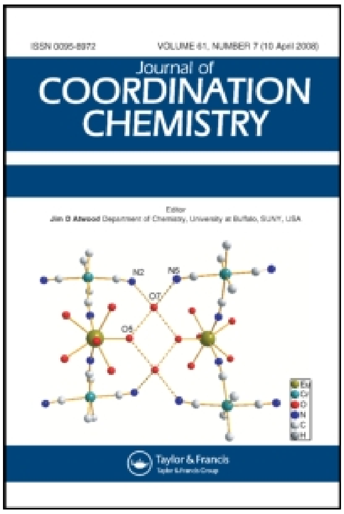

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PREPARATION, ELECTROCHEMISTRY AND THERMAL ANALYSIS OF TWO PALLADIUM(II) COMPLEXES WITH 1-AMINOPYRENE AND DERIVATIVES

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PREPARATION, ELECTROCHEMISTRY AND THERMAL ANALYSIS OF TWO PALLADIUM(II) COMPLEXES WITH 1-AMINOPYRENE AND DERIVATIVES

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Two palladium(II) complexes with aminopyrene and a derivative have been synthesized and characterized. In complex **1**, $Pd(apyr)_2Cl_2$ (apyr = 1-aminopyrene), the pyrenyl-π-electrons do not conjugate with d-electrons of the metal, whereas complex **2**, $Pd(pmpa)Cl_2$ (pmpa = *N*-(2-pyridylmethylene)-1-pyrenylamine) is a conjugated, planar molecule. Due to this, the oxidation potential and the electronic spectrum of the pyrenyl group of pmpa is significantly influenced by formation of the complex. Both iodine doped complexes show semiconductor properties (2.4×10^{-4} S cm^{-1} for **1** and 1.0×10^{-4} S cm^{-1} for **2**). TG-DTG curves for **1** shows a single step decomposition. However, curves for complex **2** show a two-step decomposition, corresponding to the organic ligand pmpa. The iodine doped compounds are more stable than the original complexes. The quantity of doped iodine for **1** and **2** is 23 and 14%, respectively.

KEY WORDS: palladium(II), aminopyrene, iodine, stacking compounds.

INTRODUCTION

The concept of using organic donor-acceptor complexes or π-radicals as building blocks in the design of synthetic organic metals and superconductors has brought about a rich and new area of chemistry. A series of molecular donors such as tetrathiafuhalene (TTF) and its derivatives has been widely investigated.[1] Several new charge transfer complexes with condensed aromatic compounds have been characterized, in which there are relatively short distances between the donor and acceptor planes.[2] It has been of interest to explore general approaches to the

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chemical synthesis of metal complex assembled with π-π interactions of aromatic rings.[3] Recently, we synthesized a Cu(I) complex with aminopyrene and showed that the formation of metal complexes can play an important role in the control of the distance of stacking planes.[4] In this paper we report the preparation, electrochemistry and thermal analysis of two palladium(II) complexes with aminopyrene and its derivatives.

EXPERIMENTAL

Reagents

All ligands are illustrated in Figure 1.1-Aminopyrene (apyr) was used as purchased (Tokyo KaSei, Japan), *N*-(2-pyridylmethylene)-1-pyrenylamine (pmpa) and *N*-Sallicylidene-1-pyrenylamine (spa) were prepared by the condensation of 1-aminopyrene with salicylaldehyde and picolinic aldehyde in methanol, respectively. The yellow precipitates formed were filtered and washed with methanol, then dried *in vacuo*, and finally characterized by elemental analyses and infrared spectra. All solvents were purified according to literature procedures. Other materials for preparation were of reagent grade and used as purchased.

Preparation of Complexes

$Pd(apyr)_2Cl_2$ (**1**)

Here, 0.1 mmol 1-aminopyrene in 10 cm^3 of MeOH was added to 2.0 cm^3 of $PdCl_2$-HCl/H_2O mixture (0.0512 mol dm^{-3} $PdCl_2$ in 0.1 mol dm^{-3} HCl) and stirred for 30 min; a dark-red precipitate separated, which was filtered, washed with methanol (twice) and finally dried *in vacuo*. Anal. calcd. for $C_{32}H_{22}N_2PdCl_2$: C, 62.75; H, 3.60; N, 4.58%. Found: C, 62.63; H, 3.96; N, 4.61%.

$Pd(pmpa)Cl_2$ (**2**)

The dark-red product was synthesized by the same method as above, by reacting the ligand with $PdCl_2$ in a 1:1 molar ratio. Anal. calc. for $C_{22}H_{14}N_2PdCl_2$: C, 54.57; H, 3.00; N, 5.79%. Found: C, 54.64; H, 3.07; N, 6.07%.

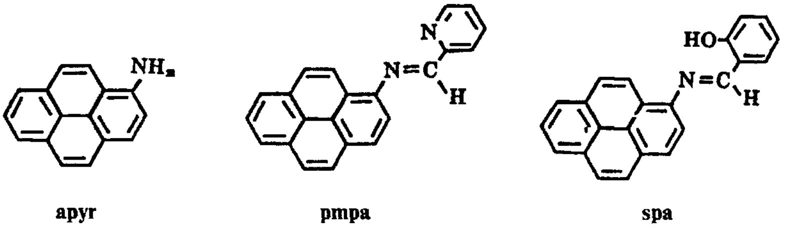

Figure 1 Structures of the ligands.

The same products **1** and **2** were obtained when $PdCl_2$-HCl/H_2O was replaced by $Pd(CH_3CN)_2Cl_2$ in the synthesis.

Physical Measurements

Carbon nitrogen and hydrogen contents were determined using a Carlo-Erba 1106 elemental analyser. IR spectra were recorded on a Muttson Alpha Centaura FT-IR spectrometer in the 4000–400 cm^{-1} region using KBr pellets. Electronic spectra were obtained on a Shimazu UV 240 spectrophotometer. Cyclic voltammetric measurements were carried out on a Yanbian Yongheng 402-A function generator in conjunction with a Dahua LM-15 X-Y recorder. A three-electrode cell comprising a glassy carbon electrode, a platinum-wire counter electrode, and an AgCl/Ag reference electrode was used. The TG-DTG runs, under non-isothermal conditions, were carried out on a Perkin-Elmer TGA-7 Delta series thermogravimetrie analyser equipped with a 3700 Data Station. Measurements were performed in a dynamic pure nitrogen atmosphere at a flow rate of 20 cm^3 min^{-1} from 50 to 700°C. The heating rate was 5°C min^{-1} and sample mass range was 3–5 mg. Electric conductivities were measured on a DDS-11A conductivity meter.

RESULTS AND DISCUSSION

The preparation of the complexes was accomplished in methanol. The dark-red products are very stable in the solid state and are insoluble in ordinary solvents except for DMF and DMSO. We have tried to grow crystals for X-ray structure analysis, but this failed due to decomposition of the complexes in solution after several days. Slowing the rate of reaction in MeOH by diffusion gave some very long fibre (about 2–3 cm). In the light of these results, we proposed that these complexes would be linked by a rather strong infinite stacking of the pyrene planes to form a polymer structure.[4]

Although salicilydeneimine complexes of palladium have been known for some time,[5] $Pd(spa)Cl_2$ can not be prepared using the same method as for **1** and **2**. Elemental analysis and IR spectra confirmed that the dark-red product separated from reaction systems involving spa was the same as **1**. The Schiff bond in spa is decomposed when the ligand coordinates to palladium. In contrast to this result, pmpa forms complex **2**. The most important difference between the two ligands are the considerable ability of the nitrogen atom in the pyridyl group of pmpa to bind strongly to palladium in the one case. The phenolate oxygen of spa is a hard base, its ability to bind to soft metal is poor; therefore the d-electrons of the palladium mainly back-donate to the π^* orbital of the C=N bond, which is weakened and finally decomposed to the stable amine complex.

The IR spectra of free 1-aminopyrene shows primary amine bands at 3200–3400 cm^{-1} (main peak at 3333 cm^{-1}). When it is condensed with salicylaldehyde and picolinic aldehyde, these bands disappear. The C=N stretch cannot be clearly assigned; it is obscured by bands of the condensed aromatic ring at 1650–1600 cm^{-1}. The amino nitrogen coordination in **1** is clearly indicated by the shift of $\nu(NH)$ (3209 cm^{-1} for **1**, $\Delta\nu = 124$ cm^{-1}). This shift is larger than we have found in the complex $[Cu(apyr)_3]ClO_4$,[4] in which the $\Delta\nu(NH)$ is 64 cm^{-1}. The amine-palladium coordination bond in this complex is rather strong.

Electronic spectra of **1** and **2** in DMF show strong ligand bands (Table 1); d-d absorptions are masked. Only a broad shoulder near 500 nm could be assigned to the singlet to triplet transition of the complexes.[5] Compared with the free ligands the π-electron bands (350–410 nm) of the pyrenyl group are not significantly changed for **1**, but they are changed for **2** and give rise to a number of shoulders.

The molar conductance of a *ca* 0.5 m mol dm^{-3} solutions of the two complexes in DMF is 18.7 S cm^2 mol^{-1} for **1** and 14.5 S cm^2 mol^{-1} for **2**, respectively, indicating nonelectrolytic behavior.[6]

Cyclic voltammograms were studied in DMF. All oxidation processes are irreversible; only E_{pa} data are presented in Table 1. No metal-centred redox can be assigned. Two stage oxidation of apyr is concerned with a one electron oxidation of the aromatic amine (E_{ap}-NH_2 0.72 V) and a one π-electron loss in the pyrenyl group (E_{ap} pyr 1.28 V).[7] The oxidation peak of the amine disappears when coordinated to the metal or is condensed. Cyclic voltommograms of **1** showed an oxidation peak (E_{ap} pyr 1.30 V); the potential is almost the same as for the ligand. When the complex decomposed after oxidation, a small peak (E_{ap}-NH_2) appeared. Cyclic voltammograms of pmpa showed a one-electron oxidation of the pyrenyl group. Although **2** showed similar CV to the ligand, in contrast with **1**, the potential E_{ap} (pyr) is significantly shifted (from 1.22 V to 1.54 V). The different results for the two complexes can be explained by the difference in their structures. The nitrogen atom in **1** is tetrahedral, and there is no conjugation of the pyrenyl π-electrons with the d-electrons of the metal. The imine nitrogen in **2** is planar and coordinates to palladium forming a conjugated planar molecule. Due to this reason the π-electrons are stabilized and the oxidation potential shifted. This is in accordance with the electronic spectra.

Halogen doping of planar, conjugated electron-donor compounds has been showed to be an effective strategy for the synthesis of electrically conductive materials consisting of partially oxidized molecular stacks.[8] Although the complexes are insulators, their electric conductivity is significantly increased when the complexes are iodine-doped by gaseous diffusion (50°C, five days). Data for electrical conductivity were measured at room temperature using pellet samples. Both complexes showed semiconductor properties (2.4×10^{-4} S cm^{-1} for **1** and 1.0×10^{-4} S cm^{-1} for **2**).

TG-DTG curves for complex **1** showed a single step decomposition (124–503°C), corresponding to the two aminopyrene ligands and loss of mass of 70.64% (calc. 71.03%). However, TG-DTG curves for **2** show a two-step decom-

TABLE 1 Electronic Spectral Data and Electrochemical Potentials for the Ligands and the Complexes in DMF

comp.	λ_{max}/nm ($\varepsilon \times 10^{-3}$/$dm^3$ mol^{-1} cm^{-1})					E_{pa}($-NH_2$)	E_{pa}(pyr)/V
apyr	265sh(10.6)	276sh(15.2)	284(18.6)	360sh(13.3)	368(13.9)	0.72	1.28
	382(14.1)	406(12.8)					
Pd(apyr)$_2$Cl$_2$	265sh(10.6)	275sh(12.0)	283(18.0)	338(7.48)	365sh(9.50)	–	1.30
	382(10.4)	408(8.42)	440sh(1.68)	485sh(0.29)			
pmpa	268sh(13.8)	275sh(15.7)	284(16.4)	325sh(9.74)	338(11.0)	–	1.22
	358(12.6)	380(13.0)	405(11.6)	440sh(1.99)			
Pd(pmpa)Cl$_2$	268(11.1)	278(10.0)	318sh(7.54)	326(8.11)	355(5.70)	–	1.54
	370sh(5.07)	382sh(4.56)	410sh(3.04)	440sh(1.77)	500sh(0.63)		

* All the potentials vs AgCl/Ag.

position, the first step (75–341 °C) corresponding to the removal of a pyridyl group from the ligand, and the second step (341–600 °C) corresponding to the removal of the remainder of pmpa. The doped compounds begin to lose iodine at about 130 °C. The quantities of iodine calculated by TG-DTG was 23% for **1** and 14% for **2**. This is in accordance with the molecular structures of the complexes; **1** has two ligands with pyrene and it loses electrons to form $Pd(apyr)_2Cl_2{}^{2+} \cdot 2I^-$; **2** has only one ligand with pyrene: it loses one electron forming $Pd(pmpa)Cl_2{}^{+} \cdot I^-$.

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