

Palladium and platinum complexes of 2-(2'-carboxyphenylazo)-4-methylphenol: Synthesis, structure and spectral properties

SARMISTHA HALDER^a, MICHAEL G B DREW^b and SAMARESH BHATTACHARYA^{a,*}^aDepartment of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700 032^bDepartment of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UKe-mail: sbhattacharya@chemistry.jdvu.ac.in

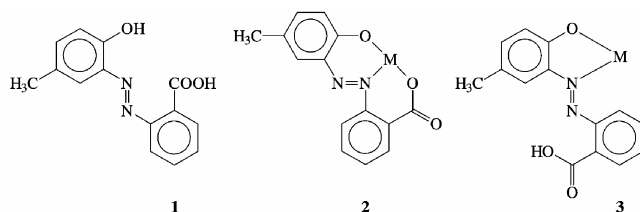
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Abstract. Reaction of 2-(2'-carboxyphenylazo)-4-methylphenol (H_2L) with $[M(PPh_3)_2Cl_2]$ ($M = Pd, Pt$) affords mixed-ligand complexes of type $[M(PPh_3)(L)]$. Structures of both the complexes have been determined by X-ray crystallography. Both the complexes are square planar, where the 2-(2'-carboxyphenylazo)-4-methylphenol is coordinated to the metal center, via dissociation of the two acidic protons, as a dianionic tridentate O,N,O-donor, and the fourth position is occupied by the triphenylphosphine. These complexes show intense MLCT transitions in the visible region.

Keywords. 2-(2'-carboxyphenylazo)-4-methylphenol; palladium and platinum complexes; crystal structure; spectral properties.

1. Introduction

There has been considerable current interest in palladium and platinum complexes, largely because of their potential catalytic and biological applications.¹ As properties of such complexes depend primarily on the coordination environment around the metal center, complexation of these metals by ligands of selected types is of significant importance. For the present study we have selected 2-(2'-carboxyphenylazo)-4-methylphenol (**1**) as the principal ligand. Ligand **1** has been abbreviated as H_2L , where H_2 stands for the two potentially dissociable protons,



viz. the phenolic proton and the carboxylic proton. This ligand has three types of potential donor sites,

viz. the phenolate oxygen, the azo nitrogens and the carboxylate oxygens. However, this ligand has been observed to display different modes of coordination in its complexes. It is known to bind to metal ions as a dianionic tridentate O,N,O-donor (**2**) utilizing all the three types of donor atoms forming two adjacent six-membered chelate rings.² It has also been observed to coordinate metal ion as a monoanionic bidentate N,O-donor (**3**) utilizing the phenolate oxygen and the first azo-nitrogen forming a five-membered chelate ring.³ In this latter coordination mode (**3**) the carboxylate oxygens are disposed so far away from the metal center that none of them can participate in the coordination. To interact with ligand **1** two reactive complexes of palladium and platinum, viz. *trans*- $[Pd(PPh_3)_2Cl_2]$ and *cis*- $[Pt(PPh_3)_2Cl_2]$ have been chosen. The primary objective of the present study has been to synthesize mixed-ligand complexes of the two metals incorporating ligand **1** and find out the coordination mode of ligand **1** in them. Reactions of ligand **1** with the chosen palladium and platinum compounds have indeed afforded mixed-ligand complexes of type $[M(PPh_3)(L)]$ ($M = Pd$ and Pt), in which ligand **1** has been found to bind the metal centers in the tridentate fashion (**2**). The chemistry of these two complexes is described in this paper with special reference to their synthesis, structure and spectral properties.

*For correspondence

2. Experimental

2.1 Materials

Palladium chloride and chloroplatinic acid were obtained from Arora Matthey, Kolkata. Triphenylphosphine, *para*-cresol and anthranilic acid were purchased from E Merck, India. The *trans*-[Pd(PPh₃)₂Cl₂] and *cis*-[Pt(PPh₃)₂Cl₂] complexes were prepared by following reported procedures.⁴ The 2-(2'-carboxyphenylazo)-4-methylphenol ligand was prepared by coupling diazotized anthranilic acid with *para*-cresol. All other chemicals and solvents were reagent-grade commercial materials and were used as received.

2.2 Synthesis of [Pd(PPh₃)(L)]

To a solution of 2-(2'-carboxyphenylazo)-4-methylphenol (40 mg, 0.16 mmol) in ethanol (40 mL) was added *trans*-[Pd(PPh₃)₂Cl₂] (100 mg, 0.14 mol) followed by triethylamine (35 mg, 0.35 mmol). The resulting mixture was then heated at reflux for 4 h to yield a reddish-purple solution. The solvent was then evaporated to give a solid mass, which was subjected to purification by thin layer chromatography on a silica plate. With 1 : 40 acetonitrile-benzene as the eluant a reddish-purple band separated, which was extracted with 1 : 1 dichloromethane-acetonitrile.

Evaporation of this extract gave [Pd(PPh₃)(L)] as a dark crystalline solid. Yield: 67%.

Analysis: Calc. for C₃₂H₂₅N₂O₃PPd: C, 61.69; H, 4.02; N, 4.50%. Found: C, 61.03; H, 4.04; N, 4.66%.

2.3 Synthesis of [Pt(PPh₃)(L)]

This complex was obtained as a violet crystalline solid by following the same above procedure using *cis*-[Pt(PPh₃)₂Cl₂] instead of *trans*-[Pd(PPh₃)₂Cl₂]. Yield: 70%.

Analysis: Calc. for C₃₂H₂₅N₂O₃Pt: C, 54.00; H, 3.52; N, 3.94%. Found: C, 54.79; H, 3.44; N, 4.01%.

2.4 Physical measurements

Microanalyses (C, H, N) were done using a Heraeus Carlo Erba 1108 elemental analyzer. NMR spectra in CDCl₃ solutions were recorded on a Bruker Avance 300 NMR spectrometer. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer.

2.5 X-ray crystallographic analysis for complexes [Pd(PPh₃)(L)] and [Pt(PPh₃)(L)]

Single crystals of [Pd(PPh₃)(L)] and [Pt(PPh₃)(L)] were obtained by slow evaporation of a solution of

Table 1. Summary of structure determination of [Pd(PPh₃)(L)] and [Pt(PPh₃)(L)].

Formula	C ₃₂ H ₂₇ N ₂ O ₄ PPd	C ₃₃ H _{26.5} N _{2.5} O ₃ Pt
Formula weight	640.93	732.12
Crystal system	Triclinic	Triclinic
Space group	Pī	Pī
Z	2	2
a (Å)	8.9220(8)	8.9281(8)
b (Å)	12.1191(8)	12.2229(8)
c (Å)	14.0058(9)	14.1454(9)
α (°)	74.078(6)	73.643(6)
β (°)	83.647(7)	83.715(7)
γ (°)	69.911(8)	69.359(8)
V (Å ³)	1367.47(19)	1386.0(2)
μ (mm ⁻¹)	0.778	5.159
Crystal size (mm ³)	0.15 × 0.20 × 0.25	0.05 × 0.05 × 0.30
T (K)	150	150
D _{calc} (g/cm ³)	1.557	1.754
λ (Å)	0.71073	0.71073
No. of reflections measured	9583	10658
No. of unique reflections	7628	8833
R ₁ indices (F > 4σ(F))	0.0707	0.0679
wR ₂	0.1976	0.1745
GOF	0.99	1.06

the complex in 1:1 dichloromethane-acetonitrile. Selected crystal data and data collection parameters are given in table 1. Data were collected on a Marresearch Image Plate system using graphite monochromated MoK α radiation. X-ray data reduction and structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs.⁵ The structures were solved by the direct methods.

3. Results and discussion

3.1 Synthesis and structure

Reaction of 2-(2'-carboxyphenylazo)-4-methylphenol (H₂L, **1**) with *trans*-[Pd(PPh₃)₂Cl₂] proceeds smoothly

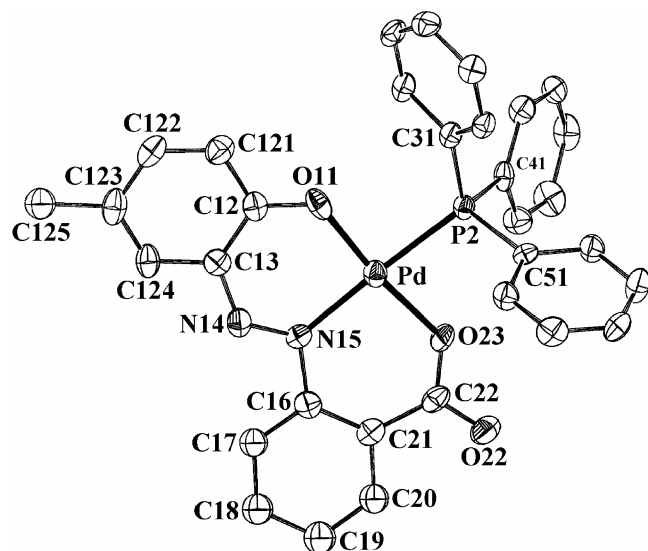


Figure 1. View of the [Pd(PPh₃)(L)] complex.

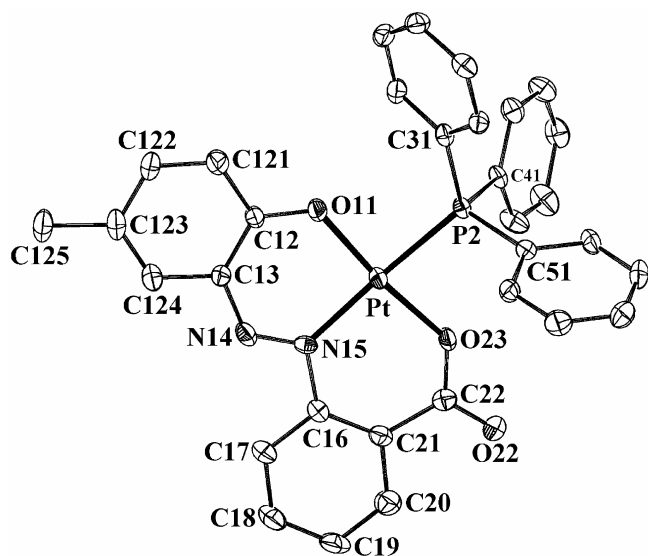


Figure 2. View of the [Pt(PPh₃)(L)] complex.

in refluxing ethanol in the presence of triethylamine to afford the expected mixed-ligand palladium complex, viz. [Pd(PPh₃)(L)], in a decent yield. The analogous platinum complex, [Pt(PPh₃)(L)], has been obtained from a similar reaction of ligand **1** with *cis*-[Pt(PPh₃)₂Cl₂]. The observed elemental (C, H, N) analytical data of the two complexes are found to be consistent with their compositions. Formulation of these complexes indicates that in both of them ligand **1** is probably coordinated to the metal center as a dianionic tridentate O,N,O-donor (**2**). In order to verify the binding mode of ligand **1** in these two complexes, structures of both the complexes have been determined by X-ray crystallography. The structures are shown in figures 1 and 2, and some relevant bond parameters are presented in table 2. Both structures are similar and it may be noted here that though the palladium and platinum starting materials have different geometries, they have afforded complexes of similar composition and stereochemistry. In each complex the ligand **1** is coordinated to the metal center in the expected tridentate fashion (**2**). A triphenylphosphine is also coordinated to each metal center. The central metal ion is thus sitting in a NO₂P coordination sphere in both the complexes, which is distorted significantly from ideal square-planar geometry, as reflected in all the bond parameters around the metal centers. The M–N, M–O and M–P (M = Pd and Pt) distances are all quite normal, and so are the phenolic C–O, carboxylate C–O and azo N–N distances within the coordinated ligand **1**.^{2,6}

3.2 ¹H NMR spectra

¹H NMR spectra of both the [M(PPh₃)(L)] (M = Pd and Pt) complexes have been recorded in CDCl₃ solution. In the palladium complex broad signals are observed within 7.3–7.7 ppm due to the coordinated PPh₃ ligand. The methyl signal of the O,N,O-coordinated ligand (L) is observed at 2.30 ppm and out of the seven expected aromatic proton signals for this ligand, five are clearly observed at 6.34 (*d*, *J* = 8.6),⁷ 7.06 (*d*, *J* = 10.8), 7.60 (*s*), 7.82 (*d*, *J* = 9.3) and 8.34 (*d*, *J* = 9.1) ppm. The other two expected triplets from the L ligand could not be identified, because of their overlap with the PPh₃ signals. In the platinum complex the broad PPh₃ signals are observed within 7.4–7.8 ppm. Out of the expected signals for the ligand L, the methyl signal is observed at 2.35 ppm and four aromatic proton signals are observed at 6.35 (*d*, *J* = 8.8), 7.18 (*d*, *J* = 9.0), 8.08 (*d*, *J* = 7.6)

Table 2. Selected bond lengths (Å) and angles (°) for [Pd(PPh₃)(L)] and [Pt(PPh₃)(L)].

[Pd(PPh ₃)(L)]		[Pt(PPh ₃)(L)]	
Bond lengths (Å)			
Pd–O(11)	1.924(5)	Pt–O(11)	1.964(6)
Pd–N(15)	2.043(4)	Pt–N(15)	2.052(6)
Pd–O(23)	1.987(4)	Pt–O(23)	1.990(6)
Pd–P(2)	2.2938(15)	Pt–P(2)	2.2878(18)
C(12)–O(11)	1.297(7)	C(12)–O(11)	1.307(9)
N(14)–N(15)	1.260(6)	N(14)–N(15)	1.272(9)
C(22)–O(22)	1.227(7)	C(22)–O(22)	1.236(11)
C(22)–O(23)	1.296(7)	C(22)–O(23)	1.294(10)
Bond angles (°)			
O(11)–Pd–N(15)	93.34(18)	O(11)–Pt–N(15)	93.1(2)
N(15)–Pd–O(23)	93.53(18)	N(15)–Pt–O(23)	93.5(2)
O(11)–Pd–O(23)	173.09(18)	O(11)–Pt–O(23)	173.3(2)
N(15)–Pd–P(2)	177.61(13)	N(15)–Pt–P(2)	177.10(17)

Table 3. Electronic spectral data in dichloromethane solution.

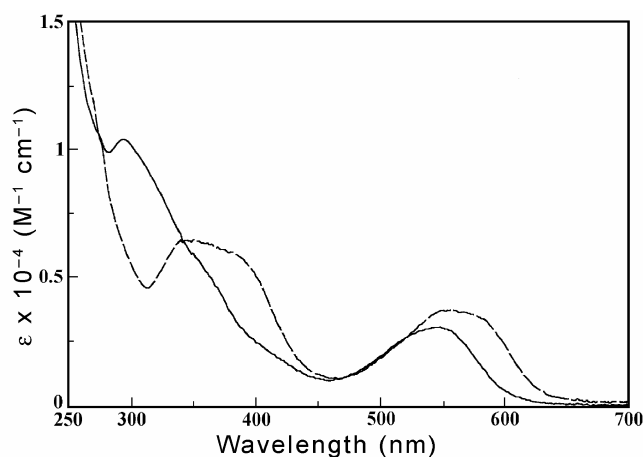
Compound	Electronic spectral data λ_{\max} (nm) ($\epsilon/M^{-1} \text{cm}^{-1}$)
[Pd(PPh ₃)(L)]	548(3100), 361*(5200), 293(10400)
[Pt(PPh ₃)(L)]	581(3400), 551(3700), 386(5800), 339(6500)

*Shoulder

and 8.41 (*d*, *J* = 9.3) ppm, while detection of two triplets and a singlet has not been possible because of overlap problem. ³¹P NMR spectra of both the [M(PPh₃)(L)] (M = Pd and Pt) complexes have also been recorded in CDCl₃ solution. A clean signal is observed at 20.67 ppm for the palladium complex and at 22.07 ppm for the platinum complex.

3.3 IR spectra

Infrared spectra of both the [M(PPh₃)(L)] (M = Pd and Pt) complexes are similar. Each complex shows several sharp bands of different intensities in the 1700–400 cm⁻¹ region. Assignment of each individual band to a specific vibration has not been attempted. However, three sharp and strong bands observed near 1630, 1483 and 1390 cm⁻¹ in both the complexes are attributable respectively to the coordinated carboxylate, azo (–N=N–) and phenolic C–O fragments. In the uncoordinated 2-(2'-carboxyphenylazo)-4-methylphenol these bands are observed at 1701, 1593 and 1402 cm⁻¹ respectively. The observed shift is attributable to complexation. Three strong bands observed near 750, 695 and 530 cm⁻¹ in both the complexes are attributable to the coordinated PPh₃ ligand.

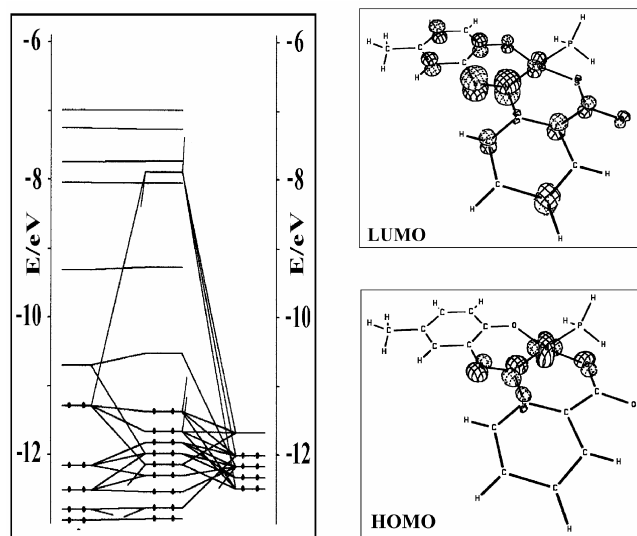
**Figure 3.** Electronic spectra of the [Pd(PPh₃)(L)] complex (—) and the [Pt(PPh₃)(L)] complex (-----) in dichloromethane solution.

3.4 Electronic absorption spectra

The [Pd(PPh₃)(L)] and [Pt(PPh₃)(L)] complexes are soluble in dichloromethane, chloroform, acetone, acetonitrile, etc. producing reddish-purple and violet solutions respectively. Electronic spectra of these complexes have been recorded in dichloromethane solutions. Each complex shows several intense absorptions in the visible and ultraviolet regions. Spectral

Table 4. Composition of molecular orbitals.

Compound	Contributing fragments	% Contribution of fragments to						
		HOMO	HOMO-1	HOMO-2	HOMO-3	LUMO	LUMO + 1	LUMO + 2
[Pd(PPh ₃)(L)]	Pd	78	88	78	71	12	1	0
	L	18	11	21	27	87 (N = N 49)	99	100
[Pt(PPh ₃)(L)]	Pt	65	47	43	55	10	2	0
	L	30	50	53	45	87 (N = N 49)	97	100

**Figure 4.** Partial molecular orbital diagram of the [Pd(PPh₃)(L)] complex.

data are given in table 3 and the spectra are shown in figure 3. While the absorptions in the ultraviolet region are assignable to transitions within the ligand orbitals, origin of those in the visible region was not clear. To have a better understanding of the nature of absorptions in the visible region, qualitative EHMO calculations have been performed on computer-generated models of both the complexes,⁸ where the phenyl rings of the triphenylphosphines have been replaced by hydrogens. The results are found to be qualitatively similar for both the complexes. Compositions of selected molecular orbitals are given in table 4. A partial MO diagram for the [Pd(PPh₃)(L)] complex is shown in figure 4. The highest occupied molecular orbital (HOMO) and the next three filled orbitals (HOMO-1, HOMO-2 and HOMO-3) have major contributions from the metal *d*-orbitals.⁹ The lowest unoccupied molecular orbital (LUMO) is localized almost entirely on the O,N,O-donor ligand (L) and is concentrated largely on the azo (N=N)

fragment. The next two vacant orbitals (LUMO + 1 and LUMO + 2) are localized on other parts of the same ligand (L). The lowest energy absorption in the visible region is therefore assignable to an allowed transition from the filled metal *d*-orbital (HOMO) to the vacant π^* (azo)-orbital of the L ligand (LUMO). It is relevant to note here that such metal-to-ligand charge-transfer transition is relatively less common in complexes of palladium and platinum.¹⁰ The other absorptions in the visible region may be assigned to similar charge-transfer transitions from the filled metal *d*-orbitals to the vacant ligand (L) orbitals.

4. Conclusions

The present study shows that 2-(2'-carboxyphenylazo)-4-methylphenol (H₂L, **1**) can readily coordinate a metal ion in the dianionic tridentate O,N,O-fashion (**2**) via dissociation of the two acidic protons. This is manifested in the formation of the stable mixed-ligand complexes of palladium and platinum of type [M(PPh₃)(L)] (M = Pd and Pt). Attempts to bind this ligand (**1**) to other platinum group of metals in the same tridentate fashion (**2**) leading to the formation of interesting homoleptic and heteroleptic complexes are currently in progress.

5. Supplementary material

Crystallographic data for the [Pd(PPh₃)(L)] and [Pt(PPh₃)(L)] complexes in the CIF format have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 614148 for the [Pd(PPh₃)(L)] complex and 614147 for the [Pt(PPh₃)(L)] complex.

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