SYNTHESES AND SPECTROSCOPIC STUDIES ON SOME PLATINUM GROUP METAL COMPLEXES WITH OXAZEPAM AS LIGAND

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ABSTRACT

The preparation and characterization of some rhodium(III), iridium(III), palladium(II) and platinum(II) halide complexes with oxazepam, 7-chloro-1,3-dihydro-5-phenyl-3hydroxy-2H-1,4-benzodiazepin-2-one are reported. The obtained complexes of the type ML_3X_3 (M = Rh, Ir) and ML_2X_3 (M = Pd, Pt) with the exception of the rhodium and palladium iododerivatives which have 1:6 and 1:4 metal:ligand ratios, respectively, have been studied and characterized through vibrational and electronic spectra, ¹H and ¹³C NMR studies, conductivity measurements and magnetic susceptibility data. The wavelengths of the principal electronic absorption peaks have been accounted for quantitatively in terms of the crystal field theory and the various parameters have been calculated. The most convincing structural evidence supports an octahedral stereochemistry for the rhodium and iridium derivatives and a square planar geometry for the palladium and platinum compounds with terminal halides and terminal ligands, acting as monodentate only in all the metal complexes through the nitrogen atom in the 4-position.

INTRODUCTION

Studies have been made recently on the complex formation of 1,4-benzodiazepines as ligands [1-7] in order to study their behaviour towards metal ions in the coordination. Although the benzodiazepines have wide application in the pharmaceutical industry, relatively little is known on their behaviour as ligands.

The most important factor in stimulating our interest in the study of the coordination properties of 1,4-benzodiazepines as ligands towards the metals of the platinum group has been the fact that the complexes of the group VIII metals have been reported to have considerable antibacterial power; in addition, platinum complexes induce lysis in lysogenic bacteria [8-11]. We hope that the study of the stereochemistries and of the chemical reactivity of their coordination compounds will help to determine what relationship exists between chemical structure and biological activity of these drugs in the belief that geometrical factors can determine the chemical reactivity and

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pharmacological activity. Furthermore, it is well known that the metal complexes of ligands which have biological activity are more active than the free ligands [12, 13].

We now report the preparation and characterization of rhodium(III), iridium(III), palladium(II) and platinum(II) halide complexes with 7-chloro-1,3-dihydro-5-phenyl-3-hydroxy-2H-1,4-benzodiazepin-2-one, commercially known as Oxazepam or Adumbran, and hereafter abbreviated adu.



This drug is widely prescribed for its important biological activity such as muscle relaxant and anticonvulsivant. The crystal and molecular structure of this ligand has been previously reported [14]; it consists of infinite layers of molecules linked by a net of hydrogen bonds of the type N-H···OH and N-H···O=C, and packed by Van der Waals forces. The diazepine ring is in the boat conformation and the remarkable stability of the seven-membered ring is due to ring annelation and to the presence of the C=N double bond.

RESULTS AND DISCUSSION

The metal complexes, which have been prepared according to the methods reported in the Experimental Section, are listed in Table 1, together with the analytical data and colours. Working with rhodium(III) and iridium(III) we have obtained complexes of the type $M(adu)_n X_3$ (M = Rh, X = Cl and Br, n = 3; X = I, n = 6; M = Ir, X = Cl, Br and 1, n = 3), while in the case of palladium(II) and platinum(II) the complexes were of type $M(adu)_n X_2$ (M = Pd, X = Cl and Br, n = 2; X = I, n = 4; M = Pt, X = Cl, Br and I, n = 2).

These derivatives have been characterized through conductivity measurements, room temperature magnetic moment studies, electronic, infrared and far infrared spectra, ¹H and ¹³C NMR studies. The solid state electronic spectra, the ligand field parameters, the most important infrared data in the 4000-50 cm⁻¹ range and the ¹³C NMR assignments are shown in the Tables 2-5. The compounds are powder-like or microcrystalline, diamagnetic, soluble in N,N'-dimethylformamide (DMF), nitromethane, dimethylsulfoxide, stable at room temperature, insensitive to atmospheric oxygen and moisture.

The conductivity measurements in DMF or nitromethane agree with the

TABLE 1

Compounds	Colour	Found %			Required %		
		C	Н	N	C	Н	N
[Rh(adu).Cl.].H.O	brown	49.6	3.0	7.5	49.7	3.2	7.7
[Rh(adu),Br,]	light brown	45.0	3.1	7.0	44.9	2.8	7.0
Rh(adu), 11,	grey-green	49.3	3.4	7.6	49.0	3.0	7.6
[Ir(adu),Cl,]·2H,O	dark brown	45.1	3.0	7.0	45.2	3.1	7.0
[Ir(adu), Br.]	dark brown	42.0	2.6	6.5	41.8	2.6	6.5
[Ir(adu), L]. 5H,O	red-violet	S5.7	2.7	5.4	35.5	2.8	5.5
[Pd(adu),Cl,] • 2H,O	lemon-yellow	46.3	3.0	7.1	45.8	3.3	7.1
[Pd(adu),Br,]·2H,O	yellow	41.1	2.9	6.3	41.1	3.0	6.4
[Pd(adu),]I,	grey	48.1	2.6	7.4	47.8	2.9	7.4
$Pt(adu), Cl_1 \cdot 2H_0$	orange	41.4	2.8	6.2	41.2	3.0	6.4
[Pt(adu),Br,]·2H,O	grey-green	36.9	2.5	5.8	37.4	2.7	5.8
$[Pt(adu)_{2}I_{2}]$	brown	35.3	2.2	5.1	35.2	2.2	5.5

Analytical data and other physical properties

cited formulae, Table 1, i.e. the rhodium and iridium derivatives with a 1:3 metal:ligand ratio and the palladium and platinum complexes with a 1:2 metal:ligand ratio are non conducting, while the complexes $[Rh(adu)_6]I_3$ and $[Pd(adu)_4]I_2$ show conductivity values typical of 1:3 and 1:2 electrolytes respectively (242.3 and 146.1 ohm⁻¹ cm² mol⁻¹ in nitromethane) [15].

The typical bands of the ligand appear in the IR spectra of the complexes,

TABLE 2

Electronic spectra and ligand field parameters (cm⁻¹)

Compounds	d-d bands		ν_2/ν_1	Ligand field parameters			
	$^{1}A_{1g} \rightarrow ^{1}T_{1g}$	$^{1}A_{1g} \rightarrow ^{1}T_{2g}$		Δ	в'	β	Z*
$[Rh(adu), Cl,] \cdot H, O$	23 920	29 850	1.25	24 975	405	0.56	0.59
[Rh(adu), Br,]	23 200	29 400	1.27	24 262	427	0.59	0.68
[Rh(adu),]I,	24 200	29 700	1.23	25 217	373	0.52	0.47
$[Ir(adu), Cl,] \cdot 2H, O$	30 770	34 720	1.13	$31\ 621$	258	0.39	
[Ir(adu), Br,]	30 120	34 250	1.14	30 999	271	0.41	
$[Ir(adu)_{3}I_{3}] \cdot 5H_{2}O$	29 850	33 900	1.14	30 713	265	0.40	
	${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$	C.T.		Δ			
$[Pd(adu), Cl_{2}] \cdot 2H_{2}O$	24 400	29 600		26 500			
Pd(adu).Br. 1.2H.O	23 530	31 050		25 630			
[Pd(adu)]]I	25 000	30 700		$27\ 100$			
Pt(adu),CI,] • 2H,O	26 180			$28\ 280$			
[Pt(adu),Br,]·2H,O	25 320	30 1 20		$27\ 4\ 20$			
[Pt(adu) ₂ I ₂]	25 000	28 800		27 100			

B is taken to be 720 and 660 cm⁻¹ for the free gaseous Rh³⁺ and Ir³⁺ ions, respectively.

TABLE 3

400

v(C≈O) v(C=N)Compounds v(OH) $\nu(\rm NH)$ adu (solid) 3340 s 3210 s 1710 vs, 1690 vs 1600 s $[Rh(adu)_{3}Cl_{3}] \cdot H_{2}O$ 1710 sh, 1690 vs 3390 m 3210 m 1570 s 1718 m, 1690 m [Rh(adu),Br,] 3400 ms 3220 m 1550 vs 3230 m 1719 m, 1690 m 1552 s [Rh(adu),]I, 3380 m $[Ir(adu)_3Cl_3] \cdot 2H_2O$ 1715 s, 1680 vs 1557 m 3410 m 3210 m [Ir(adu), Br,] 3410 m 3220 m 1710 s, 1695 s 1575 m [lr(adu), I,] • 5H, O 3380 m 3190 m 1712 m, 1695 ms 1560 ms [Pd(adu)2Cl2] · 2H2O 3440 s 3200 s 1710 vs 1595 ms $[Pd(adu)_{2}Br_{2}] \cdot 2H_{2}O$ 1702 vs 1555 ms 3430 ms 3200 s 1717 vs, 1690 s 1555 s 3200 m [Pd(adu),]I₂ 3410 m $[Pt(adu)_2Cl_2] \cdot 2H_2O$ 3400 s 3210 s 1700 vs 1575 ms $[Pt(adu)_{2}Br_{2}] \cdot 2H_{2}O$ 1568 ms 3440 s 3200 s 1712 vs 3410 s 3220 ms 1711 s, 1698 s 1570 s [Pt(adu),I,]

Most important infrared bands (cm⁻¹)

TABLE 4

¹³C chemical shifts (ppm/Me₄Si) of adu and of its palladium(II) chloro-complex

Assignments	adu	$[Pd(adu)_2Cl_2] \cdot 2H_2O$		
C(2)	169.70	169.67		
C(5)	162.26	162.31		
C(11)	137.93	137.91		
C(10)	137.65	137.63		
C(8)	131.70	131.73		
C(15)	130.40	130.45		
C(13, 17)	129.17	100.10		
C(6)	129.13	129.16		
C(14, 16)	128.30	128.34		
C(12)	127.76	127.76		
C(7)	126.57	126.59		
C(9)	123.11	123.09		
C(3)	82.75	82.71		

and the ligand can be recovered by chemical decomposition of the compounds.

Electronic spectral studies

Solid state electronic spectra suggest an octahedral configuration for rhodium(III) and iridium(III); the position of the electronic absorption bands and their most probable assignments are given in Table 2. The diamagnetic nature of these metal complexes indicates octahedral surroundings of the donor atoms around the metal ions producing a strong field.

Rhodium derivatives show a band at 23 200-23 920 cm⁻¹ and a second

TABLE 5

Far infrared spectra (450-100 cm⁻¹)

Compounds	ν(MX)	ν(M—L)	Other bands
adu	-	_	417 m, 379 m, 345 s, 322 m, 278 m, 209 w,
			186 mw, 167 m, 146 m, 121 m
$[Rh(adu)_3Cl_3] \cdot H_2O$	336 m, 298 m	268 m, 202 m	420 m, 373 m, 350 ms, 324 m, 278 m, 210 w,
			185 mw, 168 mw, 149 m, 118 m
[Rh(adu)3Br3]	193 m, 168 m	265 m, 220 m	419 m, 372 m, 344 m, 322 m, 276 m, 204 w,
			181 mw, 171 m, 148 m, 120 m
[Rh(adu) ₆] I ₃	-	266 m	410 m, 382 m, 354 m, 324 m, 280 m, 206 w,
			187 mw, 170 m, 150 m, 120 m
[lr(adu) ₃ Cl ₃]•2H ₂ O	334 m, 291 m	266 m, 204 m	422 m, 370 m, 350 m, 320 m, 278 m, 210 m,
• • •			182 m, 168 m, 148 m, 116 m
[Ir(adu) ₃ Br ₃]	190 m. —	268 m, 200 m	423 m, 373 m, 350 m, 321 m, 279 m, 212 m,
			185 m, 167 m, 150 m, 117 m
[Ir(adu),I3] •2H2O	158 m, 126 m	275 ms, 220 ms	418 m, 376 m, 346 m, 321 m, 282 m, 208 m,
			190 m, 170 m, 148 m, 116 m
[Pd(adu) ₂ Cl ₂ [•2H ₂ O	335 vs ^a	290 ms	416 m, 354 ms, 322 s, 278 m, 208 m, 190 m,
			174 m, 149 m, 119 m
$[Pd(adu)_{2}Br_{2}] \cdot 2H_{2}O$	262 m	304 ms	418 m, 380 m, 350 s, 325 m, 276 m, 211 w,
			183 mw, 172 m, 148 m, 115 m
$[Pd(adu)_4]I_2$		300 m	417 m, 375 m, 344 s, 320 m, 275 m, 208 w,
			187 mw, 169 m, 147 m, 118 m
$[Pt(adu)_2Cl_2] \cdot 2H_2O$	325 vs ^a	224 m	413 m, 372 m, 349 s, 280 m, 204 w, 188 mw,
			170 m, 149 m, 120 m
$[Pt(adu)_2Br_1] \cdot 2H_2O$	233 ms	220 m	410 m, 375 m, 343 s, 322 m, 278 m, 208 w,
			187 mw, 168 m, 151 m, 120 m
[Pt(adu) ₂ I ₂]	195 ms	223 m	415 m, 380 m, 346 s, 324 m, 278 m, 207 w,
			187 mw, 170 m, 148 m, 116 m

^aOverlapping a ligand band, which markedly reinforced.

band in the 29 400–29 700 cm⁻¹ range. These two peaks are the two expected spin allowed transitions to the $t_{2g}^5 e_g^1$ configuration and they are not obscured by charge-transfer absorptions. The values of 10Dq and B', as calculated from the position of these bands by means of the equations [16]

$$v_1 = \Delta - 4B' + 86(B')^2/\Delta$$

 $v_2 = \Delta + 12B' + 2(B')^2/\Delta$

are reported in Table 2 and are well within those found for other trivalent rhodium complexes [17-22]. These bands are in the wavelength range expected for RhN₃X₃ chromophores [23] using the law of the average environment, and for a RhN₆ chromophore as regards the iodo-derivative.

As for the iridium complexes, the two observed absorption bands are in the ranges expected for the two spin allowed transitions from the ground state ${}^{1}A_{1g}$. The 10Dq and B' values, obtained with the same type of calculation above reported are as expected for IrN₃X₃ chromophores (Table 2).

The values of B', of the order of 52–59% and 39–41% of the free ion values in the rhodium and iridium derivatives, respectively, suggest a considerable orbital overlap with a strong covalency in the metal-ligand σ bond. The nephelauxetic parameter shows the expected order with respect to the metals Rh(III) > Ir(III). The β values of our complexes were compared with

the β values of other rhodium(III) and iridium(III) derivatives in order to find out the position of the ligand in the nephelauxetic series. Our ligand can be placed in the middle of this series, among the nitrogen donors and we suggest the following order

 $\label{eq:F-SXC_6H_4SeO_2>H_2O>(CH_3)_2SO\simeq CH_3CONH_2>(NH_2)_2CO> \\ thiazolidine-2-thione(N-bonded)>NH_3>adu>terizidone(N-bonded)> \\ benzoxazole-2-thione(N-bonded)>S>(C_2H_5O)_2PSe^->Cl^->Br^-.$

The effective ionic charges for the rhodium complexes studied here, calculated using the available methods [16], are in the 0.47–0.68 range (Table 2), considerably below the formal +3 oxidation state.

The electronic spectra of the diamagnetic palladium(II) and platinum(II) derivatives are indicative of square planar geometries [24, 25], Table 2. The bands in the range 23 530–25 000 cm⁻¹ and 25 000–26 180 cm⁻¹ for the palladium and platinum derivatives respectively may be assigned to the transition ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$. In the UV region there is a strong absorption between 28 800–31 050 cm⁻¹, which may be due to a charge-transfer band.

By assuming a value of $F_4 = 60 \text{ cm}^{-1}$ for the Slater—Condon interelectronic repulsion parameter both for palladium and platinum [26], it is possible to derive from the above reported first spin-allowed d-d transition the values of Δ_1 , see Table 2. The splitting parameter increases in the expected order Pt > Pd and it places the ligand in the spectrochemical series of the nitrogen donors.

Infrared spectral studies

The meaningful IR absorption bands involving the potential donor atoms of the ligand in the free and complexed form are reported in Table 3.

The stretching values of the OH, NH and C=O groups are clearly affected by the presence of hydrogen bonds of the type NH···OH and C=O···HN as shown by the molecular structure of the ligand [14]. On passing from the free ligand spectrum to those of the complexes we observe that the directions of the shifts of the bands related to $\nu(OH)$, $\nu(NH)$, $\nu(C=O)$ and $\nu(C=N)$ are the same in all the complexes; this fact indicates that the bonding pattern must be similar in all the derivatives.

The ν (OH) stretching mode shows upward shifts allowing us to conclude that the oxygen atom is not involved in the coordination to the metals; we suggest that this blue shift is most likely due to a partial breakdown of the hydrogen bonds after the complexation.

The vibrational mode attributed to v(NH) appears unchanged at the same value as in the free ligand or shows shifts towards lower energies too small to imply coordination through this group.

The exact assignments of the other peaks are not easy, as the vibrations of the ligand conjugate with each other and they can be separated into group vibrations only with difficulty and, as a consequence, any suggestion on the coordination mode based on the IR conclusions must be considered tentative. However in all the complexes, with the exception of the palladium and platinum chloro- and bromo-derivatives, the ν (C=O) mode can be associated with the split band in the 1719—1680 cm⁻¹ range, practically unchanged or showing very small upward or downward shifts with respect to the free ligand values, 1710 and 1690 cm⁻¹. The above mentioned palladium and platinum halocomplexes, however, exhibit just a single very strong band in the 1712—1700 cm⁻¹ range. The band at 1600 cm⁻¹ in the free ligand attributed to the prevailing contribution of ν (C=N) vibrational mode, undergoes red shifts of ca. 35 cm⁻¹ on passing to the spectra of the complexes.

These facts could allow us to propose a coordination through the nitrogen atom in the 4-position of the diazepine ring. Such a coordination was also suggested by the conclusions reached from the electronic spectra studies, which are indicative of the presence in the complexes of nitrogen containing chromophores.

The medium-strong bands present in the range $3550-3500 \text{ cm}^{-1}$, $\nu(\text{OH})$, and at some 1660 cm⁻¹, $\delta(\text{HOH})$ in the water containing complexes only, Table 1, clearly confirm the presence of water of crystallization. Since vibrational modes such as wagging, twisting and rocking activated by coordination to the metal have not been found in the expected ranges [27], it appears that coordinated water is not present. These results are consistent with the thermogravimetric studies, using TG and DTG techniques; in fact this water is lost in the 60–120°C range. The observed and calculated weight losses agree with the presence of one, two, or five water molecules, as reported in Table 1.

Magnetic resonance studies

The free ligand, adu, and a representative complex $[Pd(adu)_2Cl_2] \cdot 2H_2O$, have been extensively studied through ¹H and ¹³C NMR spectroscopy. The ¹H NMR spectrum obtained from a freshly prepared DMSO d₆ solution of the ligand is shown in Fig. 1.

The chemical shift of the benzene groups proton resonances centres in the range 7.10-7.70 ppm; the singlet at 10.81 ppm is attributed to the proton of the imino group. The resonances of the OH and CH groups appear as doublets at 6.37 and 4.77 ppm respectively, with a J value of 0.04 ppm; this clearly indicates coupling between these two hydrogen atoms.

On going from the free ligand spectrum to that of the $[Pd(adu)_2Cl_2] \cdot 2H_2O$ complex in the same solvent, see Fig. 2, we observe the proton resonances of the phenyl rings and of the hydrogen of the NH group unchanged at the same values above reported, while the spectrum shows a completely and significantly different profile as regards the chemical shifts of the protons of the CH and OH groups. We observe, in fact, the disappearance of the two series of doublets, replaced by a broad signal at some 6.40 ppm related to the OH group and by a well resolved singlet at 4.79 ppm related to the CH group.





This behaviour can be explained by considering the fact that, owing to the coordination, the structural conditions favourable to the protons coupling of the OH and CH groups are not yet present and, as a consequence, the two doublets disappear. It has been shown, for the free ligand [14], that the presence of the carbon—nitrogen double bond is responsible for the great stability of the seven membered diazepine ring in the boat conformation; most likely, a possible coordination of the ligand through the nitrogen of the C=N group, as suggested by the analysis of the electronic and IR spectra, could destabilize the boat conformation of the above ring and, as a consequence, this fact makes impossible the coupling of the OH and CH groups protons and is accompanied by the disappearance of the doublets.

The ¹³C NMR spectra of the ligand and of the palladium chloroderivative were obtained in freshly prepared DMSO- d_6 solutions; the proton-noise decoupled ¹³C NMR spectrum of the ligand is shown in Fig. 3, while Fig. 4



Fig. 2. 'H NMR spectrum of the [Pd(adu)₂Cl₂] · 2H₂O complex.



Fig. 4. ¹³C D-INEPT (up) and proton decoupled (down) spectra of the ligand.

contains ¹³C spectrum of the ligand obtained with the proton decoupled INEPT technique (D-INEPT) adapted for the selection of the signals of (C-H) doublets (up), compared with the proton-noise decoupled spectrum (down); the ¹³C proton-noise decoupled NMR spectrum of the palladium complex is shown in Fig. 5.

The ¹³C NMR spectrum of the free ligand shows thirteen peaks; the assignments have been deduced from the D-INEPT spectrum (that allowed us to identify the quaternary carbon atoms) and from the "proton-coupled" spectrum in which the signal multiplicity and the values of J_{CH}^n have been evaluated. Using the figure reported in the Introduction, the relative assignments are listed in Table 4.

As for the palladium chloro-complex, Fig. 5, it is clear that the presence of a metal ion induces a systematic perturbation of the resonance conditions of the C(i) nuclei of the ligand, characterized by a moderate decrease in intensity and broadening of all the peaks, and in particular of those corresponding to C(3), C(10), C(11) and C(7).



Fig. 5. ¹³C proton-noise decoupled NMR spectrum of the complex $[Pd(adu)_2Cl_2] \cdot 2H_2O$.

This behaviour, in good agreement with the available literature data [6], is, as a whole, quite consistent with coordination of the metal atom via the N(4) nitrogen of the diazepine ring and excludes the possibilities of different coordinations.

Far infrared spectra

In the far IR spectra of the complexes the bands of the free ligand are still present at approximately the same wavenumbers; see Table 5.

Taking into account the results of the electronic spectra studies and the similar behaviour of the vibrational modes (in the near i.r. spectra) of the groups having potential donor atoms that were in keeping with a coordination through the nitrogen of the C=N group, fully confirmed by the NMR results, we can propose the same type of coordination for all the complexes.

Rhodium(III) and Iridium(III) complexes

The complexes of the type $M(adu)_3X_3$ (M = Rh, Ir) show two halogen independent bands in the 200-275 cm⁻¹ range and a second set of two bands between 126 and 336 cm⁻¹, which decrease in frequency as the mass of the halogen increases. The halogen independent bands, absent in the spectra of the starting materials used in this study and in derivatives of the rhodium(III) and iridium(III) containing O-bonded ligands [17], can be attributed to metal-nitrogen stretching modes [23, 28-31]; no bands are present in the range where $\nu(M-O)$ usually lies for these metals.

In the $[Rh(adu)_6]I_3$ derivative, metal—halogen absorptions are not found in the range usually observed for the derivatives of this metal containing covalently bonded iodide atoms, in accordance with the conductivity measurements. In this complex a single band is present at 266 cm⁻¹, absent in the spectra of the starting materials; it can be assigned to a metal—ligand vibration involving the nitrogen atom, N(4), of the diazepine ring.

Palladium(II) and platinum(II) complexes

The spectra of the $M(adu)_2X_2$ complexes (M = Pd, Pt; X = Cl, Br, I) show new halogen independent bands in the 290-304 cm⁻¹ and 220-224 cm⁻¹ ranges for the palladium and platinum derivatives respectively, Table 5, which can be assigned to metal-nitrogen vibrational modes in very good agreement with published data [29, 32]. No bands are present in the range where $\nu(M-O)$ usually lies for these metals. As for the metal-halide bands, we observe a band in the 195-335 cm⁻¹ range, whose frequency depends on the halogen present in the complex. The position and multiplicity of the $\nu(M-N)$ and $\nu(M-X)$ modes are indicative of a *trans* square-planar D_{2h} symmetry with terminal halides: these complexes show, in fact, just one $\nu(M-N)$ vibration (b_{2u}) and one $\nu(M-X)$ vibration (b_{3u}) .

In the far i.r. spectrum of the complex $[Pd(adu)_4]I_2$, no bands are present in the expected range where the $\nu(Pd-I)$ mode usually lies, but only a medium absorption band is observed, clearly due to $\nu(Pd-N)$; this is the vibration of e_u symmetry in the D_{4h} symmetry point group. The absence of palladium—iodine stretching mode is in accord with the conductivity measurements results.

EXPERIMENTAL

The ligand adu, commercially available in high purity grade, was used without further purification.

Preparation of the complexes

The rhodium and iridium derivatives were obtained by adding an ethanolic solution of the ligand to an aqueous solution of RhX₃ and $(NH_4)_3IrX_6$ (X = Cl, Br, I); metal/ligand molar ratios from 1:1 to 1:6. The solution was refluxed under vigorous stirring for about 6–18 h; the compounds, which precipitated spontaneously or after concentration to small volume on rotary evaporator, were filtered, washed with cold water and dried over P_4O_{10} .

The palladium and platinum complexes were obtained in the same way as the rhodium and iridium ones starting with K_2MCl_4 (M = Pd, Pt), in the presence of KBr and KI in the case of the bromo- and iodo-derivatives; metal/ligand molar ratios from 1:1 to 1:4. The solution was refluxed and vigorously stirred for about 4-5 h in the case of the chloro-derivatives and for times from 3 to 48 h in the case of the bromo- and iodo-complexes. The compounds, which precipitated spontaneously, were washed many times with cold water and dried over P_4O_{10} .

We have obtained complexes only in the metal/ligand ratios reported in Table 1.

Infrared spectra

The infrared spectra have been recorded in the $4000-50 \text{ cm}^{-1}$ range with a Perkin-Elmer 180 spectrophotometer of the Instruments Centre of Modena University. The spectra in the $4000-400 \text{ cm}^{-1}$ range were measured for KBr discs or Nujol mulls. Far infrared spectra were measured for Nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen.

Electronic spectra

The electronic spectra have been recorded with a Shimadzu MPS-50L spectrophotometer in the solid state in the 5000-45 000 cm⁻¹ range, the method of Venanzi and coworkers being used [33].

Nuclear magnetic resonance spectra

The ¹H and ¹³C NMR spectra were recorded on freshly prepared solutions of the ligand and of the complexes in DMSO-d₆ with a Varian XL 200 spectrometer of the Instruments Centre of Modena University, working at 50 and 200 MHz. The chemical shift values, $\delta H(i)$ and $\delta C(i)$ are expressed in p.p.m. relative to tetramethylsilane; a negative shift corresponds to a decrease in the resonance frequency.

Magnetic susceptibility measurements

These were carried out by the Gouy method at room temperature. Molecular susceptibilities were corrected for diamagnetism of the component atoms by use of the Pascal constants.

Conductivity measurements

These measurements were carried out with a WTW LBR type conductivity bridge at 25° C for 10^{-3} M solutions in dimethylformamide or nitromethane.

Analyses

Carbon, nitrogen and hydrogen were determined with a Carlo Erba 1106 elemental analyser.

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