Pergamon

PII: S0277-5387(97)00432-4

Polyhedron Vol. 17, Nos. 11-12, pp. 2065-2072, 1998

0277-5387/98 $19.00+0.00

Palladium(II) and platinum(II), (IV) complexes of acetamidrazones

M. Teresa Cocco,[b] Valentina Onnis,[b] Gustavo Ponticelli*[a] and Antonio Spanu[a]

[a] Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, Via Ospedale 72, 09124 Cagliari, Italy

[b] Dipartimento Farmaco Chimico Tecnologico, Via Ospedale 72, 09124 Cagliari, Italy

(Received 28 July 1997; accepted 21 October 1997)

Abstract—Palladium(II) and platinum(II),(IV) complexes with N^1-acylacetamidrazones (**L1**–**L5**) and N^1-acyl-2-phenylacetamidrazones (**L6**–**L9**) are described. The complexes have been prepared by reaction of the corresponding metal chloride with the ligand in the required stoichiometrical ratio and were characterized by chemical analyses and physical measurements. The stereochemistry has been assigned on the basis of IR, far IR spectroscopy, electronic reflectance spectra and molar conductivity values. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: palladium(II) chloride; platinum(II),(IV) chloride; N^1-acylacetamidrazone ligands; complexes; synthesis.

The amidrazones RC(=NH)NHNHR′ (R, R′ = H, alkyl, aryl) have been studied very little as ligands of transition metals [1]. Some published results are available on the structure and catalytic activity of nickel(II) and copper(II) complexes with amidrazones [2], and the structure of cobalt(II) complexes with N^1-aryl-substituted arylamidrazones [3]. Furthermore in the literature were found only the X-ray structure for two novel oxopersulphidoamidrazone tungstate complexes $WO(S_2)_2[RC(=NH)NHNH]$ where $R = CH_3$, C_2H_5 [4]; in the molecular structures the tungsten atom is coordinated by a terminal oxoligand, to two persulphido S_2^{2-} ligands and one bidentate amidrazone ligand. The coordination polyhedron of the tungsten atom is pentagonal bipyramidal, whose two axial ligands are formed by terminal oxoatom and the *N*(H) coordinating atom of the NHNH in amidrazone [4].

The antibacterial activity of first transition metals complexes with picolinamidrazones derivatives [5] and the antibacterial and antitumoral activities of platinum(II) complexes with N^1-phenylsubstituted amidrazones [6] have been also reported.

While, as far as the acetamidrazone complexes are concerned, at the best of our knowledge no references are available. The amidrazones were previously utilized by us in the synthesis of potential biologically active heterocyclic compounds. For example N^1-acetylacetamidrazone **L1**, N^1-ethoxycarbonylacetamidrazone **L2** and N^1-ethoxycarbonyl-2-phenylacetamidrazone **L6** were used as starting materials for the synthesis of imidazole derivatives that have shown a moderate antimicrobial activity [7,8].

EXPERIMENTAL

Solvents and reagents were purified according to standard laboratory techniques.

Microanalysis were carried out with a Fisons EA 1108 elemental analyser.

The IR spectra were recorded in the 4000–180 cm^{-1} range with a Perkin–Elmer mod. 983; the near IR spectra were recorded in KBr pellets, while the far IR spectra were recorded in Nujol mulls (CsI). The electronic reflectance spectra were recorded with a Varian Cary 5 in the 50,000–15,000 cm^{-1} range.

The conductivity measurements were carried out with a WTW, LBR model, conductance bridge at 25°C for 10^{-3} M solution in DMF.

The ^{1}H NMR spectra of ligands and complexes were taken in DMSO-d_6 solution with a Varian Unity

---

* Author to whom correspondence should be addressed.

300 spectrometer. The chemical shifts are given in ppm relative to TMS as internal standard. The ^1H NMR spectra of the complexes, taken in DMSO-d_6 solution showed no signals due to the complexes, probably because the DMSO substituted the ligand in the complexes. It was not possible to register the ^1H NMR spectra of the complexes in $CDCl_3$ since they are insoluble in this solvent.

The mass spectra of the complexes were taken via the solid inlet from solid samples in glass capillary sealed on the other end with excitations energies 16–70 eV with a Fisons QMD 1000 spectrometer in EI mode. Unfortunately the molecular peak of all the complexes was not obtained even though the conditions for the mass spectral measurements were varied. Typical by the mass spectra of all complexes were mainly those of the corresponding *N*^{1}-acylacetamidrazone ligand.

The *N*^{1}-acetyl-,*N*^{1}-ethoxycarbonyl- and *N*^{1}-benzoylacetamidrazones (**L1, L2, L6**) were prepared according to established procedures [9].

Synthesis of N^1-benzoylacetamidrazones (**L3–L5, L7–L9**)

A mixture of ethyl acetimidate derivative (0.01 mol) and the appropriate acylhydrazine (0.01 mol) in 50 ml of anhydrous ethanol was heated at 70–75°C for 1–2 min and then kept at room temperature for one night. The precipitate was collected by filtration, throughly washed with ethyl ether and recrystallized from the solvent indicated below.

N^1-benzoylacetamidrazone (**L3**) was obtained from ethylacetimidate and benzoyl hydrazine in 87% yield; M.p. 163–165°C (ethanol); Found: C, 61.0; H, 6.3; N, 23.6%. Calc. for $C_9H_{11}N_3O$: C, 61.0; H, 6.2; N, 23.6%.

^1H NMR (DMSO-d_6): δ 1.91 (s, 3H, CH_3), 6.22 (br s, 2H, NH_2), 7.37, 7.88 (m, 5H, Ar), 9.66 (br s, 1H, NH).

N^1-(4-methylbenzoyl)acetamidrazone (**L4**) was obtained from ethylacetimidate and 4-methylbenzoyl hydrazine in 78% yield; M.p. 185°C (ethanol); Found: C, 62.7; H, 6.9; N, 21.5%. Calc. for $C_{10}H_{13}N_3O$: C, 62.8; H, 6.8; N, 21.5%.

^1H NMR (DMSO-d_6): δ 1.92 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 6.27 (br s, 2H, NH_2), 7.15, 7.77 (m, 4H, Ar), 9.65 (br s, 1H, NH).

N^1-(4-chlorobenzoyl)acetamidrazone (**L5**) was obtained from ethylacetimidate and 4-chlorobenzoyl hydrazine in 86% yield; M.p. 180°C (ethanol); Found: C, 51.0; H, 4.7; N, 20.0%. Calc. for $C_9H_{10}ClN_3O$: C, 51.1; H, 4.8; N, 20.0%.

^1H NMR (DMSO-d_6): δ 1. (s, 3H, CH_3), 6.31 (br s, 2H, NH_2), 7.36, 7.96 (m, 4H, Ar), 9.84 (br s, 1H, NH).

N^1-benzoyl-2-phenylacetamidrazone (**L7**) was obtained from ethyl phenylacetimidate and benzoyl hydrazine in 82% yield; M.p. 175–6°C (ethanol); Found: C, 71.2; H, 6.0; N, 16.9%. Calc. for $C_{15}H_{15}N_3O$: C, 71.1; H, 6.0; N, 16.6%.

^1H NMR (DMSO-d_6): δ 3.49 (s, 2H, CH_2), 6.33 (br s, 2H, NH_2), 7.30, 7.86 (m, 10H, Ar), 9.74 (br s, 1H, NH).

N^1-(4-methylbenzoyl)-2-phenylacetamidrazone (**L8**) was obtained from ethyl phenylacetimidate and 4-methylbenzoyl hydrazine in 70% yield; M.p. 170–72°C (acetonitrile); Found: C, 71.7; H, 6.4; N, 15.7%. Calc. for $C_{16}H_{17}N_3O$: C, 71.9; H, 6.4; N 15.7%.

^1H NMR (DMSO-d_6): δ 2.30 (s, 3H, CH_3), 3.47 (s, 2H, CH_2), 6.38 (br s, 2H, NH_2), 7.30, 7.75 (m, 9H, Ar), 9.68 (br s, 1H, NH).

N^1-(4-chlorobenzoyl)-2-phenylacetamidrazone (**L9**) was obtained from ethyl phenylacetimidate and 4-chlorobenzoyl hydrazine in 70% yield; M.p. 180°C (ethanol); Found: C, 62.8; H, 5.0; N, 14.7%. Calc. for $C_{15}H_{14}ClN_3O$: C, 62.6; H, 4.9; N, 14.6%.

^1H NMR (DMSO-d_6): δ 3.66 (s, 3H, CH_2), 6.40 (br s, 2H, NH_2), 7.30, 7.93 (m, 9H, Ar), 9.93 (br s, 1H, NH).

Synthesis of the palladium(II) complexes

A mixture of the $PdCl_2$ (0.18 g, 1 mmol) and the ligand in the appropriate stoichemiometrical ratio was heated for 48 h at reflux in the solvent indicated below. The **A1, A6** complexes were prepared in ethanol using ligand and salt in 3 : 1 ratio. The palladium complexes with amidrazones **L3–L5** and **L7–L9** were prepared in acetone, using ligand and salt in 2 : 1 ratio.

$Pd(L1)_2Cl_2$ (**A1**). To an ethanolic solution (10 ml) of $PdCl_2$ (0.18 g, 1 mmol) *N*^{1}-acetylacetamidrazone (**L1**) (0.24 g, ~2 mmol) was added and the resulting mixture was heated at reflux with stirring for 6 h. The formed precipitate was collected by filtration, washed with hot ethanol (5 ml) and dried *in vacuo* over P_4O_{10}. Yield: 0.20 g, 50%.

Synthesis of the platinum(II) complexes

A mixture of the $PtCl_2$ (0.27 g, 1 mmol) and the ligand (3 mmol) was heated for 6 h at reflux in the acetone. The complex **B1** was prepared in ethanol utilizing ligand and salt in 2 : 1 ratio.

$[Pt(L3)_2 \cdot L3 \cdot 2H_2O$ (**B3**). To a Me_2CO solution (20 ml) of $PtCl_2$ (0.27 g, 1 mmol) *N*^{1}-benzoylacetamidrazone (**L1**) (0.24 g, ~2 mmol) was added and the resulting mixture was refluxed for 6 h. The formed precipitate was filtered off, washed with hot Me_2CO (10 ml) and dried *in vacuo* over P_4O_{10}. Yield: 0.3 g, 65%.

Synthesis of the platinum(IV) complexes

$Pt(L2)_2Cl_4$ (**B2**). To a Me_2CO solution (20 ml) of $PtCl_4$ (0.34 g, 1 mmol) *N*^{1}-ethoxycarbonylacetamidrazone (**L2**) (0.3 g, ~2 mmol) was added and the resulting mixture was refluxed for two days. The formed precipitate was filtered off, washed with hot Me_2CO (10 ml) and dried *in vacuo* over P_4O_{10}. Yield: 0.19 g, 30%.

RESULTS AND DISCUSSION

In this work we describe the preparation of N^1-acylacetamidrazones (**L1**–**L5**) and N^1-acyl-2-phenylacetamidrazones (**L6**–**L9**) and their complexes with Pd(II), Pt(II) and Pt(IV) (Scheme and Figure 1).

The synthesis of acetamidrazones was carried out in mild conditions. Short heating of a mixture of acetimidates and acylhydrazines in ethanol gave high yield of **L1**–**L9** at almost pure state. The ^1H NMR data, recorded in DMSO-d_6 solution, provide evidence for only an amide hydrazone tautomeric species. The complexes were prepared by heating at reflux the salts and an excess of acetamidrazones. A variety of experimental conditions were tested changing the solvent and the ligand/salt ratio. Depending on reaction conditions and on starting compounds, ionic or neutral complexes were obtained.

For **L1**, **L2** and **L6** we isolated complexes of formula $M(L)_2Cl_2$ where M = Pd(II), Pt(II) and $Pt(L)_nCl_4$; $n = 2, 4$. For **L3**–**L5**, **L7**–**L9** we have obtained complexes of the type $Pt(L)_2 \cdot L \cdot mH_2O$; while for **L3**–**L5** and **L7** we have isolated $Pd(L)_2 \cdot mH_2O$ complexes and for **L8** and **L9**, also $Pd(L)_2Cl_2 \cdot mH_2O$ type complexes, where $m = 0$–2, were isolated.

For the formation of complexes $Pt(L)_3 \cdot mH_2O$ and $Pd(L)_2 \cdot mH_2O$ without halogens, we can hypothesize that in these reactions HCl is free and that metal ions are coordinated with two anionic ligands.

To establish the coordination behaviour of the ligands and the stereochemistry of the complexes, all the isolated complexes have been studied by infrared, electronic reflectance spectra and by conductivity molar measurements in DMF.

Analytical and physical data of the complexes are reported in Table 1. These compounds are microcrystalline and/or powderlike, coloured from yellow to deep brown, generally soluble in DMF or DMSO and insoluble in other organic solvents. All the attempts made for recrystallize our palladium(II) and platinum(II), (IV) complexes for a X-ray structural investigation were unsuccessful.

The conductivity molar values are typical of non-conductors, except for complexes **B2** and **B6**, that are characteristic respectively of uni-univalent and uni-bivalent electrolites.

The ν(NH) and ν(CO) of the near infrared spectra for the complexes and ligands are reported in Table 2. Generally in the near infrared spectra of the complexes the ν(NH) are shifted to lower energy in the 36–200 cm^{-1} range when compared with the parent ligands. This shift is characteristic for a coordination of a NH_2 or NH group to the metallic ion [10–12]. In some cases **A1**, and **B6** the ν(NH) is either not shifted or moved to higher wavenumbers shifted with respect to the free ligand [13]. Generally the complexes with **L1** show the ν(CO) shifted to lower wavenumbers with respect to that of the free ligand, this fact has confirmed that the oxygen of the CO is involved in the coordination of the metal (Table 2).

In the far infrared spectra of **L1** complexes ν(M—N) [14] and ν(M—O) are present at 380–372 cm^{-1} and 450–429 cm^{-1}respectively, so that the complexes can be described as $[M(L1)_2]Cl_2$, (M = Pd, Pt) (Table 3). The low conductivity values typical for non electrolytes, can be explained by postulating that the complexes are rearranged in solution.

These infrared assignement for $M(L1)_2Cl_2$ complexes could be confirmed by an X-ray investigation [15] on a cobalt(II) complex $Co(L1)_2Cl_2 \cdot H_2O$, which has shown that this complex is ionic and that the

$$\underset{\displaystyle OC_2H_5}{R\text{-}C{=}NH} + H_2NNHCOR' \rightarrow \underset{\displaystyle NH_2}{R\text{-}C{=}NNHCOR'}$$

L 1 -L9

L	R	R'	L	R	R'
L1	CH_3	CH_3	L6	$C_6H_5CH_2$	OC_2H_5
L2	CH_3	OC_2H_5	L7	$C_6H_5CH_2$	C_6H_5
L3	CH_3	C_6H_5	L8	$C_6H_5CH_2$	$4\text{-}CH_3C_6H_4$
L4	CH_3	$4\text{-}CH_3C_6H_4$	L9	$C_6H_5CH_2$	$4\text{-}ClC_6H_4$
L5	CH_3	$4\text{-}ClC_6H_4$			

Scheme 1.

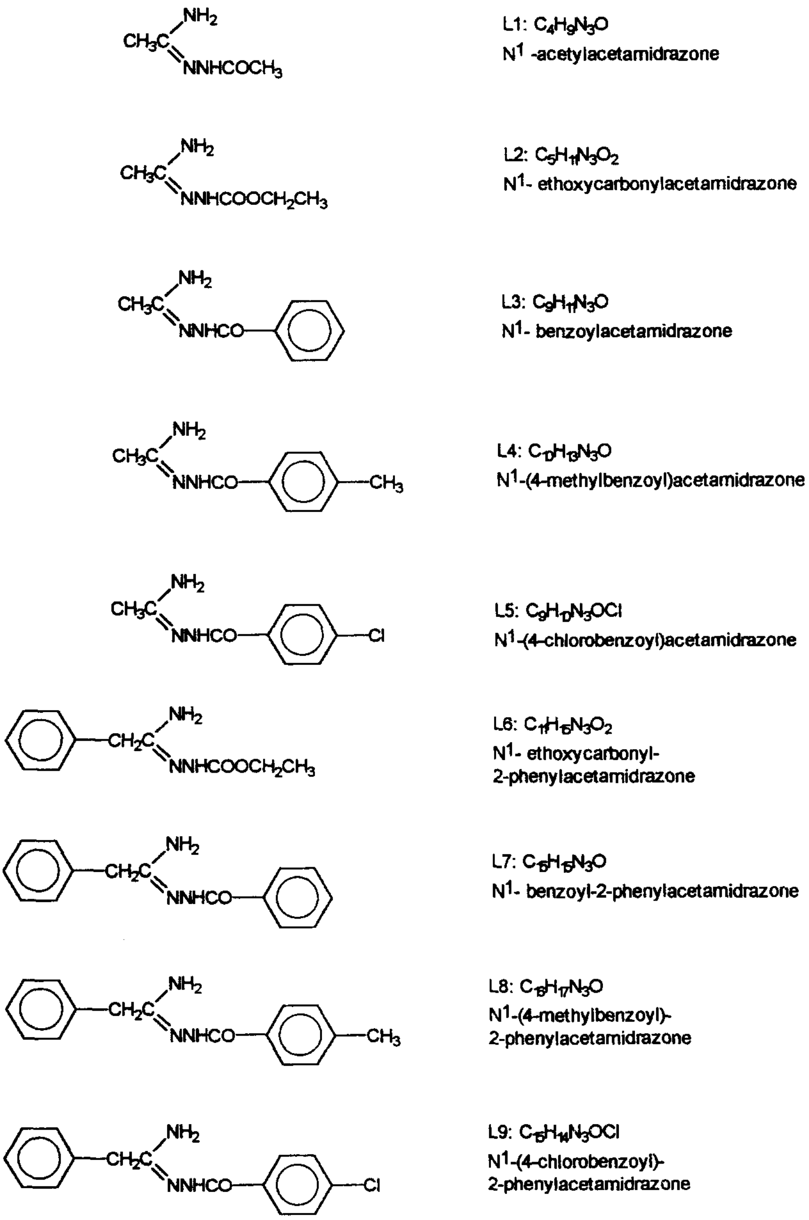

Fig. 1. **L1**–**L9** ligands.

complex is octahedral with two **L1** chelate coordinated molecules via N^3 and O of CO, two water molecules coordinated to the cobalt ion and two chloride ions out of the coordination sphere.

The reflectance electronic spectra of $[M(L)_2]Cl_2$ complexes where M = Pd(II) and Pt(II) (Table 4) are indicative of a square planar geometry [16,17]. The bands in the 26,180–23,000 cm^{-1} range could be assigned to the ν_1 transition $^1A_{1g} \rightarrow {}^1B_{1g}$. In the UV spectra there are strong absorptions in the 44,400–30,490 cm^{-1} range that may be due to the charge transfer band $L \rightarrow M$. By assuming a value of $F_2 = 10F_4 = 600$ cm^{-1} for the Slater Condon interelectronic repulsion parameters [18] it is possible to derive from the first spin-allowed transition d-d the value $\Delta = \nu_1 + 3.5F_2$. These values lie in the 28,280–25,630 cm^{-1} range.

The complexes of **L2** and **L6** do not show the negative shift of the ν(CO) and there is a negative shift of ν(NH) when compared with the free ligand.

For **A6**, **B2** and **B6** complexes, the presence of a not shifted or a shifted ν(NH) band to higher wavenumbers respect to the free ligand has been attributed to the presence of the free ligand, so that these compounds can be respectively described as $[Pd(L6)_2Cl_2] \cdot L6$, $[Pt(L2)Cl_4] \cdot L2$ and $[Pt(L6)_2Cl_4] \cdot$

Table 1. Analytical and physical data

Mark	Complex	M.p. (°C)	Colour	Found (calc.) %			Λ_M (DMF)
A1	$Pd(L1)_2Cl_2$	^{a}	tan	23.0(23.6)	3.9(4.4)	19.9(20.6)	—
A3	$Pd(L3)_2 \cdot H_2O$	254	tan	45.0(45.3)	4.7(4.2)	17.3(17.6)	—
A4	$Pd(L4)_2 \cdot 2H_2O$	229	tan	45.6(45.9)	5.1(5.4)	15.8(16.1)	—
A5	$Pd(L5)_2 \cdot 2H_2O$	216	light yellow	38.1(38.3)	4.4(3.9)	15.5(14.9)	6
A6	$Pd(L6)_2Cl_2$	302	light yellow	30.7(31.2)	3.4(3.4)	17.6(18.2)	6
A7	$Pd(L7)_2 \cdot 2H_2O$	227	tan	55.8(55.7)	5.0(4.4)	11.9(12.3)	—
A8	$Pd(L8)_2Cl_2$	216	tan	54.8(54.1)	4.7(4.5)	11.9(11.8)	7
A9	$Pd(L9)_2Cl_2 \cdot H_2O$	273	light tan	46.4(46.6)	4.1(3.7)	11.6(10.9)	—
B1	$Pt(L1)_2Cl_2$	^{a}	medium grey	19.6(19.4)	3.2(3.7)	39.9(39.9)	—
B2	$Pt(L2)_2Cl_4$	185	ivory	19.4(19.1)	3.9(3.8)	13.3(13.4)	90
B3	$Pt(L3)_3 \cdot 2H_2O$	210	lilac	42.5(42.6)	5.0(4.6)	16.5(16.6)	5
B4	$Pt(L4)_3$	219	yellow	47.7(47.0)	6.0(4.9)	16.9(16.4)	10
B5	$Pt(L5)_3 \cdot H_2O$	237	yellow	41.0(40.9)	4.5(3.6)	15.9(15.9)	3
B6	$Pt(L6)_4Cl_4$	185	pearl grey	19.7(19.3)	3.5(3.6)	16.9(16.9)	149
B7	$Pt(L7)_3$	207	ivory	56.8(56.7)	4.3(4.5)	13.8(13.2)	6
B8	$Pt(L8)_3 \cdot H_2O$	212	light yellow	56.6(56.9)	5.4(5.1)	12.4(12.4)	8
B9	$Pt(L9)_3$	214	ivory	51.9(51.2)	4.4(3.8)	12.2(11.9)	4

^{a} Compounds that decompose without melting.

— Insoluble or little soluble.

Table 2. Absorption bands in the near IR spectra (4000–500 cm^{-1} range)

Mark	Compound	ν(N—H)	$\Delta\nu$	ν(C═O)
L1	$C_4H_9N_3O$	3393 msbr, 3197 sbr		1658 s, 1686 s
A1	$Pd(L1)_2Cl_2$	3341 s, 3357 sbr	36	1642 s, 1632 s
B1	$Pt(L1)_2Cl_2$	3335 vsbr	48	1642 vs, 1632 vs
L2	$C_5H_{11}N_3O_2$	3378 ms, 3268 sh, 3218 ms, 3188 sh		1685 s
B2	$Pt(L2)_2Cl_4$	3442 mw, 3250 vs, 3115 vsbr	143	1718 vs, 1700 vs
L3	$C_9H_{11}N_3O$	3480 ms, 3460 ms, 3400 s, 3200 vs		1633 vs
A3	$Pd(L3)_2 \cdot H_2O$	3420 ms, 3180 s	60	1650 s
B3	$Pt(L3)_3 \cdot 2H_2O$	3498 m, 3356 ms, 3180 s	124	1647 vs
L4	$C_{10}H_{13}N_3O$	3456 s, 3198 sbr		1643 s
A4	$Pd(L4)_2 \cdot 2H_2O$	3418 ms, 3180 s	38	1646 vs
B4	$Pt(L4)_3$	3398 sh, 3270 sh	58	1645 vs
L5	$C_9H_{10}ClN_3O$	3414 vs, 3399 m, 3300 m		1628 s
A5	$Pd(L5)_2 \cdot H_2O$	3420 msbr, 3185 vsbr	115	1620 s
B5	$Pt(L5)_3 \cdot H_2O$	3337 s	77	1661 vs
L6	$C_{11}H_{15}N_3O_2$	3419 m, 3346 vw, 3240 ms, 3198 ms		1712 m, 1701 m
A6	$Pd(L6)_3Cl_2$	3240 s, 3215 vsbr, 3120 s	204	1756 mw, 1737 mw
B6	$Pt(L6)_4Cl_4$	3421 w, 3277 vs, 3185 s, 3124 sh	142	1725 vs, 1704 s
L7	$C_{15}H_{15}N_3O$	3432 ms, 3297 mbr, 3152 sbr		1621 s
A7	$Pd(L7)_2 \cdot 2H_2O$	3402 ms, 3330 ms	30	1650 s
B7	$Pt(L7)_3$	3430 s, 3202 sh	200	1650 vs
L8	$C_{16}H_{17}N_3O$	3460 s, 3195 s		1631 s
A8	$Pd(L8)_2Cl_2$	3480 m, 3405 m, 3322 m	55	1650 s
B8	$Pt(L8)_3 \cdot H_2O$	3330 vs	130	1650 vs
L9	$C_{15}H_{14}ClN_3O$	3420 ms, 3307 ms, 3150 s		1614 s
A9	$Pd(L9)_2Cl_2 \cdot H_2O$	3402 m, 3250 ms, 3140 s	170	1650 s
B9	$Pt(L9)_3$	3378 ms, 3270 s, 3170 vsbr	42	1658 vs

Table 3. Absorption bands in the far IR spectra (500–180 cm^{-1} range)

Mark	Compound	ν(M—O)	ν(M—N)	ν(M—X)	Other bands
L1	$C_4H_9N_3O$				472w, 394 vwbr, 345 m, 322 sh, 313 sh, 300 w, 273 w, 248 mw, 218 m
A1	$Pd(L1)_2Cl_2$	450 mw	380 m		439 mw
B1	$Pt(L1)_2Cl_2$	429 wbr	372 m		323 w
L2	$C_5H_{11}N_3O_2$				410 m, 320 m, 301 w, 273 wbr, 242 mw, 220 m
B2	$Pt(L2)_2Cl_4$		381 m	340 sh, 330 vsbr, 318 sh	396 mbr
L3	$C_9H_{11}N_3O$				445 m, 433 m, 409 w, 395 w, 365 vw, 344 ms, 320 w, 311 w, 300 mw, 275 mw, 242 ms, 220 m
A3	$Pd(L3)_2 \cdot H_2O$		340 mw		
B3	$Pt(L3)_2 \cdot 2H_2O$		337 mw		456 w, 420 vw, 355 wbr
L4	$C_{10}H_{13}N_3O$				470 m, 460 sh, 422 mw, 381 sh, 366 m, 339 ms, 321 m, 312 sh, 299 mw, 272 mw, 243 m, 221 ms
A4	$Pd(L4)_2 \cdot 2H_2O$		347 mw		
B4	$Pt(L4)_2$		312 w		
L5	$C_9H_{10}ClN_3O$				465 m, 380 vs, 372 sh, 351 sh, 321 w, 310 s, 229 sh, 272 m, 242 m, 219 m
A5	$Pd(L5)_2 \cdot 2H_2O$		348 m, 340 m		363 sh
B5	$Pt(L5)_4 \cdot H_2O$		335 m		351 mw, 262 mw, 440 w, 394w
L6	$C_{11}H_{15}N_3O_2$				474 ms, 405 vwbr, 353 w, 320 w, 310 w, 300 w, 273 mw, 242 mw, 220 m, 202 m
A6	$Pd(L6)_3Cl_2$		383 s		
B6	$Pt(L6)_4Cl_4$		365 vw	333 s	344 ms
L7	$C_{15}H_{15}N_3O$				495 m, 460 m, 412 wbr, 392 w, 381 vw, 349 ms, 333 vw, 323 ms, 313 sh, 300 mw, 272 m, 266 sh, 242 ms, 220 ms
A7	$Pd(L7)_2 \cdot H_2O$		344 m		
B7	$Pt(L7)_3$		320 m		280 mw
L8	$C_{16}H_{17}N_3O$				470 s, 456 sh, 424 m, 407 vw, 381 sh, 366 ms, 339 s, 322 ms, 300 w, 277 w, 243 m, 218 s, 206 w
A8	$Pd(L8)_2Cl_2$		345 sh		336 ms
B8	$Pt(L8)_2 \cdot H_2O$		322 m		491 w, 390 vw br, 257 m
L9	$C_{15}H_{14}ClN_3O$				479 m, 457 m, 416 vw, 391 w, 367 m, 348 m, 332 w, 318 sh, 312 ms, 300 m, 296 sh, 273 m, 243 ms, 219 ms
A9	$Pd(L9)_2Cl_2 \cdot H_2O$		[a]	353 vs	
B9	$Pt(L9)_3$		320 m		443 w

[a] ν(Pd—N) is covered by ν(Pd—Cl).

Table 4. Reflectance spectra (50,000–15,000 cm^{-1} range)

Mark	Compound	Bands[a]
A1	$[Pd(L1)_2Cl_2]$	30,675, 23,800(25,900)
B1	$[Pt(L1)_2Cl_2]$	26,180(28,280)
B2	$[Pt(L2)Cl_4]\cdot L2$	32,895, 32,050, 29,850
A3	$[Pd(L3)_2]\cdot H_2O$	44,440, 36,360, 29,410, 24,690(26,790)
B3	$[Pt(L3)_2]\cdot L3\cdot 2H_2O$	41,670, 35,710, 27,030
A4	$[Pd(L4)_2]\cdot 2H_2O$	33,900, 32,260, 28,570, 25,000(27,100)
B4	$[Pt(L4)_2]\cdot L4$	35,710, 28,170
A5	$[Pd(L5)_2]\cdot 2H_2O$	42,550, 34,480, 32,260, 25,000(27,100)
B5	$[Pt(L5)_2]\cdot L5\cdot H_2O$	40,820, 28,570
A6	$[Pd(L6)_2Cl_2]\cdot L6$	30,490, 23,310(25,410)
B6	$[Pt(L6)_2Cl_2]Cl_2\cdot 2L6$	30,860, 29,500
A7	$[Pd(L7)_2]\cdot 2H_2O$	41,670, 26,670, 23,810(25,910)
B7	$[Pt(L7)_2]\cdot L7$	44,440, 36,360, 32,790, 26,320(28,420)
A8	$[Pd(L8)_2]Cl_2$	44,440, 31,250, 23,810(25,910)
B8	$[Pt(L8)_2]\cdot L8\cdot H_2O$	41,670, 36,360, 30,300, 25,640(27,740)
A9	$[Pd(L9)_2]Cl_2\cdot H_2O$	44,440, 40,000, 32,260, 23,530(25,630)
B9	$[Pt(L9)_2]\cdot L9$	42,550, 37,730, 30,300, 25,000

[a] The values of Δ are shown in brackets.

2L6. For the absence of the ν(M—Cl) bands in the expected range, we can conclude that the complexes can be described as $[M(L)_2]Cl_2\cdot m$L.

Some platinum(IV) complexes as **B2** and **B6** show IR absorption bands at 340, 330, 318 and at 333 cm^{-1} respectively, assigned to ν(Pt—Cl) [19,20]. All the complexes with **L2** and **L6** show a band in the 381–359 cm^{-1} range assigned to ν(M—N) [14] (Table 3).

From the infrared spectra and conductivity molar values equal to 149 cm^2 Ω^{-1} mol^{-1}, characteristic for an unibivalent electrolyte, we can describe **B6** as $[Pt(L6)_2Cl_2]Cl_2\cdot 2L6$, while **B2** has a $\Lambda_M = 90$ cm^2 Ω^{-1} mol^{-1} which can be explained by postulating that in DMF is present a partial dissociation of the complex $Pt(L2)_2Cl_4$ described as $[Pt(L2)Cl_4]\cdot L2$.

The shape of the reflectance electronic spectra of the Pt(IV) complexes [21,22] (Table 4) and the far infrared spectra confirm that these compounds are hexacoordinate.

In conclusion the bidentate chelate N^1-acylacetamidrazone derivatives **L** have shown some different patterns of coordination: **L1** coordinates with nitrogen of the N^2 and oxygen of carbonylic group, **L2** and **L6** with the nitrogens of N^3 and N^1. **L3**–**L5** and **L7**–**L9** coordinate only two molecules of the anionic species with the nitrogens of N^3 and N^1. Furthermore all the studied compounds are generally non-electrolytes because the complexes are rearranged in solution: we can suggest a square planar stereochemistry for $M(L)_2Cl_2$ (M = Pd(II), Pt(II)) and a distorted octahedral structure for $Pt(L)_nCl_4$ ($n = 2, 4$) where L = **L1**, **L2** and **L6**. For $M(L)_n\cdot mH_2O$ complexes, where L = **L3**–**L8**, M = Pd(II), $n = 2$; M = Pt(II), $n = 3$, $m = 0$–2, we can suggest a square planar geometry. For the **L9** $Pd(L9)_2Cl_2\cdot H_2O$ and $Pt(L9)_3$ complexes also square planar structure can be suggested.

REFERENCES

1. Jerchel, D. and Kuhn, R., *Annales*, 1950, **56,** 185.
2. Gerbeleu, N. V., Palanciuc, S. S., Simonov, Yu. A., Dvorkin, A. A., Bourosh, P. N., Reetz, M. T., Arion, V. B. and Tollner, K., *Polyhedron*, 1995, **14,** 521.
3. Bezuglaya, Z. V., Zaitsen, B. E., Ivlieva, K. M., Avramenko, B. I. and Stepanov, B. I., *Koord. Khim.*, 1987, **13,** 191.
4. Du, S., Zhu, N. and Wu, X., *Polyhedron*, 1994, **13,** 301.
5. Samus, N. M., Toleva, A. D., Tsapkov, V. I., Burdenko, T. A. and Videlingam, A. H., *Khim. Farm. Zh.*, 1992, **26,** 75.
6. Pelova, R., Spassowska, N., Manieva, L. and Taxirov, S., *Pharmazie*, 1987, **42,** 251.
7. Cocco, M. T., Congiu, C., Plumitallo, A., Schivo, M. L. and Palmieri, G., *Farmaco*, 1987, **42,** 347.
8. Cocco, M. T., Olla, C., Onnis, V., Schivo, M. L. and De Logu, A., *Farmaco*, 1992, **47,** 229.
9. Glover, E. E., Rowbottom, K. T. and Bishop, D. C., *J. C. S. Perkin I*, 1972, **23,** 2927.
10. Ponticelli, G., *Inorganica Chimica Acta*, 1971, **5,** 461.
11. Schlessinger, G. G., *Bull. New Jersey Acad. Sci.*, 1967, **12,** 42.
12. Curtis, N. F., Raimond, R. W. and Curtis, Y. M., *J. Chem. Soc.* (A), 1968, 182.
13. Sing, P. P. and Rivest, R., *Can. J. Chem.*, 1968, **46,** 2361.

14. Sacconi, L. and Sabatini, A., *J. Inorg. Chem.*, 1963, **25,** 1389 and references therein.
15. Cocco, M. T., Ianelli, S., Ponticelli, G., *Cryst. Struct. Comm.*, submitted.
16. Efimenko, I. A., Kurbakova, A. P. and Matovic, Z. D., *Transition Metal Chem.*, 1994, **19,** 539.
17. Pinna, R., Ponticelli, G. and Preti, C., *J. Inorg. Nucl. Chem.*, 1975, **37,** 1681.
18. Latham, A. R., Hascall, V. and Gray, G., *Inorg. Chem.*, 1965, **4,** 788.
19. Massacesi, M., Pinna, R. and Puggioni, G., *J. Inorg. Biochem.*, 1987, **28,** 95.
20. Floris, G., Padiglia, A., Ponticelli, G. and Puggioni, G., *Transition Metal Chem.*, 1992, **17,** 145.
21. Ponticelli, G., Matovic, Z. D., Miletic, V. D., Efimenko, I. A., Kurbakova, A. P. and Radanovic, D. J., *Bull. Chem. Techn. Mac.*, 1996, **15,** 9.
22. Azarita, T. N. and Bora, T., *Polyhedron*, 1984, **3,** 121.