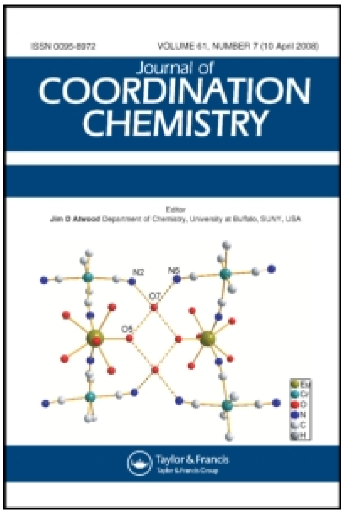

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REACTION BETWEEN $[PdCl_4]^{2-}$ AND 5,5-DIMETHYL-2-THIOXOIMIDAZOLIDIN-4-ONE

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REACTION BETWEEN $[PdCl_4]^{2-}$ AND 5,5-DIMETHYL-2-THIOXOIMIDAZOLIDIN-4-ONE

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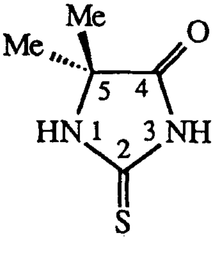
The reaction between 5,5-dimethyl-2-thioxoimidazolidin-4-one (H_2L) and $[PdCl_4]^{2-}$ has been studied in aqueous solution by potentiometric and spectrophotometric measurements. In the presence of the palladium salt, H_2L is completely monodeprotonated (HL^-); from spectrophotometric measurements, only two complexes having 1:1 and 1:2 Pd/ligand mol ratios have been identified. Potentiometric titrations, carried out on solutions with 1:1, 1:2, 1:3 and 1:4 metal/ligand mol ratios, show that these complexes must be formulated as $Pd(HL)_2$ and $[Pd_2(HL)_2(\mu\text{-}H_2O)(\mu\text{-}OH)]^+$. Ionization constants of the pure ligand and formation constants of the complexes give pH distribution curves of the various species and the spectra of the two complexes. From MeOH, *S*-coordinated $Pd(H_2L)_nCl_2$ (n = 2–4) complexes have been separated in the solid state; from water, two complexes of formula $Pd(H_2L)(HL)Cl$ and $Pd(HL)Cl$ have been obtained with HL^- *N,S*-coordinated to the metal.

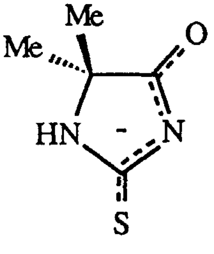
KEYWORDS: tetrachloropalladate(2-), 5,5-dimethyl-2-thioxoimidazolidin-4-one, potentiometric measurements, spectrophotometric measurements, formation constants

INTRODUCTION

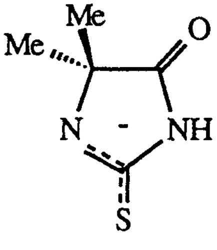
5,5-Dimethyl-2-thioxoimidazolidin-4-one can act as a neutral (H_2L) or anionic (HL^-) ligand,[1–5] since H_2L has two ways of losing a proton. However, it has been



H_2L



HL^-



HL^-

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proved[6–8] that the N(3)-H proton is more acidic than N(1)-H; consequently, we expect *N,S*-coordination to occur through N(3) in inner complexes. Using 5,5-dimethyl-2-thioxoimidazolidin-4-one with some mercury(II) salts, we prepared numerous complexes with this ligand both in its neutral H_2L and anionic HL^- form and were able to clarify its reactivity towards mercury(II).[1,2,4,5] However, while for complexes with H_2L X-ray crystal structures afforded information on coordination, as far as regards the inner complexes, crystalline compounds suitable for X-ray structure determination were never obtained. In addition, due to the low solubility of the inner mercury(II) complexes it was not possible to carry out studies in solutions. Pursuant to our interest in the coordination chemistry of 5,5-dimethyl-2-thioxoimidazolidin-4-one, we will now report the results of an investigation of the reactivity of this ligand towards $[PdCl_4]^{2-}$, both in solution and in the solid state. The choice of the palladium salt as reagent was suggested by the very few potentiometric and spectrophotometric measurements reported for this salt[9–13] in the literature.

EXPERIMENTAL

Materials

5,5-Dimethyl-2-thioxoimidazolidin-4-one was prepared according to the literature.[14] K_2PdCl_4 was purchased from Fluka and used without purification. All starting solutions of K_2PdCl_4 were prepared in 0.1 M NaCl in order to avoid the formation of species other than $[PdCl_4]^{2-}$.

Preparation of complexes

Thirty cm^3 of an MeOH solution containing the appropriate amount of 5,5-dimethyl-2-thioxoimidazolidin-4-one (2, 3 and 4 mmol) was added to 10 cm^3 of an aqueous methanolic solution of K_2PdCl_4 (1 mmol). For the 1:2 and 1:4 ratios, the initial yellow precipitate slowly changes colour (see Table 1). After filtration and several washings with MeOH, the solid products were dried in a desiccator over P_4O_{10} for 24 h. Elemental analyses of the complexes obtained, $Pd(H_2L)_nCl_2$ (n = 2, 3 and 4), are reported in Table 1. In order to prepare the inner complexes, K_2PdCl_4 (1 mmol dissolved in 10 cm^3 of water) was added to a refluxing aqueous solution of the ligand (1 or 2 mmol) at pH 8 (KOH). Brown products, separated by

Table 1 Colours and elemental analyses of the Pd(II) complexes with 5,5-dimethyl-2-thioxoimidazolidin-4-one (H_2L).

Compound*	Colour	Found (Calcd.)%			
		C	H	N	S
$Pd(H_2L)_4Cl_2$	yellow	31.5(31.9)	4.3(4.3)	14.6(14.9)	16.9(17.0)
$Pd(H_2L)_3Cl_2$	mustard	29.7(29.5)	3.7(4.0)	13.9(13.8)	15.9(15.8)
$Pd(H_2L)_2Cl_2$	light brown	25.7(25.8)	3.6(3.5)	11.6(12.0)	14.2(13.8)
$Pd(H_2L)(HL)Cl$	brown	27.6(28.0)	3.5(3.5)	12.5(13.1)	15.0(14.9)
$Pd(HL)Cl$	dark brown	21.4(21.1)	3.1(2.5)	10.2(9.8)	11.5(11.3)

* Conductivity measurements carried out in DMSO solutions show that only the species $Pd(H_2L)_nCl_2$ are ionic compounds.

centrifugation and washed with water and Et_2O, were dried in a desiccator over P_4O_{10} for 24 h (see Table 1). All compounds were diamagnetic powders.

Spectrophotometric measurements

Spectrophotometric measurements were performed using a Hewlett-Packard 8452A spectrophotometer equipped with a thermostatted cell. The complete spectrum in the 190–820 nm range was recorded (resolution ±2 nm) as an MSDOS file for subsequent elaboration in about 1 sec.

Potentiometric measurements and data treatment

Potentiometric titrations were performed on a Metrohm 654 pH-meter equipped with a Dosimat 655 automatic titrator, at an ionic strength of 0.1 (NaCl) and at 25°C in water. The concentrations of the solutions of ligand and palladium salt (ligand/metal ratios close to 1:1, 2:1, 3:1 and 4:1) used for the titrations were $\approx 10^{-3}$ M. Some 25 cm^3 of each solution were titrated with 0.1 M KOH under a nitrogen atmosphere, and for each ligand/metal ratio three different titrations were performed (60 experimental points with a time delay between two consecutive base additions of 90s). A combined pH glass electrode for highly alkaline solutions (Metrohm 6.0203.101) was used. Its standard potential together with the pK_w value was determined by titration of hydrochloric acid with KOH under the same conditions.

Potentiometric data for the electrode standardization were analyzed by our BASIC program GRANPLOT, based on the Gran equation.[15] The ionization constants of the pure ligand and the formation constants of its complexes with Pd(II) were calculated by a slightly modified version of the PSEQUAD program.[16]

Infrared measurements

I.r. spectra were recorded in KBr discs (3500–400 cm^{-1}) and in Nujol mulls (450–200 cm^{-1}) using a Perkin-Elmer 983 instrument, collected with a Perkin-Elmer 7500 Data Station.

RESULTS AND DISCUSSION

Solid state

From MeOH, in the presence of a small amount of water to dissolve K_2PdCl_4, complexes of general formula $Pd(H_2L)_nCl_2$ (n = 2–4) have been obtained as solids; shifts of infrared bands verified in the complexes with respect to the free ligand (see Table 2) are similar to those found for analogous complexes of mercury(II)[1,2,4,5] and indicate that the ligand is coordinated to the palladium through the sulphur atom; in particular, the upward shift of the strong band at 1742 cm^{-1}, due to $\nu(CO)$, and the slight downward shift of $\nu(CS)$ (495 cm^{-1}), accompanied by a noteworthy decrease of intensity, are characteristic of *S*-coordination.[1,2,4,5] In the inner complexes obtained from water, *N*,*S*-coordination is predictable; in these complexes the most significant band is always that due to $\nu(CO)$, which upon coordination,

Table 2 Selected infrared bands (cm^{-1}) for the ligand (H_2L), its anion (HL^-) as sodium salt and the Pd(II) complexes.

Compound	ν(NH)	ν(CO)	ν(CN)	ν(CS)	δ(CS)
H_2L^a	3220 sh 3179 s	1742 vs	1529 vs 1290 vs 1132 vs	495 ms	351 ms
$Pd(H_2L)_4Cl_2$	3220 sh 3100 sh	1770 vs 1750 vs	1550 vs 1270 vs 1120 vs	485 m	360 m
$Pd(H_2L)_3Cl_2$	3190 s 3110 sh	1770 s 1750 vs	1540 s 1270 s 1130 s	490 w	350 w
$Pd(H_2L)_2Cl_2$	3200 sh	1770 s 1740 s	1530 m 1200 s 1145 s	490 w	
$NaHL^a$	3239 vs	1640 vs	1483 vs 1305 vs 1160 vs	450 m	355 m
$Pd(H_2L)(HL)Cl$	3197 mbr	1750 sh 1720 s	1500 s 1230 w 1160 m	483 w	348 w
Pd(HL)Cl	3190 sh	1720 s	1500 m 1130 w	483 w	

^{a}From Ref. 1.

undergoes upward shifts from 1640 cm^{-1}, found in NaHL, to frequencies which are intermediate between those found in H_2L and HL^-.

Solution

The UV spectra of eleven solutions of K_2PdCl_4 and H_2L prepared according to a Job scheme are collected in Figure 1. A Job plot, using absorbance values at 260 nm, indicates the formation of a 1:2 metal/ligand complex; however, Job plots at different wavelengths (for example at 220 nm) suggest also the presence of a 1:1 complex. In order to confirm these stoichiometries, two new sets of solutions were prepared, keeping constant the concentrations of H_2L and $[PdCl_4]^{2-}$, respectively. In the first ($[H_2L]$ = constant), the $[H_2L]/[[PdCl_4]^{2-}]$ mol ratios range from 14.2 to 0.9: for ratios higher than 2, the spectra show three isosbestic points at 221, 250.5 and 272 nm, thus confirming that under these conditions constant stoichiometry exists. Figure 2 reports spectra of solutions having ratios higher than 2. In the second experimental set, having $[PdCl_4]^{2-}$ constant, the $[H_2L]/[[PdCl_4]^{2-}]$ mol ratios range from 0 to 1.12; all spectra with ratios lower than 1 pass through two, well-identified isosbestic points at 213.4 and 230.5 nm, as reported in Figure 3, clearly indicating the existence of constant stoichiometry. Potentiometric data for all the ligand/metal ratios used in the titrations have been fitted very well by using these two complexes having 1:1 and 1:2 metal/ligand ratios, according to the model obtained from the spectrophotometric measurements. The ionization constants of the pure ligand and the formation constants of its complexes with Pd(II) are reported in Table 3. As discussed in a previous paper,[7] the ligand first loses the N(3)-H proton at pH = 8.21, then N(1)-H at pH = 11.26. In the presence of $[PdCl_4]^{2-}$, the N(3)-H proton of the coordinated ligand is lost at pH < 3. In the 1:2

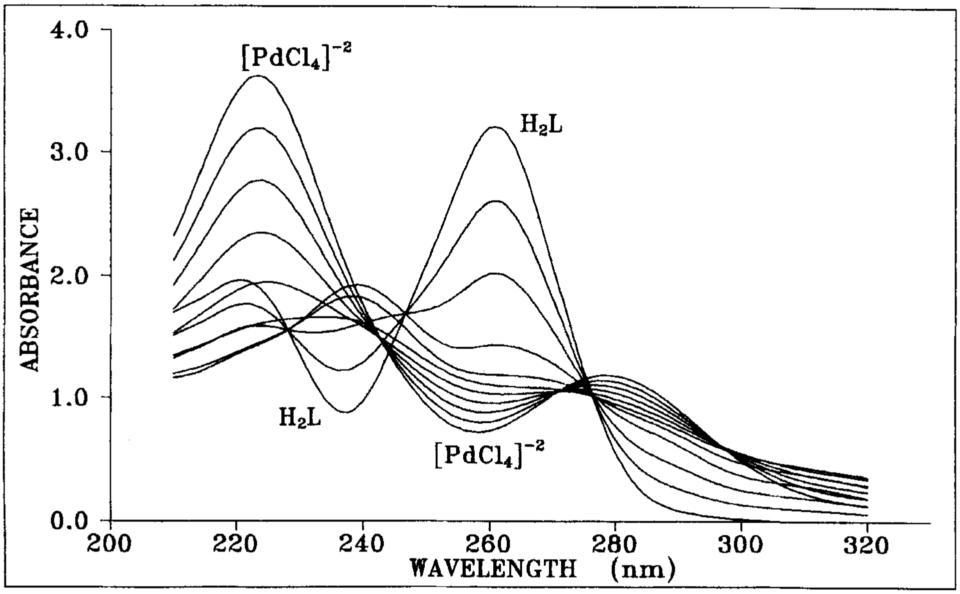


Figure 1 Spectra of the eleven solutions prepared according to the Job method; $[H_2L] = [K_2PdCl_4] = 1.946 \times 10^{-4}$ mol dm^{-3}; t = 25°C; $\mu = 0.1$ (NaCl).

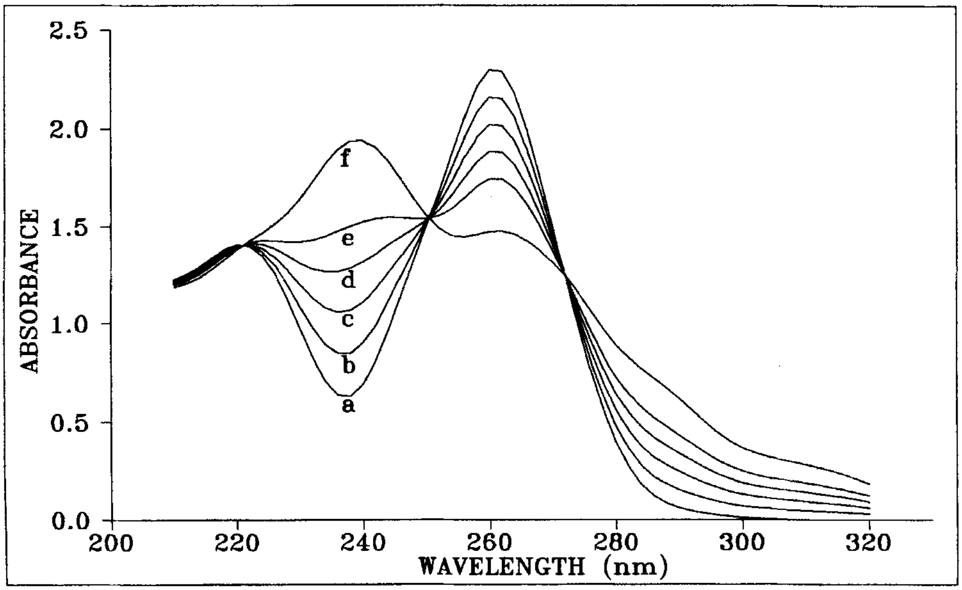


Figure 2 Isosbestic points obtained with $[H_2L] \gg [K_2PdCl_4]$; $[H_2L] = 1.390 \times 10^{-4}$ mol dm^{-3} and $[K_2PdCl_4]$ = a) 0.0, b) 9.725×10^{-6}, c) 1.945×10^{-5}, d) 2.918×10^{-5}, e) 3.890×10^{-5} and f) 5.835×10^{-5} mol dm^{-3}; (t = 25°C; $\mu = 0.1$ (NaCl). The spectra of solutions having the $[H_2L]/[K_2PdCl_4]$ ratio lower than 2 do not pass through the isosbestic points.

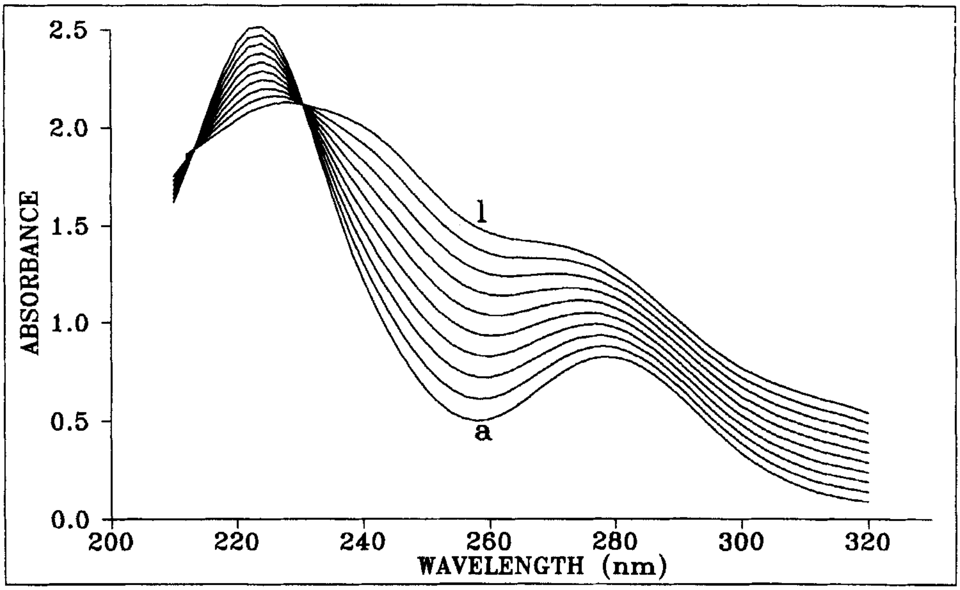
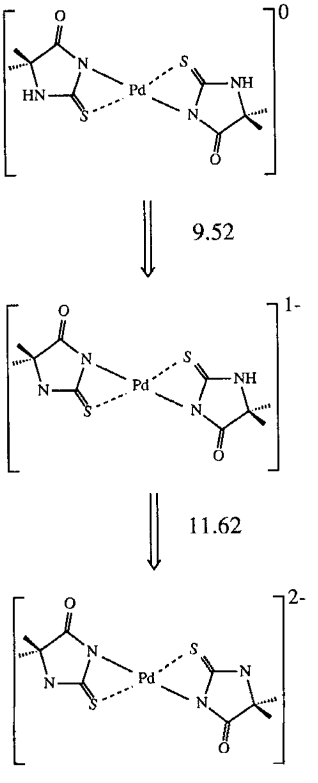


Figure 3 Isosbestic points obtained with $[K_2PdCl_4] \gg [H_2L]$; $[K_2PdCl_4] = 1.351 \times 10^{-4}$ mol dm^{-3} and $[H_2L]$ = a) 0,0, b) 1.382×10^{-5}, c) 2.764×10^{-5}, d) 4.146×10^{-5}, e) 5.528×10^{-5}, f) 6.910×10^{-5}, g) 8.292×10^{-5}, h) 9.674×10^{-5}, i) 1.106×10^{-4}, l) 1.244×10^{-4} mol dm^{-3}; (t = 25°C; μ = 0.1 (NaCl). The spectra of solutions having the $[H_2L]/[K_2PdCl]$ ratio higher than 1 do not pass through the isosbestic points.

metal/ligand complex, four protons are titrated: the first two are lost at pH < 3, the others at pH = 9.52 and 11.62. On the basis of these results, the 1:2 complex could be formulated as $Pd(HL)_2$, with a square planar arrangement around the palladium(II), as reported in Scheme 1. The first deprotonation of this complex concerns the loss of an N(1)-H proton of one of the two coordinated anionic ligands at pH = 9.52, a value that is 1.74 pH units lower than that of the same deprotonation

Table 3 Log β_{pqr} and pK values for the complexes $M_pL_qH_r$ ($\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$)). All the species are identified by the bold letters which are used in Fig. 4.

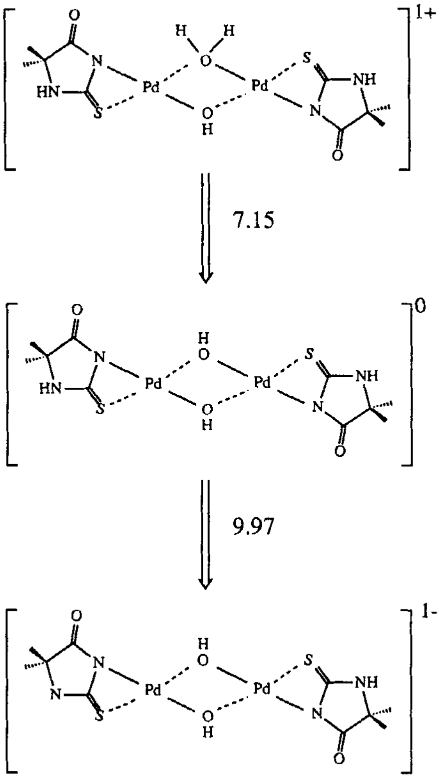
p	q	r	logβ	pK	Symbol
0	1	2	19.47 ± .01	8.21	**a**
0	1	1	11.26 ± .01	11.26	**b**
0	1	0			**c**
1	2	2	44.10 ±	9.52	**d**
1	2	1	34.58	11.62	**e**
1	2	0	22.96		**f**
2	2	1	45.46	7.15	**g**
2	2	0	38.31	9.97	**h**
2	2	−1	28.34	>11.5	**i**
2	2	−2			



Scheme 1

in HL$^-$. This result is in good agreement with expectations, since the complex is not charged. The second deprotonation at pH = 11.62 agrees well with the loss of a proton from the negatively charged complex; this value is comparable with the deprotonation of HL$^-$ and is 1.12 pH units higher than that found in the deprotonation of 3,5,5-trimethyl-2-thioxoimidazolidin-4-one.[7] Complexes of the same formula $M(HL)_2$ (M = Pd, Pt) with thiohydantoin (2-thioxoimidazolidin-4-one) have been reported;[17] however, on the basis of the complexity of ^{1}H NMR spectra recorded in d_6-DMSO, the two ligands were thought to bind the metal through both *S*,*N*(1) and *S*,*N*(3). This hypothesis could not be completely ruled out by the potentiometric data, even if the loss of the N(3)-H proton of the free ligand occurs at pH = 8.21, a value much lower than that at pH = 9.52 found for $Pd(HL)_2$.

In the 1:1 metal/ligand complex, six protons for two metal atoms are titrated: the first three protons are lost at pH < 3, two at pH = 7.15 and 9.97 and the last at pH > 11.6. Evidently, under conditions of 1:1 complex formation, two water molecules are involved in coordination to the metal. From these results, the 1:1 complex might be formulated with a water molecule and a hydroxo group bridged between two palladium atoms as reported in Scheme 2. This complex is thought to involve ligand binding to palladium through *S*,*N*(3). Such a complex should still lose



Scheme 2

three protons; the last deprotonation, not reported in Scheme 2, occurs at $pH > 11.6$ and is not detectable, the other two losses occur at $pH = 7.15$ and 9.97. We think that the deprotonation at $pH = 7.15$ could be due to the μ-water, even if this value could be acceptable also for the N(1)-H proton loss from a positively charged complex; however, the value of 9.97, only 0.45 pH units higher than the analogous deprotonation of $Pd(HL)_2$, supports our assignment since once again it occurs from a neutral complex.

The concentrations of the various species in solution as a function of the pH are reported in Figure 4 for the four ligand/metal ratios used in the potentiometric measurements. All the species are identified by the bold letters reported in Table 3, except **I**, which indicates the species $[PdCl_4]^{2-}$. In plots to the left, the concentrations of the various species (reported as %) refer to the analytical concentration of the ligand, while those to the right refer to the analytical concentration of the metal. As can be seen for the 4:1 and 3:1 $[H_2L]/[[PdCl_4]^{2-}]$ mol ratios, $Pd(HL)_2$ is the only complex present in solution; its first deprotonation starts at $pH = 7$ and reaches a maximum at $pH = 10$, when the second deprotonation starts. For the 1:1 ratio, at $pH = 2$, the palladium is present at about 50% as $[Pd_2(HL)_2(\mu\text{-}H_2O)(\mu\text{-}OH)]^+$ and the remaining 50% as $[PdCl_4]^{2-}$(~25%) and $Pd(HL)_2$(~25%).

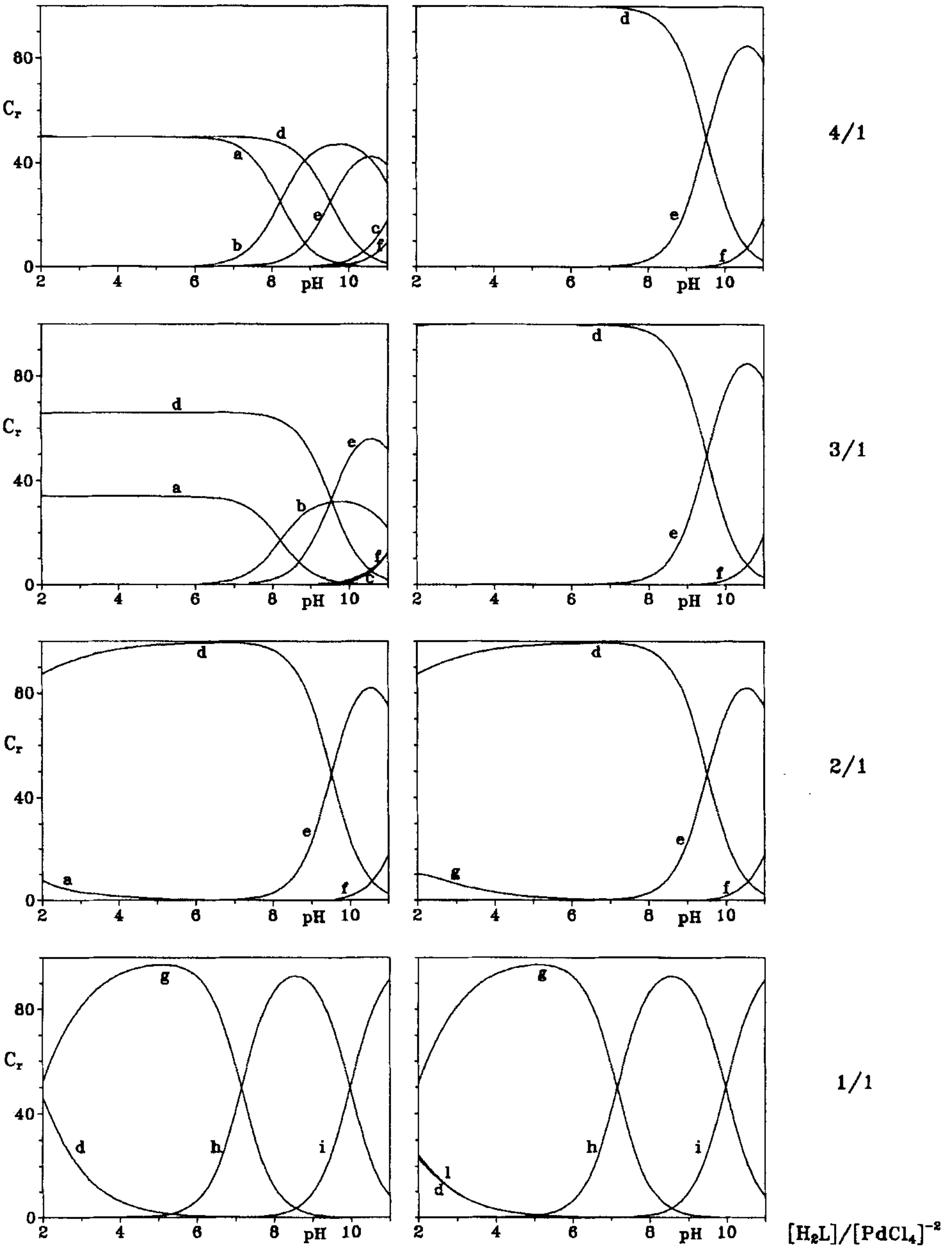


Figure 4 Distribution curves of the various species present in solution for the four ligand/metal mol ratios as a function of pH. The concentrations (reported as %) refer to analytical concentration of the ligand to the left and of the metal to the right; **a** = H_2L, **b** = HL^-, **c** = L^{-2}, d = $Pd(HL)_2$, **e** = $[Pd(HL)L]^-$, **f** = $[PdL_2]^-$, **g** = $[Pd_2(HL)_2(\mu\text{-}H_2O)(\mu\text{-}OH)]^+$, **h** = $Pd_2(HL)_2(\mu\text{-}OH)_2$, **i** = $[Pd_2(HL)L(\mu\text{-}OH)_2]^-$ and **l** = $[PdCl_4]^{2-}$.

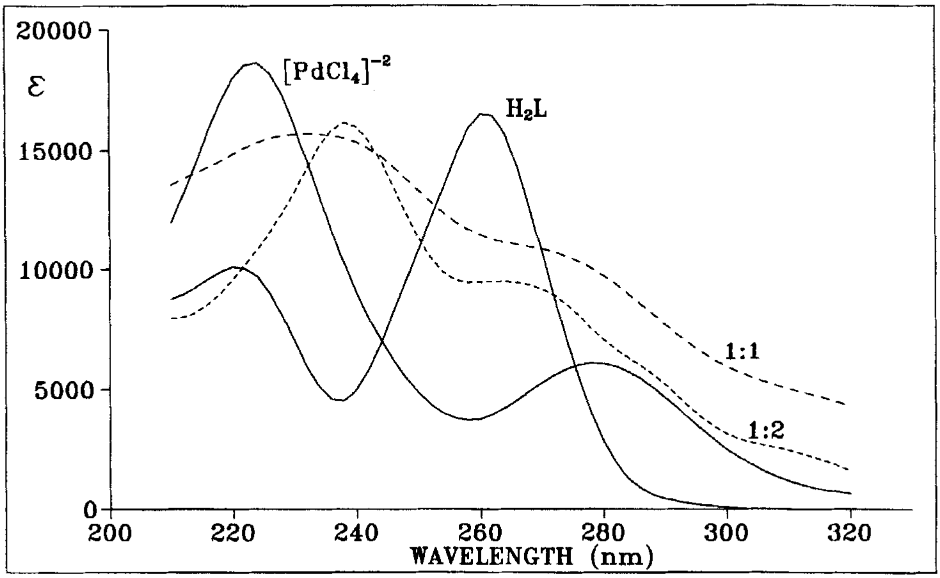


Figure 5 Absorption spectra of H_2L and $[PdCl_4]^{2-}$, together with those of $Pd(HL)_2$ (1:2) and $[Pd_2(HL)_2(\mu\text{-}H_2O)(\mu\text{-}OH)]^+$ (1:1), calculated from the distribution curves.

UV spectra of the $Pd(HL)_2$ and $[Pd_2(HL)_2(\mu\text{-}H_2O)(\mu\text{-}OH)]^+$ complexes were calculated from the distribution curves of the various species in solution and are reported as in Figure 5, together with those of H_2L and $[PdCl_4]^{2-}$. Using the cumulative formation constants β_{pqr} reported in Table 3, and the ε values of Figure 5, the experimental spectra were reproduced in very good agreement.

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