Palladium(II) Complexes of N,N-Co-ordinating Arylazouracil Ligands: Infrared Spectroscopy, Thermal Properties, and X-Ray Crystal Structure of *trans*-Bis(6-amino-1,3-dimethyl-5-phenylazouracilato)palladium(II)†

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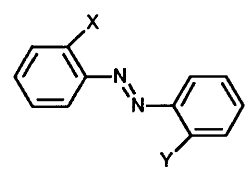
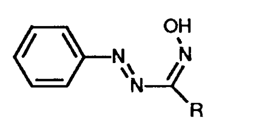
Palladium(II) forms the complexes $[PdL_2]$ (**1**)—(**4**) on reaction of tetrachloropalladate(II) with 6-amino-5-arylazouracil derivatives (uracil = pyrimidine-2,4-dione) in ethanolic media, with the exception of 6-amino-5-(2′-chlorophenylazo)-3-methyluracil (HL^5) which leads to the complex $[Pd(HL^5)_2Cl_2]$ (**5**). The crystal structure of the complex bis(6-amino-1,3-dimethyl-5-phenylazouracilato)palladium(II), $[PdL^1_2]$ (**1**), was determined by *X*-ray crystallography. The complex crystallizes in the monoclinic system, space group $P2_1/c$, with a = 7.404(2), b = 9.537(1), c = 17.420(4) Å, β = 99.38(2)°, Z = 2, and R = 0.043. The structure consists of discrete $[PdL^1_2]$ molecules (L^1 = 6-amino-1,3-dimethyl-5-phenylazouracilate), in which L^1 acts as a bidentate ligand through the nitrogen atom of the deprotonated amino group and the nitrogen atom of the azo group bonded to the phenyl ring, to give a square-planar PdN_4 geometry with palladium(II) at the inversion centre. The entire molecule is planar with the exception of the phenyl rings which are twisted by 84.4(2)° about the C–N bond away from the co-ordination plane in order to overcome interligand steric crowding. On the basis of i.r. and thermal data a *trans*-square-planar structure is proposed for (**5**), the ligand being co-ordinated through the nitrogen atom of the 6-amino group. In the temperature range 230—320 °C this complex eliminates two molecules of HCl to give $[PdL^5_2]$ (**6**). The solid-state parameters and mechanism for this reaction were determined.

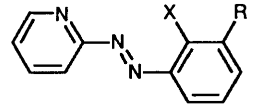
The palladium(II) chemistry of arylazo ligands has primarily grown around azobenzene (**I**), arylazo-oximes (**II**), 2-(arylazo)-pyridines (**III**), and related species. Azobenzene undergoes palladation at the azo-nitrogen and *ortho*-carbon producing a five-membered chelate ring and leading to the dimer $[Pd_2L_2Cl_2]$.[1,2] 2-Alkylthio- and 2-(alkylsulphinyl)-azobenzenes function as tridentate C,N,S-ligands affording [Pd(L)Cl] complexes in which two five-membered chelate rings are produced. When these ligands also have a 2′-hydroxy group analogous O,N,S-co-ordinated complexes can be obtained.[3,4] *o*-Hydroxy-azobenzenes act in aqueous ethanol as N,O-bidentate ligands in complexes $[PdL_2]$, whereas, in dry ethanol, orthometallation is the preferred reaction furnishing the C,N-co-ordinated complex $[Pd_2L_2Cl_2]$.[4] These complexes undergo chelative dehydro-halogenation in aqueous media leading to (after addition of donor D) [Pd(L)D] complexes containing a C,N,O-tridentate ligand.[4] Analogous O,N,O complexes have been obtained from *o,o′*-hydroxyazobenzenes.[4,5] Arylazo-oximes co-ordinate as bi-dentate ligands to palladium(II) through azo and oximato nitrogens yielding either $[PdL_2]$ or $[Pd_2L_2Cl_2]$ complexes.[6] Finally, with 2-(arylazo)pyridines, $[PdLCl_2]$ and [Pd(L)Cl] complexes have been obtained, in which the ligand is N,N- and N,N,O-co-ordinated to Pd^{II}, respectively.[7]



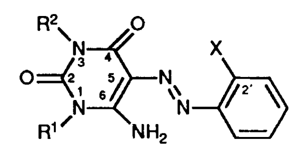
(**I**) X = H, OH, SR, or S(O)R
Y = H or OH



(**II**) R = Me, Ph, or C_6H_4Me-*p*



(**III**) R = Me
X = OH or H



(**IV**)	R^1	R^2	X	
	Me	Me	H	HL^1
	Me	Me	Et	HL^2
	Me	Me	Cl	HL^3
	Me	H	Cl	HL^4
	H	Me	Cl	HL^5

Over the last years we have concentrated on metal complexes of various modified 6-amino-5-arylazouracil ligands (uracil = pyrimidine-2,4-dione) (**IV**).[8,9] This group of ligands have proved to be extremely interesting with the ability to form various kinds of solid complexes.[10] In this paper, we report on the interaction of Pd^{II} with this new type of azo ligands containing an amino group in the uracil ring *ortho* to an azo group. This amino group might co-ordinate to Pd^{II} producing either a five- or a six-membered N,N-azo ring.

† *trans*-Bis(1,3-dimethyl-2,4-dioxo-5-phenylazo-κ*N*′-pyrimidin-6-yl-amido-κ*N*)palladium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

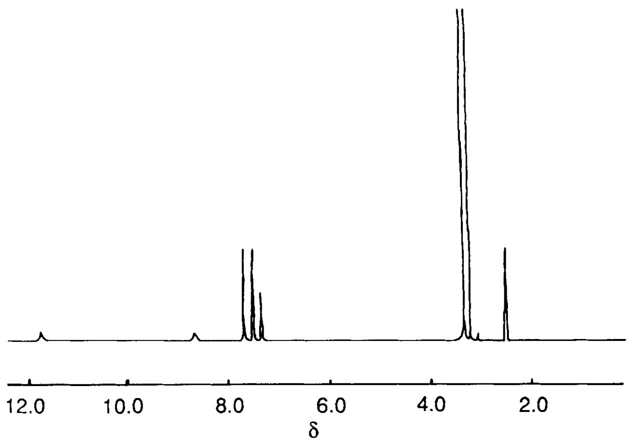


Figure 1. Proton n.m.r. spectrum of HL^1

Experimental

6-Amino-5-arylazo-1,3-dimethyluracil derivatives (**IV**) were prepared as described earlier.[8] The salt $K_2[PdCl_4]$ was purchased from Aldrich Chemicals.

Microanalyses of C, H, and N were performed with a Perkin-Elmer 240C analyser. Palladium was determined thermogravimetrically as PdO with a Mettler TG-50 thermobalance. Infrared spectra were recorded in the 4 000—180 cm^{-1} range on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets, ^1H and ^{13}C n.m.r. spectra on a Bruker AM300 spectrometer, using $(CD_3)_2SO$ as solvent. Thermal gravimetric analysis (t.g.a.) studies were carried out on a Mettler TG-50 thermobalance, using samples varying in weight from 9 to 10 mg and a heating rate of 5 °C min^{-1} in a nitrogen atmosphere. Differential scanning calorimetry (d.s.c.) curves were recorded on a Mettler differential scanning calorimeter (DSC-20) at a heating rate of 5 °C min^{-1} in the air. Analytical and spectroscopic data are presented in Table 1.

Preparation of the Complexes.—To a heated, stirred solution of $K_2[PdCl_4]$ (0.33 g, 1 mmol) in ethanol–water (20:1, 100 cm^3) was added over 15 min the 6-amino-5-arylazo-1,3-dimethyluracil derivative (2 mmol) and the mixture was refluxed for 1 h. In all cases, the precipitate was filtered off, washed with ethanol, and dried with diethyl ether. Crystals of $[PdL^1_2]$ (**1**) suitable for *X*-ray analysis were obtained by slow evaporation of a solution of the complex in ethanol–water (20:1) at 4 °C.

X-*Ray Data Collection and Structure Determination of* $[PdL^1_2]$ (**1**).—Single-crystal data collection was performed at ambient temperature with a Nicolet P3F diffractometer using graphite-monochromatized Mo-K_α radiation (λ = 0.710 69 Å). The unit-cell parameters for the orange crystal selected were obtained from least-squares refinement of 25 well centred reflections ($15 < 2\theta < 24°$).

Crystal data. $C_{24}H_{24}N_{10}O_4Pd$, specimen 0.1 × 0.15 × 0.3 mm, *M* 622.9, monoclinic, space group $P2_1/c$, a = 7.404(2), b = 9.537(1), c = 17.420(4) Å, β = 99.38(2)°, U = 1 213.5(4) Å^3, Z = 2, D_c = 1.70 g cm^{-3}, $F(000)$ = 632 μ(Mo-K_α) = 8.1 cm^{-1}.

A total of 2 507 independent reflections were collected by ω-scan technique ($3 < 2\theta < 53°$) at variable scan speed of 2.0—20.0° min^{-1}. Of these, 1 451 were considered as observed ($|F_o| > 5\sigma|F_o|$). Intensities of three check reflections measured after every 57 reflections showed only statistical variation. The data were corrected for Lorentz and polarization effects and for dispersion.

The structure was solved by using the SHELXS program system and subsequent ΔF synthesis.[11] The approximate position of the hydrogen atom bonded to N(6) was obtained from a ΔF map as well as the strongest hydrogen-atom maximum of each methyl group. The other hydrogen atoms were placed at calculated positions (C–H 1.0 Å). All non-hydrogen atoms were refined anisotropically whereas the hydrogen atoms were not refined. The function minimized was $\Sigma w(\Delta F)^2$, were $w = 1/\sigma(F^2)$, resulting in the final R value 0.043 (R' = 0.034). Scattering factors were those included in the program and anomalous dispersion corrections were applied.[12] All calculations were done on a VAX 8650 computer and the refinements and all subsequent calculations with XTAL programs.[13]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The chosen 6-amino-5-arylazouracil derivatives contain a weak acidic proton at the 6-amino group, which is involved in the tautomeric equilibrium (1). I.r. and ^1H n.m.r. results lead to

$$\underset{(\mathbf{V})}{C^6(NH_2){=}C^5(N{=}NR)C^4{=}O} \rightleftharpoons \underset{(\mathbf{VI})}{C^6({=}NH)C^5(N{=}NR){=}C^4(OH)} \qquad (1)$$

the conclusion that these uracil derivatives exist, in solid state and solution, predominantly in form (**V**). The i.r. spectra show two bands due to ν(C=O) stretching vibrations in the range 1 615—1 715 cm^{-1} and lack bands assignable to ν(O–H) in the high-frequency region. Moreover, in solution, ^1H n.m.r. spectra show that 6-amino-5-arylazouracil derivatives are stabilized by the establishment of a hydrogen bond between the 6-amino and the azo groups in form (**V**). Owing to this bond, free rotation of the amino group is hindered and, therefore, the resonances corresponding to these two protons occur at different chemical shifts (^1H n.m.r. spectrum for HL^1 is given in Figure 1), in the range δ 11.5—12.2 for the proton involved in the hydrogen bond and 8.5—9.1 for the other. The downfield shift of the former occurs because the nearby azo group has a deshielding effect. The concentration dependence of the ^1H n.m.r. chemical shifts of the two protons indicates a lack of significant intermolecular association. The hydrogen bond can be removed by heating the solution, both protons appearing as a single peak in the range δ 9.7—10.4. This hydrogen bond must contribute to the planarity of these 6-aminoaryl-5-azouracil derivatives. An analogous strong hydrogen bond has been observed in 6-aminouracil derivatives substituted at the 5 position by carbonyl and nitroso groups.[14–16]

When the amino proton dissociates both N(6) and N(8) must be the likely binding sites to the Pd^{II}. However, N(8), O(4) chelate co-ordination mode cannot be ruled out since it has been observed in the metal complexes of 6-amino-5-nitrosouracils having a similar prototropic equilibrium.[16,17] On the other hand, HL^5 has an additional weak proton at the N(3) endocyclic nitrogen atom of the pyrimidine ring, which, after proton dissociation, might co-ordinate to Pd^{II}. In addition, cyclopalladation involving the N(7) nitrogen atom of the azo group and C(2), the *ortho* carbon atom of the phenyl ring, might also occur.

The reactions of these 6-amino-5-arylazouracil derivatives and $K_2[PdCl_4]$ in ethanolic medium yielded orange, air-stable $[PdL_2]$ complexes (**1**)—(**4**) in good yield, with the exception of HL^5 which afforded yellow $[Pd(HL^5)_2Cl_2]$ (**5**). The analogous complex $[PdL^5_2]$ (**6**) was prepared in a high degree of purity by thermal elimination of HCl from (**5**) (see below). Although the

Table 1. Analytical[a] and physical data for the palladium complexes

Complex	Analysis (%) C	H	N	Pd	M.p.[b] (°C)	Colour	Yield (%)	I.r./cm^{-1} ν(N–H)	ν(N=N)
(1) $[PdL^1_2]$	46.1 (46.3)	3.8 (3.9)	22.2 (22.5)	16.8 (17.1)	>300	Orange	80	3 357vs	1 371vs
(2) $[PdL^2_2]$	49.4 (49.5)	4.7 (4.7)	20.3 (20.6)	15.7 (15.7)	>300	Orange	69	3 351vs	1 373vs
(3) $[PdL^3_2]$	41.3 (41.7)	3.1 (3.2)	20.2 (20.5)	15.4 (15.4)	>300	Orange	85	3 365vs	1 373vs
(4) $[PdL^4_2]$	39.5 (39.8)	2.5 (2.7)	21.5 (21.1)	16.3 (16.0)	>300	Orange	74	3 030m, 3 361vs	1 400vs
(5) $[Pd(HL^5)_2Cl_2]$[c]	35.5 (35.9)	2.6 (2.7)	18.9 (19.0)	14.4 (14.4)	230	Yellow	67	3 302m, 3 424m	1 396vs
(6) $[PdL^5_2]$	40.0 (39.8)	2.8 (2.7)	21.4 (21.1)	16.3 (16.0)	>300	Orange	*d*	3 020m,[e] 3 315vs	1 405vs

[a] Calculated values are given in parentheses. [b] With decomposition. [c] ν(Pd–Cl) 326 cm^{-1}. [d] Obtained by heating $[Pd(HL^5)_2Cl_2]$. [e] Wide band.

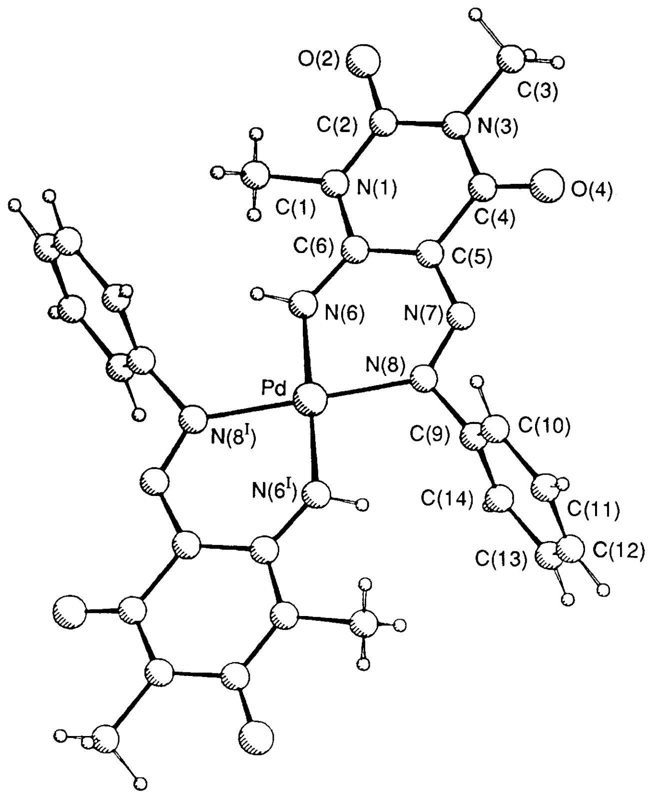


Figure 2. A perspective view of the $[PdL^1_2]$ molecule with the atom labelling

reaction between an aqueous solution of HL^5 containing 1 molar equivalent of KOH and $K_2[PdCl_4]$ also led to complex (**6**), it was not pure. All attempts to obtain complexes analogous to (**5**) with the remaining ligands in an ethanolic medium containing a few drops of HCl were unsuccessful.

Complexes $[PdL_2]$.—The evidence concerning the structures of the complexes has been primarily derived from i.r. spectral results, since ^1H and ^{13}C n.m.r. spectra could not be obtained because of the low solubility of the complexes in $(CD_3)_2SO$. In addition, the *X*-ray crystal structure of $[PdL^1_2]$ (**1**) was determined.

Crystal structure of $[PdL^1_2]$. The structure consists of discrete $[PdL^1_2]$ molecules. A perspective drawing of the molecule is given in Figure 2 together with the atomic labelling scheme. Atomic co-ordinates are listed in Table 2 and selected bond lengths and angles in Table 3.

Molecules of $[PdL^1_2]$ have C_i symmetry. The ligand HL^1 acts in a N,N-bidentate manner through the nitrogen atom of the deprotonated amino group and the nitrogen atom of the azo group bonded to the phenyl ring. This co-ordination mode has also been observed in the complex $[CuL^1_2]$·dmso (dmso = dimethyl sulphoxide).[18] Because the palladium atom is on a centre of symmetry, the two ligands are placed in a *trans* arrangement and the co-ordination of the four nitrogen atoms is necessarily planar. The two Pd–N bond distances are in the range usually found for related bonds in other palladium(II) complexes.[19–22]

The entire L^1 anion is practically planar with the exception of the phenyl rings which are twisted 84.4(2)° away from the co-ordination plane. The structure of the molecule is such that H(6), the hydrogen atom on N(6) of the amino group, and C(9^I), C(10^I), and C(14^I), the carbon atoms of the phenyl of the other co-ordinated ligand, are brought in close proximity, thus preventing H(6) participating in intermolecular hydrogen-bond formation. Indeed, if the phenyl rings were to lie in the molecular plane, then H(6)···C(9^I) and H(6)···C(10^I) contacts would be much shorter than the corresponding sum of the van der Waals radii (2.9 Å).[23] These close contacts are relieved in two ways. First, the phenyl ring is moved away from the H(6) atom so that the N(7)–N(8)–C(9) and the Pd–N(8)–C(9) angles, which might be expected to have approximately the same value, are 110.6(4) and 119.6(3)°, respectively. Moreover, the N(6)–Pd–N(8^I) external angle opens to 92.8(2)° while the internal angle is 87.2(2)°. Secondly, the phenyl ring is twisted 84.4(2)° about C(9)–N(8) bond with respect to the co-ordination plane as illustrated in Figure 2. This increases the H(6)···C(10^I) contact to 2.56 Å. This and the C(9^I)···H(6) contact of 2.22 Å are both less than 2.9 Å, the sum of the van der Waals radii, indicating that an important interligand steric crowding still remains in the structure. A further twist of the phenyl ring would increase the C(10^I)···H(6) contact distance but would reduce the C(14^I)···H(6) contact distance of 2.59 Å found. Thus, the balance of the C(10^I)···H(6) and C(14^I)···H(6) contacts seems to be the more important factor affecting the twist angle in this structure. This interpretation is supported by the *X*-ray crystal structure of the compound $[H_2L^1][AuCl_2]·1.5H_2O$.[9] In this compound, the absence of steric crowding between N(8)-protonated $[H_2L^1]^+$ cations allows the planarity of the whole $[H_2L^1]^+$ cation and N(7)–N(8)–C(9) and H(8)–N(8)–C(9) angles are very close to 120°.

The structure of (**1**) is a good example of a four-co-ordinated bis(chelate) of Pd^{II} (ref. 24) in which planar ligands arising from

Table 2. Fractional atomic co-ordinates for $[PdL^1{}_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Pd	0.000 0(0)	0.000 0(0)	0.000 0(0)
N(1)	−0.003 7(6)	0.372 0(5)	0.132 6(3)
C(1)	0.130 4(9)	0.332 9(6)	0.200 6(4)
C(2)	−0.063 7(7)	0.508 1(8)	0.128 9(3)
O(2)	−0.009 2(6)	0.594 4(4)	0.180 5(2)
N(3)	−0.190 8(7)	0.548 2(4)	0.064 9(3)
C(3)	−0.265 6(9)	0.691 6(6)	0.064 7(4)
C(4)	−0.247 6(8)	0.463 4(6)	0.000 2(3)
O(4)	−0.349 4(5)	0.510 5(5)	−0.055 7(2)
C(5)	−0.179 4(7)	0.319 1(6)	0.007 7(3)
C(6)	−0.049 7(7)	0.274 9(6)	0.072 9(3)
N(6)	0.020 3(6)	0.150 3(5)	0.079 7(3)
N(7)	−0.255 0(6)	0.236 5(5)	−0.051 8(3)
N(8)	−0.209 3(6)	0.108 6(5)	−0.059 1(3)
C(9)	−0.325 9(7)	0.043 6(5)	−0.125 0(3)
C(10)	−0.457 8(9)	−0.051 5(6)	−0.112 3(4)
C(11)	−0.565 2(9)	−0.113 3(7)	−0.177 2(4)
C(12)	−0.539 4(8)	−0.081 3(7)	−0.251 0(4)
C(13)	−0.408 1(8)	0.012 9(9)	−0.262 9(3)
C(14)	−0.298 2(8)	0.075 8(6)	−0.199 2(3)

Table 3. Bond lengths (Å) and angles (°) for $[PdL^1{}_2]$* with e.s.d.s in parentheses

Pd–N(6)	1.985(5)	C(5)–C(6)	1.426(7)
Pd–N(8)	2.004(4)	C(5)–N(7)	1.349(7)
N(1)–C(1)	1.464(7)	C(6)–N(6)	1.294(7)
N(1)–C(2)	1.371(9)	N(7)–N(8)	1.278(7)
N(1)–C(6)	1.392(7)	N(8)–C(9)	1.457(7)
C(2)–O(2)	1.237(8)	C(9)–C(10)	1.377(9)
C(2)–N(3)	1.391(7)	C(9)–C(14)	1.376(8)
N(3)–C(3)	1.476(8)	C(10)–C(11)	1.402(9)
N(3)–C(4)	1.394(7)	C(11)–C(12)	1.364(10)
C(4)–O(4)	1.215(7)	C(12)–C(13)	1.364(10)
C(4)–C(5)	1.465(8)	C(13)–C(14)	1.399(8)
N(6)–Pd–N(8)	87.2(2)	N(1)–C(6)–C(5)	116.7(5)
N(6)–Pd–N(8^{I})	92.8(2)	N(1)–C(6)–N(6)	119.8(5)
C(1)–N(1)–C(2)	116.8(4)	C(5)–C(6)–N(6)	123.5(5)
C(1)–N(1)–C(6)	119.1(5)	Pd–N(6)–C(6)	128.0(4)
C(2)–N(1)–C(6)	123.8(4)	C(5)–N(7)–N(8)	123.4(4)
N(1)–C(2)–O(2)	122.1(5)	Pd–N(8)–N(7)	129.6(3)
N(1)–C(2)–N(3)	118.0(5)	Pd–N(8)–C(9)	119.6(3)
O(2)–C(2)–N(3)	119.9(6)	N(7)–N(8)–C(9)	110.6(4)
C(2)–N(3)–C(3)	117.4(5)	N(8)–C(9)–C(10)	119.8(5)
C(2)–N(3)–C(4)	124.4(5)	N(8)–C(9)–C(14)	119.0(5)
C(3)–N(3)–C(4)	118.2(4)	C(9)–C(10)–C(11)	118.1(6)
N(3)–C(4)–O(4)	119.9(5)	C(9)–C(14)–C(13)	119.5(6)
N(3)–C(4)–C(5)	114.7(5)	C(10)–C(9)–C(14)	121.1(5)
O(4)–C(4)–C(5)	125.3(5)	C(10)–C(11)–C(12)	121.2(6)
C(4)–C(5)–C(6)	121.7(5)	C(11)–C(12)–C(13)	120.2(6)
C(4)–C(5)–N(7)	112.7(5)	C(12)–C(13)–C(14)	119.9(5)
C(6)–C(5)–N(7)	125.5(5)		

* I $-x, -y, -z$.

π delocalization are forced to deviate from planarity in order to overcome interligand steric crowding and to prevent distortion of the square-planar PdN_4 co-ordination sphere toward the energetically disfavoured tetrahedral geometry. To the best of our knowledge, there is only one palladium(II) complex described in the literature having non-planar four-co-ordination, *trans*-bis[(phenylazo)acetaldehyde oximato]palladium(II).[21]

The co-ordinated HL^1 ligand assumes a *trans* configuration and has bond lengths and angles which do not differ significantly from those reported for other compounds of HL^1.[9,18]

Table 4. Intramolecular and intermolecular contacts (Å) for $[PdL^1{}_2]$

H(6) ··· C(10^{I})	2.56	H(6) ··· H(10^{I})	3.00
H(6) ··· C(14^{I})	2.59	C(3) ··· O(2)	2.698(7)
H(6) ··· C(9^{I})	2.22	C(1) ··· O(2)	2.700(7)
H(6) ··· N(8^{I})	2.70	C(3) ··· O(4)	2.710(7)
N(8) ··· N(6^{I})	2.889(7)	H(6) ··· H(14^{I})	3.03
N(6) ··· C(9^{I})	2.929(7)	C(1) ··· N(6)	2.751(7)
C(4) ··· O(4^{III})	3.292(7)	O(2) ··· C(13^{IX})	3.420(8)
O(4) ··· O(4^{III})	3.191(6)	O(4) ··· C(3^{II})	3.423(8)
O(2) ··· C(1^{IV})	3.298(8)	N(3) ··· O(4^{II})	3.428(6)
N(1) ··· O(4^{V})	3.322(6)	C(5) ··· N(3^{V})	3.441(8)
O(4) ··· C(13^{VI})	3.372(6)	O(4) ··· C(12^{VI})	3.448(7)
C(13) ··· C(2^{VII})	3.416(8)	C(4) ··· C(2^{V})	3.483(8)
C(12) ··· C(1^{VIII})	3.410(9)	O(2) ··· C(12^{X})	3.491(7)

I $-x, -y, -z$; II $1 - x, 1 - y, -z$; III $-1 - x, 1 - y, -z$; IV $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; V $-x, 1 - y, -z$; VI $-1 - x, y + \frac{1}{2}, -z - \frac{1}{2}$; VII $x, -y + \frac{1}{2}, z - \frac{1}{2}$; VIII $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; IX $x, -y + \frac{1}{2}, z + \frac{1}{2}$; X $1 + x, y - \frac{1}{2}, z + \frac{1}{2}$.

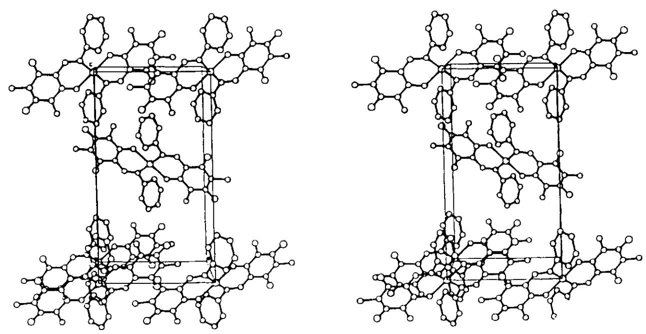


Figure 3. Stereoview of the packing of the molecules within the unit cell

The twisting of the phenyl is expected to reduce its π conjugation to the bound arylazopyrimidine moiety. In good agreement with this the N(8)–C(9) distance of 1.457(7) Å compares favourably with the value of 1.47 Å for a C–N single bond. Moreover, it is 0.03 Å larger than those reported for other HL^1 compounds, in which the ligand is planar. Although such a difference is not necessarily significant, it is in the expected direction. The C(5)–N(7) bond distance of 1.349(7) Å indicates a greater delocalization in this part of the HL^1 ligand. The N=N [1.278(7) Å] and C(5)–N(7) distances are in agreement with those reported for protonated and co-ordinated arylazouracil ligands in which one of the nitrogen atoms is involved in a σ bond to the hydrogen and metal atoms, respectively.[9,18]

The phenyl and pyrimidine rings are essentially planar, as expected. In the pyrimidine ring there are some steric interactions involving the exocyclic groups, as is evidenced by the short C(1) ··· O(2), C(1) ··· N(6), C(3) ··· O(2), and C(3) ··· O(4) contact distances of 2.700(7), 2.751(7), 2.698(7), and 2.710(7) Å, respectively, which are approximately 0.6 Å less than the sum of their van der Waals radii.[23]

Figure 3 illustrates the arrangement of the $[PdL^1{}_2]$ molecules in the unit cell. Intermolecular contacts less than 3.5 Å are listed in Table 4 and indicate that only van der Waals forces are present between molecules.

I.r. results. The similarity of the i.r. spectra (Table 1) of the complexes suggests an analogous co-ordination mode for all five ligands. Thus, all the complexes display a sharp ν(N–H) band of the deprotonated N-co-ordinated 6-amino group in the region 3 300—3 350 cm^{-1}. Furthermore, the N=N stretching bands are shifted (by *ca.* 140 cm^{-1}) to lower wavenumber relative to the unco-ordinated ligands, indicating that a nitrogen atom of the azo group is involved in the co-ordination to Pd^{II}. In view of this and the above *X*-ray results for (**1**), the four remaining $[PdL_2]$ complexes must also exhibit a *trans*-square-planar structure, as indicated in Figure 2.

$[Pd(HL^5)_2Cl_2]$ (**5**).—The i.r. spectrum of complex (**5**) exhibits in the range 3 300—3 425 cm^{-1} absorption bands due to N–H stretching vibrations of the free amino group, as well as a shift of the N=N stretching vibration band toward lower frequencies, indicating that the ligand is bonded to the Pd^{II} through a nitrogen atom of the azo group. The two remaining positions of the co-ordination sphere are occupied by two chlorine atoms, since the far-i.r. spectra display a band at 326 cm^{-1} assignable to the Pd–Cl stretching vibration. The presence of only one band of such type might indicate a *trans*-square-planar geometry (C_{2h}) for this complex. This geometry has been further supported by the results of the thermal study of the complex. T.g.a. and d.s.c. curves for (**5**) (Figure 4) show in the temperature range 230—320 °C a weight-loss effect of 10.37%, in accordance with the value of 9.90% required for the elimination of two molecules of HCl. The expected endothermic effect for this elimination is observed from d.s.c. curve at around 280 °C (ΔH = 99.8 kJ mol^{-1}). After this process the intermediate product is stable in the range 320—370 °C. Above this latter temperature, the t.g.a. curve indicates strong decomposition which finishes at 450 °C, giving PdO as a final product. This decomposition can be observed from d.s.c. curve as an exothermic effect around 420 °C corresponding to pyrolysis of the organic moiety.

To verify the HCl elimination and to identify the nature of the intermediate product, the i.r. spectrum of a sample heated to 320 °C and rapidly cooled to room temperature was recorded. The spectrum of the orange intermediate product is very similar to those of the $[PdL_2]$ complexes. In view of this, the thermal process occurring in the solid state must be as in the Scheme. In this reaction, by heating, one of the hydrogen atoms of the 6-amino group is bonded to a neighbouring co-ordinated chlorine atom, leading to HCl elimination and either subsequent or simultaneous co-ordination of the amino group to the Pd^{II}.

Because the thermally isolated complex $[PdL^5{}_2]$ (**6**) has a *trans*-square-planar geometry, the starting complex $[Pd(HL^5)_2Cl_2]$ must also exhibit this type of geometry, in good accordance with the above i.r. results for this complex.

Kinetic Parameters and Mechanism.—The kinetic parameters were determined using the general equation (2) for reactions in

$$d\alpha/dt = f(\alpha)k(T) \quad (2)$$

the solid state[25] where α is the molar fraction of the decomposed product at time *t*, varying in the range 0—1, and $k(T)$ is the rate constant of the reaction the temperature dependence of which is described by the Arrhenius equation (3) where *A* is the pre-

$$k(T) = A\cdot\exp(E_a/RT) \quad (3)$$

exponential factor, E_a the activation energy, *R* the gas constant, and *T* the temperature in K.

After separation of variables and integration the equation becomes (4) where the function $g(\alpha)$ is the mathematical expres-

$$\int_0^1 d\alpha/f(\alpha) = \int_{T_1}^{T_2} k(T)dt = g(\alpha) \quad (4)$$

sion of the physical model according to which the solid-state reaction is assumed to occur. Under isothermal conditions the equation $g(\alpha) = k(T)t$ relates the kinetics parameters A, E_a, and

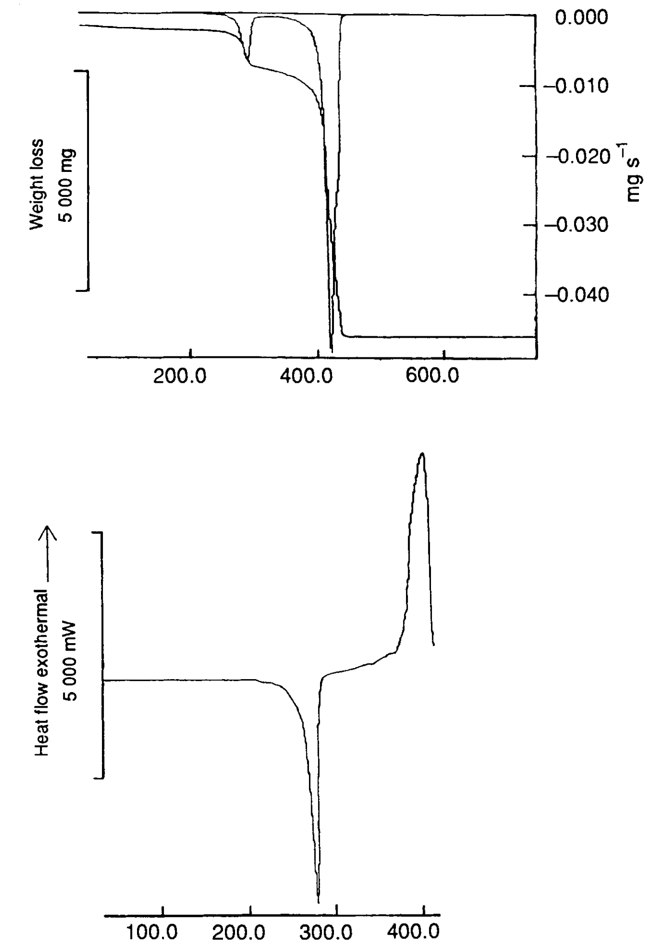
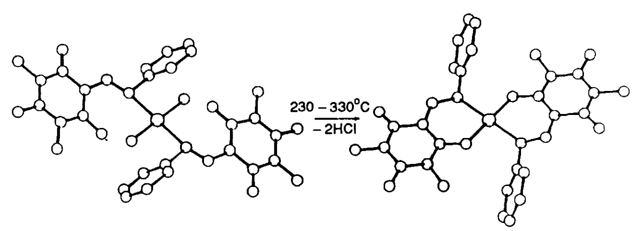


Figure 4. T.g.a. (top) and d.s.c. curves for $[Pd(HL^5)_2Cl_2]$



(**5**) (**6**)

Scheme.

$g(\alpha)$. The determination of this equation enables the establishment of the relation between α and time, and thus enables prediction of the progress of the reaction as a function of time at constant temperature *T*. However, the solution of this equation requires knowledge of the function $g(\alpha)$, this being the main difficulty in solid kinetics. Nevertheless, it has been shown that the activation energy is independent of the $g(\alpha)$ used and can be calculated from the expression[26] (5) where Δt is the time

$$\ln \Delta t = E_a/RT + ct \quad (5)$$

increment between the point corresponding to α = 0.2—0.8 and *T* is the isothermal temperature. From the slope of a plot of ln Δt *versus* $1/T$ for the different isothermal measurements E_a/R is obtained.

Table 5. Experimental values from isothermal runs for the compound $[Pd(HL^5)_2Cl_2]$

T/K	$t_{0.2}$ (min)	$t_{0.8}$ (min)	Δt (min)	$t_{0.2}/t_{0.8}$	Kinetic parameters
563	1.50	3.60	2.10	0.416	E_a = 197.2 kJ mol^{-1}
568	1.03	2.50	1.47	0.412	$\ln k_0$ = 40.71
573	0.85	2.00	1.15	0.425	r = 0.994
578	0.54	1.30	0.76	0.415	$\Delta H^{\ddagger}$ = 170.7 kJ mol^{-1}
583	0.34	0.82	0.48	0.414	$\Delta S^{\ddagger}$ = −42 J K^{-1} mol^{-1}
					r = 0.998

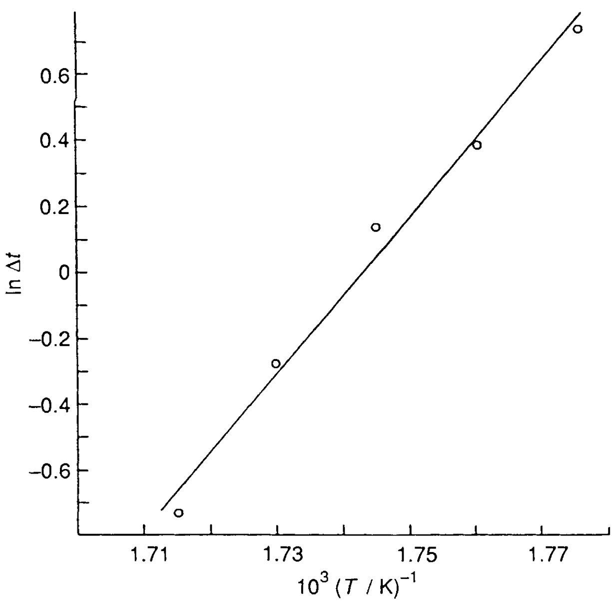


Figure 5. Plot of ln Δt *vs.* $1/T$ for $[Pd(HL^5)_2Cl_2]$

The experimental values of T, $t_{0.2}$, $t_{0.8}$, Δt, and $t_{0.2}/t_{0.8}$ from the different isothermal curves are shown in Table 5, together the E_a value obtained from the plot of ln Δt *versus* $1/T$ (Figure 5). From the ratio $g(\alpha_{0.2})/g(\alpha_{0.8}) = t_{0.2}/t_{0.8}$, two mechanisms are possible:[26] nucleation growth with $n = 2$ $\{g(\alpha) = [-\ln(1-\alpha)]^{\frac{1}{2}}$; Avrami's law$\}$ and nucleation controlled with $n = 1.5$ $[g(\alpha) = \alpha^{1/n}$; power law]. However, as the $t_{0.2}$ and $t_{0.8}$ values from $t = g(\alpha)/k(T)$ for the power law represent the best agreement with the experimental value of the ratio $t_{0.2}/t_{0.8}$ a nucleation-controlled mechanism is proposed.

If for the reaction an associative chemical mechanism is assumed, the formation of a six-bond activated complex (octahedral), requires, based on a crystal-field model, 12.56 Dq ($Dq \approx 25$ kJ mol^{-1}, ref. 27) and consequently a value of the activation energy about 300 kJ mol^{-1} is expected, which is greater than E_a = 197.2 kJ mol^{-1} obtained. In view of this an associative interchange mechanism is proposed, in which the transition state displays substantial bonding of the chloro and amino groups to Pd^{II}. In good accordance with this, the entropy of activation (Table 5) calculated from expression (6) is $\Delta S^{\ddagger}$ = −42 J K^{-1} mol^{-1}.

$$\ln kh/kT = \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT \quad (6)$$

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