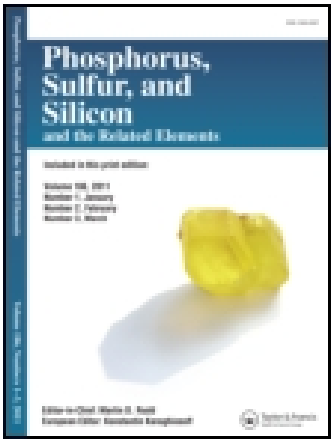

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Palladium(II) and Platinum(II) Complexes of N-Phenyl- and N-Ethyl-N′-pyrimidin-2-ylthiourea

Samir S. Kandil [a]
[a] Department of Chemistry, Faculty of Applied Science , Umm Al-Qura University , Makkah, Kingdom of Saudi Arabia
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PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF *N*-PHENYL- AND *N*-ETHYL-*N*′-PYRIMIDIN-2-YLTHIOUREA

Samir S. Kandil
Department of Chemistry, Faculty of Applied Science, Umm Al-Qura University, Makkah, Kingdom of Saudi Arabia

***Palladium(II) and platinum(II) complexes of* N-*ethyl*-N′-*pyrimidin-2-ylthiourea*(HL^1) *and* N-*phenyl*-N′-*pyrimidin-2-ylthiourea* (HL^2) *have been prepared, and the complexes* $[M(HL)Cl_2]$, $[Pt(L)_2]$, $[Pd(HL^1)_2]Cl_2$, *and* $[Pd(L^2)_2]$ *(where* $M = Pd^{II}$ *or* Pt^{II}*) were characterized. The spectroscopic data are consistent with coordination of thioureas as neutral or monoanionic ligands to* Pd^{II} *and* Pt^{II} *through S and a pyrimidine-N. The IR spectra show shifts of CS and pyrimidine ring stretch bands to lower and higher frequencies, respectively. The* ^1H *NMR spectra differentiate between H(4′) and H(6′) resonances and indicate downfield shifts for all protons of pyrimidine [H(4′), H(5′), and H(6′)], two resonances for two N−H protons for complexes containing the neutral ligand (HL), and only one N−H proton chemical shift for complexes containing the monoanion (L).* ^{13}C *NMR chemical shifts of pyrimidine carbons are correlated with the type of bonding between* Pd^{II} *or* Pt^{II} *and pyrimidine-N. The magnetic susceptibilities suggest a diamagnetic planar structure for all complexes.*

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Pt(II) and Pd(II) complexes; spectroscopic studies; thiourea derivatives

INTRODUCTION

The ability of thioureas and their deprotonated anions to coordinate to metal centers as either neutral, monoanionic, or dianionic ligands has been established.[1–6] Contrary to N,S-chelated thioureas, metal complexes of O,S-chelated ones have been widely investigated.[7–10] As such, studies of this type of thiourea have revealed interesting practical applications, including liquid–liquid extraction, reverse-phase high performance liquid chromatographic separation, and fluorimetric detection of the platinum group metals, as well as the selective online preconcentration of ultra-traces of palladium, followed by its determination by atomic absorption spectrometry.[11] This class of compounds is also used as complementary nonleaving ligands in many of prospective platinum(II)-based anticancer

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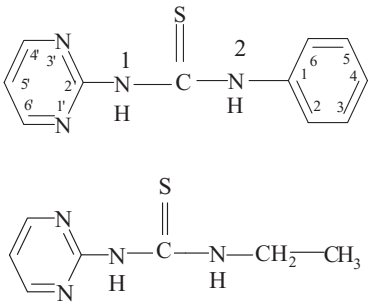
Author's permanent affiliation: Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt.
Address correspondence to Samir S. Kandil, Department of Chemistry, Faculty of Applied Science, Umm Al-Qura University, Makkah, P.O. Box 1455, Kingdom of Saudi Arabia. E-mail: kandilsamir@hotmail.com

complexes, in order to fine-tune the chemical and physical properties of the complexes and thereby influence both the target selection and the reactivity of the metal ion.[7, 12] However, such applications with N,S-chelated thioureas are awaiting studies of more diverse ligands, though complexes with bidentate nitrogen–sulfur donors are found to be potential fungicidal,[13] antiviral,[14] analgesic,[15] antibacterial,[16] and anticancer[17] agents. Pyrimidine is the parent heterocycle of a group of compounds in living systems,[18] and many pyrimidines or their derivatives have remarkable biological activity.[19] Metal complexes of 2-aminopyrimidines, as modeling ligands of DNA nucleobases, were studied in order to examine the affinity of metal centers for exocyclic amine vs. endocyclic amine nitrogens. In most cases, especially with palladium(II) and platinum(II), the 2-aminopyrimidines coordinate as monodentate ligands through a pyrimidine ring nitrogen.[20]

The present work is aimed at describing the synthesis and characterization of platinum(II) and palladium(II) complexes with two bifunctionally ligands, *N*-ethyl-*N*′-pyrimidin-2-ylthiourea (HL^1) and *N*-phenyl-*N*′-pyrimidin-2-ylthiourea (HL^2) (Scheme 1).



Scheme 1 Structures of *N*-ethyl-*N*′-pyrimidin-2ylthiourea (HL^1) and *N*-phenyl-*N*′-pyrimidin-2ylthiourea (HL^2).

RESULTS AND DISCUSSION

The reaction between ethylisothiocyanate or phenylisothiocyanate with 2-aminopyrimidine in toluene and actonitrile, respectively, under refluxing conditions yielded the two ligands HL^1 and HL^2.

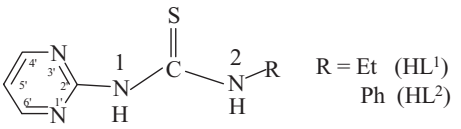
The elemental analyses and ^1H and ^{13}C NMR assignments, as well as the appearance of the highest ion peak at *m/z* 182 and 230 in the E.I. mass spectra of HL^1 and HL^2, respectively, confirm the preparation of the two ligands HL^1 and HL^2. The two ligands exist in the thione (thioketo) form in DMSO solution, as revealed by the appearance of two ^1H NMR signals due to protons of the N1H and N2H groups, respectively, and the appearance of a ^{13}C NMR signal assigned to the carbon of the C=S group (see the Experimental section). Interaction of aqueous $[MCl_4]^{2-}$ or MCl_2 in acetone ($M = Pd^{II}$ or Pt^{II}) with $HL^1$and HL^2 in 1:1 and 1:2 molar ratios (metal:ligand) produced solid complexes having 1:1 and 1:2 stoichiometries. The analytical and physical data of HL^1 and HL^2 complexes with palladium(II) and platinum(II) are given in Table I. The preparation of $[Pd(HL^2)Cl_2]$ has been reported during the progress of this work, but no thorough characterization data are reported.[21] Attempts to recrystallize the complexes for a X-ray structural investigation were unsuccessful. All the isolated solid complexes are air stable for extended periods of time, and are insoluble in water and common organic solvents, but are readily soluble

Table I Analytical and some physical data of HL^1 and HL^2 and their palladium(II) and platinum(II) complexes

Compound	Color	Yield (%)	Found (Calcd) %				Λ_M[b]	UV-Vis bands (λ_{max}, cm^{-1})
			C	H	N	S		
HL^1	White	72	46.18	5.43	30.73	17.35		36,630;29,200
$C_7H_{10}N_4S$ (182)[a]			(46.15)	(5.49)	(30.76)	(17.58)		
$[Pd(HL^1)Cl_2]$	Orange	65	23.63	2.91	15.44	8.48	8	35,800;22,760
$C_7H_{10}N_4SCl_2Pd$ (359)			(23.39)	(2.78)	(15.59)	(8.91)		
$[Pt(HL^1)Cl_2]$	Reddish-brown	68	18.98	2.35	12.32	6.96	12	35,870;22,150
$C_7H_{10}N_4SCl_2Pt$ (448)			(18.75)	(2.23)	(12.50)	(7.14)		
$[Pd(HL^1)_2]Cl_2$	Brown	62	31.53	3.78	21.43	11.56	122	35,940;21,920
$C_{14}H_{20}N_8S_2Cl_2Pd$ (541)			(31.10)	(3.70)	(20.70)	(11.83)		
$[Pt(L^1)_2]$	Yellow	65	29.78	3.43	19.65	11.18	7	35,760;22,300
$C_{14}H_{18}N_8S_2Pt$ (557)			(30.16)	(3.25)	(20.09)	(11.50)		
HL^2	White	85	57.21	4.38	24.76	13.73	—	36,100;28,570
$C_{11}H_{10}N_4S$ (230)			(57.39)	(4.34)	(24.36)	(13.91)		
$[Pd(HL^2)Cl_2]$	Brown	70	32.75	2.50	13.45	7.62	3	35,970;21,900
$C_{11}H_{10}N_4SCl_2Pd$ (407)			(32.43)	(2.46)	(13.76)	(7.86)		
$[Pt(HL^2)Cl_2].H_2O$	Brown	68	25.87	2.76	10.55	6.01	12	35,700;20,800
$C_{11}H_{12}N_4OSCl_2Pt$ (514)			(25.68)	(2.33)	(10.89)	(6.22)		
$[Pd(L^2)_2]$	Dark-brown	65	45.65	3.15	19.32	10.85	9	35,590;21,700
$C_{22}H_{18}N_8S_2Pd$ (564)			(46.81)	(3.19)	(19.85)	(11.35)		
$[Pt(L^2)_2]$	Brown	69	39.93	3.18	16.87	9.35	8	35,700;21,200
$C_{22}H_{18}N_8S_2Pt$ (653)			(40.42)	(2.76)	(17.15)	(9.80)		

[a]Formula mass.
[b]Molar conductivity ($\Omega^{-1}cm^2\ mol^{-1}$) measured in DMF.

Table II ^{1}H and ^{13}C NMR spectra (ppm) of HL^1 and $HL^2$and their palladium and and platinum complexes[a]



Compound	H(4′)	H(5′)	H(6′)	N1H	N2H	CS	C(2′)	C(4′)	C(5′)	C(6′)
HL^1	8.65	7.15	8.645	11.13	10.57	179.5	164.1	158.6	116.1	158.6
$[Pd(HL^1)Cl_2]$	9.28	7.40	8.82	11.76	9.28	172.6	162.2	154.3	118.0	161.7
$[Pt(HL^1)Cl_2]$	8.90	7.35	8.79	12.23	9.35	165.7	161.0	155.5	116.4	160.3
$[Pd(HL^1)_2]Cl_2$	9.33	7.41	8.84	11.82	10.36	172.7	162.2	154.1	118.1	161.7
$[Pt(L^1)_2]$	9.32	7.45	8.63	—	10.09	162.3	160.8	158.6	116.2	160.0
HL^2	8.71	7.15	8.71	13.21	11.05	178.9	158.8	157.9	139.2	157.9
$[Pd(HL^2)Cl_2]$	9.27	7.40	8.81	11.76	9.27	172.7	161.6	160.9	137.9	153.3
$[Pt(HL^2)Cl_2].H_2O$	9.35	7.40	8.85	12.29	9.55	173.7	162.6	160.4	140.2	158.5
$[Pd(L^2)_2]$	8.85	7.63	8.69	—	9.35	165.4	163.1	161.8	138.3	153.9
$[Pt(L^2)_2]$	8.76	7.37	8.69	—	9.07	168.9	161.6	156.7	138.5	160.7

[a]Spectra were recorded in d_6-DMSO as a solvent.

in DMF and DMSO. The molar conductivities measured in DMF (10^{-3}M) at 25°C and showed values in the 5–12 Ω^{-1} cm^2 mol^{-1} range, indicating the non-electrolytic nature of all the complexes with exception of $[Pd(HL^1)_2]Cl_2$, which behaves as a 1:2 electrolyte ($\Lambda_m = 122\ \Omega^{-1}.\ cm^2.mol^{-1}$).[22]

Infrared Spectra

The infrared spectra of HL^1 and HL^2 (Table S1, Supplemental Materials, available online) show N1H and N2H stretching vibrations at 3012, 3149 and 3041, 3218 cm^{-1}, respectively, [23,24] which are shifted to higher wavenumbers in the spectra of $[M(HL)Cl_2]$ and $[Pd(HL^1)_2]Cl_2$, but the N1H band disappears in $Pt(L)_2$ and $Pd(L^2)$. Also, compounds HL^1 and HL^2 show CS stretching bands at 798 and 813 cm^{-1}, respectively, which are lowered by 50–60 cm^{-1} in their complexes. These indicate coordination of the sulfur atom to Pd(II) and Pt(II) in all complexes in the form of thione or thiol.[25] The disappearance of N1H stretch in $[Pt(L)_2]$ and $[Pd(L^2)_2]$, with the appearance of a new band at 1585 cm^{-1}, assignable to ν(C=N) of an imine linkage created upon deprotonation, indicates coordination of thiolo-S. An upward shift of the pyrimidine ring vibration (C=C)+ ν(C=N) from 1589 and 1525 cm^{-1} in the spectra of the free ligands to 1604–1635 and 1552–1566 cm^{-1} in its complexes, is consistent with the coordination of one nitrogen atom of pyrimidine ring to a metal.[26–30] Bonding of sulfur and pyrimidine-N atoms to the metals is further supported by the appearance of new bands in the far infrared region (Table II) in the complexes due to ν(M−S)[25,31] and ν(M−N).[32–35] The coordination of the chloro ligand is indicated by the appearance of a new band at 326 cm^{-1} in palladium(II) complexes, assigned to ν(Pd−Cl). [35,36]

Magnetic Moments and Electronic Spectra

The magnetic susceptibilities indicate diamagnetic behavior for all complexes. The d^8 configuration is especially likely to form planar diamagnetic compounds. The electronic

spectra of the complexes show charge transfer bands (Table I) at 21,000–22,000 cm^{-1}, the tails of which obscure the weaker d–d transitions.[37]

^{1}H NMR Spectra

The ^{1}H NMR data of the complexes (Table II) when compared with those of the free ligands point to the following: (i) One ^{1}H NMR signal corresponding to an N2H proton is appreciably upfield-shifted from 10.57 and 11.05 ppm in the free HL^1 and HL^2 to 9.30–9.85 and 9.55–9.07 ppm in the complexes, whereas the other N1H signal is downfield-shifted from 13.21 and 11.13 ppm in the free ligands to 11.76–12.29 ppm in most complexes, but disappeared in $[Pt(L^1)_2]$ and $[M(L)_2]$. This indicates coordination of thiono-S atom to palladium(II) and platinum(II) ions in $[M(HL)Cl_2]$ and $[Pd(HL^1)_2]Cl_2$, effecting reduced electron density around N1H by the electron-withdrawing effect of the metal ion and decreased the anisotropic effect of C═S on N2H proton as a result of reducing its π-electron character and/or decreasing the number of unshared pairs of electrons from two to one upon coordination. But in the $[M(L^2)_2]$ and $[Pt(L^2)_2]$, thiolo-S atoms are coordinated to platinum(II). The formation of thiolo-S involves tautomerization between N1H and C═S groups followed by deprotonation of the thiol, SH, group with the formation of imine linkage. (ii) The pyrimidine protons H(4′) and H(6′), which are equivalent and appear as a doublet at 8.65 ppm [as a result of coupling with H(5′)] in the free ligands, are split into two doublets of two nonequivalent protons and are downfield-shifted to 9.28–9.47 and 8.81–8.95 ppm in the complexes. This result is indicative of coordination of one pyrimidine nitrogen to palladium and platinum ions, making the two protons magnetically nonequivalent.[5,38] Some selected spectra are presented in Figures S1–S7 (Supplemental Materials, available online).

^{13}C NMR Spectra

The ^{13}C NMR chemical shifts of the complexes (Table II), when compared with those of the free ligands, point to the following: (a) The ^{13}C NMR signals corresponding to C(6′) and C(5′) of pyrimidine undergo small downfield shifts, but C(2′) and C(4′) undergo an upfield shift as compared to their corresponding δ values in the free ligand. This may be attributed to the fact that coordination of one nitrogen of pyrimidine ring through its lone pair to palladium(II) and platinum(II) ions may lead to two opposing effects: (1) the electron withdrawing effect of M(II) ions through σ-bonding, which decreases the electron density around all carbon atoms of the pyrimidine ring, especially the nearer ones C(2′) and C(4′), resulting in downfield shifts (higher ppm) for all carbon signals of the ring; or (2) π-back bonding through d_π–p_π interaction between Pd(II) and a π^* orbital located on the ring, and more particularly, N, i.e., N becomes softer in the aromatic ring and is able to accept an electron pair from the soft metals, thereby also increasing electron density at all carbons with the ring and resulting in upfield shifts for them. A compromise between these two effects leads to small upfield shifts for resonances of C(2′) and C(4′) from δ 164.2 and 158.6 ppm in the free ligand to 162.2–161.5 and 155.65–154.3 ppm in the complexes and downfield shifts for signals due to C(6′) and C(5′) from δ 158.6 and 116.1 ppm in the free ligand to 161.65–159.8 and 118.05–116.35 ppm in the complexes, respectively. (b) The ^{13}C NMR signal corresponding to thiocarbonyl carbon (C═S) is upfield-shifted from δ 179.5 and 178 ppm in the free HL^1 and HL^2, respectively, to 172.6–164.3 ppm in the complexes.

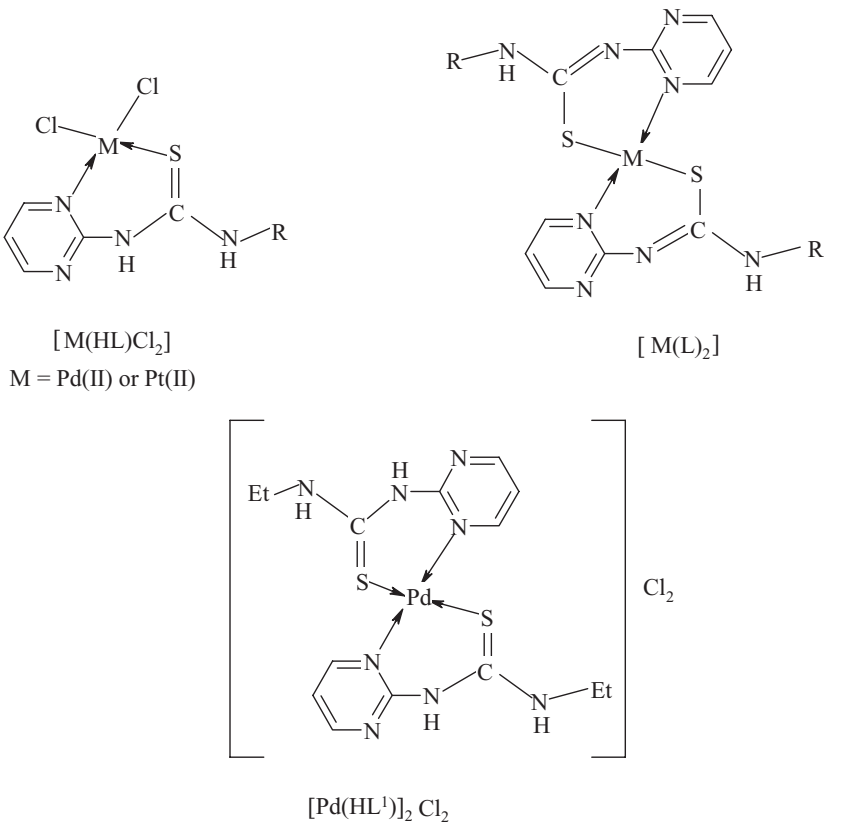


Figure 1 Proposed chemical structures of the prepared complexes.

This upfield shift is indicative of coordination of thiono-S to M(II), resulting in reduced bond order of the CS bond upon complexation; thiolo-S is bonded to platinum(II) in $[Pt(L)_2]$, which results in the thiomide changing into thioimine, i.e., HN−C=S to N=C−S−Pt(II).

From the foregoing discussion, we propose that the structures of these complexes can be formulated as shown in Figure 1.

EXPERIMENTAL

Measurements

IR spectra were recorded as KBr discs on a Perkin-Elmer 683 spectrophotometer in the 4000–200 cm^{-1} range. Electronic spectra were recorded as nujol mulls on a Shimadzu 240 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained with a Jeol JNM ECA 500 operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C measurements, using DMSO-d_6 as solvent with tetramethylsilane as a reference. The mass spectra were recorded on a Finnigan Mat 312 (70 eV) spectrometer. Magnetic susceptibilities were measured by the Gouy method. Diamagnetic corrections were made using Pascal's constants. Microanalyses of C, H, N, and S were performed by the Microanalytical Center, King Abdul Aziz University, Jeddah,

KSA. Molar conductances in DMF were measured at room temperature using a conductance bridge of the type YSI model 32.

Synthesis of *N*-Ethyl-*N*′-pyrimidin-2-ylthiourea (HL^1)

The ligand HL^1 was prepared by boiling under reflux an equimolar ratio of 2-aminopyrimidine and ethylisothiocyanate for 12 h in anhydrous toluene. The reaction product was filtered off and crystallized from toluene. White, needle-like crystals of *N*-ethyl-*N*′-pyrimidin-2-ylthiourea (HL^1) (yield: 70%; mp 162–163°C) were obtained. The ligand was characterized by elemental analysis (Table I), by mass spectrometry, and ^{1}H NMR, ^{13}C NMR, and IR spectral measurements as follows: MS: *m/z* 182 (M^+, molecular ion peak) and *m/z* 148, 139, 96 assignable to the cations $PmN{=}C{=}NCH_2CH_3^+$, (Pm = pyrimidine) $PmNHC(S)H^{+\cdot}$, and $SCNCH_2CH_3^+$, respectively. ^{1}H NMR (δ, 500 MHz, d^6-DMSO): 11.13 {1H, N1H, s}, 10.57 {1H, N2H, s}, 8.65 {2H, two equivalent $H(4')_{pm}$ and $H(6')_{pm}$, d}, 7.15 {1H, $H(5')_{pm}$, d}, 3.58{2H, CH_2, q} and 1.16{3H, CH_3, t, $^3J = 6.32$ Hz}. ^{13}C NMR (δ, 125MHz, d^6-DMSO): 179.6 {C=S}, 158.1 {C(2′)}, 158.0 {C(4′, 6′)}, 116.1 {C(5′)}, 40.2{solvent + CH_2} and 14.3{CH_3}. IR (KBr disc, cm^{-1}): 3149 $\nu(N^1{-}H)$, 3012 $\nu(N^2{-}H)$, 1581 and 1529 ν(C=N + C=C of pyrimidine) and 768 ν(C=S).

Synthesis of *N*-Phenyl-*N*′-pyrimidin-2-ylthiourea (HL^2)

The ligand (HL^2) was synthesized by boiling equimolar quantities of 2-aminopyrimidine and phenylisothiocyanate under reflux for 24 h in acetonitrile. The reaction product was filtered off and recrystallized from glacial acetic acid, and white, needle-like crystals of *N*-phenyl-*N*′-pyrimidin-2-ylthiourea (HL^2) (yield: 75%; mp 212°C) were obtained. This ligand was characterized as shown in Table I and below. MS: *m/z* 230 (M^+, molecular ion peak) and *m/z* 196, 135, 95 assignable to cations of $PhN{=}C{=}NPm^+$,. $PhNCS^+$, and $PmNH_2^+$, respectively. ^{1}H NMR (δ, 500 MHz d^6-DMSO): 13.21 {1H, N1H, s}, 11.05 {1H, N2H, s}, 8.71{2H, two equivalent H(4′) and H(6′), d}, 7.72 {2H, H(2) and H(6), d}, 7.37 {2H, H(3) and H(5), t, $^3J = 7.55$ Hz} and 7.23 {2H, $H(4)_{Ph}$ and $H(5')_{Pm}$, m}. ^{13}C NMR (δ, 125 MHz, d^6-DMSO): 178.9 {C=S}, 159.2 {C(2′)}, 158.4 {C(4′, 6′)}, 139.2 {C(5′)}, 129.0{C(1)}, 126.3{C(2,6)}, 125.1{C(3,5)} and 116.0{C(4)}. IR (KBr disc, cm^{-1}): 3149 $\nu(N^1{-}H)$, 3012 $\nu(N^2{-}H)$, 1581 and 1529 ν(C=N + C=C of pyrimidine) and 768 ν(C=S).

Synthesis of Palladium(II) and Platinum(II) Complexes

$[Pd(HL)Cl_2]$ was prepared according to the following procedure. First, a solution of $[PdCl_4]^{2-}$ was made by boiling $PdCl_2$ (0.0025 mol) in conc. HCl (10 mL), cooling, and then diluting with distilled H_2O (30 mL). Secondly, a hot solution of HL^1 or HL^2 (0.0025 mol) in EtOH (25 mL) was mixed with this tetrachloropalladate(II) solution. The mixture was heated with stirring for 24 h under refluxing conditions. The orange precipitated complex, which formed while the solution was hot, was filtered off, washed with hot EtOH followed by Et_2O, and dried in vacuo over silica gel.

$[Pd(HL^1)_2]Cl_2$ was prepared by an analogous method employed to obtain $[Pd(HL)Cl_2]$, except that a hot solution of HL^1(0.005 mol) in EtOH (50 ml) was mixed with the aqueous tetrachloropalladate (0.0025 mol). The crude product was washed successively with H_2O, hot EtOH, and Et_2O, and then dried in vacuo over silica gel.

$[Pt(HL)Cl_2]$ was prepared by addition of a solution HL^1 or HL^2 in ethanol to an aqueous solution of $K_2[PtCl_4]$ under reflux, in a 1:1 ligand:metal molar ratio. The mixture was heated with stirring for 12 h and then cooled. The resulting solid was filtered off; washed with H_2O, EtOH, and Et_2O; and dried in vacuo over silica gel.

$[M(L)_2]$ was prepared by heating a mixture of the $PdCl_2$ or $PtCl_2$ (0.002 mol) and the ligand HL^1(0.004mol) or HL^2 (0.004 mol) for 2 h under reflux temperature in Me_2CO (50 mL). The precipitated products were collected by filtration, washed with Me_2CO, and dried in vacuo over silica gel.

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