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'Model Complexes' of Palladium(II) and Platinum(II) with Pyrazole- and Pyrimidine-derived Ligands of Biological Interest

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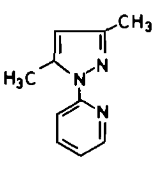
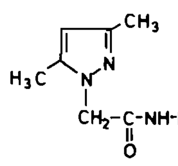
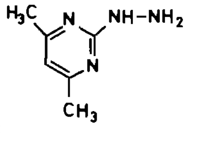
The remarkable anti-tumour activity of *cis*-dichlorodiammine platinum(II) [1] and related species has stimulated research in the design and synthesis of a considerable number of 'model metal complexes' [2] which could mimic the interaction of metal ions with DNA. As part of our current research programme [3] of investigating the coordination characteristics of biologically important diazoles and diazines, we report here the synthesis and spectroscopical identification of six new Pd(II) and Pt(II) complexes of the type $MLCl_2$ [where L = a pyrazole- or pyrimidine-derived ligand – (i) 3,5-dimethyl-1-(2′-pyridyl)pyrazole (DPyPz) [4], (ii) α-(3,5-dimethyl-1-pyrazolyl)acetohydrazide (DPzH) [5]; (iii) 2-hydrazino-4,6-dimethylpyrimidine HDPym) [6] which might have potential anti-cancer activity.


(DPyPz)


(DPzH)


(HDPym)

Experimental

The ligands were synthesised and characterised as described earlier [4–6].

Preparation of the Pd(II) and Pt(II) Complexes

To an alcoholic solution (30 ml) of the ligand (2.5 mmol)** was added with stirring an aqueous solution of K_2PtCl_4 (2.5 mmol; 1.0 g in 50 ml water) or of $PdCl_2$ (2.5 mmol, 0.45 g in 20 ml water) at water bath temperature. The resulting mixture was kept over a water bath for 30 min, by which time the desired compound (Table I) had settled down. It was filtered, washed well with water and alcohol and finally dried over anhydrous $CaCl_2$.

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**2.5 mmol ligand – 0.43 g DPyPz; 0.42 g DPzH and 0.35 g HDPym.

TABLE I. Analytical Data and Some Important Properties of the Compounds.

Compound (Colour)	Elemental Analyses: Found (Calcd)			Electronic Spectral data in DMF in kK (ε)	FIR data in cm^{-1}	
	%Pd/Pt	%C	%N		νM–N (ring)	νM–Cl
$Pd(DPyPz)Cl_2$[a]	30.60	33.73	10.62	26.45(210.9), 35.72(3409.5);	295(w), 260(ms)	305(ms); 280(ms)
(Pinkish yellow)	(30.42)	(34.22)	(10.67)	37.32(3841.5)		
$Pt(DPyPz)Cl_2$[a]	44.37	28.00	9.71	33.01(4088.5);	300(ssh); 275(ms)	330(s); 315(s)
(Pinkish yellow)	(44.41)	(27.33)	(9.57)	37.17(7405.0)		
$Pd(DPzH)Cl_2$[b]	31.21	23.81	16.24	34.48(3268.0)	300(w); 470(ms)[d]	310(ms); 285(ms)
(Yellow)	(30.86)	(24.30)	(16.20)	37.87(2542.0)	470(ms)[d]	285(ms)
$Pt(DPzH)Cl_2$[b]	45.73	20.02	12.79	37.32(7204.0)	300(ssh); 460(ms)[d]	340(ms); 325(w)
(Light yellow)	(44.92)	(19.36)	(12.90)			
$Pd(HDPym)Cl_2$[c]	41.53	27.77	21.89	32.25sh (1118.0);	260(ms). 490(s)[d]	295(s), 280(w)
(Reddish yellow)	(41.58)	(28.05)	(21.82)	37.45(2858.0)		
$Pt(HDPym)Cl_2$[c]	48.19	17.68	13.80	37.00(11,720.0)	270(ms), 480(ms)[d]	330(ms); 320(s)
(brown)	(48.26)	(17.82)	(13.85)			

[a] DPyPz = 3,5-dimethyl-1-(2′-pyridyl)pyrazole. [b] DPzH = α-(3,5-dimethyl-1-pyrazolyl)acetohydrazide. [c] HDPym = 2-hydrazino-4,6-dimethylpyrimidine. [d] Metal nitrogen frequency due to hydrazine residue.

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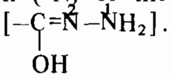
The metal contents in the complexes were determined gravimetrically as palladium dimethyl glyoximate and as metallic platinum. The C, H and N analyses were carried out in the microanalytical laboratory. Physico-chemical measurements were done as reported earlier [4–6].

Results and Discussion

Analytical and physico-chemical data are compiled in Table I. The compounds are insoluble in water and other organic solvents; they are, however, appreciably soluble in coordinating solvents like DMF The Λ_m values in DMF solution indicate the non-electrolytic nature of the complexes [$\Lambda_m \approx 5–20$ mho cm^2]. The compounds are all diamagnetic in nature, as expected indicating square-planar configuration for all the complex species. The electronic spectra in DMF showed no absorption maxima below 26.00 kK; the noticeable bands in the 33.0–38.0 kK range, associated with high molar extinction coefficients ($\epsilon \sim 2{,}000–12{,}000$), may be ascribed to $M \rightarrow L\pi^*$ CT phenomena with possible inter and/or intra ligand transitions [7]. The band appearing at 26.45 kK in the case of Pd(DPyPz)Cl$_2$ can be safely assigned to $^1A_{1g} \rightarrow {}^1E_g$ transitions [8] in a planar configuration.

In view of the neutral bidendate functioning of the concerned ligands [4–6], the complexes could be presumed to have *cis*-configurations. The participation of ring nitrogen and that of hydrazine tail (in the case of DPzH and HDPym complexes) are ascertained from the vibrational spectra of the complexes (Table I) The (+) ve shifts of the ring vibrational modes in the metal complexes compared to the uncomplexed ligands indicate possible attachment through respective ring nitrogen atoms; the appearance of new bands in the far IR region at ~300 and 270 cm^{-1} attributed to νM–N(ring) [9] gives support to this position. The band appearing at ~480 cm^{-1} range can then be assigned to νM–N (hydrazine residue) [10] In case of M(DPzH)Cl$_2$, the bonding of the ligand to Pd or Pt is expected [5] to occur through iminic nitrogen of pyrazole ring as well as the amide nitrogen (^{2}N) of the hydrazide residue in its 'imidol' form  $[-\underset{\displaystyle OH}{\underset{|}{C}}=\overset{2}{N}-\overset{1}{N}H_2]$.

The IR bands at ~1600(s) cm^{-1} [ν_{asym} (C=$\overset{2}{N}$)], ~1550 (ms) cm^{-1} [ν,(NCO-)], ~1290(s) cm^{-1} [ν_{sym} (C=$\overset{2}{N}$)] and ~1060 (ms) cm^{-1} [ν(C–O-)] which occur in the metal complexes definitely stand in favour of the above proposition [11]. The far IR spectra of all the species showed the presence of two strong to medium-strong Pd–Cl [at 305 and 285 cm^{-1}] and Pt–Cl [at 330 and 320 cm^{-1}] stretching vibrations (A_1 and B_1 in C_{2v} symmetry) confirming *cis*-geometry [12]. The reported complexes might have anti-cancer activity

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