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Metal Complexes of Pyrimidine-derived Ligands. VII*. Palladium(II), Platinum(II) and Rhodium(III) Complexes with 3,5-Dimethyl-1-(4′,6′-dimethyl-2′-pyrimidyl)pyrazole, a Potential Anti-cancer Agent

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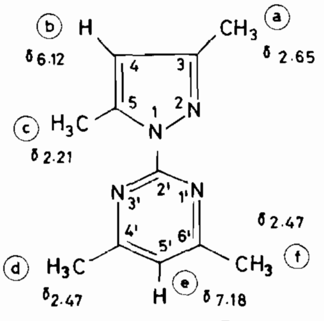
Abstract

Using 3,5-dimethyl-1-(4′,6′-dimethyl-2′-pyrimidyl)pyrazole (DPymPz) as a coordinating ligand, palladium(II), platinum(II) and rhodium(III) complexes of the type [M(DPymPz)X_2] (M = Pd(II), X = Cl, Br, I, SCN, ClO_4, NO_2, NO_3; M = Pt(II), X = Cl, Br, SCN, NO_2) and [Rh$(DPymPz)_2X_3$] (X = Cl, Br, I) habe been isolated in the solid state and characterized on the basis of analytical, magnetic and spectral (diffuse reflectance, UV–Vis, IR and ^{1}H NMR) properties, together with powder X-ray diffraction studies. The Pd(II) and Pt(II) complexes are square-planar as expected and the Rh(III) species have pseudo-octahedral geometry. The calculated ligand field parameters are in favour of the proposed stereochemistry of the complexes. IR data point out the pyrazolyl nitrogen (tertiary) and one of the pyrimidyl nitrogens of DPymPz as bonding sites in forming these complexes.

Introduction

Investigations relating to the interactions of platinum metal ions with nucleic acids and their constituents have attained a special status because these metal ions are primarily known to play a significant role in the cause and treatment of malignancy [1, 2]. The high specificity of a *cis*-environment around Pt(II) in cisplatin has actually excited tremendous global interest in studies relating to the design, synthesis and characterization of model complexes [3] which could mimic the interactions of metal ions with DNA. A fair number of *cis*-Pt(II) complexes with N-donor ligands containing labile anions have been well characterized for their cytostatic activities [4–6]. Complexes of other metal ions, particularly those of Ni(II), Zn(II), Pd(II), Rh(III) and Ru(III) [7], in this field show promising activity with less toxic effects, sometimes even superior to the well-known Pt(II) species. In the present paper, the syntheses and physicochemical characterizations of Pd(II), Pt(II) and Rh(III) complexes with a bidentate (N–N) donor ligand (*viz.* 3,5-dimethyl-1-(4′,6′-dimethyl-2′-pyrimidyl)pyrazole) [8], a potential anticancer agent [9], are reported.



[DPymPz]

Fig. 1. The [DPymPz] ligand molecule.

Experimental

The platinum metal salts used were purchased from Johnson-Matthey (London). The title ligand was synthesized and characterized as described earlier [8]. Palladium(II) perchlorate was prepared by adding dilute perchloric acid dropwise to dissolve the freshly precipitated $Pd(OH)_2$ and was kept in a desiccator over fused $CaCl_2$; dark brown crystals of $Pd(ClO_4)_2 \cdot 4H_2O$ were deposited.

Preparation and Analyses of Reported Complexes

[M(DPymPz)Cl_2] (M = Pd(II) or Pt(II))

The aqueous acidic solution of each metal(II) chloride (pH ~ 3–4) (2.5 mmol in 20 ml water) was mixed with an ethanolic solution of the ligand (2.5 mmol, 0.50 g) and the resultant yellowish brown solution was refluxed for 15 min at water-bath

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temperature and then left at room temperature (~30 °C). The precipitated compounds were filtered off, washed well with ice-cold water–ethanol (1:1) mixture and finally dried over fused $CaCl_2$.

[M(DPymPz)X_2] (M = Pd(II), X = Br, I, SCN, NO_3, NO_2; M = Pt(II), X = Br, I, SCN)

The diacido complexes were prepared by metathesis reactions which involve, in each case, refluxing an aqueous suspension of [M(DPymPz)Cl_2] (M = Pd(II), Pt(II)) with two molar proportions of the ammonium or sodium salts of corresponding anions at water-bath temperature for 30 min. The resulting solution on cooling to room temperature gradually yielded a microcrystalline product, with varying colours in each case, which was collected as before.

[Rh(DPymPz)$_2X_2$]X (X = Cl, Br, I)

An aqueous solution of $RhCl_3 \cdot H_2O$ (2.5 mmol in 20 ml water) was refluxed with an ethanolic solution of the ligand (5.0 mmol, 1.0 g) for about 3 h, after which a pale yellow solution resulted. This, on concentration and cooling, deposited pale yellow crystals of the bis-chelate corresponding to the composition Rh(DPymPz)$_2Cl_3$. If the solution after reflux were concentrated in the presence of a saturated aqueous solution of KBr or KI, the corresponding diacido complex was formed. The product was filtered off in each case, washed with a few drops of ethanol, then ether, and dried in air.

Analytical results, together with the colour, magnetic moment and conductance values of the complexes, are presented in Table I. The metals (Pd or Pt)

TABLE I. Analytical and some Physical Data for the Pd(II), Pt(II) and Rh(III) Complexes of DPymPz

Complex[a] (colour)	Elemental analyses, found(calc.) (%)			Molar conductance λ_m (mho cm^2 mol^{-1}) in 1×10^{-3} M solution in DMF (30 °C)	Far IR data (cm^{-1})		
	Pd, Pt, Rh	C	N		ν(M–N)(Pym)	ν(M–N)(pz)	ν(M–X)
$PdLCl_2$	28.1	34.7	14.7	20	242(w)	258(w)	305(m)
(creamy yellow)	(27.9)	(34.5)	(14.1)				280(m)
$PdLBr_2$	22.7	28.6	11.5	14			
(yellowish red)	(22.0)	(28.0)	(11.8)				
$PdLI_2$	18.8	23.6	9.4	8			
(dark brown)	(18.4)	(23.9)	(9.8)				
$PdL(SCN)_2$	25.1	31.8	19.5[b]	15	244(w)	262(w)	
(red)	(25.7)	(31.1)	(19.9)				
$PdL(NO_2)_2$	26.6	32.1	20.5[c]	10	240(w)	260(w)	
(pinkish yellow)	(26.4)	(32.8)	(21.9)				
$PdL(NO_3)_2$	24.7	30.1	19.4[d]	12	246(m)	258(m)	
(reddish yellow)	(24.6)	(30.8)	(19.3)				
$PdL(ClO_4)_2$	21.4	26.2	11.2	17	242(w)	260(w)	
(pale brown)	(21.2)	(26.8)	(10.9)				
$PtLCl_2$	41.6	28.1	11.6	16	248(m)	268(m)	335(m),
(creamy yellow)	(41.0)	(28.3)	(11.0)				320(ms)
$PtLBr_2$	35.2	23.0	11.5	14			
(brown)	(35.8)	(23.6)	(10.8)				
$PtL(SCN)_2$	38.2	25.3	16.7[b]	8	244(m)	262(w)	
(yellowish brown)	(38.9)	(25.6)	(16.5)				
$PtL(NO_2)_2$	39.8	27.0	17.7[c]	16	246(w)	262(w)	
(yellow)	(39.6)	(26.8)	(17.2)				
$Rh(L)_2Cl_3$		43.7	18.7	22	450(m)	390(ms)	245(ms)
(pale yellow)		(42.2)	(17.9)				
$Rh(L)_2Br_3$		35.9	15.1	18			
(reddish brown)		(35.2)	(15.2)				
$Rh(L)_2I_3$		29.6	12.6	13			
(brown)		(29.6)	(12.4)				

[a] L = one molecule of 3,5-dimethyl-1-(4',6'-dimethyl-2'-pyrimidyl)pyrazole. [b] Including nitrogen present as thiocyanate. [c] Including nitrogen present as nitrite. [d] Including nitrogen present as nitrate.

were estimated by standard analytical procedures [10]. Magnetic susceptibilities of the compounds were measured by a Gouy balance using Hg[Co(SCN)$_4$] as the calibrant. The diffuse reflectance spectra of the complexes were taken with a Cary 17D spectrophotometer with a reflectance attachment model No. 1711. The electronic spectra of the solutions of the metal complexes were recorded using the same spectrophotometer using DMF as solvent. IR spectra were recorded on a Perkin-Elmer spectrometer (model No. 577) using CsI phase. X-ray powder diffraction photographs of the ligand and a few representative complexes of Pd(II) and Pt(II) were taken with a Debye-Scherrer camera of diameter 114.6 nm using a copper target (Cu Kα = 1.542 Å); operating voltage was 33 kV with tube current of 10 mA; time of exposure was 8 h. The 80 MHz PMR spectra of the ligand and some Pd(II) and Pt(II) complexes in DMSO-d$_6$ were recorded on a Varian CFT-20 NMR spectrometer.

Results and Discussions

Analytical data of the reported Pd(II), Pt(II) and Rh(III) complexes (Table I) support the formulations given therein. Conductivity measurements (Table I) in DMF indicate that Pd(II) and Pt(II) complexes are non-electrolytes, while Rh(III) complexes behave as (1:1) electrolytes, the species being truly represented as [Rh(DPymPz)$_2$X$_2$]X. The overall solubility of the complexes in common solvents is very poor. All the reported Pd(II), Pt(II) and Rh(III) species are diamagnetic, as expected.

Electronic Spectra

In the electronic absorption spectra of Pd(II) and Pt(II) (d^8 system) in a square-planar environment, three spin-allowed transitions ($^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$) are expected; on the basis of Gaussian analyses of the reflectance spectra of the examined Pd(II) or Pt(II) complexes (except the iodo derivatives) (Fig. 2 shows a representative curve), four bands are obtained at 18 200, 20 400, 25 640 and 32 260 cm^{-1}. The first low-energy spin-allowed band in the region 18 200 cm^{-1} has been assigned to the transition $b_{2g}(xy) \rightarrow b_{1g}(d_{x^2-y^2})$, *i.e.*, $^1A_{1g} \rightarrow {}^1A_{2g}$, comparable to the transition assigned by Jørgensen [11], although in MCl$_4^{2-}$ (M = Pd(II), Pt(II)) this transition was observed between ~16 700–17 600 cm^{-1}. The blue shift is ascribed to the stereochemical difference between the ligand and the chloride ion. The bands at 25 640 and 32 260 cm^{-1} are spin-allowed transitions which probably originate from the transitions $a_{1g}(z^2) \rightarrow b_{1g}(x^2-y^2)$ (*i.e.*, $^1A_{1g} \rightarrow {}^1B_{1g}$) and $e_g(yz, zx) \rightarrow b_{1g}(x^2-y^2)$ (*i.e.*, $^1A_{1g} \rightarrow {}^1E_g$), respectively. The transitions in increasing order of energy suggest square-planar environment around the metal ion [12]. The values of Δ_1 (~25 000 cm^{-1}), Δ_2 (~9500 cm^{-1}) and Δ_3 (~3900 cm^{-1}) were calculated from known relationships [12]. The values of Δ_1 were found to be larger than the combined values of Δ_2 and Δ_3. These observations strongly suggest square-planar geometry of the complexes.

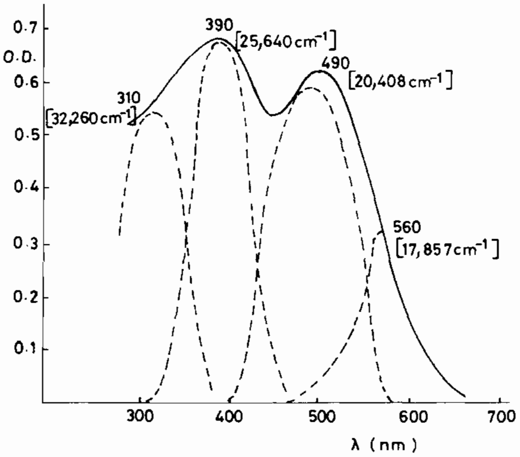

Fig. 2. Gaussian analysis of the reflectance spectrum of a representative Pd(II) complex.

The electronic absorption spectra of the DMF solutions of the complexes do not show ligand field bands in the visible region; they exhibit strong absorption peaks below 23 000 cm^{-1} which probably envelope the expected bands in a square-planar environment [13]. A number of spectral bands between 31 250–42 550 cm^{-1} with high extinction values of the order 10^4 l cm^{-1} mol^{-1} are noticeable; these are ascribed to MLCT bands with possible inter/intra ligand transitions [14].

The diamagnetic spin-paired Rh(III) (d^6 system) with octahedral stereochemistry belongs to the $^1A_{1g}$ ground state. Two absorption bands observed in the regions 21 640–22 390 cm^{-1} and 29 600 to 30 315 cm^{-1} are attributable to two spin-allowed transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ (α_1) and $^1A_{1g} \rightarrow {}^1T_{2g}$ (α_2), respectively, for the $(t_{2g})^5(e_g)^1$ configuration. The first two bands in the regions of 15 000–15 500 cm^{-1} and 19 200–19 600 cm^{-1} may be taken as the split components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in octahedral complexes [15]. The complexes might have a lower symmetry than O_h as $^1A_{1g}$ splits into $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ in order of increasing energy in D_{4h} symmetry. The observed lower-energy absorption bands, which are split to a very much greater extent, indicate that the examined species are *trans*-isomers [16]. The values of different crystal field parameters [α_2/α_1 ~ (1.36–1.39), 10 Dq (23 628–24 594 cm^{-1}), B (497–551 cm^{-1}), β (0.69–0.72), F_2 (870–950 cm^{-1}), F_4 (57–63 cm^{-1})] and ligand field stabilization energy (121–126 kcal/mol) were calculated from

TABLE II. ^{1}H NMR Chemical Shifts of DPymPz and some of its Pd(II) and Pt(II) Complexes in DMSO-d_6

Protons	a	b	c	d	e	f
Free ligand	2.55	6.12	2.21	2.47	7.18	2.47
Pd(DPymPz)Cl_2	2.65	6.45	2.23	2.49	7.43	2.50
Pd(DPymPz)Br_2	2.68	6.48	2.24	2.50	7.44	2.56
Pd(DPymPz)$(NO_2)_2$	2.63	6.45	2.21	2.49	7.36	2.54
Pd(DPymPz)$(ClO_4)_2$	2.56	6.46	2.24	2.48	7.35	2.50
Pt(DPymPz)$(NO_2)_2$	2.68	6.47	2.24	2.48	7.30	2.52
Pt(DPymPz)$(SCN)_2$	2.56	6.30	2.20	2.52	7.32	2.52

known relationships [17] and are in good agreement with an octahedral Rh(III) ion. Decreased values of B as compared to a corresponding free ion value of 720 cm^{-1} suggest a considerable overlap with a strong covalency in the metal–ligand σ-bond. Reduced values of B are also associated in the reduction of effective cationic charge which can be calculated as follows:

$$B = 472 + 28q + 50(z^* + 1) - \frac{500}{(z^* + 1)}$$

q = number of electrons in the partly filled 4d levels in the Rh(III) ion

The z^* values ($\sim$1.50–1.56) are considerably below the formal (+3) oxidation state of Rh(III). In DMF, the complexes, in addition to the d–d bands, exhibit bands around 32 500 cm^{-1} which can be assigned to π–π^*(C≡N) transitions of the ligands.

^{1}H NMR Spectra

^{1}H NMR spectra of a few Pd(II) and Pt(II) complexes (two representative spectra are shown in Fig. 3) as compared to that of the free ligand reveal that there is an appreciable downfield shift (Table II) of almost all the protons present in the ligand. However, the aromatic protons at the (b) and (c) positions (Fig. 1) are found to suffer maximum downfield shifts owing to them having positions closest to the binding sites of the ligand [18]. The observed changes in chemical shifts (Table II) on complexation may be ascribed to an electric field effect caused by complexation through π-bonding [19]. Therefore, it is highly probable that the title ligand exhibits a neutral bidentate function through the N2 of the pyrazole and the N1$'$ of the pyrimidine ring (this is further substantiated later by far IR data).

IR Spectra

The IR spectrum of the uncomplexed ligand (DPymPz) furnishes recognisable bands in the region 1600–1400 and at 1000 and 750 cm^{-1} due to the ν(C···C) + ν(C···N) and out-of-plane deformations, respectively, of both the 1,2-diazole (pyrazole) and the 1,3-diazine (pyrimidine) systems. In the spectra of the metal complexes these bands experience positive shifts ($\Delta\nu \sim$ 10–15 cm^{-1}) which tentatively point to the participation of the ring hetero-nitrogens (*viz.* N2 and N1$'$) in complexation, which is in agreement with earlier observations [8, 20]. Evidence for a metal–nitrogen bond in the case of Pd(II), Pt(II) and Rh(III) complexes is shown by the appearance of bands in the regions 240–266 and 450–490 cm^{-1} which can be safely assigned to ν(M(II)–N) [21], (M(II) = Pd(II), Pt(II)), ν(Rh(III)–N) [22, 23], respectively, in accordance with the assignments given by earlier workers.

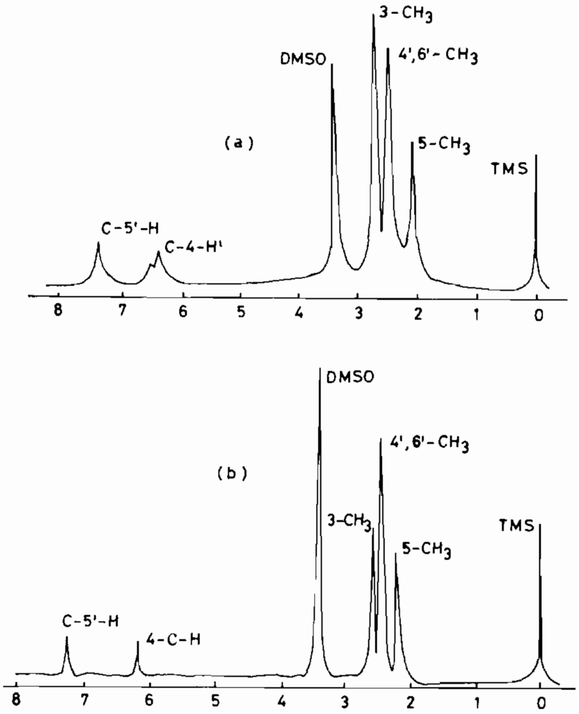

Fig. 3. ^{1}H NMR spectra of representative Pd(II) and Pt(II) complexes in DMSO-d_6.

Chloro complexes

The far IR spectra of the present Pd(II) and Pt(II) complexes show the presence of two strong to medium–strong ν(Pd–Cl) (at 305 and 285 cm^{-1})

and ν(Pt–Cl) (at 335 and 320 cm^{-1}) stretching vibrations (A_1 and B_1 in C_{2v} symmetry) confirming *cis*-geometry [24]. In case of the chloro complex of Rh(III), *trans*-configuration [25] is suggested due to the appearance of one ν(Rh–Cl) (medium–strong) band at 275 cm^{-1}.

Thiocyanate complexes

In the cyanate complexes of Pd(II) and Pt(II), a strong sharp band around 2105–2115 cm^{-1} and a weak band at 2060–2085 cm^{-1} are observed due to ν(C≡N) stretching of the coordinated thiocyanate group [26]. The ν(C–S) stretching band is located near 690–710 cm^{-1}, indicating a sulphur-bonded (SCN) group [27], which is quite consistent with the soft character of Pd(II) and Pt(II). Due to accidental degeneracies caused by the heavy metal ion, only one band is obtained in the region 2160 cm^{-1} instead of two split bands in the case of *cis*-attachment of the thiocyanate group [28]. The absence of a medium intensity band around 500–460 cm^{-1} can be assigned to the absence of δ_{NCS} of a N-bonded thiocyanate [29].

Nitrito complexes

In the case of nitrito complexes of Pd(II) and Pt(II), four bands are obtained at 1400–1410(vs,br), 1310(ms)–1320(vs), 1270(s)–1285(ms) and 830(s)–840(s) cm^{-1}, which are assigned to the split components $\nu_{as}(NO_2)$, $\nu_{sym}(NO_2)$ and δ_{ONO} vibrations. The splitting of the $\nu_{sym}(NO_2)$ vibration indicates a *cis*-bonded nitrito group [30]. In each case, ν_{as}-(NO_2) as well as $\nu_{sym}(NO_2)$ vibrations are raised to higher frequency regions, suggesting that the nitrito group is coordinated through the nitrogen atom in these complexes [31]. The *cis*-isomers exhibit, in addition, a third fairly broad band in the region 1345–1330 cm^{-1}, probably due to the lower symmetry of the *cis*-compounds [32].

Nitrate complex

The $Pd(DPymPz)(NO_3)_2$ complex shows three bands at 1430(ms), 1315(s) and 830(s) cm^{-1}. The first two bands can be assigned to the components of ν_3 and the last one to ν_2 vibration of a monodentate nitrate group in C_{2v} symmetry [33]. The splitting of some bands arises from the lower symmetry of these compounds due to the two nitro groups being in the *cis*-position.

Perchlorate complex

In the case of $Pd(DPymPz)(ClO_4)_2$, the IR band of the perchlorate group due to a Cl–O stretching frequency at 1100 cm^{-1} is split into three components at 1080, 1110 and 1145 cm^{-1}. The extent of splitting suggests that the perchlorate ion is coordinated as a monodentate one in C_{3v} symmetry [34]. The *cis*-attachment of the anions in these complexes could not be proved by dipole moment measurements as the Pd(II) and Pt(II) complexes are insoluble in benzene.

Powder X-ray Diffraction

The photographs of the Pd(II) and Pt(II) complexes under study contain a large number of lines, many of which are weak. This suggests that the complexes crystallize in low symmetry [35]. X-ray powder patterns showed no trace of unreacted ligand in the metal complexes [36].

Conclusions

Based on the interpretations of the above experimental data obtained through various physicochemical measurements, it may be reasonably accepted that the mono ligated complexes of Pd(II) and Pt(II) with 3,5-dimethyl-1-(4′,6′-dimethyl-2′-pyrimidyl)pyrazole with different counterions are square-planar *cis*-complexes, whereas the bis-complexes of Rh(III) are essentially octahedral.

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