Asian Journal of Chemistry Vol. 7, No. 3 (1995), 465–470

Studies on Platinum(II) and Palladium(II) Complexes of some Substituted Pyrazole-5-ones, Pyrazoles, Arylhydroxy Pyrazoles and Pyrano Pyrazoles

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The coordination behaviour of several pyrazole-5-ones and pyrazoles derivatives with platinum(II) and palladium(II) metals have been reported by the isolation and characterization of the resulting complexes. These complexes possess a square planer structures (*cis*-form) as revealed from IR and NMR spectral data. The ligands were coordinated mainly through the N—N linkage of the pyrazole ring.

INTRODUCTION

Many substituted pyrazole-5-ones, pyrazoles and their analogues have recieved a special attention, because of their metal binding properties at various positions[1–10]. On the other hand, metal complexes of pyrazole-based ligands are known to play a significant role in many biological processes including anti-bacterial and antitumour activities[11–14].

As a continuation of our previous work in this field[15, 16], we are presenting herein two types of potential reactions. First, the reaction of nine different pyrazole-5-ones, pyrazoles with the complex *cis*-$[Pt(DMSO)_2Cl_2]$. Second, the reaction of 3-methyl pyrazole-5-one, arylhydroxy pyrazoles, and 1H,4H-pyrano[2,3-c]pyrazole-4-one with the complex *trans*-$[Pd(DMSO)_2Cl_2]$, in an attempt to obtain *cis*-complexes analogues to so-called cisplatin, *i.e.*, *cis*-$[Pt(NH_3)_2Cl_2]$, that might have biological activity.

EXPERIMENTAL

Melting points of the synthesized complexes were determined with a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra of choosen complexes were taken on a Bruker WH90 DS spectrometer equipped with ASPECT 2000, 32K Computer, operating at 22.63 MHz. IR spectra for Nujol mulls were obtained on an SP 2000 spectrometer at a range between 4000–200 cm^{-1}. Elemental analysis were carried out on CHN Analyzer type 1106 (Carlo Erba).

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Preparation of the starting meaterials:

1. Pyrazole-5-ones, pyrazoles, arylhydroxy pyrazoles and pyrano pyrazole were prepared according to the reported procedurs[17-24]
2. The *cis*-dichlorobis (dimethyl sulphoxide) platinum(II); *cis*-$Pt(DMSO)_2Cl_2$] and the analogues palladium complex, *i.e.*, *trans*-[$Pd(DMSO)_2Cl_2$] were prepared and characterized as described in the literature[25].

Preparation of the complexes:

The platinum(II) and palladium(II) complexes of pyrazole derivatives were prepared according to previous procedure[16], which is as follows:

$$[M(DMSO)_2Cl_2] + L \xrightarrow{\text{solvent}} [MLCl_2] + 2DMSO$$

M = Pt, *cis*-; Pd, *trans*, L = pyrazole ligands

An equimolar quantities of the complex [$M(DMSO)_2Cl_2$] and the ligand (pyrazoles) were mixed together in ethanol or chloroform under nitrogen atmosphere at ambient temperature. The reaction mixture was stirred for several hrs, and in the mean time, the suspension turned clear coloured solution. Slow evaporation of some of the solvent leaves the crystalline product. The crystals were washed several times with hexane and dried *in vacuuo* for several hrs. The yield is almost quantitative.

RESULTS AND DISCUSSION

In the present work, the series of platinum(II) complexes of the ligands (Ia, b, c; IIa, b, c, d, e; III) and palladium(II) complexes of the ligands (Ia, IV; Va, b) (Scheme 1) were prepared from the direct raction between the complexes *cis*-[$Pt(DMSO)_2Cl_2$] or *trans*-[$Pt(DMSO)_2Cl_2$] and the corresponding pyrazole analogues ligands (I–V). All of these complexes were isolated as coloured solids and are soluble in various solvents, *e.g.*, DMSO and DMF.

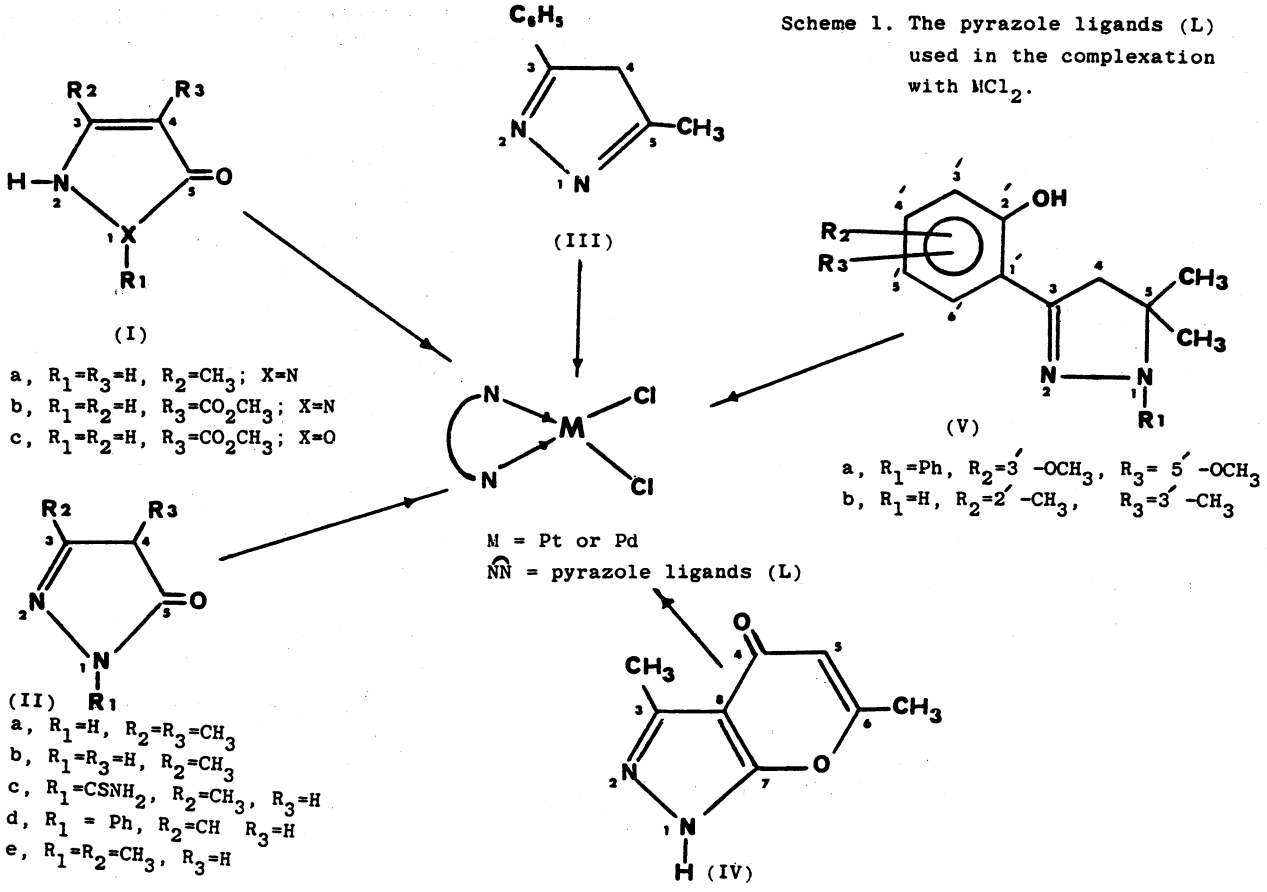
The synthesized platinum and palladium complexes were characterized and their structures were assigned on the basis of CHN elemental analyses, IR and NMR spectroscopy. The elemental analysis of most of the complexes obtained were satisfactory. The physical properties of the complexes are listed in Table-1. Their IR spectral data showed characteristic bands for the stretching frequencies, *e.g.*, M—Cl and M—N bonds. A double bands at *ca.* 315 and 350 cm^{-1} are due to ν(M—Cl)[16] and assigned as *cis*-platinum and *cis*-palladium (since the *trans*-isomer gives only single band). Other double bands at *ca.* 450 and 585 cm^{-1} are attributed to the ν(M—N) for these complexes, *i.e.*, a three member ring chelating complexes *via* both nitrogen atoms of the pyrazole unit were obtained. It is quite often for the pyrazole units to behave as a bidentate ligands *via* its both nitrogens[17], with one exception for the ligands (Ic), in which platinum could well be coordinated *via* nitrogen and oxygen atoms of this unit. Other IR stretching frequencies, such as N—H, C=N, C=C and C=O also observed in the spectra (Table-1). ν(N—H) and ν(N—OH) in complexes containing these two functional groups were overlapped to give one broad band between 3500–3000 cm^{-1}.

TABLE-1
PHYSICAL PROPERTIES OF THE PLATINUM(II) AND PALLADIUM(II) COMPLEXES

Ligand (L)	M	Colour	m.p. (Dec.) (°C)	Characteristic IR data (cm^{-1})*					
				ν(N—H)	ν(C—N)	ν(C=N)	ν(C=C)	ν(M—Cl)	ν(M—N)
Ia	Pt	yellow	182–184	3500–3200 b	1330, m, b	1525 b	1595 s	352, 322 m	543, 520 m
b^x	Pt	light brown	120–122	3400–3200 b	1380 w	1550 m	1605 m	340, 315 m	460, 440 s
c^y	Pt	yellow orange	122–124	3220–3100 b	1390 m	—	1580 m	340, 320 s	528, 490 s, 315^z m
IIa	Pt	yellow orange	94–96	3500–3000 vb	1320 m	1610 m, 1550 m	—	350, 315 b	585 b
b	Pt	brownish	188	3400–3200 b	1335 b	1605 m, 1530 b	—	350, 332 s	542, 520 b
c	Pt	yellow orange	182–184	3550–3300 b	1320 w	1600 m, 1560 m	—	355, 342 m	465, 450 s
d	Pt	yellow	103–105	—	1320 w	1555 m	1605 m	340, 320 sh	545, 530 s
e	Pt	greenish	196–198	—	1325 w	1620 m, 1510 m	—	323, 318 s	518, 495 s
III	Pt	yellow orange	230–232	3200–3000 b	1310 s	1510 m	1590 m	350, 312 s	518, 480 m
$Ia^{x'}$	Pd	yellow orange	250	3400–3200 b	1300 b	1570 m	1630 m	350,300 m	550 b
$IV^{y'}$	Pd	brown	298	3500–3320 b	1305 b	1550 m	1595 s	350, 320 m	560, 530 m
Va	Pd	brown	300	—	1315 w	1580 m	1600 m	325, 310 m	440, 425 m
b	Pd	brown	214	3500–3410 b	1310 w	1580 m	166 m, b	330, 300 w	440, 420 w

*Abbreviations: s, strong; m, medium; w, weak; sh, shoulder and b, broad bands.
x, y Frequencies at 1750 and 1740 cm^{-1} are due to —$COOCH_3$ respectively.
x′, y′ Frequencies at 1710 and 1640 cm^{-1} are due to C=O respectively.
z Frequency at 315 cm^{-1} is due to Pt-O (ref. 28).

Scheme 1. The pyrazole ligands (L) used in the complexation with MCl_2.



In order to obtain some additional information about the complexes obtained, we investigated the ^{1}H NMR spectral data of some of these complexes, *e.g.*, (IIb-d; III; IV; Va, b) (Table-2). The ^{1}H NMR spectral data for complexes (IIb, c) gave signals of chemicals shifts between 5.2–5.4 ppm, integrate to one proton (H-4). This confirms that enol form of pyrazole-5-ones is more predominant than keto form in these complexes[26].

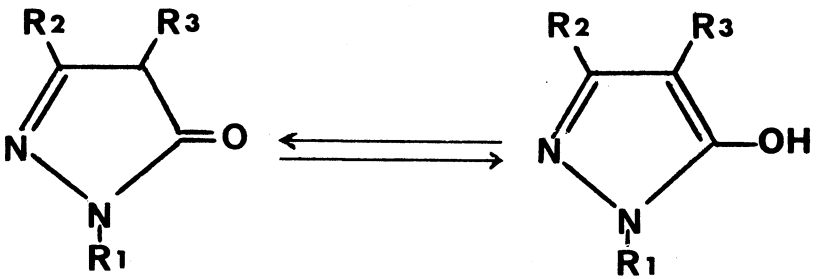


TABLE-2

^{1}H NMR SPECTRAL DATA* FOR SOME OF THE Pt(II) AND Pd(II) COMPLEXES

Ligand (L)	M	^{1}H NMR-data
II b^x	Pt	δ2.24, s, 3H, C3—CH_3; δ5.42, s, 1H, H-4
c^x	Pt	δ2.26, s, 3H, C3—CH_3; δ5.2, s, 1H, H-4
d^x	Pt	δ8.15–9.0, m, 5H, Ph, δ4.4, s, 2H —CH_2; δ3.12, s, 3H, CH_3
III^x	Pt	δ7.24–7.7, m, 5H, Ph; δ3.5, s, 2H, —CH_2; δ2.7, s, 3H, CH_3
IV^y	Pd	δ2.5, s, 3H, C3—CH_3; δ5.76, s, 1H, H-5; δ2.32, s, 3H, C6—CH_3
V a^y	Pd	δ1.39, s, 6H, C5—CH_3; δ2.64, s, 2H, H-4; δ3.82, s, 3H, C4—OCH_3; δ3.86, s, 3H, C6′—OCH_3; δ6.1, d, 1H, H-5′; δ6.22, d, 1H, H-3′; δ7.4–7.92, m, 5H, 1-Ph
b^y	Pd	δ1.32, s, 6H, C5—CH_3; δ2.55, s, 2H, H-4; δ2.06, s, 3H, C3′—CH_3; δ2.06, s, 3H, C4′—CH_3; δ7.62, d, 1H, H-5′, δ6.76, d, 1H, H-6′

*Downfield from internal TMS, using:
(x) $CDCl_3$, (y) DMSO-d_6 as solvents

Abbreviations: s, singlet, d, doublet; m, multiplet signals.

The ^{1}H NMR spectral data of other complexes confirmed the proposed structures (Scheme 1).

As a conclusion, pyrazole analogues ligands coordinate with platinum and palladium metals *via* both nitrogen atoms to give complexes analogues to so-called *cis*-platin; *cis*-$[Pt(NH_3)_2Cl_2]$ of a known biological activity as an antitumour agent. Our present complexes might have biological activity, since we have already shown their similar platinum and palladium complexes derived from some β-carboline alkaloids have a good activity aganist some tumour cells and virsuses[27]. Further investigations are in progress at our laboratories.

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(*Received*: 4 July 1994; *Accepted*: 1 November 1994) AJC-891