

NOTES

Studies on Some N-Donor Heterocyclic Mixed Ligand Complexes of Palladium(II) and Platinum(II).

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Complexes of the type $ML'L_2Cl_2$ where $M = Pd(II)$ and $Pt(II)$ $L =$ imidazole, 1-methyl imidazole, 1-vinyl imidazole and $L' =$ pyridine ML_2L'' where $H_2L'' =$ oxalic acid were prepared. The complexes were characterised by IR, UV-Visible spectra, electrical conductivity and 1H NMR data. All the complexes have square planar geometry.

A number of platinum metal complexes with imidazole and substituted imidazoles have been reported¹⁻⁸. A few complexes of these metals with some N-donor heterocyclic bidentate ligands were also reported⁹. In this work the synthesis and characterisation of a few mixed ligand complexes of Pd(II) and Pt(II) with 1-vinyl imidazole (1-VIm), 1-methyl imidazole (1-MeIm), imidazole (Im), pyridine (Py) and oxalic acid ($H_2C_2O_4$) are reported.

Preparation of the complexes

(i) $MLL'Cl_2$ ($M = Pd, Pt$; $L = Im, 1-MeIm, 1-VIm$; $L' = Py$): These complexes were prepared by mixing the metal chlorides and the ligands in 1 : 1 : 1 molar ratio in alcoholic solution. On stirring the solution for ~ 1 minute yellow precipitate occurred. It was filtered, washed with alcohol and dried in a desiccator.

(ii) ML_2L'' ($M = Pd$; $L'' = C_2O_4^{2-}$): PdL_4Cl_2 was prepared as reported earlier⁷. This was dissolved in distilled water and solution of oxalic acid in water was added in 1 : 1 molar ratio. On stirring the solution for ca 5 minutes yellow precipitate occurred. It was filtered, washed several times with water and dried. This method failed to yield the platinum complex.

The elemental analyses values (Table-1) of the complexes correspond to the molecular formulae assigned to them. All the complexes are light yellow and stable decomposing above 200°C. The non-electrolytic nature of the complexes was indicated by the conductivity values¹⁰ ($10-20 \text{ mol}^{-1} \text{ cm}^2 \text{ ohm}^{-1}$) in DMF at 25°C.

The IR spectra of the complexes $PdImPyCl_2$, $PtImPyCl_2$, and $PdIm_2C_2O_4$ show broad band in the region $3200-3400 \text{ cm}^{-1}$ due to symmetric NH stretch. The IR spectra of imidazole at ca 1573 cm^{-1} assignable to fundamental ring stretching mode has been shifted to ca 1600 cm^{-1} and the NH bending at ca 1145 cm^{-1} is also raised to ca 1150 cm^{-1} when complexes were formed.

TABLE 1
ANALYTICAL DATA ON THE COMPLEXES OF PALLADIUM(II)
AND PLATINUM(II)*

Complexes	Found (Calc)%			
	Metal	Nitrogen	Carbon	Hydrogen
PdImPyCl ₂	31.21 (32.76)		28.85 (29.57)	2.61 (2.79)
Pd1-VImPyCl ₂	29.78 (30.35)	12.11 (11.68)		
PtImPyCl ₂	48.03 (47.21)		23.34 (23.34)	2.33 (1.91)
PdIm ₂ C ₂ O ₄	28.86 (29.01)		27.58 (26.06)	2.62 (2.73)
Pd1-MeIm ₂ C ₂ O ₄	27.11 (26.96)	16.67 (14.19)		
Pt1-VImPyCl ₂	43.21 (44.41)	9.11 (9.56)		

*The value for chlorine also agree well with theoretical values.

TABLE-2
THE ¹H NMR SHIFTS OF THE COMPLEXES. (IN PPM)

Compound	C ₂ -H	C ₄ -H	C ₅ -H	Vinyl protons*		
				H _α	H _β	H _r
Im	7.4	6.87	6.87			
1-VIm	8.0	7.66	7.06	7.24	4.93	5.54
PdIm ₂ C ₂ O ₄	7.5	6.9	6.55			
Pd1-VImPyCl ₂	8.4	8.2	7.7	7.33	5.0	5.34
Pt1-VImPyCl ₂	8.33	7.66	7.25	5.66	5.0	5.14*

* -1-Vinyl imidazole.

The NH out-of-plane bending at *ca* 618 cm⁻¹ has not been observed to be shifted on complexation. In case of pyridine νC = N band at *ca* 1429 cm⁻¹ has been shifted to higher frequency on complexation showing the co-ordination of pyridine N to metal¹¹. Also, free oxalic acid has bands ν_{as}(C = O) at *ca* 1690 cm⁻¹ and δ(O - C = O) at *ca* 700 cm⁻¹. These are raised to *ca* 1700 cm⁻¹ and *ca* 730 cm⁻¹ respectively on complexation indicating M-O bonding¹².

A number of bands occur in the 500-250 cm⁻¹ region. These may be due to ν(M - O), ν(M - Cl), ν(M - N), δ(M - Cl) etc. But the spectra are too complicated to be assigned. However, the sharp band at *ca* 275 cm⁻¹ for PdImPyCl₂ and Pd1-VImPCL₂ is tentatively assigned to ν(M - Cl) stretch.

Three d-d transitions are expected for square planar MX₄²⁻ ion¹³. However, in the present complexes studied, palladium complexes in DMF solution show two spin-allowed d-d bands viz. ¹A_{1g} → ¹A_{2g} and ¹A_{1g} → ¹B_{1g} at *ca* 21000 cm⁻¹ and

ca 27000 cm^{-1} respectively. In the case of platinum complexes, two bands are observed at ca 23, 255 cm^{-1} and ca 34, 482 cm^{-1} regions. They are tentatively assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$ respectively.

The magnetic moment as determined on a Gouy balance using solid $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a standard indicate the diamagnetic nature of the complexes.

The ${}^1\text{H}$ NMR shifts (values in ppm) of Im, 1-VIm and their complexes with Pd(II) and Pt(II) are tabulated in Table-2. The signal for N-H proton is not observed in our range (0–10 ppm).

As compared to the spectra of the free ligands the signals for all the ring protons are shifted down-field in the complexes revealing lowering of electron density. This may be suggestive of some charge delocalisation to vacant metal d-orbital on complexation. There is also π -type spin delocalisation from the free ligand to the vacant metal d-orbital. All the vinyl protons in the complex show upfield shift perhaps because of solvent effect. The $\text{C}_2\text{-H}$ and $\text{C}_3\text{-H}$ protons of Py have shifts 8.5 and 6.99 respectively¹⁴. When complexes are formed the $\text{C}_2\text{-H}$ proton-shift intermingles with $\text{C}_2\text{-H}$ proton of 1-VIm. Also, the $\text{C}_3\text{-H}$ proton-shift mixes with $\text{C}_4\text{-H}$ proton of Im.

In the light of forgoing discussion square planar geometry with the chlorine atoms in *trans* position may be assigned to the mixed ligand complexes. Also, the formation of these mixed ligand complexes indicate that imidazole and pyridine can coordinate simultaneously as both are small aromatic ring systems complexing through a tertiary N atom. The greater availability of the lone pair electron on imidazole tertiary N atom than on the pyridine does not stand in the way of complex formation by the latter. Probably because of low affinity for oxygen donor ligands, the $\text{PtIm}_2\text{C}_2\text{O}_4$ could not be isolated.

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