

Substituted Imidazole Complexes of Palladium(II) & Platinum(II)[†]

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Compounds of the type PdL_2X_2 [L = 2-methylimidazole, 2-ethylimidazole, 2-isopropylimidazole, 2-ethyl-4(5)-methylimidazole and 4-methylimidazole; X = Cl, Br] have been obtained by reacting PdX_2 with the ligands in 1:2 molar ratio. Reactions of PdX_2 with ligands in 1:4 molar ratio result in PdL_4X_2 . Compounds of the type PtL_2X_2 [L = 2-methylimidazole, 2-ethylimidazole, 2-isopropylimidazole and 4-methylimidazole; X = Cl, Br, I] have been prepared from K_2PtCl_4 and the ligands, but complexes of the type PtL_4Cl_2 are obtained from $Pt(DMSO)_2Cl_2$. The compounds have been assigned square-planar geometries on the basis of analyses, molar conductivity measurements, IR and electronic spectral data.

Imidazoles are versatile ligands which may coordinate to metal ions either in neutral or in anionic form¹⁻⁸. A number of platinum metal compounds with imidazoles have been reported⁹⁻¹⁵. In continuation of our earlier work on palladium(II) compounds of substituted imidazoles¹⁶, we report here complexes of 2-methylimidazole(2-MeIm), 2-ethylimidazole(2-EtIm), 2-isopropylimidazole (2-*i*-PrIm) and 4-methylimidazole (4-MeIm) with Pd(II) and Pt(II), and also 2-ethyl-4(5)-methylimidazole {2-Et-4(5)-MeIm} complexes of Pd(II).

The ligand samples were supplied by M/s BASF (W. Germany) and were used as such. Samples of $PdCl_2$ and K_2PtCl_4 were obtained from M/s Arora-Matthey. $PdBr_2$ was prepared by dissolving palladium hydroxide ($PdO \cdot xH_2O$) in 48% HBr and concentrating the solution to near dryness repeatedly. The hydroxide was prepared from acidic solution of $PdCl_2$ neutralised with NaOH. $Pt(DMSO)_2Cl_2$ was prepared according to the known procedure¹⁷. The infrared and UV-visible spectra of the compounds were recorded on Karl-Zeiss spectrophotometers in nujol mull, HCB mull and in DMF solution. Far infrared spectra were recorded on a Fourier Far-IR30 instrument at RSIC, Madras.

Preparation of complexes: (i) PdL_2X_2 (L = 2-MeIm, 4-MeIm, 2-*i*-PrIm, 2-Et-4(5)-MeIm; X = Cl, Br)—To a mixture containing ethanolic solutions of PdX_2 (1.5 mmol in 10 ml) and the ligand (3 mmol in 10-15 ml) was added 5 ml of triethylorthoformate

(TEOF). Any precipitate (4-MeIm) obtained initially was dissolved again in hot ethanol. The resulting solution was evaporated to half or to one-third of the original volume and cooled when the compound crystallized. In the case of 2-EtIm and 4-MeIm, the mixture was evaporated to dryness and the compounds were obtained by treating the mass with water after keeping the same overnight in a desiccator. A mixture containing solution of ligand, PdX_2 and TEOF was refluxed for ~3 hr in the case of complex with 2-*i*-PrIm. It was then evaporated to half the original volume; the crystals appeared after keeping overnight. Preparation of $Pd(2-Et-4(5)-MeIm)_2Cl_2$ required refluxing for 90 min whereas the corresponding bromo compound required evaporation of the refluxed liquid to dryness, followed by vigorous stirring of the mass with hot water.

(ii) $Pd(2-MeIm)_4Cl_2$ — $PdCl_2$ (~1.5 mmol) was dissolved in DMF (2 ml) followed by the addition of acetone (50 ml). To this solution was added the ligand (6 mmol) dissolved in acetone (20 ml) when the white crystals of the complex were obtained.

(iii) PdL_4X_2 (L = 2-EtIm, 2-*i*-PrIm, 2-Et-4(5)-MeIm, 4-MeIm)—To a mixture containing ethanolic solutions of PdX_2 (1.5 mmol in 10 ml) and the ligand (6 mmol in 10 ml) was added 5 ml of TEOF when a white compound precipitated. Excess of TEOF was required to precipitate $Pd(2-Et-4(5)-MeIm)_4X_2$, while refluxing for 1 hr followed by reduction of volume by 50% and addition of diethylether was necessary to obtain $Pd(4-MeIm)_4X_2$.

(iv) $cis-PtL_2I_2$ (L = 2-MeIm, 2-EtIm, 2-*i*-PrIm, 4-MeIm)—These compounds were prepared by the same method as used for the imidazole compounds¹¹.

(v) $cis-PtL_2X_2$ (L = 2-MeIm, 2-EtIm, 2-*i*-PrIm and 4-MeIm)—These compounds were prepared by a method similar to that used earlier by Reedijk *et al.*¹¹ for the preparation of $cis-PtIm_2X_2$ compounds.

(vi) PtL_4Cl_2 (L = 2-MeIm, 2-EtIm, 2-*i*-PrIm)— $cis-Pt(DMSO)_2Cl_2$ (~0.5 mmol) was dissolved in DMF (3 ml) and heated to ~70°C. To this solution was added the ligand (~2 mmol) and it was heated for 30 min. The solution was cooled and excess of acetone was added when a white precipitate was obtained; it was filtered, washed with acetone, ether and dried. These compounds were very hygroscopic and hence the reactions were carried out in a moisture-free atmosphere.

The chloro and bromo compounds of ML_2X_2 (M = Pd, Pt) series are light-yellow and deep-yellow respectively while the compounds of the ML_4X_2 series

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Table 1—Melting Point, Analytical† and Far IR Data of Palladium(II) and Platinum(II) Complexes

Complexes	m.p. (°C)	Found (Calc), %		$\nu(\text{M-X})$ (cm^{-1})
		M	X	
$\text{Pd}(\text{2-MeIm})_2\text{Cl}_2$	295	32.0(31.2)	21.3(20.8)	355s
$\text{Pd}(\text{2-MeIm})_2\text{Br}_2$	300 ^a	25.7(24.7)	38.1(37.1)	205s
$\text{Pd}(\text{2-EtIm})_2\text{Cl}_2$	260	29.0(28.8)	20.1(19.2)	330s
$\text{Pd}(\text{2-EtIm})_2\text{Br}_2$	290	22.5(23.2)	34.8(34.8)	220s
$\text{Pd}(\text{2-}i\text{-PrIm})_2\text{Cl}_2$	230	26.5(26.8)	17.6(17.9)	330s
$\text{Pd}(\text{2-}i\text{-PrIm})_2\text{Br}_2$	245 ^a	22.5(21.3)	32.7(32.8)	215s
$\text{Pd}(\text{2-Et-4(5)-MeIm})_2\text{Cl}_2$	255	27.7(26.8)	16.6(17.8)	344s
$\text{Pd}(\text{2-Et-4(5)-MeIm})_2\text{Br}_2$	275	22.9(21.9)	32.3(32.8)	258m
$\text{Pd}(\text{4-MeIm})_2\text{Cl}_2$	225	31.4(31.2)	21.5(20.8)	345s
$\text{Pd}(\text{4-MeIm})_2\text{Br}_2$	240	25.4(24.7)	36.8(37.1)	270s
$\text{Pd}(\text{2-MeIm})_4\text{Cl}_2$	280 ^a	20.9(21.0)	14.4(14.04)	
$\text{Pd}(\text{2-MeIm})_4\text{Br}_2$	240	17.8(17.9)	26.4(26.8)	
$\text{Pd}(\text{2-EtIm})_4\text{Cl}_2$	285	19.4(18.9)	13.0(12.6)	
$\text{Pd}(\text{2-EtIm})_4\text{Br}_2$	290 ^a	16.4(16.3)	24.8(24.5)	
$\text{Pd}(\text{2-}i\text{-PrIm})_4\text{Cl}_2$	260	17.2(16.9)	11.8(11.3)	
$\text{Pd}(\text{2-}i\text{-PrIm})_4\text{Br}_2$	252	15.0(15.06)	22.7(22.6)	
$\text{Pd}(\text{2-Et-4(5)-MeIm})_4\text{Cl}_2$	200	18.3(17.2)	11.0(11.5)	
$\text{Pd}(\text{2-Et-4(5)-MeIm})_4\text{Br}_2$	175	14.0(15.0)	21.6(22.6)	
$\text{Pd}(\text{4-MeIm})_4\text{Cl}_2$	210	19.9(21.0)	13.3(14.0)	
$\text{Pd}(\text{4-MeIm})_4\text{Br}_2$	234	17.8(17.9)	26.7(26.8)	
$\text{Pt}(\text{2-MeIm})_2\text{Cl}_2$	255	46.1(45.4)	16.2(16.5)	330s, 325s
$\text{Pt}(\text{2-MeIm})_2\text{Br}_2$	320	38.3(37.6)	30.65(30.79)	225s, 200m, sh
$\text{Pt}(\text{2-MeIm})_2\text{I}_2$	320 ^a	31.1(31.8)	39.8(41.4)	
$\text{Pt}(\text{2-EtIm})_2\text{Cl}_2$	230	43.4(42.75)	14.81(15.49)	335s, 325s
$\text{Pt}(\text{2-EtIm})_2\text{Br}_2$	315	36.0(35.66)	28.1(29.2)	220s, 207m
$\text{Pt}(\text{2-EtIm})_2\text{I}_2$	305	31.0(30.43)	38.0(39.59)	
$\text{Pt}(\text{2-}i\text{-PrIm})_2\text{Cl}_2$	290	41.5(40.12)	14.9(14.6)	338s, 325s
$\text{Pt}(\text{2-}i\text{-PrIm})_2\text{Br}_2$	270	34.4(33.92)	26.85(27.78)	225ms, 207w
$\text{Pt}(\text{2-}i\text{-PrIm})_2\text{I}_2$	308	30.03(29.15)	36.0(37.9)	
$\text{Pt}(\text{4-MeIm})_2\text{Cl}_2$	183	45.35(45.0)	16.8(16.5)	330s, b
$\text{Pt}(\text{4-MeIm})_2\text{Br}_2$	180	36.60(37.59)	29.67(30.79)	220s, b
$\text{Pt}(\text{2-MeIm})_4\text{Cl}_2$		31.7(32.8)	10.8(11.9)	
$\text{Pt}(\text{2-EtIm})_4\text{Cl}_2$	300 ^a	28.8(29.9)	10.0(10.9)	
$\text{Pt}(\text{2-}i\text{-PrIm})_4\text{Cl}_2$	275 ^a	26.0(27.6)	9.8(10.05)	

† Satisfactory C, H & N analyses were obtained; ^adec.

are white in colour. The metals were analysed using standard procedures¹⁸ and halogens were estimated as silver halides. Microanalyses of C, H and N were obtained from CDRI, Lucknow. The analyses conform fairly to the compositions ML_2X_2 for neutral species and ML_4X_2 for those of ionic variety (Table 1). They are generally insoluble in common organic solvents. However, ML_2X_2 compounds are soluble in DMF and DMSO, and ML_4X_2 compounds are soluble in water. All the compounds have high melting points (200–300°C) and some decompose without any sharp melting point. Compounds of the type, $\text{Pt}(\text{4-MeIm})_2\text{X}_2$ have, however, melting points around 180°C (Table 1). The molar conductivities of ML_2X_2 (M = Pt, Pd) complexes in DMF reveal their non-electrolytic character but those of the ML_4X_2 variety are 1:2 electrolytes having molar conductance values in the range 200–220 $\text{mhos cm}^2 \text{mol}^{-1}$.

The infrared spectra of 2-MeIm, 2-EtIm, 2-*i*-PrIm and 4-MeIm exhibit medium to strong bands at ~ 3140 , $\sim 3030 \text{ cm}^{-1}$ and broad bands in the range $3000\text{--}2500 \text{ cm}^{-1}$ in HCB mulls; the latter broad bands are expected for strong N–H...N type of hydrogen bonding. The ML_4X_2 complexes reveal bands in the region $3150\text{--}2600 \text{ cm}^{-1}$ with multiple splittings; the pattern of bands, however, differs from those in the ligands perhaps due to the difference in nature of hydrogen bonding modes. In ML_2X_2 complexes the broad band in the region $3000\text{--}2500 \text{ cm}^{-1}$ almost disappears but three to four medium or weak intensity bands appear. These bands are due to $\nu\text{C-H}$ vibrations of methyl or ethyl groups. The bands at $\sim 3300\text{--}3250 \text{ cm}^{-1}$ in palladium and at $\sim 3225\text{--}3175 \text{ cm}^{-1}$ in platinum complexes are comparatively broad and are expected for $\nu\text{N-H}$ vibrations associated with some intermolecular hydrogen bonding.

The assignment of pure $\nu\text{N}-\text{H}$ frequency is quite complicated in almost all these complexes and also in the ligands because of the presence of hydrogen bonding and close proximity of $\nu\text{C}-\text{H}$ vibrations. The frequency shifts in the region $1600\text{--}660\text{ cm}^{-1}$ are normally less than 25 cm^{-1} except in the 4-MeIm and 2-Et-4(5)-MeIm complexes where the shifts are of the order of $\sim 40\text{ cm}^{-1}$. Also, some bands present in the ligands are found to split and some occur with decreased intensity or disappear completely. Further, increase in size of the substituent (2-Me to 2-Et or 2-Et to 2-*i*-Pr) has practically no effect on the spectra of the ligands, but change in position of the substituent (2-Me to 4-Me) shows moderate shifts ($\Delta\nu \sim 30\text{--}50\text{ cm}^{-1}$) of spectral bands of the ligands.

The PdL_2Cl_2 complexes exhibit one strong band at $\sim 350\text{ cm}^{-1}$, and PdL_2Br_2 complexes show a band in the region $250\text{--}200\text{ cm}^{-1}$ (Table 1). The observance of only one $\nu\text{M}-\text{X}$ mode indicates that the halogens are at *trans* positions^{19,20}. The PtL_2X_2 complexes, on the other hand, exhibit a pair of bands at $\sim 330\text{ cm}^{-1}$ for $\nu\text{Pt}-\text{Cl}$ and at $\sim 220\text{ cm}^{-1}$ for $\nu\text{Pt}-\text{Br}$ ^{19,20}. Sometimes these bands are broad where the split components may not be well resolved. A number of other bands also occur in this region due to $\nu\text{M}-\text{N}$, $\nu\text{M}-\text{L}$, $\delta\text{M}-\text{X}$ etc. but the spectra are too complicated to allow any definite prediction.

In the UV-visible region, two bands at $24000\text{--}25000\text{ cm}^{-1}$ and $30,000\text{ cm}^{-1}$ in PdL_2X_2 complexes are observed; these may be due to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1E_g$ transitions. However, only one band at $\sim 30,000\text{ cm}^{-1}$ is observed in PtL_2X_2 complexes which may be due to $^1A_{1g} \rightarrow ^1E_g$ transition, though three *d-d* transitions are expected for MX_4^{2-} ions²¹. In $\text{Pd}(4\text{-MeIm})_2\text{Cl}_2$, however, all the three bands occur; the band at $19,600\text{ cm}^{-1}$ is assigned to $^1A_{1g} \rightarrow ^1A_{2g}$ transition. The PtL_2I_2 species show a pair of bands; the latter band is due to $\text{Pt} \rightarrow \text{I}$ charge-transfer. The ionic species show only strong and broad charge-transfer bands above $40,000\text{ cm}^{-1}$ in aqueous solution.

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References

- 1 Taylor C E & Underhill A E, *J chem Soc (A)*, (1969) 368.
- 2 Goodgame D M L, Goodgame M, Hayward P J & Rayner-Canham G W, *Inorg Chem*, **7** (1968) 2447.
- 3 Reedijk J, *Inorg chim Acta*, **34** (1969) 517.
- 4 Reedijk J, *J inorg nucl Chem*, **33** (1971) 179.
- 5 Massacesi M & Ponticelli G, *J inorg nucl Chem*, **36** (1974) 2209.
- 6 Krushna C H, Mahapatra C & Dash K C, *J inorg nucl Chem*, **39** (1977) 1253.
- 7 Wellemans J A, Hulsbergen F B, Verbiest J & Reedijk J, *J inorg nucl Chem*, **40** (1978) 143.
- 8 Brockema R J, Durville P F M, Reedijk J, Smith J A, *Transition met Chem*, **7** (1982) 25.
- 9 Ghosh S P, Bhattacharjee P, Dubey L & Mishra L K, *J Indian chem Soc*, **54** (1977) 230.
- 10 van Kralingen C G & Reedijk J, *Inorg chim Acta*, **30** (1978) 171.
- 11 van Kralingen C G, deRidder J K & Reedijk J, *Inorg chim Acta*, **36** (1979) 69.
- 12 Biagini Cingi M, Lanfredi A T M, Tiripicchio A, van Kralingen C G & Reedijk J, *Inorg chim Acta*, **39** (1980) 265.
- 13 Graves B, Hodson D L, van Kralingen C G & Reedijk J, *Inorg Chem*, **17** (1978) 3007.
- 14 Navarro Ranninger M C & Gayso M, *Ann Quim*, **74** (1978) 717 & 722.
- 15 Navarro Ranninger M C, *J appl Crystallogr*, **12** (1979) 420 & 1254.
- 16 Hazarika T N & Bora T, *Transition met Chem*, **7** (1982) 210.
- 17 Price J H, Williamson A N, Schramm R F & Wayland B B, *Inorg Chem*, **11** (1972) 1280.
- 18 Vogel A I, *A text book of quantitative inorganic analysis*, 4th Edn (The English Language Book Society, London), 1978, 474.
- 19 Ferraro J R, *Low frequency vibrations of inorganic and coordination compounds* (Plenum Press, New York), 1971, 165.
- 20 Nakamoto K, *Infrared and Raman Spectra of inorganic and coordination compounds*, 3rd Edn (John Wiley, New York), 1978, 322.
- 21 Livingstone S E, *The chemistry of ruthenium, rhodium, palladium, osmium, iridium and platinum, Monograph Vol 25* (Pergamon Press, London), 1973, 1286.