

Synthesis and Characterization of Some Iridium(III) Complexes with N-donor Ligands

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Iridium(III) chloride is found to form complexes of types $(LH)_2[IrCl_3L]$ and $(L'H)[IrCl_4L'_2]$ and $(L''H)_3[IrCl_6] \cdot 2H_2O$, where L = 2-methylimidazole (2-MeIm), 2-ethylimidazole (2-EtIm), 1-methylimidazole (1-MeIm), 1-n-butylimidazole (1-n-BuIm), 1,2-dimethylimidazole; L' = imidazole (Im), 1,2-dimethyl-5-nitroimidazole (1,2-Me₂-5-NO₂Im) and L'' = α -picoline (α -pic), β -picoline (β -pic), γ -picoline (γ -pic). The compounds have been characterized by elemental analyses, molar conductance measurements and IR, UV-visible and ¹H NMR spectral studies. The compounds have octahedral geometry with pyridine nitrogen of imidazoles and picolines as donor site. Thermal studies indicate continuous loss of ligands with formation of Ir-metal at ca. 900°C in some cases.

Key Words: Iridium (III), Imidazole, Picoline, Octahedral geometry.

INTRODUCTION

Imidazole and substituted imidazole compounds of platinum metals, particularly of platinum(II), platinum(IV), palladium(II), palladium(IV), ruthenium(III) and rhodium(III) were studied by a number of workers^{1–6}. Attention is also focussed on the imidazolium compounds of ruthenium metal to study some biochemical activity⁷. Nitroimidazoles^{8, 9} and their complexes with metals like Pt, Ru and Rh¹⁰ are known to be effective radiosensitizers and chemotherapeutic agents. The radiosensitizing ability of some nitroimidazole complexes of Ru(II) toward hypoxic tumour cells have already been established¹¹. Aqueous solutions of Ir(III), Ru(III) and Rh(III) oxidize olefins¹². In this paper, the synthesis and structural characterization of some iridium(III) chloride complexes of imidazoles and picolines have been attempted.

EXPERIMENTAL

Hydrated iridium(III) chloride ($IrCl_3 \cdot xH_2O$) of Arora-Matthey Ltd. was first digested with aqua-regia and then with conc. HCl several times before use. The imidazoles (FlukaAG, BASF, Aldrich) and picolines (Fluka) were used directly.

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Hydrochloric and nitric acids were of BDH (AR) grade and used as such. The IR spectra of the compounds as nujol-mull smears were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer-883 spectrophotometer, while a Shimadzu UV-Vis spectrophotometer UV-240 was used for recording the electronic spectra in aqueous solution with quartz cell of 1 cm thickness. Solid diffused reflectance spectra using BaSO_4 as reference were also carried out.

The molar conductances of the complexes in water (*ca.* 10^{-3} M) were recorded at room temperature with a digital conductivity meter type CM-180, using a dip type platinum cell. Thermograms were recorded on Shimadzu thermal analyser-DT30 and decomposition temperatures were obtained by Ketan melting point apparatus. The ^1H NMR spectra in DMSO-d_6 were recorded at IIT, Mumbai.

Chlorine was estimated as AgCl gravimetrically. The analyses of carbon, hydrogen and nitrogen were obtained microanalytically at CIL, Punjab University, Chandigarh.

Synthesis of Imidazolium-tetrachlorobis(imidazole) iridate(III), $(\text{ImH})[\text{IrCl}_4\text{Im}_2]$

To a digested solution of $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (*ca.* 0.5 g), imidazole (*ca.* 0.45 g) in conc. HCl was added in molar ratio of 1 : 4 followed by the addition of 20 mL of ethanol. The mixture was refluxed for 2.5 h and then evaporated slowly almost to dryness on a water bath and kept over fused CaCl_2 for 3 d. The compound formed was washed several times with ethanol, filtered off and dried in *vacuo*. Yield : 0.86 g (*ca.* 90%)

A similar preparative procedure has been adopted for the synthesis of other nine compounds taking *ca.* 0.55, 0.64, 0.55, 0.83, 0.64, 0.94 and 0.62 g of 2-MeIm, 2-EtIm, 1-MeIm, 1-n-BuIm, 1,2-Me₂Im, 1,2-Me₂-5-NO₂Im and α, β, γ -pic respectively with *ca.* 0.5 g of $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$. The corresponding yields are 0.95 g (*ca.* 90%), 1.03 g (*ca.* 90%), 0.95 (*ca.* 90%), 1.20 (*ca.* 90%), 1.03 (*ca.* 90%), 1.15 (*ca.* 80%) and 0.78 g (*ca.* 70%).

RESULTS AND DISCUSSION

The analytical data, colour, decomposition temperature, molar conductivity of the compounds are included in Table-1. All the compounds are highly soluble both in DMSO and water. Molar conductance values in water indicate that $(\text{LH})_2[\text{IrCl}_5\text{L}']$ is 1 : 2 electrolyte whereas $(\text{L}'\text{H})[\text{IrCl}_4\text{L}'_2]$ behaves as 1 : 1 electrolyte and the type $(\text{L}''\text{H})_3[\text{IrCl}_6] \cdot 2\text{H}_2\text{O}$ is 1 : 3 electrolyte.

The IR spectra of the compounds reveal that most of the bands observed in the imidazoles^{5, 6, 8, 13} and picolines¹⁴. It has also been observed that the spectra of ligands reveal only small band shifts on complexation. Thus, the compound, $(\text{ImH})[\text{IrCl}_4\text{Im}_2]$ gives ring stretching vibrations at 1585 (m), 1480 (w), 1435 cm^{-1} (s) with band shift $\Delta\nu$ *ca.* 5–12 cm^{-1} compared to free imidazole. Similarly, the ring stretching vibrations of 2-MeIm, 2-EtIm, 1-MeIm, 1-n-BuIm, 1,2-Me₂Im and 1,2-Me₂-5-NO₂Im show a shift of *ca.* 5–50 cm^{-1} upon complexation. Variation in position of alkyl groups in the ring as well as their nature may cause this large band shift. It is found that α -, β - and γ -picolinium compounds exhibit bands due

to $\nu(\text{CC})$, $\nu(\text{CC}, \text{CN})$ and C—H symmetrical and antisymmetrical bending of —CH₃ group at *ca.* 1645–1280 cm⁻¹ with band shift $\Delta\nu$ *ca.* 5–50 cm⁻¹. Picolines exhibit various types of in-plane CH bending, ring breathing and ring deformation at *ca.* 1100–700 cm⁻¹ with band shift *ca.* 62–2 cm⁻¹ on complexation. The C_{ar}—CH₃(s) (C_{ar} = aromatic carbon) stretching frequency of picolines shows a shift of *ca.* 5 cm⁻¹ complex formation. The $\nu(\text{NH})$ and $\gamma(\text{NH})$ vibrations are cited to be informative in deciding the coordination sites in a number of ligands. These frequencies in many imidazole and substituted imidazole complexes of platinum metals are found to change considerably ($\Delta\nu$ *ca.* 30–50 cm⁻¹)⁵. In the compounds, (ImH)[IrCl₄Im₂], (2-MeImH)₂[IrCl₅(2-MeIm)] and (2-EtImH)₂[IrCl₅(2-EtIm)] $\nu(\text{NH})$ is observed at 3040 (wbd), 3125 (wbd) and 3143 cm⁻¹ (wbd) respectively indicating a shift of *ca.* 25–105 cm⁻¹. Also, one medium to strong $\nu(\text{Ir—Cl})$ band at 335 cm⁻¹ has been observed in the complexes, which is indicative of *trans*-imidazoles in an octahedral arrangement¹⁵.

TABLE-1
CHARACTERIZATION DATA OF Ir(III) COMPLEXES WITH N-DONOR LIGANDS

Compounds (colour)	Found (Calcd.) %				Decomp. temp. (°C)	Mol. cond., (Λ_M) (mol ⁻¹ ohm ⁻¹ cm ²)
	C	H	N	Cl		
(2-MeImH) ₂ [IrCl ₅ (2-MeIm)] (dark green)	22.9 (23.3)	3.2 (3.2)	13.4 (13.6)	28.5 (28.7)	220	196
(2-EtImH)[IrCl ₅ (2-EtIm)] (green)	26.9 (27.3)	3.5 (3.9)	12.4 (12.7)	26.7 (26.9)	185	220
(1-MeImH) ₂ [IrCl ₅ (1-MeIm)] (light brown)	23.1 (23.3)	3.1 (3.2)	13.3 (13.6)	28.5 (28.7)	160	216
(1-n-BulmH) ₂ [IrCl ₅ (1-n-Bulm)] (chocolate)	33.0 (33.9)	4.9 (5.1)	11.0 (11.3)	23.2 (23.9)	120	210
(1,2-Me ₂ ImH) ₂ [IrCl ₅ (1,2-Me ₂ Im)] (light green)	27.0 (27.3)	3.4 (3.9)	12.0 (12.7)	26.5 (26.9)	190	204
(ImH)[IrCl ₄ Im ₂] (light yellow)	20.4 (20.0)	2.9 (2.4)	15.9 (15.6)	26.0 (26.3)	180	124
(1,2-Me ₂ -5-NO ₂ ImH)-[IrCl ₄ (1,2- Me ₂ -5-NO ₂ Im) ₂] (yellow)	24.4 (23.8)	2.2 (2.9)	16.7 (16.6)	18.0 (18.7)	255	157
(α -picH) ₃ [IrCl ₆]·2H ₂ O (brown)	29.5 (29.9)	3.3 (3.9)	5.7 (5.8)	29.0 (29.4)	120	387
(β -picH) ₃ [IrCl ₆]·2H ₂ O (brown)	29.6 (29.9)	3.8 (3.9)	5.5 (5.8)	29.1 (29.4)	122	385
(γ -picH) ₃ [IrCl ₆]·2H ₂ O	29.3 (29.9)	3.5 (3.9)	5.9 (5.8)	29.1 (29.4)	180	380

Four transitions of d-d origin, (¹A_{1g} → ³T_{1g}), (¹A_{1g} → ³T_{2g}), (¹A_{1g} → ³T_{1g}) and (¹A_{1g} → ¹T_{2g}) are described for IrCl₆³⁻ ion at 16,300, 17,900, 24,100 and 28,100

cm^{-1} respectively¹⁶. The intensities of spin-forbidden bands are high for Ir(III) compounds, because the large spin-orbit coupling coefficient causes significant mixing of spin states¹⁶. The ligand field band observed in the range 16,949–16,393 cm^{-1} for 1-MeIm, 1-n-BuIm, 1,2-Me₂Im and 1,2-Me₂-5-NO₂Im compounds of Ir(III) has been assigned to $^1A_{1g} \rightarrow ^3T_{1g}$ transition in an octahedral environment. With the exception of (1-MeImH)₂[IrCl₅(1-MeIm)], all other compounds exhibit $^1A_{1g} \rightarrow ^3T_{2g}$ transition in the region 20,615–18,450 cm^{-1} . Imidazolium, 2-methylimidazolium and 2-ethylimidazolium complexes do not exhibit first spin-allowed transition $^1A_{1g} \rightarrow ^1T_{1g}$, while the other complexes give bands in the range 24,155–20,747 cm^{-1} . Imidazolium compounds exhibit second spin-allowed transition ($^1A_{1g} \rightarrow ^1T_{2g}$) in the region 27,933–28,330 cm^{-1} , while picolinium compounds do not display this band.

In aqueous solution, the electronic spectra on each complex (1-n-BuImH)₂[IrCl₅(1-n-BuIm)] and (1,2-Me₂-5-NO₂ImH)[IrCl₄(1,2-Me₂-5-NO₂Im)₂] reveal only one band at 30,720 cm^{-1} (ϵ_{max} 1,50,000 $10^{-2} \text{ m}^2 \text{ mol}^{-1}$) and 31,546 cm^{-1} (ϵ_{max} 2,55,000 $10^{-2} \text{ m}^2 \text{ mol}^{-1}$) respectively. Each of the Im, 2-MeIm, 2-EtIm, 1-MeIm, 1,2-Me₂Im, α -, β - and γ -pic compounds of Ir(III) exhibit one band in the range 33,333–30,500 cm^{-1} (ϵ_{max} = 969–3150 $10^{-2} \text{ m}^2 \text{ mol}^{-1}$) in addition to four transitions in the ranges 16,667–18,200 cm^{-1} , 18,182–21,250 cm^{-1} , 23,256–24,100 cm^{-1} and 27,027–28,610 cm^{-1} , which could be assigned ($^1A_{1g} \rightarrow ^3T_{1g}$), ($^1A_{1g} \rightarrow ^3T_{2g}$), ($^1A_{1g} \rightarrow ^1T_{1g}$) and ($^1A_{1g} \rightarrow ^1T_{2g}$) transitions respectively, with comparatively small extinction coefficient values. The large extinction coefficient values in many cases indicate considerable mixing of *d-d* bands with charge-transfer bands.

The chemical shifts of the ring C—H and N—Me protons of 1-MeIm as a free ligand¹⁷ and coordinated ligand are discussed. Compared to the spectra of free 1-MeIm, the NMR signals of all the protons of coordinated 1-methylimidazole

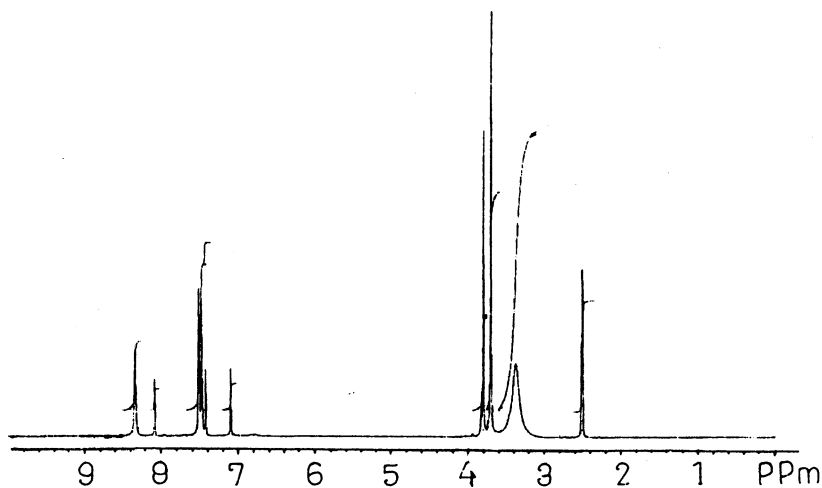


Fig. 1. ^1H NMR spectra (in ppm) in DMSO- d_6 of (1-MeImH)₂[IrCl₅(1-MeIm)]

are shifted to lower field (Fig. 1). The chemical shift for H-2 proton is 0.75 ppm and for H-4 proton it is 0.42 ppm in 1-methylimidazolium ion while the shifts for H-2 and H-4 protons are 0.50 ppm and 0.32 ppm respectively for coordinated 1-MeIm. Similarly, the shift of H-5 proton is 0.57 ppm for 1-methylimidazolium ion but is 0.18 ppm for coordinated ligand. Thus, 1-methylimidazolium ion exhibits more downfield shift than the coordinated ligand. The shift of 1-methyl proton is small; these are 0.13 ppm and 0.03 ppm in the coordinated 1-MeIm and 1-methylimidazolium ion respectively. The area of the NMR signals in $(1\text{-MeImH})_2[\text{IrCl}_5(1\text{-MeIm})]$ almost satisfied the ratio of equivalent protons 2 : 2 : 2 : 1 : 1 : 1 : 6 : 3. In many cases, expected multiplicity of the NMR signals were not obtained, probably due to the long range coupling of the ring protons.

The thermal studies of $(\text{ImH})[\text{IrCl}_4\text{Im}_2]$, $(1,2\text{-Me}_2\text{-5-NO}_2\text{ImH})[\text{IrCl}_4(1,2\text{-Me}_2\text{-5-NO}_2\text{Im})_2]$, $(2\text{-MeImH})_2[\text{IrCl}_5(2\text{-MeIm})]$, $(1,2\text{-Me}_2\text{ImH})_2[\text{IrCl}_5(1,2\text{-Me}_2\text{Im})]$ and $(1\text{-n-BuImH})_2[\text{IrCl}_5(1\text{-n-BuIm})]$ indicate that the complexes lose all imidazolium ions and imidazole ligands in the range of temperature *ca.* 460–570°C. Further, continuous weight loss occurs and forms Ir-metal at *ca.* 900°C (Fig. 2). All other weight loss processes for each compound give either sharp or broad exothermic peaks whose number and position almost coincide with DTG peaks.

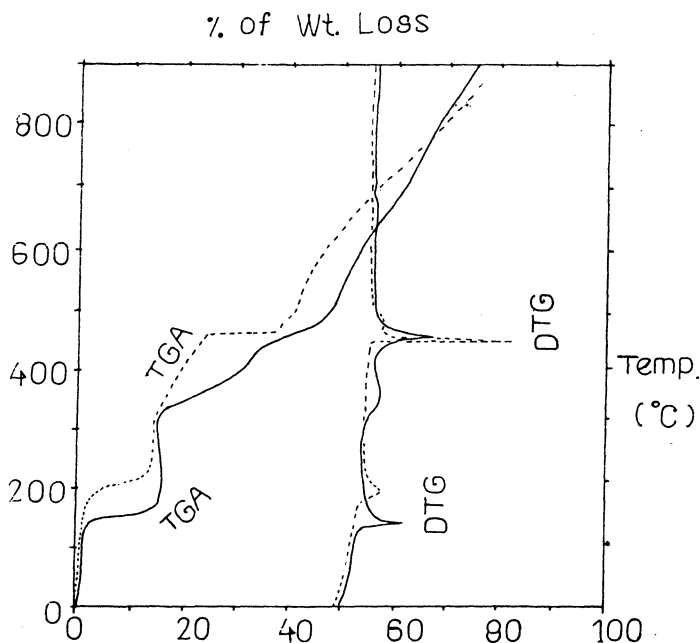


Fig. 2. Thermograms of $(1\text{-n-BuImH})_2[\text{IrCl}_5(1\text{-n-BuIm})]$ (.....) and $(\text{ImH})[\text{IrCl}_4\text{Im}_2]$ (.....)

Weight loss occurs gradually with three or four major inflexions.

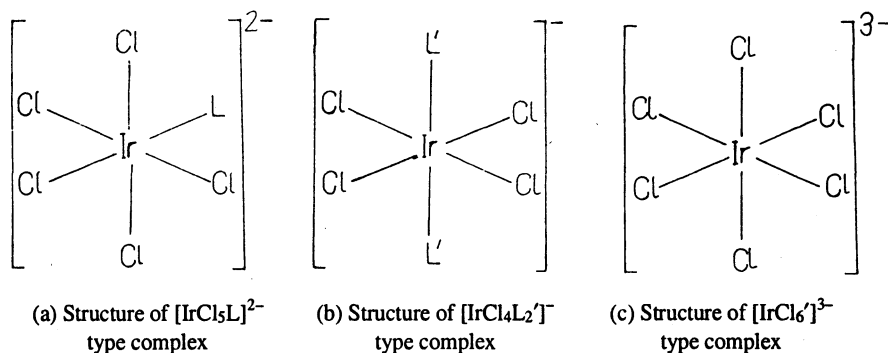


Fig. 3

From the above data, the structure of the compounds can tentatively be proposed as below (Figs. 3a, b and c).

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