

# Synthesis and Characterisation of New Octahedral Complexes of Rh(III) and Ir(III)

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**Abstract**— Octahedral complexes of Rh(III) and Ir(III) have been prepared with the tetradentate Schiff bases derived from a 2:1 molar condensation of salicylaldehyde with ethylenediamine and o-phenylenediamine. The complexes were characterised on the basis of their elemental analysis, IR, 1H, NMR and FAB mass spectra. The IR spectral data revealed that the Schiff bases behave as tetradentate and are coordinated to Rh and Ir via nitrogen and oxygen.

**Keywords**—Characterisation, Octahedral complexes, Schiff bases

## I. INTRODUCTION

THE complexes of transition metals with Schiff bases show better biological activity than the free ligands [1]. Although there is a wealth of information concerning transition metal complexes with Schiff bases, it is largely confined to the first row metals, such as copper, iron, cobalt, nickel [2] and according to our knowledge no study has been reported for complexes with rhodium and iridium before. The only reports of complexes of almost similar types of ligands, are those with the metal centres being iron, cobalt, zinc and copper(II) [3].

Rh(I), Rh(II) and Rh(III) complexes have shown interesting anticancer properties. Some rhodium metallointercalators exhibit specific DNA binding, suggesting that they represent a new type of DNA-targeting agents [4]. Dimeric  $\mu$ -acetato dimers of rhodium(II) as well as monomeric square planar rhodium(I) and octahedral rhodium(III) complexes have shown interesting antitumour properties. The dirhodium tetraacetate complex,  $[Rh_2(CH_3COO)_4(H_2O)_2]$ , is much more inhibitory towards *Escherichia coli* DNA polymerase I and exhibits good antitumour activity against P388 lymphocytic leukemia and sarcoma 180 but little activity against L1210 and B16 melanoma [5]. Recent structural studies suggest that the antitumour activity of di-rhodium(II) carboxylates may bear analogy to that of cisplatin by binding to adjacent guanines on DNA [6]. Earlier, Rajput *et al* [7-8] reported the preparation of a series of cyclooctadiene rhodium complexes with a substituted pyridine. Particular emphasis was placed on ferrocenyl, phenyl and other aromatic systems as substituents

on the pyridine ring. The antitumor activity of the complexes was compared based on structural differences. The role played by the position and nature of substituent on the pyridyl ligand was evaluated. Several rhodium complexes showed significant activity for both the WHCO1 and ME180 cancer cell lines. It appears that derivitisation of the pyridyl ligand is related to enhanced toxic activity. However the major drawback was that the rhodium complexes were only partially soluble in aqueous environment.

In this paper, the reactions of tetradentate Schiff bases with the metals Rh(III) and Ir(III) are reported. These ligands were prepared by condensing the respective diamine with the corresponding aldehyde [9].

## II. EXPERIMENTAL

### A. General procedure for the synthesis of Schiff bases [1-2]

Schiff bases were prepared from the condensation of the respective diamine with the corresponding aldehyde in a molar ratio 1:2, respectively, using methanol as a solvent at ca. 45 °C. The reaction mixture was stirred for 3 hours. The precipitates were filtered off, washed several times with methanol and finally dried under vacuum for 4 hours.

#### 1. Preparation of ligand 1

Yellow shiny crystalline solid. Yield 85%. Anal. Calcd. for  $C_{16}H_{16}O_2N_2$ : C, 71.64 %; H, 5.97 %; N 10.44 %. Found: C 71.15 %; H 5.98 %; N 10.26 %. M.p.: 120-122 °C.  $^1H$  NMR: (400 MHz,  $d_6$ -DMSO): 13.00 (2H, br s), 8.40 (2H, s), 7.30 (4H, dd), 6.95 (2H, d), 6.85 (2H, t), 3.95 (4H, s). IR (KBr): 1634 (vs), 1581 (w), 1498 (s), 1461 (s), 1284 (s), 940 (m), 806 (w). EI-MS:  $m/z$  269 [M].

#### 2. Preparation of ligand 2

Orange powder. Yield 90%. Anal. Calcd. for  $C_{20}H_{16}O_2N_2$ : C, 75.94%; H, 5.06%; N 8.86 %. Found: C 75.68%; H 5.08%; N 8.73 %. M.p.: 180-183 °C.  $^1H$  NMR: (400 MHz,  $d_6$ -DMSO): 12.95 (2H, br s), 8.95 (2H, s), 7.60 (2H, d), 7.40 (4H, dd), 6.85 (4H, dd). IR (KBr): 1613 (s), 1584 (w), 1561 (w), 1462 (vs), 1370 (s), 1276 (w). EI-MS:  $m/z$  317 [M].

### B. General procedure for the synthesis of rhodium complexes [3-4] and iridium complexes [5-6]

Complexes [3-6] were prepared by the same general procedure with stoichiometric amounts of ligands and metal chlorides in a 1:1 mole ratio. To an ethanolic solution of either  $RhCl_3 \cdot 3H_2O$  or  $IrCl_3 \cdot 3H_2O$  the appropriate amount of Schiff base were added. The reaction mixture was refluxed for 8-10

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hours under stirring. The complexes which precipitated on cooling were filtered off, washed with cold methanol and the diethyl ether and the products dried *in vacuo* for 4 hours.

### 1. Preparation of complex 3

Dark green powder. Yield 65 %.  $^1\text{H}$  NMR: (400 MHz,  $d_6$ -DMSO): 8.06 (s, 2H), 7.46 (dd, 2H,  $J=0.7\text{Hz}$ ,  $J=3.4\text{Hz}$ ), 6.41 (dd, 2H,  $J=1.8\text{Hz}$ ,  $J=3.4\text{Hz}$ ), 3.92 (s, 4H). EA: Calc. For  $\text{C}_{16}\text{H}_{14}\text{Cl}_3\text{N}_2\text{O}_2\text{Rh}$ : C, 40.41 %; H, 2.97 %; N 5.89 %. Found: C 44.31 %; H 2.67 %; N 5.85 %. M.p.: 225-227 °C. IR (KBr): 1607  $\text{cm}^{-1}$  (C=N, imine). EI-MS:  $m/z$  438.95 [M - Cl] $^+$

### 2. Preparation of complex 4

Dark brown powder. Yield 68 %.  $^1\text{H}$  NMR: (400 MHz,  $d_6$ -DMSO): 8.95 (2H, s), 7.60 (2H, d), 7.40 (4H, dd), 6.85 (4H, dd). EA: Calc. for  $\text{C}_{20}\text{H}_{14}\text{Cl}_3\text{RhN}_2\text{O}_2$ : C, 45.88 %; H, 2.70 %; N 5.35 %. Found: C, 45.31 %; H 2.12 %; N 5.69 %. M.p.: 185-187 °C. IR (KBr): 1610  $\text{cm}^{-1}$  (C=N, imine). EI-MS:  $m/z$  490.96 [M - Cl] $^+$

### 3. Preparation of complex 5

Dark yellow powder. Yield 70 %.  $^1\text{H}$  NMR: (400 MHz,  $d_6$ -DMSO): 13.00 (2H, br s), 8.40 (2H, s), 7.30 (4H, dd), 6.95 (2H, d), 6.85 (2H, t), 3.95 (4H, s). EA: Calc. for  $\text{C}_{16}\text{H}_{14}\text{Cl}_3\text{IrN}_2\text{O}_2$ : C, 34.02 %; H, 2.53 %; N 4.96%. Found: C 34.35 %; H 2.21 %; N 4.80 %. M.p.: 160-163 °C. IR (KBr): 1595  $\text{cm}^{-1}$  (C=N, imine). EI-MS:  $m/z$  529.01 [M - Cl] $^+$

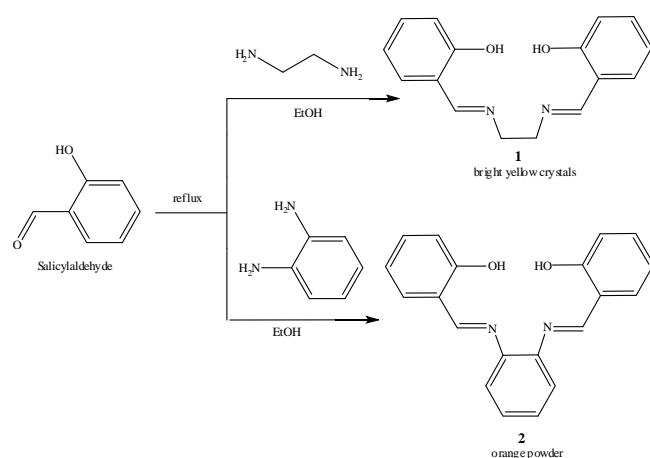
### 4. Preparation of complex 6

Brown powder. Yield 72 %.  $^1\text{H}$  NMR: (400 MHz,  $d_6$ -DMSO): 11.02 (s, 1H), 7.89 (s, 1H), 7.24 (d, 1H,  $J=1.7\text{Hz}$ ), 7.22 (dd, 1H,  $J=0.9\text{Hz}$ ,  $J=1.7\text{Hz}$ ), 7.20 (d, 1H,  $J=1.7\text{Hz}$ ), 7.12 (d, 1H,  $J=1.7\text{Hz}$ ), 7.10 (d, 1H,  $J=1.7\text{Hz}$ ), 6.96 (m, 1H), 6.88 (m, 1H), 5.43 (s, 1H). EA: Calcd. for  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2\text{IrCl}_3$ : C, 39.18 %; H, 2.30 %; N 4.56 %. Found: C, 39.29 %; H, 2.61 %; N 4.25 %. M.p.: 210-212 °C. IR (KBr): 1596  $\text{cm}^{-1}$  (C=N, imine). EI-MS:  $m/z$  579.02 [M - Cl] $^+$

## III. RESULTS AND DISCUSSION

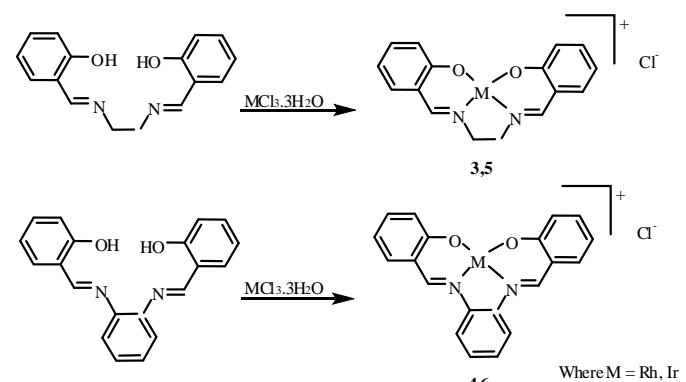
The two ligands **1** and **2** were readily prepared in good yield by condensation of salicylaldehyde and ethylenediamine (**1**), salicylaldehyde and *o*-phenylenediamine (**2**), respectively, with a 2:1 molar ratio. **1** is bright yellow crystalline material and **2** an orange powder. The prepared ligands are soluble in MeOH, DMSO,  $\text{CH}_2\text{Cl}_2$  and EtOH, and insoluble in nonpolar

solvents e.g. *n*-pentane. The ligands are tetradentate in nature having an  $\text{N}_2\text{O}_2$  donor site capable of complexing transition metal ions.<sup>1</sup> (Scheme 1).



Scheme 1: Synthesis of the Schiff base ligands

Stable Rh(III) and Ir(III) complexes were prepared with Schiff bases derived from a condensation of salicylaldehyde with ethylenediamine and *o*-phenylenediamine (Scheme 2).



Scheme 2: Synthesis of the complexes

TABLE I  
ELEMENTAL ANALYSIS OF LIGANDS AND COMPLEXES

Compound Formular	Mw	Yield %	M.p. °C	Analysis found (Calcd.)/%		
				C	H	N
<b>1.</b> $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$	268.1	85	120-122	71.15 (71.64)	5.98 (5.97)	10.26 (10.44)
<b>2.</b> $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2$	316.4	90	180-183	75.68 (75.94)	5.08 (5.06)	8.73 (8.86)
<b>3.</b> $\text{C}_{16}\text{H}_{14}\text{Cl}_3\text{RhN}_2\text{O}_2$	475.6	65	225-227	44.31 (40.41)	2.67 (2.97)	5.85 (5.89)
<b>4.</b> $\text{C}_{20}\text{H}_{14}\text{Cl}_3\text{RhN}_2\text{O}_2$	523.6	68	185-187	45.31 (45.88)	2.12 (2.70)	5.69 (5.35)
<b>5.</b> $\text{C}_{16}\text{H}_{14}\text{Cl}_3\text{IrN}_2\text{O}_2$	564.9	70	160-163	34.35 (34.02)	2.21 (2.53)	4.80 (4.96)
<b>6.</b> $\text{C}_{20}\text{H}_{14}\text{Cl}_3\text{IrN}_2\text{O}_2$	612.9	72	210-212	39.29 (39.18)	4.25 (4.56)	4.25 (4.56)

Elemental analyses, melting points, colours and molecular weights are given in Table I and are in good agreement with the actual composition. All the complexes were microcrystalline solids with a colour ranging from brown to dark green. They were insoluble in water, but soluble in DMF, DMSO, THF and CHCl<sub>3</sub>. They are very stable and do not decompose in air.

#### A. <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectra of the prepared ligands and complexes were carried out in d<sub>6</sub>-DMSO. The intensities of all the resonance lines were determined. The chemical shift observed for the OH protons at ca (13.1 ppm) is not observed in the complexes and this confirms the bonding of oxygen to the metal ions. The presence of a sharp singlet for the –C(CH)=N protons (8.9 ppm) indicates that the magnetic environment is equivalent for all protons, suggesting the presence of a planar ligand in the complexes. The multiplets of the aromatic protons appeared within the range 6.9 to 7.6 ppm and are not affected by chelation.

#### B. FT-IR Spectra

The two Schiff base ligands show a strong IR band in the 1613–1634 cm<sup>-1</sup> region characteristic of azomethine absorption (CH=N). This band shifted to lower frequencies (10–20 cm<sup>-1</sup>) and appeared at 1593–1624 cm<sup>-1</sup> in the metal complexes, indicating coordination of the nitrogen atom of Schiff base to the metal. If the Schiff bases coordinated via the nitrogen atom, a reduction in the >(C=N) frequency due, to a lowering of electron density is to be expected. There is, however, a tendency of this band of Schiff base ligands of aromatic diamines to shift to lower frequencies on coordination to the metal than occurs with those of aliphatic diamines. This is due to electron delocalisation over the whole molecule on complexation. Thus, the IR spectra give clear evidence that bonding of the ligand to the metal ion can occur through nitrogen and oxygen atoms and that the ligands act in a tetradentate manner.

#### C. FAB mass spectra

Mass spectroscopy, which is mainly applied in the analysis of biomolecules, has been increasingly used as a powerful structural characterization technique in coordination chemistry. The mass spectra of the ligands, show peaks at m/z = 269 and 317 respectively, corresponding to molecular weights of 268.31 and 316.35 respectively. The molecular peaks for the complexes of Rh(III) were observed at m/z = 438.95 and 490.96 and those for the Ir(III) complexes were observed at 529.01 and 579.02 and these are in good agreement with a loss of a Cl ion from the respective complexes.

Therefore, these results complemented previous characterizations of the complexes as having octahedral species with tetradentate Schiff bases as ligands.

#### IV. CONCLUSION

Four new rhodium and iridium complexes have been synthesised and these have been fully characterised. Crystal structure elucidation of the rhodium and iridium complexes is currently under investigation in our laboratories.

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