

Synthesis and characterization of new Schiff base ligands

Haleden Chiririwa and Edison Muzenda

Abstract— Four new Schiff base ligands [1-4] have been prepared by a 2:1 molar condensation of ethylenediamine with 4-methoxy-benzaldehyde, 4-chloro-3-nitrobenzaldehyde, 2,3-dimethoxybenzaldehyde and 2,3,4-trimethoxybenzaldehyde. The ligands were characterised on the basis of their elemental analysis, IR spectroscopies, ^1H , ^{13}C NMR and ESI-mass spectrometry.

Keywords— Characterisation, condensation, ethylenediamine, ligands, Schiff bases

I. INTRODUCTION

This work originates from our interest in developing a new class of bidentate and tetradentate ligands [1-5] and to the best of our knowledge these Schiff base ligands that we have prepared are new and have not been reported in the literature. The chemistry of the transition metal complexes of Schiff-base ligands has played an important role in the development of coordination chemistry as a whole [6]. In this context, a great deal of information regarding the properties of synthetic Schiff-base ligands of potential interest has been accumulated during the last decades [7]. Several of these compounds have been characterized and used as models for biological systems [8]. Complexes of transition metals with Schiff bases have been reported to show better biological activity than the free ligands [9], however the activity of some ligands has been found to be more than their respective metal chelates [10]. 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 [11,12] and silver [13]. Silver(I) triphenylphosphine complexes have been increasingly studied because of their interesting structure as well as their antimicrobial and anticancer properties [14-16]. According to our knowledge no study has been reported for complexes with platinum and palladium before and hence attempts have been made to complex these novel ligands with platinum and palladium.

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II. EXPERIMENTAL

All manipulations were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques unless otherwise stated. All other glassware was thoroughly dried at 210 °C for at least four hours prior to use.

Solvents and reagents

Hexane and pentane were refluxed and distilled from calcium hydride (CaH_2), tetrahydrofuran (THF), diethyl ether (Et_2O) and toluene were dried over sodium-wire and benzophenone, dichloromethane was dried over P_2O_5 under nitrogen. Methanol was refluxed over magnesium turnings and iodine. After the purification procedures the solvents were stored under nitrogen in Teflon sealed storage bottles. All reagents were purchased from Aldrich and used without further purification. Palladium and platinum were obtained as chloride salts from Johnson-Matthey. Anhydrous magnesium sulphate or sodium sulphate were used for drying reaction solutions.

Instrumentation

Melting points were determined on the Kofler hotstage microscope (Reichert Thermovar) and are uncorrected. Microanalysis data was obtained from the University of Cape Town's Microanalytical Laboratory using a Carlo Erba EA1108 elemental analyser. Infrared Spectra were recorded on a Perkin-Elmer 1000 FT-IR spectrometer, at the University of Cape Town, as KBr discs for solids. All data are given in wavenumbers (cm^{-1}).

^1H , ^{13}C and spectra were recorded on either a Varian Unity-400 (^1H : 400 MHz; ^{13}C : 100.6 MHz) or Varian Mercury-300 (^1H : 300 MHz; ^{13}C : 75.5 MHz) spectrometer at ambient temperatures. ^1H NMR spectra were referenced internally using residual protons in the deuterated solvent (CDCl_3 : δ 7.27; DMSO: δ 2.50 ppm) and values reported relate to tetramethylsilane (δ 0.00). ^{13}C NMR were similarly referenced internally to the solvent resonance CDCl_3 : δ 77.0; DMSO: δ 39.4 and with values reported relative to tetramethylsilane (δ 0.00). All chemical shifts are quoted in δ (ppm) and coupling constants, J , in Hertz (Hz). Mass spectra (EI) were recorded using a JEOL-MATE(II) GC-MS instrument at UCT.

General procedure for the synthesis of the schiff base ligands

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.

A. Preparation of 1

Product was obtained as a white crystalline powder in 83% yield. M.p.: 125-127 °C. ¹H NMR: (400 MHz, CDCl₃) δ_H 8.64 (s, 2H), 7.95 (d, 2H, *J* = 8.5 Hz), 7.24 (dd, 2H, *J* = 0.7 Hz, *J* = 2.0 Hz), 7.27 (dd, 2H, *J* = 0.6 Hz, *J* = 2.1 Hz), 4.01 (s, 4H), 2.17 (s, 6H) ¹³C NMR: (400 MHz, CDCl₃) δ 158.45, 136.96, 135.57, 131.73, 129.52, 129.27, 127.50, 61.34. EA: Calc. for C₁₈H₁₈Cl₂N₂O₂: C, 59.19 %; H, 4.97 %; N 7.67 %. Found: C, 59.39 %; H, 4.72 %; N 7.42 %. IR (KBr): 1617 cm⁻¹ (C=N, imine). EI-MS: *m/z* 336.74 [M - CH₃O]⁺.

B. Preparation of 2

Product was obtained as a yellow crystalline solid in 85% yield. M.p.: 145-147 °C. ¹H NMR: (400 MHz, CDCl₃) δ_H 8.30 (s, 2H), 8.22 (s, 2H), 7.83 (d, 2H, *J* = 8.3 Hz), 7.58 (d, 2H, *J* = 8.3 Hz), 4.03 (s, 4H). ¹³C NMR: (400 MHz, CDCl₃) δ 158.8, 149.86, 135.93, 132.14, 131.89, 128.80, 124.53, 61.11. EA: Calc. for C₁₆H₁₂Cl₂N₄O₄: C, 48.58 %; H, 3.04 %; N 14.18 %. Found: C, 48.19 %; H, 3.12 %; N 14.42 %. IR (KBr): 1614 cm⁻¹ (C=N, imine). EI-MS: *m/z* 363.66 [M - Cl]⁺

C. Preparation of 3

Product was obtained as a yellow crystalline solid in 88% yield. M.p.: 145-147 °C. ¹H NMR: (400 MHz, CDCl₃) δ_H 8.65 (s, 2H), 7.51 (d, 2H, *J* = 1.6 Hz), 7.03 (t, 2H, *J* = 7.8 Hz), 6.92 (d, 2H, *J* = 1.6 Hz, *J* = 2.1 Hz), 4.00 (s, 4H), 3.85 (s, 6H), 3.77 (s, 6H). ¹³C NMR: (400 MHz, CDCl₃) δ 158.54, 152.74, 149.36, 129.96, 124.04, 118.88, 114.24, 61.91, 61.67, 58.85. EA: Calc. for C₂₀H₂₄N₂O₄: C, 67.40 %; H, 6.79 %; N, 7.86 %. Found: C, 67.19 %; H, 6.12 %; N, 7.72 %. IR (KBr): 1618 cm⁻¹ (C=N, imine). EI-MS: *m/z* 326.69 [M - CH₃O]⁺

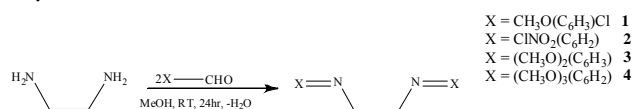
D. Preparation of 4

Product was obtained as a yellow crystalline solid in 92% yield. M.p.: 154-155 °C. ¹H NMR: (400 MHz, CDCl₃) δ_H 8.52 (s, 2H), 7.66 (s, 2H), 6.66 (s, 1H), 3.93 (s, 4H), 3.87 (s, 6H), 3.85 (s, 6H), 3.83 (s, 6H). ¹³C NMR: (400 MHz, CDCl₃) δ 158.10, 122.90, 122.17, 107.70, 62.01, 61.81, 60.87, 56.03. EA: Calc. for C₂₂H₂₈N₂O₆: C, 63.45 %; H, 6.78 %; N, 6.73 %. Found: C, 63.19 %; H, 6.52 %; N, 6.72 %. IR (KBr): 1625 cm⁻¹ (C=N, imine). EI-MS: *m/z* 386.44 [M - CH₃O]⁺

III. RESULTS AND DISCUSSION

The new Schiff base ligands **1** – **4** (Table 1) were prepared by condensation of aldehydes with the respective diamines

(Scheme 1). They were characterised by IR spectroscopy as well as ¹H and by ¹³C NMR.



Scheme 1 Synthetic route to Schiff base ligands

¹H NMR data suggests that the four ligands have symmetrical structure with two imine groups. Four methylene protons are found at *ca.* 4.00 ppm as singlets. Methylene protons on the methoxy substituent are observed as sharp singlets at around 3.77 – 3.87 ppm for ligands **3** and **4** but for ligand **1** the signal is observed at 2.17 ppm. The multiplets in the region 6.92 – 7.95 ppm are due to aromatic protons and the singlets observed at 8.30 – 8.65 ppm are assigned to the C=N protons.

The infrared spectra of the four ligands show stretching vibrations, (C-H) of the phenyl groups are in the region 3115 – 3015 cm⁻¹, while, (C-H) vibrations of the =CH- groups are observed as expected in the region 2970-2860 cm⁻¹[17]. Also strong bands appeared at about 1613 cm⁻¹ and these bands are attributed to the C=N stretching vibration [18].

Table 1: Schiff base ligands prepared

Ligand	Name	Structure
1	bis(2-chloro-4-methoxybenzylidene)ethane-1,2-diamine	
2	bis(4-chloro-3-nitrobenzylidene)ethane-1,2-diamine	
3	bis(2,3-dimethoxybenzylidene)ethane-1,2-diamine	
4	bis(2,3,4-trimethoxybenzylidene)ethane-1,2-diamine	

Physical properties of Schiff base ligands

Ligands **1** – **4** were isolated as crystalline solids which were all air stable solids and obtained in very good yields ranging between 83 – 92 % (Table 2).

Table 2 Yields and physical properties of ligands **1-4**.

Ligand	Yield (%)	Colour	Melting point (°C)
1	83	White	125-127
2	85	yellow	135-137
3	88	yellow	145-147
4	92	yellow	154-155

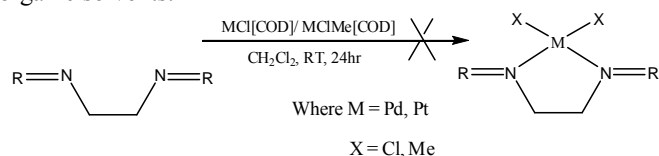
The mass spectra of Schiff base ligands are given in Table 3. The molecular ion peaks are in agreement with that calculated from their respective elemental analysis and fragmentation starts by loss of the methoxy group for ligands **1**, **3** and **4** but by initial loss of a chloride for ligand **2**.

Table 3 Mass spectra^a data of Schiff base ligands **1-4**

Ligand	Molar mass (g/mol)	Molecular fragment	Assignment
1	365.24	336.74	[M-CH ₃ O] ⁺
2	395.20	363.66	[M-Cl] ⁺
3	356.42	326.69	[M-CH ₃ O] ⁺
4	416.47	386.44	[M-CH ₃ O] ⁺

Attempted Complexation of Schiff base ligands with platinum and palladium

Attempts to complex the Schiff base ligands with either palladium or platinum precursors gave mixtures of products which were difficult to characterise due to their insolubility in organic solvents.

**Scheme 2** Attempted synthesis of palladium and platinum complexes with Schiff base ligands

IV. CONCLUSION

Four new ligands have been synthesised and these have been fully characterised. The synthesis of the platinum and

palladium and gold complexes needs to be investigated further. Crystal structures of the Schiff base ligands are to be elucidated. More data on these complexes need to be elucidated by solubilising the already prepared complexes as these complexes are only soluble in DMSO. Nevertheless, the fact that the complexes we attempted to synthesise are not very soluble in organic solvents suggests that there is considerable scope for the improvement of solubility by variation of the substituents at the imine carbon atoms. The possibility to prepare more soluble complexes is currently under investigation in our laboratories.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to the National Research Foundation, DST-NRF Centre of Excellence in Catalysis and Anglo Platinum Corporation for funding this project and the University of Cape Town for use of facilities.

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