Inorganica Chimica Acta 442 (2016) 1–9

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, characterisation and antimicrobial activity of new palladium and nickel complexes containing Schiff bases

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ARTICLE INFO

Article history:
Received 22 August 2015
Received in revised form 11 November 2015
Accepted 12 November 2015
Available online 19 November 2015

Keywords:
Schiff's base
2-(3,4-Dimethoxyphenyl)ethanamine
Palladium
Nickel
Complex
Antimicrobial activity

ABSTRACT

New Schiff base ligands were synthesized by condensation of 2-(3,4-dimethoxyphenyl)ethanamine with 2-hydroxy benzaldehyde (**L^1H**) and 2′-hydroxy acetophenone (**L^2H**) respectively. Reaction of **L^1H** or **L^2H** with Na_2PdCl_4 or $NiCl_2{\cdot}6H_2O$ in 2:1 ratio obtained four new coordination complexes $[M(L^{1-2})_2]$ (where M = Pd(II); **1** and **2** and M = Ni(II); **3** and **4**). Both the ligands and four complexes were characterised by elemental analysis, FT-IR and UV–Vis, spectroscopy. **L^1H**, **L^2H**, **1** and **2** were also characterised by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The molecular structures of **1** and **3** were determined by single crystal X-ray diffraction. The spectroscopic and crystal structure data showed that the ligands coordinated to M (II) ion in a bidentate monoanionic (O^-, N) fashion. The Pd—O and Pd—N bond lengths in **1** are 1.984(11) and 2.020(12) Å in **3** the Ni—O and Ni—N bond lengths are 1.8222(13) and 1.9262(15) Å respectively. The C=N bond length in **3** found 1.290(2) Å which was shorter than 1.310(19) Å in **1**. The bond angles provided square planar geometry around Pd(II) and Ni(II) in both **1** and **3**. There exists C—H···O type (2.50–2.52 Å) intermolecular hydrogen bonding in both **1** and **3** resulting in supramolecular structures. The antimicrobial activity of new Schiff base ligands and their Pd(II) and Ni(II) complexes against pathogenic microbial strains by agar well diffusion method was conducted. All the ligands and complexes showed significant antibacterial and antifungal activities. The bacterial and fungi growth inhibition activity of ligands has been increased on complexation as well as among complexes palladium complexes were found better antibacterial and antifungal agents than the nickel complexes of corresponding ligands. Ligand **L^1H** and the complex **2** showed highest antibacterial activity against *Pseudomonas desmolyticum* and highest antifungal activity against *Candida albicans.*

1. Introduction

Transition metal complexes of Schiff base ligands have been extensively studied due to their ease of preparation, availability of low cost raw materials, and formation of stable and chelated coordination complexes with most of the transition metals [1]. Applications of Schiff bases and their transition metal complexes have been largely investigated in the fields of biochemistry [2], catalysis [3] and medicine [4].

Schiff base ligands synthesized generally by condensation of aldehydes or ketones with aliphatic or aromatic amines. Their transition metal complexes have been evaluated for their variety of biological properties [5] such as antibacterial [6], antioxidant [8,21a], antifungal and anti-HIV [7], anticancer [9], antiamoebic [10a], herbicidal [11] activities. Investigation of biological activities Schiff bases derived from compounds (amines, aldehydes or ketones) of biologically important, for example isatin [7], 2-azetidinone [12a], cephalothin [12b] and their metal complexes have been the current interest. In this regard metal complexes of Schiff bases never been prepared from 2-(3,4-dimethoxyphenyl)ethanamine, a dimethyl derivative of dopamine, which is a starting material for many neurotransmitting agents [13] and other biologically important compounds [14] and investigated their biological activities.

Transition metal complexes are potential to show biological activity and are the current area of research [8c]. Schiff base ligands derived are very effective metal chelators on coordination, chelated complexes enhance the biological activity under the identical experimental conditions [15].

Azomethine (>C=N—) group of Schiff bases play an important role in the antimicrobial activities. The actual mechanism of increased activity of complexes is expected due to other than

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http://dx.doi.org/10.1016/j.ica.2015.11.017
0020-1693/

structural factors like solubility, dipole moment and cell permeability [16] and also their enzymatic action. A possible mode of increased toxicity may be considered in the light of Tweedy's chelation theory [17].

Therefore we have reported herein the synthesis, characterisation and evolution of antimicrobial activities such as antibacterial and antifungal activities of Schiff base ligands **L^1H** and **L^2H** derived from 2-(3,4-dimethoxyphenyl)ethanamine, 2-hydroxy benzaldehyde and 2-hydroxy acetophenone and their Pd(II) and Ni(II) complexes [M(**L^{1-2}**)$_2$] (**1–4**).

2. Experimental

2.1. Materials

2-(3,4-Dimethoxyphenyl)ethylamine (97%) and Na_2PdCl_4 (98%) were obtained from Sigma Aldrich, India. 2-Hydroxy benzaldehyde (99.5%) and 2′-Hydroxy acetophenone (99%) were purchased from Merck Specialities Pvt. Ind. Ltd. $NiCl_2{\cdot}6H_2O$ was obtained from S.D. Fine-Chem Ltd., India. All solvents (EtOH, MeOH, Pet-ether, Hexane, $CHCl_3$ and MDC) were of reagent grade and used without further purification. The microorganisms used in this study are *Klebsiella aerogenes* (*K. aerogenes*) [NCIM-2098], *Escherichia coli* (*E. coli*) [NCIM-5051], *Pseudomonas desmolyticum* (*P. desmolyticum*) [NCIM-2028] and *Staphylococcus aureus* (*S. aureus*) [NCIM-5022] as pathogenic bacterial strains and *Aspergillus flavus* (*A. flavus*) [NCIM-544] and *Candida albicans* (*C. albicans*) [NCIM-3100] as pathogenic fungal strains. These microorganisms were purchased from National Chemical Laboratory (NCL), Pune, India. These strains were maintained on nutrient agar slant at 4 °C. Standard antibiotics Ciprofloxacin and Fluconazole were purchased from Hi Media, Mumbai, India.

2.2. Analytical methods

Elemental analysis (C, H and N) was performed on a LECO–CHSNO – 9320 type elemental analyser. ^{1}H and $^{13}C\{^1H\}$ NMR spectra of ligands and Pd(II) complexes were recorded in $CDCl_3$ or DMSO-d_6 solutions on a Bruker WM-400 spectrometer (400 MHz) using TMS as an internal standard. The FT-IR spectra of all the compounds were recorded by scan method in the range of 4000–500 cm^{-1} with an Agilent FT-IR spectrometer. UV–Vis, spectra were recorded on UNI-CAM-UV 2-100 spectrophotometer. Melting points of ligands and complexes were determined with a Gallenkamp melting point apparatus in an open capillary and are reported uncorrected. Single crystal X-ray diffraction data of **1** and **3** were collected on a Bruker SMART APEX CCD-based X-ray diffractometer with Mo Kα-radiation (λ, 0.71073 Å, at T 193 K). The molecular structures of **1** and **3** were solved by direct methods and refinement was carried out with SHELXL-97 [18] package and empirical absorption correction has been applied (SADABS). All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions.

2.3. Synthesis of ligands *L^1H* and *L^2H*

2-(3,4-Dimethoxyphenyl)ethanamine (200 mg, 1.1 mmol) was dissolved in 20 ml of dry ethanol and this solution was stirred for 0.5 h at room temperature. 2-Hydroxy benzaldehyde (0.115 ml, 1.1 mmol) or 2′-hydroxy acetophenone (0.133 ml, 1.1 mmol) dissolved in 20 ml of dry ethanol was added to the above solution drop wise with stirring. The mixture was stirred further for 1.5–2.0 h at room temperature during which the solution changes to yellow colour. The progress of the reaction was monitored on TLC using pet-ether and ethyl acetate (70%:30%) as mobile phase. After completion, the reaction solution was concentrated by rotary evaporator which resulted yellow precipitate. The yellow precipitate was washed with hexane or petroleum ether (10 ml × 2) and then dried under vacuum. The dry solid was recrystallized from a mixture (1:1) of chloroform and hexane gave yellow single crystals of **L^1H** or **L^2H**.

L^1H: Yellow Crystalline solid; Yield: 290 mg (93%); M.P.: 122–123 °C; Element. *Anal.* Calc. (Found) for $C_{17}H_{19}NO_3$: C, 71.56 (71.16); H, 6.71(6.63); N, 4.91(4.96%); FT-IR (ν, cm^{-1}): 3418, 2992, 2957, 2835, 1634, 1588, 1515, 1333, 1261, 1138, 1025, 851, 761, 655, 554; UV–Vis, λ_{max} in nm: 261, 279, 315, 408; ^{1}H NMR ($CDCl_3$, δ ppm): 13.44 (s, 1H, OH), 8.18 (s, 1H, CH═N), 7.270–7.313 (t, 1H, H4), 7.160–7.184 (d, 1H, H6), 6.864–6.962 (d, 1H, H3), 6.707–6.848 (m, 4H, H5, H11, H14, H15), 3.849 (s, 3H, —OCH_3), 3.807 (s, 3H, —OCH_3), 3.817–3.837 (q, 2H, =NCH_2), 2.934–2.968 (t, 2H, —CH_2Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 36.241 (C9), 55.222 (OCH_3), 55.412 (OCH_3), 59.909 (C8), 111.748 (C5), 112.725 (C11), 116.458 (C14), 118.372 (C15), 118.557 (C10), 120.587 (C4), 131.528 (C3), 131.765 (C1), 132.192 (C6), 147.176 (C13), 148.492 (C12), 160.772 (C2), 165.849 (C7).

L^2H: Yellow Crystalline solid; Yield: 310 mg (94%); M.P.: 125–126 °C. Element. *Anal.* Calc. (Found) for $C_{18}H_{21}NO_3$: C, 72.22 (72.32); H, 7.07(7.08); N, 4.68(4.75%); FT-IR (ν, cm^{-1}): 3392, 2934, 2912, 2836, 1607, 1516, 1454, 1230, 1137, 1024, 857, 816, 763, 653, 566, 527; UV–Vis: λ_{max} in nm: 257.6, 277, 319, 392; ^{1}H NMR ($CDCl_3$, δ ppm): 16.55 (s, 1H, OH), 7.443–7473 (d, 1H, H6), 7.249–7.292 (t, 1H, H4), 6.907–6.937 (d, 1H, H3), 6.723–6.825 (m, 4H, H5, H11, H14, H15), 3.853 (s, 3H, OCH_3), 3.815 (s, 3H, OCH_3), 3.785–3.802 (t, 2H, =NCH_2), 2.993–3.027 (t, 2H, ArCH_2), 2.180 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ ppm): 14.211 (CH_3), 35.605 (C9), 50.222 (C8), 55.257 (OCH_3), 55.454 (OCH_3), 111.848 (C5), 112.819 (C11), 116.429 (C14), 118.093 (C15), 118.703 (C10), 120.582 (C4), 128.608 (C3), 131.924 (C1), 132.252 (C6), 147.230 (C13), 148.537 (C12), 163.883 (C2), 172.402 (C7).

2.4. Synthesis of palladium complexes, [Pd(*L^{1-2}*)$_2$] (*1–2*)

The $Na_2[PdCl_4]$ (100 mg, 0.3 mmol) was dissolved in 10 ml of water and the solution was stirred for 5 min. A solution of ligand **L^1H** (194 mg, 0.68 mmol) or **L^2H** (203 mg, 0.68 mmol) made in 20 ml of acetone was added to the above solution with vigorous stirring and the stirring was continued further for 1.5–2.0 h. The progress of the reaction was monitored by TLC using pet-ether and ethyl acetate (50:50) as mobile phase. The resulting orange solution was extracted into 100 ml of chloroform. The chloroform layer was washed with water (25 ml × 3) and treated with anhydrous sodium sulfate crystals. The solvent was evaporated to dryness on rotary evaporator to obtain an orange-red powder. The orange-red powder subjected to recrystallization in a 1:1 mixture of chloroform and hexane gave yellowish-orange coloured crystals of **1** or **2** after 24 h.

1: Yellow-orange crystalline solid; Yield: 390 mg (85%); M.P.: 190–192 °C; Element. *Anal.* Calc. (Found) for $C_{34}H_{36}N_2PdO_6$: C, 60.49(60.30); H, 5.38(5.27); N, 4.15(4.18%); FT-IR: (ν, cm^{-1}): 3444, 2921, 1618, 1599, 1514, 1447, 1321, 1231, 1143, 1023, 912, 760, 583, 438; UV–Vis, λ_{max} in nm: 257.8, 280.7, 392; ^{1}H NMR ($CDCl_3$, δ ppm): 7.383 (s, 1H, CH═N), 7.219–7.544 (t, 1H, H4), 7.059–7.083 (d, 1H, H3), 6.905–6.926 (d, 1H, H6), 6.782–6.832 (m, 3H, H11, H14, H15), 6.537–6.576 (t, 1H, H5), 3.951–3.987 (t, 2H, NCH_2), 3.853 (s, 3H, OCH_3), 3.777 (s, 3H, OCH_3), 3.067–3.103 (t, 2H, CH_2Ar).

2: Yellow-orange crystalline solid; Yield: 400 mg (84%); M.P.: 191–192 °C; Element. *Anal.* Calc. (Found) for $C_{36}H_{40}N_2PdO_6$: C, 61.49(61.42); H, 5.73(5.65); N, 3.98(3.98%); FT-IR: (ν, cm^{-1}):