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Ruthenium and osmium complexes of novel carbohydrate derived salen ligands: Synthesis, characterization and *in situ* ligand reduction

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ABSTRACT

Synthesis and characterization of two ruthenium(II) and osmium(II) complexes (**1** and **2**) having carbohydrate derived salen ligand and *in situ* ligand reduction are reported. The1,2-*O*-isopropylidene-3,5-diazido-3,5-dideoxy-α-D-xylopyranoside (**L1**) was reduced by catalytic hydrogenation using continuous flow hydrogen reactor in the presence of salicylaldehyde to form the corresponding bis-imino derivative **H_2L2**. The ligand **H_2L2** has been transformed to **H_2L3** upon reduction of one of the imine bonds in consequence to the oxidation of the leaving PPh_3 group to $POPh_3$. Systematic spectroscopic characterization, ^1H and ^{13}C NMR, mass spectrometry, electronic spectra reveals the composition of the complexes. X-ray crystal structures of both the complexes are reported. Detailed electrochemical studies reveal the redox behaviour of the complexes and DFT calculations help to get the idea about the intense lowest-energy absorption for these two complexes.

1. Introduction

Choice of ligand is fundamental for the use of predefined metal chelating core keeping their physico-chemical properties such as fluorescence, photoactivity intact [1–11]. Primarily carbohydrate ligands bound to the periphery of the metal ion influence the solubility of the complexes and enhances their biocompatibility to great extent. In addition, due to their intrinsic biological property, carbohydrates add the site-specific character to the complexes they are bound to [10–13].

Owing to their compatibility with various organic functionalities and the stability in the cellular environment, Schiff bases are attractive choice as ligands for transition metal complexes to be used for various applications [14–21]. The ease of synthesis and versatility to form complexes have made them one of the most studied ligand systems for transition metal coordination chemistry [22–25]. 'Salens' are the tetradentate dianionic Schiff base ligands similar to porphyrins. It is easy to tune their electronic and steric properties through modular synthesis [26,27,17]. The ease of preparation of salens triggered extensive studies on metal–salen complexes in catalysis, storage/release of gases, chemosensing, development of functional materials etc. [28–32]. Moreover, the tetradentate salens are capable of providing the structural rigidity to the complex essential for drug-like behaviour.

The present paper describes the synthesis of a novel carbohydrate derived salen ligand achieved by the reduction of known 1,2-*O*-isopropylidene-3,5-diazido-3,5-dideoxy-α-D-xylopyranoside followed by imine formation with salicylaldehyde and subsequent preparation of a ruthenium and an osmium complex with the synthesized ligand. In addition, the *in situ* site specific imine reduction is quite unusual in literature. The novel complexes were authenticated by spectroscopic and crystallographic studies and their electronic properties were assumed by DFT studies.

2. Experimental

2.1. Materials

Reactions were carried out using dry solvents under inert atmosphere. The starting materials $RuCl_3{\cdot}xH_2O$, NH_4OsCl_6, triphenylphosphane, formaldehyde, KOH, salicylaldehyde were purchased from Sigma–Aldrich and used without purification. Analytical grade solvents were obtained from commercial suppliers and dried by usual methods prior to use. $[RuCl_2(CO)_2(PPh_3)_2]$, $[OsCl_2(CO)_2(PPh_3)_2]$ and 1,2-*O*-isopropylidene-3,5-di-azido-3,5-dideoxy-α-D-xylofuranoside were synthesized using literature procedures [33,34]. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance 500 NMR spectrometer at 500 MHz (^1H) and 125 MHz (^{13}C) or JEOL ECS 400 spectrometer at 400 MHz (^1H) and 100 MHz (^{13}C) using TMS as the internal standard. Elemental analyses were

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determined on a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were recorded on a Perkin–Elmer Spectrum RXI spectrophotometer with samples prepared as KBr pellets. Electronic spectra were recorded on HITACHI U-4100 spectrometer. Electrochemical measurements were carried out using a PAR model 273 potentiostat. A platinum disk working electrode, a platinum wire auxiliary electrode and an aqueous Ag/AgCl were used in a three electrode configuration. Electrochemical measurements were made under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potential. Mass spectra were recorded on a Q-Tof Micromass spectrometer by positive-ion mode electrospray ionization. Optimization of ground-state structures and energy calculations for all the complexes were carried out by density functional theory (DFT) method using the Gaussian 03 package, where B3LYP was chosen as the basis function and 631 g(d,p) basis set was taken for H, C, N, O and SDD basis set for Ru or Os.

X-ray diffraction measurements of **1** and **2** were performed on a Bruker SMART APEXII CCD area-detector diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). For both the crystals, X-ray data reduction was carried out using the Bruker SAINT program. The structures were solved by direct methods using the SHELXS-97 program and refinement using SHELXL-97 program. X-ray data reduction, structure solution and refinement were done using the SHELXL-97 program package [35].

For the ruthenium complex **1**, single crystals were obtained by slow diffusion of methanol solution. The unit cell dimensions were determined by a least squares fit of 674 of machine centred reflections ($0^\circ < \theta < 18^\circ$) for **1**. Thirty-six standard reflections were used to check the crystal stability toward X-ray exposure showed no significant intensity reduction over the course of data collection. Five final cycles of refinement converged with discrepancy indices $R[F^2 > 2\sigma(F^2)] = 0.0690$ and $wR(F^2) = 0.0755$ for **1.**

For the osmium complex **2**, Single crystals were obtained by slow diffusion of benzene solution. The unit cell dimensions were determined by a least squares fit of 5283 of machine centered reflections ($0^\circ < \theta < 23^\circ$) for **2**. Thirty-six standard reflections were used to check the crystal stability toward X-ray exposure showed no significant intensity reduction over the course of data collection. Five final cycles of refinement converged with discrepancy indices $R[F^2 > 2\sigma(F^2)] = 0.0450$ and $wR(F^2) = 0.0894$ for **2**.

2.2. Synthesis of ligand

H_2L2:A solution of compound **L1** (500 mg, 2.1 mmol) and salicylaldehyde (490 L, 4.6 mmol) in methanol (100 mL) was passed through 10% Pd–C CatCart in a H-Cube Continuous Flow Hydrogen Reactor (Thales Nano, Hungary) at 60 °C with a flow rate of 1 mL/min. The methanolic solution collected in the receiving flask was evaporated *in vacuo* and the syrupy residue was purified by flash chromatography using *n*-hexane–EtOAc (3:1) as eluent to afford pure compound **H_2L2** (735 mg, 89%) as light yellow foam. ^{1}H NMR ($CDCl_3$, 400 MHz) : 13.02 (bs, 1H, O*H*), 12.57 (s, 1H, O*H*), 8.40, 8.27 (2s, 2H, 2C = C*H*), 7.26–6.85 (m, 8H, Ar*H*), 6.10 (d, 1H, *J* 3.6 Hz, H-1), 4.66 (m, 1H, H-4), 4.56 (d, 1H, *J* 3.6 Hz, H-2), 4.01 (d, 1H, *J* 3.6 Hz, H-3), 3.77 (m, 2H, H-5a, H-5b), 1.58, 1.34 (2s, 6H, 2isopropylidene-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) : 167.6, 167.4, 160.9, 160.8, 133.2, 132.6, 132.0, 131.5, 119.1, 118.7, 118.5, 118.2, 117.1, 116.9, 112.1 (ArC), 105.2 (C-1), 85.6 (C-2), 79.0, 75.0, 58.3 (C-5), 26.9, 26.2 (2isopropylidene-CH_3). HRMS calcd. for $C_{22}H_{24}N_2O_5Na$ $(M+Na)^+$: 419.1583, found: 419.1579.

2.3. Synthesis of complexes

[Ru(L3)(CO)(PPh_3)] (**1**): To a refluxing solution of compound **H_2L2** (40 mg, 0.1 mmol) and Et_3N (28 L, 0.2 mmol) in dry toluene (10 mL) was added $[Ru(CO)_2(PPh_3)_2Cl_2]$ (75.2 mg, 0.1 mmol) and the mixture was refluxed for 12 h under N_2 atmosphere. With the progress of the reaction, the color of the solution turned light green. The resulting solution was evaporated *in vacuo*. The green solid residue was purified by flash chromatography using *n*-hexane–EtOAc (3:1) to afford pure compound **1** (55 mg, 70%). Single crystals were obtained by slow diffusion of methanol solution. ^{1}H NMR ($CDCl_3$, 500 MHz) : 7.61–6.22 (m, 23H, Ar*H*), 5.66 (d, 1H, *J* 4.0 Hz, H-1), 4.95 (d, 1H, *J* 4.0 Hz, H-2), 4.24 (d, 1H, *J* 2.0 Hz, H-4), 4.11 (bd, 1H, *J* 11.5 Hz, H-5a), 3.89 (dd, 1H, *J* 3.0 Hz, 13.0 Hz, H-3), 3.79 (m, 1H, H-5b), 3.69 (dd, 1H, *J* 3.0 Hz, 13 Hz, CH_2–NH), 3.54 (bd, 1H, *J* 13.0 Hz, CH_2–NH), 3.30 (bd, 1H, N*H*), 1.42, 1.29 (2s, 6H, 2isopropylidene-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) : 165.1 (*C*O), 133.8(3), 133.7(3), 133.4, 133.3, 133.2, 132.9, 130.8, 130.0, 129.7, 129.6(3), 127.8(3), 127.7(3), 125.4, 123.3, 121.9, 120.1, 114.8, 114.4, 111.6(3) (Ar*C*), 102.7 (C-1), 80.9 (C-2), 75.4 (C-4), 66.6 (*C*H_2–NH), 66.5 (C-3), 49.8 (C-5), 26.2, 26.0 (2isopropylidene-*C*H_3). HRMS calcd. for $C_{41}H_{40}N_2O_6PRu$ (M^+): 789.1667, found: 789.1670.

[Os(L3)(CO)(PPh_3)] (**2**): To a refluxing solution of compound **H_2L2** (40 mg, 0.1 mmol) and Et_3N (28 L, 0.2 mmol) in 2-methoxy ethanol (10 mL) was added $[Os(CO)_2(PPh_3)_2Cl_2]$ (84 mg, 0.1 mmol) and the mixture was allowed to stir at 155 °C for 12 h under N_2 atmosphere. The color of the solution turned greenish brown with the progress of the reaction. The resulting solution was evaporated *in vacuo* and the green residue was purified by flash chromatography using *n*-hexane–EtOAc (3:1) to afford pure compound **2** (45 mg, 50%). Single crystals were obtained by slow diffusion of benzene solution. ^{1}H NMR ($CDCl_3$, 400 MHz) : 7.65–6.36 (m, 23H, ArH), 5.74 (d, 1H, *J* 3.6 Hz, H-1), 5.02 (d, 1H, *J* 3.6 Hz, H-2), 4.32 (bs, 1H, H-4), 3.98 (m, 1H, H-5a), 3.85 (dd, 1H, *J* 2.8 Hz, 12.8 Hz, CH_2–NH), 3.74 (m, 1H, H-5b), 3.61 (dd, 1H, *J* 4.8 Hz, 12.8 Hz, CH_2–NH), 3.55 (m, 1H, H-3), 3.31 (m, 1H, N*H*), 1.50, 1.37 (2s, 6H, 2isopropylidene-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) : 167.7 (*C*O), 133.6, 133.4, 133.2(2), 132.6(2), 132.1, 132.0(3), 131.9, 131.5(2), 128.7(2), 128.6(2), 128.4(3), 119.1(2), 118.8(2), 118.4, 118.2, 117.1(2), 116.9(2), 112.1 (Ar*C*), 105.2 (C-1), 85.6 (C-2), 79.1 (C-4), 75.0 (*C*H_2–NH), 58.3 (C-3), 53.4 (C-5), 26.8, 26.2 (2isopropylidene-*C*H_3). HRMS calcd. for $C_{41}H_{40}N_2O_6POs$ (M^+): 879.2239, found: 879.2222.

The quantum yields of **H_2L2**, **1** and **2** were estimated by comparison with standard (quinine sulphate) of known quantum yield (0.577). Determination of the quantum yield was accomplished by comparison of the wavelength-integrated intensity of the samples to that of the standard. The optical density of samples and reference were kept below 0.05. The quantum yield of the samples were calculated using.

$$Q = Q_R(I/I_R)(OD_R/OD)\cdot(\eta^2/\eta^{R2})$$

where *Q* is the quantum yield, *I* is the integrated intensity, *OD* is the optical density, and *n* is the refractive index. The subscript *R* refers to the reference fluorophore(quinine sulphate) of known quantum yield. Samples and reference were excited at the same wavelength (315 nm).

3. Results and discussion

The known 1,2-*O*-isopropylidene-3,5-diazido-3,5-dideoxy-α-D-xylopyranoside (**L1**) was reduced by catalytic hydrogenation using continuous flow hydrogen reactor in the presence of salicylaldehyde to form the corresponding bis-imino derivative **H_2L2** in very good yield. The organometallic complexes [RuL3(CO)(PPh_3)] (**1**) and [OsL3(CO)(PPh_3)] (**2**) were synthesized by refluxing respective $[MCl_2(CO)_2(PPh_3)_2]$ (M = Ru/Os) with ligand **H_2L2** in the presence of triethylamine. For the synthesis of complex **1**, refluxing toluene