Polyhedron 31 (2012) 167–175

Contents lists available at SciVerse ScienceDirect

Polyhedron

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

Encapsulating ruthenium and osmium with tris(2-aminoethyl)amine based tripodal ligands

Soumik Mandal [a], Dipravath K. Seth [b], Parna Gupta [a,*]

[a] Department of Chemical Sciences, Indian Institute of Science Education and Research, Kolkata, BCKV Main Post Office, Mohanpur 741252, West Bengal, India
[b] Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700032, India

ARTICLE INFO

Article history:
Received 21 July 2011
Accepted 7 September 2011
Available online 17 September 2011

Keywords:
Ru/Os-complex
Tris(2-aminoethyl)amine Schiff base
Coordination cage
Fluorescence
DFT calculation
Geometry optimization

ABSTRACT

The reaction of a series of tripodal ligands, $H_3L^{1,2}$ and L^{3-6}, with $[M(PPh_3)_2Cl_2]$ (M = Ru, Os) affords a family of coordination cage compounds of the type $[M^{III}L^{1,2}]$ (**1–4**) or $[M^{II}L^{3-6}](BPh_4)_2$ (**5–12**). The Schiff base ligands (H_3L^1, L^3, L^5) have been synthesized by condensation of tris(2-aminoethyl)amine with salicylaldehyde, pyridine-2-aldehyde and 1-methyl-2-imidazolecarboxaldehyde. These ligands were further reduced and subsequently methylated to form the new ligands (H_3L^2, L^4, L^6). Single crystal X-ray diffraction studies of **1** and **2** show that the tripodal ligand wraps around the metal center as a hexadentate ligand to form a cage. All the synthesized compounds have been thoroughly characterized by ESI-MS, FT-IR, UV–Vis and NMR spectroscopic methods. To the best of our knowledge, this is the first ever report of osmium complexes with tris(2-aminoethyl)amine based tripodal ligands. DFT calculations were performed to obtain geometry optimized structures of all the other complexes (**3–12**).

1. Introduction

The importance of tripodal tetraamine ligands in coordination chemistry has been amply demonstrated over many years [1–4]. A large number of such ligands, also known as podands, have been prepared, and metal complexes containing these ligands have been shown to exhibit a wide variety of physical and chemical properties [5,6]. The binding sites in these podands are hard (mostly N and O), and therefore stabilize transition metal centers very well [7–10]. They have drawn much attention in recent years, mainly due to their possession of spheroidal cavities which enable them to efficiently sequester metal ions. They also have demonstrated their potential use in the synthesis of polynuclear structures [11–16].

Tris(2-aminoethyl)amine is one of the most rigorously used tripodal tetramine frameworks, due to its variable coordination modes leading to variety of structural assembles [17–21]. It was first synthesized long ago, dating back to 1896 [22], and it is still highly relevant, due to its versatility as a ligand, and also for the interesting applications of its complexes in the synthesis of novel materials [23–25] and medicine [26–28]. One of the ways in which the basic ligand skeleton of a tripodal tetraamine ligand can be altered is the formation of Schiff bases [29–33]. The metal complexes of Schiff bases based on tris(2-aminoethyl)amine are very interesting as they show good anion receptive properties [34] and emission patterns [35–37]. The interesting photophysical properties help these classes of complexes to find application in molecular recognition [38,39].

The tris(2-aminoethyl)amine molecule has a flexible tripodal structure with three aminoethyl groups showing multidentate coordination modes. Interestingly, the coordination chemistry of the tris(2-aminoethyl)amine Schiff base based tripodal ligand has remained largely unexplored. A literature survey shows that the chemistry of this type of ligand with the 4d series of metals, except ruthenium, is not so well known [40,41]. In the present study, tris(2-aminoethyl)amine is allowed to react with salicylaldehyde, pyridine-2-aldehyde and 1-methyl-2-imidazolecarboxaldehyde to form Schiff bases, then these ligands were further reduced and subsequently the imine(–CH=N–) nitrogen atoms were methylated. All six ligands (Fig. 1) were allowed to react with ruthenium and osmium precursors to form coordination cage [42,43] complexes through N,O or N,N chelating atoms. This study reports the first synthesis and complete characterization of osmium complexes with tris(2-aminoethyl)amine based ligands. All the complexes are expected to be chiral because of the spiral coordination arrangement of the achiral ligands around the metal. The CD spectra of $[RuL^1]$ (**1**), $[OsL^1]$ (**2**) and $[RuL^2]$ (**3**) indicate the presence of a racemic mixture for each in solution, as expected. Interestingly, there are considerable changes in the emission pattern as well as the wavelength of emission between these ligands and their corresponding complexes. DFT calculations were performed to obtain geometry optimized structures of the ruthenium ($[RuL^2]$ (**3**), $[RuL^3(BPh_4)_2]$ (**5**), $[RuL^4(BPh_4)_2]$ (**7**), $[RuL^5(BPh_4)_2]$ (**9**)

* Corresponding author. Tel.: +91 3473279130; fax: +91 3473279131.
E-mail address: parna.gupta@gmail.com (P. Gupta).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.09.010

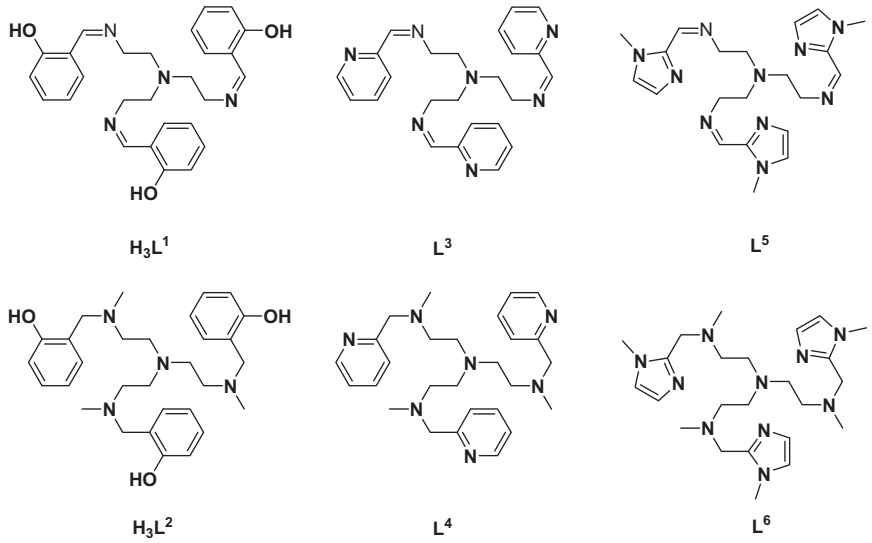

Fig. 1. Schematic diagram of the ligands $H_3L^{1,2}$, L^3–L^6.

and $[RuL^6(BPh_4)_2]$ (**11**)) and osmium ($[OsL^2]$ (**4**), $[OsL^3(BPh_4)_2]$ (**6**), $[OsL^4(BPh_4)_2]$ (**8**), $[OsL^5(BPh_4)_2]$ (**10**) and $[OsL^6(BPh_4)_2]$ (**12**)) complexes and to establish the nature of the orbitals involved in the transition processes and to correlate the structural parameters with the spectroscopic properties of the complexes. An account of the chemistry of the complexes of the tris(2-aminoethyl)amine based tripodal ligands is presented here, with special reference to their formation, structure and spectral and electrochemical properties.

2. Experimental

2.1. Materials and methods

The starting materials $RuCl_3.3H_2O$, $(NH_4)_2[OsCl_6]$, tris(2-aminoethyl)amine, salicylaldehyde, pyiridine-2-aldehyde, 1-methyl-2-imidazolecarboxaldehyde and triphenylphosphine were purchased from Sigma–Aldrich and were used without purification. All the solvents were dried by the usual methods prior to use. $[Ru(PPh_3)_3Cl_2]$, $[Ru(CO)_2(PPh_3)_2Cl_2]$ and $[Os(PPh_3)_3Cl_2]$ were prepared according to the reported procedures [44–46].

2.2. Synthesis of the ligands

2.2.1. H_3L^1

To a solution of salicylaldehyde (1 g, 8.20 mmol) in ethanol (20 mL) was added tris(2-aminoethyl)amine (0.40 g, 2.73 mmol) in absolute ethanol (20 mL). A yellow precipitate was formed immediately. The mixture was refluxed and stirred for 2 h, the resulting solid was filtered off, washed with diethyl ether, and dried in air to obtain the desired compound.

Yield 1.13 g (90%); *Anal.* Calc. for $C_{27}H_{40}N_4O_3$: C, 69.20; H, 8.60; N, 11.96. Found: C, 69.10; H, 8.80; N, 11.90%; ESI-MS *m/z*: 458.88 (M^+), 311.87 $(M–CH_2CH_2N{=}CHPhOH)^+$, 165.99 $(M^+–\{CH_2CH_2N{=}CHPhOH\}_2)^+$; ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.75 (m, 6H), 3.45 (m, 6H), 5.98 (d, 3H), 6.50 (t, 3H), 6.84 (t, 3H), 7.18 (t, 3H), 7.72 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ, ppm): 166.09 (N=C), 116.68 (aromatic ring), 118.48 (aromatic ring), 131.75 (aromatic ring), 161.05 (aromatic ring), 57.89 (NCH_2CH_2), 55.80 (NCH_2CH_2); IR (cm^{-1}, KBr pellet): 3436 (b, νO–H, typical for intramolecular hydrogen bonded O–H), 3000–2800 (ν_{C-H}), 1632 ($\nu_{C=N}$), 1610, 1582, 1498, 1459, 1430, 1337, 756.

2.2.2. L^3

To a solution of pyridine-2-aldehyde (1 g, 9.34 mmol) in ethanol (20 mL) was added tris(2-aminoethyl)amine (0.46 g, 3.11 mmol) in dry toluene (50 mL). The mixture was refluxed and stirred overnight, and the resulting liquid evaporated to dryness, affording an oily substance. The oily mass upon washing with cold ethanol gives the pure ligand.

Yield: 0.64 g (50%); *Anal.* Calc. for $C_{24}H_{27}N_7$: C, 69.71; H, 6.58; N, 23.71. Found: C, 69.45; H, 6.55; N, 23.92%; ESI-MS *m/z*: 414.83 $(M)^+$, 147.94 $(NCH_2CH_2N{=}CHPy)^+$. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.05 (–CH, 3H), 8.57 (3H, d, aromatic ring), 7.6–8.35 (9H, aromatic ring), 3.76 (6H, t, NCH_2CH_2), 2.96 (6H, t, NCH_2CH_2); ^{13}C NMR (500 MHz, $CDCl_3$, δ, ppm): 162.64 (N=C), 154.38 (aromatic ring), 149.24 (aromatic ring), 136.44 (aromatic ring), 124.52 (aromatic ring), 121.18 (aromatic ring), 59.73 (NCH_2CH_2), 55.22 (NCH_2CH_2). IR (cm^{-1}, KBr pellet): 3435–2850 (ν-H), 2850, 1651 ($\nu_{C=N}$), 1587, 1469, 1436, 774.

2.2.3. L^5

To a solution of 1-methyl-2-imidazolecarboxaldehyde (1 g, 9.08 mmol) in dry methanol (50 mL) was added tris(2-aminoethyl)amine (0.44 g, 3.01 mmol) in dry toluene (50 mL). The mixture was refluxed and stirred for overnight, and then the resulting liquid was purified by column chromatography. Yield 0.96 g (76%); *Anal.* Calc. for $C_{21}H_{30}N_{10}$: C, 59.69; H, 7.16; N, 33.15. Found: C, 60.01; H, 7.25; N, 33.08%; ESI-MS *m/z*: 422.89 $(M)^+$; ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.88–2.92 (br, 6H, NCH_2CH_2), 3.64–3.67 (br, 6H, NCH_2CH_2), 3.89 (s, 9H, N-CH_3), 6.86 (d, 3H, imidazole ring), 7.04 (d, 3H, imidazole ring), 8.25 (s, 3H, CH); ^{13}C NMR (500 MHz, $CDCl_3$, δ, ppm): 153.77 (N=C), 142.96 (imidazole ring), 128.92 (imidazole ring), 124.63 (imidazole ring), 60.25 (NCH_2CH_2), 55.29 (NCH_2CH_2), 35.15 (N–CH_3); IR (cm^{-1}, KBr pellet): 3400–2352 (ν-H), 1651 ($\nu_{C=N}$), 1479, 1439, 1288, 764.

2.2.4. Synthesis for H_3L^2, L^4 and L^6

H_3L^2, L^4 and L^6 were prepared by similar procedures [47]. A detailed method is given for one representative case.

To a solution of H_3L^1 (0.50 g, 1.09 mmol) in dry methanol, $NaBH_4$ (0.22 g, 6 mmol) was added slowly at low-temperature (~5 °C). The mixture was stirred overnight at room temperature. The solvent was evaporated and 20 mL water was added. The aqueous solution was treated with dilute hydrochloric acid until pH 7–8 was reached. The solution was extracted with dichloromethane