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Naphthyridine–imidazole hybrid ligands for the construction of multinuclear architecture

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ABSTRACT

Reaction of 2-imidazolyl-5,7-dimethyl-1,8-naphthyridine (L^1) with $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) affords the dinuclear complex $[Rh(COD)Cl]_2(\mu\text{-}L^1)$ (**1**). Elimination of chloride from the metal coordination sphere leads to a self-assembled tetranuclear macrocycle $[Rh(COD)L^1]_4[ClO_4]_4$ (**2**). A subtle alteration in the ligand framework results in the polymeric chain compound $\{Rh(COD)(L^2)\}_n(PF_6)_n$ (**3**) (L^2 = 2-imidazolyl-3-phenyl-1,8-naphthyridine). In all these complexes, the imidazole nitrogen and one of the naphthyridine nitrogen (away from the imidazole substituent) bind the metal. The 'parallel' and 'perpendicular' dispositions of nitrogens are observed in these compounds contributing to different Rh···Rh separations. The L^1 ligand adopts planar configuration, whereas the naphthyridine–imidazole rings deviate from planarity in L^2 yielding a polymeric structure. The extent of deviation is less in the polymeric structure $\{Mo_2(OAc)_4(L^2)\}_n$ (**4**) in which the ligand exhibits weak axial interactions to the metal.

1. Introduction

The desire to make new and complex structures has been a motivating factor for the intensive study of metalla-supramolecular chemistry. The applications of metal-containing supramolecular assemblies in gas storage [1–4], catalysis [5–8], single-molecule-magnetism [9–11], separation [12–14], sensor [15–18] and many other areas have afforded credence to this chemistry. Numerous multitopic ligands have been designed and metal components (including secondary building units, or SBU) have been developed [19–21]. Pyridine based ligands were one of the first to be used in the construction of metallamacrocycles [22–24]. Multi-site ligands containing multiple imidazole units have also been used in recent years [25,26]. The general scheme employed for the ligand design involves the covalent attachment of donor units on a desired organic platform. Ligand systems incorporating different types of donor moieties have shown prospects for the construction of homo- and heterometallic metallamacrocycles. Pyridine carboxylic acid has been employed for the construction of Pt and Pd based molecular squares [27,28]. Dunbar et al. have reported several heterobimetallic metallacycles consisting of Re_2/Pt and Re_2/Zn units [29,30]. Imidazole carboxylic acids have been employed for the construction of molecular polygons with 'Cp^*Rh' corners [31]. The disposition of metal-binding sites in the ligand framework and the directionality of the metal precursor dictate the topology of the resultant structure. The present work describes our recent effort to synthesize multinuclear compounds from a composite N-donor ligand.

We have employed naphthyridine–imidazole hybrid ligands (Scheme 1) for the synthesis of multinuclear compounds. The naphthyridine and imidazole nitrogens offer prospect for multimetal assemblies. The square-planar metal component 'Rh(COD)' (COD = 1,5-cyclooctadiene) has been chosen as the metal-containing unit. By judicious alteration in the ligand framework, and in the metal coordination sphere as well, dinuclear $[Rh(COD)Cl]_2(\mu\text{-}L^1)$ (**1**), tetranuclear macrocycle $[Rh(COD)L^1]_4[ClO_4]_4$ (**2**) and polymeric $\{Rh(COD)(L^2)\}_n(PF_6)_n$ (**3**) have been synthesized (Scheme 2). In this report, we make an attempt to rationalize their structures based on the ligand conformation and the metal-ion geometry.

2. Results and discussion

2.1. $[Rh(COD)Cl]_2(\mu\text{-}L^1)$ (**1**)

Addition of L^1 to the $[Rh(COD)Cl]_2$ in dichloromethane disrupts the dimeric structure and affords **1** in high yield. Molecular structure of **1** consists of two 'Rh(COD)Cl' units bridged by L^1 (Fig. 1). The terminal nitrogens of imidazolyl (N_1) and naphthyridine ($N_8{'}$) units bind to two independent Rh centers. The coordinating geometry around each Rh center is square planar and the metrical parameters are similar to those reported for Rh^I-COD compounds [32]. The angle between the naphthyridine (NP) plane and the

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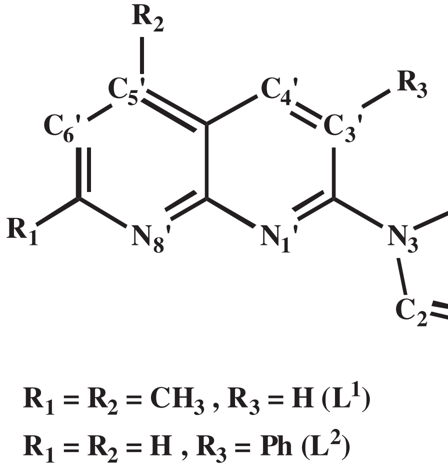


Scheme 1. Ligands used in the present study and the numbering scheme.

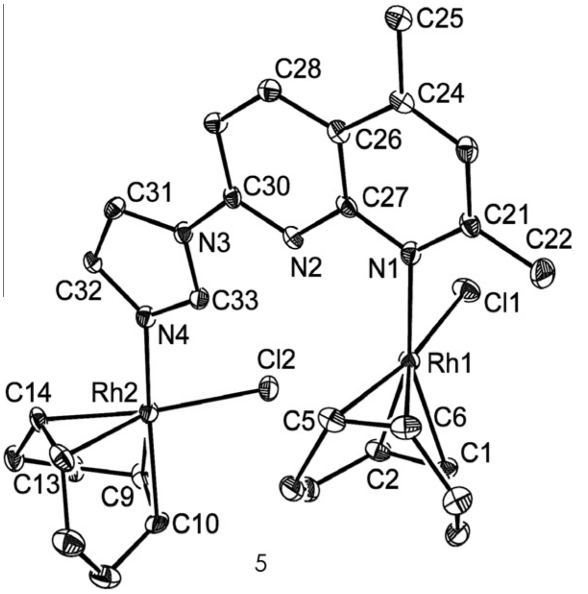


Fig. 1. ORTEP diagram (50% probability thermal ellipsoid) of **1** with important atoms labeled. Hydrogen atoms omitted for the sake of clarity. Selected bond distances (Å) and angles (°): Rh1–N1 2.124(3), Rh1–Cl1 2.3833(11), Rh1–C1 2.104(4), Rh1–C2 2.106(4), Rh1–C5 2.123(4), Rh1–C6 2.128(4), Rh2–Cl2 2.3910(10), Rh2–N4 2.105(3), Rh2–C9 2.094(4), Rh2–C10 2.103(4), Rh2–C13 2.127(4), Rh2–C14 2.137(4), N1–Rh1–Cl1 86.95(9), N4–Rh2–Cl2 90.64(9), N2–C30–N3–C33 2.9(5), Rh1···Rh2 6.1004(7).

imidazole (Im) plane is 3.9° (φ N2–C30–N3–C33 = 2.9(5)°). The non-bonded Rh···Rh distance is 6.1004(7) Å.

The ^{1}H NMR of **1** reveals a 2:1 composition of 'Rh(COD)' and L^1. However, the NMR spectrum exhibits two sets of NP protons in the ratio 1:0.7, clearly indicating a mixture of compounds in solution (see Fig. S1). The methyl protons appear as two singlets at δ 2.67, 2.71 ppm. In addition, broad signals are observed for COD protons at δ 1.84, 2.49, 4.21, 4.59 ppm. Based on the NMR data, the presence of Rh(COD)Cl(κN_1-L^1), Rh(COD)Cl($\kappa N_{8'}$-L^1) and the original dimer $[Rh(COD)Cl]_2$ is proposed. Interestingly, the ESI-MS exhibits high-intensity signals at 905, 681, 659, 435 attributed to $\{Rh_2(COD)_2(Cl)(L^1)_2\}^+$, $\{Rh_2(COD)_2(Cl)(L^1)\}^+$, $\{Rh(COD)(L^1)_2\}^+$, $\{Rh(COD)(L^1)\}^+$, respectively. The assignment is based on mass and isotropic distribution pattern.

2.2. $[Rh(COD)L^1]_4[ClO_4]_4$ (**2**)

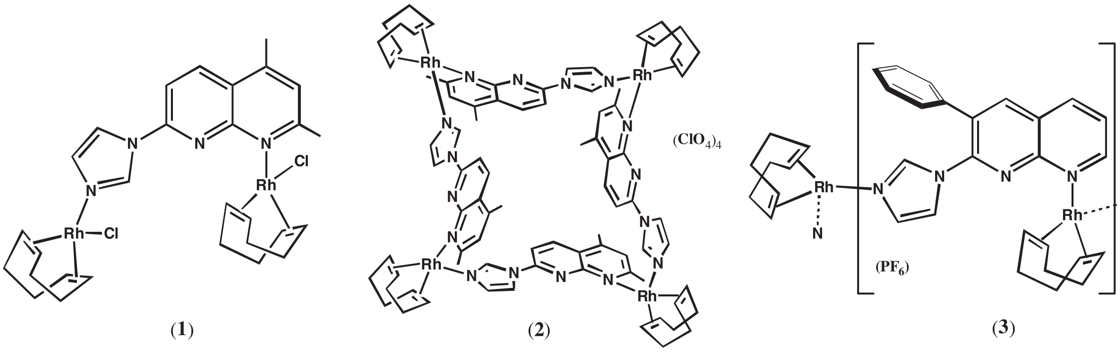
Removal of chlorides from $[Rh(COD)Cl]_2$ by $TlClO_4$ and subsequent addition of L^1 provided a cyclic tetramer $[Rh(COD)L^1]_4[ClO_4]_4$ (**2**). Molecular structure of **2** is confirmed by X-ray crystallography. The tetracationic core consists of four 'Rh(COD)' units bridged by four L^1 ligands (Fig. 2(a)). The molecule crystallizes in the tetragonal I41/a space group and only one 'Rh(COD)L^1' is observed in the asymmetric unit. Each Rh is connected to the neighboring metal by L^1 ligand through the terminal nitrogens of the Im and NP units. The four metals form an equilateral quadrangle of 8.5652(7) Å, each Rh makes an angle of 87.742(1)° with two adjoining metals, and four metals do not reside on the same plane (see Fig. 2(b)). The L^1 adapts a planar configuration (φ N2–C10–N3–C12 = 0.1(6)°). The Rh···Rh distance is 8.5652(7) Å, longer than the corresponding metal···metal distance in **1** by 2.47 Å.

The tetrameric compound **2** is also obtained from the dimer **1**. Treatment of **1** by Tl^I salt and subsequent addition of one equivalent of L^1 provided the cyclic tetramer **2**. Evidently, the removal of chloride allows the propagation of the structure aided by the linker L^1 culminating in a cyclic tetranuclear structure.

The iridium analog $[Ir(COD)L^1]_4[OTf]_4$ has been synthesized following a similar procedure using $[Ir(COD)Cl]_2$, TlOTf and L^1. The ORTEP diagram and the important bond parameters are provided in the supporting information.

Although the coordination motif of the L^1 is identical in both dimer structure **1** and tetrameric structure **2**, some significant differences are noted. The 'parallel' and 'perpendicular' disposition of the coordinating nitrogens are the characteristic features of compounds **1** and **2** (Fig. 3). This results in different metal···metal separations (6.1004(7) for **1** and 8.5652(7) Å for **2**).

All NP and COD protons exhibit broad signals in the ^{1}H NMR spectrum. The ESI-MS spectrum of complex **2** reveals signal at



Scheme 2. Line drawings of metallo-assemblies **1**–**3**.