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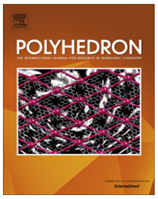

# Synthesis and structural characterization of Rh(III) complexes containing diamino ligands of types $\{D(C_6H_4NH_2)_2\}$ and $\{D(C_6H_4CH_2NHEt)_2\}$ (D = O, S) bearing different spacers

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ABSTRACT

The reaction of the diamino ligands of general formula $\{\boldsymbol{D}(C_6H_4NH_2)_2\}$ [$\boldsymbol{D}$ = O ($\boldsymbol{L^1}$); S ($\boldsymbol{L^2}$)] and $\{\boldsymbol{D}(C_6H_4CH_2NHEt)_2\}$ [$\boldsymbol{D}$ = O ($\boldsymbol{L^3}$); S ($\boldsymbol{L^4}$)] with $RhCl_3{\cdot}3H_2O$ yielded neutral coordination complexes $[Rh^{III}(\boldsymbol{L^n})Cl_3]$ [$n$ = 1 (**1**); $n$ = 2 (**2**); $n$ = 3 (**4**); $n$ = 4 (**5**)]. Compound **1** in *N*,*N*-dimethylformamide solution promoted the formation of the neutral complex $[Rh^{III}(\boldsymbol{L^1})(dmf)Cl_3]$ (**3**). A zwitterionic complex $[Rh^{III}(H\boldsymbol{L^4})Cl_4]$ (**6**) was obtained from the reaction of $\boldsymbol{L^4}$ with $RhCl_3{\cdot}3H_2O$ as a minor compound. All complexes were characterized in solution by NMR and by vibrational spectroscopy in solid state. Crystal structures of the chlorohydrates $[H_2\boldsymbol{L^3}]Cl_2{\cdot}H_2O$, $[H_2\boldsymbol{L^4}]Cl_2$, and the complexes **2**–**6** were identified by X-ray diffraction studies. Molecular structures of the complexes revealed different coordination patterns of the diamino ligands $\boldsymbol{L^n}$ as well as the formation of chelate rings of five-, six-, and eight members. The presence of N–H groups in the title compounds enhanced the formation of hydrogen bond networks that were analyzed on the basis of a graph set analysis approach, displaying rings at the first to third level.

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## 1. Introduction

Transition metal complexes derived from potentially tridentate pincer-type ligands have been widely studied for their interesting structural characteristics and the role that they perform as catalysts [1,2]. In particular, tridentate ligands containing both hard and soft donor atoms have shown a vast reactivity toward transition metals such as $Ni^{II}$, $Zr^{III,\ IV}$, and $Co^{II}$ [3–5]. In this context, some metal complexes of $Ni^{II}$, $Pd^{II}$, $Fe^{II}$, and $Co^{II}$ containing tridentate pincer-type ligands, bearing nitrogen as donor atom, have been used as catalysts for the ethylene polymerization [6–8]. In regard to structural features, it has been reported that wide-bite-angle chelating ligands such as DPEphos and Xantphos, bearing oxygen and phosphorus acting as donor atoms in a *P–O–P* core, have an effect on the *meridional* or *facial* coordination to some *d*-block elements [9,10]. In connection with this, for several transition metal complexes of bidentate ligands that also contain oxygen (hard donor) and phosphorus (soft donor), it has been noted that the hard donor atom readily undergoes de-coordination from the metal center in the coordination entity [11,12]. This hemilability plays a key role in several catalytic transformations such as alkyne carbothiolation [13], alkene and alkyne hydroacylation with β-S-substituted aldehydes [14], or hydroamination of vinylarenes [15].

On the other hand, the hemilability of pincer-type ligands can be tuned by using different central donor atoms or by varying the size of the pendant arms. We have recently reported the different coordination modes of diamino ligands such as $\boldsymbol{L^1}$ and $\boldsymbol{L^2}$ towards $Pd^{II}$ and $Pt^{II}$; in these compounds we demonstrated that the hard oxygen atom remains uncoordinated ($\kappa^2N$ mode) whereas the soft sulfur can be coordinated to the noble metals ($\kappa N\kappa S$ and $\kappa^2N\kappa S$ modes) [16]. To the best of our knowledge, there is just another structural report of transition metals containing similar diamino ligands, where the $Zn^{II}$ complex displayed an *N*-monodentate behavior of $\boldsymbol{L^1}$ [17].

In this paper, we describe the coordination studies of $\boldsymbol{L^1}$–$\boldsymbol{L^4}$ ligands to rhodium(III) central atom, where the ligands have different $\boldsymbol{D}$ donor atoms ($\boldsymbol{D}$ = O, S) as well as different moieties used as spacers ($C^{sp2}$–$NH_2$ in $\boldsymbol{L^1}$ and $\boldsymbol{L^2}$ versus $C^{sp2}$–$CH_2$–NHEt in $\boldsymbol{L^3}$ and $\boldsymbol{L^4}$). We noticed the influence of the wide-bite-angle of $\boldsymbol{L^n}$ ligands on the coordination modes. Additionally, the effect of the donor strength of either oxygen or sulfur atoms in the Rh local geometries was also analyzed. Overall, the characterization in

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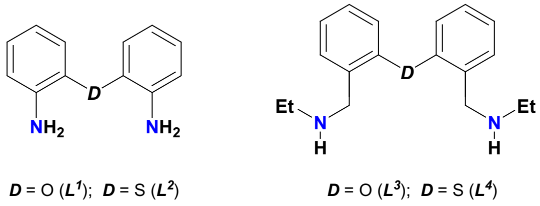

**Fig. 1.** Structure of ligands $\boldsymbol{L^1}$–$\boldsymbol{L^4}$ with different pendant groups.

solution and in solid state of six complexes of rhodium(III) proved the wide versatility of the $\boldsymbol{L^n}$ ligands (Fig. 1), on the basis of the observed κ$^2$*N* and κ*N*κ*S* bidentate modes, or the κ$^2$*N*κ*O* and κ$^2$*N*κ*S* tridentate modes.

## 2. Experimental

### 2.1. Materials and measurements

All the manipulations of air and moisture sensitive materials were carried out under dinitrogen atmosphere using Schlenk techniques. Solvents were dried according to the standard methods and distilled before their use. $RhCl_3 \cdot 3H_2O$ and ethylamine 2.0 M in methanol were purchased from Aldrich and used as received. The $\boldsymbol{L^1}$ and $\boldsymbol{L^2}$ ligands [18–20] and the *bis*-(2-formylphenyl)ether or *bis*-(2-formylphenyl)thioether [21,22] starting materials used for the synthesis of the $\boldsymbol{L^3}$ and $\boldsymbol{L^4}$ ligands, respectively, were prepared by reported methods. Melting points were recorded on a Mel-Temp II apparatus and are reported without correction. Elemental analyses were performed on a Perkin–Elmer Series II CHNS/O Analyzer 2400. Mass spectra were recorded at Cinvestav–México on a HReLC1100/MSDTOF Agilent Technology equipment. Infrared spectra were recorded on a FT-IR 200 Perkin–Elmer spectrophotometer in the 4000–400 cm$^{-1}$ range using KBr pellets. Raman spectra in the solid state were recorded in the 4000–100 cm$^{-1}$ range on a Perkin–Elmer spectrum GX NIR FT-Raman spectrophotometer with 10–280 mW laser power and 4 cm$^{-1}$ resolution. NMR spectra were recorded on a Varian NMRS 400 spectrometer; $^1$H (399.78 MHz) and $^{13}$C{$^1$H} (100.53 MHz) spectra were obtained in DMSO-d6 and $CDCl_3$. Chemicals shifts (ppm) of $^1$H and $^{13}$C{$^1$H} spectra are relative to the frequency of $SiMe_4$. NMR assignments of the ligands $\boldsymbol{L^1}$–$\boldsymbol{L^4}$ and complexes **1**–**6** were performed by two-dimensional heteronuclear and mononuclear experiments (COSY, HSQC, and HMBC). Suitable yellow single-crystals of chlorohydrates $[H_2\boldsymbol{L^3}]Cl_2 \cdot H_2O$ and $[H_2\boldsymbol{L^4}]Cl_2$ were formed by addition of hydrochloric acid (0.1 mL) to an acetonitrile saturated solution (5 mL) of the neutral $\boldsymbol{L^n}$ ligand. Single crystals of complexes **2**·DMF (orange), **3** (brown), *mer*-**4** (red), 6·MeCN (red), and **5** (yellow) were obtained by slow evaporation of dimethylformamide (for **2** and **3**), methanol (for **4**), toluene–methanol (1:1 ratio, for **5**), and acetonitrile (for **6**) saturated solutions.

X-ray diffraction data of $[H_2\boldsymbol{L^3}]Cl_2 \cdot H_2O$, $[H_2\boldsymbol{L^4}]Cl_2$, and complexes **2**–**6** were collected at room temperature on an Oxford Diffraction Gemini CCD diffractometer with either graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) for $[H_2\boldsymbol{L^3}]Cl_2 \cdot H_2O$, **2**·DMF, **3**, **4**, and **6**·MeCN, or Cu Kα radiation ($\lambda$ = 1.54184 Å) for $[H_2\boldsymbol{L^4}]Cl_2$ and **5**. Data were integrated, scaled, sorted, and averaged using the CrysAlis software package. By using Olex2 [23], the structures were solved with the SHELXS [24] structure solution program using Direct Methods and refined with the SHELXL [24] refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were kept fixed with a common isotropic displacement parameter. In the crystal structure of compound **2**·DMF, the solvent molecule displayed positional disorder over two positions, with the main component having an occupancy of 0.529(14). The disorder was treated with rigid bond restraints by using restraints such as SAME, SIMU, DELU, and FLAT. Crystallographic data are given in Table 2 and selected bond and angles are given in Table 3.

### 2.2. Synthesis of $\boldsymbol{L^3}$ and $\boldsymbol{L^4}$

The ligands $\boldsymbol{L^3}$ and $\boldsymbol{L^4}$ were prepared by linear synthesis from diphenylether and diphenylthioether, respectively (see Scheme 1), following the general method below described.

A mixture of either *bis*-(2-formylphenyl)ether or *bis*-(2-formylphenyl)thioether [21,22] in 15 mL of toluene with ethylamine 2.0 M in methanol, catalytic amounts of sulfuric acid (three drops, 98%), and 1.00 g of sodium sulfate anhydrous was refluxed for 25 h. Then, the mixture was cooled to room temperature and the sodium sulfate was filtered off; the solution was evaporated to dryness and a yellow oil was obtained. The oil was dissolved in 10 mL of dichloromethane and extracted with water (3 × 15 mL). The organic phase was dried with sodium sulfate anhydrous, filtered, and evaporated to give a yellow oil that was identified as the corresponding diimine.

$Na[BH_4]$ was added to a solution of 0.50 g of a given diimine in 10 mL of methanol; the mixture was stirred for 12 h at room temperature. The white suspension was evaporated to dryness; aqueous KOH 2.5 (10 mL) and 10 mL of ethyl acetate were added to the white solid formed. The mixture was stirred for 15 min and extracted with ethyl acetate (2 × 10 mL). The organic phase was separated and dried with sodium sulfate anhydrous; a yellow oil was obtained by evaporation of the solvent to dryness to give the corresponding diamine.

#### 2.2.1. Synthesis of $\{O(2\text{-}C_6H_4CH_2NHEt)_2\}$ ($\boldsymbol{L^3}$)

*Bis*-(2-formylphenyl)ether (0.500 g, 2.212 mmol), ethylamine 2.0 M solution (4 mL, 8.0 mmol). Yellow oil (0.382 g, 1.364 mmol). $Na[BH_4]$ (0.412 g, 10.9 mmol). Yield 62% (0.239 g). *Anal.* Calc. for $C_{18}H_{24}N_2O \cdot 0.75H_2O$: C, 72.57; H, 8.63; N, 9.40. Found; C, 72.76; H, 8.79; N, 9.27%. IR data (KBr, cm$^{-1}$): 3290 (NH); 3065, 2965 ($CH_{aromatics}$); 1580, 1484 (C=C); 1231 (C—O—C). $^1$H NMR ($CDCl_3$) $\delta$ = 7.38 (dd, 2H, H3 $^3J$ = 7.99, $^4J$ = 1.39 Hz), 7.18 (dd, 2H, H5, $^3J$ = 7.00, $^3J$ = 7.99 Hz), 7.02 (dd, 2H, H4, $^3J$ = 7.00, $^3J$ = 7.99 Hz), 6.74 (d, 2H, H6, $^3J$ = 7.99 Hz), 3.85 (s, 4H, $CH_2NH$), 2.65 (q, 4H, $CH_2$, $^3J$ = 7.19 Hz), 2.53 (s, 2H, N*H*), 1.10 (t, 6H, $CH_3$, $^3J$ = 7.19 Hz). $^{13}$C{$^1$H} NMR ($CDCl_3$) $\delta$ = 155.1 (C1), 130.6 (C2, C3), 128.5 (C5), 123.5 (C4), 117.9 (C6), 48.8 ($C$H$_2$NH), 43.4 ($C$H$_2$), 15.2 ($C$H$_3$).

**Table 1**
Structural features observed in complexes $[Rh(\boldsymbol{L^n})Cl_m]$ ($m$ = 3, 4).

| Compound | Coordination mode of the ligand $\boldsymbol{L^n}$ | Number and size of chelate rings | $Rh^{III}Cl_m$ geometrical isomerism | Sum of internal angles around $Rh^{III}$ (°) |
|---|---|---|---|---|
| **2**·DMF | κ$^2$*N*κ*S* ($\boldsymbol{L^2}$: tridentate) | Two five-membered | *fac* ($m$ = 3) | 1610.6 |
| **3** | κ$^2$*N* ($\boldsymbol{L^1}$: bidentate) | One eight-membered | *fac* ($m$ = 3) | 1610.0 |
| **4** | κ$^2$*N*κ*O* ($\boldsymbol{L^3}$: tridentate) | Two six-membered | *mer* ($m$ = 3) | 1616.9 |
| **5** | κ$^2$*N*κ*S* ($\boldsymbol{L^4}$: tridentate) | Two six-membered | *mer* ($m$ = 3) | 1608.1 |
| **6**·MeCN | κ*N*κ*S* ($\boldsymbol{L^4}$: bidentate) | One six-membered | *cis* ($m$ = 4) | 1609.9 |

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