

Proceedings

# Synthesis and structural characterization of a novel amine-bis(phenolate)ligand<sup>†</sup>

Laura Rodríguez-Silva<sup>1,\*</sup>, M. Isabel Fernández-García<sup>1</sup>, Esther Gómez-Fórneas<sup>1</sup>, Sandra Fernández-Fariña<sup>2</sup>, Luis M. González-Barcia<sup>2</sup> and María J. Romero<sup>2</sup>

<sup>1</sup> Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, Lugo, 27002, Spain.

<sup>2</sup> Departamento de Química Inorgánica, Facultade de Química, Campus Vida, Universidade de Santiago de Compostela, Santiago de Compostela, 15782, Spain.

\* Correspondence: laura.rodriguez@usc.es

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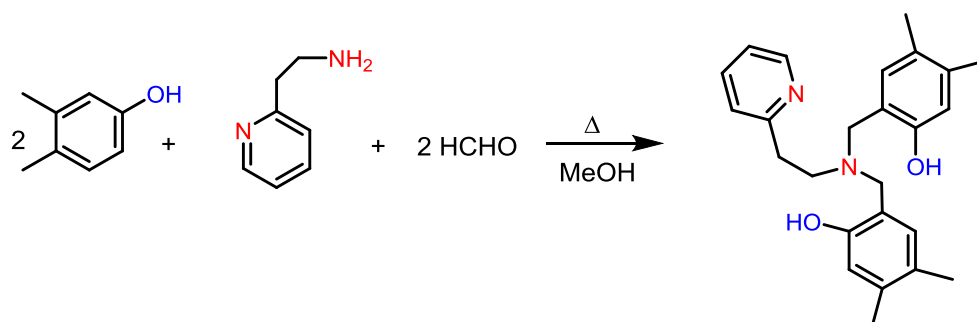
**Abstract:** The substituted amine-bis(phenol) compound N,N-bis-(4,5-dimethyl-2-hydroxybenzyl)-N(2-pyridylethyl)amine (H<sub>2</sub>L) was prepared through a Mannich reaction utilizing two equivalents of a substituted phenol, two equivalents of formaldehyde and a single equivalent of a secondary amine. The organic compound, which may act as a tripodal ligand in coordination complexes, has been characterized by elemental analysis, IR, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies, mass spectrometry (ES) and X ray diffraction spectroscopy.

**Keywords:** Mannich reaction, bis(phenolate), tripodal ligand.

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## 1. Introduction

The chemical activity of natural molecules like metalloenzymes can be of inspiration to design new synthetic compounds with tailored functions to be used for the most diverse technological applications. During such processes, it is most crucial to understand how the template natural system really works, and what are the minimal indispensable structural components that must be kept or mimicked in order to retain the function of interest. The use of chelating tetradentate amine-bis(phenolate) ligand has recently played an increasingly important role in transition-metal catalyst design and modelling of metalloenzyme active-sites. During several years we have studied the different behaviour exhibited by these ligands, mainly due to the potential reduction capacity showed by the chemical group which leads to a great variety of coordination patterns. In this work we report the preparation, structure determination and characterization of a novel tetradentate tripodal ligand.



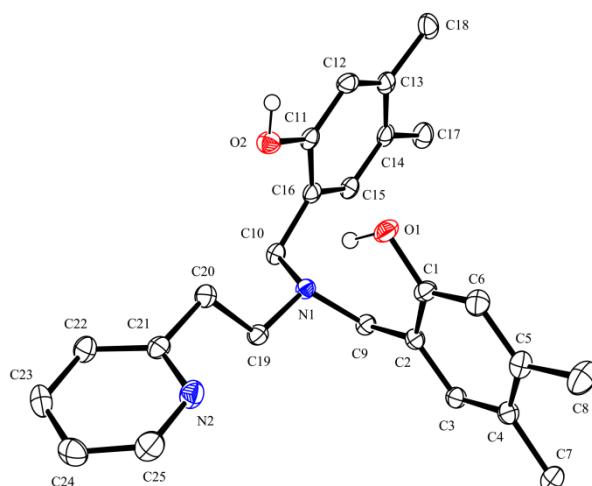
Scheme I

## 2. Methods

The substituted amine-bis(phenol) compound H<sub>2</sub>L was prepared from a Mannich reaction (Scheme 1) according to the literature [1,2], utilizing two equivalents of a substituted phenol, two equivalents of formaldehyde and a single equivalent of a secondary amine refluxing in methanol for 3 h. After cooling a white powder at almost quantitative yield was obtained. White crystals of H<sub>2</sub>L, suitable for single crystal X-ray diffraction studies, were obtained by slow evaporation of methanol solution of the ligand. The compound was also characterised by elemental analysis, IR, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Ligand H<sub>2</sub>L: Anal Calc. for C<sub>25</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.8; H, 7.7; N, 7.1. Found: C, 76.9; H, 7.7; N, 7.1%. MS ES (m/z): 391.2; IR (KBr, cm<sup>-1</sup>): E(O-H) 3266.6, E(C-O) 1284.5, <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 8,9 (s br, 2H, OH), 8.6, 7.6, 7.2 and 7.1 (4H pyridine), 6.8 (s, 2H, phenyl), 6.6 (s, 2H, phenyl), 3.7 (s, 2H, CH<sub>2</sub>), 3.1 (t, 2H, N-CH<sub>2</sub>), 2.9 (t, 2H, C-CH<sub>2</sub>), 2.1 (s, 6H, CH<sub>3</sub>), 2.0 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 160.4 (pyridine), 155.1 (C-OH), 149.5-117.3 (phenyl, pyridine), 54.2 and 52.9 (N-CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 19.9 and 10.0 (CH<sub>3</sub>).

## 3. Results and Discussion

The H<sub>2</sub>L compound, reported here for the first time, exhibits spectral and structural features similar to those expected based on comparisons to related species. Single crystals of N,N-bis(4,5-dimethyl-2-hydroxybenzyl)-N-(2-pyridylethyl)amine (H<sub>2</sub>L) suitable for X-ray diffraction studies were obtained by slow evaporation of a saturated solution in methanol at room temperature. ORTEP diagram of H<sub>2</sub>L (Fig. 1), is shown with selected bond lengths and angles collected in the corresponding figure caption, and relevant experimental parameters are presented in Table 1. This ligand exhibits intramolecular hydrogen bonding between phenol and amine functional groups, as has been observed for related amine bis(phenols) [1-4]. Heavy atom (O...N) interatomic distances are consistent with the presence of hydrogen bonds, and are within the range of those reported for similar amine bis(phenolate) ligands.



**Figure 1.** ORTEP diagram for H<sub>2</sub>L shown with 50% displacement ellipsoids and the numbering scheme for non-hydrogen atoms shown. Hydrogen atoms are drawn arbitrarily small for clarity. Selected bond distances (Å) and angles (°) for H<sub>2</sub>L: N1–C9 1.478(3); N1–C10 1.484(3); N1–C19 1.471 (3); N2–C21 1.42(3); N2–C25 1.333(3); O1–C1 1.370(0); O2–C11 1.366(3); O2...N1 3.015; O1...N1 2.590; C9–N1–C19 111.24(16); C10–N1–C19 113.16(17); C9–N1–C10 110.76 (16); C21–N2–C25 117.6 (2); O1–C1–C2 120.22 (19); O1–C1–C6 119.1 (2); O2–C11–C12 122.8 (2); O2–C11–C16 117.12 (19).

**Table 1.** Crystal data and structure refinement for H<sub>2</sub>L.

|   |   |
|---|---|
| Empirical formula                         | C <sub>25</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub> |
| Formula weight                            | 390.51  |
| Temperature                               | 100 (2) K   |
| Wavelength [Å]                            | 0.71073 Å   |
| Crystal system                            | Triclinic   |
| Space group                               | P -1  |
|   | a = 9.609 (3) Å; α = 100.717 (5) <sup>o</sup>                 |
|   | b = 9.614 (3) Å; β = 101.364 (5) <sup>o</sup>                 |
|   | c = 12.852 (4) Å; γ = 106.963 (5) <sup>o</sup>                |
| Volume [Å <sup>3</sup> ]                  | 1075.2 (6) Å <sup>3</sup>                                     |
| Z   | 2   |
| D <sub>calcd.</sub> [g cm <sup>-3</sup> ] | 1.206 mg/m <sup>3</sup>                                       |
| (μ)                                       | 0.076 mm <sup>-1</sup>  |
| F (000)                                   | 420   |
| Size                                      | 0.61 × 0.32 × 0.27 mm   |
| Total data                                | 17284   |
| Unique data                               | 4406 [R(int) = 0.0377]  |
| R Indices [I > 2σ(I)]                     | R1 = 0.0650, wR2 = 0.1896                                     |
| R Indices (all data)                      | R1 = 0.0836; wR2 = 0.2049                                     |

In the molecular depiction of H<sub>2</sub>L, the aminic nitrogen atom adopts a distorted pyramidal geometry, with the sum of angles about N1 equal to 335.21°. Weak

hydrogen bonding is observed between the phenol OH and oxygen atoms of methanol solvent, with O...O interatomic distances of 2.706 Å, MeOH and amine O...N 3.015 Å, and the phenol OH and neighboring phenol oxygen, with O...O interatomic distances of 2.691 Å.

The  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) exhibit a broad singlet at 9.44 ppm attributed to the phenol OH. Other spectral features in the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra support the proposed structural formulation depicted in Scheme I, and are consistent with the solid-state structures of  $\text{H}_2\text{L}$ . The equivalence of the proton signals corresponding to the methylene adjacent to the phenol residue suggests that the hydrogen bonding observed in the solid state is not present in  $\text{CDCl}_3$  solution. Band at  $3266,6\text{ cm}^{-1}$  in the FT-IR spectra is assigned as the phenolic OH stretch. These values are consistent with those reported in the literature for related ligands [1,2].

#### 4. Conclusions

The tetradentate tripodal ligand  $\text{H}_2\text{L}$  has been synthesized and characterized by different techniques, including X-ray diffraction studies. This organic compound is capable of coordinating different metal centres, leading different topologies, for instance, leaving two *cis* positions in octahedral geometries or imposing  $\text{C}_3$  symmetry in four- and five-coordinate metal centres.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. L. Rodriguez, E. Labisbal, A. Sousa-Pedrares, J. A. Garcia-Vazquez, J. Romero, M. L. Duran, J. A. Real, A. Sousa, *Inorg. Chem.* **2006**, *19*, 7903-7914.
2. E. Labisbal, L. Rodríguez, O. Souto, A. Sousa-Pedrares, J. A. García-Vázquez, J. Romero, A. Sousa, M. Yáñez, F. Orallo, J. A. Real, *Dalton Trans.* **2009**, 8644-56.
3. A. K. Bowsera, A. M. Anderson-Wilea, D. H. Johnstonb, B. M. Wilea, *Appl. Organometal. Chem.* **2016**, 32–39
4. R. K. Dean, C. I. Fowler, K. Hasan, K. Kerman, P. Kwong, S. Trudel, D. B. Leznoff, H. Kraatz, L. N. Dawe, C. M. Kozak, *Dalton Trans.* **2012**, 4806–4816

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