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## CRYSTAL STRUCTURE OF *N,N'*-BIS(3-METHOXYSALICYLIDENE)-1,4-DIAMINOBTANE

M. A. Vázquez- Fernández, M. I. Fernández, B. Fernández, A. M. Gonzalez-Noya, Marcelino Maneiro, M. J. Rodríguez-Doutón

*Dpto. de Química Inorgánica. Facultad de Ciencias. Univ. de Santiago de Compostela. Lugo 27002 (Spain).*

### ABSTRACT

Three multidentate Schiff-base ligands were obtained by condensation of different diamines (1,3-diaminopropane, 1,3-diamino-2,2-dimethylpropane, 1,4-diaminobutane) and 3-methoxy-2-hydroxybenzaldehyde to yield  $H_2L^n$  ( $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$ , respectively). The ligands have been characterised by elemental analysis, IR, and  $^1H$  and  $^{13}C$  NMR spectroscopies, mass spectrometry (ES) and X-ray diffraction.

### INTRODUCTION

Our interest in this kind of dicompartmental ligands derives from the known ability of ligands containing six potential donor atoms to stabilise high oxidation states of metal ions. These ligands present adequate conditions to be useful in the synthesis of octahedral complexes, occupying the equatorial positions around the metal centre. In previous papers we reported the synthesis, structures and properties of Mn(III) complexes with Schiff-base ligands<sup>1</sup>. At this goal we have designed the dianionic ligands,  $H_2L^n$ , that contain an inner site with N- and O- donor atoms (two imine nitrogen and two phenol oxygen atoms) and an outer coordination site with four O-donor atoms (two phenoxo and two methoxy groups).

### RESULTS AND DISCUSSION

The hexadentate Schiff bases,  $H_2L^n$ , were prepared<sup>2</sup> by condensation of the appropriate diamine with 3-methoxy-2-hydroxybenzaldehyde in methanol. This mixture was heated at reflux in a round-bottomed flask fitted with a Dean Stark trap to remove the water produced during the reaction. After heating for 3 h, the solution was concentrated to yield a yellow solid. The product was collected by filtration, washed with diethyl ether and dried in air. White crystals of  $H_2L^3$ , suitable for single crystal X-ray diffraction studies, were obtained by slow evaporation of the methanol solution of the ligand. The characteristics of the ligands are:

Ligand  $H_2L^1$ : M.p. 101 °C. Anal. Calc. for  $C_{19}H_{22}N_2O_4$ : C, 66.6; H, 6.5; N, 8.2. Found: C, 66.0; H, 6.5; N, 8.3%. MS ES (m/z): 343; IR (KBr,  $cm^{-1}$ ):  $\nu(O-H)$  3230,  $\nu(C=N)$  1631,  $\nu(C-O)$  1256.  $^1H$  NMR (DMSO- $d_6$ , ppm):  $\delta$  8.54 (s, 2H), 6.74-7.02 (m, 6H), 3.76 (s, 6H), 3.67 (t, 4H), 2.06 (m, 2H).  $^{13}C$  NMR (DMSO- $d_6$ , ppm):  $\delta$  166.9 (C=N), 152.7 (C-OCH<sub>3</sub>), 148.9 (C-OH), 32.2 (CH<sub>2</sub>).

Ligand  $H_2L^2$ : M.p. 82 °C. Anal. Calc. for  $C_{21}H_{26}N_2O_4$ : C, 68.1; H, 7.1; N, 7.6. Found: C, 67.7; H, 7.3; N, 7.4%. MS ES (m/z): 371; IR (KBr,  $cm^{-1}$ ):  $\nu(O-H)$  3439,  $\nu(C=N)$  1632,  $\nu(C-O)$  1254.  $^1H$  NMR (DMSO- $d_6$ , ppm):  $\delta$  8.51 (s, 2H), 6.76-7.03 (m, 6H), 3.77 (s, 6H), 3.47 (s, 4H), 0.98 (s, 6H).  $^{13}C$  NMR (DMSO- $d_6$ , ppm):  $\delta$  167.3 (C=N), 152.6 (C-OCH<sub>3</sub>), 148.8 (C-OH), 24.3 (CH<sub>3</sub>).

Ligand H<sub>2</sub>L<sup>3</sup>: M.p. 148 °C. Anal. Calc. for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>: C, 67.4; H, 6.8; N, 7.9. Found: C, 67.2; H, 6.9; N, 7.8%. MS ES (m/z): 357; IR (KBr, cm<sup>-1</sup>): ν(O-H) 3250, ν(C=N) 1629, ν(C-O) 1255. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm): δ 8.52 (d, 2H), 6.73-7.00 (m, 6H), 3.75 (s, 6H), 3.65 (t, 4H), 1.70 (q, 4H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, ppm): δ 166.6 (C=N), 153.1 (C-OCH<sub>3</sub>), 148.9 (C-OH), 28.7 (CH<sub>2</sub>).

The crystal structure of H<sub>2</sub>L<sup>3</sup>, with the numbering scheme, is shown in figure 1. Selected bond lengths and angles, as well as potential hydrogen bonds and bonding scheme are listed in tables 1 and 2, respectively.

The crystal structure reveals that H<sub>2</sub>L<sup>3</sup> exists as discrete molecules. The C(7)-N(8) distance of 1.280 Å is consistent with a C=N double bonding of the imine group. The two oxygen O(11) atoms corresponding to the phenolic groups show C-O distances O(11)-C(2) of 1.354 Å, according to the expected single bonds.

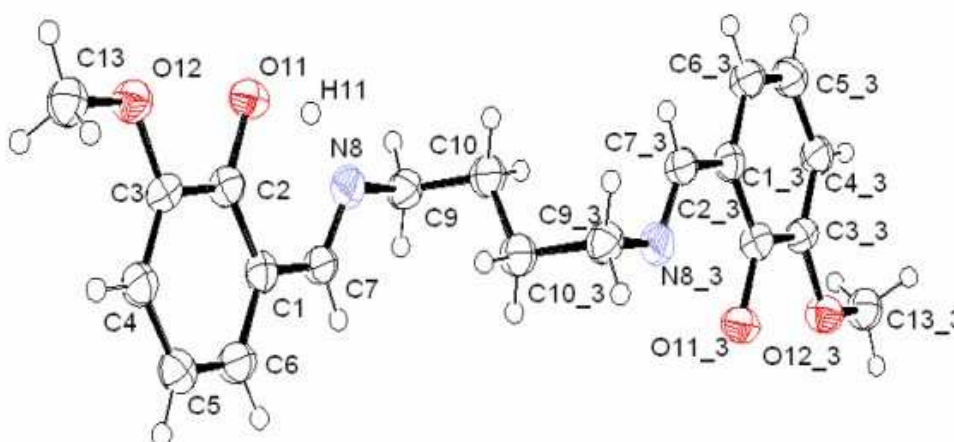


Figure1. Crystal structure of H<sub>2</sub>L<sup>3</sup>

Intramolecular hydrogen bonds exist between imine nitrogen atoms N(8) and their neighbouring phenol oxygen atoms O(11). Other intermolecular hydrogen bonds exist between the imine carbon atoms C(7) and the phenol oxygen atoms O(11) of neighbouring molecules (see table 2).

**Table 1:** Selected bond lengths (Å) and angles (°) for H<sub>2</sub>L<sup>3</sup>

O(11)-H(11)	1.340(11)	C(7)-N(8)-C(9)	118.5(3)
N(8)-H(11)	1.400(5)	N(8)-C(9)-C(10)	111.3(3)
N(8)-C(9)	1.465(5)	N(8)-C(9)-H(9A)	109.4
C(7)-N(8)	1.280(5)	C(2)-O(11)-H(11)	107.0(4)
C(2)-O(11)	1.354(4)	C(3)-O(12)-C(13)	115.8(3)
O(12)-C(13)	1.435(5)	C(4)-C(3)-O(12)	125.9(4)
C(3)-O(12)	1.371(4)	O(11)-C(2)-C(3)	118.8(3)

**Table 2:** Hydrogen bonds

D-H...A (Å)	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O(11)-H(11)...N(8)	1.34	1.40	2.5694	139
C(7)-H(7)...O(11)*	0.93	2.50	3.3386	150

Symmetry operations\* = -1/2+x, 1/2-y, -1/2+z

## REFERENCES

1. Costes, J. P.; Dahan, F.; Donnadieu, B.; Fernández-García, M. I.; Rodríguez-Douton, M. J. *Dalton Trans.* **2003**, 3776-3779.
2. Bermejo, M. R.; Fernández, M. I.; Gómez-Fórneas, E.; González-Noya, A.; Maneiro, M.; Pedrido, R.; Rodríguez, M. J. *Eur. J. Inorg. Chem.* **2007**, 3789-3797.