

**SYNTHESIS OF DICOMPARTIMENTAL SCHIFF BASE LIGANDS.
CRYSTAL STRUCTURE OF (N-N'-BIS(3- METHOXY or 3-
ETHOXY)SALICYLIDENE)-1,2-DIAMINE-2-METHYLPROPANE**

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The condensation of 3-methoxy or 3-ethoxy-2-hydroxybenzaldehyde and 1,2 diamine -2-methylpropane, to yield at the dianionic hexadentate Schiff base ligands H_2L^n (H_2L^1 , H_2L^2 respectively). The ligands have been characterised by elemental analysis, IR, 1H and ^{13}C NMR spectroscopies and mass spectrometry (ES). The crystal structure of the two ligands was solved by X-ray crystallography, revealing its ability to bind metal centres.

INTRODUCTION

These ligands present adequate conditions to be useful in the synthesis of complexes. Our interest in this kind of dicompartmental ligands derives from the known ability of ligands containing six potential donor atoms to stabilize high oxidation states of metal ions. This is the case of the complex Mn (III) in which we have been working¹. The structure of these molecules can be prepared octahedral complexes with N₂O₂ donor atoms 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^{1,2}. 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 or ethoxy groups).

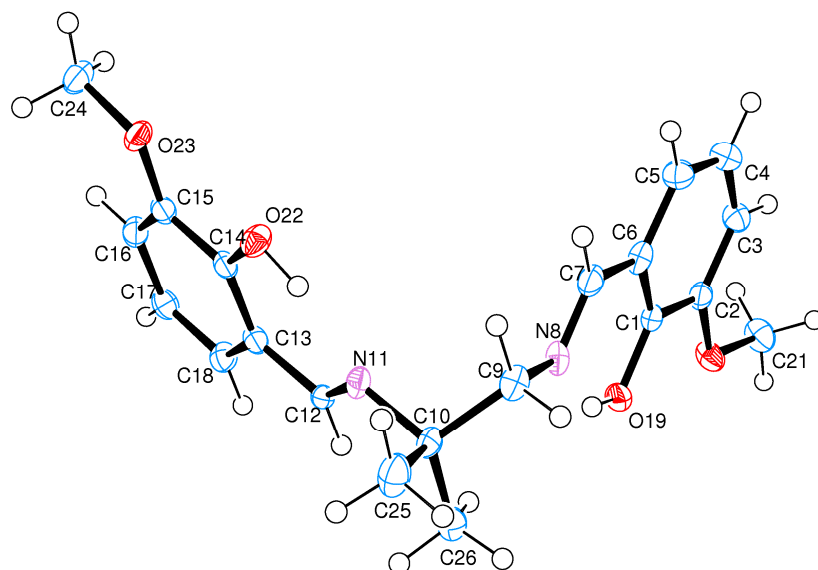
RESULTS AND DISCUSSION

The hexadentate Schiff bases H_2L^n were prepared according to the literature by condensation of 3-methoxy or 3-ethoxy-2-hydroxybenzaldehyde the with 1,2 diamine -2-methylpropane in methanol¹. 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. Yellow crystals of H_2L^1 and H_2L^2 , suitable for single crystal X-ray diffraction studies, were obtained by slow evaporation of the methanol solution of the ligands. The characteristics of the ligands are:

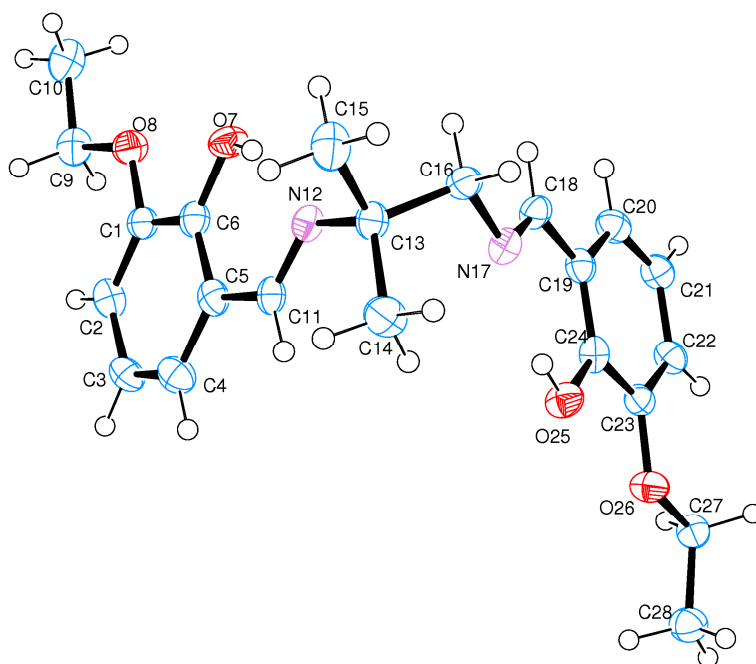
Ligand H_2L^1 (1): M.p. 122.9 ° C. Anal. Calc. for $C_{20}H_{24}N_2O_4$: C, 67.4; H,6.8; N, 7.9. Found: C, 67.3; H, 6.7, N, 7.8%. MS ES (m/z): 357; IR (KBr, cm^{-1}): $\nu(O-H)$ 3439, $\nu(C=N)$ 1628, $\nu(C-O)$ 1256. 1H NMR (DMSO- d_6 , ppm): δ 8.53, 8,50 (s, 2H), 6.77-7,01 (m, 6H), 3.83 (m, 6H), 3.76 (t, 4H), 1.37 (t, 6H), ^{13}C NMR (DMSO- d_6 , ppm): δ 163.3 (C=N), 148.9 (C-OCH₂CH₃), 152.9 (C-OH), 25.7 (CH₃).

Ligand H_2L^2 (2): M.p. 97.7 ° C. Anal Calc. for $C_{22}H_{28}N_2O_4$: C, 67.9; H, 7.3; N, 7.9. Found: C, 68.0; H, 7.7; N, 7.6 %. MS ES (m/z): 385.3; IR (KBr, cm^{-1}): $\nu(O-H)$ 3423,

$\nu(\text{C}=\text{N})$ 1628, $\nu(\text{C}-\text{O})$ 1254. ^1H NMR (DMSO- d_6 , ppm): δ 8.53-8.50 (s, 2H), 6.75-7.00 (m, 6H), 4.04 (m, 4H), 3.75 (s, 4H), 1.30 (m, 6H), 1.37 (s, 6H). ^{13}C NMR (DMSO- d_6 , ppm): δ 163.3 (C=N), 147.9 (C-OCH₂CH₃), 152.4 (C-OH), 25.7 (CH₃).



The crystal structure of H_2L^1 (**1**) and H_2L^2 (**2**), with the numbering scheme, is shown in figure 1, 2. Selected bond lengths and angles, as well as potential hydrogen bonds and bonding scheme, are listed in table 1 and 2, respectively.



The crystal structure reveals that H_2L^1 and H_2L^2 exists as discrete molecules. The C(12)-N(11), C(7)-N(8) distances of 1.272, 1.279 Å for **1** and C(11)-N(12), C(18)-N(17) distances of 1.262, 1.278 Å for **2** is consistent with a C=N double bonding. The two oxygen O(22) and O(19) for **1** and O(7) and O(25) atoms are forming phenolic groups, and they present C-O distances of 1.35 Å, corresponding to the expected single bonds.

Figure 1,2 . Ortep representation (50% probability) of H_2L^1 and H_2L^2

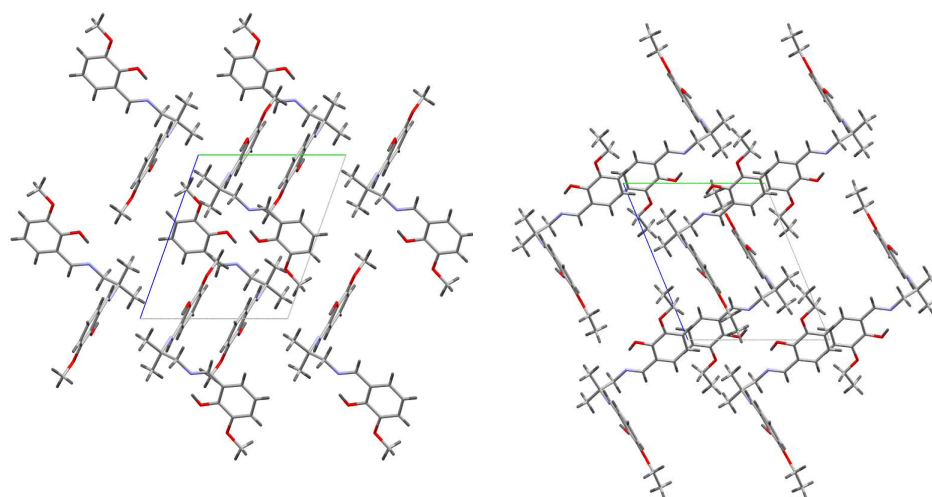
Intramolecular hydrogen bonds exist between imine nitrogen atoms N(8), N(11)for **1** and N(12) N(17) for **2** and their neighbouring phenol oxygen atoms O(2) (see table 2). Intramolecular hydrogen bonds exist between imine carbon and phenol oxygen atoms of neighbouring molecules (see table 2)

Table 1: Selected bond lengths (Å) and angles (°) for H₂L¹ and H₂L²

C(12)-N(11),	1.272(3)	C(7)-N(8)	1.279(3)
C(14)-O(22)	1.351(3)	C(1)-O(19)	1.354(3)
C(12)-N(11)-C(10)	122.9(2)	N(11)-C(10)-C(9)	106.65(19)
C(11)-N(12),	1.262(6)	C(18)-N(17)	1.278 (6)
C(6)- O(7)-	1.339(6)	C(24)-O(25)	1.360(5)
C11-N12-C13	123.3 4	N(12)-C(13)-C(16)	107.4(4)

Table 2: Hydrogen bonds

D-H...A (Å)	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (Å)
O(19) --H(19) ..N(8)	0.96	1.73	2.5839	146
O(22) --H(22) ..N(11)	0.93	1.72	2.5891	154
C(9) --H(9B) ..O(19)	0.99	2.55	3.4451	151
O(7) --H(7) ..N(12)	0.91	1.81	2.5929	143
O(25) --H(25) ..N(17)	0.78	1.87	2.5944	152
C(18) --H(18) ..O(7)	0.95	2.59	3.4538	152

Figure 3. Packing of **1** and **2** normal a

These ligands from a branched chain diamine causes a larger spatial constraints presented a folded structure². The ligands presented above from diamines with unbranched chains have a structure deployed³. This may influence the formation of metal complexes because of their greater rigidity.

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