

[A0028] **SYNTHESIS OF MULTIDENTATE SCHIFF BASE LIGANDS. CRYSTAL STRUCTURE OF (N-N'-BIS(3-ETHOXYALICYLIDENE)-1,3-DIAMINO-2,2-DIMETHYLPROPANE**

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ABSTRACT

The hexadentate Schiff base ligands were prepared by condensation of 3-ethoxy-2-hydroxybenzaldehyde and different diamines (1,3-diaminopropane, 1,3-diamino-2,2-dimethylpropane, 1,4-diaminobutane) 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, 1H and ^{13}C NMR spectroscopies and mass spectrometry (ES). The crystal structure of the H_2L^2 ligand was solved by X-ray crystallography, revealing its ability to bind metal centres.

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^{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 ethoxy groups).

RESULTS AND DISCUSSION

The hexadentate Schiff bases H_2L^n were prepared according to the literature³, by condensation of the appropriate diamine with 3-ethoxy-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^2 , 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. 81.7 °C. Anal. Calc. for $C_{21}H_{26}N_2O_4$: C, 68.1; H, 7.1; N, 7.6. Found: C, 68.2; H, 7.2; N, 7.6%. MS ES (m/z): 371; IR (KBr, cm^{-1}): $\nu(O-H)$ 3250, $\nu(C=N)$ 1632, $\nu(C-O)$ 1251. 1H NMR (DMSO- d_6 , ppm): δ 8.35 (s, 2H), 6.77-6.92 (m, 6H), 4.10 (c, 4H), 3.72 (t, 4H), 2.08 (t, 2H), 1.47 (t, 6H). ^{13}C NMR (DMSO- d_6 , ppm): δ 165.8 (C=N), 152.2 (C-OCH₂CH₃), 147.9 (C-OH), 31.9 (CH₂).

Ligand H_2L^2 : M.p. 98 °C. Anal. Calc. for $C_{23}H_{30}N_2O_4$: C, 69.3; H, 7.6; N, 7.1. Found: C, 69.2; H, 7.7; N, 7.1%. MS ES (m/z): 399; IR (KBr, cm^{-1}): $\nu(O-H)$ 3437, $\nu(C=N)$ 1637, $\nu(C-O)$ 1248. 1H NMR (DMSO- d_6 , ppm): δ 8.50 (s, 2H), 6.71-7.02 (m, 6H), 4.01 (m, 4H), 3.52 (s, 4H), 1.32 (m, 6H), 0.90 (s, 6H). ^{13}C NMR (DMSO- d_6 , ppm): δ 167.5 (C=N), 147.9 (C-OCH₂CH₃), 152.6 (C-OH), 24.3 (CH₃).

Ligand H_2L^3 : M.p. 135.4 °C. Anal. Calc. for $C_{22}H_{28}N_2O_4$: C, 68.7; H, 7.3; N, 7.3. Found: C, 68.9; H, 7.4; N, 7.3%. MS ES (m/z): 385; IR (KBr, cm^{-1}): $\nu(O-H)$ 3242, $\nu(C=N)$ 1624, $\nu(C-O)$ 1251. 1H NMR (DMSO- d_6 , ppm): δ 8.32 (s, 2H), 6.80-6.90 (m, 6H), 4.10 (c, 4H), 3.63 (s, 4H), 1.80 (m, 4H), 1.47 (t, 6H). ^{13}C NMR (DMSO- d_6 , ppm): δ 165.2 (C=N), 152.6 (C-OCH₂CH₃), 148.0 (C-OH), 28.6 (CH₃).

The crystal structure of H_2L^2 , 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 table 1 and 2, respectively.

The crystal structure reveals that H_2L^2 exists as discrete molecules. The C(9)-N(1) distance of 1.2753 Å is consistent with a C=N double bonding. The two oxygen O(2) atoms are forming phenolic groups, and they present C–O distances of 1.3501 Å, corresponding to the expected single bonds.

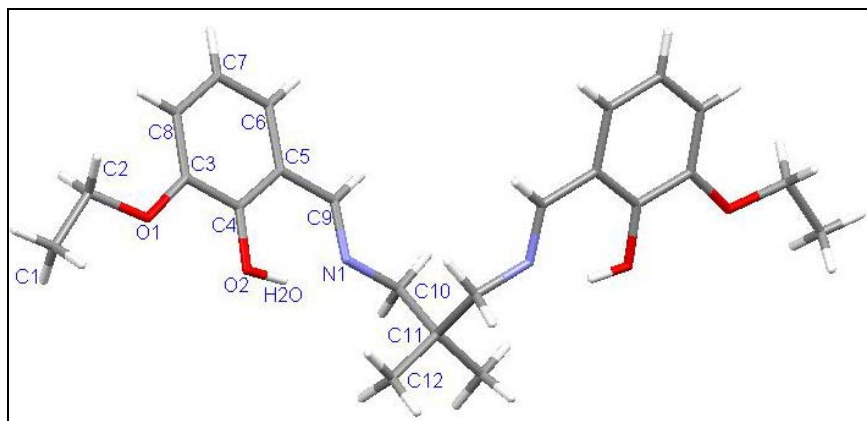


Figure 1. Crystal structure of H_2L^2

Intramolecular hydrogen bonds exist between imine nitrogen atoms N(1) and their neighbouring phenol oxygen atoms O(2) (see table 2).

Table1: Selected bond lengths (Å) and angles (°) for H_2L^2

C(9)-N(1)	1.2753(15)	C(9)-N(1)-C(10)	120.36(9)
N(1)-C(10)	1.4563(14)	N(1)-C(10)-C(11)	111.27(8)
C(4)-O(2)	1.3501(13)	N(1)-C(10)-H(10A)	109.4
C(2)-O(1)	1.4371(13)	N(1)-C(9)-H(9)	119.2
O(1)-C(3)	1.3692(13)	C(3)-O(1)-C(2)	117.29(9)
O(2)-H(2O)	0.9390(15)	O(2)-C(4)-C(3)	118.36(10)
C(9)-H(9)	0.9500(15)	C(4)-O(2)-H(2O)	104.7(9)

Table2: Hydrogen bonds

D-H...A (Å)	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O(2)-H(2O)...N(1)	0.932(16)	1.713(16)	2.5737(12)	152.0(13)

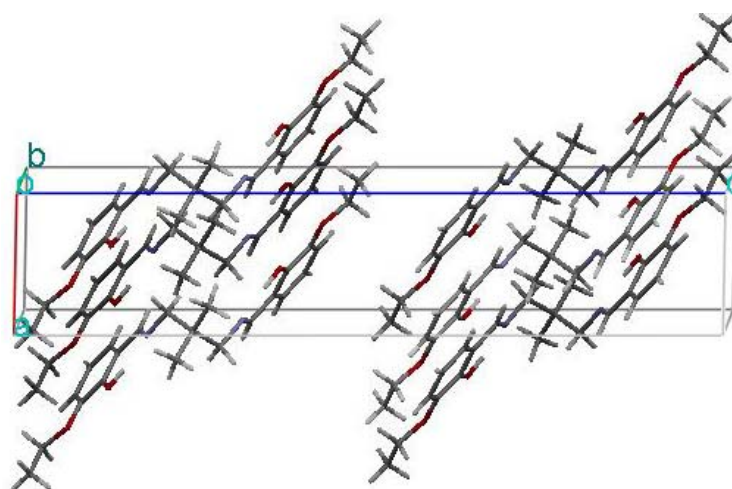


Figure 2. Packing of H_2L^2 normal b

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