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[a023]

CRYSTAL STRUCTURE OF (N-N'-BIS(3-ETHOXYSALICYLIDENE)-1,2-DIAMINOPROPANE

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ABSTRACT

Three hexadentate Schiff base ligands were obtained by condensation of 3-ethoxy-2-hydroxybenzaldehyde and different diamines (1,2-diaminoethane, 1,2-diaminopropane, 1,2-diamino-2-metylpropane) 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 spectroscopic techniques, 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 potencial 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]. 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[2] by condensation of the 3-ethoxy-2-hydroxybenzaldehyde with the appropriate diamine 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. Yellow crystals of H_2L^2, suitable for single crystal X-ray diffraction studies, were obtained by slow evaporation of methanol solution of the ligand. The characteristiques of the ligands are :

Ligand H_2L^1: M.p.144 ºC. Anal. Calc. for $C_{20}H_{24}N_2O_4$: C, 67.4; H, 6.8; N, 7.9. Found: C, 67.2; H, 6.9; N, 7.9%. MS ES (m/z): 357; IR (KBr, cm^{-1}): ν(O-H) 3448, ν(C=N) 1633, ν(C-O) 1250. ^1H NMR (DMSO-d_6, ppm): δ 8.54 (s, 2H), 6.74-6.99 (m, 6H), 4.05 (c, 4H), 3.92 (t, 4H), 1.30 (t, 6H). ^{13}C NMR (DMSO-d_6, ppm): δ 167.7 (C=N), 147.8 (C-OCH_2CH_3), 152.6 (C-OH), 58.9 (CH_2).

Ligand H_2L^2: M.p.91 ºC. Anal Calc. for $C_{21}H_{26}N_2O_4$: C, 68.0; H, 7.0; N, 7.6. Found: C, 67.7; H, 6.8; N, 7.6%. MS ES (m/z): 371; IR (KBr, cm^{-1}): ν(O-H) 3446, ν(C=N) 1632, ν(C-O) 1248. ^1H NMR (DMSO-d_6, ppm): δ 8.53/ 8.50 (s, 2H), 6.72-6.97 (m, 6H), 4.02 (m, 4H), 3.99/3.75 (m, 2H), 1.36 (m, 3H), 1.31 (s, 6H). ^{13}C NMR (DMSO-d^6, ppm): δ 167.8/165.9 (C=N), 147.7 (C-OCH_2CH_3), 152.4 (C-OH), 20.6 (CH_3).

Ligand H_2L^3: M.p.88 ºC. Anal Calc. for $C_{22}H_{28}N_2O_4$: C,68.7; H, 7.3; N, 7.2. Found: C,68.5; H, 6.9; N,7.2%. MS ES (m/z): 385; IR (KBr, cm^{-1}): ν(O-H) 3435, ν(C=N) 1628, ν(C-O) 1254. ^1H NMR (DMSO-d_6, ppm): δ 8.54/8.51 (s, 2H), 6.70-7.04 (m, 6H), 4.00 (m, 4H), 3.74 (s, 2H), 1.35 (s, 6H), 1.31 (s, 6H). ^{13}C NMR (DMSO-d^6, ppm): δ 167.9/163.3 (C=N), 147.8 (C-OCH_2CH_3), 152.4 (C-OH), 25.7 (CH_3).

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. The crystal structure reveals that H_2L^2 exists as discrete molecules. The C(11)-N(1) and C(41)-N(4) distances of 1.2717(18) and 1.2733(17) Å respectively, are consistent with a C=N double bonding of the imine groups. The two oxygen O(130) and O(430) atoms are forming phenolic groups show C–O distances O(130)-C(13) of 1.3516(16) and O(430)-C(43) of 1.3486(15) Å, according to the expected single bonds.

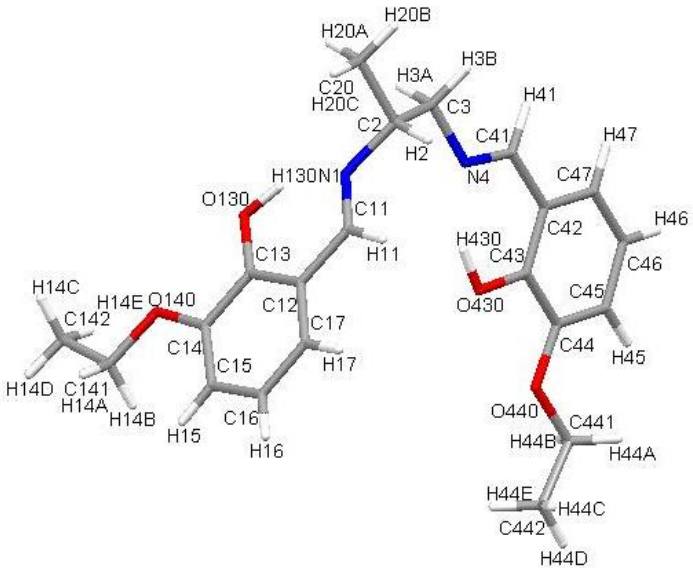

Figure 1: Crystal structure of H_2L^2.

Intermolecular hydrogen bonds exist between imine nitrogen atoms N(1) and N(4) and their neighbouring phenolic oxygen atoms O(130) and O(430) (see Figure 2 and table 2).

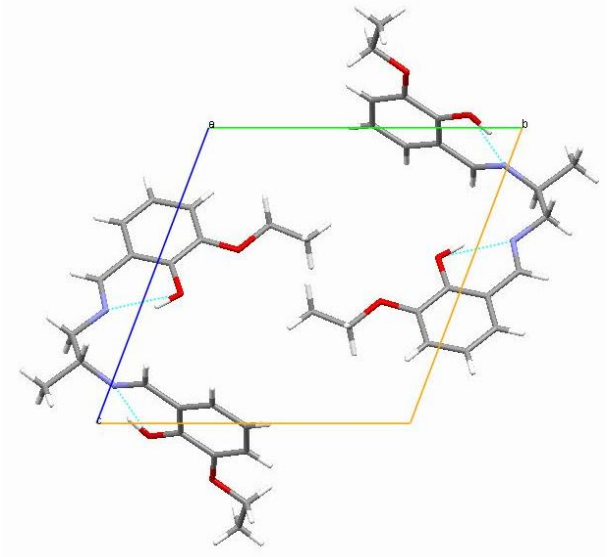

Figure 2: Packing and intermolecular hydrogen bonds of H_2L^2

Table 1: Selected bond lengths (Å) and angles (º) for H_2L^2

N(1)-C(11)	1.2717(18)	N(4)-C(41)	1.2733(17)
N(1)-C(2)	1.4635(17)	C(3)-N(4)	1.4631(17)
C(13)-O(130)	1.3516(16)	C(43)-O(430)	1.3486(15)
C(14)-O(140)	1.3645(16)	C(44)-O(440)	1.3682(16)
O(140)-C(141)	1.4412(17)	C(441)-O(440)	1.4354(16)
O(130)-H(130)	0.97(2)	O(430)-H(430)	0.94(2)
C(11)-H(11)	0.978(15)	C(45)-H(45)	0.95
C(11)-N(1)-C(2)	119.28(12)	C(41)-N(4)-C(3)	117.73(12)
N(1)-C(2)-C(3)	108.50(11)	N(4)-C(3)- C(2)	111.51(12)
C(14)-O(140)-C(141)	116.43(11)	C(44)-O(440)-C(441)	117.10(10)
O(130)-C(13)-C(14)	118.59(12)	O(430)-C(43)-C(44)	118.44 (12)

Table 2: Hydrogen bonds

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
O(130)-H(130)···N(1)	0.97(2)	1.67(2)	2.5701(17)	152.5(19)
O(430)-H(430)···N(4)	0.93(2)	1.75(2)	2.6112(18)	151.8(18)

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