Crystal structure of H_4L (N-N'-Bis(o-hydroxybenzoyl) 1,4 -diaminobutane

G. González-Riopedre, M.I. Fernández-Garcia, M. Maneiro, A. M Gonzalez-Noya, Y Perez , B. Fernández, M.A. Vázquez-Fernández

Dpto. de Química Inorgánica. Facultad de Ciencias. Univ. de Santiago de Compostela. Lugo 27002 (Spain). misabel.fernandez.garcia@usc.es

ABSTRACT

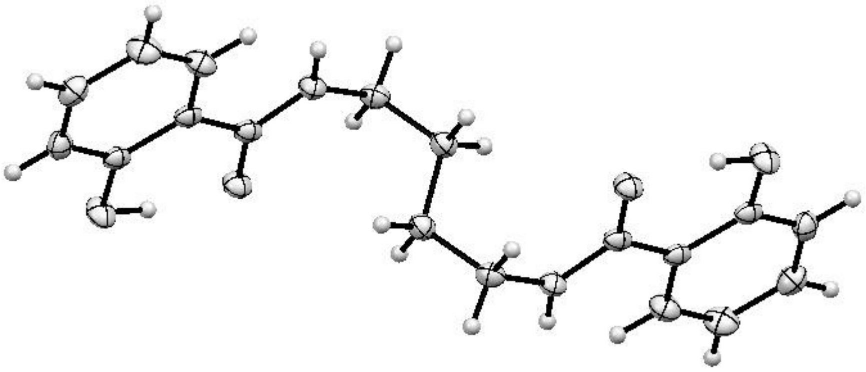
A bis-amide bis-phenoxy N_2O_2 ligand was obtained from the 2:1 molar reaction of phenyl salicylate and the diamine, 1,4-Diaminobutane, to yield H_4L. The ligand has been characterised by elemental analysis, IR, and ^1H and ^{13}C NMR spectroscopies, mass spectrometry (ES) and X ray diffraction spectroscopy.

INTRODUCTION

Our interest in this type of ligands derives from the known ability of ligands containing amide groups to stabilise high oxidation states of metal ions when coordinated with the deprotonated nitrogen atom. The oxygen amide atom of these ligands can act as a bridge between neighbouring metallic atoms and afford multi-dimensional and supramolecular structures. For this purpose, we selected the tetraanionic H_4L bisamido-bisphenoxy ligand. We have thought that the utilization of tetranionic bis-amide bis-phenoxi ligands should favour the aggregation of neighbouring complexes through these donors atoms[1] (amide and phenoxo oxygen). In previous papers we reported on the synthesis, structures and properties of Mn(III) complexes with asymmetrical trianionic amido-imino-phenoxo ligands. Herein, we present the tetraanionic ligand, H_4L^n that contain six potential donor atoms: two amide nitrogen, two phenoxo and two amide oxygen atoms.

RESULTS AND DISCUSSION

H_4L were prepared according to the literature[2], in this case by reaction in a 2:1 molar reaction of phenyl salicylate and the diamine at 180-190 º for 1 h. The product was treated with diethyl ether to obtain a white powder at almost quantitative yield. White crystals of H_4L, 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 ^1H and ^{13}C NMR spectroscopy.
Ligand H_4L: M.p.110 ºC. Anal Calc. for $C_{18}H_{20}N_2O_4$: C,65.8; H, 6.1; N, 8.5. Found: C,66.2; H, 5.6; N,8.6%. MS ES (m/z): 329; IR (KBr, cm^{-1}): ν(N-H) 3407, ν(O-H) 3057, ν(amido I) 1643, ν(amido II) 1586, ν(C-O) 1259. ^1H NMR (DMSO-d^6, ppm): δ 9.17 (s: singlet, 2H), 7.20-7.80 (m: multiplet, 4H), 3.34-3.28 (m, 4H), 1.55 (m, 2H). ^{13}C NMR (DMSO-d^6, ppm): δ 133.9 (C-OH), 161.6 (C=O), 27.5 (CH_2), 39.0 (CH_2).
Crystal data and structure refinement for H_4L are listed in table 1. Crystal structure, 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 2 and table 3. In the crystal structure of the title ligand $C_{18}H_{20}N_2O_4$ .exists two not-identical parts divided by the C14-C14B. The slight asymmetry given is showed by the slight different distances collected in Table 2.
The C(11)-O(15) and C(11B)-O(15B) distances of 1.259 and 1.257 Å respectively are consistent with C=O double bonding of amide groups. The oxygen O(20) and O(20B) atoms are forming phenolic groups, and they present distances O(20)-C(2) and O(20B)-C(2B) of 1.357 and 1.354 Å respectively, corresponding to the expected single bonds. O(20)-H(20) distances 0.98 (4) Å are longer than the O(20B)-H(20B) 0.96 Å.



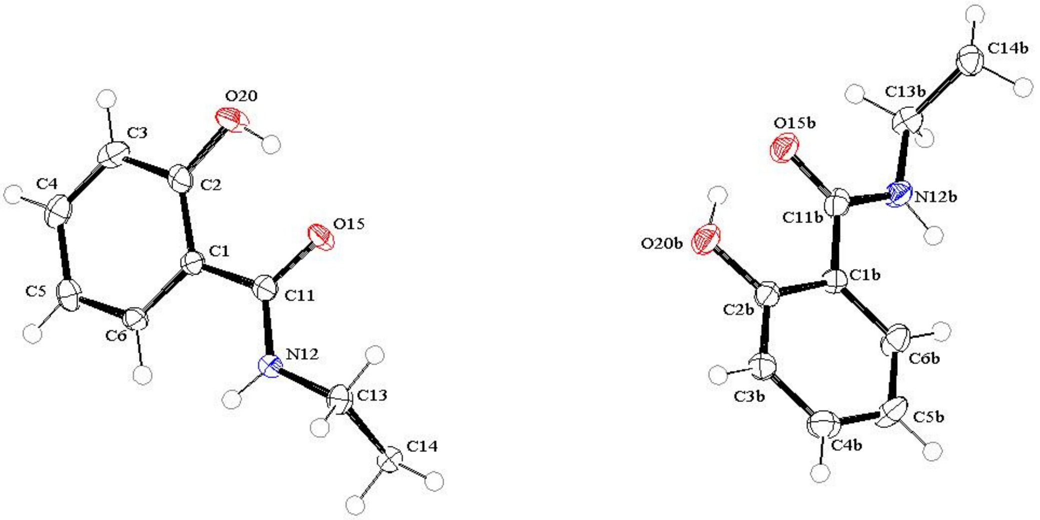


Figure 1. Molecular structure of $C_{18}H_{20}N_2O_4$ showing the atomic numbering scheme

Table 1. Crystal data and structure refinement for H_4L

Empirical formula	C18 H20 N2 O4
Formula weight	328.3
Wavelength [Å]	0.71073 Ǻ
Temperature [K]	100 (2) K
Crystal system	Monoclinic
Space group	$P2_1/C$
a	15.9570(5))Ǻ
b , β	10.1221(4) Ǻ β = 92.288(2)°
c	9.8254(4) Ǻ
Volume [Å3]	1585.72(10)A^3
Z	4
Dcalcd. [g cm-3]	1.375 mg/m^3
μ [mm-1]	$0.098mm^{-1}$
F(000)	696
Total data	13279
Unique data	2963
Final *R* indices	R1= 0.0710 wR2= 0.1053

Table 2: Selected bond lengths (Ǻ)and angles (º) for H_4L

O(20)-C(2)	1.357(2)	O(20B)-C(2B)	1.354(2)
O(20) - H(20)	0.98(24)	O(20B) - H(20B)	0.96 (2)
O(15)-C(11))	1.2593(19)	O(15B-C(11B)	1.257(2)
C(1) - C(2)	1.414 (2)	C(1B) - C(2B)	1.406 (2)
C(1) - C(11)	1.482 (2)	C(1B) - C(11B))	1.491 (2)
C(11) - N(12)	1.330(2)	C(11B) - N(12B)	1.333(2)
N(12)- C(13)	1.465(2)	N(12B)- C(13B)	1.459 (2)
N(12)- H(12)	0.851(2)	N(12B)- H(12B)	0.873(14)
C(13) - C(14)	1.519(2)	C(13B) - C(14B)	1.517 (3)
C(2) – O(20)-H(20)	102.5(14)	C(2B) – O(20B)-H(20B)	100.7(16)
O(15)-C(11)-C(1)	120.13(15)	O(15B)-C(11B)-C(1B)	120.47(15)
N(12)-C(13)- H(13A)	109.2	N(12B)-C(13B)- H(13C)	109.1
N(12)-C(11)-C(1)-	118.75(15)	N(12B)-C(11B)-C(1B)-	118.60(16)
C(11)-N (12)-C(13)	124.18(16)	C(11B)-N (12B)-C(13B)	123.57(15)
N(12)-C(13)-C(14-)	112.18(15)	N(12)-C(13)-C(14-)	112.70(15)

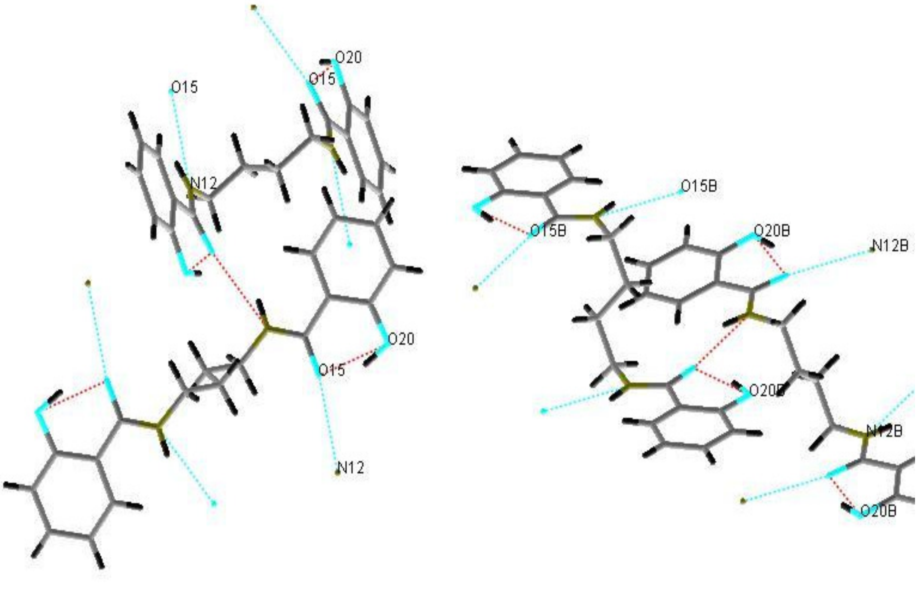


Figure 2. Stick diagram for H_4L showing the hydrogen bonding

Table 3.- Hydrogen bonds (Ǻ) for H_4L

D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**(DHA)**
Intra1 O(20) --H(20) ..O(15)	0.99(2)	1.63(2)	2.552(18)	154.5(18)
Intra1 O(20B) --H(20B) ..O(15B)	0.96(3)	1.63(3)	2.547(17)	157(3)
N(12) --H(12) ..O(15)**	0.85(2)	2.18(2)	2.952(19)	150.1(18)
N(12B) --H(12B) ..O(15B)*	0.87 152)	2.34(16)	3.066(16)	141.2(16)

symmetry operations: * = x,1/2-y, ½+z ** = -x, ½+y,-1/2-z

This molecule has intramolecular hydrogen bonds between the phenolic oxygens (O(20) and O(20B)) and amide oxygens (O(15), O(15B).Another hydrogen bond is the interaction between the amide nitrogen and amide oxygen N(12)--H(12)..O(15), and N(12B)--H(12B)..O(15B)* of a neighboring molecule. Moreover π- stacking interactions are further appreciated between the benzene rings (Table 3, Figure 2). N(12) --H(12) ..O(15)**

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