

Crystal structure of H₄L (N-N'-Bis(o-hydroxybenzoyl) 1,3-diamino-2,2-dimethylpropane)

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ABSTRACT

A bis-amide bis-phenoxi N₂O₂ ligand was obtained from the 2:1 molar reaction of phenyl salicylate and the diamine, 1,3-Diamino-2,2-dimethylpropane, to yield H₄L. The ligand has been characterised by elemental analysis, IR, and ¹H and ¹³C 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 tetraionic H₄L 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 atoms¹ (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 tetranionic ligand, H₄Lⁿ that contain six potential donor atoms: two amide nitrogen, two phenoxo and two amide oxygen atoms.

RESULTS AND DISCUSSION

H₄L were prepared according to the literature², in this case by reaction in a 2:1 molar reaction of phenyl salicylate and the diamine at 180-190 ° for 1 h. The product was treated with diethyl ether to obtain a white powder at almost quantitative yield. White crystals of H₄L, 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 ¹³C NMR spectroscopy.

Ligand H₄L: M.p.138 ° C. Anal Calc. for C₁₉H₂₂N₂O₄: C, 66.6; H, 6.5; N, 8.2. Found: C,66.8; H, 6.4; N, 8.1%. MS ES (m/z): 343; IR (KBr, cm⁻¹): ν(N-H) 3377, ν(O-H) 3063, ν(amido I) 1682, ν(amido II) 1549, ν(C-O) 1250. ¹H NMR (DMSO-d⁶, ppm): δ 8.84 (NH), 7.79-6.68 (H aromat.), 3.28 (CH₂), 0.91 (CH₃). ¹³C NMR (DMSO-d⁶, ppm): δ 160.9 (C-OH), 169.4 (C=O),136.7 (aromat.), 39.9 (CH₂), 25.6 (CH₃).

Crystal data and structure refinement for H₄L 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 C₁₉H₂₂N₂O₄ the imine group is coplanar with the aromatic ring with an N-C-C-C torsion angle of -174.2 (2)° (C6—C8—N10—C11 -174.2 (2), C15—N16—C17—C19 177.6 (2)). The dihedral angle between the benzenes rings in the molecule is 133.56(5)°.

The C(8)-O(9) and C(17)-O(18) distances of 1.250 and 1.255 Å respectively are consistent with C=O double bonding of amide groups. The oxygen O(7) and O(25) atoms are forming phenolic groups, and they present distances O(7)-C(1) and O(25)-C(24) of 1.367 and 1.354 Å respectively, corresponding to the expected single bonds. C-C distances in the aminic chain C(11)-C(12) 1.534 (4) Å are longer than the C-C distances in the aromatic ring, C(2)-C(3) 1.383 Å, which is consistent with a single bond and

double bond parameters respectively.

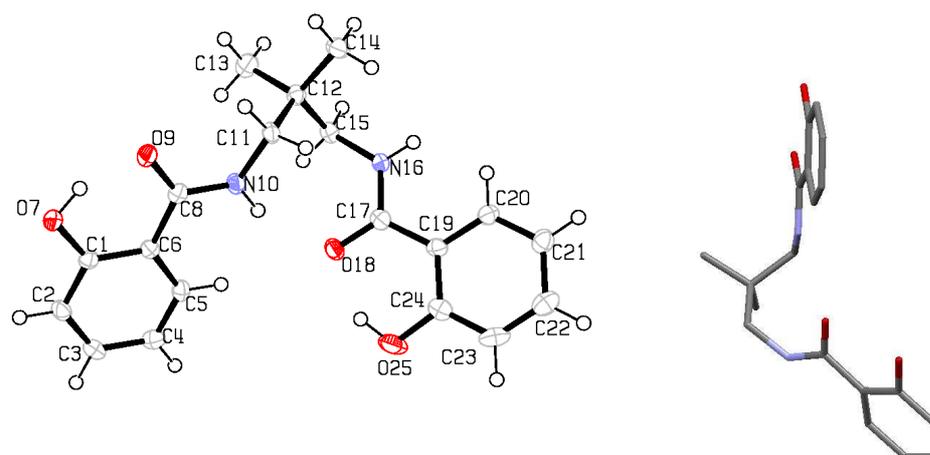


Figure 1. Molecular structure of $C_{19}H_{22}N_2O_4$ showing the atomic numbering scheme

Table 1. Crystal data and structure refinement for H_4L

Empirical formula	$C_{19}H_{22}N_2O_4$
Formula weight	342,39
Wavelength [\AA]	0,71073 \AA
Temperature [K]	100 (2) K
Crystal system	Monoclinico
Space group	$P2_1/C$
a	6,5353 (3) \AA
b, β	18,0973 (8) \AA $\beta = 91,221(2)^\circ$
c	14,6850 (8) \AA
Volume [\AA^3]	1736,42 (15) \AA^3
Z	4
Dcalcd. [g cm^{-3}]	1,31 mg/m^3
μ [mm^{-1}]	0,092 mm^{-1}
F(000)	728
Total data	15863
Unique data	3534
Final R indices	$R1 = 0.0526$ $wR2 = 0.1061$

Table 2: Selected bond lengths (\AA) and angles ($^\circ$) for H_4L

C(1)-O(7)	1,367(3)	C(24)-O(25)	1,354(4)
O(7) - H(7)	0,93(4)	O(25) - H(25)	0,94(4)
C(8) - O(9)	1,250(3)	C(17) - O(18)	1,255(3)
C(8) - N(10)	1,334(4)	N(16) - C(17)	1,336(4)
N(10)-C(11)	1,459(3)	C(15) - N(16)	1,460(4)
N(10)- H(10)	0,91(3)	N(16) - H(16)	0,89(3)
C(24)- O(25)	1,354 (3)	C(11)-H(11B)	0,990(3)
C(11) - C(12)	1,534(4)	C(12) - C(13)	1,533(4)
C(12) - C(14)	1,532(4)	C(12) - C(15)	1,534(4)
C(17) - C(19)	1,481(4)	C(6)-C(8)-N(10)	118,7(3)
C(8)-N(10)-H(10)	122,3(15)	C(12)-C(15)-N(16)	114,5(2)
O(18)-C(17)-C(19)	120,3(3)	O(18)-C(17)-C(19)	120,3(3)
C(11)-C(12)-C(14)	107,1(2)	C(11)-C(12)-C(13)	110,6(2)
C(13)-C(12)-C(15)	107,4(2)	C(14)-C(12)-C(15)	110,1(2)
C(11)-C(12)-C(15)	111,5(2)		

Table 3.- Hydrogen bonds (Å) for H₄L

D-H...A	d(D-H)	d(H...A)	d(D...A)	(DHA)
Intra1 O(7) --H(7) ..O(9)	0,93(3)	1,63(3)	2,498(2)	154(3)
Intra1 N(10)--H(10)..O(18)	0,91(2)	2,03(2)	2,860(3)	152(2)
N(16) --H(16) ..O(7)**	0,89(3)	2,20(2)	3,082(3)	170(2)
Intra1 O(25)--H(25)..O(18)	0,94(4)	1,72(4)	2,570(2)	148(4)
C(2) --H(2) ..O(25)*	0,95	2,55	3,244(3)	130
Intra 1 C(11)--H(11B) ..O(9)	0,99	2,39	2,801(3)	104
Intra1 C(15)--H(15A) ..O(18)	0,99	2,43	2,794(3)	101
C(20) --H(20) ..O(7)**	0,95	2,47	3,364(3)	157

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

This molecule has hydrogen bonds O(7)-H(7)...O(9) and O(25)--H(25)..O(18) between the phenolic oxygens (O(7) and O(25)) and amide oxygens (O(9), O(18)). Another intramolecular hydrogen interaction is the N(10)--H(10)..O(18) bond, between the amide nitrogen and phenolic oxygen. Intramolecular hydrogen bonds are also C(11)--H(11B) ..O(9) and C(15)--H(15A) ..O(18), between amine carbons and amide oxygens. It also presents an intermolecular hydrogen bond between the nitrogen N(16) - H(16) and the phenolic oxygen O(7)** of a neighboring molecule. Moreover π -stacking interactions are further appreciated between the benzene rings (Table 3, Figure 2).

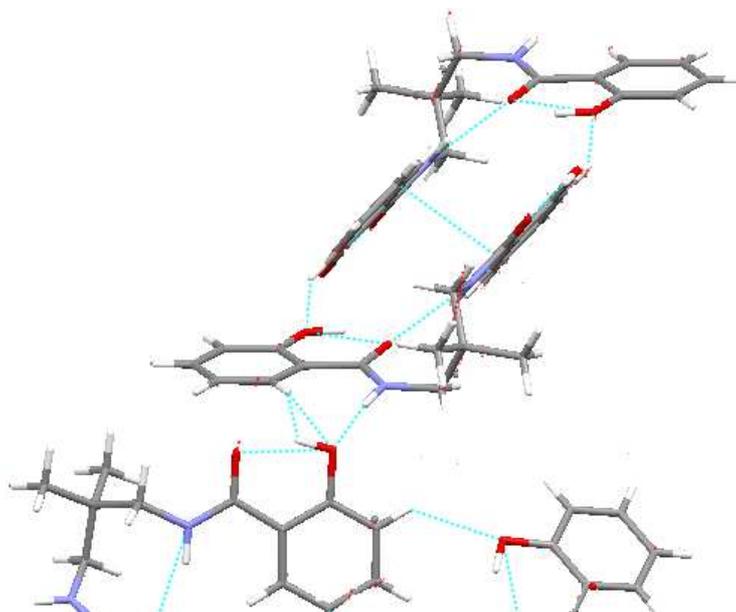


Figure 2. Stick diagram for H₄L showing the hydrogen bonding

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