Crystal structure of H_4L (N-N'-Bis(o-hydroxybenzoyl) propylenediamine

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ABSTRACT

One bis-amide bis-phenoxi N_2O_2 ligand was obtained from the 2:1 molar reaction of phenyl salicylate and the diamine, 1,3-Diaminopropane , to yield H_4L. The ligand has been characterised by elemental analysis, IR, and ^1H ^{13}C NMR spectroscopies, mass spectrometry (ES) and Xray difraction.

INTRODUCTION

Our interest in this kind 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. 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. At this goal we has designed the tetranionic ligand, H_4L^n that contain six potential donor atoms: two amide nitrogen, two phenoxo and two amide oxygeatoms.

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 characteristiques of the ligand is:

Ligand H_4L: M.p.177 ºC. Anal Calc. for $C_{17}H_{18}N_2O_4$: C,64.9; H, 5.7; N, 8.9. Found: C,63.8; H, 6.1; N,9.1%. MS ES (m/z): 315; IR (KBr, cm^{-1}): ν(N-H) 3377, ν(O-H) 3077, ν(amido I) 1645, ν(amido II) 1545, ν(C-O) 1246. ^1H NMR (DMSO-d^6, ppm): δ 8.81 (s: singlet, 2H), 6.83-6.88 (m: multiplet, 4H), 7.37 (t: triplet, 2H), 7.80 (d: doublet, 2H), 3.34-3.48 (m, 4H), 1.82 (q, 2H). ^{13}C NMR (DMSO-d^6, ppm): δ 161.3 (C-OH), 169.7 (C=O), 37.4 (CH_2), 29.6 (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, the title ligand $C_{17}H_{16}N_2O_4$ exhibits crystallographic twofold rotation symmetry. In the ligand H_4L exists two identical parts and so indicate carbon atoms to the number 12. The imine group is coplanar with the aromatic ring with an N-C-C-C torsion angle of -177.48(15) º. The dihedral angle between the benzenes rings in the molecule is 126.98(5) º.

The C(8)-O(9) and C(8)- distance of 1,253, are consistent with. C=O double bonding of amide groups. The oxygen O(7) atom is forming phenolic group, and they present C–O distances are forming and O(7)-C(6) of 1.357 (3) Å, corresponding to the expected single bonds. C-C distances chain amine C (11) - C (12) 1.522 (1) Å are longer than the distances C-C aromatic ring C (2) - C (3) 1.383 Å, which is consistent with a single bond and double bond parameters respectively.

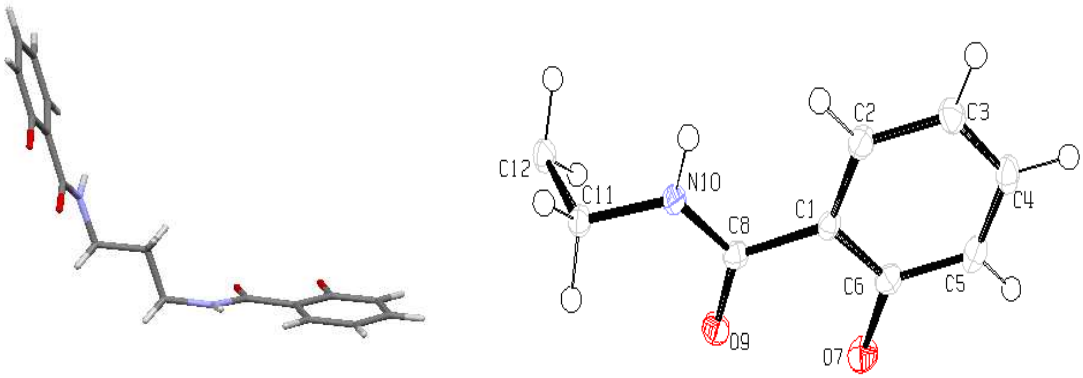

Figure 1. Molecular structure of $C_{17}H_{18}N_2O_4$ showing the atomic numbering scheme

Table 1. Crystal data and structure refinement for H_4L

Empirical formula	$C_{17}H_{18}N_2O_4$
Formula weight	314.32
Wavelength [Å]	0.71073 Á
Temperature [K]	100 (2) K
Crystal system	Monoclínico
Space group	*C*2/*c*
a	14.8511 (3) Á
b , β	8.0798 (2) Á . 106.013 (10)º
c	12.8368 (3) Á
Volume [Å3]	1480.57 (6) A^3
Z	4
Dcalcd. [g cm-3]	1.401 mg/m^3
μ [mm-1]	0.101mm^{-1}
F(000)	728
Total data	1514
Unique data	1502
Final *R* indices	R1= 0.0425 wR2= 0.1156

Table2: Selected bond lengths (Á)and angles (º) for H_4L

H(10) - N(10)	0.89(2)	C(11) - H(11A)	0.990(2)
C(6) - O(7)	1.357(3)	C(11) - H(11B)	0.990(2)
C(8) - O(9)	1.253(2)	C(11) - C(12)	1.522 (2)
C(8) - N(10)	1.331(3)	C12—H12A	0.99
N(10) - C(11)	1.458(3)	C12—H12B	0.99
C(2)-C(1)-C(8)	123.8(2)	H(11A)-C(11)-C(12)	109.2(2)
C(6)-C(1)-C(8)	118.2(2)	C(11)-C(12)-C(11)	111.2(2)
C(1)-C(6)-O(7)	120.9(2)	C(11)-C(12)-H(12A)	109.4(1)
C(5)-C(6)-O(7)	118.6(2)	H(12A)-C(12)-H(12A)	108.0(3)
C(1)-C(8)-O(9)	120.6(2)	H(12A)-C(12)-H(12B)	0.0
C(1)-C(8)-N(10)	118.2(2)	H(11A)-C(11)-C(12)	109.2(2)
O(9)-C(8)-N(10)	121.2(2)	N(10)-C(11)-H(11A)	109.2(2)
H(10)-N(10)-C(8)	120.4(13)	N(10)-C(11)-C(12)	112.3(2)
H(10)-N(10)-C(11)	115.9(13)	H(11A)-C(11)-H(11B)	107.9(2)

Table3.- Hydrogen bonds

D-H...A	d(D-H)	d(H...A)	d(D...A)	(DHA)
O(7)-H(7)-----O(9)	0.93(3)	1.63(3)	2.483(13)	154 (13)
N(10) –H(10) O(7)*	0.89(2)	2.03(2)	2.8509(18)	153.0(19)

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

This molecule has intramolecular hydrogen bond O (7) - H (7) ... O (9) between the phenolic oxygen O (7) and amide oxygen O(9). It also presents an intermolecular hydrogen bond between the nitrogen N (10) - H (10) and the phenolic oxygen O (7) of another molecule. π interactions is further appreciated - stacking between the benzene rings (Table 3, Figure 2).

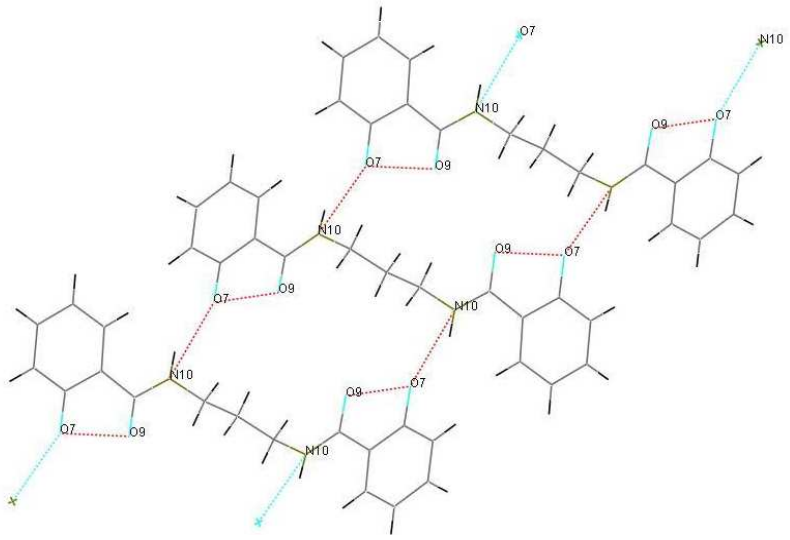

Figure 2. Stick diagram for H_4L showing the hydrogen bonding

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