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[a042]

Crystal structure of H_4L^1 (*N-N'*-Bis(o-hydroxybenzoyl)ethylenediamine)

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ABSTRACT

Three bis-amide bis-phenoxy N_2O_2 ligands were obtained from the 2:1 molar reaction of phenyl salicylate and the diamines (1,2-diaminoethane, 1,3-diaminopropane and 1,4-diaminobutane) to yield H_4L^n (H_4L^1, H_4L^2, H_4L^3 respectively). The ligands have been characterised by elemental analysis, IR, and ^{1}H ^{13}C NMR spectroscopies, mass spectrometry (ES) and X-ray diffraction.

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 tetraanionic bis-amide bis-phenoxy ligands should favour the aggregation of neighbouring complexes through these donors atoms[1] (amide and phenoxo oxygen). In previous papers we reported the synthesis, structures and properties of Mn(III) complexes with asymmetrical trianionic amido-imino-phenoxo ligands. At this goal we have designed the tetraanionic ligands, H_4L^n that contain six potential donor atoms: two amide nitrogen, two phenoxo and two amide oxygen atoms.

RESULTS AND DISCUSSION

H_4L^n were prepared according to the literature[2], in this case by a 2:1 molar reaction of phenyl salicylate and the diamines with methanol at 180-190 ºC for 1 h. The product was treated with diethyl ether to obtain a white powder at almost quantitative yield. White crystals of H_4L^{10}, 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_4L^1: M.p.180 ºC. Anal. Calc. for $C_{16}H_{16}N_2O_4$: C, 64.0; H, 5.4; N, 9.3. Found: C,64.0; H, 5.5; N,9.4%. MS ES (m/z): 301; IR (KBr, cm^{-1}): ν(N-H) 3407, ν(O-H) 3060, ν(amido I) 1642, ν(amido II) 1550, ν(C-O) 1254. ^{1}H NMR (DMSO-d^6, ppm): δ 8.87 (s, 2H), 6.83-6.88 (m, 4H), 7.37 (t, 2H), 7.78 (d, 2H), 3.48 (d, 2H). ^{13}C NMR (DMSO-d^6, ppm): δ 160.7 (C-OH), 170.0 (C=O), 39.3 (CH_2).

Ligand H_4L^2: 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. ^{1}H NMR (DMSO-d^6, ppm): δ 8.81 (s, 2H), 6.83-6.88 (m, 4H), 7.37 (t, 2H), 7.80 (d, 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).

Ligand H_4L^3: M.p.127 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. ^{1}H NMR (DMSO-d^6, ppm): δ 9.17 (s, 2H), 7.20-7.80 (m, 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 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 1.

The crystal structure reveals that H_4L exists as discrete molecules. The C(14)-O(15) and C(8)-O(9) distances of 1,257 y 1,260 Å respectively, are consistent with. C=O double bonding of amide groups. The two oxygen O(1) and O(22) atoms are forming phenolic groups, and they present C-O distances O(1)-C(2) de 1,360(4) and O(22)-C(21) of 1,351(4) Å, corresponding to the expected single bonds. The distance O(1)-H (1) de 0,99(4) Å is longer than distance O(22)-H(22) of 0,91(3) Å.

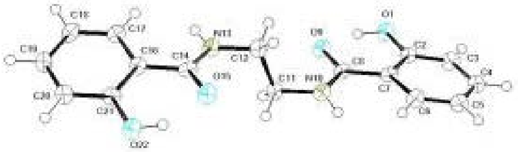

Figure 1. Crystal structure of H_4L^1.

3d structure from X-ray data [3]

Intermolecular hydrogen bonds exist between nitrogen atoms N(10) and N(13) and their neighbouring phenolic oxygen atoms O(1) and O(22). Other intramolecular hydrogen bonds exists between the phenolic oxygen atoms O(1) and O(9), O(22)–O(15) and O(22)-O(15) (see table 2 and figure 2).

Table1: Selected bond lengths (Å)and angles (º) for H_4L^1.

O(1)-C(2)	1,360(4)	O(22)-C(21)	1,351(4)
O(1)-H (1)	0,99(4)	O(22)-H(22)	0,91(3)
C(8)-O(9)	1,260(4)	C(14)-O(15)	1,257(4)
C(8)-N(10)	1,342(5)	C(14)-N(13)	1,340(4)
N(10)-C(11)	1,455(5)	N(13)-C(12)	1,449(4)
N(10)-H(10)	0,90(4)	N(13)-H(13)	0,89(4)
C(11)-C(12)	1,523(5)		
C(2)-O(1)-H(1)	103(3)	C(21)-O(22)-H(22)	106(3)
O(1)-C(2)-C(3)	119,3(3)	O(22)-C(21)- C(20)	119,4 (3)
C(6)-C(7)-C(8)	123,4(3)	C(17)-C(16)-C(14)	122,7(3)
C(8)-N(10)-C(7)	119,3(3)	C(14)-N(13)-C(12)	122,7 (3)
N(10)-C(11)-C(12)	112,2(3)	N(13)-C(12)-C(11)	111,7(3)

Table2: Hydrogen bonds

D-H...A	d(D-H)	d(H...A)	d(D...A)	(DHA)
N(10) --H(10) ..O(1)**	0.90(4)	2.13(4)	2.952(4)	152(3)
N(13) --H(13) ..O(22)*	0.90(3)	2.13(4)	2.926(4)	147(3)
Intra 1 O(1) --H(1) ..O(9)	0.99(3)	1.57(3)	2.502(3)	156(3)
Intra O(22) --H(22) ..O(15)	0.91(3)	1.67(4)	2.504(3)	152(3)
Intra O(22) --H(22) ..O(15)	0.94(4)	2.60(3)	2.910(4)	100(2)

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

REFERENCES

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2. H. Ojima, K. Aichi, *Nippon Kagaku Kaishi*, 1967, **88 (3)**, 329-333.
3. Left button of mouse to move the molecule, right button to display an options menu.