SYNTHESIS AND CRYSTAL STRUCTURES OF A POLIAZA RECEPTOR MACROLIGAND: 1,3-BIS(2-NITROBENZYLIDENEAMINO)PROPAN-2-OL

PERLA ELIZONDO MARTÍNEZ, NANCY PÉREZ RODRÍGUEZ, CECILIA RODRÍGUEZ DE BARBARÍN, SUSANA LÓPEZ CORTINA, SARA RODRÍGUEZ DE LUNA

Facultad de Ciencias Químicas, UANL, Ave Pedro de Alba S/N, Cd Universitaria, San Nicolás de los Garza, N. L. C.P. 662451

Abstract. The asymmetric unit of the title compound $C_{17}H_{16}N_4O_5$, contains one molecule of the compound (L3) (1,3-bis(2-nitrobenzylideneamino)propan-2-ol). The molecule shows a chiral C atom but the absolute structure was not possible to be determined by X-ray diffraction. The molecule shows intermolecular hydrogen bonding involving the hydroxy group and an imine nitrogen atom of a symmetry related molecule. The molecular distribution shows weak interactions between oxygen atoms of the nitro groups and two different C—H groups of benzene rings. The extended weak H bond formation, using the NO_2 groups, probably gives a more stable crystal structure. The molecule represents a precursor of a polyaza macrocylic ligands.

1. Introduction

The new Schiff base acyclic ligand in the title compound (L3), has been synthesized as a receptor and a chemical precursor of a variety of acyclic and macrocyclic multidentate ligands and metal complexes [1-4].

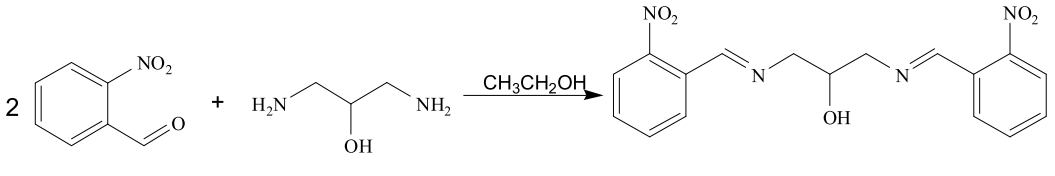
The polydentate azamacroligands have been of considerable interest in terms of structure chemistry, affinity with heavy metals and environmental and technological applications [5-8]. During the past years an extensive work has been carried out in the synthesis of this type of compounds which has culminated in the production of materials used in the extraction of heavy metals, as a catalyst, in the construction of diodes and molecular memories [9-11] is why the importance of both its synthesis as determining its structure on this applications can predict.

2. Experimental

2.1. *Synthesis*

All the reactants used to obtain the ligand were analytic grade from Sigma-Aldrich Chemical Company Inc., USA. IR spectra were measured on an IR-FT Nicolet 550 Model Magna-IR Spectrometer and ATR-FT Perkin Elmer Spectrum 1. Elemental analyses (C, H, N) were performed using a Perkin Elmer Instruments Series II 2400 CHNS-O. Single crystals diffraction data were collected on a Siemens P4 diffractometer.

In order to obtain L3, 1,3-Diaminopropan-2-ol (penOH) (3.61 g) was added to a dissolution of 2-nitrobenzaldehyde (DNB) (12.08 g) in ethanol (80 mL). The mixture was stirring for 25 minutes and a yellow solid came out. The solid was filtered off, and purified. Suitable crystals were obtained as colorless plates from ethanol solution by slow evaporation of the solvent at 298 K. The title compound was characterized by IR (KBr disc) and elemental analysis, which are in agreement with the X-ray structure.



DNB penOH **L3**

Yield 71%. P.f.: 98.52 ºC. analysis found (calc. for $C_{17}H_{16}N_4O_5$): 57.38 (57.33)% C, 4.49 (4.12)% H, 15.70 (16.39)% N. IR (KBr): O-H= 3366 cm^{-1}, N=C = 1637 cm^{-1}, $ArNO_2$ = 1529 cm^{-1} y NO_2 = 1352 cm^{-1}.

2.2. X-ray diffraction

Pertinent crystal data and other crystallographic parameters are listed in Table 1. Diffraction data were collected at room temperature (294-298 K) using the Mo-K radiation (=0.71073 Å), through standard procedures [12]. Raw data were corrected for absorption effects, either using suitable Ψ-scans data [13], or a Gaussian face-indexed correction, if available [14].

Crystal data 1,3-Bis(2-nitrobenzylideneamino)propan-2-ol

$C_{17}H_{16}N_4O_5$	D_x = 1.451 Mg m^{-3}
M_r = 356.34	Melting point: 371.52 K
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2c -2ac	Cell parameters from 67 reflections
a = 7.299 (4) Å	θ = 4.8–12.0°
b = 7.688 (3) Å	μ = 0.11 mm^{-1}
c = 29.071 (12) Å	T = 297 (2) K
V = 1631.4 (13) $Å^3$	
Z = 4	Plate, pale yellow
F_{000} = 744	0.60 × 0.60 × 0.08 mm

Data collection

Bruker P4 diffractometer	R_{int} = 0.088
Radiation source: fine-focus sealed tube	θ_{max} = 25.0°
Monochromator: graphite	θ_{min} = 2.7°
T = 297(2) K	h = - 8? 8
P = kPa	k = - 1? 9
ω scans	l = - 34? 1
Absorption correction: none	3 standard reflections
3381 measured reflections	every 97 reflections
1473 independent reflections	intensity decay: 2.9%
1141 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.045	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.119	$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max} < 0.001$
1473 reflections	$\Delta\rho_{max}$ = 0.19 e $Å^{-3}$
239 parameters	$\Delta\rho_{min}$ = - 0.21 e $Å^{-3}$
1 restraints	Extinction correction: none
constraints	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: structure-invariant direct methods	Flack parameter:

Refinement of F2 against all reflections. The weighted R-factor wR and goodness of fit S are based on F2, conventional R-factors R are based on F, with F set to zero for negative F2. The threshold expression of F2 > 2sigma(F2) is used only for calculating R-factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Hydrogen atoms bonded to C atoms were included in calculated positions, using the riding method, with C—H distances constrained to 0.93 (aromatic CH) and 0.97 Å (methylene CH_2) and Uiso(H) = 1.2Ueq(carrier C). The Hydrogen atom of the OH group was not constrained but let it refined isotropically.

Data collection: XSCANS [12]; cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL-Plus [15]; program(s) used to refine structure: SHELXTL-Plus; molecular graphics: SHELXTL-Plus and Mercury [14]; software used to prepare material for publication: SHELXTL-Plus.

3. Results and discussion

Compound (L3), Fig 1a, crystallizes with one molecule per asymmetric unit. Benzene rings are planar (r.m.s. deviation from planarity: 0.0076 and 0.0094 Å) and they make a dihedral angle of 80.7 (1)°. The nitro groups bonded to each benzene ring are rotated at an angle of 38.7 (3) and 47.6 (2)° respectively. The conformation of the central chain is described by torsion angles, C7—N2—C8—C9, 140.6 (4)°, N2—C8—C9—C10, 62.1 (5)°, C8—C9—C10—N3, -166.1 (3)°, C11—N3—C10—C9, -116.7 (4)°. The conformation showed is a trans-gauche-trans, stabilized in the solid state, and it is less common that all trans conformation in aliphatic systems. The heteroatoms, may coordinate to a metal center, giving a free arrangement of the molecules in order to be used as a versatile ligand complexation.

The molecule shows a chiral atom, C9, but the absolute structure was not possible to be determined because the compound is organic with no heavy atoms in it. The molecule shows an intermolecular hydrogen bond involving the OH group and a symmetry related N atom of an imine group (O3—H3B···N3 2.23 (8) Å). There exist two weak H bond between a C—H of a benzene ring with symmetry related O of NO_2 group (N1—O2···H3C 2.489 and N4—O4···H15A 2.450 Å respectively) as shown in Fig 1b. The extended weak H bond formation, using the NO_2 groups, probably gives a more stable crystal structure. The X-ray structure agree well with elemental analysis.

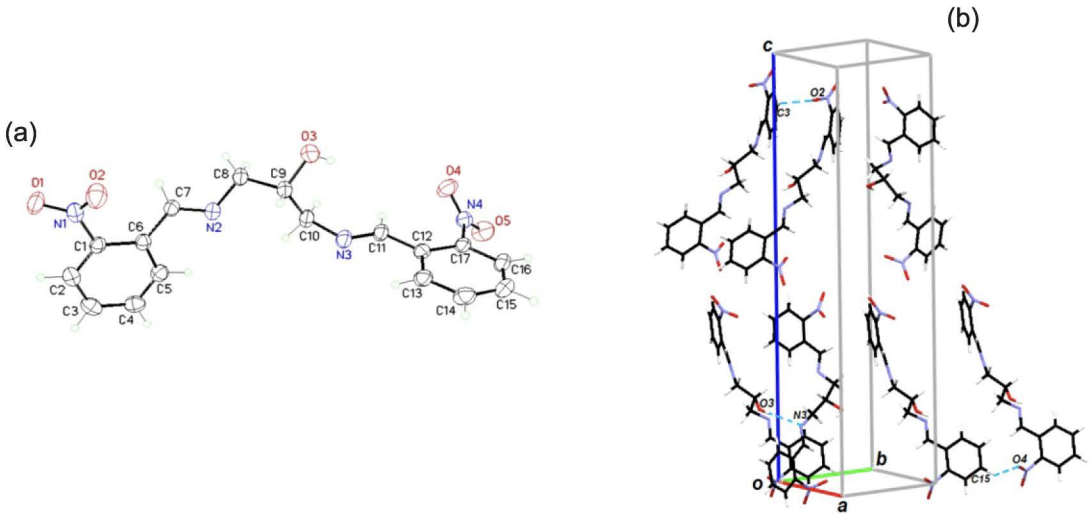


Figure 1a. Molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. 1b. Molecular packing structure of (I) showing hydrogen bond and two week interactions between O of nitro groups and H atoms of a C—H groups of the benzene rings (dashed bonds).

4. Acknowledgments

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5. Appendix

The following data are included in Appendix

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

Atomic displacement parameters (Å2)

Geometric parameters (Å, °)

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