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ORIGINAL ARTICLE

Synthesis, characterization and theoretical study of a new asymmetrical tripodal amine containing morpholine moiety

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Abstract A new asymmetrical tripodal amine, $[H_3L^2]Br_3$ containing morpholine moiety was prepared from reacting of one equivalent of *N*-(3-aminopropyl)morpholine and two equivalents of tosylaziridine, followed by detosylation with HBr/CH_3COOH. The products were characterized by various spectroscopic methods such as FAB-MS, elemental analysis, ^{1}H and ^{13}C NMR spectroscopy. The crystal structure of the hydrobromide salt of the latter amine, $[H_3L^2]Br_3$, was also determined. For triprotonated form of the ligand L^2 we can consider several microspecies and/or conformers. A theoretical study at B3LYP/6-31G** level of theory showed that the characterized microspecies is the most stable microspecies for the triprotonated form of the ligand. It was shown that the experimental NMR data for $[H_3L^2]Br_3$ in solution have good correlation with the corresponding calculated data for the most stable microspecies of $[H_3L^2]^{3+}$ in the gas phase.

1. Introduction

Tetradentate tripodal ligands have the general structure depicted in Fig. 1 and consist of a central donor atom X attached to three arms, each of which also contains at least one methylene group and a donor atom Y. A large number of such ligands containing identical sets or combinations of the donor atoms N, S, O and P are known (Blackman, 2005).

These tetradentate tripodal tetraamine ligands thus contain a single tertiary N atom, which 'caps' the tripod, and one N-donor atom on each arm. Various methods are available for the synthesis of tripodal tetraamine ligands, with the route of choice generally dictated by the nature of the donor atoms

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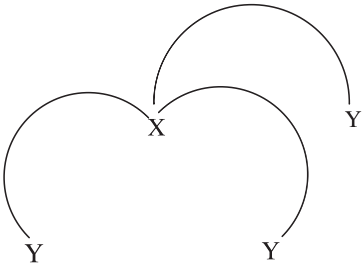


Figure 1 General structure of a tetradentate tripodal ligand.

on the three arms. All routes have in common the alkylation of the N atom of ammonium ion, or a primary or secondary amine precursor, with this N atom becoming the tertiary N atom of the resulting tripodal ligand. Bromo- and chloroalkylphthalimides are useful for the synthesis of ligands having aliphatic donor atoms as these can alkylate both primary and secondary N atoms at elevated temperatures, and deprotection using acid then gives the amine directly (Blackman, 2005). In previous works we have reported some symmetrical and asymmetrical tripodal tetramines (Keypour and Stotter, 1979; Keypour et al., 1998a,b). The first example of a tetradentate aliphatic tripodal amine ligand with all arms of different lengths was prepared by fusing 2,3-diphthalimidoethylpropylamine and *N*-(4-bromobutyl)phthalimide at 160 °C, with subsequent deprotection using HCl (Keypour et al., 2000). Herein, we report the synthesis and characterization of a novel asymmetrical tripodal amine containing morpholine moiety from the reaction of one equivalent of *N*-(3-aminopropyl)morpholine and two equivalents of tosylaziridine, followed by detosylation with HBr/CH_3COOH. The latter amine was prepared in a two-step method. The products of each step were exactly characterized. Also, in this paper, we report a theoretical study on triprotonated forms of the present polyamine. We show that the characterised microspecies in the solid state for the triprotonated form of the present amine is more stable than any other possible microspecies (see Scheme 1).

2. Experimental

2.1. Chemical and starting materials

N-(3-aminopropyl)morpholine was commercial product from Fluka and was used without further purification. Solvents were of reagent grade purified by the usual methods. Tosylaziridine was prepared according to the literature method (Hata et al., 1980)

2.2. Physical measurements

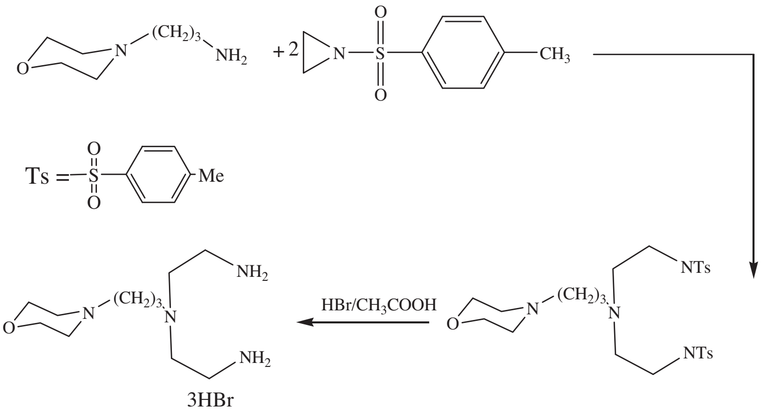
FAB mass spectra were recorded using a Kratos-MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the matrix. Elemental analyses were carried out using a Perkin–Elmer, CHNS/O elemental analyzer model 2400. ^1H and ^{13}C NMR spectra were obtained using a Bruker Avance 500 MHz spectrometer.

2.3. X-ray crystal structure determination

Vapor diffusion of diethyl ether into a solution of $[H_3L^2]Br_3$ in mixture of acetonitrile and methanol, afforded crystal suitable for study by X-ray crystallography. The details of the X-ray crystal data, and of the structure resolution and refinement, are given in Table 1. Measurements were made on a Bruker SMART CCD area diffractometer. All data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for all the crystal structures obtained (Sheldrick, 1996). Complex scattering factors were taken from the program package SHELXTL (Shelextl, 1997). The structure was solved by direct methods which revealed the position of all non-hydrogen atoms. The structure was refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using ORTEP-3 (Farrugia and Appl, 1997).

2.4. Synthesis of L^1

Tosylaziridine (9.91 g, 50 mmol) was dissolved in dry benzene (10 ml). A mixture of *N*-(3-aminopropyl)morpholine (3.60 g, 25 mmol) and dry benzene (10 ml) was added dropwise at a rate of about 10 ml/40 min. The system was fitted with a drying tube to prevent the absorption of water. It was also placed in a cool water bath to prevent the temperature from going above 25 °C. When the addition was finished, the mixture was stirred between 20 and 25 °C for about 12 h. Then it was heated to about 30 °C for 48 h and allowed to cool. Then the resulting precipitate was collected, washed with a small



Scheme 1 The synthesis processes of $[H_3L^2]Br_3$.