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ScienceDirect
Polyhedron 27 (2008) 1631–1638
POLYHEDRON
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Synthesis of two new tripodal ligands and their cyclocondensation with 2-[2-(2-formylphenoxy)ethoxy]benzaldehyde in the presence of manganese(II) and cadmium(II) metal ions

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Received 25 November 2007; accepted 21 January 2008
Available online 17 March 2008

Abstract

Two new asymmetric tripodal tetraamine ligands, 2-((bis(2-aminoethyl)amino)methyl)benzenamine (L^2) and 2-(((2-aminoethyl)(3-aminopropyl)amino)methyl)benzenamine (L^3) were synthesized and characterized. [1+1] Macrocyclic Schiff-base complexes containing 1,2-diphenoxyethane head units and a 2-aminobenzyl pendant arm, were synthesized as $[MnL^4(MeOH)](ClO_4)_2$ (**1**), $[MnL^5(MeOH)](ClO_4)_2$ (**2**), $[CdL^4(H_2O)](NO_3)_2$ (**3**) and $[CdL^5(H_2O)](NO_3)_2$ (**4**) from the metal ion templated cyclocondensation reactions of 2-[2-(2-formylphenoxy)ethoxy]benzaldehyde with the (L^2) or (L^3) tripodal tetraamine ligands. The crystal structure determination of (**1**) and (**4**) showed that the complex cations that had formed consisted of pentagonal bipyramidally coordinated Mn(II) and Cd(II) ions, centrally located in a N_3O_2 macrocycle, with one 2-aminobenzyl pendant arm. Supporting ab initio HF-MO calculations have been undertaken using the standard 3-21G* and 6-31G* basis sets.

Keywords: Macrocyclic complexes; Schiff-base; Cadmium complex; Manganese complex; Pendant arm

1. Introduction

Interest in macrocycles with pendant arms is growing on account of their unique coordination and structural properties, their utility in enzyme mimicking studies, and their applications as radiopharmaceuticals and magnetic resonance imaging reagents [1–3]. Macrocycles having a pendant arm of a primary amino group are important because this arm can be used to attach the macrocycles to other small molecules [4] or to monoclonal antibodies [5,6]. The preparation of monofunctionalized macrocycles, however, is usually more elaborate than the synthesis of polyfunctionalized ligands (*e.g.*, through extensive alkylation of the secondary amino groups in azamacrocycles) [7,8]. The development of simple methods for the preparation of monofunctionalized macrocyclic ligands that can be metallated with various transition metal ions is needed. We [9–11] and others [12,13] have previously reported a one-step synthesis of Schiff base macrocyclic complexes bearing a primary amino group in the pendant arm via a template condensation between a dicarbonyl and tripodal aliphatic tetramines. As an extension of this idea, in this work we report on the synthesis and characterization of two new asymmetric tripodal tetraamine ligands, in each case containing one primary aromatic amine and two primary aliphatic amines (Scheme 1). We report also on the cyclocondensation of these ligands with

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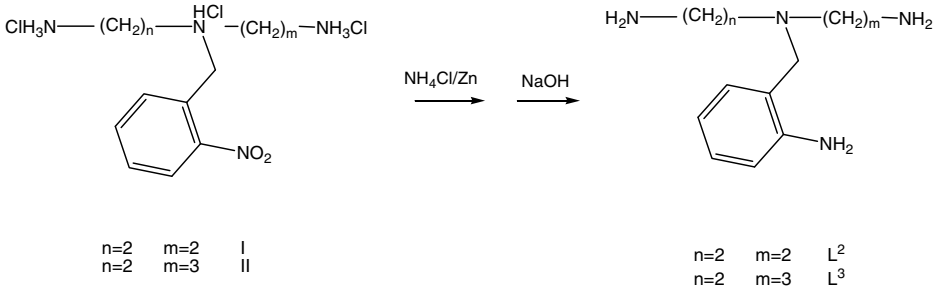
doi:10.1016/j.poly.2008.01.036



Scheme 1.

2-[2-(2-formylphenoxy)ethoxy]benzaldehyde in the presence of Mn(II) and/or Cd(II) ions.

2. Experimental

2.1. Starting materials

All solvents were of reagent grade quality and were purchased commercially. *N*1-(2-Nitrobenzyl)-*N*1-(2-aminoethyl)-ethane-1,2-diaminetrishydrochloride (I), *N*1-(2-nitrobenzyl)-*N*1-(2-aminoethyl)propane-1,3-diaminetrishydrochloride (II) and 2-[2-(2-formylphenoxy)ethoxy]benzaldehyde were synthesized according to the literature method [14,15].

2.2. Instrumentation

NMR spectra were obtained using a Bruker A V 300 MHz spectrometer. Infrared spectra were recorded in KBr pellets using a BIO-RAD FTS-40A spectrophotometer (4000–400 cm^{-1}).

2.3. X-ray crystal structure determination

Vapor diffusion of diethyl ether into a solution of $[MnL^4(CH_3OH)](ClO_4)_2$ and $[CdL^5(H_2O)](NO_3)_2$ in MeOH afforded pale yellow crystalline needles. X-ray data for $[MnL^4(CH_3OH)](ClO_4)_2$ were measured on a STOE IPDS-II two circle diffractometer at 293 °C, using graphite monochromated Mo Kα X-ray radiation ($\lambda = 0.7107$ nm) for $[MnL^4(CH_3OH)](ClO_4)_2$. X-ray data for $[CdL^5(H_2O)](NO_3)_2$ were also measured on a Bruker SMART-1000 diffractometer. Other crystallographic data are summarized in Table 1.

A full minimization of the structure for each macrocyclic complex was performed at the ab initio HF level of theory using gradient techniques with the GAUSSIAN-98 set of programs [16], on a Pentium-PC computer with a 3000 MHz processor. The effective core potential (ECP) standard basis set LanL2DZ [17] was utilized for the cadmium and manganese metal ions. The full-electron standard basis set 3-21G* or 6-31G* [18] were used for all other atoms. A starting semi-empirical structure for the ab initio 3-21G* calculations was obtained using the HYPERCHEM 5.02 program [19]. The resulting structures of the 3-21G* calculations were then used for the 6-31G* basis set.

2.4. Synthesis

2.4.1. Ligand synthesis

2.4.1.1. 2-((Bis(2-aminoethyl)amino)methyl)benzenamine (L^2). A mixture of *N*1-(2-nitrobenzyl)-*N*1-(2-aminoethyl)ethane-1,2-diaminetrishydrochloride (I) (3.47 g, 10 mmol), ammonium chloride (4 g) and water (2 ml) in 100 ml of ethanol was heated to boiling and 3 g of zinc dust was added. When the solution was pale green it was filtered. The volume was then reduced to 20 ml by rotary evaporation. Excess water was added to the mixture and the pH was adjusted to 12 with potassium hydroxide. The solution was extracted with chloroform (×3). The chloroform extracts were combined and dried over anhydrous sodium sulfate. The dried extracts were then reduced to a small volume on a rotary evaporator. The product was obtained as an oil. Yield (1.3 g, 62%). *Anal.* Calc. for ($C_{11}H_{20}N_4 + 1/10CHCl_3$): C, 60.53; H, 9.20; N, 25.44. Found: C, 60.61; H, 9.23; N, 25.31%. IR (Nujol, cm^{-1}) 3360, 3380 $\nu(NH_2)$, 3082 $\nu(CH)$; ^1H NMR δ_H ($CDCl_3$, ppm) 2.59 (t, 4H), 2.75 (t, 4H), 3.08 (NH_2, 6H, b), 3.56 (s, 2H), 6.62 (m, Ph, 2H), 6.91 (m, Ph, 2H); ^{13}C NMR δ_C ($CDCl_3$, ppm) 39.95, 58.81, 59.87,115.11, 116.30, 123.41, 129.90, 131.27, 147.47.

2.4.1.2. 2-(((2-Aminoethyl)(3-aminopropyl)amino)methyl) benzenamine (L^3). The ligand (L^3) can be readily prepared by the above procedure except using *N*1-(2-nitrobenzyl)-*N*1-(2-aminoethyl)propane-1,3-diaminetrishydrochloride (II) (3.61 g, 10 mmol) instead of (I). Yield (1.4 g, 63%) *Anal.* Calc. for ($C_{12}H_{22}N_4 + 1/11CHCl_3$): C, 62.28; H, 9.55; N, 24.03. Found: C, 62.22; H, 9.39; N, 24.13%. IR (KBr, cm^{-1}) 3361 and 3385 (NH_2), 3070 (CH); ^1H NMR δ_H ($CDCl_3$, ppm) 1.52 (m, 2H), 2.19, 2.40, 2.60 (m, 14H), 3.79 (s, 2H), 7.25–7.88 (b, 4H); ^{13}C NMR δ_C ($CDCl_3$, ppm) 29.49, 38.97, 39.52, 51.10, 56.22, 58.16, 114.84, 116.82, 122.35, 127.78, 130.04, 146.32.

2.5. Preparation of the complexes

2.5.1. General procedure

All the complexes were readily prepared by template condensation. The required amine (0.5 mmol) in methanol (10 ml) was added dropwise to a mixture of the appropriate manganese (II) or cadmium (II) salts (0.5 mmol) in methanol