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Synthesis and crystal structure of some new cadmium (II) macrocyclic Schiff-base complexes containing piperazine moiety

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ABSTRACT

The metal templated Cd(II) cyclocondensation of 2,6-diacetylpiridine or 2,6-pyridinedicarbaldehyde and two different amines containing piperazine moieties have been investigated. The resulting ligands, L^1 and L^2 are 16- and L^3 and L^4 17-membered pentaaza macrocycles. The complexes have been characterized by a variety of methods including IR, ^1H, ^{13}C NMR, DEPT, COSY(H,H), HMQC(H,C), FAB spectrometry and conductivimetry measurements. The crystal structures of $[CdL^2Cl](CH_3OH)ClO_4$ (2) and $[CdL^4(NO_3)(H_2O)]$-ClO_4 (4) have been also determined, and it was shown that the geometry of the Cd(II) ion in the complexes is slightly distorted pentagonal pyramidal and pentagonal bipyramidal, respectively. The gas-phase structures of ligands, L^2 and L^4 and their Cd(II) complexes have also theoretically studied.

1. Introduction

The capability of metal ions to promote the template synthesis of macrocyclic ligands has been studied extensively and depends on several factors related to the ligand characteristics, as well as on the nature of the metal ion [1]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and type of donor atoms presenting in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation. For transition metal ions, features such as the nature and magnitude of crystal-field effects play also an important role [2]. One of the features of non-rigid large ring macrocyclic ligands is their ability to fold to give, for example, *cis*-octahedral complexes with tetradentate macrocycles. Attempts to study the size match selectivity of azamacrocycles have involved the synthesis of ligands with rigid backbones to prevent the folding which can otherwise occur [3–5]. One way of achieving this is to build a 1,4-piperazine ring into the backbone of the macrocycle. However, the preferred chair conformation of 1,4-piperazine is unfavorable for chelation, and in open chain structures tends to give rise to oligomeric species with the 1,4-piperazine units bridging between metal with large metal ions [6–10]. 1,4-Piperazine has been observed to give metal chelates in which it has a boat conformation [11,12]. Thermodynamic studies of complex formation by 1,4-piperazine-N,N′-diethanoate indicate, from stability constant measurements, that the 1,4-piperazine ring does not form chelates with small metal cations [13]. Piperazine is rarely used as a building block in macrocycles synthesis and only a few examples of macrocycles containing piperazine moieties have been reported. Piperazine itself is achiral but the use of the easily available chiral piperazines as building blocks leads to chiral macrocycles .Therefore, piperazine is an excellent choice as a versatile building block for synthesisizing achiral or chiral macrocycles [14]. More et al. synthesised a few number of pentaaza macrocyclic complexes containing a 1,4-piperazine backbone [15]. Nelson and others have also reported the synthesis of pentaaza 15-, 16- and 17-membered macrocyclic rings with Cd(II) metal ion [16,17]. We have recently prepared some novel manganese (II) macrocyclic Schiff-base complexes containing piperazine moiety [18]. In this work we describe the Cd(II) templated [1 + 1] cyclocondensation of 2,6-diacetylpyridine or 2,6-pyridinedicarbaldehyde and two linear tetra-amines containing piperazine moiety which gave the complexes $[CdL^{1-4}]^{2+}$ (Fig. 1) as shown in Scheme 1. These complexes are based on the 16-, and 17-membered pentaaza macrocycles. The crystal structures of $[CdL^2Cl](ClO_4)(CH_3OH)$ and $[CdL^4(NO_3)(H_2O)]ClO_4$ are also reported.

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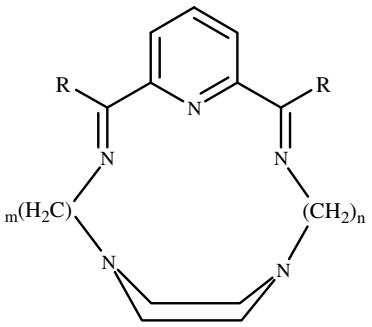


	m	n	R
L^1	2	3	H
L^2	2	3	CH_3
L^3	3	3	H
L^4	3	3	CH_3

Fig. 1. Ligands under discussion in this paper.

2. Experimental

2.1. Starting materials

2,6-Pyridinedicarbaldehyde was prepared according to the literature method [19]. N,N′(2-aminoethyl)(3-aminopropyl)piperazine was synthesized according to the literature method [18]. 2,6-Diacetylpyridine, N,N′-bis(3-aminopropyl)piperazine, 2-aminoethyl piperazine and the metal salts were commercial products (from Merck, Aldrich and Fluka) and were used without further purification. Solvents were of reagent grade purified by the usual methods.

Caution! Perchlorate salts are potentially explosive. Only small amount of material should be prepared and handled with great care.

2.2. Instrumentation

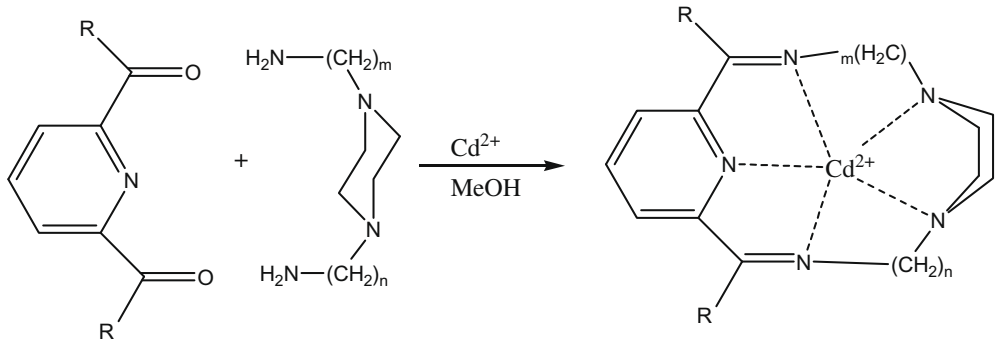
Elemental analyses were performed in a Carlo-Erba EA microanalyser. FT-IR spectra in the 4000–400 cm^{-1} region were recorded from KBr pellets on Bruker VECTOR 22 and Perkin–Elmer GX spectrophotometers. FAB mass spectra were recorded using a Kratos-MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the matrix. Conductivimetry measurements were carried out in 10^{-3} mol dm^{-3} dimethylformamide solutions at 20 °C using a CARISON GLP32 conductivimeter. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 and 400 MHz using DMSO as solvent.

2.3. X-ray crystal structure determination

X-ray data for $[CdL^4|(NO_3)(H_2O)]^+$ was performed on STOE IPDS-II two circle diffractometer, using graphite monochromated Mo Kα X-ray radiation (λ = 0.7107 nm). The data collection was performed at room temperature using the ω-scan technique and using the STOE X-AREA software package [20]. The crystal structures were solved by direct methods [21] and refined by using X-STEP32 crystallographic software package [22]. All of the non-hydrogen atoms were refined anisotropically. All of hydrogen atoms were located in ideal positions. X-ray data for $[CdL^2Cl]^+$ were measured on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) at 20 °C using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for all the crystal structures obtained [23]. Complex scattering factors were taken from the program package SHELXTL [24]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. Crystal data and structure refinement for both complexes are shown in Table 1.

2.4. Computational method

The geometries of the ligands, L^2 and L^4 and their Cd(II) complexes in the gas phase were fully optimized at DFT (B3LYP) [25] level of theory using the GAUSSIAN 98 set of programs [26]. The ligands were studied using by two different 6-31G* and lanl2dz basis sets [27]. The latter basis set was also used for calculation of the complexes. The standard 6-311+G* basis set was also used for single-point calculations on the structure of ligands derived from above calculations. Vibrational frequency analyses, calculated at the same level of theory, indicate that all optimized structures



	m	n	R
L^1	2	3	H
L^2	2	3	CH_3
L^3	3	3	H
L^4	3	3	CH_3

Scheme 1. The template condensation between 2,6-diacetylpyridine or 2,6-pyridinedicarbaldehyde and two amines with piperazine moiety in the presence of cadmium(II) ion.