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Cd(II) complexes with pendant armed oxa- and azamacrocyclic ligands

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ABSTRACT

The coordination capability of the pendant-arm macrocyclic ligands – with different sizes, nature and number of the donor atoms – dioxotriaza 17-membered (L^1) and pentaaza 17-membered (L^2) towards nitrate and perchlorate Cd(II) salts, has been investigated. The complexes were prepared in 1:1 metal/ligand molar ratio. The characterization carried out by elemental analysis, FAB mass spectrometry, IR and NMR spectroscopy, conductivity measurements, together with the crystal structure of the complexes $[CdL^1(CH_3CN)](ClO_4)_2{\cdot}CH_3CN$ and $[CdL^2](ClO_4)_2$ confirms the formation of mononuclear complexes in all cases. The X-ray diffraction of $[CdL^1(CH_3CN)](ClO_4)_2{\cdot}CH_3CN$ complex presents a mononuclear endomacrocyclic structure with the metal ion coordinated by the five donor atoms from the macrocyclic framework, the amine group from the pendant-arm and one acetonitrile molecule, in a distorted pentagonal bipyramid geometry. The complex $[CdL^2](ClO_4)_2$ is also mononuclear, but the cadmium ion is in a distorted trigonal prism environment coordinated by the six nitrogen donor atoms from the ligand. In both cases, the perchlorate ions do not participate in the coordination to the metal ion, but they are involved in numerous hydrogen bond interactions inter- and intramolecular with phenoxy and amino-groups.

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1. Introduction

The oxaaza and azamacrocyclic ligands have been a subject of extensive investigation in the coordination chemistry research during last decades [1–3]. It is mainly due its ability to form complexes with different metal ions or anionic species with considerable potential in such areas as catalysis, modelling of metalloenzyme, molecular recognition, etc. [4–6].

The host–guest interactions and the selectivity of metal ions with this sort of ligand is governed, between other factors, on the cavity and chelate ring size, ligand rigidity and the number and nature of the donor atoms. The presence of pendant-arms into the macrocyclic skeleton have attracted a great deal of interest owing to the fact that the ligating groups attached to the macrocyclic backbone can offer additional donor groups to produce important changes in the control of the stability, selectivity, stereochemistry and certain thermodynamic parameters [7–10], or promote the formation of dinuclear or polynuclear metal complexes with interaction between the metal centres. The use of pendant-armed groups can also increase the coordination capability of the macrocyclic ligand as they can encapsulate the metal ion into the macrocyclic hole [11]. In this way, some macrocyclic ligands were designed to act as selective sequestering agents for "soft" metal ions of environment importance such as cadmium, mercury or lead [12–14]. In particular, cadmium is an environment pollutant which inhibits RNA polymerase activity in vivo [15,16], and reacts readily with proteins and other biological molecules, and so the macrocyclic chemistry of cadmium complexes with multidentate ligands such that may have important utility as antagonist for treatments of heavy-metal poisoning have attracted much attention [17–20]. Although many studies have been made on cadmium(II) macrocyclic complexes, no many crystal structures have been reported and most of them resulted to be mononuclear [21–24].

As continuation of our work on the coordination capability of oxa and azamacrocyclic ligands [25–28] and in order to gain insight into the structures and stabilities of macrocyclic coordination complexes with Cd(II) ion, we report in this paper the coordination ability of two new pendant-arm macrocyclic ligands, L^1 and L^2 (Scheme 1). The X-ray crystal structure of cadmium perchlorate complexes is also reported.

2. Experimental

2.1. Chemicals and starting materials

The precursor macrocyclic ligand L^0 [29] and 2,2′-(etane-1,2-diildiamine)bisbenzaldehyde [30], were synthesized as described

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in the literature. Salicylaldehyde, tris(2-aminoethyl)amine, anhydrous Na_2SO_4, $NaBH_4$, nitrate and perchlorate salts were commercial products (from Alpha and Aldrich) and were used without further purifications. Solvents were of reagent grade and were purified by the usual methods.

Caution: Although no problems were encountered during the course of this work, attention is drawn to the potentially explosive nature of perchlorates.

2.2. Synthesis of macrocyclic ligands

Ligand L^1: To a hot methanol (30 ml) solution of the precursor macrocyclic ligand L^0 (1 mmol, 0.38 g), salicylaldehyde (1 mmol, 0.12 g) dissolved in methanol (30 ml) was added dropwise. The mixture was refluxed during 1 h. After the solution was allowed to cool to room temperature, $NaBH_4$ (0.38 g, 10 mmol) was added slowly. The solution was concentrated to dryness and the crude solid was extracted with water–chloroform. The organic layer was dried over anhydrous Na_2SO_4 and evaporated until 5 ml. The addition of ether caused separation of a pale yellow solid characterized as L^1: $C_{29}H_{38}N_4O_3$ (MW: 490): C, 68.5; H, 7.8; N, 11.0. Found: C, 68.4; H, 7.7; N, 10.6%. Yield: 45%. IR (KBr, cm^{-1}): 3670–3580 [ν(O–H)], 3434 [ν(N–H)], 1594, 1544, 1492 [ν(C=C)]. FAB-MS, *m/z*: 491 $[L^1+H]^+$. Colour: pale yellow.

The ligand L^2 was prepared by addition of (tris(2-aminoethyl)amine) (2 mmol, 0.30 mL) dissolved in methanol to a hot solution in methanol (75 ml) of 2,2′-(ethane-1,2-diildiamine)bisbenzaldehyde (2 mmol, 0.54 g). The mixture was refluxed for 4 h and after the solution was allowed cool to room temperature, $NaBH_4$ (0.76 g, 20 mmol) was added slowly, the solid filtered off and evaporated to dryness. The residue was then extracted with water–chloroform and the organic layer was dried over anhydrous Na_2SO_4 and evaporated to yield a white oil. By recrystallization of this oil in acetonitrile the ligand L^2 was obtained as white solid. *Anal.* Calc. for $C_{22}H_{34}N_6$ (MW: 382): C, 69.1; H, 8.9; N, 22.0. Found: C, 69.0; H, 8.6; N, 21.8%. Yield: 52%. IR (KBr, cm^{-1}): 3269 [ν(N–H)], 1604, 1514, 1458 [ν(C=C)]. FAB-MS, *m/z*: 383 $[L^2+H]^+$. Colour: white.

2.3. Synthesis of metal complexes-general procedure

The appropriate metal salt (0.25 mmol) in a 1:1 Cd:L^n molar ratio was dissolved in acetonitrile (10 ml) and added to a stirred and refluxing solution of the macrocyclic ligand (0.25 mmol) in acetonitrile (30 ml). The reaction mixture was refluxed for 3 h and concentrated in a rotary evaporator until *ca.* 5–6 ml. The product obtained was filtered off and dried.

2.3.1. $[CdL^1](NO_3)_2$

Anal. Calc for $C_{29}H_{38}N_6O_9Cd$: C, 47.9; H, 5.2; N, 11.6. Found: C, 47.8; H, 5.4; N, 10.9%. Yield: 62%. IR (KBr, cm^{-1}): 3260 [ν(N–H)], 1608, 1492, 1458 [ν(C=C)], 1383, 1080, 832, 766 [$\nu(NO_3^-)$]. FAB-MS (*m/z*): 665 $[CdL^1(NO_3)]^+$, 603 $[CdL^1]^+$. Λ_M/Ω^{-1} cm^2 mol^{-1} (in CH_3CN): 152 (1:1). Colour: white.

2.3.2. $[CdL^1(CH_3CN)](ClO_4)_2{\cdot}CH_3CN$

Anal. Calc. for $C_{33}H_{44}N_6O_{11}Cl_2Cd$: C, 45.9; H, 5.1; N, 9.7. Found: C, 46.0; H, 5.0; N, 9.5%. Yield: 78%. IR (KBr, cm^{-1}): 3262 [ν(N–H)], 1605, 1493, 1458 [ν(C=C)], 1100, 622 [$\nu(ClO_4^-)$]. FAB-MS (*m/z*): 703 $[CdL^1(ClO_4)]^+$, 603 $[CdL^1]^+$. Λ_M/Ω^{-1} cm^2 mol^{-1} (in CH_3CN): 268 (2:1). Colour: white.

2.3.3. $[CdL^2](NO_3)_2{\cdot}H_2O$

Anal. Calc. for $C_{22}H_{34}N_8O_7Cd$: C, 41.6; H, 5.3; N, 17.6. Found: C, 42.2, H, 5.4; N, 17.5%. Yield: 47%. IR (KBr, cm^{-1}): 3168 [ν(N–H)], 1607, 1499, 1458 [ν(C=C)], 1384, 1082, 825, 760 [$\nu(NO_3^-)$]. FAB-MS (*m/z*): 555 $[CdL^2(NO_3)]^+$, 494 $[CdL^2]^+$. Λ_M/Ω^{-1} cm^2 mol^{-1} (in CH_3CN): 148 (1:1). Colour: white.

2.3.4. $[CdL^2](ClO_4)_2$

Anal. Calc. for $C_{22}H_{34}N_6O_8Cl_2Cd$: C, 38.1; H, 4.9, N, 12.1. Found: C, 37.9; H, 4.7, N, 11.8%. Yield: 53%. IR (KBr, cm^{-1}): 3156 [ν(N–H)], 1605, 1500, 1460 [ν(C=C)], 1100, 625 [$\nu(ClO_4^-)$]. FAB-MS (*m/z*): 594 $[CdL^2(ClO_4)]^+$, 494 $[CdL^2]^+$. Λ_M/Ω^{-1} cm^2 mol^{-1} (in CH_3CN): 300 (2:1). Colour: white.

2.4. Physical measurements

Elemental analyses were performed in a Carlo-Erba EA microanalyser. IR spectra were recorded as KBr discs on a Bruker IFS-66V spectrophotometer. FAB mass spectra were recorded using a Kratos-MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the matrix. Conductivity measurements were carried out in 10^{-3} mol dm^{-3} acetonitrile solutions at 20 °C using a WTW LF3 conductivimeter. NMR spectra were recorded on a Bruker 500 MHz.

2.5. Crystal structure determination

Measurements were made on a Bruker SMART CCD 1000 area diffractometer. All data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for all the crystal structures obtained [31]. Complex scattering factors were taken from the program package SHELXTL [32]. 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. The hydrogen atoms were located in their calculated positions and refined using a riding model, except the hydrogen atoms from the amine groups in $[CdL^2](ClO_4)_2$ which were located and refined isotropically.

3. Results and discussion

L^1 and L^2 pendant-armed macrocyclic ligands were each readily obtained from a one-pot synthesis from the precursors reagents in satisfactory yield and purity without the need for column chromatography. The ligands were characterized by different techniques: elemental analysis, FAB-MS, IR, ^1H and ^{13}C NMR spectroscopy.

FAB mass spectrometry provides evidence for the presence of only L^1 (*m/z* 491, assignable to $[L^1+H]^+$), and L^2 (*m/z* 383, assignable to $[L^2+H]^+$). The IR spectra show no bands corresponding to primary amino-group in L^1 and carbonyl group in L^2, further confirm that the introduction of the pendant-arm in L^1 and the cyclization for L^2 took place.

The NMR spectra of both ligands were recorded using deuterated chloroform as solvent, and confirm the integrity of the ligands and their stability in solution. The assignment of the signals was based upon standard COSY, DEPT-135 and HMQC measurements. The aromatic region of the ^1H NMR spectrum of L^1 shows two multiplet signals at δ 7.5–6.5 ppm belonging to the aromatic rings; the ethylene protons signal appears at δ 4.4 ppm as a singlet. The benzyl and salicyl protons appear as a singlet and multiplet at δ 3.7 and 3.6 ppm, respectively. The signal of the ethylene groups of the macrocyclic framework is observed at δ 2.5 ppm as a multiplet. Finally, the ethylenic protons of the pendant-arm are observed as triplet at δ 2.4 and 2.2 ppm.

The ^1H and ^{13}C NMR signal data, together with the labelling scheme, for L^2 is collected in Table 1. The proton spectrum shows a multiplet signal due to the aromatic proton in the range δ 7.4–6.6 ppm. The signals of the tris-ethylene amine protons (H_9–H_{12})

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