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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.

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 $[CdL^1]^+$. $\Lambda_M/\Omega^{-1}\,cm^2\,mol^{-1}$ (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 $[CdL^1]^+$. $\Lambda_M/\Omega^{-1}\,cm^2\,mol^{-1}$ (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 $[CdL^2]^+$. $\Lambda_M/\Omega^{-1}\,cm^2\,mol^{-1}$ (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 $[CdL^2]^+$. $\Lambda_M/\Omega^{-1}\,cm^2\,mol^{-1}$ (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

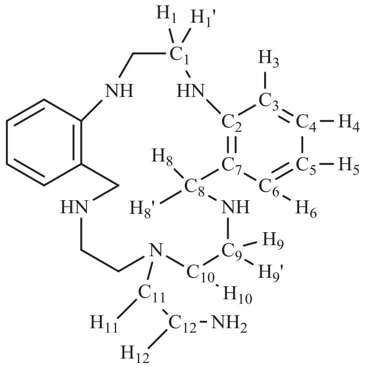
L^1 and L^2 pendant-armed macrocyclic ligands were each readily obtained from a one-pot synthesis from the precursors reagents in satisfactory yield and purity without the need for column chromatography. The ligands were characterized by different techniques: elemental analysis, FAB-MS, IR, ^1H and ^{13}C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

Table 1
^1H and ^{13}C NMR spectra assignment for L^2 in $CDCl_3$.



^1H		^{13}C	
Assignment	δ (ppm)	Assignment	δ (ppm)
		C_1	42
H_1	3.5 (s, 4H)	C_2	148
H_8	3.8 (s, 4H)	C_3, C_4, C_5, C_6	130–109
H_{10}	2.5 (m, 4H)	C_7	124
H_9, H_{12}	2.6 (m, 6H)	C_8	52
H_{11}	2.4 (m, 2H)	C_9	46
H_3, H_4, H_5, H_6	7.4–6.6 (m, 8H)	C_{10}	53
		C_{11}	56
		C_{12}	39

appear as different multiplets in the range δ 2.6–2.4 ppm, whilst the other ethylene protons (H_1) are singlet at δ 3.5 ppm. Finally, the benzyl protons appear as singlet at δ 3.8 ppm.

The coordination capability of L^1 and L^2 towards Cd(II) hydrated nitrate and perchlorate salts was studied. The complexes were characterized by elemental analysis, IR, molar conductivity, FAB-MS and NMR spectroscopy.

3.1. Structural studies of the complexes

Adequate crystals for suitable X-ray diffraction of formulae $CdL^1(CH_3CN)](ClO_4)_2{\cdot}CH_3CN$ and $[CdL^2](ClO_4)_2$ were obtained by recystallization of the complexes in acetonitrile. The details of the X-ray crystal structures solution and refinement are given in Table 2. The X-ray studies reveal the presence of similar mononuclear endomacrocyclic complexes consistent with the cation $[CdL^n]^{2+}$ and two well separated perchlorate ions. One acetonitrile molecule is also coordinated to cadmium ion in the complex with L^1. The crystal structure of the $[CdL^1(CH_3CN)](ClO_4)_2{\cdot}CH_3CN$ and $[CdL^2](ClO_4)_2$ complexes is also reported.

3.1.1. Crystal structure of $CdL^1(CH_3CN)](ClO_4)_2{\cdot}CH_3CN$

By slow concentration of a solution of the perchlorate Cd(II) complex with L^1 in acetonitrile, crystals suitable for X-ray diffraction with formula $CdL^1(CH_3CN)](ClO_4)_2{\cdot}CH_3CN$ were obtained. The molecular structure of the complex and selected bond lengths (Å) and angles (°) relating to the coordination environment of the metal are given in Fig. 1. Crystal data and structure refinement are given in Table 2.

The molecular structure shows a mononuclear endomacrocyclic complex in a distorted pentagonal bypyramid environment, being the metal atom coordinated by the three nitrogen and two oxygen donor atoms from the macrocyclic backbone and the amino nitrogen atom from the pendant-arm. The seventh coordination position is occupied by an acetonitrile molecule, remaining the phenoxy group from the pendant-arm uncoordinated and protonated. The equatorial plane of the distorted pentagonal bipyramid can be considered to be formed by the all macrocyclic backbone donor atoms [N(1)N(2)N(3)O(1)O(2), rms = 0.5104(2) Å]. The axial positions are formed by the secondary amino-group of the pendant-arm, N(4), and the coordinated acetonitrile molecule, N(1S), as these two donor atoms show the biggest angle to the metal ion N(4)–Cd(1)–N(1S) 162.52(15)°.

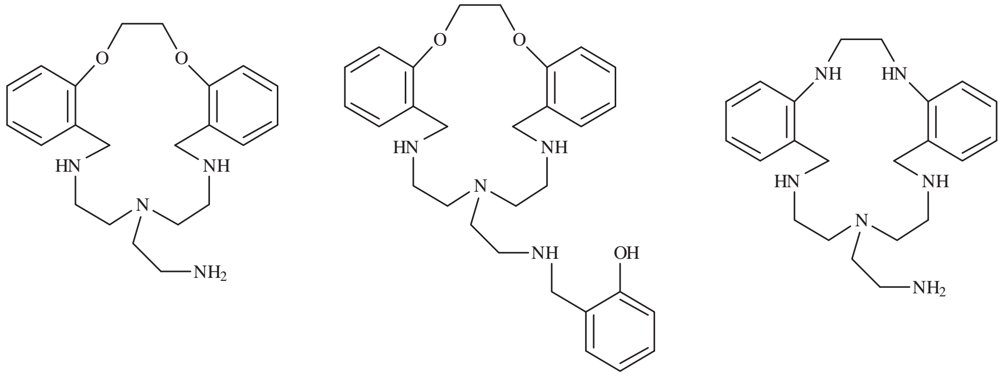
The Cd–N bond distances corresponding to the acetonitrile group [Cd(1)–N(1S), 2496(5) Å] and the tertiary amine [Cd(1)–N(2), 2.426(4) Å] are longer than the corresponding to the secondary amines (average value, 2.345 Å). The longest coordinated bond distances correspond to the ether group, which coordinates to the metal ion in asymmetric mode [Cd(1)–O(2) 2.547(5) and Cd(1)–O(1) 2.652(3) Å].

The macrocyclic ring is slightly twisted, showing a perpendicular disposition of the aromatic rings, with a dihedral angle between the planes that contain the rings of 78.34°.

The crystal structure shows that one oxygen atom of a perchlorate group is disordered in two positions. The perchlorate ions do not participate in the coordination to the metal ion, but they are involved in hydrogen bond interactions with the amino-groups from the macrocycle. Also, an intramolecular hydrogen bond interaction between the amino-group N4–H4A and the ether oxygen atom O3 has been observed.

3.1.2. Crystal structure of $[CdL^2](ClO_4)_2$

The molecular structure of the cation belonging to $[CdL^2]^{2+}$ complex, together with selected bond lengths and angles relating to the coordination environment of the metal is present Fig. 2. The metal ion present a N6 coordination environment inside the



L^0 L^1 L^2

Scheme 1.

Table 2
Crystal data and structure refinement for $[CdL^1(CH_3CN)](ClO_4)_2\cdot CH_3CN$ and $[CdL^2](ClO_4)_2$.

	$[CdL^1(CH_3CN)](ClO_4)_2\cdot CH_3CN$	$[CdL^2](ClO_4)_2$
Empirical formula	$C_{33}H_{44}N_6O_{11}Cl_2Cd$	$C_{22}H_{34}N_6O_8Cl_2Cd$
Formula weight	884.04	693.85
T (K)	298(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
Unit cell dimensions		
a (Å)	11.0786(18)	8.7909(19)
b (Å)	12.600(2)	18.282(4)
c (Å)	14.498(2)	17.348(4)
α (°)	100.148(3)	
β (°)	98.381(3)	102.133(4)
γ (°)	97.437(3)	
V (Å^3)	1945.7(5)	2725.8(10)
Z	2	4
D_{calc} (Mg m^{-3})	1.509	1.691
Absorption coefficient (mm^{-1})	0.762	1.055
$F(000)$	908	1416
Crystal size (mm^3)	$0.40 \times 0.09 \times 0.09$	$0.55 \times 0.40 \times 0.33$
θ (°)	1.66–26.43	1.64–27.15
Index ranges	$-13 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 18$	$-11 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 23$, $0 \leqslant l \leqslant 22$
Reflections collected	22111	32850
Independent reflections (R_{int})	7940 (0.0372)	6000 (0.0292)
Completeness to θ	99.3% (26.43°)	99.2% (27.15°)
Absorption correction	empirical	empirical
Maximum and minimum transmission	0.9345 and 0.7502	0.7222 and 0.5946
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	7940/0/480	6000/0/386
Goodness-of-fit (GOF) on F^2	1.059	1.057
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0456$, $wR_2 = 0.1060$	$R_1 = 0.0309$, $wR_2 = 0.0848$
R indices (all data)	$R_1 = 0.0790$, $wR_2 = 0.1272$	$R_1 = 0.0376$, $wR_2 = 0.0886$
Largest difference peak and hole (e Å^{-3})	0.834 and −0.520	0.886 and −5.62

macrocyclic hole by the five nitrogen donor atoms from the macrocyclic backbone and the nitrogen amino-group from the pendant-arm. The geometry around the metal ion can be described as distorted trigonal prism. The triangular faces of the trigonal prism are defined by N(1)N(2)N(5) and N(3)N(4)N(6) with a dihedral angle between the faces of 5.41°, and the Cd^{2+} ion slightly displaced towards N(1)N(2)N(5) face.

The longest Cd–N bond distance do not corresponds to the tertiary amine [Cd(1)–N(1) 2.426(2) Å], but for one of the secondary amines [Cd(1)–N(3) 2.447(2) Å]. The other Cd–N amines are similar [range 2.336(2)–2.396(2) Å].

In this case, the ligand is folded with a dihedral angle between the planes containing the aromatic rings of 82.17°, as the ligand must accommodate all the nitrogen atoms near the metal center.

Again, the perchlorate anions remain without coordination to the metal, but numerous hydrogen bond interactions between them and the amino-groups of the ligand are present in the crystal structure.

3.2. Spectroscopic studies

Microanalytical data of the complexes were in accord in all cases with the presence of mononuclear species of the type $[CdL^n]X_2$. xH_2O. yCH_3CN ($X = NO_3^-$ or ClO_4^-).

FAB mass spectra confirm the mononuclear nature of the complexes. All complexes show the peaks attributable to different fragmentation species, including $[CdL(X)]^+$ or $[CdL]^{2+}$.

The secondary amine stretches ν(N–H) that appear at 3434 and 3269 cm^{-1} in the IR spectrum of the free ligands, $L^1$and L^2, respectively, undergo a shift toward high frequencies in the IR spectra of the complexes, suggesting the coordination to the metal ion. In the spectra of the nitrate complexes the band at 1380 cm^{-1} associated with the presence of ionic nitrate [33],is accompanied by several bands in the region associated with nitrate vibrations and these clearly identify the coordinated nitrate groups [34]. The perchlorate complexes feature absorptions attributable to ionic perchlorate at 1100 and 626 cm^{-1} [35]. The lack of splitting of this band indicates that these groups are not coordinated to the metal centres [33,35b].

Molar conductivity data measured at room temperature using acetonitrile as solvent showed the presence of ionic counterions since they are in the range reported in that solvent for 1:1 electrolytes in the case of nitrate complexes, and 2:1 for the perclorates[36]. Those values are indicative of the different coordinative capacity between nitrate and perchlorates anion and are in agreeing with the results obtained from the IR and X-ray studies.

The ^{1}H NMR spectra of Cd(II) complexes with L^2 were recorded immediately after dissolution in CD_3CN at different temperatures (between 238 and 338 K).

The spectra are similar, and at room temperature the aliphatic signals show a poor resolution and are broadened, suggesting the presence of different conformers in solution, probably due to the rapid coordination/decoordination of the amine pendant group in the NMR time scale. When the temperature is decreased from 298 to 238 K, even better resolution of the aliphatic region of the spectrum is observed, a higher number of signals are present due the presence of the conformers, resulting a more complicated spectra.

If the temperature is raised from 298 to 338 K a better resolution of the aliphatic region of the spectrum is observed, due probably to the increase in the interchange rate between the different

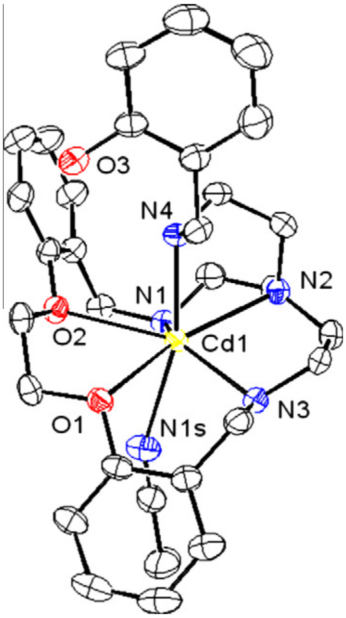


Fig. 1. Crystal structure of $[CdL^1(CH_3CN)]^{2+}$ ion; Selected bond lengths (Å) and angles (°): Cd(1)–N(3) 2.312(4), Cd(1)–N(1) 2.329(4), Cd(1)–N(4) 2.393(3), Cd(1)–N(2) 2.426(4), Cd(1)–N(1S) 2.496(5), Cd(1)–O(2) 2.547(3), Cd(1)–O(1) 2.652(3), N(3)–Cd(1)–N(1) 131.57(14), N(3)–Cd(1)–N(4) 101.76(13), N(1)–Cd(1)–N(4) 109.25(13), N(3)–Cd(1)–N(2) 76.80(14), N(1)–Cd(1)–N(2) 75.23(14), N(4)–Cd(1)–N(2) 76.88(13), N(3)–Cd(1)–N(1S) 84.35(15), N(1)–Cd(1)–N(1S) 77.10(14), N(4)–Cd(1)–N(1S) 162.52(15), N(2)–Cd(1)–N(1S) 120.59(15), N(3)–Cd(1)–O(2) 144.36(12), N(1)–Cd(1)–O(2) 78.99(12), N(4)–Cd(1)–O(2) 79.06(11), N(2)–Cd(1)–O(2) 136.18(12), N(1S)–Cd(1)–O(2) 86.46(14).

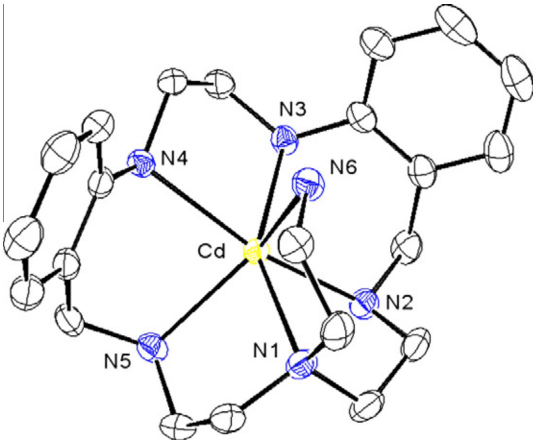


Fig. 2. Crystal structure of $[CdL^2]^{2+}$; Selected bond lengths (Å) and angles (°): Cd–N(2) 2.336(2), Cd–N(6) 2.365(2), Cd–N(5) 2.365(2), Cd–N(4) 2.396(2), Cd–N(1) 2.426(2), Cd–N(3) 2.447(2), N(2)–Cd–N(6) 107.41(10), N(2)–Cd–N(5) 106.34(9), N(6)–Cd–N(5) 127.59(9), N(2)–Cd–N(4) 151.98(8), N(6)–Cd–N(4) 87.66(9), N(5)–Cd–N(4) 80.58(8), N(2)–Cd–N(1) 77.01(8), N(6)–Cd–N(1) 73.91(9), N(5)–Cd–N(1) 76.09(8), N(4)–Cd–N(1) 130.66(8), N(2)–Cd–N(3) 82.09(8), N(6)–Cd–N(3) 93.92(8), N(5)–Cd–N(3) 129.60(8), N(4)–Cd–N(3) 73.23(8), N(1)–Cd–N(3) 151.10(8).

Table 3
^1H and ^{13}C NMR spectra assignment for $[CdL^2](ClO_4)_2$ in CD_3CN at 338 K.

^1H		^{13}C	
Assignment	δ (ppm)	Assignment	δ (ppm)
H_1	3.5 (m, 2H)	C_1	43
H'_1	3.7 (m, 2H)	C_2	145
H_3, H_4, H_5, H_6	7.5–7.2 (d, t, 8H)	C_3, C_4, C_5, C_6	134–116
H_8	4.5 (sb, 2H)	C_7	127
H'_8	3.8 (db, 2H)	C_8	53
H_9	2.9 (m, 2H)	C_9	48
H'_9, H_{10}	2.6 (m, 6H)	C_{10}	56
H_{11}	2.3 (sb, 2H)	C_{11}	56
H_{12}	1.8 (sb, 2H)	C_{12}	40

conformers. For sample, the ^1H NMR spectrum at 338 K for complex $[CdL^2](ClO_4)_2$ (Table 3) shows the aromatic protons at downfield as two triplets and two doublets. Between δ 4.5 and 3.6 ppm two signals are assigned to the geminal H_8 and H'_8 protons. The signals of H_1 and H'_1 protons of the ethylene bridge between the aromatic rings, H_1 and H'_1, are observed at δ 3.55 ppm as two broad multiplets. The H_9 and H'_9 as consequence of the coordination are not equivalent and are showing at δ 2.6 and 2.9 ppm together with H_{10}. Finally, at highfield appear the signals of H_{11} and H_{12} at δ 2.35 and 1.85 ppm, respectively. The signals of the primary and secondary amines are also observed as broad signals at different chemical displacements in the spectrum.

For complexes with L^1 in CD_3CN the ^1H NMR spectra presented broad signals showing probably a rapid conformational interconversion in solution, again due to the coordination/decoordination of the pendant group. However, the different temperatures NMR study was not useful in the assignment of the spectra. They showed that, in general, all the proton resonances are shifted downfield when compared with the free ligand due to the complexation.

Titrations by ^1H NMR of L^2 with Cd(II) nitrate and perchlorate salts were carried out in CD_3CN at room temperature. In both cases the signals of the ligand shift slightly at downfield due to the coordination to the metal ion. Also, those signals are broad and decrease in intensity as more salt is added, due to a slow ligand/complex interchange in the NMR time scale. This phenomenon is well appreciated in the aromatic region, but the aliphatic signals are poorly resolved, probably due the presence of different conformers in solution at room temperature. From this titration we can conclude the existence only the 1:1 metal/ligand of the species, because once 1:1 relation is reached, not changes are observed in the spectra when the metal salt concentration is increased. However, the formation constant of those complexes could not be determined.

4. Conclusion

Two new pendant-arms macrocyclic ligands (L^1 and L^2) derived from a dioxotriaza 17-membered and pentaaza 17-membered precursors, respectively, have been synthesized and characterized. The coordination behaviour of those ligands with nitrate and perchlorate cadmium(II) salts was studied. The synthesis of the complexes was carried out in acetonitrile in a 1:1 cadmium:ligand molar ratio. Mononuclear species were obtained in all cases. The crystal structure of $[CdL^1(CH_3CN)](ClO_4)_2 \cdot CH_3CN$ and $[CdL^2](ClO_4)_2$ were determinated by X-ray diffraction. In both cases the Cd ion is endomacrocyclicly coordinated by all the donor atoms of the macrocyclic backbone and the pendant-arm group. In the first case the heptacoordination environment around the metal is completed by an acetonitrile molecule and the geometry can be described as distorted pentagonal bipyramid. The coordination geometry around cadmium in $[CdL^2](ClO_4)_2$ complex can be better described as distorted trigonal prism.

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Appendix A. Supplementary material

CCDC 912578 and 912579 contain the supplementary crystallographic data for [CdL^1(CH$_3$CN)](ClO$_4$)$_2$·CH$_3$CN and [CdL^2](ClO$_4$)$_2$, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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