# Palladium(II) Complexation by *p*-Cyclophane Receptors. A Solution and Solid State Study

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The coordination properties of the macrocyclic ligands 1,4,7,16,19,22-hexamethyl-1,4,7,16,19,22-hexaaza[9.9]-*p*-cyclophane (**L1**) and 1,4,7-trimethyl-19,22,28,31-tetraoxa-1,4,7,14,23-pentaaza[9.25]-*p*-cyclophane (**L2**) have been studied by means of potentiometric and $^1$H and $^{13}$C measurements in aqueous solution. **L1** is composed of two equal triamine binding units connected by *p*-phenylene spacers. **L2** presents a similar molecular architecture, a triamine moiety of **L1** being replaced by a cyclic $N_2O_4$ binding unit. **L1** can form both mono- and dinuclear complexes in aqueous solution, while **L2** gives only mononuclear species. The potentiometric data indicate that in the **L1** dinuclear complex each metal is coordinated by a triamine moiety. In the **L2** mononuclear complex the Pd(II) ion is coordinated by the $N_3$ unit. The $N_2O_4$ moiety does not show any binding ability toward Pd(II), but exhibits a high tendency to protonate. These solution data are confirmed by the crystal structures of $[Pd_2Cl_2\textbf{L1}](ClO_4)_2 \cdot H_2O$ (a) and $[PdCl\textbf{L2}H_2(H_2O)](ClO_4)_3$ (b). In complex a, each Pd(II) ion is four coordinated by the three amine groups of the triaza moiety and a chloride anion, in a square planar geometry. In the mononuclear complex b, the metal is coordinated by the $N_3$ moiety, with a coordination environment almost equal to that found in complex a. The $N_2O_4$ moiety is diprotonated and encapsulates in its cavity a water molecule, held by a hydrogen-bond network. The solution structures of the **L1** and **L2** complexes have been studied by means of $^1$H and $^{13}$C NMR measurements. The analysis of the NMR data reveals that the dinuclear **L1** complex and the **L2** mononuclear one show structural features in solution almost equal to those found in the solid state. Solution and solid state data indicate that the Pd(II) complexation gives a marked stiffening of the macrocyclic structures.

## Introduction

Macrocycles containing two binding polyamine subunits linked by two chains are known to form dinuclear complexes and can be used to force two metal ions at almost fixed distances. Structural factors, such as ligand flexibility and disposition of the donors, have been shown to play significant roles in determining the strength of the interaction between the polyaza receptor and the metal cations.[1−6] Aromatic moieties can act as rigid spacers between two binding subunits and, therefore, are often introduced as integral parts of macrocyclic frameworks.

Cyclic ligands containing aromatic rings in their framework, cyclophanes, have received much attention for the recognition of lipophilic species.[7−11] More recently, polyazacyclophanes also have been synthesized and employed in metal ion complexation studies.[2−6,13,14] The presence of rigid aromatic moieties gives particular ligational properties to the ligands defining preorganized binding lodgings for the metal ions within the ligand itself.

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Recently, we reported the synthesis and binding properties toward Cu(II) of ligands **L1** and **L2**.[4b,e] **L1** is composed of two
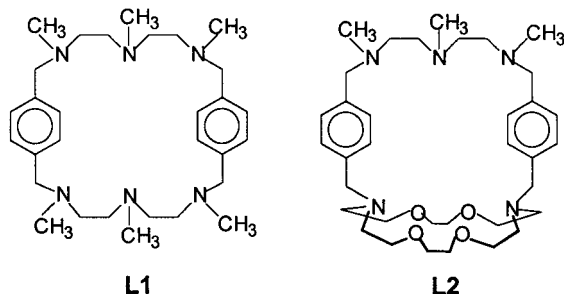
triamine chains connected by *p*-phenylene spacers and behaves as a ditopic receptor for Cu(II) in aqueous solution. It can form a binuclear $[Cu_2L1]^{4+}$ complex, in which each metal is coordinated by a triamine moiety.[4b] In the case of **L2**, only the triamine unit can bind Cu(II), and only mononuclear complexes are formed in aqueous solution.[4e] The presence in both macrocycles of *p*-xylene spacers, the short ethylenic chains connecting the amine groups, and nitrogen methylation lead to a stiffening of the macrocycles, which strongly affects the coordination geometry and the thermodynamic stability of the complexes.

Aiming to shed further light on the role played by steric requirements of metals and flexibility of ligands in determining the structural features in *p*-cyclophane complexes, we have now analyzed the coordination behavior of **L1** and **L2** toward Pd(II) coordination. Compared to Cu(II), Pd(II) has a higher tendency to impose its own geometry on ligands. Therefore, the formation of complexes with rigid structure is expected.

## Experimental Section

**Synthesis.** Ligands **L1**[4b] and **L2**[4e] were prepared as previously described.

**(a) [Pd₂Cl₂L1](ClO₄)₂·H₂O.** A solution of K₂PdCl₄ (5.9 mg, 0.02 mmol) in water (5 cm³) was slowly added to an aqueous solution (5 cm³) containing **L1**·6HCl·1.5H₂O (7.4 mg, 0.01 mmol). The pH was adjusted to 7 with 0.01 M NaOH. The solution was kept at room temperature for 3 h, and then NaClO₄·H₂O (29 mg, 0.2 mmol) was added. Pale yellow crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature of this solution. Yield: 8 mg (80%). Anal. Calcd for C₃₀H₅₂Cl₄N₆O₉Pd₂: C, 36.27; H, 5.07; N, 8.46. Found: C, 36.3; H, 5.1; N, 8.5. *CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive; these compounds must be handled with great caution!*

**(b) [PdClL2H₂(H₂O)](ClO₄)₃.** A solution of K₂PdCl₄ (2.9 mg, 0.01 mmol) in water (5 cm³) was slowly added to an aqueous solution (15 cm³) containing **L2**·5HClO₄ (11.5 mg, 0.01 mmol). The pH was adjusted to 4 with 0.01 M NaOH. Pale yellow crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature of this solution. Yield: 9 mg (84%). Anal. Calcd for C₃₅H₆₁Cl₄N₅O₁₇Pd: C, 39.21; H, 5.73; N, 6.53. Found: C, 39.3; H, 5.7; N, 6.5.

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**Table 1.** Crystal Data and Structure Refinement for [Pd₂Cl₂**L1**](ClO₄)₂·H₂O (**1**) and [PdCl**L2**H₂(H₂O)](ClO₄)₃ (**2**)

| | 1 | 2 |
|---|---|---|
| empirical formula | C₃₀H₅₀Cl₄N₆O₉Pd₂ | C₃₅H₆₁Cl₄N₅O₁₇Pd |
| fw | 993.36 | 1072.09 |
| radiation | Mo Kα, graphite monochromated | |
| temp, K | 293(2) | 293(2) |
| wavelength, Å | 0.710 69 | 0.710 69 |
| space group | $P\bar{1}$ | $Pca2_1$ |
| $a$, Å | 10.4690(11) | 23.739(5) |
| $b$, Å | 13.307(2) | 13.370(5) |
| $c$, Å | 15.152(2) | 14.903(5) |
| $\alpha$, deg | 74.980(10) | 90.000(5) |
| $\beta$, deg | 78.190(9) | 90.000(5) |
| $\gamma$, deg | 83.480(12) | 90.000(5) |
| $V$, Å³ | 1991.5(4) | 4730(3) |
| $Z$ | 2 | 4 |
| $D_c$, g/cm³ | 1.657 | 1.505 |
| $\mu$, mm⁻¹ | 1.227 | 0.690 |
| $F(000)$ | 1008 | 2224 |
| cryst size, mm | 0.3 × 0.3 × 0.4 | 0.5 × 0.5 × 0.5 |
| R1[a] [$I > 2(I)$] | 0.0790 | 0.0641 |
| wR2[b] | 0.1910 | 0.1510 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w[(F_o^2 - F_c^2)2]/\sum[(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (0.00661P)^2 + 29.22P]$; $P = [(max(F_o^2) + 2(F_c^2)]$).

**X-ray Structure Analysis.** Analyses on single crystals of [Pd₂Cl₂**L1**]-(ClO₄)₂·H₂O and [PdCl**L2**H₂(H₂O)](ClO₄)₃ were carried out with an Enraf-Nonius CAD4 X-ray diffractometer that uses equatorial geometry. A summary of the crystal data is reported in Table 1.

Prismatic pale yellow crystals of [Pd₂Cl₂**L1**](ClO₄)₂·H₂O (approximate size 0.3 × 0.3 × 0.4 mm) and [PdCl**L2**H₂(H₂O)](ClO₄)₃ (approximate size 0.5 × 0.5 × 0.5 mm) were mounted on the diffractometer and used for data collections at room temperature with graphite-monochromated Mo Kα radiation. Cell parameters for both compounds were determined by least-squares refinement from the angular settings of 25 carefully centered reflections ($14° < 2\theta < 24°$). The intensities of two standard reflections per compound were monitored periodically during data collection, and no loss of intensity was observed.

A total of 5193 ($2\theta = 50°$) and 4307 ($2\theta = 50°$) reflections for [Pd₂Cl₂**L1**](ClO₄)₂·H₂O and [PdCl**L2**H₂(H₂O)](ClO₄)₃, respectively, were collected. Intensity data for both collections were corrected for Lorentz and polarization effects; absorption corrections were applied, and the data were reduced to $F_o^2$. The structure was solved by Patterson methods, SHELXS-86.[15] Isotropic least-squares refinement was performed by means of SHELXL93[16] running on a Pentium 200 computer. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of non-hydrogen atoms were refined with full matrix against $F^2$, according to the least-squares process. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[17] Molecular plots were produced by the program ORTEP.[18]

**(a) [Pd₂Cl₂L1](ClO₄)₂·H₂O.** The compound crystallizes in the triclinic family, space group $P\bar{1}$ ($Z = 2$). Anisotropic thermal parameters have been used for the palladium, chloride and nitrogen atoms, and the carbon atoms have been refined isotropically. Some hydrogen atoms were located during the refinement, the rest were fixed in ideal positions, and finally all of them were isotropically refined using the riding model. The disordered oxygen atoms of the perchlorate groups were optimized and refined with a common isotropic temperature factor; 3678 unique reflections were used to refine, and the final agreement factors for 289

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refined parameters were R1 = 0.0790, wR2 = 0.1910 (for the 3077 observed reflections with $F_o > 4\sigma(F_o)$), and R1 = 0.0976, wR2 = 0.2403 (for all data). R1 = $\sum||F_o| - |F_c|/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/w(F_o^2)^2]$. Residual electron density: (largest maxima and minima) 0.916 and −1.027 e·Å$^{-3}$.

**(b) [PdClL2H$_2$(H$_2$O)](ClO$_4$)$_3$.** Crystals of the compound belong to the orthorhombic space group $Pca2_1$ ($Z = 4$). Anisotropic thermal parameters have been used for all palladium, chloride, oxygen, and nitrogen atoms. The carbon atoms and perchlorate oxygen atoms were isotropically refined. The hydrogen atoms have been introduced in calculated positions, and their coordinates were refined according to those of the linked carbon atoms; 4257 unique reflections were used to refine, and the final agreement factors for 319 refined parameters were R1 = 0.0641, wR2 = 0.1510 (for the 1881 observed reflections with $F_o > 4\sigma(F_o)$), and R1 = 0.2360, wR2 = 0.2262 (for all data). R1 = $\sum||F_o| - |F_c|/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/w(F_o^2)^2]$. Residual electron density (largest maxima and minima): 0.741 and −1.187 e·Å$^{-3}$.

**EMF Measurements.** Equilibrium constants for complexation reactions of Pd(II) with ligands were determined by pH-metric measurements (pH = −log [H$^+$]) in 0.1 mol dm$^{-3}$ NMe$_4$Cl at 298.1 ± 0.1 K, by using potentiometric equipment that has been already described.[19] The combined glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO$_2$-free NMe$_4$OH solutions and determining the equivalent point by Gran's method,[20] which allows determination of the standard potential E°, and the ionic product of water (p$K_w$ = 13.83(1) at 298.1 K in 0.1 mol dm$^{-3}$ NMe$_4$Cl). 1 × 10$^{-3}$ to 2 × 10$^{-3}$ mol dm$^{-3}$ ligand and metal ion concentrations were employed in the potentiometric measurements, three titration experiments (about 100 data points each) being performed in the pH range 2−8.5. Ligand protonation constants were taken from refs 4b and 4f. NMe$_4$OH (0.1 mol dm$^{-3}$) was used as titrating base. Due to some slowness encountered in the complexation reactions, potentiometric titrations were performed with waiting times of at least 10 min between successive titrant additions, to ensure the attainment of equilibrium.

The computer program HYPERQUAD[21] was used to calculate the equilibrium constants from emf data. In this program the sum of the weighted square residuals on the observed emf values is minimized. The weights were derived from the estimated errors in emf (0.2 mV) and titrant volume (0.002 cm$^3$). The most probable chemical model was selected by following a strategy based on the statistical inferences applied to the variance of the residuals, $\sigma^2$. The sample standard deviation should be 1, in the absence of systematic errors and when a corrected weighting scheme is used. However, the agreement is considered good for standard deviation values smaller than 3 ($\sigma^2 < 9$). Values of $\sigma^2$ lower than 6 were obtained for all of the refined equilibrium models in the present work.
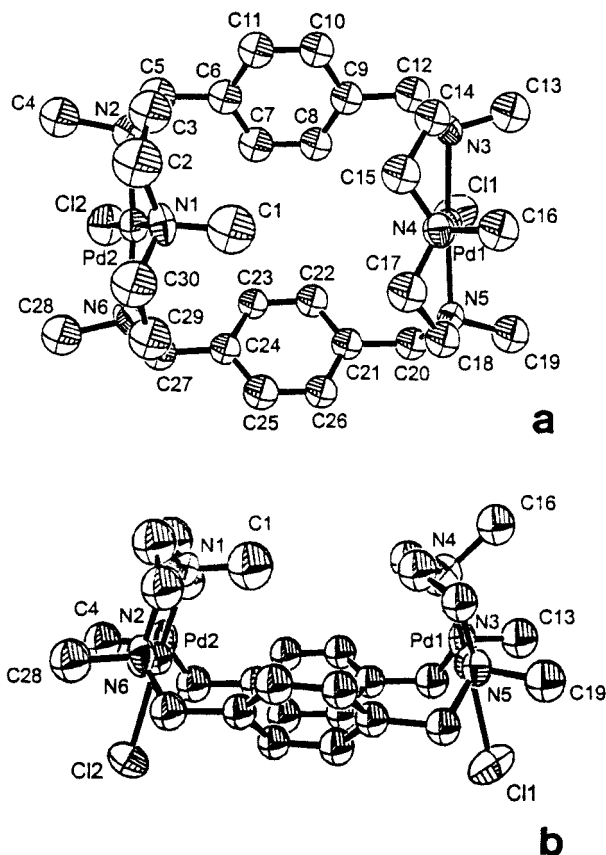
All titrations were treated either as single sets or as separated entities, for each system, without significant variation in the values of the determined constants.

**NMR Spectroscopy.** $^1$H and $^{13}$C NMR spectra were recorded on Varian UNITY300 and UNITY400 spectrometers operating at 299.95 and 399.95 MHz for $^1$H and at 75.43 and 100.58 MHz for $^{13}$C. The spectra were obtained at room temperature in D$_2$O solutions. For the carbon spectra dioxane was used as external reference ($\delta$ = 67.4 ppm), and for the proton spectra the solvent signal was used. The pH was calculated from the measured pD values using the correlation pH = pD − 0.4.[22]

## Results and Discussion.

**Description of the Structure of [Pd$_2$Cl$_2$L1](ClO$_4$)$_2$·H$_2$O.** The crystal structure consists of [Pd$_2$Cl$_2$L1]$^{2+}$ cations, perchlo-

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**Figure 1.** ORTEP drawing of the [Pd$_2$Cl$_2$**L1**]$^{2+}$ cation: (a) top view; (b) side view.

rate anions, and water solvent molecules. Figure 1 shows an ORTEP[18] drawing of [Pd$_2$Cl$_2$**L1**]$^{2+}$, and Table 2 lists selected angles and distances for the metal coordination environment. The complex cation shows a noncrystallographic symmetry plane containing the metal centers, the chloride ions, the N1 and N4 donor atoms, and the C1 and C16 methyl groups.

Each palladium atom is localized in a N$_3$ subunit, 7.08 Å apart from each other, coordinated by three nitrogens and a chloride anion, in a square planar arrangement. In the coordination environment of Pd1, the four donors are almost coplanar and the metal is displaced 0.024(5) Å from the mean plane defined by the donor atoms (maximum deviation 0.048(6) Å for N4). Similarly, Pd2 lies 0.082(5) Å out of the plane defined by the N1, N2, N6, and Cl2 donors, shifted toward the other Pd(II) ion. Both N−Pd−N angles are less than 90° because of the short ethylenic chains.

The coordination planes of the two metals forms a dihedral angle of 32.0(2)°. The macrocycle adopts a boat conformation with the chloride ions located on the same side. The two aromatic rings are rather close to each other, the shortest distance being 3.63(2) Å for C8···C22, and define two planes forming a dihedral angle of 66.0(5)°. The planes defined by the aromatic rings C6−C7−C8−C9−C10−C11 and C21−C22−C23−C24−C25−C26 form respectively dihedral angles of 79.1(4)° and 76.7(4)° with respect to the coordination plane of Pd1, and of 73.5(4)° and 77.2(4)° with respect to the coordination plane of Pd2. As a consequence, the complex gives rise to a nearly parallelepipedic cavity of approximate dimensions 4 × 5 × 7 Å. The N2−C5−C6, N3−C12−C9, N5−C20−C21, and N6−C27−C24 angles show some molecular strain, their angular values being 114(1)°, 116(1)°, 116(1)°, and 115(1)°, respectively.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for $[Pd_2Cl_2\mathbf{L1}](ClO_4)_2 \cdot H_2O$

| | | | | | |
|---|---|---|---|---|---|
| Pd(1)−N(4) | 2.001(13) | N(1)−Pd(2)−N(6) | 86.6(5) | N(4)−Pd(1)−N(5) | 85.3(5) |
| Pd(1)−N(5) | 2.089(11) | N(1)−Pd(2)−N(2) | 84.2(5) | N(4)−Pd(1)−N(3) | 84.6(5) |
| Pd(1)−N(3) | 2.099(11) | N(6)−Pd(2)−N(2) | 165.9(5) | N(5)−Pd(1)−N(3) | 169.2(5) |
| Pd(1)−Cl(1) | 2.301(5) | N(1)−Pd(2)−Cl(2) | 178.5(4) | N(4)−Pd(1)−Cl(1) | 178.7(3) |
| Pd(2)−N(1) | 2.005(12) | N(6)−Pd(2)−Cl(2) | 94.2(4) | N(5)−Pd(1)−Cl(1) | 95.6(4) |
| Pd(2)−N(6) | 2.072(12) | N(2)−Pd(2)−Cl(2) | 95.3(4) | N(3)−Pd(1)−Cl(1) | 94.5(4) |
| Pd(2)−N(2) | 2.082(11) | | | | |
| Pd(2)−Cl(2) | 2.295(4) | | | | |

It is worth noting that the macrocycle **L1** presents a high rigidity in its binuclear Pd(II) complex. Closest comparisons can be found in the binuclear Cu(II) complex with the same ligand, $[Cu_2Cl_2\mathbf{L1}]^{2+}$.[4b] In this complex each Cu(II) ion is coordinated by a $N_3$ unit and a chloride anion, and the overall conformation of the molecule is similar to that found in the present Pd(II) complex. In both $[Cu_2Cl_2\mathbf{L1}]^{2+}$ and $[Pd_2Cl_2\mathbf{L1}]^{2+}$ compounds the ligand is boat-shaped. In $[Cu_2Cl_2\mathbf{L1}]^{2+}$ both of the $N_3$ binding subunits assume almost equal conformations, with the methyl groups bound to the benzylic nitrogens pointing outside the cavity and the central ones pointing inside. The C−C−N−C and N−C−C−N torsional angles of both aliphatic chains show a gauche−trans alternate sequence ($g-t-g-t-t-g-t-g$). In the present complex, only the N2−N1−N6 moiety shows a similar conformation, with an equal $g-t$ alternate sequence. On the contrary, the N3−N4−N5 chain displays a different sequence of the torsional angles ($g-g-g-t-t-g-g-g$); in other words, the C12−N3−C14−C15 and C20−N5−C18−C17 torsional angles show a $g$ conformation, while the corresponding C5−N2−C3−C2 and C27−N6−C29−C30 exhibit a $t$ conformation. As a consequence of the different conformations of the two $N_3$ moieties, the methyl group C1 points inside the macrocyclic cavity, while the C16 one points outside. Finally, it is to be noted that the N1−C2−C3−N2 and N6−C29−C30−N1 torsional angles in the N1−N3 unit, as well as the N3−C14−C15−N4 and N4−C17−C18−N5 ones in the N3−N5 moiety, adopt an equal $g$ conformation.

**Description of the Structure of $[PdCl\mathbf{L2}H_2(H_2O)](ClO_4)_3$.** The crystal structure consists of $[PdCl\mathbf{L2}H_2(H_2O)]^{3+}$ cations and perchlorate anions. Figure 2 shows an ORTEP[18] drawing of the complex cation, and Table 3 lists selected angles and distances for the coordination environment.

The Pd atom is located in the $N_3$ subunit, coordinated by the three methylated nitrogen atoms and a chloride ion, in a square planar arrangement. Considering the mean plane determined by the four donors (maximum deviation 0.184(1) Å for N1), the metal is shifted 0.098 Å toward the cavity described by the benzyl units and the $N_2O_4$ moiety. It is of interest that the $N_3$ binding subunit shows a conformation very similar to that found for the N2−N1−N6 moiety in the $[Pd_2\mathbf{L1}Cl_2]^{2+}$ cation. In fact, the aliphatic chain shows a $g-t$ alternate sequence of torsional angles and the methyl group C1 points inside the macrocyclic cavity.

The aromatic rings linking the $N_3$ and the $N_2O_4$ subunits form a dihedral angle of 42.6(7)°.

As far as the protonated $N_2O_4$ moiety is concerned, the least-squares plane defined by the $N_2O_4$ heteroatoms (maximum deviation 0.89(1) Å for N3) forms a dihedral angle of 45.9(4)° with the corresponding mean planes defined by the donor atoms in the coordination environment of the metal ion. It is to be noted that both nitrogens of this subunit are protonated. This diprotonated moiety binds through hydrogen bonds with a water molecule, which is shifted by 1.02(2) Å from the mean plane defined by the $N_2O_4$ heteroatoms toward the Pd atom. The O5 oxygen of the water molecule forms two strong hydrogen bonds



**a**



**b**
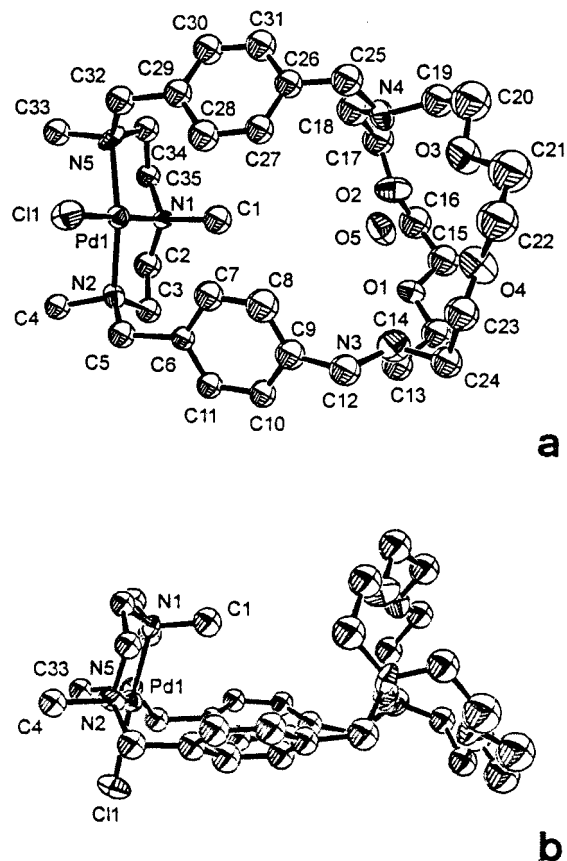
**Figure 2.** ORTEP drawing of the $[PdCl\mathbf{L2}H_2(H_2O)]^{3+}$ cation: (a) top view; (b) side view.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for $[PdCl\mathbf{L2}H_2(H_2O)](ClO_4)_3$

| | | | |
|---|---|---|---|
| Pd(1)−N(1) | 2.017(13) | N(1)−Pd(1)−N(2) | 86.4(5) |
| Pd(1)−N(2) | 2.046(13) | N(1)−Pd(1)−N(5) | 86.3(6) |
| Pd(1)−N(5) | 2.082(14) | N(2)−Pd(1)−N(5) | 163.4(6) |
| Pd(1)−Cl(1) | 2.316(5) | N(1)−Pd(1)−Cl(1) | 176.4(4) |
| | | N(2)−Pd(1)−Cl(1) | 93.2(4) |
| | | N(5)−Pd(1)−Cl(1) | 95.0(4) |

with N3 and N4 (O5···N3 2.93(3) Å and O5···N4 2.96(2) Å). The water molecule shows also short contacts with the oxygens of the $N_2O_4$ moiety (O5···O1 2.85(2) Å, O5···O2 2.94(2) Å, O5···O3 2.83(2) Å, and O5···O4 2.98(2) Å). Examples of water molecules encapsulated in macrocyclic structures and held by hydrogen-bond networks have been recently reported.[23,24] Closest comparison can be found in the water clathrates formed by the oxa−aza macrobicyclic ligands, which contain the same $N_2O_4$ moiety. Similarly to the present complex, in both cases a water molecule is encapsulated in the macrobicyclic cavity, interacting via hydrogen bonds with the $N_2O_4$ unit.[24]

**Pd(II) Complex Formation in Aqueous Solution.** As encountered in other investigations of Pd(II) complexes,[25] it is difficult to determine the stability constants of the complexes with this metal ion with polyamines because the aqua ion undergoes hydrolysis even at pH = 1, and its complexes are

**Table 4.** Logarithms of the Equilibrium Constants Determined in 0.1 mol dm$^{-3}$ NMe$_4$Cl at 298.1 K for the Complexation Reactions of Pd$^{2+}$ with **L1** and **L2**

| | log $K$ | |
|---|---|---|
| reaction | **L1** | **L2** |
| Pd$^{2+}$ + L + Cl$^-$ = PdClL$^+$ | | 23.7(1)$^a$ |
| Pd$^{2+}$ + L + Cl$^-$ + H$^+$ = PdClLH$^{2+}$ | | 31.1(1) |
| Pd$^{2+}$ + L + Cl$^-$ + 2H$^+$ = PdClLH$_2$$^{3+}$ | 37.44(8) | 36.7(1) |
| PdClL$^+$ + H$^+$ = PdClLH$^{2+}$ | | 7.4 |
| PdClLH$^{2+}$ + H$^+$ = PdClLH$_2$$^{3+}$ | | 5.6 |
| 2Pd$^{2+}$ + L + 2Cl$^-$ = Pd$_2$Cl$_2$L$^{2+}$ | 42.9(1) | |
| 2Pd$^{2+}$ + L + 3Cl$^-$ + H$^+$ = Pd$_2$Cl$_3$LH$^{2+}$ | 47.3(1) | |

$^a$ Values in parentheses are standard deviations on the last significant figure.

too stable to be investigated using the customary pH method. As a consequence, thermodynamic data for the binding of Pd(II) in aqueous solution by amine ligands are rare.[25−27] Fortunately, in 0.1 mol dm$^{-3}$ NMe$_4$Cl solution at acidic pH's, PdCl$_4$$^{2-}$ is in equilibrium with the Pd(II) complexes with polyamines.[28] Using Cl$^-$ as competing ligand, exchange equilibria can be followed by both spectrophotometry and pH-metric titrations. Speciation of the complexes formed by the ligands was performed in 0.1 mol dm$^{-3}$ NMe$_4$Cl aqueous solution by computer analysis of the potentiometric data using the HYPERQUAD[21] program. The calculated equilibrium constants are listed in Table 4.

As far as the macrocyclic ligand **L1** is considered, it is to be noted that its ligational properties are strictly related to its ditopic nature, i.e., to the presence of two separated binding subunits. In fact **L1** presents a marked tendency to form both mononuclear and binuclear Pd(II) complexed species (Table 4). It is to be noted that the unprotonated [Pd**L1**]$^{2+}$ complex is not formed in aqueous solution, while a [PdCl**L1**H$_2$]$^{3+}$ complex is formed in large amounts in aqueous solutions containing Pd(II) and **L1** in a 1:1 molar ratio. This behavior suggests that the [Pd**L1**]$^{2+}$ presents a marked tendency to bear protonation and indicates that proton binding occurs on an uncoordinated N$_3$ binding moiety. The metal is coordinated by the other N$_3$ subunit and completes its coordination environment with a chloride anion.

Both mononuclear and binuclear complexed species abound in solutions containing the ligand and the metal ion in equimolecular quantities (Figure S1a, Supporting Information) over all of the pH range. On the other hand, for 2:1 Pd(II):**L1** molar ratios the formation of mononuclear complexes is depressed; the mononuclear species [PdCl**L1**H$_2$]$^{3+}$ is formed only in acidic media (Figure S1b, Supporting Information), while the binuclear [Pd$_2$**L1**Cl$_2$]$^{2+}$ complex is the principal species above pH 4, being unique for pH > 5.

These observations agree with the involvement of two identical moieties of the ligand in the coordination to both first and second Pd$^{2+}$ ions, as observed in the molecular structure of the [Pd$_2$Cl$_2$**L1**]$^{2+}$ complex (Figure 1). In other words, the presence of the rigid spacers in **L1** between the two triamine chains prevents the metal ion from binding to both N$_3$ sets of **L1** donors. Finally, the binuclear [Pd$_2$Cl$_2$**L1**]$^{2+}$ complex can bind a proton at acidic pH's giving a [Pd$_2$Cl$_3$**L1**H]$^{2+}$ protonated complex. Protonation of [Pd$_2$Cl$_2$**L1**]$^{2+}$ implies detachment of a coordinated nitrogen atom, which is replaced by a chloride anion in the coordination environment of a Pd(II) ion.

As far as **L2** is concerned, only mononuclear Pd(II) complexes are observed in aqueous solution. **L2** presents an N$_3$ and a cyclic N$_2$O$_4$ binding subunit. The features of the Pd(II) complexes are strongly influenced by their ditopic structures. As can be noted from Table 4, besides a [PdCl**L2**]$^+$ complex, the metal ion forms a stable complex with mono- and diprotonated species of **L2**. The equilibrium constants for the successive addition of H$^+$ to the [PdCl**L2**]$^{2+}$ complex are significantly high, revealing that protonation occurs on a ligand moiety not involved in the coordination to the metal ion. In other words, the Pd(II) ion and the protons occupy two almost independent binding sites. Thus, protonation of the [PdCl**L2**]$^+$ complex strongly competes with the formation of binuclear species in acidic or neutral solutions. On the other hand, also in alkaline media **L2** does not form binuclear complexes. As a matter of fact, separation of Pd(II) hydroxide is observed from slightly alkaline solutions containing Pd(II) and **L2** in molar ratio greater than 1:1.

The stability constant of the [PdCl**L2**]$^+$ complex (log $K$ = 23.7) is very similar to that previously found for the mononuclear Pd(II) complex with the ligand 2,5,8-trimethyl-2,5,8-triazanonane (log $K$ = 24.9),[26] where the metal ion is coordinated by three methylated nitrogens and one chloride ion. This observation indicates that the metal ion is bound by the triaza subunit of the ligand, while the N$_2$O$_4$ moiety is not involved in metal coordination and can bind up to two protons at slightly acidic pH.
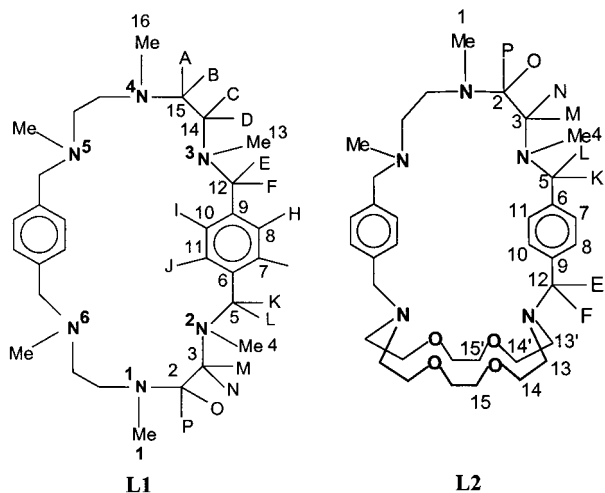
These conclusions about metal and proton binding by **L2** in aqueous solution are confirmed by the crystal structure of the [PdCl**L2**H$_2$]$^{3+}$ cation, which shows the metal coordinated by the triaza moiety, while the acidic protons are located on the N$_2$O$_4$ subunit. Furthermore, the electronic spectrum of the [PdCl**L2**]$^+$ complex in aqueous solution (pH 7) shows a charge-transfer band at 350 nm ($\epsilon$ =750 mol$^{-1}$ dm$^3$ cm$^{-1}$), which can be attributed to the presence of a N$_3$PdCl chromophore.[25c]

These data indicate that the N$_2$O$_4$ moiety does not have any binding ability toward Pd(II) in aqueous solutions. On the other hand, it is well-known that receptors containing the [2.2]kriptofix unit can bind small molecules or ions, such as ammonium cations, through the formation of hydrogen bonds.[1a,e,11] In the present case, the crystal structure of the [PdCl**L2**H$_2$(H$_2$O)]$^{2+}$ cation shows that a water molecule is encapsulated inside the N$_2$O$_4$ moiety of **L2**, held by a hydrogen-bond network.

**NMR Studies.** The $^{13}$C NMR spectrum of the free amine **L1** in aqueous solution shows six resonances, appearing at 43.7 ppm (attributed to the four methyl groups linked to the benzylic

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**Chart 1**





**Figure 3.** Aliphatic regions of the ${}^1$H and ${}^{13}$C NMR spectra of ligand **L1** (a) and of [Pd$_2$Cl$_2$**L1**]$^{2+}$ (b) and ${}^1$H$-{}^1$H homonuclear and ${}^1$H$-{}^{13}$C heteronuclear correlation for the [Pd$_2$Cl$_2$**L1**]$^{2+}$ complex (D$_2$O solution, pH 6).

nitrogens), 44.6 ppm (the two methyl groups C1 and C16, Chart 1), 53.4 and 53.7 ppm (the carbons of all of the ethylenic chains), 62.4 ppm (the four benzylic carbons), 131.8 ppm (the eight secondary aromatic carbons), and 138.3 ppm (the four tertiary carbon atoms of the aromatic rings). The ${}^1$H spectrum shows two singlets at 1.97 and 2.04 ppm (relative intensities 2:1, corresponding to the hydrogens of the four equivalent methyl groups C4 and the two equivalent methyl groups C1, respectively), a broad band at 2.23 ppm (for the hydrogen atoms of all of the ethylenic chains), a singlet at 3.12 ppm (the benzylic hydrogens), and a singlet at 7.12 ppm (the protons of the aromatic rings). These spectral features indicate a $D_{2h}$ time-averaged symmetry of the ligand in aqueous solution.

Coordination of Pd(II) to give the dinuclear [Pd$_2$Cl$_2$**L1**]$^{2+}$ complex leads to a dramatic loss of symmetry of the macrocycle. The ${}^{13}$C NMR spectrum of this complex in aqueous solution shows 16 different signals, four of which are attributed to the methyl carbons C1, C4, C13, and C16, two to the benzylic carbons C5 and C12, four to the carbons of the ethylenic chains C2, C3 and C14, C15, and six to the aromatic carbon atoms C6−C11 (Table S10, Supporting Information).

The ${}^1$H NMR spectrum is very complicated because all hydrogen atoms linked to the magnetically nonequivalent carbon atoms present different chemical shifts. However, 2D-NMR ${}^1$H−${}^1$H homonuclear and ${}^1$H−${}^{13}$C heteronuclear correlations (Figure 3) allow unequivocal assignment of all ${}^1$H and ${}^{13}$C resonances. From the heteronuclear cross peak correlation for the aliphatic region, it can be observed that the four methyl groups show four single correlations, due to equivalence of their protons, while each methylenic carbon displays two cross peaks correlating with two different proton chemical shifts. On the other hand, in the homonuclear correlation all of the expected cross peaks corresponding to the involved spin systems are observed. Four main features can be outlined from the NMR data: (i) the proton resonance of one (H1) of the four different methyl groups is remarkably upfield shifted in comparison with the other ones; (ii) the benzylic hydrogens EF and KL display two different spin systems, the signals of K and E hydrogens appearing at higher field than those for F and L hydrogens; (iii) the protons of the ethylenic chains give two different spin systems, ABCD and MNOP, A, B, O, and M hydrogens being the most shielded; and (iv) the protons of the aromatic rings show a GHIJ spin system (Table S10, Supporting Information).

All of the NMR results indicate that the complex has a $C_s$ symmetry, with a symmetry plane passing through the two
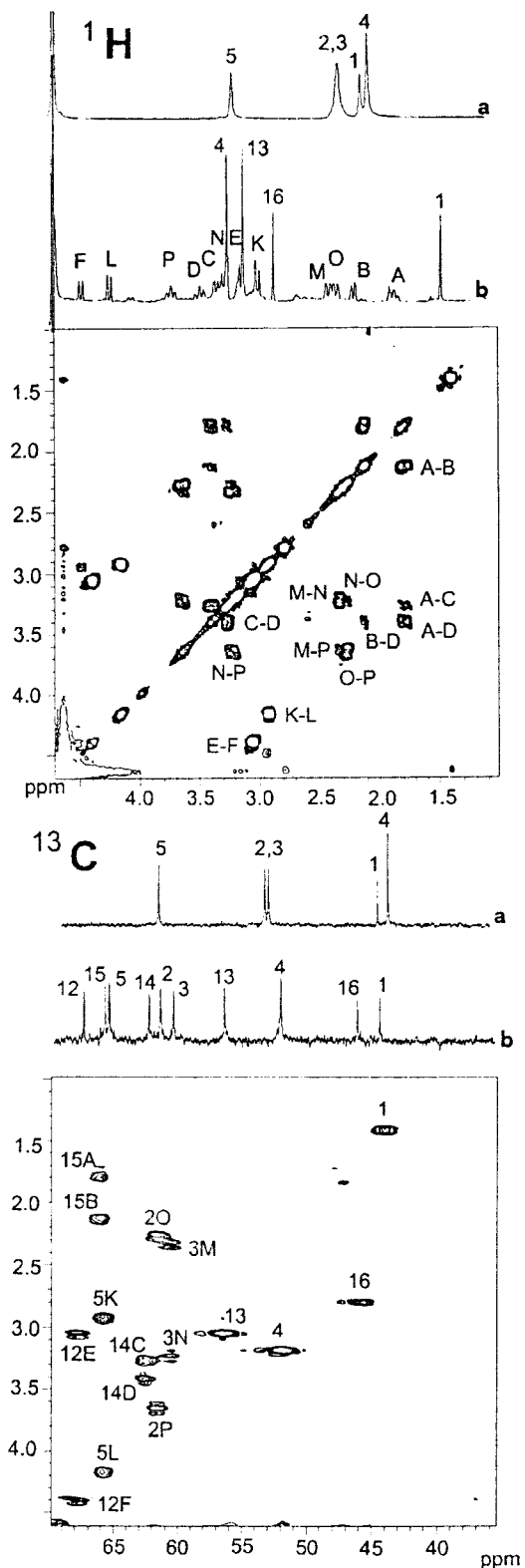
nitrogens N1 and N4 and the methyl groups C1 and C16. This symmetry is almost equal to that found in the crystal structure of the [Pd$_2$Cl$_2$**L1**](ClO$_4$)$_2$ complex, which displays (Figure 1) a noncrystallographic symmetry plane defined by the metal centers, the chloride ions, the N1 and N4 donor atoms, and the C1 and C16 methyl groups.
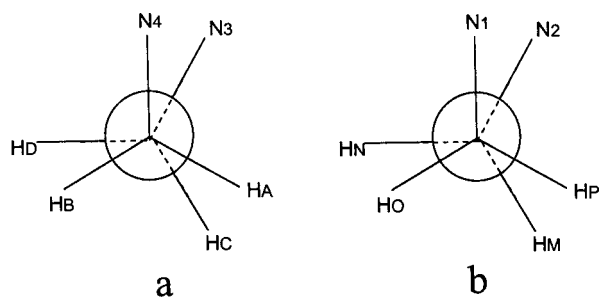
**Figure 4.** Schematic representations of the conformations of the C2−C3 (a) and C14−C15 (b) ethylenic chains.

Furthermore, computer simulation allows a more detailed analysis of the proton spin systems. The determination of the coupling constants of the ethylenic chains is interesting in that it can give information on the conformation of the macrocycle in aqueous solution. In both spin systems MNOP and ABCD, the zero value of the vicinal coupling constants for protons M−O and B−C ($J_{BC} = J_{MO} = 0$) indicates that the O−C2−C3−M and B−C15−C14−C dihedral angles are near 90°, as sketched in Figure 4. On the other hand, the values of the vicinal coupling constants for the protons A−C, B−D, N−O, and M−P are typical of a gauche conformation for the corresponding A−C15−C14−C, B−C15−C14-D, N−C2−C3−O, and M−C2−C3−P dihedral angles, as expected for N−C−C−N chelating units. The high values of the $J_{AD}$ and $J_{NP}$ coupling constants indicate that the A and D protons as well as the N and P ones assume a trans disposition. These observations point out that the BD and AC couples of hydrogens of the N1−C2−C3−N2 unit as well as the PM and NO couples of the N3−C14−C15−N4 unit are in a partially eclipsed orientation, as schematically drawn in Figure 4.

Further information about the conformation of the macrocycle in aqueous solution can be obtained by the analysis of the $^1$H chemical shifts of the two methyl groups 1 and 16. In the binuclear complex the resonance of the protons of methyl group 1 is significantly shifted upfield (ca. 1.5 ppm) with respect to that of the protons of methyl group 16. This effect can be reasonably explained considering that in the [Pd$_2$Cl$_2$**L1**]$^{2+}$ cation the methyl group 1 points inside the macrocyclic cavity delimited by the two benzylic units, as observed in the crystal structure of the [Pd$_2$Cl$_2$**L1**](ClO$_4$)$_2$ compound (see Figure 1), and therefore its resonance is strongly influenced by the shielding cones of the aromatic rings. On the contrary, the methyl group 16 points outside the cavity. Similar effects are also observed for the protons of the ethylenic chains and for the benzylic hydrogens. The crystal structure of [Pd$_2$Cl$_2$**L1**]$^{2+}$ evidences that two vicinal protons of the C2−C3 ethylenic chain (O and M) and the two geminal protons of carbon C15 (A and B) of the C14−C15 ethylenic chain are displaced almost inside the macrocyclic cavity. Therefore, their resonances are markedly shifted upfield with respect to those of the remaining ethylenic hydrogens (N, P and C, D) which are positioned outside the cavity. Similarly, upfield shifts are also observed for the signals of the K and E benzylic protons, located inside the cavity, with respect to those of the F and L ones, positioned outside (see Figure 3).

These observations point out that the macrocycle assumes in solution the same conformation found in the [Pd$_2$Cl$_2$**L1**](ClO$_4$)$_2$ solid complex.

As far as the mononuclear [PdCl**L2**H$_2$]$^{3+}$ complex is concerned, the NMR spectra also indicate a $C_s$ symmetry of the macrocycle, with a symmetry plane passing through the nitrogen atom N1, the linked methyl group 1, and the Pd(II) ion and bisecting the O−CH$_2$−CH$_2$−O ethylenic chains. In this case, the $^{13}$C NMR spectrum recorded in aqueous solution shows 16 different resonances, of which two are attributed to the methyl carbons C1 and C4, two to the benzylic carbons C5 and C12, two to the carbons of the ethylenic chain C2−C3, four to the aromatic carbon atoms C6−C9, and six to the ethylenic carbons C13, C13′, C14, C14′, C15, and C15′ of the N$_2$O$_4$ unit. Although in the $^1$H NMR spectrum the signal of the hydrogens of the N$_2$O$_4$ unit cannot be confidently attributed, the proton NMR parameters for the N$_3$ unit are similar to those found in the [Pd$_2$Cl$_2$**L1**]$^{2+}$ complex (Table S10, Supporting Information). For instance, all protons of the ethylenic chain C2−C3 and of the two benzylic carbons C5 and C12 have different chemical shifts, and the chemical shift of the methyl group 1 is remarkably upfield shifted in comparison with the signal of the methyl groups 4 (ca. 1.5 ppm). This observation indicates that in the [PdCl**L2**H$_2$]$^{3+}$ complex the methyl group 1 points inside the macrocyclic cavity, as actually observed in the crystal structure of the [PdCl**L2**H$_2$(H$_2$O)]$^{3+}$ cation.

These observations lead to the conclusion that both the dinuclear [Pd$_2$Cl$_2$**L1**]$^{2+}$ and the mononuclear [PdCl**L2**H$_2$(H$_2$O)]$^{3+}$ complexes maintain in aqueous solution almost the same structure found in the solid state.

**Concluding Remarks**

Ligands **L1** and **L2** form stable [Pd$_2$Cl$_2$**L1**]$^{2+}$ and [PdCl**L2**H$_2$]$^{3+}$ complexes in aqueous solution. In the former each Pd(II) ion is coordinated by a triamine unit, and in the latter the metal is coordinated by the triamine binding moiety, while the N$_2$O$_4$ unit is protonated. A water molecule, which is a simple example of a neutral guest molecule, is encapsulated in the N$_2$O$_4$ moiety, held by a hydrogen-bond network.

In both **L1** and **L2** complexes, Pd(II) coordination gives a noticeable stiffening of the macrocyclic backbone. Actually, the structural features of the two [Pd$_2$Cl$_2$**L1**]$^{2+}$ and [PdCl**L2**H$_2$]$^{3+}$ complexes, found in the solid state, are retained in aqueous solution. This effect can be reasonably ascribed to the strict stereochemical requirements of the Pd(II) ion, coupled with the rigidity of the ligand frameworks.

**Supporting Information Available:** Tables of crystallographic and experimental data, complete atomic positional parameters, anisotropic temperature factors, and bond distances and angles for [Pd$_2$Cl$_2$**L1**](ClO$_4$)$_2$·H$_2$O and [PdCl**L2**H$_2$(H$_2$O)](ClO$_4$)$_3$; $^1$H and $^{13}$C chemical shifts for the [Pd$_2$Cl$_2$**L1**]$^{2+}$ and [PdCl**L2**H$_2$]$^{3+}$ complexes and coupling constants for the [Pd$_2$Cl$_2$**L1**]$^{2+}$ complex; distribution diagrams of the species for the system **L1**/Pd(II); experimental data points and theoretical titration curves for the systems Pd(II)/**L1** and Pd(II)/**L2**. This material is available free of charge via the Internet at http://pubs.acs.org.