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Small Azaparacyclophanes as Potential Selective Scavengers of Mercury. Crystal Structure of the Complex $Hg_2(L1)Cl_4$ (L1 = 16,17,19,20-Tetramethyl-2,6,9,13-tetraaza[14]paracyclophane)

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The ligational properties of the macrocycles 16,17,19,20-tetramethyl-2,6,9,13-tetraaza[14]paracyclophane (**L1**) and 2,6,9,13-tetraaza[14]paracyclophane (**L2**) and of its dibenzylated open-chain counterpart 1,12-dibenzyl-1,5,8,12-tetraazadodecane (**L3**) toward Hg^{2+} are reported. The equilibrium constants have been determined by potentiometry at 298.1 K in 0.15 mol dm^{-3} NaCl. Competition of the ligands with chloride anions for the coordination of Hg^{2+} was required for the determination of the stability constants due to the high stability of the complexes formed. **L1** and **L2** selectively complex Hg^{2+} over first transition series metal ions and particularly over Cu^{2+}. NMR measurements prove that just three of the four nitrogen donors in ligands **L1** and **L2** are involved in the coordination to Hg^{2+}; the remaining benzylic nitrogen atom is not coordinated. NMR spectra also show a strong diamagnetic shielding (*ca.* 2 ppm) for one of the protons in the central methylene groups of the propylenic chain linked to the uncoordinated benzylic nitrogen. These signals appear for $[Hg\mathbf{L1}]^{2+}$ at 0.3 ppm and for $[Hg\mathbf{L2}]^{2+}$ at −0.4 ppm. The crystal structure of $[Hg_2\mathbf{L1}Cl_4]$ agrees with the NMR studies. Crystals of $[Hg_2\mathbf{L1}Cl_4]$ ($C_{20}H_{36}Cl_4Hg_2N_4$) are monoclinic space group $P2_1/c$, with $a = 10.360(2)$ Å, $b = 17.535(2)$ Å, $c = 14.918(1)$ Å, $\beta = 105.98(1)°$, $Z = 4$, $R_1 = 0.0471$, $wR_2 = 0.1064$. The tetrahedral coordination polyhedra around the Hg^{2+} ions are formed in one case by the benzylic nitrogen atom and the two consecutive nitrogen atoms of the central part of the bridge and one chloride anion and, in the other case, by the remaining benzylic nitrogen and three chloride anions. Both coordination polyhedra are strongly distorted, particularly the one involving three nitrogen atoms of the bridge.

Introduction

Probably the initial main goal in macrocyclic chemistry was the achievement of ligands able to complex selectively target metal ions.[1] With the greater awareness of environmental hazards, the design of sequestering agents of heavy metal ions has become a topic of current interest. It is advantageous to prepare ligands that can be easily attached to solid supports and therefore used in a variety of separation techniques. Recently, we have reported on the synthesis and reactivity of a series of tri-, tetra- and pentaazacyclophanes whose molecular architecture was made up of the corresponding polyamine chain interrupted by a single *p*-phenylene subunit.[2−4]

The presence of the *p*-phenylene subunit within the macrocyclic framework prevents the simultaneous coordination of all the nitrogen atoms to a single metal center. We demonstrated that coordination of Cu^{2+} and Zn^{2+} by the polyazacyclophane 16,17,19,20-tetramethyl-2,6,9,13-tetraaza[14]paracyclophane (**L1**) or 2,6,9,13-tetraaza[14]paracyclophane (**L2**) occurs through three of the four nitrogen atoms present in the ligand;[3,4] one of the benzylic nitrogens remains uncoordinated. This feature allowed us the use of the metal complex of these ligands for self-addressing their functionalization reactions.[5] Indeed, while random functionalization occurred when treating the free macrocycles with several alkylating agent, selective monofunctionalization at the benzylic position was achieved when using the Zn^{2+} complexes of either **L1** or **L2**. This represents an easy and accessible way to obtain a new family of compounds and allows the introduction of functional groups permitting their incorporation into polymeric supports.

Ligands **L1** and **L2** appear to posses some of the characteristics that could make them appropriate separating agents for hazardous metals. In order to test these expectations we have studied the coordination capabilities of these ligands toward Hg^{2+}. For comparison, we have also studied the Hg^{2+} coordination chemistry of the dibenzylated open-chain counterpart 1,12-dibenzyl-1,5,8,12-tetraazadodecane (**L3**).

Experimental Section

Materials. Ligands **L1** and **L2** were synthesized as described[2] and handled as their perchlorate salts. (*Caution!* Perchlorate salts can be explosive and must be handled with care. Compounds should not be

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Table 1. Crystallographic Data for Hg_2(**L1**)Cl_4

M_r	875.51	λ/Å	0.71073
cryst color	colorless	μ(Mo Kα)/cm^{-1}	12.12
cryst size/cmm	0.15 × 0.25 × 0.20	Θ limits/deg	1−25
formula	$C_{20}H_{36}Cl_4Hg_2N_4$	*hkl* range	(0, 0, −17) to (12, 20, 17)
cryst sym	monoclinic	drift cor	1.00−1.64
space group	$P2_1/c$	no. of obsd reflcns ($I > 2\sigma(I)$)	2041
a/Å	10.360(2)	F(000)	1648
b/Å	17.535(2)	ψ-scan	0.74−1.00
c/Å	14.918(1)	DIFABS	0.92−1.21
β/deg	105.98(1)	R_1[a]	0.0471
V/Å^3	2605(1)	wR_2[b]	0.1064
Z	4	max shift error peaks	0.001
temp (°C)	20	max and min/e·Å^{-3}	1.42, −1.89
D_c/g·cm^{-3}	2.219	no. of variables	277

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma |F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2$ $w = 1/[\sigma^2(F_o)^2 + (0.0661P)^2 + 29.22P]$; $P = [(\max(F_o^2) + 2(F_c)^2])$.

heated as solids). The synthesis of **L3** will be described elsewhere.(6) All the ligands gave satisfactory elemental analysis. NaCl used as background electrolyte in the pH-metric titration was from Merck. $NaClO_4$ was purified as reported.(7) Stock solutions of Hg^{2+} were prepared from their nitrate salts and standardized with EDTA.

Synthesis of Hg_2(L1)Cl_4. Evaporation of aqueous solutions containing 0.110 mmol Hg^{2+} and 0.055 mmol of **L1** in 50 cm^3 of H_2O in the presence of an excess of NaCl yielded a powdered sample of Hg_2(**L1**)Cl_4. Crystals suitable for X ray diffraction were obtained by slow recrystallization of the above product in aqueous solution.

Emf Measurements. The potentiometric titrations were carried out, in 0.15 mol dm^{-3} NaCl at 298.1 ± 0.1 K, as described.(8) The acquisition of the emf data was performed with the computer program PASAT.(9) The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-ion concentration probe by titration of accurately known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by the Gran's method,(10) which gives the standard potential, $E°'$, and the ionic product of water ($pK_w = 13.73(1)$).

The computer program HYPERQUAD(11) was used to calculate the protonation and stability constants. All the protonation constants of the ligands were re-determined under the experimental conditions employed.(26) Due to the high stability of the Hg^{2+} complexes of polyamines **L1**−**L3**, competition between protonation of the free ligands and complex formation is not significant enough to derive the values of the stability constants, and competition with formation of Hg^{2+} chloro complexes was used. The stability constants for the formation of Hg^{2+} chloro complexes were taken from ref 12. DISPO(13) program was used to obtain distribution diagrams. The titration curves for each system (*ca.* 200 experimental points corresponding to at least three measurements, pH range investigated 2−10, and concentration of ligands ranging from 1×10^{-3} to 5×10^{-3} mol dm^{-3} and that of the metal ions from 1×10^{-3} to 2×10^{-3} mol dm^{-3}) were treated either as a single set or as separated curves without significant variations in the values of the stability constants. Finally, the sets of data were merged together and treated simultaneously to give the final stability constants.

Spectroscopy. The ^1H and ^{13}C NMR spectra were recorded on Varian UNITY 300 and UNITY 400 spectrometers, operating at 299.95 and 399.95 MHz for ^1H and at 75.43 and 100.58 MHz for ^{13}C. The spectra were obtained at room temperature in D_2O solutions. For the ^{13}C NMR spectra dioxane was used as a reference standard ($\delta = 67.4$ ppm) and for the ^1H spectra the solvent signal. The pH was calculated from the measured pD values using the correlation, pH = pD − 0.4.(14) The UV/vis spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer.

X-ray Structure Analysis. Analysis on single crystals of Hg_2(**L1**)Cl_4 were carried out with an Enraf-Nonius CAD-4 single-crystal diffractometer (λ = 0.710 73 Å). The unit cell dimensions were measured from the angular settings of 25 reflections with θ between 15 and 25°. The space group was $P2_1/c$. A total of 5182 reflections were measured in the *hkl* range (0, 0 , −17) to (12, 20, 17) between θ limits $1 < \theta < 25°$. $\omega - 2\theta$ scan techniques and a variable scan rate with a maximum scan time of 60 s per reflection were used. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 3600 s. Profile analysis was performed on all reflections;(15) a semiempirical absorption correction, Ψ-scan based, was performed.(16) A total of 4577 "unique" reflections from which 2041 were with $F_o > 4\sigma(F_o)$. Lorenz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structure was solved by the Patterson method using the program SHELXS-86(17) running on a Pentium 100 computer. Isotropic least-squares refinement was performed by means of the program SHELXL-93(18) converging to $R = 0.10$, at this stage additional empirical absorption correction was applied using DIFABS.(19) The maximum and minimum absorption correction factors were 0.92 and 1.21, respectively. Hydrogen atoms were geometrically placed. Tables 1 and 2 present details of the crystal data and the atomic coordinates.

During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined, except aromatic carbons which were isotropically refined. The hydrogen atoms were refined with a common thermal parameter. The final conventional agreement factors were $R_1 = 0.0471$ and $wR_2 = 0.1064$. Atomic scattering factors were taken from the ref 20. Molecular plots were produced by the program ORTEP.(21)

Results and Discussion

In Table 3 are shown the stability constants for the formation of Hg^{2+} complexes of the polyazacyclophanes **L1**−**L2** deter-

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Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic or Equivalent Thermal Parameters ($Å^2 \times 10^3$) for Hg_2(**L1**)Cl_4, with their Esd's in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Hg(1)	1556(1)	767(1)	2372(1)	57(1)
Hg(2)	1382(1)	−2435(1)	−933(1)	49(1)
Cl(1)	−1013(4)	−2652(2)	−1606(3)	58(1)
Cl(2)	2470(4)	−1836(2)	−2049(3)	56(1)
Cl(3)	2574(5)	−3640(3)	−286(3)	76(1)
Cl(4)	552(4)	694(2)	759(3)	49(1)
N(1)	2107(11)	−1603(6)	301(7)	36(3)
N(2)	3544(14)	1117(7)	3267(9)	62(4)
N(3)	390(13)	1155(7)	3428(9)	58(4)
N(4)	678(13)	−394(6)	2812(8)	43(3)
C(1)	4619(15)	536(8)	2193(9)	42(3)
C(2)	5068(16)	−156(8)	2594(10)	51(4)
C(3)	4808(14)	−839(8)	2049(10)	53(3)
C(4)	4034(14)	−790(8)	1056(8)	38(3)
C(5)	3775(15)	−67(8)	663(9)	41(3)
C(6)	4050(14)	591(8)	1249(9)	39(3)
C(20)	5784(18)	−226(10)	3594(11)	71(5)
C(30)	5235(18)	−1596(9)	2505(11)	67(5)
C(50)	3094(14)	3(8)	−348(8)	40(3)
C(60)	3705(16)	1370(8)	765(10)	52(4)
C(7)	3550(14)	−1503(7)	538(10)	41(4)
C(8)	1526(16)	−1767(8)	1058(9)	46(4)
C(9)	1651(16)	−1164(8)	1806(10)	52(4)
C(10)	410(14)	−950(7)	2055(10)	42(4)
C(11)	−461(16)	−152(8)	3118(12)	57(5)
C(12)	−15(19)	476(10)	3853(11)	68(5)
C(13)	1117(18)	1734(10)	4087(12)	73(6)
C(14)	2565(20)	1591(10)	4517(10)	72(6)
C(15)	3475(17)	1755(8)	3924(11)	55(4)
C(16)	4615(14)	1207(8)	2801(10)	43(4)

Table 3. Logarithms of the Stability Constants for the Formation of Hg(II) Complexes of the Ligands **L1**, **L2**, and **L3** Determined at 298.1 K in 0.15 mol dm^{-3} NaCl

reaction	**L1**	**L2**	**L3**
$Hg + L + 2H + 2Cl \leftrightarrows [HgH_2LCl_2]$[b]		36.88(8)[a]	38.20(4)
$Hg + L + H + Cl \leftrightarrows [HgHLCl]$	30.60(2)	26.70(2)	29.4(1)
$Hg + L + Cl \leftrightarrows [HgLCl]$	22.63(5)	21.88(3)	
$Hg + L \leftrightarrows [HgL]$			21.60(3)
$Hg + L + H_2O \leftrightarrows [HgL(OH)] + H$	10.9(1)	12.08(6)	12.13(7)

[a] Numbers in parentheses are standard deviations in the last significant figure. [b] The stability constants taken from ref. 12 for the chloro complexes of Hg^{2+} are as follows: $Hg^{2+} + Cl^- \leftrightarrows [HgCl]^+$, log $K = 6.74$; $Hg^{2+} + 2Cl^- \leftrightarrows [HgCl_2]$, log $K = 13.22$; $Hg^{2+} + 3Cl^- \leftrightarrows [HgCl_3]^-$, log $K = 14.20$; $Hg^{2+} + 4Cl^- \leftrightarrows [HgCl_4]^{2-}$, log $K = 15.20$; $Hg^{2+} + Cl^- + H_2O \leftrightarrows [HgCl(OH)] + H^+$, log $K = 3.05$. [c] Charges omitted for clarity.

mined by potentiometry at 298.1 ± 0.1 K in 0.15 mol dm^{-3} NaCl. For comparison the stability constants for the formation of Hg^{2+} complexes of the related dibenzylated open-chain polyamine **L3** have been also included in the same table. The high stability of these complexes made necessary the use of competing procedures to determine the stability constants since hydrogen ions do not compete significantly with Hg^{2+} in the pH range 2−10. Competition of **L1**−**L3** with chloride ions for the coordination of Hg^{2+} was used. All three ligands present similar speciation models (see Table 3); the only difference among them being that azaparacyclophane **L1**, containing a durene spacer in between the polyamine bridge, does not form a diprotonated mononuclear species.

In order to test the 1:1 metal:ligand stoichiometries inferred from the pH-metric studies we have recorded the UV spectrum for all three systems since the bands of the aromatic moieties of these ligands are strongly affected by the coordination of the metal. The UV spectrum of the free ligand **L2** at pH = 8.5, where the nonprotonated mononuclear species predominates, displays two absorption bands centered at 204 and 221 nm; addition of Hg^{2+} yields UV spectra which display just a single broad band in this region centered at 219 nm with a clear increase of the molar absorptivity. The absorption of this band increases progressively until a molar ratio Hg^{2+}:**L2** 1:1 ($\epsilon = 2.9 \times 10^4$ mol^{-1} dm^3 cm^{-1}) is reached. Further Hg^{2+} additions do not produce more spectral changes. UV spectra for the ligand **L3** were recorded at pH values 6.5, 8.5, and 10.5 in correspondence with the maximum formation of the complex species $[HgH_2$**L3**$Cl_2]^{2+}$, [Hg**L3**$]^{2+}$, and [Hg**L3**(OH)$]^+$, respectively. In all three cases the bands at 211 and 220 nm present in the spectrum of the free ligand collapsed into a single broad band place at *ca.* 217 nm of much higher intensity. Plots of absorbance vs molar ratio Hg^{2+}:**L3** give for the three pH values clear breaks for 1:1 molar ratios confirming also in this case the formation of complexes of this stoichiometry . **L1** behaves similarly for the concentrations at which the spectra were recorded ($[Hg^{2+}] = 1 \times 10^{-4}$ mol dm^{-3}). However, for higher concentrations precipitation was observed for molar ratios Hg^{2+}:**L1** over 1. Recrystallization of this precipitate afforded crystals of the neutral binuclear complex $[Hg_2$**L1**$Cl_4]$ whose crystal structure will be discussed below.

One of the main characteristics of the metal coordination chemistry of ligands **L1** and **L2** derives from the presence of the aromatic spacer which imposes enough strain to prevent simultaneous coordination of both benzylic nitrogens to a single metal center. Therefore, it was found that Cu^{2+} or Zn^{2+} are just coordinated by three out of the four nitrogen atoms present in **L2** [3,4] which results in marked stability drops with respect to analogous complexes of polyazacycloalkanes or open-chain polyamines.[22]

In order to obtain structural information we have performed a NMR study of the mononuclear Hg^{2+} complexes of these ligands. The ^1H NMR spectrum of **L1** in D_2O shows, throughout all the pH range, 2-fold symmetry with singlet signals for the benzylic protons (H1), for all the methylene protons of the central ethylenic chain (H5), and for the methyl groups of the spacer (HB3) and two triplet signals corresponding to protons H2 and H4 of the propylenic chains and a multiplet signal attributed to protons (H3) of the central methylene groups (see Chart 1). **L2** reflects the same symmetry with a similar pattern for the signals of the aliphatic chains and a singlet signal for the aromatic protons (HB2). The ^{13}C NMR spectra of both ligands are also consistent with this symmetry; **L1** displays eight signals and **L2** seven signals corresponding to half of the carbon atoms present in the molecules. The spectra recorded for molar ratios Hg^{2+}:L < 1 show both the signals of the complex species and of the free ligand due to the great rigidity imposed in the ligand by the coordination of the Hg^{2+} ions (Figure 1A). When the molar ratio reaches the value of 1 just the signals of the complex species are observed (Figure 1, parts B and C). Addition of Hg^{2+} removes the symmetry of the ligands and both the ^1H and ^{13}C NMR spectra present as many signals as proton or carbon nuclei are in the ligands. It is to be noted, that even the methyl groups of the durene spacer in **L1** appear as four different signals (see Figure 1C). These NMR spectra may be explained in terms of an asymmetric coordination of the metal ion to the macrocyclic nitrogen atoms. In this sense, a coordination of the metal by three of the four nitrogen atoms of the macrocycle, like that observed for Hg(1) in the crystal structure of the compound $[Hg_2$**L1**$Cl_4]$, would fully agree with these spectral patterns. The NMR spectra of the Hg^{2+} complexes of **L3** are, however, different. The 2-fold symmetry showed by the open-chain dibenzylated free-ligand is preserved

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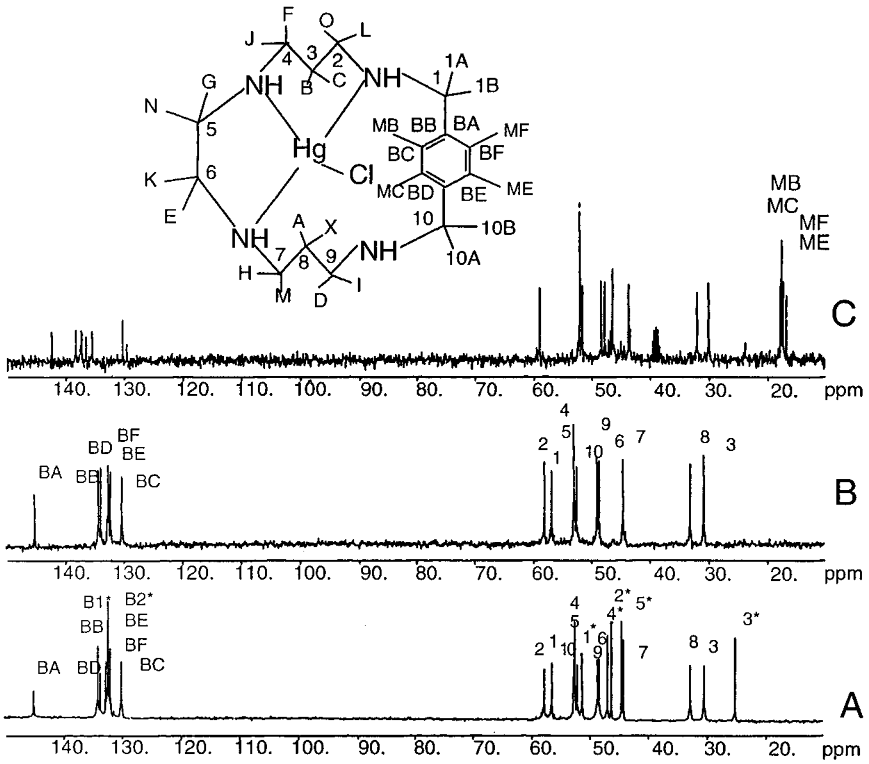
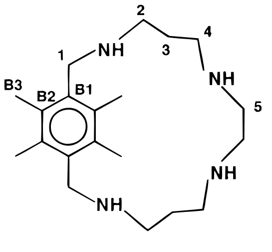
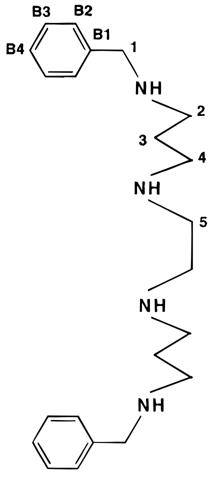


Figure 1. ^{13}C NMR spectra of the systems: **(A)** Hg^{+2}−**L2** in an excess of ligand, **(B)** Hg^{+2}−**L2** in 1:1 metal:ligand ratio, and **(C)** Hg^{+2}−**L1** in 1:1 metal:ligand ratio. Asterisks correspond to signals for free ligand.

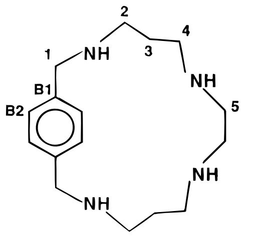
Chart 1



L1



L3



L2

in the $[HgL3]^{2+}$ complex. These spectral features reveal a more symmetric participation of the nitrogen donors in the coordination to the metal and could probably denote the involvement of all four nitrogens atoms in the coordination to the metal as is usually observed for other open-chain polyamines.

It is of interest to analyze the strong diamagnetic shielding experienced by one of the methylene protons of the bridge in the macrocyclic ligands. In Figure 2 are plotted the 2D NMR $^{1}H-^{1}H$ and $^{1}H-^{13}C$ spectra of the system Hg^{2+}−**L2**. It can be seen that the signal at −0.4 ppm belongs to one of the protons of the central methylene of the propylenic chain linked to the unbounded nitrogen and presents cross-peaks with the other proton of this methylene group as well as with all the other protons of the propylenic chain. Such an effect could be accounted for by the conformation adopted by the macrocycle upon coordination to Hg^{2+} which would produce this hydrogen to be embedded in the electron cloud of the aromatic ring. A similar situation is observed in the system Hg^{2+}−**L1** for the signal at 0.3 ppm.

These solution studies are partly supported by the structure of the solid compound $[Hg_2$**L1**$Cl_4]$. The structure consists only of discrete neutral $[Hg_2$**L1**$Cl_4]$ binuclear units. An ORTEP[21] drawing of the compound is shown in Figure 3, and some selected bond angles and distances are listed in Table 4. The structure comprises two different distorted tetrahedral Hg^{2+} environments, with the coordination sites being formed in one case by one benzylic nitrogen (N(2)), the two consecutive nitrogens in the chain (N(3), N(4)) and one chloride anion (Cl(4)) (site A), and the other one by the remaining benzylic nitrogen (N(1)) and three chloride anions (Cl(1), Cl(2), Cl(3)) (site B). The distance between both metal ions is 7.456(1) Å. In site A, all the Hg−N distances are different (see Table 4, Figure 3); the shortest distance being Hg(1)−N(2) which just forms part of the six-membered chelate ring and the largest one Hg(1)−N(4) which only pertains to the five-membered chelate; the remaining bond distance (Hg(1)−N(3)) are comprised between these two. Hg(1) is placed 3.24(1) Å above the aromatic ring. The Hg−N distance in site B is within the distance range found in site A. It is of interest to notice the differences in the Hg−Cl distances found for both coordination sites. The three Hg−Cl distances in site B are markedly larger that the one in site A, possibly influenced by the differing number of bonded nitrogens in each site. Each Hg^{+2} displays a distorted tetrahedral geometry (see Figure 3B) being site A more distorted than site B. It should be noted that the very narrow angle N(3)−Hg(1)−N(4) (76°) of the five-membered chelate ring is significantly reduced from the standard tetrahedral angle, with the opposite angle Cl(4)−Hg(1)−N(2) considerably opened up to compensate. In this site Hg is located 1.04 Å

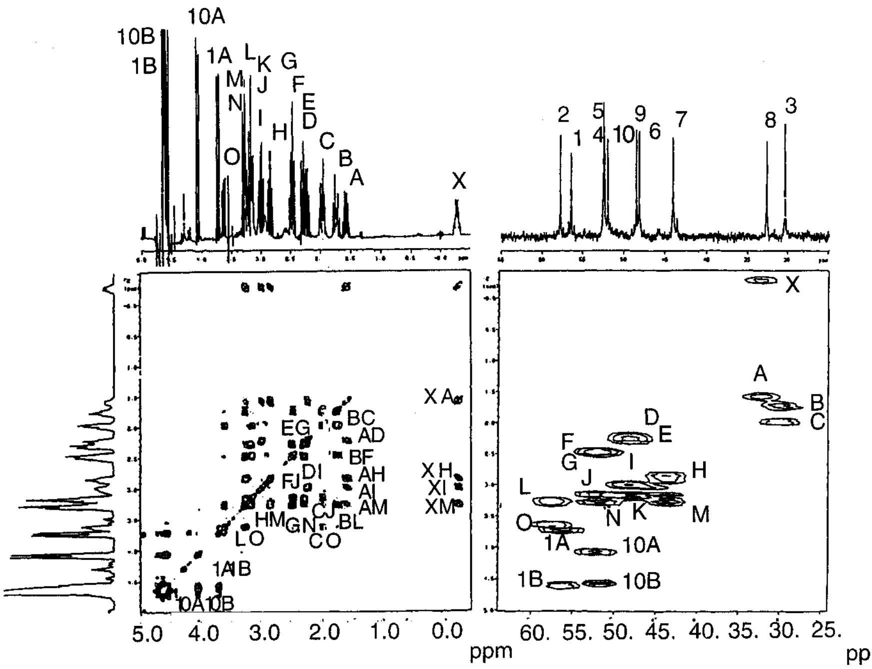


Figure 2. ^{1}H−^{1}H and ^{1}H−^{13}C 2D NMR spectra in D2O solution for the system Hg^{+2}−**L2** in 1:1 metal:ligand ratio and neutral pH.

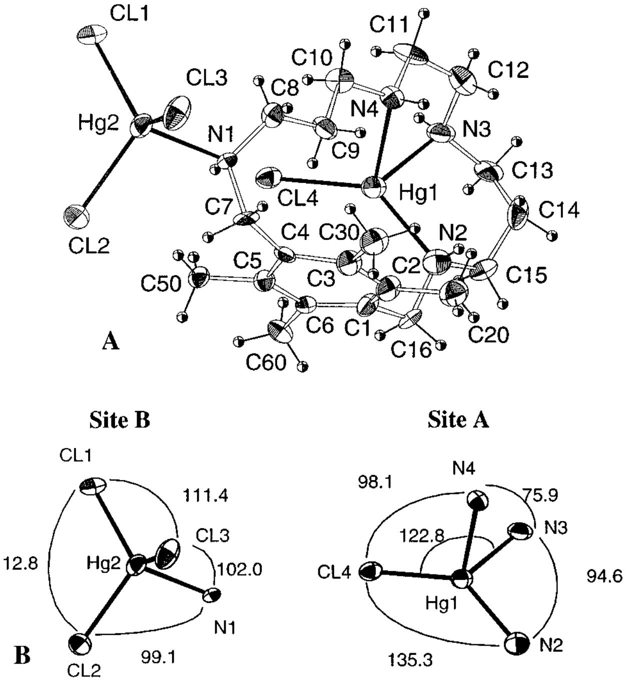


Figure 3. (A) ORTEP drawing of the neutral [Hg$_2$(**L1**)Cl$_4$] molecule. (B) ORTEP drawing showing the coordination sites of both mercury atoms. Thermal ellipsoids are drawn at the 30% probability level.

above the mean plane defined by the macrocycle. The angles of coordination site B are much less distorted. A somewhat similar situation was reported for the Hg^{2+} complex of the *anti* isomer of the macrocycle 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine.[23] The torsion angles along the polyamine bridge reflect the presence of the five- and six-membered chelate rings as well as that of the aromatic spacer. In fact torsion angles in the portion of the chain around coordination site A are as follows: C(13)−C(14)−C(15)−N(2)−83(2)°, N(3)−C(13)−C(14)−C(15) 78(2)°, N(4)−C(11)−C(12)−N(3) 66(1)°. The torsion angles are much larger around the monodentate amine group: C(8)−C(9)−C(10)−N(4) 177(1), N(1)−C(8)−C(9)−C(10) 130(1)°.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Hg$_2$(**L1**)Cl$_4$

Hg(1)−N(2)	2.22(1)	Hg(2)−N(1)	2.31(1)
Hg(1)−N(3)	2.34(1)	Hg(2)−Cl(1)	2.441(4)
Hg(1)−Cl(4)	2.351(4)	Hg(2)−Cl(2)	2.491(4)
Hg(1)−N(4)	2.40(1)	Hg(2)−Cl(3)	2.508(4)
N(2)−Hg(1)−N(3)	94.6(5)	N(1)−Hg(2)−Cl(1)	119.9(3)
N(2)−Hg(1)−Cl(4)	135.3(3)	N(1)−Hg(2)−Cl(2)	99.1(3)
N(3)−Hg(1)−Cl(4)	122.8(4)	Cl(1)−Hg(2)−Cl(2)	112.8(1)
N(2)−Hg(1)−N(4)	115.6(5)	N(1)−Hg(2)−Cl(3)	102.0(3)
N(3)−Hg(1)−N(4)	75.9(4)	Cl(1)−Hg(2)−Cl(3)	111.4(2)
Cl(4)−Hg(1)−N(4)	98.1(3)	Cl(2)−Hg(2)−Cl(3)	110.4(2)

Also of interest is that one of the hydrogen atoms (H(9B)) of the central methylene (C(9)) of the propylenic chain points directly to the center of the aromatic ring and lies just 2.47(2) Å above its mean plane while the other one is at 2.80(2) Å. H(9B) is also the proton being closest to Hg(1) (Hg(1)−H(9B) 2.93(1) Å). If a conformation like this one was to be kept in solution for the mononuclear complex, which seems very likely on the basis of the NMR studies, this short distance would probably explain the strong diamagnetic shielding observed for this proton in the ^{1}H NMR spectrum.[24]

In Figure 4 is shown the crystal packing of this compound. It is noticeable that the aromatic rings, although displaced, lie parallel each other with mean distances of 3.7 Å showing the contribution of stacking to the tri-dimensional arrangement of the structure.

All these data permit to one make estimates of the selectivity toward metal ions achieved by these azaparacyclophane receptors. Regarding stability, the full complexation of Hg^{2+} at pH values as low as 2 when NaClO$_4$ instead of NaCl was used as background electrolyte, together with the fact that chloride anions are present in the crystals even if they are separated from solutions with stoichiometric amounts of this anion, clearly indicates that these anions have to be considered in the computation of the stability data (Table 3). The tentative number of chlorides introduced in the computation responds to

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(24) Johnson, C. E. Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, 29,1, 1012.

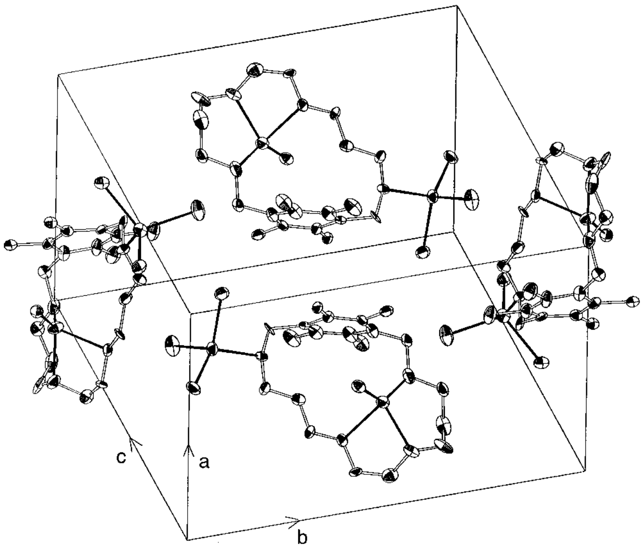

Figure 4. ORTEP drawing of the crystal packing of [$Hg_2(\mathbf{L1})Cl_4$].

the best fitting between experimental and theoretical data and to the chemical knowledge of the system provided by the NMR and the X-ray structure.

Concerning the equilibrium data in Table 3 it deserves to be noted that despite three nitrogen atoms are probably involved in the coordination to Hg^{2+} by cyclophanes **L1** and **L2** and four in the coordination by the dibenzylated ligand (**L3**), their stability constants do not differ greatly. This may be attributed to the particular coordination chemistry of the soft Hg^{2+} which does not have any ligand field stabilization and readily adopts coordination numbers between 2 and 4.[25] This situation contrasts to that found for complexes of bivalent transition metal ions or other post-transition metal ions with cyclophanes **L1** and **L2** which display reduced stability with respect to analogous tetraamines that do not contain the single aromatic spacer.[3,4] For instance while the logarithm of the stability constant for $[Cu(\mathbf{L2})]^{2+}$ was found to be 13.02(1),[3] that for the Cu^{2+} complex of the linear ligand 1,5,8,12-tetraazadodecane was 21.7 and that for complex with the cyclic 1,4,8,11-tetraazacyclotetradecane (cyclam) was 27.2.[25]

This stability trend poses interesting points regarding selective coordination of Hg^{2+}. Either cyclic or open-chain saturated tetraamines present close stability constants for Cu^{2+} and Hg^{2+}. For instance, the logarithms of the stability constants for the Cu^{2+} and Hg^{2+} complexes of cyclam are 27.2 and 23.0, those for the cyclic ligand 1,4,8,12-tetraazacyclopentadecane are 24.4 and 23.7, and those for 1,4,7,10-tetraazacyclododecane 24.6 and 25.5 for Cu^{2+} and $Hg^{2+,}$ respectively.[25]

In our case the big gap in stability between the complexes of Hg^{2+} (see Table 3) and those of all the other first series transition or post-transition metal ions including Cu^{2+} would permit the selective recognition of Hg^{2+} over all those metal ions. Such behavior together with the easy monofunctionalization procedure of these cyclophanes would allow one for removing selectively Hg^{2+}.[5] We are currently exploring these possibilities.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, torsion angles, anisotropic displacement parameters, calculated hydrogen coordinates, and isotropic displacement parameters and a distribution diagram of the species existing in equilibria for the system $Hg^{+2}-\mathbf{L2}-Cl^-$ ($[Hg^{+2}] = [\mathbf{L2}] = 10^{-3}$ mol dm^{-3}; $[Cl^-] = 0.15$ mol dm^{-3}) (9 pages). Ordering information is given on any current masthead page.

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(26) The stepwise protonation constants for the ligands **L1**, **L2**, and **L3** determined in 0.15 mol dm^{-3} NaCl at 298.1 K are: **L1**; log $K_{H\mathbf{L1}}$= 10.49(1), log $K_{H_2\mathbf{L1}} = 9.11(1)$, log $K_{H_3\mathbf{L1}} = 7.31(2)$, log $K_{H_4\mathbf{L1}} = 4.11$-(2); **L2**; log $K_{H\mathbf{L2}} = 9.91(2)$, log $K_{H_2\mathbf{L2}} = 9.18(1)$, log $K_{H_2\mathbf{L2}} = 7.67$-(2), log $K_{H_4\mathbf{L2}} = 4.24(4)$; **L3**; log $K_{H\mathbf{L3}} = 9.69(1)$, log $K_{H_2\mathbf{L3}} = 8.87(1)$, log $K_{H_2\mathbf{L3}} = 7.36(2)$, log $K_{H_4\mathbf{L3}} = 4.82(2)$.