Inorg. Chem. **2007**, *46*, 7818–7826

Inorganic Chemistry
Article

Exploring the Interaction of Mercury(II) by N_2S_2 and NS_3 Anthracene-Containing Macrocyclic Ligands: Photophysical, Analytical, and Structural Studies

Abel Tamayo,[†,‡] Bruno Pedras,[‡] Carlos Lodeiro,*[,‡] Lluis Escriche,*[,†] Jaume Casabó,[†] José Luis Capelo,[‡] Berta Covelo,[‡] Raikko Kivekäs,[§] and Reijo Sillanpää[||]

*Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain,
REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova
de Lisboa, 2829-516 Monte de Caparica, Portugal, Department of Chemistry, University of
Helsinki, 00014 Helsinki, Finland, and Department of Chemisty, University of Jyväskylä,
40351 Jyväskylä, Finland*

Received March 13, 2007

The complexation properties toward Hg(II) of six macrocyclic ligands, 3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L1**), 7-(9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L2**), 7-(10-methyl-9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L3**), 7,7′-[9,-10-anthracenediylbis(methylene)]bis-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L4**), 1,4,7-trithia-11-azacyclotetradecane (**L5**), and 11,-(anthracen-9-ylmethyl)-1,4,7-trithia-11-azacyclotetradecane (**L6**), were studied. The stoichiometries of the formed species were determined from absorption and fluorescence titrations. In these anthracene-containing macrocycles, a fluorescent quenching of the emission was found upon Hg(II) addition. The X-ray crystal structure of $[HgCl_2(\mathbf{L2})]\cdot 1/2CH_2Cl_2$ was determined. The asymmetric unit contains two independent $[HgCl_2(\mathbf{L2})]$ molecules and one dichloromethane molecule. Each Hg(II) ion is coordinated by the pyridine nitrogen, the two sulfur atoms of one **L2** molecule, and two chloride ions. Analytical studies using solvent extraction separation of Hg(II) from aqueous solutions were performed to determine the Hg(II) extraction capability of ligands **L1**, **L2**, and **L5**.

Introduction

It is well-known that Hg(II) is a global pollutant with complex and unusual chemical and physical properties.[1] In general, some heavy-metal ions such as Hg(II), Cd(II), and Pb(II) are dangerous because they tend to bioaccumulate, increasing the concentration of the chemical in biological organisms over time. Natural biological processes can produce methylated forms of mercury, which bioaccumulate more than a million-fold and concentrate in living organisms, especially fish.[2] This is the factor by which the main pathway for mercury to humans is through the food chain and not by inhalation. These forms of organic mercury (monomethylmercury and dimethylmercury) are highly toxic,[3] cause neurotoxicological disorders,[4] and are the main aim of many analytical papers.[5] Up to now, several methods and techniques have been used for mercury detection, such as nuclear magnetic resonance spectroscopy,[6] atomic absorption spec-

---

* To whom correspondence should be addressed. E-mail: lodeiro@dq.fct.unl.pt. Fax: + 351 21 2948385 (C. L.), E-mail: lluis.escriche@uab.es. Fax: + 34 93/581-2497 (L. E.).

[†] Universitat Autònoma de Barcelona.

[‡] Universidade Nova de Lisboa.

[§] University of Helsinki.

[||] University of Jyväskylä.

(1) (a) Vernet, P. *Heavy Metals in the Environment*; Elsevier Science: New York, 1991. (b) Leermakers, M.; Baeyens, W.; Quevauviller, P.; Horvat, M. *Trends Anal. Chem.* **2005**, *24*, 383−393.

(2) (a) Southworth, G. R.; Turner, R. R.; Peterson, M. J.; Bogle, M. A.; Ryon, M. G. *Environ. Monit. Assess.* **2000**, *63*, 481−494. (b) Hrabik, T. R.; Watras, C. J. *Sci. Total Environ.* **2002**, *297*, 229−237. (c) Sorensen, J. A.; Kallemyn, L. W.; Sydor, M. *Environ. Sci. Technol.* **2005**, *39*, 9237−9243.

(3) (a) Tai, H. C.; Lim, C.; *J. Phys. Chem. A* **2006**, *110*, 452−462. (b) Havarinasab, S.; Hultman, P. *Autoimmun. Rev.* **2005**, *4*, 270−275.

(4) Day, J. J.; Reed, M. N.; Newland, M. C. *Neurotoxicol. Teratol.* **2005**, *27*, 629−641.

(5) (a) Liu, Y.; Zai, Y.; Chang, X.; Guo, Y.; Meng, S.; Feng, F. *Anal. Chim. Acta.* **2006**, *575*, 159−165. (b) Capelo, J. L.; Lavilla, I.; Bendicho, C. *Anal. Chem.* **2000**, *72*, 4979−4984. (c) Capelo, J. L.; Maduro, C.; Mota, A. M. *J. Anal. At. Spectrom.* **2004**, *19*, 414−416.

10.1021/ic700489e CCC: $37.00

trometry,[7] electrospray ionization mass spectrometry,[8] solvent extraction,[9] chromogenic sensors,[10] fluorescence spectroscopy, etc. Most systems using fluorescence spectroscopy for detecting Hg(II) are based on the complexation enhancement of the fluorescence quenching effect (CHEQ), and only a few are based on fluorescence enhancement upon chelation effect (CHEF).[11]

Although synthetic macrocyclic compounds have been known for over 85 years, the number of publications on this field has substantially increased over the last three decades. In 1987, the year of the Chemistry Nobel Prize share by Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen, many works appeared in the literature concerning the design and synthesis of new macrocycles for sensing highly toxic metal ions, especially mercury.[12] In addition to detection, the removal of mercury ions from wastewater is of great concern in the environmental field of pollution reduction. Thioether-containing macrocycles have been shown to be useful for Hg(II) extraction from aqueous solution,[13] as a result of the well-known affinity of Hg(II) for sulfur atoms.

We have previously reported the synthesis and complexation ability toward Pd(II), Zn(II), Cu(II), Co(II), and Ni(II), of thioether-containing macrocycles 3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L1**) 7-(9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L2**), 7-(10-methyl-9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L3**), 7,7′-[9,10-anthracenediylbis(methylene)]bis-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L4**), 1,4,7-trithia-11-azacyclotetradecane (**L5**), and 11,-(anthracen-9-ylmethyl)-1,4,7-trithia-11-azacyclotetradecane (**L6**).[14] In the present article, we focus on the interactions of these six azathiamacrocycles with both inorganic and organic mercury, and their usefulness as fluorescent chemosensors for mercury detection. Such interactions have been studied in solution via absorption and fluorescence titrations and in the solid state via the synthesis of Hg(II) complexes. Additionally, analytical solvent extraction studies of Hg(II) from aqueous solutions have been carried out to explore the mercury-removal capabilities of these thioether-containing macrocycles.

Table 1. Crystal and Structure Refinement Data for $[HgCl_2(\mathbf{L2})]\cdot 1/2CH_2Cl_2$

empirical formula	$C_{28.5}H_{31}Cl_3HgN_2S_2$
fw	772.61
cryst syst, space group	triclinic, $P\bar{1}$
unit cell dimensions (Å, deg)	$a = 10.1828(2)$, $\alpha = 113.4430(10)$
	$b = 17.5508(4)$, $\beta = 99.491(2)$
	$c = 18.1227(5)$, $\gamma = 99.5980(10)$
V (Å^3)	2832.55(12)
Z, ρ_{calcd} (g.cm^{-3})	4, 1.812
F(000)	1516
cryst size (mm^3)	$0.16 \times 0.12 \times 0.06$
absorption coefficient (mm^{-1})	5.886
θ range (deg)	1.27−25.67
max./min.transmission	0.698/0.238
reflns collected	31 761
independent reflns (R_{int})	10 712 (0.0589)
final R indices [$I > 2s(I)$]	R1 = 0.0398, wR2 = 0.0909
final R indices (all data)	R1 = 0.0669, wR2 = 0.1107

Experimental Section

General Remarks. All of the reactions were carried out using standard Schlenk techniques. Solvents were dried by conventional methods and distilled under N_2(g) before being used. Elemental analyses were performed on a Carlo Erba EA-1108 instrument by the Chemical Analysis Service of the Universitat Autònoma de Barcelona or on a Thermo Finnigan-CE Flash-EA 1112-CHNS Instrument by the Chemical Analysis Service of the REQUIMTE, DQ, Universidade Nova de Lisboa. Conductivity measurements were carried out using a Cyberscan 500 conductimeter. IR spectra were recorded using a PerkinElmer FT-1710 instrument. NMR spectra were recorded on a Bruker 250 MHz AC Instrument. Organic reagents and transition-metal salts were purchased from Merck and Aldrich and used as received. Mass spectra were recorded using a HP298S GC/MS system. Ligands **L1**−**L6** were prepared as previously reported.[14]

X-ray Crystal Structure Determinations. A single crystal of $[HgCl_2(\mathbf{L2})]\cdot 1/2CH_2Cl_2$ was analyzed by X-ray diffraction, and a summary of the crystallographic data is reported in Table 2. Crystallographic measurements were performed on a Enraf Nonius FR590 CCD diffractometer at −100 °C using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using the program *SHELXS97*.[15] All of the non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program

---

(6) Helm, M. L.; Helton, G. P.; VanDerveer, D. G.; Grant, G. J. *Inorg. Chem.* **2005**, *44*, 5696−5706, and references therein.

(7) Capelo, J. L.; Maduro, C.; Mota, A. M. *Ultrason. Sonochem.* **2006**, *13*, 98−106. Ubillus, F.; Alegria, A.; Barbera, R.; Farre, R.; Lagarda, M. J. *Food Chem.* **2000**, *71*, 529−533.

(8) Williams, S. M.; Brodbelt, J. S.; Marchand, A. P.; Cal, D.; Mlinaric-Majerski, K. *Anal. Chem.* **2002**, *74*, 4423−4433, and references therein.

(9) Reddy, M. L. P.; Francis, T. *Solvent Extr. Ion Exch.* **2001**, *19*, 839−863, and references therein.

(10) (a) Kao, T.-L.; Wang, C.-C.; Pan, Y.-T.; Shiao, Y.-J.; Yen, J.-Y.; Shu, C.-L.; Lee, G.-H.; Peng, S.-M.; Chung, W.-S. *J. Org. Chem.* **2005**, *70*, 2912−2920, and references therein. (b) Martínez, R.; Espinosa, A.; Tárraga, A.; Molina, P. *Org. Lett.* **2005**, *26*, 5869−5872.

(11) (a) Yang, Y. K.; Yook, K. J.; Tae, J. *J. Am. Chem. Soc.* **2005**, *127*, 16760−16761. (b) Zhang, G.; Zhang, D.; Yin, S.; Yang, X.; Shuai, Z.; Zhu, D. *Chem. Commun.* **2005**, *16*, 2161−2163. (c) Guo, X.; Qian, X.; Jia, L. *J. Am. Chem. Soc.* **2004**, *126*, 2272−2273. (d) Nolan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 14270−14721. (e) Hennrich, G.; Walther, W.; Resch-Genger, U.; Sonnenshein, H. *Inorg. Chem.* **2001**, *40*, 641−644. (f) Zhao, Y.; Lin, Z.; He, C.; Wu, H.; Duan, C. *Inorg. Chem.* **2006**, *45*, 10013−10015.

(12) (a) Feng, K.; Hsu, F.-L.; Bota, K.; Bu, X. R. *Microchem. J.* **2005**, *81*, 23−27. (b) Matsushita, M.; Meijler, M. M.; Wirsching, P.; Lerner, R. A.; Janda, K. D. *Org. Lett.* **2005**, *7*, 4943−4946. (c) Nolan, E. M.; Lippard, S. J. *J. Mater. Chem.* **2005**, *15*, 2778−2783. (d) Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Borsari, L.; Giorgi, C.; Valtancoli, B.; Lodeiro, C.; Lima, J. C.; Parola, A. J.; Pina, F. *Dalton Trans.* **2004**, *4*, 591−597. (e) Bianchi, A.; Berni, E.; Bencini, A.; Fornasari, P.; Giorgi, C.; Lima, J. C.; Lodeiro, C.; Melo, M. J.; Parola, A. J.; Pina, F.; Valtancoli, B. *Dalton Trans.* **2004**, *14*, 2180−2187.

(13) (a) Baumann, T. F., Reynolds, J. G., *Chem. Commun.* **1998**, *16*, 1637−1638. (b) Nelson, A. J., Reynolds, J. G., Baumann, T. F., Fox, G. A., *Appl. Surf. Sci.*, **2000**, *167*, 205−215. (c) Baumann, T. F.; Reynolds, J. G.; Fox, G. A. *React. Funct. Polym.* **2000**, *44*,111−120.

(14) (a) Tamayo, A.; Lodeiro, C.; Escriche, L.; Casabó, J.; Covelo, B.; González, P. *Inorg. Chem.* **2005**, *44*, 8105−8115. (b) Tamayo, A.; Casabó, J.; Escriche, L.; Lodeiro, C.; Covelo, B.; Brondino, C. D.; Kikevás, R.; Sillampää, R. *Inorg. Chem.* **2006**, *45*, 1140−1149. (c) Tamayo, A.; Escriche, L.; Casabó, J.; Covelo, B.; Lodeiro, C. *Eur. J. Inorg. Chem.* **2006**, *15*, 2997−3004.

(15) Sheldrick, G. M. *SHELXS97, A Program for the Solution of Crystal Structures from X-ray Data*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for $[HgCl_2(\mathbf{L2})]\cdot 1/2CH_2Cl_2$

Hg(1)		Hg(2)	
Hg(1)−N(11)	2.396(5)	Hg(2)−N(21)	2.569(5)
Hg(1)−Cl(12)	2.4135(16)	Hg(2)-Cl(22)	2.4249(18)
Hg(1)−Cl(11)	2.4856(17)	Hg(2)-Cl(21)	2.4438(17)
Hg(1)−S(12)	2.7476(17)	Hg(2)−S(22)	2.5915(17)
Hg(1)−S(11)	2.9321(17)	Hg(2)−S(21)	2.9945(18)
N(11)−Hg(1)−Cl(12)	153.95(13)	Cl(22)-Hg(2)-Cl(2)	114.31(7)
N(11)−Hg(1)−Cl(11)	88.73(12)	Cl(22)−Hg(2)−N(21)	143.67(14)
Cl(12)−Hg(1)−Cl(11)	117.28(6)	Cl(21)−Hg(2)−N(21)	87.85(12)
N(11)−Hg(1)−S(12)	73.88(14)	Cl(22)−Hg(2)−S(22)	110.46(7)
Cl(12)−Hg(1)−S(12)	97.59(6)	Cl(21)−Hg(2)−S(22)	125.92(6)
Cl(11)−Hg(1)−S(12)	102.48(5)	N(21)−Hg(2)−S(22)	72.59(13)
N(11)−Hg(1)−S(11)	70.36(13)	Cl(22)−Hg(2)−S(21)	81.98(6)
Cl(12)−Hg(1)−S(11)	95.33(5)	Cl(21)−Hg(2)−S(21)	94.38(6)
Cl(11)−Hg(1)−S(11)	120.49(6)	N(21)−Hg(2)−S(21)	67.28(13)
S(12)−Hg(1)−S(11)	121.95(5)	S(22)−Hg(2)−S(21)	120.81(5)

SHELXL97.[16] Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Special computations for the crystal structure discussions were carried out with *PLATON*.[17] Drawings were produced with *XP-SHELXTL*[18] and *Mercury*.[19] CCDC 298744 contains the supplementary crystallographic data for this article. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44−1223-336033.

Spectrophotometric and Spectrofluorimetric Measurements. Absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer and fluorescence emission on a Horiba-Jobin-Yvon SPEX Fluorolog 3.22 spectrofluorimeter at the Universidade Nova de Lisboa. The linearity of the fluorescence emission versus concentration was verified for the concentration range used (10^{-4}−10^{-6} M). A correction for the absorbed light was performed when necessary. The absorptions and fluorescence titrations were performed by adding microliter amounts of acetonitrile solutions of $Hg(ClO_4)_2\cdot 3H_2O$ to dichloromethane solutions of the corresponding ligand. $[\mathbf{L1}] = 4.33 \times 10^{-5}$ M; $[\mathbf{L2}] = 4.73 \times 10^{-5}$ M and $\lambda_{exc} = 368$ nm (or $[\mathbf{L2}] = 2.0 \times 10^{-5}$ M and $\lambda_{exc} = 388$ nm); $[\mathbf{L3}] = 4.59 \times 10^{-5}$ M, $[\mathbf{L4}] = 5.55 \times 10^{-5}$ M and $\lambda_{exc} = 376$ nm; $[\mathbf{L5}] = 5.50 \times 10^{-5}$ M and $\lambda_{exc} = 377$ nm; $[\mathbf{L6}] = 5.14 \times 10^{-5}$ M and $\lambda_{exc} = 368$ nm (or $[\mathbf{L6}] = 2.0 \times 10^{-5}$ M and $\lambda_{exc} = 385$ nm). Luminescence quantum yields were measured using a solution of sublimated anthracene in cyclohexane as a standard [$\Phi_F = 0.36$].[20]

Analytical Measurements. Mercury was determined in a Flow Injection System consisting of a four channel Gilson (Villiers le Bel, France) Minipuls 2 peristaltic pump, a four channel Ismatec (Glattbrugg, Switzerland) programmable peristaltic pump model Reglo Digital MS-4/12, a PerkinElmer (Uberlingen, Germany) membrane gas−liquid separator, a six-port injection valve (Supelco, Bellefonte, PA) with a 500 μl loop, and a Fisher and Porter (Warminster, PA) flow meter (0−100% N_2, 200 mL min^{-1}). Ismatec Tygon tubing type R3607 of different internal diameters (2.06 and 3.15 mm id) was used for carrying the reducing agent, carrier solution, and waste solution. The initial conditions for cold-vapor generation using $SnCl_2$ as a reducing agent were established in a previous work,[21] in which a 5% mass v^{-1} $SnCl_2$ solution in 10% v/v^{-1} HCl was used as a reducing stream with a 3 mL min^{-1} flow rate and a 3% v v^{-1} HCl solution was used as carrier with a 10 mL min^{-1} flow rate. A 200 mL min^{-1} flow-rate of carrier gas (N_2) was used. Mercury atomic absorbance was measured with a Thermo (Cambridge, U.K.) atomic absorption spectrometer model Solar S2 equipped with a homemade quartz tube. The quartz tube was kept at room temperature during operation. A mercury hollow-cathode lamp (Thermo) operated at 4 mA was used as a radiation source. The mercury line at 253.7 nm and a slit width of 0.5 nm were used for measurements. An inorganic mercury stock standard solution (Merck, Darmstat, Germany, 1 g l^{-1}) was used. All of the stock standard solutions were stored in a refrigerator at 4 °C and protected from light. Working standard solutions were prepared just before use by the appropriate dilution of the stock standard solution. Sn(II) chloride used as reducing agent was prepared by dissolving the appropriate mass of Sn(II) chloride dehydrated (Panreac: Barcelona, Spain) in concentrated hydrochloric acid and diluted with ultrapure water. Diluted hydrochloric acid (Merck) was used as a carrier.

$[Hg(\mathbf{L2})](ClO_4)_2$. A dichloromethane solution of **L2** (100 mg, 0.22 mmol, 4 mL) was added dropwise to an acetonitrile solution of $Hg(ClO_4)_2\cdot 3H_2O$ (87 mg, 0.22 mmol, 4 mL). The resulting solution was stirred at room temperature for 2 h, and the solvent was partially removed to ca. 3 mL. Diethyl ether was slowly infused into the solution, producing powdery precipitate, which was filtered off and washed with diethyl ether. Yield 150 mg (81%). Anal. Calcd for $C_{28}H_{30}N_2S_2O_8Cl_2Hg$: C, 39.19; H, 3.52; N, 3.26; S, 7.47. Found: C, 39.42; H, 3.70; N, 3.41; S, 7.31. ^1H NMR (250 MHz, DMSO-d_6): $\delta = 1.58$ (m, 4H, $-S-CH_2-C\mathit{H_2}-CH_2-N-$); 2.25 (m, 4H, $-S-C\mathit{H_2}-CH_2-CH_2-N-$); 2.40 (m, 4H, $-S-CH_2-CH_2-C\mathit{H_2}-N-$); 4.22 (s, 4H, $-Py-C\mathit{H_2}-S-$); 4.33 (s, 2H, $An-C\mathit{H_2}-N-$); 7.32 (m, 2H, $\mathit{An}-CH_2-N-$); 7.50 (m, 2H, $\mathit{An}-CH_2-N-$); 7.61 (d, $^3J_{H,\,H} = 7.67$ Hz, 2H, $-\mathit{Py}-CH_2-S-$); 8.05 (m, 2H, $\mathit{An}-CH_2-N-$); 8.15 (m, 2H, $\mathit{An}-CH_2-N-$); 7.65 (t, $^3J_{H,\,H} = 7.67$ Hz, 1H, $-\mathit{Py}-CH_2-S-$); 8.53 (s, 1H, $\mathit{An}-CH_2-N-$) ppm. $^{13}C\{^1H\}$ NMR (DMSO-d_6): $\delta = 26.66$ ($-S-CH_2-\mathit{C}H_2-CH_2-N-$); 29.22 ($-S-\mathit{C}H_2-CH_2-CH_2-N-$); 37.65 ($-Py-\mathit{C}H_2-S-$); 50.76 ($An-\mathit{C}H_2-N-$); 52.33 ($-S-CH_2-CH_2-\mathit{C}H_2-N-$); 124.51, 140.84, 162.61 ($-\mathit{Py}-CH_2-S-$); 125.00, 125.27, 125.80, 127.30, 128.89, 129.92, 130.55, 130.85 ($\mathit{An}-CH_2-N-$) ppm. Conductivity (CH_3CN, 1×10^{-3} M): 248 $\mu S\ cm^{-1}$. UV−vis (CH_2Cl_2) $\lambda = 338$ ($\epsilon = 3520$); 356 (5951); 374 (7930); 394 nm (6448 $M^{-1}\ cm^{-1}$). IR (KBr pellet): 3434, 3051, 2942, 1593, 1570, 1453, 1420, 1143, 1114, 1086, 1001, 896, 789, 738, 602 cm^{-1}.

$[HgCl_2(\mathbf{L2})]$. A dichloromethane solution of **L2** (100 mg, 0.22 mmol, 4 mL) was added dropwise to an ethanol solution of $HgCl_2$ (87 mg, 0.22 mmol, 4 mL). A beige precipitate formed while stirring overnight. The solid was vacuum-filtered and washed with diethyl ether to yield the complex as a beige solid (142 mg, 76%). Crystals suitable for X-ray diffraction with the formula $[HgCl_2(\mathbf{L2})]\cdot 1/2CH_2Cl_2$, were obtained by slow diffusion of diethyl ether into a dichloromethane solution. Anal. Calcd for $C_{28}H_{30}N_2S_2Cl_2Hg$: C, 46.06; H, 4.14; N, 3.83; S, 8.77. Found: C, 45.81; H, 3.94; N, 3.74; S, 8.51. ^1H NMR (250 MHz, DMSO-d_6): $\delta = 1.45$ (m, 4H, $-S-CH_2-C\mathit{H_2}-CH_2-N-$); 2.20 (m, 4H, $-S-C\mathit{H_2}-CH_2-CH_2-N-$); 2.40 (m, 4H, $-S-CH_2-CH_2-C\mathit{H_2}-N-$); 3.81 (s, 4H, $-Py-$

---

(16) Sheldrick, G. M. *SHELXL97, A Program for the Refinement of Crystal Structures from X-ray Data*; University of Göttingen, Göttingen, Germany, 1997.

(17) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2004.

(18) *XP in SHELTXL, Interactive Molecular Graphics. Version 5.1*; Bruker Analytical X-ray Systems: Madison, WI, 1998.

(19) *MERCURY 1.4.1. Software for Visualising Crystal Structures*; The Cambridge Crystallographic Data Centre: Cambridge, U.K., 2005.

(20) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971.

(21) Capelo, J. L.; Rivas, G. M.; Oliveira, L. G.; Vilhena, C.; Santos, A. C.; Valada, T.; Galesio, M.; Oliveira, P.; Gomes da Silva, M. D. R.; Gaspar, E. M.; Alves, S.; Fernandez, C.; Vaz, C. *Talanta.* **2006**, *68*, 813−818.

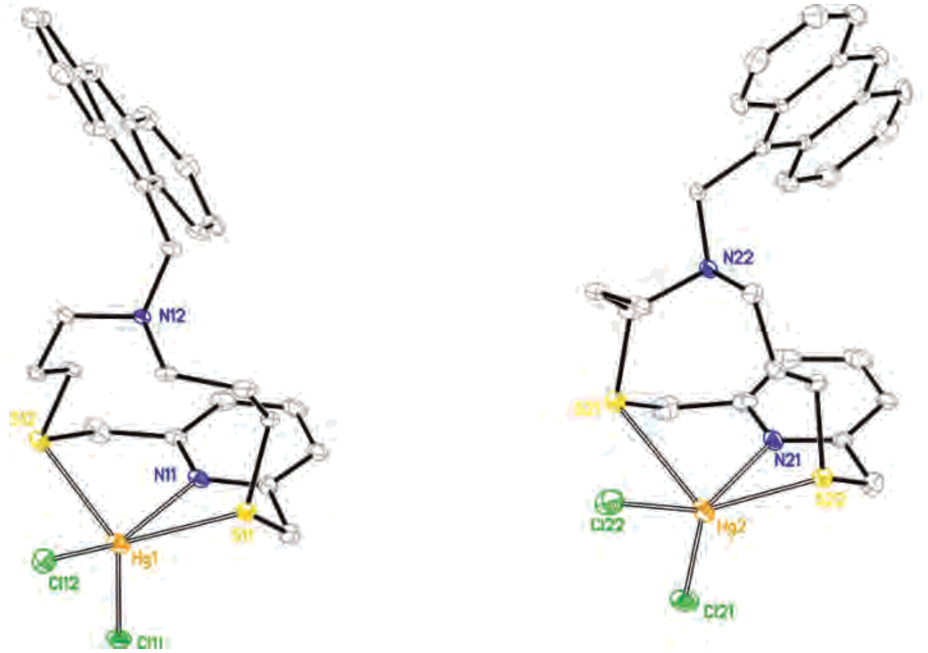


Figure 1. Displacement ellipsoid representation of the two independent molecules of complex [$HgCl_2$(**L2**)]·1/2CH_2Cl_2 with the atom-numbering scheme adopted. Hydrogen atoms and dichloromethane molecules are omitted for clarity. Ellipsoids are drawn at 30% probability level.

CH_2−S−); 4.36 (s, 2H, An−CH_2−N−); 7.33 (d, $^3J_{H,\ H} = 7.15$ Hz, 2H, −*Py*−CH_2−S−); 7.44 (m, 4H, *An*−CH_2−N−); 7.86 (t, $^3J_{H,\ H} = 7.15$ Hz, 1H, −*Py*−CH_2−S−); 8.04 (d, 2H, *An*−CH_2−N−); 8.30 (d, 2H, *An*−CH_2−N−); 8.52 (s, 1H, *An*−CH_2−N−) ppm. $^{13}C\{^1H\}$ NMR (DMSO-d_6): $\delta = 27.95$ (−S−CH_2−CH_2−CH_2−N−); 29.85 (−S−CH_2−CH_2−CH_2−N−); 37.75 (−Py−CH_2−S−); 51.90 (An−CH_2−N−); 53.89 (−S−CH_2−CH_2−CH_2−N−); 122.93, 139.10, 158.04 (−*Py*−CH_2−S−); 125.64, 125.79, 125.33, 126.48, 127.95, 129.62, 131.10, 131.51, 131.70 (*An*−CH_2−N−) ppm. Conductivity (Acetone, 1×10^{-3} M): 11 μS cm^{-1}. IR (KBr pellet): 3456, 3061, 2922, 2851, 2786, 1575, 1454, 1231, 1090, 888, 804, 726 cm^{-1}.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great caution.

Results and Discussion

Synthesis of Hg(II) Complexes. The complexation reactions between **L2** and 1 equiv of $Hg(ClO_4)_2$ or $HgCl_2$ yielded microcrystalline solids whose elemental analyses fit the formulas Hg(**L2**)$(ClO_4)_2$ and Hg(**L2**)$(Cl)_2$, respectively. The conductimetry measurements, performed in acetonitrile solution, show that the perchlorate-containing compound behaves as a 2:1 electrolyte. This data indicates that, at least in solution, no perchlorate ion is coordinated to the Hg(II) centers and suggest that this complex should be formulated as [Hg(**L2**)]$(ClO_4)_2$. On the other hand, the chloride-containing compound behaves as a nonelectrolyte in acetone solution, which reveals the existence of strong interactions between chloride and metal ions, and therefore, this complex should be formulated as [$HgCl_2$(**L2**)]. These bonds between chloride ions and Hg(II) centers, would be responsible for the differences between the ^{1}H NMR spectra of both Hg(II) complexes. For instance, the ^{1}H NMR chemical shift of the methylene group −Py−CH_2−S− is more downfield shifted in [Hg(**L2**)]$(ClO_4)_2$ than in [$HgCl_2$(**L2**)],[22] which could be attributed to different shielding effects caused by the Hg^{2+} and $HgCl_2$ cores of the [Hg(**L2**)]$^{2+}$ and [$HgCl_2$(**L2**)] complexes, respectively. The existence of such $HgCl_2$ cores in [$HgCl_2$(**L2**)] was also confirmed by single-crystal X-ray diffraction analysis.

Figures 1 and Table 1 show a displacement ellipsoid representation and selected bond lengths and angles of complex [$HgCl_2$(**L2**)]·1/2CH_2Cl_2. The asymmetric unit contains two closely related [$HgCl_2$(**L2**)] units and one dichloromethane molecule. Both Hg(II) ions are coordinated by the pyridine nitrogen atom, the two sulfur atoms of a macrocyclic ligand, and two chloride ions. These five donor atoms make up a highly distorted square-based pyramid around the Hg(II) centers. The values of the angular parameter of trigonal distortion are 0.53 for Hg(1) and 0.30 for Hg(2), which indicate that the coordination geometry around Hg(2) is closer to a square pyramid than that for Hg(1).[23] In no cases was the amine nitrogen atom of **L2** is bonded to the metal ion, and this macrocyclic ligand adopts a folded conformation. The Hg−N_{py} bond lengths (2.396(5) and 2.569(5) Å for Hg(1) and Hg(2), respectively) are close to the average distance obtained from the Cambridge Structural Database (CSD) for pentacoordinated Hg(II) complexes with Hg−N_{py} moieties.[24] Although the four Hg−S bond lengths (2.7476(17)and 2.9321(17) for Hg(1), and 2.5915(17) and 2.99545(18) Å for Hg(2)) lie within the range

---

[22] The ^{1}H NMR chemical shift of the −Py−CH_2−S− methylene group is 3.76 ppm for **L2**, 4.22 ppm for [Hg(**L2**)]$(ClO_4)_2$, and 3.81 ppm for [$HgCl_2$(**L2**)].

[23] The value of the angular parameter of trigonal distortion τ ranges from 0 for a perfect square pyramid to 1 for a perfect trigonal bipyramid. Addison, A. W.; Rao, T. N.; Reedjik, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, *7*, 1349−1356.

[24] References and analyses of crystallographic data can be found in the Supporting Information.

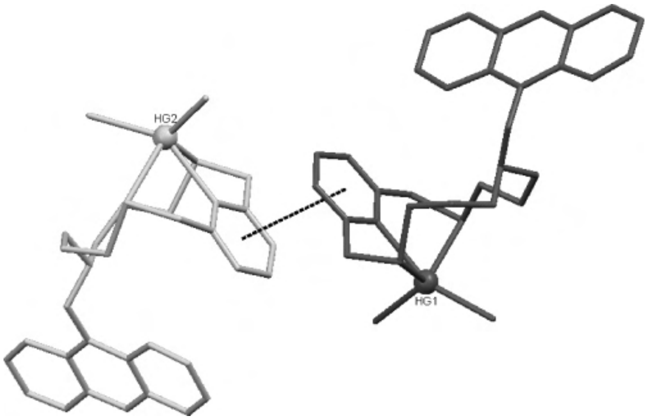


Figure 2. View of the supramolecular dimers of [$HgCl_2$(**L2**)] generated by $\pi\cdots\pi$ interactions.

found for thioether-containing Hg(II) complexes; two of them are slightly larger than the average distance found for such related complexes.[24] The four Hg−Cl distances, which range from 2.4135 to 2.4856 Å, do not significantly differ from the most common distance found for other pentacoordinated Hg(II) complexes (2.438 Å).[24] The nature of the macrocyclic ligand allows the formation of supramolecular architectures based on $\pi\cdots\pi$[25] and C−H$\cdots\pi$[26] interactions. The $\pi\cdots\pi$ interactions involving the pyridine rings (d[Cg$\cdots$Cg] = 3.700 Å, dihedral angle $\alpha = 3.64°$) join two macrocyclic complexes to form supramolecular dimers (Figure 2). The C−H$\cdots\pi$ interactions among the anthracene moieties create polymeric chains (Figure 3) whose Cg$\cdots$H distances range from 2.6485 to 3.0145 Å. Nonclassical hydrogen bonds C−H$\cdots$Cl involving the dichloromethane solvate molecule join these chains to form a 3D supramolecular network.

It is important to note that, although numerous structures of Hg(II) complexes have already been reported, the structure of [$HgCl_2$(**L2**)]·1/2CH_2Cl_2 is the fourth one in which a Hg(II) ion is coordinated by a NS_2Cl_2 donor set.

Spectrophotometric and Spectrofluorometric Studies: Hg(II) Titrations. Aliphatic amines closely bonded to fluorophore moieties are involved in the electron-transfer quenching, which makes it possible to signal the presence of metal cations in polyamine systems. The stronger the involvement of these nitrogen atoms in the complexation, the stronger the effect on the luminescence of the ligand.[27] Metal ions coordinated to such nitrogen atoms prevent photoinduced electron transfer (PET) quenching from the lone pair of electrons of each nitrogen atom to the fluorophore moieties. It was reported that d^{10} transition-metal ions such as Cd(II), Ag(I), Cu(I), or Zn(II) enhance the fluorescence of this kind of ligands because these ions usually do not introduce low-energy metal centered or charge-separated excited states into the molecules, so that the electron-transfer or energy-transfer phenomena cannot usually occur. Although Hg(II) is a d^{10} ion, and as such, it could be expected that it would enhance the fluorescence of these ligands, Hg(II) usually quenches the fluorescence emission via the enhancement of spin−orbit coupling due to heavy-atom effects.[28] As a consequence, most of the systems reported for the detection of Hg(II) are based on CHEQ effects.

Strong changes in the absorption and emission spectra of dichloromethane solutions of **L1**−**L6** were observed upon addition of Hg(II) salts. Figure 4 shows the absorption titrations of the anthracene-containing macrocycles **L2**, **L3**, **L4**, and **L6** with $Hg(ClO_4)_2$·$3H_2O$. In all of the titrations, the addition of the metal ion causes a red shift of the anthracene band and the apparition of a new band around 300 nm. The changes of the anthracene band are attributed to interactions between the metal ion and the aliphatic nitrogen,[14a] whereas the changes around 300 nm are attributed to the involvement of the sulfur atoms in the coordination.[14c] In addition, in those pyridine-containing macrocycles (**L2**, **L3**, and **L4**), the changes around 300 nm could be also attributed to the involvement of the pyridine moieties in the complexation.[29] The insets of Figure 4 show that these changes occur until the addition of 1 equiv of metal ion for **L1**, **L3**, and **L6**, and 2 equiv for **L4**. These data suggest that each macrocyclic moiety is coordinated to one metal center, and therefore, each molecule of **L4** is simultaneously coordinated to two metal ions. Both macrocyclic units of **L4** probably behave as independent binding units because the mobility provided by the 9,10-dimethylanthracene linker allows **L4** to adopt conformations in which the two binding units are considerably distant from each other. New bands around 280 nm appear as a consequence of Hg(II) addition over dichloromethane solutions of **L1** and **L5**. In both cases, a plateau is reached after the addition of 1 equiv of metal ion.

Figure 5 shows the fluorescence titrations of **L2** and **L6** with $Hg(ClO_4)_2$·$3H_2O$. Although initial additions of metal ion increase the fluorescence of the ligand, supplementary additions cause a partial quenching of the fluorescence. As stated before, the addition of Hg(II) is expected to quench the fluorescence emission via the enhancement of spin−orbit coupling, so the initial increase of the fluorescence observed in both fluorescence titrations was certainly an unexpected behavior. These increases could be explained by the protonation of small amounts of the ligands because the protonation of their aliphatic amines prevents PET from their nitrogen atoms to the anthracene moieties, which significantly increases the fluorescence of the species.[30] Such protonations are probably due to the presence of water in the metal-ion solutions, which act as an acid.[31] To verify this hypothesis,

---

(25) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, *21*, 3885−3896.

(26) Nishio, M. *Cryst. Eng. Comm.* 2004, **6**, 130−158.

(27) (a) Albelda, M. T.; Díaz, P.; García-España, E.; Lima, J. C.; Lodeiro, C.; de Melo, J. S.; Parola, A. J.; Pina, F.; Soriano, C. *Chem. Phys. Lett.* **2002**, *353*, 63−68. (b) de Melo, J. S.; Pina, J.; Pina, F.; Lodeiro, C.; Parola, A. J.; Lima, J. C.; Albelda, M. T.; Clares, M. P.; García-España, E.; Soriano, C. *J. Phys. Chem. A* **2003**, *107*, 11307−11318.

(28) (a) McClure, D. S. *J. Chem. Phys.* **1952**, *20*, 682−689. (b) Burress, C. N.; Bodine, M. I.; Elbjeirami, O.; Reibenspies, J. H.; Omary, M. A.; Gabbaie, F. P. *Inorg. Chem.* **2007**, *46*, 1388−1395.

(29) (a) Cao, Z.; Zhang, Q.; Peyerimhoff, S. D. *Chem.*−*Eur. J.* **2001**, *7*, 1927−1935. (b) Aucejo, R.; Alarcon, J.; Garcia-España, E.; Llinares, J. M.; Marchin, K. L.; Soriano, C.; Lodeiro, C.; Bernardo, M. A.; Pina, F.; Pina, J.; Seixas de Melo, J. *Eur. J. Inorg. Chem.* **2005**, *21*, 4301−4308.

(30) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3−40.

(31) These protonation processes were also observed when ligands **L2**, **L3**, **L4**, and **L6** were titrated with Pd(II), Cu(II), Ni(II), and Co(II).

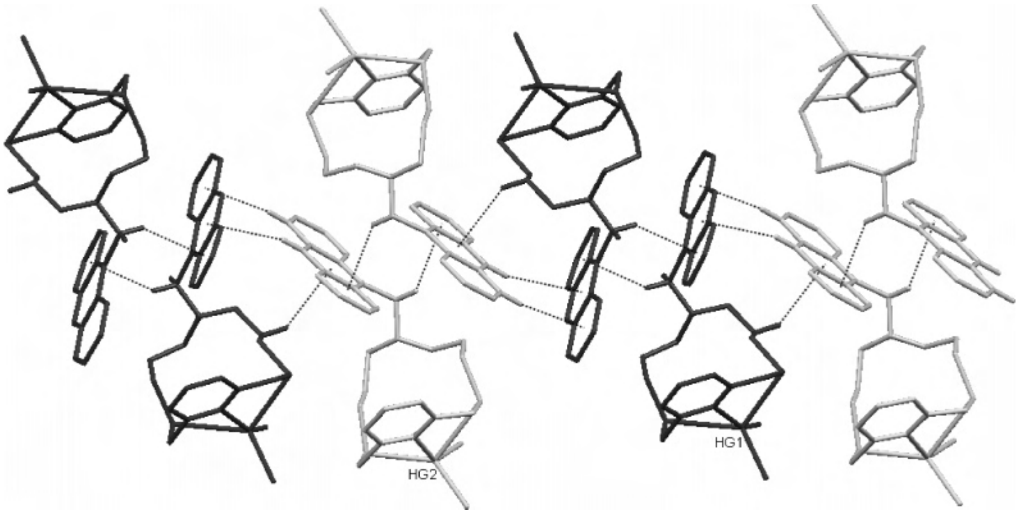


Figure 3. View of the 1D network of [HgCl$_2$(**L2**)] obtained by C−H···π interactions.

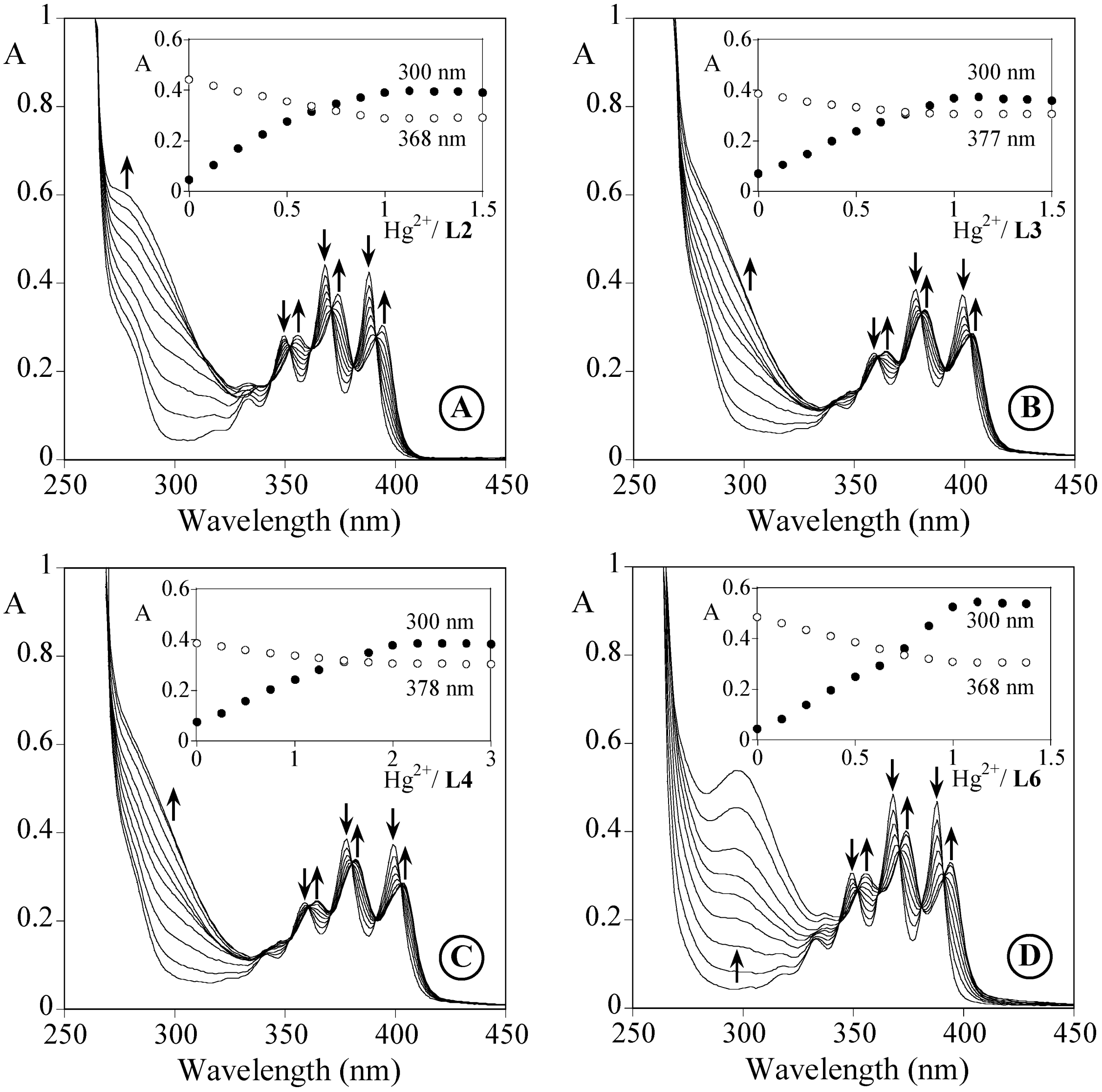


Figure 4. Absorption spectra of dichloromethane solutions of **L2** (**A**), **L3** (**B**), **L4** (**C**), and **L6** (**D**) as a function of added Hg(ClO$_4$)$_2$·3H$_2$O. The insets show the absorbances at 300 and 368 nm for **L2** and **L6**, 300 and 277 nm for **L4**, and 300 and 378 nm for **L4**. [**L2**] = 4.73 × 10^{-5} M, [**L3**] = 4.59 × 10^{-5} M, [**L4**] = 5.55 × 10^{-5} M, [**L6**] = 5.14 × 10^{-5} M.

the emission spectra of **L2**H$^+$ and **L6**H$^+$ in the presence/absence of 1 equiv of Hg(II) were also recorded (Figure 6).

As could be seen in Figure 6 and in Table 3, the addition of Hg(II) to dichloromethane solutions of **L2**H$^+$ or **L6**H$^+$

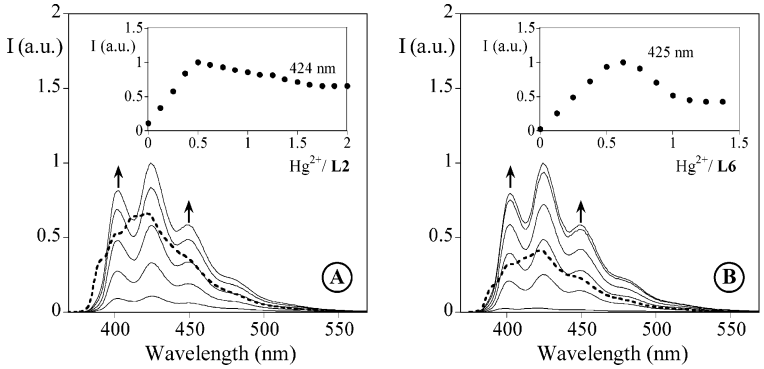


Figure 5. Emission spectra of dichloromethane solutions of **L2** (**A**) and **L6** (**B**) as a function of increasing amounts of $Hg(ClO_4)_2 \cdot 3H_2O$. The insets show the normalized fluorescence intensity at 424 nm for **L2** and 425 nm for **L6**. [**L2**] = 4.73 × 10^{-5} M, λ_{exc} = 368 nm; [**L6**] = 5.14 × 10^{-5} M, λ_{exc} = 368 nm.

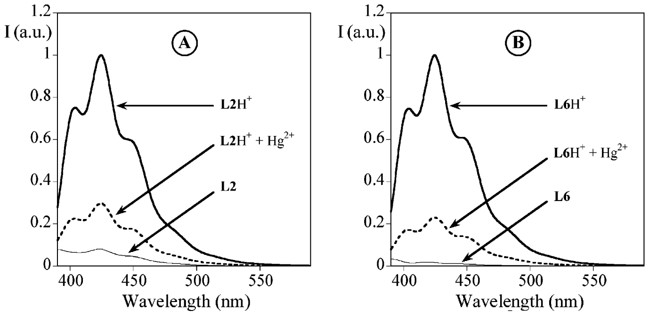


Figure 6. Emission spectra of dichloromethane solutions of **L2** (**A**) and **L6** (B) in their free (solid lines) and monoprotonated forms (bold lines). The dashed lines represent the emission spectra obtained after adding 1 equiv of $Hg(ClO_4)_2 \cdot 3H_2O$ to dichoromethane solutions of the protonated ligands. [**L2**] = 2.0 × 10^{-5} M, λ_{exc} = 388 nm. [**L6**] = 2.0 × 10^{-5} M, λ_{exc} = 385 nm.

Table 3. Quantum Yields in Dichloromethane at 298 K

	F
L2	0.027[a]
L2 + $1H^+$	0.394[a]
L2 + $1Hg^{2+}$	0.060
L2 + $1H^+$ + $1Hg^{2+}$	0.094
L3	0.064[a]
L3 + $1H^+$	0.459[a]
L3 + $1Hg^{2+}$	0.128
L3 + $1H^+$ + $1Hg^{2+}$	0.164
L4	0.018[a]
L4 + $2H^+$	0.458[a]
L4 + $2Hg^{2+}$	0.042
L4 + $2H^+$ + $2Hg^{2+}$	0.097
L6	0.010[b]
L6 + $1H^+$	0.341[b]
L6 + $1Hg^{2+}$	0.045
L6 + $1H^+$ + $1Hg^{2+}$	0.109

[a] From ref 14a. [b] from ref 14c.

leads to significant quenching of the fluorescence intensity. These results are in agreement with the simultaneous presence of protonated and complexed species in the early stages of the titration of **L2** and **L6** with $Hg(ClO_4)_2$ and with the increase of the complexed/protonated ratio in the last stages of such titrations, which indicates that the Hg(II) ions can replace the protons of the protonated forms of **L2** and **L6**.

It is important to note that, although the protonation processes were clearly observed in the fluorescence titrations of **L2**−**L4** and **L6** with Hg(II), these processes were not easily observed in the analogous absorption titrations. This is attributed to the fact that the protonation of small amounts of the ligands produces strong changes in their fluorescence spectra because the increase of the fluorescence intensity due to the protonated species is considerably greater than the decrease of the fluorescence intensity due to the complexated ones. On the contrary, the protonation of small amounts of the ligands does not produce strong changes on their absorption spectra, and therefore the absorption spectra of the protonated and complexated species are not different enough to allow the observation of both kinds of species. Such differences between the absorption spectra of protonated and complexated species can be evaluated by comparing the absorption spectra of the dichloromethane solutions of the ligands as a function of added H^+ (Figures S1−S4 of the Supporting Information) with those as a function of added Hg(II) (Figure 4).

To perform a speciation study between organic and inorganic mercury, the same experiments were carried out using the organic derivates methyl mercury chloride and phenyl mercury chloride. Taking ligands **L2**, **L3**, and **L6** as examples, no significant modifications of the absorption and emission spectra were observed. The lack of complexation could be attributed to steric hindrance of the cavities of the 14-membered macrocycles, which are unable to encapsulate those metal centers directly bonded to phenyl rings or methyl units.

Hg(II) Extraction. Extraction experiments were performed to assess the capability of ligands **L1**, **L2**, and **L5** to remove mercury from aqueous solution. These ligands were dissolved in dichloromethane to a concentration of 1 × 10^{-5} M. Then, 2.5 mL of these solutions were mixed with 2.5 mL of aqueous solutions containing 4 × 10^{-7} M of Hg(II). All of the aqueous solutions were buffered with universal buffer to pH 2−10. Blanks were performed in triplicate at each pH. The mixtures were shaken in a vortex for 5 min. Finally, 0.5 mL of the aqueous phases was used for mercury determination. As can be seen in Figure 7, only ligand **L2** was able to effectively remove Hg(II) from aqueous solution. Because ligands **L1** and **L5** are more hydrophilic than the anthracene derivative **L2**, their mercury complexes are presumably more water-soluble than those of **L2**. This argument is in agreement with the larger mercury-removal capacity of **L2**.

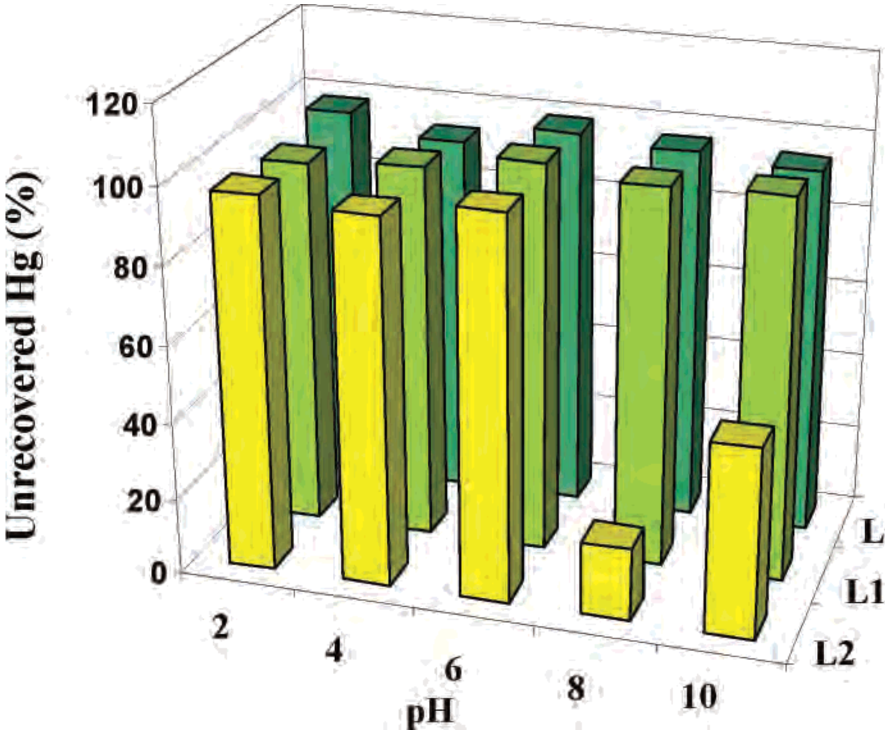
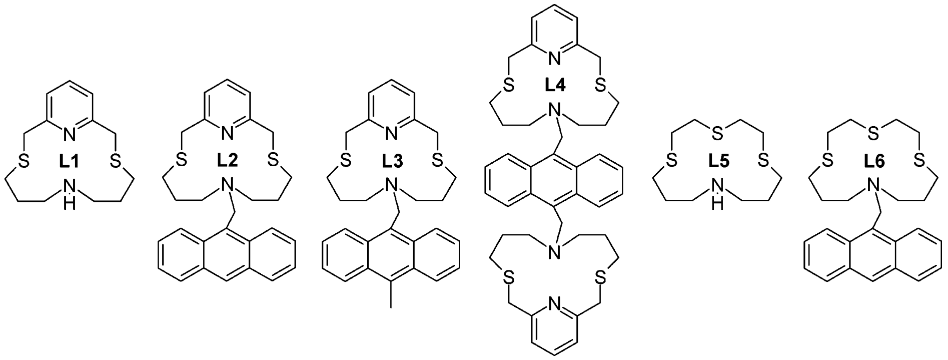


Figure 7. Unrecovered Hg(II) remaining in aqueous phase after treatment with dichloromethane solutions of **L1**, **L2**, and **L5** at different pH values.

Scheme 1



The extraction capability of **L2** has been shown to be pH-dependent. At pH 2−4, mercury extraction from the aqueous solution to the organic phase was unsuccessful. However, the extraction capability is quite high at pH 8 (81%, $n = 3$), although it decreases to 51% as the pH is increased to 10. This narrow extraction range is constrained by two pH-dependent processes, which avoid the extraction of Hg(II). The first one (at low pH values), is associated with the protonation of **L2**, which decreases its coordinating properties and increases its solubility in water. The second one (at high pH values), is associated with the formation of hydroxide-containing species, which prevents mercury extraction to the organic phase.

Preliminary analytical Hg(II) extractions have been also performed in the presence of Na(I) and Ca(II) ions. In both cases, any of these metal ions changes the observed and reported results. On the basis of our results with ligand **L2**, we could postulate that this system is sensitive to Hg(II) at pH 8, but taking into account the results previously published using the same receptor,[14a] we could conclude that this ligand is not, at least in these conditions, selective for Hg(II).

Conclusions

Two new Hg(II) complexes containing ligand 7-(9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene (**L2**) have been successfully synthesized and characterized. Single-crystal X-ray structural data for [$HgCl_2$(**L2**)]·1/2CH_2Cl_2 show two different complex molecules in which a mercury center is coordinated to two chloride ions, the pyridine nitrogen, and both thioether sulfur atoms of one **L2** molecule. This structure is the fourth one in which a mercury center is coordinated by a NS_2Cl_2 donor set.

The addition of $Hg(ClO_4)_2·3H_2O$ to dichloromethane solutions of **L2**, **L3**, **L4**, and **L6** simultaneously produces protonation and complexation processes. As observed in the fluorescence titrations of **L2** and **L6** with Hg(II), initial additions of metal ion increase the fluorescence of the ligand as a result of its partial protonation. In spite of that, later additions decrease the fluorescence intensity as a result of metal complexation, which suggests that Hg(II) ions can efficiently remove the protons from the protonated molecules to yield complexed species. The emission spectra recorded after the addition of Hg(II) to solutions of **L2**H$^+$ and **L6**H$^+$ confirmed this hypothesis.

The capability of ligands **L1**, **L2**, and **L5** to remove mercury from aqueous solution has been explored. **L2** has been proven to be able to effectively remove Hg(II) by shaking equal amounts of a dichloromethane solution of this ligand with a mercury-containing water solution. The extraction capability of **L2** is pH-dependent, being maximal between pH 8 and 10.

Acknowledgment. This work was supported by the Spanish Government (CYCIT) under project CTQ2004-04134 and by the Catalan Government (DURSI) via Grant FI2002-00320 (A.T.). Financial support by the Fundação para a Ciência e Tecnologia (Portugal) and FEDER (project POCI/QUI/55519/2004) is also acknowledged. B.P. acknowledges the Ph.D. grant given by the FCT (Science and Technical Foundation) from Portugal (SFRH/BD/27786/2006).

Supporting Information Available: X-ray crystallographic data in CIF format for [HgCl$_2$(**L2**)]·1/2CH$_2$Cl$_2$. CSD searches for pentacoordinated Hg(II) complexes with Hg−N$_{\text{(pyridine)}}$, Hg−S$_{\text{(thioether)}}$, or Hg−Cl bonds and for Hg(II) centers coordinated by NS$_2$-Cl$_2$ donor sets. Absorption spectra of dichloromethane solutions of **L2**−**L4** and **L6** as a function of added H$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700489E