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Macrocyclization of cyclic thiosemicarbazones with mercury salts

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Abstract—A new cyclic Schiff base L^1H_3 derived from benzil and thiosemicarbazide has been prepared in the presence of $NaBH_4$. Reactions of the new molecule and the cyclic 5-methoxy-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]triazine-3-thione L^2H_2 with mercury chloride and nitrate are reported. Complexes of 1:2 stoichiometry are obtained from L^1H_3, but the reactions from L^2H_2 yield complexes of the macrocyclic Schiff base 5,6,11,12-tetraphenyl-1,2,4,7,8,10-hexaaza-cyclododeca-4,6,10,12-tetraene-3,9-dithione L^3H_2, which indicates the macrocyclization of L^2H_2. A mechanism for the cyclization reaction based on the rupture of the C–N single bond in L^2H_2 is proposed. The electrochemical results of complex L^3Hg makes it and its precursors, L^2H_2 and L^3H_2, outstanding candidates for mercury determination by appropriate electrode modification. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Schiff base macroligands derived from thiosemicarbazide and their complexes are of significant interest for their pharmacological properties as antibacterial and anticancer agents.[1–8] Macrocyclic ligands allow selective complexation and extraction of metallic cations and anions of environmental importance.[9–12] In particular, the accidental liberation of mercury in the environment poses dreadful toxicity problems, but only recent studies have considered the reactivity of macroligands containing sulfur to entrap this metal.[13–18]

In the last few years, a great deal of research has been aimed to design compounds highly selective and sensitive to heavy metal ions, in order to detect, and if possible, remove them. Among the many different strategies proposed, the preparation of electrochemical and fluorescent sensors should be highlighted.[19–21]

The number and relative position of the donor atoms and the cavity size in macrocyclic compounds confer these molecules with special reactivity. From specific dicarbonyl and diamine precursors, the structure of the condensation product can be conditioned by controlling the reaction conditions. Thus, [1+1], [1+2] and [2+2] condensation products, open chain and cyclic structures can be obtained by selecting the appropriate solvent, pH, temperature and the presence of metal ions. Metal salts have been used as templates to yield macrocyclic Schiff bases from diamine and dicarbonyl precursors.[22,23] In these cases the size of the metal, its charge, acidic character and favorable geometries have to be considered.

In previous papers, we have reported the preparation of several macroligands derived from thiosemicarbazide and benzil.[24,25] The obtained results showed the importance of the reaction conditions to get different condensation products: open chain, cyclic L^2H_2 and macrocyclic L^3H_2 compounds. We have also studied their complexation reactions with transition metals ions, in order to know the structural features of the formed complexes and their potential use in determination of metals.[26–29] Some of the studied copper complexes have been used for the preparation of sensitive potentiometric sensors for this metal.[30] The aim of this work is to get hydrogenated molecules from the same precursors, which would permit to obtain new ligands with functionalized pendant arms by subsequent reactions, and to study the interaction of the obtained new molecules and the previously published [1+1] and [2+2] condensation products,[25,27] (see Scheme 1) with mercury chloride and nitrate to determine their conduct towards this toxic metal. The compounds have been characterized by elemental analysis, mass spectrometry, IR and ^1H and ^{13}C NMR spectroscopy. We also explored the electrochemical behavior of the complexes by cyclic voltammetry in order to check their potentiality as sensors for mercury.

Keywords: thiosemicarbazones; mercury complexes; nitrogen macrocycles; templates.

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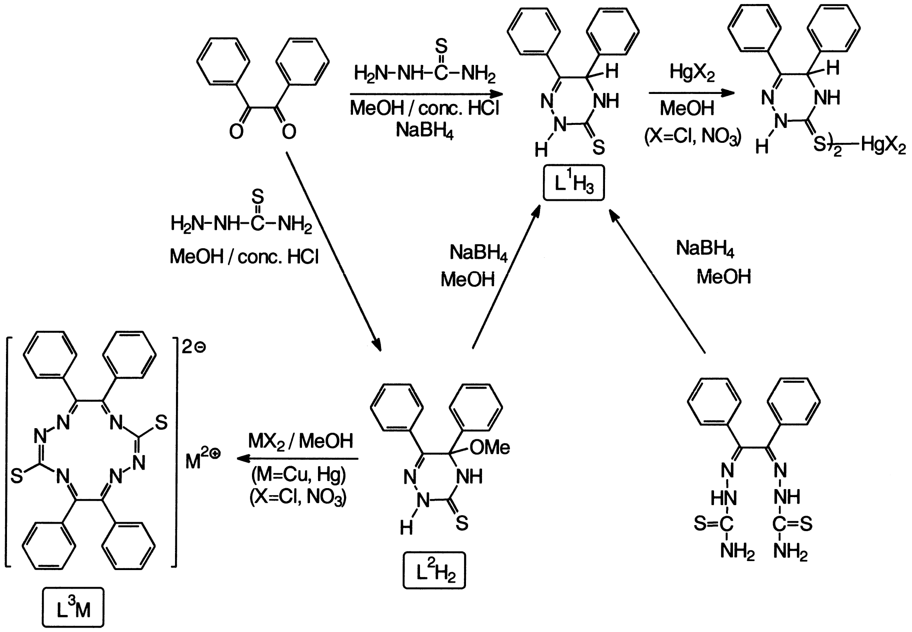


Scheme 1. Reaction of benzil and thiosemicarbazide studied in this work.

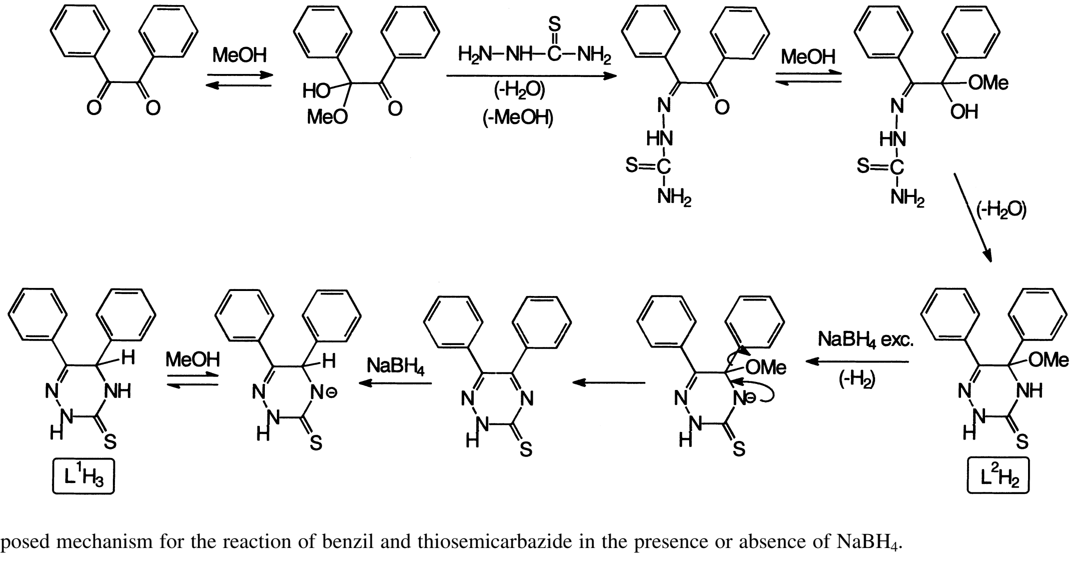
2. Results and discussion

The reactions of benzil with thiosemicarbazide in various conditions are summarized in Scheme 1. Compounds L^1H_3 and L^2H_2 were obtained in the presence or absence of $NaBH_4$, respectively. Compound L^2H_2 was easily transformed into L^1H_3 with $NaBH_4$. The latter compound was also obtained in low yield by $NaBH_4$ reduction of benzilbisthiosemicarbazone (Scheme 1). All analytical data are in agreement with the proposed structures for L^1H_3 and L^2H_2 (see Section 4).

All attempts to reduce the remaining imine group present in L^2H_2 and in the new L^1H_3 resulted unsuccessful in our hands.

A plausible mechanism for the formation of L^1H_3 and L^2H_2 is outlined in Scheme 2. Benzil dissolved in MeOH in acidic medium should be in equilibrium with the various possible ketal and hemiacetal forms, which react with thiosemicarbazide to form benzilthiosemicarbazone. The latter should be also in equilibrium with the hemiacetalic form whose intramolecular reaction leads to L^2H_2. In the absence of $NaBH_4$ the reaction ends here. But its presence induces the loss of MeOH, probably due to acid–base reaction with the relatively highly acidic NH bond. The elimination of MeOH, which has also been observed when L^2H_2 was treated with strongly basic organometallic compounds (MeHgCl or Me_2SnCl_2), led to the formation of a strongly electrophilic double bond that was easily reduced in situ by $NaBH_4$. The electron-donor effect of the NH makes the remaining C=N bond much less electrophilic and unable to react with $NaBH_4$.

Complexation of L^1H_3 with mercury(II) chloride or nitrate gave the corresponding complexes of metal/organic-ligand



Scheme 2. Proposed mechanism for the reaction of benzil and thiosemicarbazide in the presence or absence of $NaBH_4$.

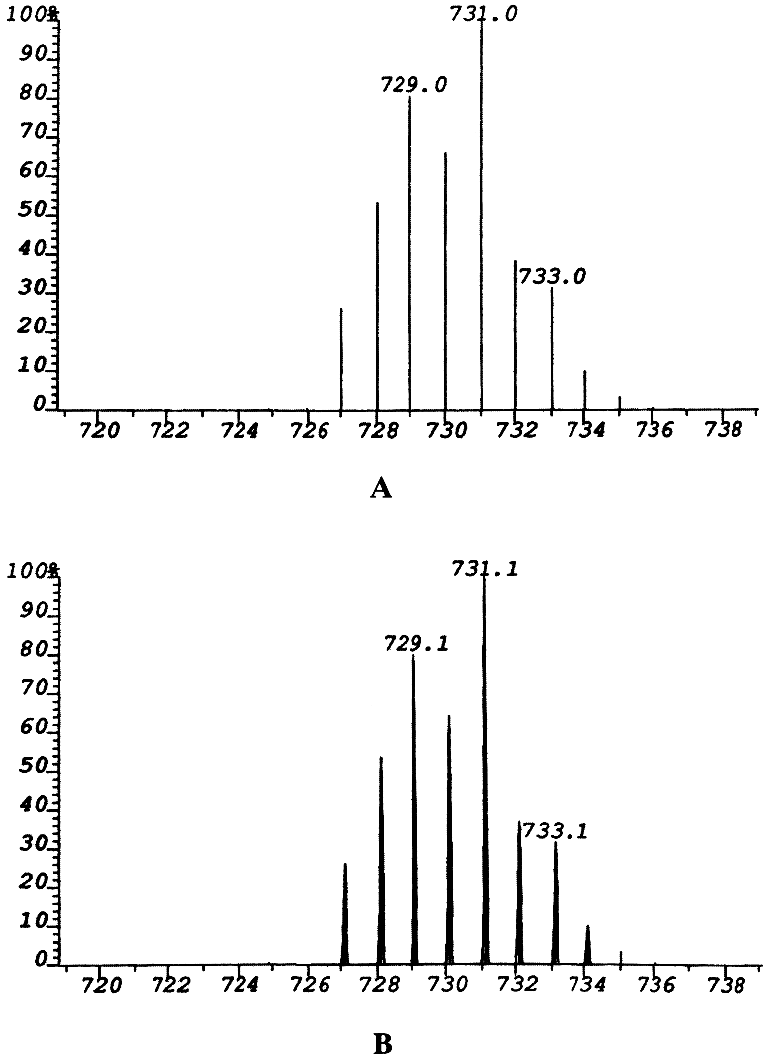


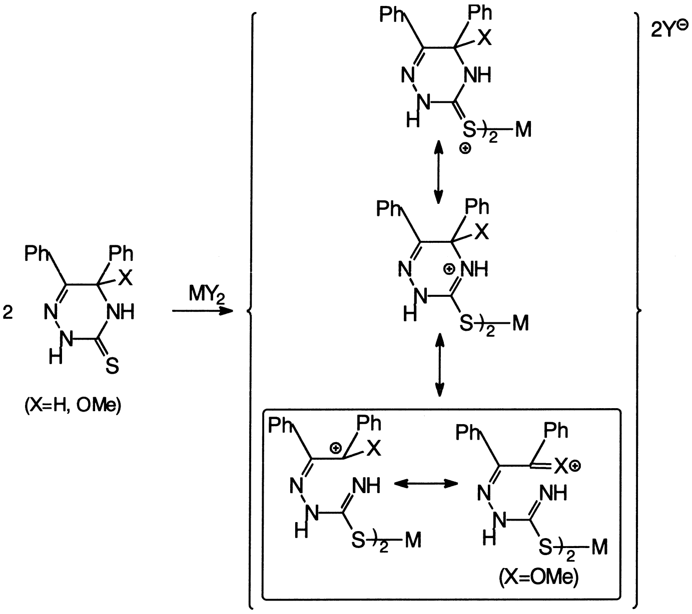
Figure 1. Experimental (trace A; FAB+) and theoretical (trace B) mass spectrum of L^3Hg with enlarged isotope distribution.

1:2 stoichiometry. Their mass spectra show two peaks at 735.5 and 268 amu, which correspond to the $C_{30}H_{25}N_6S_2Hg$ fragment and to the molecular ion of L^1H_3, respectively. These data and the fact that conductivity measurements in DMF agree with the complexes as being non-electrolytes indicate that L^1H_3 is not modified by complexation, acts as a neutral ligand and that chloride and nitrate ions are bonded to the mercury atom.

The IR spectrum of $[Hg(L^1H_3)_2(NO_3)_2]$ shows poorly resolved bands for the amine stretching vibrations shifted to lower frequency, which suggests hydrogen bonding between the molecules of the ligand in the complex. The bands assigned to the thioamide I, and specially those to the thioamide IV, have been shifted. This indicates that the sulfur atom is bonded to the metal ion, each L^1H_3 ligand acting as monodentate, with the mercury coordination sphere completed by the nitrate anions. IR spectrum of the chloride complex shows similar modifications with respect to the free ligand, implying a similar coordination pattern for the mercury ion. Therefore, it can be assumed that in these complexes the mercury is in a pseudo-tetrahedral environment, with two chloride ions and two organic ligands bonded to the metal ion. The shift to higher field observed for the thione carbon atom in the ^{13}C NMR spectra of both complexes agrees with the coordination of the ligand to the metal by the sulfur atom.[14,31]

We also studied the reactions of L^2H_2 with mercury chloride and nitrate in order to compare its reactivity with the new cyclic L^1H_3. The reaction with $Hg(NO_3)_2$ or $HgCl_2$ gives a mercury complex, whose mass spectrum shows peaks at 731 and 530 amu, corresponding to the $C_{30}H_{21}N_6S_2Hg$ and $C_{30}H_{22}N_6S_2$ species, respectively (Fig. 1). These data suggest that the ligand does modify its structure when complexing with mercury. On the other hand, ^1H NMR spectrum of this complex shows the absence of both amine nitrogens and OMe group thus indicating the loss of the methoxy group and the secondary amine hydrogens. ^{13}C NMR spectrum confirms the absence of the methoxy group and the presence of two imine carbons. IR spectra show the absence of both amine and nitrate ion vibrations, the shift to lower frequencies suffered by the thioamide I and IV bands, and the presence of absorptions corresponding to two imine groups.

All this evidence points to the formation of the L^3Hg macrocycle shown in Scheme 1. Therefore, in contrast to L^1H_3, the



Scheme 3. Behavior of ligands L^1H_3 and L^2H_2 in the presence of Hg(II) (see text).

coordination of L^2H_2 with mercury(II) led to a macrocyclization process, which yields a complex of the macrocycle L^3H_2 acting as a bidentate anion ligand by loss of the amine secondary hydrogens. Last but not least, we have studied the reaction of L^3H_2, previously isolated from the reaction between L^2H_2 and copper(II) chloride, with mercury nitrate. The reaction yields a solid, whose IR, mass and NMR spectra are totally coincident with those obtained from the complex isolated from the reaction of L^2H_2 with mercury nitrate. This, in our belief, confirms the macrocyclization reaction.

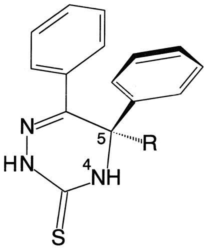


Figure 2. Calculated structures (AM1 semiempirical method) of ligands L^1H_3 and L^2H_2 (see text).

Concerning its mechanism, it may be assumed that both L^1H_3 and L^2H_2 form in a first step a complex by means of sulfur coordination as shown in Scheme 3. The positive charge developed in this atom should be delocalized through the nitrogens, but in the case of L^2H_2, the presence of the methoxy group should weaken the C–N bond as the hyperconjugative resonance forms of Scheme 3 suggest.

The results of AM1 semiempirical calculations on these molecules support this assumption. The optimized geometries of L^1H_3 and L^2H_2 displayed C(5)–N(4) bond lengths (Fig. 2) of 1.459 and 1.465 Å, respectively. Protonation at sulfur, which has been used in the calculations to mimic coordination to the metal, elongates those bonds to 1.473 and 1.491 Å, respectively, i.e. less than 1% for L^1H_3 but ca. 2% for L^2H_2.

Once the C(5)–N(4) bond is broken, the two ligands bonded to the metal might interact in the way shown in Fig. 3, the

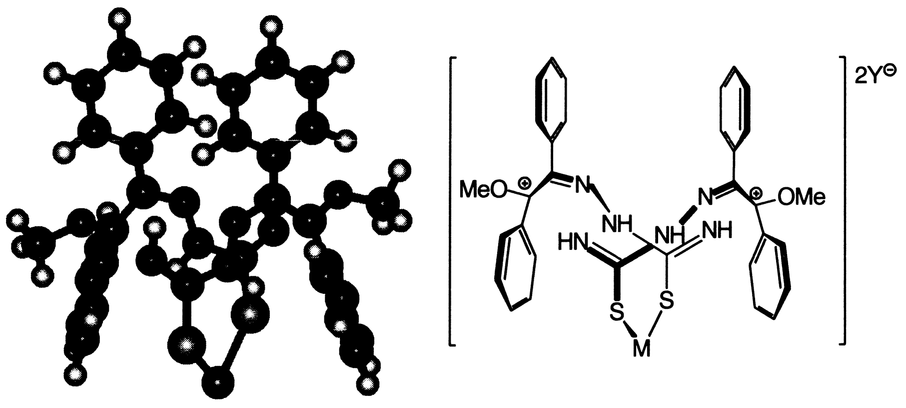
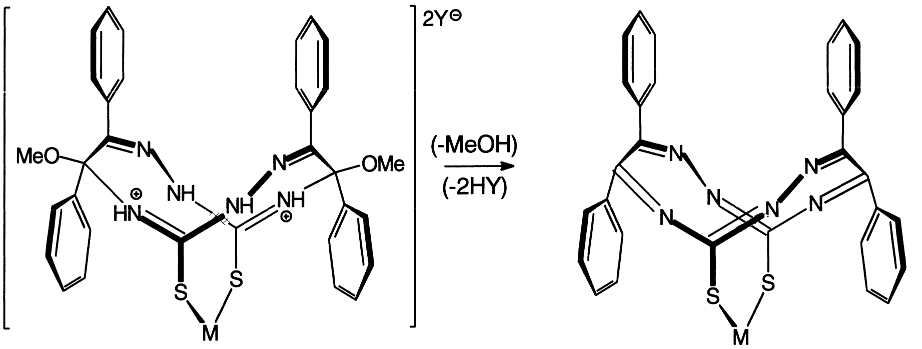


Figure 3. Calculated structure for the possible transition state of Hg(II) templated macrocyclization of L^2H_2.



Scheme 4. Expected intermediate in the Hg(II) templated macrocyclization of L^2H_2.

metal being an excellent template to induce the observed formation of the macrocycle.

When the new C–N bonds are formed, the counter ions acting as a base take two protons from the macrocyclic structure and two molecules of methanol are lost as shown in Scheme 4.

Cyclic voltammograms of L^1H_3, L^2H_3 and L^3H_2 in DMF exhibit irreversible cathodic waves in the range expected for this kind of molecules.[32] The cyclic voltammogram of [L^3Hg], between 0.0 and −1.6 V (Fig. 4), shows a cathodic peak at −0.517 V associated with an anodic one at −0.468 V. This couple corresponds with the reversible redox mercury process. At more negative potentials two peaks corresponding to ligand reduction processes are observed (−0.750 and −1.350 V). One of them is slightly shifted in relation with those of the free ligand (−0.720 and −1.350 V), which is in agreement with its bonding to the mercury ion.

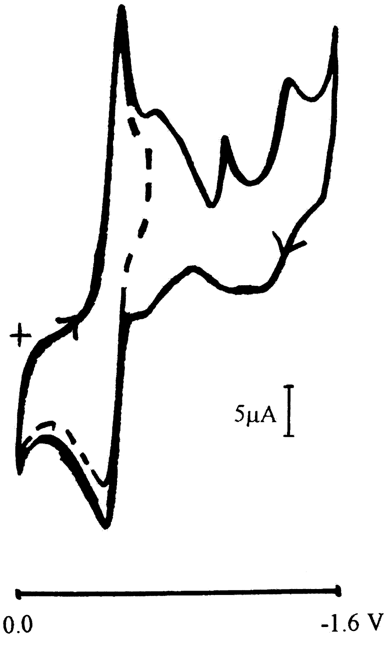


Figure 4. Cyclic voltammogram of L^3Hg.

3. Conclusions

The reaction of benzil with thiosemicarbazone in methanol in the presence of $NaBH_4$ led to a six-membered ring heterocycle L^1H_3 that forms stable 2:1 complexes with Hg(II) as a neutral ligand. The resulting heterocycle retains a N=C bond whose low electrophilic character prevents its reduction by the hydride.

In the absence of $NaBH_4$ a different heterocycle L^2H_2 is obtained that contains a MeO group. Interestingly, the presence of the methoxy group induces a different outcome of its reaction with Hg(II) as compared to L^1H_3: the ring opens and two molecules of L^2H_2, anchored by the metal, react to give a macrocycle that binds as an anionic bidentate ligand to the metal. Semiempirical calculations support the proposed metal-template mechanism.

The electrochemical results of complex L^3Hg makes it and its precursors, L^2H_2 and L^3H_2, outstanding candidates for mercury determination by appropriate electrode modification.

4. Experimental

Microanalyses were carried out using a Perkin–Elmer 2400 II CHNS/O Elemental Analyser. IR spectra in the 4000–400 cm^{-1} range were recorded as KBr pellets on a Bomen-100 spectrophotometer. Conductivity data were measured using freshly prepared DMF solutions (ca. 10^{-3} M) at 25°C with a Metrohm Herisau model E-518 instrument. ^1H and ^{13}C NMR spectra were recorded on a spectrophotometer Bruker AMX-300 using dimethylsulfoxide-d_6 as solvent and TMS as internal reference. Fast atom bombardment mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol (*m*NBA) as the matrix. Electronic impact spectrum was recorded in the same instrument. Electrochemical measurements were performed with a BAS CV 27 voltammograph and a BAS A-4 XY register using a glassy carbon (ϕ 5 mm) as working electrode, a platinum wire as auxiliary, and a double junction, with porous ceramic wick, Ag/AgCl as reference electrode, standardized for the redox couple ferricinium/ferrocene ($E_{1/2}=+0.400$ V, $\Delta E_p=60$ mV). Cyclic voltammetry studies of ligands and complex were carried out on 0.01 M solutions in dimethylformamide containing 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte. The range of potential studied was between +1 to −1.6 V. All solutions were purged with nitrogen for five minutes before measurement and the working electrode was polished before each experiment with diamond paste. The procedure was performed at room temperature and nitrogen atmosphere was maintained over the solution during the measurements. IUPAC names of compounds were obtained from ChemWeb: (http://cwgen.chemweb.com/autonom/autonomsearch.html).

4.1. Preparation of organic molecules

4.1.1. 5,6-Diphenyl-4,5-dihydro-2*H*-[1,2,4]triazine-3-thione, L^1H_3. A solution of thiosemicarbazide (1.00 g, 10.64 mmol) in 80 ml of absolute methanol, 22 ml of 2 M HCl and 0.6 ml of conc. HCl was added to a solution of benzil (2.31 g, 10.64 mmol) in 80 ml of the same solvent and some drops of conc. HCl under reflux. After 30 min $NaBH_4$ (5.20 g, 159.00 mmol) was added in small amounts, with effervescence. The reaction mixture was heated under reflux for 8 h, and then the solvent was evaporated about a half of the volume and a white solid was formed, which was collected by filtration and recrystallized from CH_2Cl_2 (yield 73%), mp 196°C. Anal.; Found: C, 67.35; H, 4.78; N, 15.33; S, 11.73; Calc. for $C_{15}H_{13}N_3S$. C, 67.42; H, 4.87; N, 15.73; S, 11.99. *m/z* (EI): 267 ($C_{15}H_{13}N_3S$, 100%). Selected spectroscopic data: IR (cm^{-1}): 3375, 3187 and 3073 (NH), 1597 (C=N), 1559 (thioamide I), 846 (thioamide IV). ^1H NMR (300 MHz): (1H, s) 11.5; (1H, s) 9.7; (2H, m) 7.7; (8H, m) 7.5–7.2; (H, s) 5.7. ^{13}C NMR (75 MHz): 171.1 (CS); 145.3 (CN); 139.2–125.9 (Ph); 51.53 (CR_3).

To a solution of benzilbisthiosemicarbazone (1.00 g, 2.91 mmol) (prepared by the procedure previously published)[24] in 800 ml of absolute methanol under reflux was added (1.08 g, 28.80 mmol) of $NaBH_4$ in small amounts, with effervescence. The mixture was refluxed for 8 h, and then the solution was concentrated until a white solid precipitated, which was filtered off and recrystallized in CH_2Cl_2, (yield 15%). From the remaining solution, a dark yellow oil was obtained.

To a warm solution of L^2H_2 (0.50 g, 1.68 mmol) in 200 ml of absolute methanol, was added $NaBH_4$ (0.64 g, 17.00 mmol) in small amounts, with effervescence. After 6 h under reflux, the solvent was partially removed and a white solid was formed, which was filtered off, and recrystallized in CH_2Cl_2, (yield 68%).

4.1.2. 5-Methoxy-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]-triazine-3-thione, L^2H_2. A solution of thiosemicarbazide (1.14 g, 12.50 mmol) in methanol (150 ml), hydrochloric acid (25 ml, 2 M), 1 ml of conc. HCl and a solution of benzil (2.63 g, 12.50 mmol) in methanol (100 ml) were alternatively added dropwise and slowly with strong stirring in 75 cm^3 of methanol. After finishing the addition of all reactants, the mixture was stirred over 8 h. Overnight a crystalline solid was formed, which was filtered off, washed and dried in vacuo (yield 95%), mp 222°C. Anal.; Found: C, 64.45; H, 5.09; N, 14.05. Calc. for $C_{16}H_{15}N_3OS$: C, 64.64; H, 5.05; N, 14.14%. *m/z* (FAB): 298 ($C_{16}H_{15}N_3SO+1$, 35%). Selected spectroscopic data: IR (cm^{-1}): 3184 and 3131 (NH); 1608 (C=N), 1550 (thioamide I), 846 (thioamide IV). ^1H NMR (300 MHz): (1H, s) 12.1; (1H, s) 10.0; (2H, m) 7.5, (8H, m) 7.4–7.2; (3H, s) 3.1. ^{13}C NMR (75 MHz): 169.7 (CS); 142.4 (CN); 141.7–126.5 (Ph); 83.2 (CH_3O) and 50.7 (CR_3).

4.1.3. 5,6,11,12-Tetraphenyl-1,2,4,7,8,10-hexaaza-cyclododeca-4,6,10,12-tetraene-3,9-dithione, L^3H_2. A solution of copper chloride dihydrate (0.23 g, 0.70 mmol), in methanol (50 ml) was added to a solution of L^2H_2 (0.41 g, 1.40 mmol) in methanol (50 ml). The mixture was stirred for 2 h at room temperature. The cream solid L^3H_2 formed was filtered off, washed several times with methanol and dried in vacuo (yield 79%), mp 205°C. Anal.; Found: C, 67.82, H, 4.28, N, 15.75, S, 12.13; Calc. for $C_{30}H_{22}N_6S_2$: C, 67.92, H, 4.15, N, 15.85, S, 12.07. *m/z* (FAB): 530.1 ($C_{30}H_{22}N_6S_2$, 100%). Selected spectroscopic data: IR (cm^{-1}): 3057 (NH), 1599 and 1581 (C=N), 1480 (thioamide I), 866 (thioamide IV). ^1H NMR (300 MHz): (11H, m) 7.5–7.3. ^{13}C NMR (75 MHz): 166.9 (CS), 156.6, 156.0 (CN), 134.9–128.6 (Ph).

4.2. Synthesis of mercury complexes

4.2.1. Derivatives of L^1H_3. $[Hg(L^1H_3)_2(NO_3)_2$. A solution of mercury(II) nitrate monohydrate (0.64 g, 1.87 mmol) in 30 ml of absolute methanol was added to a solution of L^1H_3 (1.00 g, 3.74 mmol) in 50 ml of the same solvent. The mixture was stirred for 12 h at room temperature. The pale yellow solid formed was filtered off, washed successively with absolute methanol and ether, and dried in vacuo (yield 87%), mp 132–134°C. Λ_M (DMF, Ω^{-1} cm^2 ml^{-1}): 45. *m/z* (FAB): 735.3 ($C_{30}H_{25}N_6S_2Hg$, 65%). Selected spectroscopic data: IR (cm^{-1}): 3180, 3107 and 3064 (NH), 1614 (C=N), 1573 (thioamide I), 838 (thioamide IV). ^1H NMR (300 MHz): (2H, m) 7.8; (8H, m) 7.5–7.2; (1H, s) 6.1; (2H, br.) 3.2. ^{13}C NMR (75 MHz): 163.1 (CS); 148.1 (CN); 137.0–126.0 (Ph); 52.2 (CR_3).

$[Hg(L^1H_3)_2Cl_2]$. A methanolic solution, 25 ml, of mercury(II) chloride (0.26 g, 0.97 mmol) was added to a solution of L^1H_3 (0.50 g, 1.95 mmol) in 75 ml of methanol, at room temperature. After being stirred and refluxed for 8 h, the pale yellow solution was concentrated until a solid was obtained, which was filtered off, washed with methanol and dried in vacuo (yield 83%), mp 138°C. Λ_M (DMF, Ω^{-1} cm^2 ml^{-1}): 16. *m/z* (FAB): 735.5 ($C_{30}H_{25}N_6S_2Hg$, 10%), 268 ($C_{15}H_{13}N_3S$, 65%). IR (cm^{-1}): 3170, 3103 and 3062 (NH), 1615 (C=N), 1570 (thioamide I), 838 (thioamide IV). ^1H NMR (300 MHz): (1H, s) 12.1; (1H, s) 10.4; (2H, m) 7.8; (8H, m) 7.5–7.2 (1H, s) 5.9. ^{13}C NMR (75 MHz): 166.6 (CS); 146.6 (CN); 137.7–125.7 (Ph); 51.1 (CR_3).

4.2.2. Derivatives of L^2H_2. $[L^3Hg]$. A suspension of $Hg(NO_3)_2 \cdot H_2O$ (2.55 g, 7.43 mmol) in 100 ml of absolute methanol was added to a solution of L^2H_2 (1.11 g, 3.70 mmol) in 200 ml of anhydrous methanol, at room temperature. The mixture was stirred for 20 h and the pale yellow solid formed was filtered off, washed with methanol and dried in vacuo (yield 59%), mp 218°C (D). Λ_M (DMF, Ω^{-1} cm^2 ml^{-1}): 25. *m/z* (FAB): 731 ($C_{30}H_{21}N_6S_2Hg$, 30%), 530 ($C_{30}H_{22}N_6S_2$, 5%). Selected spectroscopic data: IR

(cm^{-1}): 1601 and 1581 (C=N), 1491 (thioamide I), 815 (thioamide IV). ^1H NMR (300 MHz): (m) 7.4–7.1. ^{13}C NMR (75 MHz): 174.7 (CS); 154.3 and 153.2 (CN); 135.4–128.1 (Ph).

A solution of $HgCl_2$ (0.88 g, 3.20 mmol) in 11 ml of methanol was added to a solution of L^2H_2 (1.93 g, 6.50 mmol) in 200 ml of the same solvent at room temperature. The solution was stirred for 12 h and partially concentrated. The yellow solid formed was filtered off, washed with methanol and dried in vacuo (yield 30%), mp 218°C (D). *m/z* (FAB): 731 ($C_{30}H_{21}N_6S_2Hg$, 30%); 530 ($C_{30}H_{22}N_6S_2$, 15%). Selected spectroscopic data: IR (cm^{-1}): 1602 and 1597 (C=N), 1485 (thioamide I), 815 (thioamide IV). ^1H NMR (300 MHz). (m) 7.4–7.2. ^{13}C NMR (75 MHz): 174.7 (CS); 154.3 and 153.2 (CN); 135.4–128.1 (Ph).

To a suspension of the macrocyclic ligand L^3H_2 (0.13 g, 0.24 mmol) in 150 ml of absolute methanol was added a suspension of $Hg(NO_3)_2{\cdot}H_2O$ (0.08 g, 0.24 mmol) in 15 ml of the same solvent. The mixture was stirred for 12 h. The white solid obtained was filtered off, washed with methanol and dried in vacuo. The filtrate was concentrated and a yellow solid precipitated (yield 65%), mp 218°C (D). *m/z* (FAB): 731.1 ($C_{30}H_{21}N_6S_2Hg$, 40%), 529 ($C_{30}H_{21}N_6S_2$, 20%). Selected spectroscopic data: IR (cm^{-1}): 3055 (NH), 1601 and 1597 (C=N), 1485 (thioamide I), 815 (thioamide IV). ^1H NMR (300 MHz): (m) 7.4–7.1.

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