

## Ionic Recognition by 7-Nitro-1,3,5-triaza Adamantane: First Thermodynamic Study

Angela F. Danil de Namor,<sup>\*,†</sup> Nwanyinnaya A. Nwogu,<sup>†</sup> Jorge A. Zvietcovich-Guerra,<sup>†</sup> Oscar E. Piro,<sup>‡</sup> and Eduardo E. Castellano<sup>§</sup>

Laboratory of Thermochemistry, Chemical Sciences, Faculty of Health and Medical Sciences, University of Surrey, Guildford, GU2 7XH, U.K., Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata and Institute IFLP (CONICET), C. C. 67, 1900 La Plata, Argentina, and Instituto Física de São Carlos, Universidade de São Paulo, C. P. 369, 13560 São Carlos (SP), Brazil.

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A thermodynamic study involving 7-nitro-1,3,5-triaza adamantane, **1**, and its interaction with metal cations in nonaqueous media is first reported. Solubility data of **1** in various solvents were used to derive the standard Gibbs energies of solution,  $\Delta G_s^\circ$  in these solvents. The effect of solvation in the different media was assessed from the Gibbs energy of transfer taking acetonitrile as a reference solvent. <sup>1</sup>H NMR studies of the interaction of **1** and metal cations were carried out in CD<sub>3</sub>CN and CD<sub>3</sub>OD and the data are reported. Conductance measurements revealed that this ligand forms lead(II) or zinc complexes of 1:1 stoichiometry in acetonitrile. It also revealed a stoichiometry of two molecules of **1** per mercury(II) and two cadmium (II) ions per molecule of **1**. The addition of silver salt to **1** led to the precipitation of the silver-**1** complex which was isolated and characterized by X-ray crystallography. At variance with conductance measurements in solution, in the solid state the X-ray structure shows a 1:1 stoichiometry in the Hg(II) complex. The thermodynamics of complexation of **1** and these cations provide a quantitative assessment of the selective behavior of this ligand for ions of environmental relevance.

## Introduction

Adamantane<sup>1</sup> is the name given by IUPAC to the hydrocarbon tricyclo [3,3,1,1] decane compound.<sup>2</sup> Its derivatives<sup>3–6</sup> found applications in medicine to the extent that hundreds of papers have been written on the use of amantadine and amantadone as antiviral agents for some types of influenza.<sup>7–11</sup> In fact, the National Advisory Committee on Immunisation has recommended the prophylactic use of amantadine against influenza for the 2005–2006 period except in Canada due to the increased rate of resistance to this drug among influenza A viruses from tests carried out in that season.<sup>12</sup> Other applications are those involving the use of adamantanes to fight soman poisoning in mice.<sup>13</sup> The anti-Parkinson and antispastic activity of adamantane has also been discussed in the literature.<sup>14</sup>

Among adamantanes, those with nitrogen atoms in bridgehead junctions have received a great deal of attention.<sup>15</sup> The synthetic procedures for their preparation, chemical, physical, and spectroscopic properties have been discussed. It has been claimed that some derivatives can be used as a solid rocket or as a hybrid rocket fuel when in hydrocarbon solutions, as polymer stabilizers, modifying agents for rubbers, additives to fuel-lubricating materials, corrosion inhibitors, and for the regeneration of ion exchange anions when complexed with metal cation salts.

On the basis of our previous work on the macrocycles known as cryptands<sup>16–25</sup> containing nitrogen atoms at bridgehead positions and their interaction with metal cations in water and nonaqueous solvents, we decided to carry out a detailed investigation on aza adamantanes and their cation complexing properties. For this purpose, the 7-nitro-1,3,5-triaza adamantane,

**1**, was selected. This compound was prepared in 1967,<sup>15,26</sup> and the synthetic procedure was modified subsequently by several workers.<sup>15</sup> Despite the increased interest in these compounds, there is not a detailed investigation on the solution thermodynamics of **1** or its complexing properties. A preliminary study of this ligand involving transition metal cations has been reported.<sup>27</sup> However, nothing is known on the interaction of this ligand with heavy metal cations despite of the fact that this compound has donor atoms that can provide suitable sites for interaction with heavy metal cations that are ions of environmental concern. If so, this compound can be used as pendant arms in the functionalization of calixarenes and calixpyrroles. This is an area of considerable interest for our Group given the possibility of anchoring this ligand to the polymeric matrices and then being used as recyclable decontaminating agents<sup>28–34</sup> for removal of heavy metals from water. However before proceeding with these studies, the complexing properties of this compound for these cations need to be investigated. Therefore, we report for the first time the following:

(i) the solubility of **1** and derived standard Gibbs energies of solution in various solvents at 298.15 K. In an attempt to assess the different solvation effects of the solvent on this compound, transfer Gibbs energies,  $\Delta G_t^\circ$  from a reference solvent to another are calculated;

(ii) <sup>1</sup>H NMR spectroscopic data on the interactions of **1** with metal cations in CD<sub>3</sub>CN and CD<sub>3</sub>OD;

(iii) conductance measurements to establish the composition of the metal-ion complexes in acetonitrile solution;

(iv) thermodynamics of cation complexation in acetonitrile; and

(v) solution data that are compared with X-ray crystallographic studies on the silver and mercury complexes of this ligand.

\* To whom correspondence should be addressed.

<sup>†</sup> University of Surrey.

<sup>‡</sup> Universidad Nacional de La Plata and Institute IFLP (CONICET).

<sup>§</sup> Universidade de São Paulo.

## Experimental Section

**Chemicals.** Nitromethane,  $\rho$ -formaldehyde, and ammonium acetate were all purchased from Aldrich and were used without further purification.

Metal-ion perchlorate salts ( $\text{LiClO}_4$ , 99%;  $\text{NaClO}_4$ , 98%;  $\text{KClO}_4$ , 99%;  $\text{Mg}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ , 99%;  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ , 99%;  $\text{Sr}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ , 98%;  $\text{Ba}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ , 98%;  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , 98%;  $\text{Cd}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ , 98%;  $\text{Hg}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ , 9.99%;  $\text{AgClO}_4$ , 97%;  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ , 98%) used in the experiments were purchased from Aldrich. The perchlorate salts were dried over  $\text{P}_4\text{O}_{10}$  under vacuum for several weeks and the  $^1\text{H}$  NMR was used to check for the presence of water in the salts before use.

Deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ), deuterated methanol ( $\text{CD}_3\text{OD}$ ), deuterium oxide, and tetramethylsilane (TMS) were all purchased from Aldrich.

Acetonitrile, MeCN (HPLC grade, Fisher UK Scientific International) was dried by refluxing with calcium hydride under a nitrogen atmosphere.<sup>35</sup>

Methanol (MeOH) and ethanol (EtOH), HPLC grade) purchased from Fisher were used without further purification.

**Synthesis of 7-Nitro-1,3,5-triaza Adamantine.** The ligand was prepared by following a previously reported procedure<sup>24</sup>

Elemental analysis was performed at the University of Surrey. Analytical calculations for the ligand ( $\text{C}_7\text{H}_{12}\text{N}_4\text{O}_2$ ): % C, 45.65; H, 6.57; N, 30.42. Found: % C, 45.81; H, 6.77; N, 30.40.

$^1\text{H}$  NMR, ( $\text{CD}_3\text{CN}$ ) at 298 K,  $\delta$  (ppm): 4.41 and 4.05 (6H, 2d,  $\text{N}-\text{CH}_2-\text{N}$ ) and 3.77 (6H, s,  $\text{N}-\text{CH}_2-\text{C}$ ).

**Isolation of Metal Ion Complexes of the Ligand.** Aqueous solutions of silver nitrate or mercury perchlorate ( $1.135 \times 10^{-1} \text{ mol dm}^{-3}$ ) and the ligand ( $0.6 \text{ mol dm}^{-3}$ ) were prepared. A volume of the solution of the ligand (7 mL) was added to the silver nitrate or mercury perchlorate solutions in separate tubes. A precipitate was formed in each of the tubes that was dissolved in methanol and water, filtered, and covered with aluminum foil. The mixture was left for 14 days until crystals were formed. These were filtered out, dried, and employed in the X-ray structure determination procedure.

**Solubility Measurements.** To determine the solubility of this ligand in the various solvents, the method described by Danil de Namor et al.<sup>36,37</sup> was used. Thus saturated solutions of 7-nitro-1,3,5-triaza adamantane in the appropriate solvent were prepared and the mixtures were left in a thermostatted bath at  $298.15 \pm 0.02 \text{ K}$  for several days until equilibrium was attained between the solid and its saturated solution.

The crucibles were numbered and preweighed and aliquots of the saturated solution were placed into the crucibles and analyzed gravimetrically in triplicate by allowing the solvents to evaporate. Then the crucibles containing the solid were left in desiccators over  $\text{CaCl}_2$ . The crucibles were weighed until a constant weight was attained. Separate blank experiments were carried out to ensure the absence of any nonvolatile material in the pure solvent.

Solvate formation was monitored by placing a small amount of the ligand on a watch glass over a saturated atmosphere of the appropriate solvent placed at the bottom of a closed desiccator.<sup>38</sup>

**$^1\text{H}$  NMR Measurements.** A Bruker DRX-500 pulse Fourier transform NMR spectrometer was used. The operating conditions for routine proton measurement involved pulse or flip angle of  $30^\circ$ , spectra width (SW) of 20.7 ppm, spectral frequency (SF) of 500.150 MHz, delay time of 0.3 s, acquisition time (AQ) of 3.17 s, and a line broadening of 0.3 Hz. Solutions of **1** ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) were prepared in the appropriate deuterated

solvent and placed in 5 mm NMR tubes. Tetramethylsilane (TMS) was used as the internal reference.

To study the complexation with metal-ion salts, these salts ( $3 \times 10^{-3} \text{ mol dm}^{-3}$ ) were added in excess to solutions of the ligand in the appropriate solvent. Chemical shift changes relative to that for the free ligand in the appropriate solvent were calculated.

**Conductance Measurements.** A Wayne-Kerr Auto Balance Universal bridge, type B642 was used to carry out conductance measurements. The conductivity cell constant was performed as described by Danil de Namor et al.<sup>39</sup> For each experimental run, fresh solutions of the ligand **1** and metal-ion salts were prepared. The conductance cell was filled with a solution of the metal cation salt (concentration range  $5 \times 10^{-5}$  to  $5 \times 10^{-4} \text{ mol dm}^{-3}$ ) and this was used for the experiment. The solution in the cell was allowed to attain equilibrium and then the ligand (concentrations in the  $1 \times 10^{-3}$  to  $3 \times 10^{-3}$  range) was added to the vessel in a stepwise titration using a hypodermic syringe. The conductivity was recorded after each addition and the molar conductance was calculated. A plot of molar conductance versus the ligand–metal ion concentration ratio was used to determine the stoichiometry of the complex.

**Titration Calorimetry.** Stability constants (expressed as  $\log K_s$ ) and enthalpies of complexation,  $\Delta H_c$ , of the ligand with the metal-cation with perchlorate as the counterion in acetonitrile were determined using the Thermal Activity Monitor (TAM 2277) calorimeter. The calorimeter was calibrated using the standard reaction involving the complexation of 18-crown-6 with barium chloride in water at 298.15 K.<sup>40</sup>

Microcalorimetric titrations were then performed to calculate the stability constant and the heat of complexation of the reaction.<sup>41,42</sup> For these experiments, the vessel was filled with a solution of **1** in acetonitrile ( $8 \text{ cm}^3$ ,  $6 \times 10^{-4}$  to  $1 \times 10^{-3} \text{ mol dm}^{-3}$ ). A solution of the metal cation salt about 10 times more concentrated than that of the ligand was then injected from a  $0.5 \text{ cm}^3$  gastight Hamilton syringe into the vessel. About 26 injections were made. This syringe attached to a computer operated syringe, drove at an average of 30 min intervals. Blank experiments were carried out for each reaction which was performed in duplicate.

**Potentiometric Titrations.** The stability constant value for mercury(II) and adamantane in acetonitrile was higher than 6, so potentiometric titrations were carried out to calculate the stability constant (expressed as  $\log K_s$ ) in this solvent. For this experiment, the electrochemical vessel containing the indicator mercury electrode was filled with a solution of tetra-*n*-butylammonium perchlorate (TBAP  $0.05 \text{ mol dm}^{-3}$ ,  $35 \text{ cm}^3$ ) in acetonitrile. The reference electrode was from Russell, and the internal electrolyte was a saturated solution of LiCl in ethanol.

## Results and Discussion

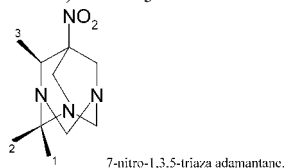
**Solubility Studies of **1** in Various Solvents.** Solubility data for **1** in various solvents are recorded in Table 1. These are the result of several analytical measurements carried out on the same saturated solution. The standard deviation of the data is also included in this table. Solvate formation was observed when **1** was exposed to a saturated atmosphere of chloroform. Given that the calculation of the standard Gibbs energy of solution,  $\Delta G_s^\circ$  requires the same composition of **1** in the solid and the saturated solution, this parameter was not calculated in chloroform.

This ligand is strongly protonated in water; its solubility could not be quantitatively obtained. In fact the protonation constant of some triaza adamantanes in water and in dimethylsulfoxide

**TABLE 1: Solubilities and Standard Gibbs Energies of Solution of 7-nitro-1,3,5-triaza adamantane in Various Solvents at 298.15 K with Derived Standard Transfer Gibbs Energies from Acetonitrile<sup>a</sup>**

solvent	solubility (mol dm <sup>-3</sup> )	$\Delta G_s^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_t^\circ$ (MeCN $\rightarrow$ s) (kJ mol <sup>-1</sup> )
MeCN	$(4.0 \pm 1.7) \times 10^{-2}$	8.0	0
DCM	$(1.7 \pm 0.8) \times 10^{-1}$	4.4	-3.6
DMF	$(7.6 \pm 3.3) \times 10^{-2}$	6.4	-1.6
THF	$(4.6 \pm 0.2) \times 10^{-2}$	7.7	-0.3
EtOH	$(8.6 \pm 0.2) \times 10^{-3}$	11.8	3.8
MeOH	$(2.5 \pm 0.1) \times 10^{-2}$	9.2	1.2
Tol	$(1.6 \pm 0.7) \times 10^{-2}$	10.3	2.3
H <sub>2</sub> O	protonated	protonated	protonated
CHCl <sub>3</sub>	solvate formation		

<sup>a</sup> Abbreviations: dichloromethane, DCM; *N,N*-dimethylformamide, DMF; tetrahydrofuran, THF; acetonitrile, MeCN; methanol, MeOH; toluene, Tol; ethanol, EtOH; water, H<sub>2</sub>O; chloroform, CHCl<sub>3</sub>.

**TABLE 2: <sup>1</sup>H NMR Chemical Shift Changes for 7-Nitro-1,3,5-triaza Adamantane upon Addition of Metal Cations (as Perchlorate) in CD<sub>3</sub>CN at 298 K**

metal cation	H-1, $\Delta\delta$ (ppm)	H-2, $\Delta\delta$ (ppm)	H-3, $\Delta\delta$ (ppm)
Zn <sup>2+</sup>	0.32	0.38	0.21
Cd <sup>2+</sup>	0.11	0.11	0.08
Hg <sup>2+</sup>	0.37	0.43	0.73
Pb <sup>2+</sup>	0.33	0.43	0.22

Chemical Shifts (in ppm) for **1** (free ligand) in deuterated acetonitrile: H-1, 4.41; H-2, 4.05; H-3, 3.77.

has been reported in the literature.<sup>15</sup> This is to be expected given that these are amines and as such these compounds have affinity for the proton. We have monitored the possibility of protonation of **1** by conductivity measurements. It is expected that a neutral ligand such as **1** should act as an electrical insulator. However, in an aqueous medium the solution possesses conductivity due to the protonation of the ligand in water. In the absence of solvation and conductance, solubility data were used to derive the standard Gibbs energy of solution,  $\Delta G_s^\circ$  referred to the standard state of 1 mol dm<sup>-3</sup>. These are also listed in Table 1. Taking acetonitrile as the reference solvent, the standard transfer Gibbs energy,  $\Delta G_t^\circ$  of **1** was calculated. The data show that the difference in solvation of **1** in one solvent relative to acetonitrile is indeed very small.

Judging from the  $\Delta G_t^\circ$  values as shown in Table 1, the solvation trend for **1** follows the sequence DCM > DMF > THF > MeCN > MeOH > Tol > EtOH.

**<sup>1</sup>H NMR studies on cation complexation.** Data for the <sup>1</sup>H NMR chemical shift changes that **1** undergoes in the presence of mercury(II), zinc(II), lead(II), and cadmium(II) cations in CD<sub>3</sub>CN are listed in Table 2. Within the concentrations used, Ag<sup>+</sup> formed a precipitate when complexed with **1** in CD<sub>3</sub>CN, therefore we were unable to detect chemical shift changes for this system in this solvent. The most significant chemical shift changes are observed for Hg<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> ions, while the smallest downfield shift was observed for Cd<sup>2+</sup>. However, the chemical shift changes exhibited by H-1, H-2 and H-3 protons for Zn<sup>2+</sup> and Pb<sup>2+</sup> are quite similar. To a much lesser extent, a

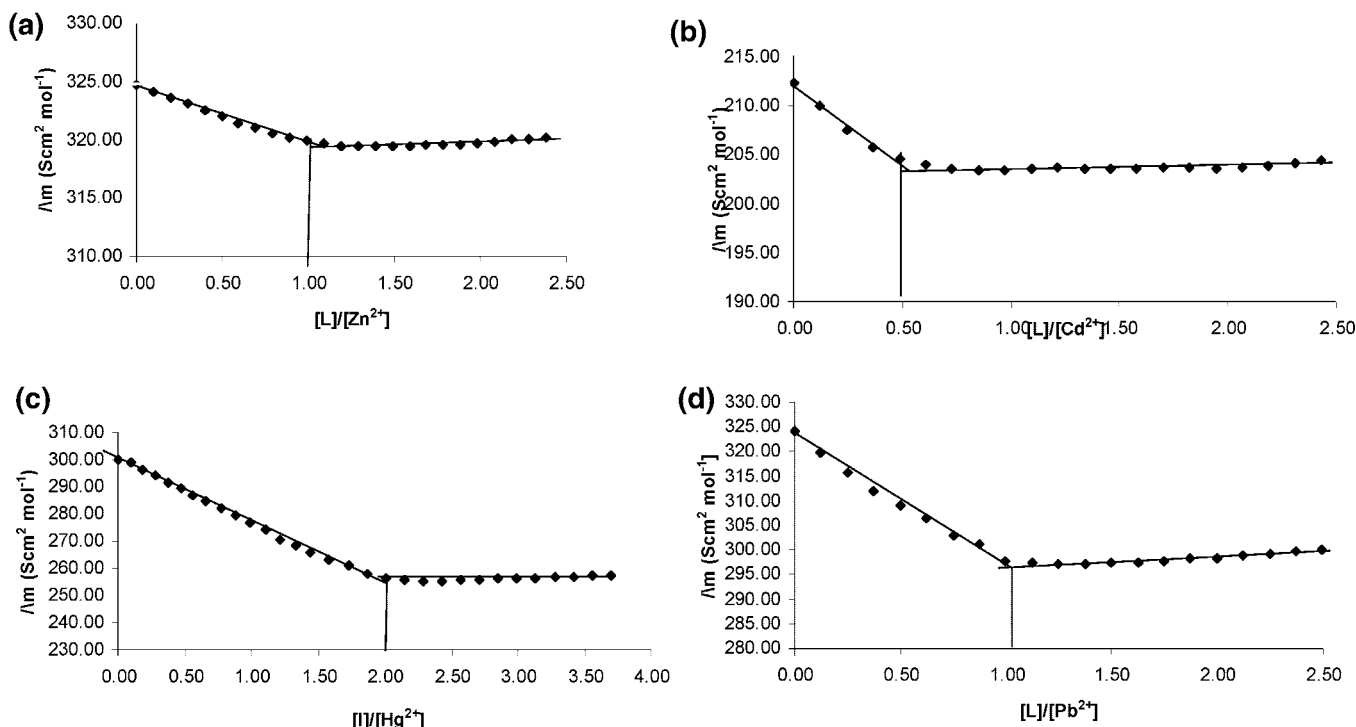
similar trend is observed for Cd<sup>2+</sup> in CD<sub>3</sub>CN. However, this trend is not observed for mercury(II). For this cation and **1**, the most pronounced downfield shift is observed for H-3 followed by a less pronounced downfield shift for H-2 and H-1 protons. These shifts appear to indicate that the interaction of the former cations with this ligand differ at least in strength from that of Hg<sup>2+</sup> and this ligand in solution. No significant chemical shift changes were observed for any of the alkali and alkaline-earth metal cations in this solvent.

As far as CD<sub>3</sub>OD is concerned, no significant chemical shift changes were observed by the addition of metal cation salts to this ligand except for silver and mercury(II). Thus the addition of the silver salt leads to distortion of all the peaks while in the presence of mercury(II) this was only observed for H-3 proton.

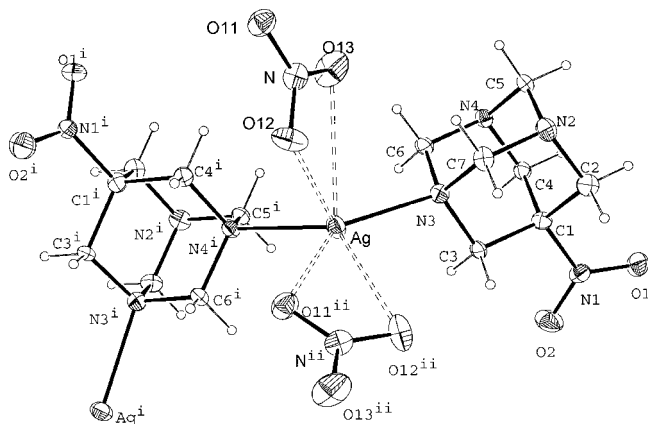
In an attempt to establish the composition of the metal-ion complexes, conductance measurements were carried out and these are described in the following section.

**Conductance Measurements and X-ray Diffraction Studies.** The addition of a solution of the ligand (non-conducting) to a metal-ion salt solution placed in the conductance cell led to significant changes in conductance due to complex formation in the case of mercury(II), zinc(II), lead(II), and cadmium(II) in acetonitrile. Plots of molar conductance,  $\Lambda_m$ , against the ligand to metal cation concentration ratios for the titration of these salts with **1** in this solvent are shown in Figure 1. Thus the initial molar conductance of the metal cation salt (as perchlorate) in the absence of the ligand falls within the values previously reported in this solvent.<sup>40,43</sup> The size effect in moving from the single to the complex cation is reflected in the decrease in conductance observed in going from A to B. This is to be expected as the mobility of the complex must be lower than that of the single cation unless solvation of the latter is remarkably high or a substantial degree of ion pair formation occurs between the free cation and the counterion relative to that of the metal ion complex and its counterpart. The most interesting feature of these results is that while 1:1 complexes are formed in the interaction of **1** with either Pb<sup>2+</sup> or Zn<sup>2+</sup>, this is not the case for Hg<sup>2+</sup> and Cd<sup>2+</sup>. It is found that two molecules of **1** binds to a Hg<sup>2+</sup> ion and that one molecule of **1** binds two Cd<sup>2+</sup> ions. Because of the precipitation of the silver complex by the addition of **1** to silver perchlorate or vice versa the composition of this complex from conductance measurements could not be established but instead, we were able to obtain suitable single crystals for structural X-ray diffraction studies. Also the unusual composition of the mercury(II) complex led us to its isolation and again, suitable crystals were obtained and the corresponding X-ray structure determined. Atomic fractional coordinates and equivalent displacement parameters as well as anisotropic thermal parameters for the non-H atoms and hydrogen atoms and isotopic displacement parameters for silver and mercury(II) complexes of **1** are available on request. Figures 2 and 3 respectively are ORTEP<sup>44</sup> drawings of these complexes. The silver complex crystallizes as C<sub>7</sub>H<sub>12</sub>AgN<sub>4</sub>O<sub>2</sub>·NO<sub>3</sub>. As shown in Figure 2, the silver cation bridges the N atoms of neighboring adamantane ligands and subtends two more short contacts of two neighboring solvent molecules giving rise to an infinite three-dimensional supramolecular arrangement. This figure also shows the extended structure generated by the above-mentioned contacts to the silver cation. In the mercury complex, C<sub>7</sub>H<sub>12</sub>HgN<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>, the metal cation is bonded to two chloride ions and two neighboring, symmetry related, adamantane ligands, giving rise to an infinite supramolecular chain along the crystal *b*-axis. Comparison of 10 atoms of adamantane skeleton in both complexes by using the Kabsch's procedure<sup>45</sup>

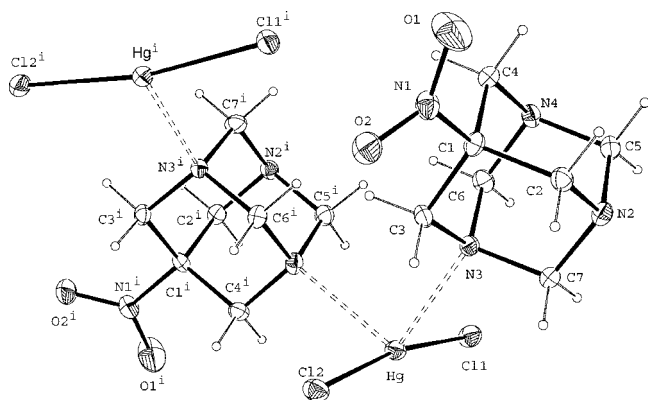




**Figure 1.** Conductometric titration curve of **1** with (a) zinc(II), (b) cadmium(II), (c) mercury(II), and (d) lead(II) metal cations in acetonitrile at 298.15 K.



**Figure 2.** X-ray crystallography of the **1**-silver complex.



**Figure 3.** X-ray crystallography of **1**-mercury complex.

showed them to be essentially identical with an overall rms derivation from homologous atoms of 0.023 Å.

Having established the composition of the complexes and knowing from previous studies the concentration range at which metal cation salts of mercury, lead, zinc, and cadmium are

predominantly in their ionic forms in solution,<sup>40</sup> thermodynamic data referred to a properly characterized process in acetonitrile can be derived and this is now discussed.

**Thermodynamics of Complexation of **1** and Metal Cations in Acetonitrile.** Stability constants and derived standard Gibbs energies, enthalpies, and entropies of complexation of **1** with metal cations (mercury(II), zinc(II), lead(II), and cadmium(II)) in acetonitrile at 298.15 K are listed in Table 3. Calorimetric titrations also provide information regarding the composition of the metal-ion complexes. In all cases, agreement was found between the stoichiometry of complex formation derived from conductometry and calorimetry. It may be argued that thermodynamics does not provide structural information. On the other hand, it is indisputable that any model proposed must fit the experimental data. This is indeed the case as reflected in the standard deviation of the data.

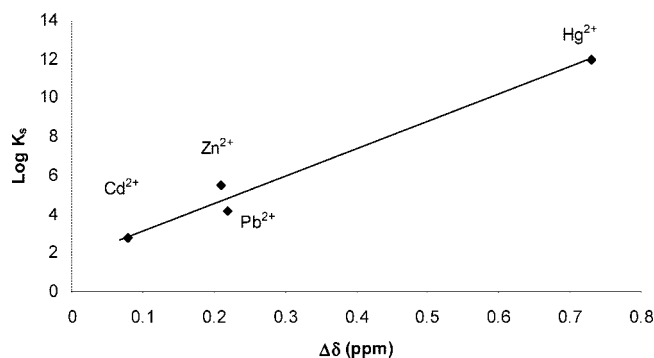
For all systems, the processes are enthalpically controlled and entropically unfavored except for the formation of the 1:2 (ligand/metal cation) complex of cadmium(II) which is entropically favored. For the 2:1 complexation reaction between **1** and mercury(II), the stability constant value is well beyond the scope of titration calorimetry. Therefore stability constants for this system were determined by potentiometry. The results show that the formation of the 1:1 complex (eq 1) is characterized by a similar stability to that of the 2:1 complex (eq 2) although the enthalpies and entropies differ as a result of their full compensation.



Computer simulation studies show that for  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  complexes the cation interacts with the three nitrogen atoms of the ligand and a fourth coordination is provided by the nitrogen

**TABLE 3: Thermodynamics of Complexation of 1 with Metal Cations (Mercury(II), Zinc(II), Lead(II), and Cadmium (II)) in Acetonitrile at 298.15 K**

cation	L:M <sup>n+</sup>	log K <sub>s</sub>	ΔG <sub>c</sub> <sup>o</sup> kJ mol <sup>-1</sup>	ΔH <sub>c</sub> <sup>o</sup> kJ mol <sup>-1</sup>	ΔS <sub>c</sub> <sup>o</sup> JK <sup>-1</sup> mol <sup>-1</sup>
Hg <sup>2+</sup>	1: 1	12.0 ± 0.2 <sup>a</sup>	-68.5 ± 0.2 <sup>a</sup>	-96.4 ± 0.2 <sup>b</sup>	-94
	2: 1	12.0 ± 0.1 <sup>a</sup>	-68.5 ± 0.0 <sup>a</sup>	-90.2 ± 0.0 <sup>b</sup>	-73
Zn <sup>2+</sup>	1: 1	5.5 ± 0.1 <sup>b</sup>	-31.4 ± 0.1	-62.4 ± 0.3 <sup>b</sup>	-104
Pb <sup>2+</sup>	1: 1	4.2 ± 0.1 <sup>b</sup>	-24.0 ± 0.1	-65.1 ± 0.1 <sup>b</sup>	-139
Cd <sup>2+</sup>	1: 1	2.8 ± 0.2 <sup>b</sup>	-16.0 ± 0.2	-20.4 ± 0.1 <sup>b</sup>	-15
	1: 2	1.6 ± 0.1 <sup>b</sup>	-9.1 ± 0.1	-7.3 ± 0.1 <sup>b</sup>	+6

<sup>a</sup> Potentiometry. <sup>b</sup> Calorimetry.**Figure 4.** Correlation between log K<sub>s</sub> values for 1:1 complexes and Δδ values (ppm) for H-3 in CD<sub>3</sub>CN at 298 K.

atom of the solvent. This is the arrangement that leads to the lowest energy (higher stability). In fact the enthalpy values associated with the complexation of **1** with these cations are quite close. However, the lower stability of the lead relative to the zinc complex is attributed to the higher loss in entropy of the former relative to the latter.

As far as the cadmium complex is concerned, molecular modeling calculations suggest that the arrangement of the highest stability (lower energy) is that in which one cadmium cation is bonded to the three nitrogen atoms of the ligand and one molecule of acetonitrile, while the second cadmium cation is bonded to one of the oxygens of the nitro group and to three molecules of acetonitrile. It should be noted that there is a correlation between the log K<sub>s</sub> values corresponding to the formation of 1:1 complexes and the Δδ values for H-3 (Table 2) resulting from the addition of metal cation salts to the ligand in deuterated acetonitrile as shown in Figure 4.

## Conclusions

From the above discussion the following conclusions are drawn:

(1) This is the first detailed thermodynamic study of cation interactions involving the

7-nitro-1,3,5-triaza adamantane **1** ligand.

(2) The behavior of **1** with metal cations in acetonitrile is quite versatile in that complexes of different compositions are formed depending on the nature of the metal cation. Thus, in solution two **1** ligands bind to a mercury cation forming 2:1 complex, while two symmetry related adamantanes coordinate each Hg(II) ion in the polymeric 1:1 complex found in the solid state. The most interesting feature of these results is that this ligand interacts selectively with cations of environmental relevance following the sequence for 1:1 complexes Hg(II) > Zn(II) > Pb(II) > Cd(II).

Attempts to attach adamantane functionalities as pendant arms in calix[4]arene and calix[4]pyrrole are now in progress.<sup>46</sup>

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