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ORIGINAL ARTICLE

Study on the interaction between dinaphthosulfide-substituted macrocyclic diamides and some metal ions: experimental measurements vs. quantum mechanical calculations

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Abstract Complexation properties of dinaphthosulfide-substituted macrocyclic diamides **1** and **2** with some metal cations that have been obtained by conductometric method are described with quantum mechanics calculations. To do this, the most stable structures of ligands, Hg^{2+}-ligand complexes, ligand-MeOH and ClO_4^-–MeOH are optimized at HF/Lanl2dz level of theory and the most important interactions are analyzed by atoms in molecules (AIM) theory. These calculations predict the existence of strong interaction between Hg^{2+} cation and ligands **1** and **2**, particularly, S–Hg^{2+} interaction. The different conductometric behaviors of complexation of ligands **1** and **2** with metal ions are interpreted on the basis of the calculated intramolecular hydrogen bonds in ligands and intermolecular hydrogen bonds between ligands and methanol as a solvent and perchlorate as a counter ion. In addition, binding energies between Hg^{2+} and ligands are also calculated by HF/Lanl2dz level of theory. Results show that all theoretical predictions are in line agreement with the experimental data.

Keywords Ab initio · AIM theory · Complexation · Conductometry · Hydrogen bonding · Macrocyclic diamides

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Introduction

Macrocyclic diamides complexation properties have not been studied extensively, and few attempts have been made to measure their stability constants [1–4]. The macrocyclic amides have complexation properties that are complementary to the all-oxygen crowns, which strongly form complexes with alkali metal ions, and to the all-nitrogen cyclams, which strongly form complexes with heavy metal cations. Introduction of polar amide donors in the ring of macrocycle plays an important role in the enhancement of the selectivity of cations. In particular, cations with high charge density are usually favored [5–7]. Thus, amide based cyclic ligands, which are able to complex cations other than alkali and alkaline earth metal cations have received extensive attention. The macrocyclic amides represent characteristics of both a hydrogen bond donor and a hydrogen bond acceptor through which complex neutral molecules [8–10].

The synthesis and complexation properties of sulfur-containing macrocyclic diamides are attracting the interest of researchers, because of their ability to coordinate transition metal ions [11–13].

In this article, we have developed investigations on new dinaphthosulfide-substituted macrocyclic diamides with 15, 16 and 17-membered rings synthesized by Shockravi et al. [11]. These ligands are considered as multidentate macrocycles including amidic nitrogenes. In this study, the conductometric behavior of complexation and quantum chemical calculations of 15-membered macrocyclic diamide **1** containing –CH_2CH_2– group attached to the amide groups are reported and compared with previous studied 18-membered macrocyclic diamide **2** [11] containing –$(CH_2)_2NH(CH_2)_2$– group attached to the amide groups (Fig. 1). The presence of the amide groups in the structures

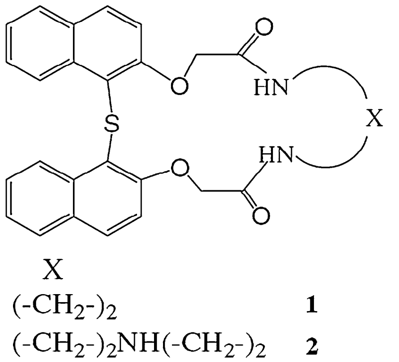

Fig. 1 Structure of macrocyclic diamides **1** and **2**

of these ligands makes them able to form intra- and intermolecular hydrogen bondings. In this study, we have optimized their conformations and showed that the intramolecular hydrogen bonds are formed between NH amide-carbonyl and NH amide-ethereal oxygen. The ability of inter- and intramolecular hydrogen bonding affects conductometric behavior of these macrocycles in methanol. The conductometric behavior of complexation of ligands **1** and **2** in methanol as a protic solvent has been interpreted on the basis of their ability to form inter- and intramolecular hydrogen bonds. This interpretation has been confirmed by quantum chemical calculations of intramolecular hydrogen bonds in free ligands and intermolecular hydrogen bonds between free ligands and methanol as a solvent, and between free ligands and perchlorate ion as a counter ion.

Experimental

Reagent grade $NaClO_4$, $KClO_4$, all nitrate salts and methanol were purchased from Merck. The other perchlorate salts were purchased from Aldrich and Fluka except for $Ca(ClO_4)_2$ that was prepared based on our previous reported procedure [11].

All purchased materials were of the highest purity available and used as received. The macrocyclic diamide **1** was prepared as the previously reported procedure [11].

Conductance measurements were carried out with a metrohm 712 conductometer equipped with a circulator. The conductometric procedure and calculation of the formation constants of the resulting complexes in methanol are according to our earlier study [11] except that the mole ratio data greater than one has not been considered in computer fitting of the molar conductivity-mole ratio data. The conductance measurements were repeated three times for each system.

Results and discussion

Conductometric studies

The molar conductivity of perchlorate salts of Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Pb^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} and the nitrate salts of Mg^{2+}, Ni^{2+}, La^{3+}, Ce^{3+}, Sm^{3+} and Tl^+, at a constant salt concentration (5.0×10^{-5} mol L^{-1}) was monitored while increasing the concentration of macrocyclic diamide **1** in methanol solvent at 25 °C. The observed molar conductivity as a function of ligand/cation mole ratio plots is shown in Fig. 1 of supporting information, Figs. 2 and 3. The formation constant of the ligand **1**-cation (Cd^{2+}, Pb^{2+}, and Hg^{2+}) complexes in methanol at 25.00 ± 0.03 °C computed by fitting of the molar conductivity-mole ratio data, are listed in Table 1. The stability of the resulting 1:1 complexes decreases in the order $Hg^{2+} > Pb^{2+} \gg Cd^{2+}$. The comparison of these values with the formation constants of ligand **2** complexes [11] indicates that the order is the same but the formation constant of Hg^{2+} complexes has decreased from

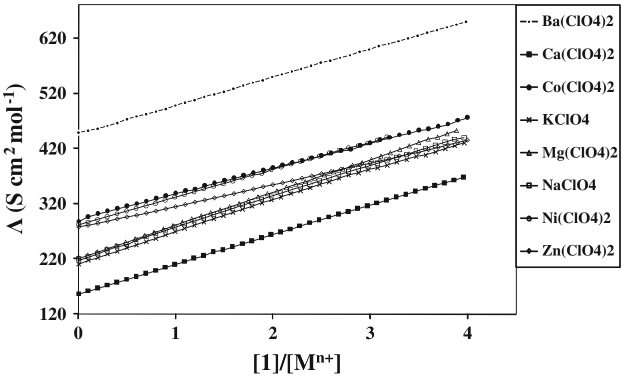

Fig. 2 Molar conductivity (S cm^2 mol^{-1}) versus [**1**]/[M^{n+}] for various cations in methanol at 25 °C

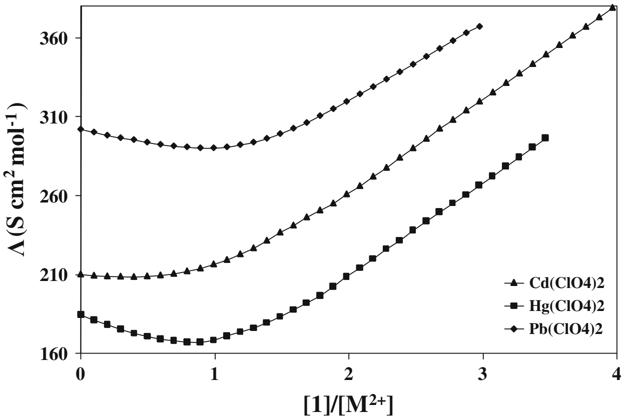

Fig. 3 Molar conductivity (S cm^2 mol^{-1}) versus [**1**]/[M^{2+}] for Hg^{2+}, Pb^{2+}, and Cd^{2+} in methanol at 25 °C

Table 1 Formation constants for ligand **1**- and ligand **2**-metal ion complexes in methanol at 25 °C

Cation (Ionic radius, Å)[a]	Ligand **1** Log K_f ± SD[b]	Ligand **2**[c] Log K_f ± SD[b]
Cd^{2+} (0.97)	2.74 ± 0.09	2.81 ± 0.04
Pb^{2+}(1.19)	4.77 ± 0.09	4.64 ± 0.05
Hg^{2+} (1.02)	4.90 ± 0.09	6.49 ± 0.05

[a] Ref. [24]

[b] SD = Standard deviation

[c] Ref. [11]

$\log K_f = 6.49 \pm 0.05$ in Hg^{2+}-ligand **2** to $\log K_f = 4.90 \pm 0.09$ in Hg^{2+}-ligand **1** because of the decreasing coordination number from 6 in ligand **2** to 5 in ligand **1** (Figs. 4, 6).

The conductance behavior of ligand **1** is different from ligand **2** studied in our previous investigation [11]. For ligand **2**, it has been shown, in all cases, that there is a gradual decrease in the molar conductivity with an increase in the ligand concentration, and in the cases of Hg^{2+} and Pb^{2+}, the conductivity first decreases and then begin to level off at a mole ratio greater than one (1:1). This is an indication of the formation of fairly stable 1:1 complexes in solution. However, the conductance behavior of ligand **1** can be divided as follows:

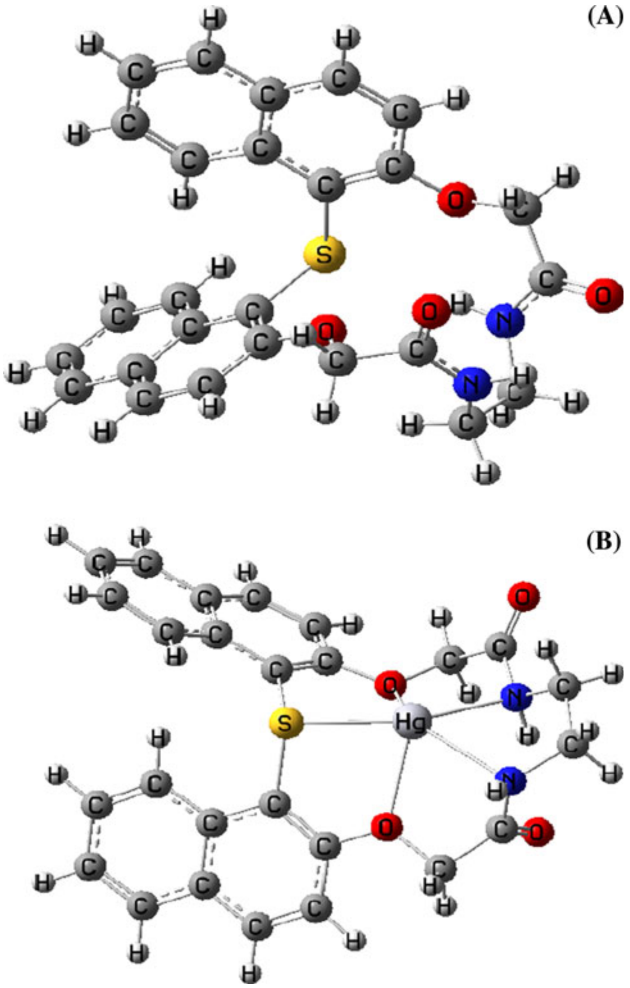

Fig. 4 Optimized structure of the lowest-energy conformation (within 6 ones) of free ligand **1** (**a**) and Hg^{2+}-**1** complex (**b**) in the gas-phase

- For all nitrates and the most perchlorates including Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, there is a gradual increase in the molar conductivity without any change in the slope with increasing the ligand **1** concentration (Fig. 1 of supporting information and Fig. 2). These behaviors do not indicate the formation of cation–ligand complexes in solution.
- In the case of perchlorate salts of Cd^{2+}, Hg^{2+} and Pb^{2+}, the molar conductivity first decreases up to the [ligand]/[cation] mole ratio one and then increases (Fig. 3).

The hydrogen bond between perchlorates and methanol as a solvent has been studied by IR, Raman [14] and NMR [15, 16] spectroscopic methods. The results indicated that the methanol molecule is associated with perchlorate anion through hydrogen bonding as $(ClO_4^- \cdots HOCH_3)$ units [14]. The other conclusion showed that “the perchlorate ion is a weaker proton acceptor than the oxygen atom of methanol” [14–16].

The study of cations-methanol interactions have also indicated that cations with high charge density such as Zn^{2+}, Mg^{2+} and Al^{3+} have important and strong electrostatic interaction with methanol but as the size of cation increases, ultimately such interaction to the cation becomes less important and the methanol molecules revert almost completely to their normal state [16]. On the basis of these studies, we interpret the conductometric behaviors as following:

- The ligand–cation complexes are not formed because of the intense solvation of cation by methanol. The perchlorate (or nitrate) salts can be solvated as Eq. 1.

$$M(ClO_4)_n \xrightarrow{CH_3OH} M^{n+} \cdots OHCH_3 + n(ClO_4^- \cdots HOCH_3) \quad (1)$$

The dotted line is indicative of electrostatic interaction in the case $M^{n+} \cdots OHCH_3$, and hydrogen bonding in the latter case.

With adding the methanolic solution of ligand **1** to methanolic solution of salt, methanol releases perchlorate in $ClO_4^- \cdots HOCH_3$ system and prefers to interact with ligand **1** through hydrogen bonding by which the conductivity increases. In other words, the hydrogen bonded macrocyclic diamide **1** with methanol $(L_1 \cdots HOCH_3)$ has stronger interaction with methanol and it replaces the perchlorate ion which is weaker proton acceptor in $(ClO_4^- \cdots HOCH_3)$ units. This can be stated as Eq. 2.

$$n(ClO_4^- \cdots HOCH_3) + L_1 \cdots HOCH_3 \rightarrow (n-1)(ClO_4^- \cdots HOCH_3) + CH_3HO \cdots L_1 \cdots HOCH_3 + ClO_4^- \quad (2)$$

In which the macrocyclic diamide **1** is denoted as L_1.

- The complex is formed between ligand **1** and cation due to intense tendency of soft donor atoms of ligand including S and N to soft cations with lower charge density such as Hg^{2+}, Pb^{2+}, and Cd^{2+} or may be due to the weak solvation of these cations by methanol solvent. Therefore, once the ligand is added, it is observed that a gradual decrease in the molar conductivity occurred up to the mole ratio one (Fig. 3).
  This behavior is indicative of the lower mobility of the ligand–cation complexes compared to the solvated ones. At ligand to cation mole ratio greater than one, the conductance increases quickly according to Eq. 2.

For ligand **2**, no increment in the molar conductivity is observed at mole ratio greater than one [11], this is due to its lower or higher tendency to interact with hydrogen bonded methanol-perchlorate system, as indicated by Eqs. 3 and 4, respectively.

$$n(ClO_4^- \cdots HOCH_3) + L_2 \cdots HOCH_3 \rightarrow \text{ no interaction} \quad (3)$$

or

$$n(ClO_4^- \cdots HOCH_3) + L_2 \cdots HOCH_3 \rightarrow (n\text{-}1)(ClO_4^- \cdots HOCH_3) + ClO_4^- \cdots L_2 \cdots HOCH_3 \quad (4)$$

In above equations, the macrocyclic diamide **2** is denoted as L_2. Therefore, the cations such as Hg^{2+} and Pb^{2+} interact strongly with ligand **2** and lead to complex formation, hence, the molar conductivity decreases until mole ratio one and then approximately becomes constant according to Eq. 3. For metal cations that don't interact or interact weakly with macrocyclic diamide **2**, very slightly decrease in molar conductivity plots is observed according to Eq. 4.

Quantum mechanics calculations

Quantum chemical calculations are found to be extremely helpful in the understanding of hydrogen bonding and ligand–metal interactions. Therefore, an attempt is made to use quantum chemistry to obtain more information about molecular structure and interactions of present compounds. For this purpose, Gaussian 03 [17], and AIM2000 [18] programs are utilized to optimize the geometrical structures and to analyze bond critical points between ligands and solvent, transition metal ion (Hg^{2+}) and its counter ion (ClO_4^-). A critical point is that gradient of electron density vanishes. As a typical result, the interactions of ligands **1** and **2** with Hg^{2+}, methanol, and ClO_4^- are taken into consideration. The ligands are large molecules which have many conformations. It is statistical point of view that a molecule is more likely to be found in a configuration with lower energy. The lower the energy of a configuration is, the more likely it is to be found. In this study an attempt is made to try six conformations for both ligands **1** and **2**. The conformation with the lowest gas phase energy is chosen for further studies. To recognize the lowest-energy conformation, optimization should be done for bond lengths, angles, and torsions as variables. This is done by keyword OPT. It is common to accelerate the convergence rate by pre-optimization with semi-empirical methods. PM3 is used as a pre-optimization method for all calculations. True minimum is guaranteed by NImag = 0 (number of imaginary frequencies) in the output of FREQ keyword. Two kinds of computer, i.e., a G5 server (from HP) with Xeon processor and 4 GB RAM, and a Core™ 2 Due processor with 2 GB RAM have been used for calculations. HF/Lanl2dz level of theory has been considered as an ab initio method. Optimization can be done in a solvent by use of SCRF OPT keywords. This option has not been considered and all calculations are done in the gas phase. Figures 4a, b show the optimized structures of free ligand **1** and **1**-Hg^{2+} complex, respectively. The bonds between Hg^{2+} and oxygens and nitrogens are based on the critical points between them taken from the output of AIM program. In this article, all non-covalent bonds have been shown by dotted lines. The optimized structure of ligand **2** and **2**-Hg^{2+} complex has been previously represented [11]. It must be noted that one may find a conformation with lower-energy than the presented conformations. Since, these structures explain the experimental behaviors of ligands, we did not consider more conformations. However, one can obtain potential energy surface (PES) by SCAN keyword. To obtain the further chemical information about the intermolecular interaction, Bader theory of atoms in molecules (AIM) was used by AIM2000 program [19, 20]. In addition, it is common to calculate binding energy between cation and ligand to obtain more information about the strength of cation binding to ligand. Bader's theory of atoms in molecules offers a useful tool for classifying different kinds of interactions. Bader and Essen have reported different categories of critical points [21]. For shared (covalent) interactions the electron density at bond critical point is of order $>10^{-1}$ a.u. The Laplacian of the electron density $(\nabla^2\rho(r_c))$ is a measure of local concentrations of electron density and may be positive or negative. A negative value of Laplacian denotes electron concentration while a positive Laplacian shows depletion of the electron density. It has been reported that for hydrogen bonded systems, nobel-gas dimmers and ionic systems, electron density is of order $\sim 10^{-2}$ a.u. and for Van der Waals complexes, it is of order $\sim 10^{-3}$ a.u. and the Laplacian is positive [19]. Figure 5 shows intramolecular interactions of free ligands **1** and **2** based on the AIM data. One can find all of the molecular graphs in the supporting information file. As shown in Fig. 5a there are six intramolecular interactions in free ligand **1**. Five of these six interactions belong to the hydrogen bonding. Details of electron densities ($\rho(r_c)$) at critical points are shown in Table 2. The Laplacian ($\nabla^2\rho$) values at critical points are shown in the supporting information file. AIM2000 gives Laplacians that need to be multiplied by -4π to obtain the correct values [22]. The data in the supporting information have been corrected. Figure 5b shows seven intramolecular interactions for free ligand **2**. The related data have been shown in Table 2 and in supporting information. In this conformation, the C_1–H_4 interaction with $\rho = 0.0004$ a.u. belongs to the Van der Waals interaction.

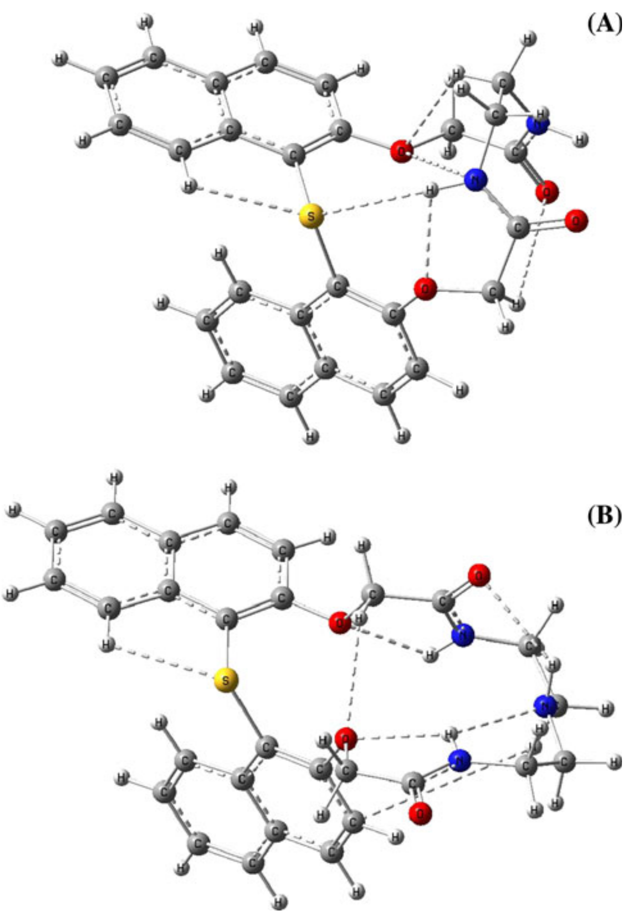

Fig. 5 Molecular graphs of free ligand **1** (**a**) and ligand **2** (**b**) by HF/Lanl2dz

To build Gaussian job function (Gjf) for ion-ligand complex, optimized structure of free ligands are modified. Optimization (OPT) and frequencies analyses (FREQ) are done by HF/Lanl2dz level of theory. Figure 6 shows atoms in molecules (AIM) analyses for Hg^{2+}-ligands compounds (for critical points see supporting information). As are shown in these figures, Hg^{2+} has strong interaction with all nitrogen, ethereal oxygen and sulfur atoms. This is completely in line agreement with conductometric data that show the existence of strong interaction between some transition metal ions and ligands. The electron densities of these critical points are summarized in Table 2. S–Hg^{2+} interaction in both complexes is strong. In both complexes N–Hg^{2+} is stronger than O–Hg^{2+}. Experimental data showed that for ligand **1** the conductance reduces up to 1:1 molar ratio of ligand/metal ion and then it increases. However, this is not the case for ligand **2**. There is no direct confirmation for the mechanism of the process. One conjecture is about intermolecular hydrogen bond between methanol and ligands. If the interaction between ligand **1** and methanol is stronger than the interaction between counter ion (ClO_4^-) and methanol, one may suppose that at molar ratio higher than 1:1, the counter ion is released and the conductance increases. To accept or reject this idea, one needs molecular information about interaction between above species. Quantum chemical calculation plays important role in this subject. However, it should be noted that contrary to the experimental data that are determined in solution phase, all calculations are in gas phase. The binding energies for ClO_4^-–MeOH, ClO_4^--ligand **1**, ClO_4^--ligand **2**, MeOH-ligand **1**, and MeOH-ligand **2** interactions were calculated using ab initio methods (Tables 2, 3 of supporting information). But, these results cannot interpret the experimental behaviors. Therefore, these interactions are investigated by AIM analyses. As before, to test the real local minima for these complexes, OPT and FREQ keywords are used. Figures 7 and 8 show the molecular shape of these interactions at HF/Lanl2dz level of theory. The molecular shape of ClO_4^-–MeOH has been shown in Fig. 9. Calculations with higher levels of theory are the subject of our further study and will be presented later. The details of AIM analyses for ClO_4^-–MeOH, MeOH-ligand **1**, ClO_4^--ligand **1**, ClO_4^--ligand **2**, and MeOH-ligand **2** are shown in Table 2 and supporting information. The number of critical points in above species is high. This leads that the systems to be more complex and the conclusion not to be straightforward. Recently, researchers made an attempt to relate stabilization energy to the sum of electron densities of bond critical points [23]. In these studies, it has been found that the calculated total

Table 2 Electron density (in e/a^3) of bond critical points for free ligands **1** and **2**, Hg^{2+}-ligand **1**, Hg^{2+}-ligand **2**, MeOH-ligand **1**, MeOH-ligand **2**, ClO_4^--ligand **1**, ClO_4^--ligand **2**, and MeOH–ClO_4^- and their total electron density

Compound	Bond											Σρ
Ligand **1**	O1–H2[a]	O3–H1	O4–N1	O4–H3	S–H2	S–H4						
ρ	0.0202	0.0012	0.0039	0.0109	0.0087	0.0131						0.0580
Ligand **2**	O1–H1	N2–H1	O3–H2	O4–H3	O1–H6	S–H5	C1–H4					
ρ	0.0179	0.0170	0.0092	0.0185	0.0068	0.0124	0.0004					0.0822
Hg^{2+}-ligand **1**	O1–Hg^{2+}	N1–Hg^{2+}	N2–Hg^{2+}	O3–Hg^{2+}	S–Hg^{2+}	O2–H1	S–H2	C1–H3	H4–H5			
ρ	0.0469	0.0374	0.0614	0.038	0.064	0.0128	0.0119	0.0126	0.0124			0.2974
Hg^{2+}-ligand **2**	O1–Hg^{2+}	N1–Hg^{2+}	N2–Hg^{2+}	N3–Hg^{2+}	O3–Hg^{2+}	S–Hg^{2+}	O2–H1	S–H2	C1–H3			
ρ	0.0426	0.0358	0.0657	0.0406	0.0351	0.0474	0.0102	0.0118	0.009			0.2982
MeOH-ligand **1**	O1–H1	O2–H1	O1–H5	O5–H4	S–H6	O4–H3	O3–H2					
ρ	0.0097	0.0192	0.0156	0.0016	0.0128	0.0308	0.0232					0.1129
MeOH-ligand **2**	O1–H1	O2–H2	O3–H3	N1–H5	C1–H4	N2–H6	O4–H7	S–H8				
ρ	0.0186	0.0334	0.019	0.0164	0.0004	0.0057	0.0076	0.0124				0.1135
ClO_4^--ligand **1**	O1–H1	O3–H3	O3–C1	O2–H2	O2–N	O5–H5	O6–H5	O4–H4	S–H5	S–H6		
ρ	0.0104	0.0049	0.0043	0.007	0.0034	0.0051	0.0183	0.0024	0.0076	0.0131		0.0765
ClO_4^--ligand **2**	O1–H1	O5–H8	N2–H2	O2–H3	O2–H5	O3–H4	O3–H6	O4–H6	O4–H7	N3–H9	S–H10	
ρ	0.0054	0.0043	0.0187	0.0038	0.0136	0.005	0.0033	0.0047	0.0036	0.0056	0.0120	0.0800
MeOH–ClO_4–	O1–H1	O3–H2	O2–H3									
ρ	0.0034	0.0034	0.0187									0.0255

[a] The numbered atoms are presented in supporting information

electron density of water clusters varies linearly with the stabilization energy. This is a good trick for the present work to estimate the stabilization due to the interaction between different species by summing electron density of total bond critical points. The last column of Table 2 summarizes this value for all calculated interactions. The data clearly show that there is a strong interaction between transition metal ion (Hg^{2+}) with both ligands **1** and **2**. Total electron density for Hg^{2+}-ligand **1** is 0.2974 a.u., and for Hg^{2+}-ligand **2** is 0.2982 a.u. So, it can be concluded that ligand **2** has stronger interaction with Hg^{2+}. However, it should be noted that both free ligands are in methanol as a solvent. The electron density difference between Hg^{2+}-ligand and MeOH-ligand for ligand **1** is 0.1845 a.u., and for ligand **2** is 0.1847 a.u. Therefore, it is clear that the replacement of methanol by Hg^{2+} is more readily occurred for ligand **2** than ligand **1**.

As has been noted in above sentences, AIM predicts that the interaction between Hg^{2+}-ligand **2** is stronger than Hg^{2+}-ligand **1**. It is common in the literature to calculate binding energy of complexation to compare the interaction between ligand and cations.

The binding energy of complexation between ligand (L) and cation (M^{n+}) is defined as follows:

$$\Delta E = E_{L-M^{n+}} - E_L - E_{M^{n+}} \quad (5)$$

Where, E_L, $E_{M^{n+}}$, and $E_{L-M^{n+}}$ are free ligand, cation, and complex energies, respectively.

Table 3 shows the results of above energies for ligand **1**, ligand **2**, and their complex with Hg^{2+}. Since for both complexation processes, the same cation (Hg^{2+}) has been considered, we have not calculated the cation energy. Results show that the binding energy for ligand **2**-Hg^{2+} is greater than ligand **1**-Hg^{2+}. In other words, binding energy calculations as AIM data are in line with experimental data.

As a final point, we try to use AIM data to explain the different behaviors of ligands **1** and **2** after the complexation. After 1:1 mole ratio, there is free ligand in the solution. All of the Hg^{2+} is in the complex form, and free ligands may interact with methanol or perchlorate ion, or even may prefer to be free. The total electron density difference between ligand **1**-MeOH and free ligand **1** is 0.0549 a.u., and between ligand **2**-MeOH and free ligand **2** is 0.0313 a.u.. It is clear that the tendency of methanol to interact with the ligand **1** and to release perchlorate is higher than ligand **2**. So, we can conclude that quantum results (even in the gas phase) predict correctly the different behaviors of two above complexations. In future, we

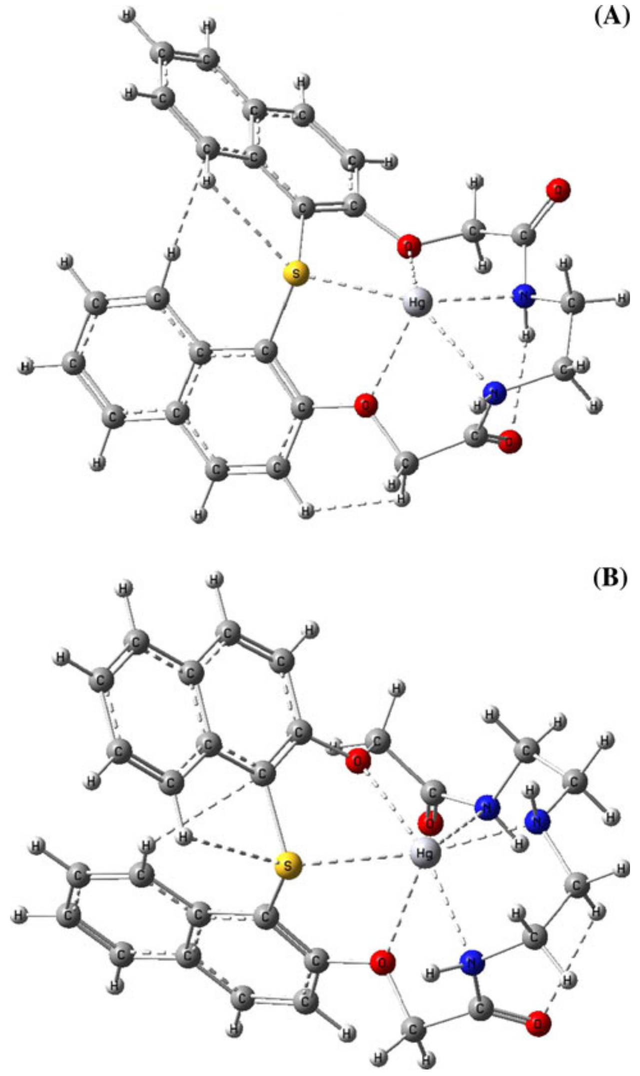

Fig. 6 Molecular graphs of Hg^{2+}-**1** (**a**) and Hg^{2+}-**2** (**b**) complexes by HF/Lanl2dz

Table 3 Electronic energies of ligands **1** and **2**, and their complex with Hg^{2+}

Species	Electronic energy in a.u.
Ligand **1**	−1415.23177
Ligand **2**	−1548.2966
Ligand **1**-Hg^{2+}	−1456.0632
Ligand **2**-Hg^{2+}	−1589.1772
ΔE^{a}_{bind}	−40.8314
ΔE^{b}_{bind}	−40.8806
$\Delta\Delta E^{c}_{bind}$	30.8735

[a] Binding energy for the complex formation of Ligand **1**-Hg^{2+}

[b] Binding energy for the complex formation of Ligand **2**-Hg^{2+}

[c] The difference of binding energy between Ligand **1**-Hg^{2+} and Ligand **2**-Hg^{2+} in kcal/mol. Note that 1 a.u. equals to 627.5095 kcal/mol

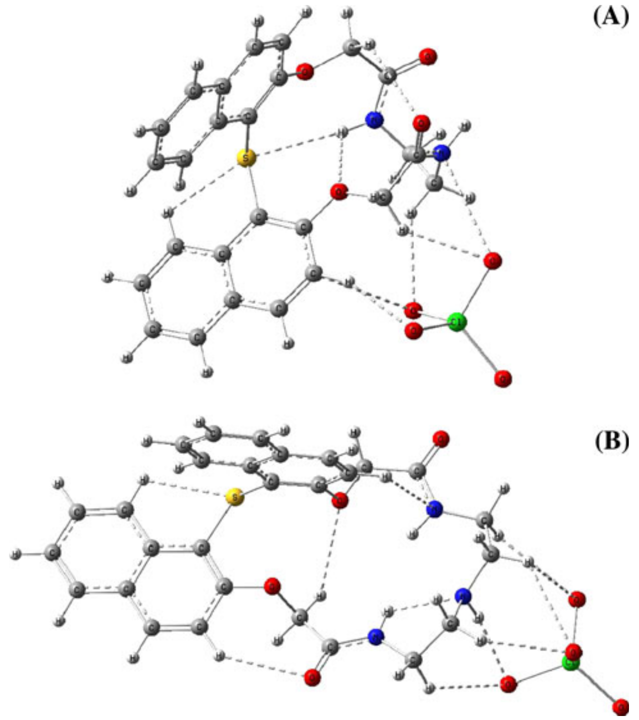

Fig. 7 Molecular graphs of ClO_4^--ligand **1** (**a**) and ClO_4^--ligand **2** (**b**) by HF/Lanl2dz

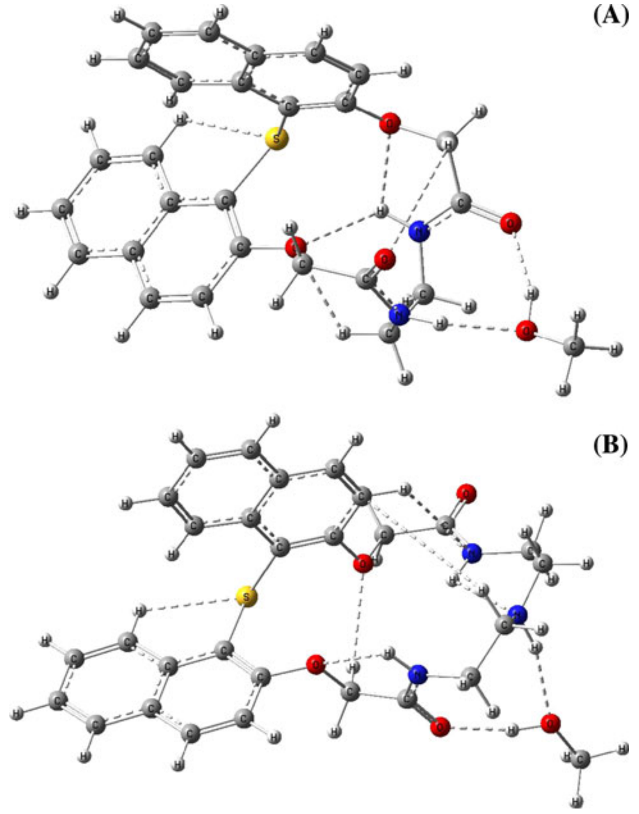

Fig. 8 Molecular graphs of MeOH-ligand **1** (**a**) and MeOH-ligand **2** (**b**) by HF/Lanl2dz

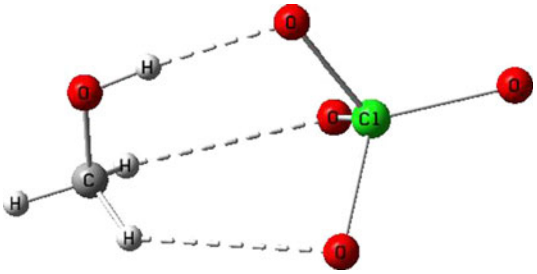

Fig. 9 Molecular graph of MeOH–ClO_4^- by HF/Lanl2dz

will try to use more sophisticated levels of theory (such as MP2) to study these complexation in more details.

Conclusion

In this article, complexation between different cations and two dinaphthosulfide-substituted macrocyclic amids (L_1, and L_2) have been studied by conductometric and ab initio methods. The experimental results show that for some cations, there is not any interaction between ligands and cations, while for some others there is a strong interaction. Two different behaviors of the complexation have been observed. In the first one, after 1:1 mole ratio of ligand/cation, a horizontal line is obtained which means that with addition of more free ligands, it is not occurred new process. For the second one, after 1:1 mole ratio of ligand/cation the slope increases abruptly. To prove the conjectured mechanism, we have used AIM theory. AIM data show that there is more tendency for ligand **1** to interact with methanol, by which the counter ion is released. With increasing the mobility of this ion the conductance increases.

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