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ORIGINAL PAPER

Cation recognition of thiacalix[2]thianthrene and p-tert-butylthiacalix[2]thianthrene and their conformers and complexes with Zn(II), Cd(II) and Hg(II): a theoretical investigation

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Abstract The structures of thiacalix[2]thianthrene, p-tert-butylthiacalix[2]thianthrene and their complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} were obtained using B3LYP/LanL2DZ and HF/LanL2DZ calculations. The structures of the most stable conformers of thiacalix[2]thianthrene and p-tert-butylthiacalix[2]thianthrene optimized at either the B3LYP/LanL2DZ or HF/LanL2DZ level are in good agreement with their corresponding X-ray crystallographic structures. The binding energies of cations, Zn^{2+}, Cd^{2+} and Hg^{2+} to thiacalix[2]thianthrene and to p-tert-butylthiacalix[2]thianthrene conformers, and the thermodynamic properties of their associations were obtained. The relative selectivities of both thiacalix[2]thianthrene and thiacalix[2]thianthrene conformer are in same order: $Zn^{2+} >> Hg^{2+} > Cd^{2+}$.

Keywords Thiacalix[2]thianthrenes · p-Tert-butylthiacalix[2]thianthrene · Zinc · Cadmium · Mercury · Cation recognition · Quantum chemical calculations

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Introduction

Calix[4]arene derivatives were used widely as receptors for cations, anions and neutral molecules [1–3]. In the search for receptors exhibiting selective binding toward toxic metal ions such as Hg^{2+}, Pb^{2+} and Cd^{2+} present in the environment, calix[4]arene derivatives are widely studied for their recognition of these toxic metal ions. Various sulfur-containing calix[4]arene derivatives, such as substituted calix[4]arene dithianes [4], N,N-dimethyl dithiocarbamoyl and thioether groups attached to the calix[4]arene [5], the calix[4]arene containing azathiol [6] and thiacalix[4]arenes [7] were found to selectively bind to Hg^{2+}. Therefore, calix[4]arenes containing sulfur atoms are expected to bind strongly to Cd^{2+} and Hg^{2+} but only a few studies of these complexes have been published. Numerous studies have focused on the sulfur-containing calix[4]arenes such as sulfonylcalix[4]arenes [8–10], thiacalix[4]arenes [11], p-tert-butylthiacalix[4]arene [12, 13], tetraamino-p-tert-butylthiacalix[4]arene conformers [14] and their complexes with transition ions [15–17], but their complexation with Cd^{2+} and Hg^{2+} have seldom been investigated. Since thiacalix[2]thianthrene and p-tert-butylthiacalix[2]thianthrene, in which the thianthrene cores are combined, have now been synthesized and their X-ray crystallographic structures [18, 19] obtained, the conformational structures of these two receptors, their binding abilities with toxic metal ions, and the structure of their complexes are now of great interest to environmental scientists.

In this work, the conformer structures of the thiacalix[2]thianthrene and p-tert-butylthiacalix[2]thianthrene receptors and their complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} were

investigated using quantum chemical computations. The binding energies and thermodynamic properties of all studied complexes and their highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and their energy gaps have been determined.

Computational details

Geometrical structures of thiacalix[2]thianthrene (**L1**), p-tert-butylthiacalix[2]thianthrene (**L2**) and their complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} were determined using Becke's

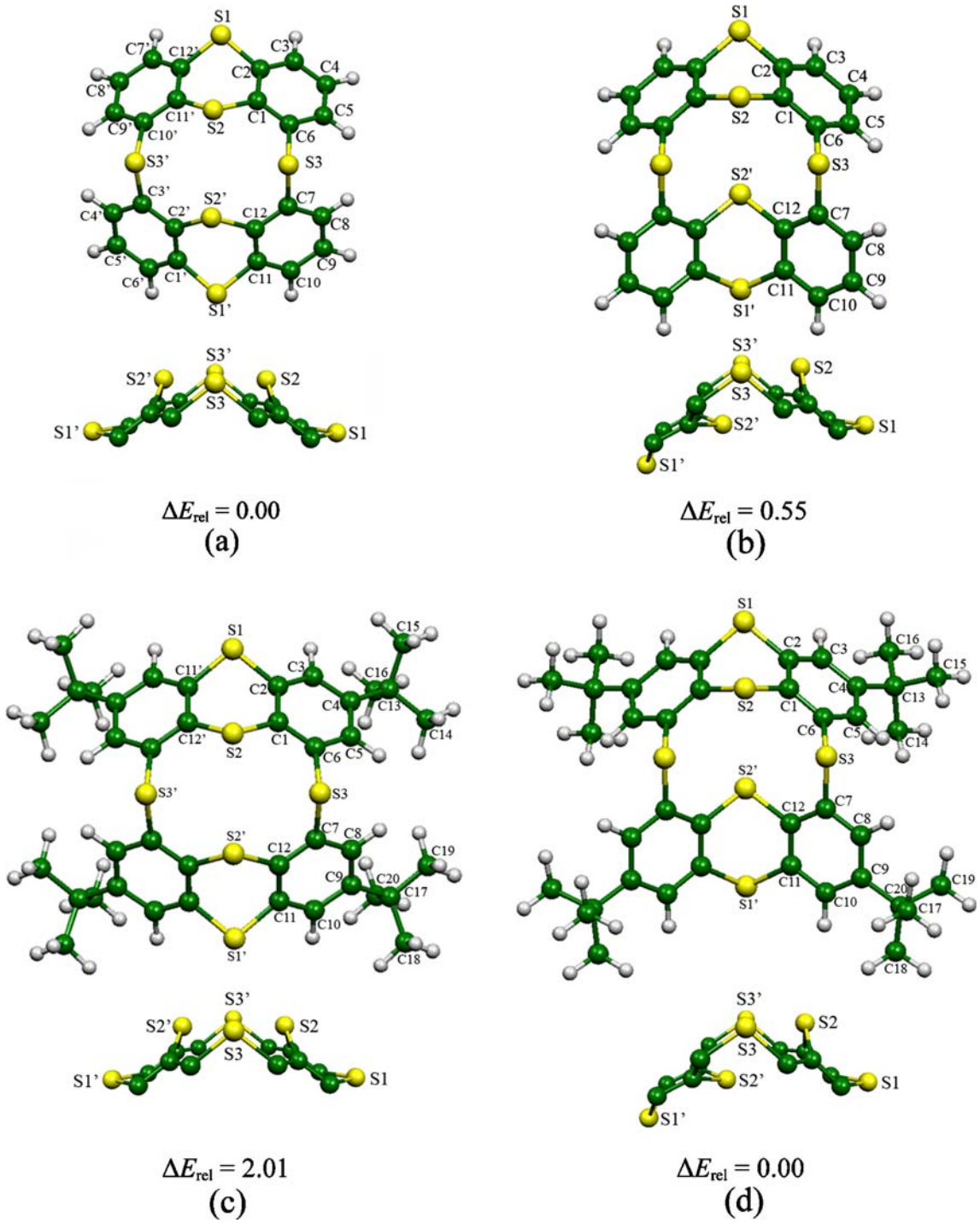

Fig. 1 The B3LYP/LANL2DZ-optimized structures of thiacalix[2]thianthrene conformers (**a**) **L1**, (**b**) **L1′**, p-tert-butylthiacalix[2]thianthrene conformers (**c**) **L2** and (d) **L2′**. *Top* Top view (full structure), *bottom* side view (for clarity, partial structure was displayed). Relative energies are in kcal mol^{-1}

three parameter exchange functional with the Lee–Yang–Parr correlation functional (B3LYP) [20–22] using the Los Alamos LanL2DZ split-valence basis set [23–25]. Density functional theory (DFT) calculations were performed with zero-point vibrational energy (ZPVE) corrections. Vibrational analyses were carried out on the minima. All computations were performed with the GAUSSIAN 03 program [26]. Molecular graphics of all studied molecules were generated with the MOLEKEL 4.3 program [27].

Table 1 Selected geometrical data for the structure of the thiacalix[2]thianthrene **L1** and **L1′** conformer, optimized at the B3LYP/LanL2DZ and HF/LanL2DZ levels

Data[a]	**L1**			**L1′**	
	X-ray[b]	B3LYP/LanL2DZ[c]	HF/LanL2DZ[d]	B3LYP/LanL2DZ	HF/LanL2DZ
Bond length (Å)					
S1-C2	1.7552	1.8409	1.7900	1.8487	1.8284
S2-C1	1.7691	1.8467	1.7828	1.8457	1.8316
C1-C2	1.3982	1.4115	1.4026	1.4074	1.3969
C2-C3	1.3877	1.4059	1.4040	1.4055	1.3908
C3-C4	1.3677	1.4044	1.3793	1.4094	1.3922
C4-C5	1.3830	1.4049	1.4091	1.4140	1.3914
C5-C6	1.3858	1.4084	1.3763	1.4042	1.3952
C1-C6	1.3993	1.4163	1.4208	1.4146	1.3998
C6-S3	1.7824	1.8660	1.8493	1.8603	1.8386
S3-C7	1.7888	1.8660	1.8492	1.8570	1.8371
C7-C8	1.3894	1.4084	1.3763	1.4052	1.3956
C8-C9	1.3885	1.4049	1.4091	1.4161	1.3937
C9-C10	1.3763	1.4044	1.3793	1.4088	1.3911
C10-C11	1.3874	1.4059	1.4040	1.4073	1.3928
C11-C12	1.4011	1.4115	1.4026	1.4049	1.3943
C7-C12	1.4024	1.4163	1.4208	1.4155	1.4002
C11-S1′	1.7619	1.8409	1.7899	1.8493	1.8290
C12-S2′	1.7789	1.8468	1.7828	1.8375	1.8219
Bond angle (º)					
C11′-S1-C2	103.68	100.49	107.07	98.39	98.39
S1-C2-C1	121.86	121.15	126.66	119.99	120.03
C2-C1-S2	123.06	120.98	124.06	119.83	118.76
C1-S2-C12′	103.93	101.24	108.89	97.82	98.12
C1-C2-C3	120.43	121.09	119.38	121.41	120.94
C2-C3-C4	120.26	119.70	120.31	120.95	119.64
C2-C1-C6	118.74	118.82	119.98	118.10	119.19
S2-C1-C6	117.95	120.14	115.84	122.06	122.05
C1-C6-S3	120.07	121.58	122.20	121.04	121.62
C6-S3-C7	101.50	101.58	98.08	103.37	103.78
Dihedral angle (°)					
S1-C2-C3-C4	171.73	174.26	178.11	-179.85	179.67
C2-C3-C4-C5	1.32	1.36	1.61	1.51	1.52
C3-C4-C5-C6	1.30	1.20	-0.82	-0.06	0.20
S1-C2-C1-S2	1.03	1.78	-4.52	-1.40	-1.48
S2-C1-C6-S3	1.17	-0.86	7.18	-1.94	-0.79

[a] Atomic numbering as defined in Fig. 1

[b] Taken from ref. [15]

[c] Root mean square deviations (RMSD) for bond length, bond angle and dihedral angle are 0.0490 Å, 1.73° and 1.49°, respectively

[d] RMSD for bond length, bond angle and dihedral angle are 0.0264 Å, 2.89° and 4.74°, respectively

Table 2 Selected geometrical data for the structure of p-tert-butylthiacalix[2]thianthrene **L2** and **L2′** conformers, optimized at the B3LYP/LanL2DZ and HF/LanL2DZ levels

Data[a]	**L2**			**L2′**	
	X-ray[b]	B3LYP/LanL2DZ	HF/LanL2DZ	B3LYP/LanL2DZ	HF/LanL2DZ
Bond length (Å)					
S1-C2	1.7507	1.8428	1.8233	1.8487	1.8303
S2-C1	1.7638	1.8450	1.8300	1.8457	1.8295
C1-C2	1.3738	1.4112	1.3969	1.4074	1.3908
C2-C3	1.3914	1.4017	1.3860	1.4055	1.3928
C3-C4	1.3702	1.4128	1.3992	1.4094	1.3947
C4-C5	1.3900	1.4089	1.3940	1.4140	1.4006
C5-C6	1.3890	1.4091	1.3985	1.4042	1.3900
C1-C6	1.3864	1.4119	1.3956	1.4146	1.4001
C6-S3	1.7729	1.8672	1.8456	1.8603	1.8391
S3-C7	1.7746	1.8672	1.8456	1.8570	1.8379
C7-C8	1.3873	1.4091	1.3985	1.4052	1.3907
C8-C9	1.3837	1.4089	1.3940	1.4161	1.4033
C9-C10	1.3834	1.4128	1.3992	1.4088	1.3936
C10-C11	1.3824	1.4017	1.3860	1.4073	1.3949
C11-C12	1.3808	1.4112	1.3969	1.4049	1.3882
C7-C12	1.4022	1.4119	1.3956	1.4155	1.4005
C11-S1′	1.7643	1.8428	1.8233	1.8493	1.8309
C12-S2′	1.7642	1.8450	1.8300	1.8375	1.8201
C4-C13	1.5267	1.5453	1.5406	1.5454	1.5406
C13-C14	1.4562	1.5491	1.5435	1.5574	1.5503
C13-C15	1.4561	1.5574	1.5504	1.5492	1.5439
C13-C16	1.4346	1.5574	1.5503	1.5575	1.5503
Bond angle (°)					
C11′-S1-C2	101.92	100.57	100.37	98.39	98.38
S1-C2-C1	120.60	120.94	120.65	119.99	119.84
C2-C1-S2	121.96	121.24	120.24	119.83	119.16
C1-S2-C12′	102.40	101.02	100.79	97.82	97.88
C1-C2-C3	121.25	121.35	121.48	121.41	121.45
C2-C3-C4	121.59	121.23	121.23	120.95	120.97
C2-C1-C6	117.68	117.89	117.95	118.10	118.17
S2-C1-C6	120.12	120.81	121.72	122.06	122.67
C1-C6-S3	120.43	121.39	122.05	121.04	121.39
C6-S3-C7	100.93	101.93	103.31	103.37	103.91
C4-C13-C14	113.71	112.30	112.33	109.29	109.42
C9-C17-C18	107.58	109.44	109.52	112.27	112.25
Dihedral angle (°)					
S1-C2-C3-C4	174.31	174.34	174.44	-179.85	-179.98
C2-C3-C4-C5	0.83	1.44	1.62	1.51	1.62
C3-C4-C5-C6	2.88	1.21	1.18	-0.06	0.17
S1-C2-C1-S2	-0.96	1.46	0.88	-1.40	-1.60
S2-C1-C6-S3	2.25	-0.86	-1.32	-1.94	-1.02
C5-C4-C13-C14	26.22	-0.10	-0.32	-59.67	-60.31
C10-C9-C17-C18	-67.40	-59.31	-58.95	0.68	0.95

[a] Atomic numbering as defined in Fig. 1

[b] Taken from ref. [15]

[c] RMSD for bond length, bond angle and dihedral angle are 0.0632 Å, 1.01° and 10.53°, respectively

[d] RMSD for bond length, bond angle and dihedral angle are 0.0520 Å, 1.44° and 10.66°, respectively

The Mulliken electronegativity (χ), chemical hardness (η) and electronic chemical potential (μ) for all optimized molecules using orbital energies of the HOMO and LUMO were calculated at the B3LYP/LanL2DZ and HF/LanL2DZ levels of theory. The chemical indices η, μ and χ were derived from the first ionization potential (I) and electron affinity (A) of the N-electron molecular system with a total energy (E) and external potential ($v(\vec{r})$) using the formulas $\chi = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} = -\mu \cong \frac{1}{2}(I+A)$ and $\eta = -\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} \cong \frac{1}{2}(I-A)$, with the first ionization potential and electron affinity being $I=E(N-1) - E(N)$ and $A=E(N) - E(N+1)$ [28]. According to Koopman's theorem [29], I and A were computed from the HOMO and LUMO energies using the formula $I=-E_{\mathrm{HOMO}}$ and $A=-E_{\mathrm{LUMO}}$.

Binding energy ($\Delta E_{\mathrm{binding}}$), preorganization energy ($\Delta E_{\mathrm{preorg}}$) of hosts and complexation energy ($\Delta E_{\mathrm{complex}}$) for complexation are defined by the following formulae:

$$\Delta E_{\mathrm{binding}} = E_{\mathrm{complex}} - \left(E_{\mathrm{free-host}} + E_{\mathrm{guest}}\right) \quad (1)$$

$$\Delta E_{\mathrm{preorg}} = E_{\mathrm{complexed-host}} - E_{\mathrm{free-host}} \quad (2)$$

$$\Delta E_{\mathrm{complex}} = E_{\mathrm{complex}} - \left(E_{\mathrm{complexed-host}} + E_{\mathrm{guest}}\right) \quad (3)$$

Therefore,

$$\Delta E_{\mathrm{complex}} = \Delta E_{\mathrm{binding}} + \Delta E_{\mathrm{preorg}} \quad (4)$$

The binding selectivity of receptor **L1** and **L2** as host molecules to metal cations Zn^{2+}, Cd^{2+} and Hg^{2+} as guests was derived from definition of the selectivity coefficient from [30]. Therefore, the selectivity coefficient, K_X^{LS} termed as a ratio of association constant of complexation to their least stable complex species $\left(\frac{K_X}{K_{LS}}\right)$ [17, 31] was used as binding selectivity of receptor **L1** and **L2**.

Results and discussion

Conformers of receptors and their binding sites

The B3LYP/LanL2DZ-optimized structures of thiacalix[2]thianthrene conformers (**L1** and **L1′**) and p-tert-butylthiacalix[2]thianthrene conformers (**L2** and **L2′**) are shown in Fig. 1. The selected B3LYP/LanL2DZ and HF/LanL2DZ-optimized geometrical data for the conformers of thiacalix[2]thianthrene and p-tert-butylthiacalix[2]thianthrene are listed in Tables 1 and 2. The B3LYP/LanL2DZ and HF/LanL2DZ-optimized structures of conformers **L1** and **L2** correspond to the X-ray structures, and their selected geometrical data are compared with the X-ray crystallographic data given in Table 1. This comparison revealed that both the B3LYP/LanL2DZ and HF/LanL2DZ-optimized structures of the most stable conformers of thiacalix[2]thianthrene (**L1**) and p-tert-butylthiacalix[2]thianthrene (**L2**) are in good agreement with their corresponding X-ray crystallographic data. The relative stabilities of the conformers of thiacalix[2]thianthrene and p-tert-butylthiacalix[2]thianthrene are in the order: **L1** > **L1′** and **L2′** > **L2**, see Fig. 1.

Two binding sites in each conformer of these receptors toward the cations M, $M^{2+}=Zn^{2+}$, Cd^{2+} and Hg^{2+} were found; one site is in the 4-S cavity and the other in the 2-S cavity of the thianthrene ring. As the all studied complexes were formed by four conformers (**L**) and three cations (M), 12 configurations were obtained. Therefore, the notation for these complex configurations is defined as **L**/M and **L**/M′ for the cation located in the 4-S and the 2-S cavities, respectively (Figs. 2, 3).

The sizes of the 4-S cavity of the conformers **L1** and **L2** in terms of distances between two diagonally opposite S atoms as (S2⋯S2′) x (S3⋯S3′) are 3.804×5.441 Å for **L1** and 3.793×5.471 Å for **L2**, and the sizes of the conformers **L1′** and **L2′** are (S2⋯S2′)×(S3⋯S3′)= 3.589×5.067 Å and 3.598×5.088 Å, respectively. The sizes of the 2-S cavity of the conformers **L1**, **L1′**, **L2** and **L2′** defined as (S1⋯S2) are 3.315, 3.248, 3.793 and 3.250 Å, respectively.

Thiacalix[2]thianthrene complexes and their associations

The B3LYP/LanL2DZ optimized structures of the thiacalix[2]thianthrene complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} are shown in Fig. 2. This figure shows that coordination bond lengths (denoted by M⋯S) of the complexes for the same thiacalix[2]thianthrene conformers are in the order: Hg⋯S > Cd⋯S > Zn⋯S. Relative energies of the thiacalix[2]thianthrene complexes with Zn^{2+}, Cd^{2+} and Hg^{2+}, obtained using the B3LYP/LanL2DZ and HF/LanL2DZ calculations are shown in Table 3. These show that the relative energies of the complexes obtained at the HF/LanL2DZ level are overestimated as compared with their corresponding structures computed at the B3LYP/LanL2DZ level. The relative stabilities of the complex of thiacalix[2]thianthrene conformers with Zn^{2+}, Cd^{2+} and Hg^{2+}, based on the B3LYP/LanL2DZ calculations are, in order: **L1′**/Zn > **L1**/Zn > **L1**/Zn′ > **L1′**/Zn′, **L1′**/Cd > **L1**/Cd > **L1**/Cd′ > **L1′**/Cd′ and **L1′**/Hg > **L1**/Hg′ > **L1**/Hg > **L1′**/Hg′ (see Fig. 2). Nevertheless, the most stable complex species optimized at either the B3LYP/LanL2DZ or HF/LanL2DZ level are **L1′**/Zn, **L1′**/Cd and **L1′**/Hg.

The binding abilities of the thiacalix[2]thianthrene conformers toward Zn^{2+}, Cd^{2+} and Hg^{2+}, in terms of binding energy and thermodynamic properties of their associations, are given in Table 4. Based on the largest value of the selectivity coefficient of each group of complexes as listed in Table 4, the relative selectivities of the thiacalix[2]thianthrene are, in order: $Zn^{2+} >> Hg^{2+} > Cd^{2+}$, which corresponds to the

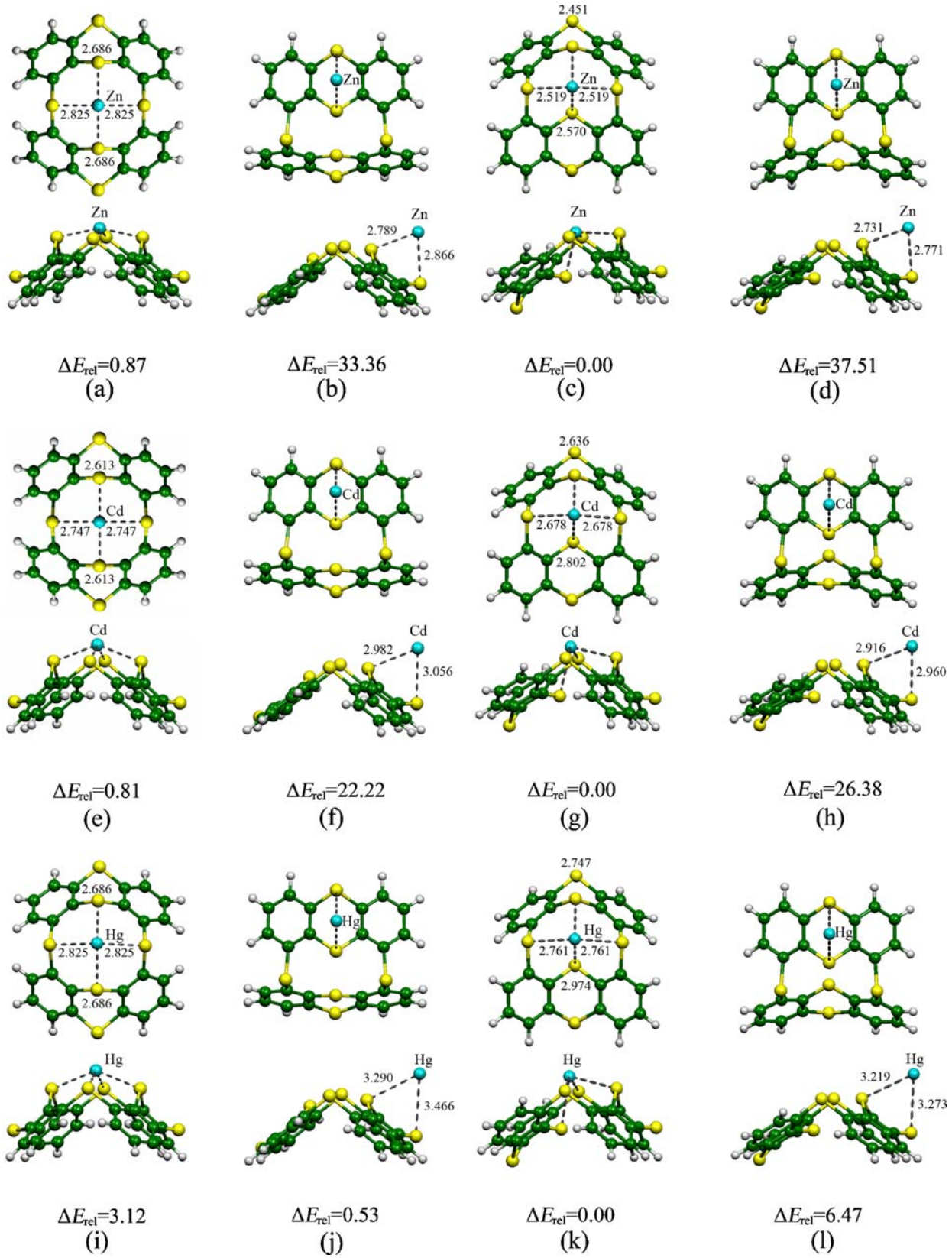

Fig. 2 B3LYP/LANL2DZ-optimized structures of thiacalix[2]thianthrene complexes as (**a**) **L1**/Zn, (**b**) **L1**/Zn′, (**c**) **L1′**/Zn, (**d**) **L1′**/Zn′, (**e**) **L1**/Cd, (**f**) **L1**/Cd′, (**g**) **L1′**/Cd, (**h**) **L1′**/Cd′, (**i**) **L1**/Hg, (**j**) **L1**/Hg′, (**k**) **L1′**/Hg and (**l**) **L1′**/Hg′. *Top* Top views, *bottom* side views. Relative energies, based on the most stable species of each complexes (Zn, Cd and Hg complexes) are in kcal mol^{-1}; bond distances are in Ångstroms

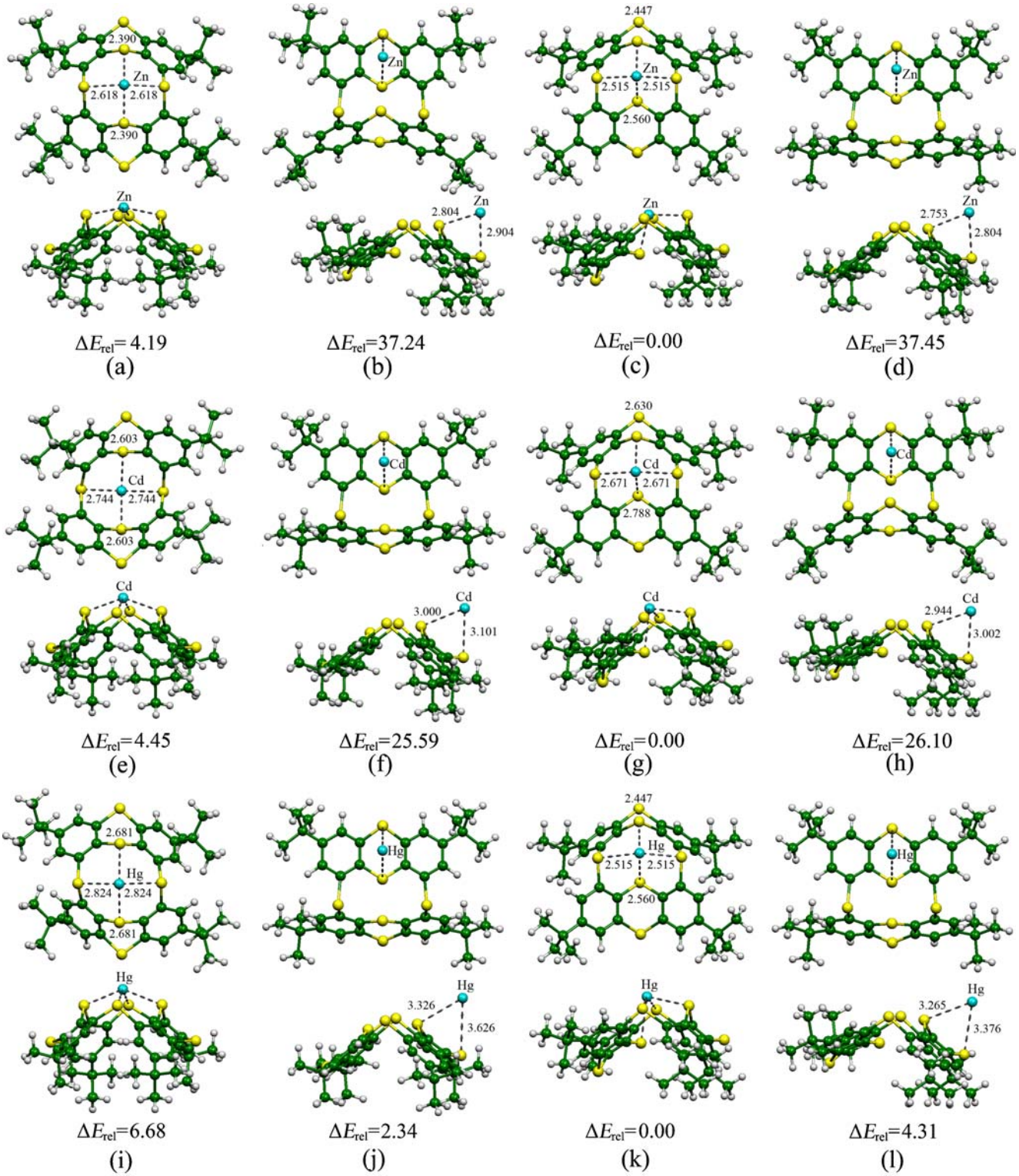

Fig. 3 B3LYP/LANL2DZ-optimized structures of p-tert-butylthiacalix[2]thianthrene complexes as (**a**) **L2**/Zn, (**b**) **L2**/Zn′, (**c**) **L2′**/Zn, (**d**) **L2′**/Zn′, (**e**) **L2**/Cd, (**f**) **L2**/Cd′, (**g**) **L2′**/Cd, (**h**) **L2′**/Cd′, (**i**) **L2**/Hg, (**j**) **L2**/Hg′, (**k**) **L2′**/Hg and (**l**) **L2′**/Hg′. *Top* Top views, *bottom* side views. Relative energies, based on the most stable species of each complexes (Zn, Cd and Hg complexes) are in kcal mol^{-1}; bond distances are in Ångstroms

Table 3 Relative energies of thiacalix[2]thianthrene (**L1**) and p-tert-butylthiacalix [2]thianthrene (**L2**) complexes with Zn^{2+}, Cd^{2+} and Hg^{2+}, computed at the B3LYP/LanL2DZ and HF/LanL2DZ levels with zero-point vibrational energy (ZPVE) corrections

Complex	ΔE_{rel} [a, b]	
	B3LYP/LanL2DZ + ZPVE	HF/LanL2DZ + ZPVE
L1 system		
L1/Zn	0.87	2.47
L1/Zn′	33.36	57.57
L1′/Zn	0.00	0.00
L1′/Zn′	37.51	50.47
L1/Cd	0.81	2.16
L1/Cd′	22.22	48.43
L1′/Cd	0.00	0.00
L1′/Cd′	26.38	41.66
L1/Hg	3.12	4.50
L1/Hg′	0.53	40.73
L1′/Hg	0.00	0.00
L1′/Hg′	6.47	34.02
L2 system		
L2/Zn	4.19	3.71
L2/Zn′	37.24	60.09
L2′/Zn	0.00	0.00
L2′/Zn′	37.45	52.72
L2/Cd	4.45	3.45
L2/Cd′	25.59	51.11
L2′/Cd	0.00	0.00
L2′/Cd′	26.10	43.85
L2/Hg	6.68	5.52
L2/Hg	2.34	42.48
L2′/Hg	0.00	0.00
L2′/Hg′	4.31	35.38

[a] Relative energies are compared to the most stable for their corresponding complexes of which masses are equivalent

[b] In kcal mol^{-1}

order: **L1′**/Zn >> **L1**/Hg′ > **L1′**/Cd. The three complexes **L1′**/Zn, **L1′**/Cd and **L1**/Hg′ are the most thermodynamically favorable complexes with the Zn^{2+}, Cd^{2+} and Hg^{2+}, respectively. This is because the ionic sizes of Zn^{2+} (1.53 Å) and Cd^{2+} (1.71 Å) in the complexes **L1′**/Zn and **L1′**/Cd completely fit into the 4-S cavity of conformer **L1′**. However, the Hg^{2+} is able to fit into the 4-S cavity of conformer **L1′** but, thermodynamically, it prefers to be coordinated by two sulfur atoms of the 2-S cavity, see Fig. 2j,k.

The preorganization energies of the thiacalix[2]thianthrene conformers to form complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} are within the range of 3.63–8.87, 4.08–11.59 and 5.89–14.14 kcal mol^{-1}, respectively. Based on the highest values of selectivity coefficients of the thiacalix[2]thianthrene complexes, Zn^{2+} and Cd^{2+} ions are likely located in the 4-S cavity of the conformer **L1′**, and Hg^{2+} is located in the 2-S cavity of the conformer **L1**.

p-tert-butylthiacalix[2]thianthrene complexes and their associations

The B3LYP/LanL2DZ optimized structures of the p-tert-butylthiacalix[2]thianthrene complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} are shown in Fig. 3. The figure shows that coordination bond lengths of the complexes for the same p-tert-butylthiacalix[2]thianthrene conformers are, in order: Hg···S > Cd···S > Zn···S. Relative energies of the thiacalix[2]thianthrene complexes with Zn^{2+}, Cd^{2+} and Hg^{2+}, obtained using B3LYP/LanL2DZ and HF/LanL2DZ calculations are shown in Table 4. The relative stabilities for the complex the p-tert-butylthiacalix[2]thianthrene conformers with Zn^{2+}, Cd^{2+} and Hg^{2+}, based on the B3LYP/LanL2DZ method are, in order: **L2′**/Zn ≈ **L2**/Zn >> **L2**/Zn′ ≈ **L2′**/Zn′, **L2′**/Cd ≈ **L2**/Cd >> **L2**/Cd′ ≈ **L2′**/Cd′, and **L2′**/Hg > **L2**/Hg′ > **L2**/Hg > **L2′**/Hg′, respectively, see Fig. 3. Nevertheless, the most stable complex species optimized at either the B3LYP/LanL2DZ or HF/LanL2DZ level are **L2′**/Zn, **L2′**/Cd and **L2**/Hg′. The binding abilities of the p-tert-butylthiacalix[2]thianthrene conformers toward Zn^{2+}, Cd^{2+} and Hg^{2+}, in terms of binding energy and thermodynamic properties of their associations are given in Table 4. Based on the largest value of the selectivity coefficient of each group of complexes as listed in Table 4, the relative selectivities of the thiacalix[2]thianthrene are, in order: Zn^{2+} >> Hg^{2+} > Cd^{2+}, which corresponds to the order: **L2′**/Zn >> **L2**/Hg′ > **L2′**/Cd. These three complexes **L2′**/Zn, **L2′**/Cd and **L2**/Hg′ are the most thermodynamically favorable complexes with Zn^{2+}, Cd^{2+} and Hg^{2+}, respectively. The reason for this is the same as mentioned for the thiacalix[2]thianthrene complex, i.e., the ionic sizes of Zn^{2+} and Cd^{2+} in the complexes **L2′**/Zn and **L2′**/Cd fit into the 4-S cavity of conformer **L2′** and Hg^{2+} thermodynamically prefers to be coordinated by two sulfur atoms of the 2-S cavity (Fig. 3j, k).

The preorganization energies of the p-tert-butylthiacalix[2]thianthrene conformers to form complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} are within the range of 4.46–17.06, 4.73–12.35 and 6.30–14.62 kcal mol^{-1}, respectively. Based on the highest values of selectivity coefficients of the p-tert-butylthiacalix[2]thianthrene complexes, Zn^{2+} and Cd^{2+} ions are likely located in the 4-S cavity of conformer **L2′**, and Hg^{2+} is located in the 2-S cavity of conformer **L2**.

Chemical reactivity and selectivity

The B3LYP/LanL2DZ energies E_{LUMO}, E_{HOMO}, frontier molecular orbital energy gap, ($\Delta E_{HOMO-LUMO}$) and chemi-

Table 4 Preorganization energies, thermodynamic quantities of the thiacalix[2]thianthrene and p-tert-butylthiacalix[2]thianthrene conformers, complexation and binding energies of the complexes with Zn^{2+}, Cd^{2+} and Hg^{2+}, and selectivity coefficients computed at the B3LYP/LanL2DZ level with ZPVE corrections

Complex	Host			Host/guest				
	ΔE_{preorg} [a]	ΔH^{O}_{preorg} [a]	ΔG^{O}_{preorg} [a]	$\Delta E_{complex}$ [a]	$\Delta E_{binding}$ [a]	ΔH^{O}_{298} [a]	ΔG^{O}_{298} [a]	K_X^{LS} [b]
L1 system								
L1/Zn	8.87	8.95	8.30	-269.58	-260.71	-261.19	-251.68	1.89×10^{45}
L1/Zn′	6.27	5.78	7.20	-234.49	-228.22	-228.28	-220.43	2.34×10^{22}
L1′/Zn	3.63	3.73	3.57	-265.76	-262.13	-262.63	-252.71	1.07×10^{46}
L1′/Zn′	4.09	4.20	3.03	-228.70	-224.62	-224.62	-217.15	9.13×10^{19}
L1/Cd	11.59	11.08	13.54	-233.84	-222.26	-223.23	-210.92	2.47×10^{15}
L1/Cd′	6.09	5.60	7.02	-206.94	-200.85	-200.84	-193.22	2.63×10^{2}
L1′/Cd	4.84	4.95	4.72	-228.46	-223.62	-223.98	-214.24	6.71×10^{17}
L1′/Cd′	4.08	3.61	4.79	-201.32	-197.24	-197.16	-189.92	1.00×10^{0}
L1/Hg	14.14	13.63	16.12	-244.65	-230.51	-231.36	-219.21	2.97×10^{21}
L1/Hg′	26.76	8.08	9.09	-259.86	-233.10	-232.99	-226.05	3.06×10^{26}
L1′/Hg	5.89	5.97	5.80	-240.07	-234.18	-234.42	-224.84	3.96×10^{25}
L1′/Hg′	6.23	5.77	6.79	-233.94	-227.71	-227.49	-221.17	8.05×10^{22}
L2 system								
L2/Zn	17.06	10.32	27.45	-297.18	-280.12	-280.46	-271.41	5.15×10^{45}
L2/Zn′	6.82	5.97	9.57	-253.89	-247.08	-247.10	-239.37	1.67×10^{22}
L2′/Zn	4.46	4.67	4.47	-286.77	-282.31	-282.70	-273.37	1.42×10^{47}
L2′/Zn′	4.75	4.44	5.84	-249.61	-244.86	-244.83	-237.31	5.23×10^{20}
L2/Cd	12.35	11.88	15.22	-252.75	-240.40	-240.78	-230.34	4.05×10^{15}
L2/Cd′	6.71	6.44	6.99	-225.98	-219.26	-219.13	-212.20	2.03×10^{2}
L2′/Cd	5.40	5.65	5.20	-248.24	-242.84	-243.07	-234.01	1.98×10^{18}
L2′/Cd′	4.73	4.42	5.84	-221.47	-216.74	-216.68	-209.05	1.00×10^{0}
L2/Hg	14.62	14.12	17.58	-263.38	-248.75	-249.04	-238.77	6.13×10^{21}
L2/Hg′	9.72	8.93	12.00	-262.81	-253.09	-252.84	-246.64	3.58×10^{27}
L2′/Hg	6.30	6.55	6.04	-259.73	-253.43	-253.50	-244.81	1.63×10^{26}
L2′/Hg′	7.04	6.74	7.32	-256.16	-249.12	-248.87	-242.25	2.17×10^{24}

[a] In kcal mol−1

[b] Selectivity coefficient defined as $\frac{K_X}{K_{LS}}$ where the least stable complex (LS) is related to its complexes' system

cal indices of the thiacalix[2]thianthrene, p-tert-butylthiacalix[2]thianthrene conformers and their complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} are shown in Table 5. This table shows that all the existing complexes are markedly more reactive than their free receptors and cations. As reactivity is a function of the energy gap, the energy gaps of all studied compounds can be considered as their reactivities. Therefore, the reactivities of the metal cations (Zn^{2+}, Cd^{2+} and Hg^{2+}) complexes in which the cation is coordinated to four sulfur atoms of the 4-S cavity (S2, S2′, S3 and S3′) of either the conformer **L1** or **L1′** are higher than those complexes of which the cation is coordinated to the two sulfur atoms of the 2-S cavity (S1and S2). It was found that reactivities of the **L1** and **L2** (denoted by M/2-S) complexes in which the metal cation is located close to their 2-S cavity ($\Delta E_{HOMO\text{-}LUMO}$=0.49 to 0.76 eV) are always higher than (denoted by M/4-S) complexes in which the metal cation is located in the 4-S cavity ($\Delta E_{HOMO\text{-}LUMO}$=1.55 to 3.32 eV, see Table 5). On the other hand, the M/2-S complexes are soft acids as compared with their M/4-S complexes. Nevertheless, acidities for all the complexes are much softer than their free metal cation. The relative reactivities for all the complexes and their components are, in order: **L1′**/Zn′ ≈ **L1′**/Cd′ > **L1′**/Hg′ ≈ **L2′**/Cd′ > **L2′**/Zn′ > **L1**/Cd′ ≈ **L2′**/Hg′ > **L1**/Zn′ > **L2**/Cd′ > **L2**/Zn′ > **L1**/Hg′ > **L2**/Hg′ > **L1′**/Hg ≈ **L2′**/Hg > **L1**/Hg > **L2**/Hg > **L1′**/Cd ≈ **L2′**/Cd > **L1**/Cd > **L2**/

Table 5 The B3LYP/LanL2DZ energies E_{LUMO} and E_{HOMO} and frontier molecular orbital energy gap, $\Delta E_{HOMO-LUMO}$ and chemical hardness of the thiacalix[2]thianthrene, p-tert-butylthiacalix[2]thianthrene conformers and their complexes with Zn^{2+}, Cd^{2+} and Hg^{2+}

Species	E_{LUMO}[a]	E_{HOMO}[a]	$\Delta E_{HOMO-LUMO}$[a]	η[a]
Zn^{2+}	-0.65	-6.20	5.55	2.78
Cd^{2+}	-0.71	-5.99	5.28	2.64
Hg^{2+}	-0.41	-6.48	6.07	3.03
L1	-1.28	-5.99	4.71	2.35
L1′	-1.22	-6.10	4.87	2.44
L1/Zn	-9.09	-12.41	3.32	1.66
L1/Zn′	-10.88	-11.48	0.60	0.30
L1′/Zn	-9.44	-12.44	2.99	1.50
L1′/Zn′	-11.05	-11.54	0.49	0.24
L1/Cd	-9.74	-12.27	2.53	1.27
L1/Cd′	-10.86	-11.43	0.57	0.29
L1′/Cd	-10.01	-12.27	2.26	1.13
L1′/Cd′	-10.99	-11.48	0.49	0.24
L1/Hg	-10.37	-12.30	1.93	0.97
L1/Hg′	-11.02	-11.73	0.71	0.35
L1′/Hg	-10.69	-12.25	1.55	0.78
L1′/Hg′	-11.18	-11.70	0.52	0.26
L2	-1.03	-5.71	4.68	2.34
L2′	-0.93	-5.80	4.87	2.44
L2/Zn	-8.76	-11.84	3.07	1.54
L2/Zn′	-10.26	-10.91	0.65	0.33
L2′/Zn	-8.79	-11.81	3.02	1.51
L2′/Zn′	-10.39	-10.94	0.54	0.27
L2/Cd	-9.12	-11.70	2.59	1.29
L2/Cd′	-10.23	-10.86	0.63	0.31
L2′/Cd	-9.39	-11.67	2.29	1.14
L2′/Cd′	-10.37	-10.88	0.52	0.26
L2/Hg	-9.77	-11.73	1.96	0.98
L2/Hg′	-10.37	-11.13	0.76	0.38
L2′/Hg	-10.10	-11.65	1.55	0.78
L2′/Hg′	-10.50	-11.08	0.57	0.29

[a] In eV

Cd > **L1′**/Zn > **L2′**/Zn ≈ **L2**/Zn > **L1**/Zn > **L2** > **L1** > **L1′** > **L2′** > Cd^{2+} > Zn^{2+} > Hg^{2+}.

A plot of the Gibbs free energies of the complexations of thiacalix[2]thianthrene (**L1**) and p-tert-butylthiacalix[2]thianthrene (**L2**) complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} cations against sizes of cations is shown in Fig. 4. It shows that the relative selectivities of either the **L1** or **L2** are in the same order: Zn^{2+} >> Hg^{2+} > Cd^{2+}. Comparing these three cations, it was concluded that the **L1** or **L2** selectively recognize Zn^{2+}. This is because the ionic size of Zn^{2+} is a perfect fit to the 4-S cavity of the **L1′** and **L2′** conformers.

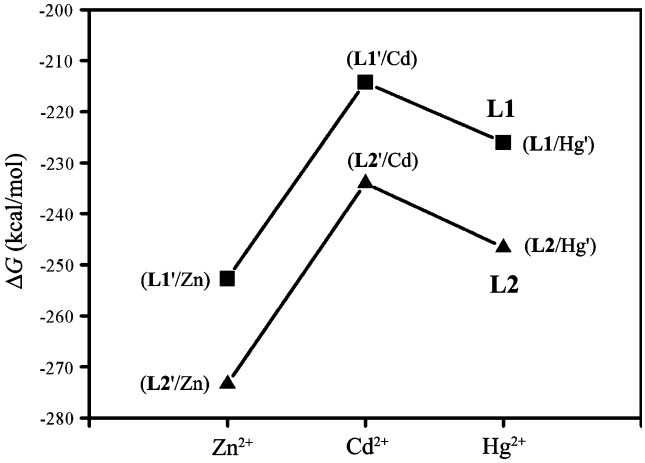

Fig. 4 Plot of Gibbs free energies of the complexations of thiacalix[2]thianthrene (**L1**) and p-tert-butylthiacalix[2]thianthrene (**L2**) complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} cations against cation size. Preferred complex species are shown in parentheses

Conclusions

The thiacalix[2]thianthrene **L1** and **L1′** conformers and p-tert-butylthiacalix[2]thianthreneare **L2** and **L2′** conformers were found. The optimized structures of **L1** and **L2** are in good agreement with their corresponding X-ray crystallographic structures. It was found that the coordination bond lengths of the complexes for the same receptor conformers are, in order: Hg···S > Cd···S > Zn···S. The relative stabilities of the conformers of thiacalix[2]thianthrene and p-tert-butylthiacalix[2]thianthrene are, in order: **L1** > **L1′** and **L2′** > **L2**, respectively. The relative stabilities for the complex conformers of the thiacalix[2]thianthrene with Zn^{2+}, Cd^{2+} and Hg^{2+} are, respectively, in order: **L1′**/Zn > **L1**/Zn > **L1**/Zn′ > **L1′**/Zn′, **L1′**/Cd > **L1**/Cd > **L1**/Cd′ > **L1′**/Cd′ and **L1′**/Hg > **L1**/Hg′ > **L1**/Hg > **L1′**/Hg′ and of the p-tert-butylthiacalix[2]thianthrene with Zn^{2+}, Cd^{2+} and Hg^{2+}: **L2′**/Zn ≈ **L2**/Zn >> **L2**/Zn′ ≈ **L2′**/Zn′, **L2′**/Cd ≈ **L2**/Cd >> **L2**/Cd′ ≈ **L2′**/Cd′, and **L2′**/Hg > **L2**/Hg′ > **L2**/Hg > **L2′**/Hg′. The relative selectivities of either the thiacalix[2]thianthrene or thiacalix[2]thianthrene are in the same order: Zn^{2+} >> Cd^{2+} > Hg^{2+}. Comparing these three cations, it was concluded that **L1** or **L2** selectively recognize Zn^{2+}.

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