



# Molecular design of macrocyclic compounds for complete removal of thallium(I) from wastewater

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## Abstract

Design of new adsorbents for complete removal of thallium(I) from wastewater is of significant importance. Based on the theory of binding ability between crown ether and metal ion, a kind of Tl(I)-selected crown ether, thio-18-crown-6 ether, was designed. Subsequently, modeling calculations were performed to investigate the microscopic interaction between 18-crown-6 ether and its sulfur-substituted derivatives with Tl<sup>+</sup>. The results showed that thio-18-crown-6 ether generally showed higher affinity to Tl<sup>+</sup> than 18-crown-6. The stabilities of these complexes ranked in an order of 5S-18C6 > 4S-18C6(II) > 2S-18C6(I) > 2S-18C6(II) > 6S-18C6 > 3S-18C6 > 18C6 > 1S-18C6. The binding energies of 5S-18C6 with free Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>, which are usually impurity ions in thallium-containing wastewater, were more negative than with Tl<sup>+</sup>, indicating more affinity of 5S-18C6 toward these free two-valence ions. However, after the influence of solvent (water) was taken into account, 5S-18C6 showed fairly high selectivity to Tl(I) over Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>. Therefore, 5S-18C6 should be a proper compound which has the promising potential to be adopted for the complete and selective removal of Tl(I) from wastewater. Further synthesis and adsorption experiments are needed to verify this prediction.

**Keywords** Molecular design · Thallium · Removal · Molecular modeling calculation · Wastewater

## Introduction

Thallium is a highly toxic element. It is more acutely toxic to mammals than heavy metals, e.g., Hg(II), Pb(II), Cd(II), Zn(II), and Cu(II) (Zitko 1975). In geochemical systems, thallium occurs almost exclusively as the monovalent thallos cation Tl(I), which usually substitutes for K(I) or Rb(I) in such silicates as alkali feldspars or mica. In hydrothermal systems, thallium is mainly associated with sulfides such as pyrite, sphalerite, or marcasite (Tatsi and Turner 2014).

The industrial facilities that produce or use Tl and its compounds are not the major sources of Tl release to the

environment. Rather, the main sources are industrial processes including coal combustion, smelting operations (mainly lead and zinc), and cement plants (Antón et al. 2013). Industrial wastewater produced from mining, treatment, and smelting of sulfide ores has become an emerging pollutant in recent years and has caused serious thallium contamination incidents. For instance, collapse of a thallium-containing tailing pond in Spain in 1998, 189 cases of Tl poisoning in Southwest China in the 1960s and 1970s, Tl pollution from the wastewater discharge of a lead/zinc smelting plant on drinking water source of northern branch of Pearl River in southern China in 2010, and Tl-polluted Hejiang River in Guangxi province of China in 2013 (Liu et al. 2014; Wan et al. 2014; Xiao et al. 2012) have been reported.

For the treatment of thallium-containing wastewater, complete removal of thallium is necessary due to its high toxicity and mobility. Thallium-containing wastewater usually contains low concentration of Tl(I) and much higher concentration of heavy metal ions, e.g., Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>. So, it is not an easy task to achieve the complete removal of Tl(I).

Many methods including precipitation (Minami et al. 1990), solvent extraction (Sato and Sato 1992), floatation, electrochemical deposition, and adsorption (Twidwell and Williams-Beam 2002), have been developed to remove

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thallium from contaminated wastewater. Among them, a large number of investigations have focused on adsorption method due to the following reasons: (1) adsorption is known as one of the most effective techniques for the removal/recovery of metal ions because of its high removal efficiency, high capacity, and simplicity in operation (Wen et al. 2014). (2) The process of adsorption implies the presence of an “adsorbent” that could be well designed with strong affinity toward thallium so that to completely remove thallium from wastewater with very low concentration of thallium and much higher levels of impurity ions. (3) Adsorption process has been widely used in commercial for metal ions removal/recovery (e.g., gold industry, water purification, and gallium recovery from Bayer liquor), and it has the potential for industrial application once the thallium adsorbents are developed. Adsorbents such as Prussian Blue analogues (Sangvanich et al. 2010; Vincent et al. 2014), biosorbents (Dashti Khavidaki and Aghaie 2013), and metal oxides (Wan et al. 2014; Yantasee et al. 2007) have exhibited good affinity to Tl(I). However, the selectivity of these adsorbents toward Tl(I) is easily affected by coexisting cations, since the adsorption of thallium is either through electrostatic attraction or cation ion exchange. Therefore, it is an important work to design new adsorbents with high selectivity to Tl(I) over other impurity ions, so as to achieve the complete removal of Tl(I) from wastewater.

Crown ether, firstly synthesized by Pedersen in 1967 (Pedersen 1967), is one of the macrocyclic compounds which are well known for their complexing affinity and selectivity toward metal ions. Crown ether can form complexes with salts of most metallic elements including all IA and IB group, most IIA group, some IIB group, and a few IIIA, IIIB, and IVB group of the periodic table. These compounds appear to be salt-polyether complexes formed by ion-dipole interaction between the cation and the negatively charged oxygen atoms symmetrically placed in the crown ether ring. The conditions necessary for the formation and the factors influencing the stability and selectivity of the macrocyclic complexes mainly include (1) the relative sizes of the ion and the hole in the crown ether ring; (2) the number, coplanarity, and symmetrical placement of the oxygen atoms; (3) the basicity of the oxygen atoms; (4) the acid-base character of metal ions; and (5) steric hindrance in the crown ether ring (Jabbari et al. 1993; Pedersen 1967). Therefore, according to different complexation properties between crown ether and cation, it is possible to design special crown ether with selectivity to particular ions. Based on this, crown ether and their derivatives have been widely applied in ion recognition, selective transport and separation of metals, second-sphere coordination, ion transport, macrocyclic liquid crystals, and ion-selective electrodes (Al-Kahtani et al. 2014). For the recovery/removal of metal ions by crown ether-based materials, Izatt and co-workers (Izatt et al. 2015; Izatt et al. 2012) have developed a series of products which have been widely applied in

commercial, e.g., platinum group metals separation, bismuth removal from copper electrolyte, mercury separation and recovery from commercial sulfuric acid, cadmium removal, and rhenium recovery. This technology has been proved efficient with good economic benefits by industrial application. However, thallium selective adsorbents based on crown ether have not been reported in literature so far. In this paper, based on the specific property of Tl(I), the design of Tl(I)-selected crown ether was carried out. Subsequently, simulated calculations including structure optimization of designed crown ether-Tl(I) complexes, binding energies, charge transfer and electron density, and thermal properties were conducted to verify the design results.

## Molecular design

As mentioned above, the binding ability and selectivity of crown ether to metal ion depend on several factors: viz. the relative size of the cation to crown ether cavity, type of donor atom, conformation, and polarity of the solvent. Generally, the relation between ion size and cavity size of crown ether plays an important role in the selectivity of crown ether toward metal ions. Thallium is a metallic element with ionic diameters (Tl(I)) 3.0 Å (Izatt et al. 1985). Tl(I) matches best the cavity size of 18-crown-6 (18C6, 2.6–3.2 Å (Maeda et al. 1979)) (Table 1). Therefore, Tl(I) could form stable complexes with 18-crown-6 and its derivatives.

Furthermore, since there are many impurity ions in the wastewater, the affinity of designed crown ethers toward Tl(I) needs to be enhanced. The complexation process of the crown ether with cation can be dealt with by the HSAB principle (Tamura et al. 1980), hard-hard or soft-soft interaction between acceptor and donor cause strong interaction. According to HSAB principle, an oxygen atom is a hard base, the complexation between crown ether and hard ions, e.g., alkaline earth ions, takes place easily. Substitution of the cyclic oxygen atoms by other atoms such as nitrogen, sulfur could significantly affect the crown ether’s complexation property. For instance, Jabbari et al. (Jabbari et al. 1993) found that the substitution of two oxygen atoms by two nitrogens in the 18C6 increases the stability of the  $Ag^+$ -18C6 complexes significantly. This is because  $Ag^+$  is soft acids, and they

**Table 1** Diameters of cavity in different crown ether

Crown ether	Diameters of cavity (Å)
12-crown-4	1.2–1.5 (Pedersen 1967)
15-crown-5	1.7–2.2 (Maeda et al. 1979)
18-crown-6	2.6–3.2 (Maeda et al. 1979)
21-crown-7	3.4–4.3 (Shamsipur et al. 1980)

interact more strongly with nitrogen atoms of the ring as boundary bases softer than oxygen. Tl(I) is classified as a soft acid, so the binding force between  $Tl^+$  and oxygen atoms in the crown ether ring is not so strong. If the oxygen atoms are substituted by sulfur, which is a typical soft base, the resulted crown ethers would be expected to have a much larger extractability and higher selectivity for  $Tl^+$  in the wastewater.

Therefore, thio-18C6 might be a potential material which could be used for the selective removal of Tl(I) from wastewater. However, there are many kinds of thio-18C6, which thio-18C6 has the most affinity toward Tl(I)? It is not possible to synthesize all kinds of these thio-crown ether and investigate their affinity toward Tl(I). Molecular modeling calculation is a good method to solve this problem. Molecular modeling calculation has been widely recognized and proved as a powerful tool for the design of new molecular ligands with specified properties, and for explaining their coordination mechanism with cation. Furthermore, accurate theoretical calculations can provide ways to obtain important chemical and physical information that cannot be easily obtained by experimental approaches. In this study, we carried out a DFT-based study to understand the microscopic interaction between different thio-18C6 and  $Tl^+$  so that to predict the selectivity of these crown ether toward Tl(I).

## Methods of calculation

The Material Studio (Version 5.0) software package was used for all calculations. All the simulations were performed with the COMPASS forcefield. Geometry-optimized and spin-unrestricted density functional theory (DFT) calculations have been performed using the DMol<sup>3</sup> model in the framework of a generalized-gradient approximation (GGA), which is suitable

for crown ether system and the calculation accuracy is high (Hazra et al. 2013). The geometry of the molecule was fully optimized using Becke–Lee–Yang–Parr (BLYP) hybrid exchange–correlation functional and a double numeric plus polarization (DNP) basis set. The frequency, population, and electronic density were also calculated at the same level. No constraint was applied to bond distances, bond angles, or dihedral angles in the calculations and all atoms were free to optimize.

## Results and discussion

### Structure optimization

The optimized geometric structures of 18-crown-6 (18C6), eight selected thio-18-crown-6 (1S-18C6–6S-18C6) and their complexes with  $Tl^+$  are given in Figs. 1 and 2. The calculated geometric parameters of these crown ether and complexes are listed in Table 2. Note that, we selected thio-crown ether containing spacing position sulfur atoms for calculation, since it has been reported that thio-crown ether show stronger affinity to soft ions when the sulfur atoms are located in spacing position. In addition, the result of 4S-18C6(II)- $Tl^+$  was not included because the geometry optimization did not converge.

In the calculated optimized structures of 18C6, two O atoms pointed upward and the remaining four pointed downward from the backbone. This structure has also been observed in the X-ray analysis of the crystalline 18C6 (Dunitz et al. 1974) and reported by Ali et al. (Ali et al. 2008). After one O atom was substituted by S atom (1S-18C6), the optimized structure showed that four O atoms still pointed downward, the remaining one O atom pointed upward, but the S

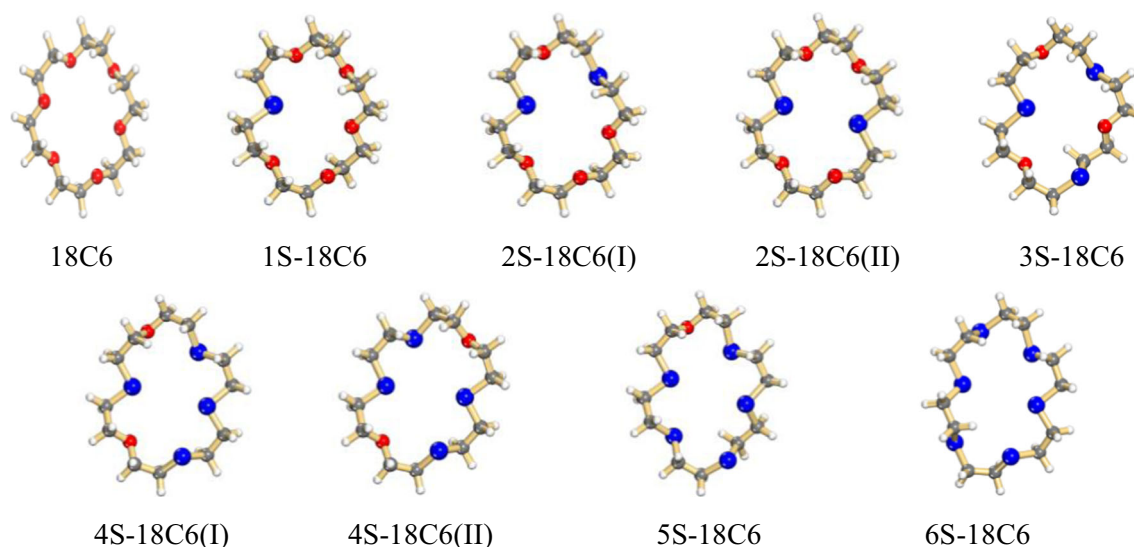
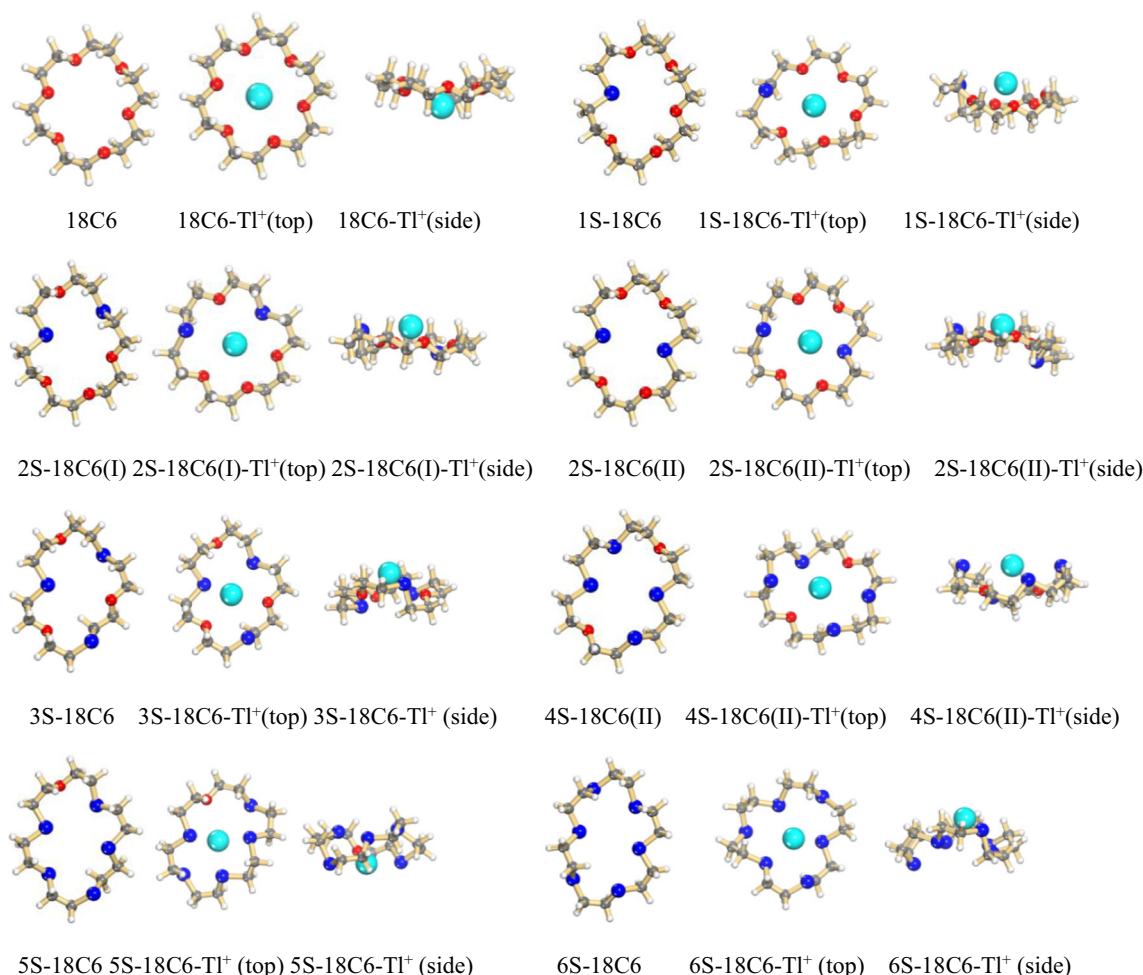


Fig. 1 Optimized structure for free 18C6 and different thio-18C6



**Fig. 2** Optimized structure for free crown ether and their complexes with TI<sup>+</sup>

atom pointed inward from the ring. As a result, the ring became a little “slim.” The distance between the O atom and S atom was only 4.239 Å, much shorter than that of two para-position O atoms in 18C6 (5.133 Å). For 2S-18C6(I) in which one O atom was located in the middle of two S atoms, its optimized structure was almost the same with 1S-18C6. However, in the case of 2S-18C6(II) which contains two para-position S atoms, the two S atoms pointed toward each other and their distance became even shortened (4.055 Å). When three O atoms were substituted by S atoms (3S-18C6), the structure was quite different with the former crown ether. Two O atoms and one S atoms pointed downward, one O atom and one S atom pointed upward, and the remaining S atom pointed inward. The optimized structures of 4S-18C6(I) and 4S-18C6(II) were similar with 2S-18C6(II), in which three atoms (two O atoms and one S atom) pointed downward, one S atom pointed upward, and the remaining S atom pointed inward. For 5S-18C6 and 6S-18C6, their optimized structure was also quite different. In the structure of 5S-18C6, three atoms (two S atoms and one O atom) pointed downward, two S atoms pointed upward, and the remaining one S atom

pointed inward. The optimized structure of 6S-18C6 showed that four S atoms pointed downward, one S atom pointed upward, and the remaining one S atom pointed inward.

Figure 2 showed that for 18C6-TI<sup>+</sup>, the structure of 18C6 kept almost unchanged. The TI<sup>+</sup> ion sited at the center but below the oxygen plane of 18C6. However, in the case of thio-crown ether-TI<sup>+</sup> complexes, all of the crown ether structures have undergone major distortion. In the optimized structure of 1S-18C6-TI<sup>+</sup>, S atom and two O atoms were forced from inward and downward to upward, since TI<sup>+</sup> ion sited above the ring plane. Similar distortions were observed in 2S-18C6(I)-TI<sup>+</sup>, 2S-18C6(II)-TI<sup>+</sup>, and 4S-18C6(II)-TI<sup>+</sup>. It is interesting that 3S-18C6 did not change its structure greatly from the top view of 3S-18C6-TI<sup>+</sup>. However, from side view, it is clear that the ring plane became quite distorted, and TI<sup>+</sup> ion sited opposite to the distortion direction. In the case of 6S-18C6, it not only changed its cavity shape but also distorted its ring plane to complex with TI<sup>+</sup>. It is interesting to note that TI<sup>+</sup> ion sited below the ring plane in the structure of 5S-18C6-TI<sup>+</sup>, which is different with all other thio-crown ether-TI<sup>+</sup> complexes.

**Table 2** Calculated geometric parameters of free crown ether and their complexes with  $Tl^+$ 

Crown ethers and complexes	Coordination bonds length (Å)				Average covalent bonds length (Å)			Cavity size <sup>a</sup> (Å)	
	$Tl^+-O$		$Tl^+-S$		C–C	C–O	C–S	Diameters	$\Delta D$
	Minimum	Maximum	Minimum	Maximum					
18C6	/	/	/	/	1.5136	1.4210	/	3.48	/
/1S-18C6	/	/	/	/	1.5162	1.4227	1.8375	2.38	/
/2S-18C6(I)	/	/	/	/	1.5179	1.4224	1.8358	2.75	/
2S-18C6(II)	/	/	/	/	1.5172	1.4228	1.8370	2.19	/
3S-18C6	/	/	/	/	1.5205	1.4239	1.8363	2.65	/
4S-18C6(I)	/	/	/	/	1.5214	1.4237	1.8378	2.24	/
4S-18C6(II)	/	/	/	/	1.5217	1.4218	1.8363	2.26	/
5S-18C6	/	/	/	/	1.5255	1.4265	1.8372	2.54	/
6S-18C6	/	/	/	/	1.5252	/	1.8376	2.37	/
18C6- $Tl^+$	2.885	3.078	/	/	1.5119	1.4352	/	3.66	0.18
1S-18C6- $Tl^+$	2.909	3.142	3.323	/	1.5131	1.4356	1.8419	3.37	0.99
2S-18C6(I)- $Tl^+$	3.029	3.290	3.227	3.272	1.5162	1.4335	1.8401	3.80	1.05
2S-18C6(II)- $Tl^+$	3.029	3.208	3.170	3.257	1.5168	1.4328	1.8405	3.72	1.53
3S-18C6- $Tl^+$	2.935	4.295	3.177	3.232	1.5204	1.4327	1.8430	2.91	0.26
4S-18C6(I)- $Tl^+$	3.199	3.298	3.168	3.413	1.5205	1.4331	1.8404	3.37	1.13
5S-18C6- $Tl^+$	3.027	/	3.104	3.478	1.5248	1.4351	1.8410	2.23	-0.31
6S-18C6- $Tl^+$	/	/	3.080	4.853	1.5241	/	1.8447	3.49	1.12

<sup>a</sup> The cavity size is the minimum diameter between two donor atoms located at para-position, and DD is the difference of the minimum diameter between free macrocycle and its complex

According to Table 2, the calculated length of C–C bonds and C–O bonds in 18C6 were 1.5136 Å and 1.4210 Å, respectively, which are consistent with the research of Diao et al. (Diao and Wang 2009). The cavity size of 18C6 we calculated was 3.48 Å, a little larger than the reported value of 2.7–3.2 Å (Maeda and Kimura 1979). All the thio-18C6 cavity sizes were smaller than 18C6. Comparing these free crown ether with corresponding complexes with  $Tl^+$ , the lengths of C–C bonds in complexes were almost invariable, and the length of C–O bonds in complexes was lengthened by 0.009–0.013 Å, still the length of C–S bonds in complexes was lengthened by 0.003–0.007 Å. The minimum cavity sizes for all crown ether except 5S-18C6 were enlarged by 0.18–1.53 Å. On the contrary, the cavity size of 5S-18C6 was minified by 0.31 Å to coordinate with  $Tl^+$ .

## Binding energies

Binding energies (BE) is the most important property for metal ion selectivity with crown ether (Ali et al. 2008). Generally, the systematic energy will decrease during the course of new complex formation. The decreased energy is binding energy, which is generally related to the stability of corresponding complex. A stable complex always gives a negative binding energy. Hence, the stability of complexes

will improve with the increase of negative value of binding energy. In this study, the binding energies were calculated as follows:

$$BE = E_{\text{crown ether-Tl}^+} - (E_{\text{crown ether}} + E_{\text{Tl}^+}) \quad (1)$$

where  $E_{\text{crown ether-Tl}^+}$ ,  $E_{\text{crown ether}}$ , and  $E_{\text{Tl}^+}$  refer to the energy of the crown ether- $Tl^+$  complexes, crown ether, and  $Tl^+$  respectively. The calculated values of binding energy are given in Table 3. It is seen from Table 3 that the binding energies of thio-18C6- $Tl^+$  complexes were generally more negative than that of 18C6, except 1S-18C6- $Tl^+$ .

**Table 3** Calculated binding energies of crown ether- $Tl^+$ 

Complexes	Binding energies (kJ/mol)
18C6- $Tl^+$	-279.11
1S-18C6- $Tl^+$	-265.79
2S-18C6(I)- $Tl^+$	-290.22
2S-18C6(II)- $Tl^+$	-286.40
3S-18C6- $Tl^+$	-280.83
4S-18C6(II)- $Tl^+$	-301.41
5S-18C6- $Tl^+$	-308.88
6S-18C6- $Tl^+$	-288.55

This means the substitution of O atom by S atom from the ring of 18C6 will usually increase the binding capability to  $Tl^+$ , which is consistent with our prediction. It is interesting to find that the binding energies of thio-18C6 to  $Tl^+$  did not increase or decrease with the number of S atom. 1S-18C6- $Tl^+$  had the lowest binding energy, even lower than 18C6- $Tl^+$ . The binding energy of 5S-18C6- $Tl^+$  was the highest, indicating 5S-18C6 had the highest binding affinity with  $Tl^+$  among these thio-18C6. The position of S atom has some influence on the binding energies of thio-18C6 to  $Tl^+$ . For instance, 2S-18C6(I)- $Tl^+$  had higher binding energies than 2S-18C6(II)- $Tl^+$ . According to binding energies, the binding capability to  $Tl^+$  of these crown ether ranks in an order of 5S-18C6 > 4S-18C6(II) > 2S-18C6(I) > 2S-18C6(II) > 6S-18C6 > 3S-18C6 > 18C6 > 1S-18C6.

### Charge transfer and electron density

Charge transfer is a chemical process whereby electric charge is transferred from a donor to an acceptor when the coordination reaction occurred. In this study, the charge transfer ( $Q_t$ ) was defined as the charge difference between free crown ether and its corresponding moiety in complex, which was equal to that of between free metal ion and its corresponding moiety in complex. The calculated charge transfer between crown ether and  $Tl^+$  in complexes is shown in Table 4. Table 4 indicates that during the complexation, negative charge (electrons) did transfer from crown ether to metal ion, as a result the positive charge on crown ether increased while the charge on  $Tl^+$  decreased. The amount of charge transfer ranked in an order of 6S-18C6 > 5S-18C6 > 3S-18C6 > 4S-18C6(II) > 2S-18C6(II) > 2S-18C6(I) > 1S-18C6 > 18C6, which was quite different from the order of binding energies (Table 3). Generally, the complexation between crown ether and metal ion may involve the covalent and electrostatic interaction. The former is mainly the charge transfer interaction from the crown to the cation and

the latter is the ion-dipole interaction. Therefore, it is reasonable that the amount of charge transfer seems not to correlate with binding energy since the electrostatic interaction may also play an important role during the complexation.

### Thermal properties

The calculated thermal properties of complexation process, the entropy of formation  $\Delta S_f$ , the enthalpy of formation  $\Delta H_f$ , and the thermal free energy of formation  $\Delta G_f$  are listed in Table 5. As can be seen from Table 5,  $\Delta G$  values were negative, indicating the spontaneous nature of the complexation process (Ganesan et al. 2013; Vasudevan and Lakshmi 2012). The entropy change  $\Delta S_f$  for the coordination reaction was also slightly negative; this might be because these complexes became more rigid after coordination (Ramakrishnan et al. 2016). The fact that the change in the enthalpy  $\Delta H_f$  was big and negative showed an exothermic process for the complexation of crown ether with  $Tl^+$ . These thermal parameters of formation show that the complexes of 18C6 and thio-18C6 with  $Tl^+$  are stable and easy-to-form. Calculations also predict that the stabilities of these complexes ranked in an order of 5S-18C6 > 4S-18C6(II) > 2S-18C6(I) > 2S-18C6(II) > 6S-18C6 > 3S-18C6 > 18C6 > 1S-18C6, which was consistent with the binding energies.

### Selectivity

According to our calculations, 5S-18C6 has the most affinity toward  $Tl(I)$ . However, as previously mentioned, the purpose of this paper is to design macrocyclic compounds which have high selectivity to  $Tl(I)$  over ions like  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$ . Therefore, the binding energies between 5S-18C6 and these impurities ions are calculated and listed in Table 6. It is worth noticing that all the binding energies of 5S-18C6 with these ions were much more negative than 5S-18C6- $Tl^+$ . It

**Table 4** The charge transfer ( $Q_t$ ) between crown ethers and  $Tl^+$  in complexes and the electron density on ring plane of crown ether in complexes

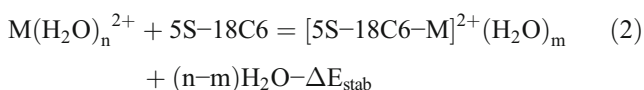
Complexes	Charge transfer						Average electron density on ring plane (e/Bohr <sup>3</sup> )
	Crown ether			$Tl^+$			
	Free	Complexation	$Q_t$ (e)	Free	Complexation	$Q_t$ (e)	
18C6- $Tl^+$	0	0.274	0.274	1	0.727	-0.273	0.454
1S-18C6- $Tl^+$	0	0.330	0.330	1	0.668	-0.332	0.537
2S-18C6(I)- $Tl^+$	0	0.379	0.379	1	0.619	-0.381	0.425
2S-18C6(II)- $Tl^+$	0	0.399	0.399	1	0.600	-0.400	0.343
3S-18C6- $Tl^+$	0	0.527	0.527	1	0.472	-0.528	0.298
4S-18C6(II)- $Tl^+$	0	0.489	0.489	1	0.513	-0.487	0.337
5S-18C6- $Tl^+$	0	0.546	0.546	1	0.456	-0.544	0.214
6S-18C6- $Tl^+$	0	0.615	0.615	1	0.383	-0.617	0.140

**Table 5** The entropy of formation ( $\Delta S_f$ ), the enthalpy of formation ( $\Delta H_f$ ), and the Gibbs energy of formation ( $\Delta G_f$ )

Complexes	$\Delta S_f$ (J/mol)	$\Delta H_f$ (kJ/mol)	$\Delta G_f$ (kJ/mol)
18C6-Tl <sup>+</sup>	-90.57	-255.96	-228.97
1S-18C6-Tl <sup>+</sup>	-89.19	-252.02	-225.44
2S-18C6(I)-Tl <sup>+</sup>	-89.60	-277.00	-250.30
2S-18C6(II)-Tl <sup>+</sup>	-89.73	-273.72	-246.98
3S-18C6-Tl <sup>+</sup>	-89.66	-270.05	-243.33
4S-18C6(II)-Tl <sup>+</sup>	-89.77	-289.78	-263.03
5S-18C6-Tl <sup>+</sup>	-89.46	-296.57	-269.91
6S-18C6-Tl <sup>+</sup>	-89.60	-276.54	-249.84

implies that the Tl<sup>+</sup> complex is less stable than these complexes. As a result, there would be no selectivity of 5S-18C6 toward Tl(I) over Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>, which is opposite to our intention.

It should be noted that in our calculations, we did not take the influence of solvent into consideration. Actually, in aqueous solution, water molecular will significantly affect the complexation. The importance of solvent effect for the selectivity of crown ether against metal ions has been predicted by Pedersen (1967) when he firstly synthesized crown ether and proved by many researches (Bajaj and Poonia 1988; Izatt et al. 1991) after that. In this paper, the system we concerned is thallium-containing wastewater, in which hydrated species is a more realistic system than the complex itself. According to literature reported, Tl<sup>+</sup> is very weakly hydrated in solution and no Tl(H<sub>2</sub>O)<sub>n</sub><sup>+</sup> ions are formed (Lee 1972). However, for Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>, they usually exist as Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, Pb(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, Cu(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, and Cd(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> in aqueous solutions (Cooper and Armentrout 2010; Díaz et al. 2000; Velghe 1977). Therefore, in aqueous system, the coordination between crown ether (5S-18C5) and these ions is represented by

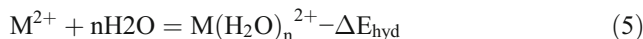
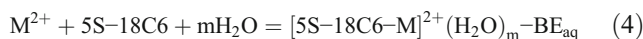
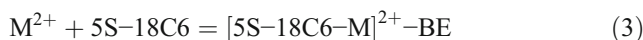


where  $n$  and  $m$  are the number of hydrating water molecules to the ion and those to the complex, respectively.  $\Delta E_{stab}$  is the stabilization energy in the aqueous solution.

**Table 6** Binding energies (BE), binding energies in aqueous solution (BE<sub>aq</sub>), hydration energies ( $\Delta E_{hyd}$ ), and stabilization energies ( $\Delta E_{stab}$ ) for the cation complex of 5S-18C6

Cation	BE (kJ/mol)	BE <sub>aq</sub> (kJ/mol)	$\Delta E_{hyd}$ (kJ/mol)	$\Delta E_{stab}$ (kJ/mol)
Zn <sup>2+</sup>	-1443.86	-1311.43	-1414.20	102.77
Pb <sup>2+</sup>	-858.23	-801.72	-752.93	-48.80
Cu <sup>2+</sup>	-2598.88	-2619.77	-2594.43	-25.34
Cd <sup>2+</sup>	-1166.76	2314.416	-1223.83	3538.25

Equation (2) could be divided into the following process:



where BE, BE<sub>aq</sub>, and  $\Delta E_{hyd}$  designate the binding energy, that in aqueous solution and the hydration energy.  $\Delta E_{stab}$  is then estimated:

$$\Delta E_{stab} = BE_{aq} - \Delta E_{hyd} \quad (6)$$

We assumed  $m = 2$  and calculated the  $\Delta E_{stab}$  for Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>. The results are also listed in Table 6. It is shown in Table 6 that the  $\Delta E_{stab}$  of hydrated Pb<sup>2+</sup> and Cu<sup>2+</sup> with 5S-18C6 complexes were -48.80 kJ/mol and -25.34 kJ/mol, respectively, which were much less than their binding energies and also much less than the binding energy of 5S-18C6-Tl<sup>+</sup>. In the case of Zn<sup>2+</sup> and Cd<sup>2+</sup>, the stabilization energies were positive, indicating the unlikely formation of hydrated Zn<sup>2+</sup> and Cd<sup>2+</sup> with 5S-18C6 complexes in aqueous solution. Table 6 clearly showed that although the larger complexation energies were gained by the free complexes formation, the hydrated Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>-5S-18C6 complexes were unstable or even unlikely formed in aqueous solution, since their hydrated ions have a comparable stability with their crown complexes. Therefore, we could predict that in thallium-containing wastewater, 5S-18C6 would have high selectivity to Tl<sup>+</sup> over Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>.

## Conclusions

In order to design crown ether with high affinity and selectivity to Tl<sup>+</sup>, we performed simulation calculations. From the calculated and analytical results, the following conclusions could be drawn:

- (1) The calculated optimized structures of 18C6 was consistent with the reported X-ray analysis of the crystalline 18C6, indicating the reliability of calculation. For free crown ether, the structure of thio-18C6 was quite different with 18C6 by the point direction of O atoms or S atoms, and by cavity size. In the case of complexes, the structure of 18C6 kept almost unchanged. However, all the thio-crown ether structures have undergone major distortion to meet the coordination request with Tl<sup>+</sup>. Since the diameter of Tl<sup>+</sup> is a little larger than the cavity of these crown ethers, Tl<sup>+</sup> did not sit into the ring plane but sited above or under the ring plane.
- (2) All the calculated thio-18C6 cavity sizes were smaller than 18C6. The lengths of C-C bonds in complexes were almost invariable, while the length of C-O bonds and C-

S bonds in complexes was lengthened. The cavity sizes for all crown ethers were enlarged by 0.18–1.53 Å after complexation except 5S-18C6.

- (3) According to the calculated binding energies, thio-18C6-Tl<sup>+</sup> complexes were generally more negative than that of 18C6, meaning the substitution of O atom by S atom from the ring of 18C6 increased the binding capability to Tl<sup>+</sup>. The binding energies of thio-18C6 to Tl<sup>+</sup> did not increase or decrease with the number of S atom. 5S-18C6 had the highest binding affinity toward Tl<sup>+</sup> among these thio-18C6. The binding capability to Tl<sup>+</sup> of these crown ethers ranked in an order of 5S-18C6 > 4S-18C6(II) > 2S-18C6(I) > 2S-18C6(II) > 6S-18C6 > 3S-18C6 > 18C6 > 1S-18C6.
- (4) During the complexation of crown ether with Tl<sup>+</sup>, a negative charge transferred from crown ether to metal ion, as a result, the positive charge on crown ether increased while charge on Tl<sup>+</sup> decreased. The amount of charge transfer order was different from the order of binding energies. This is because the complexation involved both charge transfer and electrostatic interaction.
- (5) The thermal property calculations showed that the complexation  $\Delta G$  values were negative, indicating the spontaneous nature of the complexation process. The predicted stability orders of complexes according to thermal properties were consistent with the order of binding energies.
- (6) The binding energies of 5S-18C6 with free Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup> were more negative than 5S-18C6-Tl<sup>+</sup>. However, after we took into account the influence of solvent (water), 5S-18C6 showed fairly high selectivity to Tl(I) over Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup> because their hydrated ions-5S-18C6 complexes were unstable or even unlikely formed in aqueous solution.

Therefore, 5S-18C6 should be a compound which has the promising potential to be adopted for the complete and selective removal of Tl(I) from wastewater. However, the preparation of 5S-18C6 based adsorbents and adsorption experiments needs to be conducted to verify this prediction. These experiments are in progressing.

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