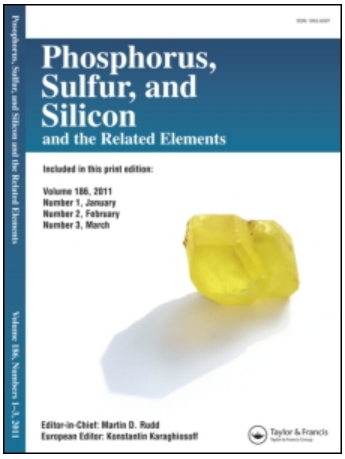

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Spectrophotometric Study of Complexation of Tri-Aza Dibenzosulfide and Dibenzosulfoxide Macrocyclic Compounds with Heavy Metal Ions

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*The complexation reactions between 7,10,13-triaza-1-thia-4,16-dioxa-20,24-dimethyl-2,3;17,18-dibenzo-cyclooctadecane-6,14-dione (**TTD**) and 7,10,13-triaza-1-sulfoxo-4,16-dioxa-20,24-dimethyl-2,3;17,18-dibenzo-cyclooctadecane-6,14-dione (**TSD**) macrocycles with Ag^{+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Sr^{2+}, Tl^{+}, and Zn^{2+} ions have been studied in ethanol and methanol solutions at 25°C. The complexes formed between macrocycles (**TTD**) and (**TSD**) with these metals cations had a stiochiometry of 1:1 and 1:2, respectively. The stability constants of the resulting complexes were determined and found to decrease in the order $Cu^{2+} > Zn^{2+} > Ag^{+} > Tl^{+} > Cd^{2+} > Pb^{2+} > Sr^{2+}$ with macrocycle (**TTD**) and $Tl^{+} > Zn^{2+} > Cd^{2+} > Pb^{2+} > Cu^{2+} > Ag^{+} > Sr^{2+}$ with macrocycle (**TSD**).*

Keywords Copper; formation constant; macrocycle; spectrophotometry; thallium; zinc

INTRODUCTION

Crown ethers, which were first discovered by Pederson in 1967,[1] are now important as a class of heteromacrocycles in the view of synthesis and complexation properties for various cations and anions as well as ionic and neutral molecules.[2,3]

Macrocyclic diamides and corresponding aza crown compounds have gained a great deal of attention due to their wide applications in chemistry. This is generally due to their high capability in selective and

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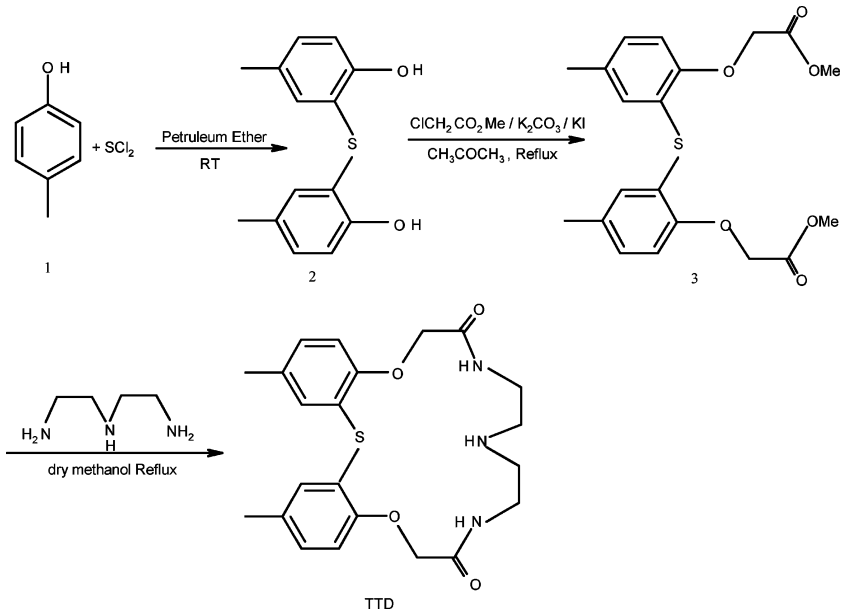
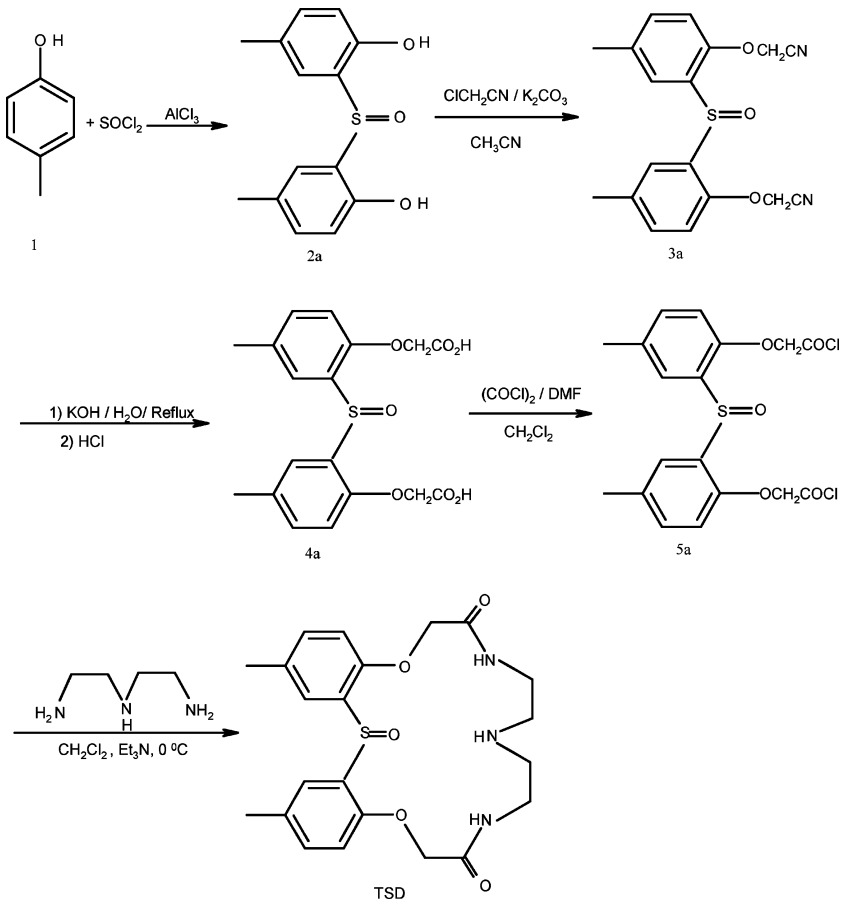
effective complexation with variety of transition and heavy metals, molecular ions, and neutral molecules, and there is an increasing interest in the preparation of them.[4] *The use of thia-containing macrocycles as building blocks in such systems yields the potential of binding soft metals, this behavior is based on HSAB (hard-soft acid and base) concept, sulfur is classified with soft base, some soft acids, such as Ag (I), Pt (II), Hg (II), Cu (II), and Zn (II) can bind very strongly with ligands containing sulfur atoms.*[5]

Since most of heavy metal cations are toxic,[6] their complexation studies are competitive area of research. The investigation of the reaction conditions and the design of a highly selective ligand for removal of these cations is of particular importance. Determination of formation constants of complexes of these cations are performed by different methods such as: ^{1}H NMR studies,[7] spectrophotometric,[8] conductometric,[9] polarographically,[10] square wave polarography,[10] and potentiometric[12] methods.

We have synthesized two triaza macrocycles **TTD** and **TSD** in our previous works as are shown in Schemes 1 and 2.[13] Herein, we wish to report the complexation and stabilities of macrocycles **TTD** and **TSD** with heavy metal cations Ag^+, Cd^{2+}, Cu^{2+}, Pb^{2+}, Sr^{2+}, Tl^+, and Zn^{2+}.



SCHEME 1 Synthesis of macrocycle **TTD**.



SCHEME 2 Synthesis of macrocycle **TSD**.

RESULTS AND DISCUSSION

The electronic absorption spectra of macrocycles with various concentrations are represented in Figures 1 and 2. Examination of Figures 1 and 2 indicate that the electronic spectra of these macrocycles are largely depending on the concentration. Increasing the macrocycle **TTD** and **TSD** concentrations result in increasing the absorbance of both bands for both macrocycles at (248–254 and 278–286), and (230–246 and 280–284) nm, respectively. This behavior can be ascribed to the association of the molecules through intermolecular hydrogen bonding. The complexation behavior of these two macrocycles with Ag^{+}, Cd^{2+},

TABLE I Maximum Wavelengths of Complextion of Macrocycles-M^{n+}

	λmax(nm)						
Macrocycle	Cu(II)	Zn(II)	Ag(I)	Tl(I)	Cd(II)	Pb(II)	Sr(II)
TTD	216	216	218	216	214	212	212
TSD	212	212	212	214	212	212	212

Cu^{2+}, Pb^{2+}, Sr^{2+}, Tl^{+}, and Zn^{2+} are studied and the maximum absorption wavelengths are shown in Table 1. The electronic spectra of the complextion of these two marocycles with above cations are shown in Figures 3 and 4, respectively.

The formation constant of complexes are calculated by fitting the observed absorptions of the ligands at various [M^{n+}] / [L] mole ratios by using a nonlinear least-squares program KINFIT.[14] Two of the typical

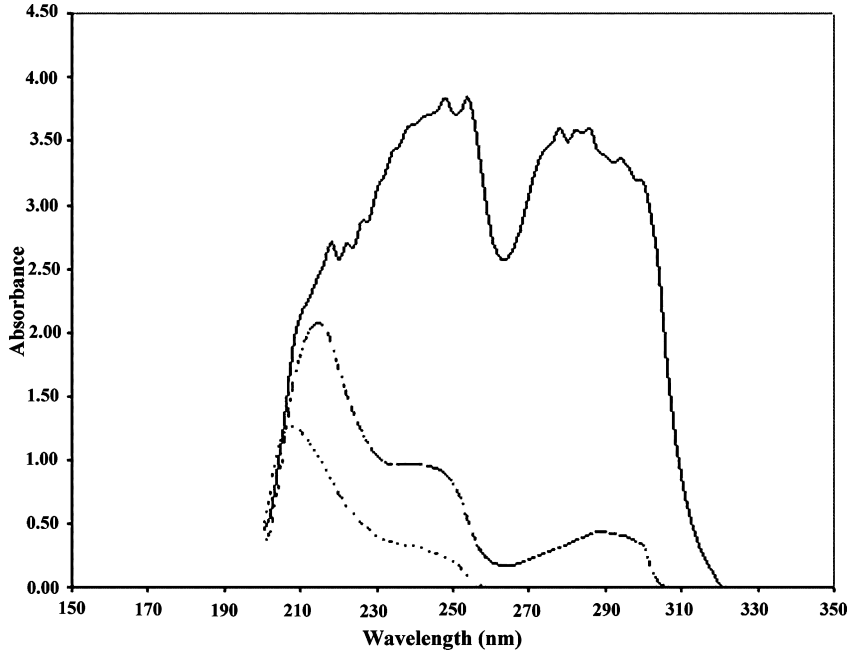


FIGURE 1 Electronic spectra of macrocycle **TTD** in different concentrations: –(2×10^{-3} mol l^{-1}); —·— (1.2×10^{-4} mol l^{-1}), and ….. (3.59×10^{-5} mol l^{-1}) in ethanol.

TABLE II Formation Constants of M^{n+} with Macrocycle TTD (in ethanol, at 25°C) and Macrocycle TSD (in methanol, at 25°C)

	$LogK_f$						
Macrocycle	Cu(II)	Zn(II)	Ag(I)	Tl(I)	Cd(II)	Pb(II)	Sr(II)
TTD	4.28 ± 0.09	1.99 ± 0.08	1.56 ± 0.06	0.79 ± 0.15	0.73 ± 0.04	0.45 ± 0.11	0.64 ± 0.02
TSD	0.74 ± 0.15	1.29 ± 0.14	0.68 ± 0.02	2.28 ± 0.05	0.90 ± 0.15	0.87 ± 0.02	0.67 ± 0.02

fitting curves of macrocycles with cations using the above software are illustrated in Figure 5 and 6. The fitting curves of complexation process for both ligands are in very good agreement with calculated and experimental data. The results of formation constants are shown in Table 2.

As is evident from Table 2, the stability of the complexes of these heavy metal ions with **TTD** decreases in the order of $Cu^{2+} > Zn^{2+} > Ag^{+} > Tl^{+} > Cd^{2+} > Pb^{2+} > Sr^{2+}$. This means that Cu^{2+} ion with the least soft character and with a good fit condition for **TTD** cavity, forms

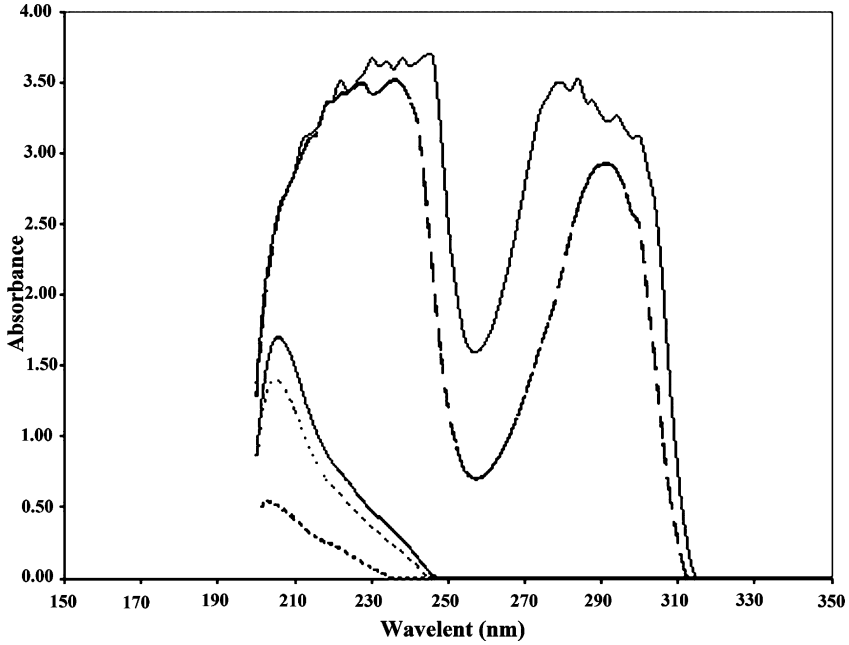


FIGURE 2 Electronic spectra of macrocycle **TSD** in different concentrations: –(03 × 10^{-5} mol l^{-1}); —- (5.03 × 10^{-4} mol l^{-1}); (5.03 × 10^{-5} mol l^{-1}); . . . . (3.09 × 10^{-5} mol l^{-1}); and . . . . (1.03 × 10^{-6} mol l^{-1}) in methanol.

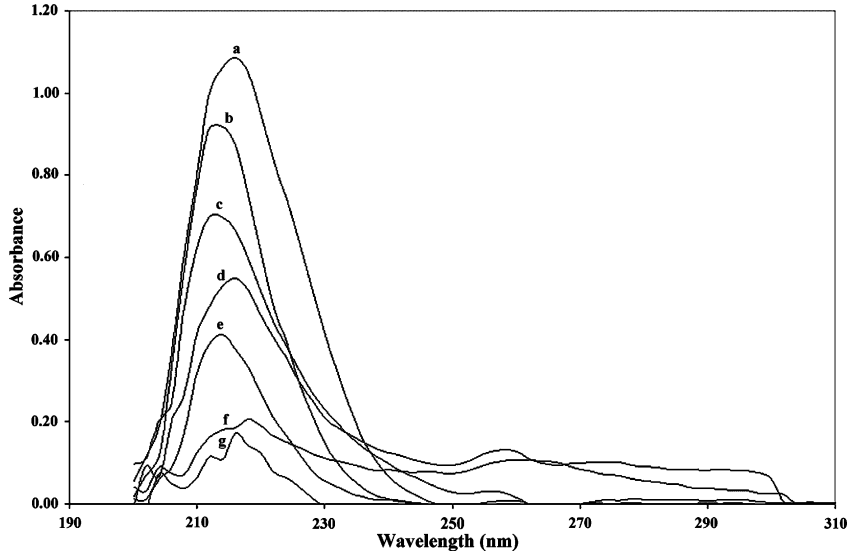


FIGURE 3 Electronic spectra of complex of macrocycle **TTD**–M^{n+}: (a) Tl^{+}; (b) Sr^{2+}; (c) Pb^{2+}; (d) Cu^{2+}; (e) Cd^{2+}; (f) Ag^{+}, and (g) Zn^{2+}.

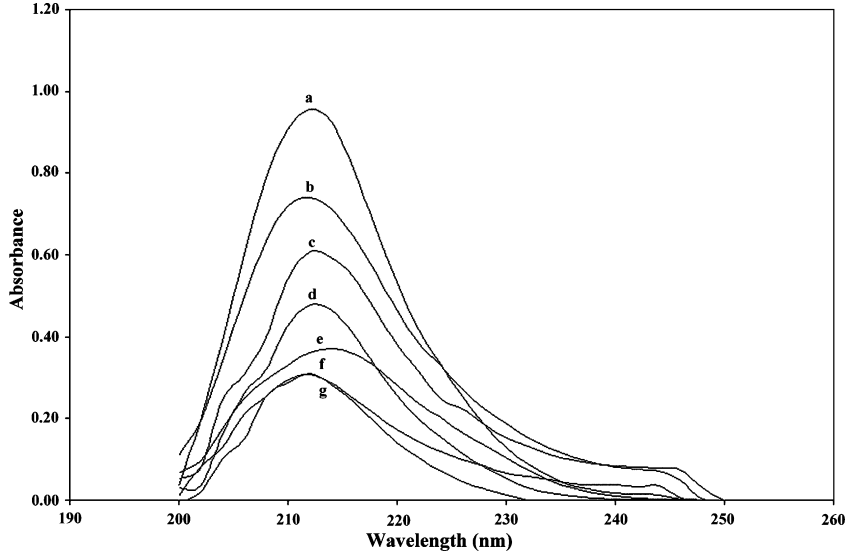


FIGURE 4 Electronic spectra of complex of macrocycle **TSD** – M^{n+}: (a) Sr^{2+}; (b) Pb^{2+}; (c) Cu^{2+}; (d) Cd^{2+}; (e) Tl^{+}; (f) Ag^{+}; and (g) Zn^{2+}.

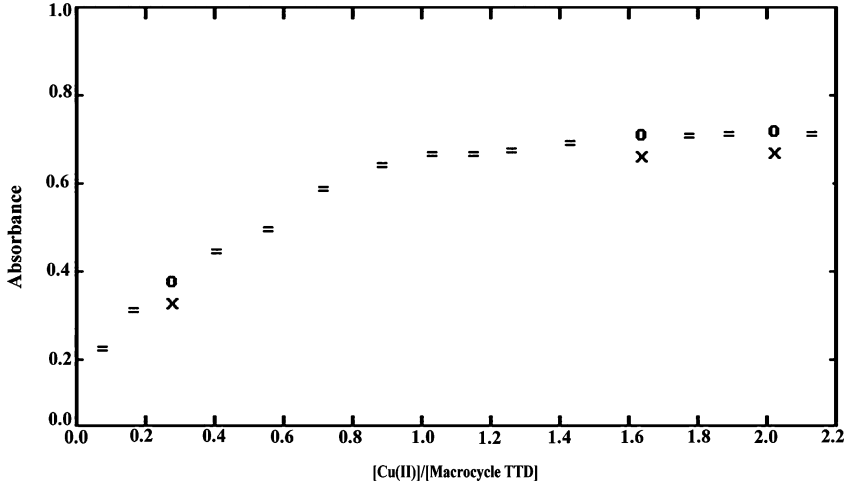


FIGURE 5 Fitting curve of macrocycle **TTD**–Cu^{2+} with ML (= presents fitting; × presents experimental data; and 0 presents calculated data).

the most stable complex with **TTD** as a relatively hard donating ligand. It seems that the increased nature of covalent bonding character of the Cu^{2+} ion could explain the larger value of the stability constant of **TTD-**Cu^{2+} complex than the other six complxes in the protic solvent. The stability order of complexes with **TSD** is changed to Tl^{+} > Zn^{2+} > Cd^{2+} > Pb^{2+} >Cu^{2+} > Ag^{+} > Sr^{2+}, in which Tl^{+} ion with a good

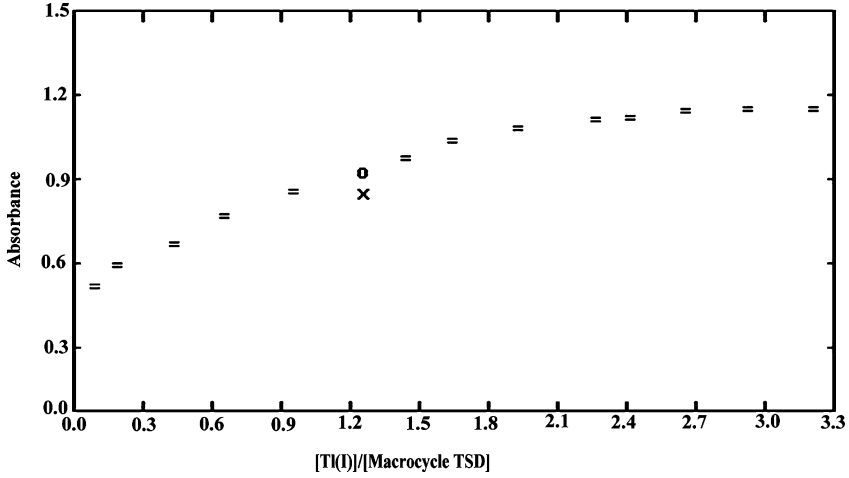


FIGURE 6 Fitting curve of macrocycle **TSD**–Tl^{+} with ML_2 (= presents fitting; × presents experimental data; and 0 presents calculated data).

fit condition for **TSD** cavity, forms the most stable complex with this ligand. As is seen from the Table 2, the Tl^{+}ion forms a more stable complex with **TSD** than other ions in protic solvent system. This observation seems reasonable, since the Tl^{+}ion is bound in the complex by an ion- dipole interaction with a covalent contribution.[15]

Based on the analytical data obtained in these experiments, it seems the macrocycle **TTD** allows 1:1 complexation process with the cations in its cavity. This process is apparently occurred in 1: 2 ratio by macrocycle **TSD**. This may be because of formation of strong interamolecular hydrogen bonding in the cavity of macrocycle **TSD** between NH and S=O groups. Thus, this situation could provide a suitable conditions for 1: 2 ratio complexation in which the formation constants trends are generally lower than the macrocycle **TTD**. This could be because of more rigidity of the macrocycle **TSD** due to S=O group which is also found in our previous studies.[13c] In this case, the macocycle may not be flexible enough to keep the ions in its cavity. As a result, the formation of 1: 2 guest-host system will be more preferable.

EXPERIMENTAL

Apparatus

A Milton Roy Model 1201 photomultiplier tube spectrophotometer was interfaced with an IBM PCS-486 microcomputer by the spectro program that was developed to convert the absorption data acquire with the spectrometer was used. The KINFIT software was used for fitting of experimental and calculated data.

Reagents and Material

All experiments were performed with analytical reagent grade chemicals and pure solvents. Doubly distilled water was used for preparation of aqueous solutions.

Macrocycles were synthesized and reported previously.[13] Macrocycle **TTD** stock solution (3.59×10^{-3} mol l^{-1}) was prepared in ethanol and macrocycle **TSD** stock solution (3.09×10^{-3} mol l^{-1}) was prepared in methanol. Stock solutions of Ag^{+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Sr^{2+}, Tl^{+}, and Zn^{2+} were made by dissolving an appropriate of high purity nitrate salts of these cations (Merck, Germany) in distilled water, respectively. Working solutions were prepared by appropriate dilution of stock solution.

Procedure

Absorption spectra of macrocycles **TTD** and **TSD** are recorded in different concentrations between 200 and 500 nm and the results are shown

in Figures 1 and 2. The absorption spectra of complexes of **TTD** and **TSD** with Ag^{+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Sr^{2+}, Tl^{+}, and $Zn^{2+}$are shown in Figures 3 and 4. The optimum concentrations of macrocycle **TTD** and **TSD** were found in 3.59×10^{-5} mol l^{-1} and 3.09×10^{-5} mol l^{-1}, respectively. The stock solution concentrations of cations for complextion with macrocycles **TTD** and **TSD** were 8.95×10^{-4}, 8.83×10^{-4}, 7.07×10^{-4}, 9.01×10^{-4}, 5.96×10^{-4}, 5.26×10^{-4}, and 8.59×10^{-4} mol l^{-1}, respectively. The absorption of each complex of macrocycles **TTD** and **TSD** with cations in their maximum absorption wavelength are determined in different $[M^{+n}]$ / [L] mole ratio for determination of formation constants.

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