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Thermodynamics studies of fluorescence quenching and complexation behavior of thallium(I) ion with some polyazamacrocycles

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Abstract

The mechanism of fluorescence quenching and stability of the complex formation of thallium(I) ion with polyazamacrocycles [12]aneN_3, Me_3[12]aneN_3, [12]aneN_4, [14]aneN_4, [18]aneN_6 and Me_6[18]aneN_6 were studied in methanol solution at different temperatures spectrofluoromertrically. The factors affecting the mechanism of fluorescence quenching and complexation behavior were found as the size of polyazamacrocycle and substitution of methyl groups on nitrogen atoms of the macrocyclic ring. All the ligands studied form a 1:1 complex at 2.5×10^{-5} M concentration of the thallium(I) at temperatures 15, 20, 25 and 30 °C. Linear Stern–Volmer plots were obtained for [12]aneN_3, Me_3[12]aneN_3 and [14]aneN_4 (first group). In contrast, in the cases of [12]aneN_4, [18]aneN_6 and Me_6[18]aneN_6 systems (second group) an upward curvature was observed in the corresponding Stern–Volmer plots. From the temperature dependence of the fluorescence quenching, it is demonstrated that the mechanism of the quenching process is probably static for the first group. However, in the case of second group, both the static and dynamic mechanisms contribute to the quenching process of the thallium fluorescence. The formation constants of thallium with groups and thermodynamic parameters ΔH°, ΔS° and ΔG° have been determined and the influence of number of members in macrocycle and the substitution of the methyl groups on nitrogen atoms of the macrocyclic ring on the stability of the complexes is discussed. A green emission was observed for the Tl^+-Me_6[18]aneN_6 complex at room temperature.

Keywords: Thallium; Fluorescence quenching mechanism; Complexation; Polyazamacrocycle

1. Introduction

The fluorescent properties of the thallium are well characterized by Steffen and Sommermeyer who found some promising features for such studies in both aqueous and non-aqueous media [1]. Recently, the optical properties of thallium(I), lead(II) and bismuth(III) hexafluoroacetylacetonates have been reported by Strasser and Vogler [2]. The s^2 ions of heavy main group metals (e.g., Tl^+, Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+}) are characterized by low-energy sp triplets [3,4]. Generally, complexes of these metal ions are colorless and their longest-wavelength sp absorptions appear in the UV spectral region. The chloro complexes of these ions show visible phosphorescence under ambient conditions [3,4]. The wavelength of this emission depends on the metal ion and its coordination number. The emission colors of the chloro complexes vary from blue to red. Compounds, which emit from the triplet state under ambient conditions have attracted much recent attentions [5]. This interest is largely related to the application of triplet emitters in organic light emitting diode (OLED) technology [6]. In particular, phosphorescent metal complexes are promising materials. Tris pyrazolyl hydridoborato–thallium(I) complexes show a photoluminescence [7].

The monovalent thallium ion is a polarizabale soft ion [8] with an ionic radius of 1.49 Å [9], which has been suggested as a probe for potassium ion in biological systems [10,11]. It can substitute for K^+ ion activation of some important enzymes such as ATPase [12] and pyruvate kinase [13].

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Thus, information about the stability and selectivity of Tl^+ complexes with macrocyclic ligands are of special interest [14].

In the present study, we investigated the effects of some added polyazamacrocycles (i.e., [12]aneN_3, Me_3[12]aneN_3, [12]aneN_4, [14]aneN_4, [18]aneN_6 and Me_6[18]aneN_6) on the fluorescence quenching of the thallium(I) ion and attempted to clarify mechanisms and bindings of the ligands to thallium(I) in methanol solution at different temperatures, using the Stern–Volmer method [15].

2. Experimental

Reagent grade [12]aneN_3 (1,5,9-triazacyclododecane), Me_3[12]aneN_3 (trimethyl-1,5,9-triazacyclododecane), [12]aneN_4 (1,4,7,10-tetraazacyclododecane) and [14]aneN_4 (1,4,8,11-tetraazacyclotetradecane) were purchased from Aldrich, and [18]aneN_6 (1,4,7,10,13,16-hexaazacyclooctadecane), and Me_6[18]aneN_6 (1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazaoctadecane,), from Fluka, were of the highest purity available and used as received. Analytical grade $TlNO_3$ and spectroscopy grade methanol (both from Merck) were used throughout.

The fluorescence spectra were recorded by a Perkin-Elmer model LS 50B spectrofluorimeter equipped with a thermostated cell compartment. At all temperatures used, the accuracy of temperature measurement was ±0.1 °C. The thallium(I) fluorescence intensity was measured at the maximum emission wavelength of 360 nm after excitation of solutions at 232 nm. Stock solutions of quenchers were prepared, and small volumes were added with a microsyringe to a known volume of 2.5×10^{-5} M of Tl^+ ion solution directly in quartz cuvette. The results of the quenching reactions between the thallium ion and polyazamacrocycle ligands were analyzed according to the Stern–Volmer equation [15]. No effort was made to remove the oxygen dissolved in the solvent as it has been shown that the fluorescence of thallium is not quenched by molecular oxygen so that the fluorescence intensity is unaffected by the presence of oxygen in solution at atmosphere pressure. Absorption spectra were obtained using a Shimadzu 2100 UV–visible spectrophotometer.

3. Results and discussion

The fluorescence spectra of Tl^+ ion in methanol at different excitation wavelengths were obtained and a wavelength 232 nm was selected as the most convenient excitation wavelength for further studies. Maximum fluorescence emission occurs at 360 nm (inset of Fig. 1). The formation constant of different Tl^+–polyazamacrocycle complexes were determined using the Stern–Volmer method. Sample spectra is shown in Fig. 1. As seen, an increase in the ligand concentration results in the decreased thallium fluorescence intensity at 360 nm. The physical origin of fluorescence quenching arising from the addition of a quenching agent (ligand) to the thallium fluorescence can be divided into two distinct mechanistic classes namely, dynamic and static quenching. In dynamic (collisional) quenching, the decrease in fluorescence is due to a collision between the metal and the quencher. In contrast, static quenching can arise from the formation of a dark complex between the thallium and the quenching agent. Quenching can also occur via many trivial processes, such as attenuation of the excitation light by the fluorophore itself or other absorbing species. Except for trivial processes, the quenching mechanisms involve very close contact between the excited state of a fluorescent species and the quencher and are sometimes referred to as contact quenchers.

As will be shown later, the quenching of fluorescence observed in this study most probably arises from static

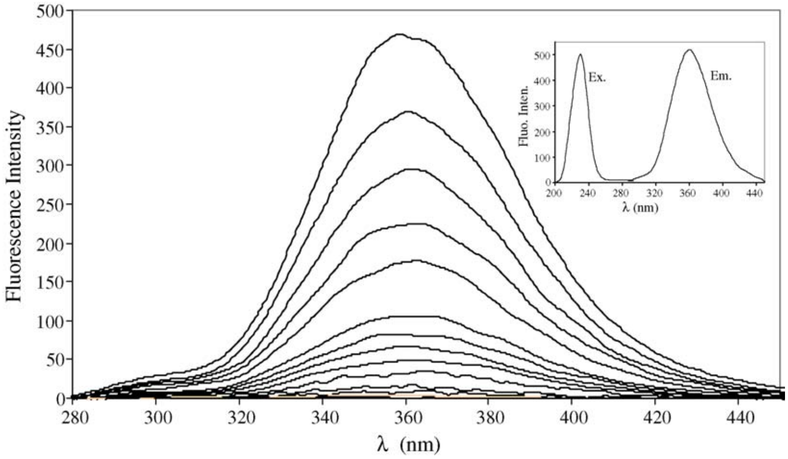


Fig. 1. Emission spectra of 2.5×10^{-5} M thallium(I) in methanol with added [12]ane N_4 concentrations of 0, 7.0×10^{-6}, 1×10^{-5}, 1.3×10^{-5}, 1.6×10^{-5}, 1.9×10^{-5}, 2.2×10^{-5}, 2.4×10^{-5}, 3.0×10^{-5}, 3.6×10^{-5}, 4.2×10^{-5}, 4.7×10^{-5}, 5.9×10^{-5} and 10^{-4} M from the largest to the smallest emission at 288 K. (Insert) Excitation and emission spectra of 2.5×10^{-5} M solution of thallium(I) in methanol solution at 298 K, the excitation and emission slits were 10 nm, each spectra is a result of the average of three scans and intensity in arbitrary unit's a.u.

quenching and is presumably due to the formation of a non-fluorescent complex between the ligand and thallium.

For the association of thallium ion (M) and a ligand (L)

$$\mathrm{M} + \mathrm{L} \leftrightarrow \mathrm{M} - \mathrm{L} \tag{1}$$

the following relationship between the fluorescence intensity in the absence (I_o) and presence (I) of the quenching agent can be obtained:

$$\frac{I_o}{I} = 1 + K_{\mathrm{sv}}[L] \tag{2}$$

where K_{sv} is the corresponding equilibrium (association) constant for the complexation reaction, Eq. (1). This equation is generally known as the Stern–Volmer relation [16]. The typical results of the fluorescence titrations plotted according to the Stern–Volmer equation are given in Fig. 2. In the Stern–Volmer plots, the five-membered (M–N–C–C–N–) ligands (i.e., [12]aneN_4, [18]aneN_6 and Me_6[18]aneN_6) showed an upward curvature, whereas the six-membered (M–N–C–C–C–N–) ligands (i.e., [12]aneN_3, Me_3[12]aneN_3 and [14]aneN_4) showed a straight line, and we attempted to explain the mechanism of these two groups of quenching processes. In fact, the curvature of the plots suggested that more than one mechanism is involved in the quenching of fluorescence of thallium by the five-membered ligands (Fig. 3).

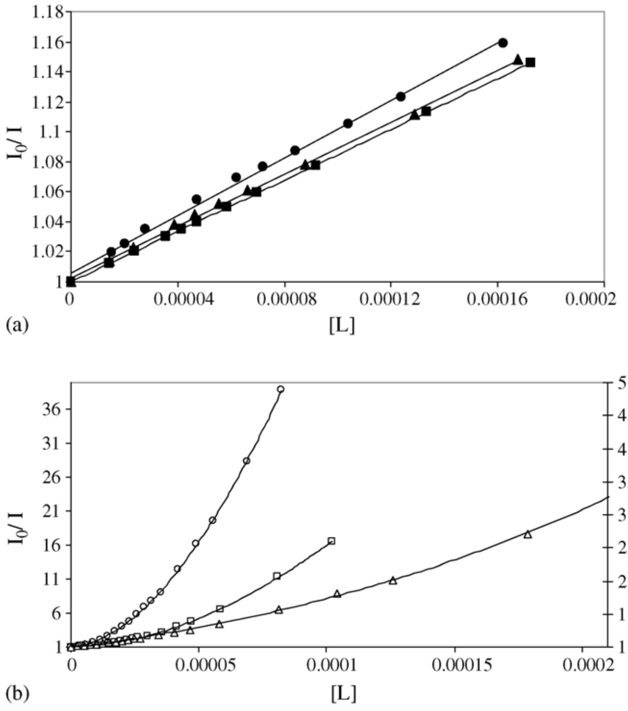


Fig. 2. (a) The Stern–Volmer plot for quenching processes of thallium(I) by polyazamacrocycles (six-membered) in methanol at 298 K: (●) Me_3[12]aneN_3, (▲) [12]aneN_3, (■) [14]aneN_4. (b) The Stern–Volmer plot for quenching processes of thallium(I) by polyazamacrocycles (five-membered) in methanol at 298 K: (◯) Me_6[18]aneN_6 and (□) [12]aneN_4 left scale; (△) [18]aneN_6 right scale.

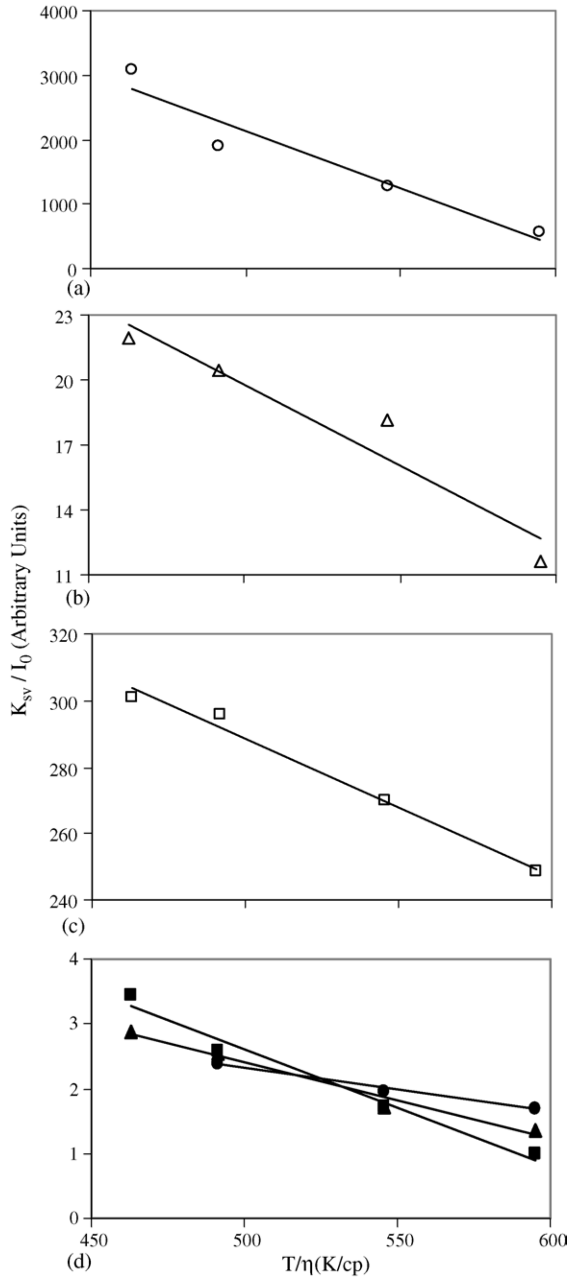


Fig. 3. Dependence of the quantity K_{sv}/I_o on T/η for (a) Me_6[18]aneN_6, (b) [18]aneN_6, (c) [12]aneN_4 and (d): (●) Me_3[12]aneN_3, (▲) [12]aneN_3, (■) [14]aneN_4. The viscosity of the solution, η, is expressed in centipoise and is taken to be that of methanol, at each temperature; [CRC Handbook of Chemistry and Physics (1987)].

In the case of dynamic (collisional) quenching, the corresponding Stern–Volmer equation is given by Eq. (3):

$$\frac{I_o}{I} = 1 + K_q[L] \tag{3}$$

$$I_o = k_f\,\tau_o \tag{4}$$

where K_q is the bimolecular collisional quenching constant, which is generally referred to as the Stern–Volmer collisional quenching constant, k_f the rate constant of fluorescence process and τ_o denotes the excited-state lifetime of the fluorescence in the absence of the quencher. It should be noted that the Stern–Volmer equation has the same mathematical form for both types of quenching mechanism (static and dynamic). In fact, from a comparison between Eqs. (2) and (3), it can readily be seen that the only difference between the two different forms of the Stern–Volmer equation lies in the physical nature of the quenching constants. In the diffusion-controlled limit, the bimolecular rate constant can be expressed by the Smoluchowski equation [16]:

$$k_0 = \frac{4\pi N_0 R(D_M + D_L)}{1000} \tag{5}$$

where N_0 is Avogadro's number, R the distance of closest approach between the metal and the ligand and D_M and D_L are the diffusion coefficients of the fluorophore and the quencher, respectively. Here, k_0 is the diffusion-controlled bimolecular rate constant and is related to K_q by the quenching efficiency κ, as:

$$K_q = \kappa k_0 \tag{6}$$

For dilute solutions, the diffusion coefficient for each species can be determined from the Stokes–Einstein equation [16]:

$$D = \frac{k_B T}{6\pi R\eta} \tag{7}$$

$$\frac{K_q}{I_o} \propto \frac{T}{\eta} \tag{8}$$

where k_B is the Boltzmann's constant, T the absolute temperature, R the radius of the species and η is the solvent viscosity. Hence, for an efficient dynamic quencher, K_q is expected to vary with T/η. Distinguishing between dynamic and static quenching processes can be straightforward, as the dynamic bimolecular rate constant k_0 and, consequently, the bimolecular collisional quenching constant, K_q, will increase with temperature (i.e., $K_q/I_o \propto T/\eta$, Eq. (8)), compared to the decrease in static quenching constants with temperature, as a result of the decreased stability and subsequent break-up of the non-fluorescent ground state complexes (Fig. 3).

It is also possible to distinguish between these two mechanisms of quenching by simple examination of the absorption spectrum of the system under study. Since collisional quenching only affects the excited state of the fluorophore then there are typically no changes in fluorophore absorption spectra whereas ground state complex formation and subsequent static quenching frequently results in the absorption spectrum being altered.

When both dynamic and static fluorescence quenchings occur together, then a modified form of the Stern–Volmer equation is used, equation (9), and a steady-state fluorescence plot of I_o/I versus $[L]$ will usually result in an upward curving (the equation is second order in $[L]$, Fig. 2b).

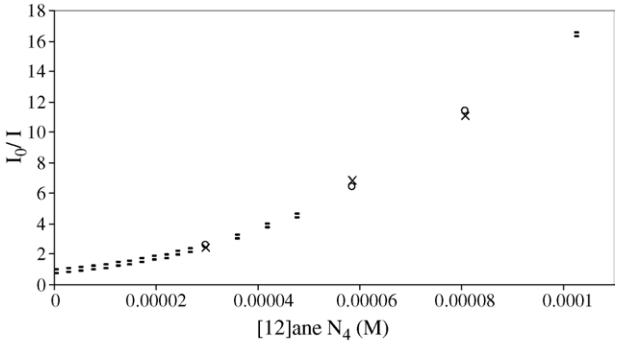


Fig. 4. Computer fit of relative fluorescence intensity as a function of ligand (quencher) concentration in methanol at 298 K: (×) experimental point, (○) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

$$\frac{I_o}{I} = (1 + K_q[L])(1 + K_{sv}[L]) \tag{9}$$

In Eq. (9), the first part is related to the dynamic quenching and the second part to the static quenching. The expansion of the parentheses of Eq. (9) yields:

$$\frac{I_o}{I} = 1 + (K_{sv} + K_q)[L] + K_{sv}K_q[L]^2 \tag{10}$$

The data shown in Fig. 2 were fitted to Eq. (10) for the determination of K_q and K_{sv} values by using a non-linear least-squares curve-fitting program KINFIT [17]. A sample computer fit of the relative fluorescence intensity–quencher concentration data is shown in Fig. 4. In Table 1 are given the bimolecular collisional constant and static quenching constant obtained from computer fitting of the relative fluorescence intensity–quencher concentration data for [12]aneN$_4$, [18]aneN$_6$ and Me$_6$[18]aneN$_6$ in methanol solution at 298 K.

On the basis of Eq. (8), dependence of K_{sv}/I_o on the quantity T/η with a negative slope (Fig. 3) indicates that the dynamic quenching does not play a significant role in the quenching of thallium fluorescence by polyazamacrocycle ligands. This conclusion is supported by the fact that the magnitudes of K_q values evaluated from Eq. (10) are much lower than the corresponding K_{sv} (first group in Table 1) values calculated for static quenching of thallium (i.e., for the case where the fluorescence quenching occurred in a static process by forming a non-fluorescent complex). The slopes of the Stern–Volmer plots, therefore, are equivalent to the equilibrium constants for the thallium complex formation. However, in order to obtain the true values of the formation constants of the complexes, K_{sv}, it is necessary to correct the initial concentrations of ligand for the amounts due to the formation of the complex. To correct for this effect, an iteration procedure was applied for the evaluation of the complex formation constants. Since the free ligand concentration is unknown, the total amount of the added ligand was used as a starting point for the Stern–Volmer plot. The calculated free ligand concentration, corrected by the formation of complex

Table 1
Stability constants and bimolecular collisional quenching constants, for the thallium(I) complexes with some polyazamacrocycles ligands at 298 K, and the thermodynamic parameters of the complex formation[a]

Legend	$\log K_{sv}$[b]	$\log K_q$[b]	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	$\Delta G^\circ_{(298\,K)}$ (kJ mol^{-1})
Six-membered					
[12]aneN_3	2.95 ± 0.01	<1	−36.5 ± 7.2	−66.1 ± 24.5	−16.8 ± 0.1
Me_3[12]aneN_3	2.98 ± 0.01	<1	−17.5 ± 1.6	−1.6 ± 5.4	−17.0 ± 0.1
[14]aneN_4	2.92 ± 0.01	<1	−58.4 ± 9.1	−141.4 ± 30.9	−16.3 ± 0.1
Five-membered					
[12]aneN_4	4.84 ± 0.01	4.27 ± 0.02	−11.4 ± 0.7	60.2 ± 2.3	−29.3 ± 0.1
[18]aneN_6	3.86 ± 0.01	3.53 ± 0.08	−31.5 ± 5.6	−32.3 ± 18.8	−21.9 ± 0.1
Me_6[18]aneN_6	5.76 ± 0.01	3.31 ± 0.09	−80.5 ± 1.9	−161.2 ± 40.2	−32.5 ± 0.2

[a] Values for the standard enthalpy and standard entropy are obtained as the slopes and the negative of the intercepts of plots of $\ln K_{sv}$ vs. $1/T$. Values of the standard free energy (at 298 K) are calculated from the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Standard errors are presented.

[b] The units of K_{sv} and K_q are l mol^{-1}.

species, was then used for the next iteration process. Convergence was achieved after three iterations. The values of the complexation constant K_{sv} derived from the slope of the Stern–Volmer plot in methanol solution at 298 K are listed in Table 1.

The values of ΔS° and ΔH° (presented in Table 1) were evaluated from a linear van't Hoff plot, thereby in essence treating these two thermodynamic parameters as constants at the experimental temperature range employed (288–304 K). The resulting thermodynamic parameters for the complexation of Tl^+ ion with [12]aneN_3, Me_3[12]aneN_3, [12]aneN_4, [14]aneN_4, [18]aneN_6 and Me_6[18]aneN_6 along with the corresponding standard errors are presented in Table 1. A comparison between the ΔG° values of the resulting 1:1 complexes of Tl^+ ion showed that the five-membered ligands ([12]aneN_4, [18]aneN_6 and Me_6[18]aneN_6) form much more stable thallium complexes than the six-membered ligands ([12]aneN_3, Me_3[12]aneN_3 and [14]aneN_4). The results indicated that the five-membered ligands provide a more favorable conformation for the Tl^+ ion binding with the donating nitrogen atoms of the ligands.

The observed trend in the 1:1 complexes of five-membered and six-membered ligands with Tl^+ ion is consistent with the complexation constants reported in the literature for analogous complexes with a relatively large metal ion such as Pb^{2+} [18–20]. The stability sequence of the 1:1 Tl^+ complexes with tri-, tetra- and hexaaza-macrocycles, in methanol solution is Me_6[18]aneN_6 > [12]aneN_4 > [18]aneN_6 > $(Me)_3$[12]aneN_3 ≥ [12]aneN_3 > [14]aneN_4.

Five-membered ligand rings have minimum strain energy with large metal ions of high coordination number and thus small N-M-N angle. Molecular mechanics calculations show that as the metal ion gets larger, the ligand ring flattens and the hydrogens rotate into eclipsed positions, with a rise in strain energy. Thus, complexes of large metal ions are destabilized by six membered ligand rings. This rule holds for both macrocyclic and acyclic ligands [18–20]. From the data given in Table 1 it is obvious that, in the case of the five-membered ligands studied, the stability of the resulting Tl^+ ion complexes with Me_6[18]aneN_6 and [12]aneN_4 is higher than that with [18]aneN_6. This is most probably due to the slow exchange rate between the free and complexed Tl^+ with Me_6[18]aneN_6 and [12]aneN_4, as it compared with the fast exchange rate of the Tl^+-[18]aneN_6 system which occurred via a bimolecular exchange mechanism [21]. However, in the cases of the Me_6[18]aneN_6 and [12]aneN_4 complexes with Tl^+ ion, the predominant exchange mechanism is a dissociative pathway [21,22].

As is obvious from Table 1, the stability constants of the resulting Tl^+ ion complexes with both two groups of ligands in the presence of $–NCH_3$ groups was increased in comparison with the corresponding ligands bearing –NH groups. This is due to the inductive electron pumping of the methyl groups of the Me_3[12]aneN_3 and Me_6[18]aneN_6 ligands, which increase the basicity of the donating nitrogen atoms of the macrocyclic rings over those of [12]aneN_3 and [18]aneN_6, respectively.

Fig. 5 shows the fluorescence spectra of thallium in the presence of increasing concentration of Me_6[18]aneN_6 in methanol solution. As it is seen, addition of the ligand results in the appearance of a new emission maximum at 415 nm in the expense of gradual quenching of the thallium emission maxima at 360 nm through a well-defined isosbestic point at 390 nm, presumably due the formation of a 1:1 complexation in solution. Obviously, the Tl^+-Me_6[18]aneN_6

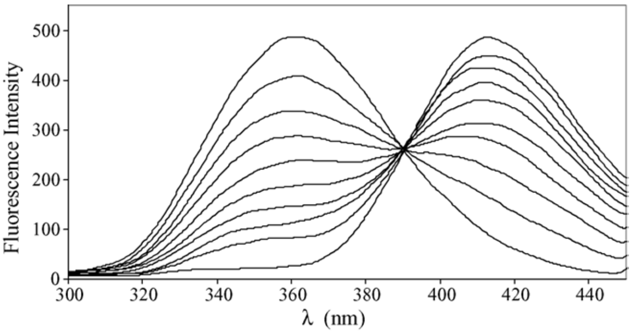
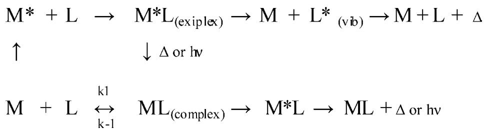


Fig. 5. Emission spectra of 2.5 × 10^{-5} M thallium(I) at 298 K in methanol with added Me_6[18]aneN_6 concentrations of 0, 2.5 × 10^{-6}, 3.1 × 10^{-6}, 5.8 × 10^{-6}, 7.9 × 10^{-6}, 9.5 × 10^{-6}, 1.2 × 10^{-5}, 1.4 × 10^{-5}, 1.6 × 10^{-5}, 1.9 × 10^{-5}, 2.5 × 10^{-5} and 10^{-4} M from the largest to the smallest emission in 360 nm.



Scheme 1.

complexation will result in a strong emission shift of about 55 nm towards longer wavelengths (green emission) indicating that the environment of thallium in a methanol solution containing Me_6[18]aneN_6 is quite different from that in the absence of the ligand. It should be noted that only in the case of Me_6[18]aneN_6 the 415 nm band of thallium complex was so intense and comparable with the 360 nm band of the free thallium ion, and in the other cases the complexed form did not show any fluorescence in this spectral region. The existence of the new emission band in Tl^+-Me_6[18]aneN_6 is indicative of the formation of an exciplex between the excited thallium(I) ion and the ligand. Thus, it is believed that the internal conversion step should deliver energy to the ligand via vibrational excitation for two reasons. First, the fact that nonradiative decay must be much faster than in the quenchee by itself implies involvement of the quencher as an active participant in the process. Second, there are cases in which chemical transformation of the quencher indicates that energy in some form must be transferred. Possible mechanistic pathways for the quenching and complexation of Tl^+-polyazamacrocycles are suggested in Scheme 1, from which the observation of such green emission process can be deduced.

Based on the proposed mechanistic pathways shown in Scheme 1, two factors seem to be responsible for the observation of the new emission band: (a) high binding energy of the exciplex (M*L), and (b) low dissociation rate (k_{-1}) of the Tl^+ complex (ML). As it is seen from Table 1, binding in the Tl^+-Me_6[18]aneN_6 system is much more exothermic than that of other systems, i.e., in the excited complex the thallium binding of the nitrogen atoms of ligand are relatively strong. The more negative ΔS° and ΔH° values for Tl^+-Me_6[18]aneN_6 complex than those of the other Tl^+–ligand complexes has been regarded as an indication of a considerable structural transformation caused by the coordination of the Me_6[18]aneN_6 ligand to the metal centre of Tl^+-Me_6[18]aneN_6. In contrast to the Tl^+-Me_6[18]aneN_6 system, the M^*L complex can decay rapidly to the ground state via non-radiative process for [12]aneN_3, Me_3[12]aneN_3, [12]aneN_4, [14]aneN_4, [18]aneN_6, and it is reasonable to assume that its $\nu = 0$ vibration level lies close to its luminescent states.

Another important quenching process, which has been used to describe quenching mechanism is fluorescence resonance energy transfer (FRET). FRET is the transfer of the excited state energy from the initially excited thallium, M*, to a complex, ML, which is typically non-fluorescent (Figs. 1 and 6). The M* resonance emission spectrum typically overlaps with the absorption spectrum of the ML.

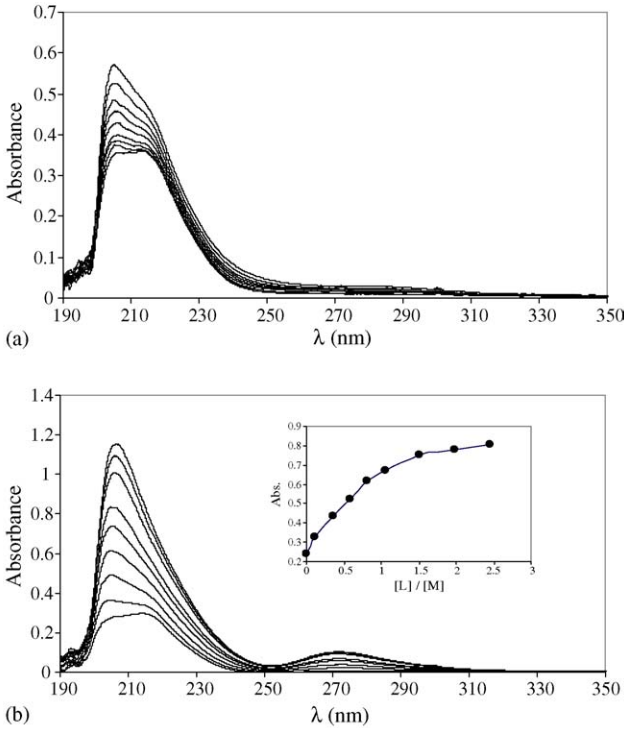


Fig. 6. UV absorption spectra of 2.5×10^{-5} M thallium(I) in methanol with added ligand. (a) [12]aneN_3 concentrations of 0, 1.0×10^{-5}, 2.1×10^{-5}, 2.6×10^{-5}, 4.1×10^{-5}, 5.6×10^{-5}, 7.1×10^{-5}, 9.0×10^{-5} and 1.1×10^{-4} M from the smallest to the largest absorbance. (b) Me_6[18]aneN_6 concentrations of 0, 2.9×10^{-6}, 8.6×10^{-6}, 1.4×10^{-5}, 2.0×10^{-5}, 2.6×10^{-5}, 3.7×10^{-5}, 4.8×10^{-5} and 5.9×10^{-5} M from the smallest to the largest absorbance. (Insert) The absorbance–mole ratio plot at wavelength of 204 nm.

The absorption spectra of 2.5×10^{-5} M thallium(I) ion recorded at 25 °C in methanol solution with increasing concentrations of ligand in the UV range of 190–350 nm are given in Fig. 6. The absorption spectrum of thallium shows dual bands, one at 204 nm and another at 216 nm (Fig. 6), and the emission spectra appeared at 360 nm in methanol (Fig. 1). Sample spectra of first and second group are shown in Fig. 6. On addition of ligand, the absorption intensity of both the bands increases gradually (Fig. 6). It is also observed that the position of the absorption maximum show a blue shift. In the case of Tl^+-Me_6[18]aneN_6 a new band at wavelength of 275 nm was observed in absorption spectra (Fig. 6b). It should be noted that all of the polyazamacrocycles used have low absorption intensity at the wavelength range of 190–350 nm in the concentration ranges studied, so extinction coefficients are small ($10^2 < \varepsilon < 4 \times 10^3$). The increases of absorption bands present in the spectrum of thallium due to addition of ligand clearly indicates that thallium was complexed by ligand. The resulting absorbance–mole ratio plot is shown in inset of Fig. 6b. On the other hand, the emission intensity decreases significantly due to fluorescence quenching of thallium by the gradual addition of ligand, without any change in the position of the emission band. It is well known that apart from changes in absorption spectra, the exciplex formation also causes enhancement of absorption intensity and quenching of fluorescence. The exciplex formation quenching is a process, which competes with emission for depopulation of the excited state; thus the fluorescence decreases in proportion to the yield. Another possible quenching mechanism may act by a FRET process is also discussed above.

The results of complexation of several macrocyclic ligands with thallium ion in methanol solution by fluorescence spectroscopy have already been reported by Parham and Shamsipur [22]. It is interesting to note that, in the cases of 18-crown-6 and dicyclohexyl-18-crown-6 ligands, the addition of ligands to a methanol solution of Tl^+ resulted in a blue shift (308 nm) in fluorescence spectrum of thallium ion through a well-defined isosbestic point [22]. Kunkely and Vogler have also reported that the coordination compounds $TlTp^{3-R}$ with Tp^{3-R} = hydridotris-3-R-pyrazolyl-1-yl-borate anion (R = *tert*-butyl, phenyl, 2-thienyl and *p*-tolyl) show a photoluminescence which originates from the metal-centered sp triplet of the Tl^+ ion at room temperature [7].

The electronic spectra of simple main group metal complexes with heavy s^2 ions such as Tl^+ are characterized by metal-centered MC $s \rightarrow p$ transitions which are modified by the ligands. Generally, complexes of these metal ions (e.g. Tl^+, Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+}) are colorless and their longest-wavelength sp absorptions appear in the UV spectral region. The chloro complexes of these ions show a visible phosphorescence under ambient conditions [3,4,23]. The wavelength of this emission depends on the metal and its coordination number. The emission colors of the chloro complexes vary from blue to red [2].

4. Conclusions

Linear plot of relative fluorescence intensity versus concentration of quencher (polyazamacrocycle) corresponds to a first order quenching which indirectly indicates the formation of a complex with 1:1 stoichiometry, i.e., an exciplex. A general model for fluorescence quenching by exciplex formation involves the formation of a M*L complex which then may form an equilibrium complex or dissociate back into M and L, as indicated in Scheme 1. The equilibrium complex is the species which is directly responsible for the fluorescence quenching.(upward curvature for more stable thallium complexes with five membered ligands). The modified Stern–Volmer plots for $Me_6[18]aneN_6$, $[18]aneN_6$ and [12]aneN4 as quenchers depicted the coexistence of both static and dynamic mechanisms of quenching with the static mechanism being predominant, due to the formation of non-fluorescent complexes in the ground state (with the exception of $Me_6[18]aneN_6$). A new emission signal with about 55 nm shift (green shift) was observed for the 18-membered ligand, $Me_6[18]aneN_6$. It was concluded that the appearance and wavelength of this emission depends on the coordination number and exchange kinetics of metal ion, while the conformational changes in the ligands caused formation of an excited state complex (exciplex).

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