



**SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF
CHARGE-TRANSFER COMPLEXES DERIVED FROM
THREE SYMMETRICALLY SUBSTITUTED 4,4'-BIS-
(1,3,5-TRIAZINYLAMINO)STILBENE-2,2'-DISULFONATE
DERIVATIVES WITH SOME π -ACCEPTORS.
PART ONE : CHLORANILIC ACID**

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ABSTRACT

Fluorescent brighteners (FBs) have become a part of everyday life and culture. One important class of fluorescent brighteners (FBs) is triazine-stilbene derivatives, which are widely used to create intense and bright white shades in textiles, pulps and papers. It is possible to improve the chemical and physical properties of triazine-stilbene derivatives by studying their complexation behavior. For this purpose, three new charge-transfer complexes were obtained by the interaction between three symmetrically substituted 4,4'-bis-(1,3,5-triazinylamino)stilbene-2,2'-disulfonate derivatives with chloranilic acid. The structures of these complexes were characterized by using elemental analysis, IR and electronic absorption spectroscopy. Based on elemental analyses and photometric titrations, the stoichiometry of the complexes (donor : acceptor molar ratios) was determined to be 1 : 2 for all three complexes. The formation constant (K_{CT}), molar extinction coefficient (ϵ_{CT}) and other spectroscopic data have been determined using the Benesi-Hildebrand method and its modifications.

Key words: Fluorescent brighteners, Triazine-stilbene derivatives, Charge-transfer, Chloranilic acid.

INTRODUCTION

Fluorescent brighteners (FBs) are substances, which normally have a system of conjugated double bonds and electron-donating groups to show the high fluorescence

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activity. FBs are primarily applied to textiles to enhance their whiteness and brightness and are commonly added to textile substrates at various manufacturing steps in order to increase their apparent whiteness and to provide an additional layer of protection against UV-A and UV-B radiation^{1,2}. They increase the whiteness by absorbing light in ultraviolet region (330-380 nm) and re-emitting more visible light at a longer wavelength in the blue region, via fluorescence, with a typical maximum at (430-440 nm) wavelength³. One important class of FBs is based on triazine-stilbene derivatives, which are widely used to create intense and bright white shades when incorporated in plastic, textiles, pulp and paper or when applied to textiles through washing with laundry detergents⁴. Until now, many triazine-stilbene derivatives, involving linear and nonlinear optical materials, photovoltaic materials, light emitting diodes, photoinduced electron transfer sensors, fluorescent switchers, chemosensors, pH chemosensing materials, biofunctional materials and new medicine have been prepared⁵⁻¹⁵. In this paper, we report herein the synthesis and spectral properties of three charge-transfer complexes formed between three triazine-stilbene derivatives; namely sodium (E)-6,6'-(ethene-1,2-diyl)bis(3-(4-(dimethyl-amino)-6-(2-hydroxyethylamino)-1,3,5-triazin-2-yl-amino) benzenesulfonate (**TS1**), sodium (E)-6,6'-(ethene-1,2-diyl) bis(3-(4-(2-hydroxyethyl-amino)-6-morpholino-1, 3, 5-triazin-2-yl-amino)benzene-sulfonate (**TS2**) and sodium (E)-6,6'-(ethene-1,2-diyl) bis(3-(4-(diethylamino)-6-(2-hydroxyethylamino)-1,3,5-triazin-2-yl-amino) benzene-sulfonate (**TS3**) as donors with chloranilic acid (CLA). The chemical structures of the synthesized compounds were characterized by the analysis of UV-vis and IR spectra as well as elemental analysis.

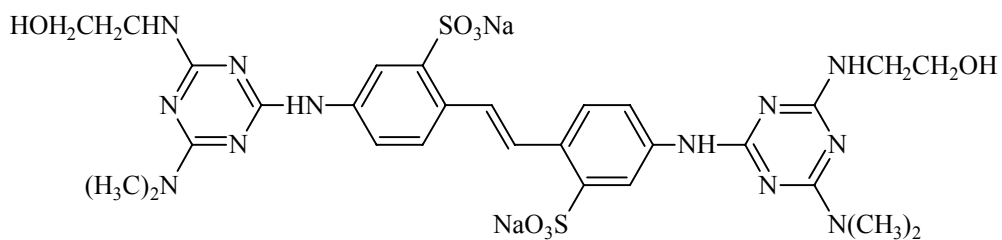
EXPERIMENTAL

Materials and instruments

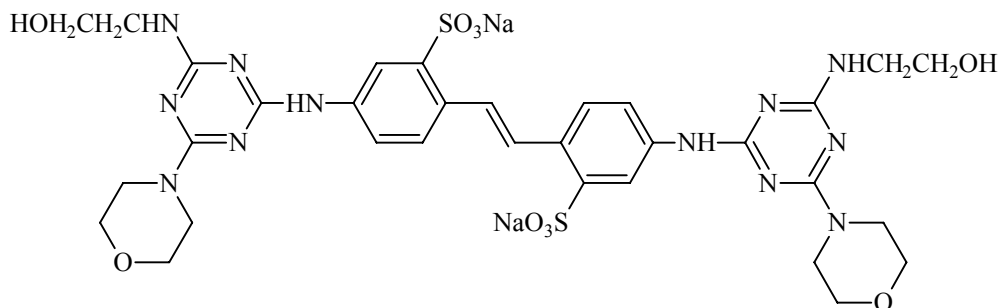
The three symmetrically substituted 4,4'-bis-(1,3,5-triazinylamino)stilbene-2,2'-disulfonate donors (**TS1**, **TS2** and **TS3**; Formula I) were obtained by synthesis according to the literature methods¹⁶. The chloranilic acid (CLA) acceptor was purchased from the Sigma-Aldrich Chemical Company and was used without further purification. The elemental analyses of the carbon, hydrogen and nitrogen content were performed using a Perkin-Elmer CHN 2400 (USA). The electronic absorption spectra of the donors, the acceptor and the synthesized complexes were recorded in methanol over a wavelength range of 200-800 nm using a Perkin-Elmer Lambda 25 UV/Vis double-beam spectrophotometer. The instrument was fitted with a quartz cell that had a path length of 1.0 cm. The infrared (IR) spectra using KBr discs within the range of 4000-400 cm^{-1} for the complexes were recorded on a Shimadzu FT-IR spectrophotometer with 30 scans at 2 cm^{-1} resolution.

Synthesis

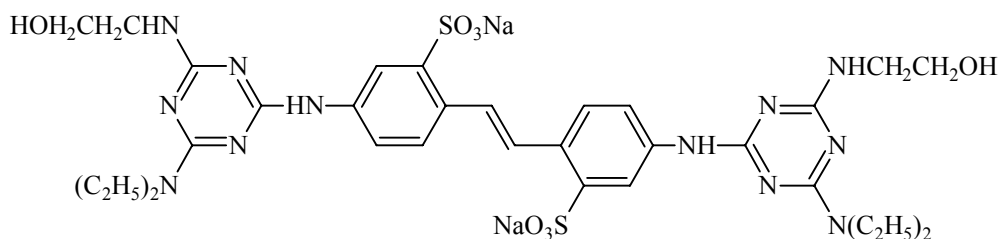
The solid charge-transfer complexes of the **TS1**, **TS2** and **TS3** donor with the CLA acceptor were prepared by mixing 1 mmol of each donor in pure-grade methanol (20 mL) with 1 mmol of CLA acceptor in methanol (20 mL). The mixtures were stirred for approximately 30 min and allowed to evaporate slowly at room temperature resulting in the precipitation of the solid complexes. The resultant complexes were filtered and washed well with methanol. Then, the synthesized complexes were collected and dried under vacuum over anhydrous calcium chloride for 24 h.



TS1



TS2



TS3

Formula I: Chemical Structure of triazine-stilbene derivatives; TS1, TS2 and TS3

RESULTS AND DISCUSSION

Analytical results

The analytical data and elemental analysis (C, H and N) of the synthesized complexes are shown in Table 1. The elemental analysis data for the prepared complexes are in agreement with the molar ratio obtained from the spectrophotometric titrations. The resulting elemental analysis values are in good agreement with the calculated values. The stoichiometry of the prepared complexes with the CLA acceptor was found to have a 1 : 2 ratio. Based on the obtained data, the prepared complexes were formulated as [(TS)(CLA)₂] (TS: **TS1**, **TS2** or **TS3**). The [(**TS1**)(CLA)₂], [(**TS2**)(CLA)₂] and [(**TS3**)(CLA)₂] complexes have a red, violet and dark brown, respectively. All the complexes are insoluble in cold and hot water, but easily soluble in DMSO and DMF.

Table 1: Analytical data of the synthesized complexes

Complex	Molecular formula	Mwt. g/mol	Elemental analyses					
			C%		H%		N%	
			Found	Calc.	Found	Calc.	Found	Calc.
[(TS1)(CLA) ₂]	C ₄₀ H ₃₈ N ₁₂ O ₁₆ Cl ₄ Na ₂ S ₂	1193.96	40.39	40.20	3.22	3.18	14.00	14.07
[(TS2)(CLA) ₂]	C ₄₄ H ₄₂ N ₁₂ O ₁₈ Cl ₄ Na ₂ S ₂	1278.20	41.27	41.31	3.24	3.28	13.10	13.14
[(TS3)(CLA) ₂]	C ₄₄ H ₄₆ N ₁₂ O ₁₆ Cl ₄ Na ₂ S ₂	1249.96	42.30	42.24	3.63	3.68	13.59	13.44

Stoichiometry

Figure 1 shows the electronic absorption spectra of the reactants, donors (**TS1**, **TS2** or **TS3**) (5.0×10^{-4} M) and CLA acceptor (5.0×10^{-4} M), along with those of the prepared complexes. These spectra revealed the presence of the absorption bands that correspond to the CT interactions. These bands are observed at (320, 525), (350, 530) and (330, 520) nm for the [(**TS1**)(CLA)₂], [(**TS2**)(CLA)₂] and [(**TS3**)(CLA)₂] complexes, respectively. These detected absorption bands well known to be characteristic of the formation of new charge-transfer complexes. The stoichiometry of the synthesized charge-transfer complexes formed between the donors and the acceptor was obtained from the determination of the conventional spectrophotometric molar ratio according to previously published protocols¹⁷. Representative spectrophotometric titration plots based on these characterized absorption bands are shown in Fig. 1. Based on this figure, the complex formation occurred with a ratio (TS : acceptor) of 1 : 2. These stoichiometry values are consistent with the elemental analyses.

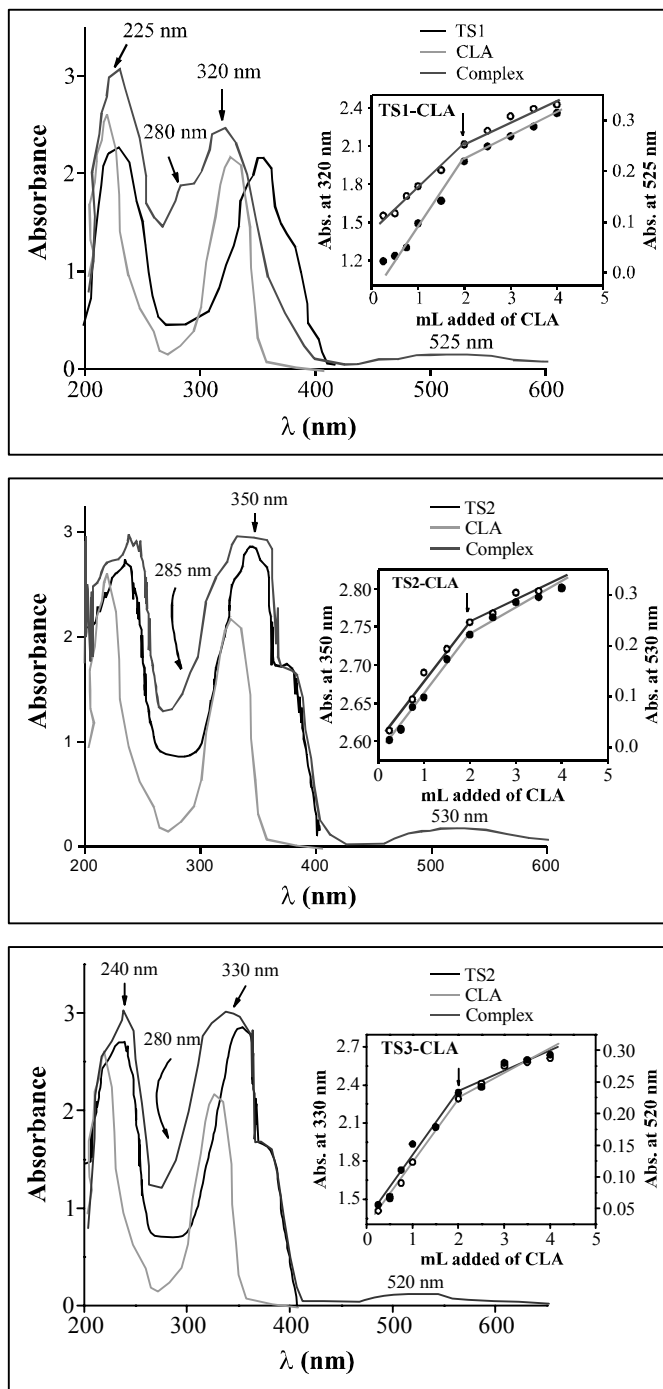


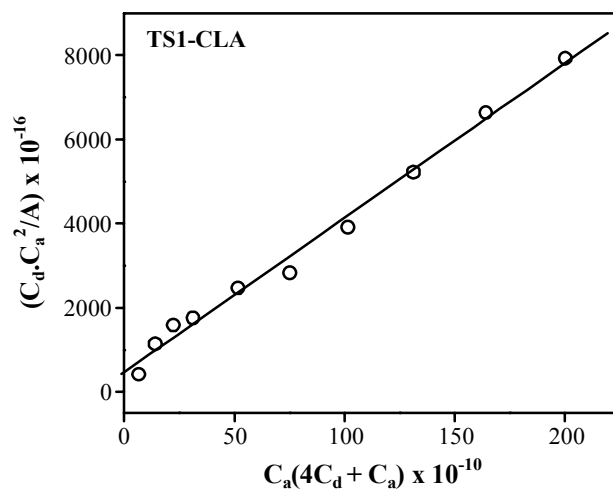
Fig. 1: Electronic spectra of the donors, CLA acceptor and the synthesized complexes coupled with spectrophotometric titration spectra

The spectroscopic data

The 1 : 2 modified Benesi–Hildebrand plots (Fig. 2)^{18,19} were constructed to calculate the formation constant (K_{CT}) and the extinction coefficient (ϵ_{CT}) for each complex. The obtained K_{CT} and ϵ values associated with the synthesized complexes are given in Table 2. The energy of the complex (E_{CT}), the oscillator strength (f), the transition dipole moment (μ) and the standard free energy (ΔG°), were calculated for the formed complexes as described elsewhere²⁰⁻²³. The calculated values of these spectroscopic data for the complexes are presented in Table 2. In general, all the complexes exhibit high values for the formation constants (K_{CT}). These high K_{CT} values reflect the high stabilities of the prepared complexes due to the strong donation of the triazine-stilbene derivatives. The [(TS3)(CLA)₂] complex exhibited higher value for the oscillator strength (f), which indicates a strong interaction between the donor-acceptor pairs (TS3 and CLA). The ϵ values of the complexes decrease in the following order: [(TS1)(CLA)₂] > [(TS2)(CLA)₂] > [(TS3)(CLA)₂].

Table 2: Spectroscopic data of the synthesized complexes (25°C)

Complex	λ_{\max} (nm)	K (Lmol ⁻¹)	ϵ_{\max} (Lmol ⁻¹ cm ⁻¹)	E_{CT} (eV)	f	μ	ΔG° (KJ mol ⁻¹)
[(TS1)(CLA) ₂]	525	7.93×10^8	2.72×10^4	2.37	0.235	5.118	-39.362
[(TS2)(CLA) ₂]	530	13.14×10^8	2.69×10^4	2.35	0.233	5.121	-40.617
[(TS3)(CLA) ₂]	520	19.86×10^8	2.37×10^4	2.39	0.205	4.756	-41.641



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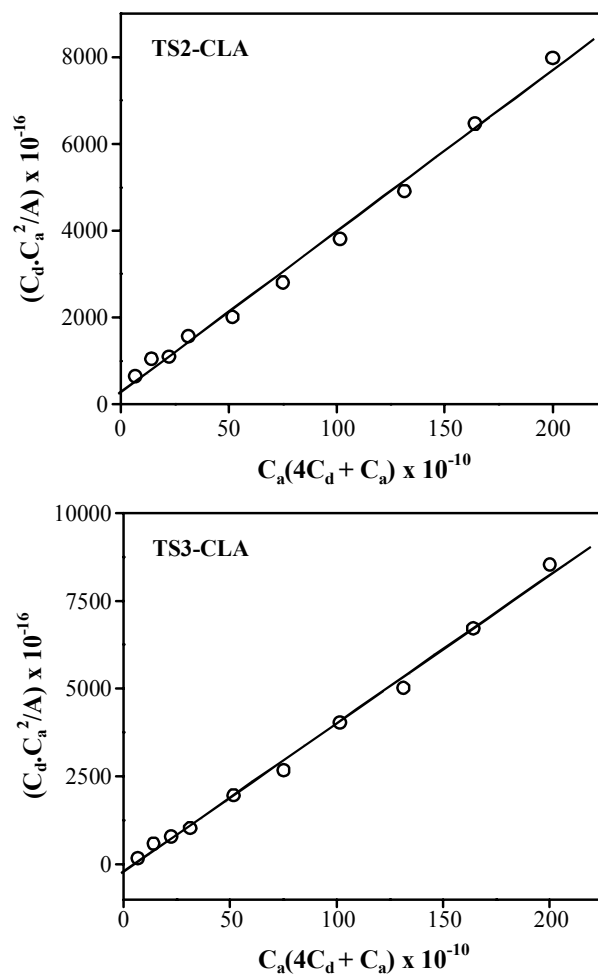


Fig. 2: The 1 : 2 Benesi-Hildebrand plot of TS1-CLA, TS2-CLA & TS3-CLA complexes

The obtained values of the standard free energy change (ΔG°) for the [(TS3)(CLA)₂], [(TS2)(CLA)₂] and [(TS1)(CLA)₂] complexes are -41.64, -40.62 and -39.36 KJmol⁻¹, respectively. These negative values indicate that the interaction between the donors and the CLA is spontaneous²⁴.

IR spectra

Infrared spectral studies shed light on the donation location in the donor species and the differences occur in the spectra of the obtained charge-transfer complexes. The infrared absorption spectra of the synthesized molecular complexes were recorded in the frequency range 4000-400 cm⁻¹ using a KBr disc, and their peak assignments for the important characteristic IR spectral bands are provided in Table 3.

Table 3: Infrared frequencies^(a) (cm⁻¹) and tentative assignments for TS1, TS2 and TS3 complexes with CLA acceptor

Donors			Acceptor	Complexes			Assignments ^(b)
TS1	TS2	TS3	CLA	TS1-CLA	TS2-CLA	TS3-CLA	
3423	3374	3420	3235	3303 3073	3401	3401	ν (O-H) ν (N-H) ν (C-H); aromatic
2927	2928	2972	-	2928	2926	2976	ν (C-H) + ν_{as} (C-H)
2877	2861	2931		2850	2790	2815	Hydrogen bond
		2872		2847			
1620	1616	1614	1664 1630	1742 1677 1650	1752 1655 1626	1655 1622	ν (C=O), CLA
1575	1567	1570	-	1608 1575	1590	1591	δ_{def} (N-H) Ring breathing bands
1529	1541	1516	-	1552	1538	1541	ν (C=C)
1490	1492	1488		1487	1480	1483	δ (C-H) deformation
1402	1442	1412		1465	1443	1412	
	1416			1416	1412		
1286	1357	1358	1368	1369	1350	1360	ν (C-C) + ν (C-O) +
1187	1303	1308	1263	1206	1281	1228	ν_{as} (C-N)
1078	1276	1225	1207	1109	1223	1178	
1021	1226	1180	1168	1065	1176	1079	
	1180	1080			1111	1022	
	1108	1024			1075		
	1078				1019		
	1021						
993	888	983	981	986	893	901	δ_{rock} ; NH
903	832	894	851	905	838	840	δ (CH) in-plane bending
829	805	829	752	847	775	778	
801	699	806		786	714	690	
717		782		768			
		695					

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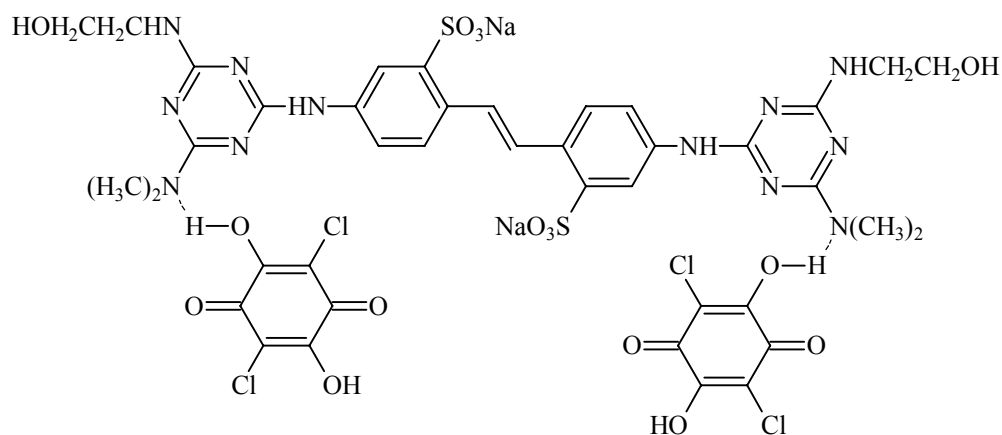
Donors			Acceptor	Complexes			Assignments ^(b)
TS1	TS2	TS3	CLA	TS1-CLA	TS2-CLA	TS3-CLA	
625	626	625	690	689	625	626	$\delta(\text{C-N})$ out-of-plane bending
540	543	544	569	647	576	577	skeletal vibration
				525	543	544	CNC deformation

(a): s, strong; w, weak; m, medium; sh, shoulder; v, very; vs, very strong; br, broad.
 (b): ν , stretching; ν_{ss} , symmetrical stretching; ν_{as} , asymmetrical stretching; δ , bending

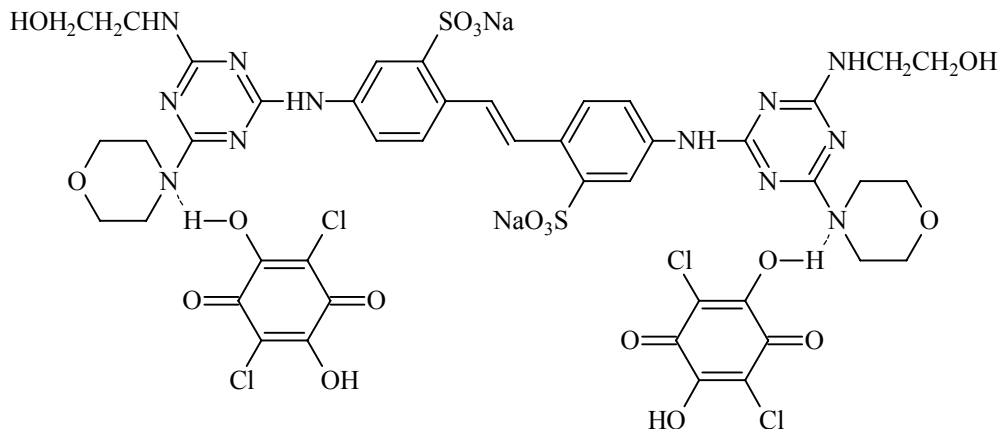
A comparison of the relevant IR spectral bands of the free donors and CLA acceptor with the corresponding bands in the IR spectra of the isolated solid CT complexes clearly indicated that the characteristic bands of the donors exhibit small shifts in frequency and changes in their band intensities. This result could be attributed to the expected changes in symmetry and electronic configurations upon the formation of the CT complexes. The IR spectra of the complexes are characterized by a broad medium band that appears between 2400-2800 cm^{-1} , which does not appear in the spectra of the free donors or those of the CLA acceptor. These broadened peaks can be attributed to the stretching vibration of the intermolecular hydrogen bond in the complex formed through the transfer of a proton from the acidic center of CLA acceptor to the donors as dictated by acid–base theory²⁵⁻³⁰.

Structural interpretation

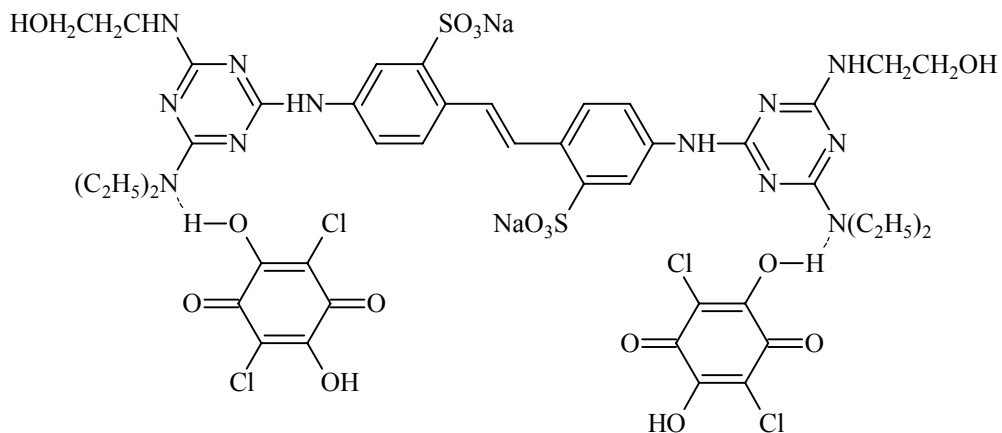
The structures of the [(TS1)(CLA)₂], [(TS2)(CLA)₂] and [(TS3)(CLA)₂] CT complexes are confirmed by elemental analysis, spectrophotometric titration and IR spectra. The proposed structures of these CT complexes are shown in Formulas II-IV.



Formula II: Suggested structural formula of [(TS1)(CLA)₂] complex



Formula III: Suggested structural formula of [(TS2)(CLA)₂] complex.



Formula IV: Suggested structural formula of [(TS3)(CLA)₂] complex

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Accepted : 21.09.2013