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IR, ¹H-NMR, UV-Vis AND THERMAL STUDIES ON THE RHODAMINE 6G CHARGE-TRANSFER COMPLEXES

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ABSTRACT. Charge-transfer (CT) complexes formed between Rhodamine 6G (Rh6G) as donor with iodine, CLA and PA as acceptors have been studied spectrophotometrically. The synthesis and characterization of Rhodamine 6G CT-complexes of iodine, [(Rh6G)₂]I⁺.I₃⁻, chloranilic acid (CLA), [(Rh6G)(CLA)] and picric acid (PA) [(Rh6G)(PA)] were described. These complexes are readily prepared from the reaction of Rh6G with I₂, CLA and PA with CHCl₃ solvent. Mid and far IR, ¹H-NMR, UV-Vis techniques, elemental analyses (CHN) and thermal studies, characterize the three new Rhodamine 6G charge-transfer complexes. Modified Benesi-Hildebrand method was applied to the determination of association constant and molar extinction coefficient.

KEY WORDS: Rhodamine 6G, Charge transfer complexes, Picric acid, Chloranilic acid, Iodine, Thermal studies

INTRODUCTION

Rhodamine is a family of related chemical compounds, fluorone dyes. Examples are Rhodamine 6G and Rhodamine B. They are used as a dye and as a dye laser gain medium. They are often used as a tracer dye within water to determine the rate and direction of flow and transport [1].

Charge-transfer materials have become very important in the recent years due to their efficiency in the field of magnetic, electrical conductivity and optical properties [2, 3]. Generally, charge-transfer complexes play an important role in biological systems as well as in the field of drug receptor binding mechanism [4, 5].

Charge-transfer complexes using organic species are intensively studied [6, 7], which are accompanied by transfer of an electron from the donor to the acceptor, Also, protonation of the donor from acidic acceptors are generally route for the formation of ion pair adducts [8-10]. Recently there are some references dealing with the interactions of charge transfer of Rodamine 6G with oleic acid [11], DNA complexes [12] and derivatives of Rodamine 6G with amino acid tryptophan and DNA base guanine [13]. Following, our studies of charge transfer complexes [14-22], this work was undertaken to investigate spectroscopically the CT complexes formed between Rhodamine 6G (Rh6G) as donor with iodine, CLA and PA as acceptors.

EXPERIMENTAL

The general chemical structure of Rhodamine 6G donor and acceptors are given in Scheme 1.



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Scheme 1. General chemical structure of donor and acceptors.

Sample preparation

Rhodamine-6G charge transfer complexes

The solid CT-complex of (Rh6G) with a π -acceptor like (CLA and PA) and a σ -acceptor like (I₂) were prepared by mixing 1 mmol of the donor in chloroform (10 mL) with 1 mmol of each acceptor in the same solvent with constant stirring for about 15 min. The solutions were allowed to evaporate slowly at room temperature; the resulted complexes in the solid state were filtered and washed several times with little amount of solvent and dried under vacuum over anhydrous calcium chloride. The charge-transfer complexes [(Rh6G)/(CLA)] (brown), [(Rh6G)/(PA)] (red) and [(Rh6G)/(I₂)] (orange) were formed with the empirical formula C₃₄H₃₃O₇NCl₃, C₃₄H₃₄O₁₀N₄Cl and C₅₆H₆₂N₄O₆Cl₂I₄, respectively.

Tools of analysis

The electronic spectra of the donors, acceptors and the resulted CT complexes were recorded in the region of 200-800 nm using a Jenway 6405 spectrophotometer (UK) with quartz cells of 1.0 cm path length. Photometric titrations were performed [23] at 25 °C for the reactions of (Rh6G) with σ - and π -acceptor in methanol and/or chloroform. The concentration of the donor in the reaction mixtures was kept fixed at 1.0×10^{-4} M, while the concentration of acceptors (I₂, PA and CLA) were changed over a wide range from 0.25×10^{-4} to 4.00×10^{-4} M, which produced solutions with (donor : acceptor) molar ratios varying from 1:0.25 to 1:4.00.

The infrared spectra of the reactants and the resulted CT complexes were recorded as KBr discs using a Bruker IFS 113V FT-IR spectrometer (Germany) in the wavenumber range 4000-400 cm⁻¹. ¹H-NMR spectra were obtained on Varian spectrometer Gemini 200 MHz (USA) using d_6 -DMSO as solvent.

Thermogravimetric analysis (TGA) was performed on Shimadzu TGA 50H (Japan) in a standard platinum TGA pans, samples 2-5 mg and heated from 25 °C to 600°C at a rate of 10°C/min under nitrogen flow rate to the furnace sample 30 mL/min. The amount and rate change in the weight of each resulted compound were recorded as a function of temperature to determine thermal stability.

RESULTS AND DISCUSSION

The elemental analysis data (CHN) of the Rhodamine 6G charge transfer complexes are listed in Table 1. From this table, it can be seen that the resulting values match with the theoretical values and the predicted CT-complexes conform to the molar ratios produced from the photometric titration curves.

Complexes		C%		H%		N%		Physical data	
(FW)	MW	Found	Calc.	Found	Calc.	Found	Calc.	Color	$\begin{array}{c} \Lambda m \\ (\Omega^{\text{-1}} \text{cm}^{\text{-1}} \text{ mol}^{\text{-1}}) \end{array}$
$[(Rh6G)_2]I^+.I_3^- \\ (C_{56}H_{62}N_4O_6Cl_2I_4)$	1466	45.22	45.84	3.97	4.23	3.61	3.82	Orange	54
[(Rh6G)(CLA)] (C ₃₄ H ₃₃ N ₂ Cl ₃ O ₇)	687	58.78	59.39	4.68	4.80	3.89	4.07	Brown	21
$[(Rh6G)(PA)] \\ (C_{34}H_{32}N_5O_{10}Cl)$	708	57.19	57.63	4.37	4.52	9.70	9.89	Red	26

Table 1. Elemental analysis CHN and physical parameters data of the CT-complexes formed in the reaction of the Rh6G with iodine, CLA, and PA.

Rhodamine 6G-iodine CT-complex

The electronic absorption spectrum of Rh6G/iodine complex was measured in chloroform. The complex was formed by adding X mL of 5.0×10^{-4} M (iodine) (X = 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00 mL) to 1.00 mL of 5.0×10^{-4} M Rhodamine 6G. The volume of the mixtures in each case was adjusted to 10 mL with the same solvent. The concentration of Rh6G in the reaction mixture was kept fixed at 0.5×10⁻⁴ M while the concentration of iodine was varied over the range of 0.125×10^{-4} M to 1.50×10^{-4} M. These concentrations produce donor : I₂ ratios extending along the range from 1:0.25 to 1:3.00. The electronic absorption spectra of the 1:1 ratio in $CHCl_3$ together with the reactants I_2 and Rh6G were discussed. The spectrum has two absorption bands which were absent in the spectra of the free reactants (iodine and Rh6G). The bands at 384 and 283 nm are due to the CT-complex formed in the reaction of Rh6G with I₂ in chloroform solvent. Photometric titration curves based on these two absorption bands were performed. These photometric titration curves were obtained according to the known methods [23] by the plot of the absorbance against the X mL of the added acceptor. The equivalence points shown in these curves clearly indicate that the formed CT-complex between Rh6G and iodine is 1:1. Both elemental analysis and thermal measurements also support formation of 1:1 complex. The two absorption bands at 384 and 283 nm are known [24-26] to represent a characteristic feature for the formation of the triiodide ion (I_3) . Accordingly, the formed complex is formulated as $[(Rh6G)]_2l^+.I_3^-$. To study the stability of Rh6G/iodine complex, it was necessary to calculate the values of the equilibrium constant, K, the extinction coefficient ε , and the oscillator strength, f, of the iodine complex. The 1:1 modified Benesi-Hildebrand equation [27] was used in these calculations.

$$C^{o}_{A}C^{o}_{D} l/A = 1/K\varepsilon + (C^{o}_{A} + C^{o}_{D})/\varepsilon$$
⁽¹⁾

where, C_a° and C_d° are the initial concentrations of the acceptor (I₂) and the donor Rh6G, respectively, and A is the absorbance of the strong bands at 283 and 384 nm. When the C_a° . C_d° /A values are plotted against the corresponding C_a° + C_d° values, straight lines are obtained with a slope of 1/ ϵ and intercept of 1/ ϵ for the reactions in CHCl₃. The oscillator strength f was obtained from the approximate formula [28].

The oscillator strength values together with the corresponding energy of charge transfer interaction, E_{CT} , ionization potential, I_p , and dipole moment, μ , are given in Table 2. The trend of the values in this Table reveals that the $[(Rh6G)_2]I^+$. I_3^- shows high values of both the equilibrium constant (K) and extinction coefficient (ϵ). This high value of (K) reflects the high stability of the iodine complex as a result of the expected high donation of the Rh6G which contain donating groups like; alkyl, C=C, NH, and C=O groups.

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Table 2. Spectrophotometric data of Rh6G-iodine CT-complex.

Complex	λ_{max} nm	E _{CT}	K L.mol ⁻¹	$\begin{array}{c} \epsilon_{max} \\ L.mol^{-1}.cm^{-1} \end{array}$	$f \times 10^2$	μ (Debyes)	Ip (eV)
$[(Rh6G)_2]I^+.I_3^-$	384	3.24	2.19×10 ⁴	4.98×10 ⁴	0.65	72.9	7.82

The oscillator strength f was obtained from the approximate formula;

$$f = (4.319 \times 10^{-9}) \varepsilon_{\text{max}} \cdot v_{1/2}$$
⁽²⁾

where $v_{1/2}$ is the band-width at half-intensity in cm⁻¹. The transition dipole moment (μ) of the Rh6G CT-complex, has been calculated from the following equation;

$$\mu = 0.0958 [\varepsilon_{max} v_{1/2} / v_{max}]^{\frac{1}{2}}$$
(3)

The ionization potential (I_p) of the free (Rh6G) donor was determined according to the CT band of iodine complex using the following relationship;

$$I_p(ev) = 5.76 + 1.53 \times 10^{-4} \quad v_{\rm CT} \tag{4}$$

The energy of the charge-transfer E_{CT} of the Rh6G iodine complex was calculated using the following equation;

$$E_{CT} = (hv_{CT}) = 1243.667 / \lambda_{CT} \ (nm) \tag{5}$$

where, λ_{CT} is the wavelength of the complexation band.

A general mechanism for the formation of $[(Rh6G)_2]I^+.I_3^-$ complex is proposed as follows, 2[Rh6G]+I_2 \rightarrow [Rh6G]₂I⁺.I⁻

$$[Rh6G]_2I^+. \Gamma + I_2 \rightarrow [Rh6G]_2I^+. I_3^-$$
(6)

The mid infrared spectra of Rh6G and the resulted CT-complex, $[Rh6G]_2I^+$.I₃⁻, were recorded from KBr discs. The spectral bands are resolved and assigned into their vibrational modes and given in Table 3. As expected, the bands characteristic for the Rh6G unit in $[Rh6G]_2I^+$.I₃⁻ are shown with small changes in band intensities and frequency values of aromatic ring, NH, and C=O groups. This proves that the charge transfer transition occurs as π - σ * and/or n- σ *. The blue shifted $v_{(N-H)}$ vibration in case of $[(Rh6G)_2]I^+$.I₃⁻ complex rather than free Rh6G from 3465 to 3374 cm⁻¹, respectively, indicates that the lone pair of electrons on the nitrogen atom of the -NH group is involved in the complexation process between Rh6G donor with iodine.

The far infrared spectrum of $[Rh6G]_2I^+.I_3^-$ CT complex was recorded using Nujol mulls dispersed on polyethylene windows within the region 50-400 cm⁻¹. The spectrum has characteristic bands of the triiodide ion, I_3^- at 123, 99 and 68 cm⁻¹. These bands were assigned to the $v_{as(I-I)}$, $v_{s(I-I)}$ and $\delta(I_3^-)$, respectively. These three absorptions do not exist in the spectrum of the free donor, Rh6G. However, the I_3^- ion may be linear (D_{och}) or non linear (C_{2v}). Group theoretical analysis indicates that the I_3^- with C_{2v} symmetry displays three vibrations $v_s(I-I)$; A₁, $v_{as}(I-I)$; B₂ and $\delta(I_3^-)$; A₁, all are infrared active [24, 29, 30] in agreement with the observed three infrared bands for [Rh6G]₂I⁺.I₃⁻. Accordingly, the formed iodine complex is formulated as [Rh6G]₂I⁺.I₃⁻.

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Table 3. Infrared frequencies^(a) (cm⁻¹) and tentative assignments for Rh6G donor and [(Rh6G)₂]1⁺.I₃⁻ complex.

Rh6G	$[(Rh6G)_2]I^+.I_3^-$	Assignments ^(b)
3465 s,br	3374 s	ν _(N-H) ; Rh 6G
3160 ms	3145 vw	$v_{(CH)}$;CH ₂ +CH ₃ + aromatic
3102 m	2973 mw	
2974 ms		
1717 s	1698 s	$v_{(C=C)} + v_{(C=O)} + v_{(C=N)}$
1650 ms	1647 s	Phenyl
1563 m	1608 vs	-
1525 s	1530 s	
1498 ms	1501 s	
1439 ms	1446 mw	
1366 ms	1364 s	
1266 mw	1318 vs	
1242 ms	1242 ms	
809 s	813 ms	Aromatic rings
739 s	727 mw	_

(a): s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad. (b): v, stretching; δ , bending.



Figure 1. TGA/DTG thermal diagram of [(Rh 6G)₂]I⁺.I₃⁻ CT complex.

TGA and DTG curves of the [Rh6G]₂I⁺.I₃⁻CT complex are shown in Figure 1. Table 4 gives the maximum temperature values, T_{max}^{0} C, together with the corresponding weight loss for each step of the decomposition reactions of Rh6G/iodine complex. The obtained data strongly support the structure proposed for the reported complex. The thermal decomposition of the Rh6G-iodine CT-complex in inert atmosphere proceeds approximately with four essential degradation steps as shown in Figure 1. The first stage of degradation takes place at DTG_{max}= 190 °C and accompanied by a weight loss of 16.28% corresponding to the loss of one iodine molecule. Theoretically, the loss of this molecule corresponds to a weight loss of 17.32%. The second decomposition stage occurs at a maximum temperature of 240 °C. The weight loss associated with this step is 11.24% corresponding to the loss of two ester moieties (2COOC₂H₃) and in good agreement with the theoretical weight loss values of 9.96%. The third decomposition step is located at 287 °C and corresponds to the loss of second iodine molecule with a weight loss 19.56% against the calculated value of 17.32%. The final decomposition step

is observed at $DTG_{max} = 358$ and 410 °C assigned to the decomposition of the two organic moieties of Rh6G. Thermal products obtained as a residue at 800 °C correspond to polluted carbon atoms.

Table 4. The maximum temperature, $T_{max}/^{\circ}C$, and weight loss values of the decomposition stages for the $[(Rh6G)_2]I^{+}.I_3^{-}$ complex.

Decomposition	т /%С	Lastanasias	% weight losses		
Decomposition	I_{max}/C	Lost species	Found	Calc.	
First stage	190	I ₂	16.28	17.32	
Second stage	240	2COOC ₂ H ₅	11.24	9.96	
Third stage	287	I_2	19.56	17.32	
Fourth stage	358 and 410	2 Rh6G moieties	34.26	37.39	
Residue		Carbon residual	18.66	18.01	

The general thermal behaviors of the Rh6G/iodine CT complex in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in Figure 2 and Table 5. The kinetic parameters have been evaluated using the Coats-Redfern equation [31]. The kinetic parameters, E, Δ H, Δ S and Δ G calculated with Coats-Redfern equation, are tabulated in Table 5. Taking the first decomposition step as a criterion, the values of the activation entropies, $-\Delta$ S in the [Rh6G]₂I⁺.I₃⁻ CT complex indicate that the activated complex have a more ordered structure than the reactants.



Figure 2. Kinetic diagrams of Coats Redfern (CR) equation for [(Rh6G)₂]I⁺.I₃⁻ CT complex at first step (190 °C).

Table 5. Kinetic data of the [(Rh6G)₂]I⁺.I₃⁻ CT complex at the essential stage.

Complex	Parameters*	Coats-Redfern equation
$[(Rh6G)_2]I^+.I_3^-$	ΔE^*	97.8
	А	$3.29 \times 10^{+4}$
	ΔS^*	-126
	ΔH^*	92.7
	$\Delta \mathrm{G}^{*}$	165
	r	0.9904

^{*}Units of parameters: E in kJmole⁻¹, A in s⁻¹, Δ S in kJmole⁻¹K⁻¹, Δ H and Δ G in kJmole⁻¹.

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 ΔG is positive for reaction for which ΔH is positive and ΔS is negative. The reactions for which ΔG is positive and ΔS is negative are considered as unfavorable or non-spontaneous. It is clear that the thermal decomposition process of Rh6G/iodine complex is non-spontaneous, i.e. the complex is thermally stable.

Charge-transfer complexes of Rh6G/CLA and Rh6G/PA systems

Charge-transfer interactions of Rhodamine 6G with chloranilic acid (CLA) and picric acid (PA) as π -acceptors were investigated spectrophotometrically and found to form stable n- π^* CT-complexes of [(Rh6G)(CLA)] and [(Rh6G)(PA)]. The donor site participated in CT complexation is lone pair of electron on –NH group of Rh6G. These complexes are easily synthesized from the reaction of Rh6G with CLA and PA using CHCl₃ solvent. ¹H-NMR, IR, elemental analyses, and UV-Vis techniques characterize the two Rhodamine 6G charge transfer complexes. Benesi-Hildebrand and its modification methods were applied to the determination of association constant (K), molar extinction coefficient (ϵ). The physical and analytical data of the two new solid CT-complexes CHN contents are tabulated (Table 1).

The recorded electronic absorption spectra are those of the chloroform solutions of Rh6G, CLA, PA and their mixtures using the same solvent as a blank. The spectra clearly indicate that the Rh6G/CLA and Rh6G/PA complexes have obviously absorption bands at 348 and 345 nm, respectively, which are hyperchromic shift than the reactants. The electronic absorption spectra of the donor (Rh6G) with acceptors CLA and PA molar ratios (Rh6G : acceptor) 1:1 CT complexes were performed. Photometric titration at 348 and 345 nm for the reaction between Rh6G with CLA and PA, respectively, in chloroform were carried out as follows: concentration of CLA and PA (C_a) was varied over the range of 0.25 x 10⁻⁴ - 3.00 x 10⁻⁴ M, whereas that of the donor was kept fixed at 1.00 x 10⁻⁴ M (Rh6G) C_d .

The 1:1 modified Benesi-Hildebrand equation was used to estimated the values of the equilibrium constant, K (L mol⁻¹), and the extinction coefficient, ε (L mol⁻¹ cm⁻¹), for the Rh6G/CLA and Rh6G/PA complexes. Where, C_a^o and C_d^o are the initial concentrations of acceptors and the donor, respectively, while A is the absorbance at the mentioned CT bands. The values of (ε) and (K) for the two CT complexes are calculated according to the slope and intercept of the linear relationship of ($C_A^o + C_D^o$) against ($C_A^o C_D^o$)/A. Table 6, contain the calculated values of the spectroscopic data such as; ε , K, μ and f. Generally, these complexes show high values of both the formation constant (K) and the extinction coefficients (ε). These high values of K confirm the expected high stabilities of the formed CT-complexes as a result of the expected high donation of the Rh 6G. The equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents to it such as nitro and halo groups.

Table 6. Spectrophotometric results of the CT-complexes of (A): [(Rh6G)(CLA)] and (B): [(Rh6G)(PA)] CT-complexes.

Solvent	λ_{max}	E _{CT}	K	ε _{max}	f	μ	Ip
	(nm)	(eV)	$(L.mol^{-1})$	$(L.mol^{-1}.cm^{-1})$	x 10 ⁺²	(Debyes)	(eV)
Α	348	3.57	1.01x10 ⁺⁴	2.62 x 10 ⁺⁴	0.34	50.40	7.61
В	345	3.60	1.12x 10 ⁺⁴	2.68 x 10 ⁺⁴	0.38	30.70	7.63

The infrared spectra of the obtained CT complexes [(Rh6G)(CLA)] and [(Rh6G)(PA)] were measured and their band assignments are listed in Table 7. The IR spectra of the two CT complexes of CLA and PA are characterized by a group of weak/very weak bands appearing in the region 2800-2500 cm⁻¹, which are not present in the spectra of the free donor and acceptors.

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These bands are attributed to the stretching vibration of a proton attached to the donation site of the donor [32]. These results due to the protonation of the ⁺NH group of the donor through one proton transfer from the two acidic centers on the CLA acceptor from one (OH) sides to the basic center on the donor ⁺NH group. On the other hand the intermolecular hydrogen bond occurs in PA acceptor from OH group to the basic center nitrogen atom. Such assumption is strongly supported by the appearance of an absorbance band between 1648 and 1560 cm⁻¹ due to ⁺NH₂ deformation, and all absorbed bands near 800 cm⁻¹ which are attributed to NH₂ rock. This is further supported by the disappearance or decrease in the stretching vibrational mode of the OH group of PA or CLA (acceptors) caused by intermolecular hydrogen bond formation. Accordingly, the hydrogen bonding interaction between the donor and the acceptors can be formulated as Figure 3. The donor and acceptor bands in the [(Rh6G)(CLA)] and [(Rh6G)(PA)] CT complexes show a small shift in wavenumber and a reduced intensity when compared with the free reactants.



Figure 3. Structures of: (A): [(Rh6G)(CLA)] and (B): [(Rh6G)(PA)].

¹H-NMR spectra of Rh6G and the two CT complexes in DMSO were performed. The ¹H-NMR data and chemical shifts (ppm) provide evidence regarding the interaction site between donor and acceptor species. In the [(Rh6G)(CLA)] and [(Rh6G)(PA)] CT complexes, H signal of the OH acceptor (8.90 ppm) entirely disappears due to deprotonation from acceptor to donor. In addition, shift to high field is observed, in H of NH (Rh6G) from 4.00 ppm to 3.50 ppm for Rh6G/CLA and to 3.49 ppm for Rh6G/PA, respectively. This indicates that one of the OH protons is transferred to the N atom of the donor NH group.

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CLA	PA	Rh6G/CLA	Rh6G /PA	Assignments
3235 s, br	3416 br	3438 vw	3409 s	v(O-H); H-bonded
	3103 ms	3233 s,br	3237 s, br	v(C-H); aromatic
	2980 sh	3024 vw	3029 vw	$v_s(C-H)$
	2872 w	2976 w	2976 w	$v_{as}(C-H)$
			2933 vw	
			2873 vw	
		2800-2500 vw	2800-2500 vw	Hydrogen bonding
1664 ms	1861 ms	1716 s	1707 s	v(C=O); NO ₂ of PA
1630 vs	1632 vs	1672 ms	1649 ms	v(C=C)
	1608 vs	1648 s	1632 ms	v(C=N)
	1529 vs	1607 vs	1607 vs	Ring breathing bands
		1560 ms	1566 s	
		1529 vs	1528 s	
		1500 vs	1500 s	
	1432 s	1446 s	1469 ms	C-H deformation
			1448 s	
1368 s	1343 ms	1366 vs	1364 vs	v(C-C)
1263 vs	1312 w	1304 s	1309 vs	v(C-N)
1207 w	1263 w	1266 w	1267 sh	v(C-O)
1168 w	1150 ms	1242 w	1184 s	Phenyl
	1086 s	1186 s	1163 w	
		1132 ms	1139 ms	
		1078 ms	1077 ms	
981 vs	917 vs	982 s	941 w	(C-H) bend
851 vs	829 w	884 mw	911 w	Aromatic rings
		838 vw	885 w	
			838 w	
			814 ms	
752 vs	781 s	781 vw	784 ms	Skeletal vibrations
690 vs	732 s	753 vw	738 ms	
	703 s	738 vw	707 s	
569 vs	522 ms	612 s	613 s	δ(ONO); PA
		570 s	553 w	CNC deformation
		553 vw		
		451 s		

Table 7. Infrared frequencies $^{(a)}$ (cm⁻¹) and tentative assignments for CLA, PA, [(Rh6G)(CLA)] and [(Rh6G)(PA)] compounds.

(a): s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad. (b): v, stretching; δ , bending.

CONCLUSIONS

Charge-transfer interactions between Rhodamine 6G (Rh6G) as donor with iodine, chloranilic acid (CLA) and picric acid (PA) as acceptors were studied spectrophotometrically in chloroform. The results showed stoichiometry 1:1 for all reactions to form CT-complexes. The spectral data indicate that the intermolecular hydrogen bonds formed between the donor and (CLA and PA) acceptors, via a lone pair of electrons on the nitrogen atom of Rh6G with phenolic OH groups in the case of each acceptor. The CT complexes were confirmed on the basis of infrared, ¹H-NMR and thermal measurements (TGA). The donor property of Rh6G controls mainly through electronic factors (ethyl and aromatic groups). So the stability constant increase as the ethyl and aromatic groups increases.

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REFERENCES

- 1. Schäfer, F.P. Dye Lasers, 3rd ed., Springer-Verlag: Berlin; 1990.
- 2. Ulanskki, J. Synth. Met. 1990, 39, 13.
- 3. Hashem, H.A.; Refat, M.S. Surf. Rev. Lett. 2006, 13, 439.
- 4. Mandal, R.S.; Lahiri, C. J. Indian Chem. Soc. 1999, 76, 347.
- 5. Feng, J.; Zhong, H.; Xuebau, B.D. Ziran Kexueban 1999, 27, 691.
- 6. Das, S.K.; Krishnamoorthy, G.; Dofra, S.K. Can. J. Chem. 2000, 78, 191.
- 7. Jones, G.; Jimenez, J.A.C. Tetrahedron Lett. 1999, 40, 8551.
- 8. Smith, G.; Bott, R.C.; Rae, A.D.; Willis, A.C. Aust. J. Chem. 2000, 53, 531.
- 9. Smith, G.; Lynch, D.E.; Bott, R.C. Aust. J. Chem. 1998, 51, 159.
- 10. Smith, G.D.; Lynch, E.K.; Byriel, A.; Kennard, C.H.L. J. Chem. Crystallogr. 1997, 27, 307.
- 11. Wieja, K.; Tarakowski, R.; Siegoczyński, R.M.; Rostocki, A.J. *High Pressure Research* **2010**, 30, 130.
- 12. Vladimirov, E.; Ivanova, A.; Rosch, N. J. Phys. Chem. B 2009, 113, 4425.
- 13. Doose, S. ChemPhysChem 2005, 6, 2277.
- 14. Refat, M.S.; El-Zayat, L.A.; Yeşilel, O.Z. Spectrochim. Acta Part A 2010, 75, 745.
- 15. Refat, M.S.; Al. Didamony, Hamdy; Abou El-Nour, Khlood M.; El-Zayat, Lamia; Adam, A.A. Arabian J. Chem. 2011, 4, 105.
- 16. Refat, M.S.; Sadeek, S.A.; Khater, H.M. Spectrochim. Acta Part A 2006, 64, 778.
- 17. Refat, M.S.; El-Didamony, A.M. Spectrochim. Acta Part A 2006, 65, 732.
- Refat, M.S.; Grabchev, I.; Chovelon, J.-M.; Ivanova, G. Spectrochim. Acta Part A 2006, 64, 435.
- 19. Refat, M.S.; Ahmed, H. Al-Didamony; El-Zayat, L.A. Can. J. Anal. Sci. Spec. 2006, 51, 147.
- Refat, M.S.; Killa, H.M.A., Grabchev, I.; El-Sayed, M.Y. Spectrochim. Acta Part A 2007, 68, 123.
- 21. Refat, M.S.; El-Zayat, L.A.; Yeşilel, O.Z. Polyhedron 2008, 27, 475.
- 22. Refat, M.S.; Ahmed, H.A.; Grabchev, Ivo; El-Zayat, L.A. Spectrochim. Acta Part A 2008, 70, 907.
- 23. Skoog, D.A. *Principle of Instrumetal Analysis*, 3rd ed., Saunders College Publishing: New York; **1985**; Ch. 7.
- 24. Kiefer, W.; Bernstein, H. J. Chem. Phys. Lett. 1972, 16, 5.
- 25. Anderews, L.; Prochaska, E.S.; Loewenschuss, A. Inorg. Chem. 1980, 19, 463.
- 26. Kaya, K.; Mikami, N.; Udagawa, Y.; Ito, M. Chem. Phys. Lett. 1972, 16, 151.
- 27. Abu-Eittah, R.; Al-Sugeir, F. Can. J. Chem. 1976, 54, 3705.
- 28. Tsubomura, H.; Lang, R. J. Am. Chem. Soc. 1964, 86, 3930.
- 29. Maki, A.G.; Forneris, R. Spectrochim. Acta 1967, 23A, 867.
- 30. Parrett, F.W.; Taylor, N.J. J. Inorg. Nucl. Chem. 1970, 32, 2458.
- 31. Coats, A.W.; Redfern, J.P. Nature (London) 1964, 201, 68.
- 32. Bellamy, L.J. *The Infrared Spectra of Complex Molecules*, Chapman and Hall: London, **1975**; p 290.