STRUCTURAL AND THERMAL INVESTIGATIONS OF NOVEL CHARGE-TRANSFER COMPLEXES OF THYMOL AND THE ACCEPTORS PICRIC ACID, CHLORANILIC ACID, 1,3-DINITROBENZENE AND *p*-CHLORANIL

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Thymol (Thy) is a widely known anti-microbial agent and can be found as one of the components of many essential oils. Intermolecular charge-transfer complexes between the Thy as a donor and picric acid (PA), chloranilic acid (CLA), 1,3-dinitrobenzene (DNB) or *p*-chloranil (*p*-CHL) as a π-acceptor have been structurally and thermally studied in methanol at room temperature. Based on elemental analyses (CHN) and photometric titrations, the stoichiometry of the complexes (Thy: acceptor molar ratios) was determined to be 1:1 for all four 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. The newly synthesized CT complexes have been characterized via elemental analyses (CHN), IR, ^{1}H-NMR, and electronic absorption spectroscopy. Thermogravimetric analyses (TG) were also used to investigate the thermal stability of the synthesized solid CT complexes.

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Introduction

The term charge-transfer complex (CTC) was first introduced by Mulliken[1,2] and has been widely discussed by Foster[3]. Mulliken[4,5] demonstrated that the charge-transfer interactions within a molecular complex that consists of an electron donor, D, and an electron acceptor, A, involve a resonance with a transfer of charge from D to A:

$$D + A \rightleftarrows D^+A^- \rightleftarrows D^+ + A^- \qquad (1)$$
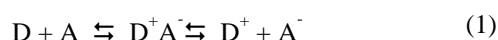
Charge-transfer complexation is of great importance in chemical reactions, including addition, substitution, condensation[6,7], biochemical and bioelectrochemical energy-transfer processes[8], biological systems[9], and drug–receptor binding mechanisms. For example, drug action, enzyme catalysis, ion transfers through lipophilic membranes[10], and certain π-acceptors have successfully been used in the pharmaceutical analysis of some drugs in pure form or in pharmaceutical preparations[11-17]. Furthermore, charge-transfer complexation is also of great importance in many applications and fields, such as in non-linear optical materials, electrically conductive materials[18-21], second-order non-linear optical activity[22], microemulsions[23], surface chemistry[23], photocatalysts[24], dendrimers[25], solar energy storage[26], organic semiconductors[27], and the investigation of redox processes[28]. Charge-transfer complexes that use organic species are intensively studied because of their special type of interaction, which is accompanied by the transfer of an electron from the donor to the acceptor[29,30]. In addition, the protonation of the donor from acidic acceptors is a route for the formation of ion-pair adducts[31-33].

Considerable attention has recently been devoted to the formation of stable charge-transfer complexes that result from the reaction between acceptors and drugs or biological compounds. This interest stems from the significant physical and chemical properties of these complexes. For example, the complexation of charge-transfer complexes with drugs has been recognized as an important phenomenon in the drug-receptor binding mechanism and in many other biological processes. Herein, the CT interaction between the anti-microbial agent thymol and four acceptors are investigated. Thymol (Thy, $C_{10}H_{14}O$), a phenol derivative, is the main constituent in natural essential oils from many herbs, such as Thyme, Oregano and winter savory[34-36]. Thymol has an antimicrobial effect on bacteria, fungi, and yeasts. It is able to inhibit both Gram-positive and Gram-negative bacteria, including the potential pathogenic strains of *Bacillus subtilis*, *Escherichia coli*, *Klebsiella pneumonia* and *Staphylococcus aureus* also . Amongst the identified natural anti-microbial agents (thymol, carvacrol, citronella, eugenol and terpinen-4-ol), thymol showed the highest antibacterial activity against *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*[37]. Due to its bactericidal action against oral bacteria, it is commonly incorporated in mouthwashers. Thymol and essential oils rich in thymol, have proved beneficial in medical[38,39], food[40], agricultural[41], veterinarian and pest control applications[42].

The purpose of the work reported here was to study the structural and thermal stability of charge-transfer complexes formed between thymol with picric acid (PA), chloranilic acid (CLA), 1,3-dinitrobenzene (DNB) and *p*-chloranil (*p*-CHL). The elemental analysis, infrared (IR),

^{1}H-NMR and electronic absorption spectroscopy were used to interpret the behavior of the interactions. The spectroscopic physical data were analyzed in terms of the formation constant (K_{CT}), the molar extinction coefficient (ε_{CT}), the standard free energy ($\Delta G°$), the oscillator strength (f), the transition dipole moment (μ), the resonance energy (R_N) and the ionization potential (I_D). The thermal behaviors of the obtained complexes have also been investigated.

Experimental

Chemicals

All chemical used were of high grade of purity. Thymol (Thy) (MF=$C_{10}H_{14}O$) was obtained from Sigma-Aldrich Chemical Company, USA with a stated purity of more than 99.6% and was used without further purification. Picric acid (2,4,6-trinitrophenol, PA), 1,3-dinitrobenzene (DNB), chloranilic acid (CLA) and *p*-chloranil (*p*-CHL) were purchased from Merck Chemical Company and were also used as received.

Synthesis

The solid CT products of Thy with PA, CLA, DNB and *p*-CHL were synthesized by mixing equimolar amounts of Thy donor with each acceptor in methanol. The mixtures were stirred for 20 min, and allowed to evaporate slowly at room temperature, which resulted in the precipitation of the solid CT complexes. The separated complexes were filtered off, washed well with little amounts of methanol, and then collected and dried under vacuum over anhydrous calcium chloride for 24 h.

Photometric titration

Photometric titration measurements were carried out for the reactions of Thy with PA, CLA, DNB and *p*-CHL against methanol as a blank at wavelengths of 354, 285, 300 and 284 nm, respectively. A 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50 or 4.00 mL aliquot of a standard solution (5.0×10^{-4} M) of the appropriate acceptor in MeOH was added to 1.00 ml of 5.0×10^{-4} M Thy, which was also dissolved in MeOH. The total volume of the mixture was 5 mL. The concentration of EC (C_d) in the reaction mixture was maintained at 5.0×10^{-4} M, whereas the concentration of the acceptors (C_a) changed over a wide range of concentrations (0.25×10^{-4} M to 4.00×10^{-4} M) to produce solutions with an acceptor molar ratio that varied from 4:1 to 1:4. The stoichiometry of the molecular CT complexes was obtained from the determination of the conventional spectrophotometric molar ratio according to known methods[43] using a plot of the absorbance of each CT complex as a function of the C_d:C_a ratio. Modified Benesi–Hildebrand plots[44,45] were constructed to allow the calculation of the formation constant, K_{CT}, and the absorptivity, ε_{CT}, values for each CT complex in this study.

Instrumentation

The elemental analyses of the carbon, hydrogen and nitrogen contents were performed by the microanalysis facility at Cairo University, Egypt, using a Perkin-Elmer CHN 2400 (USA). The electronic absorption spectra of methanolic solutions of the donor, acceptors and resulting CT complexes were recorded over a wavelength range of 200-800 nm using a Perkin-Elmer Lambda 25 UV/Vis double-beam spectrophotometer at Taif University, Saudi Arabia. The instrument was equipped with a quartz cell with a 1.0 cm path length. The mid-infrared (IR) spectra (KBr discs) within the range of 4000-400 cm^{-1} for the solid CT complexes were recorded on a Shimadzu FT-IR spectrophotometer with 30 scans at 2 cm^{-1} resolution. The Raman laser spectra of the samples were measured on a Bruker FT-Raman spectrophotometer equipped with a 50 mW laser at Taif University, Saudi Arabia. ^{1}H-NMR spectra were collected by the Analytical Center at King Abdul Aziz University, Saudi Arabia, on a Bruker DRX-250 spectrometer operating at 250.13 MHz with a dual 5 mm probe head. The measurements were performed at ambient temperature using DMSO-d_6 (dimethylsulfoxide, d_6) as a solvent and TMS (tetramethylsilane) as an internal reference. The ^{1}H-NMR data are expressed in parts per million (ppm) and are internally referenced to the residual proton impurity in the DMSO as solvent. Thermogravimetric analysis (TGA) was performed under an air atmosphere between room temperature and 800 °C at a heating rate of 10 °C/min using a Shimadzu TGA–50H thermal analyzer at the Central Lab at Ain Shams University, Egypt.

Results and discussion

Elemental analyses results

Elemental analyses (C, H, and N) of the Thy CT complexes were performed, and the obtained analytical data are as follows:

1 [(Thy)(PA)]: $C_{16}H_{17}N_3O_8$; Mol. wt.=379.32; Orange; Anal. Calcd.: C, 50.62; H, 4.48; N, 11.07. Found: C, 51.01; H, 4.37; N, 10.73.

2 [(Thy)(CLA)]; $C_{16}H_{16}Cl_2O_5$; Mol. wt.=359.20; Dark red; Anal. Calcd.: C, 53.45; H, 4.45. Found: C, 53.61; H, 4.54.

3 [(Thy)(DNB)]; $C_{16}H_{18}N_2O_5$; Mol. wt.=318.32; Pale brown; Anal. Calcd.: C, 60.32; H, 5.65; N, 8.80. Found: C, 60.50; H, 5.37; N, 8.67

4 [(Thy)(*p*-CHL)]; $C_{16}H_{14}Cl_4O_3$; Mol. wt.=396.10; Orange yellow; Anal. Calcd.: %C, 48.47; %H, 3.53. Found: %C, 48.40; %H, 3.59.

The resulting values are in good agreement with the calculated values, and the suggested values are in agreement with the molar ratios determined from the photometric titration curves.

The stoichiometry of all complexes was found to be 1:1 ratios. Based on the obtained data, the formed charge-transfer complexes were formulated as [(Thy)(PA)], [(Thy)(CLA)], [(Thy)(DNB)] and [(Thy)(p-CHL)].

Electronic absorption spectra

Figure 1 shows the electronic absorption spectra of the Thy donor, acceptors and the formed CT complexes. These spectra revealed new absorption bands that are attributed to the CT interactions. These bands are observed at 354, 285, 300 and 284 nm for the Thy/PA, Thy/CLA, Thy/DNB and Thy/p-CHL complexes, respectively. These peak absorbance values that appeared in the spectra assigned to the formed CT complexes were measured and plotted as function of the C_d: C_a ratio according to the known method. Photometric titration plots based on these measurements (Figure 2) confirmed the complex formation at a ratio (Thy: acceptor) of 1:1 in all cases. The formation constant (K_{CT}) and the molar absorptivity (ε) of these complexes were calculated by applying the 1:1 modified Benesi–Hildebrand equation in Eqn. (2)[44]:

$$\frac{C_a C_d}{A} = \frac{1}{K\varepsilon} + \frac{(C_a + C_d)}{\varepsilon} \qquad (2)$$

where C_a and C_d are the initial concentrations of the electron acceptor and the electron donor, respectively, and A is the absorbance of the strongly detected CT band. Plotting $(C_a C_d)/A$ values versus the corresponding $(C_a + C_d)$ values for the formed EC charge-transfer complexes, straight line are obtained supporting our finding of the formation of 1:1 complexes. In the plots, the slope and intercept equal $1/\varepsilon$ and $1/K\varepsilon$, respectively. The modified Benesi–Hildebrand plots are shown in Figure 3 and the values of both K_{CT} and ε associated with the complexes are given in Table 1. These complexes exhibit high values of both the formation constant (K_{CT}) and the extinction coefficients (ε). These high values of K_{CT} reflect the high stabilities of the formed CT complexes. 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[46]. The data reveal that the [(Thy)(CLA)] complex shows a higher K_{CT} value compared with the other complexes, reflecting the relatively higher powerful electron acceptance ability for CLA.

Calculation of the spectroscopic and physical data

The spectroscopic and physical data, such as the standard free energy ($\Delta G°$), the oscillator strength (f), the transition dipole moment (μ), the resonance energy (R_N), and the ionization potential (I_P), were estimated for samples dissolved in methanol at 25 °C. The oscillator strength (f) is a dimensionless quantity used to express the transition probability of the CT-band From the CT absorption spectra[47], and can be estimated using the approximate formula[48]:
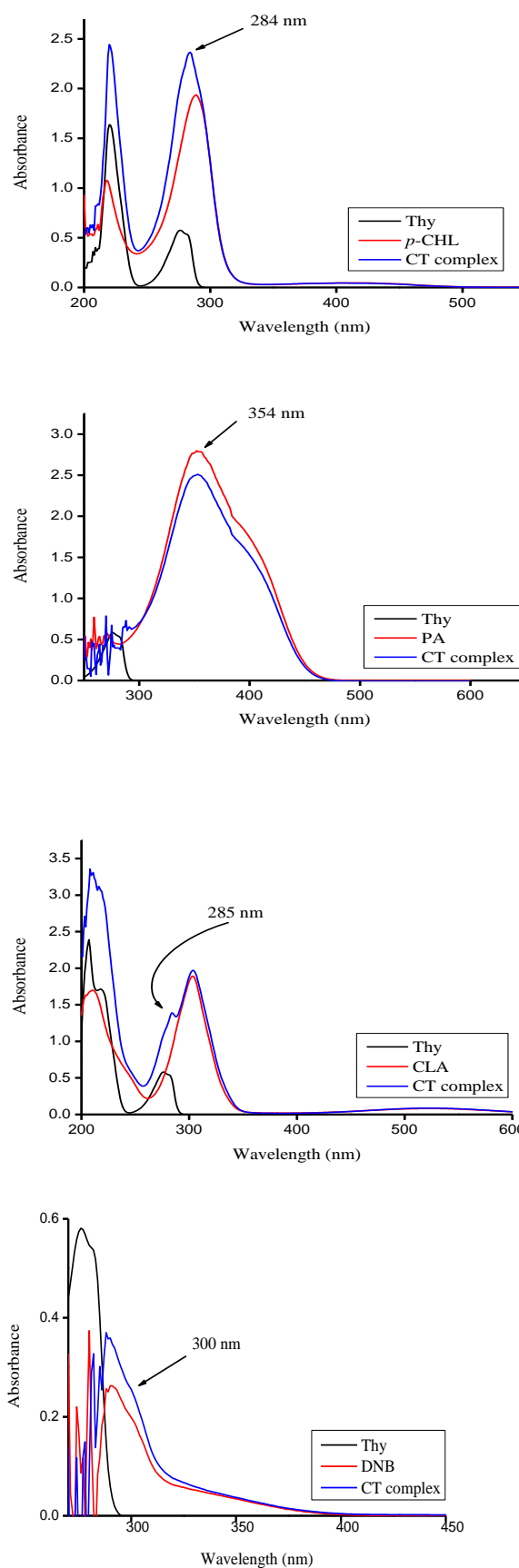

Figure 1.Electronic absorption spectra of Thy CT complexes at the detectable peak.

$$f = 4.319 \times 10^9 \int \varepsilon_{CT} d\nu \qquad (3)$$

where $\int \varepsilon_{CT} d\nu$ is the area under the curve of the extinction coefficient of the absorption band in question plotted as a function of frequency. To a first approximation,

$$f = 4.319 \times 10^{-9} \varepsilon_{CT} \nu^{1/2} \qquad (4)$$

where ε_{CT} is the maximum extinction coefficient of the CT band, and $\nu_{\frac{1}{2}}$ is the half-bandwidth in cm^{-1} (i.e., the width of the band at half the maximum extinction). The transition dipole moments (μ) of the Thy CT complexes have been calculated from Eq. 5[49]:

$$\mu = 0.0958 \left[\varepsilon_{CT} \frac{\nu_{1/2}}{\nu_{max}} \right]^{1/2} \qquad (5)$$

The transition dipole moment can be used to determine if a particular transition is allowed; the transition from a bonding π orbital to an antibonding π^* orbital is allowed because the integral that defines the transition dipole moment is nonzero. The ionization potentials (I_P) of the Thy donor in the charge-transfer complexes were calculated using the empirical equation derived by Aloisi and Pignataro represented in Eq. 6[50]:

$$I_P(eV) = 5.76 + 1.53 \times 10^{-4} \nu_{CT} \qquad (6)$$

where ν_{CT} is the wavenumber in cm^{-1} that corresponds to the CT band formed from the interaction between the donor and the acceptor. The electron-donating power of a donor molecule is measured by its ionization potential, which is the energy required to remove an electron from the highest occupied molecular orbital. Briegleb and Czekalla[51] theoretically derived the following relationship to obtain the resonance energy (R_N):

$$\varepsilon_{CT} = \frac{7.7 \times 10^{-4}}{\dfrac{h\nu_{CT}}{R_N} - 3.5} \qquad (7)$$

where ε_{CT} is the molar absorptivity coefficient of the CT complex at the maximum of the CT absorption, ν_{CT} is the frequency of the CT peak, and R_N is the resonance energy of the complex in the ground state, which contributes to the stability constant of the complex (a ground-state property). The energy values (E_{CT}) of the n$\rightarrow\pi^*$ and π–π^* interactions between the donor (EC) and the acceptors were calculated using the equation derived by Briegleb[52]:

$$E_{CT} = h\nu_{CT} = \frac{1243.667}{\lambda_{CT}} \qquad (8)$$

where λ_{CT} is the wavelength of the CT band of the formed complex. The standard free energy of complexation $(\Delta G°)$ for each complex was calculated from the formation constants using the equation derived by Martin et al.[53]:
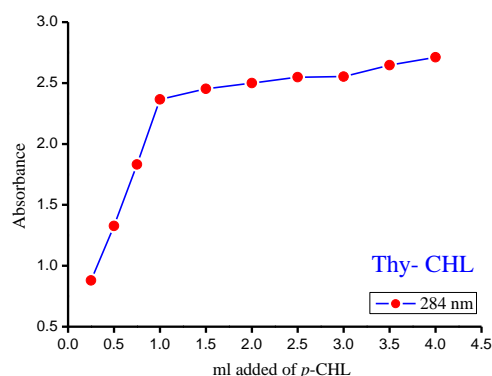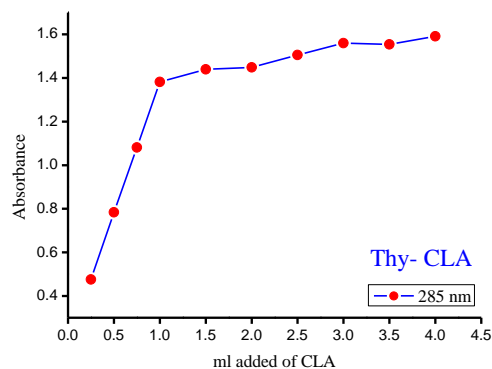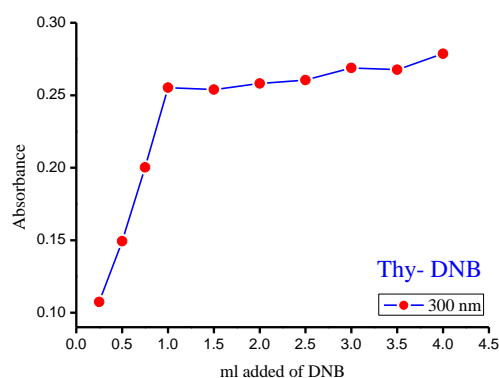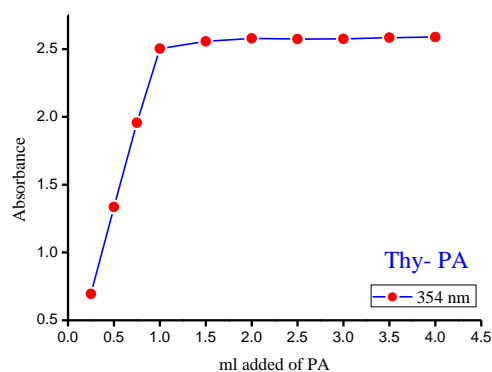

Figure 2. Photometric titration curves for Thy CT complexes at detectable peaks.

$$\Delta G = -2.303RT \lg K_{CT} \qquad (9)$$

where $\Delta G°$ is the free energy change of the CT complex (kJmol^{-1}), R is the gas constant (8.314 Jmol^{-1}K), T is the absolute temperature in K, and K_{CT} is the formation constant of the complex (Lmol^{-1}) at room temperature.

The calculated spectroscopic and physical values (f, μ, I_P, R_N and $\Delta G°$) for the Thy CT complexes using these equations are presented in Table 1. [(Thy)(CLA)] complex exhibits considerably higher values of both the oscillator strength (f) and the transition dipole moment (μ). CLA is a strong electron acceptor to form stable CT complexes with the donors. Beside this function, CLA is a strong acid (pK$_1$=1.07 and pK$_2$= 2.24)[54], hence a proton transfer from CLA to the donors is expected. The observed high values of f indicate a strong interaction between the donor–acceptor pairs with relatively high probabilities of CT transitions[55]. Further evidence for the nature of CT interactions is the calculation of the standard free energy change ($\Delta G°$). The obtained values of $\Delta G°$ for the Thy/PA, Thy/CLA, Thy/DNB and Thy/p-CHL complexes are -35.8, -36.1, -35.4 and -36 kJmol^{-1}, respectively; these negative values indicate that the interaction between Thy and the acceptors is exothermic and spontaneous[56, 57].

IR spectra

The IR absorption spectra of the Thy solid CT complexes were recorded in the frequency range 4000-400 cm^{-1} using KBr disc. These spectra are shown in Figure 4 while their band assignments are given in Table 2. In the IR spectra of the [(Thy)(PA)] and [(Thy)(CLA)] complexes, the characteristic bands of Thy observed at 3613 cm^{-1}, which is assigned to ν(O-H) stretching vibration, shifted to lower value and reduced in intensity after complexation. Also, the IR spectra of these complexes are characterized by weak bands that appear between 2400-2800 cm^{-1}, which does not appear in the spectra of the free Thy donor or those of the PA and CLA acceptors. These peaks are due to hydrogen bonding in the complex formed through the transfer of a proton from PA or CLA to the -OH group of the Thy donor. These observations clearly indicate that the complexation occurs through the protonation of the –OH group in the Thy donor via a proton-transfer phenomenon from the acidic center of each acceptor to the lone pair of electrons on the Thy oxygen atom based on acid–base theory[59-63]. Thus, one can say that the charge-transfer molecular complexes between Thy and PA or CLA acceptors are stabilized by hydrogen bonding. Because DNB and p-CHL acceptors lack acidic centres, the molecular complexes can be concluded to form through $\pi \rightarrow \pi^*$ charge migration from the HOMO of the donor to the LUMO of the acceptor. The $\pi \rightarrow \pi^*$ CT complex is formed via the benzene ring (electron-rich group) of the Thy and the DNB and p-CHL reagents (electron acceptor). The group of bands are exhibited at 2920 and 2843 cm^{-1} in [(Thy)(DNB)] complex, and at 2890 and 2836 cm^{-1} in [(Thy)(p-CHL)] complex were assigned to symmetric stretching vibrations of the ν(C-H) with different position wavenumbers compared with the free Thy.
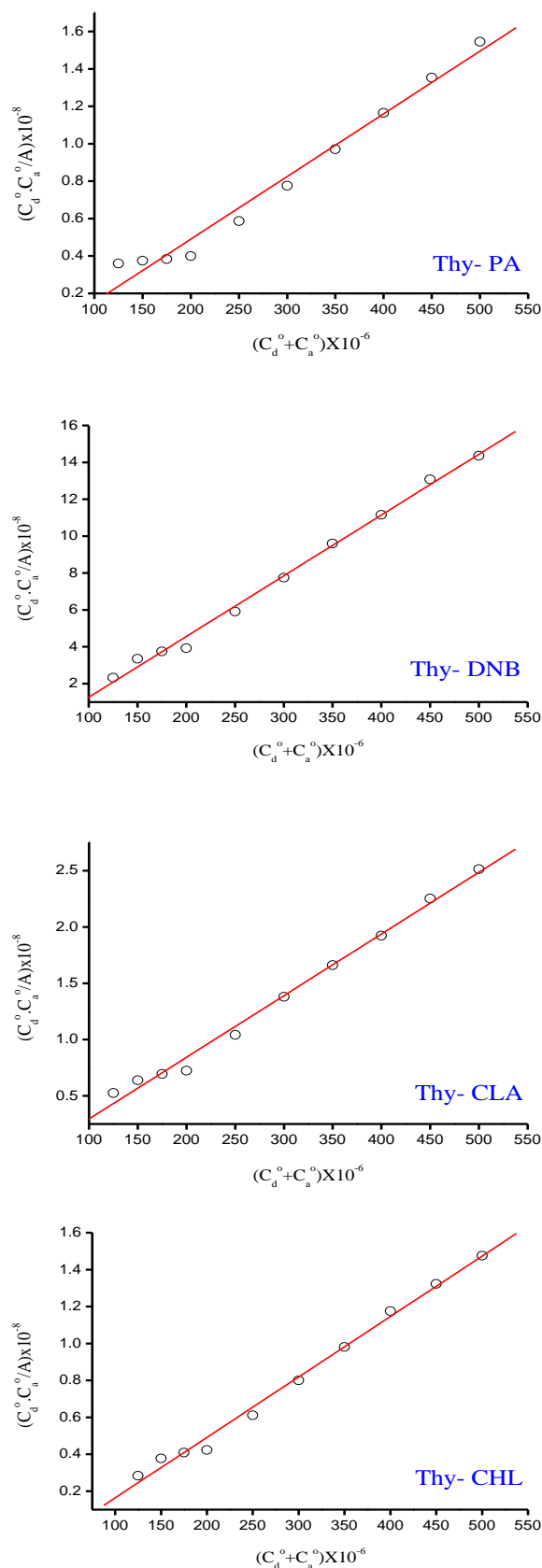

Figure 3. The modified Benesi-Hildebrand plots of Thy CT complexes at detectable peaks.

Table 1. Spectrophotometric results of the Thy CT complexes

Complex	CT-absorption, nm	E_{CT}, eV	K (Lmol^{-1})	ε_{max} (L mol^{-1} cm^{-1})	f	μ	I_p	R_N	$\Delta G°$ (25 °C) (kJ mol^{-1})
[(Thy)(PA)]	354	3.513	1.86×10^4	2.99×10^4	12.89	31.14	10.08	0.99	-35,771
[(Thy)(CLA)]	285	4.364	2.16×10^4	1.83×10^4	39.40	48.85	11.13	1.23	-36,146
[(Thy)(DNB)]	300	4.146	1.62×10^4	3.04×10^4	27.39	23.60	10.86	1.10	-35,426
[(Thy)(p-CHL)]	284	4.379	2.00×10^4	3.06×10^4	37.73	47.72	11.15	1.24	-35,949
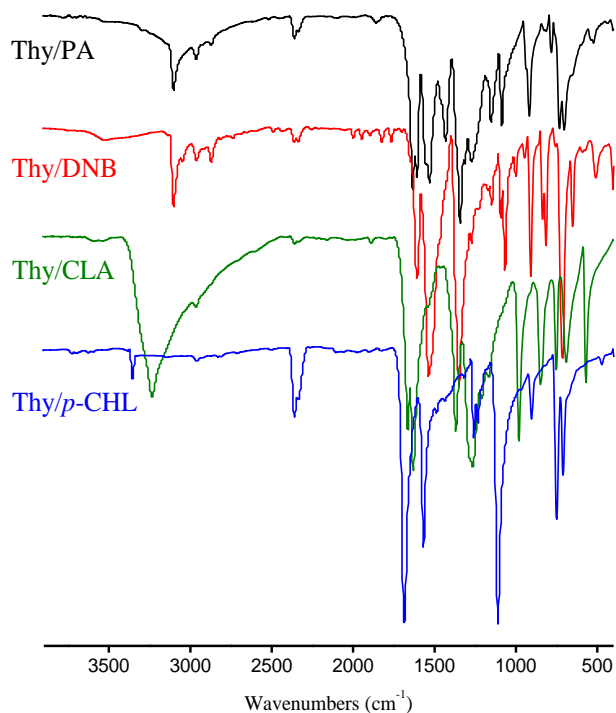
Figure 4. Infrared spectra of Thy CT complexes.

The stretching vibration of ν(C=O) absorption band in free *p*-CHL appeared at 1685 cm^{-1}, but under complexation this band is still un-shifted. Also, the bands associated with ν(C-Cl) vibration that appeared at 903, 750 and 709 cm^{-1} in free *p*-CHL were shifted to lower wavenumbers and decreasing in the intensities of the characteristic peaks, these results due to the increasing in the electron density around *p*-CHL moiety. These observations proved that the complexation of Thy with DNB and *p*-CHL take place via the $\pi\rightarrow\pi^*$ transition. Based on these data, the suggested complexation mechanism between Thy donor and acceptors is illustrated in Scheme 1.

^{1}H-NMR spectra

The 400 MHz nuclear magnetic resonance (^{1}H-NMR) spectra of the Thy complexes were measured in DMSO-d_6 at room temperature. The chemical shifts (δ) of the different types of protons of the complexes are;

[(Thy)(PA)] complex; *(2-isopropyl-5-methylphenyl)oxonium 2,4,6-trinitrobenzenolate*; ^{1}H NMR (400 MHz, DMSO-d_6): 1.59 (d, 6H, 2C*H*$_3$), 2.59 (s,

3H, C*H*$_3$), 3.21 (m, 1H,C*H*(CH$_3$)$_2$), 7.26 (d, 1H, Ar-*H*, C$_4$ thymol), 7.39 (d, 1H, Ar-*H*, C$_3$ thymol), 7.63 (s, 1H, Ar-*H*, C$_6$ thymol), 9.00 (s, 2H, Ar-*H*, picric acid ring), 12.2 (s, 2H, Ar-O*H*$_2$$^+$, thymol).

[(Thy)(CLA)] complex; *(2-isopropyl-5-methylphenyl)oxonium 2,5-dichloro-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate*; ^{1}H-NMR (400 MHz, DMSO-d_6): 1.60 (d, 6H, 2C*H*$_3$), 2.59 (s, 3H, C*H*$_3$), 3.21 (m, 1H,C*H*(CH$_3$)$_2$), 7.25 (d, 1H, Ar-*H*, C$_4$ thymol), 7.40 (d, 1H, Ar-*H*, C$_3$ thymol), 7.63 (s, 1H, Ar-*H*, C$_6$ thymol), 11.9 (s, 1H, Ar-O*H*, CLA ring), 12.2 (s, 2H, Ar-O*H*$_2$$^+$, thymol).

[(Thy)(DNB)] complex; *2-isopropyl-5-methylphenol compound with 1,3-dinitrobenzene (1:1)*; ^{1}H-NMR (400 MHz, DMSO-d_6): 1.18 (d, 6H, 2C*H*$_3$), 2.40 (s, 3H, C*H*$_3$), 3.19 (m, 1H,C*H*(CH$_3$)$_2$), 4.27 (s, 1H, O*H*), 6.89 (d, 1H, Ar-*H*, C$_4$ thymol), 7.22 (s, 1H, Ar-*H*, C$_6$ thymol), 7.37 (d, 1H, Ar-*H*, C$_3$ thymol), 8.07 (d, 2H, Ar-*H*, C$_4$, C$_6$ dinitrobenzene ring), 8.19 (t, 1H, Ar-*H*, C$_5$ dinitrobenzene ring), 8.47 (s, 1H, Ar-*H*, C$_2$ dinitrobenzene ring)
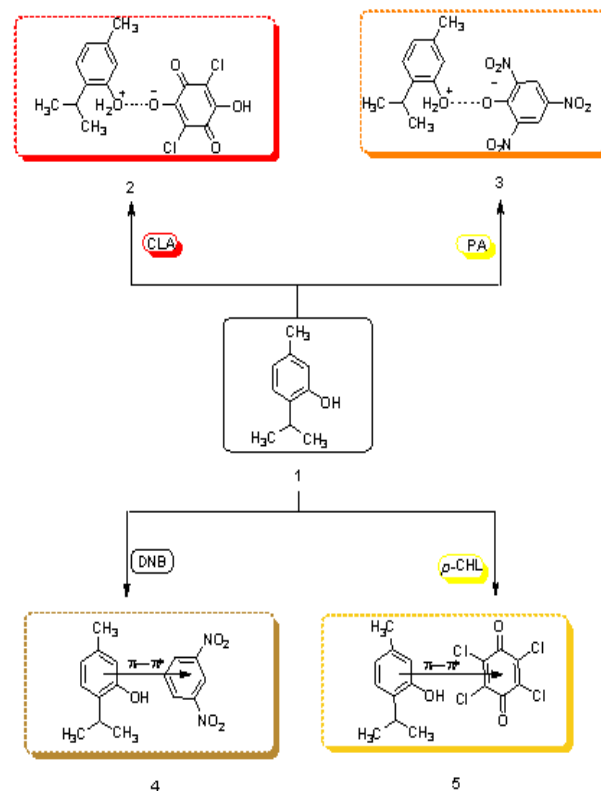

Scheme 1. Complexation mechanism between Thy donor and acceptors.

Table 2. Characteristic infrared frequencies (cm^{-1}) and tentative assignments of Thy, PA, CLA, DNB, *p*-CHL and their CT complexes.

| Thy | PA | CLA | DNB | *p*-CHL | [(Thy)(acceptor)] complex | | | | Assignments[(a)] |
					PA	CLA	DNB	*p*-CHL	
3613									ν(O-H)
		3235	3110	3354	3103	3256	3103	3355	
2963	2980				2965	2966	2920	2890	ν(C-H)
2872	2872				2760	2778	2843	2836	Hydrogen bond
	1861				1858		1824		ν(C=O)
1626	1632	1664		1685	1633	1665		1685	ν(NO$_2$)
	1608	1630	1608		1609	1631	1609		
1516			1538	1567	1530	1541	1537	1568	ν(C=C)
1460	1432			1487	1431	1462		1437	δ(CH) deformation
1419	1343	1368	1364	1316	1342	1369	1349	1317	
1290	1312	1263			1313	1265	1271	1258	ν(C-O)
1216	1263	1207			1272	1209		1233	ν(C-N)
1160	1150	1168	1150		1152	1168	1148	1110	ν(C-C)
1087	1086		1069		1085		1068		
946	917	981	914	903	918	982	909	896	ν(C-Cl)
868	829	851	837		782	849	815		
	781	752	727	750	732	752	712	740	ν(C-Cl) + δ(NO$_2$)
593	652	690	663	709	703	691	651	701	
579	522	569			523	569	510	473	

^{a} ν, stretching; ν_s, symmetrical stretching; ν_{as}, asymmetrical stretching; δ, bending.

[(Thy)(*p*-CHL)] complex; *2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione compound with 2-isopropyl-5-methylphenol (1:1)*; ^{1}H-NMR (400 MHz, DMSO-d$_6$): 1.62 (d, 6H, 2C**H**$_3$), 2.59 (s, 3H, C**H**$_3$), 3.30 (m, 1H,C**H**(CH$_3$)$_2$), 4.67 (s, H, Ar-O**H**, thymol), 7.12 (d, 1H, Ar-**H**, C$_4$ thymol), 7.40 (s, 1H, Ar-**H**, C$_6$ thymol), 7.77 (d, 1H, Ar-**H**, C$_3$ thymol).

The three aromatic protons of Thy appear at δ 7.37-7.77 (C$_3$), 6.89-7.26 (C$_4$) and 7.22-7.63 (C$_6$) ppm. The aliphatic protons of Thy appear at δ 1.18-1.62 ppm (6H), 2.40-2.59 ppm (3H) and 3.19-3.30 (1H), corresponds to the protons of 2CH$_3$, CH$_3$ and CH groups, respectively. The intensities and chemical shifts of the aromatic and aliphatic signals have been significantly affected by the complxation and the accompanying changes in the structural configuration. The new peak observed at 12.2 ppm in [(Thy)(PA)] complex, which is not detected in the spectrum of the free Thy donor, is attributed to the formation of a hydrogen bond between PA and Thy. The peak at δ = 11.94 ppm, which is assigned to the –OH proton of free picric acid[64], was absent in the spectrum of this complex. Together, these data indicate that the hydroxyl and phenolic groups are involved in the formation of the CT complex between Thy and PA.

In the [(Thy)CLA] complex, the phenolic proton (–OH) signal, which is observed at approximately δ~9.15 ppm in the spectrum of the free CLA acceptor[57], decreased in intensity with an down-field shift for the non-hydrogen-bonded one (δ~11.9) in the spectrum of the CT complex. Instead, a new peak is observed at 12.2 ppm, attributing to two protons of OH$_2^+$. This situation confirmed the transfer of the phenolic proton of CLA to the (-OH) group of Thy.
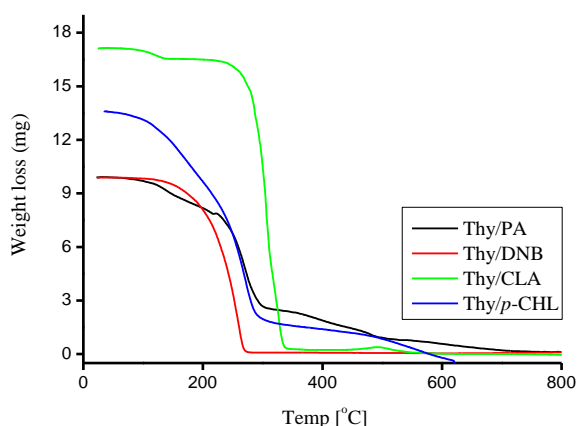
Thermal analysis

The thermogravimetric analysis (TG) provided information about the thermal stabilities of the prepared charge-transfer complexes and about the differences in the physical behavior of the starting and resulting compounds. In order to verify charge-transfer interaction between Thy donor and acceptors and thermal stability of the new CT complexes, the thermogravimetric analysis of Thy CT complexes were carried out over the temperature range of 25-800 °C under an air atmosphere using 9.9, 9.87, 17.12 and 13.60 mg samples for [(Thy)(PA)], [(Thy)(CLA)], [(Thy)(DNB)] and [(Thy)(*p*-CHL)] complexes, respectively. The TG curves were redrawn as mg mass loss versus temperature. Figure 5 shows the thermograms for Thy CT complexes and thermal analyses data are listed in Table 3. The obtained data indicate that the [(Thy)(PA)] complex decomposes in three clear decomposition steps within the 25-800 °C temperature range. The first decomposition step within the temperature range 25-152 °C has a weight loss about 12.20% and is attributed to the liberation of NO$_2$ molecule. The second decomposition step existed within the 152-300 °C temperature range and is reasonably explained by the loss of 5C$_2$H$_2$, 2NO$_2$ and CO$_2$ molecules.

The final decomposition step found within the temperature range 300-800 °C which corresponds to the liberation of 2C$_2$H$_2$, CO$_2$ and 3/2H$_2$ molecules. This step is associated with a total weight loss of 25.77%, which is in good agreement with the calculated value (26.10%). The [(Thy)(CLA)] complex is thermally stable in the 25-675 °C temperature range. The thermal decomposition of the complex is a two-steps process.

Table 3. Thermal decomposition data for the Thy CT complexes.

| Complex | Stage | TG range, °C | Mass loss, % | | Detected fragments |
			Found	Calculated	
[Thy)(PA)] ($C_{16}H_{17}N_3O_8$)	I	25-152	12.20	12.13	NO_2
	II	152-300	62.03	61.69	$5C_2H_2 + 2NO_2 + CO_2$
	III	300-800	25.77	26.10	$2C_2H_2 + CO_2 + 3/2H_2$
[Thy)(CLA)] ($C_{16}H_{16}Cl_2O_5$)	I	25-220	3.97	3.34	CO_2
	II	220-675	96.03	96.60	$6C_2H_2 + Cl_2 + 3CO_2 + 2H_2$
[Thy)(DNB)] ($C_{16}H_{18}N_2O_5$)	I	25-800	100.00	99.90	$7C_2H_2 + 2NO_2 + 2CO_2 + 2H_2$
[Thy)(p-CHL)] ($C_{16}H_{14}Cl_4O_3$)	I	25-345	86.16	86.34	$6C_2H_2 + 2Cl_2 + CO_2$
	II	345-600	13.84	13.63	$C_2H_2 + CO_2$

The first mass loss step occurs between 25-220 °C corresponds to the loss of CO_2 molecule with a weight loss of 3.97% close to the expected theoretical value of 3.34%. The second degradation step at 220-675 °C has an extremely large scale of weight loss for about 96.03%, and is attributed to the loss of $6C_2H_2$, Cl_2, $3CO_2$ and $2H_2$ molecules. The curve of [(Thy)(DNB)] complex was thermally decomposed in one decomposition step within temperature range 25-800 °C, and may be assigned to the liberation of $7C_2H_2$, $2NO_2$, $2CO_2$ and $2H_2$.

Figure 5. TG curves of Thy CT complexes.

The thermal analysis curve of the [(Thy)(p-CHL)] complex indicates that the decomposition occurs in two main stages in the temperature range of 25-600°C. The first decomposition step within the temperature range 25-345 °C corresponding to loss of $6C_2H_2$, $2Cl_2$ and CO_2 molecules representing a weight loss of 86.16% very close to the expected theoretical value of 86.34%. The second decomposition step found within the temperature range 345-600 °C which corresponds to the liberation of C_2H_2 and CO_2 molecules representing a weight loss of 13.84% very close to the expected theoretical value of 13.63%.

Conclusion

Recently, considerable attention has been devoted to the formation of stable charge-transfer complexes that result from the reaction between acceptors and drugs or biological compounds. This interest stems from the significant physical and chemical properties of these complexes. The results reported in this paper are concerned with the preparation, characterization, structural and thermal studies of novel charge-transfer complexes formed between the anti-microbial agent; thymol (Thy) and the acceptors picric acid (PA), chloranilic acid (CLA, 1,3-dinitrobenzene (DNB) and *p*-chloranil (*p*-CHL**).** It is observed that the reaction stoichiometry is 1:1, and the resulting CT complexes were shown to have the general formula: [(Thy)(acceptor)]. The interaction between the Thy and PA or CLA acceptors was stabilized by hydrogen bonding. The obtained complexes were thermally stable. Physical parameters such as formation constant (K_{CT}), molar extinction coefficient (ε_{CT}) and other spectroscopic data have also been determined.

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