

SPECTROPHOTOMETRIC AND THERMAL STUDIES

OF CHARGE TRANSFER COMPLEX OF 1,10-

PHENANTHROLINE

AS AN ELECTRON DONOR WITH π -ACCEPTOR

p-NITROPHENOL

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INTRODUCTION

Charge transfer interaction within a molecular complex formed as a result of an electron donor, D and electron acceptor, A, involves resonance with a transfer of charge from D to A as were shown by Mulliken [1,2]. Therefore, the excited state of the complex is easily achieved by direct excitation in the charge transfer band of the complex [3]. In general, the charge transfer complexation occurs as an ionic bond in simple low-radical pair interaction. Charge transfer complexes play an important role in biological system as well as in the field of drug acceptor binding mechanism [4, 5].

$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ molecular complexes of 1,10-phenanthroline derivatives with chloranil, picric acid and chloranilic acid were investigated spectrophotometrically [6] and also the spectral data of the complexes obtained on the reaction of iodine with twin site donors such as 1,10-phenanthroline and its methyl and chloro derivatives, 1,7- and 4,7-phenanthroline and 2,2'-bipyridine were studied

[6]. Charge transfer interaction of π acceptor p-Nitrophenol (PNP) and other para position phenols with N,N'-bis[2-hydroxyethyl]-1,4,6,8-naphthalenediimide (BHENDI) were investigated spectrophotometrically and spectroscopically [8]. Charge transfer (CT) complexes of 1,10-phenanthroline derivatives with aromatic phenols derivatives were prepared and investigated [6]. The interest to study these particular organic compounds has antibacterial activity. These compounds are used as parent material in pharmaceutical insecticides and the excess of thiocarbamides can be determined as charge transfer complexes. 1,10-phenanthroline and its derivatives show high catalytic activity [9-11] and phenols are more acidic than alcohols.

In continuation of our studies on charge-transfer interaction [12-14], the present chapter is concerned with the study of the behaviour of 1,10-phenanthroline (Phen) which is hygroscopic and acts as a donor towards complexation with p-Nitrophenol (PNP) as π -acceptor. The stoichiometry of the charge transfer complex under investigation was determined by using Benesi-Heldebrand methods[15].

The molecular compound of the 1,10-phenanthroline with PNP is prepared and investigated by instrumental techniques such as FTIR, TGA-DTA, and electronic absorption spectra.

II. EXPERIMENTAL

1,10-phenanthroline (Merck), p-Nitrophenol (Thomas Baker), methanol (Merck) analytical grad (AR) were used without further purification.

Stoichiometry is determined using the Benesi-Hildebrand method (straight line method) from stock solutions of acceptor and donor. On the other hand, the formation constant (K_{CT}) of the CT complex has been determined by Benesi-Hildebrand equation [15] which is valid under the condition $[A]_0 \gg [D]_0$ or $[D]_0 \gg [A]_0$, for 1:1 donor-acceptor complexes [16-18]. The concentration of donor was kept fixed at 6×10^{-6} M and that of the acceptor changed from 8×10^{-5} to 7.56×10^{-5} M. The electronic absorption spectra of the complexes were measured in methanol at room temperature.

The preparation of the molecular complex and the working procedure are the same as described elsewhere [19, 20] and in the chapter 4. The electronic spectra of the donor, acceptor and the resulting CTC in methanol were recorded in the region of 700-200nm using a Shimadzu UV-visible spectrophotometer model UV 1700 Pharma spec with a 1 cm quartz cell paths length and the FTIR spectroscopy of the reactants and the CT complex were recorded using KBr disc on the FTIR spectrometer model spectrospec 2020, the thermal analysis (TGA and DTA) was carried under nitrogen atmosphere with a heating rate of 20 °C/min for thermogravimetric analysis TGA-DTA using Shimadzu model DTG-60H thermal analyzers, the solid CT complex prepared by mixture of fine powder of 1 mmol each of acceptor and donor.

III. RESULT AND DISCUSSION

3.1 Observation of CT bands and determination of formation constant

Taking into consideration the presence of an electron donating group in the electron donor system under investigation, on mixing the methanol solution of the donor and acceptor according to the condition $[A]_0 \gg [D]_0$ or $[D]_0 \gg [A]_0$ for 1:1 donor-acceptor complexes [16-18], different wavelength, λ_{CT} of CT transition relative to donor and acceptor is observed. This fact is further supported by measurement of the absorption of CT complex of 1,10-phenanthroline with π -acceptor p-Nitrophenol in methanol which gave CT characteristic broad bands that absorbed in the UV region, in which neither the donor nor the acceptor separately absorbed.

The electronic absorption spectra of mixtures of charge transfer complexes of different and excess concentration of p-Nitrophenol with fixed concentration of 1,10-

phenanthroline were recorded in methanol at room temperature are shown in Fig.1 and data are reported in Table 1 for determination of formation constant and molar extinction coefficient. The change in the absorption intensity to higher side for CT complex while adding the acceptor part in the reaction mixture are reported in Table

1. In comparison with the reactants spectra new absorption bands at 316 nm and 233 nm are obtained and the longest wavelength peak consider as CT peak [21], which shift due to $n \rightarrow \pi^*$ transition, i.e., involving the transfer of an electron from HOMO of the donor to the LUMO of the acceptor is shown in scheme 3 of chapter 3, the absorption intensities of these two new bands increases as the concentration of the acceptor is increased. The Phen is relatively electron rich and PNP is relatively electron poor compound. When a solution contains both an electron rich and electron poor compound, they tend to associate with one another in loose interaction known as electron-donor-acceptor (EDA) complexes [22]. The new, low energy absorptions are observed in

solutions containing both a donor and an acceptor by Mulliken [23] as charge transfer interactions involving the excitation of an electron on the donor to empty orbital on the acceptor

The formation constant (K_{CT}) for the CT complex of donor-acceptor, with molar extinction coefficient (ϵ_{CT}) were determined by the Benesi-Heldebrand [15] equation using the absorbance of the CT complex.

$$\frac{[D]_0}{AK} = \frac{1}{C} \frac{1}{\epsilon C} + \frac{1}{[A]} \frac{1}{\epsilon C} \quad \text{or} \quad \frac{[A]_0}{AK} = \frac{1}{C} \frac{1}{\epsilon C} + \frac{1}{[D]} \frac{1}{\epsilon C}$$

$$\frac{1}{AK} = \frac{1}{C} \frac{1}{\epsilon C} + \frac{1}{[A]} \frac{1}{\epsilon C} \quad \text{or} \quad \frac{1}{AK} = \frac{1}{C} \frac{1}{\epsilon C} + \frac{1}{[D]} \frac{1}{\epsilon C}$$

where $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and donor, respectively, A is the absorbance of the donor-acceptor mixture at λ_{CT} measured against the solvent as reference and ϵ_{CT} is the molar extinction coefficient. K_{CT} is the formation constant of the CT complex. In this case a very good linear plot is obtained. This typical case is shown in Fig. 2. The correlation coefficient for this plot was about 0.9. The values of ϵ_{CT} and K_{CT} are determined from such plot which are $4.401 \times 10^5 \text{ l cm}^{-1} \text{ mol}^{-1}$ and $2.303 \times 10^3 \text{ l mol}^{-1}$ respectively, and also transition energy of CT complex is calculated to be 3.935 eV. The values of the formation constant (K_{CT}) are dependent on the nature and geometry of acceptors and donors. The stoichiometry of the CT complex of 1,10-phenanthroline with PNP is found to be 1:1, is likely to occur derivatives of 1,10-phenanthroline form CT complexes with aromatic nitrophenols [5, 24]. The result is confirmed by the application of straight line method [15].

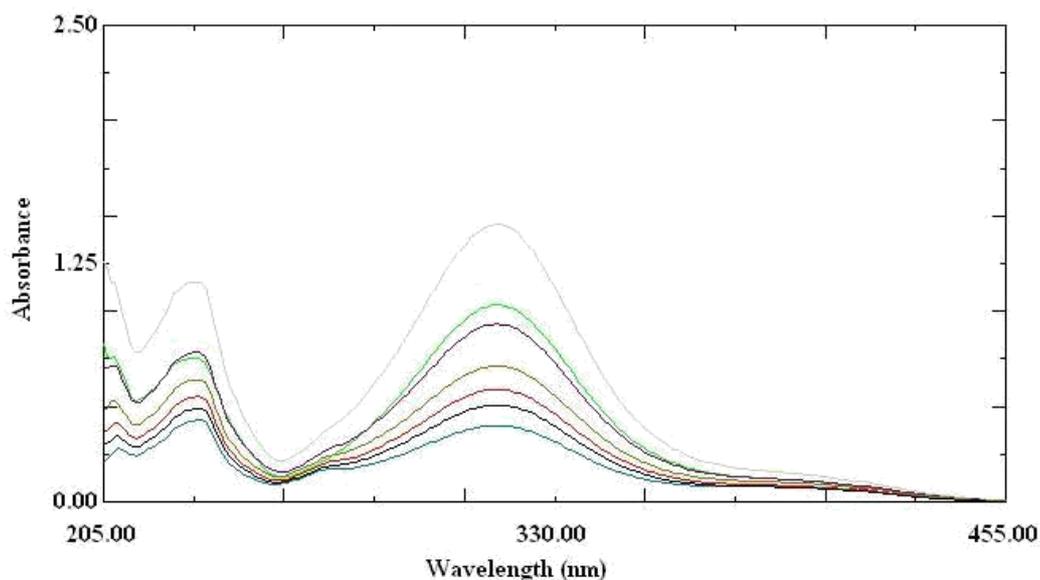


Fig. 1. Electronic absorption spectra of mixture of charge transfer complexes of; (1) Phen ($4.5 \times 10^{-5} \text{ M}$) + PNP ($8 \times 10^{-3} \text{ M}$); (2) Phen ($4.5 \times 10^{-5} \text{ M}$) + PNP ($1.06 \times 10^{-4} \text{ M}$); (3) Phen ($4.5 \times 10^{-5} \text{ M}$) + PNP ($1.2 \times 10^{-4} \text{ M}$); (4) Phen ($4.5 \times 10^{-5} \text{ M}$) + PNP ($1.8 \times 10^{-4} \text{ M}$); (5) Phen. ($4.5 \times 10^{-5} \text{ M}$). + PNP ($2 \times 10^{-4} \text{ M}$); (6) Phen. ($4.5 \times 10^{-5} \text{ M}$). + PNP ($2.64 \times 10^{-4} \text{ M}$) and (7) Phen. ($4.5 \times 10^{-5} \text{ M}$) + PNP ($7.56 \times 10^{-4} \text{ M}$) in methanol at room temperature.

Table 1

Absorption data for spectrophotometric determination of stoichiometry and formation constant (K_{CT}) and molar extinction coefficient (ϵ_{CT}) of the CT complex of Phen and PNP in methanol at room temperature

Concentration of acceptor ($\times 10^{-4}$ M)	Concentration of donor (M)	Absorbance at λ_{CT} 316 nm	Formation constant (K_{CT}) $l \text{ mol}^{-1}$	Molar extinction coefficient (ϵ_{CT}) $l \text{ cm}^{-1} \text{ mol}^{-1}$
0.80	6×10^{-6}	0.406	2.303×10^3	4.401×10^5
1.06		0.513		
1.20		0.588		
1.80		0.769		
2.00		0.906		
2.64		1.092		
7.56		1.457		

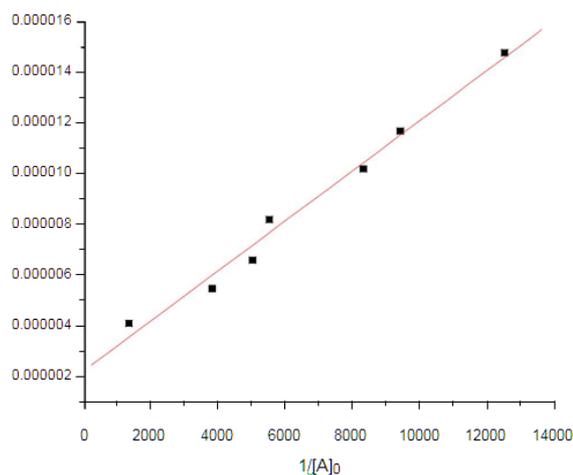


Fig.2. Benesi-Hildebrand plot of the charge transfer complex of 1,10-phenanthroline with p-Nitrophenol, $[A]_0/A$ vs. $1/[D]_0$ in methanol at room temperature

3.2 Determination of free energy (ΔG°)

The values of K_{CT} were used to calculate $-\Delta G^\circ$ values according to the equation [25, 26]

$$\Delta G^\circ = -RT \ln K_{CT}$$

The complex is found to have a $-\Delta G^\circ$ as $17.897 \text{ kJ mol}^{-1}$ indicating the formation of the complex are exothermic and spontaneous.

3.3 Comparative study of FTIR spectroscopy of CT complex and reactants

A careful investigation of the important characteristic peaks of the FTIR spectra of 1,10-phenanthroline, PNP and their 1:1 CTC are recorded using FTIR spectrometer model interspec 2020 and shown in Fig. 3. Assignments of the characteristic infrared spectral bands of the free acceptor and donor as well as the formed CT complex are reported in Table 2. However, it is observed that the formation of CTC is strongly supported by observing the main infrared bands of the reactant 1,10-phenanthroline and PNP in the product spectrum. However, the position of the most bands of donor and acceptor in the complex spectrum show shift in the frequency as well as some changes in their intensities compared with those of the free phen and PNP. This could be attributed due to expected symmetry and electronic structure changes upon the formation of CT complex. In general, the CTC spectrum show the characteristic bands due to various modes of vibration of the acceptor part, shift to lower wavenumber while those of the donor part also acquire a counter shift. The shift of the nCH bands of the donor to higher wavenumber is considered to be a criterion for CTC interaction type [27] involving the transfer of an electron from HOMO of the donor to the LUMO of the acceptor [26]. These types of bands are due to the stretching mode of proton attached to a quaternary nitrogen atom [28].

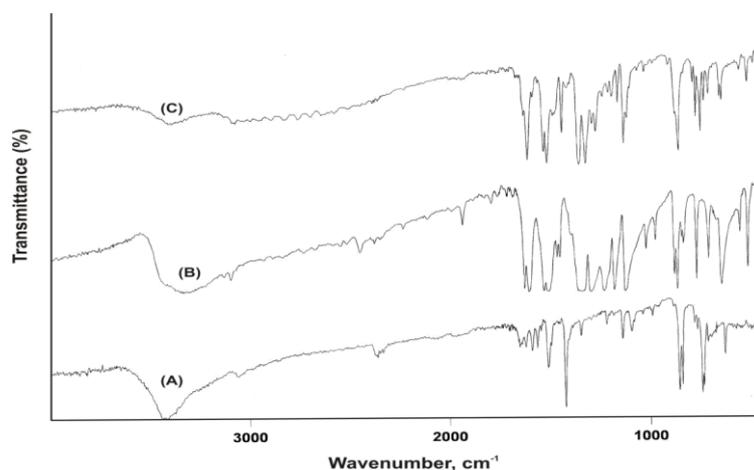


Fig. 3. FTIR spectra of (A) 1,10-phenanthroline; (B) p-Nitrophenol; (C) charge transfer complex of p-Nitrophenol and 1,10-phenanthroline

Table 2
 Infrared frequencies^a (cm⁻¹) and band assignments for (A) 1,10-Phen (B) PNP
 and (C) [(Phen) (PNP)] compounds

A	B	C	Assignments ^b
	3321 vs, br	3384 m, br	v(O-H) of PNP; CTC v(⁺ NH)
3059 w	3084 w	3064 w	v(C-H); aromatic
2960 w	2980 w	2955 w	v(C=C); CH aromatic
	2948 w	2950 w	v _s (C-H); CH ₂ – CH ₃
		2930 w	
		2878 w	Hydrogen bonding
		2811 w	

		2744 mw	
		2682 w	
		2625 w, br	
1690 w	1613 mw	1650 sh	$\nu(\text{C}=\text{C})$; aromatic
	1589 vs	1592 vs	$\nu_{\text{as}}(\text{NO}_2)$; PNP
1587 m	1492 vs	1494 vs	$\delta(\text{CH})$; CH def
1509			
1500		1463 sh	$\delta(\text{CH})$; aromatic
1422 vs	1325 vs	1422 s	$\nu_{\text{as}}(\text{CN})$
1339 w		1334 s	
	1278 vs	1303 s	$\nu(\text{C}-\text{O})$; C-OH
		1270 w	
	1218 vs	1214 w	$\nu_{\text{s}}(\text{NO}_2)$; PNP
	1169 s	1187 w	
	1106 vs		
1138 mw	1007 w	1102 vs	$\nu_{\text{s}}(\text{CN})$
1091		1094 sh	
1037 mw	963 w	1042 w	$\delta(\text{CH})$; in-plane bend
988 w	850 vs	1009 w	
854 vs	819 w	889 w	
837 s		840 vs	
778 w	757 s	766 w	$\delta(\text{CH})$; CH-rock
762 w		752 m	
740 s	627 vs	730 s	
694 w	694 s	711 w	$\delta(\text{NH})$; NH def
622 m	628 vs	688 w	
637 mw		634 w	
		622 w	
525	536 mw	535 w	$\delta(\text{CH})$; out-of-plan
447	496 s	493 w	
411	417 w	465 w	
		405 w	

a br, broad; m, medium; s, strong; sh, shoulder; w, weak; ν , stretching, δ , bending.

b stretching and bending.

The stretching vibrations of the (C=N) and (C=C) peaks appear at 1422 cm^{-1} (very strong) and 1690 cm^{-1} (weak), in 1,10-phenanthroline, respectively, and stretching vibration of -OH, -NO₂ and C=C peaks appear at 3321 cm^{-1} (very strong, broad), 1589 cm^{-1} (very strong) and 1613 cm^{-1} (medium, weak), respectively for p-Nitrophenol which is more acidic than alcohol [7]. The infrared spectrum of CTC complex shows a medium

broad band for the N^+-H-O^- within the range $3224-3500\text{cm}^{-1}$ and stretching vibrations of the $C=N$, $C=C$ and NO_2 peaks appear at 1422 (very strong), 1650 cm^{-1} (sh) and 1592 cm^{-1} (very strong), respectively. It is also observed that some peaks for 1,10-phenanthroline and p-Nitrophenol do not appear in the FTIR spectrum of CT complex of them. This behaviour is in accordance with the charge migration from the donor to the acceptor [29, 30], which give an additional evidence for interaction between 1,10-phenanthroline and PNP. Therefore, the FTIR data provided evidence for the existence of a new bands of medium weak intensity in the spectrum of CTC prepared and indicated the formation of quaternary amine species i.e., ^+NH , from which a labile proton is expected. Therefore, these results reveal that the CT complex has just some changes in their band intensities and shift of some band frequency values.

3.4. Comparative study of thermograms for 1,10-phenanthroline, p-Nitrophenol and their CT complex

Thermal analysis was carried out using a Shimadzu model DTG-60H thermal analyzers for 1,10-phenanthroline, PNP and their CT complex. A heating rate of $20\text{ }^\circ\text{C}/\text{min}$ within the temperature range of $25-800\text{ }^\circ\text{C}$ was used.

The combined TGA and DTA thermograms for charge transfer complex along with acceptor and donor are presented in Fig. 4. It is clearly observed that [(Phen) (PNP)] exhibit three step degradation (Fig. 4. C) which is typical thermal behavior of derivatives of PNP as reported elsewhere [8]. In first step, 3.558% of the compound is lost at around $142.2\text{ }^\circ\text{C}$ which is thought to be a consequence of crystallization. This can also be reflected by the existence of corresponding endothermic peak ($\Delta H = 21.547\text{ J/gm}$) observed on DTA thermograms. The second major weight loss (81.563%) is due to the decomposition of charge transfer complex into its constituents. The PNP is less aromatic (less carbon content) which is thus lost first. Therefore, this weight loss in CT complex is attributed to the loss of PNP prior to 1,10-phenanthroline, as clearly mirrored the first weight loss in TGA thermogram of PNP (Fig. 4.B). However, the large difference in the ΔH values, corresponding to loss of PNP which are estimated from DTA thermograms (Fig. 4. B and C) is in perfect agreement with bonding between the hydrogen of PNP and the aromatic nitrogen of 1,10-phenanthroline in the complex. Table 3 presents the most important thermal analysis data obtained from the TGA-DTA thermograms. It is also interesting to note that the third degradation step exhibited by charge transfer complex at around $499.7\text{ }^\circ\text{C}$ is the final loss of the carbon residue and azocyanine as well, resulting from the full decomposition of 1,10-phenanthroline is likely due to derivatives of 1,10-phenanthroline [9, 31]. This step can also be observed in the TGA thermogram of donor (Fig. 4. A) with slight difference in ΔH values of the second step (Fig.4.A) and the first step (Fig. 4.C) corresponding to this weight loss which is due to charge transfer complex formation.

IV. CONCLUSIONS

The electron donor 1,10-phenanthroline reacts with the π -acceptor p-Nitrophenol in methanol at room temperature to form the charge transfer complex. The forgoing discussion has shown that 1,10-phenanthroline forms with PNP 1:1 molecular complex in which phen was found to act as a n donor or a hydrogen acceptor. Further, the TGA-DTA thermograms of the solid state CT complex of phen and PNP supported for interaction between donor and acceptor by some change in enthalpy(ΔH), degradation temperature and weight loss for phen, PNP and their CT complex. It is also observed that FTIR data provides evidence for the existence of new

bands of CTC with some changes and indicate the formation of quaternary amine species (^+NH). Formation constant, molar extinction coefficient, free energy, enthalpy, degradation temperature and weight loss are also estimated.

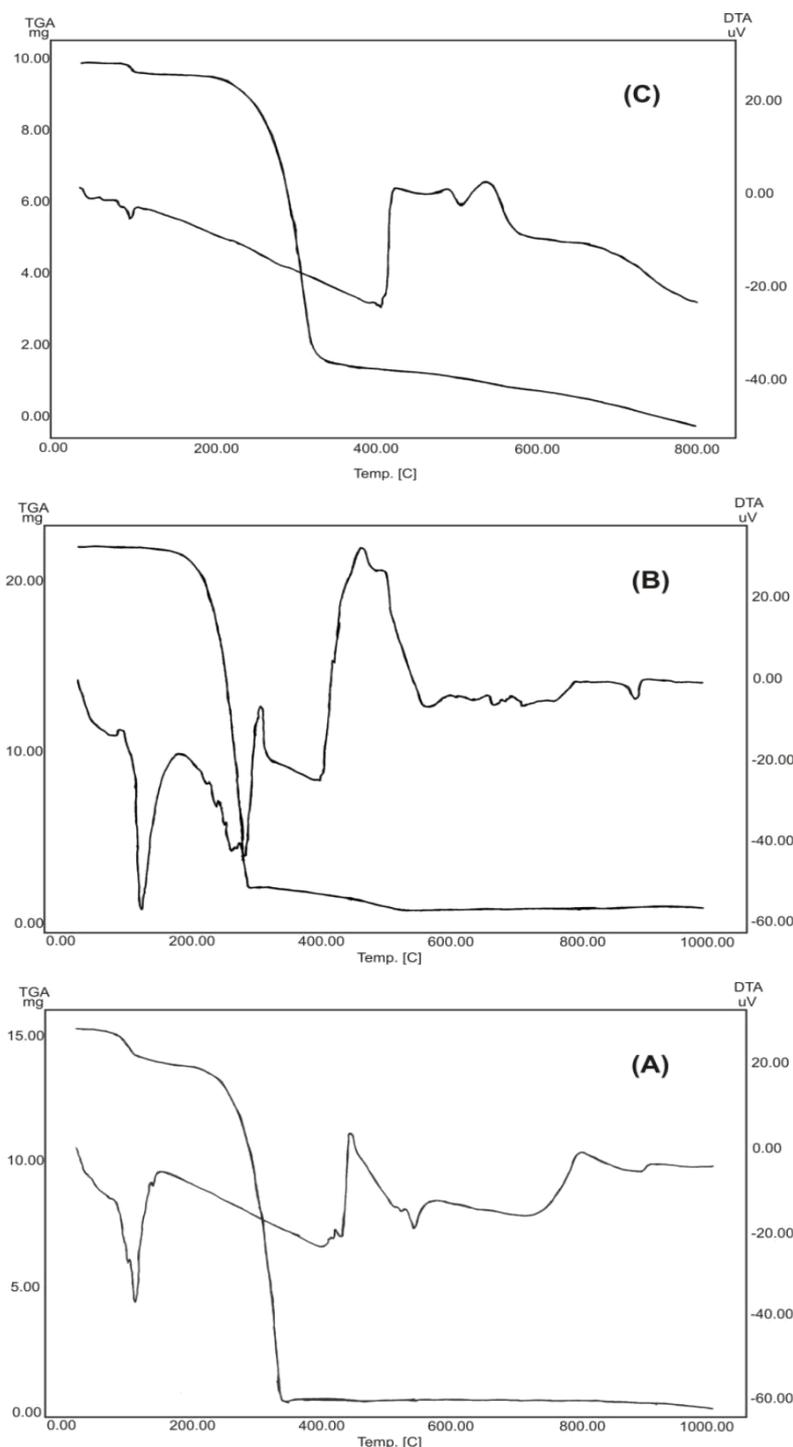


Fig. 4. TGA-DTA curves for (A) 1,10-phenanthroline; (B) p-Nitrophenol; (C) charge transfer complex of 1,10-phenanthroline and p-Nitrophenol.

Table 3

Weight loss, enthalpy (ΔH), and degradation temperature (T), for CT complex of 1,10-Phen and PNP, 1,10-phenanthroline and p-Nitrophenol.

Step	CT Complex of Phen 1,10-phenanthroline & PNP			1,10-phenanthroline			p-Nitrophenol		
	Weight loss (%)	ΔH (J/gm)	T ($^{\circ}C$)	Weight loss (%)	ΔH (J/gm)	T ($^{\circ}C$)	Weight loss (%)	ΔH (J/gm)	T ($^{\circ}C$)
I	3.56	+21.55	142.37	9.37	+121.69	111.93	87.26	+64.34	254.83
II	81.56	+729.80	298.99	87.22	-117.10	280.67	6.04	+600.64	226.09
III	5.65	-127.36	499.77						

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